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THE ELECTROLYTIC FORMATION OF PERSULPHATE. PART I.

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Various studies have been done on the electrolytic formation of persulphate, but most of them seem to be unsystematic for reason that their primary purpose is the determination of the best conditions for the manufacture of persulphate, the theoretical side of the problem being necessarily neglected.

M. Berthelot⁽¹⁾ considers that the formation of persulphuric acids is a process of oxidation by the hydrogen peroxide formed at the anode. K. Elbs and O. Schönherr⁽²⁾, on the other hand, attribute this formation to two discharged HSO_4 -ions united together in an analogous manner to the formation of the chlorine molecule by the union of two discharged Cl-ions when hydrochloric acid is electrolysed. Then again, F. Foerster⁽³⁾, in his book, states that the oxidation of SO_4 -ions by anodic oxygen is responsible for the persulphate formation, and gives a complicated interpretation of the mechanism of the anodic reactions.

When the present writer⁽⁴⁾ gave explanations for Kolbe's reaction, the electrolytic oxidation of fatty acids, on the basis of the peroxide theory, he suggested, from the result of electrolysis of dilute solutions of ammonium and potassium sulphates, that the electrolytic formation of the persulphate might be similarly explained.

Experimental.

A spiral of thin Pt-wire was used as the anode, immediately after being treated according to the method employed by Goard and Rideal⁽⁵⁾, and rotated at the center of a porous cylinder, which stood at the center of a beaker and made the anode chamber. The cathode was also a spiral Pt-wire placed

(1) *Compt. rend.*, **90** (1880), 269; *ibid.*, **112** (1891), 1418.

(2) *Z. Elektrochem.*, **1** (1894), 417.

(3) "Elektrochemie wässriger Lösungen," 1923.

(4) *Complete Abst. Japanese Chem. Literatures (Nippon Kwagaku Soran)*, 2nd Series, **6** (1932), 85B.

(5) *Trans. Faraday Soc.*, **19** (1924), 740.

against the inner wall of the beaker. The anolyte, 90.0 c.c. at the commencement, was kept at 16–18°C. by circulating water through a glass tubing immersed in the cylinder. The anolyte was stirred by the rotation of the anode. The same amount of electricity, 828 coulombs, was supplied in each electrolysis.

The analysis of the electrolysed solution was performed as follows: a 40.0 c.c. portion out of the anolyte which was about 89.5 c.c. after electrolysis in each case was mixed with a sodium acetate solution sufficient for making it acid with regard to acetic acid and then titrated with potassium sulphite with iodine as indicator. This titration gave the amount of Caro's acid present. Another 40.0 c.c. portion was treated with a ferrous sulphate solution at about 50°C., being adequately acidified with sulphuric acid when necessary and was then back-titrated with potassium permanganate, which gave the total amount of the peroxidic oxygen, i. e. persulphuric acid, Caro's acid and hydrogen peroxide. The potassium sulphite solution was prepared with potassium pyrosulphite⁽⁶⁾ and was stored under nitrogen. Coloured sulphate solutions, such as those of Fe and Cu, could not be titrated with the sulphite solution. For the estimation of the total peroxidic oxygen of such solutions potassium bichromate was employed instead of permanganate, with barium diphenyl-sulphonate as indicator.

Experiment 1. Influences of Current Density and H⁺-Concentration. This was rather a repetition of what had been done by Elbs and Schönherr⁽⁷⁾. A 10 N sulphuric acid free from ammonium sulphate was denoted by (0 : 10), and a solution of 2 and 8 N respectively with regard to the sulphate and sulphuric acid by (2 : 8), and so on. The solutions employed here were (0 : 10), (2 : 8), (4 : 6), (6 : 4), (8 : 2), and the saturated solution of ammonium sulphate which was 7.88 N and contained no free sulphuric acid. The current efficiencies are shown in Tables 1 and 2. No hydrogen peroxide was detected in any of above cases with titanium sulphate. Amounts of Caro's acid were small in all cases, although they increased with total amount of peroxidic oxygen, which itself increased with the rise of the current density.

The highest current efficiency with regard to this peroxydic product was obtained in the case of the saturated solution of ammonium sulphate with the current density 1.6 amp./cm.², which amounted to 2.5%. Therefore, nothing conclusive can be deduced out of the current efficiency with respect to Caro's acid.

(6) F. Foerster, *Z. physik. Chem.*, **110** (1924), 476. S. Glasstone and A. Hickling, *J. Chem. Soc.*, **1933**, 829.

(7) *Z. Elektrochem.*, **2** (1895), 245.

Table 1. Current Efficiencies with Regard to Caro's Acid.

Solution \ Current density	0.05 amp./cm. ²	0.10	0.20	0.40	0.80	1.60
(0 : 10)	0.3%	0.3	0.4	1.4	2.2	2.4
(2 : 8)	0.7	0.5	1.2	1.1	1.7	2.5
(4 : 6)	0.6	0.6	0.7	0.9	0.9	1.0
(6 : 4)	0.4	0.5	0.6	0.8	1.4	1.8
(8 : 2)	0.8	1.6	1.6	1.9	0.8	1.4
The saturated solution of (NH ₄) ₂ SO ₄	2.2	2.3	0.9	1.1	1.9	2.5

Table 2. Current Efficiencies with Regard to the Total Peroxidic Oxygen.

Solution \ Current density	0.05 amp./cm. ²	0.10	0.20	0.40	0.80	1.60
(0 : 10)	2.2%	3.3	4.6	21.4	45.8	63.7
(2 : 8)	18.0	28.6	41.5	56.3	76.9	87.5
(4 : 6)	35.5	38.9	56.3	63.9	78.2	74.5
(6 : 4)	49.5	56.7	69.0	74.4	83.4	83.1
(8 : 2)	57.3	60.6	74.4	81.1	87.2	92.0
The saturated solution of (NH ₄) ₂ SO ₄	59.6	60.5	68.9	84.2	82.4	89.0

Increase of the current density was favourable, in general, to the anodic oxidation, and the effect of the increase on the current efficiency with respect to the total peroxidic oxygen was the greatest in the case of (0 : 10) among the six solutions; the more concentrated was the solution with regard to ammonium sulphate, the less marked was the effect. When part of the free sulphuric acid was replaced by the sulphate, there were more OH⁻-ions brought into existence as the result of H⁺- and SO₄⁻-ions uniting themselves together to form acid sulphate.

The difference of the current efficiencies generally observed between (0 : 10) and (2 : 8) was greater than any other succeeding pairs. This is because the difference of OH⁻-concentrations was presumably the greatest in this case. When solutions were more concentrated with respect to ammonium sulphate, for instance (8 : 2), the OH⁻-concentrations were considerably greater than that of (0 : 10), so that fairly high current efficiencies were obtainable even with the smallest current density (Fig. 1). One of the highest current efficiencies was obtained with the saturated solution of am-

monium sulphate in spite of its comparatively smaller concentration and also of its being neutral at the beginning. If this solution had been so concentrated as 10N, it is very probable that its current efficiency might have been greater than any other.

Elbs and Schönherr's view can hardly account for these facts, but OH-ions discharged at the anode seem to the writer to play an important rôle in the persulphate formation. S. Glasstone and A. Hickling⁽⁸⁾ proposed that hydrogen peroxide is the effective oxidizing agent in anodic oxidation of certain inorganic salts. In the present case, however, it is not the primary concern whether hydrogen peroxide or nascent oxygen is the oxidizing agent, though for convenience's sake the latter is assumed to be the case. It is evident, anyhow, that increase of OH' is favourable to the persulphate formation in this experiment when solutions with the same total concentration of the sulphate radical are electrolysed.

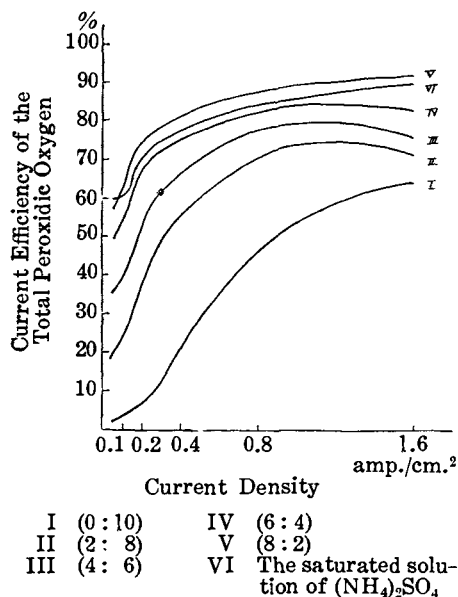


Fig. 1.

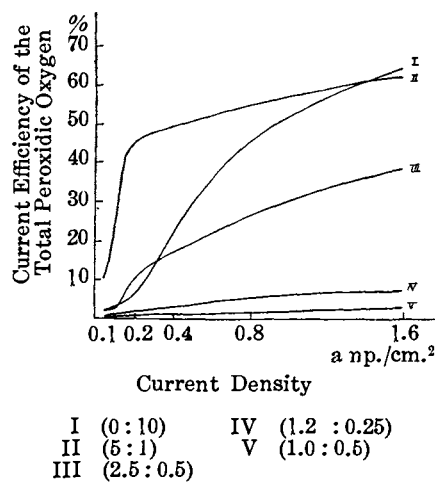


Fig. 2.

Experiment 2. Influence of Concentration. A solution which was 5 and 1N with regard to ammonium sulphate and sulphuric acid respectively was denoted (5:1) and so on. Four solutions, (5:1), (2.5:0.5), (1.25:0.25), and (1.0:0.5), were electrolysed with the same current densities as before, and the current efficiencies of these solutions are shown in Fig. 2.

(8) *J. Chem. Soc.*, **1932**, 2345, 2800; *ibid.*, **1933**, 829.

Differences of current efficiencies of above solutions can easily be understood from the view point of concentration. That the current efficiencies of (0:10) of Experiment 1 and (5:1) of this experiment were alike is noteworthy, considering the far greater concentration of the former with respect to the sulphate radical. This point can be explained by the fact that the latter had greater OH'-concentration. The difference between (1.25:0.25) and (1.0:0.5), both of which had the same total concentration of the sulphate radical, is similarly explicable.

Experiment 3. Influences of Various Cations. A 7N sulphuric acid solution and those which were 2 and 5 N respectively with regard to sulphate and sulphuric acid were electrolysed. The copper solution which was obtained by saturating 5N sulphuric acid with copper sulphate was nearly normal with regard to the sulphate. The current efficiencies of these solutions are shown in Table 3 and Fig. 3.

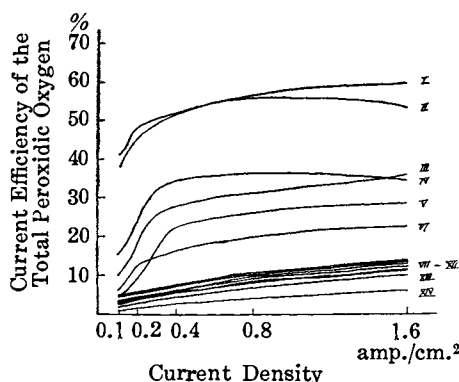
Table 3. Current Efficiencies with Regard to the Total Peroxidic Oxygen of Solutions which were 2 and 5 N Respectively with Regard to the Corresponding Sulphate and Sulphuric Acid.

Current density Sulphate	0.10 amp./cm. ²	0.20	0.40	0.80	1.60
K ₂ SO ₄	36.4%	46.0	51.3	59.2	60.1
(NH ₄) ₂ SO ₄	10.4	17.6	24.4	30.8	36.2
Na ₂ SO ₄	3.3	8.5	22.2	26.2	27.8
H ₂ SO ₄	3.2	3.8	4.3	8.0	12.3
MgSO ₄	1.0	1.8	6.3	8.3	12.0
Li ₂ SO ₄	0.6	1.5	3.8	4.8	10.3
Al ₂ (SO ₄) ₃	3.5	4.8	6.3	9.3	12.6
CdSO ₄	1.0	1.8	4.6	8.6	10.9
Fe ₂ (SO ₄) ₃	2.3	2.6	4.3	4.8	6.5
CuSO ₄	3.0	4.0	6.4	7.1	9.2
ZnSO ₄	1.0	1.0	1.8	3.1	4.7

These sulphates can be classified into two according to the current efficiencies of corresponding solutions. Sulphates of K, NH₄, and Na are one class and the others, i. e. those of Li, Mg, Zn, Fe(ferric), Al, Cu, and Cd, are the other.

One characteristic property common to the three former sulphates is the capability of forming the acid sulphate. Its formation which causes the

increase of OH' -concentration can possibly account for higher current efficiencies of these solutions. Why, then, did the potassium sulphate solution give the highest current efficiencies? Let the writer explain. According to A. Kailan and E. Leisek⁽⁹⁾ different alkali metal ions have different effects on



- I 2N K_2SO_4 , 5N H_2SO_4
- II 1N K_2SO_4 , 1N ZnSO_4 , 5N H_2SO_4
- III 2N $(\text{NH}_4)_2\text{SO}_4$, 5N H_2SO_4
- IV $\frac{1}{2}\text{N}$ K_2SO_4 , $1\frac{1}{2}\text{N}$ ZnSO_4 , 5N H_2SO_4
- V 2N Na_2SO_4 , 5N H_2SO_4
- VI 1N $(\text{NH}_4)_2\text{SO}_4$, 1N ZnSO_4 , 5N H_2SO_4
- VII-XII 2N sulphate, 5N H_2SO_4 ; sulphates being those of H_2 , Mg, Li, Al, Cd and Fe(III)
- XIII 1N CuSO_4 , 5N H_2SO_4
- XIV 2N ZnSO_4 , 5N H_2SO_4

Fig. 3.

persulphate decomposition. To verify their result, 20N sulphuric acid was electrolysed for half an hour with a current density of 0.8 amp./cm.² To each of three 10 c.c. portions of the anolyte after electrolysis was added potassium, ammonium, and sodium sulphates respectively enough to make the solution normal with regard to the corresponding sulphate. These three solutions as well as a blank one were titrated, after allowing them to stand for $1\frac{1}{2}$ hours at 85–90°C. with frequent stirring.

The total peroxidic oxygen of the blank, K_2SO_4 , $(\text{NH}_4)_2\text{SO}_4$, and Na_2SO_4 solutions were respectively 35.0, 19.7, 34.2, and 4.9% of the theoretical current efficiency. Thus Na-ions proved to be the most effective, K-ions coming next, and NH_4 -ions being the least on persulphuric acid decomposition.

Furthermore, different solubilities of various persulphates have to be taken into consideration. It can be assumed that the region of the anolyte which is very close to the anode is exceedingly concentrated with respect to persulphuric acid, compared with the bulk of the solution; consequently its decomposition by cations is extraordinarily vigorous there. The solubilities of $\text{K}_2\text{S}_2\text{O}_8$ and $(\text{NH}_4)_2\text{S}_2\text{O}_8$ at 0°C. are 1.73 and 36.7 parts respectively in 100 parts of the saturated solution. This vast difference of solubilities of these two persulphates may be the probable cause, by which the decomposing effect of cations was more than compensated, and which gave rise to the greatest current efficiency in the case of potassium sulphate.

(9) *Monatsh.*, 50 (1928), 403.

The reason why the other sulphates did not have any marked effect (except a slightly negative one with Zn-salt) remains to be investigated. The effect of replacing half the amount of potassium in the K_2SO_4 solution with zinc and the corresponding case of $(NH_4)_2SO_4$ (Fig. 3) can be explained in the same way as above. In the case of the solution ($\frac{1}{2}N K_2SO_4$, $1\frac{1}{2}N ZnSO_4$, $5N H_2SO_4$) the influence of Zn-salt was more marked.

It is interesting to examine whether there was any catalytic effect of cations on persulphate decomposition in Experiment 1. The cations concerned therewith were H^+ in (0:10) and NH_4^+ and H^+ in the other five solutions. As mentioned above, $(NH_4)_2SO_4$ added to 20N sulphuric acid which had been electrolysed caused more persulphate to be decomposed than in the blank solution, hence, H^+ had, if any, less effect on persulphate decomposition than NH_4^+ . Therefore, these five solutions of Experiment 1 which contained ammonium sulphate were more affected, but not less certainly, by cations on the decomposition in question than 10N sulphuric acid. Nevertheless, the more concentrated the solutions were with regard to NH_4^+ , the greater were the current efficiencies.

Summary.

1. Sulphuric acid and ammonium sulphate solutions were electrolysed in order to see the influences of the current density and OH^- -concentration.

2. Influence of various cations, H^+ , K^+ , NH_4^+ , Na^+ , Li^+ , Mg^{++} , Zn^{++} , Fe^{+++} , Al^{+++} , Cu^{++} , and Cd^{++} , was studied and some were explained to have connexion with persulphate formation.

3. A new suggestion was made that OH^- plays an important rôle in persulphate formation, and this suggestion will clearly explain the results of the present investigation which may otherwise be obscure.

The author wishes to thank Dr. S. Glasstone, F.I.C., of the University of Sheffield for his deep interest in the present investigation.

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

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Mixtures showing minima in the viscosity versus concentration curves. Mixtures of alcohols with benzene have been treated by several investigators with recent views to the molecular complexity of liquids. Despite that the mixture of ethyl alcohol with benzene has an eutectic point on the freezing point curve, the molecular weight of the alcohol in benzene as determined by the freezing point method has been found abnormally high for concentrations above 0.278 mol. % alcohol according to Gibbons⁽¹⁾ or 0.383 mol. % alcohol according to Peterson and Rodebush.⁽²⁾ The mean molecular weight calculated from Gibbons's data if it is taken at the concentration range from 1.8 to 35.5 mol. % is 170 or 3.7 times the formal molecular weight. Such an anomalous phenomenon of association as observed in the case of the alcohol in benzene has been quite recently criticized by Müller and Mortier.⁽³⁾ The van Arkel association⁽⁴⁾ which signifies that the molecular polarization P of dipole substances dissolved in a solvent polar or non-polar is simply related to the concentration by van Arkel's formula

$$P = \frac{4\pi}{3} n \left(\alpha + \frac{\mu^2}{3kT + cn\mu^2} \right)$$

(α is the optical polarization, n the number of dipole per c.c., μ the dipole moment, k the Boltzmann constant, and c a constant) does not fit for the case in question. Substances with van Arkel's association scarcely indicate molecular complex cryoscopically and ebullioscopically as it is a well known fact that alcohols give normal molecular weights in dilute aqueous solutions. They point out that although propyl alcohol appears to obey the above rule at very low concentration, yet the constant c thereby gives about 60, whereas the normal value lies between 1.1 and 1.8, and conclude that even at extremely high dilution the reciprocal action of the alcohol molecules seems to

(1) W. A. Gibbons, *J. Phys. Chem.*, **21** (1917), 48.

(2) J. M. Peterson and W. H. Rodebush, *J. Phys. Chem.*, **32** (1928), 709.

(3) F. H. Müller and P. Mortier, *Physik. Z.*, **10** (1935), 371.

(4) A. E. v. Arkel and J. L. Snoek, *Trans. Faraday Soc.*, **30** (1934), 707.

become greater than the separating force of the solvent and such effect is attributed to the anomalous position of the dipole within the alcohol molecules.

Gundermann⁽⁵⁾ observes that the pairs of butyl alcohol-benzene and especially ethyl alcohol-benzene do not obey the theory of Debye which tells that the dielectric constant of liquids decreases as the square of the applied voltage. As to the former pair the decrease of dielectric constant with voltage is qualitatively understood from the Debye theory, but the latter pair behaves anomalously in such a manner that the effect indicates relatively high value at low concentration of the alcohol, but too low at high concentration, the pure alcohol, however, showing little effect against field intensity. He attributes this to the association of the alcohol molecules in benzene solution.

The anomalous behaviour of benzene towards alcohols has also been known in the measurement of infra-red absorption spectra. Freymann⁽⁶⁾ notices that in the mixtures of butyl alcohol and ethyl alcohol with benzene the characteristic frequency band of OH-group at 0.9631μ shifts intensively to 0.9778μ , and that the same band of alcohols also shifts to longer wave in the dilution of the alcohols with benzene, but that such phenomenon is scarcely observed with other solvents.

The viscosity of mixtures of benzene with alcohols, especially with ethyl and propyl alcohols studied by Dunstan⁽⁷⁾, indicates a distinct minimum against the composition in each system. No adequate reason has been given for binary liquid mixtures which exhibit minima in the viscosity versus concentration curves. If we take an analogy to the phenomena of some inorganic salts such as NH_4^- , K^- , Rb^- , and Cs^- halides in consideration,⁽⁸⁾ the viscosity minimum would be elucidated by the dissociation of alcohol molecules as Dunstan supposes, but such opinion is not only opposite to the recent view above cited, but also gives unsatisfactory results in actual calculation, since midway of the curves cannot be expressible by such method of calculation in which two solutional viscosities of both components must be postulated at the same time. Therefore, so far as the present knowledge of alcohols-benzene mixtures is concerned, we are reduced to assume that the anomalous change of association of alcohol molecules occurs in benzene solution, a change tends probably to greater association.

(5) H. Gundermann, *Ann. Physik.*, [5], **6** (1930), 545.

(6) R. Freymann, *Compt. rend.*, **193** (1932), 923.

(7) A. E. Dunstan, *J. Chem. Soc.*, **85** (1904), 817; **87** (1905), 11; *Z. physik. Chem.*, **49** (1904), 590.

(8) T. Ishikawa and T. Baba, *this Bulletin*, **10** (1935), 153.

In this series of papers⁽⁹⁾ the authors have developed the Ishikawa formula for the viscosity of binary mixtures standing on the fundamental hypothesis that the associations of both components are invariant throughout the concentration when no chemical change on their mixing. A reflection shall be given on this point.

If there happens some anomalous (increasing or decreasing) change of association in one component, say, component 2 in its greatest dilution with component 1 where the quantity of component 2 is quite enough to change its original association a_2 into a'_2 statistically, component 2 in the opposite case in quantity may also suffer change in association more or less, the degree of which, however, is not always the same in both the extremities, say, a_2 tends statistically to a'_2 in this case. If such is the case, the viscosity change with composition between these extremities may be expressible by the following formula :

$$\begin{aligned}\eta &= \frac{\eta_1 k_1 a_1 (1 - z_m)}{k_1 a_1 (1 - z_m) + k_2 a'_2 z_m} + \frac{\eta_2 k_2 a'_2 z_m}{k_1 a_1 (1 - z_m) + k_2 a'_2 z_m} \\ &= \frac{\eta_1}{1 + K' \frac{z_m}{1 - z_m}} + \frac{\eta_2}{1 + K'' \frac{1 - z_m}{z_m}}\end{aligned}$$

in which $K' = \frac{k_2 a'_2}{k_1 a_1}$ and $K'' = \frac{k_1 a_1}{k_2 a'_2}$.

It is easily understood by simple calculation that the necessary condition under which η as expressed by the above formula takes a minimum is $K'K'' > 1$.

Provided that the anomalous behaviour of benzene towards alcohols attributes wholly to the change of association of alcohols as defined above and to no further interactions between both the component molecules, viscosity curves between the two extremities must be completely expressible by this formula.

The viscosity data for these mixtures are adopted from the studies of Dunstan, Fischler, and Bhide and Watson.⁽¹⁰⁾ The calculated values are listed in the third column in each table from Tables 1 to 4, and how they are compared with observed values is clearly seen from Fig. 1, in which the curves are all traced by use of the calculated values, putting the viscosities of benzene at given temperatures as unity.

(9) T. Ishikawa, this Bulletin, **4** (1929), 5, 25, 149, 288; **5** (1930), 47, 117; **8** (1933), 280, 293; **9** (1934), 155; **10** (1935), 153, 248.

(10) A. E. Dunstan, *loc. cit.* J. Fischler, *Z. Elektrochem.*, **19** (1913), 126. B. W. Bhide and H. E. Watson, *J. Chem. Soc.*, **1927**, 2101.

For the system ethyl alcohol (2)-benzene (1) the K' (1.754) thus obtained is, as recent views demand, much greater than the normal K (0.466) as calculated on the assumption that no change of association occurs on mixing the two liquids, their ratio giving 3.76. This value is quite coincident with the value 3.7 as the abnormal value of the association of the alcohol already explained at the beginning of this paper.

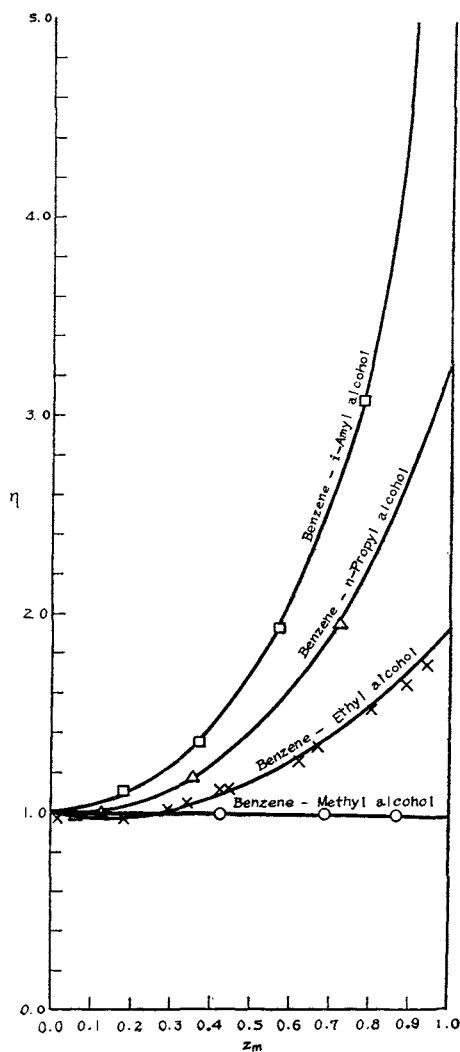


Fig. 1.

Table 1. Benzene—Methyl alcohol, 25°C. (Fischler).

z_m	η obs.	η calc.
0.0000	0.005758	—
0.4235	0.005723	0.005720
0.6879	0.005684	0.005681
0.8684	0.005645	0.005643
1.0000	0.005608	—

$$K' = 0.619, K'' = 1.603. K'K'' = 0.99.$$

Table 2. Benzene—Ethyl alcohol, 25°C. (Dunstan).

z_m	η obs.	η calc.
0.0000	0.005821	—
0.0192	0.005668	0.005778
0.1874	0.005669	0.005669
0.2927	0.005885	0.005840
0.3421	0.006071	0.005977
0.4267	0.006465	0.006287
0.4485	0.006514	0.006395
0.6235	0.007282	0.007398
0.6692	0.007758	0.007758
0.8067	0.008837	0.008956
0.8923	0.009545	0.009848
0.9475	0.01013	0.01048
1.0000	0.01113	—

$$K' = 1.754, K'' = 1.453. K'K'' = 2.55.$$

Table 3. Benzene-*n*-Propyl alcohol, 25°C. (Dunstan).

z_m	η obs.	η calc.
0.0000	0.005978	—
0.0631	0.005917	0.005934
0.1291	0.005989	0.005990
0.3554	0.007028	0.006952
0.7243	0.01167	0.01167
1.0000	0.01962	—

$$K' = 1.701, K'' = 2.246. K'K'' = 3.82.$$

Table 4. Benzene-*i*-Amyl alcohol, 30°C. (Bhide and Watson).

z_m	η obs.	η calc.
0.0000	0.00562	—
0.1813	0.00621	0.00607
0.3714	0.00760	0.00760
0.5707	0.0108	0.0108
0.7802	0.0173	0.0173
1.0000	0.0321	—

$$K' = 1.712, K'' = 3.355. K'K'' = 5.74.$$

For other systems the anomalies of the association of alcohols are not so great as that of ethyl alcohol, but their products $K'K''$'s still take greater values than unity, although K'' 's seem to approach to their normal K 's.

The anomalous change of molecular complexity of ethyl alcohol is also observed in viscosity determination with other solvents such as nitromethane, cyanobenzene, and allyl mustard oil.⁽¹¹⁾ With respect to these mixtures other physical properties to be needly explained are little known except that nitromethane has van Arkel's association.

Tables 5, 6, and 7 and Fig. 2 show the coincidence between the observed and calculated viscosities.

Table 5. Ethyl alcohol-Nitromethane (Wagner).

z_m	η obs.	η calc.
0.0000	1.0000	—
0.0579	0.9015	0.9043
0.1153	0.8210	0.8249
0.2290	0.7037	0.7042
0.4505	0.5704	0.5652
0.6518	0.5143	0.5143
0.8288	0.5003	0.5114
1.0000	0.5335	—

$$K' = 2.231, K'' = 1.268. K'K'' = 2.83.$$

Table 6. Ethyl alcohol-Cyanobenzene (Wagner).

z_m	η obs.	η calc.
0.0000	1.0000	—
0.0073	0.9958	0.9941
0.0147	0.9883	0.9880
0.0297	0.9784	0.9771
0.0607	0.9539	0.9560
0.1273	0.9210	0.9206
0.2703	0.8949	0.8823
0.3718	0.8785	0.8780
0.6346	0.9091	0.9264
1.0000	1.0768	—

$$K' = 2.000, K'' = 0.925. K'K'' = 1.85.$$

(11) J. Wagner, *Z. physik. Chem.*, **46** (1903). 867.

Table 7. Ethyl alcohol-Allyl mustard oil (Wagner).

z_m	η obs.	η calc.
0.0000	1.0000	—
0.0611	0.9237	0.9279
0.1275	0.8523	0.8551
0.2790	0.7331	0.7331
0.4810	0.6512	0.6349
0.6902	0.5995	0.5917
0.7769	0.5879	0.5879
1.0000	0.6100	—

$$K' = 1.823, K'' = 1.221. K'K'' = 2.23.$$

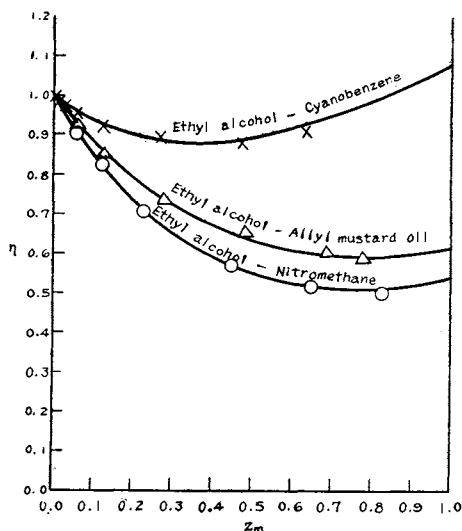


Fig. 2.

The mixture of acetic acid and benzene has been a subject in recent years for the same object of study as in alcohols-benzene mixtures. Bury and Jenkins⁽¹²⁾ observe with a cryoscopic method that the molecular form of acetic acid in benzene is completely dimeric at all concentrations greater than ca 3 mol. % acetic acid. Beckmann and Liesche⁽¹³⁾ obtain with an ebullioscopic determination that acetic acid in benzene is not completely dimeric, but partially suffers molecular dissociation to give 0.87 times the dimolecular weight for the mean value between 0.9 and 9.4 mol. % acetic acid. Dadiou and Kohlrausch⁽¹⁴⁾ study the Raman effect of this mixture and of mixtures of acetic acid in other solvents such as ether, alcohol, and water, and point out that the deepest frequency 440 of acetic acid is markedly weakened in benzene solution, and moreover that

Table 8. Benzene-Acetic acid, 25°C. (Dunstan).

z_m	η obs.	η calc.
0.0000	0.005978	—
0.0355	0.005941	0.005965
0.1295	0.005907	0.005942
0.2289	0.005962	0.005960
0.2769	0.005969	0.005988
0.5822	0.006658	0.006637
0.7081	0.007341	0.007344
0.8666	0.008932	0.009007
1.0000	0.01174	—

$$K' = 0.711, K'' = 3.108. K'K'' = 2.21.$$

(12) C. R. Bury and H. O. Jenkins, *J. Chem. Soc.*, **1934**, 688.(13) E. Beckmann and O. Liesche, *Z. physik. Chem.*, **92** (1917), 421.(14) A. Dadiou and K. W. F. Kohlrausch, *Physik. Z.*, **31** (1930), 514.

the powerful frequency 1432 is replaced by two weak frequencies, these phenomena being not observed in other solvents.

Dunstan⁽¹⁵⁾ who makes viscosity determinations on this mixture confirms a distinct minimum existing at 16.7 mol. % acetic acid at 25°C.

Opposite to alcohols-benzene mixtures, acetic acid in benzene suffers molecular dissociation, and the ratio of the anomalous K' (0.711) to the normal K (0.820) is 0.867, which is quite equivalent to the 0.87 calculated from Beckmann and Liesche's data above explained.

The variation of the product $K'K''$ with temperature. Substances which behave anomalous association in non-polar or polar liquids with van Arkel's association are, in most cases, hydroxylated, carboxylated, and some chlorinated compounds. Acetone-carbon bisulphide⁽¹⁶⁾ is an example of the second case, and ethylene dichloride-benzene and tetrachloroethane-benzene⁽¹⁷⁾ are good examples of the last case.

For one more example of hydroxylated compounds phenol-diphenyl-methylamine, and for chlorinated compounds ethylene dichloride-benzene will be considered below, since the measurements done by Bramley⁽¹⁸⁾ and by Faust⁽¹⁹⁾ respectively on these mixtures are convenient for the consideration

Table 9. Phenol—Diphenylmethylamine (Bramley).

z_m	$\eta_{19.8^\circ}$		$\eta_{20.1^\circ}$	
	obs.	calc.	obs.	calc.
0.0000	0.2010	—	0.1104	—
0.0580	0.1877	0.1884	0.1048	0.1050
0.1214	0.1752	0.1755	0.0995	0.0996
0.2011	0.1614	0.1618	0.0935	0.0937
0.2803	0.1502	0.1502	0.0885	0.0885
0.3536	0.1411	0.1410	0.0845	0.0844
0.4933	0.1306	0.1286	0.0798	0.0789
0.5728	0.1226	0.1216	0.0764	0.0758
0.7106	0.1145	0.1144	0.0730	0.0729
0.8307	0.1097	0.1109	0.0715	0.0718
0.9084	0.1090	0.1098	0.0708	0.0717
1.0000	0.1096	—	0.0722	—

$$K' = 1.648, K'' = 1.150.$$

$$K'K'' = 1.895.$$

$$K' = 1.440, K'' = 1.190.$$

$$K'K'' = 1.714.$$

(15) A. E. Dunstan, *J. Chem. Soc.*, **87** (1905), 11.

(16) O. Faust, *Z. physik. Chem.*, **79** (1912), 97.

(17) W. Herz and W. Rathmann, *Z. Elektrochem.*, **19** (1913), 589.

(18) A. Bramley, *J. Chem. Soc.*, **109** (1916), 10.

(19) O. Faust, *loc. cit.*

Table 9 (*Concluded*).

z_m	η_{30°		η_{40°		η_{60°		η_{80°	
	obs.	calc.	obs.	calc.	obs.	calc.	obs.	calc.
0.0000	0.0709	—	0.0474	—	0.0253	—	0.01585	—
0.0537	0.0673	0.0676	0.0451	0.0458	0.02495	0.0250	0.01586	0.01586
0.1000	0.0650	0.0653	0.0440	0.0444	0.0247	0.0247	0.01585	0.01587
0.1557	0.0626	0.0628	0.0428	0.0431	0.02445	0.0245	0.01589	0.01590
0.2384	0.0597	0.0597	0.0415	0.0415	0.02415	0.0242	0.01594	0.01594
0.3403	0.0570	0.0567	0.0402	0.0399	0.02395	0.0239	0.01603	0.01603
0.4843	0.0542	0.0539	0.0388	0.0385	0.02375	0.0236	0.01624	0.01619
0.6720	0.0519	0.0519	0.0377	0.0377	0.0237	0.0237	0.01650	0.01649
0.8187	0.0513	0.0513	0.0376	0.0377	0.0240	0.0240	0.01682	0.01683
0.9074	0.0510	0.0512	0.03785	0.0380	0.02435	0.0244	0.01708	0.01706
1.0000	0.0513	—	0.03835	—	0.02480	—	0.01735	—

$K'=1.791, K''=0.812. K'=1.557, K''=0.916. K'=1.081, K''=1.163. K'=0.908, K''=1.197.$
 $K'K''=1.455. K'K''=1.585. K'K''=1.257. K'K''=1.086.$

Table 10. Benzene—Ethylene dichloride (Faust).

z_m	η_{0°		$\eta_{19.4^\circ}$		η_{50°	
	obs.	calc.	obs.	calc.	obs.	calc.
0.0000	0.00850	—	0.00619	—	0.00418	—
0.1000	0.00843	0.00840	0.00615	0.00613	0.00422	0.00422
0.2000	0.00837	0.00837	0.00615	0.00615	0.00428	0.00423
0.3000	0.00835	0.00840	0.00620	0.00621	0.00435	0.00435
0.5000	0.00868	0.00868	0.00645	0.00645	0.00455	0.00455
0.7000	0.00933	0.00926	0.00690	0.00689	0.00492	0.00486
1.0000	0.01077	—	0.00800	—	0.00565	—

$K'=1.132, K''=1.295. K'=0.997, K''=1.370. K'=0.721, K''=1.664.$
 $K'K''=1.466. K'K''=1.366. K'K''=1.200.$

of the temperature variation of the product $K'K''$. Figs. 3 and 4 show the points of the observed values lying on the calculated curves.

As seen from the footnotes of Tables 9 and 10, the decrease of the product $K'K''$ with rising temperature is a strong indication that the anomalous molecular complexity decreases with rise of temperature. This tendency expects that at sufficiently high temperature where the anomaly disappears or where they are truly chemically indifferent with each other the product $K'K''$ tends to unity.

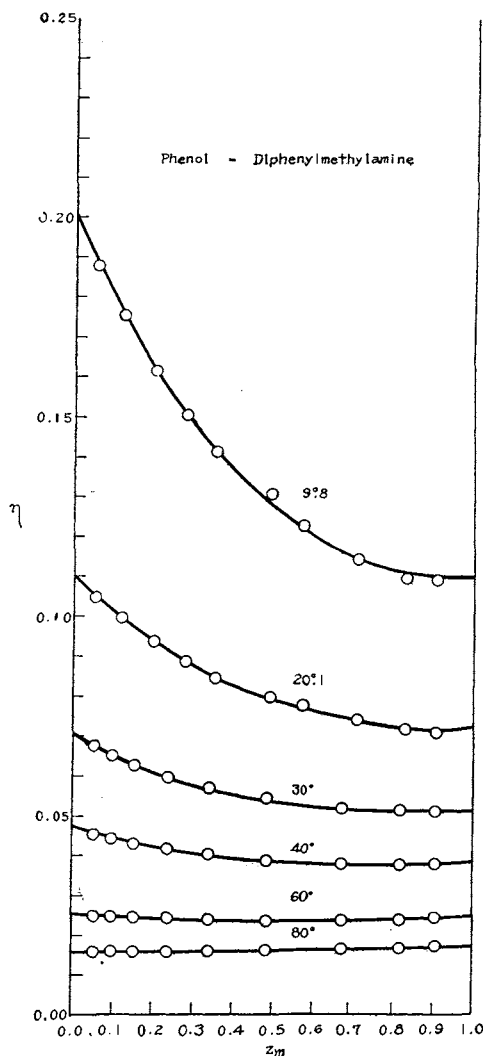


Fig. 3.

It is also noticed from these examples that the condition $K'K'' > 1$ under which anomaly of molecular complexity occurs is not always followed by a minimum in the viscosity versus concentration curves.

A further comparison of the product $K'K''$ in the formula newly proposed for liquid mixtures with the corresponding term in the Thiesen formula for gaseous mixtures. In Part II⁽²⁰⁾ we have made a little comparison of the Ishikawa formula with the Thiesen formula for gaseous mix-

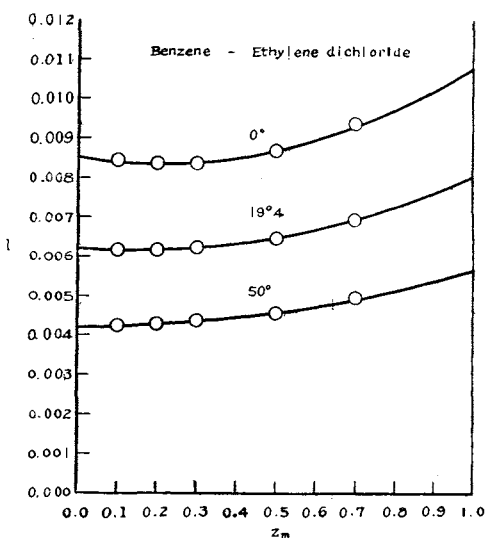


Fig. 4.

tures. The type of the Thiesen formula has been rigorously supported by the classical kinetic theory of gases,⁽²¹⁾ the general form of which runs:

(20) T. Ishikawa, this Bulletin, 4 (1929), 5.

(21) J. P. Kuenen, "Eigenschaften der Gase," Leipzig 1919. H. Schmick, *Physik. Z.*, 29 (1928), 633.

$$\eta = \frac{\eta_1}{1 + A_1 \frac{z_m}{1 - z_m}} + \frac{\eta_2}{1 + A_2 \frac{1 - z_m}{z_m}},$$

$$A_1 = \left(\frac{\sigma}{S_1} \right)^2 \frac{1 - \frac{m_1}{m_1 + m_2} \theta_1}{0.797} \sqrt{\frac{m_1 + m_2}{2m_2}} \frac{T + C_{12}}{T + C_1},$$

$$\theta_1 = \frac{m_1}{2(m_1 + m_2)} + \frac{1}{4} \frac{m_1^2}{m_1^{1/2}(m_1 + m_2)^{3/2}} \ln \frac{\sqrt{m_1 + m_2} + \sqrt{m_2}}{\sqrt{m_1 + m_2} - \sqrt{m_2}}.$$

A_2 , θ_2 take the similar forms as A_1 and θ_1 respectively, in which m_1 , m_2 are the molecular weights of components 1 and 2; S_1 , S_2 the molecular diameters of components 1 and 2; $\sigma = \frac{1}{2}(S_1 + S_2)$; C_1 , C_2 the Sutherland constants of components 1 and 2; C_{12} the corresponding constant due to the attraction between a molecule of kind 1 and a molecule of kind 2; and T the absolute temperature.

Judging from the form of the formula newly proposed, one may imagine that no apparent difference is observed between these two formulae. It is of great interest, however, to note here that for gaseous mixtures whether or not the viscosity indicates a maximum the product $A_1 A_2$, the corresponding term to the product $K'K''$ in our case, is always less than or equal to unity (see Table 11), whilst for liquid mixtures $K'K''$ is always greater than or equal to unity.

Table 11.

Mixtures showing a maximum.		
Mixture	$A_1 A_2$	Observers
H ₂ - CH ₄	0.624	Azumi, Graham, Trautz and Sorg.
H ₂ - C ₂ H ₆	0.528	Azumi.
H ₂ - C ₃ H ₈	0.517	Thomsen, Trautz and Stauf.
H ₂ - C ₃ H ₆	0.508	Azumi.
H ₂ - C ₃ H ₄	0.462	Azumi.
H ₂ - NH ₃	0.597	Thomsen, Trautz and Heberling.
H ₂ - CO ₂	0.404	Graham, Puluj, Thomsen, Breitenbach, Trautz and Kurz.
H ₂ - SO ₂	0.339	Trautz and Weizel.
H ₂ - NO	0.467	Graham.
H ₂ - N ₂ O	0.401	Graham, Trautz and Kurz.
H ₂ - HCl	0.430	Trautz and Narath.
H ₂ - Cl ₂	0.341	Thomsen.
He - Ar	0.575	Tänzler, Trautz and Kipphan, Trautz and Binkele.
He - Kr	0.454	Nasini and Rossi.
CH ₄ - NH ₃	0.977	Jung and Schmick.
NH ₃ - C ₂ H ₄	0.997	Thomsen, Trautz and Heberling.

Table 11 (*Concluded*).

Mixtures showing no maximum.		
Mixture	$A_1 A_2$	Observers
H ₂ - CO	0.491	Graham, Trautz and Baumann.
H ₂ - O ₂	0.457	Kleint, Graham, Trautz and Melster.
H ₂ - N ₂	0.496	Graham, Kleint, Trautz and Baumann.
H ₂ - Air	0.485	Graham.
H ₂ - He	0.806	Gille, Trautz and Kipphan, Trautz and Baumann.
H ₂ - Ar	0.411	Trautz and Ludewigs, Trautz and Binkele.
H ₂ - Ne	0.547	Trautz and Binkele.
He - Ne	0.739	Trautz and Kipphan.
Ne - Ar	0.968	Trautz and Kipphan, Trautz and Binkele.
NH ₃ - N ₂	0.940	Thomsen, Trautz and Heberling.
NH ₃ - O ₂	0.901	Thomsen, Trautz and Heberling.
NH ₃ - Air	0.973	Jung and Schmick.
NH ₃ - CO ₂	0.901	Thomsen.
NH ₃ - Cl ₂	0.704	Thomsen.
Air - CO ₂	0.985	Jung and Schmick.
Air - HCl	0.966	Jung and Schmick.
Air - H ₂ S	0.978	Jung and Schmick.
CO - N ₂	1.00	Trautz and Melster.
CO ₂ - N ₂ O	1.00	Trautz and Kurz.
CO ₂ - SO ₂	0.989	Jung and Schmick.
O ₂ - CO ₂	0.996	Graham.
CO - O ₂	1.00	Graham, Trautz and Melster.
N ₂ - O ₂	0.973	Graham, Kleint, Trautz and Melster.
CH ₄ - O ₂	0.923	Graham.
CH ₄ - C ₂ H ₂	0.983	Azumi.
CH ₄ - C ₂ H ₆	0.967	Trautz and Sorg.
CH ₄ - C ₃ H ₈	0.898	Trautz and Sorg.
C ₂ H ₂ - C ₃ H ₆	0.985	Azumi.
N ₂ - C ₂ H ₄	1.01	Trautz and Melster.
CO - C ₂ H ₄	1.01	Trautz and Melster.
C ₂ H ₄ - O ₂	1.06	Trautz and Melster.
C ₂ H ₄ - Air	1.00	Breitenbach.
C ₂ H ₆ - C ₃ H ₈	1.01	Trautz and Sorg.
C ₃ H ₆ - C ₃ H ₈	0.982	Azumi.
C ₃ H ₈ - N ₂ O	1.05	Trautz and Kurz.
C ₃ H ₈ - CO ₂	1.04	Trautz and Kurz.

Although the formula for gaseous mixtures stands on a sound theoretical basis, a closer investigation⁽²²⁾ informs us that in the case where a maximum occurs the calculated viscosities are not quite coincident with the observed viscosities, giving some more or less functional divergence. On the other hand, our formula affords no such divergencies as clearly recognized from the figures above given.

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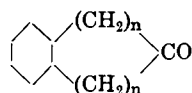
(22) H. Azumi, *Bull. Inst. Phys. Chem. Research*, **11** (1932), 1103.

ON THE FORMATION OF SYMMETRICAL DIBENZO-CYCLO-DOCOSANE-DIONE.

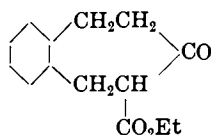
By Mioji UENAKA and Bennosuke KUBOTA.

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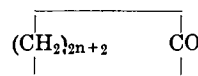
Researches designed to synthesize isocyclic ketones with a benzene ring condensed at the ortho-position have engaged our attention since the researches of Ruzicka and his collaborators⁽¹⁾ in the preparation of many-membered alicyclic ketones. In a previous paper⁽²⁾ one of the authors described a method of synthesizing a seven-membered cyclic ketone, *o*-benzo^{4:5}-cycloheptanone-(1) [benzene-(pentanone-3-ylene)_{1,2}] (I, $n = 2$), which is the parent ketone of ethyl 3-ketophen-heptamethylene-2-carboxylate (II) identified by Titley⁽³⁾ only as its phenylhydrazone.



I

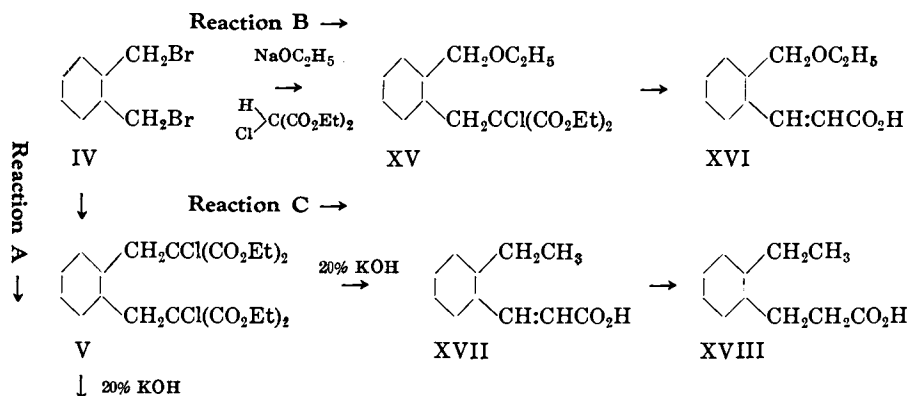


II



III

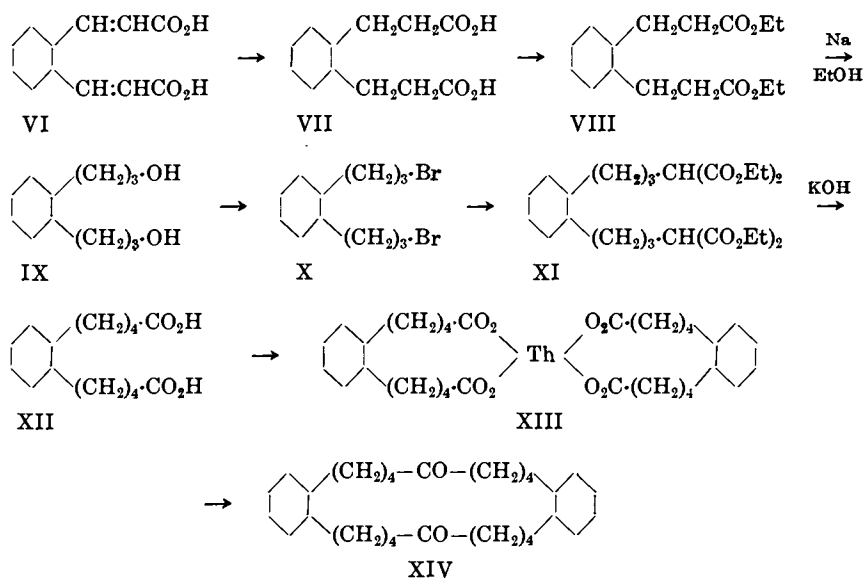
Following the compound with $n = 2$ in I we have further proceeded to the preparation of a series of ketones of this type intending to compare their properties with those of the alicyclic ketone III already known, and we have attempted to synthesize a compound with $n = 4$ in I. The course of reactions, however, resulted in the formation of a diketone XIV, symmetrical dibenzo-cyclo-docosane-dione, as shown below :



(1) Ruzicka, *Helv. Chim. Acta*, **9** (1926), 230.

(2) This Bulletin, **6** (1931), 103.

(3) Titley, *J. Chem. Soc.*, **1928**, 2571.



Starting from *o*-xylylene dibromide, *o*-phenylene-diacrylic acid was prepared by the method described by Perkin; but the reaction of *o*-xylylene dibromide with chloro-sodio-malonic ester was not so simple as we expected. When monochloro-malonic ester having a boiling point of 221–225° (corr.) was used (undoubtedly containing some dichloro-ester), the reaction, instead of taking course A, went through B and D (see experimental part), and thus resulted in the formation of *o*-(ethoxymethyl)-cinnamic acid (XVI) and phthalic alcohol diethyl-ether (XIX). This difficulty was partially overcome by preparing a monochloro-malonic ester having a boiling point 221–222°, by slightly modifying the usual method⁽⁴⁾.

o-Phenylene-diacrylic acid (VI) was reduced to *o*-phenylene-dipropionic acid (VII) with 2% sodium amalgam. A small amount of β -(*o*-ethylphenyl)-propionic acid (XVIII) was formed along with acid VII, when a crude acid of VI was reduced. The presence of XVIII indicates that reaction C partly took place during the hydrolysis of *o*-xylylene-dichloro-malonic ester (V) with concentrated alcoholic potash (although we have not isolated acid XVII). The scission of three molecules of carbon dioxide from *o*-xylylene-dimalonic ester (H substituted for Cl in V) by the action of concentrated alcoholic potash has already been reported by H.T. Lo⁽⁵⁾, and the present case shows that a similar reaction also occurs to some extent in the decomposition of the dichloro-derivative of *o*-xylylene-dimalonic ester mentioned above.

(4) Conrad, Bischoff and Guthzeit, *Ann.*, **209** (1881), 218.

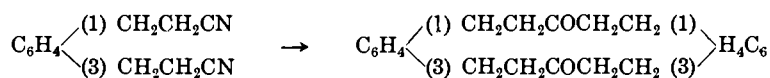
(5) H. T. Lo, this Bulletin, **5** (1930), 326.

o-Phenylene-dipropionic acid diethyl ester (VIII) was reduced with sodium and alcohol to *o*-phenylene-dipropyl alcohol (IX) having a melting point 56–57°. This gave a liquid bromide (X) when treated with dry hydrogen bromide.

The condensation of malonic ester and *o*-phenylene-dipropyl bromide (X) took place readily (formation of XI), and a syrupy tetracarboxylic acid was obtained by the saponification of the ester XI; this on being heated up to 160° evolved carbon dioxide and yielded *o*-phenylene-divaleric acid (XII). The thorium salt of this acid was submitted to high vacuum dry distillation. When the distillation pressure was lower than 0.01 mm. the oily distillate partly crystallized into flat needles, which on recrystallisation gave a sharp melting point of 133.5° (corr.). The analytical results of this compound agreed with $n = 4$ in I, but the molecular weight determination by Rast's method (in camphor) gave a double molecular weight which corresponds to XIV: a dibenzo-cyclo-docosane-dione. The remaining part of the the distillate was redistilled and fractionated. Although the lower fraction (110–195° / 0.004 mm.) was found to yield a minute quantity of XIV after a few months, no other definite compound could be obtained by treating the liquid fractions with semicarbazide, *p*-nitrophenylhydrazine, etc.

According to the results of Ruzicka⁽⁶⁾, and Ziegler⁽⁷⁾ in preparing alicyclic ketones, an eleven-membered ring proved to be one of the most difficultly formed ketones, while a twenty-two-membered cyclic diketone was obtained with better result. In our case we could obtain only a twenty-two-membered cyclic diketone in a yield of about 0.2%, but could not isolate the monoketone (I, $n = 4$). This shows that the difficulty of the formation of an eleven-membered ring is emphasized in the case of alicyclic compounds, with a condensed aromatic ring.

A similar reaction occurring in the meta-position of benzene, first observed by Titley⁽⁸⁾, was later confirmed by Ziegler⁽⁹⁾ in the case of *m*-phenylene-dipropionitrile.



In this reaction the dinitrile, undergoing cyclisation, merely formed a diketone and practically no monoketone. The formation of such cyclic diketones as XIV in the cyclisation of *o*-C₆H₄[(CH₂)_nCOOH]₂ series must further be investigated.

(6) L. Ruzicka, *Helv. Chim. Acta*, **11** (1928), 672.

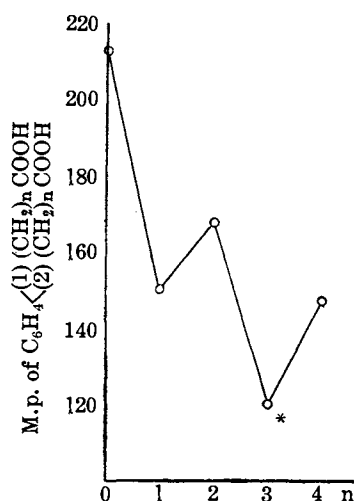
(7) K. Ziegler, *Ann.*, **513** (1934), 43.

(8) A. F. Titley, *J. Chem. Soc.*, **1928**, 2575.

(9) K. Ziegler, *Ann.*, **511** (1934), 6.

In regard to the odour of the diketone XIV, while the odour of the oily distillate reminds us of cedar oil, owing, perhaps, to the presence of a minute trace of the monoketone (I, $n = 4$), the diketone is odourless, as is the case with the alicyclic twenty-two-membered diketone obtained by Ruzicka⁽⁹⁾.

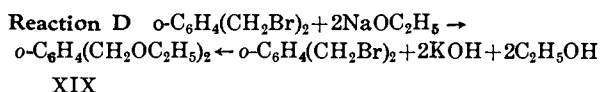
Although, up to the present, we have not obtained sufficient data concerning the dicarboxylic acid series $o\text{-C}_6\text{H}_4[(\text{CH}_2)_n\text{COOH}]_2$, there seems to exist a similar melting point rule as in the case of the aliphatic series $\text{HOOC}(\text{CH}_2)_n\text{COOH}$, the melting point of an acid having an even number n being higher than that of the acid $n-1$, as can be seen in the following diagram.



Experimental.

I. Preparation of *o*-Phenylene-diacrylic Acid (VI).

This acid was obtained by the procedure described by Perkin. For this reaction it was found necessary to use monochloro-malonic ester of good quality; otherwise *o*-xylylene dibromide remained unattacked, or was partly acted upon by the sodium derivative of monochloro-malonic ester, and also giving rise to the following reaction:



The product consisted mainly of phthalic alcohol diethylether (XIX) and partly of acid XIII (described below) formed through reaction B. Therefore, in order to avoid the formation of these by-products the usual method of preparing monochloromalonic ester had to be modified.

(i) *Monochloro-malonic ester*. Dry chlorine was passed into malonic ester for a short time; the yellow solution was gently heated up to 55°, when a sudden reaction took place and hydrogen chloride was evolved. The vessel was then cooled in running water and the addition of chlorine continued until the liquid became yellow. The temperature of the ester was kept at about 30° throughout the reaction. The main part of the product boiling at 221-222° (corr.) was redistilled under reduced pressure (b.p. 116-117°/16 mm.).

(ii) *o*-Xylylene dibromide (IV). The presence of moisture during the bromination of *o*-xylene resulted in a considerably decreased yield of the dibromide. The crude dibromide was washed with chloroform and dried on a porous plate, m.p. 89°. This was used for the preparation of *o*-phenylene-diacrylic acid.

From the reagents described above, a maximum yield of 80% of *o*-phenylene-diacrylic acid was obtained. The crude acid was washed with alcohol, and then with benzene.

(iii) *o*-(Ethoxymethyl)-cinnamic acid (XVI). This acid was found to be formed by reaction B when monochloro-malonic ester having a higher boiling point (221-225°) was

* Observed by E. Takai. M.p. 119-120° (corr.)

used. This indicates that the presence of dichloro-malonic ester (b.p. 234°) favours reaction B. The crude product of XVI was separated from *o*-phenylene-diacrylic acid by treating the mixture with benzene (*o*-phenylene-diacrylic acid is practically insoluble in benzene). The acid XVI was then recrystallized from a mixture of acetone and water, m.p. 130-130.5° (corr.). (Found: C, 69.79; H, 7.15; mol. wt., 203 (camphor), 205 (titration). Calc. for $C_{12}H_{14}O_3$: C, 69.87; H, 6.85%; mol. wt., 206.) The presence of the ethoxyl group in the acid was proved qualitatively by the usual Zeisel method. The presence of a double bond in the side chain was confirmed by the addition of bromine (see v) and hydrogen (see vi).

(iv) *Ethyl o-(ethoxymethyl)-cinnamate*. B.p. 140-141°/2 mm. (uncorr.); n_D^{22} 1.5460. (Found: C, 71.54; H, 7.93. Calc. for $C_{14}H_{18}O_3$: C, 71.75; H, 7.75%.)

(v) β -(*o*-Ethoxymethyl)- α,β -dibromopropionic acid, C_6H_4 $\begin{cases} (1) CH_2OC_2H_5 \\ (2) CHBrCHBrCOOH \end{cases}$. Acid XVI (0.2 g.) was dissolved in 10 c.c. carbon tetrachloride and 0.17 g. bromine in 5 c.c. carbon tetrachloride was added; the solution was gently heated on the water bath for a minute, when absorption of bromine took place. The solution was then left at room temperature for an hour, then washed with sodium bisulphite solution and water, and dried over sodium sulphate. After evaporating the solvent, the residue was dissolved in benzene and recrystallized by adding some petroleum ether. Colourless crystals resembling dandelion leaves separated; when heated in a capillary tube it darkened at 155° and melted into a black liquid at 168-169° (corr.). (Found: Br, 42.4. Calc. for $C_{12}H_{14}O_3Br_2$: 43.7%.)

(vi) *o-(Ethoxymethyl)-hydrocinnamic acid*. This acid was prepared by reducing acid XVI with 2% sodium amalgam. It was recrystallized from petroleum ether in colourless needles melting at 85°, and found to be soluble in water and in benzene. (Found: C, 69.38; H, 7.85. Calc. for $C_{12}H_{16}O_3$: C, 69.19; H, 7.75%.)

II. *o*-Phenylene-dipropionic Acid (VII). *o*-Phenylene-diacrylic acid (1 mol) was readily reduced by 2% sodium amalgam (6 atoms Na), and *o*-phenylene-dipropionic acid was obtained in a yield of 80-90%. When dried at 100°, a leafy sublimate was found to separate from the crude product. The sublimate, recrystallized from water, melted at 102.5°. No depression of the melting point was observed on mixing it with β -(*o*-ethylphenyl)-propionic acid prepared from *o*-xylylene-dimalonic ester⁽¹⁰⁾. This indicates that reaction C also occurs when the ester V is saponified with a 20-25% alcoholic potash.

Ethyl *o*-phenylene-dipropionate (VIII) was prepared by refluxing one part of acid with three to five parts of a 5% alcoholic solution of hydrogen chloride for three hours. The product was washed with dilute soda solution and water successively, and dried over calcium chloride; b.p. 192-193°/8 mm. (corr.) (b.p. given by Titley⁽¹¹⁾ 200-202°/12 mm.); n_D^{22} 1.4962; d_4^{22} 1.0763; MR_D obs. 75.52 (calc. 75.56).

III. *o*-Phenylene-dipropyl Alcohol (IX). Ethyl *o*-phenylene-dipropionate was reduced to this alcohol by Bouveault Blanc's method: one part of ester VIII was dissolved in seven parts of absolute alcohol and the solution was added to a flask containing one part of metallic sodium in the course of about fifteen minutes. The flask was then

(10) *Loc. cit.*, (5).

(11) Titley, *J. Chem. Soc.*, 1928, 2578.

heated in an oil bath (120°) until the sodium was completely dissolved (A further addition of absolute alcohol was sometimes required for the complete dissolution of sodium). The solution was then slightly cooled and two parts of water added to saponify the ester which had not been reduced. It was then heated on the water bath for two hours. Ethyl alcohol was removed from the solution by steam distillation, and the residue was cooled, extracted four times with ether, washed with water, and dried over potassium carbonate. The solvent was removed and the syrupy residue was cooled to 0°. Crystallization of alcohol IX was induced by scratching the inner wall of the vessel with a glass rod, but as the alcohol crystallized with some difficulty, crystallization was effected in later runs by inoculating with the crystalline alcohol previously obtained. The product was drained on a porous plate. The yield of the crude product amounted to 30-40% of the theoretical. Increase in the yield of alcohol IX could not be attained by increasing the quantity of sodium. A considerable excess of sodium gives a rather poor yield as may be seen in the following table.

Na (atoms)/1 mol Ester VIII	8(theoret.)	12.1	12.4	16.9	18.0	23.9
Yield of Alcohol IX (%)	—	40	45	31	25	16

The alcohol was recrystallized from carbon tetrachloride. Lustrous scales, m.p. 56-57°. It is very soluble in alcohol, moderately soluble in carbon tetrachloride and difficultly soluble in ligroin. (Found: C, 73.97; H, 7.85; mol. wt., 184 (in camphor). Calc. for $C_{12}H_{18}O_2$: C, 74.17; H, 7.75%; mol. wt., 194.)

p-Xenyl-carbamate of *o*-phenylene-dipropyl alcohol⁽¹²⁾, $C_6H_4[(CH_2)_3OCONHC_6H_4C_6H_5]_2$. M.p. 187°. (Found: N, 4.94. Calc. for $C_{28}H_{36}N_2O_4$: N, 4.79%.)

The ester VIII which had not been reduced, was recovered from the alkaline mother liquor as the free acid (VII) and was used in a subsequent run.

IV. *o*-Phenylene-dipropyl Bromide (X). Thirty grams of *o*-phenylene-dipropyl alcohol (IX) was heated to 130-140° in a glycerine bath and dry hydrogen bromide passed into it for five hours (three times the calculated quantity of hydrogen bromide was required). The heavy oil product was washed with dilute soda solution and then with water, dried over potassium carbonate, and distilled under reduced pressure. Yield, 35 g. B.p. 187-189°/7.5 mm. (corr.); n_D^{25} 1.5670; d_4^{25} 1.4824. (Found: Br, 50.1; MR_D , 70.13. Calc. for $C_{12}H_{16}Br_2$: Br, 50.0%; MR_D , 70.52)

V. *o*-Phenylene-divaleric Acid (XII). A sodium ethylate solution, prepared by dissolving 4.9 g. of metallic sodium in 60 g. of absolute alcohol, was slowly added to 68 g. of malonic ester. *o*-Phenylene-dipropyl bromide (X) (33.5 g.) dissolved in 100 c.c. dry ether was slowly added to the sodio-malonic ester solution. Precipitation of sodium bromide took place immediately after the addition of the bromide. After heating the mixture over a 50-watt carbon lamp for three hours, the excess of malonic ester was removed by distilling it under reduced pressure, and the residue was saponified by heating with 20% alcoholic potash (45 g. potassium hydroxide) on the water bath for six hours. The alcohol

(12) The authors wish to thank Mr. T. Akita for preparing and identifying this compound.

was then driven off and the residue was dissolved in some water and the oily matter insoluble in the alkaline solution was removed by shaking with ether. *o*-Phenylene-dipropyl malonic acid separated as a syrupy mass on neutralizing the solution with dilute hydrochloric acid. The viscous acid was dissolved in ether and dried over anhydrous sodium sulphate; after removal of the ether, the syrupy residue was heated to 120-160°, when it decomposed into *o*-phenylene-divaleric acid (XII) and carbon dioxide. A part of the crude product was purified by dissolving it in a dilute sodium carbonate solution and heating on the water bath for an hour with the addition of animal charcoal. The acid thus obtained was recrystallized from a mixture of acetone and water. Colourless crystals, m.p. 148-149° (corr.). The yield was 90% of the theoretical. (Found: C, 68.98; H, 8.34; mol. wt., 285 (in camphor), 280 (titration, as dibasic acid). Calc. for $C_{16}H_{22}O_4$: C, 69.02; H, 7.97%; mol. wt., 278.) It is soluble in acetic acid, alcohol, chloroform, and acetic ester, difficultly soluble in cold water, and insoluble in petroleum ether.

VI. **The Symmetrical Dibenzo-cyclo-docosane-dione (XIV).** Twenty grams of *o*-phenylene-divaleric acid was dissolved in 1 l. of water by neutralizing it with sodium carbonate. Fourteen grams of thorium chloride, dissolved in 400 c.c. of water, was slowly added to the former solution with constant mechanical stirring. The yield of the thorium salt was 29.4 g. This was divided into two portions and each portion placed in a 30 c.c. distilling flask provided with a large side tube. The salt was subjected to high vacuum dry distillation by heating the flask in salt bath ($LiNO_3$ - $NaNO_3$ - KNO_3) of 160° and then gradually raising the temperature to about 400° in the course of eight to ten hours, the pressure meanwhile being 0.008-0.009 mm. A light yellow, viscous substance distilled over from 190° (bath temperature), a part of it solidifying into long needles after four to six hours from the beginning of distillation. The total yield of the distillate was 2.4 g. This was placed in an ice box for a few days, and the crystals were then separated. The solid product is soluble in ordinary organic solvents. It was recrystallized from ligroin with great ease. Yield, 25 m.g., m.p. 133.5° (corr.). In a third run, when 6.7 g. of the salt was used, the yield of the solid product was 4.5 mg. In this case the distillation was carried out under a comparatively high pressure, i.e., 0.01-0.1 mm., and the product was found to give small oblong plates only after a few weeks' cooling in an ice box. These crystals, when recrystallized from ligroin by inoculating with the flat needles previously obtained, were changed into needle-like crystals identical with those obtained in the first distillation. (Found: C, 83.18; H, 9.43; mol. wt., 430, 439 (in camphor). Calc. for $C_{30}H_{40}O_2$: C, 83.27; H, 9.39%; mol. wt. 432.)

The semicarbazone was prepared in the usual way by adding semicarbazide acetate to the ketone (XIV) and adding alcohol until solution was complete. The reaction mixture was allowed to stand overnight at room temperature when a flocculent mass separated. The alcoholic solution was diluted with water and the flocculent precipitate was collected. As the product was difficultly soluble in absolute alcohol and practically insoluble in other solvents, it was successively washed with hot water, alcohol, ligroin, and dried in vacuum. Decomp. pt. 205-208° (corr.) (turns red). (Found: N, 14.8, 13.6. Calc. for $C_{32}H_{46}O_2N_6$: N, 15.4%). Yellow microscopic needles, probably the *p*-nitrophenylhydrazone were obtained by treating XIV with *p*-nitrophenylhydrazine; m.p. 168-172°. The substance was so scarce that analysis was impossible.

The remaining liquid part of the distillate was treated with semicarbazide, *p*-nitrophenylhydrazine, etc., but no definite product could be obtained. It was therefore redistilled and the two following fractions were collected: (1) 110-195/0.004 mm., (2)

195–250/0.004 mm. On standing for five months, 0.8 mg. of ketone XIV was found to have crystallized from fraction (1); no change was observed in fraction (2). Both fractions were treated with semicarbazide etc., but no derivative could be obtained. The analytical results of the fractions were: (1) C, 86.22; H, 9.51; (2) C, 87.07; H, 9.47%.

Summary.

The synthesis of an eleven-membered carbon ring attached to the ortho-position of benzene was attempted. The dry distillation of the thorium salt of *o*-phenylene-divaleric acid resulted in the formation of a twenty-two-membered diketone ring. Several new compounds incidental to the synthesis are reported.

In concluding, the authors wish to thank Mr. S. Tsutsumi and Mr. H. Yamura for the valuable assistance given us.

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DECENOIC ACID $C_{10}H_{18}O_2$ IN SPERM HEAD OIL.*

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Whilst in preceding papers⁽¹⁾ the separation of denticetic acid ($\Delta^{5:6}$ -dodecenoic acid) from sperm blubber and head oils was described, the present paper deals with the separation of a decenoic acid—a lower homologue of denticetic acid—from sperm head oil. The only one decenoic acid in natural fats recorded in the literature is $\Delta^{9:10}$ -decenoic acid discovered by Grün and Wirth⁽²⁾ as an extremely minor constituent of butter fat; the presence of decenoic acid in sperm head oil has so far never been known before the present experiment.

In a previous experiment⁽³⁾ of the separation of hexadecenol and tetradecenol in the unsaponifiable matter of sperm head oil, the liquid oil obtained by removing the crystalline solid was first subjected to the methanolysis, and

* Translated from the Japanese text published in *J. Chem. Soc. Japan*, **56** (1935), 1313.

(1) This Bulletin, **10** (1935), 563, 570.

(2) *Ber.*, **55** (1922), 2197.

(3) This Bulletin, **10** (1935), 573.

the resulting mixture of methyl esters and free unsaponifiable matter was fractionated, by which a fraction boiling below $180^\circ/15$ mm. was separately collected. This fraction was saponified, and the fatty acids and the unsaponifiable matter were separated in the usual way.

Whilst the unsaponifiable matter was worked up further in the previous experiment, the fatty acids obtained above were used in the present experiment. They were fractionated, and a fatty acid fraction boiling below $160^\circ/15$ mm. was separated. For the separation of unsaturated acids, this fraction was treated by the bromo-ester distillation method of Grün and Janko.⁽⁴⁾ In this method the fatty acid fraction was converted into the methyl esters, and then brominated in ethereal solution. The product was distilled under reduced pressure, by which the saturated methyl esters were removed as distillate. The residue containing the bromides derived from the unsaturated methyl esters was debrominated, and the product was saponified to regenerate the unsaturated acids, which were then fractionated to yield decenoic acid.

The decenoic acid thus obtained was converted into the methyl ester, and the latter was oxidised with potassium permanganate in acetone. After the oxidation products were saponified to liberate the free acid from the acid ester, azelaic acid $HOOC \cdot (CH_2)_7 \cdot COOH$ was identified, and formic acid $H \cdot COOH$ was also detected. Accordingly the constitution of decenoic acid is to be represented by the formula $CH_2=CH \cdot (CH_2)_7 \cdot COOH$. It is thus seen that decenoic acid in sperm head oil is identical with $\Delta^{9:10}$ -decenoic acid which was found by Grün and Wirth in butter fat.⁽⁵⁾

Experimental.

1. **Separation of Decenoic Acid.** In a previous experiment⁽³⁾ of the separation of hexadecenol and tetradecenol, the sperm head oil having saponification value 147.7, iodine value (Wijs) 53.4 and unsaponifiable matter 36.52% was first pressed to remove the solid portion, and the liquid portion obtained in a yield of about 80% was subjected to the methanolysis. The product (10 kg.) consisting of the methyl esters and the free unsaponifiable matter was fractionated, and a fraction boiling below $180^\circ/15$ mm. was separately collected. This fraction was saponified, the resulting soap solution was extracted with

(4) *Z. Deuts. Oel-u. Fett-Ind.*, **41** (1921), 553, 572.

(5) Grün stated that he and his co-workers found dodecenoic ($\Delta^{11:12}$?) and tetradecenoic ($\Delta^{13:14}$?) acids besides $\Delta^{9:10}$ -decenoic acid in butter fat (*Z. angew. Chem.*, **37** (1924), 228). It should be noted that whilst decenoic acid in sperm head oil is found to be identical with that in butter fat, dodecenoic and tetradecenoic acids in sperm head oil were confirmed to be $\Delta^{5:6}$ -dodecenoic (denticetic) and $\Delta^{5:6}$ -tetradecenoic (physeteric) acids, respectively; neither $\Delta^{11:12}$ -dodecenoic nor $\Delta^{13:14}$ -tetradecenoic acid was found in sperm head oil.

ether, and the fatty acids and the unsaponifiable matter were separated in the usual way. Whilst the unsaponifiable matter was used for the isolation of hexadecenol and tetradecenol, the fatty acids were used for the present experiment. These were fractionated, and there was obtained 282 g. of a fraction boiling below $180^{\circ}/15$ mm. and having neutralisation value 301.9 and iodine value 26.2. This fatty acid fraction was refractionated, giving 61 g. of a fraction which distilled below $160^{\circ}/15$ mm. and had neutralisation value 338.2 and iodine value 18.3. This was converted into methyl esters, and the latter were brominated in ethereal solution under cooling with ice. After the ethereal solution had been freed from the excess of bromine by washing with sodium thiosulphate solution, it was washed with water and then dehydrated over anhydrous sodium sulphate. On distilling off the solvent from the ethereal solution, the product of bromination was distilled under 5 mm. When the distillation was continued up to $120^{\circ}/5$ mm., the rate of the distillation of saturated esters became very slow, and the operation was stopped. The residue containing the bromides derived from unsaturated esters was debrominated with zinc powder and sulphuric acid in methanol solution, and the product was saponified, yielding 9 g. of unsaturated acids. These were subjected to a further fractionation, by which the distillation began at $141^{\circ}/15$ mm., and 1.5 g. of a fraction boiling at 143 – $148^{\circ}/15$ mm. was separately collected as decenoic acid $C_{10}H_{18}O_2$ (Found: C, 70.47; H, 10.70. Calc. for $C_{10}H_{18}O_2$: C, 70.53; H, 10.66%). It had the following constants: d_4^{15} 0.9238, d_4^{20} 0.9203, n_D^{15} 1.4507, n_D^{20} 1.4488, molecular refraction (based on the data at 15°) 49.56 (calc. for $C_{10}H_{18}O_2$ F_1 : 49.45), neutralisation value 328.3 (calc. 329.7), iodine value 134.0 (calc. 149.2).

Hydrogenation of the decenoic acid yielded capric acid $C_{10}H_{20}O_2$ which, after being recrystallised from 70% alcohol, showed neutralisation value 325.1 (calc. 325.9), m.p. 30 – 30.5° and mixed m.p. 30.5 – 31° .⁽⁶⁾ Unlike other mono-ethylenic acids, the decenoic acid yielded no crystalline dihydroxy derivative by oxidation with a dilute alkaline solution of potassium permanganate.

2. **Oxidation of Methyl Decenoate.** The decenoic acid obtained above was converted into the methyl ester by means of hydrogen chloride in methanol solution. The methyl ester (1.0 g.) was dissolved in 10 c.c. of acetone, and 4 g. of finely powdered potassium permanganate was added in small portions. After heating for 4 hours on the water-bath under reflux condenser the acetone was removed by distillation, and 30 c.c. of water was added to the residue. 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 with 300 c.c. of ether, and the ethereal solution was treated with potassium carbonate solution in order to dissolve out the acidic oxidation products as their potassium salts. The aqueous solution containing the potassium salts was heated on the water-bath with the addition of a little potassium hydroxide to saponify the acid ester. On decomposing the potassium salts with hydrochloric acid, the acidic substances liberated were taken up with ether. The ethereal solution was washed with brine, and ether was removed by distillation. The residue consisted mainly of a crystalline solid having a strong penetrating odour; yield 0.7 g. It was treated with petroleum ether, and the petroleum ether solution was separated from the insoluble portion. On distilling off the solvent from the petroleum ether solution, there was obtained a small amount of residue which had a smell of

(6) The specimen of capric acid used for the mixed melting point test was separated from the seed oil of *Cinnamomum pedunculatum*; m.p. 30.5 – 31° .

formic acid and was soluble in water. The distillate of petroleum ether had also a smell of formic acid. On warming the aqueous solution of the residue with solutions of silver nitrate, metallic silver was deposited. When reduced with hydrochloric acid and metallic magnesium, the aqueous solution gave a smell of formaldehyde, the presence of which was confirmed by the violet colouration when the mixture of this solution, fresh milk and hydrochloric acid containing a trace of ferric chloride were heated gently.

The portion insoluble in petroleum ether yielded azelaic acid $C_9H_{16}O_4$ on recrystallisation from benzene; neutralisation value 594.2 (calc. 596.5), m.p. and mixed m.p. 105-106°⁷⁾ (Found: C, 57.28; H, 8.69. Calc. for $C_9H_{16}O_4$: C, 57.41; H, 8.57%).

Summary.

A decenoic acid has been separated from sperm head oil. Its methyl ester was oxidised with potassium permanganate in acetone, and after the saponification of the acid ester contained in the oxidation products, azelaic acid was identified. The presence of formic acid in the oxidation products was also indicated. Accordingly the decenoic acid in sperm head oil is proved to be $\Delta^{9:10}$ -decenoic acid, having the formula $CH_2=CH \cdot (CH_2)_7 \cdot COOH$.

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7) The specimen of azelaic acid used for the mixed melting point test was prepared by the ozonolysis of oleic acid; m.p. 105-106°.

THE HIGHLY UNSATURATED ALCOHOLS IN SPERM BLUBBER OIL.*

By Yoshiyuki TOYAMA and Goroku AKIYAMA.

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In a former study on the unsaponifiable matter of sperm blubber oil, one of the authors⁽¹⁾ separated and identified oleyl alcohol as the chief constituent together with such substances as cetyl alcohol, octadecanol and cholesterol, but other unsaponifiable constituents present in a minor proportion were not closely examined. Later, we⁽²⁾ have attempted to separate and investigate these minor constituents, and recently described the results of our experi-

* Translated from the Japanese text published in *J. Chem. Soc. Japan*, **56** (1935), 1316.

(1) Toyama, *J. Soc. Chem. Ind., Japan*, **30** (1927), 527.

(2) This Bulletin, **10** (1935), 579.

ments in which zoomaryl alcohol ($\Delta^9:10$ -hexadecenol) was separated and its constitution was established. The present paper deals with the highly unsaturated alcohols which are present as minor constituents in the unsaponifiable matter of this oil. A review of the literature shows that the following facts have hitherto been reported in connection with the highly unsaturated alcohols in sperm oil. One of the authors, in his previous study on the unsaponifiable matter of sperm blubber oil, indicated the presence of some highly unsaturated alcohols by the fact that bromination of a fraction of the unsaponifiable matter of this oil yielded a small amount of ether insoluble bromides and also petroleum ether insoluble bromides having high Br-contents. Also Hilditch and Lovern⁽³⁾ stated the presence of some highly unsaturated alcohols (mainly di-ethylenic) among C_{18} - and C_{20} -unsaturated alcohols in sperm blubber oil. According to André and François⁽⁴⁾ the liquid fraction of the unsaponifiable matter of sperm oil contains, in addition to oleyl alcohol, alcohols of higher molecular weight and higher unsaturation than oleyl alcohol, and yields a petroleum ether insoluble bromide having the formula $C_{22}H_{42}OBr_4$. It is thus seen that, although the presence of some highly unsaturated alcohols has already been pointed out by several authors, our knowledge of the individual constituents of these highly unsaturated alcohols has hitherto been scanty.

In the previous experiment of the separation of zoomaryl alcohol in sperm blubber oil, the unsaponifiable matter of this oil was separated into 5 fractions by fractional distillation, and the lowest fraction boiling below $188^\circ/5$ mm. was worked up further for the isolation of zoomaryl alcohol. Since the highly unsaturated alcohols originally present in the unsaponifiable matter in a small proportion were deemed to have been concentrated in the highest fraction, the latter was used for the present experiment. A small amount of solid saturated alcohols was removed from this fraction, and the liquid alcohols were brominated. The ether insoluble bromides were separated and then debrominated to regenerate the highly unsaturated alcohols. These were then converted into acetates, and the latter were separated into 12 fractions by fractional distillation. The 3rd fraction had saponification and iodine values which agreed with those calculated for the acetate ($C_{22}H_{36}O_2$) of a highly unsaturated alcohol $C_{20}H_{34}O$. The free alcohol obtained on saponification of this fraction showed an elementary composition which corresponded to the formula $C_{20}H_{34}O$, and yielded on bromination an ether insoluble bromide of the formula $C_{20}H_{34}OBr_8$. The 1st and 2nd fractions showed saponification values which were a little higher than the value calculated for $C_{22}H_{36}O_2$, and

(3) *J. Soc. Chem. Ind.*, **48** (1929), 365 T.

(4) *Compt. rend.*, **185** (1927), 279.

consequently these fractions were thought to contain, in addition to the acetate of $C_{20}H_{34}O$, the acetates of some highly unsaturated alcohols of lower molecular weight (possibly the acetates of $C_{18}H_{32}O$ and $C_{16}H_{30}O$). A saturated alcohol $C_{20}H_{42}O$ was separated from the hydrogenation product of the free alcohols from the 1st-3rd fractions, and it was oxidised with chromic acid, yielding arachidic acid $C_{20}H_{40}O_2$. Accordingly the highly unsaturated alcohol $C_{20}H_{34}O$, which is present as its acetate in these fractions, is a primary alcohol having no branched chain of carbon atoms. The 12th fraction showed a saponification value which was a little higher than that calculated for the acetate ($C_{24}H_{38}O_2$) of an alcohol $C_{22}H_{36}O$, but the iodine value of this fraction agreed with the value calculated for $C_{24}H_{38}O_2$. The free alcohol yielded an ether insoluble bromide having the formula $C_{22}H_{36}OBr_{10}$. Hence the alcohol, which was present as its acetate in the 12th fraction, was deemed to consist mainly of $C_{22}H_{36}O$. The fact that the saponification value of the 12th fraction was higher than the value calculated for $C_{24}H_{38}O_2$ is presumably ascribed to the contamination of the acetates of some polyvalent alcohols (possibly some highly unsaturated alcohols belonging to the selachyl alcohol group). A further investigation is yet wanted to confirm these postulations. The hydrogenation product of the free alcohol yielded, after repeated recrystallisation, a saturated alcohol which showed an acetyl value corresponding to $C_{22}H_{46}O$.

It is thus seen from the results of the present experiment that the highly unsaturated alcohols in the unsaponifiable matter of sperm blubber oil contain two alcohols $C_{20}H_{34}O$ and $C_{22}H_{36}O$ as chief constituents. These two alcohols have the formula just corresponding to eicosatetraenoic acid $C_{20}H_{32}O_2$ and clupanodonic acid $C_{22}H_{34}O_2$ which occur in sperm blubber and other marine animal oils as chief constituents of highly unsaturated acids. Although no individual constituents of highly unsaturated alcohols other than $C_{20}H_{34}O$ and $C_{22}H_{36}O$ have been found with certainty in the present experiment, it is very probable that a further investigation, starting with a large quantity of material, may bring out a sufficient evidence for the presence of several individual constituents of highly unsaturated alcohols corresponding to those of highly unsaturated acids in marine animal oils. Postulating from the relations of the constitutions of physeteryl and zoomaryl alcohols⁽⁵⁾ and the corresponding fatty acids in marine animal oils, two highly unsaturated alcohols $C_{20}H_{34}O$ and $C_{22}H_{36}O$ in sperm blubber oil may have ethylenic linkings in the same positions as eicosatetraenoic⁽⁶⁾ and clupanodonic acids,⁽⁷⁾ i.e., these

(5) Toyama and Tsuchiya, this Bulletin, **10** (1935), 573; Toyama and Akiyama, this Bulletin, **10** (1935), 579.

(6) Toyama and Tsuchiya, this Bulletin, **10** (1935), 296.

(7) Toyama and Tsuchiya, this Bulletin, **10** (1935), 441.

alcohols may possibly be identified as the alcohols obtained on reducing the carboxyl group of the corresponding highly unsaturated acids. We are intended to confirm this by subsequent experiments. Whilst the alcohol $C_{20}H_{34}O$ (eicosatetraenol), for which we propose the name catadonyl alcohol,⁽⁸⁾ has never been recorded in the literature, the docosapentenol (clupanodonyl alcohol) $C_{22}H_{36}O$ was prepared by Tsujimoto and Kimura⁽⁹⁾ by the reduction of methyl clupanodonate, but its occurrence in natural oils has never been reported before our experiment.

Experimental.

1. **The Preparation of Ether Insoluble Bromides from High Boiling Fraction and the Regeneration of Highly Unsaturated Alcohols by Debromination.** A specimen of sperm blubber oil having saponification value 126.8, iodine value (Wijs) 82.6 and unsaponifiable matter 38.98% was heated with barium hydroxide solution under pressure, and a mixture of barium soaps and free unsaponifiable matter was obtained, from which the latter was extracted with acetone. The unsaponifiable matter was separated into 5 fractions by fractional distillation, the yield of the highest fraction boiling at 195–198°/5 mm. being 1,680 g. from 10,070 g. of unsaponifiable matter. For the details of the above experiment the previous paper⁽²⁾ should be consulted.

The highest fraction obtained above showed acetyl value 182.6 and iodine value 96.8. This fraction (1,670 g.) was divided into three batches, and each of them was dissolved in about 10 times its quantity of acetone. The solution was cooled down to about –10°, the separated solid (yield 70 g. in total, iodine value 14.5) was filtered, and on distilling off the solvent from the filtrate there was obtained the liquid portion having iodine value 100.9. The liquid portion (1,570 g. in total) was brominated in the following manner: this was divided into 3 batches consisting of 520–530 g., and each of them was dissolved in about 10 times its quantity of ether. The solution was cooled down to about –10°, and an excess of bromine (about 400 g.) was added in the course of 5 hours under constant stirring. After the completion of the addition of bromine, the solution was allowed to stand in the cold for 2 hours more and then the precipitate of insoluble bromides (53.5 g. in total) was filtered and washed with cold ether until the precipitate became white. The filtrate together with the washings was washed with sodium thio-sulphate solution to remove the excess of bromine, and after subsequent washing with water and dehydration over anhydrous sodium sulphate, the solvent was distilled. The residue was then dissolved in about 10 times its quantity of petroleum ether, the solution was cooled down to about –10°, and the precipitated bromides (35 g. in total) were filtered off. The ether insoluble bromides had Br-content 69.50% and melted to a tar-like matter at about 240°. The petroleum ether insoluble bromides had Br-content 64.40% and turned black at about 150°. Fifty-three g. of ether insoluble bromides were mixed with 27 g. of zinc powder, and 80 c.c. of ethyl alcohol was added to the mixture. The liquid was heated on the water-bath under a reflux condenser, and 80 c.c. of 5 N hydrochloric acid in ethyl alcohol was added in the course of 1.5 hours. After heating 1 hour more, the supernatant solution was decanted off. The residue was again treated with 27 g. of zinc powder, 80 c.c. of ethyl alcohol and 80 c.c. of 5 N hydrochloric acid in

(8) Derived from Catadontidae.

(9) *J. Soc. Chem. Ind., Japan*, **28** (1925), 390.

ethyl alcohol as before, and then the solution was separated from the insoluble substances which were thoroughly washed with ethyl alcohol. The united solutions and the washings were diluted with a large quantity of water, and the debrominated product, which separated as an oily layer, was collected by using ether. The highly unsaturated alcohols (15.3 g.) thus obtained by debromination of ether insoluble bromides had acetyl value 166.7, iodine value 383.9⁽¹⁰⁾ and n_D^{20} 1.4926. They showed a drying power and had a peculiar smell like the highly unsaturated acids in marine animal oils. A portion of the highly unsaturated alcohols was subjected to hydrogenation, and the product was recrystallised from 90% ethyl alcohol, yielding the recrystallised product and the portion recovered from the mother liquor (Table 1). The latter was, however, suspected to contain more or less unsaturated alcohols which escaped a complete hydrogenation. The acetyl values (saponification values of the corresponding acetates) calculated for $C_{18}H_{38}O$, $C_{20}H_{42}O$, and $C_{22}H_{46}O$ are shown in Table 2.

Table 1.

	M.p.	Acetyl value
Recrystallised product	64°	156.8
Portion recovered from the mother liquor	57°	171.5

Table 2.

	$C_{18}H_{38}O$	$C_{20}H_{42}O$	$C_{22}H_{46}O$
Acetyl value	179.6	164.9	152.3

2. Fractionation of Highly Unsaturated Acetates. The highly unsaturated alcohols were heated with acetic anhydride, and 15.8 g. of the resulting acetates were fractionally distilled with the results shown in Table 3.

Table 3.

Fraction	B.p. (°C./5 mm.)	Saponif. value	Iodine value	n_D^{20}	Yield (g.)
1	185-202	173.2	296.4	1.4798	0.8
2	202-207	171.6	303.0	1.4800	1.0
3	207-211	169.1	308.3	1.4804	1.3
4	211-213	168.3	309.9	1.4808	1.0
5	213-215	168.1	310.8	1.4809	1.2
6	215-217	167.9	312.0	1.4810	1.2
7	217-218	167.5	313.6	1.4817	1.3
8	218-219	166.1	315.9	1.4828	1.7
9	219-220	165.8	318.1	1.4835	1.4
10	220-221	164.2	325.5	1.4839	1.5
11	221	163.7	333.0	1.4843	1.3
12	221-225	165.1	349.9	1.4868	1.5
Residue and loss	—	—	—	—	0.6

The saponification and iodine values of the fraction (3) are close to the corresponding values (saponification value 168.8, iodine value 305.6) for the acetate $C_{22}H_{36}O_2$ of a highly unsaturated alcohol $C_{20}H_{34}O$. The free alcohol obtained on saponification of this fraction was found to have the formula $C_{20}H_{34}O$ by elementary analysis (Found: C, 82.31;

(10) This value is thought to be a little too high.

H, 11.89. Calc. for $C_{20}H_{40}O$: C, 82.68; H, 11.80%).⁽¹¹⁾ The hydrogenated product of the free alcohol showed acetyl value 164.4 (calc. for $C_{20}H_{42}O$: 164.9) and m.p. 62.5–63° after recrystallisation from 90% ethyl alcohol (Found: C, 80.19; H, 14.20. Calc. for $C_{20}H_{42}O$: C, 80.45; H, 14.19%). The melting point of *n*-eicosanol is recorded as 65–65.5°. ⁽¹²⁾ On brominating the free alcohol in ethereal solution, there was obtained 56% of an ether insoluble bromide which showed Br-content 68.82% (calc. for $C_{20}H_{34}OBr_8$: 68.77%) and turned black at about 240°.

The saponification values of the fractions (1) and (2) are a little higher than the value calculated for the acetate $C_{22}H_{36}O_2$ of an alcohol $C_{20}H_{34}O$, but on hydrogenating the free alcohol liberated from the fractions (1) and (2), there was obtained the same product having acetyl value 164.3 and m.p. 62.5–63° as that described in the case of the fraction (3).

The saturated alcohol (0.8 g.) described above, m.p. 62.5–63°, was dissolved in 30 c.c. of glacial acetic acid, and 3.5 g. of chromic acid was added. The solution was heated on the water-bath under a reflux condenser for 2 hours. On cooling it was diluted with water, and the oxidation products were extracted with 500 c.c. of ether. The ethereal solution was washed with water and then with potassium hydroxide solution by which the acidic oxidation products were converted into the potassium salts and separated from the ethereal solution. The aqueous solution containing the potassium salts was decomposed with hydrochloric acid, and the insoluble acidic substances were separated and recrystallised from 95% ethyl alcohol. The product showed neutralisation value 181.5 (calc. for $C_{20}H_{40}O_2$: 179.6) and m.p. 73.5–74°. No depression of melting point was observed when the product was admixed with a pure specimen of arachidic acid $C_{20}H_{40}O_2$ (m.p. 74.5–75°).

The highest fraction (12) showed a saponification value which is considerably higher than the value calculated for the acetate $C_{24}H_{38}O_2$ of a highly unsaturated alcohol $C_{22}H_{36}O$, but the free alcohol obtained on saponification of this fraction showed an elementary composition corresponding to the formula $C_{22}H_{36}O$ (Found: C, 83.28; H, 11.38. Calc. for $C_{22}H_{36}O$: C, 83.47; H, 11.47%). On brominating the free alcohol in ethereal solution, there was obtained 57% of an ether insoluble bromide which had Br-content 71.45% (calc. for $C_{22}H_{36}OBr_{10}$: 71.65%) and turned black at about 240°. The hydrogenation product showed acetyl value 152.2 (calc. for $C_{22}H_{46}O$: 152.3) and m.p. 67–67.5° after repeated recrystallisation from 90% ethyl alcohol. The melting point of *n*-docosanol $C_{22}H_{46}O$ is recorded as 70–70.5°. ⁽¹³⁾

Summary.

The high boiling fraction of the unsaponifiable matter of sperm blubber oil was brominated in ethereal solution, and the ether insoluble bromide was separated and then debrominated to regenerate the highly unsaturated alcohols. These were converted into acetates, and the latter were fractionated. An examination of the resulting fractions showed that the highly unsaturated alcohols of sperm blubber oil contained two individual alcohols $C_{20}H_{34}O$ and $C_{22}H_{36}O$ as chief components.

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(11) For the elementary analyses we are indebted to Mr. Tsuchiya.

(12) Adam and Dyer, *J. Chem. Soc.*, **127** (1925), 70.

(13) Bleyberg and Ulrich, *Ber.*, **64** (1931), 2504.

GEWINNUNG DER FESTEN FIBER AUS REISSTROH.

Von Munenari TANAKA.

Eingegangen am 27. November 1935. Ausgegeben am 28. Januar 1936.

Es gibt wenig Arbeiten über die Isolierung der α -Zellulose aus Reisstroh. Früher glaubte man, es gäbe überhaupt keine röhrenförmige Zellulose im Stroh. Diesmal ist es nun dem Verfasser nach fünfjähriger Forschung gelungen, röhrenförmige Zellulose im Stroh zu isolieren.

Zur Isolierung wird zuerst die Zellulose mit "Nibe"⁽¹⁾ (*Hydrangea paniculata* Sieb.) verstärkt, und dann mit Myrrhe⁽²⁾ oder Weihrauch⁽³⁾ zusammengebracht wie bei der Färbungsmethode der Zellulose mit Küpenfarbstoff. Diese Zellulose lässt man endlich mit Ammoniumcarbonat und Natriumbicarbonat schwellen. Zu diesem Zwecke wurden die Blattscheiden anstatt der Halme benutzt, da die ersteren viel mehr Zellulose als die letzteren enthalten.

Beispiel: 100 g. Stroh werden mit 70 g. Ätznatron in 15 Liter Wasser erhitzt und nach 40 Min. wird das Produkt mit Wasser gewaschen. Die Zellulose wird darauf mit 7 g. "Nibe" und 1/2 Liter Wasser etwa 15 Min. unter Zufügung von wenig Natriumperoxyd aufgekocht und gut gewaschen. Dann werden zur Zellulose 800 c.c. heisses Wasser 7 g. Myrrhe (5% ig verdünnt mit Natriumbicarbonat), 0.1 g. Brankit hinzugefügt, und ein paar Minuten stehen gelassen. Dazu kommen 1.5 g. Oxalsäure und 6 g. Chlorkalk und endlich erhält man bei der Zugabe der Mischung von 5 g. Natriumbicarbonat und Ammoniumcarbonat bei 50° feste Fiber. Die Ausbeute beträgt 20% des Ausgangsmaterials. Die Analyse dieses Produkts ist folgende: (1) Wassergehalt 7.15%; (2) Elementaranalyse: (A) Subst., 5.612 mg.; Asche, 0.013 mg.; C, 45.7%; H, 6.7%; (B) Subst., 5.086 mg.; Asche, 0.045 mg.; C, 46.2%; H, 6.9%.

Diese feste Fiber ist etwas stärker als Naturwatte. Der Unterschied zwischen dem künstlichen und dem Naturprodukt besteht darin, dass das künstliche nicht gedreht ist.

Kobe College.

(1) Wiesner, „Die Rohstoffe der Pflanze,“ Bd. II, 391.

(2) Köhler, „Medizinal Pflanzen,“ Bd. I, 303-306.

(3) *Ibid.*, Bd. I, 299.

ÜBER DEN UNTERSCHIED IN DER ISOTOPENZUSAMMEN- SETZUNG VON LUFT- UND WASSERSAUERSTOFF.

(Vorläufige Mitteilung.)

Von Noriyoshi MORITA und Toshizo TITANI.

Eingegangen am 3. Dezember 1935. Ausgegeben am 28. Januar 1936.

Beim Vergleich von zahlreichen Versuchen über den Deuterium-Gehalt von gewöhnlichem Wasser sowie die elektrolytische Trennung von Sauerstoffisotopen, kam uns die Vermutung, dass der Sauerstoff in der Luft, den wir Luftsauerstoff nennen wollen, spezifisch schwerer sei als der Wassersauerstoff, der im Wasser mit Wasserstoff gebunden ist. Um diese Vermutung näher zu prüfen haben wir ein Experiment durchgeführt, dessen Ergebnisse wir vorläufig mitteilen wollen.

Zunächst wurde leichtes oder Deuterium-armes Wasser durch die fraktionierte Elektrolyse von gewöhnlichem Wasser hergestellt. Durch nochmalige Elektrolyse dieses leichten Wassers konnten wir den leichten Wasserstoff, dessen D-Gehalt schätzungsweise kleiner als 1 Atom in 30,000 war, sich entwickeln lassen. Den so erhaltenen leichten Wasserstoff haben wir separat mit dem Luft- und Wassersauerstoff zu Wasser rekombiniert und die Dichten des jeweils entstehenden Wassers miteinander verglichen. Dazu verwendeten wir die folgenden drei Sorten von Sauerstoff: Sauerstoff (I) war Luftsauerstoff. In der Praxis verwendeten wir die atmosphärische Luft, die im voraus gut gereinigt und getrocknet war. Sauerstoff (II) war Wassersauerstoff, der durch teilweise Elektrolyse aus gewöhnlichem Wasser gewonnen wurde. In diesem Sauerstoff (II) kann man die extreme Verschiebung der Isotopenzusammensetzung inolge der elektrolytischen Trennung erwarten, weil nur 5% vom gesamten Elektrolysierwasser gespalten worden war. Sauerstoff (III) war ebenfalls durch die Elektrolyse erhaltener Wassersauerstoff. Aber in diesem Fall wurde die Elektrolyse fast bis zum Ende durchgeführt, d.h. 95% vom totalen Volumen elektrolytisch gespalten. Infolgedessen muss Sauerstoff (III) dieselbe Isotopenzusammensetzung wie der Sauerstoff, der im Wasser chemisch verbunden ist, besitzen.

Die Rekombination von so hergestelltem Sauerstoff mit dem leichten Wasserstoff führten wir über dem auf 300° bis 350°C. erhitzten Kupferkatalysator durch, der aus Kupferoxyd durch die Reduktion mittels Wasserstoffs hergestellt worden war. Wir verwendeten immer den Wasserstoff in grossem Überschuss, um den Sauerstoff vollständig reagieren zu lassen.

Dabei funktionierte der Kupferkatalysator auch als ein sehr effektives Reservoir für den Sauerstoff. Nach dem Experiment wurde der leichte Wasserstoff noch lange Zeit über den erhitzten Katalysator durchgeleitet, um ihn vollständig vom gebundenen Sauerstoff zu befreien und den verwendeten Sauerstoff restlos in Wasser zu verwandeln. Auf diese Weise wurden drei Sorten von Wasser je aus den drei Sorten von Sauerstoff und dem leichten Wasserstoff hergestellt. Die so gewonnenen Arten von Wasser wurden alle sorgfältig gereinigt und ihre Dichte wurde je mit der des Standardwassers mittels eines Quarzschwimmers verglichen. Aus diesem Experiment ergab sich folgendes:

(1) Das Wasser, das aus dem Sauerstoff (III), d.h. dem kompletten Sauerstoff aus Wasser entstand, erwies sich durchschnittlich um 2% schwerer als das Wasser aus dem Sauerstoff (II), der durch die partielle Elektrolyse des Wassers hergestellt wurde. Daraus folgt, dass der Trennfaktor von Sauerstoffisotopen unter den von uns verwendeten Versuchsbedingungen d.h. bei der Elektrolyse von 2N NaOH Lösung zwischen Nickel-Elektroden $O^{18}/O^{16} = 1.01$ ist. Dieser Wert erwies sich als gut übereinstimmend mit den von Johnston⁽¹⁾ sowie von Taylor und seinen Mitarbeitern⁽²⁾ gefundenen.

(2) Wie erwartet erwies sich das Wasser aus dem Luftsauerstoff (I) spezifisch schwerer als das aus dem Wassersauerstoff (III) gewonnene. Der Unterschied betrug durchschnittlich 8%. Diesen Unterschied darf man fast ausschliesslich auf den Unterschied im spezifischen Gewicht oder in der Isotopenzusammensetzung zwischen Luft- und Wassersauerstoff zurückführen. Denn unter den von uns verwendeten Versuchsbedingungen war erstens irgendeine isotopische Trennung im Sauerstoff ganz ausgeschlossen und zweitens konnte eine eventuell vorhandene minimale Trennung von Wasserstoffisotopen auf die oben geschilderten Experimentalresultate (1) und (2) keinen merklichen Einfluss ausüben. Nimmt man an, dass das Isotopenverhältnis $O^{18}:O^{16} = 1:500$ ist, dann folgt aus diesem Resultat, dass der Luftsauerstoff um 4% reicher an O^{18} als der Wassersauerstoff ist, oder dass der Verteilungskoeffizient von O^{18} zwischen Luft/Wasser = 1.04 ist. Auf die Frage nach der Ursache dieses Unterschiedes kann man natürlich nicht sofort antworten. Aber es scheint uns interessant, dass der eben gefundene Koeffizient vielmehr dem von Urey und Greiff⁽³⁾ aus spektroskopischen Daten errechneten Verteilungskoeffizienten von O^{18} beim Austauschgleichgewicht zwischen Sauerstoff/Wasserdampf (= 1.020) nahe steht, aber nicht dem zwischen Sauerstoff/Wasser (= 1.006). Auf jeden Fall

(1) H.L. Johnston, *J. Am. Chem. Soc.*, **57** (1935), 484.

(2) P.W. Selwood, H.S. Taylor, J.A. Hipple, Jr., und W. Bleakney, *J. Am. Chem. Soc.*, **57** (1935), 642.

(3) H.C. Urey und L.J. Greiff, *J. Am. Chem. Soc.*, **57** (1935), 321.

muss bei genaueren Versuchen die oben gefundene Tatsache in Betracht gezogen werden, dass es einen ziemlich merklichen Unterschied in den Isotopenzusammensetzungen zwischen Sauerstoff in Luft und Wasser, den zwei wichtigsten Behältern von Sauerstoff, gibt und dass er schon auf die vierte Dezimalstelle des Atomgewichts des Sauerstoffs einen Einfluss ausübt. Die bisher manchmal beobachteten Diskrepanzen zwischen den von vielen Forschern veröffentlichten Daten über den Trennfaktor von Sauerstoffisotopen sowie das Vorkommenverhältnis von Wasserstoffisotopen scheinen uns mindestens teilweise durch die eben gefundene Tatsache befriedigend erklärt werden zu können. Näheres darüber soll später in diesem Bulletin erörtert werden.

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THE CONFIGURATION OF CHLOROBISDIMETHYL- GLYOXIMOAMMINE-COBALT.

By Ryutaro TSUCHIDA, Masahisa KOBAYASHI, and Akira NAKAMURA.

Received December 18th, 1935. Published January 28th, 1936.

The authors have recently published a paper⁽¹⁾ on asymmetric adsorption of quartz and proposed a convenient method for detecting molecular asymmetry. It affords the means of revealing optical activity of racemic substances even when the traditional methods for resolution are unavailable. In the present paper is given one of the conspicuous examples of this method.

The steric configuration of chlorobisdimethylglyoximoammine-cobalt [$\text{Codg}_2(\text{NH}_3)\text{Cl}$] has not yet been determined. For this non-electrolytic ammine may be assumed two possible configurations, i.e., cis- and trans-forms (Fig.). If we could prove optical activity in the ammine, the configuration should consequently be of the cis-form, i.e. [$\text{Codg}_2(\text{NH}_3)\text{Cl}$]₍₁₎. The ammine, how-

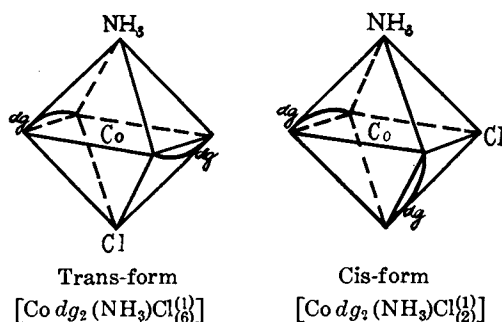
(1) R. Tsuchida, M. Kobayashi, and A. Nakamura: *J. Chem. Soc. Japan*, **56** (1935), 1339.

ever, would not combine with active acids or bases to form resolvable diastereomers and the crystals have so far failed to give any enantiomorphic faces. In order to determine the configuration the authors applied the new method making use of well-developed enantiomorphic crystals of quartz of various localities, Brazil, Kimbusen (Yamanashi Prefecture) and Naegi (Gifu Prefecture). The rock-crystals from Kimbusen were transparent quartz with large trapezohedral faces and the crystals from Naegi were smoky quartz with well-defined form and beautiful lustre. The latter species occurs often as twins of the Dauphiné type and it has been supposed to have irregular internal structure in spite of its well-defined external form. One of the purposes of using this species was to have some information about the internal structure of this interesting mineral. The authors, therefore, chose a left-handed single crystal and a right-handed twin of the Dauphiné type.

The ammine prepared from chloropentammine cobaltic chloride by the method of Tschugaëff⁽²⁾, was dissolved in water at 50°C. and 10 c.c. of the warm saturated solution was shaken with *g* g. of quartz powder. When cold the supernatant solution was syphoned out for polarimetry. It rotated the plane of polarized light by α_c degrees for the C-line in a 4 cm. tube.

Locality	Crystal	<i>g</i>	α_c
Brazil	right-handed	1.03	-0.03
	left-handed	3.94	+0.00
Kimbusen	right-handed	2.43	-0.05
	left-handed	1.42	+0.02
Naegi	right-handed	5.55	-0.02
	left-handed	2.93	+0.03

structure in itself adsorbs molecules of one of the antipodes of the ammine more strongly than the other. In other words, the phenomenon of asymmetric adsorption takes place. The configuration of the ammine has thus been determined as $[\text{Co}dg_2(\text{NH}_3)\text{Cl}_{(2)}^{(1)}]$ instead of $[\text{Co}dg_2(\text{NH}_3)\text{Cl}_{(6)}^{(1)}]$.



(2) L. Tschugaëff, *Ber.*, **39** (1906), 2695.

It is noteworthy that, so far as the sign of rotation is concerned, $[\text{Co}(\text{dg}_2(\text{NH}_3)\text{Cl})_2^{(1)}]$ shows the same effect as similarly configured cobalt amines, e.g., $[\text{Co}(\text{en}_2(\text{NH}_3)\text{Cl})_2^{(1)}]^{--}$, in spite of their different electrical charges. We may, therefore, assume that similar configurations give rise to similar asymmetric adsorption⁽³⁾.

It is also interesting to note that the smoky quartz from Naegi shows the same specificity as other rock-crystals, though the effect produced by the right-handed twin crystal was observed a little less than that of the corresponding left-handed single crystal. It may, therefore, be concluded that the mineral species retains, at least locally, the same asymmetric structure as shown by the external form. As the left-handed quartz from Brazil had scarcely shown the effect, the experiment was repeated with greater quantities of the quartz, but the results were always negative, while the smallest quantity of the corresponding right-handed quartz was sufficiently effective. This fact may be explained by assuming that the crystal was racemic, as in the case of the twin of the Brazil law, in spite of its external asymmetric form. The utmost caution should, therefore, be paid to the choice of crystals.

The authors have tried similar experiments with quartz powder covered with monoatomic layer of nickel, as was used in the researches by Schwab, Rost and Rudolph⁽⁴⁾ on asymmetric catalysis. The results, however, were negative.

The authors wish to express sincere thanks to Prof. Y. Shibata for his kind advice and suggestions and also to Mr. K. Masutomi for the fine crystals from Brazil and Kimbusen.

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(3) *J. Chem. Soc. Japan*, **56** (1935), 1342.

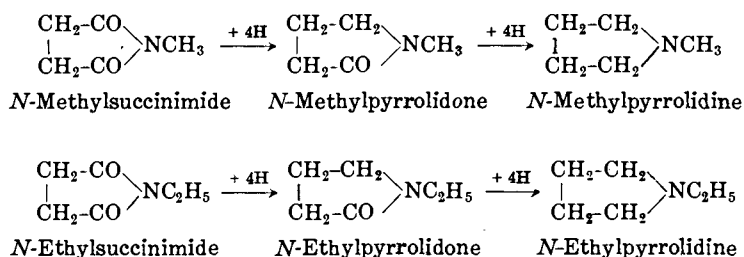
(4) *Kolloid-Z.*, **68** (1934), 157.

ELECTROLYTIC REDUCTION OF N-METHYLSUCCINIMIDE AND N-ETHYLSUCCINIMIDE.

By Buhei SAKURAI.

Received October 24th, 1935. Published February 28th, 1936.

The reduction, especially total reduction, of the cyclic imides of aliphatic acids is very difficult, and it seems to be almost impossible to carry out such reduction through purely chemical methods alone. But it may be accomplished electrolytically by using a lead or a zinc amalgam cathode, which has a strong reducing power. As reported in the preceding paper⁽¹⁾ the present writer carried out electrolytic reduction of succinimide using a zinc amalgam cathode and succeeded in its total reduction with a fairly satisfactory yield of pyrrolidine; and then he proceeded to similar reduction with *N*-methylsuccinimide and *N*-ethylsuccinimide. In these cases reduction goes through the same process as in the case of succinimide:



E. Spath⁽²⁾ and his collaborator reduced several derivatives of succinimide using a very high current density and a lead cathode prepared with special care, and succeeded in total reduction, corresponding reduction products being obtained. A. Luckes⁽³⁾ reduced *N*-methylsuccinimide in sulphuric acid solution with a current of 0.1 amp./sq. cm., and obtained *N*-methylpyrrolidone.

The present writer tried electrolytic reduction of *N*-methylsuccinimide, using a zinc amalgam cathode⁽⁴⁾ in a 50% sulphuric acid solution, at a current density as high as 100–125 amp./100 sq. cm., all the while avoiding any rise of temperature, and thus could carry the reduction over the stage of *N*-methylpyrrolidone and obtain *N*-methylpyrrolidine.

(1) B. Sakurai, this Bulletin, **10** (1935), 311.

(2) E. Spath and F. Breush, *Monatsh.*, **50** (1928), 349.

(3) R. Luckes, *Collection Czechoslov. Chem. Comm.*, **2** (1930), 531–44.

(4) B. Sakurai, this Bulletin, **7** (1932), 155.

As for *N*-ethylsuccinimide, as far as the present writer knows, no reports on its electrolytic reduction have been published. In the first place a 10% sulphuric acid solution, a lead cathode, and a current of 2.5 amp./100 sq. cm. were used, and the cathodic solution was extracted with chloroform without interfering with its acidity following the example of Lyman⁽⁵⁾, the reduction product being thus easily separated. The product was subjected to distillation under reduced pressure. A liquid, which distilled at 107° under 20 mm. was ascertained to be *N*-ethylpyrrolidone by its chemical properties and the results of analysis. Then the concentration of sulphuric acid was increased to 50%, the current density was raised to 100 amp./100 sq. cm., and a zinc amalgam cathode was used to effect a powerful reduction and the experiment resulted in the formation of *N*-ethylpyrrolidine.

Experimental.

The materials for electrolysis were prepared according to the method of Ladenberg⁽⁶⁾.

1. **Complete Reduction of *N*-Methylsuccinimide.** Cathode: zinc amalgam placed in a cylindrical vessel of biscuit, area 15 sq. cm.; cathodic solution: 3 g. of methylsuccinimide dissolved in 100 c.c. of 50% sulphuric acid; anode: cylindrical lead; anodic solution: 50% sulphuric acid; current density: 133 amp./100 sq. cm.; temperature: below 30°; time of electrolysis: 8 hours; current quantity: 224 F./mol.

As the rise of temperature has a harmful influence upon electrolysis as in the case of succinimide, a spiral lead tube was inserted in the cylindrical vessel of biscuit which contained the solution, cold water was passed rapidly through the lead spiral, and the apparatus was immersed in water, so that it was cooled from both inside and outside, while the cathodic solution was constantly stirred throughout the electrolysis.

When the electrolysis was over, the cathodic solution was taken out and shaken with a small quantity of chloroform, unchanged substances and *N*-methylpyrrolidone being thus extracted. The solution was then made strongly alkaline by adding a caustic soda solution and then was subjected to steam distillation. *N*-Methylpyrrolidine, the complete reduction product, distilled over with vapour. The distillate was made acid with hydrochloric acid. From the solution the gold salt of *N*-methylpyrrolidine was obtained in a bright yellow substance in the yield of 8.86%. The gold salt melted at 215°. (Found: Au, 46.5. Calc. for $C_6H_{12}N \cdot AuCl_4$: Au, 46.3%.) Its picrate was found to melt at 220°.

2. **Partial Reduction of *N*-Ethylsuccinimide.** Cathode: cylindrical lead plate of 100 sq. cm. placed in a cylindrical vessel of biscuit; cathodic solution: 10 g. of ethylsuccinimide dissolved in 100 c.c. of 10% sulphuric acid solution; anode: lead plate; anodic solution: 10% sulphuric acid solution; current density: 3.0 amp./100 sq. cm.; temperature: 28°; time of electrolysis: 21 hours; current quantity: 29.9 F./mol.

The electrolytic apparatus was placed in water, but this time the cooling from inside was dispensed with. Stirring was again continued during electrolysis.

After the electrolysis was finished, the cathodic solution was treated with chloroform to extract *N*-ethylpyrrolidine. When the chloroform was distilled off, about 8 g. of a liquid remained. When this liquid was subjected to vacuum distillation, 6 g. of a liquid

(5) Lyman, *J. Am. Chem. Soc.*, **55** (1933), 295-8.

(6) Ladenberg, *Ann.*, **215** (1882), 211.

distilling at 107° under 20 mm. was obtained. Its specific gravity was 1.0553, and when it was dissolved in 50% sulphuric acid and was oxidized with potassium permanganate solution, it changed back into *N*-ethylsuccinimide. On the other hand, when it was dissolved in 50% sulphuric acid and was electrolytically reduced under the conditions which will be described in the next experiment, it changed into *N*-ethylpyrrolidine. (Found: C, 62.3; H, 10.2; N, 11.98. Calculated for $C_6H_{11}ON$: C, 63.7; H, 9.37; N, 12.39%.) From the above results this substance was evidently *N*-ethylpyrrolidone where only one carbonyl group had undergone reduction.

3. **Complete Reduction of *N*-Ethylsuccinimide.** The conditions of the electrolysis and the treatment of the product after electrolysis were almost the same as in the case of *N*-methylsuccinimide. The double gold chloride of *N*-ethylpyrrolidine obtained in the yield of 18.3%. (Found: Au, 44.84. Cal. for $C_6H_{11}NAuCl_4$: Au, 44.87%.) Its picrate, closely resembling that of *N*-methylpyrrolidine, was bright yellow needle crystals and melted at 185°. These and other properties all well agree with those observed by Brown⁽⁷⁾.

In conclusion the writer expresses his sincere thanks to Dr. Motooki Matsui, President of the Kyoto Imperial University, for his helpful advice.

(7) J. W. Brown, *Ber.*, **44** (1911), 1252-60.

ÜBER DIE DAMPFPHASEHYDROLYSE.⁽¹⁾

Von Shigeaki YAMASAKI.

Eingegangen am 2. November 1935. Ausgegeben am 28. Februar 1936.

In einer früheren Arbeit⁽²⁾ hat der Verfasser zusammen mit T. Titani gefunden, dass der organische Ester wie Äthylacetat oder Benzylchlorid im Dampfzustand durch den Wasserdampf nicht hydrolysiert wird. Anschliessend daran wurde untersucht, ob dieselbe Reaktion durch den Zusatz von homogenen Katalysatoren⁽³⁾ oder Gasen beschleunigt werde. Obwohl der Versuch noch nicht abgeschlossen ist und die bisherigen Ergebnisse sich als negativ erwiesen, erfolgt hier nur eine kurze Mitteilung, weil der Verfasser an der Fortführung der Versuche im hiesigen Laboratorium verhindert ist.

Die verwendeten Katalysatoren waren Chlorwasserstoff und Jod. Der erste wurde als 5 N wässrige Lösung und der letzte als Esterlösung dem dampfförmigen Gemisch aus Äthylacetat und Wasser zugesetzt und bei 200°C. während verschiedener Zeitdauer erhitzt. Die sonstige Versuchsanordnung sowie die analytische Methode des Reaktionsprodukts waren genau dieselben

(1) Ergänzung der Arbeit von S. Yamasaki und T. Titani, dieses Bulletin, **9** (1934), 501.

(2) *Loc. cit.*

(3) Die heterogene Katalyse für die Hydrolyse sowie Esterbildung in Dampfphase ist schon wohl bekannt.

wie früher. Die Versuchsergebnisse ergaben sich ebenfalls als negativ, wie aus Abb. 1 ersichtlich ist, wo die zersetzten Mengen des Esters im Vergleich zur Versuchsdauer eingetragen sind.

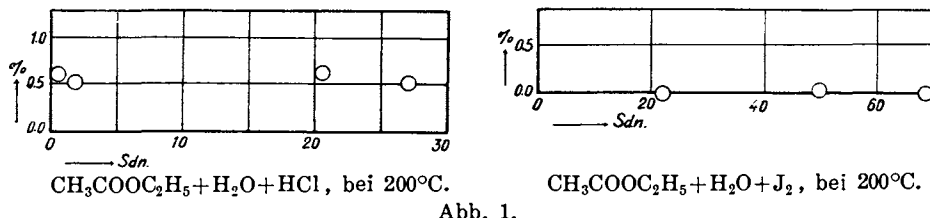


Abb. 1.

Im zweiten Versuch wurde versucht die Reaktionen durch den Zusatz von Gasionen zu katalysieren. Zu diesem Zweck wurde das Reaktionsgemisch bei 200°C. durch Röntgenstrahlen aus Molybden-Antikathode bestrahlt. Die Versuchsergebnisse sind in Tabelle 1 zusammengestellt.

Tabelle 1. Versuche mit Röntgenstrahlen.

Reaktionsgemisch	Intensität der Röntgenstrahlen		Versuchsdauer in Stunden	Prozentuale Zersetzung (%)
	Kilovolt	Milliamp.		
CH ₃ COOC ₂ H ₅ allein	20	1	1	0.00
CH ₃ COOC ₂ H ₅ + H ₂ O	20	1	1	0.00
CH ₃ COOC ₂ H ₅ + H ₂ O + HCl	20	1	1	0.50
wie oben	20	1	1.6	0.45
CH ₃ COOC ₂ H ₅ + H ₂ O + J ₂	20	1	1	0.03
wie oben	20	1	1	0.04
C ₂ H ₅ Br + H ₂ O	20	1	1	0.05
wie oben	30	4	2	0.03
C ₆ H ₅ Br + H ₂ O	20	1	1	0.06

Die Halogen-haltigen Verbindungen wurden zugesetzt oder verwendet um das Absorptionsvermögen des Reaktionsgemisches für die Röntgenstrahlen zu erhöhen. Die Versuchsdauer war sehr kurz im Vergleich mit den der erst genannten Versuche, aber mindestens wurden während dieser Zeitdauer keine Spuren einer hydrolytischen Reaktion innerhalb des Messfehlers gefunden.

Herrn Prof. T. Titani habe ich für die Anregung zu dieser Arbeit herzlichst zu danken. Ebenso bin ich Herrn Prof. I. Nitta, der die Röntgenapparat zur Verfügung gestellt hat, zum besten Dank verpflichtet.

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und

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DI-8-OXYCHINOLIN-INNERKOMPLEXSALZ DES ZWEIWERTIGEN SILBERS⁽¹⁾.

Von Yuichi NAKATSUKA.

Eingegangen am 4. November 1935. Ausgegeben am 28. Februar 1936.

Wir kennen bisher noch recht wenige Salze von zweiwertigem Silber. Man findet in der Literatur etwa folgende: Tetrapyridinsilber(II)-persulfat⁽²⁾ und -nitrat⁽³⁾; Di-*o*-phenanthrolin-silber(II)-persulfat, -chlorat, -perchlorat, -nitrat und -hydrosulfat⁽⁴⁾; Di- α, α' -dipyridylsilber(II)-persulfat, -hydrosulfat, -perchlorat und -nitrat⁽⁵⁾; Tri- α, α' -dipyridylsilber(II)-nitrat, -chlorat und -perchlorat⁽⁶⁾; Penta- α, α' -dipyridyldisilber(II)-persulfat⁽⁶⁾; Picolinsaures Silber(II)⁽⁷⁾; Chinolinsaures Silber(II)⁽⁸⁾; Silber(II)-fluorid⁽⁹⁾. Ausgenommen von Silber(II)-fluorid, das direkt aus den Bestandteilen dargestellt wurde, wurden alle anderen Salze durch anodische Oxydation bzw. durch Oxydation mittels Persulfates gewonnen.

Mir gelang es nun, das Di-8-oxychinolinsilber(II) auf ganz anderem Wege, d.h. ohne Gebrauch von besonderem Oxydationsmittel darzustellen, worüber in der vorliegenden Arbeit ebenso wie über die entsprechenden Silber(I)- und Kupfer(II)-verbindungen berichtet wird.

Fügt man zu einer abgekühlten Silberacetatlösung eine alkoholische Lösung von 8-Oxychinolin, so erhält man gelbes Di-8-oxychinolin-

silber(I) von der Formel (10). Falls die Silberacetatlösung dagegen heiss ist, so scheiden sich grüne Kristalle

(1) Vorgetragen am 5. April 1935 auf der Hauptversammlung der Japanischen Chemischen Gesellschaft.

(2) G. A. Barbieri, *Gazz. chim. ital.* **42** II (1912), 7.

(3) G. A. Barbieri, *Ber.*, **60** (1927), 2424.

(4) W. Hieber u. F. Mühlbauer, *Ber.*, **61** (1928), 2149.

(5) G. T. Morgan u. F. H. Burstall, *J. Chem. Soc.*, **1930**, 2594; G. A. Barbieri, *Atti accad. Lincei*, [6], **16** (1932), 44.

(6) G. T. Morgan u. F. H. Burstall, a.a.O.

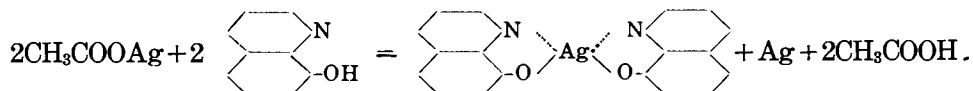
(7) G. A. Barbieri, *Atti accad. Lincei*, [6], **17** (1933), 1078.

(8) A. Burada, *Ann. Sci. Univ. Jassy*, **20** (1934), 71.

(9) O. Ruff u. M. Giese, *Z. anorg. allgem. Chem.*, **219** (1934), 143.

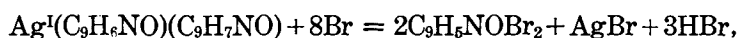
(10) Der räumliche Bau dieses Salzes wurde neulich als tetraedrisch festgestellt: Fr. Hein u. H. Regler, *Naturwiss.*, **23** (1935), 320.

von Di-8-oxychinolinat des zweiwertigen Silbers zusammen mit metallischem Silber nach folgender Gleichung ab:



Wie die Gleichung zeigt, oxydiert das eine von zwei einwertigen Silberatomen das andere zum zweiwertigen Zustand, und andererseits scheidet sich dieses selbst in metallischem Silber aus. Behandelt man das Komplexsalz-Silber-Gemisch mit Pyridin und lässt die pyridinische Lösung eindunsten, so kristallisiert das Salz mit einem Mol Pyridin rein aus.

8-Oxychinolin lässt sich, wie allgemein bekannt, sehr leicht bromometrisch titrieren⁽¹¹⁾, wobei ein Mol desselben vier Atomen Brom entspricht. Dementsprechend verbraucht ein Mol Di-8-oxychinolinsilber(I) acht Atome Brom in einer Säurelösung, damit es völlig bromiert wird⁽¹²⁾. In gleicher Weise bei Anwesenheit von Bromwasserstoffsäure behandelt, oxydiert Di-8-oxychinolinsilber(II) dagegen Bromwasserstoff, indem ein Atom Brom pro Mol Salz frei wird. Daher verbraucht in diesem Falle ein Mol des Salzes ein Atom Brom weniger als die entsprechende Silber(I)-verbindung, wie folgende Gleichungen zeigen:



Aus diesem Grunde kann man also sehr leicht beweisen, dass das Silber im zweiwertigen Zustand existiert.

Di-8-oxychinolinkupfer(II) kristallisiert aus Pyridin auch mit einem Mol Pyridin. Di-8-oxychinolinat des einwertigen Silbers bildet ebenfalls ein 1 Mol Pyridin enthaltendes Solvat. Diese drei pyridinhaltigen Salze haben überdies dieselbe säulenförmige Kristallgestalt.

Experimenteller Teil.

Di-8-oxychinolinsilber (I). Man löst 0.6 g. Silberacetat in 150 c.c. heissem Wasser. Nach Zusatz von etwas Natriumacetat fügt man in der Eiskälte unter Umrühren 20 c.c. Alkohol hinzu, der 1 g. 8-Oxychinolin gelöst enthält. Gelbe feine Säulen kristallisieren aus, die abgesaugt, mit Wasser nachgewaschen und auf Ton an der Luft getrocknet werden. Ausbeute fast quantitativ. Löslich in Pyridin und Chloroform, weniger in Alkohol, unlöslich in Wasser. (Gefunden: Ag, 27.31; N, 7.04. Berechnet für $\text{Ag}(\text{C}_9\text{H}_6\text{NO})(\text{C}_9\text{H}_7\text{NO})$: Ag, 27.17; N, 7.06%.)

(11) R. Berg, *Pharm. Ztg.*, **71** (1926), 1542.

(12) Vgl. R. Berg, *J. prakt. Chem.*, **115** (1927), 1780.

Nach dem Eintragen des Salzes in eine salzsaure Bromkaliumlösung, titriert man es mit Kaliumbromatlösung nach der bromometrischen Methode von Berg⁽¹²⁾. Als Indikator wird aber eine alkoholische Methylrotlösung nach Kolthoff verwendet. 0.0864 g. Subst. verbrauchten 17.48 c.c. N/10. Brom (Ber. 17.41 c.c.).

Trägt man das Salz in wenig Pyridin ein, so löst es sich zunächst, aber bald danach fällt das Salz mit einem Mol Pyridin in gelben Säulen aus. (Gefunden: Ag, 22.80; N, 8.88. Berechnet für $[\text{Ag}(\text{C}_6\text{H}_5\text{NO})(\text{C}_6\text{H}_7\text{NO})]\cdot\text{C}_5\text{H}_5\text{N}$: Ag, 22.66; N, 8.83%.)

Di-8-oxychinolinsilber (II). Die Darstellungsvorschrift ist wie beim Silber(I)-salze. Man löst jedoch etwas mehr als 1.2 g. Silberacetat in 200 c.c. heissem Wasser, und beim Zusatz von alkoholischem 8-Oxychinolin wird die Acetatlösung etwa auf 60° gehalten. Zuerst fällt Di-8-oxychinolinat des einwertigen Silbers aus, dessen Silber aber sogleich zum zweiwertigen Zustand oxydiert wird. Das dabei entstandene metallische Silber scheidet sich teilweise mit dem Salze gemischt und teilweise auch als Silberspiegel an der Gefässwand aus. Das Salz bildet grasgrüne viereckige Tafeln.

Zur Ermittlung der Zusammensetzung des Komplexsalzes und der Zweiwertigkeit des Silbers desselben wurde mit einem gut zerriebenen und möglichst einheitlich zusammengerührten Komplexsalz-Silber-Gemisch zuerst die Stickstoffbestimmung durchgeführt. (Gefunden: N, 5.75%.) Wenn das Komplexsalz kein Kristallwasser hat, so sollte das Gemisch von der Zusammensetzung Silber 18.72% + Komplexsalz 81.28% denselben Stickstoff- und 40.86%igen Silbergehalt ergeben. Analysenergebnisse mit derselben Probe waren folgende: Ag, 40.90%; 0.0677 g. Gemisch verbrauchten 9.80 c.c. N/10 Brom. Berechnet aus dem Stickstoffgehalt für das genommene Gemisch: 9.73 c.c. Die Analysen stimmen also mit den berechneten Werten gut überein, und daraus kann man mit Sicherheit schliessen, dass das Komplexsalz kristallwasserfrei ist und das Silber in zweiwertiger Form vorliegt.

Das Salz löst sich nicht in Wasser, ist aber löslich in Pyridin und in Chloroform. Um das Salz vom beigemengten metallischen Silber zu trennen, schüttelt man das Gemisch gut mit Pyridin. Nach dem Abfiltrieren des metallischen Silbers lässt man die pyridinische Lösung im Vakuum eindunsten, wobei das Komplexsalz in grasgrünen Säulen auskristallisiert. (Gefunden: Ag, 22.98, 22.66; N, 8.85. Berechnet für $[\text{Ag}(\text{C}_6\text{H}_5\text{NO})_2]\cdot\text{C}_5\text{H}_5\text{N}$: Ag, 22.71; N, 8.85%.) Bromometrie wurde wie beim entsprechenden Silber(I)-salz durchgeführt. 0.0994 g. Subst. verbrauchten 14.60 c.c. N/10 Brom. (Berechnet: 14.64 c.c.).

Di-8-oxychinolinkupfer (II)⁽¹³⁾. Fällt man eine natriumacetathaltige Kupferacetatlösung mit einer alkoholischen Lösung von 8-Oxychinolin, so scheidet sich Di-8-oxychinolinkupfer in einem blassgrünen Kristallpulver ab. Das Salz hat zwei Mol Kristallwasser (Salz I). (Gefunden: Cu, 16.77, 16.25; N, 7.26; H₂O, 9.40. Berechnet für $[\text{Cu}(\text{C}_6\text{H}_5\text{NO})_2]\cdot 2\text{H}_2\text{O}$: Cu, 16.40; N, 7.23; H₂O, 9.29%.) 0.1015 g. Subst. verbrauchten 18.16 c.c. N/10 Brom. (Berechnet: 18.32 c.c.) Fällt man dagegen in der Siedehitze, so erhält man gelbgrüne Nadeln. Dieses Salz enthält ein halbes Mol Wasser (Salz II). (Gefunden: Cu, 17.50; H₂O, 2.0, 3.0. Berechnet für $[\text{Cu}(\text{C}_6\text{H}_5\text{NO})_2]\cdot\frac{1}{2}\text{H}_2\text{O}$: Cu, 17.63; H₂O, 2.50%.)

(13) Bisher wurde nur das Salz als kristallwasserfrei beschrieben: Zd. H. Skraup, *Monatsh.*, **3** (1882), 541; G. Bargellini u. I. Bellucci, *Gazz. chim. ital.*, **53** (1923), 605.

Trägt man eines der beiden Salze I und II in wenig Pyridin ein, so fällt das Salz kristallwasserfrei als braungrüne sechseckige Tafeln (Salz III). (Gefunden: Cu, 17.86; N, 8.02. Berechnet für $\text{Cu}(\text{C}_9\text{H}_6\text{NO})_2$: Cu, 18.08; N, 7.97%.) Wenn man dagegen viel Pyridin verwendet, so löst sich das zuerst ausgeschiedene Salz wieder. Aus dieser Lösung erhält man beim Eindunsten grasgrüne Säulen, die ein Mol Pyridin pro Mol Salz enthalten (Salz IV). Dieses Salz verliert ziemlich schnell seinen Pyridingehalt. (Gefunden: Cu, 14.91; N, 9.71; Pyridin, 19.72. Berechnet für $[\text{Cu}(\text{C}_9\text{H}_6\text{NO})_2] \cdot \text{C}_5\text{H}_5\text{N}$: Cu, 14.76; N, 9.76; Pyridin, 18.35%.)

Herrn S. Murayama spreche ich hier meinen herzlichen Dank für seine Hilfe aus.

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ÜBER DIDIMETHYLGLYOXIM-DIAMMIN-KOBALT (III)-SALZE UND IHRE KONFIGURATION.⁽¹⁾

Von Yuichi NAKATSUKA und Hiroshi IINUMA.

Eingegangen am 5. November 1935. Ausgegeben am 28. Februar 1936.

Feigl und Rubinstein⁽²⁾ erhielten grüne Kristalle von der Formel $[\text{Co}(\text{DH}_2)_2\text{Cl}_2]$ ⁽³⁾ aus einer alkoholischen oder acetonischen Lösung von Kobaltchlorid und Dimethylglyoxim. Wenn man aber eine völlig wasserfreie acetonische Lösung von frisch entwässertem Kobaltchlorid und Dimethylglyoxim eindunsten lässt, so kristallisiert dagegen nach Thilo und Heilborn⁽⁴⁾ ein rotes mit dem Feiglschen grünen Salz isomeres echtes Chlorid $[\text{Co}(\text{DH}_2)_2]\text{Cl}_2$ aus. Thilo und Heilborn⁽⁴⁾ haben überdies festgestellt, dass im Feiglschen Salz zwei Chloratome trans-Stellungen besetzen, also zwei Dimethylglyoxime plan konfiguriert sein müssen.

Ausgehend von diesen beiden Salzen, haben wir in der vorliegenden Arbeit (1) einige neue Kobalt(III)-komplexsalze von der allgemeinen Formel $[\text{CoA}_2(\text{DH})_2]\text{X}$ ⁽⁵⁾ dargestellt, und (2) die Konfiguration der

(1) Gekürzte Übersetzung der schon in Japanisch veröffentlichten Arbeit, *J. Chem. Soc. Japan*, **55** (1934), 630.

(2) *Ann.*, **433** (1923), 183. Vgl. dazu Hieber u. Leutert, *Ber.*, **60** (1927), 2296; Thilo u. Heilborn, *Ber.*, **64** (1931), 1441.

(3) DH_2 = Dimethylglyoxim, DH = einwertiger Dimethylglyoximrest.

(4) a.a.O.

(5) $\text{A} = \text{NH}_3$ bzw. einwertiges Amin; X = einwertiger Säurerest.

schon beschriebenen und auch der von uns zum ersten Mal erhaltenen Salze dieser Reihe daraufhin bewiesen, dass zwei Dimethylglyoximreste immer sehr fest plan koordiniert sind, wie dies bei den zwei Dimethylglyoximen im Feigl'schen Salz des zweiwertigen Kobalts der Fall ist.

Frühere Untersuchungen über die Salze der Reihe wurden fast alle von Tschugaeff⁽⁶⁾ durchgeführt. Er erhielt $[\text{Co}(\text{NH}_3)_2(\text{DH})_2]\text{Cl}$ aus $[\text{Co}(\text{NH}_3)_6]\text{Cl}_3$ und Dimethylglyoxim. Die anderen Salze wurden im wesentlichen direkt aus den Bestandteilen dargestellt, also z.B. $[\text{Coph}_2(\text{DH})_2]\text{Cl}$ durch Oxydation mittels Luftsauerstoffes einer Mischung alkoholhaltiger Lösungen von Kobaltchlorid, Dimethylglyoxim und Pyridin.

Beato und Brugger⁽⁷⁾ erhielten 1929 Komplexsalze der Reihe (A = Anilin bzw. *o*- und *p*-Toluidin) direkt aus der alkoholischen Lösung der Bestandteile, aber sie benutzten die Salze als Nachweisreagenzien von Polysulfid und bestimmten die Zusammensetzung selbst nicht.

Wir haben uns der oben erwähnten Methode von Beato und Brugger bedient, d.h. eine gemischte alkoholische Lösung von Kobaltchlorid und Dimethylglyoxim wurde nach Zusatz von Amin mit Luft oxydiert. Auf diese Weise haben wir zuerst das Chlorid, dann durch doppelte Umsetzung das Bromid, Jodid, Rhodanid, Nitrat, saure Sulfat und neutrale Sulfat dargestellt. Als Amine wurden Ammoniak, Anilin, *o*- und *p*-Toluidin, *m*-Xylidin, und α - und β -Naphthylamin gebraucht. Das von uns so erhaltene Salz $[\text{Co}(\text{NH}_3)_2(\text{DH})_2]\text{Cl}$ war dasselbe wie das von Tschugaeff aus $[\text{Co}(\text{NH}_3)_6]\text{Cl}_3$ gewonnene.

Wie im experimentellen Teil beschrieben wird, koordinieren alle diese Amine ausserordentlich leicht am Zentralkobaltatom. Wenn nun ein Molekül *o*-Phenylendiamin als zweizähliger Ligand anstelle von zwei A treten würde, müsste es sich natürlich in *cis*-Stellung binden, vorausgesetzt dass zwei Dimethylglyoximreste nicht plan konfiguriert sind. Ein solches Salz konnte aber nie erhalten werden, sondern immer trat *o*-Phenylendiamin als einzähliger Ligand an das Kobaltatom wie in dem Salz $[\text{Coph}_2(\text{DH})_2]\text{Cl}$ ⁽⁸⁾. Daraus folgt, dass die zwei Dimethylglyoximreste in einer Ebene liegen und infolgedessen zwei A in den Salzen $[\text{CoA}_2(\text{DH})_2]\text{X}$ *trans*-Stellungen besetzen müssen.

Wir haben noch ein Salz von der Zusammensetzung $\text{Co}(\text{DH})_2\text{Cl}, ph$ erhalten. Dieses Salz enthält aber kein ionogenes Chlor, was sich durch

(6) *Z. anorg. Chem.*, **46** (1905), 144; *Ber.*, **39** (1906), 2692. Vgl. dazu noch „Gmelins Handbuch der anorganischen Chemie“, 58.B, S.276f.

(7) *Anales Soc. Espanola Fisica Quim.*, **27** (1929), 822.

(8) *ph* = *o*-Phenylendiamin.

Schäumen beim Eintragen in konzentrierte Schwefelsäure erkennen lassen würde. Aus diesem Grunde hat das Salz die Formel $[Coph(DH)_2]Cl$ und nicht $[Coph(DH)_2]Cl$. Auch hier reagiert *o*-Phenylendiamin als einzähliger Ligand.

Auch wenn man von dem Thiloschen roten Salz $[Co(DH_2)_2]Cl_2$ ausgeht, kann man keine anderen Salze der allgemeinen Formel $[CoA_2(DH)_2]Cl$ erhalten. Wenn man also z.B. nach Einleitung von trockenem Ammoniak in eine acetonsche Lösung von $[Co(DH_2)_2]Cl_2$ mit getrockneter Luft oxydiert, oder anstatt des Ammoniaks Anilin gebraucht, erhält man immer dieselben Salze wie oben.

Falls man *o*-Phenylendiamin als Amin verwendet, scheiden sich zuerst gelbe Nadeln aus. Diese Kristalle verschwinden allmählich mit dem Luftzutritt, und es gelingt nicht, aus der Lösung ein kristallinisches Komplexsalz zu erhalten. Diese gelben Nadeln haben die Formel $[Coph(DH_2)_2(OH_2)]Cl_2 \cdot CH_3 \cdot CO \cdot CH_3$, worin Kobalt also zweiwertig ist. Denn dasselbe Salz wird ebenso erhalten, wenn man in einer Stickstoffatmosphäre arbeitet. Auch ist das Salz durch Säuren sehr leicht zersetzbar, während Kobalt(III)-dimethylglyoxim-komplexsalze im allgemeinen beständig gegen Säuren sind. Das Salz verliert kein Gewicht im Vakuum über konzentrierter Schwefelsäure oder bei 110° und reagiert deutlich sauer in wässriger Lösung. Diese Reaktion kann folgendermassen gedeutet werden:



Aus dem oben beschriebenen kann man schliessen, dass in allen bisher erhaltenen und von uns neu dargestellten Kobalt(III)-komplexsalzen von der allgemeinen Formel $[CoA_2(DH)_2]X$ zwei Dimethylglyoximreste sehr fest plan konfigurieren, und daher zwei A trans-Stellungen besetzen.

Experimenteller Teil.

Allgemeine Darstellungsmethoden der Salze $[CoA_2(DH)_2]X$. Zur Darstellung des Chlorids löst man 1 g. kristallisiertes Kobaltchlorid in 15 c.c. warmem Alkohol, der 1 g. Dimethylglyoxim gelöst enthält. Nach dem Erkalten trägt man etwa 4 Mole Amin auf 1 Mol Kobaltchlorid ein und oxydiert das Gemisch 5 Minuten lang durch einen starken Luftstrom oder lässt 30 Minuten unter häufigem Umrühren an der Luft stehen. Das Chlorid, das sich sehr leicht ausscheidet, wird nach dem Abfiltrieren aus warmem Wasser umkristallisiert. Fügt man dabei etwas Natriumchlorid hinzu, so wird das Salz mit besserer Ausbeute erhalten.

Das Bromid, Jodid, Rhodanid bzw. Nitrat kristallisiert mit guter Ausbeute aus einer warmen konzentrierten Lösung des Chlorids beim Zusatz eines Überschusses an Kaliumbromid, Kaliumjodid, Kaliumrhodanid bzw. Natriumnitrat.

Auf diese Weise kann man jedoch das Sulfat wegen seiner grossen Löslichkeit nicht rein erhalten. Wenn man eine alkoholische oder acetonische Lösung von Dimethylglyoxim und Amin, in welcher gepulvertes kristallisiertes Kobaltsulfat suspendiert ist, mit Luft oxydiert, erhält man unreines Sulfat. Um daraus das Sulfat rein darzustellen, ist es empfehlenswert, über das saure Sulfat zu gehen. Wenn man also zu einer konzentrierten Lösung des unreinen Sulfates halbkonzentrierte Schwefelsäure im Überschuss fügt, so kristallisiert reines saures Sulfat in guter Ausbeute aus. Dasselbe saure Sulfat erhält man auch, wenn man eine konzentrierte warme Lösung des Chlorids oder das in wenig Wasser suspendierte Chlorid mit Schwefelsäure reagieren lässt. Fügt man zu dem in möglichst wenig Wasser eingetragenen sauren Sulfat die berechnete Menge oder einen geringen Überschuss an Natriumkarbonatlösung und lässt das Gemisch erkalten oder versetzt es mit etwas Natriumsulfat, so scheidet sich das neutrale Sulfat rein aus.

Didimethylglyoxim - diammin - kobalt (III) - salze. Chlorid. Die Darstellungsmethode ist die gleiche wie die oben angegebene allgemeine Vorschrift, wobei Ammoniak als konzentrierte Lösung gebraucht wird. Dabei scheiden sich gelbe Nadeln aus. Aus Wasser umkristallisiert, erhält man sie rein als viereckige Tafeln. Gut löslich in Wasser, in Alkohol etwas löslich. (Gef.: Co, 13.12; H₂O, 20.07. Ber. für [Co(NH₃)₂(DH)₂]Cl, 5H₂O: Co, 13.15; H₂O, 20.04%.)

Bromid. Gelbe Tafeln, schlecht löslich in Wasser und Alkohol. (Gef.: Co, 14.60. Ber. für [Co(NH₃)₂(DH)₂]Br: Co, 14.64%.)

Jodid. Gelbe Nadeln, schwer löslich in Wasser, Alkohol und Aceton. (Gef.: Co, 13.15. Ber. für [Co(NH₃)₂(DH)₂]I: Co, 13.12%.)

Rhodanid. Gelbe Schuppen, schwer löslich wie das Jodid. (Gef.: Co, 14.81; H₂O, 4.52. Ber. für [Co(NH₃)₂(DH)₂]SCN, H₂O: Co, 14.80; H₂O, 4.66%.)

Nitrat. Gelbe Nadeln, ziemlich gut löslich in Wasser, schwer in Alkohol. (Gef.: Co, 15.36. Ber. für [Co(NH₃)₂(DH)₂]NO₃: Co, 15.33%.)

Didimethylglyoxim - dianilin - kobalt (III) - salze. Chlorid. Zuerst als Nadeln erhältlich; aus Wasser umkristallisiert gelbbraune Prismen, ziemlich gut löslich in Wasser, Alkohol, und Aceton. (Gef.: Co, 10.18; H₂O, 12.32. Ber. für [Co(C₆H₇N)₂(DH)₂]Cl, 4H₂O: Co, 10.12; H₂O, 12.35%.)

Bromid. Orangefarbene Nadeln, nicht gut löslich in Wasser und Alkohol. (Gef.: Co, 10.70; N, 15.32. Ber. für [Co(C₆H₇N)₂(DH)₂]Br: Co, 10.63; N, 15.13%.)

Jodid. Braune Nadeln, wenig löslich in Wasser und Alkohol. (Gef.: Co, 9.76; N, 14.25. Ber. für [Co(C₆H₇N)₂(DH)₂]I: Co, 9.81; N, 13.95%.)

Rhodanid. Orangefarbene Tafeln, schwer löslich in Wasser. (Gef.: Co, 10.45; N, 17.79; H₂O, 3.17. Ber. für [Co(C₆H₇N)₂(DH)₂]SCN, H₂O: Co, 10.70; N, 17.78; H₂O, 3.27%.)

Nitrat. Orangefarbene Nadeln, nicht gut löslich in Wasser und Alkohol. (Gef.: Co, 11.08; H₂O, 6.76. Ber. für [Co(C₆H₇N)₂(DH)₂]NO₃, 2H₂O: Co, 10.97; H₂O, 6.29%.)

Saures Sulfat. Graubraune Tafeln, ziemlich gut löslich in Wasser, wenig in Alkohol und Aceton. (Gef.: Co, 9.69; SO₄, 15.98; N, 13.83; H₂O, 5.28. Ber. für [Co(C₆H₇N)₂(DH)₂]SO₄, H₂SO₄, 3½H₂O: Co, 9.79; SO₄, 15.88; N, 13.90; H₂O, 5.30%.)

Neutrales Sulfat. Gelbe Säulen, sehr gut löslich in Wasser, auch gut in Alkohol. (Gef.: Co, 10.09; N, 14.60; H₂O, 10.85. Ber. für [Co(C₆H₇N)₂(DH)₂]SO₄, 7H₂O: Co, 10.05; N, 14.34; H₂O, 10.73%.)

Didimethylglyoxim-di-*o*-toluidin-kobalt(III)-salze. *Chlorid.* Sechseckige Prismen, ziemlich gut löslich in Wasser und Alkohol. (Gef.: Co, 9.69; H₂O, 12.10. Ber. für [Co(C₇H₇N)₂(DH)₂]Cl, 4H₂O: Co, 9.67; H₂O, 11.80%.)

Bromid. Gelbbraune Säulen, wenig löslich in Wasser. (Gef.: Co, 9.76; H₂O, 3.02. Ber. für [Co(C₇H₇N)₂(DH)₂]Br, H₂O: Co, 9.82; H₂O, 2.99%.)

Jodid. Orangefarbene Nadeln, schwer löslich in Wasser. (Gef.: Co, 9.36; N, 13.00. Ber. für [Co(C₇H₇N)₂(DH)₂]I: Co, 9.38; N, 13.32%.)

Rhodanid. Orangefarbene Nadeln, schwer löslich in Wasser. (Gef.: Co, 10.37; N, 16.87; H₂O, 3.40. Ber. für [Co(C₇H₇N)₂(DH)₂]SCN, H₂O: Co, 10.19; N, 16.90; H₂O, 3.11%.)

Nitrat. Braune Säulen, nicht gut löslich in Wasser und Alkohol. (Gef.: Co, 10.52; N, 17.30. Ber. für [Co(C₇H₇N)₂(DH)₂]NO₃: Co, 10.44; N, 17.35%.)

Saures Sulfat. Braune Prismen, gut löslich in Wasser. (Gef.: Co, 9.40; SO₄, 15.97; N, 13.77; H₂O, 3.04. Ber. für [Co(C₇H₇N)₂(DH)₂]₂SO₄, H₂SO₄, 2H₂O: Co, 9.56; SO₄, 15.35; N, 13.61; H₂O, 2.92%.)

Neutrales Sulfat. Gelbe Nadeln, sehr gut löslich in Wasser. (Gef.: Co, 9.02; N, 12.87; H₂O, 16.59. Ber. für [Co(C₇H₇N)₂(DH)₂]₂SO₄, 12H₂O: Co, 8.96; N, 12.73; H₂O, 16.37%.)

Didimethylglyoxim-di-*p*-toluidin-kobalt(III)-salze. *Chlorid.* Braune Säulen, ziemlich gut löslich in Wasser, wenig in Alkohol und Aceton. (Gef.: Co, 10.68; H₂O, 3.17. Ber. für [Co(C₇H₇N)₂(DH)₂]Cl, H₂O: Co, 10.59; H₂O, 3.24%.)

Bromid. Gelbbraune Nadeln. (Gef.: Co, 10.22. Ber. für [Co(C₇H₇N)₂(DH)₂]Br: Co, 10.12%.)

Jodid. Gelbbraune Nadeln. (Gef.: Co, 9.46; N, 13.53. Ber. für [Co(C₇H₇N)₂(DH)₂]I: Co, 9.37; N, 13.47%.)

*Rhodanid.** Gelbbraune Nadeln. (Gef.: Co, 10.63; N, 17.41. Ber. für [Co(C₇H₇N)₂(DH)₂]SCN: Co, 10.51; N, 17.45%.)

Nitrat. Braune rautenförmige Tafeln, ziemlich gut löslich in Wasser. (Gef.: Co, 10.37. Ber. für [Co(C₇H₇N)₂(DH)₂]NO₃: Co, 10.44%.)

Saures Sulfat. Rotbraune sechseckige Prismen, gut löslich in Wasser. (Gef.: Co, 8.74; SO₄, 17.91; N, 12.01; H₂O, 9.37. Ber. für [Co(C₇H₇N)₂(DH)₂]₂SO₄, 1½H₂SO₄, 7H₂O: Co, 8.59; SO₄, 17.46; N, 12.22; H₂O, 9.11%.)

Neutrales Sulfat. Rotbraune Säulen, sehr gut löslich in Wasser. (Gef.: Co, 9.18; H₂O, 14.35. Ber. für [Co(C₇H₇N)₂(DH)₂]₂SO₄, 10H₂O: Co, 9.20; H₂O, 14.04%.)

Freie Base. Aus der Lösung des Chlorids oder Sulfats der Reihe mit überschüssigem Alkali als gelbbraune flache Säulen erhältlich, schwer löslich in Wasser, wenig in Aceton, gut in Alkohol. (Gef.: Co, 10.70; H₂O, 6.80. Ber. für [Co(C₇H₇N)₂(DH)₂]OH, 2H₂O: Co, 10.61; H₂O, 6.48%.)

Didimethylglyoxim-di-*m*-xylidin-kobalt(III)-salze. *Chlorid.* Braune Säulen, ziemlich gut löslich in Wasser, Alkohol, und Aceton. (Gef.: Co, 9.70; H₂O, 6.25. Ber. für [Co(C₈H₁₁N)₂(DH)₂]Cl, 2H₂O: Co, 9.80; H₂O, 5.98%.)

Bromid. Gelbbraune Nadeln. (Gef.: Co, 9.59; N, 13.56. Ber. für [Co(C₈H₁₁N)₂(DH)₂]Br: Co, 9.66; N, 13.74%.)

Jodid. Gelbbraune Säulen. (Gef.: Co, 8.80; H₂O, 2.66. Ber. für [Co(C₈H₁₁N)₂(DH)₂]I, H₂O: Co, 8.73; H₂O, 2.66%.)

Rhodanid. Gelbbraune Nadeln. (Gef.: Co, 9.84; N, 16.74. Ber. für [Co(C₈H₁₁N)₂(DH)₂]SCN: Co, 10.00; N, 16.63%.)

Nitrat. Braune Prismen. (Gef.: Co, 9.85; H₂O, 3.53. Ber. für [Co(C₈H₁₁N)₂(DH)₂]NO₃, H₂O: Co, 9.66; H₂O, 2.95%.)

Sulfat. Entgegen der allgemeinen Vorschrift kann man dieses Salz direkt aus dem unreinen Sulfat durch Umkristallisieren aus Alkohol und Wasser darstellen. Gelbe Tafeln, sehr gut löslich in Wasser. (Gef.: Co, 9.12; N, 12.98; H₂O, 10.55. Ber. für [Co(C₈H₁₁N)₂(DH)₂]SO₄, 7 1/2 H₂O: Co, 9.13; N, 12.97; H₂O, 10.43%.)

Didimethylglyoxim-di- α -naphthylamin-kobalt(III)-salze. *Chlorid.* Rotbraune Nadeln, ziemlich gut löslich in warmem Wasser. (Gef.: Co, 9.07; H₂O, 5.88. Ber. für [Co(C₁₀H₉N)₂(DH)₂]Cl, 2H₂O: Co, 9.13; H₂O, 5.60%.)

Bromid. Rotbraune Nadelchen. (Gef.: Co, 8.48; H₂O, 6.00. Ber. für [Co(C₁₀H₉N)₂(DH)₂]Br, 2H₂O: Co, 8.53; H₂O, 5.21%.)

Jodid. Rotbraunes Pulver. (Gef.: Co, 8.22; H₂O, 1.63. Ber. für [Co(C₁₀H₉N)₂(DH)₂]I, 1/2 H₂O: Co, 8.30; H₂O, 1.27%.)

Rhodanid. Orangefarbenes Pulver, schwer löslich in Wasser. (Gef.: Co, 9.41; N, 15.57. Ber. für [Co(C₁₀H₉N)₂(DH)₂]SCN: Co, 9.32; N, 15.49%.)

Nitrat. Rotbraune Säulen, wenig löslich in Wasser und Alkohol, praktisch unlöslich in überschüssiges Nitrat enthaltendem Wasser. (Gef.: Co, 8.90; H₂O, 4.28. Ber. für [Co(C₁₀H₉N)₂(DH)₂]NO₃, 1 1/2 H₂O: Co, 8.88; H₂O, 4.07%.)

Saures Sulfat. Rotbraune Nadeln. (Gef.: Co, 8.52; SO₄, 14.40; N, 12.60. Ber. für [Co(C₁₀H₉N)₂(DH)₂]SO₄, H₂SO₄: Co, 8.77; SO₄, 14.27; N, 12.50%.)

Neutrales Sulfat. Rotbraunes Pulver. (Gef.: Co, 8.32; N, 11.93; H₂O, 11.73. Ber. für [Co(C₁₀H₉N)₂(DH)₂]SO₄, 9H₂O: Co, 8.38; N, 11.94; H₂O, 11.51%.)

Didimethylglyoxim-di- β -naphthylamin-kobalt(III)-salze. *Chlorid.* Gelbe Nadeln. (Gef.: Co, 9.33; H₂O, 2.91. Ber. für [Co(C₁₀H₉N)₂(DH)₂]Cl, H₂O: Co, 9.39; H₂O, 2.86%.)

Bromid. Orangefarbene Nadeln. (Gef.: Co, 8.40; H₂O, 8.10. Ber. für [Co(C₁₀H₉N)₂(DH)₂]Br, 3H₂O: Co, 8.32; H₂O, 7.62%.)

Jodid. Braunes Pulver. (Gef.: Co, 8.38; H₂O, 1.27. Ber. für [Co(C₁₀H₉N)₂(DH)₂]I, 1/2 H₂O: Co, 8.30; H₂O, 1.27%.)

Rhodanid. Braune Prismen. (Gef.: Co, 9.20; H₂O, 1.81. Ber. für [Co(C₁₀H₉N)₂(DH)₂]SCN, 1/2 H₂O: Co, 9.19; H₂O, 1.40%.)

Nitrat. Orangefarbene Nadelchen, ziemlich gut löslich in Wasser. (Gef.: Co, 8.40; H₂O 10.65. Ber. für [Co(C₁₀H₉N)₂(DH)₂]NO₃, 4H₂O: Co, 8.32; H₂O, 10.15%.)

Saures Sulfat. Orangefarbene Nadeln. (Gef.: Co, 8.60; SO₄, 13.68; N, 11.97; H₂O, 3.41. Ber. für [Co(C₁₀H₉N)₂(DH)₂]SO₄, H₂SO₄, 2 1/2 H₂O: Co, 8.50; SO₄, 13.80; N, 12.09; H₂O, 3.24%.)

Neutrales Sulfat. Man fällt eine warme Lösung, die auf 10 c.c. Wasser 1 g. des sauren Sulfates enthält, tropfenweise mit etwas weniger der berechneten Menge Natriumkarbonatlösung. Nach dem Erkalten kristallisiert das Salz in gelben Säulen aus. Sehr gut löslich in Wasser. (Gef.: Co, 8.67; H₂O, 9.66. Ber. für [Co(C₁₀H₉N)₂(DH)₂]SO₄, 7H₂O: Co, 8.60; H₂O, 9.18%.)

Freie Base. Erhältlich wie die entsprechende *p*-Toluidinverbindung als schwer lösliche gelbe Schuppen. (Gef.: Co, 9.55; N, 13.69; H₂O, 5.85. Ber. für [Co(C₁₀H₉N)₂(DH)₂]OH, 2H₂O: Co, 9.40; N, 13.36; H₂O, 5.73%.)

Didimethylglyoxim-di-*o*-phenylendiamin-kobalt(III)-chlorid. Man trägt in eine Lösung, die auf 30 c.c. Alkohol 1 g. kristallisiertes Kobaltchlorid und 1 g. Dimethylgly-

oxim enthält, 1 g. *o*-Phenylendiamin ein, und oxydiert das Gemisch mit Luft. Das ausgeschiedene Salz wird aus Wasser umkristallisiert. Es bildet in Wasser sehr gut lösliche, schwarzbraune Kristalle. In konzentrierte Schwefelsäure eingeworfen, schäumt es heftig als Kennzeichen eines echten Chlorides. (Gef.: Co, 9.74; N, 18.63; H₂O, 11.89. Ber. für [Coph₂(DH)₂]Cl₂·4H₂O: Co, 9.63; N, 18.30; H₂O, 11.76%.)

Chloro-didimethylglyoxim-*o*-phenylendiamin-kobalt(III). Nach Zusatz von 0.4 g. *o*-Phenylendiamin und 2 c.c. norm. Ätznatron zu 20 c.c. Alkohol, der 1 g. kristallisiertes Kobaltchlorid und 1 g. Dimethylglyoxim gelöst enthält, leitet man in die Lösung sehr lange Luft ein. Die erhaltene Kristalle werden mit etwas Wasser gewaschen und aus Methanol umkristallisiert. Rotbraune Tafeln, schwer löslich in Wasser, ziemlich gut in Alkohol. Reaktion mit konzentrierter Schwefelsäure zeigt, dass das Salz kein ionogenes Chlor enthält. Bei der trockenen Destillation gibt das Destillat die Jodoformreaktion. (Gef.: Co, 12.23; Cl, 7.82; C₂H₅OH, 9.53. Ber. für [Coph(DH)₂]Cl, C₂H₅OH: Co, 12.22; Cl, 7.42; C₂H₅OH, 9.61%.)

Didimethylglyoxim-aquo-*o*-phenylendiamin-kobalt(II)-chlorid. Man löst 0.5 g. frisch entwässertes Kobaltchlorid und 1.2 g. Dimethylglyoxim in 20 c.c. völlig wasserfreiem Aceton, fügt dazu 0.4 g. in wenig wasserfreiem Aceton gelöstes *o*-Phenylendiamin. Reibt man einige Zeit die Gefäßwand, so scheiden sich gelbe Nadeln mit guter Ausbeute aus, die in Methanol gelöst und unter Zusatz von Äther gefällt werden können. Sehr gut löslich in Alkohol, schwer löslich in Wasser, jedoch mit deutlich saurer Reaktion. Durch Säuren sofort zersetzbar; reagiert mit konzentrierter Schwefelsäure als echtes Chlorid. Mittels der Jodoformreaktion ist Aceton nachweisbar. (Gef.: Co, 10.73; Cl, 12.82; N, 15.33. Ber. für [Coph(DH₂)₂(OH₂)]Cl₂, CH₃·CO·CH₃: Co, 10.80; Cl, 13.00; N, 15.36%.)

Zusammenfassung.

Komplexsalze der allgemeinen Formel [CoA₂(DH)₂]X, in denen A Ammoniak, Anilin, *o*- und *p*-Toluidin, *m*-Xylidin, bzw. *α*- und *β*-Naphthylamin, und X Cl, Br, J, SCN, NO₃ bzw. 1/2SO₄ ist, wurden dargestellt. Gleichzeitig wurden einige verwandte Verbindungen dargestellt.

Es wurde gezeigt, dass, wenn *o*-Phenylendiamin als A gebraucht wird, dieses zweiwertige Amin nie als zweizähliger Ligand reagiert, sondern immer einzählig ist, woraus wir schlossen, dass zwei Dimethylglyoximreste in den Komplexsalzen sehr fest plan konfigurieren müssen.

Herrn S. Murayama sind wir für seine Hilfe bei dieser Arbeit zu herzlichem Dank verpflichtet.

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DIE GESCHWINDIGKEIT DER AUSTAUSCHREAKTION DER WASSERSTOFFATOME ZWISCHEN ZUCKER UND WASSER.

(Vorläufige Mitteilung.)

Von Masao HARADA und Toshizo TITANI.

Eingegangen am 20. Januar 1936. Ausgegeben am 28. Februar 1936.

Die Austauschbarkeit der H-Atome in den OH-Radikalen von Zucker und Wasser wurde zuerst von Bonhoeffer und Brown entdeckt.⁽¹⁾ Und später wurde das Gleichgewicht dieser Austauschreaktion von Hamill und Freudenberg⁽²⁾ eingehend untersucht. Ähnliche Versuche führten wir auch aus, um die Verteilung von D-Atomen zwischen einigen Hexosen und schwerem Wasser zu untersuchen. Aber dabei schien es uns notwendig zuerst von der Geschwindigkeit der betreffenden Reaktion Kenntnis zu gewinnen. In dieser Hinsicht haben wir ein Experiment durchgeführt, dessen Ergebnisse wir vorläufig mitteilen wollen.

Zuerst wurde eine Lösung aus 2 bis 3 g. Glukose und 2 g. gewöhnlichem Wasser bzw. 1.5 N H_2SO_4 oder 1.5 N NaOH in einem mit Schliffmündung versehenen Glasrohr hergestellt. Die so bereitete neutrale, saure oder alkalische Lösung von Glukose wurde dann mit 1 c.c. von 5 prozentigem schweren Wasser versetzt und schnell vermischt. Unmittelbar darauf wurde das Glasrohr mittels des Glasschliffs an einer Vakuumdestillationsanordnung angesetzt, und 50 bis 100 mg. Wasser wurde aus der Lösung in das andere Glasröhrchen schnell abdestilliert. Dazu war durchschnittlich eine Minute erforderlich. Die so abdestillierte Wasserprobe wurde zur Dichtebestimmung gesondert aufbewahrt. Dann wurde die Abdestillation kleiner Mengen von Wasser aus derselben Lösung drei bis fünf Mal bei verschiedenen Zeiten nach der Vermischung sukzessiv wiederholt. Die letzte Probe wurde entsprechend dem Gleichgewichtszustand mindestens nach 24 Stunden vorgenommen. Die so gesammelten Wasserproben wurden separat je durch zweimalige Destillation gereinigt. Dann wurde ihre Dichte durch die Schwebemethode mittels eines kleinen Glasschwimmers bestimmt und miteinander verglichen.

(1) K. F. Bonhoeffer und G. W. Brown, *Z. physik. Chem.*, B, **23** (1933), 171.

(2) W. H. Hamill und W. Freudenberg, *J. Am. Chem. Soc.*, **57** (1935), 1427.

Aus diesem Experiment ergaben sich die folgenden Tatsachen:

(1). Das Wasser, das innerhalb einer Minute, der kürzesten Zeit die wir erreichen konnten, nach der Vermischung aus der Glukose-Lösung durch die Destillation gewonnen wurde, besass innerhalb des Messfehlers genau dieselbe Dichte wie die des Wassers, das nach mehr als 24 Stunden aus derselben Lösung abdestilliert wurde. Daraus ersieht man sofort, dass das Austauschgleichgewicht zwischen Glukose und Wasser mindestens innerhalb einer Minute erreicht wird.

(2). Wir erhielten immer dasselbe Resultat ohne Unterschied, ob wir die neutrale, saure oder alkalische Lösung der Glukose benutzten. Daher vermuten wir, dass die Austauschreaktion zwischen Glukose und Wasser sehr schnell vor sich geht.

Wir haben das Experiment auch mit Fruktose durchgeführt. Aber die Resultate erwiesen sich als genau dieselben wie oben. Die eben gefundenen Verhältnisse müssen beim Versuch über das Austauschgleichgewicht zwischen Zucker, oder vermutlich auch anderen ähnlichen organischen Verbindungen, und schwerem Wasser, besonders beim Abtrennen der Verbindungen von Wasser, in Betracht gezogen werden.

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ON THE VISCOSITY OF THE CRITICAL MIXTURE OF TERNARY SYSTEM BENZENE-ALCOHOL-WATER.

By Osamu KIMURA.

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Introduction. It is a well-known phenomenon that a liquid shows critical opalescence at its critical state. Two component system also shows this phenomenon and there are numerous investigations⁽¹⁾ on this problem. The author has studied colloid-chemically on the three component system of organic solvents⁽²⁾. The optical method seems to be superior, but from the standpoint of colloid chemistry, the viscometric method is one of the most usefull methods for studying the liquid of colloidal nature. In this paper the viscosity of three component system is measured at its critical state and some discussions concerning the colloidal properties of critical mixture are described.

Experimental. The three component system benzene-ethanol-water has been studied by the author and reported in a previous paper⁽²⁾. This system is the most familiar and the materials are easily purified. Recently the viscosity of this system was measured by Pestemer⁽³⁾, but he paid no attention to the colloidal nature at the critical state. This system shows critical opalescence at a certain temperature and composition, and when the temperature is raised, the intensity of opalescence becomes weak by and by, and at last the opalescence disappears and the total system becomes homogeneous. It must be noticed that this state which shows critical opalescence is very stable and does not change for long time if the temperature is maintained constant. The viscosity has been measured following this stadium at various temperatures. The apparatus used is a modified type of Ostwald viscosimeter, which is shown in Fig. 1.

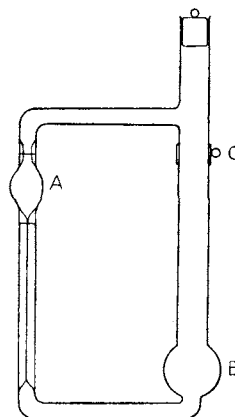


Fig. 1.

Even a slight vaporisation of a component affects the state of the system markedly, so that after pouring the liquid in viscosimeter the inlet tube is

(1) J. Friedländer, *Z. physik. Chem.*, **38** (1901), 435. V. Rothmund, *Z. physik. Chem.*, **63** (1908), 54. Wo. Ostwald, *Ann. Phys.*, (4), **36** (1911), 848.

(2) N. Sata and O. Kimura, this Bulletin, **10** (1935), 409.

(3) M. Pestemer, *Kolloid-Z.*, **65** (1933), 25.

sealed. The total apparatus is dipped in a thermostat, the temperature of which is changeable. To measure the viscosity the apparatus is rotated in left hand, C being the axis of rotation, so that the liquid in B fills the bulb A. Then it is again rotated reversely and the apparatus is fixed vertical. The transpiration time of liquid between two marks is measured by a stopwatch. On the other hand the density of the liquid is measured by Ostwald pycnometer and the viscosity is calculated. The viscosity was measured on five series of different compositions, of which three systems showed critical opalescence, and the other two did not. The compositions of these five systems are shown in Table 1, and graphically in Fig. 2. The temperature is varied from homogeneous domain to the critical point.

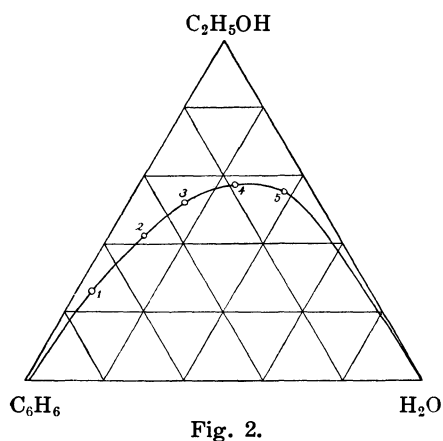


Table 1. Compositions of Five Systems in Volume Percent.

System	Ben- zene	Ethanol	Water	Remarks
1	70.3	26.2	3.5	shows opalescence
2	48.3	42.3	9.4	„
3	33.7	52.2	14.1	„
4	18.1	57.6	24.3	no opalescence
5	7.2	55.7	37.1	„

Results and Discussion. The experimental results are shown graphically in Fig. 3. It is seen that the viscosity-temperature curve has a gentle slope in homogeneous region and a steep one in the region which shows opalescence. This sudden increase of viscosity in critical region was pointed out by Friedländer and Rothmund, but the reason of this increase was not discussed. It may be easily supposed that this sudden increase of viscosity is caused by the existence of colloidal particles which are the small droplets of benzene covered with thin film of alcohol, as was reported in the previous paper. Moreover this conception is confirmed by the experimental data that the viscosity-temperature curve of the system which shows no opalescence (i.e. there is no colloidal region) has gentle slope, while that of the system which shows opalescence is very steep in colloidal region. To show this more quantitatively some considerations have been made.

Concerning viscosity-temperature relation, there are numerous formulas theoretical and empirical. Among these Andrade's formula⁽⁴⁾ is an excellent

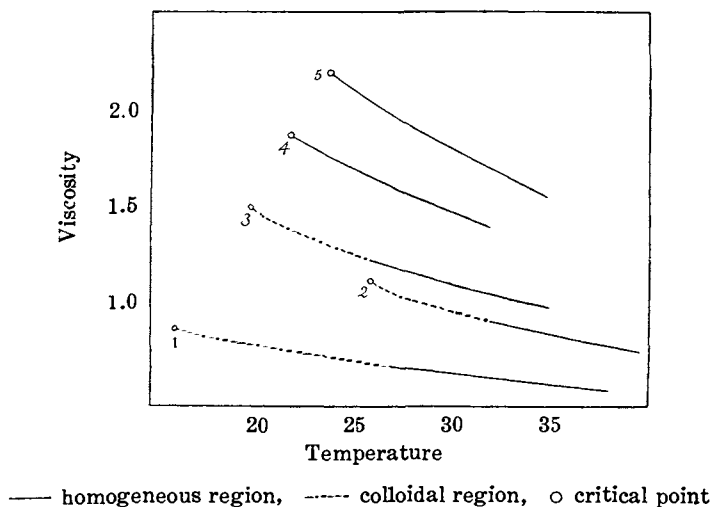


Fig. 3.

one because it is very simple and contains only two constants and furthermore it is applicable to wide range of temperature and many substances. The formula is as follows :

$$\eta = Ae^{b/T},$$

where A and b are constants, and T is the absolute temperature.

The formula was applied to the homogeneous region determining the two constants by means of the least square. The formula is highly applicable to the homogeneous region within the deviation of 0.5%. But when it is extrapolated in the colloidal region, the deviation from calculated values is remarkable and the nearer the critical point the greater the deviations. To the system which shows no opalescence it is applicable up to the critical point. This deviation is, as already explained due to colloidal nature (i.e. emulsion) of the system.

For the viscosity-concentration relation of emulsion Hatschek presented following formula :

(4) C. Andrade, *Nature*, **125** (1930), 309.

$$\eta = \eta_m \frac{1}{1 - \sqrt[3]{\phi}},$$

where η is the viscosity of emulsion, η_m that of medium, ϕ the volume of dispersed phase in unit volume of emulsion. This formula was verified experimentally by many investigators, and among those Sibree⁽⁵⁾ has carefully measured the viscosity of emulsions and concluded that Hatschek's formula is applicable to many types of emulsion very satisfactorily if not strictly. If this formula can be applied to this case, the concentration of emulsion is cal-

Table 2. System 1.

°C.	t (sec.)	d	$\eta_{\text{obs.}}$	$\eta_{\text{calc.}}$	$\Delta \eta$	ϕ
38.0	54.3	0.8403	0.5836	0.5836	0.0000	
37.0	55.2	0.8413	0.5940	0.5931	+0.0009	
36.0	55.9	0.8422	0.6021	0.6028	-0.0007	
35.0	56.7	0.8432	0.6115	0.6129	-0.0014	
34.0	57.7	0.8441	0.6229	0.6230	-0.0001	
33.0	58.7	0.8451	0.6345	0.6334	+0.0009	
32.0	59.5	0.8461	0.6438	0.6450	-0.0012	
31.0	60.5	0.8470	0.6554	0.6551	+0.0003	
30.0	61.5	0.8479	0.6670	0.6662	+0.0008	
29.0	62.5	0.8489	0.6786	0.6784	+0.0002	
28.0	63.5	0.8498	0.6902	0.6896	+0.0006	
27.0	64.5	0.8508	0.7002	0.7017	-0.0015	
26.0	65.5	0.8517	0.7135	0.7140	0.0005	0.000005
25.0	67.0	0.8527	0.7307	0.7265	0.0042	0.00004
24.0	68.0	0.8536	0.7414	0.7390	0.0024	0.00002
23.0	69.3	0.8546	0.7574	0.7527	0.0047	0.00005
22.0	70.8	0.8556	0.7747	0.7662	0.0085	0.00009
21.0	72.2	0.8565	0.7909	0.7802	0.0107	0.00011
20.0	73.7	0.8575	0.8083	0.7945	0.0138	0.00014
19.0	75.0	0.8584	0.8234	0.8090	0.0144	0.00014
18.0	76.5	0.8594	0.8409	0.8241	0.0168	0.00017
17.0	78.4	0.8603	0.8626	0.8393	0.0233	0.00023
16.3	79.6	0.8610	0.8765	0.8504	0.0261	0.00026
16.0	critical point					

(5) J. O. Sibree, *Trans. Faraday Soc.*, **26** (1930), 104; **27** (1931), 161.

Table 3. System 2.

°C.	t (sec.)	d	$\eta_{\text{obs.}}$	$\eta_{\text{calc.}}$	$\Delta \eta$	ϕ
40.0	71.4	0.8398	0.7669	0.7673	-0.0004	
39.0	73.0	0.8408	0.7850	0.7852	-0.0002	
38.0	74.7	0.8418	0.8042	0.8037	+0.0005	
37.0	76.3	0.8428	0.8224	0.8227	-0.0003	
36.0	78.1	0.8439	0.8430	0.8422	+0.0008	
35.0	79.7	0.8449	0.8613	0.8627	-0.0014	
34.0	81.7	0.8459	0.8839	0.8834	+0.0005	
33.0	83.6	0.8469	0.9055	0.9048	+0.0007	
32.0	85.5	0.8479	0.9272	0.9272	+0.0000	
31.0	88.0	0.8489	0.9554	0.9500	+0.0054	0.0000001
30.0	91.4	0.8499	0.9985	0.9734	+0.0201	0.0000087
29.0	93.1	0.8510	1.012	0.9993	+0.013	0.0000022
28.0	95.8	0.8520	1.044	1.023	+0.011	0.0000013
27.0	99.0	0.8530	1.080	1.049	+0.031	0.0000026
26.0	103.8	0.8540	1.134	1.076	+0.058	0.00016*
25.0	critical point					

Table 4. System 3.

°C.	t (sec.)	d	$\eta_{\text{obs.}}$	$\eta_{\text{calc.}}$	$\Delta \eta$	ϕ
35.0	92.4	0.8451	0.9987	0.9992	-0.001	
34.0	94.4	0.8461	1.022	1.022	0.000	
33.0	96.6	0.8471	1.047	1.046	+0.001	
32.0	98.7	0.8481	1.071	1.071	0.000	
31.0	101.0	0.8491	1.097	1.097	0.000	
30.0	103.2	0.8501	1.122	1.123	-0.001	
29.0	105.7	0.8511	1.151	1.151	0.000	
28.0	108.2	0.8521	1.176	1.178	-0.002	
27.0	110.8	0.8531	1.209	1.207	+0.002	
26.0	113.4	0.8541	1.239	1.236	+0.003	
25.0	116.8	0.8551	1.277	1.267	+0.010	0.0000005
24.0	120.0	0.8560	1.314	1.297	+0.017	0.0000002
23.0	123.2	0.8570	1.350	1.331	+0.019	0.0000003
22.0	126.7	0.8580	1.390	1.364	+0.026	0.0000007
21.0	130.4	0.8589	1.432	1.399	+0.033	0.0000013
20.0	136.8	0.8599	1.505	1.435	+0.070	0.000116
19.5	critical point					

Table 5. System 4.

°C.	t (sec.)	d	$\eta_{\text{obs.}}$	$\eta_{\text{calc.}}$	$\Delta \eta$
32.0	126.7	0.8646	1.401	1.401	0.000
31.0	130.3	0.8655	1.442	1.440	+0.002
30.0	134.0	0.8664	1.485	1.481	+0.004
29.0	137.4	0.8673	1.524	1.526	-0.002
28.0	141.1	0.8682	1.567	1.567	0.000
27.0	145.1	0.8691	1.613	1.613	0.000
26.0	148.9	0.8700	1.657	1.660	-0.003
25.0	153.3	0.8709	1.708	1.709	-0.001
24.0	157.7	0.8718	1.758	1.757	+0.001
23.0	162.2	0.8727	1.811	1.811	0.000
22.0	167.0	0.8736	1.866	1.866	0.000
21.0	critical point				

Table 6. System 5.

°C.	t (sec.)	d	$\eta_{\text{obs.}}$	$\eta_{\text{calc.}}$	$\Delta \eta$
35.0	136.0	0.8917	1.551	1.555	-0.004
34.0	140.0	0.8926	1.598	1.601	-0.003
33.0	144.4	0.8934	1.650	1.651	-0.001
32.0	149.0	0.8943	1.704	1.700	+0.004
31.0	153.2	0.8952	1.754	1.752	+0.002
30.0	157.6	0.8960	1.806	1.805	+0.001
29.0	162.1	0.8969	1.859	1.865	-0.006
28.0	166.8	0.8977	1.915	1.920	-0.005
27.0	172.4	0.8986	1.981	1.980	+0.001
26.0	177.2	0.8994	2.038	2.043	-0.005
25.0	183.2	0.9003	2.110	2.108	+0.003
24.0	189.3	0.9012	2.182	2.173	+0.009
23.0	critical point				

culated as follows. In the formula η is the viscosity of emulsion which is the observed viscosity in this case, and η_m is the viscosity of medium, which can be calculated from Andrade's formula. Then we obtain

$$\phi = \left(\frac{\eta - \eta_m}{\eta} \right)^3 = \left(\frac{\Delta \eta}{\eta} \right)^3.$$

Thus the values of ϕ were calculated for three systems which showed critical opalescence. These values are illustrated in Table 2, 3, 4, 5, and 6. In the tables the 1st column is the temperature in centigrade, the 2nd the time of transpiration between two marks, the 3rd the density, the 4th the observed viscosity, in centipoise, the 5th the viscosity calculated by using Andrade's formula, the 6th the difference between observed and calculated viscosities, and the 7th the concentration calculated from Hatschek's formula.

It is seen from the tables that the concentration of colloid particles which are supposed to be the droplets of benzene covered with thin film of alcohol is of the order of 0.0001 near the critical point and decreases as the temperature is raised. There may be some relations between the concentration and the intensity of opalescence, which also shows maximum at critical point and decreases as the temperature is raised. The experiment on this line is now in course.

Summary.

(1) The viscosity of the three component system benzene-ethanol-water was measured in the neighbourhood of critical point.

(2) To the homogeneous region Andrade's formula is strictly applicable but not to the colloidal region. This deviation is caused by the existence of colloid particles.

(3) The concentration of colloid particles was calculated by using Hatschek's formula, and it was of the order of 0.0001 near the critical point.

The author expresses his sincere thanks to Prof. N. Sata, at whose suggestion this work has been carried out.

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

By Tetsuya ISHIKAWA and Toshitomo BABA.

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The probable values of the normal K relative to that of benzene. Before closing this series of the viscosity study,⁽¹⁾ we will consult as much as available data found in the literature in order to have the probable values of the normal K .

Mixtures adopted here are (1) those the viscosity curves of which are convex or quite rarely concave towards the composition axis, and (2) these both component K 's of which in accord with Ishikawa's theory have already been known, although they indicate viscosity maxima or minima.

The following notations will be used :

K signifies the ratio of the characteristic constant (ka) of component 2 to that of component 1 in formula (1) for chemically indifferent mixtures :

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

This normal case is simply denoted by the symbol n .

In the course of the calculation we have met with cases in which K 's slightly vary as concentration, and either of the extrapolated values of K at $z_m = 0$ or $z_m = 1$ if taken much differs from the probable value of the normal K . Such anomaly is observed in the following mixtures: Acetone-*i*-propyl alcohol, carbon tetrachloride-tetrachloroethane, &c. However, further tests for these mixtures prove that they must be classified into the following case.

K' and K'' denote the ratios of the characteristic constant (ka) of component 2 to that of component 1 and that of component 1 to that of component 2 respectively, more or less differing from K and $1/K$ in formula (1) or $K'K'' > 1$ as a result of anomalous changes in molecular association :

(1) This Bulletin, **4** (1929), 5, 25, 149, 288; **5** (1930), 47, 117; **8** (1933), 280, 293; **9** (1934), 155; **10** (1935), 153, 248; **11** (1936), 8.

$$\eta = \frac{\eta_1}{1 + K' \frac{z_m}{1 - z_m}} + \frac{\eta_2}{1 + K'' \frac{1 - z_m}{z_m}} \quad (2).$$

This formula for anomalous change in association on mixing holds true for the concentration range between the two extremities close to $z_m = 0$ and $z_m = 1$, where the numbers of molecules of one component become quite enough to change its original association into some other associations statistically at extremely low concentration and at extremely high concentration diluted with the other component. This anomalous case is abbreviated by the symbol a.

For the case in which the association degree of a component varies as dilution with the other, the extrapolated value of K at $z_m = 0$ or $z_m = 1$ gives the normal K for the mixture. The mixtures of phenol, guaiacol, or benzyl benzoate with benzene or toluene in which the former components suffer molecular dissociation are examples of this case. The formulation of the viscosity-composition curves of such mixtures cannot be generally done, since the decreasing rate of the association degree with dilution depends upon its own peculiarity of the associated component against the solvating action of the other component, yet a particular case can be solved with a particular means, say, taking K or its reciprocal at each composition for test whether they are in a linear relationship with composition or not. This variable case (3) is briefly denoted by the symbol v, and both extrapolated values at $z_m = 0$ and $z_m = 1$ are written thus: e.g. 0.087-0.227 for C_6H_6 (1)- C_6H_5OH (2).

The mixture phenol-dimethylaniline is considered as one more example of the case. The viscosity-composition curves observed by Bramley at the temperatures between 10° and $180^\circ C.$ are sinuous nature as seen from Fig. 1 in which the points are the observed viscosities. Simply judging from the curves, one may imagine, as Bramley does, that the mixture appears to have a compound, but the freezing-point curve consists of two branches only, the eutectic temperature being found to be $-36.0^\circ C.$ according to Bramley.⁽²⁾ Once when we take, however, K as ordinate and z_m as abscissa, we readily see that the points at each temperature lie on a straight line. This fact shows that there occurs the molecular dissociation of phenol but no molecular compound just as the freezing-point diagram requires. The curves in Fig. 1 are traced on thus calculated viscosities (see Table 1).

(2) A. Bramley, *J. Chem. Soc.*, **109** (1916), 469.

Table 1. Phenol—Dimethylaniline, (Bramley).

z_m	10°C.		z_m	29.8°C.		59.9°C.	
	$\eta_{\text{obs.}}$	$\eta_{\text{calc.}}$		$\eta_{\text{obs.}}$	$\eta_{\text{calc.}}$	$\eta_{\text{obs.}}$	$\eta_{\text{calc.}}$
0.0000	0.2010	—	0.0000	0.0709	—	0.02530	—
0.0571	0.1964	0.1946	0.0537	0.0686	0.0687	0.02665	0.02473
0.1173	0.1850	0.1801	0.1116	0.0648	0.0650	0.02380	0.02387
0.1785	0.1639	0.1596	0.1726	0.06025	0.06003	0.02270	0.02274
0.2500	0.1347	0.1327	0.2409	0.05325	0.05352	0.02100	0.02124
0.3149	0.1094	0.1092	0.3046	0.04705	0.04721	0.01960	0.01972
0.3815	0.0869	0.0881	0.3778	0.0393	0.04025	0.01760	0.01790
0.4542	0.0696	0.0693	0.4452	0.0333	0.03448	0.01587	0.01627
0.5340	0.05315	0.0535	0.5231	0.0283	0.02373	0.01428	0.01451
0.6110	0.04185	0.0421	0.6151	0.02315	0.02335	0.01267	0.01268
0.7115	0.03145	0.0317	0.7042	0.01936	0.01928	0.01123	0.01118
0.7879	0.02586	0.0259	0.7960	0.01629	0.01616	0.01001	0.00992
0.8861	0.02076	0.0207	0.9001	0.01351	0.01356	0.00878	0.00881
1.0000	0.01654	—	1.0000	0.01173	—	0.00799	—

$$K = 0.25 + 6.05 z_m.$$

$$K = 0.50 + 3.36 z_m.$$

$$K = 0.50 + 1.93 z_m.$$

Table 2. Acetone—Phenol, (Bramley).

z_m	9.95°C.		20.05°C.	
	$\eta_{\text{obs.}}$	$\eta_{\text{calc.}}$	$\eta_{\text{obs.}}$	$\eta_{\text{calc.}}$
0.0000	0.00360	—	0.00323	—
0.0926	0.00486	0.00486	0.00429	0.00432
0.1837	0.00635	0.00636	0.00560	0.00559
0.2749	0.00868	0.00873	0.00755	0.00752
0.3761	0.01256	0.01265	0.01055	0.01061
0.4580	0.01688	0.01683	0.01379	0.01402
0.5363	0.02358	0.02338	0.01853	0.01828
0.6340	0.03670	0.03722	0.02750	0.0273
0.6982	0.0495	0.0501	0.0359	0.0357
0.7829	0.0748	0.0736	0.0497	0.0500
0.8890	0.1193	0.1194	0.0730	0.0745
1.0000	0.2010	—	0.1104	—

$$K = 0.063 (z_m = 0.0-0.20);$$

$$K = 0.0485 + 0.079 z_m$$

$$K = -0.026 + 0.228 z_m$$

$$K = 0.100 (z_m = 0.0-0.20);$$

$$K = 0.077 + 0.120 z_m$$

$$K = -0.033 + 0.316 z_m$$

$$(z_m = 0.20-0.55);$$

$$(z_m = 0.20-0.55);$$

$$(z_m = 0.55-1.0).$$

Table 2. (Concluded)

z_m	29.8°C.		40.1°C.		49.8°C.	
	$\eta_{\text{obs.}}$	$\eta_{\text{calc.}}$	$\eta_{\text{obs.}}$	$\eta_{\text{calc.}}$	$\eta_{\text{obs.}}$	$\eta_{\text{calc.}}$
0.0000	0.002950	—	0.002700	—	0.002480	—
0.0613	0.003599	0.003596	0.003279	0.003273	0.002990	0.002980
0.1302	0.004409	0.004414	0.003991	0.003987	0.003599	0.003604
0.1912	0.005212	0.005233	0.004700	0.004698	0.004219	0.004216
0.2695	0.00670	0.00656	0.005899	0.005756	0.005299	0.005133
0.3324	0.00808	0.00805	0.00711	0.00698	0.006281	0.006177
0.4179	0.01058	0.01065	0.00904	0.00908	0.00794	0.00794
0.4832	0.01319	0.01321	0.01101	0.01105	0.00950	0.00956
0.5581	0.01658	0.01682	0.01362	0.01384	0.01149	0.01175
0.6401	0.02179	0.02188	0.01742	0.01759	0.01425	0.01459
0.7213	0.02747	0.02838	0.02232	0.02219	0.01786	0.01768
0.8187	0.03922	0.03886	0.02874	0.02911	0.02247	0.02246
0.8880	0.04902	0.04873	0.03460	0.03516	0.02618	0.02615
1.0000	0.07092	—	0.04739	—	0.03279	—

$$K = 0.147$$

$$(z_m = 0.0-0.20);$$

$$K = 0.105 + 0.175 z_m$$

$$(z_m = 0.20-1.0).$$

$$K = 0.198$$

$$(z_m = 0.0-0.20);$$

$$K = 0.140 + 0.220 z_m$$

$$(z_m = 0.20-1.0).$$

$$K = 0.257$$

$$(z_m = 0.0-0.20);$$

$$K = 0.177 + 0.308 z_m$$

$$(z_m = 0.20-1.0).$$

Another example of this case in which K sometimes occurs to be composed of two or more sets of linear functions of z_m suggests the molecular dissociation of one component in two or more stages. For a good example the mixture of phenol (2) with acetone (1) measured by Bramley will be adopted here. Fig. 2 shows the K 's plotted against the composition, in which we make distinct classifications of the points in three sets of straight lines at 10° and 20°C., and in two sets at 30° and higher temperatures. In Table 2 $\eta_{\text{calc.}}$ are obtained by assuming these sets of linear relationship of K with composition. As judged from the numerical values of the cutting points of the elongations of these sets of lines at each temperature at phenol-pure axis, the degradation of phenol-associated molecules is well explained if we assume that the phenol in its pure state consists mainly of trimol at low temperatures and of dimol at high temperatures; that is, of the three sets at low temperatures the first phenol-rich set indicates the coexistence of trimol and dimol, the second the coexistence of dimol and monomol, and the third the existence of monomol only, whereas at higher temperatures the first set at phenol-rich solutions shows the coexistence of dimol and monomol, and the second the existence of monomol only, all in equilibrium with acetone molecules. The above elucidation

tion, though it indicates no appreciable presence of a molecular compound, yet the presence of dynamic equilibrium of dimol and monomol whose relative

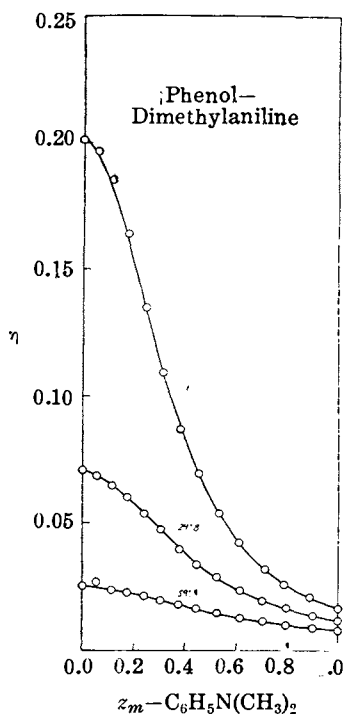


Fig. 1.

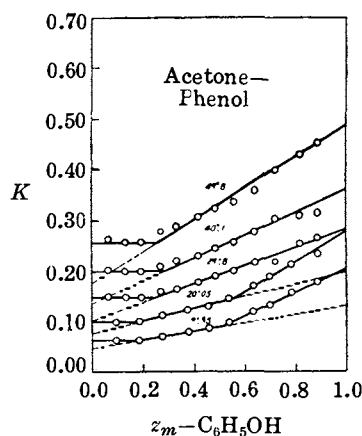


Fig. 2.

amounts to each other are nearly independent of temperature, is affirmative to the melting-point diagram observed by Schmidlin and Lang⁽³⁾ which records a greatly dissociated molecular compound $(\text{CH}_3)_2\text{CO} \cdot 2\text{C}_6\text{H}_5\text{OH}$ melting at 15°C .

ν_1 and ν_2 signify the molecular numbers of components 1 and 2 in the molecular compound in accord with formula (4):

$$\eta = \frac{\eta_1}{1 + K \frac{z_m}{1 - z_m}} + \frac{\eta_2}{1 + \frac{1}{K} \frac{1 - z_m}{z_m}} + C_0 (\eta_1^{\nu_1} \eta_2^{\nu_2})^{\frac{m}{\nu_1 + \nu_2}} (1 - z_m)^{\nu_1} z_m^{\nu_2} \quad (4),$$

where C_0 and m are constants independent of the temperature and concentration. This case in which a compound occurs is denoted by the symbol c ($\nu_1 : \nu_2$).

(3) J. Schmidlin and R. Lang, *Ber.*, **43** (1910), 2812.

An interesting system for case (4) is the water-pyridine mixture. The solvation viscosity $\delta = \eta - \eta_0$ of this mixture at 0° and 25°C. appears to consist of two terms up to 30 mol % pyridine, i.e. it is not simply proportional to $(1-z_m)^3 z_m$ or $(1-z_m)^2 z_m$, but it corresponds to the sum of some or other

Table 3. Water-Pyridine, (Hartley, Thomas, and Applebey).

0°C.

z_m	η	η_0	δ	$\delta_{\text{calc.}}$	$\eta_{\text{calc.}}$
0.0000	0.01778	—	0.00683	0.00672	—
0.0236	0.02448	0.01765	1471	1482	0.02437
0.0564	0.03218	0.01747	2110	2122	0.03229
0.0872	0.03840	0.01730	2841	2825	0.03852
0.1306	0.04548	0.01707	3468	3461	0.04532
0.1847	0.05147	0.01679	3875	3860	0.05140
0.2483	0.05521	0.01646	3927	3929	0.05506
0.2713	0.05562	0.01635	3939	3965	0.05564
0.2985	0.05560	0.01621	3939	3806	0.05586
0.3462	0.05416	0.01598	3818	3309	0.05404
0.4159	0.04905	0.01564	3341	2766	0.04873
0.4780	0.04262	0.01535	2727	1844	0.04301
0.5789	0.03298	0.01489	1899	1080	0.03333
0.6746	0.02398	0.01446	952	338	0.02526
0.8159	0.01729	0.01385	344	103	0.01723
0.9117	0.01463	0.01346	117	—	0.01449
1.0000	0.01321	—	—	—	—

 $K = 1.19.$

25°C.

z_m	η	η_0	δ	$\delta_{\text{calc.}}$	$\eta_{\text{calc.}}$
0.0000	0.00890	—	0.00226	0.00222	—
0.0240	0.01116	0.00890	446	446	0.01112
0.0515	0.01336	0.00890	708	705	0.01336
0.0890	0.01598	0.00890	944	936	0.01595
0.1312	0.01833	0.00889	1143	1142	0.01825
0.1840	0.02032	0.00889	1298	1293	0.02031
0.2522	0.02187	0.00889	1337	1334	0.02182
0.3127	0.02225	0.00888	1298	1318	0.02222
0.3450	0.02186	0.00888	1007	994	0.02206
0.4780	0.01894	0.00887	463	447	0.01881
0.6730	0.01350	0.00887	178	180	0.01334
0.8126	0.01064	0.00886	93	92	0.01066
0.8864	0.00979	0.00886	57	64	0.00978
0.9186	0.00942	0.00885	32	32	0.00949
0.9576	0.00917	0.00885	—	—	0.00917
1.0000	0.00885	—	—	—	—

 $K = 1.19.$

multiples of these concentration factors, which phenomenon undoubtedly shows the coexistence of $C_5H_5N \cdot 3H_2O$ and $C_5H_5N \cdot 2H_2O$ in solution for the concentration range. For higher concentrations up to more than 90 mol % pyridine a set of hydrates $C_5H_5N \cdot 3H_2O$ and $C_5H_5N \cdot H_2O$ exists, of which the former greatly predominates, but the dihydrate disappears.

Baud⁽⁴⁾ has determined the freezing points of the system but found no decisive hydrates owing to the existence of hidden maxima. He also points out that the volume contraction maximum occurs at 30 mol % pyridine corresponding to $C_5H_5N \cdot 2.3H_2O$, whereas Pariselle⁽⁵⁾ has observed that the density maxima at 17° and 25°C. correspond to $C_5H_5N \cdot 3H_2O$ and $C_5H_5N \cdot 3.3H_2O$ respectively. However, if we consider the volume contraction per gram at 0°, 25°, and 50°C. from the density measurements done by Faust,⁽⁶⁾ the points of maximum at these temperatures nearly lie at the same composition probably corresponding to $C_5H_5N \cdot 2.3H_2O$. These results may be fairly understood from the present study that the two hydrates $C_5H_5N \cdot 3H_2O$ and $C_5H_5N \cdot 2H_2O$ coexist in solution, and the former is more stable than the latter as clearly recognized from the concentration ranges of their existence (see Table 3) and also from the amounts of m , the stability coefficient, of these compounds, m of the former being estimated to be 2.4 up to 30 mol % and 1.8 up to more than 90 mol % or in the mean 2.1, while m of the latter to be 1.6 between 0 and 30 mol %.

Fig. 3 shows how the theoretical and observed viscosities compare graphically.

It rarely happens that anomalous change occurs in association and thence follows a further chemical change to form a molecular compound. For such a case, the formula in combination of formula (2) with the second term of formula (4) may suffice to express the nature of the viscosity-composition curve. Mixtures as that of formamide with *i*-butyl alcohol or with *i*-amyl

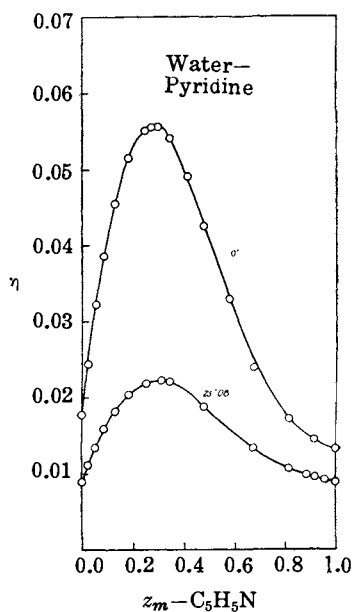


Fig. 3.

(4) E. Baud, *Bull. soc. chim.*, [4], **5** (1909), 1022.

(5) Pariselle, *Compt. rend.*, **172** (1921), 673.

(6) O. Faust, *Z. physik. Chem.*, **79** (1912), 104.

alcohol where both a maximum and a minimum display themselves at low temperatures belong to this case :

$$\eta = \frac{\eta_1}{1 + K' \frac{z_m}{1 - z_m}} + \frac{\eta_2}{1 + K'' \frac{1 - z_m}{z_m}} + C_0(\eta_1^{\nu_1} \eta_2^{\nu_2})^{\frac{m}{\nu_1 + \nu_2}} (1 - z_m)^{\nu_1} z_m^{\nu_2} \quad (5).$$

The calculation by this formula which appears to be difficult will become easy, if we remember that K' or K'' is often nearly equivalent to K or its reciprocal as in the mixtures of higher alcohols with benzene, together with the presupposition for the values ν_1 and ν_2 from the position of a maximum point in the actual curve. For example, the mixture of *i*-amyl alcohol (1) and formamide (2) as determined by Drucker and Kassel will be considered in the following. Since K of formamide is 0.34 and that of *i*-amyl alcohol is nearly 0.30 as supposed from K (0.29) of γ -amyl alcohol, the probable value for K in this mixture may be nearly 1.17 at an extremity. From the maximum points of the viscosity curves at 0° and 76.5°C., the case for which $\nu_1 = 1$ and $\nu_2 = 2$ is highly probable. After a few trials we have the following equations which are good enough to represent the nature of the curves :

$$\eta = \frac{0.0883}{1 + 1.77 \frac{z_m}{1 - z_m}} + \frac{0.0755}{1 + 1.1 \frac{1 - z_m}{z_m}} + 0.287(1 - z_m)z_m^2 \quad \text{at } 0^\circ\text{C.},$$

$$\eta = \frac{0.00951}{1 + 1.1 \frac{z_m}{1 - z_m}} + \frac{0.01255}{1 + 1.1 \frac{1 - z_m}{z_m}} + 0.0128(1 - z_m)z_m^2 \quad \text{at } 76.5^\circ\text{C.}$$

The calculated viscosities show no functional divergence from the observed viscosities as seen from Table 4 and also Fig. 4 in which the curves are drawn with the calculated values.

Peculiar systems for which the viscosity maxima often display themselves as hundreds times greater than the component viscosities are also understood as special cases of formula (4).

Acetic acid—stannic chloride and ethyl formate—stannic chloride are good examples of such cases. For the former pair a molecular compound $\text{SnCl}_4 \cdot 3\text{CH}_3\text{COOH}$ is pointed out by Stranathan and Strong with the viscosity curves the maximum points of which exactly correspond to this molecular ratio, probably independent of temperature. For the latter pair a molecular compound $\text{SnCl}_4 \cdot 2\text{HCO}_2\text{C}_2\text{H}_5$ has been confirmed by Kurnakow from the measurements of the viscosities at 30°, 40°, and 50°C. and of the fusion curve.

Table 4. *i*-Amyl alcohol—Formamide, (Drucker and Kassel).

z_m	0°C.		76.5°C.	
	$\eta_{\text{obs.}}$	$\eta_{\text{calc.}}$	$\eta_{\text{obs.}}$	$\eta_{\text{calc.}}$
0.0000	0.0883	—	0.00951	—
0.0538	0.0848	0.0848	0.00966	0.00960
0.1783	0.0836	0.0837	0.01005	0.01008
0.4571	0.0992	0.1008	0.01178	0.01183
0.6633	0.1111	0.1106	0.01311	0.01295
0.8194	0.1064	0.1053	0.01322	0.01324
0.9441	0.0858	0.0881	0.01292	0.01292
1.0000	0.0755	—	0.01255	—

Since the viscosities of both components in this type of mixtures are negligibly small as compared to the viscosity of the solution, the consideration of the true value of K is not useful for the approximate estimation of ν_1 and ν_2 in formula (4). In the following calculation, therefore, viscosity deviations are taken from formula (1) in which K is put as unity.

As clearly indicated in Table 5, a molecular compound $\text{SnCl}_4 \cdot 3\text{CH}_3\text{COOH}$ exists as some multiple of the simplest molecular ratio, 2-fold up to 5 mol %, 7-fold up to 17 mol %, and 14-fold for higher concentrations.

Similar phenomena are also seen from Table 6 for the mixture of ethyl formate and stannic chloride. In this mixture a molecular compound $\text{SnCl}_4 \cdot 2\text{HCO}_2\text{C}_2\text{H}_5$ exists as a great molecule of 30-fold of the simplest ratio at concentrations up to ca 36 mol % at 30°, 40°, and 50°C., but exists as a greater molecule of 60-fold at the concentration range from 32 to 36 mol % at 30°C., under which temperature an enormous crystallization of this compound begins, the melting point of it, however, being at 49°C. according to the same observer.

One more molecular compound $\text{SnCl}_4 \cdot \text{HCO}_2\text{C}_2\text{H}_5$ may probably exist at ca 7-fold of the simplest ratio, though the constancy of $\delta/\{(1-z_m)z_m\}^\nu$ is not sufficiently good.

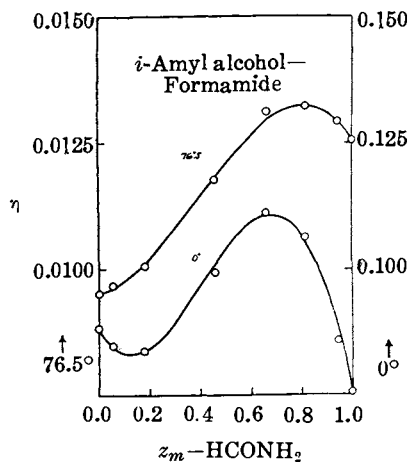


Fig. 4.

These studies suggest that the multiple number of the simplest ratio of a molecular compound at sufficiently low temperature as crystallization begins may be in close relationship with the crystal structure or probably with the dimension of the secondary structure of a crystal as judged from the magnitude of thus estimated multiple of the supposed molecular volume of the molecular compound.⁽⁷⁾

Table 5. Acetic acid—Stannic chloride, 25.2°C., (Stranathan and Strong).

z_m	η	δ	$\delta/(1-z_m)^{v_1} z_m^{v_2}$
0.0000	0.01155		
0.0244	0.02121	0.00974	19.0 }
0.0520	0.04373	0.03234	16.4 } mean $v_1 = 3 \times 2,$
0.1084	0.1897	0.1785	
0.1719	0.963	0.952	1.13 $\times 10^7$ } mean $v_2 = 1 \times 2.$
0.2290	2.582	2.571	1.13 „ } 1.13×10^7 $v_1 = 3 \times 7,$
0.2527	3.034	3.023	(1.33 $\times 10^{14}$) } $v_2 = 1 \times 7.$
0.2682	2.909	2.898	1.30 $\times 10^{14}$ }
0.2969	2.105	2.094	1.44 „ }
0.3151	1.649	1.638	1.44 „ }
0.3498	0.864	0.854	1.34 „ } mean $v_1 = 3 \times 14,$
0.3608	0.691	0.681	1.42 „ } 1.42×10^{14} $v_2 = 1 \times 14.$
0.4111	0.4234	0.4131	1.45 „ }
1.0000	0.0084		1.57 „ }
			(4.75 „)

Table 6. Ethyl formate—Stannic chloride, (Kurnakow).

30°C.

z_m	η	δ	$\delta/(1-z_m)^{v_1} z_m^{v_2}$
0.00	0.00375		
0.25	0.08788	0.08305	2.99 $\times 10^{24}$ } mean $v_1 = 2 \times 30,$
0.30	0.31158	0.30654	2.93 „ } 2.96×10^{24} $v_2 = 1 \times 30.$
0.32	0.52286	0.51773	3.22 $\times 10^{49}$ }
0.335	0.57832	0.57313	3.33 „ } 3.28×10^{49} $v_1 = 2 \times 60,$
0.36	0.44142	0.43812	3.29 „ } $v_2 = 1 \times 60.$
0.50	0.06871	0.06281	1.03 $\times 10^3$ }
0.75	0.01526	0.00828	1.02 „ } 1.03×10^3 $v_1 = 1 \times 7,$
1.00	0.00806		

(7) This Bulletin, **10** (1935), 248.

Table 6. (Concluded)

40°C.

z_m	η	δ	$\bar{c}/(1-z_m)^{\nu_1} z_m^{\nu_2}$
0.00	0.00342		
0.25	0.06384	0.05946	2.14×10^{24}
0.30	0.19034	0.18577	1.78 "
0.32	0.27615	0.27150	2.14 " mean $\nu_1 = 2 \times 30,$
0.335	0.29541	0.29071	2.22 " $2.05 \times 10^{24} \nu_2 = 1 \times 30.$
0.36	0.23514	0.23034	2.00 "
0.50	0.04952	0.04419	7.2×10^2
0.75	0.01292	0.00663	8.1 " $7.7 \times 10^2 \nu_1 = 1 \times 7,$
1.00	0.00725		

50°C.

z_m	η	δ	$\bar{c}/(1-z_m)^{\nu_1} z_m^{\nu_2}$
0.00	0.00311		
0.25	0.04904	0.04504	1.62×10^{24}
0.30	0.12463	0.12045	1.15 "
0.32	0.16102	0.15667	1.24 " mean $\nu_1 = 2 \times 30,$
0.335	0.16758	0.16327	1.24 " $1.29 \times 10^{24} \nu_2 = 1 \times 30.$
0.36	0.14237	0.13798	1.20 "
0.50	0.03753	0.03264	5.3×10^2
0.75	0.01115	0.00536	6.5 " $5.9 \times 10^2 \nu_1 = 1 \times 7,$
1.00	0.00668		

General Conclusions. The validity of the above formulas is acknowledged from a great deal of calculations already made (see Table 8). It may fairly be said that formula (1) deserves to be an ideal mixture law which has long been aimed at. The consideration of the viscosity deviation from the ideal mixture law in case where viscosity exhibits a maximum, which idea was introduced by Findlay⁽⁸⁾ and by Denison⁽⁹⁾ but failed owing to the lack of the true law of ideal mixtures, proves to be true in our case not only in determining the composition of a molecular compound but also in estimating its stability in solution.

The second term of formula (4) or (5) contains two factors, one being concentration function $(1-z_m)^{\nu_1} z_m^{\nu_2}$, the other main corresponding to the viscosity of a molecular compound. One may readily understand that the former is at once deduced from the law of probability by considering the

(8) A. Findlay, *Z. physik. Chem.*, **69** (1909), 203.

(9) R. B. Denison, *Trans. Faraday Soc.*, **8** (1912), 20.

number of encounter between reacting molecules, but one may throw doubt on the form of the latter in which C_0 is independent of concentration and temperature; that is, formula (4) or (5) the second term of which appears to superpose on the first term with respect to composition cannot be elucidative by the classical treatment of chemical equilibrium. If the viscosity of liquids is defined by $\frac{cm\nu}{\sigma}$ as Andrade⁽¹⁰⁾ proposes where m is a mass of a molecule, σ the distance between the centres of molecules, ν the vibration frequency, and c a constant, the number of molecular encounter or collision is proportional to $\frac{\nu}{\sigma}$ which is of the order of some 10^{20} per second. Although the collision probability between ν_1 molecules of kind 1 and ν_2 molecules of kind 2 to form a molecular compound is much less than this amount, the time of such encounter may be beyond comparison with the time ordinarily required for viscosity measurements, so long as a molecular compound is only statistically recognized as such the component molecules of which are freely interchangeable with the same kinds of molecules outside of its reaction sphere. Hence the fact that the viscosity of chemically reactive mixtures strictly obeys formula (4) or (5) leads to the conception that a molecular compound is not a fast-combined molecule but a molecular grouping in a statistical meaning.

Formula (4) when applied to the viscosity which exhibits a very marked maximum at low temperature may afford a clue to the study on the mechanism of crystal formation.

Formula (1) is also valid for ideal solutions of solids in liquids.

For a strong electrolyte solution (i) where there occurs no solvation or hydration, the viscosity difference (η^{**}) between the observed specific viscosity (η^*) and the viscosity caused by the inter-ionic forces according to the Falkenhagen-Vernon theory⁽¹¹⁾ obeys formula (1) as expressed in specific quantity:

$$\left. \begin{aligned} \eta^{**} &= 1 + \frac{(H-1)Kz_m}{1-z_m + Kz_m} \\ \text{or} \quad \eta^* &= 1 + A\sqrt{\frac{1000sz_m}{M_1 + (M_2 - M_1)z_m}} + \frac{(H-1)Kz_m}{1-z_m + Kz_m} \\ \text{or} \quad \eta^* &= 1 + A\sqrt{c} + \frac{(H-1)KM_1c}{1000s + (KM_1 - M_2)c} \end{aligned} \right\} \quad (6),$$

(10) E. N. Da C. Andrade, *Nature*, **128** (1931), 835; *Phil. Mag.*, **17** (1934), 497.

(11) H. Falkenhagen and E. L. Vernon, *Phil. Mag.*, **14** (1932), 537.

in which H is the specific solutional viscosity of the solute, the viscosity of solvent being taken as unity, s the density of the solution at concentration c (g. mol/litre soln.), M_1 and M_2 the formal molecular weights of the solvent and the solute, and A the Falkenhagen–Vernon constant.

For a strong electrolyte solution (ii) where there forms a solvated or hydrated compound, formula (2) for which the Falkenhagen–Vernon effect is taken into account holds true for concentrations up to saturation :

$$\eta^{**} = 1 + \frac{(H-1)Kz_m}{1-z_m + Kz_m} + C^*(1-z_m)^{v_1} z_m^{v_2} \quad (7)$$

where C^* is a constant independent of concentration.

The solutional viscosity of a solid in a liquid in accord with formulas (1), (6), and (7) is the viscosity probably 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 crystal.

At very dilute solutions where the solvation or hydration, though it happens, is not appreciable and the Falkenhagen–Dole–Vernon equation holds, formula (6) or (7) becomes

$$\eta^* = 1 + A\sqrt{c} + \frac{(H-1)KM_1}{1000s_1}c \quad (8),$$

whence it readily follows that the theoretically as yet unknown factor B of the Falkenhagen–Dole–Vernon equation is defined by

$$B = \frac{(H-1)KM_1}{1000s_1}.$$

Quite recently Sulston has made careful measurements on the temperature variation of B for aqueous solutions of KCl and K_2SO_4 . As we have had for KCl $H_{18}=0.9471$, $H_{25}=0.9765$, and $K=40.39$ and this K may be regarded to keep constancy for higher temperatures, we can estimate the

Table 7. The Solutional Viscosity of KCl.

$t^\circ\text{C.}$	B	η	$\eta_{\text{calc.}}$
18	−0.0330	0.01003	0.01003
25	−0.0140	0.00874	0.00874
35	+0.0090	0.00731	0.00731
55	+0.0400	0.00540	0.00539
65	+0.0506	0.00472	0.00471
70	+0.0545	0.00442	0.00442
75	+0.0561	0.00415	0.00416
80	+0.0613	0.00392	0.00392
85	+0.0654	0.00371	0.00370

(12) W. J. Sulston, *Proc. Phys. Soc.*, **47** (1935), 657.

Table 8. I. Mixture.

Component 1	Component 2	$t^{\circ}\text{C.}$	K	Remarks	Observer
Benzene	Toluene	25	1.23	n	Linebarger
	Diphenyl	25	0.30	n	Kendall and Monroe
	Naphthalene	25	0.49	n	"
	Chloroform	25	(1.81)	n	Linebarger
	Carbon tetrachloride	0	1.08	n	Thorpe and Rodger
	"	10	0.99	n	
	"	20	0.96	n	
	"	30	0.94		
	"	40	0.88	n	
	"	50	0.83	n	
	"	60	0.79	n	
	"	70	0.81	n	
	Ethylene dichloride	0	$K'1.13, K''1.30$	a	Faust
	"	19.4	$K'1.00, K''1.37$	a	
	"	50	$K'0.72, K''1.66$	a	
	Bromobenzene	18.2	1.06	n	Yajnik and coworkers
	"	30	1.10	n	
	"	40	1.07	n	
	Nitrobenzene	25	0.49	n	Linebarger
	<i>m</i> -Nitrotoluene	15	0.40	n	Dessart
	"	30	0.44	n	
	Methyl alcohol	25	$K'0.62, K''1.60$	a	Fischler
	Ethyl alcohol	25	$K'1.75, K''1.45$	a	Dunstan
	<i>n</i> -Propyl alcohol	25	$K'1.70, K''2.25$	a	
	<i>n</i> -Amyl alcohol	30	$K'1.71, K''3.36$	a	Bhide' and Watson
	Phenol	20	0.087-0.23	v	Bramley
	"	25	0.12 - 0.32	v	Swearingen
	<i>m</i> -Cresol	60	0.27	n	Piatti
	Guaiacol	30	0.17 - 0.29	v	Puschin and Pinter
	Ether	25	2.28	n	Linebarger
	"	10	2.35	n	I. C. T.
	"	20	2.20	n	
	"	30	2.07	n	
	Anisol	0	0.83	n	Piatti
	"	10	0.80	n	
	"	20	0.84	n	
	"	30	0.84	n	
	"	40	0.89	n	

I. Mixture. (*Continued*)

Component 1	Component 2	$t^{\circ}\text{C.}$	K	Remarks	Observer
Benzene	Anisol	50	0.94	n	I. C. T.
	„	60	0.97	n	
	Acetone	10	1.87	n	
	„	20	1.79	n	
	„	30	1.66	n	
	„	25	1.70	n	Fischler
	Acetophenone	16	0.65	n	I. C. T.
	Acetic acid	25	$K'0.71, K''3.11$	a	Dunstan
	Ethyl acetate	25	2.01	n	„
	Ethyl benzoate	25	0.69	n	Kendall and Monroe
	Benzyl benzoate	25	0.31-0.50	v	„
	„	5	0.20-0.38	v	Bingham and Sarver
	„	15	0.25-0.47	v	
	„	25	0.31-0.53	v	
	„	40	0.37-0.61	v	
	„	60	0.48-0.74	v	
	<i>m</i> -Toluidine	15	0.18	n	Dessart
	„	30	0.24	n	
	Pyridine	25	(0.76)	c(1:2)	Dunstan, Thole and Hunt
	Quinoline	25	0.46	n	I. C. T.
	Carbon bisulphide	25	0.91	n	Linebarger
	Sulphur chloride	15.5	0.78	n	De Carli
	„	20	0.78	n	
	Stannic chloride	25	$K'0.86, K''2.08$	a	Kurnakow
	„	70	$K'0.95, K''1.68$	a	

II. Mixture.

Component 1	Component 2	$t^{\circ}\text{C.}$	K	(ka) of comp. 1 rel. to (ka) of benzene	Remarks	Observer
<i>n</i> -Hexane	<i>n</i> -Decane	25	0.74	$\left. \begin{array}{l} 1.48 \\ 1.58 \\ 1.41 \\ 1.60 \end{array} \right\} \begin{array}{l} \text{mean} \\ 1.52 \end{array}$	n	Bingham, White, Thomas and Cadwell Tab. internat., 1927-1928 I. C. T. Dessart "
	"	35	0.79		n	
	"	50	0.84		n	
	"	65	0.87		n	
	Nitrobenzene	8	0.33		n	
	"	15	0.33		n	
	"	15	0.31		n	
	"	20	0.30		n	
	"	25	0.31		n	
	<i>m</i> -Nitrotoluene	15	0.28		n	
Cyclohexane	<i>m</i> -Toluidine	30	0.29	$\left. \begin{array}{l} 1.00 \\ 0.97 \end{array} \right\} \begin{array}{l} \text{mean} \\ 0.99 \end{array}$	n	"
	"	32	0.20		n	
	<i>m</i> -Nitrotoluene	15	0.36		n	
	"	30	0.46		n	
	<i>m</i> -Toluidine	15	0.33		n	
Methyl cyclohexane	"	30	0.32	$\left. \begin{array}{l} 1.14 \\ 1.14 \end{array} \right\} \begin{array}{l} \text{mean} \\ 1.14 \end{array}$	n	"
	<i>m</i> -Nitrotoluene	15	0.30		n	
	"	30	0.41		n	
	<i>m</i> -Toluidine	15	0.26		n	
<i>n</i> -Decane	"	30	0.29	$\left. \begin{array}{l} 1.13 \\ 1.20 \\ 1.28 \\ 1.32 \end{array} \right\}$	n	Bingham, White, Thomas and Cadwell
	<i>n</i> -Hexane	25	1.35		n	
	"	35	1.27		n	
	"	50	1.19		n	
Toluene	"	65	1.15	$\left. \begin{array}{l} 1.23 \\ 1.25 \\ 1.26 \\ 1.25 \end{array} \right\}$	n	Linebarger Kendall and Monroe "
	Benzene	25	0.81		n	
	Diphenyl	25	0.24		n	
	Naphthalene	25	0.38		n	
	Chlorobenzene	20	1.02		n	
	"	35	1.03		n	
	"	50	1.02		n	

II. Mixture. (*Continued*)

Component 1	Component 2	$t^{\circ}\text{C.}$	K	(k_a) of comp. 1 rel. to (k_a) of benzene	Remarks	Observer
Toluene	Bromobenzene	20	0.86) mean	1.24) mean	n	Yajnik and coworkers Dessart
	"	35	0.85) 0.86	1.24	n	
	<i>m</i> -Nitrotoluene	15	0.32) mean	1.21	n	
	"	30	0.36) 0.34	1.21	n	
	Guaiacol	30	0.18-0.24	1.67-1.25	v	Puschin and Pinter
	Benzaldehyde	17	0.57	1.23	n	
	Ethyl acetate	25	(1.63)	1.25	n	
	Ethyl benzoate	25	0.59) mean	1.22	n	
	"	25	0.60) 0.60		n	Kendall and Monroe
	Benzyl benzoate	25	0.25-0.39	1.92-1.23	v	
	<i>m</i> -Toluidine	15	0.15	(2.13?)	n	Dessart
	"	30	0.21	(1.52?)	n	
Diphenyl	Benzene	25	3.33	0.30) mean	n	Kendall and Monroe
	Toluene	25	4.10	0.30) 0.30	n	
Stilbene	Dibenzyl	125	0.95		n	Beck
	Azobenzene	125	0.86		n	
	Benzal aniline	125	0.90		n	
Dibenzyl	Stilbene	125	1.05		n	"
	Azobenzene	75	0.97		n	
Naphthalene	Benzene	25	2.04	0.49) mean	n	Kendall and Monroe
	Toluene	25	2.63	0.47) 0.48	n	
Tetralin	Methyl alcohol	25	(3.03)	0.21) mean	c(1:1)	Herz and Schuftan
	Ethyl alcohol	25	(2.22)	0.22) 0.22	c(1:1)	
	<i>n</i> -Butyl alcohol	25	$K'1.72, K''1.30$	0.21, 0.45	a	
Dekalin	<i>n</i> -Butyl alcohol	25	$K'1.63, K''1.10$	0.22, 0.40	a	"

II. Mixture. (Continued)

Component 1	Component 2	$t^{\circ}\text{C.}$	K	(ka) of comp. 1 rel. to (ka) of benzene	Remarks	Observer
Methylene chloride	Acetone	0	0.56	3.38	n	Sachanov and Rjachowsky
Chloroform	Benzene	25	(0.55)	1.82	n	Linebarger
	Carbon tetrachloride	25	0.52	1.79	n	"
	Ether	0	(1.13)	2.02	mean 1.87	Thorpe and Rodger
	"	10				
	"	20				
	"	30				
	Phenetol	0	(0.56)	1.84	c(2:1) $m = 2.62$ $C_0 = 6.08 \times 10^3$	Sachanov and Rjachowsky
	Acetone	0	(0.95)	1.88	c(2:1) $m = 2.32$ $C_0 = 1.52 \times 10^2$	Tsakalotos
	"	20				
	"	40				
Carbon tetrachloride	Benzene	0	0.96	1.08	n	Thorpe and Rodger
	"	10	1.01	0.99	n	
	"	20	1.04	0.96	n	
	"	30	1.06	0.94	n	
	"	40	1.14	0.88	n	
	"	50	1.21	0.83	n	
	"	60	1.27	0.79	n	
	"	70	1.24	0.81	n	
	Chloroform	25	1.94	0.96	n	Linebarger Herz and Rathmann
	Tetrachloroethylene	25	$K'1.44, K''0.94$	1.10, 1.68	a	
	Tetrachloroethane	25	$K'1.05, K''1.44$		a	
	Acetone	0	1.75	1.08	n	
	Acetophenone	25	0.74	0.91	n	
Ethylene dichloride	Benzene	0	$K'1.30, K''1.13$	0.77, 0.89	a	Faust
	"	19.4	$K'1.37, K''1.00$	0.73, 1.00	a	
	"	50	$K'1.66, K''0.72$	0.60, 1.39	a	
Trichloroethylene	Pentachloroethane	25	0.41	1.71	n	Herz and Rathmann

II. Mixture. (Continued)

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Component 1	Component 2	t°C.	K	(ka) of comp. 1 rel. to (ka) of benzene	Remarks	Observer
Tetrachloroethylene	Carbon tetrachloride	25	K'0.94, K''1.44	0.99, 1.35	a	Herz and Rathmann
Tetrachloroethane	Carbon tetrachloride	25	K'1.44, K''1.05	0.65, 1.01	a	Sachanov and Rjachowsky
	Ether	0	2.22	1.12 } mean	n	
	Phenetol	0	0.86	1.20 } 1.16	n	
	Acetone	0	1.05-1.85	1.80-1.02	v	
Pentachloroethane	Trichloroethylene	25	2.44		n	Herz and Rathmann Sachanov and Rjachowsky
	Ether	0	1.85-3.85	1.34-0.64	v	
	Phenetol	25	1.48	0.70	n	
Chlorobenzene	Toluene	20	0.98 } mean	1.27 } mean	n	Yajnik and coworkers
	"	35	0.97 } 0.98		n	
	"	50	0.98 } 0.98		n	
	Bromobenzene	20	0.78 } mean	1.27 } mean	n	Unkovskaja and Volova
	"	40	0.83 } 0.84		n	
	"	60	0.83 } 0.84		n	
	"	12	0.85 } 0.84	2.80-1.25	n	Kremann, Gugle and Meingast Bramley
	"	64	0.93 } 0.84		n	
	Phenol	20	0.082-0.184		v	
	Phenol	20	0.082-0.184		v	
Bromobenzene	Benzene	18.2	0.94 } mean	1.08 } mean	n	Yajnik and coworkers
	"	30	0.91 } 0.93		n	
	"	40	0.93 } 0.93		n	
	Toluene	20	1.16 } mean	1.06 } mean	n	"
	"	35	1.18 } 1.17		n	
	Chlorobenzene	20	1.28 } mean		n	
	"	40	1.21 } 1.19	1.07 } mean	n	Unkovskaja and Volova
	"	60	1.21 } 1.19		n	
	"	12	1.18 } 1.19		n	
	"	64	1.08 } 1.19	1.55-1.13	n	Kremann, Gugle and Meingast Sachanov and Rjachowsky
	Acetone	0	1.22-1.67		v	
	Acetone	0	1.22-1.67		v	

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II. Mixture. (Continued)

Component 1	Component 2	$t^{\circ}\text{C.}$	K	(ka) of comp. 1 rel. to (ka) of benzene	Remarks	Observer
Methyl iodide	Carbon bisulphide	0	1.89	0.50	n	Thorpe and Rodger
	"	10	1.64	0.58	n	
	"	20	1.64	0.58	n	
	"	30	1.45	0.66	n	
	"	40	1.39	0.68	n	
Ethyl iodide	Methyl alcohol	20	(0.29)	2.21	n	Yajnik and coworkers Sachanov and Rjachowsky
	"	45		mean	n	
	Phenetol	0	0.47	2.19	n	
Nitromethane	Ethyl alcohol	—	$K/1.27, K'/2.23$	0.39, 1.09	a	Wagner
Nitrobenzene	<i>n</i> -Hexane	8	3.03	mean	n	Tab. internat., 1927-1928
	"	15	3.03	3.03	n	
	"	15	3.23	mean	n	I. C. T.
	"	20	3.33	mean	n	
	"	25	3.23	3.26	n	Linebarger Fischler
	"	25	2.04	0.49	n	
	Benzene	25	1.32	0.49	n	Swearingen and Heck
	Methyl alcohol	25	$K/2.06, K'/1.48$	0.18, 0.53	a	
	<i>n</i> -Butyl alcohol	35	$K/1.66, K'/1.61$	0.22, 0.58	a	Wagner
	"	45	$K/1.53, K'/1.52$	0.24, 0.54	a	
	"	55	$K/1.53, K'/1.47$	0.24, 0.53	a	Drucker and Kassel
	"	65	$K/1.50, K'/1.41$	0.24, 0.51	a	
	"	75	$K/1.31, K'/1.60$	0.27, 0.57	a	De Carli
	"	80	$K/1.02, K'/3.16$	0.22, 0.72	a	
	<i>i</i> -Butyl alcohol	—	$K/1.97, K'/2.25$	0.48-0.27	a	" "
	<i>i</i> -Amyl alcohol	0	$K/1.58, K'/1.41$	0.48-0.64	a	
	Sulphur chloride	80	1.61-2.89		v	" "
	"	3	1.61-1.21		v	
	Stannic chloride	15	(1.35)		c(2:1) $m \approx 2.00$ $C_0 = 1.31 \times 10^3$	" "
	"	25	(1.70)			
	Stannic bromide	25	(1.00)			" "
	"	40	(1.00)		c(1:1)	

II. Mixture. (Continued)

Component 1	Component 2	$t^{\circ}\text{C.}$	K	(ka) of comp. 1 rel. to (ka) of benzene	Remarks	Observer
<i>m</i> -Nitrotoluene	<i>n</i> -Hexane	15	3.57 mean	0.43	n	Dessart
	"	30	3.45/3.51		n	"
	Cyclohexane	15	2.78 mean	0.40	n	"
	"	30	2.17/2.48		n	"
	Methyl cyclohexane	15	3.33 mean	mean	n	"
	"	30	2.44/2.89	0.41	n	"
Toluene	"	15	2.50 mean	0.39	n	"
	"	30	2.27/2.39	0.42	n	"
	"	15	3.13 mean		n	"
	"	30	2.78/2.96	0.42	n	"
Cyanobenzene	Ethyl alcohol	—	$K'0.92, K''2.00$	0.53, 1.58	a	Wagner
Azobenzene	Stilbene	125	1.16		n	Beck
	Dibenzyl	75	1.03		n	"
	Benzal aniline	75	1.03		n	"
Water	Methyl alcohol	20		0.68	$c(2:1)$ $m = 2.00$ $C_0 = 9.2 \times 10^2$	Traube
	"	30	(0.96)			
	"	40				
	"	50				
	"	60				
	Ethyl alcohol	0			$c(3:1)$ $m = 2.00$ $C_0 = 1.55 \times 10^3$	I. C. T.
	"	10			$c(2:1)$ $m = 1.83$ $C_0 = 4.08 \times 10^2$	
	"	20		0.70		
	"	30				
	"	40				
	"	50				
	"	60				
	"	70				
	<i>n</i> -Propyl alcohol	20		0.68	$c(3:1)$ $m = 2.00$ $C_0 = 1.31 \times 10^3$	Dunstan and Thole
	"	25			$c(4:1, 3:1, 2:1)$	Dunstan Davis, Hughes and Jones
	Allyl alcohol	30			$c(5:1)$	
	Acetone	25		0.64	$c(4:1)$	
	"	0		0.67		

II. Mixture. (Continued)

Component 1	Component 2	t°C.	K	(ka) of comp. 1 rel. to (ka) of benzene	Remarks	Observer
Water	Formic acid	15	{ (0.69) }	{ 0.68 } mean 0.67	c(1:1)	{ I. C. T. }
	"	25				
	"	35				
	"	45				
	Acetic acid	55	{ (1.29) }	0.67	c(1:1) $m = 1.68$ $C_0 = 1.16 \times 10^2$	{ I. C. T. }
	"	15				
	"	20				
	"	25				
	"	30				
	"	35				
	"	40				
	"	45				
	"	50				
	"	55				
	"	60				
	"	65				
	"	75				
	"	85				
	"	95				
	Lactic acid	25	{ 0.28 0.48 } mean 0.50	0.69	n n n c(3:1+2:1) c(3:1+1:1)	{ Dunstan Merry and Turner Hartley, Thomas and Applebey }
	Formamide	25				
	"	40				
	Pyridine	0				
		25.08	{ (1.19) }	0.66		
Methyl alcohol	Benzene	25	{ K/1.60, K'/0.62 (0.33) (3.45) 0.76 }	{ 0.67 } 0.63, 0.62	a c(1:1) n n n	{ Fischer Herz and Schuftan Yajnik and coworkers Fischler }
	Tetralin	25				
	Ethyl iodide	20				
	"	45				
	Nitrobenzene	25	{ (1.04) }	{ 0.64 } mean 0.64	c(1:2) $m = 2.00$ $C_0 = 9.2 \times 10^2$	{ Fischer Traube }
	Water	20				
	"	30				
	"	40				
	"	50				
	"	60				

II. Mixture. (Continued)

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Component 1	Component 2	t°C.	K	(ka) of comp. 1 rel. to (ka) of benzene	Remarks	Observer
Methyl alcohol	Ethyl alcohol	25	0.78	0.63	n	Bingham, White, Thomas and Cadwell
	"	35	0.84		n	
	"	45	0.86		n	
	"	55	0.91		n	
	n-Propyl alcohol	25	0.63	0.65	n	Herz and Kuhn Baker
	Ether	25	2.33-4.55		v	
	Phenetol	25	1.60	0.64	n	Mardles
	Acetic acid	25	(1.34)	0.64	c(1:2)	
	Formamide	25	0.50 mean	0.64	n	Merry and Turner
	"	40	0.55/0.53		n	
Ethyl alcohol	Benzene	25	K'1.45, K''1.75	0.69, 1.75	a	Dunstan Herz and Schuftan
	Tetralin	25	(0.45)	0.49	c(1:1)	
	Nitromethane	—	K'2.23, K''1.27		a	Wagner
	Cyanobenzene	—	K'2.00, K''0.92		a	
	Water	0			c(1:3)	I. C. T.
	"	10			m = 2.00	
	"	20			C ₀ = 1.55 × 10 ³	
	"	30			&	
	"	40	(1.43)	0.47	c(1:2)	
	"	50			m = 1.83	
	"	60			C ₀ = 4.08 × 10 ²	
	"	70		mean		
	Methyl alcohol	25	1.28	0.51	n	Bingham, White, Thomas and Cadwell
	"	35	1.19		n	
	"	45	1.16		n	
	"	55	1.10		n	
	n-Propyl alcohol	25	0.88	0.47	n	Parks and Schwenck Parks and Kelley
	i-Propyl alcohol	25	0.78	0.51	n	
	Ether	25	3.30-6.60		v	Baker
	Anisol	25	K'1.81, K''1.01	0.65-0.32	a	
	Phenetol	25	K'1.70, K''0.96	0.46, 0.85	a	"
	Acetaldehyde	0	(1.7)	0.61, 0.99	a	
	"	18	(1.9)		c(1:1, 3:1)	Leeuw
	Acetone	25	3.7-6.9	0.47-0.25	v	

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II. Mixture. (Continued)

Component 1	Component 2	$t^{\circ}\text{C.}$	K	(ka) of comp. 1 rel. to (ka) of benzene	Remarks	Observer
Ethyl alcohol	Formamide	25	0.70) mean	0.48	n	Merry and Turner I. C. T. Dunstan Wagner
	Quinoline	40	0.71) 0.71	0.51	n	
	Carbon bisulphide	25	0.89	0.48	n	
	Mercaptan	25	2.00		n	
	Allyl thiocyanide	25	2.70		n	
<i>n</i> -Propyl alcohol			$K'1.82, K''1.22$		a	Dunstan Dunstan and Thole Herz and Kuhn Parks and Schwenck Trew and Watkins Baker English and Turner
	Benzene	25	$K'2.25, K''1.70$	0.44, 1.70	a	
	Water	20			$c(1.3)$	
	"	25	(1.67)	0.40	$m = 2.00$	
	"	30			$C_0 = 1.31 \times 10^3$	
	Methyl alcohol	25	1.59	mean	n	
	Ethyl alcohol	25	1.14	0.41	n	
	<i>n</i> -Butyl alcohol	25	0.89	0.43	n	
	Ether	25	3.88-7.75	0.40	v	
	Formamide	25	$K'2.30, K''0.80$	0.55-0.27 0.15, 0.27	a, $c(1.2)$	
<i>i</i> -Propyl alcohol	Ethyl alcohol	25	1.28	0.38) mean	n	Parks and Kelley Trew and Watkins Parks and Chaffee
	<i>n</i> -Butyl alcohol	25	0.85	0.42) 0.40	n	
<i>n</i> -Butyl alcohol	Acetone	25	$K'4.76, K''0.85$	0.37, 1.47	a	Herz and Schuftan " Swearingen and Heck Trew and Watkins " " Wagner
	Tetralin	25	$K'1.30, K''1.72$	0.17, 0.38	a	
	Dekalin	25	$K'1.10, K''1.63$		a	
	Nitrobenzene	35	$K'1.48, K''2.06$	0.33, 1.01	a	
	"	45	$K'1.61, K''1.66$	0.30, 0.81	a	
	"	55	$K'1.52, K''1.53$	0.32, 0.75	a	
	"	65	$K'1.47, K''1.53$	0.33, 0.75	a	
	"	75	$K'1.41, K''1.50$	0.35, 0.74	a	
	"	80	$K'1.60, K''1.31$	0.31, 0.64	a	
	<i>n</i> -Propyl alcohol	25	1.12	0.37) mean	n	
	<i>i</i> -Propyl alcohol	25	1.17	0.35) 0.36	n	
	<i>i</i> -Butyl alcohol	25	0.63		n	
	<i>i</i> - γ -methyl butyl alcohol	25	0.89		n	
	Nitrobenzene	—	$K'3.16, K''1.02$	0.16, 0.50	a	

II. Mixture. (Continued)

Component 1	Component 2	$t^{\circ}\text{C.}$	K	(η_0) of comp. 1 rel. to (η_0) of benzene	Remarks	Observer
Phenol	Dimethyl aniline	40.2	0.60-3.10		v	Bramly
	"	59.9	0.50-2.43		v	
	"	80	0.50-2.10		v	
	"	126	0.50-1.75		v	"
	Diphenyl amine	177	1.40		n	
	"	30	0.52-0.93		v	
	"	40	0.55-0.95		v	"
	"	81	0.75		n	
	Diphenyl methyl amine	9.8	$K'1.65, K''1.15$		a	
	"	20.1	$K'1.44, K''1.19$		a	"
o-Cresol	"	30	$K'1.79, K''0.81$		a	
	"	40	$K'1.56, K''0.92$		a	
	"	60	$K'1.08, K''1.16$		a	
	"	80	$K'0.91, K''1.20$		a	
m-Cresol	Phenol	25	1.45		n	Kendall and Beaver
	m-Cresol	25	0.67		n	
	p-Cresol	25	0.68		n	
p-Cresol	Benzene	60	3.70	0.27	n	Piatti Kendall and Beaver
	Phenol	25	1.92		n	
	o-Cresol	25	1.49		n	
	p-Cresol	25	0.31-0.87		v	
Guaiacol	Phenol	25	1.72		n	"
	o-Cresol	25	1.47		n	
	m-Cresol	25	1.16-3.23		v	
	Benzene	30	3.45-5.88	0.29-0.17 0.30-0.22 0.85-0.31	v	
Guaiacol	Toluene	30	4.17-5.56		v	Puschin and Pinter
	Acetone	30	2.00-5.56		v	
	Methyl aniline	30	1.41		n	
	Dimethyl aniline	30	2.50		n	

II. Mixture. (*Continued*)

Component 1	Component 2	$t^{\circ}\text{C.}$	K	(ka) of comp. 1 rel. to (ka) of benzene	Remarks	Observer
<i>o</i> -Nitrophenol	Aniline	30	$K/1.10, K'/1.83$	0.36, 0.73	a	Bramley
	"	40	$K/0.96, K'/1.76$	0.44, 0.74	a	
	"	60	$K/0.91, K'/1.69$	0.53, 0.85	a	
	Pyridine	80	$K/0.93, K'/1.55$	0.59, 0.85	a	"
		30	(1.82)	0.43	c(2:1)	
		40	(1.54)	0.51	$m = 2.00$	
		60	(1.35)	0.59	$C_0 = 7.02 \times 10$	
		80	(1.19)	0.66		
Ether	Benzene	25	0.44	2.28	n	Linebarger
	"	10	0.43	2.35	n	I. C. T.
	"	20	0.45	2.20	n	
	"	30	0.48	2.07	n	
	Chloroform	0			c(1:2)	Thorpe and Rodger
	"	10	(0.89)	2.10	$m = 2.62$	
	"	20			$C_0 = 6.08 \times 10^3$	
	"	30				Sachanov and Rjachowsky
	Tetrachloroethane	0	0.45	2.58	n	
	Pentachloroethane	0	0.26-0.54	2.69-1.36	v	
	Methyl alcohol	25	0.22-0.43	2.91-1.49	v	Baker
	Ethyl alcohol	25	0.15-0.30	3.27-1.63	v	"
	<i>n</i> -Propyl alcohol	25	0.13-0.26	3.15-1.58	v	"
	Phenetol	25	0.48	2.15	n	Kendall and Wright
Anisol	Benzene	0	1.21	0.83	n	Piatti
	"	10	1.25	0.80	n	
	"	20	1.19	0.84	n	
	"	30	1.19	0.84	n	
	"	40	1.12	0.83	n	
	"	50	1.06	0.94	n	Baker
	"	60	1.03	0.97	n	
	"	25	$K/1.01, K'/1.81$	0.49, 0.89	a	
	Ethyl alcohol					

II. Mixture. (Continued)

Component 1	Component 2	$t^{\circ}\text{C.}$	K	(ka) of comp. 1 rel. to (ka) of benzene	Remarks	Observer
Phenetol	Chloroform	0	(1.79)	1.04	c(1:2)	Sachanov and Rjachowsky
	Tetrachloroethane	0	1.16	1.00	n	"
	Pentachloroethane	25	0.68	mean	n	"
	Ethyl iodide	0	2.12	1.04	n	"
	Methyl alcohol	25	0.63	1.03	n	Baker
	Ethyl alcohol	25	$K/0.96, K/1.70$	0.51, 0.83	a	"
	Ether	25	2.08	1.02	n	Kendall and Wright
	Diphenyl ether	25	0.54		n	"
	Aniline	0	0.29		n	Bramley
	"	10	0.32		n	
	"	20	0.37		n	
	"	30	0.39		n	
	"	40	0.41		n	
	"	60	0.47		n	
	"	80	0.54		n	
Diphenyl ether	Phenetol	25	1.85	0.56	n	Kendall and Wright
Acetaldehyde	Ethyl alcohol	0	(0.59)	0.83	c(1:1, 1:3)	Leeuw
	"	18	(0.53)	0.92		
Benzaldehyde	Toluene	17	1.75	0.71	n	Schaaf
	Sulphur chloride	3	0.89-0.53	0.89-1.47	v	De Carli
	"	13.2	0.91	0.86	n	
Acetone	"	20	1.16	0.67	n	I. C. T. Fischler Sachanov and Rjachowsky
	Benzene	10	0.53	1.87	n	
	"	20	0.56	1.79	n	
	"	30	0.60	1.66	n	
	Methylene chloride	25	0.59	1.70	n	

II. Mixture. (Continued)

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Component 1	Component 2	$t^{\circ}\text{C.}$	K	(ka) of comp. 1 rel. to (ka) of benzene	Remarks	Observer
Acetone	Chloroform	0	(1.05)	1.78	c(1:2)	Tsakalotos
	"	20			$m = 2.32$	
	"	40			$C_0 = 1.52 \times 10^2$	
	Carbon tetrachloride	0	0.57	1.89	n	Sachanov and Rjachowsky
	Tetrachloroethane	0	0.54-0.95	2.15-1.22	v	"
	Bromobenzene	0	0.60-0.82	1.78-1.30	v	"
	Water	0	0.34	1.98	c(1:5)	Davis, Hughes and Jones
	"	25	0.39	1.72	c(1:4)	"
	Ethyl alcohol	25	0.14-0.27	3.50-1.81	v	Dunstan
	<i>i</i> -Propyl alcohol	25	$K'0.85, K''4.76$	0.47, 1.92	a	Parks and Chaffee
	Phenol	9.95	See Phenol-Acetone		v	Bramley
	"	20.05			v	
	"	29.8			v	
	"	40.1			v	
	"	49.8			v	
	Guaiacol	30	0.18-0.50	1.67-0.60	v	Puschin and Pinter
	Acetic acid	25	(0.49)	1.76	c(1:2, 1:4)	Kendall and Brakeley
	Carbon bisulphide	-13	$K'1.27, K''1.16$	0.75, 1.10	a	Faust
	"	-10	$K'1.02, K''1.31$	0.93, 1.24	a	
	"	0	$K'1.42, K''0.89$	0.67, 0.85	a	
Acetophenone	Benzene	16	1.54	0.65	n	I. C. T. Sachanov and Rjachowsky Kendall and Brakeley
	Carbon tetrachloride	25	1.35	0.70	n	
	Acetic acid	25	(1.28)	0.67	c(1:1)	
Formic acid	Water	15	(1.45)	0.46	c(1:1)	I. C. T.
	"	25				
	"	35				
	"	45				
	"	55				

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II. Mixture. (Continued)

Component 1	Component 2	t°C.	K	(ka) of comp. 1 rel. to (ka) of benzene	Remarks	Observer
Formic acid	Acetic acid	15	(1.87)	0.46	c(1:1)	Davis and Jones
	"	25		mean 0.47		
	Formamide	25	(0.71)	0.48	c(1:1)	Merry and Turner
	"	40				
Acetic acid	Benzene	25	K/3.11, K'/0.71	0.32, 0.71	a	Dunstan
	Water	15				
	"	20				
	"	25				
	"	30				
	"	35				
	"	40				
	"	45				
	"	50			c(1:1)	I. C. T.
	"	55			m = 1.68	
	"	60			C ₀ = 1.16 × 10 ²	
	"	65				
	"	75				
	"	85				
	"	95				
	Methyl alcohol	25	(0.75)	0.86	c(2:1)	Mardlas Kendall and Brakeley
	Acetone	25	(2.04)	0.87	c(2:1, 4:1)	
	Acetophenone	25	(0.78)	0.85	c(1:1)	" "
	Formic acid	25	(0.53)	0.86	c(1:1)	
	"	15		mean 0.86		Davis and Jones Kendall and Brakeley
	"	25		0.89		
	Trichloroacetic acid	25	0.49	0.85	n	" "
	Ethyl acetate	25	2.33	0.85	c(1:2)	
	Ethyl benzoate	25	0.89	0.82	c(1:1)	" "
	Pyridine	35			m = 1.44	
	"	45			C ₀ = 1.4 × 10	Swearingen and Heck
	"	55			&	
	"	65			c(5:1)	
	"	75			m = 2.00	
	"	80	(0.93)	0.85	C ₀ = 3.44 × 10 ³	

II. Mixture. (Continued)

Component 1	Component 2	t°C.	K	(ka) of comp. 1 rel. to (ka) of benzene	Remarks	Observer
Acetic acid	Stannic chloride	25.2		Polym. $v_1 = 3 \times 2, 3 \times 7, 3 \times 14$ $v_2 = 1 \times 2, 1 \times 7, 1 \times 14$		} Stranathan and Strong
n-Butyric acid	Pyridine	20	(0.60)	1.32	c(3:1)	
	"	18.2	(0.60)	1.32	c(3:1)	} Yajnik and coworkers
	"	30	(0.52)	1.52	m = 1.60	
	"	40	(0.40)	1.98	C ₀ = 1.60 × 10 ²	
Lactic acid	Water	25	3.57	0.19	n	Dunstan
Trichloroacetic acid	Acetic acid	25	2.04	0.42	n	Kendall and Brakeley
Formamide	Water	25	2.08 mean	0.33 } 0.34 } 0.35 } mean 0.34 } 0.51, 0.94 0.26, 0.78 0.26, 0.46 0.26, 0.51 0.26, 0.19 0.33 }	n	} Merry and Turner
	"	40	2.00 2.04		n	
	Methyl alcohol	25	2.00 mean		n	} "
	"	40	1.82 1.91		n	
	Ethyl alcohol	25	1.43 mean		n	} "
	"	40	1.41 1.42		n	
	n-Propyl alcohol	25	K'0.80, K''2.30		a, c(2:1)	} English and Turner
	i-Butyl alcohol	25	K'0.90, K''1.90		a, c(2:1)	
	i-Amyl alcohol	25	K'1.10, K''1.60		a, c(2:1)	} "
	"	0	K'1.10, K''1.77		a, c(2:1)	
	"	76.5	K'1.10, K''1.10		a, c(2:1)	} Drucker and Kassel
	Formic acid	25	} (1.43)		0.33 }	
	"	40				
Ethyl formate	Stannic chloride	30		Polym. $v_1 = 2 \times 30, 2 \times 60, 1 \times 7$ $v_2 = 1 \times 30, 1 \times 60, 1 \times 7$		} Kurnakow
	"	40		Polym. $v_1 = 2 \times 30, 1 \times 7$ $v_2 = 1 \times 30, 1 \times 7$		
	"	50				

II. Mixture. (Continued)

Component 1	Component 2	$t^{\circ}\text{C.}$	K	(ka) of comp. 1 rel. to (ka) of benzene	Remarks	Observer
<i>i</i> -Butyl formate	Ethyl propionate ,,	20 40	1.24-0.99 1.08		v n	{ Unkovskaja and Volova
Amyl formate	Propyl acetate ,,	12 64	1.00 1.08		n n	{ Kremann, Gugl and Meingast
Methyl acetate	Ethyl acetate	25	0.94	2.16	n	Chadwell
Ethyl acetate	Benzene Toluene Acetic acid Methyl acetate Benzyl benzoate Aniline	25 25 25 25 25 0	0.50 (0.61) 0.42 1.06 0.22-0.38 0.13-0.19	2.00 } mean 2.03 } 2.03 2.05 }	n n n n v v	Dunstan Linebarger Kendall and Brakeley Chadwell Kendall and Wright I. C. T.
Propyl acetate	Amyl formate ,, Ethyl propionate ,,	12 64 20 40	1.00 0.93 1.47-0.96 1.02		n n v n	{ Kremann, Gugl and Meingast Unkovskaja and Volova
Ethyl propionate	<i>i</i> -Butyl formate ,, Propyl acetate ,,	20 40 20 40	1.01-0.81 0.93 0.68-1.04 0.98		v n v n	{ } } }
Ethyl benzoate	Benzene Toluene ,, Acetic acid Benzyl benzoate	25 25 25 25 25	1.45 1.70 } mean 1.60 } 1.69 (1.12) 0.50-0.59	0.69 0.73 0.76 0.96-0.81	n n n c(2:1) v	Kendall and Monroe Linebarger Kendall and Monroe Kendall and Brakeley Kendall and Wright
Benzyl benzoate	Benzene	25	2.00-3.23	0.50-0.31	v	Kendall and Monroe

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II. Mixture. (*Continued*)

Component 1	Component 2	$t^{\circ}\text{C.}$	K	(ka) of comp. 1 rel. to (ka) of benzene	Remarks	Observer
Benzyl benzoate	Benzene	5	2.63-5.00	0.38-0.20	v	Bingham and Sarver
	"	15	2.13-4.00	0.47-0.25	v	
	"	25	1.89-3.23	0.53-0.31	v	
	"	40	1.64-2.70	0.61-0.37	v	Kendall and Monroe Kendall and Wright "
	Toluene	60	1.35-2.08	0.74-0.48	v	
	Ethyl acetate	25	2.56-4.00	0.49-0.31	v	
Aniline	Ethyl benzoate	25	2.63-4.55	0.77-0.45	v	Bramley
	"	25	1.70-2.00	0.43-0.37	v	
	<i>o</i> -Nitrophenol	30	$K'1.83, K''1.10$		a	
	"	40	$K'1.76, K''0.96$		a	"
	"	60	$K'1.69, K''0.91$		a	
	"	80	$K'1.55, K''0.93$		a	
	Phenetol	0	3.45	0.30	n	I. C. T.
	"	10	3.12	0.33	n	
	"	20	2.72	0.38	n	
	"	30	2.54	0.40	n	
	"	40	2.43		n	
	"	60	2.11		n	
	"	80	1.86		n	
	Ethyl acetate	0	5.26-7.69	0.39-0.26	v	
Metnyl aniline	Guaiacol	30	0.71		n	Puschin and Pinter
Dimethyl aniline	Phenol	10	0.16-4.0		v	Bramley
	"	20	0.22-2.0		v	
	"	29.8	0.26-2.0		v	
	"	40.2	0.32-1.7		v	
	"	59.9	0.41-2.0		v	
	"	80	0.48-2.0		v	
	"	126	0.57-2.0		v	Puschin and Pinter
	Guaiacol	177	0.71		n	
		30	0.40		n	

II. Mixture. (Continued)

Component 1	Component 2	t°C.	K	(ka) of comp. 1 rel. to (ka) of benzene	Remarks	Observer
Diphenyl amine	Phenol	30 40 81	1.08-1.92 1.05-1.82 1.33		v v n	Bramley
Diphenyl methyl amine	Phenol	9.8 20.1	K'1.15, K'1.65 K'1.19, K'1.44		a	
	"	30	K'0.81, K'1.79		a	
	"	40	K'0.92, K'1.56		a	"
	"	60	K'1.16, K'1.08		a	
	"	80	K'1.20, K'0.91		a	
Benzal aniline	Stilbene	125	1.11		n	Beck
	Azobenzene	75	0.97		n	"
	Benzyl aniline	75	0.99		n	"
Benzyl aniline	Benzal aniline	75	1.01		n	"
m-Toluidine	n-Hexane	22 32	5.26\ mean 5.00/ 5.13	0.30	n	Dessart
	Cyclohexane	15	3.03\ mean	mean	n	
	"	30	3.13/ 3.08	0.32	n	"
	Methyl cyclohexane	15	3.85\ mean	0.31	n	"
	"	30	3.45/ 3.65	0.31	n	"
	Benzene	15	5.56	(0.18?)	n	"
	"	30	4.17	(0.24?)	n	"
	Toluene	15	6.67	(0.18?)	n	"
	"	30	4.76	(0.26?)	n	"
Pyridine	Benzene	25	(1.32)	0.76	c(2:1)	Dunstan, Thole and Hunt
	Water	0	(0.84)	0.80	c(1:3+1:2)	Hartley, Thomas
	"	25.08			c(1:3+1:1)	and Applebey
	o-Nitrophenol	30	(0.55)		c(1:2)	
	"	40	(0.65)		m = 2.00	
	"	60	(0.74)		C ₀ = 7.02 × 10	Bramley

II. Mixture. (Continued)

Component 1	Component 2	t°C.	K	(ka) of comp. 1 rel. to (ka) of benzene	Remarks	Observer
Pyridine	<i>o</i> -Nitrophenol	80	(0.84)	0.80	$c(1:1)$ $m = 1.44$ $C_0 = 1.4 \times 10$ & $c(1:5)$ $m = 2.00$ $C_0 = 3.44 \times 10^3$ $c(1:3)$ $m = 1.60$ $C_0 = 1.6 \times 10^2$	Swearingen and Heck Tsakalotos Yajnik and coworkers
	Acetic acid	35	(1.08)			
	"	45				
	"	55				
	"	65				
Butyric acid	"	75				
	"	80				
	"	20	(1.67)			
	"	18.2	(1.67)			
	"	30	(1.92)			
Quinoline	"	40	(2.50)			
	"					
Benzene	Benzene	25	2.17	0.46) mean 0.44) 0.45	n n	I. C. T. "
	Ethyl alcohol	25	1.12			
Carbon bisulphide	Benzene	25	1.10	0.91 mean 0.95 0.98	n n n n n n n n a a a	Linebarger Thorpe and Rodger Dunstan Faust
	Methyl iodide	0	0.53			
	"	10	0.61			
	"	20	0.61			
	"	30	0.69			
	"	40	0.72			
	Ethyl alcohol	25	0.50			
	Acetone	-13	$K/1.16, K'/1.27$			
	"	-10	$K/1.31, K'/1.02$			
	"	0	$K/0.89, K'/1.42$			
Mercaptan	Ethyl alcohol	25	0.37	1.32	n	Dunstan
Allyl thiocyanide	Ethyl alcohol	—	$K/1.22, K'/1.82$	0.40, 0.89	a	Wagner
Lead	Tin	400	1.15		n	Arpi "
	Bismuth	500	1.03		n	
	"	400	2.6		n	
	"	500	1.6		n	

II. Mixture. (*Concluded*)

Component 1	Component 2	$t^{\circ}\text{C.}$	K	(ka) of comp. 1 rel. to (ka) of benzene	Remarks	Observer
Tin	Lead	400	0.87		n	} Arpi
	"	500	0.97		n	
Bismuth	Lead	400	0.38		n	} "
	"	500	0.63		n	
Sulphur chloride	Benzene	15.5	1.28	0.781 mean	n	} De Carli
	"	20	1.28	0.781 (0.78)	n	
	Nitrobenzene	3	0.35-0.62	1.40-0.79	v	} "
	"	20	0.83-0.62	0.59-0.79	v	
	Benzaldehyde	3	1.89-1.12		v	} "
	"	13.2	1.10		n	
	"	20	0.86		n	} Kurnakow
Stannic chloride	Benzene	25	$K/2.08, K'/0.86$	0.48, 0.86	a	
	"	70	$K/1.68, K'/0.95$	0.60, 0.95	a	} De Carli
	Nitrobenzene	15	(0.74)	0.66	c(1:2)	
	"	25	(0.59)	0.83	$m = 2.00$	} Stranathan and Strong
	Acetic acid	25.2			$C_0 = 1.31 \times 10^2$	
	Ethyl formate	30		Polym. $v_1 = 1 \times 2, 1 \times 7, 1 \times 14$ $v_2 = 3 \times 2, 3 \times 7, 3 \times 14$		} Kurnakow
	"	40		Polym. $v_1 = 1 \times 30, 1 \times 60, 1 \times 7$ $v_2 = 2 \times 30, 2 \times 60, 1 \times 7$		
	"	50		Polym. $v_1 = 1 \times 30, 1 \times 7$ $v_2 = 2 \times 30, 1 \times 7$		
Stannic bromide	Nitrobenzene	25		0.49	c(1:1)	
	"	40	(1.00)			} De Carli

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solutional viscosity or the viscosity of ionic pair of KCl. Column 3 in Table 7 shows thus estimated solutional viscosities, the viscosities of water at the corresponding temperatures being adopted from Internat. Crit. Tables, V.

By simple calculation, we see that these viscosity values are quite sufficiently expressed by the quadratic equation :

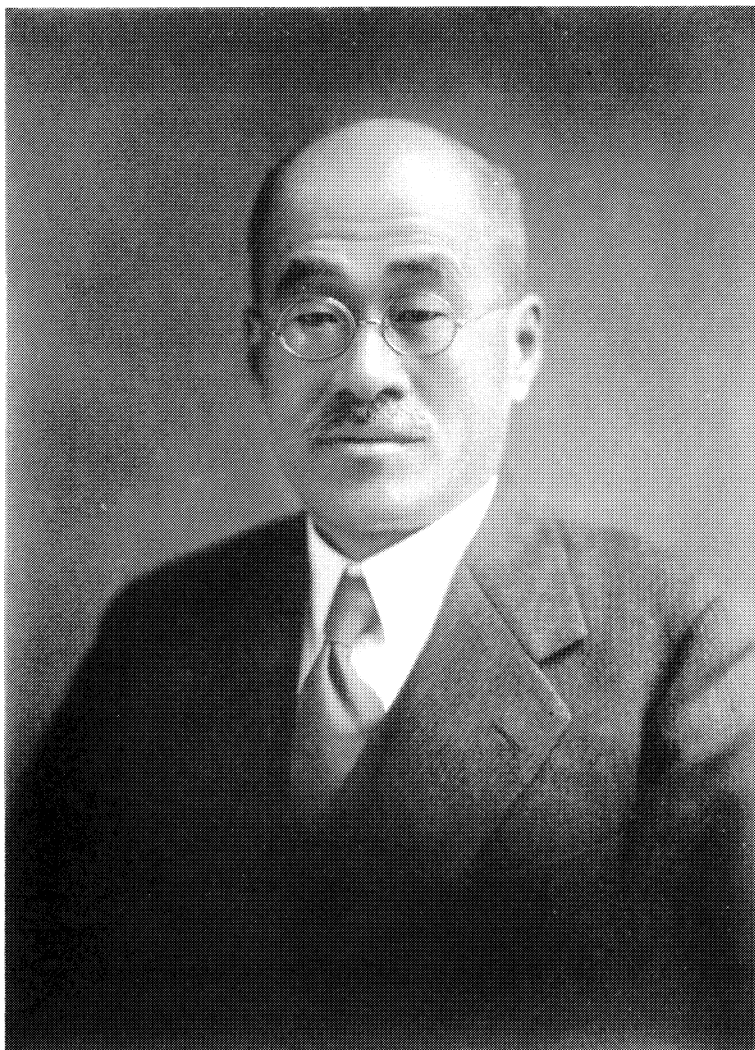
$$\eta_t = \frac{0.01533}{1 + 0.02730t + 0.0001141t^2}.$$

The fact that the equation of this type has been proved by Thorpe and Rodger⁽¹³⁾ to reproduce very closely the viscosity of numerous organic liquids without molecular complexity, and further that the magnitudes of these here obtained coefficients also are reasonably acceptable as compared with those for such liquids as ethylene chloride, carbon tetrachloride, and acid anhydrides, draws the conclusion that the solutional state of an electrolyte which is composed of its ionic pairs behave, as would be expected, like a liquid containing no molecular aggregates.

In conjunction with our study hitherto made some inquiry about the characteristic constant K along quite different lines, which we earnestly hope, may afford a clue to unveil the mysterious nature of liquids.

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Ritsko Majima

PROFESSOR RIKŌ MAJIMA.

On November 13th, 1934, Prof. Majima completed his sixtieth year and a feast in honour of him was given in Tokyo by his pupils, and in congratulation of this memorable day in his long life, a sum of contributions gathered among his pupils was presented to him, together with a souvenir of the occasion. On receiving it, he was good enough to give some part of it to the Chemical Society of Japan for the fund of a prize. Accordingly the Majima Prize was established, and from the year 1936 at every Annual Meeting of the Society, it shall be awarded to any person who has done an excellent work in organic chemistry or biochemistry. The papers collected in the present number of this Bulletin, all of which are the recent works of his pupils, are dedicated to Prof. Majima, and the expenses for publishing them are drawn from the same source.

Prof. Rikō Majima was born in Kyoto on the thirteenth day of November in 1874, as the eldest son of Toshitami Majima, a noted physician. His primary and middle school days were spent under his parents in this old city. Without finishing the middle school course, he came to Tokyo in order to prepare himself for the entrance examination of the First Higher School, which he passed successfully in 1890. Although in the middle school days he was rather a weak boy, he could now enjoy perfect health, for the restoration of which he tried every sports in his power: he was indeed once a member of the First Higher School Crew. It is evident that the health and the discipline given him by the sports enabled him to achieve the valuable works in later days. When he entered the Higher School he intended at first to make geology his life-work; but, advised by one of his seniors that his short-sightedness would be inconvenient for his study, he changed his course; and when he was admitted to the Tokyo Imperial University in 1896, he became a student in the Chemical Department of the Faculty of Science.

In the three years of the university life he studied inorganic chemistry under the late Prof. Edward Divers, physical chemistry and analytical chemistry under Prof. Kikunae Ikeda, and organic chemistry and part of physical chemistry under Prof. Joji Sakurai. He received also valuable instructions for the laboratory works from the late Prof. Tamemasa Haga, who had returned from Germany in 1898.

Immediately after his graduation in 1899, he was appointed Assistant and began to work under Prof. Sakurai. In 1903 he was promoted to the position of Assistant Professor. Thus Prof. Majima's research life was commenced, which, for convenience' sake, will be divided into three periods: the Tokyo period, the Sendai period, and the Osaka period.

One of his principal research objects in his Tokyo period was *urushiol*, the main constituent of Japan-lacquer.

In January 1907 he was ordered abroad for the study of inorganic chemistry, against his own interest in the organic branch. He was obedient to the order and his scheme was first to visit Prof. A. Werner, the brilliant initiator of the Co-ordination Theory. When he arrived in Europe, however, a telegram from the Japanese Government commanded him to take organic chemistry as his subject. This unexpected but agreeable change drove him immediately for Kiel from Zürich. It was quite natural that he should have done so, because at the Kiel University there was Prof. Harries, inventor of ozonolysis, probably the best method for the exploration of the constitution of *urushiol*.

At Kiel he was working hard upon *terpene* and partly upon *urushiol*. But unfortunately in the following year he suffered from influenza which brought pneumonia. Soon after recovery he was again infected with erysipelas which was followed by nephritis. Thus he was forced twice to lie in bed in the Kiel University Hospital. Then he had to stay at the noted spa Wildungen to ensure complete recovery. It was only after one complete summer semester had passed that he could return to the laboratory. His research work there was kept on again from the beginning of the winter semester of the year 1908 until the end of the summer in 1909.

From the winter semester of the year 1909 until the end of the summer in 1910, he stayed at Zürich under Prof. R. Willstätter, with whom he worked on some oxidation mechanism of aniline.

Then he went over to England to inspect the state of things in the study of chemistry and spent some time at the Davy-Faraday Research Laboratory of the Royal Institution in London. Then passing through the United States of America, he returned to Japan on March 3rd in the year 1911.

Just at that time the Faculty of Science of the Tōhoku Imperial University was newly founded at Sendai. ("Tōhoku" means north-east. This university is so called as Sendai is situated in the north-eastern part of Japan proper). The Faculty was ready to receive him in 1911 as one of the professors. Prof. Majima's Sendai period was thus begun and it was in this period that the works upon *urushiol* were published. For this research, in 1913 he was honoured with the Sakurai Prize from the Tokyo Chemical Society and then in 1917 with the Imperial Academy Prize from the Imperial Academy of Japan.

His research field, however, was not confined only to *urushiol*; he also found a new synthetical method for obtaining *indole* by a pyrogenetic reaction of *aniline* and *acetylene*. His endeavour was then naturally directed to the synthetical works upon various *indole* derivatives.

His interest was also directed to many natural colouring matters, e.g. *shikonin*, *carthamin*, and many other sorts of *anthocyanins* (studied partly with Miss C. Kuroda), *mangostin* and *fukugetin* (studied by M. Murakami); and also to synthetical pigments, e.g. some new classes of vat dyes (by M. Nakanishi) and various sorts of photographic sensitizers (by T. Ogata and S. Sakurai). They should specially be cited, as those studies were all executed in Prof. Majima's laboratory under his zealous encouragement.

In his endeavour to elucidate the constitution of *aconitine*, Prof. Majima showed a fair example of his character, or the spirit fighting against a difficult problem to explore the mystery wrapped in it.

Aconitine, the alkaloid of aconitum roots, has many hydroxyl-groups and, indeed, an unparalleled complex nature. Prof. Majima began the study in collaboration with T. Suginome, S. Morio, and H. Shimanuki, and is still continuing it step by step assisted by K. Tamura. Assuredly the difficulties of isolating the *aconitine* in pure state greatly puzzled him in his earlier experiments, but his strenuous efforts brought him a clear decisive result. He could isolate the four sorts of *aconitines*, i.e. *aconitine*, *mesaconitine*, *hypoaconitine*, and *jesaconitine*, in pure forms, from about sixteen different species of aconitum plants.

In 1926 he was elected Member of the Imperial Academy of Japan, and although he was rather a man in the laboratory, he was compelled gradually to take up many administrative responsibilities with relation to the universities in Japan. He became, in 1926, the Director of the Faculty of Science of the Tōhoku Imperial University, which post he held until 1928. He was appointed, in 1927, head of the Organizing Committee of the Science Faculty of the Hokkaido Imperial University which was to be established at Sapporo, and he was, in 1930, appointed Director of that newly opened Faculty, in which post, however, he remained only for a year, as an additional one to the professorship at Sendai. Meanwhile he was also a member of the Organizing Committee of the Department of the Dyestuff-Chemistry of the Tokyo University of Engineering.

In 1931 he was again a member of the Organizing Committee, this time, of the Faculty of Science of the Osaka Imperial University, and was appointed Professor and Director of this new faculty since its foundation in 1932. In 1933, he and his family left Sendai, where they had lived twenty-two long years, and removed to Osaka. Thus his Osaka period was begun.

It is the present writer's happy duty to report that he is still assiduously engaged in his research works on *aconitines*, etc., in his new laboratory, with the same health and energy as were enjoyed in his Sendai period. He

may perhaps thus be making good for the time long lost in the administrative affairs in the various universities.

Outside the universities he has been also active since 1917 as a member of the research staff of the Institute of Physical and Chemical Research, Tokyo; since 1920 as a member of the National Research Council of Japan ("Gakujutu Kenkyu Kaigi"); and since 1933 as a member of a committee of the Foundation for the Promotion of Scientific and Industrial Research of Japan ("Nippon Gakujutu Sinko Kai"). In 1924 Prof. Majima was sent to the Fifth Conference of the International Union of Pure and Applied Chemistry held at Copenhagen as the delegate of the National Research Council of Japan. In 1927 he was elected Honorary Member of the Chemical Society of Holland.

Prof. Majima's life is not complete if his literary work is left unmentioned. It is the compilation of the complete abstracts of Japanese chemical literatures. For this painstaking work he received donations from the "Keimei Kai" Foundation and was also given contributions from many supporters. Consequently he was able to found a society called "Nippon Kagaku Kenkyu Kai" in 1926, with the sole purpose of continuing the work already commenced as early as 1918 and of publishing the materials thus accumulated. In the year 1927 the first product of his endeavours appeared in the form of a book entitled "Nippon Kagaku Sōran" Vol. I, which covers the period of 1877-1900. Since then Vol. II (1901-1908), Vol. III (1909-1913), Vol. IV (1914-1917) and Vol. V (1918-1921) have all been published. Besides these a monthly magazine with the same title has also been edited by him. It publishes the complete abstracts of the current Japanese chemical literatures, beginning with the year 1927. The gap between the year 1922 and 1926 will be filled with two more volumes of the "Nippon Kagaku Sōran" which are now ready in press. Needless to say, these publications were received with enthusiasm by the Japanese chemists as well as by the whole circles of the scientists in the country.

The green old age of Prof. Majima, who has played such an important rôle in promoting the scientific education and research in Japan and especially served in elevating his special domain of organic chemistry in this country up to the present state, should heartily be congratulated not only by his pupils but by all the Japanese chemists, wishing on their part for his further aid for the future advancement of chemistry in Japan.

Sin'iti KAWAI.

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ON THE COMPOSITION OF RAPE SEED OIL.

By Riichiro YAMASAKI and Kentaro ICHIHARA.

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Numerous studies on the rape seed oil have hitherto been published, and the composition of the fatty acid mixture from the oil has been considered generally as follows:⁽¹⁾ myristic acid 1.5%, stearic acid 1.5%, arachidic acid 1.5%, oleic acid 19.5%, erucic acid 60%, linolic acid 14%, and linolenic acid 2% (total 100%). This composition corresponds to an oil with the saponification value 171 and the iodine value 88.7. But rape seed oil, as well known, has generally saponification value 172-175 and iodine value 99-103, and such a low iodine value as the above-mentioned (88.7, nondrying oil) has never been found in any of the rape seed oils prepared from the various sorts of the seed.⁽²⁾ The authors describe in this paper the quantitative determination of the composition of rape seed oil.

The sample oil employed in this study had moderate numbers for rape seed oil: $d_4^{15.5}$ 0.9147, viscosity (Redwood) at 104°F. 186 sec., at 210°F. 55 sec., flash point 278°C., cloud point -14°C., pour point -17°C., acid value 1.3, saponification value 174, iodine value (Wijs) 101, moisture 0.2%, and hexabromide value 7.66 (corresponding to 2.81% of linolenic acid by calculation).

Rape seed oil (1 kg.) was saponified with 4 N alcoholic potash, the solvent was evaporated, the residual soap was dissolved in water, and the solution

Fraction	Temperature °C./10 mm.	Yield (g.)	Saponif. value	Iodine value	Saponif. value calculated as methyl ester (F_1)
I	-200	50	200	94.6	C ₁₇ acid 199
II	200-210	400	189	132	C ₁₈ „ 189
III	210-215	25	183	86.4	C ₁₉ „ 181
IV	215-220	40	175	—	C ₂₀ „ 173
V	220-230	250	163	74.5	C ₂₁ „ 166
VI	230-235	100	160	73.3	C ₂₂ „ 159
VII	residue	85	—	—	—
	loss	50			

(1) Grün, "Analyse der Fette u. Wachse", Vol. II (1929), 44. Hilditch, Riley and Vidyarthi, *J. Soc. Chem. Ind.*, **46** (1927), 457, 462. Täufel and Bauschinger, *Z. Untersuch. Lebensm.*, **56** (1928), 253.

(2) Lewkowitch, "Chem. Tech. and Analy. of Oils, Fats and Waxes", Vol. II (1914), 262. Ubbelohde, "Chem. Analy. und Technol. d. Öle u. Fette", Vol. II (1920), 176. Grün, *ibid.*

was acidified and extracted with ether. The ethereal solution was concentrated, and the resulting fatty acid was converted into the methyl ester, which was then subjected to fractional distillation under diminished pressure. After 9 rectifications, fractions I-VII were obtained.

Fraction I was further fractionated :

Fraction	Temperature °C./25 mm.	Yield (g.)	Saponif. value	Iodine value	Saponif. value calculated as methyl ester ($\bar{F}_1$)
1	135-195	5	213	—	C ₁₅ acid 221
2	195-210	10	210	77.6	C ₁₆ „ 209
3	210-220	10	201	86.7	C ₁₇ „ 199
4	220-228	10	201	96.0	„ „ „
5	228-248	5	—	—	
6	residue	10	—	—	

From fraction 1 fatty acid mixture was liberated and separated by means of lead salt alcohol method into two following portions :

solid acid, yield 2.4 g., neutralization value 215, m.p. 57°C. ; liquid acid, yield 2.0 g., neutralization value 202, iodine value 104.

By recrystallization of the solid acid, palmitic acid was isolated and it was confirmed by mixed-melting method. The liquid acid seemed to be a mixture of oleic, linolic and a small amount of palmitic acids. The existence of myristic acid and palmitoleic acid was doubtful.

Fraction II (30 g.) was subjected to lead salt ethanol method :

solid acid, yield 3 g. ; liquid acid, yield 25 g., neutralization value 190, iodine value 144.

The above solid acid was fractionally recrystallized :

Fraction	Yield (g.)	M.p.(°C.)	Neutralization value	Iodine value
1	0.7	60.5-61	204	—
2	1.2	52.5-55	194	—
3	0.9	51-55	179	51.3

Fraction 1 was confirmed to be palmitic acid by mixing with pure acid, and fraction 3 was considered to be crude erucic acid from its neutralization and iodine values. Contrary to our anticipation, stearic acid could not be obtained ; if stearic acid were present, it would crystallize out first in the 1st

crystalline fraction before palmitic acid. Fraction 2 seemed to be a mixture of erucic acid and palmitic acid.

The liquid acid portion of fraction II was a mixture of oleic, linolic, and a minute quantity of linolenic acids, judging from the neutralization and iodine values and the yield of its hexabromide.

As the existence of oleic and linolic acids in rape seed oil was already confirmed by Toyama,⁽³⁾ isolation and identification of these acids were omitted in this study.

From fraction III liquid C₁₈-acid and solid C₂₂-acid were obtained.

Fraction IV (40 g.) was separated into two following portions by the usual method.

Solid acid, yield 16 g., neutralization value 173; liquid acid, yield 21 g., neutralization value 191, iodine value 92.7.

The solid acid was recrystallized:

Fraction	Yield (g.)	M.p.(°C.)	Neutralization value	Iodine value
1	2	33-34	167	66.6
2	3	33-34	170	73.7
3	10	—	175	—

Namely, only erucic acid was isolated and no arachidic acid seemed to exist in this oil.

Fraction V and VI were obviously methyl erucate.

Fraction VII (residue) (85 g.) was saponified and the unsaponifiable matter was extracted with ether. From the aqueous layer, mixed acids were liberated and recrystallized from methanol.

Crystal	Yield (g.)	M.p.(°C.)	Neutralization value	Iodine value
1	1	76.5-77.5	167	0.5
2	2	33-35	166	74.7
3	21.5	32-33.5	169	74.1
4	25	32-33.5	168	76.2
5	16.5	32.5-33.5	167	75.5
6	10	32-33.5	166	73.7
7	5	28-29	165	73.7

(3) *J. Soc. Chem. Ind., Japan*, **25** (1922), 1044; *Chem. Umschau, Fette, Öle, Wachse, Harze*, **30** (1923), 88.

Crystals 1 and 4 were identified with pure behenic and erucic acids respectively by the usual mixing test. On the other hand, the ethereal layer was concentrated and about 7 g. of brassicasterine⁽⁴⁾ was obtained.

Summary.

The composition of rape seed oil was determined and the contents of the fatty acids were calculated from the chemical numbers of the original oil and each fraction: behenic acid 0.8%, erucic acid 55%, oleic acid 14%, linolic acid 24%, linolenic acid 2%, and palmitic acid 3.5%. Myristic, palmitoleic, and stearic acids, however, could not be found.

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(4) Siegfeld, *Z. Nahr. Genussm.*, **17** (1904), 581. Windaus and Welsch, *Ber.*, **42** (1909), 612. Marcusson and Meyerheim, *Z. angew. Chem.*, **27** (1914), 201. Schmid and Waschkau, *Monatsh.*, **48** (1927), 139.

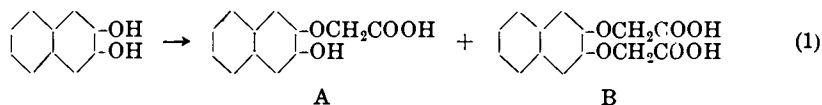
ÜBER DIE PRODUKTE DER EINWIRKUNG VON MONOCHLORESSIGSÄURE AUF NAPHTHOLE.

Von Rin-nosuke SHIBATA und Minoru OKUYAMA.

Eingegangen am 15. Oktober 1935. Ausgegeben am 28. März 1936.

Einleitung. Beim Erhitzen äquimolekularer Mengen von Monochloressigsäure mit β -Naphthol in Gegenwart von Kalilauge wird β -Naphthoxyessigsäure⁽¹⁾ kondensiert. In analoger Weise wirkt Monochloressigsäure auf Dioxynaphthalin. So hat man aus 2,3-Dioxynaphthalin 2-Naphthol-3-oxyessigsäure (Formel A) vom Schmp. 153°, in farblosen Nadeln aus Wasser gewonnen, die gegenüber 2,3-Dioxynaphthalin wesentlich gesteigerte Baumwollaffinität zeigt und bei der Faser mit diazotiertem *p*-Nitranilin einen durch Schönheit ihrer Tönung hervorragenden, roten Farbstoff ergibt, der freilich in der Echtheit hinter der Naphthol-AS-Färbung zurücksteht. Dabei hat man noch eine Spur von 2,3-Naphthalindioxyessigsäure (Formel B) erhalten, aber aus 2,7-Dioxynaphthalin, nur Mono-oxyessigsäure vom Schmp. 202–203°.

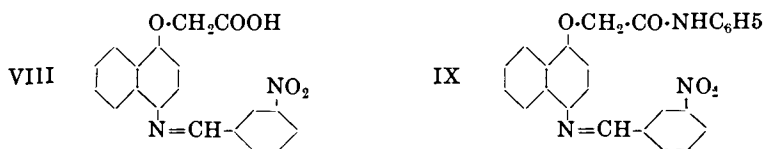
(1) F. Spitzer, *Ber.*, **34** (1901), 3191.



Verfasser hat früher bei Herrn Prof. Hans Bucherer diese Reaktion⁽²⁾ untersucht. Es handelte sich damals jedoch anfänglich darum, eine Hydroxylgruppe von Dioxynaphthalin zu besetzen, um die Reaktion mit *p*-Dimethylamino-anilin-*o*-thiosulfonsäure zu vereinfachen.

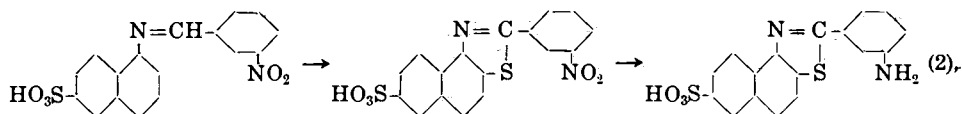
In vorliegender Arbeit wollte Verfasser weiter möglichst viele Produkte dieser Reihe synthetisieren, um den Einfluss der Oxyessigsäuregruppe des Naphthalinkerns auf die Naphthole sowie ihre Abkömmlinge in ihrer Substantivität näher unterzusuchen, wie er sich beim 2,3-Dioxynaphthalin so ausgezeichnet hatte erweisen lassen.

α -Naphthol. Zunächst haben wir aus α -Naphthol folgende Verbindungen synthetisiert: I. 1-Naphthoxyessigsäure, Schmp. 193.5°, farblose Nadeln aus Benzol; II. 4-Nitronaphthyl-1-oxyessigsäure, Schmp. 217°, gelbe Nadeln aus Xylol; III. 4-Aminonaphthyl-1-oxyessigsäure-chlorhydrat, Schmp 231°, farblose Nadeln aus Äthanol, dessen freie Base: IV. Schmp. 220–225° (zers.) und farblose Nadeln zeigte; V. 4-Nitronaphthyl-1-oxyessigsäureanilid, Schmp. 181.5°, schwach gelbe Nadeln aus Alkohol; VI. 4-Nitronaphthyl-1-oxyessigsäure-1'-Naphthyl-amid, Schmp. 241°, farblose Nadeln aus Aceton; VII. 4-Aminonaphthyl-1-oxyessigsäureanilid, Schmp. 142.5°, farblose Nadeln aus Ligroin-Benzol; VIII. *m*-Nitrobenzyliden-(1)-aminonaphthyl-(4)-oxyessigsäure, Schmp. 182.5°, gelbe, lange Blättchen aus Alkohol; IX. *m*-Nitrobenzyliden-(1)-aminonaphthyl-(4)-oxyessigsäureanilid, Schmp. 217.5°, gelbe Nadeln aus Aceton und X. *p*-Nitrobenzyliden-(1)-aminonaphthyl-(4)-oxyessigsäure, Schmp. 243°, gelborange farbige Nadeln aus Aceton.

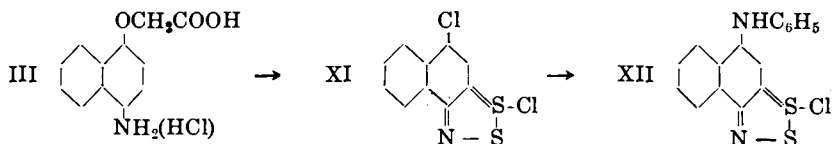


Durch die Synthese der Verbindungen II mit X wollten wir ein neues, eine Oxyessigsäuregruppe enthaltendes Thiazol gewinnen, nach dem Verfahren des D. R. P. 165 226 über Benzylidenverbindung, mit Hilfe von Schwefel und Schwefelnatrium (Gleichung 2):

(2) Näheres darüber wird vielleicht später von Herrn Prof. Bucherer veröffentlicht werden.



aber hatten gar keinen Erfolg damit. Zum selben Zweck haben wir die Verbindung III mit Schwefelchlorür nach Herz⁽³⁾ behandelt und dadurch eine gelbbraune Substanz erhalten, die mit Anilin eine in goldglänzende, tief violette Blättchen auskrystallisierende Verbindung bildet. Sie hat nach der Analyse die Zusammensetzung $\text{C}_{16}\text{H}_{11}\text{S}_2\text{N}_2\text{Cl}$ und stimmt in allen Eigenschaften mit dem Anilid überein, welches Vannotti⁽⁴⁾ nach Herz über Thiazthioniumchlorid des 1-Naphthylamins synthetisiert hat. Danach wirkt Schwefelchlorür auf die Verbindung III auf zwei Weisen: einerseits durch einen Ringverschluss zusammen mit der Aminogruppe zum Thiazthioniumchlorid, andererseits zugleich mit einer Kernsubstitution des Chloratoms durch Verdrängen der Oxyessigsäuregruppe:



Dieses Anilid färbt Wolle und tanningebeizte Baumwolle bordeauxrot, ganz wie ein basischer Farbstoff.

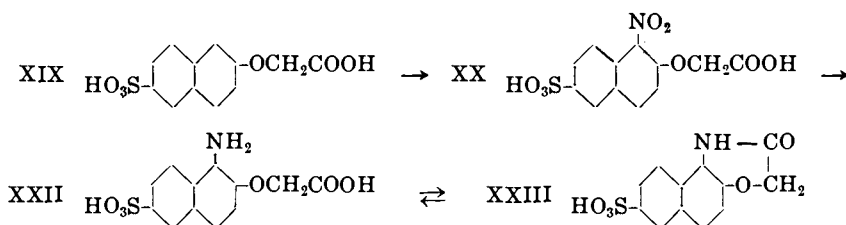
β -Naphthol. Durch Nitrierung der β -Naphthoxyessigsäure erhält man zwei Nitrokörper. Der eine, 1-Nitroverbindung XIII, gelbe Nadeln aus Eisessig vom Schmp. $191-192^\circ$, bildet das Hauptprodukt, dessen Anilid XV bei 169° schmilzt und aus Alkohol gelbe Mikrokrystalle darstellt. Der andere XIV, der daneben entsteht schafft auch gelbe Nadeln aus Eisessig, welche zwischen 157 und 185° schmilzt, liefert jedoch ein ganz anderes Anilid XVI, welches aus Äthanol schwach gelbe, lange, etwas biegsame Nadeln vom Schmp. 217° darstellt. Durch Reduktion gibt der erste sowie sein Anilid ein und dasselbe Produkt XVII vom Schmp. $218-219^\circ$, welches aus Alkohol farblose Nadeln darstellt und nichts anderes als das innere Anhydrid der 1-Aminonaphthyl-2-oxyessigsäure ist, der zweite dagegen eine braungelbe Substanz XVIII vom Schmp. $187-188^\circ$, vielleicht 6-Aminonaphthyl-2-oxyessigsäure, welche aus Alkohol in Nadeln krystallisiert.

(3) Richard Herz, D.R.P. 360690 (Frdl. XIV. 908).

(4) F. Vannotti, Dissertation der Eidg. Techn. Hochschule, Zürich (1933).

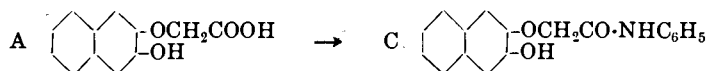
2-Naphthol-6-sulfosäure. Zunächst wendet man Schäffersche Säure als Naphthol an, um möglicherweise durch Einführung der Sulfogruppe die Anhydridbildung der 1-Aminonaphthyl-2-oxyessigsäure zu verhindern und um ferner damit auch ein Thiazol über die entsprechende Benzylidenverbindung zu synthetisieren.

2-Naphthoxyessig-6-sulfosäure XIX bildet ein Dinatriumsalz, welches aus Wasser mit 2 Mol. Krystallwasser farblose Blättchen darstellt, wohingegen man aus der verd. Salzsäure Mononatriumsalz ohne Krystallwasser erhält. Durch Nitrierung gewann man 1-Nitrokörper XX, das Hauptprodukt und konnte aus dessen Mutterlauge ausserdem etwas 4-Nitrokörper XXI, ein Nebenprodukt in braungelben Nadeln, isolieren. Durch Reduktion gab 1-Nitrokörper XX wieder inneres Anhydrid XXIII, welches man jedoch durch Kochen mit Natronlauge in freie Oxyessigsäure XXII verwandeln kann:



Aber es ist uns noch nicht gelungen, daraus ein Thiazol zu synthetisieren. 1-Aminonaphthyl-2-oxyessig-6-sulfosäure XXII ist diazotierbar und kuppelt sich mit β -Naphthol zu einem blautichigen, roten, sauren Farbstoff.

2,3-Dioxynaphthalin-6-sulfosäure. Zur Erlangung der Substantivität der 2-Naphthol-3-oxyessigsäure sollte man sie weniger wasserlöslich machen. Es wäre also zweckmässiger, die Säure in ihr Anilid (Formel C) zu verwandeln:

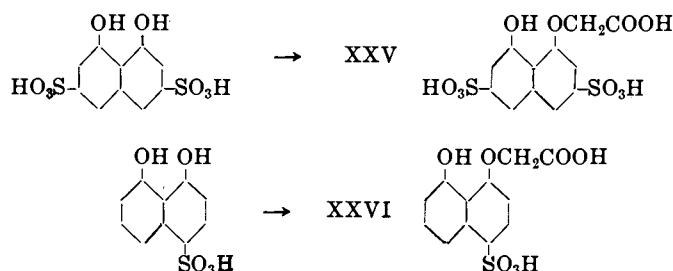


Im Gegensatz zu diesem allgemeinen Gedanken hat man zunächst 2,3-Dioxynaphthalin-6-sulfosäure angenommen. Statt, wie aus 2,3-Dioxynaphthalin und Monochloressigsäure, bei Gegenwart von Soda hauptsächlich Mono-oxyessigsäure und nur spurweise Dioxyessigsäure zu bekommen, verläuft die Reaktion mit 2,3-Dioxynaphthalin-6-sulfosäure gerade umgekehrt. Das heisst, die entsprechende Dioxyessigsäure XXIV ist das einzige Produkt. Man konnte dies nicht verhindern, weder durch Anwendung von weniger Soda, noch durch sonstigen milderen Kondensationsverfahren, z.B. Natriumacetat statt Soda und niedrigerer Temperatur. Dioxyessigsäure XXIV hat Kuppungsfähigkeit, obwohl die so gewonnenen Azofarbstoffe wegen ihres unschein-

baren, hellorangen Farbtons technisch wertlos sind. Beide sind vielleicht die Folge des Vorhandenseins der Sulfogruppe in 6-Stellung.



1,8-Dioxynaphthalin-sulfosäure. Nächst der 2,3-ortho-Stellung hat man die 1,8-peri-Abkömmlinge untersucht. Als Einwirkungsprodukt der Monochloressigsäure auf die Chromotropsäure in Gegenwart von Soda entsteht allein die entsprechende Mono-oxyessigsäure XXV, deren Mononatriumsalz in farblosen Nadeln aus Wasser krystallisiert.



Sie koppelt sich mit dem diazotierten *p*-Nitranilin zu einem roten Azofarbstoff, der als Säurefarbstoff Wolle in einem klaren, leuchtend roten Farbton färbt.

Auf dieselbe Weise gewinnt man aus Dioxynaphthalin-sulfosäure S auch nur eine Monooxyessigsäure XXVI, die aus Wasser in farblosen Nadeln krystallisiert und sich mit dem diazotierten *p*-Nitranilin zu einem roten Azofarbstoffe koppelt, der als Wollfarbstoff dient.

In beiden Fällen wurde durch Einführung einer Oxyessiggruppe der Farbton der Farbstoffe mit der Veränderung des ursprünglich blaustichigen Rots in klares, reines Rot beeinflusst. Das Verhalten der Farbstoffe gegen die Metallbeize wurde so beeinflusst, dass die Farbveränderung durch Nachbehandlung augenscheinlich schwächer wurde.

Diese Untersuchung ist noch im Gang, aber vorliegende Mitteilung möchten wir doch hier bringen, als einen kleinen Beitrag zur Festschrift für unseren hochverehrten Professor Dr. Rikō Majima, und dabei ihm auch hier unsre besten Glückwünsche aussprechen.

An dieser Stelle sagen wir auch der Japanische Gesellschaft zur Förderung der Wissenschaft und Industrie für ihre grosszügige Unterstützung unseren verbindlichsten Dank.

Beschreibung der Versuche.

I. α -Naphthol. (1) α -Naphthoxyessigsäure.⁽¹⁾⁽⁵⁾ 20 g. α -Naphthol wurde in 72 g. Kalilauge (1:2) gelöst. Nach Verdünnen mit 200 c.c. Wasser wurde die Lösung bei 100° unter Umrühren erhitzt, wobei man innerhalb von etwa 2 Stunden eine Lösung von 19 g. Monochloressigsäure in 90 c.c. Wasser langsam zufließen lässt. Nach vollständigem Eintropfen der Lösung wurde alles noch eine halbe Stunde lang erwärmt. Den Reaktionsendpunkt erkennt man, wenn die Kupplungsfähigkeit verschwindet. Nach beendeter Reaktion wurde das Gemisch abgekühlt und mit verd. Salzsäure deutlich sauer auf Lackmuspapier angesäuert, woraufhin Oxyessigsäure ausschied. Man saugt die Niederschläge ab, wäscht mit kochendem Wasser, trocknet und löst alles in 80 c.c. Alkohol. Nach dem Entfärben mit Tierkohle lässt man die Lösung in 160 c.c. Wasser einfließen, worauf die Säure in farblosen Säulchen auskrystallisiert. Nach dem Umkrystallisieren aus Benzol zeigte das reine Präparat den Schmp. 193.5°. Die Ausbeute betrug 20-25 g. α -Naphthoxyessigsäure ist leicht löslich in Äthanol, Methanol, Äther, Aceton, Essigester sowie Toluol und ein wenig löslich in Benzol sowie Schwefelkohlenstoff. Sie hat keine Kupplungsfähigkeit.

(2) 4-Nitronaphthyl-1-oxyessigsäure.⁽¹⁾⁽⁵⁾ 17 g. α -Naphthoxyessigsäure in 60 c.c. Eisessig wurden bei 20-30° mit 26 c.c. Salpetersäure von 40° B $\acute{e}$ nitriert. Man saugt die so gewonnene gelbe Paste ab und wäscht sie mit Eisessig, danach mit Wasser aus, trocknet und krystallisiert sie aus Eisessig um. Schöne gelbe Säulchen vom Schmp. 215°-216°. Die Ausbeute betrug 15 g. Nach dem Umkrystallisieren aus Xylol Schmp. 217°. Sie ist leicht löslich in Äthanol, Methanol, Aceton, Eisessig sowie Essigester und ein wenig in Äther, Benzol, Toluol, Xylol sowie in Wasser.

(3) 4-Aminonaphthyl-1-oxyessigsäure.⁽¹⁾ 5 g. feinpulveriger Nitrokörper in 40 c.c. Eisessig wurden bei 100-110° mit 8 g. Zinnpulver und 20 c.c. konz. Salzsäure reduziert, nach Beendigung der Reaktion mit 400 c.c. heissem Wasser verdünnt und heissfiltriert. Man entfernt das in die Lösung übergegangene Zinn mittels Schwefelwasserstoff und engt das Filtrat unter vermindertem Druck ein, wodurch man Chlorhydrat des Aminokörpers in farblosen Nadeln vom Schmp. 230° (zers.) gewinnt. Die Ausbeute betrug 4,1 g. Die freie Base kann man aus der alkalischen wässerigen Lösung durch Ansäuern mittels Essigsäure isolieren. Nach Umkrystallisieren aus Äthanol zeigt die reine, freie Base den Schmp. 220-225° (zers.) und stellt farblose Nadeln dar.

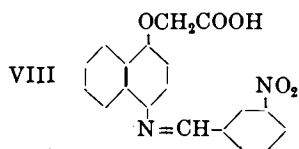
Behandelt man die Salzsäurelösung des Aminokörpers mit Natriumnitrit, so tritt eine blaue Farbe⁽⁶⁾ auf. Der diazotierte Aminokörper kuppelt sich mit β -Naphthol zu einem violettroten Azofarbstoff.

Der Aminokörper ist in verd. Alkalien leicht löslich, aber kaum in verd. Mineralsäure und ein wenig löslich in heissem Wasser, in organischen Lösungsmitteln aber meistens nicht löslich, jedoch in Essigester wieder ziemlich leicht löslich. Für Analyse wurde die Substanz über Benzylidenverbindung (Formel VIII) gereinigt. (Gef.: N, 5,55. Ber. für $C_{12}H_{12}NO_3Cl$: N, 5,53%.)

(4) *m*-Nitrobenzyliden-(1)-aminonaphthyl-(4)-oxyessigsäure. Durch 2-stündiges Kochen von 5 g. Aminokörper in 20 c.c. verd. Natronlauge und 20 c.c. Wasser mit 4 g. *m*-Nitro-

(5) B.H. Ingham, *J. Chem. Soc.*, **1931**, 895.

(6) Jacobs und Heiderbergér, *J. Am. Chem. Soc.*, **39** (1917), 2217, erklärten diese Erscheinung als einer partiellen Oxydation.



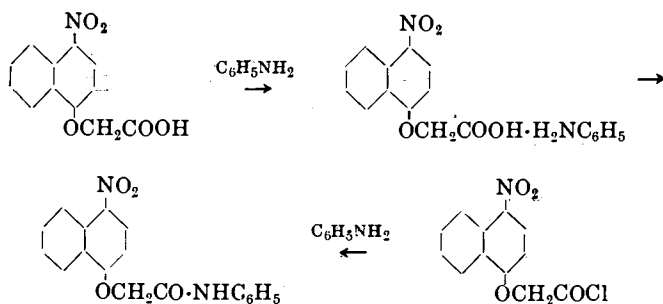
benzaldehyd scheidet die Benzylidenverbindung in gelben Blättchen aus. Zieht man den Krystallbrei aus und erwärmt ihn mit verd. Essigsäure, so erhält man die Säure im freien Zustand. Rohausbeute 4.5 g. Nach Umkrystallisieren aus Alkohol zeigt sie den Schmp. 182,5°. Durch Kochen mit verd. Mineralsäure spaltet sie sich leicht in den Aminokörper und in Aldehyd. Sie ist leicht löslich in Äthanol, Methanol, Äther, Aceton, Toluol sowie Essigester und ein wenig in Benzol. (Gef.: N, 7.65. Ber. für $C_{19}H_{16}N_2O_6$: N, 7.63%.)

(5) *1-Nitronaphthyl-4-oxyessigsäureanilid*. 1-Nitronaphthyl-4-oxyessigsäure wirkt durch gelindes Erwärmen leicht auf Anilin, wodurch sich eine lockere Verbindung bildet, vielleicht von der Zusammensetzung $C_{18}H_{16}N_2O_5 \cdot C_6H_5NH_2$, die so unbeständig ist, dass sie sich durch Kochen in organischen Lösungsmitteln schon abgespalten. Nach sorgfältigem Umkrystallisieren aus Alkohol erhielt man aus ihr schwachgelbe, feine Nadelchen, welche bei 124–125° fast völlig schmelzen, aber gänzlich erst bei 218°.

Durch 10-stündiges Kochen einer Lösung von 2.5 g. Nitrokörper in 10 g. Anilin erhält man aber 2.5 g. Anilid vom Schmp. 181.5° in schwachgelben Nadeln, was ganz mit dem Anilid, das man über dem Säurechlorid synthetisiert hat, übereinstimmt (Mischschmelzpunkt). (Gef.: N, 9.02. Ber. für $C_{18}H_{14}N_2O_4$: N, 8.70%.)

In eine Suspension von 7.5 g. gut getrockneter Nitrokörper in 80 c.c. Benzol wurden 6 g. Phosphorpentachlorid in 60 c.c. Benzol unter Umrühren langsam getropft. Nach 2-stündigem Erhitzen engt man die Benzollösung auf etwa ein Drittel des Volums ein, fügt dasselbe Volum Petroläther hinzu, und lässt alles so stehen, worauf das Säurechlorid in schwachgelben Nadeln ausscheidet. Nachdem Umkrystallisieren aus Benzol-Ligroin wurden 7.8 g. vom Schmp. 96° erhalten.

Durch Eintun von 2.5 g. Säurechlorid in 2.5 g. Anilin tritt sofort die Reaktion ein, wobei sich Gas und Wärme entwickeln. Man lässt sich alles durch Erhitzen lösen, fügt die dreifache Menge Alkohol hinzu, worauf das Anilid in schwachgelben Nadeln ausscheidet. Nach Umkrystallisieren aus Alkohol wurden 3.3 g. vom Schmp. 181.5° erhalten. Die Reaktion verläuft also folgendermassen:



Das Anilid ist in Aceton, Nitrobenzol sowie Anilin leicht löslich und beim Kochen ziemlich leicht löslich in Alkohol, Benzol sowie Methanol. Man kann das Anilid in Mineralsäure erwärmen, ohne dass es sich zersetzt.

(6) *1-Nitronaphthyl-4-oxyessigsäure-1'-naphthylamid*. Aus 2 g. α -Naphthylamin in 10 c.c. Alkohol und 2.5 g. Säurechlorid wurde 2.5 g. Naphthylamid gewonnen. Nach

Umkrystallisieren aus Aceton fast farblose Nadeln vom Schmp. 241° , welche in Wasser, verd. Säure u. Alkalien beständig sind. Es ist in den meisten organischen Lösungsmitteln wenig löslich. (Gef.: N, 7.67. Ber. für $C_{22}H_{16}N_2O_4$: N, 7.52%.)

(7) *1-Aminonaphthyl-4-oxyessigsäureanilid*. 1.4 g. 1-Nitronaphthyl-4-oxyessigsäureanilid in 90 c.c. Alkohol wurde mit 2 g. Zinnpulver und 7 c.c. konz. Salzsäure reduziert. Nach weiterem 30 Minuten langen Erhitzen filtriert man heiss und kühlt das farblose Filtrat ab; dann scheidet das Zinndoppelsalz aus, das man mit verd. Natronlauge behandelt. Die so ausgeschiedene Base wurde mit Äther aufgenommen. Nach Eindampfen des Äthers wurde 1.1 g. Base vom Schmp. 136° erhalten. Nach Umkrystallisieren aus Benzol-Ligroin Schmp. 142.5° . Es stellt etwas rötlich gefärbte, weisse Nadeln dar, welche in Aceton leicht und in Methanol, Äthanol, Äther, Benzol, Toluol und verd. Essigsäure beim Kochen löslich sind, wobei es den Lösungen eine schwach violette Fluoreszenz sich verleiht. (Gef.: N, 9.83. Ber. für $C_{18}H_{16}N_2O_2$: N, 9.58%.)

(8) *m-Nitrobenzyliden-(1)-aminonaphthyl-(4)-oxyessigsäureanilid*. Durch 30 Minuten langes Erhitzen einer Alkohollösung von 0.25 g. Aminokörper (VII) und 0.25 g. *m*-Nitrobenzaldehyd bekam man 0.4 g. Benzylidenverbindung vom Schmp. 216° .

Nach Umkrystallisieren aus Aceton, Schmp. 217.5° , schöne gelbe Nadeln, welche in Aceton, Benzol, Toluol und Essigester beim Kochen leicht löslich und in Methanol, Äthanol und Äther nur ganz wenig löslich sind. In verd. Mineralsäure verseifen sie sich leicht. (Gef.: N, 9.69. Ber. für $C_{25}H_{19}N_3O_4$: N, 9.88%.)

(9) *p-Nitrobenzyliden-(1)-aminonaphthyl-(4)-oxyessigsäureanilid*. Aus 1-Aminonaphthyl-4-oxyessigsäureanilid und *p*-Nitrobenzaldehyd wurde durch einstündiges Kochen ihrer Alkohollösung die entsprechende *p*-Nitrobenzylidenverbindung synthetisiert; goldgelbe Nadeln vom Schmp. 243° aus Aceton. (Gef.: N, 9.89. Ber. für $C_{25}H_{19}N_3O_4$: N, 9.88%.)

(10) *Einwirkung des Schwefelchlorürs auf 1-Aminonaphthyl-4-oxyessigsäure*. In eine Suspension von 2 g. gut getrockneten gepulverten Chlorhydrats der 1-Aminonaphthyl-4-oxyessigsäure (Formel III) in 50 c.c. wasserfreiem Benzol wurden 2 g. Chlorschwefel in 50 c.c. wasserfreiem Benzol innerhalb von 2 Stunden bei 40° getropft. Danach wurde die Temperatur allmählich auf 85° gesteigert. Nach 10 stündigem Erhitzen unter stetigem Umrühren und Luftfeuchtigkeitsabschluss wurde das gesamte Gemisch abgekühlt. Man saugt die Niederschläge ab, wäscht mit Benzol aus und trocknet im Vakuum. Die Rohausbeute beträgt 2 g. Dieses Thiazthioniumsalz hat keinen Schmp. und kein Lösungsmittel. Mit Anilin stellt es ein Anilid dar; z.B. werden 4 g. davon in eine Lösung von 6 g. Anilin und 10 g. Eisessig langsam getan. Erst dieses Gemisch löst sich und färbt sich blutrot. Bald aber scheidet das Anilid in goldglänzenden, rotbraunen Blättchen aus. Nach einige Stunden langem Stehenlassen verdünnt man es mit 20 c.c. eines aus 20 c.c. Eisessig, 20 c.c. Wasser und 30 c.c. 2 N Salzsäure bestehenden Säuregemisches, filtriert dies dann ab, wäscht mit dem Säuregemisch aus und trocknet alles im Vakuum über Ätznatron. Die Rohausbeute beträgt 3.5 g. Zur Analyse wurde es aus einem Säuregemisch, das aus 160 c.c. 2 N Salzsäure und 200 c.c. 2 N Eisessig bestand, umkrystallisiert. Aus der anfänglichen Mutterlauge wurde 0.6 g. 1-Aminonaphthyl-4-oxyessigsäure zurückgewonnen. (Gef. für Anilid XII: C, 58.25; H, 3.68; N, 8.62; S, 19.02; Cl, 10.66. Ber. für $C_{16}H_{11}N_2S_2Cl$: C, 58.10; H, 3.33; N, 8.47; S, 19.36; Cl, 10.74%.)

II. β -Naphthol. (11) *2-Naphthoxyessigsäure*. Aus 5 g. β -Naphthol und 7 g. Monochloressigsäure in Gegenwart von 27 g. Kalilauge (1:2) wurden nach Spitzer⁽¹⁾ 6-7 g. rohe 2-Naphthoxyessigsäure gewonnen. Man löst sie in verd. Ammoniak, verdünnt sie mit

Wasser auf 500 c.c. und filtriert sie. Man schüttelt das Filtrat mit Äther, um das unveränderte β -Naphthol zu trennen. Man säuert die wässrige Lösung mit konz. Salzsäure an, filtriert die abgeschiedenen Niederschläge und wäscht sie mit Wasser. Nach dem Umkrystallisieren aus Wasser wurden 5 g. reine Naphthoxyessigsäure vom Schmp. 156° erhalten. Aus dem Ätherabfalle wurde 0.7–0.8 g. Naphthol zurückgewonnen.

(12) *Einwirkung der Salpetersäure.* 2-Naphthoxyessigsäure wurde ganz genau nach Spitzer nitriert. Man erhält aus 24 g. Oxyessigsäure 26.7 g. rohes Nitroprodukt vom Schmp. 161–181°. Nach 2-maligem Umkrystallisieren aus Eisessig zeigte die reine 1-Nitro-2-naphthoxyessigsäure den Schmp. 191–192°. Sie stellt gelbe Nadeln dar, die in Äther und Benzol bei Zimmertemperatur und in Äthanol und Eisessig durch Kochen löslich sind. Es gibt mit Anilin ein Anilid vom Schmp. 169°, Spitzer hat dagegen 139° angegeben.

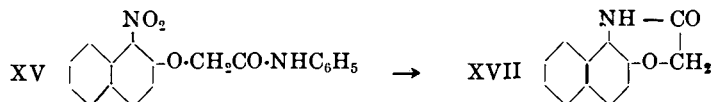
Aus der Mutterlauge beim Umkrystallisieren wurde das zweite Produkt vom Schmp. 157–185° isoliert. Das ist ein isomerer Körper, der ein anderes Anilid vom Schmp. 217° ergibt.

(13) *Anilid des Nitrokörpers.* (A) Durch 10 Minuten langes Erwärmen bei 150–160° einer Lösung von 5 g. 1-Nitronaphthyl-2-oxyessigsäure (Schmp. 185–192°) in 10 g. Anilin wurden 3.9 g. Anilid vom Schmp. 168.5–171° gewonnen. Nach Umkrystallisieren aus Alkohol zeigte die reine 1-Nitronaphthyl-2-oxyessigsäureanilid den Schmp. 169°, was mit dem über Säurechlorid synthetisierten Präparat ganz identisch ist. Sie ist löslich in heissem Äthanol und Anilin. (Gef.: N, 9.00. Ber. für $C_{18}H_{14}O_4N_2$; N, 8.69%.)

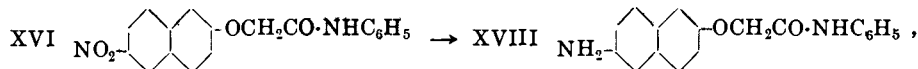
(B) Andererseits wurde durch 20 Minuten langes Erhitzen einer Lösung von 8.2 g. des Produkts vom Schmp. 157–185° in 50 g. Anilin 2.1 g. Anilid vom Schmp. 213–218° erhalten. Nach einmaligem Umkrystallisieren aus Äthanol gab das neue Anilid schwachgelbe, lange Nadeln vom Schmp. 217°. Nach der Analyse ist es auch ein Anilid eines Mononitrokörpers. (Gef.: N, 9.05. Ber. für $C_{18}H_{14}O_4N_2$; N, 8.69%.)

Daraus erhellt dass das zweite Produkt aus einem isomeren Mononitrokörper bestand.

(14) *Reduktion des Anilids.* (A) 2 g. Anilid in 150 c.c. Alkohol wurden mittels 3 g. Zinnpulver und 8 c.c. konz. Salzsäure behandelt. Nach 15 Minuten langem Kochen filtriert man heiss und fügt 100 c.c. Wasser hinzu. Das Produkt wurde mit Äther aufgenommen, nachdem man alles mit Natronlauge alkalisch gemacht hat. Verdampft man den Äther und krystallisiert den Rückstand aus Äthanol um, so gewinnt man 0.5 g. farblose Nadeln vom Schmp. 218–219°, was mit dem inneren Anhydrid der 1-Aminonaphthyl-2-oxyessigsäure identisch ist (Mischschmelzpunkt). Das Anilid wurde also zerstört.



(B) Aus dem Anilid des isomeren Nitrokörpers konnte man aber in derselben Weise leicht den entsprechenden Aminokörper gewinnen, der aus Alkohol gelbbraune Nadeln vom Schmp. 187–188° darstellt:



wobei die Stellung der NO_2 - und der NH_2 -Gruppe fraglich ist. (Gef.: N, 9.75. Ber. für $C_{18}H_{16}O_2N_2$; N, 9.58%.)

III. Schöffersche Säure. (15) *2-Naphthoxyessig-6-sulfosäure*. Aus 20 g. 2-Naphthol-6-sulfosaurem Natrium, 10 g. Monochloressigsäure, 8.4 c.c. Natronlauge (40° Bé) und 100 c.c. Wasser wurden 22 g. 2-Naphthoxyessig-6-sulfosaures Natrium erhalten, dessen Dihydrat glänzende weisse Tafeln darstellt. (Gef.: Na, 12.60; H₂O (Trocknen beim Xylolsiedepunkt über P₂O₅ in Vakuum), 9.89. Ber. für C₁₂H₈O₆SN₂ · 2H₂O: Na, 12.70; H₂O, 9.94%. Gef. für getrocknete Subst.: Na, 14.04. Ber. für C₁₂H₈O₆SN₂: Na, 14.11%.)

Nach Umkrystallisieren aus verd. Salzsäure erhält man Mononatriumsalz, welches krystallwasserfrei ist. (Gef.: Na, 7.40. Ber. für C₁₂H₈O₆SN₂: Na, 7.56%.)

(16) *1-Nitronaphthyl-2-oxxyessig-6-sulfosäure*.⁽⁷⁾ In 15 c.c. Salpetersäure (D = 1.397) wurde 5 g. 2-Naphthoxyessig-6-sulfosaures Natrium bei 20° getan. Nach weiterem 12-stündigen Umrühren bei 15–20° wurden der nitrierten Masse 30 g. Eiswasser zugefügt. Man neutralisiert sie bei Kälte mit etwa 25 c.c. Natronlauge (40° Bé), versetzt sie mit 25 c.c. gesättigter Kochsalzlösung, lässt sie über Nacht stehen und saugt die dann ausgeschiedenen Niederschläge ab. Nach 5-maligem Umkrystallisieren aus Wasser gewinnt man 4 g. 1-Nitrokörper in gelben Nadeln. (Gef.: Na, 12.45; N, 3.62. Ber. für C₁₂H₇O₆NS Na₂: Na, 12.64; N, 3.77%.)

Ausserdem wurde durch Einengen des von der nitrierten Masse abgesaugten Filtrats 0.7 g. als zweite Ausbeute gewonnen. Nach dem Umkrystallisieren, erst aus verd. Natronlauge, dann 5-mal aus Wasser wurde die Substanz in gelbbrauner Nadeln erhalten. Das ist ein Nebenprodukt, vielleicht 4-Nitrokörper. (Gef.: Na, 12.59; N, 3.51. Ber. für C₁₂H₇O₆NSNa₂: Na, 12.64; N, 3.77%.)

(17) *Reduktion des Nitrokörpers*. In ein siedende Lösung von 1 g. Nitrokörper in 0.5 c.c. 20%iger Essigsäure und 2 c.c. Wasser wurde 0.5 g. Eisenpulver getan. Nach 40 Minuten langem Erhitzen wurde alles abgekühlt, mit Natronlauge neutralisiert, nochmals erwärmt und filtriert, worauf 0.8 g. Aminokörper gewonnen wurde. Nach Umkrystallisieren aus Wasser stellt das Produkt etwas rötlich gefärbte Blättchen dar, deren Analyse mit der Zusammensetzung des inneren Anhydrids des erforderlichen Aminokörpers übereinstimmt. (Gef.: Na, 7.52; N, 4.73. Ber. für C₁₂H₈O₅NSNa: Na, 7.64; N, 4.65%.)

1 g. Anhydrid wurde in 5 c.c. Natronlauge (40° Bé) und 5 c.c. Wasser gekocht und heissfiltriert. Beim Abkühlen scheidet 1 g. 1-Aminonaphthyl-2-oxxyessig-6-sulfosäure in weissen Blättchen aus. Zur Analyse wurde die Substanz einige Male in folgender Weise umkrystallisiert. Man löst die Substanz in einer kleinen Menge Wasser, fügt etwas Natronlauge (40° Bé) hinzu und lässt sie in der Kälte stehen. Man saugt die ausgeschiedenen Krystalle ab und wäscht sie erst mit gesättigter Kochsalzlösung, dann mit Wasser und zuletzt mit Alkohol und trocknet sie. Nach der Analyse entsteht sie aus Dinatriumsalz. (Gef.: Na, 13.15; N, 4.13. Ber. für C₁₂H₉O₆NSNa₂: Na, 13.49; N, 4.11%.)

Durch Kochen mit Mineralsäure geht das Natriumsalz wieder in inneres Anhydrid über.

IV. *Peri- u. o-Dioxynaphthalinsulfosäure*. (18) *1,8-Dioxynaphthalin-3,6-disulfosäure*. 5 g. Chromotropsäure wurden in einer Lösung von 4.3 g. kalz. Soda und 9 c.c. Wasser gelöst, worauf man unter Umrühren allmählich innerhalb von etwa 2 Stdn. eine vorher mit Soda neutralisierte Lösung von 1.9 g. Monochloressigsäure in 9 c.c. Wasser tropfeln, währenddem die Temperatur im Ölbad auf etwa 100° stehen bleiben muss. Nachdem man alles hinzugefügt hat, erhitzt man eine weitere halbe Stunde bei 100° und lässt es

(7) D.R.P. 58614 (Frdl. III. 438).

abkühlen. Man krystallisiert die abgesaugten Krystalle aus verdünnter aus 20 c.c. konz. Salzsäure und 40 c.c. Wasser bestehender Salzsäure um. Die Ausbeute beträgt 2.2 g. weisse Nadeln, welche nach der Analyse Mononatriumsalz der entsprechenden Monooxyessigsäure sind. (Gef.: Na, 5.72; S, 16.01. Ber. für $C_{15}H_9O_{10}S_2Na$: Na, 5.75; S, 16.00%.) Aus der Mutterlauge konnte man 3 g. unveränderte Chromotropsäure zurückgewinnen. (Gef.: Na, 12.28; S, 17.40. Ber. für $C_{10}H_6O_8S_2Na_2$: Na, 12.63; S, 17.60%.)

(19) *Monochloressigsäure auf 1,8-Dioxynaphthalin-4-sulfosäure.* 5 g. Dioxynaphthalinsulfosäure S wurden genau nach Vorschrift (18) behandelt, wodurch man 3 g. grauweiße, rohe Monooxyessigsäure gewann. Nach Umkrystallisieren aus Wasser reine weisse Nadeln. (Gef.: S, 10.64; keine Asche. Ber. für $C_{12}H_{14}O_7S$: S, 10.78%.) Dabei betrug die unveränderte, aus dem Abfall bei der Alkoholwäsche zurückgewonnene Dioxynaphthalinsulfosäure S, 2 g. (Gef.: Na, 6.19; S, 8.84. Ber. für $C_{10}H_7O_5Na_2S \cdot 6H_2O$: Na, 6.21; S, 8.64%.)

(20) *Monochloressigsäure auf 2,3-Dioxynaphthalin-6-sulfosäure.* Durch Behandlung von 5.3 g. 2,3-Dioxynaphthalin-6-sulfosaurem Natron nach Vorschrift (18) wurden 5.5 g. grauweißer Niederschlag gewonnen. Nach Umkrystallisieren aus Wasser 3.8 g. reine 2,3-Dioxyessignaphthalin-6-sulfosäure in weissen Nadeln erhalten. (Gef.: S, 8.38; Na, 6.62. Ber. für $C_{14}H_{11}O_9SNa$: S, 8.46; Na, 6.10%.)

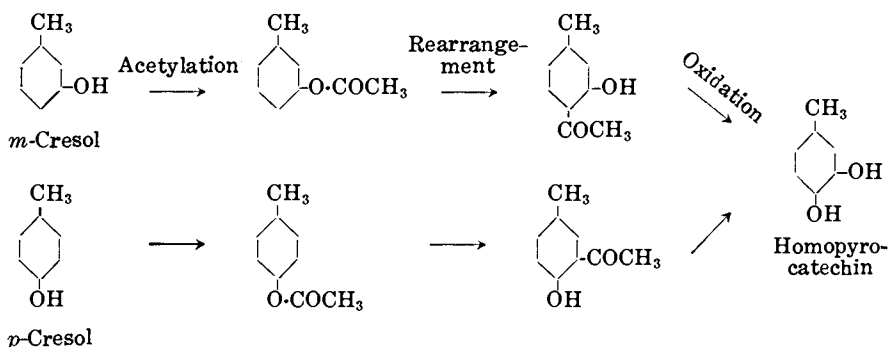
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**SYNTHESIS OF VANILLIN FROM CRESOLS. I.
SYNTHESIS OF HOMOPYROCATECHIN.**

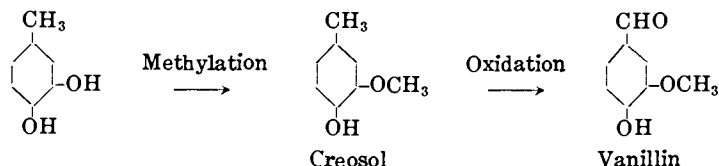
By **Kashichi ONO** and **Minoru IMOTO**.

Received October 16th, 1935. Published March 28th, 1936.

The pyrocatechin-derivatives play important rôles in nature as vanillin, adrenalin, urushiol, zingerone, capsaicin, etc. Our factory has succeeded in the industrial preparation of vanillin from safrol, one of the principal constituents of camphor oil, and is now pursuing further studies with a view to a more effective preparation of vanillin and related compounds. This paper concerns the synthesis of homopyrocatechin from cresols. Homopyrocatechin, which has been prepared by the demethylation of creosol, is an intermediate compound of importance for many useful pyrocatechin-derivatives. Our scheme for the synthesis is as follows :



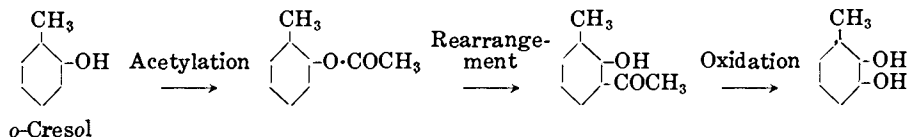
And in addition, the methylation and subsequent oxidation of homopyrocatechin into creosol and vanillin are reported preliminarily.



Through Fries rearrangement of *m*-cresol acetate with aluminum chloride, the acetyl group was rearranged to ortho and para positions to the hydroxyl group.⁽¹⁾ But the ratio of quantities of ortho and para products can be controlled to a certain extent by the conditions. On rearranging at 160°, we obtained 22 g. of *o*-substituted compound and only 2 g. of *p*-substituted. The separation of these is simple, for only the *o*-compound distills with steam. The oxidation of the rearranged *m*-cresyl-methylketone to homopyrocatechin was carried out by the Dakin-process⁽²⁾ with an alkaline hydrogen peroxide solution.

The case of *p*-cresol, a synthesis completely analogous to the former, is in fact simpler, for the product in Fries rearrangement is an *o*-compound and nothing more.

From *o*-cresol, we cannot obtain homopyrocatechin by similar reactions, as the following formulas show :

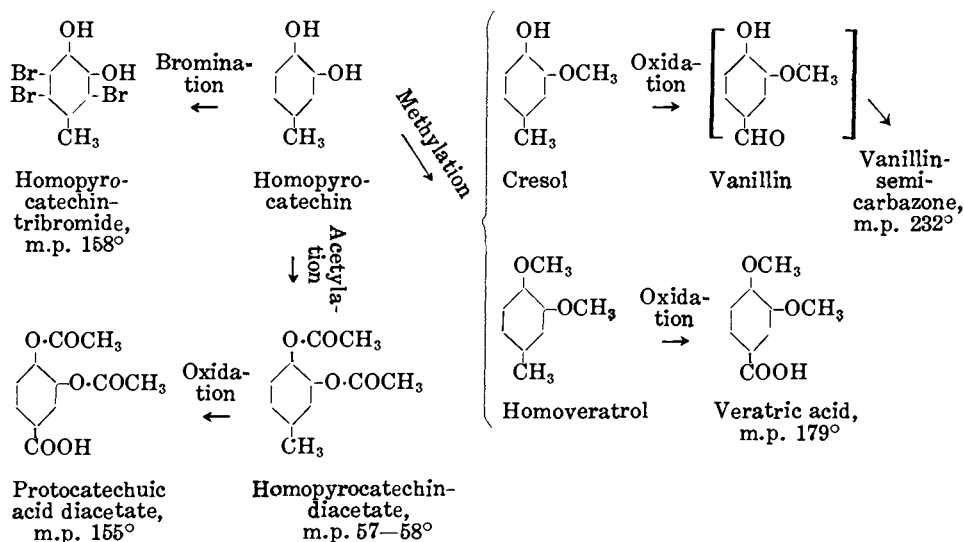


(1) K.W. Rosenmund and W. Schnurr, *Ann.*, **460** (1928), 56.

(2) H. D. Dakin, *Am. Chem. J.*, **42** (1909), 477.

But fortunately, the *o*-cresyl-methylketone would not give a definite oxidation-product by the Dakin-process, as proved experimentally in our laboratory.⁽³⁾ And the industrial separation of *o*-cresol from the raw cresol-mixture is possible.⁽⁴⁾ So in the preparation of homopyrocatechin according to our method, it is not necessary to use pure cresol, but it is enough that the cresol-mixture is somewhat free from the ortho component.

For the exact identification of the prepared homopyrocatechin, the following derivatives are synthesized :



Of these derivatives, creosol which is obtained from wood-tar, was noted recently as a new material for the vanillin-preparation.⁽⁵⁾ And although the oxidation method still remains a subject for future study we have oxidized it preliminarily with ethyl nitrite and obtained vanillin, identifying it as its semicarbazone.

Experimental.

1. **Acetylation of Cresols.** (A) *m*-Cresol. (i) To a solution of *m*-cresol (108 g.), water (70 c.c.), and potassium hydroxide (70 g.), acetic anhydride (110 g.) was added slowly. After washed with 10%-solution of potassium hydroxide, the produced acetate was distilled. Yield, 80% of the theoretical. B.p. 210–215°, n_D^{20} 1.5059, d_4^{15} 1.051. (ii) To a mixture of *m*-cresol (108 g.) and acetic anhydride (130 g.), one drop of conc. sulphuric acid was added.

(3) K. Ono and T. Oyamada, not yet published.

(4) For example, see S. Masai, *J. Soc. Chem. Ind., Japan*, **38** (1935), 217 B.

(5) H. Schulz, *Chem. Ztg.*, **59** (1935), 113.

The temperature was raised, for example, up to 95°. Yield was theoretical. B.p. 210–211°, n_D^{26} 1.4978, d_{25} 1.043.

(B) *p-Cresol*. From 250 g. of *p-cresol*, 300 g. of acetic anhydride, and one drop of conc. sulphuric acid, 280 g. of *p-cresyl acetate* was obtained. B.p. 209–211°, d_{25} 1.043, n_D^{26} 1.4972.

2. **Fries Rearrangement of Acetates.** (A) *m-Cresyl acetate*. To the ice-cooled *m-cresyl acetate* (29 g.), powdered aluminium chloride (30 g.) was added in portions and the mixture heated in an oil-bath at 130°. A violent evolution of HCl gas occurred. Temperature of the oil-bath was raised to 160° during 1.5 hours, and the reaction was then stopped. After cooling, the product was decomposed with ice-water and conc. hydrochloric acid (20 c.c.) and distilled with steam. From the distillate *m-cresyl-o-methylketone* was extracted with ether. After redistillation, it weighed 22 g. B.p. 230–235°, n_D^{27} 1.5511, d_{28} 1.081. From the residue of the steam distillation the para product crystallized out. It weighed 2.3 g. and melted at 124–126° after recrystallisation from water.

(B) *p-Cresyl acetate*. Similarly, *p-cresyl acetate* (50 g.) and aluminium chloride (60 g.) gave *p-cresyl-o-methylketone* (35 g.), melting at 50° and of somewhat yellowish colour. Recovered acetate weighed 8 g.

3. **Dakin-Oxidation.** (A) *m-Cresyl-o-methylketone*. A solution of *m-cresyl-o-methylketone* (22 g.) and sodium hydroxide (7 g.) in water (200 c.c.) was treated with 3% hydrogen peroxide solution at ordinary temperature. As seen from next case, the quantities of NaOH and H₂O₂ (both 1 mole) were insufficient. After standing a whole night, the product was extracted with ether. From the ethereal solution, unchanged *m-cresyl-o-methylketone* (15 g.) was recovered by steam distillation. The residue was extracted with ether. After drying the ethereal solution and distilling off the ether, a reddish black oil remained and it yielded a red oil (2.5 g.) boiling at 250–255°. When it was cooled, it solidified. This was the homopyrocatechin somewhat decomposed during the distillation under ordinary pressure.

(B) *p-Cresyl-o-methylketone*. To a solution of *p-cresyl-o-methylketone* (11 g.) and sodium hydroxide (7 g., double the theoretical quantity) in water (350 c.c.) was added a 3% hydrogen peroxide solution (260 g., 1.6 times the required quantity). After standing for 3.5 hours, the mixture was acidified with acetic acid and the unchanged *p-cresyl-o-methylketone* was distilled off with steam. It weighed 2 g. By extraction and redistillation there was obtained a somewhat yellowish, viscid, oily homopyrocatechin, boiling at 122° (6 mm.), 117° (4 mm.) or 114° (3 mm.). In the receiver, the oil solidified into a white, mass, but when left in the air, it became a red liquid again. (Found: C, 67.17; H, 6.76. Calc. for C₇H₈O₂: C, 67.74; H, 6.50%.)

(C) *Homopyrocatechin-tetrabromide*. A bromide was prepared according to H. Cousin.⁽⁶⁾ To a solution of homopyrocatechin in glacial acetic acid was dropped a solution of bromine in the same solvent. Hydrogen bromide was evolved. After 1.5 hours, water was added. The separated substance was recrystallized repeatedly from dil. acetic acid. Somewhat orange coloured needles were obtained, m.p. 158° (Cousin gives m.p. 162–163°). (Found: C, 22.75, 23.73; H, 1.88. Calc. for C₇H₅O₂Br₃: C, 23.27; H, 1.38%.)

(6) H. Cousin, *Ann. chim.*, (7), **13** (1898), 480.

(D) *Homopyrocatechin-diacetate*. After heating at 140–150° a mixture of homopyrocatechin (3 g.), acetic anhydride (10 g.), and anhydrous sodium acetate (2 g.) for four hours, the contents were extracted with ether, the ethereal solution washed with 10% KOH and fractionated under ordinary pressure. The obtained diacetate was a somewhat yellowish oil, boiling at 274–275°⁽⁷⁾ and having the following constants: n_D^{28} 1.4932, d_4^{28} 1.1314 and M.R. 53.44 (theoretical 52.71). On standing, it solidified and it melted at 57–58° after recrystallisation from alcohol. (Found: C, 63.38, 63.02; H, 6.10, 6.09. Calc. for $C_{11}H_{12}O_4$: C, 63.46; H, 5.78%.)

(E) *Oxidation of the homopyrocatechin-diacetate*. The diacetate (0.2 g.), mixed with 0.5 N sulphuric acid (20 c.c.), was oxidized with 2% potassium permanganate on the water-bath. The obtained diacetate of protocatechuic acid melted at 143°. After double recrystallisation from water, it was identified with the diacetate of protocatechuic acid⁽⁸⁾ by the mixed melting point.

4. **Methylation and Oxidation of Homopyrocatechin.** A mixture of homopyrocatechin (4.5 g.), caustic potash (6 g.), water (30 c.c.), and impure sodium methylsulphate (9 g.) was refluxed for 2.5 hours. Then the contents were dissolved in water, and the dimethylated ether (homoveratrol) was extracted with ether. The residue was acidified with dil. hydrochloric acid and the monomethylated ether (creosol) was extracted with ether.

(A) Homoveratrol, weighing 1.0 g., was obtained as yellowish oil from the ethereal solution. B.p. 216–218°, n_D^{28} 1.5250, d_4^{29} 1.051 (Found: M.R. 44.29; C, 70.66; H, 7.99. Calc. for $C_7H_{12}O_2F_3$: M.R. 43.65; C, 71.05; H, 7.90%). For the identification, the homoveratrol was oxidized with 2.5% potassium permanganate. It gave veratric acid, melting at 179°.

(B) Creosol was obtained as yellowish oil. It weighed 1.2 g. and smelled somewhat of guaiacol. B.p. 218–225°, n_D^{27} 1.5347, d_4^{27} 1.100.

(C) *Oxidation of Creosol*. Ethyl nitrite, prepared from sodium nitrite (2.5 g.), alcohol, and sulphuric acid by Wallach's method,⁽⁹⁾ was passed into the solution of creosol (0.3 g.) in alcohol (0.5 g.) cooled with ice and salt. NO_2 -gas evolved. The contents became red-dish-dark and some white precipitates were produced. After filtration and extraction of the filtrate with ether, the ether was evaporated off and the resulting tarry residue was extracted with hot water. To the water extract were added semicarbazide hydrochloride (0.1 g.), potassium acetate (0.1 g.), and alcohol (1 c.c.). On the next day, crystals of the resulting semicarbazone separated, were collected. M.p. 220–225°. After recrystallisation it melted at 227–229°, and proved to be vanillin-semicarbazone by the mixed melting point.

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(7) Cousin gives b.p. 264°.

(8) M. Imoto, *J. Chem. Soc. Japan*, **55** (1934), 523.

(9) O. Wallach, *Ann.*, **245** (1889), 251. M. Imoto, *J. Chem. Soc. Japan*, **55** (1934), 120.

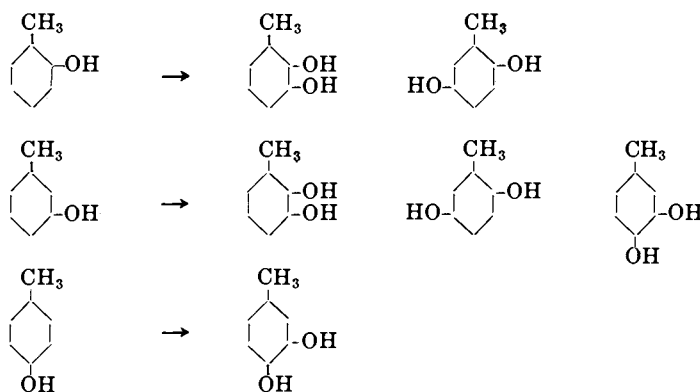
ON THE REACTION BETWEEN CRESOLS AND HYDROGEN PEROXIDE IN THE PRESENCE OF FERROUS SULPHATE.

By Kashichi ONO and Taichiro OYAMADA.

Received October 16th, 1935. Published March 28th, 1936.

In 1900, Caross, Bevan, and Heiberg⁽¹⁾ reported that benzene when oxidised with hydrogen peroxide in the presence of ferrous sulphate yielded phenol (15%) and pyrocatechin (35%). Though this reaction seems to be interesting from the standpoint of pure chemistry as well as applied chemistry, only a few investigations on this subject have hitherto been carried out.⁽²⁾

The present authors extended this reaction to three isomeric cresols with the view to examining whether the direct introduction of a hydroxyl-group into a benzene nucleus is possible as in the case of benzene itself. If this reaction is always the case, it is expected that the following compounds, which are all important not only from a scientific, but also from a technological point of view, can be obtained :



As shown in details in the experimental part, the oxidation of *o*-cresol with hydrogen peroxide in the presence of ferrous sulphate was first conducted under various conditions and the chief product of the oxidation was a black substance, which is insoluble in water, partly soluble in ether and, on combusting, leaves iron oxide. Besides this substance *p*-toluhydroquinone

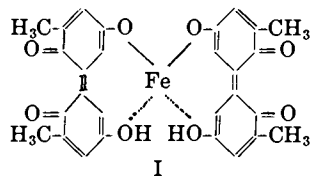
(1) *Ber.*, **33** (1900), 2015.

(2) Sommer, D.R.P. 155731. Bargellini and Monti, *Gazz. chim. ital.*, **45** (1915), 90. O. Magidson and N. Preobrashenski, *Trans. Sci.-Chem.-Pharm. Inst. (Moscow)*, **16** (1926), 65.

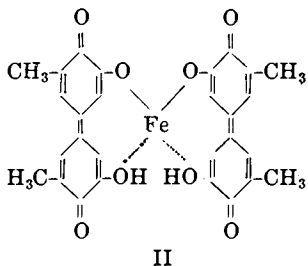
was isolated in a small amount. Although some attempts were made to separate oxidation products, the oxidation products turned out to be nothing more than the above-mentioned substances, and the expected 1-methyl-2,3-dihydroxybenzene was not isolated.

Now it is necessary to investigate the nature of this black substance in order to make clear the whole reaction. But, owing to the difficulty in purifying this substance, it was impossible to obtain a complete elucidation. After long and fruitless trials, however, it was found to be most probably a mixture of three or more substances. First, it was separated into an ether-soluble and an ether-insoluble parts. The ether-soluble part was separated into two compounds by gradual addition of petroleum ether. The precipitate first formed was represented by composition $C_{28}H_{12}O_8Fe$. On reduction with zinc dust and HCl in alcoholic solution, it gave a colourless compound melting at 202° , which was further converted into its acetate, melting at 135° , by heating with acetic anhydride and fused sodium acetate. This acetate was proved to be 2,5,2',5'-tetracetoxy-3,3'-dimethyl-diphenyl by elementary analysis and mixed melting point test. Consequently, the reduction product which melts at 202° may be 2,5,2',5'-tetrahydroxy-3,3'-dimethyl-diphenyl because of agreement in melting point and composition. From these results, it follows that the compound represented by $C_{28}H_{22}O_8Fe$ is probably a complex of Fe with two mol ditolyldiquinone, represented by formula I.

The precipitate formed last was a yellow crystalline powder melting at $163-5^\circ$ and found to be ditolyldiquinone by analysis. Moreover, this was also ascertained to be the case by converting it into 2,5,2',5'-teracetoxy-3,3'-dimethyl-diphenyl by means of reductive acetylation.



The ether-insoluble black substance was also represented by formula $C_{28}H_{22}O_8Fe$ (although the analytical data was unsatisfactory) and, on reductive acetylation, gave an acetate melting at $194-6^\circ$ in a small amount. On the other hand, Prof. Majima,⁽³⁾ in his series of researches on urushiol, tried to oxidise 1-methyl-2,3-dihydroxybenzene with $FeCl_3$ and then observed the formation of a complex compound (II).

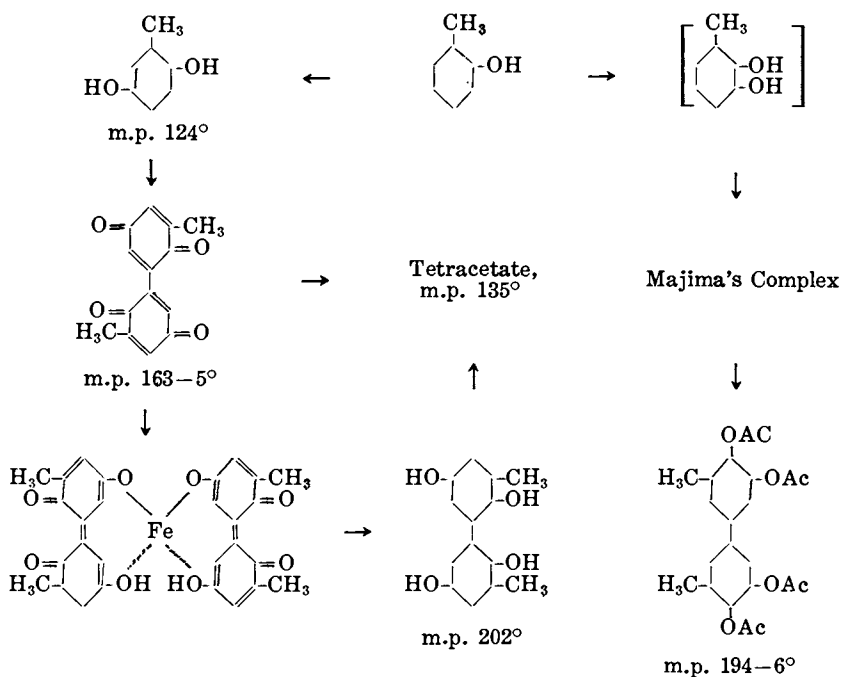


The complex obtained by the present authors seems to be in agreement with Majima's complex in appearance, composition, and the melting point of

(3) *Ber.*, **53** (1920), 1907.

the reductively acetylated product, so they may be assumed to be in all probability the same compound. Thus, 1-methyl-2,3-dihydroxybenzene which could not be isolated may be considered to have once been formed and to have undergone subsequent oxidation and condensation.

The above-described results can be summarised in the following manner :



Such a direct introduction of the hydroxyl-group into the benzene nucleus has been demonstrated already in the case of the anodic oxidation of aromatic compounds by various investigators. For instance, F. Fichter and Franz Ackermann⁽⁴⁾ obtained *p*-toluhydroquinone and 4,4'-dihydroxy-3,3'-dimethyldiphenyl from *o*-cresol by anodic oxidation. It is of interest to note that the oxidation with H₂O₂ in the presence of FeSO₄ takes place in a manner somewhat similar to that of electrolytic oxidation.

Under the same conditions as described above *m*- and *p*-cresols were oxidised. In the former case, a large amount of a black substance together with a little *p*-toluhydroquinone was isolated as in the case of *o*-cresol, and the black substance, on close examination, was proved to be a mixture of ditolydiquinone and a complex containing Fe. From the oxidation products of

(4) *Helv. Chim. Acta*, **2** (1919), 596.

p-cresol, no definite crystalline compound except a black substance was isolated. This black substance was treated in the same way as in the case of *o*-cresol. From the ether soluble part, on reductive acetylation, an acetate which melts at 145° was obtained but owing to the small quantity, a further investigation could not be carried out. From the ether insoluble part, on reduction and subsequent acetylation, an acetate melting at 250° was obtained which also could not be identified owing to the scarcity of the substance.

Experimental Part.

I. Oxidation of *o*-cresol with H_2O_2 in the presence of FeSO_4 . (a) To a mixture of 40 g. of *o*-cresol and 100 c.c. of water containing 6 g. of FeSO_4 , 300 c.c. of 2% aqueous solution of H_2O_2 was added in portions with frequent shaking and the mixture was allowed to stand overnight, when the solution became brownish red and a black resinous oil separated out. In order to drive off unacted cresol the whole oxidised mixture was subjected to steam distillation and 19 g. of *o*-cresol was obtained from the distillate. On cooling, a resinous mass solidified in the residue of the steam treatment and was collected on a filter. The filtrate separated from the black substance was thoroughly extracted with ether and then the ethereal solution evaporated, when about 2.5 g. of a reddish substance remained and gradually crystallised which was dried on a porous plate and recrystallised from benzene. It forms colourless needles melting at 124° and was identified with *p*-toluhydroquinone by elementary analysis and mixed melting point test. (Found: C, 67.68; H, 6.86. Calc. for $\text{C}_7\text{H}_8\text{O}_2$: C, 67.8; H, 6.4%.)

(b) To a mixture of 40 g. of *o*-cresol and 100 c.c. of water containing 10 g. of FeSO_4 , 300 c.c. of 2% aqueous hydrogen peroxide solution was added drop by drop with ice-cooling and vigorous stirring. After being allowed to stand for several hours at room temperature, the excess of H_2O_2 was decomposed by the addition of MnO_2 . With the intention of isolating the expected 1-methyl 2,3-dihydroxybenzene, the whole mixture was first treated with a solution of lead acetate when a brown precipitate of a lead salt was deposited. The precipitate thus obtained was washed with water, alcohol, and ether successively, decomposed with dilute sulphuric acid, and extracted with ether. From the ethereal extract a brown resinous matter was obtained, from which no definite compound could be isolated. The mixture was treated with lead acetate solution, mixed together with the washings and submitted to steam distillation, and 25 g. of unchanged *o*-cresol was recovered. The residue was filtered from the black viscous resinous matter and extracted with ether. From the ethereal solution *p*-toluhydroquinone was obtained in a small amount. The aqueous solution which had been treated with ether was evaporated to dryness under reduced pressure, from which no definite organic compound was isolated.

(c) To a mixture of 30 g. of *o*-cresol and 100 c.c. water containing 6 g. of FeSO_4 , 300 c.c. of 2% aqueous hydrogen peroxide solution was added in small portions and the temperature was maintained at 80° during the oxidation.

The investigation of oxidation products was carried out just as in case (a) and about 1 g. *p*-toluhydroquinone and a large amount of the black material were obtained.

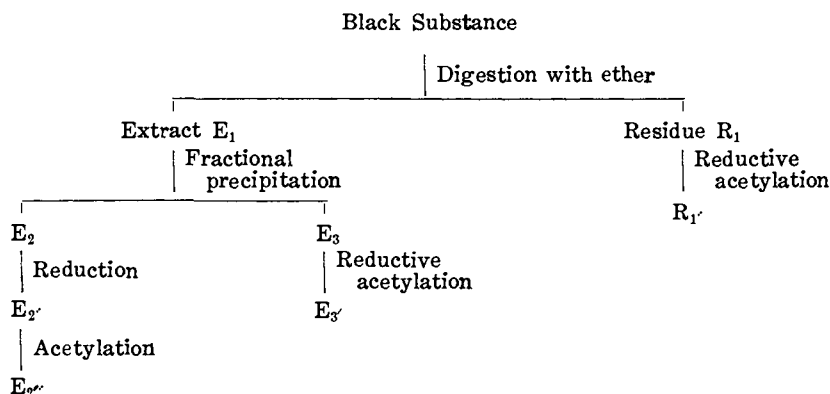
(d) A solution of 30 g. of *o*-cresol in acetone was mixed with a solution of ferrous sulphate in 100 c.c. water and the mixture heated with constant stirring on the water-bath. Three hundred c.c. of 2% aqueous solution of H_2O_2 was added to the mixture

drop by drop. From the oxidation products nothing other than the above-mentioned materials was isolated.

(e) When a large amount of FeSO_4 was used, the chief oxidation product was obtained as a black powder instead of an oily substance. Aside from this, *p*-toluhydroquinone was found in a small amount as in the above cases.

To a mixture of 30 g. of *o*-cresol and 100 c.c. of water containing 40 g. of FeSO_4 , 300 c.c. of 2% aqueous solution of H_2O_2 was added in portions with vigorous shaking. Twenty grams of a black substance and 2 g. of *p*-toluhydroquinone were obtained from the oxidation products.

II. The investigation of the black substance. As already stated, the chief oxidation product was a black substance insoluble in water. For a further investigation of this substance, it was treated as follows:



Of course, a complete separation was by no means attained in this way, but it was possible to speculate that it would be a mixture of the substances described in the introduction.

(A) *Part soluble in ether.* The black substance was thoroughly extracted with ether in a Soxhlet apparatus. On addition of petroleum ether to the ethereal solution, E_2 first and then E_3 separated out.

(a) *Complex salt (E_2).* E_2 was again dissolved in ether and fractionally reprecipitated by addition of petroleum ether. By the repetition of this process, E_2 was purified and used in a further experiment as below. (Found: C, 61.05; H, 5.13; Fe, 9.67. Calc. for $\text{C}_{28}\text{H}_{22}\text{O}_8\text{Fe}$: C, 61.99; H, 4.06; Fe, 10.14%.)

(b) *Reduction of E_2 (E_2').* To a mixture of 1 g. of E_2 in alcohol (20 c.c.) and 5 g. of zinc dust, 5 c.c. of concentrated HCl was slowly added. After an hour, the reaction mixture was filtered by suction and the solution was poured into 150 c.c. of cold water, when an almost colourless precipitate separated out. It was recrystallised from alcohol, crystalline powder melting at 202° , and giving data agreeing with 2,5,2',5'-tetrahydroxy-3,3'-dimethyl-diphenyl. (Found: C, 68.03; H, 6.10. Calc. for $\text{C}_{14}\text{H}_{14}\text{O}_4$: C, 68.29; H, 5.69%.)

(c) *Acetylation of E_2' (E_2'').* One gram of E_2' was boiled with 10 c.c. of acetic anhydride together with 2 g. fused sodium acetate under reflux for an hour. After cooling, it was poured into cold water, when a colourless precipitate separated out.

The precipitate was recrystallised from alcohol, a colourless crystalline substance melting at 135° and showing no depression of melting point by admixture with 2,5,2',5'-tetra-acetoxy-3,3'-dimethyl-diphenyl synthesized from *p*-toluhydroquinone. (Found: C, 63.56; H, 6.10. Calc. for $C_{22}H_{22}O_8$: C, 63.8; H, 5.3%.)

(d) *Purification of E₃*. E_3 was also dissolved in ether and petroleum ether was added until a yellow precipitate was just separating out. To the filtrate a large amount of petroleum ether was added to complete the precipitation, when a yellow substance was deposited. By repeating such a treatment several times, a yellow crystalline powder melting at 163.5° was obtained. The analytical data and the melting point agree with those of ditolydiquinone. This was, moreover, ascertained also by converting it into its acetate. (Found: C, 68.98; H, 4.68. Calc. for $C_{14}H_{10}O_4$: C, 69.42; H, 4.13%.)

(e) *Reductive acetylation of E₃*. Two grams of E_3 was dissolved in 15 c.c. of acetic anhydride and 5 g. of zinc dust and 3 g. of fused sodium acetate were added and the whole was boiled under reflux for an hour, when the brownish red colour of the initial mixture faded. After removal of the excess of zinc dust, the mixture was poured into cold water and left to stand. A yellowish mass separating out therefrom, and after recrystallisation from alcohol it showed a melting point 135° , agreeing with the data for 2,5,2',5'-tetracetoxy-3,3'-dimethyl-diphenyl. It was moreover identified by the mixed melting point test with a synthetical specimen which had been prepared by the reductive acetylation of ditolydiquinone, prepared from *p*-toluhydroquinone according to Brunner.

(B) *Part insoluble in ether (R₁)*. (a) *Reductive acetylation of R₁*. Twelve grams of R_1 was boiled with 20 c.c. of acetic anhydride together with 14 g. of fused sodium acetate and 10 g. of zinc dust under reflux for an hour. While hot, excess of zinc was filtered off and the solution thus obtained was poured into cold water, when a yellowish mass separated. On recrystallisation from alcohol, a colourless substance melting at 193.5° was obtained. This melting point coincides with that of 3,3'-dimethyl-4,4',5,5'-tetracetoxy-diphenyl. (Found: C, 61.25; H, 5.20; Fe, 9.56. Calc. for $C_{28}H_{22}O_8Fe$: C, 61.99; H, 4.06; Fe, 10.14%.)

III. Oxidation of *m*-cresol with H_2O_2 in the presence of $FeSO_4$. Thirty grams of *m*-cresol was oxidised under the same conditions as in case (a) for *o*-cresol. The formation of *p*-toluhydroquinone and the black material were also observed here. The investigation of the black material was carried out exactly in the same way as in the case of *o*-cresol. (A) *Part soluble in ether*. By the treatment as in the case of *o*-cresol, ditolydiquinone and the complex of Fe with it were detected. (B) *Part insoluble in ether*. From this part, no definite compound could be isolated.

IV. Oxidation of *p*-cresol with H_2O_2 in the presence of $FeSO_4$. The oxidation and the separation of the resulting products were carried out as in the above two cases. (A) *Part soluble in ether*. On reductive acetylation by means of acetic anhydride and zinc dust, it gave an acetate melting at 145° in a very small amount. (B) *Part insoluble in ether*. By reductive acetylation, an acetate melting at 250° was obtained in a small amount. These two acetates could not be identified owing to the small amounts of the substances available.

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STUDIES ON AMINO-ACIDS AND RELATED COMPOUNDS.

IX. ELECTROLYTIC OXIDATION OF PROLINE
AND γ -AMINO-BUTYRIC ACID.

By Yoshitaro TAKAYAMA.

Received October 18th, 1935. Published March 28th, 1936.

In a previous paper⁽¹⁾ it was reported briefly that the electrolytic oxidation of proline may proceed in a type similar to that of pyrrolidone-carboxylic acid. In this paper the details of the above oxidation and that of γ -amino-butyric acid are reported.

Langheld⁽²⁾ oxidized *dl*-proline with sodium hypochlorite and isolated a certain base having an odour of pyrrolidine. Recently Herbst and Clark⁽³⁾ treated proline with silver oxide, but no definite compound was obtained.

In the present experiment, proline in dilute sulphuric acid was electrolyzed in an undivided cell with a lead peroxide anode and a lead cathode under the following conditions: current quantity about 8F./mol; temperature 35°C.

In the electrolysate, no substance giving aldehydic reaction could be found. By thorough extraction with ether it was divided into two parts. The part soluble in ether was found to consist of a comparatively large amount of succinimide together with a little succinic acid. From the residual part, by treating with barium hydroxide, ammonia as well as pyrrolidine were isolated as volatile bases. The pyrrolidine was confirmed by the analysis of its chloroplatinate and by the formation of characteristic precipitates on addition of a solution of potassium bismuth iodide.

In the solution, from which volatile bases were removed, there was found some amount of amino-nitrogen, which greatly increased when the solution was boiled with barium hydroxide and, in fact, γ -amino-butyric acid was isolated in the form of its chloroplatinate. It may be a proper reasoning to consider that the above increase of amino-nitrogen means an accumulation of γ -amino-butyric acid due to the hydrolysis of pyrrolidone⁽⁴⁾, though, in reality, the base itself was not isolated.

The electrolytic oxidation of γ -amino-butyric acid was carried out just in the same manner as described above and from its electrolysate ammonia, succinic acid, and unchanged amino-acid were isolated.

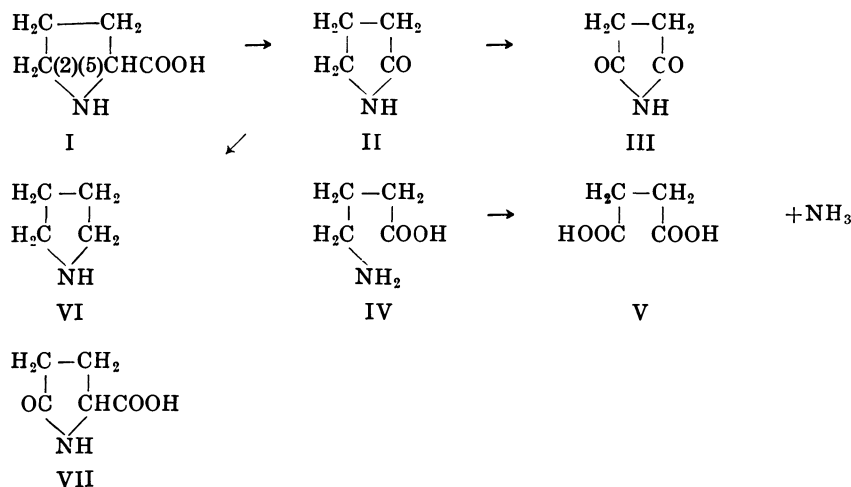
(1) Y. Takayama, this Bulletin, **8** (1933), 213.

(2) K. Langheld, *Ber.*, **42** (1909), 2373.

(3) R. M. Herbst and H. T. Clark, *J. Biol. Chem.*, **104** (1934), 769.

(4) J. Tafel and M. Stern, *Ber.*, **33** (1900), 2230.

Taking the two sets of oxidation into consideration, the mechanism of electrolytic oxidation of proline may be represented as follows:



Proline (I) was first oxidized to pyrrolidone (II) and the latter, on further oxidation, gives succinimide (III) and this course of reaction seems to be a main one, when interpreted from the amount of the final products. γ -Amino-butyric acid (IV) as well as pyrrolidine (VI) are presumed to be derived from pyrrolidone, the former by hydrolysis, the latter by reduction. As to the formation of succinic acid (V) two possible processes can be conceived: hydrolysis of succinimide and oxidation of γ -amino-butyric acid.

It was shown by E. Fischer⁽⁵⁾ that proline can be formed by the reduction of pyrrolidone-carboxylic acid (VII). In the present oxidation, as a matter of fact, not pyrrolidone-carboxylic acid⁽⁶⁾ but γ -amino-butyric acid together with pyrrolidine was obtained, thus, the reverse of the E. Fischer's reaction can not be imagined to occur in this case. It naturally leads to the conclusion that the carbon atom (5) in proline is more readily oxidizable than the carbon atom (2).

Experimental Part.

Electrolytic Oxidation of Proline. Proline (Fraenkel and Landau) m.p. 209–210° after recrystallization from *n*-butyl alcohol.

The above sample (1.151 g., 10 millimols) was dissolved in *N* sulphuric acid (27 c.c.) and electrolyzed under the following conditions: cell the same as described in part VII⁽⁷⁾;

(5) E. Fischer, *Ber.*, **44** (1911), 1332.

(6) Y. Takayama, this Bulletin, **8** (1933), 137.

(7) Y. Takayama, this Bulletin, **8** (1933), 213.

electrodes (2 cm. $\times$ 4 cm.) PbO_2 -Pb; current density 2 amp./dm².; 3.5 volts; current quantity 8 F./mol; temperature 35°C.

The electrolysate of proline (10 millimols $\times$ 2) was thoroughly extracted with ether. Ether was expelled, and the remaining crystalline mass was separated into neutral and acidic parts as usual.

Neutral part (succinimide). Crystals (0.5 g.) obtained were recrystallized from acetone, m.p. 126°. It was found to be succinimide by the determination of nitrogen as well as by the mixed melting point test (Found: N, 14.2. Calc. for $\text{C}_4\text{H}_5\text{O}_2\text{N}$: N, 14.15%).

Acidic part (succinic acid). Crystals (0.2 g.) obtained melted at 183° after recrystallization from water. It was identified as succinic acid by the determination of acid equivalent and mixed melting point test (4.419 mg. of this acid required 5.56 c.c. (0.01346 N NaOH). Calc. for $\text{C}_4\text{H}_6\text{O}_4$: 5.63 c.c.).

Volatile bases (ammonia and pyrrolidine). After removal of the part soluble in ether from the electrolysate, the residual solution was distilled with an excess of barium hydroxide under reduced pressure, the volatile bases being collected in dilute hydrochloric acid. On evaporating up the solution, a very hygroscopic crystalline mass was obtained, which was treated with absolute alcohol, and were separated into soluble and insoluble parts.

The hydrochloride (0.1 g.) insoluble in alcohol was found to be ammonium chloride by the analysis of its chloroplatinate and by the inspection of crystal forms under polarizing microscope (Found: Pt, 43.9. Calc. for $(\text{NH}_4)_2\text{PtCl}_6$: Pt, 43.96%).

On expelling the solvent from the hydrochloride solution very hygroscopic crystals were obtained, which was subjected to steam distillation with sodium hydroxide. The distillate was shaken with an excess of yellow mercuric oxide⁽⁸⁾ and filtered. After twice repeating the above treatments, the solution was distilled with steam. The free base thus obtained gave no reaction of pyrrole, it gave the characteristic crystalline precipitates of pyrrolidine when a solution of potassium bismuth iodide was added. The chloroplatinate of this base crystallized in orange rods (straight extinction), which decomposed at 210°. The result of the analysis coincided with that of chloroplatinate of pyrrolidine (Found: Pt, 35.4. Calc. for $(\text{C}_4\text{H}_9\text{N})_2\text{H}_2\text{PtCl}_6$: Pt, 35.34%).

Separation of γ -Amino-butyric Acid. After removal of part soluble in ether and volatile bases from the electrolysate, the solution was treated with CO_2 , to remove the large bulk of barium. The filtrate was concentrated under reduced pressure, and boiled with an excess of barium hydroxide. The solution, after complete removal of barium, was extracted with ether. From the ethereal extract a small quantity of succinic acid (m.p. 183°) was obtained, which remained unextracted in the previous treatments.

In the residual solution, 1.63 mg. of amino-nitrogen (74.3% of total-nitrogen) was found and it gave an intense ninhydrin reaction. From this solution yellow crystalline chloroplatinate (0.13 g.) was isolated which, after recrystallization, decomposed at 220°. It was identified as γ -amino-butyric acid by the decomposition point and by the comparison of crystalline behaviours under polarizing microscope (straight extinction, sign of elongation: negative) with those of synthetic sample. The hydrochloride of this base was prepared from the chloroplatinate, as usual, and it gave an intense ninhydrin reaction. Here again its behaviours under polarizing microscope coincided with those of synthetic hydrochloride.

To ascertain the nitrogen distribution and the presence of pyrrolidone in the electrolysate, proline (0.707 g.) was electrolyzed (7.9 F./mol) under the same conditions as already

(8) E. Abderhalden, "Handbuch der biologischen Arbeitsmethoden," 1923, I, 7, 347.

described. The volatile bases (NH_3 , pyrrolidine) and barium were removed from the electrolysate, and the amounts of amino-nitrogen as well as total nitrogen in the solution were determined. After boiling with an excess of barium hydroxide for two hours, the amounts of the two forms of nitrogen in it were again determined. The amount of amino-nitrogen (percentage to total nitrogen) reached 93.9% after this treatment, the net increase exceeding 20%.

Oxidation of γ -Amino-butyric Acid. γ -Amino-butyric acid⁽⁹⁾ was prepared by the electrolytic reduction of succinimide. It melted at 203° with decomposition (Found: N, 13.5. Calc. for $\text{C}_4\text{H}_9\text{O}_2\text{N}$: N, 13.59%. Found: Pt, 31.6. Calc. for $(\text{C}_4\text{H}_9\text{O}_2\text{N})_2\text{H}_2\text{PtCl}_6$: Pt, 31.62%).

γ -Amino-butyric acid (1.031 g., 10 millimols) in $\text{N H}_2\text{SO}_4$ (27 c.c.) was electrolyzed, current quantity being 8.25 F./mol, under the same conditions as in the case of proline. Amino-N/total-N in the electrolysate was 30.28%. The electrolysate was extracted thoroughly with ether. Succinic acid (0.2 g.) was obtained from the ethereal extract and it was recrystallized from water, which melted at 183° . The acid equivalent and silver content in its silver salt were determined (29.6 mg. acid required 5.00 c.c. (0.09972 N NaOH). Calc. for $\text{C}_4\text{H}_6\text{O}_4$: 5.02 c.c. Found: Ag, 64.8. Calc. for $\text{C}_4\text{H}_4\text{O}_4\text{Ag}_2$: Ag, 65.04%).

The residue of the ethereal extraction was treated with Ba(OH)_2 , and ammonium chloride was isolated as volatile base (Found: Pt, 43.7. Calc. for $(\text{NH}_4)_2\text{PtCl}_6$: Pt, 43.93%). After the removal of succinic acid, ammonia, and barium from the electrolysate, unchanged γ -amino-butyric acid was recovered in crystalline form (m.p. 203°).

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(9) J. Tafel and M. Stern, *Ber.*, **33** (1900), 2224.

SYNTHESIS OF β,γ -DIHYDROXY-PROPYL-GUANIDINE.

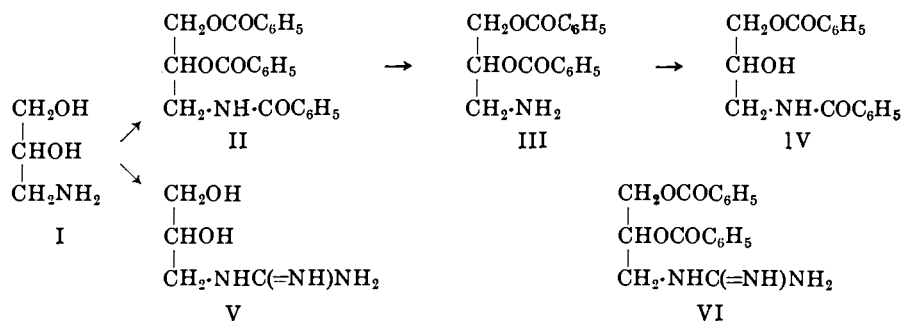
By Sin'iti KAWAI and Noboru SUGIYAMA.

Received October 25th, 1935. Published March 28th, 1936.

One of us (K.) has synthesized β -hydroxy-ethyl-guanidine⁽¹⁾. Polyhydroxy-alkyl-guanidine, as we are aware, seems not yet been described in the literature. With the object of enlarging our knowledge upon the synthetic methods of polyhydroxy-alkyl-guanidine we attempted to synthesize β,γ -dihydroxy-propyl-guanidine, on which will be briefly reported here.

Starting from glycerol we first obtained amino-propylene glycol (I).

(1) S. Kawai, *Sci. Pap. Inst. Phys. Chem. Research, Japan*, **16** (1931), 24.



Amino-propylene glycol was benzoylated to its tribenzoyl-derivative (II) from which one benzoyl group was removed to *O,O'*-dibenzoyl- γ -amino-propylene glycol (III)⁽²⁾. *O,O'*-Dibenzoyl- γ -amino-propylene glycol hydrochloride (III) and an equivalent quantity of cyanamide were heated at 120–130°C in a sealed tube, absolute alcohol, or anhydrous pyridine being chosen as the solvents. In both cases, instead of procuring the expected β,γ -dibenzoyl-propyl-guanidine (VI), the reaction proceeded in an unexpected manner, and the sole crystalline product which we gained was the *O,N*-dibenzoyl- γ -amino-propylene glycol of Bergmann (IV)⁽³⁾. When we submitted *O*-methyl-pseudo-urea (free base) to reaction in place of cyanamide, the result was the same. In all cases the reactions ended in the acyl displacement from oxygen to nitrogen.

Our trial to synthesize β,γ -dihydroxy-propyl guanidine (V) succeeded, however, when we applied free amino-propylene glycol (I) and *S*-methyl-pseudo-thiourea hydroiodide as the starting materials. The β,γ -dihydroxy-propyl-guanidine (V) was isolated and identified as its picrate.

Experimental.

Amino-propylene glycol (I). Glycerol- α -monochlorhydrin was first synthesized after R. Adams⁽⁴⁾, which was transformed into glycidol⁽⁵⁾. The latter was converted to amino-propylene glycol⁽⁶⁾ (b.p. 163–165°/18 mm.) with concentrated aqueous ammonia.

***O,N*-dibenzoyl- γ -amino-propylene glycol (IV).** Only one case will be written here for simplification. Into a sodium methylate solution (from 0.5 g. of metallic sodium and 5 c.c. of absolute methyl alcohol), which was cooled with ice water from outside, an absolute methyl alcoholic solution (10 c.c.) of *O*-methyl-pseudo-urea hydrochloride⁽⁷⁾ (2.4 g.)

(2) M. Bergmann, *Ber.*, **54** (1921), 936.

(3) *Loc. cit.*

(4) R. Adams, "Organic Synthesis," II, 33.

(5) J.U. Nef, *Ann.*, **335** (1904), 231. T.H. Rider, *J. Am. Chem. Soc.*, **52** (1930), 1521.

(6) L. Knorr and E. Knorr, *Ber.*, **32** (1899), 752.

(7) J. Stieglitz, *Ber.*, **33** (1900), 1517.

was slowly added. After standing for about an hour, the separated sodium chloride was filtered off. Into this filtered solution *O,O'*-dibenzoyl- γ -amino-propylene glycol hydrochloride (III)⁽⁸⁾ (7.28 g.) was added and the whole was shaken until dissolution was complete, temperature not being raised above 30°C.

After standing overnight the solution was concentrated to about two-thirds of its original volume under reduced pressure. Two days later the separated crystals were sucked off and were recrystallized several times from aqueous methyl alcohol. Colourless long plates, m.p. 108–109°C. Judging from its melting point and the analytical results no doubt can be inserted in its identity with the Bergmann's *O,N*-dibenzoyl- γ -amino-propylene glycol. Bergmann gives m.p. 109°C (corr.). (Found: C, 68.14, 67.99; H, 5.61, 5.69; N, 4.67, 4.50. Calc. for $C_{17}H_{17}O_4N$: C, 68.20; H, 5.73; N, 4.68%.)

β,γ -Dihydroxy-propyl-guanidine (V). Into an alcoholic solution (10 c.c.) of amino-propylene glycol (0.91 g., $\frac{1}{100}$ mol) *S*-methyl-pseudo-thiourea hydroiodide (2.18 g., $\frac{1}{100}$ mol) was added and the whole was refluxed on a steam bath for about 1.5 hours, strong evolution of mercaptan being observed. When the major part of the solvent was driven off under reduced pressure from the reaction mixture we obtained a syrupy mass, which showed no sign of crystallization even though it was kept in a vacuum desiccator for several days.

The syrup, however, exhibits positive colour-reactions of guanidine and it can be concluded that β,γ -dihydroxy-propyl guanidine hydroiodide was produced, in spite of its non-crystallizing tendency, which is presumably originated in its hygroscopic nature. The attempt to isolate the hydroiodide was then abandoned and the syrupy material was treated with a concentrated aqueous solution of sodium picrate (2.5 g.). Yellow crystals soon separated, which were collected. Yield 1.45 g. The picrate thus obtained was recrystallized several times from water. M.p. 126°C. Yellow fine prisms.

As is shown in the following analytical data, as well as the positive colour-reactions of guanidine (Sakaguchi's test, carmine red; Weber's test, blood red) it can be concluded that β,γ -dihydroxy-propyl-guanidine picrate was obtained. (Found: C, 33.26, 33.55; H, 3.71, 4.04; N, 22.89, 22.83%). Calc. for $C_{10}H_{14}O_9N_6$: C, 33.13; H, 3.90; N, 23.20%.)

The authors wish to express their hearty thanks to Prof. R. Majima for his kind advice.

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and
Tokyo Bunrika University,
Koishikawa, Tokyo.*

(8) M. Bergmann, *loc. cit.*

(9) The nitrogen analysis of guanidine derivative, arginine for instance, often shows too small amount of nitrogen.

4,5-BIS-(*m*-AMINOPHENYL)-CARBAZOLE.

By Shin-ichi SAKO.

Received October 29th, 1935. Published March 28th, 1936.

This investigation was undertaken with a view to elucidate the spatial relations of the two phenyl nuclei contained in 4,5-diphenyl-carbazole. Although the work has not so far progressed as was originally intended, it has been thought advisable, for the reasons which will be given at the end of this introduction, to communicate some of the results already obtained.

In a previous paper⁽¹⁾, a brief account was given of the structure of 4,5-diphenyl-carbazole. It was there stated that, as the two phenyl nuclei cannot occupy their normal positions owing to the collision with each other, the valencies carrying the phenyl groups will have to be in a strained condition. Assuming that the atoms of the carbazole nucleus lie in a single plane⁽²⁾, and taking into account that the molecule would assume the least strained form possible in the circumstances, it was suggested that the most probable structure representing the substance would be one in which the two phenyl nuclei lie in planes approximately perpendicular to the plane in which the carbazole nucleus lies. This is shown by Fig. 1, which is constructed on the assumption

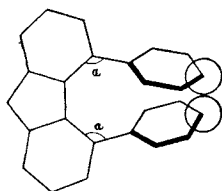


Fig. 1.

that the interatomic distances, C-C and C-N, is approximately 1.42 Å and also that valency distortion is possible only in the same planes as those in which the benzene nuclei lie. The thick lines indicate the sides of hexagons which are nearer to the reader. The directions of the valencies carrying the phenyl groups are those when the two carbon atoms of the *p*-positions of the phenyl nuclei are in mutual contact with the interatomic distance 1.42 Å,

in other words, when the angle α is 125.1°. Since, however, it is inconceivable that the two atoms which is not in actual combination should be in such close proximity, actually the angle α will be somewhat larger than this. At any rate, this figure serves to indicate that, when the molecule assumes the structure represented by Fig. 1, the intramolecular strain is not large. The

(1) Sako, this Bulletin, **9** (1934), 63.

(2) That the carbazole nucleus has a coplanar configuration has been shown by the fact that when *d*- or *l*-2,2'-diamino-1,1'-dinaphthyl is heated with HCl, inactive naphtho-carbazole is produced (Kuhn and Goldfinger, *Ann.*, **470** (1929), 183). See also Adams and Yuan, *Chem. Rev.*, **12** (1933), 289.

facile formation of 4,5-diphenyl-carbazole⁽³⁾ from 2,2'-diamino-6,6'-diphenyl-diphenyl and also of 4,5-bis-(*m*-aminophenyl)-carbazole (XV) from 2,2'-diamino-6,6'-bis-(*m*-aminophenyl)-diphenyl(XIV) may be attributed to this cause.

If Fig. 1 represents the stable form of 4,5-diphenyl-carbazole, a question which is naturally raised is whether or not there is a possibility of the rotation of the two phenyl nuclei around the bond carrying them. The observations such as those by Mills and his co-workers that benzenesulphonyl-8-nitronaphthylglycine (I)⁽⁴⁾ and 8 benzenesulphonylethylamino-1-ethyl-quinolinium iodide (II)⁽⁵⁾ can be obtained in optically active forms and the resolvability of many of the ortho-substituted diphenyl compounds due to the restricted rotation of the two nuclei seem to indicate that the rotation of the phenyl nuclei of 4,5-diphenyl-carbazole should also be restricted in a similar manner. The probability that the rotation of one of the phenyl groups will be obstructed by the other is perhaps more clearly indicated in the diagrammatical representation of this compound given in Fig. 2, which is constructed on the assumption

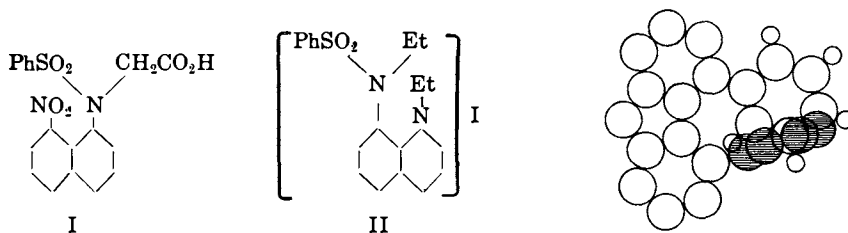


Fig. 2.

that the atoms of carbon and nitrogen may be regarded as spheres of a diameter approximately 1.42 Å, and that the hydrogen atoms as spheres of a diameter approximately one half of the diameter of the carbon atom. The carbazole nucleus is shown in the left half of the figure, and the hydrogen-atoms attached to this nucleus are omitted to simplify the diagram. The six carbon atoms of one of the phenyl groups, which are assumed to lie in the same plane as that in which the carbazole nucleus lies, are indicated in the upper-right of the figure, and the small spheres attached to five of these carbon atoms represent the hydrogen atoms⁽⁶⁾. The horizontally shaded spheres

(3) Sako, this Bulletin, **9** (1934), 70.

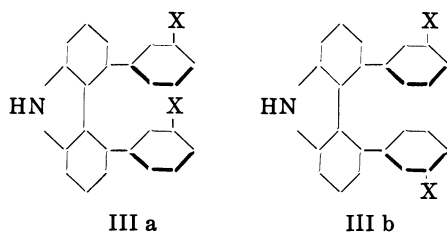
(4) Mills and Elliot, *J. Chem. Soc.*, **1928**, 1291.

(5) Mills and Breckenridge, *J. Chem. Soc.*, **1932**, 2209.

(6) That the hydrogen atoms in the nucleus do act as obstacles and are not embedded in the nuclear carbon atoms has been proved by the fact that diphenyl with only two substituents of proper size in opposite nuclei is resolvable (Turner and his co-workers, *J. Chem. Soc.*, **1932**, 2021, 2394; *ibid.*, **1933**, 135. Searle and Adams, *J. Am. Chem. Soc.*, **55** (1933), 1649. See also *Chem. Soc. Annual Reports*, **1933**, p. 258).

represent the four of the six carbon atoms of the other phenyl group which are assumed to be lying in a plane perpendicular to the plane of the paper. The positions of the two phenyl nuclei indicated in the figure are those when they are in their supposed normal positions.

It will be seen that, for the rotation of one of the phenyl nuclei by sweeping the obstacles presented by the other, the molecule will have to be distorted very considerably, the magnitude of this distortion being perhaps comparable to, if not larger than, that required in the case of the compounds I and II examined by Mills and his co-workers. The compound should there-

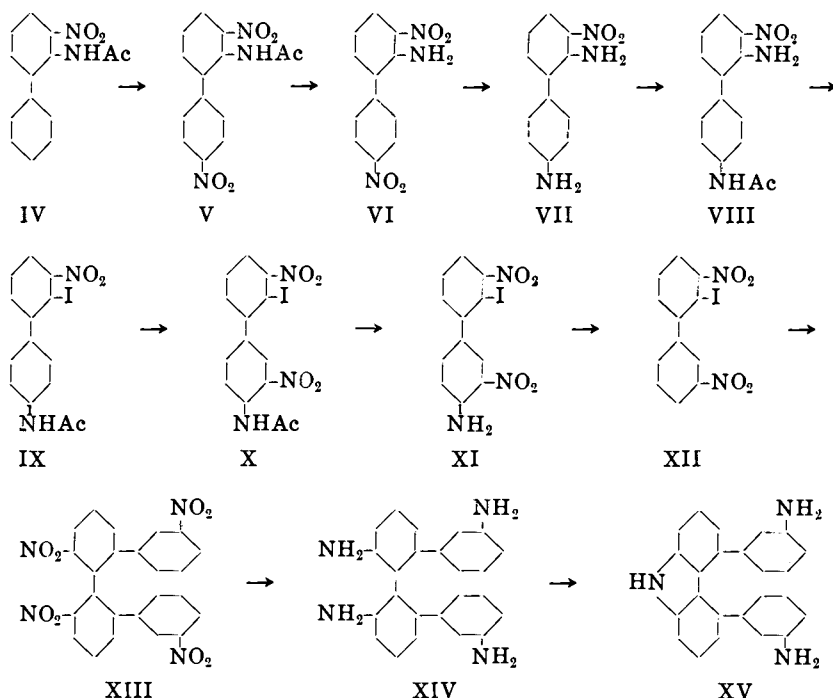


fore be represented by the structure given in Fig. 1, which appears to be the least strained condition of the molecule attainable in the circumstances. If the rotation of the phenyl nuclei are in fact thus limited, it follows that a 4,5-diphenylcarbazole derivative, which contains each of a substituent in the meta-

(or ortho-) positions of the two phenyl nuclei, should exist in a pair of geometrical isomers, one *cis* and the other *trans*, as shown respectively by the formulæ IIIa and IIIb, and that, since the transform (IIIb) does not possess a plane of symmetry, it should exist in two enantiomorphous modifications.

It seemed therefore that the simplest way to test those views stated above experimentally would be through the examination of such a type of 4,5-diphenylcarbazole derivative as indicated by formulæ IIIa and IIIb. The compound which was selected for examination was 4,5-bis-(*m*-aminophenyl)carbazole (XV) which has been obtained in the following way. 3-Nitro-2-acetamidodiphenyl (IV), which has been prepared through a series of processes from diphenyl by Sako's method⁽⁷⁾, can be successively converted into 3,4'-dinitro-2-acetamidodiphenyl (V), 3,4'-dinitro-2-amino-diphenyl (VI), 3-nitro-2,4'-diaminodiphenyl (VII), 3-nitro-2-amino-4'-acetamidodiphenyl (VIII), 2-iodo 3-nitro-4'-acetamidodiphenyl (IX), 2-iodo-3,3'-dinitro-4'-acetamidodiphenyl (X), 2-iodo-3,3'-dinitro-4'-aminodiphenyl (XI), 2-iodo-3,3'-dinitrodiphenyl (XII), and the latter treated according to the Ullmann method with copper powder. 2,2'-Dinitro-6,6'-bis-(*m*-nitrophenyl)-diphenyl(XIII), produced in this way, on reduction, passes into 2,2'-diamino-6,6'-bis-(*m*-aminophenyl)-diphenyl (XIV), which, upon heating with HCl, yields 4,5-bis (*m*-aminophenyl)carbazole (XV) :

(7) This Bulletin, 9 (1934), 65.



Scarborough and Waters⁽⁸⁾ have found that, although it contains the acetamido-group which tends to promote substitution in the same nucleus, 2-acetamidodiphenyl is nitrated in the 4'-position in the presence of acetic acid and conc. H_2SO_4 , 4'-nitro-2-acetamidodiphenyl being obtained in a good yield⁽⁹⁾. This anomalous behaviour must be attributed to the presence of conc. H_2SO_4 which in general weakens, most probably due to the salt formation, the directive influence of the acetamido-group. This view is supported by the fact that when nitrated in the presence of acetic acid alone, 2-acetamidodiphenyl affords the 5-nitro-derivative⁽¹⁰⁾ as the primary product. From these facts and also from the fact that 3-nitro-2-acetamidodiphenyl (IV) contains the nitro-group which tends to prevent substitution from occurring in the same ring, it is to be expected that the compound IV, when nitrated in the presence of conc. H_2SO_4 and acetic acid, should give mainly 3,4'-dinitro-2-acetamidodiphenyl (V). The experiment fully justified this expectation, for it has been found that under the conditions the compound (V) is produced in 73% yield. A conclusive proof of the position of the entering nitro-group has been

(8) *J. Chem. Soc.*, **1927**, 95.

(9) Sako, this Bulletin, **10** (1935), 585.

(10) Bell, *J. Chem. Soc.*, **1928**, 2773.

afforded by oxidizing 3,4'-dinitro-2-aminodiphenyl (VI), which is obtained by the hydrolysis of V, with chromic acid in acetic acid, when *p*-nitrobenzoic acid is obtained as one of the products.

The partial reduction of compounds V and VI, and 2-iodo-3,4'-dinitro-diphenyl, with sodium sulphide of which the latter can be obtained from VI by the usual method, was attempted in the hope of effecting the reduction of only the 4'-nitro-group contained in these substances. As a matter of fact, however, the partial reduction of compound VI has been found to be the only workable method, the yield of VII being 89% of the theoretical. That a nitro-group adjacent to an amino-group resists reduction with an alkaline sulphide has already been observed in the case of *o*-nitroaniline which is recovered unchanged after being heated with ammonium sulphide⁽¹¹⁾. This behaviour of *o*-nitro-aniline is in marked contrast with that of *o*-nitro-acetanilide, of which compound V is a derivative, for under similar conditions the acetylated base can be reduced with ammonium sulphide⁽¹²⁾. As will be foreseen from this, when compound V was treated with sodium sulphide, both nitro-groups appeared to be attacked, and the chance of partial reduction taking place in the desired manner only seemed remote. It has been found that when 2-iodo-3,4'-dinitro-diphenyl is heated with alcoholic sodium sulphide, the resulting substance contains no halogen. This observation is in accord with that of Beilstein and Kurbatow⁽¹³⁾ that the reaction, which occurs when *o*-chloronitro-compounds such as 1-chloro-2,4-dinitrobenzene are heated with (NH₄)₂S, K₂S, or better with KSH, is the elimination of halogen.

In the monoacetylation of 3-nitro-2,4'-diaminodiphenyl (VII), advantage was taken of the fact that the amino-group adjacent to the nitro- and also to the phenyl group is not attacked by acetic anhydride, the theoretical yield of the monoacetylated product VIII being obtained easily. This was a matter which had been anticipated, for it had been known that 3,5-dinitro-2-aminodiphenyl⁽¹⁴⁾ and 3-nitro-2-aminodiphenyl⁽¹⁵⁾, which, like compound VII, have each a nitro- and a phenyl-group in positions adjacent to the amino-group, cannot be acetylated even by boiling with acetic anhydride.

2-Iodo-3-nitro-4'-acetamidodiphenyl (IX), on nitration with nitric acid of D. 1.45–1.46, yields dinitro-compound X, but with nitric acid of D. 1.51–1.52, the trinitro-compound, 2'-iodo-3,5,3'-trinitro-4-acetamidodiphenyl (XVI). The constitution of this dinitro-compound (X) follows from the following considera-

(11) *Ber.*, **25** (1892), 987.

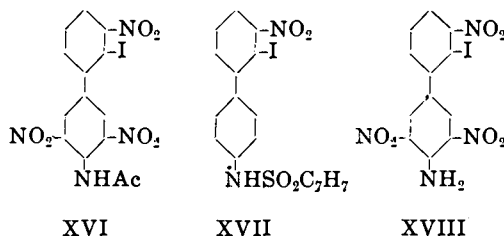
(12) Lassar-Cohn, "Arbeitsmethoden f. org. Chem. Lab.", 5 Ed., p. 861; cf. Niementowski, *Ber.*, **43** (1910), 3024.

(13) *Ber.*, **11** (1878), 2056.

(14) Bell, *J. Chem. Soc.*, **1928**, 2774.

(15) Sako, this Bulletin, **9** (1934), 68.

tions : (i) since there is a nitro-group in one of the nuclei of IX, the second nitro-group would naturally go to the other nucleus containing the acetamido-group which tends to promote substitution, and this should be more so as the nitration was conducted in the presence of nitric acid alone ; (ii) that the compound appears to be a derivative of *o*-nitroacetanilide and not that of *m*-nitroacetanilide has been shown by the fact that free base (XI) obtained by its hydrolysis does not form the hydrochloride in a dil. HCl solution, and also that the deamination of the free base (XI) through the diazonium salt resulting in 2-iodo-3,3'-dinitrodiphenyl (XII) takes place with utmost readiness ; (iii) by the nitration of 2-iodo-3-nitro-4'-*p*-toluenesulphonamidodiphenyl (XVII), a product is obtained, which, on hydrolysis, yields a trinitroamino-compound identical with that obtained by the hydrolysis of the trinitroacetamido-compound (XVI). In view of the very powerful ortho-para-directing influence exerted by the *p*-toluenesulphonamido-group as has been shown by Bell⁽¹⁶⁾, the most probable structure of this trinitro-amine would be formula XVIII.



There was no difficulty presented in the preparations of 2,2'-dinitro-6,6'-bis-(*m*-nitrophenyl)-diphenyl (XII), 2,2'-diamino-6,6'-bis-(*m*-aminophenyl)-diphenyl (XIV), and 4,5-bis-(*m*-aminophenyl)-carbazole (XV). The free base of the latter crystallized, however, with difficulty. This property, coupled with the fact that it is rather readily oxidized in the air, rendered obtaining the free base XV in pure crystalline condition impossible. The hydrochloride and the diacetyl derivative of XV could be obtained readily in a state of purity. The sharp melting point possessed by this diacetyl compound indicated that it was a single substance, but since compound XV has been produced at such a high temperature as over 200° in the presence of HCl, it is possible that the more stable form (probably the *trans* form (IIIb)) alone is produced.

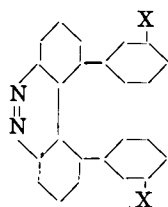
Attempts to resolve compound XV with *d*-camphor-sulphonic acid and *d*-tartaric acid have not been successful. The former acid gave no crystalline salt, and, although the latter acid gave a difficultly soluble tartarate in alcohol, the deep brown colour of this salt rendered the polarimetric examination impossible. This colour was undoubtedly caused by the oxidation in the air, which appeared to occur more readily when the base exists as a salt than when it is free. On account of this property and also of the small quantity

(16) *J. Chem. Soc.*, 1928, 2770.

of the material (XV), a detailed examination of these salts had to be postponed till a later date (as already stated, for the synthesis of XV, no fewer than fifteen stages of preparations are required).

Compound XV was then submitted to the action of *l*-menthoxyacetyl chloride, when the stable 4,5-bis-(*m-l*-menthoxyacetamidophenyl)-carbazole was obtained in 73% yield. Its sharp melting point indicated that the *l*-menthoxyacetyl derivative was a single substance, although it does not necessarily follow from the good yield that the bis-(aminophenyl)-carbazole portion of the *l*-menthoxyacetyl compound is optically inactive, since there is a possibility that the substance might have been obtained as a result of processes of optical activation, similar to those observed, for example, by Pope and Peachy⁽¹⁷⁾ with methyl-ethyl-*n*-propyl-tin-*d*-camphor-sulphonate, by Mills and Elliot⁽⁴⁾ with the brucine salt of benzenesulphonyl-8-nitro-naphthyl-glycine, and by Yuan and Adams with the brucine salt of 2'-nitro-2,5-dimethoxydiphenyl-6'-carboxylic acid. Unfortunately, however, attempts to eliminate the *l*-menthoxyacetyl group by means of hydrolysis have so far been failures. That the rotation of an active substance is greatly influenced by the nature of solvents has been demonstrated once again by the bis-*l*-menthoxyacetyl derivative of XV. Thus, although it has $[\alpha]_D -22.27^\circ$ in EtOH and -24.65° in acetone, the sign of rotation is completely reversed in benzene, in which $[\alpha]_D$ is $+14.2^\circ$.

Although, owing to lack of material, the behaviour of the active acids on XV has not been examined so thoroughly as otherwise would have been



XIX

possible, it seemed that the rather unstable nature of XV and its salts was unsuited or at least not advantageous for the investigation of this kind. It is proposed, therefore, to investigate the matter in other compounds of similar type which fulfil the conditions mentioned above, including, if possible, those containing a 6-membered ring in place of the 5-membered ring of XV, such as, for example, shown in formula XIX. From similar considerations regarding the probability of restriction

of rotation of the phenyl groups, it is apparent that, since XIX should be more highly strained than XV, the rotation of the phenyl groups will be more difficult in XIX than in XV.

Experimental.

3,4'-Dinitro-2-acetamidodiphenyl (V). A solution of 42.8 g. of 3-nitro-2-acetamidodiphenyl in 85 c.c. each of glacial acetic acid and conc. H_2SO_4 was cooled with ice and

(17) *J. Chem. Soc., Proc.*, **16** (1900), 12, 42, 116.

treated gradually with a mixture of 8.6 c.c. of fuming HNO_3 of D. 1.52, 15 c.c. of glacial acetic acid, and 15 c.c. of conc. H_2SO_4 with constant stirring, the mixed acids being added at such a rate that the temperature of the reaction mixture was maintained below $+2^\circ$. After the mixed acids had been added, stirring was continued one more hour. The mixture was then poured on ice, and the precipitated solid collected. The dried crude product weighed 49.2 g. It was dissolved in 1600 c.c. of boiling EtOH and left overnight. The yellow crystals (30.5 g.) thus separated were almost pure 3,4'-dinitro-2-acetamidodiphenyl (V). By concentration of the mother liquor, somewhat impure crystals were obtained, which on recrystallization gave a second crop (6.4 g.). The yield of V was therefore 73% of the theoretical. Pure 3,4'-dinitro-2-acetamidodiphenyl had m.p. 207.5° with previous sintering (Found: N, 14.2. Calc. for $\text{C}_{14}\text{H}_{11}\text{O}_5\text{N}_3$: N, 14.0%).

The mother liquors separated from the main product, on further concentration, deposited more soluble nitration products in crystalline condition, but they have not been investigated so far. 3,4'-Dinitro-2-acetamidodiphenyl (V), when treated with alcoholic sodium sulphide, yielded a product which contained at least two substances, one yellow and the other red, the latter being identified with compound VII by the mixed melting point method.

3,4'-Dinitro-2-amino-diphenyl (VI). 3,4'-Dinitro-2-acetamidodiphenyl (V) (37 g.) was refluxed with a mixture of 450 c.c. each of EtOH and conc. HCl on the water bath for 7 hours. The free base separated as orange needles during the heating. After cooling, the product (31.1 g.) was collected, dried, dissolved in 900 c.c. of boiling benzene, and the solution allowed to cool. The orange leaflets thus obtained, 28 g., melted at $196-197^\circ$ (Found: N, 16.5. Calc. for $\text{C}_{12}\text{H}_9\text{O}_4\text{N}_3$: N, 16.2%).

The dinitroamino-compound (VI), on oxidation with chromic anhydride in acetic acid, gave *p*-nitrobenzoic acid as one of the products, showing that in the nitration of IV, the second nitro-group entered the 4'-position: a suspension of 3,4'-dinitro-2-aminodiphenyl in 10 parts of glacial acetic acid was treated with 5 parts of chromic anhydride with agitation. The substance disappeared with the evolution of heat, forming a dark-green, thick liquid. After standing for some hours, it was diluted with water, when a yellow precipitate separated. It was collected, dissolved in dil. ammonia solution and some insoluble matter was filtered off. The filtrate, on acidifying with HCl, deposited a yellow crystalline solid, which, on recrystallization, gave yellow crystals, which showed no depression of the melting point when mixed with the authentic specimen of *p*-nitrobenzoic acid.

2-Iodo-3,4'-dinitrodiphenyl. 3,4'-Dinitro-2-aminodiphenyl (VI) (1.3 g.) was dissolved in 5 c.c. of conc. H_2SO_4 at ordinary temperature. The vessel was then surrounded by ice, and 3.5 g. of cracked ice and 0.38 g. of powdered sodium nitrite were added with stirring. After a time, 2.5 g. of ice was added and stirring continued for an hour. A large quantity of ice was then added, and some suspended matter removed by filtration. The filtrate, on addition of 1.0 g. of KI, decomposed at once, the iodo-compound being precipitated. It was dissolved in ether, and the ethereal solution was shaken with a KOH solution and dried. On removal of the ether, a crystalline solid remained, which after being treated with animal charcoal in alcohol, was twice crystallized from the solvent (50 c.c.). It formed yellow, flat needles melting at $139-140^\circ$ (Found: I, 34.33. Calc. for $\text{C}_{12}\text{H}_7\text{O}_4\text{N}_2\text{I}$: I, 34.31%). The yield was 1.4 g.

In an attempt to effect the partial reduction of the 4'-nitro-group only, the iodo-dinitro-compound was treated with sodium sulphide in EtOH and a small quantity of

water, when fine needles separated, which contained no halogen. This product has not been studied.

3-Nitro-2,4'-diaminodiphenyl (VII). The procedure described below for the partial reduction of 3,4'-dinitro-2-aminodiphenyl (VI) is the outcome of a number of comparative experiments which were made to determine the best conditions. A suspension of 26 g. of 3,4'-dinitro-2-amino-diphenyl (VI) in 600 c.c. of EtOH was mixed with a solution of 40 g. of $\text{Na}_2\text{S}\cdot 9\text{H}_2\text{O}$ in 150 c.c. of water, and refluxed on the boiling water bath for an hour. The original substance disappeared in a quarter of an hour, forming a red solution. After the requisite time, the hot solution was diluted with 250 c.c. of water, when 3-nitro-2,4'-diaminodiphenyl (VII) separated immediately in crystalline state. The red crystals were collected, washed with EtOH- H_2O , and dried. The substance thus obtained was almost pure, had m.p. $156-157^\circ$, and may be used for a further experiment. The yield was 20.5 g. or 89.1% of the theoretical. On crystallization from EtOH, it gave red crystals melting at 157° (Found: N, 18.6. Calc. for $\text{C}_{12}\text{H}_{11}\text{O}_2\text{N}_3$: N, 18.3%).

3-Nitro-2-amino-4'-acetamidodiphenyl (VIII). Acetic anhydride (6.9 g.) dissolved in a few c.c. of benzene was added to a suspension of 13.8 g. of 3-nitro-2,4'-diaminodiphenyl (VII) in 80 c.c. of benzene. The reaction commenced to occur at once, but it was heated on the boiling water bath for 30 minutes, during which time the original red crystals were replaced by the yellow crystals of the acetyl compound (VIII), which is practically insoluble in benzene. 3-Nitro-2-amino-4'-acetamidodiphenyl (VIII) thus obtained was pure and had m.p. $174-175^\circ$ (Found: N, 15.80. Calc. for $\text{C}_{14}\text{H}_{13}\text{O}_3\text{N}_3$: N, 15.50%). The yield was 16.2 g. (theoretical).

2-Iodo-3-nitro 4'-acetamidodiphenyl (IX). 3-Nitro-2-amino-4'-acetamidodiphenyl (VIII) (17.4 g.) was added in small portions to 77 c.c. of conc. H_2SO_4 at ordinary temperature with agitation. The resulting clear solution was cooled with ice water, treated with 60 g. of ice and then with 5.0 g. of NO_2Na which was added during 30 minutes. As soon as the thick foam had subsided, a large quantity of ice was added, and the red solution thus obtained treated with a solution of 14 g. of KI in the cold. Shortly afterwards, a vigorous reaction took place. External heating was not necessary, as the decomposition was complete even in the ice-cold temperature. The precipitated product was filtered and washed successively with a $\text{Na}_2\text{S}_2\text{O}_3$ solution and water. The dried crude product weighed 24.5 g. It was dissolved in 2240 c.c. of boiling alcohol and allowed to stand for crystallization. The yellow leaflets thus obtained melted at 239° with previous softening (Found: I, 33.1. Calc. for $\text{C}_{14}\text{H}_{11}\text{O}_3\text{N}_2\text{I}$: I, 33.2%). The yield of the pure substance was 22 g. or 90% of the theoretical.

2-Iodo-3-nitro-4'-aminodiphenyl and its hydrochloride. A suspension of 1.9 g. of 2-iodo-3-nitro-4'-acetamidodiphenyl (IX) in a mixture of 20 c.c. each of alcohol and conc. HCl was refluxed on the water bath for 1.5 hours during which time the original crystals were replaced by the yellow crystals of the hydrochloride of 2-iodo-3-nitro-4'-aminodiphenyl. After cooling, it was collected, washed with EtOH-conc. HCl and then with ether (Found: Cl, 9.32. Calc. for $\text{C}_{12}\text{H}_9\text{O}_2\text{N}_2\text{I}\cdot\text{HCl}$: Cl, 9.42%). The yield of the hydrochloride was 1.8 g. It can be crystallized from water.

To obtain the free base, the hydrochloride obtained above was shaken with an excess of NaOH solution and ether, and the upper layer, after being dried with K_2CO_3 , evaporated up. The residual crystals, on crystallization from EtOH, gave yellow crystals melting at $126-127^\circ$ (Found: I, 37.16. Calc. for $\text{C}_{12}\text{H}_9\text{O}_2\text{N}_2\text{I}$: I, 37.33%).

2-Iodo-3-nitro-4'-*p*-toluenesulphonamidodiphenyl (XVII). To a solution of 1.12 g. of 2-iodo-3-nitro-4'-aminodiphenyl in 3 c.c. of pyridine was added 0.66 g. of *p*-toluenesulphonyl chloride, and the reddish solution thus obtained was heated on the water bath until the colour had almost disappeared. It was then diluted with water and shaken with benzene. The benzene solution, when shaken with a CaCl_2 solution, separated a gummy material which solidified on rubbing. On crystallization from EtOH, 2-iodo-3-nitro-4'-*p*-toluenesulphonamidodiphenyl separated as beautiful yellow, transparent crystals which melted at $136-137^\circ$ (Found I, 25.44; S, 6.56. Calc. for $\text{C}_{19}\text{H}_{15}\text{O}_4\text{N}_2\text{IS}$: I, 25.69; S, 6.49%).

2-Iodo-3,3'-dinitro-4'-acetamidodiphenyl (X). At first, the preparation of this compound from 2-iodo-3-nitro-4'-acetamidodiphenyl (IX) presented unexpected difficulties, and it was only after a large number of comparative experiments, in which nitric acid of varied concentrations was employed, that this compound (X) became obtainable in an almost theoretical yield. The success of the nitration depended essentially upon the concentration of nitric acid, according to which either the dinitro-compound (X) or the trinitro-compound (XVI) was obtained exclusively.

To 40 c.c. of nitric acid of D. 1.456 which was cooled with ice water, was gradually added 7.64 g. of 2-iodo-3-nitro-4'-acetamidodiphenyl (IX) with stirring. The substance disappeared almost instantaneously after each addition. The addition of the original substance took about one hour, and the agitation was continued one more hour. Some of the product separated towards the end of the reaction. Reaction mixture was then poured into ice, and the solid thus appeared collected. The dried crude product weighed 8.6 g. On crystallization from 615 c.c. of EtOH, it formed yellow leaflets melting at $196-197^\circ$ (Found: N, 10.11. Calc. for $\text{C}_{14}\text{H}_{10}\text{O}_5\text{N}_3\text{I}$: N, 9.84%). The yield of the purified substance was 8 g. or 93.7% of the theoretical.

2-Iodo-3,3'-dinitro-4'-aminodiphenyl (XI). A suspension of 7.26 g. of powdered 2-iodo-3,3'-dinitro-4'-acetamidodiphenyl (X) in a mixture of 100 c.c. each of EtOH and conc. HCl was refluxed on the water bath for 1.5-2.0 hours. Fifty c.c. of water was then added to the hot mixture, and the crystalline product thus separated filtered after cooling. The substance (6.5 g.) was the almost pure free base (XI). Crystallized from EtOH, it formed yellow needles which melted at $178-178.5^\circ$ (Found: N, 11.22. Calc. for $\text{C}_{12}\text{H}_8\text{O}_4\text{N}_3\text{I}$: N, 10.91%).

2'-Iodo-3,5,3'-trinitro-4-acetamidodiphenyl (XVI). 2-Iodo-3-nitro-4'-acetamidodiphenyl (IX) (0.57 g.) was added during 15 minutes and with stirring to 6 c.c. of fuming HNO_3 of D. 1.52 which was cooled in an ice bath. After a short time (it has been found essential that the reaction mixture should be poured into ice without delay, for otherwise an amorphous product would result, from which no crystalline substance can be isolated), the reaction mixture was poured on ice and the yellow solid thus separated collected and dried. It was dissolved in 300 c.c. of boiling EtOH and the solution, after being concentrated, left overnight. The crystals thus obtained, on one more crystallization from EtOH, yielded slightly yellow needles melting at $263-264^\circ$ (Found: N, 11.96. Calc. for $\text{C}_{14}\text{H}_9\text{O}_7\text{N}_4\text{I}$: 11.86%). The yield of the pure substance was 0.4 g. .

2'-Iodo-3,5,3'-trinitro-4-aminodiphenyl (XVIII). This base was obtained by the hydrolysis of 2'-iodo-3,5,3'-trinitro-4-acetamidodiphenyl (XVI) and also of the product obtained by nitrating 2-iodo-3-nitro-4'-*p*-toluenesulphonamidodiphenyl (XVII).

A mixture of 2'-iodo-3,5,3'-trinitro-4-acetamidodiphenyl (XVI), conc. HCl and EtOH was refluxed on the water bath for a long time. The free base began to appear when

there was still a considerable quantity of the original acetyl compound left unaffected in the reaction mixture. The base was purified by crystallization from EtOH, from which it separated as yellow thin needles melting at 220-221° (Found: N, 13.12. Calc. for $C_{12}H_7O_6N_4I$: N, 13.02%). It is readily soluble in cold benzene.

The same base was also obtained from 2-iodo-3-nitro-4'-*p*-toluenesulphonamidodiphenyl as follows. 2-Iodo-3-nitro-4'-*p*-toluenesulphonamidodiphenyl (XVII) (0.25 g.) was added in small portions to 0.5 c.c. of fuming HNO_3 of D. 1.51 at ordinary temperature with agitation. After some time, water was added and the precipitated product filtered off. The product, 0.29 g., after crystallization from EtOH, was dissolved in 1 c.c. of conc. H_2SO_4 by gentle heating, and the solution, after cooling, poured into water. The yellow precipitate thus obtained, on crystallization from EtOH, gave yellow needles which melted, either alone or when mixed with the base obtained by the hydrolysis of the acetyl compound (XVI), at 220-221°.

2-Iodo-3,3'-dinitrodiphenyl (XII). 2-Iodo-3,3'-dinitro-4'-aminodiphenyl (XI) (6.6 g.) was added slowly to 28 c.c. of conc. H_2SO_4 at ordinary temperature with constant stirring, and the stirring continued until the substance had disappeared (1.5 hours). With continued stirring and with cooling with ice water, it was treated with 19 g. of ice and then 1.4 g. of NO_2Na , the latter being added in small portions. After an hour, 9 g. of ice was added and stirring continued for some time. The reaction mixture was then added gradually to 280 c.c. of boiling EtOH and the solution, after being refluxed on the water bath for an hour, filtered while hot to remove a trace of the red byproduct which was deposited during the reaction. The clear filtrate was concentrated, diluted with water, and the precipitate thus obtained extracted with ether. The ether was then removed, when 6.3 g. of the crystalline product was left behind, which, on vacuum distillation, gave 6.0 g. of the distillate boiling at 239°/6 mm. Upon crystallization from EtOH, 2-iodo-3,3'-dinitrodiphenyl separated in beautiful yellow needles which melted at 130-131° (Found: N, 7.72. Calc. for $C_{12}H_7O_4N_2I$: N, 7.57%).

2,2'-Dinitro-6,6'-bis-(*m*-nitrophenyl)-diphenyl (XIII). Copper powder (1.27 g.) was added during 4 minutes to 3.70 g. of well-stirred 2-iodo-3,3'-dinitrodiphenyl (XII) which was heated in an oil bath at 190-195°. After the copper powder had been added, the heating was continued for 5 to 7 minutes more, during which time the mass solidified completely. The product was extracted with a large quantity of boiling benzene, and the blue benzene extract shaken with water to remove the colour which was due probably to the presence of a copper compound. The benzene was then evaporated off, and the yellow residue (2.35 g.) crystallized from glacial acetic acid. 2,2'-Dinitro-6,6'-bis-(*m*-nitrophenyl)-diphenyl thus obtained was yellow needles melting at 259.5-260° (Found: N, 11.70. Calc. for $C_{24}H_{14}O_8N_4$: N, 11.52%). The yield of the pure substance was 90.5% of the theoretical. Compound XIII was not so easily soluble in cold benzene, but once dissolved by heating, it did not crystallize from this solvent even when it was greatly concentrated. One gram of it dissolves in about 55 c.c. of boiling acetic acid.

2,2'-Diamino-6,6'-bis-(*m*-aminophenyl)-diphenyl (XIV). A suspension of 3.9 g. of powdered 2,2'-dinitro-6,6'-bis-(*m*-nitrophenyl)-diphenyl (XIII) in a solution of 26 g. of stannous chloride in 96 c.c. of glacial acetic acid which contains dry HCl was gently heated with occasional shaking until a clear solution resulted, dry HCl being passed in all the time. It was observed that, when the reaction mixture was heated at a higher temperature (over 70° or so), the product separated as a gelatinous mass which redissolved

when HCl was passed into the cooled mixture, showing that the solubility of the product decreases with the decrease of the HCl content in the reaction mixture. When the reaction was over, the solvent was removed by distillation in vacuum, and the residue dissolved in water, made alkaline, and the free base collected. It was purified by vacuum distillation and then by crystallization from EtOH, from which 2,2'-diamino-6,6'-bis-(*m*-aminophenyl)-diphenyl (XIV) separated as almost colourless, large crystals which melted at 169-170° (Found: N, 15.43. Calc. for $C_{24}H_{22}N_4$: N, 15.30%). The yield of the pure crystals was 2.5 g. The tetramino-compound, unlike most of the aromatic amines, is sparingly soluble in ether and benzene. It is moderately soluble in EtOH when hot and sparingly so in the cold.

Attempts to isolate the tetramine as its hydrochloride from the reaction mixture were also made, but besides some other reason which has not been made clear, as the hydrochloride is very soluble even in conc. HCl, the result was not satisfactory.

4,5-Bis-(*m*-aminophenyl)-carbazole (XV). A solution of 0.61 g. of 2,2'-diamino-6,6'-bis-(*m*-aminophenyl)-diphenyl (XIV) in 20 c.c. of 0.5 N HCl solution in the nitrogen atmosphere was heated in a sealed tube in an oil bath at 200-205° for 7 hours, and then left overnight in the cold. As it is difficultly soluble even in a greatly diluted HCl, the carbazole derivative (XV) separated almost completely as a gray powdery dihydrochloride, but a few c.c. of conc. HCl was added to complete its separation, the dihydrochloride was collected, washed with dil. HCl and dried in vacuum over soda lime. The product (0.69 g.) was the almost pure dihydrochloride of XV. The method of purification such as the redissolution of the dihydrochloride in water, followed by the addition of conc. HCl after being treated with animal charcoal did not remove a trace of the impurity present. The crude product was therefore dissolved in water, made alkaline, and the base thus set free extracted with ether, when a trace of the dark impurity remained undissolved. The ethereal solution thus obtained was still somewhat coloured, but on leaving overnight with the addition of anhydrous K_2CO_3 or KOH, it became almost colourless. The ether was then removed at as low a temperature as possible to avoid oxidation of the base which tends to darken in colour at higher temperatures. The gummy residue was subsequently dried in high vacuum. It weighed 0.57 g. All attempts to purify the base by crystallization from a solvent and from mixed solvents failed, but on rubbing this gum with a small quantity of EtOH, a small portion of it was obtained as a solid form, which melted fairly sharply at 180-182° after softening at 175°.

The free base is readily soluble in ether, benzene, MeOH, and EtOH, and insoluble in petroleum ether. The solutions had a violet fluorescence, as was also observed in solutions of its salts and the acyl derivatives prepared so far. As stated above, the base, when heated at higher temperatures, darkens in colour and passes into a substance or substances insoluble or difficultly soluble in ether and benzene.

To obtain the pure dihydrochloride, the gummy base obtained above was dissolved in the calculated quantity of dil. HCl, and the dihydrochloride precipitated by the addition of a few c.c. of conc. HCl. It was collected and dried in vacuum over soda lime at ordinary temperature. It formed nearly colourless powdery crystals containing two molecules of water of crystallization (0.1858 g. of the dihydrochloride lost 0.0136 g. at 100° and 7 mm. pressure. Found: H_2O , 7.32; N, 9.42; Cl, 15.28. Calc. for $C_{24}H_{18}N_4 \cdot 2HCl \cdot 2H_2O$: H_2O , 7.86; N, 9.17; Cl, 15.48%). Aqueous solutions of the dihydrochloride darkened gradually when left in the air. This rather easily oxidisable nature was also

observed in solutions of the other salts of this base. Apparently, in solutions, these salts were oxidized more readily than the free base.

As already stated in the introduction, attempts to resolve this base with *d*-camphor sulphonic acid and *d*-tartaric acid have not been successful. No crystalline substance was formed when a conc. solution of this base in EtOH or in a mixture of EtOH and benzene was treated with *d*-camphor sulphonic acid. With *d*-tartaric acid, the base formed a difficultly soluble salt or salts in EtOH, but the deep brown colour of this salt rendered polarimetric examination impossible. Furthermore, as the material available for the investigation was very small, it was not possible to make a detailed examination of these salts.

4,5-Bis-(*m*-acetamidophenyl)-carbazole. The gummy 4,5-bis-(*m*-aminophenyl)-carbazole (XV) (0.20 g.) was dissolved in 12 c.c. of benzene and treated with an excess of acetic anhydride. The very difficultly soluble diacetyl derivative separated at once as an amorphous mass, which slowly but completely crystallized when the mixture was heated under reflux. After two hours' heating almost colourless crystals (0.21 g.) melting at 257-258° were obtained (Found: N, 9.90. Calc. for $C_{28}H_{23}O_2N_3$: N, 9.70%). There was no indication of the existence of the two forms.

4,5-Bis-(*m*-*l*-menthoxyacetamidophenyl)-carbazole. To a mixture of 0.32 g. of anhydrous K_2CO_3 and a solution of 0.20 g. of 4,5-bis-(*m*-aminophenyl)-carbazole (XV) in 20 c.c. of benzene was added 0.40 g. of *l*-menthoxyacetylchloride prepared from *l*-menthoxyacetic acid⁽¹⁸⁾ by the method of Holmes and Adams⁽¹⁹⁾, and the mixture refluxed on the water bath for two hours. It was then shaken with water to remove the excess of *l*-menthoxyacetic acid, and the upper layer, after being dried with Na_2CO_3 , evaporated up. The residual syrup, on being left in a basin, partly crystallized, but as the residual mass was not easily brought into crystallization it was rubbed with 12 c.c. of ether, and the crystals thus obtained were collected and washed. The colourless powder thus obtained weighed 0.19 g. It was dissolved in 10 c.c. of boiling EtOH, and the solution evaporated until the bulk was 6 c.c. and left overnight. In this way, all the dissolved substance (0.19 g.) slowly separated in almost colourless, well-defined crystals melting at 190-191° (Found: N, 5.77. Calc. for $C_{48}H_{59}O_4N_3$: N, 5.67%). Rotation: 0.0741 g. made up to 15 c.c. with benzene gave $\alpha_D + 0.14^\circ$ ($l = 2$), $[\alpha]_D + 14.2^\circ$, 0.0741 g. made up to 15 c.c. with EtOH gave $\alpha_D - 0.22^\circ$ ($l = 2$), $[\alpha]_D - 22.27^\circ$, 0.0852 g. made up to 15 c.c. with acetone gave $\alpha_D - 0.28^\circ$ ($l = 2$), $[\alpha]_D - 24.65^\circ$.

The ethereal mother liquor and the washings obtained above were evaporated up and the residue twice crystallized from a few c.c. each of EtOH. The crystals thus obtained (0.12 g.), though had somewhat lower melting point (188° after sintering at 185°) than the main crop, showed no depression of the melting point when they were mixed together, and possessed the same crystalline form and the same rotation as the main crop, showing that they were one and the same substance. The total yield of the *l*-menthoxyacetyl compound was therefore 0.31 g. or 73% of the theoretical.

The *l*-menthoxyacetyl compound was hydrolysed with great difficulty. Thus, in one instance, when 0.14 g. of the diacetyl compound was refluxed with a mixture of 5 c.c. of conc. HCl and 7 c.c. of EtOH for 14 hours, 0.06 g. of the original substance was recovered unchanged. In addition, there was also deposited from the reaction mixture 0.04 g. of

(18) Frankland and O'sullivan, *J. Chem. Soc.*, **99** (1911), 2329.

(19) Holmes and Adams, *J. Am. Chem. Soc.*, **56** (1934), 2093.

a crystalline hydrochloride which was quite stable in the air. The free base could be precipitated by adding alkali to its solution in water. This hydrochloride had $\alpha_D = 0$ in water, and so was the rotation of the free base in benzene. From these properties it is inferred that this hydrochloride might have been a product obtained by the removal of one of the menthoxyacetyl groups and also of the menthoxyl group of the other menthoxyacetamido-group. The analysis of the nitrogen content in the hydrochloride showed that the figure found agreed fairly well with that calculated for the monoglycolyl derivative of XV containing one molecule of water of crystallization. The conclusive proof of the structure of this substance could not be obtained on account of lack of material.

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SYNTHETISCHE VERSUCHE IN DER SELENOPHENGGRUPPE.
I. EINWIRKUNG VON CHLOR UND BROM AUF
SELENOPHEN.

Von Harusada SUGINOME und Sumio UMEZAWA.

Eingegangen am 29. Oktober 1935. Ausgegeben am 28. März 1936.

Das Selenophen (I), das dem Thiophen entsprechende Selenderivat, ist von Foa⁽¹⁾ aus bernsteinsaurem Natrium durch Erhitzen mit Phosphortriselenid in schlechter Ausbeute als ein Öl, Sdp. 147–149°/250 mm., erhalten worden. Nach ihm haben Bogert und Andersen⁽²⁾ durch Erhitzen von Bernsteinsäure mit Phosphorpentaselenid ein Öl erhalten, das dem von Foa beschriebenen Selenophen sehr ähnlich war. Kürzlich veröffentlichten Briscoe und seine Mitarbeiter⁽³⁾ eine schöne Darstellungsmethode von Selenophen aus Acetylen und Selen bei ca. 400°. Selenophen wird als schweres gelbes Öl, Sdp. 109.9–110.1°/752.1 mm., mit nicht angenehmem, an Benzol und Schwefelkohlenstoff erinnerndem Geruch erhalten.

(1) *Chem. Zentr.*, **81** (1910), I, 837; *Gazz. chim. ital.*, **39** (1909), II, 527.

(2) *J. Am. Chem. Soc.*, **48** (1926), 225.

(3) H. V. A. Briscoe und J. B. Peel, *J. Chem. Soc.*, **1928**, 1741. H. V. A. Briscoe und P. L. Robinson, *ibid.*, **1928**, 2628. McMahon, T. G. Pearson und P. L. Robinson, *ibid.*, **1933**, 1644.

Die Einwirkung von Acetylen auf Selen wurde auch von Mazza und Solazzo⁽⁴⁾ untersucht. Sie liessen reines Acetylen auf Selen bei 250–300° einwirken und isolierten durch fraktionierte Destillation ein bei 113–114° siedendes Öl, Selenophen. Die Angaben über das Selenophen in der Literatur⁽⁵⁾ sind also sehr verschieden, und es scheint uns, als ob noch nicht viele seiner Derivate synthetisch hergestellt worden seien. Da in unserem Land verhältnismässig reichlich Selen produziert wird—die Sumitomo-Bessiberg-Aktiengesellschaft stellte uns freundlicherweise eine ziemlich grosse Menge von Selendioxyd und Kammerschwamm zur Verfügung, wofür wir nochmals an dieser Stelle unseren Dank aussprechen möchten—so haben wir die vorliegende Arbeit unternommen.

Auch wir liessen Acetylen auf Selen in einem Porzellanrohr bei 350–370° einwirken. Die Resultate haben die Beschreibung von Briscoe und seinen Mitarbeitern⁽³⁾ bestätigt und zwar fanden wir, dass die Ausbeute, wenn man die Reaktion unter bestimmten Bedingungen ausführt, etwa 35% der Theorie erreichen kann.

Führt man bei tiefer Temperatur wasserfreies Chlor in das mit Schwefelkohlenstoff verdünnte Selenophen ein, so tritt Selenophen-2, 3, 4, 5-tetrachlorid (VI), ohne Chlorwasserstoffentwicklung, als einheitlich gelbe Krystalle auf. Lässt man dasselbe sich thermisch zersetzen, so bildet sich das 2, 5-Dichlorselenophen (III) welches mit demjenigen identisch ist, das durch direkte Einwirkung von Chlor auf Selenophen erhalten wurde. Bei der thermischen Behandlung verwandelt sich das Tetrachlorid (VI) in einen sehr beständigen Isomer, 2, 2, 5, 5-Tetrachlortetrahydroselenophen (VIII).

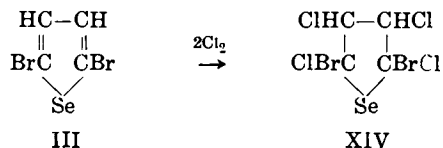
Wenn man bei Zimmertemperatur dieselbe Lösung mit einer berechneten Menge Chlor behandelt, so entstehen unter Chlorwasserstoffentwicklung 2-Chlorselenophen (II), 2, 5-Dichlorselenophen (III) und Selenophentetrachlorid (VI), während sich mit überschüssigem Chlor 2, 5-Dichlorselenophen-2, 3, 4, 5-tetrachlorid $C_4H_2Cl_6Se$ (X) neben den oben erwähnten drei Chlorderivaten (II, III, VI) bildet. Die Hexachlorverbindung wurde auch aus 2, 5-Dichlorselenophen (III) durch vorsichtige Behandlung mit Chlor gewonnen. Lässt man aber bei 50–60° Chlor auf Selenophen ohne Lösungsmittel einwirken, treten keine gelben Krystalle auf, sondern Monochlor- (II), Dichlor-selenophen (III) und Dichlorselenophentetrachlorid (X) sind dargestellt. Die Bildung von einem solchen Dihalogenselenophentetrachlorid wurde beim Behandeln des 2, 5-Dibromselenophen (III) mit Chlor bestätigt und dabei erhielten wir das dem

(4) *Chem. Zentr.*, **100** (1929), I, 1454; *Rend. accad. sci. (Napoli)*, Serie 3a, **33** (1927), 236.

(5) Die Konstanten des Selenophens von Foa sind von Richter-Anschütz, „Chemie der Kohlenstoffverbindungen“ (12 Auflage, 1931, Bd. III) angenommen worden.

Dichlorselenophentetrachlorid (X) ähnliche 2, 5-Dibromselenophen-2, 3, 4, 5-tetrachlorid (XIV).

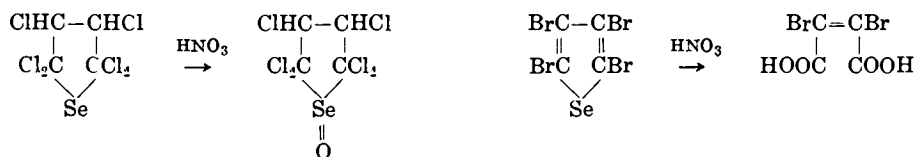
Die Einwirkung von Brom auf Selenophen wurde wie beim Chlor untersucht und gewannen wir dabei Substitutions- wie auch Additions-produkte. Unter diesen



Selenophenderivaten sind 2,3,5-Tribrom- (IV), Tetrabromselenophen (V), und 2,2,5,5-Tetrabromtetrahydroselenophen-1,1-dibromid (IX), welche beim Chlor nicht erhalten wurden. Beim Behandeln des Selenophens mit überschüssigem Brom bei tiefer Temperatur konnten wir Selenophen-2,3,4,5-tetrabromid und Hexabromverbindung, welche beim Chlor erhalten wurden, nicht gewinnen. Das oben beschriebene Dibromid (IX), färbt sich gelblich, wird mit Wasser, besonders mit wässrigem Alkali zersetzt, indem die Bromatome am Selen sich spalten, wobei das farblose 2,2,5,5-Tetrabromtetrahydroselenophen (VIII) gebildet wurde. Unter den mit Wasser zersetzten Produkten konnten wir auch ein Selenoxyd $\text{C}_4\text{H}_4\text{Br}_4\text{SeO}$ (XI) isolieren, das durch Oxydation des Tetrabromtetrahydroselenophen (VIII) mit rauchender Salpetersäure gewonnen wurde. Neuerdings haben Morgan und Burstall⁽⁶⁾ von einem mit dem oben beschriebenen Selenoxyd (XI) nahe verwandten Tetrahydroselenophen-1,1-dihydroxyd (XIII) Mitteilung gemacht. Diese Verfasser haben das interessante Dihydroxyd durch Behandlung des Tetrahydroselenophen-1,1-dibromids mit Silberoxyd dargestellt. Es scheint uns nicht ohne Interesse, dass das Dihydroxyd des halogenierten Tetrahydroselenophens unbeständig ist und Wasser abspaltet. Wir haben noch einen Beweis für die Bildung eines solchen Selenoxyd gefunden. Beim Kochen des Selenoxyds mit Cyclohexanol entsteht nämlich das Tetrabromtetrahydroselenophen (VIII). Das letztere wurde durch Anlagerung des Broms an Selenatom ins Dibromid (IX) eingeführt, welches beim Kochen mit Toluol umkehrbar ist.

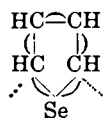
Was die Orientierungen der Halogene in den oben beschriebenen Selenophenderivaten betrifft, so können wir schliessen, dass, wie beim Thiophen oder Furan, α -ständige Wasserstoffatome leichter als β -ständige angegriffen werden. Zum Zweck des direkten Beweises für die Orientierungen der Halogene oxydierten wir natürlich die oben erhaltenen Derivate mit rauchender Salpetersäure. Dabei fanden wir, dass die Tetrahydroselenophenringe ausserordentlich widerstandsfähig gegen das Oxydationsmittel sind und Selenoxyden als Oxydationsprodukt liefern. Die halogensubstituierten Selenophenringe sind im Gegenteil gegen Salpetersäure unbeständig und geben halogenierte Maleinsäure. Zum Beispiel:

(6) *J. Chem. Soc.*, 1929, 1096.



Vor kurzem haben Gilman und Wright⁽⁷⁾ berichtet, dass das Furan ein dynamisches Gleichgewicht von mehreren Strukturformeln zu sein scheint. Hinsberg⁽⁸⁾ hat über die Thiophenformel eine aufgestellt, die freie Valenzkräfte am Schwefel annimmt. Danach stellte Steinkopf⁽⁹⁾, der sich eingehend mit der Thiophengruppe beschäftigt hat, durch Anwendung der Partialvalenztheorie eine vortreffliche Thiophenformel auf. Wir können infolgedessen die Steinkopfsche Formel ohne weiteres auf das Selenophen anwenden, womit man die Einwirkungen der Halogene auf das Selenophen genügend erklären

kann. Der Grund des ungesättigten Charakters des Selenophens beruht wahrscheinlich darauf, dass die inaktive Doppelbindung zwischen C und Se offenbar einen geringeren Grad Festigkeit besitzt als die zwischen C und C, und dass, infolge der kleineren Partialvalenzen am Se diese nicht genügen, die der benachbarten C-atome völlig abzusättigen, so dass an letzteren geringe Affinitätsbeträge übrig bleiben und sich das Bild der nebenstehenden Formel ergibt.



Bemerkenswert ist, dass Selenophen sich viel weniger aromatisch als Thiophen verhält, indem das erstere bei Einwirkung von Halogenen die Additionsprodukte leicht ergibt. Diese verlieren freiwillig oder leicht durch die thermische Behandlung Halogenwasserstoffe und so entstehen die Substitutionsprodukte. Bei den Olefinen aber bleiben die Reaktionen meist bei der ersten Phase der Addition stehen. Was die Mechanismen der Substitution von Thiophenen oder Benzolen betrifft, so könnten sie wie beim Selenophen erklärt werden, die Anlagerung an die Doppelbindungen tritt nämlich als primärer Vorgang auf und es entstehen durch nachfolgende Abspaltung substituierte Substanzen. Diesen Schluss haben schon Steinkopf⁽⁹⁾, Wieland und Bettag⁽¹⁰⁾ aus ihren Beobachtungen gezogen. Sie scheinen sie aber noch nicht an Thiophenen oder an Benzolen experimentell nachgewiesen zu haben. Doch scheint sich die Reihenfolge: Olefine, Selenophene, Thiophene, Benzole, und Furane zu ergeben.

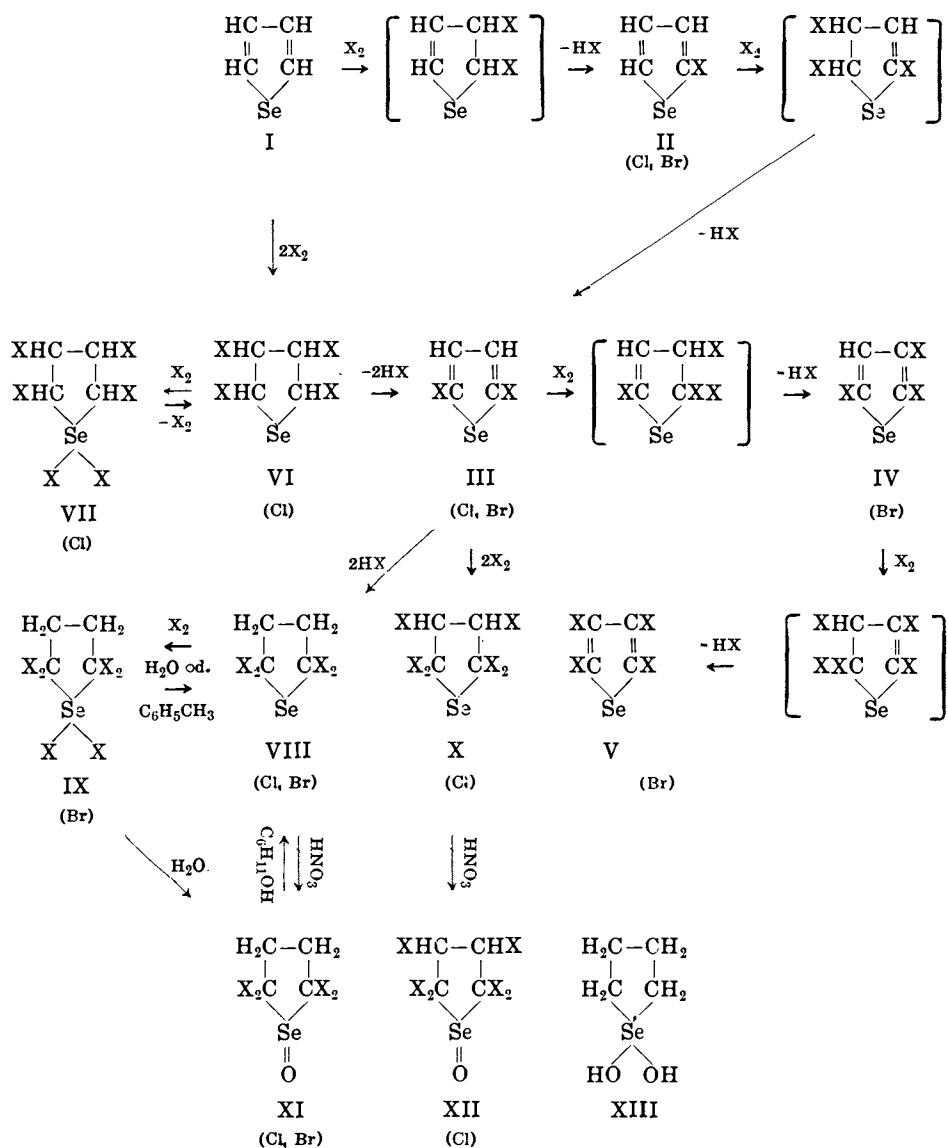
(7) *Chem. Rev.*, **11** (1932), 323.

(8) *J. prakt. Chem.*, (2), **93** (1916), 302.

(9) *Ann.*, **430** (1923), 94.

(10) *Ber.*, **55** (1922), 2246.

Die folgende Übersicht erklärt wohl die Einwirkungsmechanismen der Halogene auf Selenophen.



Beschreibung der Versuche.

Zur Darstellung des Selenophens. Im wesentlichen wurde nach den Angaben von Briscoe und seinen Mitarbeitern⁽³⁾ gearbeitet. Gereinigtes Acetylen liess man auf 20 g. Selen bei 350–370° einwirken, welches sich in einem Porzellanschiffe innerhalb eines Porzellanrohres befand. Nach der Reaktion war eine schwarze, teerartige Substanz im Schiffe geblieben. Dieser Rückstand, wie Briscoe und seine Mitarbeiter schon bemerkten, wirkt als Katalysator und zwar fanden wir, dass die Ausbeute von Selenophen durch Mischung des Selen mit dem Katalysator ziemlich zunimmt. Ferner hängt die Ausbeute von der Geschwindigkeit des Gases ab; deshalb muss man die Reaktion in ungefähr 24 Stunden zu Ende kommen lassen. Bei der Ausführung kann man die gleiche Menge dunkelbraunes Öls (Sp. Gew. = 1.47) mit derselben des angewandten Selen erhalten. Man fraktioniert das rohe Öl mittelst eines Ladenburgschen Kölbchens zweimal, wobei der Hauptanteil bei 110° überging und aus 192 g. rohem Öl 110 g. reines Selenophen erhalten wurden. Die Ausbeute des Selenophens beträgt 57% der rohen Flüssigkeit und 35% des Selen. d_4^{150} 1.5301; n_D^{150} 1.568. Gef.: C, 36.33; H, 3.14; Se, 60.01. Ber. für C_4H_4Se : C, 36.60; H, 3.08; Se, 60.36%.

Selenophen ist beständig gegen konzentrierte Salzsäure wie auch gegen Alkalien, reagiert aber auf konzentrierte Schwefelsäure sofort, wobei sich ein dunkelgrüner Niederschlag bildet, ebenso heftig ist die Reaktion auf konz. Salpetersäure.

I. Einwirkung von Chlor auf Selenophen.

2-Chlorselenophen (II). In 4 g. erwärmtes Selenophen werden 2 g. Chlor langsam bei 50–60° geleitet, wobei sich sehr heftig Chlorwasserstoff entwickelt und die Lösung dunkelbraun gefärbt ist. Nach 2 stündigem Stehenlassen bei Zimmertemperatur wird das Reaktionsgemisch mit Äther verdünnt, mit verdünntem Natriumcarbonat gewaschen und zuletzt über Glaubersalz getrocknet. Das Lösungsmittel wurde dann eingedampft und der Vakuumdestillation unterworfen. Sdp. 42°/12.5 mm. Ausbeute 3.5 g., d_4^{140} 1.6621; n_D^{20} 1.594. Gef.: C, 28.68; H, 2.14; Cl, 20.94; Se, 47.46. Ber. für C_4H_3ClSe : C, 23.97; H, 1.83; Cl, 21.36; Se, 47.71%.

Bei der Reaktion erhält man höher siedendes 2, 5 Dichlorselenophen als Nebenprodukt. Das Chlorselenophen bildet eine farblose Flüssigkeit, hat dem Chlorbenzol ähnlichen Geruch und zeigt deutlich Indopheninreaktion.

2,5-Dichlorselenophen (III). Zu 4 g. Selenophen werden 4 g. Chlor langsam bei 50–60° eingeleitet. Nach 2 stündigem Stehenlassen bei Zimmertemperatur wird das hierbei erhaltene dunkelbraune Öl mit Äther verdünnt, mit verdünntem Natriumcarbonat gewaschen und dann über Chlorcalcium getrocknet. Nach Verdunsten des Äthers wurde im Vakuum destilliert, wobei vorläufig geht Chlorselenophen über und dann wird das 2,5-Dichlorselenophen als der Hauptanteil erhalten. Sdp. 67°/12 mm. oder 71°/18 mm. Ausbeute 3.0 g. d_4^{140} 1.8372; n_D^{140} 1.606. Gef.: C, 23.83; H, 1.33; Cl, 35.48. Ber. für $C_4H_2Cl_2Se$: C, 23.95; H, 1.06; Cl, 35.38%.

Das Dichlorselenophen ist fast farblos und stark lichtbrechend, hat einen charakteristischen Geruch und zeigt Indopheninreaktion beim Erwärmen. Die bei der Fraktionierung im Kolben zurückbleibenden Anteile scheiden beim Erkalten im Eisschranke eine kleine Menge von farblosen Krystallen aus. Nach Umkrystallisation wurde sie als 2, 5-Dichlorselenophen-2, 3, 4, 5-tetrachlorid (X) identifiziert.

2, 5-Dichlorselenophen-2, 3, 4, 5-tetrachlorid (X). In ein Reagenzglas bringt man 3 g. Selenophen, erwärmt es auf 60° und leitet dann überschüssiges Chlor langsam ein, wobei sich eine etwas zähige Flüssigkeit bildet. Nach 2 stündigem Stehenlassen bei Raumtemperatur wurde sie wie oben beschrieben aufgearbeitet. Das braungefärbte, dickflüssige Öl wird im Vakuum destilliert, wobei sich eine kleine Menge noch flüssiger Anteile abdestilliert und der Rückstand beim Erkalten krystallin erstarrt. Ausbeute 3.0 g. Dieser wird aus Alkohol dreimal umkrystallisiert, wobei sich die Substanz in Rosetten ausscheidet. Schmp. 55° . Gef.: C, 14.44, 14.13; H, 0.88, 0.85; Cl, 62.00. Ber. für $C_4H_2Cl_6Se$: C, 14.04; H, 0.59; Cl, 62.21%.

Die Substanz ist leicht löslich in Äther, Benzol, Chloroform, Petroläther und Schwefelkohlenstoff, aber unlöslich in Wasser.

Oxydation von Dichlorselenophen-2, 3, 4, 5-tetrachlorid (X) mit rauchender Salpetersäure. In auf -21° abgekühlte, rauchende Salpetersäure versetzt man 0.1 g. Dichlorselenophen-2, 3, 4, 5-tetrachlorid und lässt die Temperatur des Reaktionsgemisches allmählich auf $+15^{\circ}$ steigen. Verdünnt man die dabei gebildete, klare Lösung sofort mit ca. 50 c.c. kaltem Wasser, so scheidet sich ein farbloser krystallinischer Körper aus. Man saugt diesen ab und wäscht ihn mit Alkohol und Äther. Ausbeute 0.1 g. Umkrystallisiert aus Ligroin. Feine Nadeln. Schmp. $172-172.5^{\circ}$ unter heftigem Aufschäumen. Gef.: Cl, 59.33. Ber. für $C_4H_2Cl_6SeO$: Cl, 59.43%.

Das Oxyd ist löslich in Alkohol, Äther, Ligroin und Benzol, aber schwerlöslich in Petroäther.

Selenophen-2, 3, 4, 5-tetrachlorid (VI). Man löst 3 g. Selenophen in 12 c.c. Schwefelkohlenstoff und leitet dazu 4 g. Chlor langsam bei -15° ein. Es entstehen sofort gelbe, tafelförmige Krystalle, während sich der Chlorwasserstoff noch nicht entwickelt. Es ist deutlich, dass diese Krystalle, ein Chloranlagerungsprodukt, Selenophen-2, 3, 4, 5-tetrachlorid-1, 1-dichlorid (VII) sind. Dieses Chlorderivat ist aber so unbeständig, dass sich beim Absaugen explosivartig Chlor entwickelt und sich in Selenophen-2, 3, 4, 5-tetrachlorid (VI) verändert. Beim Stehenlassen des Reaktionsgemisches bei -15° entfärbt es sich, indem die ausgeschiedenen gelben Krystalle Chloratome am Selen abspalten. Das dabei entstandene, farblose Tetrachlorid wird schnell abgesaugt und mit Schwefelkohlenstoff gründlich gewaschen. Ausbeute 2 g. Es schmilzt bei 97° unter Aufschäumen und Bräunung. Es ist in gewöhnlichen Lösungsmitteln unlöslich. Das Tetrachlorid ist ohne Zersetzung nicht umkrystallisierbar. Gef.: C, 17.66, 17.77; H, 1.64, 1.54; Cl, 52.27. Ber. für $C_4H_4Cl_4Se$: C, 17.53; H, 1.48; Cl, 52.00%.

Briscoe und Peel⁽¹¹⁾ haben auch eine Tetrachlorverbindung nach denselben Bedingungen erhalten und sie nahmen an, dass diese Chlorverbindung statt des Anlagerungsprodukts ein Substitutionsprodukt, nämlich Tetrachlorselenophen, wäre.

Ferner untersuchten wir sein Verhalten gegen rauchende Salpetersäure bei tiefer Temperatur und erhielten Oxalsäure als Oxydationsprodukt.

Thermische Zersetzung von Selenophentetrachlorid (VI). Man lässt 4 g. Selenophentetrachlorid bei 95° im Paraffinbade allmählich sich zersetzen, wobei sich heftig Chlorwasserstoff entwickelt. Nach Vollendung der Zersetzung verdünnt man die dabei gebildete, dunkelbraune Flüssigkeit mit Äther, behandelt sie mit Natriumcarbonatlösung und arbeitet sie auf. Das entstandene Öl wurde im Vakuum fraktioniert. Dichlorselenophen (III) destilliert sich bei 70.8° unter 15 mm. Ausbeute 1 g. In jeder Hinsicht ist diese

(11) *J. Chem. Soc.*, 1928, 1741.

farblose, stark lichtbrechende Flüssigkeit identisch mit dem oben beschriebenen 2,5-Dichlorselenophen (III). n_D^{15} 1.606. Gef.: Cl, 35.65. Ber. für $C_4H_2Cl_2Se$: Cl, 35.38%.

Der bei dieser Fraktionierung gebliebene Rückstand scheidet im Eisschranke prachtvolle, farblose Krystalle aus, welche abgesaugt und aus Alkohol umkrystallisiert werden. Schmp. 96–98°. Gef.: C, 17.34, 17.16; H, 1.83, 1.83; Cl, 52.17. Ber. für $C_4H_4Cl_4Se$: C, 17.58; H, 1.48; Cl, 52.00%.

Die Tetrachlorverbindung, 2,2,5,5-Tetrachlortetrahydroselenophen (VIII), ist leicht löslich in Lösungsmitteln und weitaus beständiger als das andere, welches sich bei 97° zersetzt.

Diese Tetrachlorverbindung wurde mit rauchender Salpetersäure oxydiert und ein Selenoxyd erhalten. Man versetzt 0.15 g. 2,2,5,5-Tetrachlortetrahydroselenophen in –18° abgekühltem 2 c.c. rauch. Salpetersäure. Nach einigen Minuten verdünnt man diese klare Lösung mit 50 c.c. kaltem Wasser. Es scheidet sich nach einiger Zeit ein farbloser, krystallinischer Körper aus, welcher in organischen Lösungsmitteln schwer löslich ist. Ausbeute 0.05 g. Schmp. 149–150° unter heftigem Aufschäumen. Gef.: Cl, 49.33. Ber. für $C_4H_4Cl_4SeO$: Cl, 49.11%.

II. Einwirkung von Brom auf Selenophen.

2, 2, 5, 5 - Tetrabromtetrahydroselenophen - 1, 1 - dibromid (IX). Man verdünnt 2 g. Selenophen mit 5 c.c. Schwefelkohlenstoff und lässt dann unter Schütteln im Kältegemisch bei ca. –15° aus dem Tropftrichter nach und nach eine 20%-ige Lösung von Brom darein eintropfen. Unter gelinder Bromwasserstoffentwicklung scheidet es bei der Reaktion gelbe Krystalle aus. Ist die ganze Bromlösung versetzt, so werden die gelben Krystalle sofort abgezogen und mit Schwefelkohlenstoff genügend gewaschen. Ausbeute 1 g. An der Luft zersetzt sich dieses Präparat allmählich und ist unbeständig gegen Wasser, besonders gegen wässrige Säuren und Alkalien, die dasselbe zu dem unten erwähnten, farblosen Körper sich entfärben lassen. Nach der Umkrystallisierung aus wasserfreiem Benzol schmilzt es bei 152° unter Aufschäumen und Bräunung. Gef.: C, 7.98, 8.03, 8.05; H, 1.03, 0.99, 1.01; Br, 78.10, 78.02, 78.20; Se, 12.54, 12.42, 12.48. Ber. für $C_4H_4Br_6Se$: C, 7.86; H, 0.66; Br, 78.26; Se, 12.97%.

Die Hexabromverbindung ist in gewöhnlichen Lösungsmitteln schwer löslich und zeigt keine Indopheninreaktion in der Kälte, nur eine undeutliche beim Erhitzen.

Die Brom-ionen und -moleküle, welche aus Tetrabromtetrahydroselenophen-1,1-dibromid (IX) beim Behandeln mit Wasser abgespalten wurden, wurden auf folgende Weise titriert. Das pulverisierte Dibromid 0.3907 g. wurde mit ca. 5 c.c. Wasser versetzt und mit Äther umgeschüttelt. Die Ätherschicht wurde dreimal mit Wasser gewaschen, das gesamte Wasser mit 1 g. Kaliumjodid, das in einer kleinen Menge von Wasser gelöst ist, versetzt, wobei die Jodmoleküle, welche den freien Brommolekülen entsprechen, sich befreien. Sie wurden mit Natriumthiosulfatlösung mittels Indikators von einigen Tröpfchen der Stärkelösung titriert (a). Dann wurde das Reaktionsgemisch noch einmal mit 1 g. Kaliumjodat, das in einer kleinen Menge von Wasser gelöst ist, versetzt und bis zur Entfärbung mit Natriumthiosulfat titriert (b).

Das gesamte Natriumthiosulfat (b) zeigt das gesamte Brom, welches aus dem Dibromid sich spaltet und die Differenz (b–a) entspricht den Bromionen, welche durch Hydrolyse als Bromwasserstoff aus dem Dibromid sich abspalten. Natriumthiosulfatlösung: 0.1004 N. Brom als Brommoleküle = a = 0.82 c.c. = 0.0104 g. Jod = 0.0066 g. Brom = 1.68% des Di-

bromids. $b = 12.55 \text{ c.c.}$ Brom als Bromionen $= b - a = 1.73 \text{ c.c.} = 0.1494 \text{ g.}$ Jod $= 0.0941 \text{ g.}$ Brom $= 24.09\%$ des Dibromids. Gef.: Gesamtes Br, 25.77% des Dibromids. Ber. für $\text{Br}_2/\text{C}_4\text{H}_4\text{Br}_6\text{Se}$: Br, 26.17%.

2, 2, 5, 5-Tetrabromtetrahydroselenophen (VIII). Versetzt man 3 g. gelbe Hexabromverbindung (IX) mit überschüssigem kaltem Wasser und schüttelt es, so entfärbt sich dies allmählich. Nach vollständiger Entfärbung wird das Reaktionsgemisch mit Äther wieder umgeschüttelt, wobei ein Anteil des farblosen Körpers in die Oberschicht geht, während der Rest noch unlöslich vorhanden ist. Man trennt die Ätherschicht und trocknet sie über Chlorcalcium. Verdampft man das Lösungsmittel im Vakuum bei Zimmertemperatur, bleibt ein farbloses, krystallinisches Produkt zurück, welches in Lösungsmitteln leicht löslich ist. Ausbeute 0.2 g. Aus Alkohol umkrystallisiert. Tafelförmige Krystalle. Schmp. 97° (ohne Zersetzung). Gef.: C, 10.59, 10.66; H, 1.15, 1.08; Br, 70.83, 70.79; Se, 17.43. Ber. für $\text{C}_4\text{H}_4\text{Br}_4\text{Se}$: C, 10.64; H, 0.89; Br, 70.85; Se, 17.56%.

Bei langer Aufbewahrung zersetzt sich dies allmählich von selbst unter Färbung.

Man kann das Tetrabromtetrahydroselenophen-1,1-dibromid (IX) aus Tetrabromtetrahydroselenophen (VIII) auf folgende Weise durch Bromanlagerung wiedererzeugen. Man löst 0.1 g. Tetrabromtetrahydroselenophen in 2 c.c. Schwefelkohlenstoff, versetzt es mit 0.5 c.c. Brom und bewahrt die klare Lösung 2 Tage lang bei Raumtemperatur unter Ausschluss von Feuchtigkeit auf. An der Wand des Gefäßes scheiden sich prachtvolle gelbe, tafelförmige Krystalle ab, welche abgesaugt und mit Schwefelkohlenstoff gewaschen werden. Umkrystallisiert aus wasserfreiem Benzol; winzige gelbe Krystalle. Schmp. 152° unter Aufschäumen und Bräunung. Gef.: Br, 78.15; 78.27. Ber. für $\text{C}_4\text{H}_4\text{Br}_6\text{Se}$: Br, 78.26%.

2,2,5,5-Tetrabromtetrahydroselenophen-1-oxyd (XI). Der bei der Behandlung des Hexabromderivats (IX) mit Wasser entstandene, ätherunlösliche, farblose Anteil wurde abgesaugt und mit Alkohol und Äther gewaschen. Er sintert oberhalb 120° und zersetzt sich bei 123° . Unlöslich in Alkohol, Aceton, Essigester, Benzol, Chloroform, Petroläther, Schwefelkohlenstoff und Kohlenstofftetrachlorid und schwer löslich in Äther, Toluol und Eisessig. Wir probierten die Umkrystallisation aus Toluol erfolglos, weil es zersetzt. Zur Reindarstellung sättigten wir 85 c.c. Eisessig mit 0.1 g. dieser Substanz bei ca. 60° und nach der Abkühlung versetzten mit 30 c.c. Äther. Nach einiger Zeit im Eisschranke scheiden es sich allmählich winzige, farblose Kryställchen aus. Schmp. $128.5\text{--}130^\circ$ unter Aufschäumung. Gef.: C, 10.51, 10.53; H, 1.27, 1.23; Br, 68.69. Ber. für $\text{C}_4\text{H}_4\text{Br}_4\text{SeO}$: C, 10.29; H, 0.86; Br, 68.47%.

Dieser Körper ist sehr beständig gegen chemische Reagenzien, sogar gegen erwärmte rauchende Salpetersäure. Dieses Selenoxyd wurde auch durch Oxydation des oben beschriebenen Tetrabromtetrahydroselenophens (VIII) mit rauchender Salpetersäure erhalten.

Oxydation von Tetrabromtetrahydroselenophen zu seinem Oxyd. In der auf -17° abgekühlten 1 c.c. rauchenden Salpetersäure wird 0.1 g. Tetrabromtetrahydroselenophen gelöst. Man lässt die Temperatur des Reaktionsgemisches auf Zimmertemperatur steigen und verdünnt das Gemisch sofort mit 50 c.c. abgekühltem Wasser, wobei sich ein farbloser krystallinischer Körper ausscheidet. Dies wurde abgesaugt und mit Alkohol und Äther gewaschen. Das noch nicht umkrystallisierte Präparat zersetzt sich bei 124° unter Aufschäumen. Ausbeute 0.09 g. Umkrystallisiert aus Eisessig und Äther wie oben. Schmp. 129° unter Aufschäumen. Mischschmelzpunkt mit dem Präparat, das aus Tetrabrom-

tetrahydroselenophen-1,1-dibromid abgeleitet wurde, zeigt keine Depression. Gef.: C, 10.46; H, 1.05; Br, 68.08. Ber. für $C_4H_4Br_2SeO$: C, 10.29; H, 0.86; Br, 68.47%.

Reduktion von Tetrabromtetrahydroselenophen-1-oxyd (XI) zum Tetrabromtetrahydroselenophen (VIII). Zu 2 c.c. Cyclohexanol wird 0.1 g. Selenoxyd (XI) versetzt, durch Erhitzen gelöst und die Lösung weiter noch einige Minuten erhitzt. Man bringt sie in einer Krystallisierschale und lässt sie im Vakuumexsiccator über Paraffin einige Tage lang stehen. Es scheiden sich sehr langsam prächtige, tafelförmige Krystalle aus, die aus Alkohol umkrystallisiert sind. Schmp. 96–97.5°. Mischschmelzpunkt mit authentischem Präparat zeigt keine Depression.

Behandlung von Tetrabromtetrahydroselenophen-1,1-dibromid (IX) mit kochendem Toluol. In 2 c.c. Toluol wird 0.1 g. Dibromid durch Erwärmen allmählich gelöst. In der ersten Zeit ist die Lösung braun gefärbt, aber in der Nähe des Siedepunktes entwickeln sich tränenenerregendes, bromiertes Toluol und Bromwasserstoff, während die Lösung sich entfärbt. Nach Vollendung der Bromwasserstoffentwicklung wird sie im Vakuumexsiccator über Paraffin und Alkali eingedunstet. Es scheidet sich 0.08 g. Tetrabromtetrahydroselenophen ab, welches aus Alkohol umkrystallisiert. Schmp. 95–96°. Mischschmelzpunkt mit Tetrabromtetrahydroselenophen zeigt keine Depression.

2-Bromselenophen (II). Zu wassergekühlter 10%-iger Schwefelkohlenstofflösung von 4 g. Selenophen tropft man eine 10%-ige Schwefelkohlenstofflösung von 4.8 g. Brom unter Umschütteln ein. Nach 2 stündigem Stehenlassen wird das Reaktionsgemisch mit verdünntem Natriumcarbonat gewaschen und über Chlorcalcium getrocknet. Nach Verdunsten des Lösungsmittels erhält man ein braunes Öl. Ausbeute 7.5 g. Wir versuchten anfangs sie unter atmosphärischem Druck zu destillieren, aber dabei fand die Zersetzung statt. Bei der Vakuumdestillation ging ein fast farbloses Öl über. Sdp. 59°/13 mm. Ausbeute 3.0 g. d_4^{20} 2.1003; n_D^{20} 1.635. Gef.: C, 23.03, 22.77; H, 1.36, 1.72; Br, 37.22, 37.28; Se, 37.46. Ber. für C_4H_3BrSe : C, 22.85; H, 1.44; Br, 38.03; Se, 37.69%.

Das Bromselenophen mischt sich in jedem Verhältnisse mit gewöhnlichen Lösungsmitteln, hat einen dem Brombenzol ähnlichen Geruch und zeigt deutlich Indopheninreaktion.

2, 5-Dibromselenophen (III) und 2, 3, 5-Tribromselenophen (IV). Zu 4 g. Selenophen in 10 c.c. Schwefelkohlenstoff wurden aus einem Tropftrichter 20 g. Brom in 10 c.c. Schwefelkohlenstoff unter Abkühlung und fleissigem Umrühren gebracht. Man lässt das Gemisch über Nacht bei Zimmertemperatur stehen, und bearbeitet es wie in den anderen Fällen. Das dunkelbraune, dickflüssige Öl wird im Vakuum destilliert. Nachdem das oben erwähnte Bromselenophen ca. 2.7 g. ausdestilliert, wird an zweiter Stelle 2, 5-Dibromselenophen erhalten. Sdp. 42°/0.02 mm. Ausbeute 4.1 g. d_4^{20} 2.5005; n_D^{20} 1.667. Gef.: C, 16.15, 16.62; H, 0.88, 1.24; Br, 55.09. Ber. für $C_4H_2Br_2Se$: C, 16.61; H, 0.70; Br, 55.31%.

Destilliert man die höher siedenden Anteile weiter, so erhält man noch ein Öl, das unter 0.12 mm. bei 94° kocht, und bei Raumtemperatur krystallinisch erstarrt. Ausbeute 2.9 g. Aus Alkohol kamen farblose Nadeln. Schmp. 38°. Gef.: C, 13.46, 13.31; H, 0.63, 0.75; Br, 65.04. Ber. für C_4HBr_3Se : C, 13.04; H, 0.27; Br, 65.15%.

Das Dibromselenophen ist fast farblos und stark lichtbrechend, mischt sich in jedem Verhältnisse mit organischen Lösungsmitteln und zeigt beim Erhitzen Indopheninreaktion. Auch das Tribromselenophen ist leicht löslich in Lösungsmitteln, zeigt aber beim Erhitzen nur undeutlich Indopheninreaktion.

Tetrabromselenophen (V). Selenophen ist ohne Lösungsmittel mit überschüssigem Brom unter Umschütteln in kaltem Wasser nach und nach versetzt, wobei sich sehr heftig Bromwasserstoff entwickelt. Lässt man das Reaktionsgemisch über Nacht stehen, so scheidet es farblose Nadeln aus. Ausbeute ist fast quantitativ. Schmp. 102° . In jeder Hinsicht stimmte unser Präparat mit der Beschreibung von Briscoe und Peel⁽¹¹⁾ überein. Gef.: C, 10.84, 10.63; H, 0.16; 0.17; Br, 71.48; Se, 17.68. Ber. für C_4Br_4Se : C, 10.74; H, 0.00; Br, 71.49; Se, 17.72%.

Oxydation von Tetrabromselenophen mit rauchender Salpetersäure. Trägt man 1 g. Tetrabromselenophen in 7 c.c. auf -18° abgekühlter, rauchender Salpetersäure (1.52) ein, so sinkt das Pulver grösstenteils unverändert zu Boden. Lässt man die Temperatur des Reaktionsgemisches allmählich steigen, so findet eine vollständige Lösung unter Rotfärbung und Entwicklung von Bromdämpfen statt. Giesst man die Flüssigkeit langsam in abgekühltes Wasser, so bildet sich anfangs eine krystallinische Ausscheidung, welche jedoch alsbald verschwindet. Nach einigen Tagen äthert man aus und erhält Dibrommaleinsäure. Ausbeute 0.53 g. Schmp. $120-123^{\circ}$. Die Säure wurde durch Behandlung mit Acetylchlorid und Schwefelsäure in Anhydrid⁽¹²⁾, Schmp. 116° , abgeleitet und identifiziert. Gef.: Br, 62.09. Ber. für $C_4Br_2O_3$: Br, 62.48%.

2, 5-Dibromselenophen-2, 3, 4, 5-tetrachlorid (XIV) Da Weitz⁽¹³⁾ und Rosenberg⁽¹⁴⁾ 2,5-Dibromthiophen mit überschüssigem Chlor behandelt und Tetrachlorthiophen erlangt hat, probierten wir das Verhalten des Dibromselenophens gegen überschüssiges Chlor und fanden, dass in unserem Falle nur Anlagerung statt Austausch stattfand. Im gleichen Volumen Schwefelkohlenstoff sind 2 g. Dibromselenophen gelöst und bei Raumtemperatur wird ein Überschuss von Chlor langsam hineingeleitet. Nachdem eine kleine Menge des dabei ausgeschiedenen, gelben, krystallinischen Nebenproduktes abfiltriert ist, wird das Filtrat mit Äther verdünnt und mit Natriumcarbonat behandelt. Nach der Aufarbeitung erhält man ein dickflüssiges braunes Öl. Ausbeute 2 g. Bei der Vakuumdestillation ging nur eine kleine Menge von Öl zwischen $100-105^{\circ}$ über, obwohl die Ölbadtemperatur 170° erreichte. Lässt man den Rückstand stehen, so scheiden sich nadelartige, farblose Krystalle aus, welche abgesaugt werden. Aus Alkohol umkrystallisiert, farblose Nadeln. Schmp. $70-72^{\circ}$. Gef.: C, 11.50, 11.36; H, 0.64, 0.62; Cl, 32.40, 33.14; Br, 37.40, 35.81; Se, 17.96. Ber. für $C_4H_2Cl_4Br_2Se$: C, 11.40; H, 0.47; Cl, 32.90; Br, 37.08; Se, 18.37%.

Diese Substanz ist leicht löslich in Lösungsmitteln, dem Dichlorselenophentetrachlorid (X) in mancher Hinsicht ähnlich und zeigt sogar beim Erhitzen keine Indopheninreaktion.

Für Unterstützung der Kaiserlichen Akademie sind wir ihr zu Dank verpflichtet.

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(12) O. Diels und M. Reinbeck, *Ber.*, **43** (1910), 1274.

(13) *Ber.*, **17** (1884), 795.

(14) *Ibid.*, **19** (1886), 650.

ON THE ALKALOIDS OF WHITE HELLEBORE. II.
ISOLATION OF ALKALOIDS FROM THE
SO-CALLED RESINOUS MATTERS.

By Kojiro SAITO and Harusada SUGINOME.

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In the previous communication⁽¹⁾, a method of isolating alkaloids from the roots of white hellebore was described, but no account was given of the resinous matters soluble in alcohol but insoluble in water nor in dilute acetic acid. The former authors also laid aside, and did not investigate, this part of alkaloids, considering it as resin⁽²⁾, as resinous substances⁽³⁾ or as "unlösliche Bestandteile"⁽⁴⁾. Our subsequent investigation of the so-called resinous matters has shown the presence of another series of alkaloids.

The resinous matters were treated with dilute acetic acid to remove the soluble part, which gave alkaloids similar to those described in Part I on basifying with ammonia. This operation of extraction was very tedious, so that it was repeated until the yield of the bases amounted to 0.5% of the starting material.

The brown powder, insoluble in dilute acetic acid, was then treated with ether continuously and some oily matters as well as phenolic substances were removed. The latter were proved to consist chiefly of a dihydric phenol. Unfruitful attempts were made by using various solvents to obtain a crystalline substance from the powder. On treatment with dilute alkali the brown powder was decomposed into bases freely soluble in dilute acetic acid, and acidic substances with angelic acid and an acid melting at 102°. These acids, however, were rather small in amount and the acidic substances were found to be phenolic acids sparingly soluble in ether. The crude bases thus obtained could be crystallised from dilute alcohol but isolation of the components in pure condition was unsuccessful. Then they were divided into seven fractions by fractional precipitation, as done in Part I. On neutralizing each fraction with hydrochloric acid in alcohol, the first three gave jervine hydrochloride in crystalline form. From the fourth fraction some more hydrochloride could be obtained.

(1) This Bulletin, **9** (1934), 15.

(2) Wright and Luff, *J. Chem. Soc.*, **35** (1879), 406.

(3) C. Pehkschen, *J. Chem. Soc.*, **90** (1891), 88; *J. Pharm.*, (5), **22**, 265; *Pharm. Zeit. Russ.*, **29**, 339.

(4) Salzberger, *Arch. Pharm.*, **228** (1890), 462.

The so-called resinous matters in the roots of *Veratrum grandiflorum* Loes. fil. may, therefore, be considered as a mixture of salt-like substances, consisting of alkaloids, acids, and free phenolic substances. The chief constituents of the salt-like substances are probably molecular compounds of alkaloids and phenolic compounds, while the acids, soluble in water, are combined with the alkaloids as esters.

Experiments concerning the constitution of the phenolic compounds and the isolation of other alkaloids in crystalline state are in progress.

Experimental.

Treatment of the so-called resinous matters with dilute acetic acid. After the extraction⁽⁵⁾ of the alkaloids from the powdered roots (12 kg.) with alcohol (95%) the solvent was distilled off under reduced pressure; a semi-solid residue was obtained. On treating the latter with water and light petroleum (b.p. 40-60°) a comparatively large amount of dark resinous matters, insoluble in water, separated and were collected. They were then digested successively with dilute acetic acid and with water to remove soluble basic substances and alcohol that had been absorbed. The brown powder thus obtained was next suspended in three parts of dilute acetic acid, and the mixture was stirred all day long and filtered. On basification of the filtrate with ammonia, free alkaloids were separated, which were collected, washed, and dried. The yield was 9.1 g. The amounts of the crude alkaloids obtained in each treatment were as follows:

Number of extraction	I	II	III	IV
Basic substances in g.	2.8	2.3	2.1	1.9

As may be seen from the table extraction proceeds very slowly, so that it was given up when the yield of the bases reached 0.5% of the material. At the later stage of the treatment the insoluble powder appeared to be partly decomposed by the dilute acetic acid. The yield of the insoluble powder was 302 g. or 2.5% of the roots.

The powder is sparingly soluble in water, light petroleum, and benzene; partly soluble in carbon tetrachloride, ether, acetic ester, and acetone; freely soluble in methyl and ethyl alcohol, and glacial acetic acid. When the powder is treated with dilute alcohol, in which it is sparingly soluble, it becomes viscous and resinous in appearance but can be restored by suspension in water, the absorbed alcohol being lost.

Alkaloids extracted with dilute acetic acid. This part of the alkaloids may be considered as a mixture of the bases described as portion A in Part I and those obtained from the insoluble part through hydrolysis.

Crude bases (34 g.) were dissolved in 0.5 N acetic acid (108 c.c.), diluted with water (108 c.c.) and divided into five parts by fractional precipitation with 0.5 N ammonium hydroxide. The first fraction was small in amount and brown in colour, but the amounts

(5) Compare Part I, this Bulletin, 9 (1934), 17.

of the second and third fractions were larger. The amounts of the fourth and fifth fractions were again small. To the mother liquor of the fifth fraction an excess of ammonia was added, when some more precipitates separated and were collected as the sixth fraction. The filtrate of the sixth fraction was saturated with ammonium sulphate and was extracted with chloroform. On working up the chloroform solution the seventh fraction was obtained. Each fraction thus obtained was then dissolved in alcohol and treated with hydrochloric acid in the same solvent. On being allowed to stand for a while, a crystalline hydrochloride, melting at 308° with decomposition, separated from the first, second, third, and fourth fractions. This was collected and dried; the yield was 5.6 g. or 16% of the crude bases. The salt (5.6 g.) was suspended in hot alcohol (90%, 62 c.c.) and was treated with sodium carbonate; on cooling the solution the freshly liberated base separated in colourless needles. It was collected and recrystallised from alcohol; it melted at $242-243^{\circ}$, and was proved to be jervine by mixed melting point with an authentic specimen. (Found: C, 75.70; H, 9.25. Calc. for $C_{26}H_{37}NO_3$: C, 75.86; H, 9.07%. $[\alpha]_D^{25} = -150^{\circ}$ in absolute alcohol.)

In the following table the amounts of each fraction as well as the yield of the salt are shown.

Number of fraction	I	II	III	IV	V	VI	VII
Precipitate in g.	0.3	14.8	5.3	0.1	0.1	0.4	1.5
Jervine hydrochloride in g.	0.1	4.2	1.3	trace	0	0	0

Treatment of the part insoluble in dilute acetic acid with ether. In order to remove fats and oils, free phenolic substances, and free alkaloids, the brown amorphous powder was treated first with dilute acetic acid and subsequently with ether for 26 days continuously. In the earlier stage of the process extraction proceeded fairly rapidly and a yellowish brown crystalline powder was obtained but its amount decreased gradually as the days passed. In the latter stage of the extraction brown viscous substances were obtained. After 10 days 0.5% of the material was extracted in 24 hours, while on the 24th day 0.1%. Total extract in 26 days was 55 g. or 18% of the material. On treatment of the extract with light petroleum (b.p. $40-60^{\circ}$) about 10 g. or 19% of fats and oils were removed, leaving a yellowish brown fine powder. The latter contained a trace of nitrogen, and was sparingly soluble in sodium bicarbonate, partly soluble in sodium carbonate, and almost perfectly soluble in caustic alkali. In water, light petroleum, chloroform, and benzene, it was difficultly soluble while freely soluble in methyl, ethyl alcohol, and acetic ester. It was crystallised from dilute alcohol in plates melting at 262° with decomposition. Its alcoholic solution gave a dark brown colouration with ferric chloride; it decolourised bromine water and potassium permanganate. On dissolving it in concentrated sulphuric acid it developed a colouration similar to the case of bromine water.

Decomposition of the part insoluble in dilute acetic acid with alkali. The amorphous brown powder (247 g.) purified as described above was treated with dilute alkali (1000 c.c.) when the solution rapidly turned dark brown in contact with the air owing to the absorption of oxygen, while the compact brown powder passed into lighter,

coarse, floating *bases*. After a while they were collected, washed, and dried in the air. The yield was 137 g. or 1.1% of the roots. The filtrate was saturated with carbon dioxide, when brown *phenolic substances* separated, which were collected, washed, and dried. On being treated with dilute sulphuric acid some more acidic substances were obtained. The yield of the phenolic and acidic substances altogether was 58 g. Lastly the filtrate was treated with ether continuously and *soluble acids* were extracted (ca. 26 g.). These phenolic and acidic substances rapidly turned dark brown in contact with the air through autoxidation either in an alkaline solution or in a solid state with a trace of alkali and moisture, but were comparatively stable if they were quite free from alkali as well as from moisture.

Phenolic substances. The brown phenolic substances contained no nitrogen and were comparatively difficultly soluble in ether; they gave off carbon dioxide on pyrogenetic treatment and appeared to be a phenolic acid.

Soluble acids. Among these acids angelic acid was detected. Another acid, melting at 102°, was very small in amount and was not further investigated.

Alkaloids. The bases obtained from the brown powder insoluble in dilute acetic acid had a characteristic odour and were partly soluble in benzene, ether, chloroform, acetic ester, and acetone, but sparingly soluble in light petroleum. In methyl and ethyl alcohol they were freely soluble.

Crude bases (88 g.) were dissolved in 0.5 N acetic acid (440 c.c.), the solution, after filtered from the insoluble matter, was diluted with water (440 c.c.), and the bases were fractionally precipitated. The results were similar to the other case of the fractional precipitation. Each fraction was treated with alcoholic hydrochloric acid, and jervine hydrochloride was isolated from the first to the fourth fraction; the yield was 32.8 g. or 37% of the crude bases, and 0.43% of the material. Taking into account the salt in Part I, the total yield of jervine hydrochloride amounted to 0.6% of the roots.

Number of fraction	I	II	III	IV	V	VI	VII
Precipitate in g.	4.0	25.9	40.0	1.4	0.6	0.7	1.3
Jervine hydrochloride in g.	1.5	12.5	18.8	trace	0	0	0

On treating the salt with sodium carbonate the free base was liberated and was crystallised from alcohol in colourless needles, melting at 242-243°, identified with jervine.

We are deeply indebted to Mr. K. Akagi, the Director of the Industrial Experiment Station at Kotoni near Sapporo, and Mr. K. Hayashi, the chief chemist of the institute, for affording us facilities for the investigation.

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ON THE ALKALOIDS OF WHITE HELLEBORE. III. EXPERIMENTS ON THE CONSTITUTION OF JERVINE.

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In Parts I⁽¹⁾ and II⁽²⁾ it has been shown that the constituent alkaloids of *Veratrum grandiflorum* Loes. fil. can be extracted in a yield of 2.6% referring to the roots and from these alkaloids jervine hydrochloride may be isolated in a pure state in a yield of 23%, or 0.6% of the material. In the present communication some experimental results concerned with the constitution of jervine are given.

Jervine reacts as a secondary base giving a *N*-methyl derivative on methylation with diazomethane or better with methyl iodide and potassium hydroxide. Treatment of the latter with an excess of methyl iodide in a sealed tube gives a crystalline methiodide, while the same derivative can be obtained directly from jervine by boiling with methyl iodide and anhydrous potassium carbonate. Further evidence of this is afforded by the formation of a nitroso-compound on treatment of the alkaloid with sodium nitrite and acetic acid.

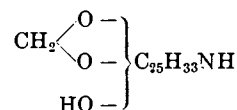
Jervine contains neither methoxyl nor carbonyl group and does not form an oxime or semicarbazone. Two oxygen atoms of the base appear to be present in the form of dioxymethylene, while the last one is in the form of an alcoholic hydroxyl group. The alkaloid dissolves in strong sulphuric acid, forming a yellow solution which becomes green on standing. It gives, however, reddish brown colouration with strong sulphuric acid together with phloroglucinol. On boiling with acetic anhydride the alkaloid yields a diacetyl derivative, melting at 176–177°, while it gives a monoacetyl compound, melting at 161–162°, with the same reagent but at room temperature. The former has been proved to be *O, N*-diacetyljervine and the latter to be *N*-acetyljervine. The *N*-methyl compound gives a monoacetyl derivative which melts at 186–187° at the boiling point of the reagent. On the other hand it furnishes no acetyl derivative at room temperature. At room temperature, therefore, the acetylation of jervine occurs at nitrogen but at the boiling point of acetic anhydride at both nitrogen and oxygen. The

(1) This Bulletin, **9** (1934), 15.

(2) *Ibid.*, **11** (1936), 163.

diacetyljervine is hydrolysed in steps as in the case of diacetyl-iso-yohimbine⁽³⁾. On hydrolysis with dilute and concentrated alcoholic caustic soda the acetyl compound furnishes the *N*-acetyl derivative and jervine respectively. Jervine has also been treated with acetic anhydride and anhydrous sodium acetate but the results are just the same as in the case of acetic anhydride only.

The functions of oxygen and nitrogen atoms of jervine have now been revealed as having two active hydrogen atoms, one in the hydroxyl and the other in the imino group. These were supported further by the results of determination of active hydrogen atoms after Zerewitinoff. Jervine may, therefore, be represented by the extended formula shown above.



Experiments concerned with the degradation of jervine are in progress.

Experimental.

Purification and properties of jervine. The alkaloid was stated by the earlier investigators to melt at various temperatures⁽⁴⁾ and to give different colouration, showing that the purity of the base was doubtful. Jervine is present in nature with many other alkaloids which are hardly crystallisable. Consequently the specimen purified by the usual method may accompany more or less another veratrum alkaloid. In view of the minor alkaloids mixed with jervine the purification of the base was fundamentally tried. Taking advantage of the easiness with which the minor alkaloids could be decomposed, it was warmed with alcoholic potash when the impurities passed into solution in brown colour. The solution was concentrated and water was added: the base separated was collected, washed, and dried. This was crystallised from alcohol, forming colourless needles, melting at 243.5–244.5°⁽⁵⁾. The base in this purity may also be obtained through repeated recrystallisation from alcohol or acetic ester. Jervine thus purified showed $[\alpha]_D^{21} = -150^\circ$ in absolute alcohol (see Part I).

Pure jervine gives no colouration with concentrated hydrochloric acid but a specimen melting at 240–241° furnishes a yellow colour reaction. The colour reaction of jervine of inferior quality with strong sulphuric acid was described by Wright and Luff⁽⁶⁾. Pure jervine, melting at 243.5–244.5°, dissolves in cold strong sulphuric acid to a yellow fluid which in a very short time successively becomes orange, green, and then decolourises after several hours, whilst the impure specimen leaves a red solution instead of decolourisation. On dilution of the coloured solution it becomes colourless but may be reversed by adding strong concentrated sulphuric acid. When jervine was kept in the air it

(3) G. Hahn and W. Schuch, *Ber.*, **62B** (1929), 2953.

(4) Will: 200°, *Ann.*, **35** (1840), 117. Pehkschen, *J. Chem. Soc.*, **90** (1891), 88; *J. Pharm.*, (5), **22**, 265; *Pharm. Zeit. Russ.*, **29**, 339. Wright and Luff: 237–239°, *J. Chem. Soc.*, **35** (1879), 411. Salzberger: 238–242°, *Arch. Pharm.*, **228** (1890), 462. Bredemann: 241°, *Chem. Zentr.*, **1906**, I, 607; *Apoth. Ztg.*, **21**, 41.

(5) On melting it decomposes slightly and the m.p. depends more or less upon the rate of heating. It was determined by the bath preheated to 180°.

(6) Wright and Luff, *J. Chem. Soc.*, **35** (1879), 410.

became impure, colouring pale yellow with a depression of melting point. For instance, it melted unsharply at 239–240° after 7 days and at 220–229°, sintering at 160°, after 7 months. The specimen, however, in a closed vessel could be kept stable, and was found quite pure after 2 years.

Methylation of jervine with diazomethane. To a solution of jervine (0.5 g.) in methanol (50 c.c.) was added an ethereal solution of diazomethane prepared from nitrosomethylurethane (2 c.c.). On allowing to stand overnight, the solvents were removed, leaving a crystalline mass. This was treated with ether to remove the unchanged substance. On distilling off the solvent, *N*-methyljervine was left in colourless crystals (0.3 g.); it crystallised from dilute alcohol, m.p. 201–202°. It was shown to have 1 mol of water of crystallisation. (Found for air dry crystals on dehydration at 120° and 20 mm.: H₂O, 4.22, 4.02. Calc. for C₂₆H₃₆O₃N·CH₃·H₂O: H₂O, 4.07%. Found for dehydrated substance: C, 76.56; H, 9.17; -CH₃, 3.79. Calc. for C₂₆H₃₆O₃N·CH₃: C, 76.18; H, 9.24; -CH₃, 3.53%.)

The behaviours of methyljervine toward organic solvents are similar to those of jervine but the former is more soluble than the latter.

Methylation of jervine with methyl iodide and potassium hydroxide. Jervine (0.5 g.) in alcohol (12 c.c.) was heated with methyl iodide (1.4 g.) and potassium hydroxide (0.7 g.) for two hours on the water bath. After cooling, potassium iodide separated, which was filtered off, and the solvent was then removed. The residue was collected by means of water and dried. The yield was 0.5 g. This was crystallised from dilute alcohol in colourless crystals, m.p. 201–202°. There was no depression of melting point on admixture with *N*-methyljervine prepared by methylation with diazomethane. (Found: -CH₃, 3.87. Calc. for C₂₆H₃₆O₃N·CH₃: -CH₃, 3.53%.)

***N*-Methyljervine methiodide and methochloride.** *N*-Methyljervine (0.5 g.) was heated in a sealed tube with methyl iodide (1 c.c.) at 100° for 6 hours. After cooling the excess of methyl iodide was distilled off when *N*-methyljervine methiodide separated in rosettes, melting at ca. 247°. It was dissolved in dilute alcohol and treated with moistened silver chloride. The silver iodide produced was filtered off and the filtrate evaporated, leaving a crystalline mass melting at 245° with decomposition. This is freely soluble in methanol and dilute alcohol, and sparingly soluble in ether and light petroleum. It recrystallised from absolute alcohol in needles melting at 252° with decomposition. The dried substance was analysed. (Found: Cl, 7.13. Calc. for C₂₆H₃₆O₃N·CH₃·CH₃Cl: Cl, 7.45%.)

The methiodide and methochloride are freely soluble in most organic solvents, especially in dilute alcohol, but they are insoluble in ether and light petroleum.

Treatment of jervine with methyl iodide and anhydrous potassium carbonate. A solution of jervine (0.5 g.) in methanol (10 c.c.) was heated with methyl iodide (1.4 g.) and anhydrous potassium carbonate (0.6 g.) on the water bath for 3 hours. It was cooled and the inorganic salt was filtered off. On removing the solvent a crystalline mass was separated; it was collected, washed, and dried. The yield was 0.6 g., m.p. 247° with decomposition. This was converted into the methochloride by treating with silver chloride as in the other case. The methochloride thus obtained, melting at 252° with decomposition, was proved to be identical with the chloride described above.

Nitrosojervine. Jervine (0.5 g.) in 2*N* acetic acid (5 c.c.) was treated with sodium nitrite (0.1 g.) in water (1 c.c.) when crystalline powders separated. These were collected,

washed, and dried. The yield was 0.5 g. After repeated crystallisation from alcohol it melted at 251-252° with decomposition. (Found: N, 6.44. Calc. for $C_{26}H_{36}O_3N\cdot NO$: N, 6.36%.)

Tetrahydrojervine. A solution of jervine (2 g) in pure glacial acetic acid (10 c.c.) was shaken in hydrogen with platinum oxide (0.42 g.). Absorption of hydrogen occurred at room temperature but it was rather slow; 198 c.c. or 1.98 mols were taken up in 24 hours. For the first one mol it took ca. 80 minutes but for the second ca. 22 hours. The solution was diluted with water, and the catalyst was removed. Tetrahydrojervine was separated by making the filtrate alkaline, collected, and washed. The yield was 2.1 g. Tetrahydrojervine was freely soluble in most organic solvents with the exception of light petroleum. It was hardly crystallisable from usual organic solvents. A solution of tetrahydrojervine in benzene was treated with light petroleum until the solution was set in turbidity. On allowing the solution to stand tetrahydrojervine crystallised out in colourless needles which, after drying, melted at 208-210°. The hydrochloride in needle crystals was made by treating an alcoholic solution with hydrochloric acid in the same solvent. It did not melt at 360°. (Found: C, 69.10; H, 9.34. Calc. for $C_{26}H_{41}O_3N\cdot HCl$: C, 69.57; H, 9.37%.)

N-Acetylervine. Jervine (5 g.) was dissolved in acetic anhydride (50 c.c.) and was allowed to stand overnight. The reaction mixture was treated with water, and a crystalline mass separated. This was collected and dried. The yield was 5.3 g. It was crystallised from dilute alcohol in stout crystals, melted at 161-162° with immediate foaming. (Found: C, 70.88, 70.63; H, 9.01, 9.15. Calc. for $C_{28}H_{39}O_4N\cdot H_2O$: C, 71.29; H, 8.77%. The air-dried substance lost 4.02% at 115° and 16 mm. Calc. for $C_{28}H_{39}O_4N\cdot H_2O$: 3.82%. Found for anhydrous substance: C, 74.23; H, 8.68%. Calc. for $C_{28}H_{39}O_4N$: C, 74.11; H, 8.67%.)

It is soluble in methyl alcohol, ethyl alcohol, acetone, chloroform, acetic ester, and benzene, but sparingly soluble in ether and light petroleum.

Diacetylervine. A solution of jervine (5 g.) in acetic anhydride (50 c.c.) was boiled on the wire gauze 1.5 hours. The excess of the acetic anhydride was distilled off under reduced pressure and the trace of the latter was removed by treating with methyl alcohol; a syrupy substance was obtained. This was then treated with water when the acetylated compound separated in crystals. It was collected, washed, and dried. The yield was 5.95 g. It was recrystallised from dilute alcohol, rosettes, m.p. 176-177°. (Found: C, 73.14, 73.17; H, 7.75, 8.23. Calc. for $C_{30}H_{41}O_5N$: C, 72.68; H, 8.34%.)

It is soluble in methyl alcohol, ethyl alcohol, acetone, acetic ester, chloroform, and benzene, but sparingly soluble in ether and light petroleum.

Hydrolysis of diacetylervine. A solution of diacetylervine (0.23 g.) in alcohol (14 c.c.) was treated with 0.1 N alcoholic caustic soda and was warmed for 4 hours on the water bath. On evaporation a crystalline mass (0.15 g.) was obtained; it was collected by means of water and dried. It was recrystallised from dilute alcohol, six-sided plates, m.p. 158-159° with decomposition. The hydrolysed substance was proved in every point to be N-acetylervine described above. This was treated once more with the same but more concentrated reagent. The mixture was heated for 6 hours. On working up the reaction mixture jervine was obtained. Moreover diacetylervine was also treated with concentrated alcoholic caustic alkali as above, jervine being obtained in one step.

Acetylation of N-methyljervine. N-Methyljervine prepared by the method described above was treated with acetic anhydride in the cold as in the case of jervine. On working up, the starting substance was recovered unchanged.

O-Acetyl-N-methyljervine. N-Methyljervine (0.3 g.) was dissolved in acetic anhydride (10 c.c.) and was kept boiling for an hour. The excess of acetic anhydride was removed under diminished pressure and the reaction product, on treating with water, was collected, washed, and dried. After crystallisation from dilute alcohol, needle crystals in rosettes melted at 186–187°. The yield was 0.07 g. (Found: C, 74.50; H, 8.96. Calc. for $C_{29}H_{41}O_4N$: C, 74.47; H, 8.84%.)

It is soluble in most organic solvents with the exception of light petroleum.

Determination of active hydrogen. Active hydrogen in jervine was determined by the method of Zerewitinoff using pyridine⁽⁷⁾ as the solvent (Found: active hydrogen, 0.54% or 2.17 atoms. Calc. for 2H in $C_{26}H_{37}O_3N$: 0.49%).

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(7) Th. Zerewitinoff, *Ber.*, **47** (1914), 2417.

A NEW BACTERIOXANTHOPHYLL,
THE YELLOW PIGMENT OF *SARCINA LUTEA*.⁽¹⁾

(Preliminary Report.)

By Teruko NAKAMURA.

Received October 29th, 1935. Published March 28th, 1936.

In recent years, inquiries into the chemical nature and biological significance of organic colouring matters have been made to a great extent, but very few pigments of microorganisms have been studied chemically. The chemical nature of most of the pigments in highly coloured bacteria is not well known, although its study would be of interest not only for the understanding of the biological rôle of the bacterial pigments themselves, but also for comparison in cases of pigments which are also found in higher plants.

The writer has studied the yellow pigment of *Sarcina lutea*⁽¹⁾ which is prevalent in air. Although the occurrence of carotenes in bacterial pigments

(1) After the completion of this manuscript, the author has found a note on the pigment of *Sarcina lutea*: E. Chargaff and J. Dieryck, *Naturwiss.*, **20** (1932), 872.

is generally accepted and moreover demonstrated by absorption spectra⁽²⁾ and by feeding experiments⁽³⁾ for the vitamin A activity, reports on the examination of carotenoids isolated as such from any bacterial growth are still meager.

The pale yellow pigmentation of *Sarcina lutea* with green fluorescence which is distinct from well known red or orange coloured carotenoids, e.g. lycopene or carotenes, seemed to furnish a new interesting material for study. The pigment was found to be carotenoidal, containing chiefly a xanthophyllic substance which gave ordinary lipochrome reactions and which revealed absorption maxima at 490, 460, and 433m μ in carbon bisulphide. The study of such hitherto undefined yellow pigment of microorganism is of interest in connection with the investigation of xanthophyllic matter in higher plants as they are conjectured to be the precursor of carotenes. The present paper is a preliminary report.

Experimental.

Isolation of the Pigment. The organism was grown on broth agar at 22°.⁽⁴⁾ The medium was slightly alkaline (pH 7.2). A solid culture was preferred to a liquid medium because on agar it was found to grow more rapidly and also to produce more pigment. The organism reached maximum pigmentation in approximately 10 days, when the growth was scraped off the surface.

The pigment was collected as follows: The cultures were extracted with cold 98% methyl alcohol in the dark at room temperature, until the cellular material became almost colourless; the pigment was taken up as a clear yellow methyl alcoholic solution with green fluorescence. The alcoholic solution was then distilled to dryness in a stream of CO₂ gas at 5° under a diminished pressure. The residue consisted of a greenish yellow matter. It was washed with a small quantity of methyl alcohol which dissolved the pigment leaving a great portion of a white residual matter undissolved. The latter was readily soluble in water and sparingly soluble in organic solvents.

The methyl alcoholic solution of the pigment was concentrated by distillation and was diluted with water until it contained 30% methyl alcohol, and the solution was extracted with ether. From the ether extract, the solvent was removed, leaving the crude pigment of greenish yellow colour, which was tested chemically and spectroscopically.

Solubility. Insoluble in H₂O, in aqueous acid (HCl), and alkaline solutions (NaOH), soluble in methyl alcohol, ethyl alcohol, ether, chloroform, carbon bisulphide, acetone, benzine, benzene, petroleum ether, and xylene. Among the above solvents it is most soluble in methyl alcohol and only slightly soluble in petroleum ether and benzine.

Colour Reactions. Blue colourations with conc. H₂SO₄, with SbCl₃, and with chloroacetic acid in chloroform. No colouration with 25% HCl, conc. HCl, HNO₃, acetic acid,

(2) V. Reader, *Biochem. J.*, **19** (1925), II, 1041.

(3) Carl A. Baumann, H. Steenbock, Mary A. Ingraham, and E. B. Fred, *J. Biol. Chem.*, **103** (1933), 339.

(4) On the improved method of cultivation, a report will be made by Mr. R. Ohtake.

and phosphoric acid. On addition of HCl or NaOH to the alcoholic solution no appreciable change was observed in the colour.

Oxidation and Reduction. The alcoholic solution was decolorized by Mg and HCl, and by H_2O_2 on standing.

Adsorption Tests. From the ether or benzine solution, the pigment could be adsorbed on several substances, e.g. Al_2O_3 , kaolin, silica, fuller's earth, and "Faserton-erde" (Fränkel), but not on $CaCO_3$.

The elution of the adsorbed pigment, however, was difficult. Only in the cases of Al_2O_3 and "Faserton-erde" the pigment could be separated in 1-5% solution of methyl alcohol in petroleum ether or benzine. This behavior is comparable with that of cryptoxanthine.⁽⁵⁾

Spectroscopic Measurements. With a hand spectroscope the following absorption maxima were read:

Solvent	Absorption maxima (m μ)		
Carbon bisulphide	490	460	(433)
Chloroform	475	445	(423)
Alcohol	467	436	(410)
Methyl alcohol	468	435	(408)
Ether	468	437	(413)
Benzine	470	440	

The third maximum placed in brackets was not distinct.

The spectrographic readings are lower than in any of the already identified carotenoids. Among similar compounds, the nearest values found in the literature are those of a short wave xanthophyll (468-469, 438-439 in alcohol),⁽⁶⁾ β -xanthophyll of Tswett which is noted by Kuhn, and of canary xanthophyll⁽⁷⁾ (472, 443, 418 in benzine). But as already mentioned the pigment of *Sarcina lutea* is not adsorbed on $CaCO_3$, while β -xanthophyll is.

Saponification. A solution of the pigment in methyl alcohol was saponified with alcoholic potash, the concentration of the alkali being 2.5%. It was kept at 50° for 2 hours in a stream of hydrogen. On expelling a portion of the alcoholic solvent by distillation, the pigment became soluble in water. From the aqueous solution it could not be extracted with ether. On acidifying, however, the pigment was taken up in ether. It was also possible to extract the pigment with ether after saturating the alkaline solution of saponification with a stream of CO_2 .

Notes. Minute quantity of a yellow crystalline substance was obtained from benzine and acetone solutions of the pigment. Further work is in progress to obtain the pigment

(5) R. Kuhn and C. Grundmann, *Ber.*, **66** (1933), 1746.

(6) R. Kuhn and H. Brockmann, *Z. physiol. Chem.*, **206** (1932), 60.

(7) H. Brockmann and O. Völker, *Z. physiol. Chem.*, **224** (1934), 209.

in pure crystalline state by the method of chromatograph ;⁽⁸⁾ thereby the pigment may be divided into components.

Summary.

The yellow pigment of *Sarcina lutea* was examined. It is a lipochromic substance with absorption maxima at 490, 460, and 433 $m\mu$ in carbon bisulphide apparently distinct from well known xanthophylls, the constitution of which had not been identified. Saponification showed the substance to be chiefly a xanthophyll-like ester. The work is being continued.

The author wishes to express her sincere thanks to Prof. R. Majima and to Dr. C. Kuroda for their advice and encouragement throughout this work. She is grateful to Prof. U. Suzuki for his kind interest. She is also indebted to Dr. T. Kodama of the Kitasato Institute for Infectious Diseases for furnishing her with the pure strain of *Sarcina lutea* and to Mr. R. Ohtake for the most valuable assistance rendered to her in the cultivation of the organism.

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(8) R. Kuhn and H. Brockmann, *Z. physiol. Chem.*, **206** (1932), 41. A. Winterstein and G. Stein, *Z. physiol. Chem.*, **220** (1933), 247.

SYNTHESIS OF 4-HYDROXY-3-ETHOXY-1-ALLYL-BENZENE
FROM 4-HYDROXY-3-METHOXY-1-ALLYL-
BENZENE (EUGENOL).

By Nenokichi HIRAO.

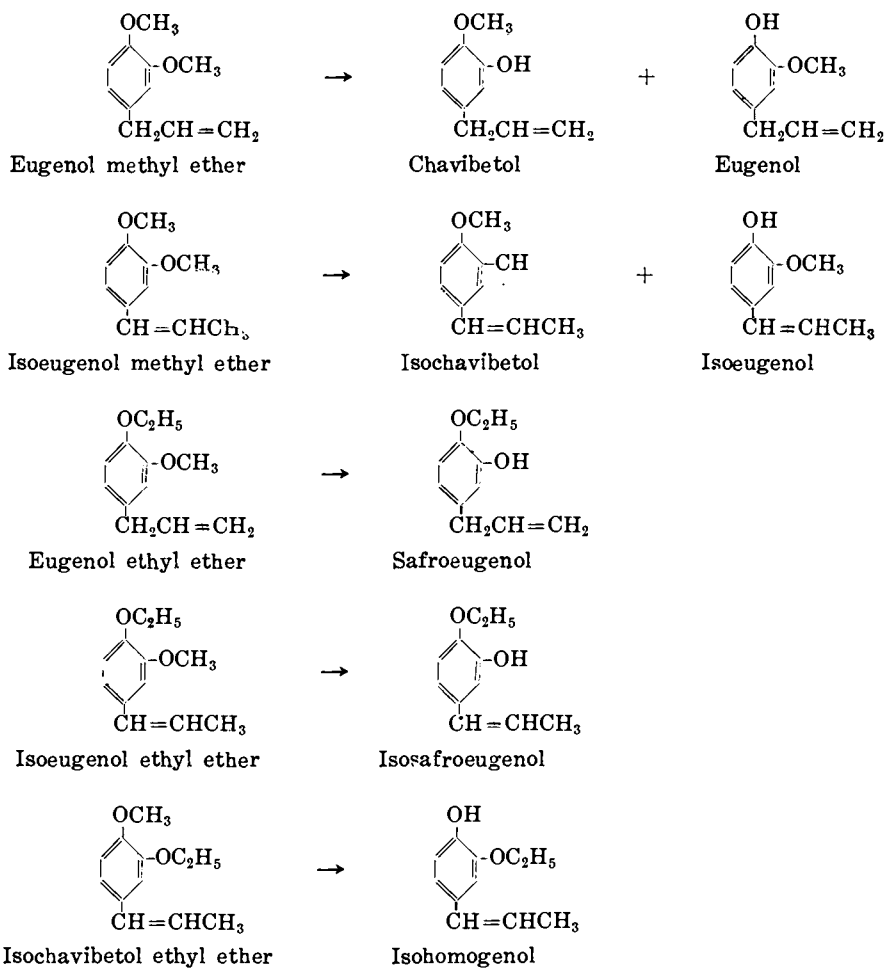
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On the basis of Grignard's reaction the author prepared eugenol and chavibetol from eugenol methyl ether⁽¹⁾, isoeugenol and isochavibetol from isoeugenol methyl ether⁽¹⁾, safroeugenol from eugenol ethyl ether⁽¹⁾, isosafroeugenol from isoeugenol ethyl ether⁽¹⁾, and 4-hydroxy-3-ethoxy-1-propenylbenzene⁽²⁾ from isochavibetol ethyl ether⁽³⁾.

(1) *J. Chem. Soc. Japan*, **52** (1931), 519.

(2) The author proposes to designate Isohomogenol.

(3) *J. Chem. Soc. Japan*, **52** (1931), 263.

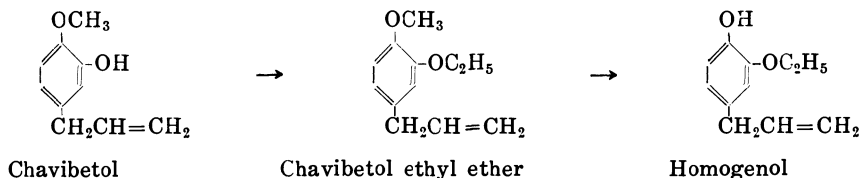


It has been considered difficult to prepare chavibetol, but the author synthesised it with ease by the above method. The mixture of chavibetol and eugenol was readily separated in their benzoates by fractional recrystallisation from petroleum ether and alcohol in turn.

Chavibetol ethyl ether, a new compound, was prepared by the ethylation of chavibetol with a good yield. It had the following constants: b.p. $114^{\circ}/6.5$ mm., d_4^{25} 1.0073, n_D^{25} 1.5231. On oxidation with potassium permanganate 4-methoxy-3-ethoxy-benzoic acid, m.p. $162-163^{\circ}$, was formed.

4-Hydroxy-3-ethoxy-1-allyl-benzene, a new compound, was prepared in a good yield by the action of Grignard's reagent on chavibetol ethyl ether. The author proposes to designate this new compound "homogenol." It is a

clear liquid with an odour resembling eugenol. In alcoholic solution a green colouration was observed upon the addition of ferric chloride.



Homogenol had the following physical constants: b.p. 114.5°/8.5 mm.; d_4^{25} 1.0344, n_D^{25} 1.5292; benzoate, m.p. 45.5°; phenylurethane, m.p. 93.5–94.5°. (Further experiment on the same line is now in progress.)

Experimental.

(1) *Action of Grignard's reagent on eugenol methyl ether.* (a) A solution of 9 g. of eugenol methyl ether in 10 g. of xylene was poured into Grignard's reagent prepared from 1.3 g. of magnesium 8 g. methyl iodide, and 10 g. of dry ethyl ether. The mixture was heated on the oil bath at 160–180° for 2 hours under a reflux condenser. After cooling to room temperature some pieces of ice and dilute acetic acid were added, and the reaction product was distilled in steam. The distillate was extracted with ether and washed with a dilute solution of sodium bicarbonate. Seven grams of a phenolic substance and 0.2 g. of a neutral oil were obtained by shaking with dilute caustic soda in usual manner. The phenolic product had a sweet taste, and the presence of chavibetol was suspected.

(b) *Isomerisation.* One part of the phenolic product and 2 parts of potassium hydroxide were mixed in a test tube, and heated on the oil bath at about 220° for one hour. The mass was dissolved in water and acidified. The crude product was obtained in a yield more than 90 per cent of theory. One part was dissolved in 3 or 4 parts of hot 50% alcohol, and then cooled to room temperature. Isochavibetol crystallised out in glistening thin plates, m.p. 95–96°, and was confirmed by mixed melting point with an authentic specimen.

(c) *Separation of eugenol and chavibetol in their benzoates.* The phenolic product (b.p. 128–129°/6 mm.) (42 g.) was added to a solution of 19 g. of potassium hydroxide and (110 g.) of alcohol, and the solution was cooled with ice. Benzoyl chloride (43 g.) was added in a thin stream with constant stirring. When the reaction was completed, about 500 c.c. of water was added and the separated benzoates collected and washed with water. The benzoates were added to 80 c.c. of hot alcohol, and on cooling 87 g. of crystals were obtained. The crystals were dissolved in 200 c.c. hot petroleum ether (b.p. 30–60°), and, on standing, 10.3 g. of magnificent crystals appeared. The melting point of these crystals was 69°, and they were identified as eugenol benzoate by mixed melting point with an authentic specimen.

About a quarter of the solvent in the mother liquor was distilled off, and then it was allowed to crystallise, when 6.5 g. of crystals, m.p. 49°, separated, which differed

from the former. They were chavibetol benzoate. The mother liquor was evaporated to half its volume, when 23 g. of crude product, m.p. 42–62°, crystallised. This is a mixture of the two benzoates. When 1 part of this mixture was treated with 2.5 parts of hot petroleum ether a small quantity of eugenol benzoate remained in crystalline state, and relatively pure chavibetol benzoate crystallised out from the solution. On repetition, it proved possible to separate the two benzoates from the mixture.

(2) **Action of Grignard's reagent on isoeugenol methyl ether.** (a) *Isoeugenol methyl ether.* To the reaction mixture of 32.8 g. of isochavibetol, m.p. 95°, 15 g. of potassium hydroxide and 30 c.c. of water, some pieces of ice and 25.2 g. of dimethyl sulphate were added, and then the mixture was shaken mechanically. The methylated product was treated in the usual manner. Yield 25.5 g.; b.p. 135°/14 mm.; d_4^{25} 1.0504; n_D^{25} 1.5655; M.R. 55.24; $C_{11}H_{14}O_2F_4$ 52.22.

(b) A solution of 9 g. of isoeugenol methyl ether and 10 c.c. of xylene was added to Grignard's reagent prepared from 1.44 g. of magnesium, 8.5 g. of methyl iodide, and 10 c.c. of ether. After the usual procedure 6 g. of a phenolic product was separated. On recrystallisation from 50% alcohol 1.3 g. of isochavibetol, m.p. 94°, was yielded. Most of the residue of the mother liquor consisted of isoeugenol, which was confirmed by the formation of its benzoate melting at 103.5°.

(3) **Action of Grignard's reagent on eugenol ethyl ether. Synthesis of safro Eugenol.** (a) *Eugenol ethyl ether.* Ethyl iodide (20.8 g.) and methanol (10 g.) were added to the reaction mixture containing 21.6 g. of eugenol, 10 g. of potassium hydroxide, and 7 c.c. of water. The mixture was boiled under a reflux condenser for an hour. Yield 22 g.; b.p. 122–125°/12 mm.; d_4^{25} 1.0099; n_D^{25} 1.5254.

(b) *Safro Eugenol.* Eugenol ethyl ether and xylene (10 g.) were added to Grignard's reagent prepared from 1.3 g. of magnesium, 8 g. of methyl iodide, and 10 g. of ether. The usual treatment yielded 3.2 g. of a phenolic product. B.p. 129.5°/20 mm.; m.p. 34.5°; d_4^{25} 1.0335; n_D^{25} 1.5304 (in supercooled state); M.R. 53.2; $C_{11}H_{14}O_2F_4$ 52.10. (Found: C, 73.83; H, 8.19. Calc. for $C_{11}H_{14}O_2$: C, 74.16; H, 7.87%.) Phenylurethane, m.p. ca. 58°.

Isomerisation. The phenolic product (0.5 g.) and potassium hydroxide (1 g.) were heated in a small test tube in the oil bath at 200° for one and a half hours. The reaction product was dissolved in water and acidified with acetic acid. Lustrous thin plates crystallised out, and after recrystallisation from 50% alcohol, they melted at 85°. They were isosafro Eugenol, and identification was established by mixed melting point with an authentic specimen.

The above data show that the phenolic product is safro Eugenol.

(4) **Action of Grignard's reagent on isoeugenol ethyl ether. Synthesis of isosafro Eugenol.** (a) *Isomerisation of eugenol ethyl ether.* In a test tube 5 g. of eugenol ethyl ether and 5 g. of potassium hydroxide were heated in the oil bath at 200° for 2 hours. The reaction mixture was dissolved in water and the separated crystals were collected and washed with water. The yield of the crystals was 4.8 g. These white crystals melted at about 61°, and after recrystallisation from 90% alcohol the melting point was raised to 63°, identical with that of isoeugenol ethyl ether.

(b) *Isosafro Eugenol.* Isoeugenol ethyl ether (4.7 g.) and xylene (15 g.) were added to Grignard's reagent prepared from 0.65 g. of magnesium, 3.8 g. of methyl iodide and 10 c.c. of ether. The mixture was treated as above, and 4.1 g. of a phenolic product was

produced in white crystals (theoretical yield 4.37 g.). Its melting point was 83°, but, after one recrystallisation from 50% alcohol, rose to 85°, identical with that of isosafroleugenol.

(5) **Action of Grignard's reagent on isochavibetol ethyl ether. Synthesis of isohomogenol.** (a) *Isochavibetol ethyl ether.* To the reaction mixture of 32 g. of isochavibetol, 12 g. of potassium hydroxide, and 20 c.c. of water, 37 g. of potassium ethyl sulphate was added, and the mixture was heated in the oil bath at 150–160° for 2 hours, and after cooling, a dilute solution of sodium hydroxide was added. Twenty three grams of white crystals were separated and readily purified by recrystallisation from 90% alcohol, m.p. 49.5° (Found: C, 74.84; H, 8.39. Calc. for $C_{12}H_{16}O_2$: C, 75.00; H, 8.33%). On oxidation with 3% potassium permanganate solution 4-methoxy-3-ethoxy-benzoic acid, m.p. 162–163°, was formed, which was identified by mixed melting point with an authentic specimen. These data show that the white crystalline substance is isochavibetol ethyl ether.

(b) *Isohomogenol.* A solution of 6.4 g. of isochavibetol ethyl ether in 30 g. of xylene was added to Grignard's reagent prepared from 0.9 g. of magnesium, 5.5 g. of methyl iodide, and 10 c.c. of dry ether, and the mixture boiled for 2 hours under a reflux condenser. Two grams of a crystalline phenolic substance was produced, and recrystallised from 50% alcohol. It melted at 53–54°. (Found: C, 74.06; H, 7.97. Calc. for $C_{11}H_{14}O_2$: C, 74.16; H, 7.89%.) The melting point of its benzoate was 87°, identical with that of isohomogenol benzoate.

(6) **Action of Grignard's reagent on chavibetol ethyl ether. Synthesis of homogenol.** (a) *Chavibetol.* In alcoholic solution, 49 g. of the pure chavibetol benzoate, m.p. 49°, described above, was saponified with 18 g. of potassium hydroxide. Yield 23 g.; b.p. 113°/8 mm. (oil bath 130°); d_{25}^{25} 1.0646, d_4^{25} 1.0613; n_D^{25} 1.5379; M.R. 48.33; $C_{10}H_{12}O_2$ 47.48.

(b) *Chavibetol ethyl ether.* In a pressure bottle, a solution of 23 g. of chavibetol, 9.3 g. of potassium hydroxide, 100 c.c. of alcohol, and 17 g. of ethyl bromide was heated at 80–90° on the water bath for 3 hours. Chavibetol (1.5 g.) was recovered. Yield 23.8 g.; b.p. 114°/6.5 mm. (oil bath 140°); d_{25}^{25} 1.0104, d_4^{25} 1.0073; n_D^{25} 1.5231; M.R. 58.23; $C_{12}H_{16}O_2$ 56.83. (Found: C, 74.82; H, 8.45. Calc. for $C_{12}H_{16}O_2$: C, 75.00; H, 8.33%.) It had a faint odour. This ethyl ether (1.7 g.) was oxidised with 2.5% potassium hydroxide solution (200 c.c.), the reaction mixture was filtered, and the filtrate acidified with acetic acid. 4-Methoxy-3-ethoxy-benzoic acid (m.p. 161–162°, 0.5 g.) was obtained as white crystals. It was identified by mixed melting point with an authentic specimen.

(c) *Homogenol.* The solution of the foregoing ethyl ether (23.8 g.) in xylene (30 c.c.) was added to Grignard's reagent prepared from magnesium (3 g.), methyl iodide (18 g.) and ether (50 g.), and the product treated in the usual manner. A phenolic product (homogenol 18.5 g.) was obtained. B.p. 112°/6.5 mm.; d_{25}^{25} 1.0375, d_4^{25} 1.0344; n_D^{25} 1.5292; M.R. 52.81; $C_{11}H_{14}O_2$ 52.10. (Found: C, 73.89; H, 8.07. Calc. for $C_{11}H_{14}O_2$: C, 74.16; H, 7.89%.) It is a colourless oil with eugenol-like odour. In alcoholic solution a greenish tinge was given with ferric chloride.

Phenylurethane. After standing for 2 months, the mixture of homogenol (1 g.) and carbanil (0.9 g.) crystallised completely, and the product was recrystallised from 80% methanol, m.p. 93.5–94.5° (sharp). (Found: C, 72.55; H, 6.50. Calc. for $C_{18}H_{19}O_3N$: C, 72.73; H, 6.40%.)

Benzoate. In ice cooling, benzoyl chloride (1.4 g.) was added to a solution of homogenol (1.65 g.) and potassium hydroxide (0.7 g.) in alcohol (10 g.). Yield of crude benzoate, 3 g. On standing, the solution of the benzoate in petroleum ether gave beautiful plates, m.p. 45.5° (sharp). (Found: C, 76.25; H, 6.52. Calc. for $C_{18}H_{18}O_3$: C, 76.60; H, 6.38%).

Isomerisation. In a small test tube, homogenol (1.3 g.) and potassium hydroxide (1.5 g.) were heated on the oil bath at 180-200° for 2 hours. The reaction mixture was dissolved in water and the solution acidified with acetic acid, when white crystals separated out. Yield 1.1 g. Benzoate was prepared and recrystallised from alcohol, m.p. 85.5-86.2°. It is identical with the isohomogenol benzoate.

In conclusion, the author wishes to express his gratitude to Dr. Kashichi Ono for his kind guidance during this investigation.

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STUDIES ON THE DERIVATIVES OF BENZOYLBENZOIC ACIDS.

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One of the authors has reported an isomeric change of halogenohydroxy-benzoyltoluic acids under the influence of concentrated sulphuric acid⁽¹⁾. They now wish to report further studies on the other derivatives of benzoylbenzoic acid.

I. Condensation of 3-Methylphthalic Anhydride with Benzene. When 3-methylphthalic anhydride was condensed with benzene, one substance, m.p. 116–117° (A), from the part insoluble in ammonia and two benzoyltoluic acids, m.p. 171–172° (B) and m.p. 126.5–127.5° (C), from the part soluble in ammonia were isolated. The analytical data of the first substance (A) corresponded to the empirical formula $C_{21}H_{16}O_2$, and it may be 1-methyl-2,3-dibenzoylbenzene (III) or diphenylmethylphthalide (I or II).

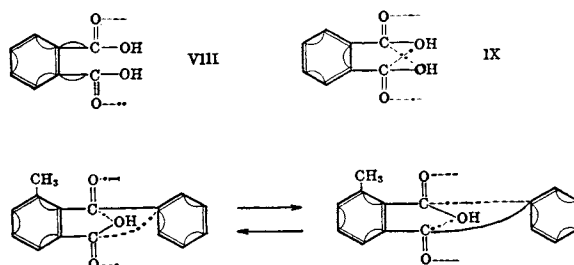
Benzoyltoluic acids (B and C) remained unaltered on being treated with concentrated sulphuric acid at room temperature. But when isomeride B was treated with concentrated sulphuric acid at 100–105°, an isomeric change

(1) *J. Chem. Soc.*, **1927**, 2516; **1930**, 1513, 1520, 1524.

Table 1.

Original	Corrected
2-(5'-Chloro-2'-hydroxybenzoyl)- 3(or 6)-methylbenzoic acid, m.p. 233-239° ⁽⁴⁾	2-(5'-Chloro-2'-hydroxybenzoyl)- 3-methylbenzoic acid
2-(5'-Chloro-2'-hydroxybenzoyl)- 6(or 3)-methylbenzoic acid, m.p. 171-171.5° ⁽⁵⁾	2-(5'-Chloro-2'-hydroxybenzoyl)- 6-methylbenzoic acid
2-(5'-Bromo-2'-hydroxybenzoyl)- 3(or 6)-methylbenzoic acid, m.p. 246-246.5° ⁽⁶⁾	2-(5'-Bromo-2'-hydroxybenzoyl)- 3-methylbenzoic acid
2-(5'-Bromo-2'-hydroxybenzoyl)- 6(or 3)-methylbenzoic acid, m.p. 163.5-164° ⁽⁷⁾	2-(5'-Bromo-2'-hydroxybenzoyl)- 6-methylbenzoic acid
2-(3'-Chloro-4'-hydroxybenzoyl)- 3(or 6)-methylbenzoic acid, m.p. 198-199° ⁽⁸⁾	2-(3'-Chloro-4'-hydroxybenzoyl)- 3-methylbenzoic acid
2-(3'-Chloro-4'-hydroxybenzoyl)- 6(or 3)-methylbenzoic acid, m.p. 188.5-189° ⁽⁹⁾	2-(3'-Chloro-4'-hydroxybenzoyl)- 6-methylbenzoic acid
2-(4'-Chloro-2'-hydroxybenzoyl)- 3(or 6)-methylbenzoic acid, m.p. 219.5-220.5° ⁽¹⁰⁾	2-(4'-Chloro-2'-hydroxybenzoyl)- 3-methylbenzoic acid
2-(4'-Chloro-2'-hydroxybenzoyl)- 6(or 3)-methylbenzoic acid, m.p. 177.5-178° ⁽¹¹⁾	2-(4'-Chloro-2'-hydroxybenzoyl)- 6-methylbenzoic acid
2-(2'-Chloro-4'-hydroxybenzoyl)- 3(or 6)-methylbenzoic acid, m.p. 218-218.5° ⁽¹²⁾	2-(2'-Chloro-4'-hydroxybenzoyl)- 3-methylbenzoic acid
2-(2'-Chloro-4'-hydroxybenzoyl)- 6(or 3)-methylbenzoic acid, m.p. 201-202° ⁽¹³⁾	2-(2'-Chloro-4'-hydroxybenzoyl)- 6-methylbenzoic acid

Now that we consider that the formula of phthalic acid is IX instead of VIII, the above-mentioned phenomena and also the reaction of ammonia on acid chloride of alkyl 3- or 4-methylphthalate⁽¹⁴⁾ and on acid chloride of methyl 3- or 4-nitrophthalate⁽¹⁵⁾ may be conveniently illustrated as shown below.



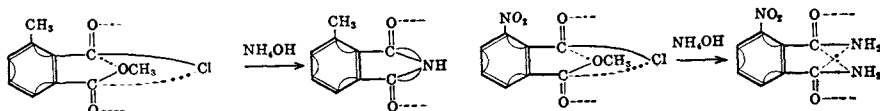
(4) (5) (6) (7) *J. Chem. Soc.*, **1927**, 2516; *ibid.*, **1930**, 1514.

(8) (9) *J. Chem. Soc.*, **1930**, 1521.

(10) (11) (12) (13) *J. Chem. Soc.*, **1930**, 1526.

(14) See pp. 187, 193.

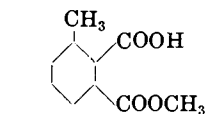
(15) See pp. 191, 200; *J. Soc. Chem. Ind., Japan*, **36** (1933), 203B.



II. Condensation of Acid Chlorides of Methyl 3- and 4-Methylphthalates with Benzene. The methyl ester of benzene-1,2,3-tricarboxylic acid, which was obtained by oxidizing methyl 3-methylphthalate (F), m.p. 114.5–115°, with potassium permanganate, melted with decomposition at 193–194°⁽¹⁶⁾. When acid chloride of methyl 3-methylphthalate (F) was condensed with benzene, 2-benzoyl-3-methylbenzoic acid (IV) and substance A (I, II or III) were obtained, but 2-benzoyl-6-methylbenzoic acid (V) could not be isolated. From these facts, it is highly probable that methyl 3-methylphthalate (F), m.p. 114.5–115°, may be 1-methyl 3-methylphthalate (X). Therefore, ethyl 3-methylphthalate (G), m.p. 86–87°, would be also 1-ethyl 3-methylphthalate (XI).

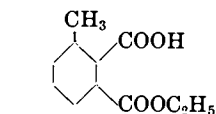
Benzoyltoluic acid, which was obtained by condensing acid chloride of methyl 4-methylphthalate (H), m.p. 89–90°, with benzene, melted at 136–138° and was proved to be identical with 2-benzoyl-5-methylbenzoic acid (XXII)⁽¹⁷⁾. Therefore, methyl 4-methylphthalate (H), m.p. 89–90°, may be 2-methyl 4-methylphthalate (XII).

On treating acid chloride of 1-methyl or 1-ethyl 3-methylphthalate and of 2-methyl 4-methylphthalate with conc. aqueous ammonia, 3-methylphthalimide (XIV), m.p. 188.5–189°⁽¹⁸⁾ and 4-methylphthalimide (XV), m.p. 194.5–195°⁽¹⁹⁾, were obtained, respectively⁽²⁰⁾.



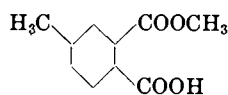
m.p. 114–115° (F)

X



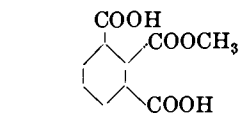
m.p. 86–87° (G)

XI



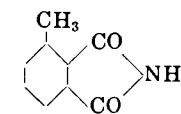
m.p. 89–90° (H)

XII



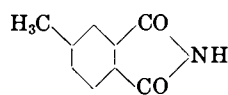
m.p. 203–205°(decomp.)

XIII



m.p. 188.5–189°

XIV



m.p. 194.5–195°

XV

(16) *Ann.*, **290** (1896), 226: 2-methyl ester of benzene-1,2,3-tricarboxylic acid (XIII), m.p. 203–205° (decomp.).

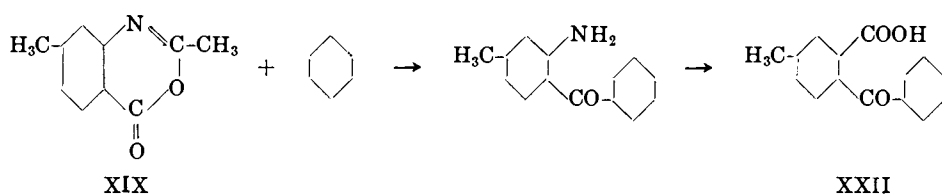
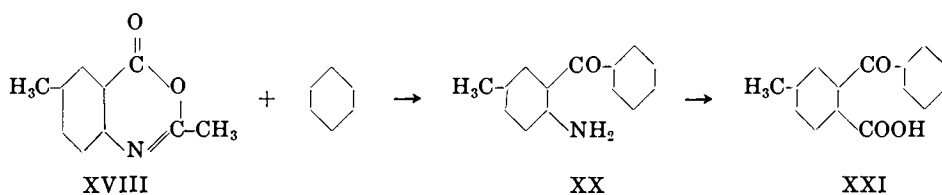
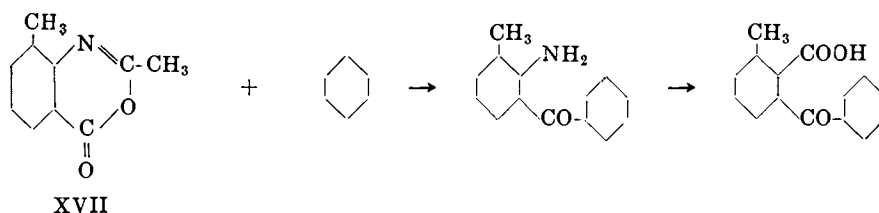
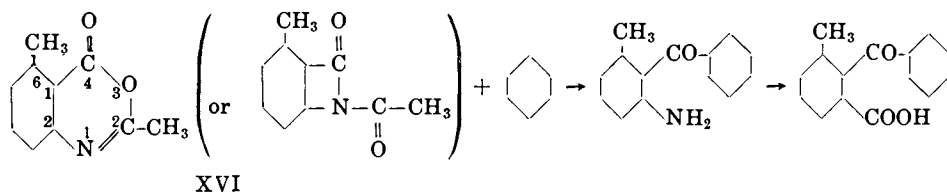
(17) *J. Chem. Soc.*, **1930**, 1518: 2-benzoyl-4 (or 5)-methylbenzoic acid (E), m.p. 145–145.5°, and also see p. 189 and 197.

(18) *Ber.*, **25** (1892), 2107; **40** (1907), 4413: m.p. 183–184°, 187°.

(19) *Monatsh.*, **12** (1891), 627: m.p. 196°.

(20) Compare p. 193.

III. An Attempt to determine the Constitutions of Benzoyltoluic Acids. As far as the authors are aware, a condensation of methyl-2-oxo-4-(toluoxazine-3,1)-derivatives with aromatic hydrocarbons or with their derivatives in the presence of aluminium chloride has not been reported. This synthesis was attempted to determine the constitutions of benzoyltoluic acids by schemes shown below. The results were not very satisfactory, yields of amino-diphenylketones being very poor.



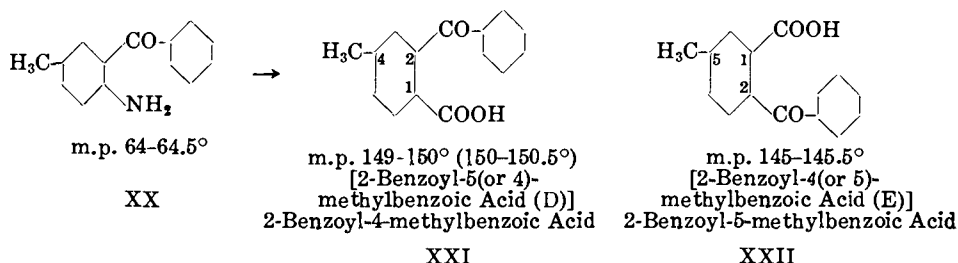
2-Amino-5-methyldiphenylketone (XX) had been already prepared by Chattaway and Lewis⁽²¹⁾, Esselen and Clarke⁽²²⁾, and Hanschke⁽²³⁾. 2-Benzoyl-4-methylbenzoic acid (XXI), which was derived from 2-amino-5-methyldiphenylketone, melted at 149–150° and was proved to be identical with 2-

(21) *J. Chem. Soc.*, **85** (1904), 594.

(22) *J. Am. Chem. Soc.*, **1914**, 321.

(23) *Ber.*, **32** (1899), 2021.

benzoyl-(5 or 4)-methylbenzoic acid (D), m.p. 150-150.5°.⁽²⁴⁾ Therefore 2-benzoyl-(4 or 5)-methylbenzoic acid⁽¹⁷⁾ (E), m.p. 145-145.5°, should be 2-benzoyl-5-methylbenzoic acid (XXII).



By analogy the authors propose the corrections of the interpretations given in the paper, "A New Isomerism of Halogenohydroxybenzoyltoluic Acids" as shown in Table 2.

Table 2.

Original	Corrected
2-(5'-Chloro-2'-hydroxybenzoyl)-5(or 4)-methylbenzoic acid (A), m.p. 239.5-240.5° ⁽²⁵⁾	2-(5'-Chloro-2'-hydroxybenzoyl)-4-methylbenzoic acid (A)
2-(5'-Chloro-2'-hydroxybenzoyl)-4(or 5)-methylbenzoic acid (B), m.p. 227.5-228.5° ⁽²⁶⁾	2-(5'-Chloro-2'-hydroxybenzoyl)-5-methylbenzoic acid (B)

IV. **Condensation of 3-Methylphthalic Anhydride with Phenol.** When 3-methylphthalic anhydride was condensed with phenol, two hydroxybenzoyltoluic acids were obtained; one melted at 220-221° (K) and the other at 197-198° (L). When these two acids were separately treated with concentrated sulphuric acid at room temperature, an isomeric change occurred, and hydroxybenzoyltoluic acid, m.p. 141-142° (K') from the former (K), and hydroxybenzoyltoluic acid, m.p. 183-184° (L') from the latter (L), were produced. The four acids K, K', L, and L' exhibit absorption bands with heads at λ 3300 and ca. 2500, 3310 and ca. 2500, 2875, and 2880 Å, respectively.

2-(2'-Hydroxybenzoyl)-benzoic acid (XXIII)⁽²⁷⁾, m.p. 171-171.5°, and 2-(4'-hydroxybenzoyl)-benzoic acid (XXIV)⁽²⁸⁾, m.p. 212-213°, have absorption bands with heads at λ 3310 and ca. 2500, and 2880, respectively. Reasoning

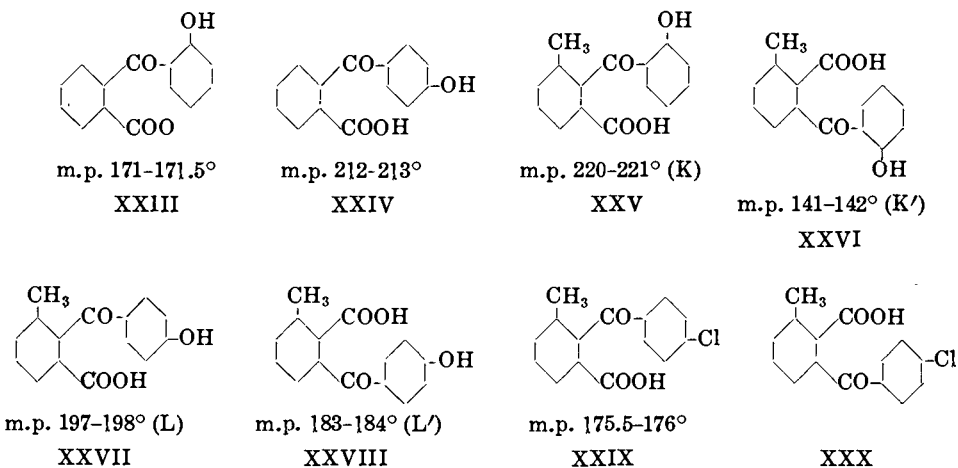
(24) *J. Chem. Soc.*, **1930**, 1518.

(25) (26) *J. Chem. Soc.*, **1930**, 1516.

(27) (28) Ullmann and Schmidt, *Ber.*, **52** (1919), 2100, 2106.

from the great similarity of these absorption bands, K or K' should have formula XXV or XXVI which has the hydroxy-group in the *o*-position to the carbonyl-group, and L or L' should have formula XXVII or XXVIII which has the hydroxy-group in the *p*-position to the carbonyl-group.

On taking into account the case of benzene, K, K', L, and L' would be 2-(2'-hydroxybenzoyl)-3-methylbenzoic acid (XXV), 2-(2'-hydroxybenzoyl)-6-methylbenzoic acid (XXVI), 2-(4'-hydroxybenzoyl)-3-methylbenzoic acid (XXVII) and 2-(4'-hydroxybenzoyl)-6-methylbenzoic acid (XXVIII) respectively.



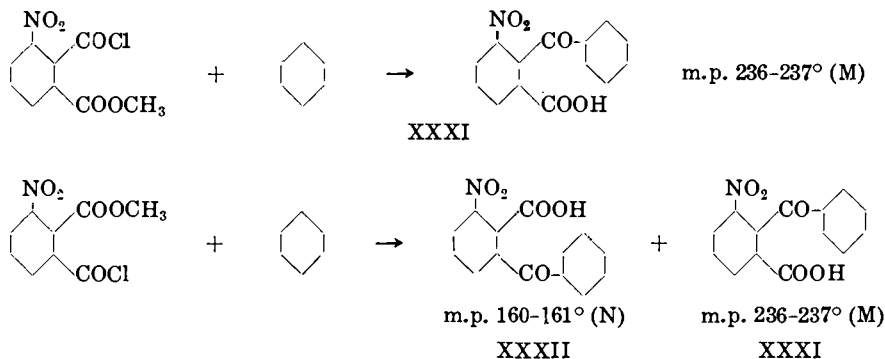
V. Condensation of 3-Methylphthalic Anhydride with Chlorobenzene.

On taking into account of the general rule, chlorobenzoyltoluic acid, m.p. 175.5-176°, which was obtained by condensation of 3-methylphthalic anhydride with chlorobenzene, should have formula XXIX or XXX, and may be 2-(4'-chlorobenzoyl)-3-methylbenzoic acid (XXIX) from the analogy with the case of benzene, but an isomeric change in concentrated sulphuric acid solution was not clear.

VI. Condensation of 3-Nitrophthalic Anhydride with Benzene. When 3-nitrophthalic anhydride was condensed with benzene, W. Lawrance⁽²⁹⁾ obtained two 2-benzoylnitrobenzoic acids, one melted at 217-221° and the other at 140-158-161° (decomp.) (or 157-160°), and concluded that the former is "6-benzoyl-2-nitrobenzoic acid" (XXXII) and the latter is "2-benzoyl-3-nitrobenzoic acid" (XXXI). The present authors, however, could isolate only one benzoylnitrobenzoic acid (M), m.p. 236-237°. When acid chloride of

(29) *J. Am. Chem. Soc.*, **42** (1920), 1874.

1- or 2-methyl 3-nitrophthalate was condensed with benzene⁽³⁰⁾, only isomeride M was isolated in the case of 1-methyl ester, and a small amount of isomeride M and a comparatively larger amount of isomeride N, m.p. 160-161°, in the case of 2-methyl ester. The present authors' experimental result support that isomerides M and N may be 2-benzoyl-3-nitrobenzoic acid (XXXI) and 2-benzoyl-6-nitrobenzoic acid (XXXII), respectively, not coincident with Lawrance's conclusions.



On treating acid chloride of 1- or 2-methyl 3-nitrophthalate with conc. ammonia, diamide of 3-nitrophthalic acid, m.p. 204-204.5° (decomp.), was obtained in both cases⁽³¹⁾.

Experimental.

I. Condensation of 3-Methylphthalic Anhydride with Benzene. Anhydrous aluminium chloride (15.4 g.) was gradually added to a solution of 3-methylphthalic anhydride (7.7 g.) in benzene (70 c.c.) with constant stirring, and then the mixture was gradually heated, boiled after 1.5 hours' heating, and maintained at a boiling state until the evolution of hydrogen chloride had almost ceased (about 2 hours). The brown coloured mass⁽³²⁾ was treated with aqueous sodium carbonate, a substance (10.7 g., 94%), m.p. 128-156°, was obtained from the soluble portion, and a substance (4.2 g.), m.p. 109-113°, from the insoluble portion. On fractionally crystallising the former from glacial acetic acid, two fractions were isolated. The less soluble crystals (4.3 g.) melted at 163-170° and the more soluble ones (1.1 g.) at 123-128°. The residue (4.8 g.), from which nothing definite could be isolated by further recrystallisation, melted at 100-160°.

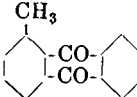
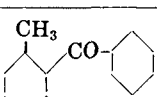
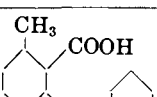
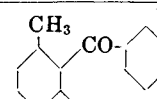
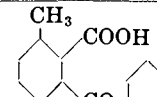
Substance A (I, II or III). The substance, m.p. 109-113°, crystallised from alcohol in colourless needles (Found: C, 84.26; H, 5.49; M, in camphor by Rast's method, 314, 303. Calculated for C₂₁H₁₆O₂: C, 83.97; H, 5.37%; M, 300.1). It melts at 116-117°, and

(30) Compare Lawrance, *ibid.*, **42** (1920), 1875.

(31) Compare p. 186, 200.

(32) From the filtrate, crude 3-methylphthalic acid (0.5 g.), m.p. 149-150° (decomp.), was recovered by extraction with ether.

Table 3.

Sample	Condition			Soluble part in ammonia					Insoluble part in ammonia  Crude : m.p. (°C.)
				Before recrystallisation			After recrystallisation		
	H ₂ SO ₄ 100% (c.c.)	Temp. (°C.)	Hours	m.p. (°C.)	Mixed with		 m.p. (°C.)	 m.p. (°C.)	
 0.1 g.	2	room temp.	15	155-165	164-169	—	—	—	—
0.5 g.	3	70-75	$\frac{3}{4}$	119-146 0.43 g.	145-164	113-125	157-165	?	169.5-172 0.05 g.
0.5 g.	2.5	100-105	$\frac{2}{3}$	121-125.5 0.35 g.	120-162	122-127.5	?	} 125.5-127 0.31 g.	167-171.5 0.1 g.
0.5 g.	2.5	100-105	$1\frac{1}{2}$	121-124° 0.23 g.	117-156	121-125.5	?		168.5-172 0.2 g.
 0.31 g.	1.6	100-105	$\frac{3}{4}$	122-125° 0.2 g.	—	122-127	—	—	168-171 0.1 g.
Residue { m.p. 100-160°, 4.8 g. m.p. 125-153°, 0.7 g.	25	100-105	$\frac{1}{2}$	110-120 4.4 g.	—	—	—	126.5-127.5 1.6 g.	— 0.83 g.

is soluble to some extent in glacial acetic acid, and appreciably in alcohol. This substance is not soluble in dilute caustic alkali, and dissolves in conc. sulphuric acid to a faintly yellow solution.

2-Benzoyl-3-methylbenzoic acid (B). When the material, m.p. 163–170°, was recrystallised several times from glacial acetic acid, fine colourless crystals, m.p. 171–172°, were obtained (Found: C, 74.85; H, 5.29. Calculated for $C_{15}H_{12}O_3$: C, 74.97; H, 5.04%). It is easily soluble in alcohol and appreciably soluble in glacial acetic acid. The solution in conc. sulphuric acid is faintly yellow. Its methyl ester melts at 106.5–107.5°.

2-Benzoyl-6-methylbenzoic acid (C). Fine colourless crystals, m.p. 126.5–127.5°, were obtained from the substance, m.p. 123–128°, by several crystallisations from glacial acetic acid (Found: C, 74.90; H, 5.43%). The solubilities of this acid are generally similar to, but greater than, those of the isomeric acid (B). Its methyl ester melts at 122.5–123°.

The results, which were obtained when 2-benzoyl-3- or 6-methylbenzoic acid was treated with conc. sulphuric acid, are given in Table 3.

Diphenylketone-2,6-dicarboxylic acid (D). 2-Benzoyl-3-methylbenzoic acid (0.88 g.) was boiled with 1% potassium permanganate solution (184 c.c.) for 27 hours. The solution was concentrated and acidified with hydrochloric acid; a substance (ca. 1 g.), m.p. 249–255°, was obtained. On recrystallising from glacial acetic acid, it melted at 255–256° (Found: C, 66.60; H, 3.93. Calculated for $C_{15}H_{10}O_5$: C, 66.65; H, 3.73%).

Diphenylketone-2,3-dicarboxylic acid (E). Diphenylketone-2,3-dicarboxylic acid, which was obtained by oxidizing the 2-benzoyl-6-methylbenzoic acid with potassium permanganate, melted at 100–125–176–186°. It was recrystallised from acetic acid or from water; fine colourless crystals, which melted with foaming at 121–125–146°, were obtained (Found for air-dried material: loss at 100–105°/28 mm., 6.30; C, 62.53; H, 4.29. Calculated for $C_{15}H_{10}O_5 \cdot H_2O$: H_2O , 6.25; C, 62.48; H, 4.20%). Its anhydrous form melts with foaming at 140–141° (Found for anhydrous material: C, 66.73; H, 3.90. Calculated for $C_{15}H_{10}O_5$: C, 66.65; H, 3.73%).

II. Condensation of Acid Chloride of Methyl 3- and 4-Methylphthalate with Benzene.

(a) *Preparation of alkyl 3- and 4-methylphthalates*. As far as the authors are aware, alkyl 3- and 4-methylphthalates have not been prepared; they synthesised these esters as summarised in Table 4. These results are not in agreement with v. Meyer's theory of esterification⁽³³⁾.

1-Methyl 3-methylphthalate (F) (0.3 g.) was boiled with 1% potassium permanganate solution (70 c.c.) for 12 hours. The solution was concentrated and acidified with hydrochloric acid; a substance, m.p. 188–207° (decomp.), was obtained. On recrystallising from acetic acid, it melted with decomposition at 193–194° (0.15 g.).

(b) *3- and 4-Methylphthalimide*. 1-Ethyl or 1-methyl 3-methylphthalate (G or F) was boiled with thionyl chloride (5 parts) for 15–30 minutes. The excess of thionyl chloride was removed by distillation under reduced pressure. On treating the residue with an excess of conc. ammonia 3-methylphthalimide (XIV), melting at 188.5–189° after recrystallisation in both cases, was obtained (Found: N, 8.99. Calculated for $C_9H_7O_2N$: N, 8.69%).

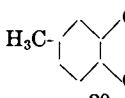
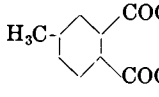
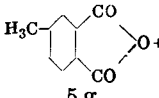
4-Methylphthalimide (XV), which was prepared by much the same method as in the case of 3-methylphthalic acid, melted at 194.5–195° (Found: C, 67.09; H, 4.57; N, 8.92; 8.64. Calculated for $C_9H_7O_2N$: C, 67.06; H, 4.38; N, 8.69%).

(33) *Ber.*, **27** (1897), 1585; also compare *Ber.*, **27** (1894), 510, 3146; **28** (1895), 182, 1254, 1468; **29** (1896), 1401.

Table 4.

Materials	Condi- tion	Crude product	Pure product
 19 g. 100 c.c.	boil 5 h.	Air-dried : m.p. 74-89° (22.3 g., 89.5%) Anhydrous : m.p. 109-114°	 Air-dried : C ₁₀ H ₁₀ O ₄ ·H ₂ O (6.3 g., 27.7%) Anhydrous : m.p. 114.5-115° (F)
 20 g. 200 c.c.	boil 1/2 h.	Soluble part in Na ₂ CO ₃ : anhydrous, m.p. 101-111.5° (2.95 g., 11.3%)	 Anhydrous : m.p. 114.5-115° (F)
		Insoluble part in Na ₂ CO ₃ : b.p. ca. 165-169°/21 mm. (15.6 g., 60.7%)	 b.p. 167-169°/21 mm.
 15 g. 5 g. 70 c.c.	boil 5 h.	Soluble part in NaOH : anhydrous, m.p. 107-112°	 Recrystallisa- tion three times from acetic acid : anhydrous, m.p. 109-112° (3.25 g.), mixed m.p. with (F) 109-114°
 10 g. 200 c.c.	boil 2 h.	Air-dried : m.p. 71-80° (5.4 g., 38.8%) Anhydrous : m.p. 77-82°	 Air-dried : C ₁₁ H ₁₂ O ₄ ·H ₂ O, m.p. 75-85° (4 g.) Anhydrous : m.p. 86-87°(G)
 4 g. 40 c.c.	boil 1 h.	Soluble part in NH ₄ OH : air-dried, m.p. 69-82° (0.63 g., 12%) Anhydrous : m.p. 73-83°	 Anhydrous : m.p. 86-87°(G)
		Insoluble part in NH ₄ OH	Diester
 10 g. 100 c.c.	boil 2 h.	Anhydrous : m.p. 85-90° (5.1 g., 42.6%)	 Air-dried : C ₁₀ H ₁₀ O ₄ ·H ₂ O Anhydrous : m.p. 89-90°(H) (4.7 g., 39.3%)

Table 4. (Concluded)

Materials	Condi- tion	
 20 g.	boil 2 h.	Pure ethyl monoester could not be isolated
 4.6 g.	boil 1 h.	
 5 g.	boil 1 h.	Diester, b.p. ca. 193-195°/27 mm. (4.6 g.)

(c) *Condensation*. When acid chloride of 1-methyl-3-methylphthalate (ca. 6 g.) was condensed with benzene (120 c.c.) in the presence of anhydrous aluminium chloride (4.5 g.), crude substance A (I, II or III)⁽³⁴⁾ (ca. 0.9 g.) and 2-benzoyl-3-methylbenzoic acid⁽³⁵⁾ (ca. 1.3 g.) were isolated but 2-benzoyl-6-methylbenzoic acid could not be separated.

Aluminium chloride (0.8 g.) was added to a solution of acid chloride of 2-methyl-4-methylphthalate (ca. 0.5 g.) and benzene (5 c.c.), and the mixture was boiled for 30 minutes. The product soluble in ammonia, on recrystallising from acetic acid, melted at 136-138° and was proved to be identical with 2-benzoyl-5-methylbenzoic acid⁽¹⁷⁾.

III. An Attempt to determine the Constitutions of Benzoyltoluic Acids. (a) *Preparation of methyl-2-oxo-4-(toluoxazine-3,1)*. 6-Methyl-2-acetoanthranil (XVI). When 2-amino-6-methylbenzoic acid (9 g.) was boiled with acetic anhydride (50 c.c.) for one hour and distilled fractionally under reduced pressure, 6-methyl-2-acetoanthranil (7 g., 86%; b.p. 145-150°/10 mm.) was obtained. It crystallised from a mixed solvent of benzene and petroleum ether in a colourless crystalline substance, m.p. 84° (Found: C, 68.47; H, 5.40. Calculated for C₁₀H₉O₂N: C, 68.54; H, 5.18%).

3-Methyl-2-acetoanthranil (XVII). After a solution of 2-amino-3-methylbenzoic acid (30 g.) in acetic anhydride (150 c.c.) was boiled for one hour, some acetic anhydride was distilled and the solution cooled; 3-methyl-2-acetoanthranil (31 g., 89%), m.p. 135-136°, separated, 2-acetyl-amino-3-methylbenzoic acid (3 g., 7.8%), m.p. 193-195° (foaming), being recovered from the filtrate on treating with water. The former was recrystallised from benzene mixed with petroleum ether, m.p. 136-137° (Found: N, 8.02%).

After recrystallisation from glacial acetic acid, 2-acetyl-amino-3-methylbenzoic acid melted with foaming at 196.5-197° (Found: N, 7.01. Calculated for C₁₀H₁₁O₃N: N, 7.25%).

5-Methyl-2-acetoanthranil (XVIII). On treating 2-amino-5-methylbenzoic acid with acetic anhydride (5 parts.), 5-methyl-2-acetoanthranil (70%, m.p. 123-124°) and 2-acetyl-

(34) See p. 191.

(35) See p. 193.

amino-5-methylbenzoic acid (30%, m.p. 177–187°) were obtained. The former crystallised from benzene in almost colourless needles (Found: N, 8.17%). The latter, on several recrystallisations from acetic acid or alcohol, showed m.p. 179–190°⁽³⁶⁾ and had no water of crystallisation (Found: N, 7.38%).

4-Methyl-2-acetoanthranil (XIX). This substance was prepared by the same method as in the above cases and melted at 102–103° (Found: N, 7.85%).

(b) **Condensation of acetoanthranil with benzene.** Acetoanthranil (50 g.) was dissolved in benzene (300 c.c.) and aluminium chloride (91 g.) gradually added with constant stirring and then the mixture boiled for 14 hours, the evolution of hydrogen chloride being very slight. The reaction mixture, after distillation in steam as usual and the addition of an excess of alkali, was extracted several times with ether, and the ethereal extract was evaporated. The resinous substance was dissolved in a small amount of alcohol, and hot dilute hydrochloric acid added; the brownish resinous substance that separated was removed. On evaporation of the alcoholic solution, a substance, m.p. 160° (decomp.), separated in 5.7% yield (5.5 g.). After the addition of alkali to the filtrate and being washed with a small amount of alcohol, substance (2 g., 3.3%, m.p. about 106°) was obtained.

2-Phenylaminodiphenylketone. After neutralisation, the former crystallised from alcohol in colourless crystals, m.p. 121.5–122° (Found: N, 5.16. Calculated for $C_{19}H_{15}ON$: N, 5.13%). It dissolves easily in ether, benzene, and glacial acetic acid. Its hydrochloride melts with decomposition at 165–167° and is hydrolysed readily in water (Found: N, 4.59. Calculated for $C_{19}H_{15}ON \cdot HCl$: N, 4.52%).

2-Aminodiphenylketone. The latter was recrystallised from alcohol; yellow long hexagonal plates, m.p. 109–110°, were obtained (Found: N, 7.08. Calculated for $C_{13}H_{11}ON$: N, 7.11%). Its hydrochloride (colourless needles) dissolves easily in water and melts with decomposition at 179–180° (Found: N, 6.07. Calculated for $C_{13}H_{11}ON \cdot HCl$: N, 5.99%).

(c) **Condensation of 3-methyl-2-acetoanthranil with benzene.** *2-Phenylamino-3-methyldiphenylketone.* 3-Methyl-2-acetoanthranil (20.3 g.) was condensed with benzene (150 c.c.) in the presence of aluminium chloride (34.1 g.), and the subsequent treatment and the separation of the reaction product were carried out as in the case of acetoanthranil. In this case, 2-phenylamino-3-methyldiphenylketone (yield as hydrochloride, 5.6 g.), m.p. 123–123.5°, was only separated (Found: N, 4.88. Calculated for $C_{20}H_{17}ON$: N, 4.88%). Its hydrochloride melts with decomposition at 166–168–173° (Found: N, 4.54. Calculated for $C_{20}H_{17}ON \cdot HCl$: N, 4.33%).

(d) **Condensation of 5-methyl-2-acetoanthranil with benzene.** 5-Methyl-2-acetoanthranil (7.3 g.), benzene (50 c.c.), and aluminium chloride (15 g.) were boiled for 22 hours with constant stirring. On treating the reaction product as in the case of acetoanthranil, crude 2-phenylamino 5-methyldiphenylketone (1.9 g., 15.9%; m.p. 159–161°), and crude 2-amino-5-methyldiphenylketone (0.1 g., 1.1%) were separated.

2-Phenylamino-5-methyldiphenylketone. It crystallised from alcohol in colourless fine needles, m.p. 163.5° (Found: C, 83.47; H, 6.26; N, 4.74. Calculated for $C_{20}H_{17}ON$: C, 83.58; H, 5.97; N, 4.88%).

2-Amino-5-methyldiphenylketone (XX). After recrystallising from alcohol, it melted at 62–63°, and was proved to be identical with Chattaway and Lewis' 2-amino-5-methyldiphenylketone⁽²¹⁾, m.p. 64–64.5°.

(36) Miller and Meyer, *Ber.*, **24** (1891), 1914; "Beilsteins Handbuch," 3 Ed., II, 1333: m.p. 193–194°.

(e) The determination of constitution of 2-benzoyl-5 (or 4)-methylbenzoic acid (D)⁽³⁷⁾. 2-Amino-5-methyldiphenylketone, which was prepared by Chattaway and Lewis' method from *p*-toluidine and benzoyl chloride, melted at 64-64.5° (Found: N, 6.78. Calculated for C₁₄H₁₃ON: N, 6.58%). The diazotized solution of 2-amino-5-methyldiphenylketone (20 g.) was added to a well agitated potassium cuprous cyanide solution at 40°, the mixture was then boiled for about ten minutes, and an oily substance (α) (18 g.) was isolated by means of ether. On keeping a long time in a vacuum desiccator, a small amount of crystals, which melted at 189-190° after being recrystallised from benzene mixed with alcohol, was obtained (Found: N, 3.48. Calculated for C₂₈H₂₃O₂N⁽³⁸⁾: N, 3.46%). The oily substance, filtered from these crystals was distilled several times under reduced pressure; a clear, almost colourless, viscous oil, b.p. 192-195°/19 mm., which contained no nitrogen, was obtained.

The above-mentioned substance (α) was refluxed with 20% hydrochloric acid (10 parts) for 10 hours; a sticky substance thus obtained was extracted with ether, and the ethereal solution was treated with dilute aqueous ammonia. On acidifying the ammoniacal solution with hydrochloric acid, a very small amount of crude 2-benzoyl-4-methylbenzoic acid, m.p. 144-148°, was obtained. After recrystallising from acetic acid, it melted at 149-150°, and at 149-150° or at 130-138° when it was mixed with a specimen of 2-benzoyl-5-(or 4)-methylbenzoic acid (D)⁽³⁷⁾, m.p. 150-150.5°, or of 2-benzoyl-4-(or 5)-methylbenzoic acid (E)⁽¹⁷⁾, m.p. 145-145.5°. Therefore 2-methyl-5-(or 4)-methylbenzoic acid (D) should be 2-benzoyl-4-methylbenzoic acid.

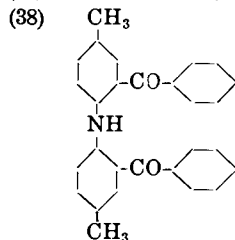
Diphenylketone-2,5-dicarboxylic acid, which was obtained from 2-benzoyl-4-methylbenzoic acid by oxidizing with potassium permanganate, melted at 291-292°.

(IV) Condensation of 3-Methylphthalic Anhydride with Phenol. Anhydrous aluminium chloride (20 g.) was added to a solution of 3-methylphthalic anhydride (10 g.) and phenol (7 g.) in acetylene tetrachloride (50 c.c.), and the mixture was heated at 130° until the evolution of hydrogen chloride had nearly ceased (about 3.5 hours). On repeated crystallisation from glacial acetic acid, two fractions were isolated from the part soluble in aqueous sodium carbonate. One melted at 212-217° (4.5 g.) and the other at 85-101° (8 g.).

2-(2'-Hydroxybenzoyl)-3-methylbenzoic acid (K). The former crystallised from acetic acid in colourless rhombic crystals (Found: C, 70.20; H, 4.89. Calculated for C₁₅H₁₂O₄: C, 70.29; H, 4.72%). It melts at 220-221° and dissolves in alkali to a faintly yellow solution.

2-(4'-Hydroxybenzoyl)-3-methylbenzoic acid (L). The latter was recrystallised three times from glacial acetic acid, a substance (3.4 g.), m.p. 195-197°, being separated. On further recrystallisation from glacial acetic acid, colourless plates, m.p. 197-198°, were

(37) *J. Chem. Soc.*, **1930**, 1518.



obtained (Found: C, 70.21; H, 4.84%). It dissolves in alkali to an almost colourless solution.

2-(2'-Hydroxybenzoyl)-6-methylbenzoic acid (K'). A solution of 2-(2'-hydroxybenzoyl)-3-methylbenzoic acid (0.8 g.) in sulphuric acid (100%, 10 c.c.) was kept for 15 hours at room temperature; on pouring the product into ice-water, a precipitate (0.74 g., m.p. 122-138°) separated. It crystallised from glacial acetic acid in faintly yellow prisms (0.5 g.) (Found: C, 70.49; H, 4.97%). It melts at 141-142° and dissolves in alkali to a faintly yellow solution.

2-(4'-Hydroxybenzoyl)-6-methylbenzoic acid (L'). After a solution of 2-(4'-hydroxybenzoyl)-3-methylbenzoic acid (0.9 g.) in 100% sulphuric acid (9 c.c.) had been kept for 15 hours at room temperature, the isolated product (0.84 g., m.p. 140-146.5°) crystallised from glacial acetic acid in colourless fine crystals, m.p. 183-184° (Found: C, 70.22; H, 4.95%). It dissolves in alkali to an almost colourless solution.

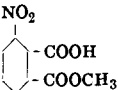
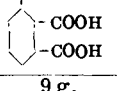
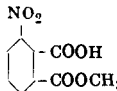
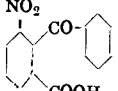
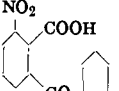
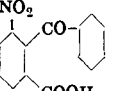
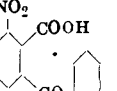
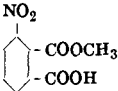
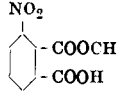
(V) **Condensation of 3-Methylphthalic Anhydride with Chlorobenzene.** 3-Methylphthalic anhydride (10 g.) was condensed with chlorobenzene (50 c.c.) in the presence of anhydrous aluminium chloride (20 g.). A substance (9.2 g.), m.p. 158-162°, was obtained from the part insoluble in ammonia and chlorobenzoyltoluic acid (10 g.), m.p. 162-169°, from the part soluble in ammonia. On recrystallising the latter from glacial acetic acid, faintly yellow 2-(4'-chlorobenzoyl)-3-methylbenzoic acid was obtained (Found: C, 65.43; H, 4.22. Calculated for $C_{15}H_{11}O_3Cl$: C, 65.56; H, 4.04%). It melts at 175.5-176°.

The authors have examined the ultra-violet absorption curves of alcoholic solutions of the above-mentioned substances (Table 5).

Table 5.

Substance	Maxima of absorption bands, Å	
1-Methyl-2,3-dibenzoylbenzene (A), m.p. 116-117°	2830,	2670
2-Benzoyl-3-methylbenzoic acid (B), m.p. 171-172°	2830,	2650
2-Benzoyl-6-methylbenzoic acid (C), m.p. 126.5-127.5°	2830,	2650
Diphenylketone-2,6-dicarboxylic acid (D), m.p. 255-256°	2820,	2650
Diphenylketone-2,3-dicarboxylic acid (E), m.p. 140-141° (foam.)	2820,	2650
1-Methyl 3-methylphthalate (F), m.p. 114.5-115°	2830,	2670
1-Ethyl 3-methylphthalate (G), m.p. 86-87°	2830,	2660
2-(2'-Hydroxybenzoyl)-3-methylbenzoic acid, m.p. 220-221° (K)	3300,	ca. 2500
2-(4'-Hydroxybenzoyl)-3-methylbenzoic acid, m.p. 197-198° (L)	2875	
2-(2'-Hydroxybenzoyl)-6-methylbenzoic acid, m.p. 141-142° (K')	3310,	ca. 2500
2-(4'-Hydroxybenzoyl)-6-methylbenzoic acid, m.p. 183-184° (L')	2880	
2-(2'-Hydroxybenzoyl)-benzoic acid, ⁽²⁷⁾ m.p. 171-171.5°	3310,	ca. 2500
2-(4'-Hydroxybenzoyl)-benzoic acid, ⁽²⁸⁾ m.p. 212-213°	2880	
2-(4'-Chlorobenzoyl)-3-methylbenzoic acid, m.p. 175.5-176°	ca. 2510	

Table 6.

 (g.)	 (c.c.)	AlCl ₃ (g.)	Conditions of condensation		Substance recovered from water solution.  (g.)	Precipitate (g.)	Fraction soluble in ammonia (γ)			Fraction insoluble in ammonia (β)	
			(°C.)	hrs.			 	 	 	 	
50	250	32.5	-80 boil	5 1/2 1/2	9 g. m.p. 206-209° (decomp.)	—	2.6 g. m.p. 148-158°	0.2 g. m.p. 200-210°	not isolated	4.6 g. m.p. 210-230°	not isolated
10	50	9	-70 boil	1 5	—	10.2	—	0.4 g. m.p. 220-224°	not isolated	combined	not isolated
10	120	6	55-60	6	—	10.8	—	not isolated			
14	100	17	-80 boil	1 5	—	—	—	0.2 g. m.p. 229-234°	not isolated	0.15 g. m.p. 210-230°	not isolated
10	50	6	-80 boil	1 5	—	—	—	0.1 g. m.p. 200-220°	not isolated	combined	not isolated
 							 				
20	200	24	-80 boil	1 4 1/2	—	—	—	0.2 g. m.p. 228-230°	3 g. (39) m.p. 155-160°	not isolated	
50	250	32.5	-80 boil	7 1/2	13.9 g. m.p. 207-215° (decomp.)	—	0.3 g. m.p. 134-140°	0.2 g. m.p. 225-230°	—	4.7 g. m.p. 223-230°	0.5 g. m.p. 148-152°
10	50	6	-80 boil	1 5	—	—	—	—	0.6 g. m.p. 146-158°	—	—

(39) On recrystallisation from glacial acetic acid, 2-benzoyl-6-nitrobenzoic acid (N) melted at 160-161° (Found: N, 5.38. Calculated for C₁₄H₉O₅N: N, 5.17%).

(VI) **Condensation of 3-Nitrophthalic Anhydride with Benzene.** 3-Nitrophthalic anhydride (50 g.) was dissolved in benzene (300 c.c.), aluminium chloride (75 g.) was added with constant stirring, and the mixture heated slowly and boiled in the course of 40 minutes. After 5 hours' boiling, the product was mixed with ice-water and, after the addition of hydrochloric acid (90 c.c.), distilled in steam. The residue was extracted with aqueous ammonia, the ammoniacal extracts were freed from ammonia, cooled, and the resinous substance that separated was removed. On acidification of the filtrate, a sticky precipitate (27.3 g.) separated. This substance was dissolved in glacial acetic acid and treated with animal charcoal, the substance (2 g.), m.p. 220–228°, thus obtained was recrystallised from glacial acetic acid; faintly yellow rhombic crystals (Found N, 5.27. Calculated for $C_{14}H_9O_5N$: N, 5.17%). 2-Benzoyl-3-nitrobenzoic acid (M) melts at 236–237°. When this acid was heated with 100% sulphuric acid (10 parts) at 100–105° for 45 minutes or kept for 17 hours at room temperature, no isomeric change occurred.

Condensation of acid chloride of 1- or 2-methyl 3-nitrophthalate with benzene. To a solution of acid chloride of 1- or 2-methyl 3-nitrophthalate in benzene, aluminium chloride was added, and the mixture boiled. On treating the product as usual, an insoluble part (β) in ammonia and an ammoniacal solution (γ) were obtained. The latter (γ) was boiled with animal charcoal, and acidified with hydrochloric acid; the resinous substance thus precipitated was recrystallised fractionally from acetic acid or purified by preparing its barium salt. The former (β) was extracted several times with boiling alcohol, and the alcoholic solution was boiled with 50% KOH solution. The fraction soluble in alkali was recrystallised fractionally from acetic acid. Their results are given in Table 6.

Diamide of 3-nitrophthalic acid. On treating acid chloride of 1-methyl 3-nitrophthalate (m.p. 97.5–99.5°)⁽⁴⁰⁾ or 2-methyl 3-nitrophthalate (m.p. 95–97°)⁽⁴¹⁾ with an excess of conc. ammonia and recrystallising from alcohol, colourless fine crystals were obtained in each case (Found: N, 20.21. Calculated for $C_8H_7O_4N_3$: N, 20.10%). They melt with decomposition at 204–204.5°⁽⁴²⁾.

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(40) *J. Chem. Soc.*, **109** (1916), 234: m.p. 97–99°.

(41) *J. Chem. Soc.*, **109** (1916), 234: m.p. 95–97°.

(42) *J. Am. Chem. Soc.*, **23** (1901), 747: m.p. 200–201° (decomp.).

ON THE DERIVATIVES OF ANTHRAHYDROQUINONE
DISULPHURIC ACID ESTERS. I. SYNTHESIS OF
SOME AZO-COMPOUNDS.

By Kenji IWAMOTO.

Received November 2nd, 1935. Published March 28th, 1936.

Bader and Vaucher⁽¹⁾ synthesised leuco-indigo disulphuric acid ester treating indigo white with pyridine salt of chlorosulphonic acid. Its alkali salt is stable and highly soluble in water. In acid solution, however, indigo is easily precipitated by the action of weak oxidising agents such as ferric chloride or sodium nitrite, due to the hydrolysis and oxidation taking place simultaneously. Inasmuch as fabrics may be dyed with indigo without the use of alkali, of the so-called Indigosol dyes belonging to this class, many are actually prepared. Schirmacher, Scharich, and Eishold⁽²⁾ synthesised the anthrahydroquinone disulphuric acid ester or its derivatives, by mixing anthraquinone or its derivatives with pyridine salt of chlorosulphonic acid, then reducing and esterifying the mixture by means of metallic powder. Moreover the fact that these compounds are soluble in water and easily oxidisable to the original quinone in acid solution has been utilized in many attempts in the field of dye-synthesis⁽³⁾. The present author synthesised the same compound and examined the properties.

Sodium salt of anthrahydroquinone disulphuric acid ester was readily prepared as yellow crystals by the method of German patent 473 471. But the isolation of alkali or alkaline earth salts of β -aminoanthrahydroquinone disulphuric acid ester proved unsuccessful owing to the great solubilities of salts. After many experiments, the author succeeded in isolating it in the form of diphenylguanidine salt. The latter is difficultly soluble in water, and may be purified by recrystallisation from alcohol in yellow crystals. On adding alkali, it is converted into the sodium salt, and free diphenylguanidine formed is removed by filtration.

Next, using this compound, the author synthesised some azo-dyes. The diazo-compound is readily prepared by the usual method as the compound is easily soluble in water. By coupling with α - and β -naphthol, dark, violet

(1) *Chimie & Industrie*, **1924**, 449.

(2) D. R. P. 473471.

(3) D. R. P. 461500, 472772, 470809, 476811.
E. P. 333506, 333507, 338891.

powders were obtained which dyed animal fibres in good colour in weak acid baths.

These dyed fabrics were reddish-violet and changed into scarlet by the action of hot ferric chloride solution. Dye from β -naphthol was pure scarlet.

Dye from α -naphthylamine was reddish-orange in alkaline solution and dyed the fibres scarlet. This turned bluish-violet with acid and again violet-red on oxidation. β -Naphthylamine derivative was also orange-red in alkaline solution and dyed the fibre reddish, which turned violet-red by the action of ferric chloride. But its shade did not come out as clear as in the case of α -derivative.

Experimental.

Sodium Salt of Anthrahydroquinone Disulphuric Acid Ester, $C_6H_4(COSO_3Na)_2C_6H_4$. Chlorosulphonic acid (8 g.) was slowly poured into pyridine (50 c.c.) cooled with ice. The mixture was then heated to 30° , anthraquinone (5 g.) was introduced in and the whole was heated to 65° . Copper powder ("Naturkupfer C") was then added in small quantities at a time with constant stirring, the temperature was raised to 70° and maintained for half an hour. After cooling, sodium hydroxide solution (10 g. NaOH) was poured in, pyridine was distilled over with steam, and the solution was filtered while hot. The filtrate was evaporated on the water-bath. On cooling, anthrahydroquinone disulphuric acid ester disodium salt was crystallised out. The yield of the crude product was 10.5 g. After two crystallisations from water, it separated in faintly yellow crystals. The solution showed violet fluorescence and anthraquinone was precipitated on treating the solution with ferric chloride. The solid salt is also unstable and decomposes into anthraquinone when it is kept in a bottle for some days or more rapidly when it is hot. In the above case, reduced iron powder or bronze powder was used as the reducing agent, but the treatment was not found effective.

Diphenylguanidine Salt of β -Aminoanthrahydroquinone Disulphuric Acid Ester, $C_6H_4(COSO_3H \cdot C_{13}H_{13}N_3)_2C_6H_3NH_2$. To well-cooled pyridine (200 c.c.) chlorosulphonic acid (48 c.c.) was added drop by drop with vigorous stirring, keeping the temperature below 5° . The salt thus obtained was warmed to 40° , β -acetaminoanthraquinone (26.5 g.) was introduced to the solution and the mixture was heated to 65° . To this suspended mixture, copper powder ("Naturkupfer C," 30 g.) was added gradually with constant stirring, while the temperature was maintained at 70° for an hour. At first the suspension was dissolved in yellow solution, and in a short time the whole was again crystallised to form a paste. After leaving overnight, the product was heated to 40° with stirring, and sodium hydroxide solution (90 g. NaOH in 300 c.c. of water) was slowly poured in until the product was dissolved. From the solution pyridine was removed by steam distillation and the copper salt was filtered off. The filtrate was cooled, 40 c.c. of hydrochloric acid was added and the brown precipitate was again removed by filtration. The solution was then neutralised with sodium bicarbonate and 400 c.c. of diphenylguanidine hydrochloride [$C_6H_5NH \cdot C(:NH) \cdot NHC_6H_5 \cdot HCl$] solution (10%) was poured in, when brown precipitate was deposited. The precipitate was collected, washed with water, and dried. Recrystallised three times from alcohol, lemon-yellow crystals were obtained. The yield was 65.5 g. after one crystallisation, 80% of the theoretical. The salt was dissolved in

hydrochloric acid and treated with ferric chloride while hot. Orange crystalline aminoanthraquinone was deposited (0.4681 g. of the salt gave 0.1294 g. aminoanthraquinone. Found: 27.94. Calculated: 27.64%).

The sodium salt was obtained as a solution by treating the diphenylguanidine salt with sodium hydroxide and filtering it. The solution was brownish-yellow with strong, green fluorescence.

Sodium Salt of Leuco- β -anthraquinone-azo- α -naphthol Disulphuric Acid Ester, $C_6H_4(COSO_3Na)_2C_6H_3N:NC_{10}H_6OH(4)$. Aminoanthrahydroquinone sulphuric acid ester diphenylguanidine salt (8.1 g., 1/100 mol) was changed into sodium salt by treating with caustic soda solution (3 g. NaOH in 30 c.c. of water), filtering, and washing with water. The yellow solution (80 c.c.) was then cooled to 0° , 10 c.c. of hydrochloric acid was added and diazotised by dropping sodium nitrite solution (0.69 g. in 7 c.c. of water). The diazo-compound was not easily soluble in water and formed carmine-red precipitate. α -Naphthol (1.45 g., 1/100 mol) with sodium hydroxide (4 g.) was dissolved in 80 c.c. of water, and to this cold solution the above diazo-solution was poured in as a thin stream with constant stirring. A violet solution obtained was stirred for two hours more and heated to 80° for an hour. This was filtered and salted out with sodium chloride and sodium bicarbonate. The dark-violet, amorphous powder was collected, washed with salt solution, and dried. It gave a deep-reddish-violet solution and dyed the animal fibre violet-red in a weak acid-bath. This colour of the dyed fabrics may be changed red by oxidation with hot ferric chloride and hydrochloric acid, but the colour shade of this changed dye is not so fine as that of the β -isomer.

Sodium Salt of Leuco- β -anthraquinone-azo- β -naphthol Disulphuric Acid Ester, $C_6H_4(COSO_3Na)_2C_6H_3N:NC_{10}H_6OH(2)$. Diazotisation and coupling were carried out similarly to the above case. On salting out the dye with sodium chloride, violet precipitate was formed. This was collected, washed with salt solution, and dried. It was very soluble in water and produced a violet-red solution. Silk was dyed violet-red from its weak acid-bath, the colour was changed into bright-scarlet when oxidised with ferric chloride solution. The solution also gives a scarlet precipitate by the action of ferric chloride. The latter was recrystallised from tetraline, from which it separated in scarlet needles, m.p. 262° . The product thus obtained is β -anthraquinone-azo- β -naphthol. Kaufler⁽⁴⁾ and Maki⁽⁵⁾ synthesised the same substance from β -diazoanthraquinone and β -naphthol, and gave m.p. 262° .

Sodium Salt of Leuco- β -anthraquinone-azo- α -naphthylamine Disulphuric Acid Ester, $C_6H_4(COSO_3Na)_2C_6H_3N:NC_{10}H_6NH_2(4)$. Diphenylguanidine salt (8.1 g., 1/100 mol) was treated with sodium hydroxide solution and the solution of sodium salt (80 c.c.) was acidified with 10 c.c. of hydrochloric acid. This was cooled well and diazotised with sodium nitrite solution until the reaction was complete when tested with potassium-iodide-starch-paper. α -Naphthylamine (1.43 g., 1/100 mol) was dissolved in hot solution of hydrochloric acid (3 c.c. in 80 c.c. of water) and cooled rapidly. To this suspension of hydrochloride, the above diazo-solution was poured in and the sodium acetate solution (20 g. in 30 c.c. of water) was added gradually with vigorous mixing. The stirring was continued for 3 hours and the mixture became brownish. On standing overnight, it was heated to 80° for an hour and made alkaline with sodium hydroxide solution. From the filtered solution, a brownish-red precipitate was produced by salting out with sodium

(4) *Chem. Zentr.*, **1904**, I, 289.

(5) *J. Soc. Chem. Ind., Japan*, **32** (1929), 348 B.

chloride. This was collected and washed with sodium chloride solution. This substance is brownish-red in aqueous solution but in acid solution the colour changed to violet, and dyed the animal fibre deep-violet in weak acid-bath. It was changed reddish-violet by the action of oxidising agent.

Potassium Salt of Leuco- β -anthraquinone-azo- β -naphthylamine Disulphuric Acid Ester, $C_6H_4(COSO_3K)_2C_6H_3N:NC_{10}H_6NH_2(2)$. This dye was synthesised similarly to the above case. As its sodium salt was very viscid, the coupled solution was made alkaline with potassium hydroxide when a deep-scarlet solution was obtained. It was filtered and salted out with potassium chloride as brownish-red powder, which was collected and washed with a solution of the same salt. It dyes the fibre orange-red and turns violet-red by oxidation. Its shade is somewhat not clear.

In conclusion, the author wishes to express his gratitude to Prof. R. Majima for his valuable suggestions, also to Dr. T. Ogata and Dr. M. Nakanishi for their kind advices. Moreover, the author's appreciation is expressed to the Nippon Gakujutu-Sinkokai for a grant toward this research.

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ÜBER DIE KATALYTISCHE HYDRIERUNG VON ROHRZUCKER.
I. HYDRIERUNG VON ROHRZUCKER MIT REDUZIERTEM
NICKEL ALS KATALYSATOR.

Von Tsuneharu TANNO.

Eingegangen am 2. November 1935. Ausgegeben am 28. März 1936.

Der Zweck dieser Untersuchung war darauf gerichtet, dass die Einwirkung von Hochdruck-Wasserstoff auf dem Rohrzucker selbst [ohne Inversion, d.h. das den Brückensauerstoff enthaltende Rohrzuckermolekül oder α -*D*-Glukopyranosido-*D*-Fruktofuranosid], in Gegenwart von Katalysator, festgestellt würde. Dabei wurden die Bedingungen, die Mechanismen und die Produkten der Reaktion von Wasserstoff auf dem Rohrzuckern versucht. Als Katalysator wurde erst das reduzierte Nickel genommen.

Die Berichte über die katalytische Hydrierung der Disaccharide bei den hohen Temperaturen und Drucken werden erst von Ipatiew⁽¹⁾ und in dieser Zeit von Adkins⁽²⁾ und Yoshikawa⁽³⁾, ausser einigen Patentbeschreibungen⁽⁴⁾,

(1) Wl. Ipatiew, *Ber.*, **45** (1912). 3226.

(2) H. Adkins u. W. H. Zartmann, *J. Am. Chem. Soc.*, **55** (1933). 4559.

(3) K. Yoshikawa, *Bull. Inst. Phys. Chem. Research, Japan*, **13** (1934), 1045. J.P. 106376 (1934).

(4) C.C. Fowler, U.S.P. 1493623 (1924). I.G. Farbenind., A-G., D.R.P. 541326 (1927); E.P. 299373 (1928); F.P. 622873 (1928).

nur bekannt gemacht. Der Bericht von Adkins und der von Yoshikawa sind im Laufe dieser Arbeit in die Öffentlichkeit gegangen.

Hier berichte ich nur kurz über die Hauptpunkte dieser Versuche und möchte in späteren Zeiten im Detail erklären.

I. Die Wirkung des Hochdruck-Wasserstoffs gegen den Rohrzucker. Der Rohrzucker unter Suspendierung in Dekalin wurde mit dem reduzierten Nickel-Katalysator und etwa 100 Atm. Wasserstoff im Autoklav erhitzt, da zeigt es sich, dass die Wirkung des Wasserstoffs gegen den Rohrzucker, sich in zwei Stufen teilend, sich entwickelt. Nämlich die Wirkung in erster Stufe verläuft bei 155–175° verhältnismässig schnell und ging zum Reaktionsende in einigen Stunden (erste Reaktion), die in zweiter Stufe verläuft bei etwa 225° auffallend langsam und endet nach 20 Stunden (zweite Reaktion).

II. Die erste Reaktion und die Reaktionsprodukte. Bei der ersten Reaktion gibt es zwei Reaktionsfälle. In einem Falle nimmt ein Rohrzucker-molekül etwa drei Wasserstoffmolekülen bei 170–175° bis zum Ende der Reaktion (Reaktion-A), in anderem Falle nimmt es bei 155–160° etwa zwei Wasserstoffmolekülen bis zum Ende der Reaktion (Reaktion-B).

In beiden Reaktionsfällen verändert sich das Anfangsmaterial (Rohrzucker) so genau dass fast kein Rohrzucker so wie reduzierender Zucker im Reaktionsprodukte gefunden werden.

Aus dem Produkte der Reaktion-A oder -B wurden *d*-Mannit und *d*-Sorbit in der gleichen Menge erhalten und die Gesamtmenge dieser beiden Hexiten entsprach der Hälfte des gebrauchten Rohrzuckers.

Aus dem Produkte der Reaktion-A wurde ein neues Methylpentit⁽⁵⁾ d.i. *l*-Gulomethylit, $C_6H_{14}O_5$, Siedp. 182–183°, $[\alpha]_D^{25} = +2.04$ (in Wasser, 2.46%) gefunden.

Bei der Reaktion-B bildet sich kein *l*-Gulomethylit und nach der Abscheidung des Mannits und Sorbits von dem Reaktionsprodukte bleibt eine harzige Substanz hinter, welche schon unter den Bedingungen der Reaktion-B nicht mit Wasserstoff wirksam ist, aber unter den Bedingungen der Reaktion-A durch zweimalige Wirkung von Wasserstoff *l*-Gulomethylit gibt.

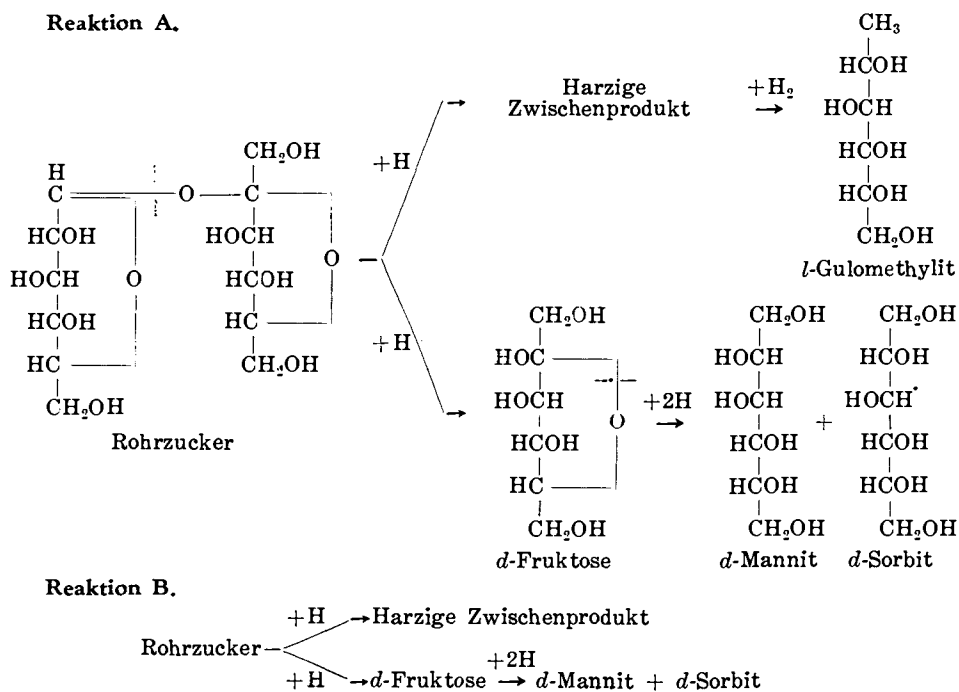
Wenn man den Fruchtzucker unter den Bedingungen der Reaktion-A mit Wasserstoff wirken lässt, so geht die Hydrierung des Fruchtzuckers sehr schnell vonstatten und aus den Produkten dieser Reaktion werden leicht *d*-Mannit und *d*-Sorbit gewonnen, aber es gibt kein *l*-Gulomethylit. Dabei zeigt es sich, dass Gulomethylit nicht aus den Fruktosidradikalen des Rohrzuckermoleküls, sondern aus dem Glukosidradikalen hergestellt worden ist.

(5) E. Votoček u. F. Valentin, *Bull. soc. chim.*, **43** (1928), 216; E. Votoček u. J. Mikšič, *ibid.*, **43** (1928), 220; E. Votoček u. F. Valentin, *Collect. trav. chim. Tchéco.*, **2** (1930), 36; E. Votoček u. V. Kučerenko, *ibid.*, **2** (1930), 47.

Mit anderen Worten, bei der Reaktion-A wirkt ein Rohrzuckermolekül mit etwa drei Wasserstoffmolekülen und dabei werden die gleiche Mengen von *d*-Mannit und *d*-Sorbit (jeder, dem Vierteln der gebrauchten Zuckermengen entsprechend) und *l*-Gulomethylit hergestellt. Aber bei der Reaktion-B, wirkt ein Rohrzuckermolekül mit etwa zwei Wasserstoffmolekülen und dabei entstehen die gleiche Mengen von *d*-Mannit und *d*-Sorbit, wie bei der Reaktion-A, und ein Zwischenprodukt welche unter den Bedingungen von Reaktion-A wieder mit Wasserstoff wirkend *l*-Gulomethylit erzeugen kann.

III. Mechanismus der ersten Reaktion. Von hier gewonnene Experimentresultate zeigt es sich, dass der Mechanismus der ersten Reaktion, bei der hydrogenolytische Hydrierung des Rohrzuckers in Anwesenheit von reduzierten Nickel-Katalysator unter der hohen Temperatur und Wasserstoffdrucken, ist wie folgend (Diagramm 1.) :

Diagramm 1. Mechanismus der ersten Reaktion.



Diese Resultate zeigen auch, dass die Hydrierung des Rohrzuckers, wie die Fälle seiner Hydrolyse erst an dem Brückensauerstoff und dann an dem Furanring und Pyranring stattgefunden werden, und vielleicht, dass der Furanring leichter als Pyranring gespalten wird.

IV. **Darstellung des Katalysators.** Da die Herstellungsverfahren des reduzierte Nickel-Katalysators auf seiner Fähigkeit charakteristischen Einfluss ausübt, es wird in besonderer Darstellungsvorrichtung (Fig. 1) vorsichtig hergestellt, um den Katalysator möglichst von einheitlichen Fähigkeiten zu gewinnen.

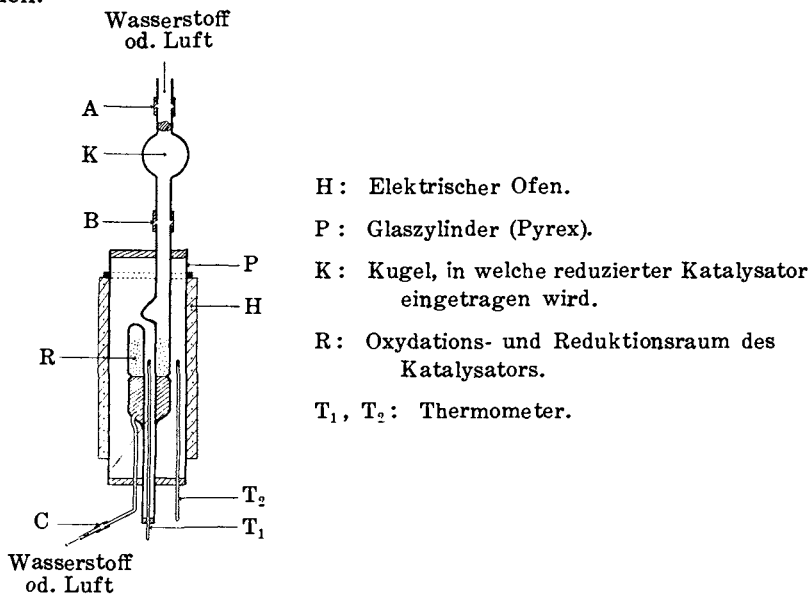


Fig. 1. Darstellungsvorrichtung des Katalysators.

Diese Vorrichtung ist dadurch gekennzeichnet, dass der Katalysator bei der einheitlichen Temperatur oxydiert und reduziert werden kann und der reduzierte Katalysator ohne Berührung nach die Luft und verhältnismässig einfach in Gebrauch gebracht werden kann.

Katalysatorpulver, welche in den Räumen R reduziert worden ist, wird in die Kugel K eingetragen und dann wird sie an beiden Enden (A und B) geschmolzend eingeschlossen. Auf dieser Weise wird der in Glaskugel eingeschlossene, reduzierte Nickel-Katalysator fertiggemacht.

Zum Schluss möchte ich Herrn Prof. Dr. R. Majima für die freundlichen Ratschläge und Herrn T. Hara für die eifrigen Hilfen meinen herzlichsten Dank aussprechen.

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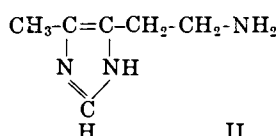
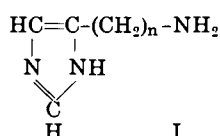
Anmerkung am 17. Februar: Nach nochmaligen Versuche wurde festgestellt dass die als *l*-Gulomethylit betrachtete Flüssigkeit ein Gemisch von Propylenglykol und Glycerin ist.

SYNTHESE VON IMIDAZOLDERIVATEN AUS
 α -AMINOSÄUREN. III. SYNTHESE VON
 ZWEI HÖHEREN HOMOLOGEN
 DES HISTAMINS.⁽¹⁾

Von Shiro AKABORI und Takeo KANEKO.

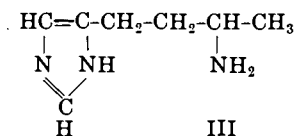
Eingegangen am 4. November 1935. Ausgegeben am 28. März 1936.

Seitdem es bekannt geworden ist, dass Histamin (bei $n = 2$) beträchtliche physiologische Wirkungen ausübt, wurden dessen verschiedene Derivate und Homologe auf synthetischen Wege dargestellt. Davon hat das von Ewins⁽²⁾ gewonnene 5-Methyl-histamin (II) etwas ähnliche physiologische Wirkungen wie Histamin, während die andern weitaus schwächere Wirkungen haben.



Wie man aus den Literaturen ersieht, verändern sich wahrscheinlich seine physiologischen Wirkungen merklich, wenn man seine Struktur nur ein wenig verändert. Wir glauben, es würde interessant sein, weiter zu forschen, in welcher Beziehung die Grösse von n in 4-(ω -Aminoalkyl)-imidazol, die die allgemeine Formel wie I hat, zu der physiologischen Wirkung steht. Von solchen Imidazolderivaten ist nur Imidazolyl-methylamin (bei $n = 1$) bekannt; die Verbindungen mit n von mehr als 3 sind noch nicht zur Synthese gekommen.

Pyman⁽³⁾ wollte die physiologische Wirkung von Imidazolyl-propylamin (bei $n = 3$) kennen lernen, aber da die Synthese dieser Verbindung Schwierigkeit bietet, bereitete er ihr Methylderivat, nämlich 1-Imidazolyl-3-aminobutan (III). Diese Verbindung dürfte aber zum Vergleich mit



Histamin ungeeignet sein, da seine Aminogruppe an sekundären Kohlenstoff gebunden ist.

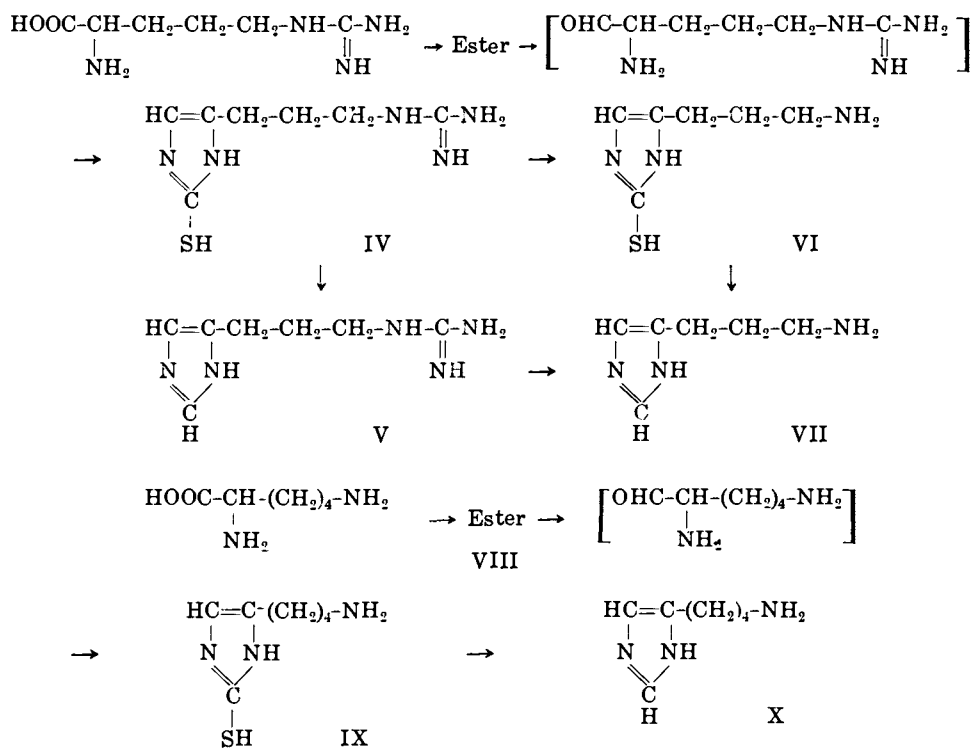
Nach Pyman⁽³⁾ haben sowohl Imidazolyl-methylamin als auch 1-Imidazolyl-3-aminobutan eine viel schwächere Wirkung (Erregungswirkung auf glatte

(1) II. Mitt., *Ber.*, **66** (1933), 159.

(2) *J. Chem. Soc.*, **99** (1911), 2052.

(3) *J. Chem. Soc.*, **111** (1917), 1125. van der Merwe, *Z. physiol. Chem.*, **117** (1928), 301.

Muskeln) als Histamin. Es ist aber oft zu beobachten, dass, wenn man in den Verbindungen, die eine kettenförmige Atomgruppe haben, die Atomzahl der Kette sukzessiv vermehrt, verschiedene Eigenschaften der Verbindungen um je ein Atom, steigend und fallend, periodisch verändert werden. Auch im bezug auf die Verbindungen, die eine allgemeine Formel wie I haben, ohne Rücksicht auf die Wirkungen aller Fälle, wo $n = 1-4$ beträgt, wird man deshalb über die Beziehung der chemischen Konstitution zu den physiologischen Wirkungen keinen endgültigen Schluss ziehen können. Deshalb versuchten wir γ -Imidazolyl-propylamin (bei I $n = 3$) und δ -Imidazolyl-butylamin (bei I $n = 4$) synthetisch darzustellen und ihre physiologischen Wirkungen mit denen des Histamins zu vergleichen. Zur Synthese wandten wir die in I. und II. Mitteilungen⁽⁴⁾ beschriebenen Methoden auf Arginin und Lysin an und konnten auf folgendem Wege zum Ziele gelangen.



Bezüglich VII und X versuchten wir ihre Wirkung auf den Uterus und Darm eines nicht schwangeren Kaninchens festzustellen. Dabei zeigte das

(4) Ber., **66** (1933), 153, 159.

erstere eine ziemlich starke Erregungswirkung, die aber schwächer als die des Histamins ist, und das andere nur eine äusserst schwache. (Diese physiologische Untersuchung wurde von Dr. T. Takase, dem Dozent im pharmakologischen Institut der Kaiserlichen Universität zu Sendai vorgenommen. An dieser Stelle sagen wir ihm für seine Güte unseren besten Dank.)

Wegen geringeren Probestoffes konnten wir keinen genauen Versuch machen, aber es ist wohl sicher, dass sich die eigentümliche starke Erregungswirkung von Histamin auf glatte Muskeln dann plötzlich vermindert, wenn n in Formel I auf 1 abnimmt oder auf mehr als 3 zunimmt, nicht aber periodisch verändert.

Experimenteller Teil.

Arginin-äthylester-dichlorhydrat. Das durch Zersetzung von 29.5 g. Arginin-flavianat durch Salzsäure erhaltene sirupöse Arginin-dichlorhydrat wird mit 350 c.c. 3.5% Chlorwasserstoff enthaltenem absolutem Alkohol 3.5 Stunden gekocht, 70 c.c. Benzol hinzugefügt, erst unter normalen Druck destilliert, bis Benzol fast abdestilliert ist, und dann unter vermindertem Druck zum Sirup konzentriert. Das so erhaltene Arginin-äthylester-dichlorhydrat kann man nicht kristallinisch erhalten. Deshalb löst man es in absolutem Alkohol, bis das Volum von 45 c.c. hat und gebraucht davon je 15 c.c. für folgende Versuche.

2-Mercapto-4-(ω -guanidinopropyl)-imidazol (IV). 15 c.c. alkoholische Lösung von Arginin-äthylester-dichlorhydrat (entsprechen 3.5 g. Arginin) wird in 25 c.c. kaltem Wasser gelöst, durch Kältemischung auf -12 bis -17° abgekühlt, unter tüchtigem Rühren 120 g. 2.3% Natriumamalgam langsam eingeworfen, während 23 c.c. 5N Salzsäure dazu getropft wird, um die Lösung sauer zu halten.

Die Reaktionsflüssigkeit wird von Quecksilber getrennt, filtriert, unterhalb 50° unter vermindertem Druck destilliert und solange konzentriert, bis das Kochsalz sich auszuscheiden beginnt. 4.5 g. Ammoniumrhodanid wird dazu gefügt, und auf dem Wasserbad zur Trockne eingedampft. Wird der Rückstand mit 100 c.c. absolutem Alkohol gekocht, unlösliche Substanz abfiltriert und aus dem Filtrat Alkohol abdestilliert, so bleibt eine sirupöse Substanz zurück. Wird sie in ein wenig Wasser gelöst und eine gesättigte wässrige Lösung von Quecksilberchlorid im Überschuss zugefügt, so scheidet sich ein harziger Niederschlag aus.

Der Niederschlag wird in heissem Alkohol gelöst, nach gewöhnlicher Weise mit Schwefelwasserstoff zersetzt, von Quecksilbersulfid abfiltriert und das Filtrat eingedampft. Die zurückbleibende sirupöse Substanz wird im warmen Butylalkohol gelöst und von unlöslicher anorganischer Substanz abfiltriert. Wird das Filtrat unter vermindertem Druck zum Sirup konzentriert und stehen gelassen, so scheiden sich hellgelbe sandige Kristalle (0.7 g.) aus, die bei $218-223^{\circ}$ unter Aufschäumen und Bräunung schmelzen. Das aus Essigsäure zweimal umkristallisierte farblose Produkt beginnt sich bei ungefähr 220° zu bräunen, schmilzt bei $236.5-237.5^{\circ}$ unter Aufschäumen und wird nach beendetem Aufschäumen zu einer braunen durchsichtigen Flüssigkeit (Gef.: N, 27.72, 28.34; Cl, 14.10; S, 13.12. Ber. für $C_7H_{13}N_5S \cdot HCl$: N, 29.72; Cl, 15.04; S, 13.61%).

Die Analysenwerte sind etwas niedriger, als man sie für $C_7H_{13}N_5S \cdot HCl$ berechnete, aber die Hünnersche Farbenreaktion für 2-Mercaptoimidazol ist stark positiv und es

entwickelt sich Ammoniak wenn man es mit Bariumhydroxyd kocht. Daraus kann man die erhaltene Substanz wohl als die gewünschte ansehen.

γ -Imidazolyl-propyl-guanidin (V). 0.3 g. Hydrochlorid von IV wird in 10 c.c. Wasser gelöst, dazu 2 g. Eisenchlorid in 10 c.c. Wasser hinzugefügt, das ganze auf dem Wasserbad 1 Stunde erhitzt und mit 20 g. Phosphorwolframsäure in 20 c.c. Wasser versetzt, wobei sich ein weisser feinpulveriger Niederschlag ausscheidet.

Da die Filtration schwierig ist, wird der Niederschlag durch Zentrifugieren getrennt, mit 5% Schwefelsäure gewaschen, wiederum durch Zentrifugieren getrennt, dann mit 10 g. Bariumhydroxyd in Mörser gut verrieben und nach Zusatz von Wasser filtriert. Wird in das Filtrat genügend Kohlensäure eingeleitet, Bariumcarbonat abfiltriert und das Filtrat auf dem Wasserbad konzentriert, so bleibt eine starke alkalische Substanz zurück. Wird diese in ein wenig Wasser gelöst, 0.7 c.c. 5 N Salpetersäure hinzugefügt und das ganze mit Eis gekühlt, so scheidet sich Imidazolyl-propyl-guanidin-dinitrat in weissen Kristallen aus. Zur Reinigung kristallisiert man sie aus Wasser zweimal um. Schmp. 183.5–184° (Bräunung und Aufschäumen). Die Analysenwerte stimmen mit Imidazolyl-propyl-guanidin-dinitrat überein (Gef.: N, 33.68. Ber. für $C_7H_{13}N_5 \cdot 2HNO_3$: N, 33.45%).

Wird zur Mutterlauge obiges Dinitrats eine Lösung von 0.4 g. Pikrinsäure in 100 c.c. heissem Wasser hinzugefügt, so scheiden sich gelbe Kristalle aus (0.1 g.). Aus Wasser umkristallisierte Kristalle schmelzen bei 258° unter Zersetzung. Das Flavianat stellt in Wasser schwerlösliche orangerote Kristalle dar, die bei 248° unter Zersetzung schmelzen.

γ -Imidazolyl-propylamin (VII). Zu Überführung von 2-Mercapto-4-(ω -guanidino-propyl)-imidazol (IV) in 2-Mercapto-imidazolyl-propylamin (VI) wird 0.2 g. Chlorhydrat des ersten mit einer Lösung von 0.8 g. kristallinen Bariumhydroxyd in 20 c.c. Wasser versetzt, nach mehrstündigen Kochen Kohlensäure eingeleitet, Bariumcarbonat abfiltriert und das Filtrat zur Trockne eingedampft, wobei eine geringe Menge sirupöse Substanz zurückbleibt. Wird eine kleine Menge davon ins Reagenz-glas genommen und der Hunderschen Reaktion unterworfen, so wird eine tiefrote Farbe erzeugt. Durch diese Farbenreaktion lässt sich vermuten, dass ein Teil des Mercapto-imidazolylderivats schon seine Mercaptogruppe verlor. Wir verzichteten darauf, 2-Mercapto-imidazolylpropylamin zu isolieren.

Die sirupöse Substanz wird in ein wenig Wasser gelöst, eine Lösung von 1.4 g. Eisenchlorid in 5 c.c. Wasser hinzugefügt, eine Stunde auf dem Wasserbad erhitzt und dann 50% Lösung von Phosphorwolframsäure hinzugefügt, wobei sich ein weisser Niederschlag ausscheidet. Dieser wird abfiltriert, mit 5% Schwefelsäure gewaschen, mit einer Lösung von 2 g. Bariumhydroxyd in 10 c.c. Wasser versetzt und nach kurzem Kochen filtriert. Das Filtrat wird durch Einleiten von Kohlensäure von Ba befreit, auf dem Wasserbad konzentriert, eine Lösung von 0.5 g. Pikrinsäure in 20 c.c. heissem Wasser hinzugefügt, wobei sich gelbe Kristalle in Nadeln ausscheiden, Ausbeute 0.2 g., 95% der Theorie. Die erst aus Alkohol und dann aus Wasser umkristallisierte Kristalle schmelzen bei 244–244.5° (unter Bräunung und Aufschäumen). Die Analysenwerte stimmen mit Imidazolyl-propylamin-dipikrat $C_6H_{11}N_3 \cdot 2C_6H_3O_7N_3$ überein (Gef.: C, 37.39; H, 3.20; N, 21.58. Ber. für $C_6H_{11}N_3 \cdot 2C_6H_3O_7N_3$: C, 37.04; H, 3.01; N, 21.62%).

γ -Imidazolyl-propylamin lässt sich auch durch Hydrolyse von γ -Imidazolyl-propyl-guanidin (V) darstellen.

0.2 g. Dinitrat von V und 2 g. kristallinisches Bariumhydroxyd werden in 5 c.c. Wasser gelöst, nach 2 stündigen Kochen mit Wasser verdünnt, genügend Kohlensäure eingeleitet, Bariumcarbonat abfiltriert, das Filtrat durch Schwefelsäure angesäuert, eine Lösung von Phosphorwolframsäure hinzugefügt, wobei sich ein weißer Niederschlag bildet. Dieser Niederschlag wird abfiltriert, durch Bariumhydroxyd zersetzt, von Barium völlig befreit und eine Lösung von 0.5 g. Pikrinsäure in 20 c.c. heissem Wasser hinzugefügt, wo sich gelbe Kristalle (0.25 g.) ausscheiden. Die aus Alkohol einmal und aus Wasser zweimal umkristallisierte Kristalle schmelzen bei 243–244° (unter Aufschäumen und Bräunung) die mit dem auf vorhergehende Weise bereiteten Präparat identisch sind.

Lysin-äthylester-dichlorhydrat (VIII). Wird 3.7 g. Lysin-dichlorhydrat (0.02 Mol) in 100 c.c. 3% Chlorwasserstoff enthaltendem absolutem Alkohol suspendiert und auf dem Wasserbad gekocht, so lösen sich seine Kristalle langsam auf. Nach 3 stündigem Kochen wird 20 c.c. Benzol hinzugefügt, zunächst unter normalem Druck etwa 60 c.c. destilliert und dann unter vermindertem Druck unterhalb 45° Alkohol fast vollständig abdestilliert. Wird zurückbleibende sirupöse Ester wieder in 15 c.c. Alkohol gelöst und im Eisschrank stehen gelassen, so scheiden sich weisse Kristalle aus (3.1 g.). Zur Reinigung werden sie in absoluten Alkohol gelöst und durch Zusatz von Äther ausgeschieden. Schmp. 143.5–144.5° (Aufschäumen). Sie sind hygroskopisch.

$[\alpha]_D^{25} = +11.69$ (0.0496 g. Subst. in 2 c.c. Alkohol). (Gef.: N, 11.49, 11.06. Ber. für $C_8H_{18}N_2O_2 \cdot 2HCl$: N, 11.34%.)

δ -(2-Mercapto-imidazolyl)-butylamin (IX). 3.7 g. Lysin-äthylester-dichlorhydrat wird in 15 c.c. Alkohol und 25 c.c. eiskaltem Wasser gelöst, durch Kältemischung auf –10 bis –15° abgekühlt und durch 120 g. 2.3% Natriumamalgam und 23 c.c. Salzsäure auf dieselbe Weise wie bei Arginin-äthylester reduziert.

Die Reaktionsflüssigkeit wird unterhalb 50° unter vermindertem Druck konzentriert, bis Kochsalz sich auszuscheiden beginnt, nach Zusatz von 4.7 g. Ammoniumrhodanid etwas erwärmt, über Nacht stehen gelassen und dann auf dem Wasserbad zur Trockne verdampft. Wird das so erhaltene Reaktionsprodukt mit 100 c.c. absolutem Alkohol erwärmt, nach dem Erkalten unlösliche anorganische Substanz abfiltriert und aus dem Filtrat Alkohol abdestilliert, so bleibt eine sirupöse Substanz zurück. Wird sie in ein wenig Wasser gelöst, nach Entfärben mit Kohle wieder konzentriert und dann 50% Kaliumcarbonat Lösung im Überschuss hinzugefügt, so scheidet sich ein weißer kristallinischer Niederschlag aus. Dieser wird abfiltriert, mit ein wenig Wasser gewaschen und getrocknet. Ausbeute 0.9 g., 26% der Theorie.

Aus Wasser wiederholt umkristallisiert, werden farblose Kristalle in Nadeln gewonnen. Schmp. 220.5–221.5° (Rötung). Wird bei der Reduktion Essigsäure statt Salzsäure benutzt, so erhält man doch ungefähr dasselbe Resultat. (Gef.: C, 48.67; H, 7.87; S, 18.05, 18.21; N, 23.85. Ber. für $C_7H_{13}N_3S$: C, 49.07; H, 7.65; S, 18.73; N, 24.55%.) 0.0849 g. Subst. wird in ein wenig Wasser gelöst und mit 0.0605 N Salzsäure titriert. Zur Neutralisierung benötigt man 8.1 c.c.; Ber. für $C_7H_{13}N_3S$ (einwertig): 8.2 c.c.

Hydrochlorid. Aus Wasser-haltigem Butylalkohol umkristallisiert, Schmp. 212–214° (Rötung und Aufschäumen).

Pikrat. Schmp. 154–155° (Aufschäumen).

δ -Imidazolyl-butylamin (X). 0.85 g. δ -(2-Mercapto-imidazolyl)-butylamin (IX) wird in 20 c.c. Wasser und 2.5 c.c. 2 N Salzsäure gelöst, dazu eine Lösung von 6.8 g. Eisenchlorid in 30 c.c. Wasser hinzugefügt, auf dem Wasserbad 40 Minuten erhitzt und dann

eine 50% wässrige Lösung von 25 g. Phosphorwolframsäure hinzugegeben, wobei sich ein weisser pulveriger Niederschlag bildet.

Da dieser feinpulverige Niederschlag schwer zu filtrieren ist, so wird er durch Zentrifugieren getrennt, mit 5% Schwefelsäure gewaschen und wieder zentrifugiert. Er wird dann in Wasser suspendiert, unter Zusatz von 35 g. kristallinischem Bariumhydroxyd auf dem Wasserbad erhitzt, nach dem Erkalten filtriert, in das Filtrat genügend Kohlensäure eingeleitet, ausgeschiedener Niederschlag von Bariumcarbonat abfiltriert und das Filtrat auf dem Wasserbad konzentriert. Wird es wieder mit Salzsäure angesäuert und zur Trockne eingedampft, so bleibt kristallinisches Hydrochlorid zurück. Da dieses aber sehr hygroskopisch ist, so wird es in ein wenig Wasser gelöst und eine 50% Lösung von Kaliumcarbonat im Überschuss hinzugefügt, wobei eine ölige, stark nach Diamin riechende Substanz ausscheidet. Wird diese ölige Substanz mit alkoholhaltigem Äther mehrmal ausgezogen, die ätherische Lösung mit Natriumsulfat getrocknet und das Lösungsmittel vollständig herausgedrängt, so erstarrt sie beim Stehen allmählich zu einer kristallinen Masse. 0.9 g. Rohprodukt wird unter vermindertem Druck destilliert und 0.6 g. Destillat vom Sdp. $204^{\circ}/6$ mm. gewonnen. Es ist anfangs ölig, wird aber beim Stehen gänzlich zu einer kristallinen Masse. Schmp. $51-53^{\circ}$.

Da das Umkristallisation schwierig ist, so wird das destillierte Produkt bei Zimmertemperatur unter vermindertem Druck über Kaliumhydroxyd aufbewahrt und dann analysiert (Gef.: C, 59.05; H, 8.53; N, 29.13. Ber. für $C_7H_{13}N_3$: C, 61.79; H, 9.64; N, 30.09%). Die Analysenwerte sind erheblich niedriger, als die berechneten. Das kommt aber vielleicht daher, dass ein Teil sich während des Wiegens in Karbonat verwandelte.

Bioxalat. 0.144 g. durch Destillation gereinigtes Imidazolybutylamin und 0.31 g. Oxalsäure werden in 1 c.c. Wasser gelöst und nach geringerem Erwärmen Aceton hinzugefügt. Dabei scheiden sich weisse Nadeln aus. Das aus wasserhaltigem Aceton umkristallisierte Produkt schmilzt bei $168.5-170^{\circ}$ unter Aufschäumen (Gef.: C, 41.46; H, 5.38, N, 13.23, 12.94. Ber. für $C_7H_{13}N_3 \cdot 2C_2H_2O_4$: C, 41.36; H, 5.37; N, 13.17%).

Dipikrat. Aus Wasser scheidet sich in gelben Nadeln aus. Schmp. $197.5-198.5^{\circ}$ (Lösung und Aufschäumen).

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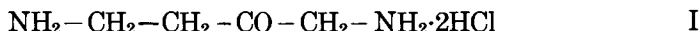
SYNTHESE VON IMIDAZOLDERIVATEN AUS α -AMINOSÄUREN. IV. EINE NEUE SYNTHESE VON HISTAMIN.

Von Shiro AKABORI und Shinji NUMANO.

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Die Synthese von Histamin wurde, wie in der ersten Mitteilung beschrieben ist, zuerst von Windaus und Vogt⁽¹⁾ durch Überführung von Imidazolypropionsäure in Histamin durch Curtiusche Reaktion ausgeführt. Später ging Pyman⁽²⁾ von Diaminoaceton aus und stellte es über viele Stufen dar. Koessler und Hanke⁽³⁾ wiederholten die Pymansche Methode und verbesserten dabei das Verfahren.

Obgleich Histamin verschiedene ausgesprochene physiologische Wirkungen auf Tiere hat und physiologisch wie pharmakologisch eine äusserst wichtige Verbindung ist⁽⁴⁾, hat man wohl doch keine anderen Aufbauverfahren, als den oben genannten. Es gibt zwar Wege zur Darstellung des Histamins, entweder durch Entcarboxylieren von Histidin⁽⁵⁾ oder durch Reduktion von Imidazolylacetonitril, das man durch Oxydation von Histidin mit Toluolsulfonsäure-chloramid⁽⁶⁾ gewinnt, sie benutzten aber Histidin als Ausgangsmaterial, sodass man beide Verfahren als richtigen Aufbauverfahren nicht bezeichnen kann. Kürzlich zeigte auch Pyman⁽⁷⁾, dass man Histamin leicht erhalten kann, wenn man Natriumrhodanid auf Diamino-ketobutan-hydrochlorid (I) einwirken lässt und das so erhaltene 2-Mercapto-histamin (III) mit Ferrichlorid oxydiert.



Dies kann man auch jedoch nicht als Aufbaumethode von Histamin ansehen, denn die Verbindung I wird durch Zersetzung des Histamins gewonnen. Pucher und Johnson⁽⁸⁾ versuchten zwar aus Diäthoxy-acetessigester Histamin zu gewinnen, es gelang ihnen aber nicht. Akabori und Kaneko (III. Mitt.)⁽⁹⁾

(1) *Ber.*, **40** (1907), 3691.

(2) *J. Chem. Soc.*, **99** (1911), 669.

(3) *J. Am. Chem. Soc.*, **40** (1918), 1761.

(4) S. Feldberg u. Schiff, „Histamin“, Berlin (1930).

(5) Ewins u. Pyman, *J. Chem. Soc.*, **99** (1911), 339. Ackermann, *Z. physiol. Chem.*, **65** (1910), 504.

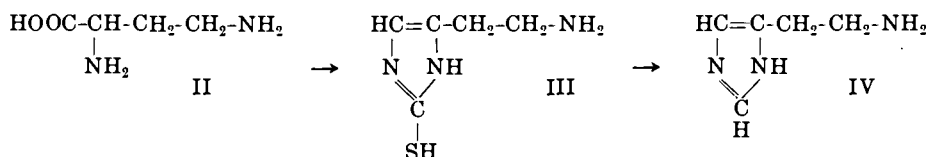
(6) Dakin, *Biochem. J.*, **10** (1916), 319; *Chem. Zentr.*, **87** (1916), II, 1142.

(7) *J. Chem. Soc.*, **1930**, 98.

(8) *J. Am. Chem. Soc.*, **44** (1922), 817.

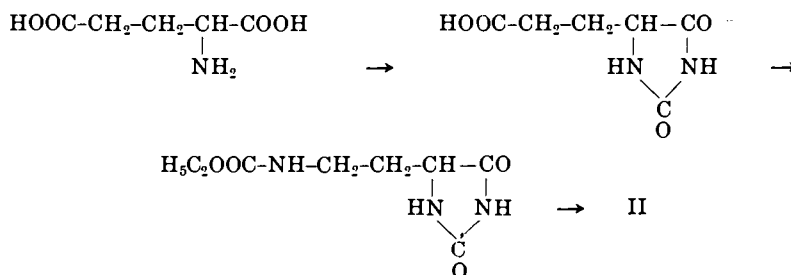
(9) Sieh. vorangehende Mitteilung.

haben das neue Verfahren auf Arginin und Lysin angewandt und zwei höhere Homologe des Histamins erhalten. Wir haben nun auf folgende Weise aus α,γ -Diaminobuttersäure (II) Histamin dargestellt.



α,γ -Diaminobuttersäure (II) wurde zuerst von E. Fischer⁽¹⁰⁾ gewonnen. Karrer und Widmer⁽¹¹⁾ gewannen *d*- α,γ -Diaminobuttersäure durch Anwendung Hoffmannschen Abbaus auf *d*-Glutamin, die Ausbeute war aber sehr schlecht.

Wir haben anfangs nach der Methode von E. Fischer *dl*- α,γ -Diaminobuttersäure synthetisch dargestellt. Da dieser Vorgang aber zu stufenartig war und die Versuche viele Schwierigkeiten machten, so sind wir von Glutaminsäure ausgegangen, indem wir dieselbe auf Dakinsche Weise⁽¹²⁾ Hydantoinpropionsäure verwandelten und durch Anwendung Curtiusschen Abbau auf diese Säure *dl*- α,γ -Diaminobuttersäure darstellten.



Diese Methode hat auch eine nicht so gute Ausbeute, aber da man Glutaminsäure leicht erhalten kann, so ist sie als einer Laboratoriumsmethode sehr bequem. Die so erhaltene Diaminobuttersäure wurde in Äthylester verwandelt und nach der in III. Mitt. erwähnten Methode 2-Mercapto-histamin synthetisch gewonnen. Obgleich die Ausbeute hierbei sehr schlecht ist, haben wir doch Hoffnung auf bessere Ausbeute, wenn die experimentellen Bedingungen verbessert werden. 2-Mercaptohistamin kann man nach Pyman⁽¹³⁾ mit Eisenchlorid quantitativ in Histamin (IV) verwandelt werden.

(10) *Ber.*, **34** (1901), 2900.

(11) *Helv. Chim. Acta*, **9** (1926), 301.

(12) *Am. Chem. J.*, **44** (1910), 58.

(13) *J. Chem. Soc.*, **1930**, 100.

Beschreibung der Versuche.

Hydantoinpropionsäure-äthylester. Werden 17.2 g. *dl*-Hydantoinpropionsäure (Schmp. 167-168.5°) in 60 c.c. absolutem Alkohol suspendiert, 10 g. trockener Chlorwasserstoff absorbiert und dann auf dem Wasserbad erhitzt, so löst sich die Säure allmählich auf. Nachdem sie sich gänzlich gelöst hat, wird sie weiter kurze Zeit gekocht, nach Zusatz von 40 c.c. Benzol destilliert, bis zum Sirup konzentriert und dann über Schwefelsäure unter vermindertem Druck getrocknet. Wird der Rückstand in heissem Benzol aufgenommen, der grösste Teil von Benzol abdestilliert und stehen gelassen, so scheiden sich Kristalle aus. Ausbeute 19.5 g. Aus Benzol umkristallisiert, so erfolgt Ausscheidung weisser Kristallen in Tafelchen. Schmp. 78-82°. (Gef.: N, 14.30. Ber. für $C_8H_{12}O_4N_2$: N, 14.00%.)

Hydantoinpropionsäure-hydrazid. Werden 5 g. obigen Esters und 1.4 g. Hydrazinhydrat in 5 c.c. absolutem Alkohol gelöst und gekocht, so beginnen sich nach kurzer Zeit Kristalle auszuschcheiden. Nach 10 stündigem Kochen giesst man das ganze in eine Schale über, bewahrt es im Vakuumexsikkator auf und entfernt Alkohol und das überschüssige Hydrazinhydrat. Kristallisiert man einmal aus Wasser um, so erfolgen 3.3 g. Hydrazid vom Schmp. 164-167°. Ausbeute 71% der Theorie. Wird noch einmal aus Wasser umkristallisiert, so bekommt man das Produkt vom Schmp. 169-171°. (Gef.: N, 29.50. Ber. für $C_6H_{10}O_3N_4$: N, 30.11%.)

Hydantoinpropionsäure-azid. 3.7 g. obigen Hydrazids werden in 20 c.c. 2 N Salzsäure gelöst, durch Kältemischung gegen -10° abgekühlt und unter Rühren eine Lösung von 1.6 g. Natriumnitrit in 10 c.c. Wasser hineingetropfelt. Während des Tröpfelns scheidet sich Azid in sandigen Kristallen aus. Nach beendeter Reaktion wäscht man mit ein wenig Wasser und trocknet unter vermindertem Druck über Schwefelsäure. Ausbeute 3.5 g., 89% der Theorie. Diese Substanz zersetzt sich bei 69-70° und schäumt plötzlich auf, wenn man sie auf konzentrierte Schwefelsäure fallen lässt. Da die Umkristallisierung schwer ist, wird das Azid sofort analysiert. (Gef.: N, 32.44. Ber. für $C_6H_7O_3N_5$: N, 35.53%.)

Hydantoinäthyl-carbaminsäure-äthylester (V). Werden 3.5 g. obigen Azids mit 12 c.c. absolutem Alkohol auf 40-60° erhitzt, so entwickelt sich das Gas lebhaft. Wird nach Aufhören der Gasentwicklung 1/2 Stunde gekocht, Alkohol destilliert und unter vermindertem Druck über Schwefelsäure getrocknet, so gewinnt man 3.4 g. Kristallmasse. Schmp. 82-88°. Sie ist in Wasser und Alkohol leicht löslich und in Benzol unlöslich. Da sie mit einer zähen Substanz vermischt und schwer umkristallisierbar ist, so führten wir sogleich folgenden Versuch aus.

α,γ -Diaminobuttersäure-dichlorhydrat. Wird obiges unreines Urethan sogleich mit 110 c.c. Wasser und 58 g. kristallinen Bariumhydroxyd 8 Stunden lang gekocht, dann durch Zusatz von Wasser auf 600 c.c. verdünnt, Kohlensäure eingeleitet, Bariumcarbonat abfiltriert, das Filtrat durch Abdampfen konzentriert, unter Zusatz von wenig Schwefelsäure Barium vollständig entfernt und dann auf dem Wasserbad zur Trockne eingedampft, so bleibt zähe harzige Diaminobuttersäure zurück. Wird dieselbe in 5 c.c. konzentrierter Salzsäure gelöst und wieder konzentriert, so scheiden sich Kristalle von Diaminobuttersäure-dichlorhydrat aus. Nach Zusatz von 30 c.c. absolutem Alkohol werden die Kristalle abfiltriert. Ausbeute 1.15 g. Zersetzungspunkt 202-204°. Das aus Essigsäure, die ein wenig Salzsäure enthält, umkristallisierte Produkt hat den Zersetzungspunkt 206.3°, der mit dem des nach der Fischerschen Methode synthetisch dargestellten Produkts übereinstimmt. (Gef.: N, 14.86. Ber. für $C_4H_{10}O_2N_2 \cdot 2HCl$: N, 14.67%.)

α,γ -Diaminobuttersäure-äthylester-dichlorhydrat. Werden 5.7 g. α,γ -Diaminobuttersäure-dichlorhydrat mit 285 c.c. absolutem Alkohol, der etwa 7% Salzsäure enthält, auf dem Wasserbad gekocht, so lösen die Kristalle langsam auf. Werden diese 8 Stundenlang gekocht, unter Zusatz von 100 c.c. Benzol destilliert und schliesslich unter vermindertem Druck zum Sirup konzentriert, so erstarrt das Produkt zu einer kristallinischen Masse. Wird es aus einer Mischung von absolutem Alkohol und Benzol umkristallisiert, so erfolgen 4.7 g. Kristalle von Schmp. 173–175° (unter Aufschäumen), die in Wasser und Alkohol leicht löslich und hygroskopisch sind. (Gef. : N, 12.62. Ber. für $C_6H_{14}O_2N_2 \cdot 2HCl$: N, 12.79%.)

2-Mercapto-histamin (III). 4.6 g. obigen α,γ -Diaminobuttersäure-äthylester-dichlorhydrats werden in einer Mischung von 10 c.c. Alkohol, 30 c.c. Wasser und 10 c.c. 5 N Salzsäure gelöst, durch Kältemischung gegen –10° abgekühlt, durch 100 g. 2.3% Natriumamalgam und zur dessen Neutralisierung erforderliche Menge von 5 N Salzsäure in üblicher Weise reduziert. Nach der beendeten Reaktion wird wiederum 4 c.c. 5 N Salzsäure zugesetzt, längere Zeit stehen lassen, von Quecksilber getrennt, das Filtrat unter vermindertem Druck auf etwa 40 c.c. konzentriert, eine Lösung von 5.5 g. Ammoniumrhodanid in ein wenig Wasser zugesetzt und auf dem Wasserbad bis zu fast vollständigen Trocknen verdampft. Werden zu diesen Rückstand 70 c.c. 95% Alkohol zugesetzt, wird dann etwas erwärmt, unlösliche Substanz abfiltriert, aus dem Filtrat Alkohol abdestilliert, der Rückstand in ein wenig Wasser gelöst und 400 c.c. der bei 40° gesättigten wässerigen Quecksilber-chlorid Lösung zugesetzt, so scheidet sich ein weisser harziger Niederschlag aus. Dieser Niederschlag verwandelt sich beim Stehen allmählich in eine kristallinische Masse. Sie wird in 100 c.c. 1 N Salzsäure gelöst, durch Einleitung von Schwefelwasserstoff zersetzt und nach Abfiltrieren von Quecksilbersulfid auf dem Wasserbad zur Trockne eingedampft. Wird der Rückstand in möglichst wenig Wasser gelöst und durch Zusatz von Alkohol ausscheiden lassen, so erfolgen 0.6 g. Kristalle, die bis auf einen geringen Teil bei 245–249° schmelzen. Da die Kristalle noch ein wenig anorganische Substanz zu enthalten scheinen, so werden sie wieder in Wasser gelöst, mit Quecksilberchlorid wiederum gefallen, mit Schwefelwasserstoff zersetzt und nach Abfiltrieren von Quecksilbersulfid das Filtrat zur Trockne eingedampft. Dann wird der Rückstand aus 80% Essigsäure umkristallisiert. Schmp. 245.5–247°. Die Analysenwerte stimmen gut mit den des Mercapto-histamin-chlorhydrat überein. Ausbeute an reinem Produkt 0.25 g. (Gef. : C, 33.76; H, 5.40; S, 17.30. Ber. für $C_5H_9N_3S \cdot HCl$: C, 33.40; H, 5.61; S, 17.85%.)

Mercapto-histamin-pikrat. Schmp. 220–222°. Nach Pyman 225° (korr.).

Histamin (IV). Werden 0.107 g. 2-Mercapto-histamin-chlorhydrat in 2 c.c. Wasser gelöst, dazu eine Lösung von 1 g. Eisenchlorid ($FeCl_3 \cdot 6H_2O$) in 15 c.c. Wasser hinzugesetzt, auf dem Wasserbad 1 Stunde erhitzt und eine Lösung von 0.3 g. Pikrinsäure in 10 c.c. heissen Wasser dazugesetzt, so scheiden sich gelbe Kristalle aus. Ausbeute 0.33 g., 97% der Theorie. Schmp. 231–234°. Aus Wasser einmal umkristallisiert, erhält man 0.3 g. vom Schmp. 233–235° (unter Zersetzung).

Beim Mischen mit dem aus Imidazoyl-propionsäure dargestellten Histamin-dipikrat, (von Schmp. 235–237°) zeigt sich ein Schmp. von 233–235°. (Gef. : C, 36.23; H, 2.28; N, 21.71. Ber. für $C_5H_9N_3 \cdot 2C_6H_3O_7N_3$: C, 35.84; H, 2.66; N, 22.15%.)

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ÜBER DIE SYNTHESE VON ALKOXY- UND OXY-CARBAZOLE.

Von Toshio HOSHINO und Kiyoshi TAKIURA.

Eingegangen am 4. November 1935. Ausgegeben am 28. März 1936.

3-Oxy-carbazol wird in gewöhnlicher Weise⁽¹⁾ aus 3-Amino-carbazol erhalten, aber nur in sehr schlechter Ausbeute, während die bekannte Darstellungsmethode von 2-Oxy-carbazol⁽²⁾ sehr kompliziert ist. Daher versuchten wir die Darstellung der genannten Substanzen nach dem Verfahren von W. Borsche⁽³⁾ durchzuführen.

Borsche stellte Carbazol aus Tetrahydrocarbazol, das aus Cyclohexanon-phenylhydrazon durch Erwärmen mit verdünnter Schwefelsäure erhalten wurde, durch Dehydrierung mit Bleioxyd in der Hitze dar. Diese Dehydrierungsmethode fanden wir aber besonders beim Alkoxyderivat nicht sehr geeignet. Daher versuchten wir die Dehydrierung nach dem Verfahren von Akabori und Saito⁽⁴⁾ und zwar mittels Pd-Schwarz zusammen mit ungesättigter Verbindung als Wasserstoff-akzeptor, und erhielten gute Resultate. So stellten wir das 3- bzw. 2-Äthoxy-carbazol aus 6- bzw. 7-Äthoxy-1,2,3,4-tetrahydrocarbazol dar.

Aus 3- bzw. 2-Äthoxy-carbazol erhielten wir das 3- bzw. 2-Oxycarbazol nach dem Verfahren von Klemenc⁽⁵⁾ und zwar durch Erhitzen mit Anilin-chlorhydrat in guter Ausbeute.

Wenn man rein aber nicht so viel oben genannten Verbindungen haben will, so empfehlen wir diese Darstellungsmethode.

Der Japanischen Gesellschaft zur Förderung der Naturwissenschaften (Nippon-Gakujutu-Sinko-Kwai) danken wir ergebenst für die finanzielle Unterstützung bei dieser Arbeit.

Beschreibung der Versuche.

Die Synthese von Carbazol. *Cyclohexanon-phenylhydrazon.* Eine Mischung äquivalenter Mengen Cyclohexanon mit Phenylhydrazin erstarrt nach anfänglicher Selbsterwärmung sehr bald zu einem schneeweißen Krystallkuchen von Phenylhydrazon. Aus

(1) Ruff u. v. Stein, *Ber.*, **34** (1901), 1683.

(2) Kehrman u. Zweifel, *Helv. Chim. Acta*, **11** (1928), 1213; D.R.P. 522960.

(3) Borsche, *Ann.*, **359** (1908), 52.

(4) Akabori u. Saito, *Proc. Imp. Acad. Tokyo*, **6** (1930), 236.

(5) Klemenc, *Ber.*, **49** (1916), 1371.

50-proz. Alkohol umkrystallisiert. Schmp. 81–82° (Angabe von Baeyer⁽⁶⁾ 74–75°). Die Ausbeute 95-Proz. der Theorie.

Tetrahydrocarbazol. 1.7 g. Phenylhydrazon wurden mit 20 c.c. 10-proz. Schwefelsäure vermischt, wobei unter Selbsterwärmung alles in Lösung ging. Beim Stehenlassen schieden sich allmählich farblose Tafeln aus, die aus 50-proz. Alkohol umkrystallisiert wurden. Ausbeute 1.6 g. (93-Proz. der Theorie). Schmp. 116–117° (Borsche 116°; Perkin und Plant⁽⁷⁾ 119°).

Borsche erhitzte bei dieser Reaktion; Perkin und Plant verwandten Essigsäure statt Schwefelsäure und erhitzten auch.

Dehydrierung von Tetrahydrocarbazol (Carbazol). 0.3 g. Tetrahydrocarbazol wurden mit 0.7 g. Zimtsäure und 0.05 g. Pd-Schwarz (nach Tausz u. v. Putnosky⁽⁸⁾) gut vermischt in einem Reagenzrohr auf 150–200° einige Minuten lang erhitzt, wobei die anfangs grünliche Schmelze rot und klar wurde. Das Reaktionsgemisch wurde mit Alkohol gekocht und heiss filtriert. Aus dem Filtrat schieden sich farblose Blättchen aus, die abfiltriert und mit verdünnten Alkohol, Alkali und schliesslich Wasser nachgewaschen wurden. Das Produkt schmolz bei 240°. Ausbeute 0.25 g. (89-Proz. der Theorie).

Akabori und Saito benutzten als Wasserstoffakzeptor Safrol statt Zimtsäure bei dieser Reaktion, aber wir fanden die letztere Substanz viel geeigneter als die erste.

Die Synthese von 3-Äthoxy-carbazol. *p*-Äthoxy-phenylhydrazin.⁽⁹⁾ 36 g. *p*-Phenetidin-chlorhydrat wurden mit 200 c.c. konzentrierter Salzsäure vermischt und dem Gemisch unter gutem Umrühren bei 0° eine Lösung von 20 g. Natriumnitrit in 100 c.c. Wasser zugetropft. Nach dem Ende der Reaktion wurde das Reaktionsgemisch bis –10° gekühlt, unter Umrühren eine gekühlte Lösung von 120 g. Zinnchlorür in 100 c.c. konzentrierter Salzsäure in kleinen Portionen zugetropft und dann 2 Stunden lang unter Kühlung stehengelassen. Das entstandene salzsaure Salz des Hydrazins wurde abfiltriert, mit gesättigter Kochsalzlösung nachgewaschen, unter Äther mit Alkali zersetzt, mit Äther aufgenommen und schliesslich mit festem Kali getrocknet. Beim Einengen des Äthers schied sich die Verbindung in schönen, farblosen Blättchen aus. Schmp. 74° unter Zersetzung (Angabe von Stolz auch 74°). Ausbeute 22.4 g. (71-Proz.).

Cyclohexanon-p-äthoxy-phenylhydrazon. 17 g. *p*-Äthoxy-phenylhydrazin, in 10 c.c. Alkohol gelöst, wurden mit 12 g. Cyclohexanon vermischt, wobei unter Selbsterwärmung Reaktion eintrat und bald farblose Tafeln entstanden. Umkrystallisation aus wenig Alkohol. Schmp. 77°. Ausbeute 23.5 g. (95-Proz.). Borsche gab keinen Schmelzpunkt.

6-Äthoxy-1,2,3,4-tetrahydro-carbazol. 26.5 g. des oben erhaltenen Hydrazons wurden mit 300 c.c. 10-proz. Schwefelsäure vermischt, wobei unter Selbsterwärmung alles bald in Lösung ging, aus der sich beim Abkühlen schöne farblose Nadeln ausschieden. Das Produkt schmolz bei 105–106° nach zweimaligem Umkrystallisieren aus 80-proz. Alkohol. Kocht man nach Borsche bei dieser Reaktion, so entsteht viel dunkelbraune harzige Substanz. Der Schmp. nach Borsche 87–88°.

Dehydrierung von 6-Äthoxy-tetrahydrocarbazol (3-Äthoxy-carbazol). 6-Äthoxy-1,2,3,4-tetrahydrocarbazol wurde mit 1/10 Teil Pd-Schwarz und 2 Teil Zimtsäure vermischt und unter CO₂-Atmosphäre 5–6 Minuten lang auf 200–250° erhitzt, wobei sich das Pd-Schwarz zusammen ballte und die Schmelze rot und klar wurde. Die Schmelze wurde dann vom

(6) Baeyer, *Ann.*, **278** (1894), 105.

(7) Perkin u. Plant, *J. Chem. Soc.*, **1921**, 1831.

(8) Tausz u. v. Putnosky, *Ber.*, **52** (1919), 1573.

(9) Stolz, *Ber.*, **25** (1892), 1663.

Pd-Schwarz dekantiert und erstarrte bald. Das fest gewordene Reaktionsgemisch wurde pulverisiert, mit verdünntem Alkali gut vermischt, abgesaugt und mit warmem Wasser mehrmals nachgewaschen. Dann wurde Exsiccator getrocknet, mit Petroläther gewaschen und aus 50-proz. Alkohol 2-mal umkrystallisiert. Farblose Blättchen vom Schmp. 106–107°. Ausbeute 80-Proz. der Theorie. (Gef.: N, 6.63. Ber. für $C_{14}H_{13}ON$ (211): N, 6.64%.)

3-Oxy-carbazol. 1 Mol 3-Äthoxy-carbazol wurde mit 3 Mol Anilinhydrochlorid vermischt und unter CO_2 -Atmosphäre 1/2 Stunde lang auf 220° erhitzt. Das Reaktionsgemisch wurde dann mit verdünnter Salzsäure auf dem Wasserbade erhitzt und abfiltriert. Der Rückstand wurde in verdünntem Alkali gelöst, die Lösung filtriert und das Filtrat mit verdünnter Salzsäure sauer gemacht, wobei sich 3-Oxy-carbazol ausschied. Aus Alkohol farblose Blättchen vom Schmp. 256–257°. Ausbeute 50–70-Proz. der Theorie. (Gef.: N, 7.54. Ber. für $C_{12}H_{11}ON$ (185): N, 7.65%.)

Die Synthese von 2-Äthoxy-carbazol. *m*-Äthoxy-phenylhydrazin wurde aus *m*-Phenetidin in gleicher Weise wie *p*-Äthoxy-phenylhydrazin dargestellt. Die Ausbeute war 33-Proz. der Theorie. Das Produkt war ölig.

7-Äthoxy-1,2,3,4-tetrahydrocarbazol. 11.8 g. Cyclohexanon-*m*-äthoxy-phenylhydrazon, das aus 10.5 g. *m*-Äthoxy-phenylhydrazin und 11 g. Cyclohexanon erhalten worden war, wurde mit 100 c.c. 10-proz. Schwefelsäure vermischt, wobei sich unter Selbsterwärmung 7-Äthoxy-1,2,3,4-tetrahydrocarbazol in farblose Nadeln mit einer Ausbeute von 10 g. ausschied. Nach Umkrystallisieren aus 50-proz. Alkohol Schmp. 120°. (Gef.: N, 6.51. Ber. für $C_{14}H_{17}ON$ (215): N, 6.50%.)

Dehydrierung von 7-Äthoxy-tetrahydrocarbazol (2-Äthoxy-carbazol). 4.2 g. 7-Äthoxy-tetrahydrocarbazol wurde mit 12 g. Zimtsäure und 0.5 g. Pd-Schwarz vermischt, 5 Minuten lang schwach gekocht und dann wie beim 3-Äthoxy-carbazol behandelt. Nach dem Nachwaschen mit Petroläther wurde das rohe 2-Äthoxy-carbazol aus Eisessig 2-mal umkrystallisiert. Farblose Tafeln vom Schmp. 216–217°. Ausbeute 3.5 g. (Gef.: N, 6.76. Ber. für $C_{14}H_{13}ON$ (211): N, 6.64%.)

2-Oxy-carbazol. 2.1 g. 2-Äthoxy-carbazol wurden mit 3.8 g. Anilinhydrochlorid 1/2 Stunden lang im Ölbad auf 240–250° erhitzt, das Reaktionsgemisch mit heisser, verdünnter Salzsäure behandelt und dann abfiltriert. Der Rückstand wurde in verdünnter Natronlauge gelöst, abfiltriert und das Filtrat nach dem Ansäuern mit Salzsäure ausgeäthert. Nach dem Abdampfen des Äthers wurde der Rückstand aus Alkohol 2-mal umkrystallisiert. Farblose Blättchen vom Schmp. 273–274°. Ausbeute 1.3 g. Viel beständiger als 3-Oxy-carbazol. (Gef.: N, 7.53. Ber. für $C_{12}H_{11}ON$ (185): N, 7.65%.)

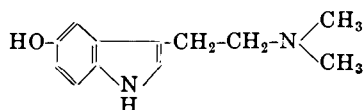
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ÜBER DIE SYNTHESE DES BUFOTENIN-METHYL-ÄTHERS
(5-METHOXY-N-DIMETHYL-TRYPTAMIN)
UND BUFOTENINS.⁽¹⁾
(SYNTHESEN IN DER INDOL-GRUPPE. XV.)⁽²⁾

Von Toshio HOSHINO und Kenya SHIMODAIRA.

Eingegangen am 4. November 1935. Ausgegeben am 28. März 1936.

Im Zusammenhang mit Versuchen zur Synthese von Eseräthol haben wir in der vorigen Mitteilung über die Synthese des Bufotenins (5-Oxy-*N*-dimethyl-tryptamin) berichtet, die von dem Äthyl-äther ausging, der aus 5-Äthoxy-indolyl-3-äthyl- β -bromid und Dimethylamin erhalten worden war. Diesmal haben wir ganz analoger Weise den Methyl-äther von Bufotenin (5-Methoxy-*N*-dimethyl-tryptamin) hergestellt, und daraus wieder das Bufotenin erhalten.



Bufotenin

Herr Dr. R.H. Manske (Canada) hat uns jüngst (3. Oktober 1935, Ottawa) freundlicherweise darauf aufmerksam gemacht, dass wir seine beiden schönen Abhandlungen⁽³⁾ übersehen hatten (Wir möchten ihm hiermit für seine Mitteilung bestens danken). In diesen Abhandlungen berichtete er über die Isolierung von *N*-Monomethyl-tryptamin (4 g.), *N*-Dimethyl-tryptamin (1 g.), Trimethyl- β -3-indolyl-äthylammonium-jodid (12.1 g.), neben regeneriertem Tryptamin (15.1 g.), aus dem Reaktionsgemisch von Tryptamin (32 g.) und Jodmethyl, ferner über die Darstellung von *N*-Dimethyl-tryptamin durch Vakuumdestillation von Trimethyl- β -3-indolyl-äthylchlorid, das aus das Jodid erhalten wird.

Im Zusammenhang mit Versuchen zur Synthese von Eserin versuchten wir die Monomethylierung von Tryptamin. Zuerst⁽⁴⁾ liessen wir auf das Amin (1 g.) Jodmethyl reagieren und konnten dabei nur regeneriertes Amin und Trimethyl- β -3-indolyl-äthylammonium-jodid isolieren. Dann probierten wir das Verfahren von Decker und Becker und isolierten dabei 3-Phenyl-3,4,5,6-tetrahydro-4-carbolin und 3-Phenyl-4-methyl-3,4,5,6-tetrahydro-4-carbolin-jodmethylat (Herr Dr. Manske schreibt in seiner Abhandlung, dass er in diesem Falle als Hauptprodukt "a neutral cherry-red resin" erhalten hat).

(1) Wieland, Konz u. Mittasch, *Ann.*, **513** (1934), 1.

(2) Hoshino u. Shimodaira, *Ann.*, **520** (1935), 19; *Proc. Imp. Acad. Japan*, **11** (1935), 227.

(3) Manske, *Can. J. Research*, **1931**, 275, 592.

(4) Hoshino u. Kotake, *Ann.*, **516** (1935), 76.

Schliesslich⁽⁵⁾ ist es uns gelungen nach dem Verfahren von Hinsberg die Monomethylierung von Tryptamin, sowie 5-Äthoxy-tryptamin durchzuführen und dadurch das *dl*-Eseräthol zu synthetisieren. Gleichzeitig⁽²⁾ haben wir aus Indolyl-3-äthyl- β -bromid sowie 5-Äthoxy-indolyl-3-äthyl- β -bromid und Methylamin bzw. Dimethylamin das *N*-Methyl- bzw. *N*-Dimethyl-tryptamin sowie 5-Äthoxy-*N*-methyl bzw. 5-Äthoxy-*N*-dimethyl-tryptamin (Bufotenin-äthyläther) dargestellt, wie bereits oben erwähnt wurde.

N-Methyl-tryptamin: Manske Schmp. 90°, Pikrat Schmp. 191°; Hoshino und Kobayashi Schmp. 89–90°, Pikrat 190–191°. *N*-Dimethyl-tryptamin: Manske Schmp. 47°, Pikrat Schmp. 168°; Hoshino und Shimodaira Schmp. 49–50°, Pikrat (Mono-) Schmp. 170–171°. Trimethyl- β -3-indolyl-äthylammonium-jodid: Manske Schmp. 197°; Hoshino und Kotake 216–117°.

Das Trimethyl- β -3-indolyl-äthylammonium-jodid bzw. 5-Methoxy-trimethyl- β -3-indolyl-äthylammonium-jodid haben wir einfach durch Kochen der alkoholischer Lösung von Tryptamin bzw. 5-Methoxy-tryptamin mit einem Überschusse von Jodmethyl bei Anwesenheit von überschüssigem Natriumcarbonat in sehr guter Ausbeute (über 90-Proz.) erhalten, während Wieland, Konz und Mittasch⁽¹⁾ zur Vorsicht Talliumäthylat statt Natriumcarbonat anwandten.

Aus dem 5-Methoxy-trimethyl- β -3-indolyl-äthylammonium-jodid haben wir nach dem Verfahren von Manske das 5-Methoxy-*N*-dimethyl-tryptamin (Bufotenin-methyläther) dargestellt.

Der Stiftung des verstorbenen Herrn Tejima zur Förderung der technischen Ausbildung sind wir für die Unterstützung bei dieser Arbeit zu grossem Dank verpflichtet. Auch möchten wir Herrn Prof. R. Majima für seine Anregungen unseren besten Dank aussprechen.

Beschreibung der Versuche.

Die Synthese des 5-Methoxy-tryptophols.⁽²⁾ 5-Methoxy-indolyl-(β)-essigsäure. 30 g. 5-Methoxy-indolyl-3-acetonitril⁽¹⁾ (siedet bei 221°/4 mm.) werden mit Kaliumhydroxyd in Methanol-Wasser-Lösung so lange gekocht, bis kein Ammoniak mehr entwickelt wird, d.h. etwa 20 Stunden lang. Nach dem Abdestillieren des Methanols nimmt man das unveränderte Nitril mit Äther auf und macht die wässrige Schicht mit Salzsäure sauer, wobei sich anfangs eine ölige Substanz ausscheidet, die beim Stehen bald krystallinisch wird (Blättchen). Die Menge betrug ca. 28 g., der Schmp. lag bei 146–147° (Gef.: N, 7.03. Ber. für C₁₁H₁₁O₃N (205): N, 6.83%).

Äthylester. Eine Lösung von 24 g. der Säure in 80 g. absolutem Alkohol wird mit HCl fast gesättigt und 1/2 Stunde lang gekocht. Der Alkohol wird in Vakuum abdestilliert und das zurückbleibende Öl mit Äther aufgenommen. Nach dem Trocknen mit Natriumsulfat wird der Äther abdestilliert und das zurückbleibende Öl in Vakuum destilliert. Die bei 202–203°/4 mm. (23 g.) übergehende Fraktion krystallisiert aus Äther

(5) Hoshino u. Kobayashi, *Ann.*, **520** (1935), 11; *Proc. Imp. Acad. Japan*, **11** (1935), 227.

in schönen farblosen Tafeln vom Schmp. 97–98° (Gef.: N, 6.32. Ber. für $C_{13}H_{15}O_3N$ (233): N, 6.03%).

Reduktion. 23 g. des Esters werden in 350 c.c. absolutem Alkohol auf dem Ölbad auf 120° erhitzt und mit 21 g. Natrium in kleinen Stückchen versetzt. Dann wird die Temperatur allmählich auf 150° gesteigert. Nach dem Verschwinden des Natriums wird etwas Wasser zugegeben, der Alkohol in Vakuum abdestilliert und nach dem Zusatz von Wasser ausgeäthert. Aus der alkalischen Lösung werden beim Ansäuern mit Salzsäure 5-Methoxy-indolyl-3-essigsäure zurückerhalten in unserem Falle 9 g. Die mit Natriumsulfat getrocknete ätherische Lösung hinterliess nach dem Abdestillieren des Lösungsmittels ein schwach braun gefärbtes Öl, das bei 194°/4 mm. schwach gelb gefärbt übergang. Ausbeute 5.5 g. Pikrat: aus Benzol wurden schöne, rot gefärbte Nadeln vom Schmp. 117–118° erhalten (Gef.: N, 13.22. Ber. für $C_{11}H_{13}O_2N \cdot C_6H_5O_7N_3$ (420): N, 13.34%).

5-Methoxy-indolyl-3-äthyl- β -bromid. 2 g. 5-Methoxy-tryptophol werden in 100 c.c. absolutem Äther bei Zimmertemperatur mit 1 g. Phosphor-tribromid, gelöst in absolutem Äther, allmählich vermischt und über Nacht stehengelassen. Die Lösung wurde von der harzigen Ausscheidung abgegossen, mit Wasser und Bicarbonatlösung gewaschen und mit Kaliumcarbonate getrocknet. Nach dem Abdunsten des Äthers hinterbleibt ein fast farbloses Öl, das schon bei kurzem Erhitzen auf dem Wasserbade schwarz wird. Ausbeute 1.3 g.

5-Methoxy-N-dimethyl-tryptamin (Bufotenin-methyläther). 1.0 g. rohes Bromid, gelöst in 4 c.c. Methanol, wird mit 4 c.c. einer 33-proz. Dimethylamin-Lösung im Einschlussrohr im siedenden Wasserbade 15 Stunden lang erhitzt. Das Reaktionsgemisch wird mit viel verdünnter Salzsäure vermischt und durch Ausschütteln mit Äther gewaschen. Die salzsaure Schicht wird mit Kaliumcarbonat getrocknet. Nach dem Abdampfen des Äthers wird der Rückstand in Vakuum destilliert. Sdp. 208–210° (Bad) bei 4 mm. Ausbeute 0.5 g. Die Substanz krystallisiert aus Äther-Petroläther. Schöne farblose Prismen vom Schmp. 66–67° (Gef.: N, 12.71. Ber. für $C_{13}H_{15}ON_2$ (218): N, 12.85%).

Monopikrat. Aus Benzol-Aceton schöne gelb gefärbte Tafeln vom Schmp. 176–177° (Gef.: N, 15.69. Ber. für $C_{13}H_{15}ON_2 \cdot C_6H_5O_7N_3$ (447): N, 15.66%).

Krystallisiert man das Pikrat aus Methanol um, so nimmt es 1 Mol Methanol auf (Gef.: N, 14.60. Ber.: N, 14.61%).

Das Dipikrat konnten wir in diesem Falle nicht isolieren.

Jodmethyolat. Aus dem Gemisch von absolutem Alkohol und Äther schöne farblose Prismen vom Schmp. 183°. Das aus natürlichen Bufotenin erhaltene O-Methyl-bufotenin-jodmethyolat schmilzt nach der Angabe von Wieland⁽¹⁾ und seinen Mitarbeitern bei 183–184° und das aus 5-Methoxy-tryptamin synthetisierte bei 182–183°. (Gef.: N, 7.76. Ber. für $C_{14}H_{21}ON_2J$ (360): N, 7.78%.)

Monopikrat. Aus Methylalkohol-Wasser schöne gelb gefärbte Prismen vom Schmp. 170–171° (Gef.: N, 14.98. Ber. für $C_{14}H_{21}ON_2 \cdot C_6H_5O_7N_3$ (461): N, 15.19%).

Dipikrat. Krystallisiert man das gelbe Monopikrat aus Methylalkohol-Wasser mit einem Überschuss von Pikrinsäure um, so erhält man rote Nadeln vom Schmp. 103–104°. Beim Umkrystallisieren des Dipikrats aus Benzol erhält man das gelbe Monopikrat. (Gef.: N, 16.04. Ber. für $C_{14}H_{21}ON_2 \cdot C_6H_5O_7N_3 \cdot C_6H_5O_7N_3$ (692): N, 16.24%.)

Das Pikrat des Jodmethylates schmilzt nach der Angabe von Wieland und Mitarbeitern⁽¹⁾ bei 84°. Es war vielleicht ein Dipikrat.

Flavianat. Aus Methylalkohol-Wasser schöne rot gefärbte Nadeln vom Zersetzungsp. 242° (Wielands Angabe 233°).

Bufotenin. 0.45 g. Bufotenin-methyläther werden in 10 c.c. Benzol gelöst und mit 1.1 g. Aluminiumchlorid auf dem Wasserbade 15 Stunden lang gekocht wobei sich eine braunrote harzige Substanz am Boden des Kolbens ansetzt. Zum Reaktionsgemisch setzt man verdünnte Salzsäure zu, wodurch die harzige Substanz in Lösung geht, und schüttelt dann mit Äther aus. Aus der Benzol-Äther-Lösung wurde keine Substanz erhalten.

Nach Zugabe von Natronlauge bis zur alkalischen Reaktion wurde durch Ausäthern eine ganz kleine Menge von Ausgangsmaterial zurückerhalten. Die alkalische Lösung wurde nochmals mit Salzsäure sauer und mit Natriumbicarbonat wieder schwach alkalisch gemacht, wobei sich die Lösung trübte. Nach dem erschöpfenden Extrahieren mit peroxydfreiem Äther wurde der schwach gelb gefärbte Äther mit Natriumsulfat getrocknet. Nach dem Abdampfen hinterblieben 0.35 g. einer öligen Substanz.

Dipikrat. Aus Methylalkohol schöne, rot gefärbte Prismen vom Schmp. 177-178°.

Monopikrat. Beim Kochen in Benzol geht das rot gefärbte Dipikrat in ein gelbes über und schmilzt auch bei 177-178°.

Die beiden Pikrate sind jeweils ganz identisch mit den betreffenden Pikraten von Bufotenin, das früher⁽²⁾ aus dem Bufotenin-äthyläther erhalten worden war.

5-Methoxy-trimethyl- β -3-indolyl-äthylammonium-jodid. 1.5 g. 5-Methoxy-tryptamin, gelöst in 30 c.c. absolutem Alkohol, wurden mit 5 g. Jodmethyl vermischt und bei Anwesenheit von 4.5 g. wasserfreiem Natriumcarbonat 5 Stunden lang auf dem Wasserbade gekocht. Das Reaktionsgemisch wurde heiss abgesaugt, der Rückstand nochmals mit absolutem Alkohol gekocht und heiss abgesaugt. Wird das gesamte Filtrat eingeeengt und stehen gelassen, so scheiden sich schöne, farblose, grosse Nadeln aus. Der Körper schmilzt bei 183° und die Mischprobe mit 5-Methoxy-bufotenin-jodmethylat bei gleichen Temperatur. Die Ausbeute betrug 1.8 g. Nach weiteren Einengen der Mutterlauge wurden noch 0.7 g. erhalten.

Trimethyl- β -3-indolyl-äthylammonium-jodid wurde ganz analogerweise aus Tryptamin, ebenfalls mit guter Ausbeute erhalten.

5-Methoxy-trimethyl- β -3-indolyl-äthylammonium-chlorid. 1.6 g. 5-methoxy-trimethyl- β -3-indolyl-äthylammonium-jodid, gelöst in 20 c.c. absolutem Alkohol, wurden mit 6 g. AgCl am Rückflusskühler 3 Stunden lang erhitzt, heiss abfiltriert, der Rückstand nochmals mit absolutem Alkohol gekocht und heiss abfiltriert. Engt man das gesamte Filtrat stark ein und lässt über Nacht stehen, so scheiden sich schöne, sehr grosse, farblose Tafeln vom Schmp. 144° aus. Die Menge betrug 0.7 g. Aus der Mutterlauge isolierten wir noch 0.5 g. der gleichen Krystalle. (Gef.: N, 10.13. Ber. für $C_{14}H_{21}ON_2Cl$ (269): N, 10.43%.)

Monopikrat schmilzt bei 170-171° und ist identisch mit dem aus 5-Methoxy-bufotenin-jodmethylat erhaltenen (Mischprobe).

5-Methoxy-N-dimethyl-tryptamin aus 5-Methoxy-trimethyl- β -3-indolyl-äthylammonium-chlorid. 0.6 g. 5-Methoxy-trimethyl- β -3-indolyl-äthylammonium-chlorid wurden im Hochvakuum auf 240-250° erhitzt, wobei unter Aufschäumen ein gelb gefärbtes Öl überging, während eine rotbraun gefärbte harzige Substanz zurückblieb. Das Öl wurde in einer kleinen Menge von Methylalkohol gelöst und Pikrinsäure zugesetzt. Das gelb gefärbte Pikrat schmolz bei 172° und seine Menge betrug 0.1 g. Nach dem Umkrystallisieren aus Methylalkohol schmolz es bei 174-175° und die Mischprobe mit dem Pikrat (174-175°) von 5-Methoxy-N-dimethyl-tryptamin ergab keine Erniedrigung.

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STUDIES ON QUINOXALINE COLOURS.

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Quinoxaline colours belong to azine colours, and are derivatives of quinoxaline (according to Hinsberg). The only technically important dyestuff of this series is Flavinduline (B) $C_{26}H_{17}N_2Cl$ which was discovered by C. Schraube in 1893⁽¹⁾, and was obtained by the action of *o*-amidodiphenylamine on phenanthraquinone in glacial acetic acid solution, followed by boiling the reaction products with dilute hydrochloric acid.

The papers related to the quinoxaline colours which have been published are very poor and a few investigators have described only unsatisfactorily Flavinduline and its properties.

The present studies have been undertaken with the view to pursue the study in greater detail and to get more exact information as to the properties of quinoxaline and its derivatives, and especially as to their dyeing character which has been explained by "chromophore theory" or "quinoid theory".

First of all, the three condensations described in the experimental parts have been studied.

Experimental.

I. The reaction of phenanthraquinone on *o*-amidodiphenylamine in glacial acetic acid solution. Preparation of the dyestuffs. *Chloride*. A mixture of 1 part of *o*-amidodiphenylamine (5 g.), 1 part of phenanthraquinone (5 g.) and about 20 parts of glacial acetic acid (100 g.) is heated on the water bath until a sample shows no increase in intensity of colour. The melt is then boiled with 20 times its volume of water, acidified with HCl (38%, 30 g.), cooled, and filtered. The dye is precipitated from the filtrate with zinc chloride.

Bromide. According to the formation process of the chloride, the melt is boiled with HBr solution (48%, 40 g. in 1500 g. water), cooled, and filtered. The dyestuff is precipitated.

Iodide. The melt is boiled with HI solution (57%, 60 g. in 1500 g. water), cooled, and filtered. The dyestuff is precipitated.

Molecular weight.

		Calculated	Found
Chloride	$C_{26}H_{17}N_2Cl \cdot \frac{1}{2}ZnCl_2$	460.5	448.1
Bromide	$C_{26}H_{17}N_2Br$	437.0	420.3
Iodide	$C_{26}H_{17}N_2I$	484.0	468.1

(1) E.P. 18374 (1893); U.S.P. 543784 (1975).

Analytical data (%).

	$C_{26}H_{17}N_2Cl \cdot \frac{1}{2}ZnCl_2$		$C_{26}H_{17}N_2Br$		$C_{26}H_{17}N_2I$	
	Calculated	Found	Calculated	Found	Calculated	Found
C	67.75	66.20	71.39	71.20	64.46	64.25
H	3.69	4.60	3.89	5.30	3.51	4.09
N	6.08	6.79	6.39	6.20	5.78	6.11
Cl	15.42	15.77	Br 18.3	18.13	I 26.23	26.19

Properties. Form and colour.

$C_{26}H_{17}N_2Cl \cdot \frac{1}{2}ZnCl_2$ yellowish red needles;
 $C_{26}H_{17}N_2Br$ brownish red needles;
 $C_{26}H_{17}N_2I$ glistening black needles.

Melting point. Melting points of these compounds are over 285°C., and difficult to be determined exactly.

Solubility.

Solvent	$C_{26}H_{17}N_2Cl \cdot \frac{1}{2}ZnCl_2$	$C_{26}H_{17}N_2Br$	$C_{26}H_{17}N_2I$
Water	very sol.	not very sol.	sparingly sol.
Alcohol	very sol.	sol.	sol.
Aniline	very sol.	very sol.	very sol.
Chloroform	sol.	sol.	sol.
Nitrobenzene	sol.	sol.	sol.
Acetone	sol.	sol.	sol.
Glacial acetic acid	very sol.	very sol.	very sol.
Benzene	insol.	insol.	insol.
Ether	insol.	insol.	insol.

Colour reaction in aqueous solutions.

Solvent	$C_{26}H_{17}N_2Cl \cdot \frac{1}{2}ZnCl_2$	$C_{26}H_{17}N_2Br$	$C_{26}H_{17}N_2I$
H ₂ O	reddish brown	reddish yellow	yellow
NaOH	greyish green	bluish yellow	yellowish brown
HCl	precipitate	precipitate	precipitate
H ₂ SO ₄ (conc.)	reddish yellow	yellow	pale yellow
	bluish red	brownish red	brownish red

Dyeing.

	Cotton	Silk	Wool
$C_{26}H_{17}N_2Cl \cdot \frac{1}{2}ZnCl_2$	yellowish brown	reddish yellow	brown
$C_{26}H_{17}N_2Br$	pale yellowish brown	reddish yellow	yellowish brown
$C_{26}H_{17}N_2I$	pale yellow	reddish yellow	greenish brown

These Dyestuffs have good affinity, especially for silk and wool.

Fastness.

	$C_{26}H_{17}N_2Cl \cdot \frac{1}{2}ZnCl_2$	$C_{26}H_{17}N_2Br$	$C_{26}H_{17}N_2I$
Light	good	good	good
Washing	good	good	good
Soap	moderate	moderate	moderate
Alkali	moderate	moderate	moderate
Acetic acid	good	good	good
Sulphuric acid	good	good	good

II. The reaction of phenanthraquinone on *o*-amidomonomethylaniline in glacial acetic acid solution. Preparation of the dyestuffs. *Chloride.* A mixture of 1 part of *o*-aminomonomethylaniline (5 g.), 1 part of phenanthraquinone (5 g.), and about 20 parts of glacial acetic acid (100 g.) is heated on the water bath until a sample shows no increase in intensity of colour. The melt is then boiled with HCl solution (38%, 25 g. in 1500 c.c. water), and filtered. The dye is precipitated from the filtrate with zinc chloride.

Bromide. According to the formation process of the chloride, the melt is boiled with HBr solution (48%, 45 g. in 1500 c.c. water), and filtered while hot. The dyestuff is precipitated on cooling.

Iodide. The melt is boiled with HI solution (57%, 60 g. in 1500 c.c. water).

Molecular weight.

		Calculated	Found
Chloride	$C_{21}H_{15}N_2Cl \cdot \frac{1}{2}ZnCl$	397.59	406.38
Bromide	$C_{21}H_{15}N_2Br$	374.91	382.80
Iodide	$C_{21}H_{15}N_2I$	421.93	430.10

Analytical data.

	$C_{21}H_{15}N_2Cl \cdot \frac{1}{2}ZnCl_2$		$C_{21}H_{15}N_2Br$		$C_{21}H_{15}N_2I$	
	Calculated	Found	Calculated	Found	Calculated	Found
C	63.39	64.09	67.21	66.89	59.72	59.04
H	3.77	4.02	4.00	4.81	3.55	4.16
N	7.40	7.20	7.46	7.53	6.63	6.64
Cl	17.80	18.05	Br 21.03	20.89	I 30.08	29.38
Zn	8.22	6.88				

Properties. *Form and colour.*

$C_{21}H_{15}N_2Cl \cdot \frac{1}{2}ZnCl_2$ brown needles ;
 $C_{21}H_{15}N_2Br$ yellow needles ;
 $C_{21}H_{15}N_2I$ glistening brownish red needles.

Melting point (Decomposition point).

$C_{21}H_{15}N_2Cl \cdot \frac{1}{2}ZnCl_2$ 200–205°C.
 $C_{21}H_{15}N_2Br$ 216–217°C.
 $C_{21}H_{15}N_2I$ 195–200°C.

Solubility.

Solvent	$C_{21}H_{15}N_2Cl \cdot \frac{1}{2}ZnCl_2$	$C_{21}H_{15}N_2Br$	$C_{21}H_{15}N_2I$
Water	sol.	sol.	sol.
Alcohol	sol.	sol.	sol.
Aniline	very sol.	very sol.	very sol.
Chloroform	sol.	sol.	sol.
Nitrobenzene	sol.	sol.	sol.
Acetone	sol.	sol.	sol.
Glacial acetic acid	sol.	sol.	sol.
Benzene	insol.	insol.	insol.
Ether	insol.	insol.	insol.

Colour reaction in aqueous solution.

Solvent	$C_{21}H_{15}N_2Cl \cdot \frac{1}{2}ZnCl_2$	$C_{21}H_{15}N_2Br$	$C_{21}H_{15}N_2I$
H ₂ O	yellow, with greenish fluorescence	yellow, with greenish fluorescence	yellow, with greenish fluorescence
NaOH	pale green precipitate	pale yellowish brown precipitate	pale greyish yellow precipitate
HCl	reddish yellow	reddish yellow	reddish yellow
H ₂ SO ₄ (conc.)	brownish red	brownish red	brownish red

Dyeing.

	Cotton	Silk	Wool
$C_{21}H_{15}N_2Cl \cdot \frac{1}{2}ZnCl_2$	brown	yellow	yellow
$C_{21}H_{15}N_2Br$	brown	yellow	yellow
$C_{21}H_{15}N_2I$	brown	yellow	yellow

These dyestuffs have good affinity for cotton.

Fastness.

	$C_{21}H_{15}N_2Cl \cdot \frac{1}{2}ZnCl_2$			$C_{21}H_{15}N_2Br$			$C_{21}H_{15}N_2I$		
	Cotton	Silk	Wool	Cotton	Silk	Wool	Cotton	Silk	Wool
Light	good	bad	bad	good	bad	bad	good	bad	bad
Washing	moderate	bad	bad	mod.	bad	bad	mod.	bad	bad
Soap	bad	bad	bad	bad	bad	bad	bad	bad	bad
Acetic acid	good	bad	bad	good	bad	bad	good	bad	bad
Sulphuric acid	moderate	mod.	mod.	mod.	bad	bad	mod.	mod.	mod.

III. The reaction of naphthoquinone on *o*-amidodiphenylamine in glacial acetic acid solution. Preparation of the dyestuffs. *Chloride.* A mixture of 1 part of *o*-amidodiphenylamine (5 g.), 1 part of naphthoquinone (5 g.) and about 20 parts of glacial acetic acid (100 g.) is heated on the water bath until the sample shows no increase in intensity of colour. The melt is then boiled with 20 times its volume of water acidified with HCl (38%, 30 g.), cooled, and filtered. The dye is precipitated from the filtrate with zinc chloride.

Bromide. According to the formation process of the chloride, the melt is boiled with HBr solution (48%, 40 g. in 1500 g. water), filtered, and cooled. The dyestuff is precipitated.

Iodide. The melt is boiled with HI solution (57%, 60 g. in 1500 g. water).

Molecular weight.

		Calculated	Found
Chloride	$C_{22}H_{15}N_2Cl \cdot \frac{1}{2}ZnCl_2$	410.75	392.5
Bromide	$C_{22}H_{15}N_2Br$	387.05	378.8
Iodide	$C_{22}H_{15}N_2I$	434.07	430.6

Analytical data (%).

	$C_{22}H_{15}N_2Cl \cdot \frac{1}{2}ZnCl_2$		$C_{22}H_{15}N_2Br$		$C_{22}H_{15}N_2I$	
	Calculated	Found	Calculated	Found	Calculated	Found
C	64.27	64.30	68.21	67.51	60.82	61.03
H	3.68	3.63	3.91	5.57	3.48	3.38
N	6.82	6.80	7.24	7.23	6.45	6.39
Cl	17.26	17.52	Br 20.65	19.74	I 29.24	29.16
Zn	7.95	7.58				

Properties. Form and colour.

$C_{21}H_{15}N_2Cl \cdot \frac{1}{2}ZnCl_2$	madder brown needles;
$C_{22}H_{15}N_2Br$	vistoris lake needles;
$C_{22}H_{15}N_2I$	vandyke red needles.

Melting point (decomposition point).

$C_{22}H_{15}N_2Cl \cdot \frac{1}{2}ZnCl_2$	278—279°C.
$C_{22}H_{15}N_2Br$	281—282°C.
$C_{22}H_{15}N_2I$	220—221°C.

Solubility.

Solvent	$C_{22}H_{15}N_2Cl \cdot \frac{1}{2}ZnCl_2$	$C_{22}H_{15}N_2Br$	$C_{22}H_{15}N_2I$
Water	very sol.	very sol.	very sol.
Alcohol	sol.	sol.	sol.
Aniline	very sol.	very sol.	very sol.
Chloroform	insol.	insol.	insol.
Nitrobenzene	sol.	sol.	sol.
Acetone	sol.	sol.	sol.
Glacial acetic acid	sol.	sol.	sol.
Benzene	insol.	insol.	insol.
Ether	insol.	insol.	insol.

Colour reaction in aqueous solution.

Solvent	$C_{22}H_{15}N_2Cl \cdot \frac{1}{2}ZnCl_2$	$C_{22}H_{15}N_2Br$	$C_{22}H_{15}N_2I$
H ₂ O	yellowish red	brownish yellow	reddish yellow
NaOH	bluish yellow (black ppt.)	pale yellow (yellowish green ppt.)	yellow (red ppt.)
HCl	reddish yellow	reddish yellow	pale yellow
H ₂ SO ₄	brownish red	brownish red	pale red

Dyeing.

	Cotton	Silk	Wool
$C_{22}H_{15}N_2Cl \cdot \frac{1}{2}ZnCl_2$	pale sudan brown	capucin yellow	deep fresh colour
$C_{22}H_{15}N_2Br$	sudan brown	golden yellow	ocher red
$C_{22}H_{15}N_2I$	pale sudan brown	pale capucin yellow	seashell colour

These dyestuffs have good affinity for silk, wool, and especially for cotton.

Fastness.

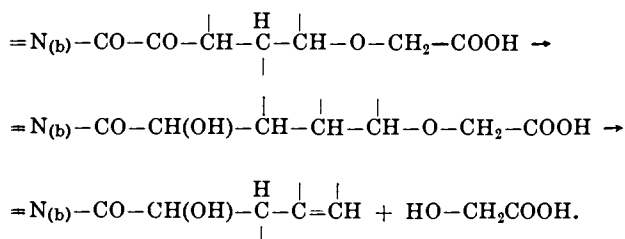
		$C_{22}H_{15}N_2Cl \cdot \frac{1}{2}ZnCl_2$	$C_{22}H_{15}N_2Br$	$C_{22}H_{15}N_2I$
Light	Cotton Silk Wool	good moderate moderate	good moderate moderate	good moderate moderate
Washing	Cotton Silk Wool	good bad bad	good bad bad	good bad bad
Soap	Cotton Silk Wool	bad bad bad	bad bad bad	bad bad bad
Acetic acid	Cotton Silk Wool	good bad moderate	good bad moderate	good bad moderate
Sulphuric acid	Cotton Silk Wool	good bad moderate	good bad moderate	good bad moderate

STUDIES ON THE STRUCTURE OF STRYCHNINE. III.
STRYCHNINOLONE AND ITS DERIVATIVES.

By Munio KOTAKE and Tadahiro MITSUWA.

Received November 9th, 1935. Published March 28th, 1936.

Leuchs and others discovered an important reaction : strychninolic acid is decomposed into strychninolone and glycolic acid when treated with alkali. Although strychninonic acid can hardly be broken up to produce glycolic acid by alkali, if it is reduced to strychninolic acid, the latter easily gives glycolic acid even by the action of dilute alkali. It is undoubtedly due to the fact that the carbonyl group of strychninonic acid is reduced to an alcoholic group. It must have therefore been assumed that, according to Leuchs's or Robinson's formula as shown below, the influence of the carbonyl or the alcohol group should extend so far as to the third carbon atom with the glycolic acid group.



It seemed to be rather unreasonable. Further careful studies on strychninolone, produced by the above reaction, might very likely throw light upon the matters in question. For this reason the present investigation was started.

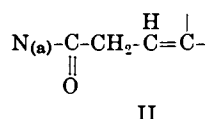
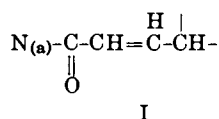
According to Leuchs's method, strychnine was oxidized with potassium permanganate in acetone solution and the formed precipitate was extracted with water. The aqueous solution was then extracted with chloroform. From the chloroform layer dihydroxystrychnine ($\text{C}_{21}\text{H}_{24}\text{N}_2\text{O}_4$, needles) was isolated as a by-product. Its hydrochloride crystallises in needles, and decomposes at 212° ; its iodomethylate is also crystalline and melts at 322° . Thus it is shown that in Leuchs's oxidation the double bond is also first to be oxidized.

Leuchs informed that, besides strychninolone, the a-form (m.p. $228-231^\circ$, $[\alpha] -112-4^\circ$), which was obtained from strychninolic acid treated with alkali, there were two more isomers: when the a-form was shaken with 0.5N alkali, the b-form (m.p. $228-230^\circ$, $[\alpha] -37^\circ$) was obtained; and when the a-form was heated with methyl alcoholic ammonia, the c-form (m.p. 252° , $[\alpha] -176^\circ$). However, there is still some doubt about the identity of the reduction products of these compounds of Leuchs's. Therefore these isomers were first of all subjected to further investigation.

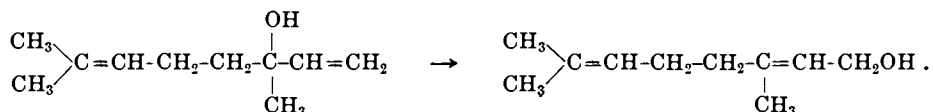
As Leuchs reported, strychninolone melting at $228-230^\circ$ was obtained by the action of alkali upon strychninolic acid, but when it was subjected to fractional crystallization, it was found that the substance melting at $238-240^\circ$, which was designated strychninolone- β , was separated from the less soluble portion, and the substance melting at 224° , which was designated strychninolone- α , was separated from the more soluble portion. It is interesting that these two compounds have the same formula $\text{C}_{19}\text{H}_{18}\text{N}_2\text{O}_3$ and are reduced to a dihydro-compound by catalytic reduction.

It is considered, therefore, that the substance melting at $228-230^\circ$ or Leuchs's strychninolone-a is a mixture of strychninolone- α (m.p. 224°) and strychninolone- β (m.p. 240°). Since these two substances give the same reduction product, they are believed to be isomeric with each other, simply showing the difference in the position of a double bond. This consideration well

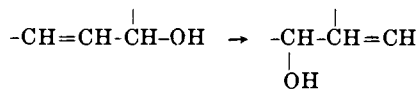
agrees with the following fact. Leuchs already reported that when acetyl-brucinolone is oxidized with potassium permanganate, there are obtained barium salts of two isomeric carboxylic acids, each of which produces oxalic acid and malonic acid. Taking the above-mentioned fact into account, the two following formulas for the two isomeric strychninolones may be considered :



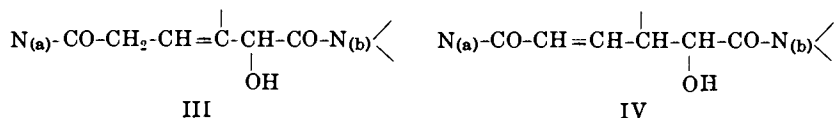
If formula II represents strychninolone- α , formula I belongs to strychninolone- β . (Such a representation is convenient to the following explanation.) The mixture of the two compounds which were found to melt at $228-230^\circ$ was shaken with 0.5N NaOH solution for five days, no visible reaction occurred. But when it was warmed with 10% KOH solution in the presence of a small amount of alcohol, γ -isomer $\text{C}_{19}\text{H}_{18}\text{N}_2\text{O}_3$ melting at 254° was obtained. It forms not only dihydro-derivative $\text{C}_{19}\text{H}_{20}\text{N}_2\text{O}_3$ but also mono-acetyl-derivative $\text{C}_{21}\text{H}_{20}\text{N}_2\text{O}_4$, and it is therefore no doubt an isomer. Since its reduction product is not identical with that of other isomers, it cannot but be considered an isomer caused by the shift of the hydroxyl group. For such an explanation the linalool-geraniol isomerism is often taken as an example :

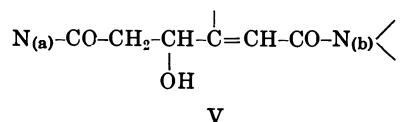


If it is assumed that such an isomeric change occurs between strychninolone- α and strychninolone- γ , the isomerism will be quite readily understood :

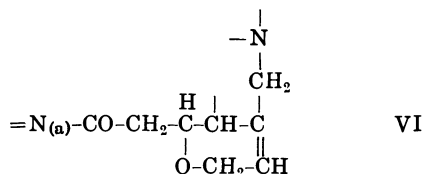


If the assumption be correct, strychninolone- α , strychninolone- β , and strychninolone- γ will be represented by formulas III, IV, and V, respectively, and the number of carbon atoms between $\text{N}_{(a)}$ and $\text{N}_{(b)}$ of the strychninolone molecule will be six :

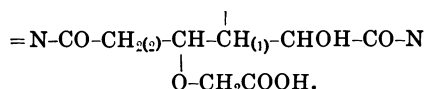




Consequently there must be an atomic group represented by VI in the strychnine molecule.



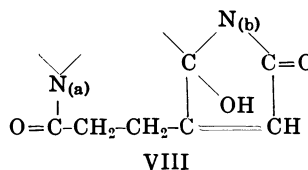
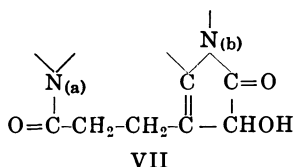
By the same explanation, the fact that glycolic acid does not split from strychninonic acid but does from strychninolic acid, may be well understood. If strychninonic acid forms an enol structure in an alkaline medium, the hydrogen atom of $\text{C}_{(1)}$ migrates to the oxygen atom of the adjacent carbonyl group and there will be no opportunity for glycolic acid to be split off. Hence it is regarded that strychninonic acid does not form an enol structure, the hydrogen atom remaining in $\text{C}_{(1)}$, and it splits readily glycolic acid.



Now a question arises whether such a compound as strychninonic acid forms an enol structure or not. Strychninone $\text{C}_{19}\text{H}_{16}\text{N}_2\text{O}_3$ (m.p. 273°), obtained from strychninolone by oxidation with chromic acid, readily dissolves in alkali in slightly yellowish colour and precipitates on passing carbon dioxide in the solution. When dihydrostrychninolone is oxidized with chromic acid, dihydrostrychninone is also obtained; the compound dissolves slowly in alkali to a colourless solution, and, moreover, does not precipitate with carbon dioxide. It may be assumed that the hydrogen atom of $\text{C}_{(2)}$ may be removed in order to split glycolic acid from strychninolic acid molecule, the keto form,

$\text{=N}_{(a)}-\text{CO}-\text{CH}_2-\text{CH}-\text{O}-\text{CH}_2-\text{COOH}$. If the assumption mentioned above is correct, glycolic acid also has to split off from strychninonic acid, but actually the reaction does not occur.

Two following isomeric formulas for strychninolones may also be considered :



Really strychninolone- δ , an isomer melting at 286° , is obtained from strychninolone-a by heating it with sodium ethylate. Strychninolone- δ can not be reduced in the presence of Pd at room temperature, but gives an acetyl derivative. Considering the fact that neostrychnine and Tafel base are not easily reduced at room temperature, the position of the double bond of these compounds may be the same with that of strychninolone- δ .

Leuchs's method, action of methyl alcoholic ammonia upon strychninolone-a, was repeated and the neutral substances in the reaction product were treated with hot water. From the more soluble portion was obtained strychninolone- γ , and from the less soluble portion a new isomer, which was recrystallized from water and melted at $241-243^\circ$. The isomer, expressed by the name strychninolone- ε , was readily reduced by catalytic reduction and gave a mono-acetyl-derivative. Since strychninolone- γ is obtained by the same method, strychninolone- ε is regarded to be produced also by the shift of OH-group. Therefore strychninolone- ε is represented by formula VIII and consequently strychninolone- δ by formula VII.

Supposing the ring of the molecule opens at one position and closes in another, one more isomer can be obtained. The confirmation of this idea is left for future investigation.

Melting points of strychninolone isomers and their derivatives

Strychninolone		Dihydro-derivative	Acetyl derivative
α C ₁₉ H ₁₈ N ₂ O ₃	224°	274°	$240-243^\circ$
β C ₁₉ H ₁₈ N ₂ O ₃	$233-240^\circ$	274°	253°
γ C ₁₉ H ₁₈ N ₂ O ₃	254°	$215-217^\circ$	260°
δ C ₁₉ H ₁₈ N ₂ O ₃ ·3H ₂ O	286°	—	$340-350^\circ$
ε C ₁₉ H ₁₈ N ₂ O ₃ ·H ₂ O	$240-243^\circ$	257°	$214-215^\circ$

Experimental Part.

Dihydroxy-strychnine. Strychnine was oxidized with potassium permanganate in acetone solution. In order to separate⁽¹⁾ the oxidized substance, the precipitate was extracted with cold water and the aqueous extract was shaken with chloroform. When the solvent

(1) *Ber.*, **41** (1908), 1711; *ibid.*, **46** (1913), 3693.

was distilled off, needle crystals were obtained. This substance was recrystallized from methanol. It bubbles at 100° , solidifies again on further heating, contracts at about 155° , and melts finally at 240° . The crystals obtained from methanol solution gave the following results by analysis: Found: C, 66.15, 66.27; H, 6.84, 6.60. Calc. for $C_{21}H_{24}N_2O_4 \cdot CH_3OH$: C, 66.00; H, 7.00%. The crystals from aqueous solution showed the following results by analysis: Found: C, 61.39, 61.23; H, 7.21, 7.12. Calc. for $C_{21}H_{24}N_2O_4 \cdot 2\frac{1}{2}H_2O$: C, 61.02; H, 7.02%. The above substance was dehydrated by heating in the xylene bath under reduced pressure and subjected to analysis: 3.618 mg. gave 9.070 mg. CO_2 and 2.264 mg. H_2O . Found: C, 68.37, 68.12; H, 7.00, 6.76. Calc. for $C_{21}H_{24}N_2O_4$: C, 68.5; H, 6.50%.

Dihydroxystrychnine Hydrochloride. When dihydroxystrychnine was dissolved in hydrochloric acid and the solution evaporated, needle crystals were obtained. They were recrystallized from water. Needles, decomposing at 212° with bubbling: (Found: C, 58.93, 59.16; H, 6.64, 6.68. Calc. for $C_{21}H_{24}O_4 \cdot HCl \cdot H_2O$: C, 59.64; H, 6.39%).

Dihydroxystrychnine-iodomethylate. Dihydroxystrychnine in methanol was treated with methyl iodide, and dihydroxystrychnine iodomethylate was obtained. It was recrystallized from water, m.p. 322° . (Found: C, 52.30, 52.18; H, 5.59, 5.21. Calc. for $C_{21}H_{24}N_2O_4 \cdot CH_3I$: C, 51.75; H, 5.29%.)

Purification of Strychninolones (Separation of α - and β -Isomers). Strychninolone obtained from strychninolic acid by the action of cold alkali was found to melt at 215 – 225° . It was subjected to fractional crystallization from methanol. The first crop of crystals melted at 238 – 240° , and further four crops, melting at 235 – 237° , 232 – 234° , 228 – 230° , and 222 – 224° , respectively, were obtained from the mother liquor. The first crop melting at 238 – 240° was recrystallized from ethyl alcohol, methanol, and other solvents, but its melting point was not raised. The portion melting at 222 – 224° was recrystallized from alcohol and its melting point was found to be 223 – 224° . The crops obtained between these two crops were finally separated into the above two substances by repeated crystallization. The substances melting at 223 – 224° or α -isomer was analyzed: Found: C, 70.38, 70.47; H, 6.03, 6.07. Calc. for $C_{19}H_{18}N_2O_3$: C, 70.80; H, 5.59%. The substance melting at 238 – 240° or β -isomer was analyzed as follows: Found: C, 70.77, 70.70; H, 5.82, 5.81. Calc. for $C_{19}H_{18}N_2O_3$: C, 70.80; H, 5.59%.

Catalytic Reduction of Strychninolone- α and Strychninolone- β . Strychninolone- α (m.p. 224°), strychninolone- β (m.p. 240°) and strychninolone-a (m.p. 228 – 230°) were respectively dissolved in alcohol or glacial acetic acid and shaken in the current of hydrogen gas for three hours in the presence of Pd-catalyst. When the absorption of hydrogen ceased, the reaction mixture was filtered in order to separate Pd, and the solvent was distilled, when the reduction product was obtained in crystalline form. It was recrystallized from methanol. The above-mentioned three substances gave the identical reduction product; needles melting at 274° . (Found: C, 70.77, 70.78; H, 6.15, 6.16. Calc. for $C_{19}H_{20}N_2O_3$: C, 70.37; H, 6.17%.)

Acetylation of Strychninolone- α . Strychninolone- α (0.5 g.) in 10 c.c. of acetic anhydride with a small amount of anhydrous sodium acetate was heated at 100° for four hours provided with an air condenser. After removal of acetic anhydride under reduced pressure, the reaction mixture was dissolved in water and shaken with chloroform. The chloroform layer was separated from aqueous solution and the solvent was distilled. When a few drops of alcohol was added to the residue, a crystalline substance appeared. It was recrystallized from ethyl alcohol or methanol. Needles, melting at 240 – 243° . (Found: C, 68.89; H, 6.05. Calc. for $C_{21}H_{20}N_2O_4$: C, 69.23; H, 5.52%.)

Acetylation of Strychninolone- β . The procedure of the acetylation of strychninolone- α was followed in every particular. Needles, m.p. 253°. (Found: C, 69.40, 69.23; H, 5.94, 5.93. Calc. for $C_{21}H_{20}N_2O_4$: C, 69.23; H, 5.52%.)

Formation of Strychninolone- γ . To strychninolone-a was mixed with 10% potassium hydroxide solution and a few drops of alcohol, and the mixture was warmed on the water bath, when the solid was dissolved in a short time. After cooling the mixture, it was treated with hydrochloric acid, when there appeared a white precipitate. Allowing the precipitate to settle down for one day, it was separated by filtration and recrystallized from alcohol. Needles, m.p. 254°; yield 70%. (Found: C, 71.15, 70.81; H, 6.05, 6.10. Calc. for $C_{19}H_{18}N_2O_3$: C, 70.80; H, 5.59%.)

Catalytic Reduction of Strychninolone- γ . Strychninolone- γ , dissolved in glacial acetic acid, was shaken in the current of hydrogen in the presence of catalytic Pd. When it ceased to absorb hydrogen, the reaction mixture was filtered to remove the catalyst and the solvent was distilled under reduced pressure, when crystalline residue was obtained. It was recrystallized from ethyl alcohol and methanol successively, prisms melting at 215°. (Found: C, 70.13, 69.90; H, 6.31, 6.46. Calc. for $C_{19}H_{20}N_2O_3$: C, 70.37; H, 6.17%.)

Acetylation of Strychninolone- γ . To strychninolone- γ , (0.4 g.), was added 10 c.c. of acetic anhydride and a small amount of anhydrous sodium acetate. The mixture was warmed at 100° for four hours, using an air condenser. Then acetic anhydride was distilled under reduced pressure, the residue dissolved in water, and the solution shaken with chloroform. When the chloroform layer was separated from the aqueous solution, the solvent distilled, and a few drops of alcohol were added to the residue, crystals separated out. They were recrystallized from ethyl alcohol or methanol. Needles, m.p. 260°. (Found: C, 69.07, 69.24; H, 6.00, 5.98. Calc. for $C_{21}H_{20}N_2O_4$: C, 69.23; H, 5.52%.)

Formation of Strychninolone- δ : Reaction of Sodium Ethylate upon Strychninolone-a. To 1 g. strychninolone-a was added a solution of sodium ethylate (prepared from 1 g. of sodium) in absolute alcohol, and the mixture was heated on the water bath under a reflux condenser for two hours. Then the alcohol was distilled. When a small amount of water, a few drops at a time, was added to the residue, needle crystals appeared. It was recrystallized from dilute alcohol. It was found to melt at 285–286° with bubbling: (Found: C, 60.54, 60.36; H, 6.46, 6.66. Calc. for $C_{19}H_{18}N_2O_3 \cdot 3H_2O$: C, 60.63; H, 6.38%). When it was dehydrated under reduced pressure on a xylene bath, 4.253 mg. of the substance lost 0.554 mg. or 13.1% of the original weight, whereas the theory requires 14%: (Found: C, 70.36, 70.68; H, 6.01, 5.92. Calc. for $C_{19}H_{18}N_2O_3$: C, 70.80, H, 5.59%).

It was subjected to reduction in the current of hydrogen gas in the presence of Pd but no reaction was observed.

Acetyl-strychninolone- δ . For the preparation of this compound the directions given in the case of acetyl-strychninolone- γ were followed. It was obtained in needles and recrystallized from methanol; its melting point was above 340°: (Found: C, 65.54, 65.49; H, 6.07, 5.54; H_2O , 4.0. Calc. for $C_{21}H_{20}N_2O_4 \cdot H_2O$: C, 65.96; H, 5.54; H_2O , 4.8. Calc. for $C_{23}H_{22}N_2O_5 \cdot H_2O$: C, 65.10; H, 5.66; H_2O , 4.2%.)

Action of Methyl Alcoholic Ammonia upon Strychninolone-a (Formation of Strychninolone- ϵ). To strychninolone-a was added methyl alcoholic ammonia (saturated at 20°) and the mixture was heated in a sealed tube for three hours. The sealed tube was allowed to cool overnight and opened. When methanol was evaporated, crystals were obtained. They were treated with hydrochloric acid and shaken with chloroform; when

the chloroform layer was separated and evaporated, crystals melting at 240° separated out. They were treated with hot water and subjected to fractional crystallization. From the more soluble part, fine needles were obtained by cooling the hot solution. They were recrystallized from water and found to melt at $240\text{--}243^{\circ}\text{C}$: (Found: C, 67.50; H, 6.21; H_2O , 5.4. Calc. for $\text{C}_{19}\text{H}_{18}\text{N}_2\text{O}_3 \cdot \text{H}_2\text{O}$: C, 67.05; H, 5.99; H_2O , 5.3%). The dehydrated substance obtained by warming in a xylene bath under reduced pressure was found to melt at 208° . (Found: C, 70.51, 70.37; H, 6.09, 5.76. Calc. for $\text{C}_{19}\text{H}_{18}\text{N}_2\text{O}_3$: C, 70.80; H, 5.59%.)

The part less soluble in water was recrystallized from methanol. Its melting point was found to be $252\text{--}253^{\circ}$ and was not lowered by admixture with strychninone- γ . Thus the identity of the compound with γ -derivative was established.

Catalytic Reduction of Strychninolone- ϵ . Strychninolone- ϵ (m.p. $240\text{--}243^{\circ}$) was dissolved in alcohol and subjected to reduction in the current of hydrogen gas in the presence of Pd-black. After shaking the mixture for three to four hours, the current of hydrogen gas was stopped and the solution was filtered in order to remove Pd-black. When the filtrate was evaporated, crystals melting at $208\text{--}210^{\circ}$ were obtained. When they were recrystallized from a large amount of methanol, unchanged strychninolone- ϵ separated first and dihydro-strychninolone- ϵ crystallized out next upon further evaporation of the solvent; its melting point was 257° . It was again recrystallized from alcohol and obtained in prisms; the melting point was still 257° . (Found: C, 68.09, 68.29; H, 6.67, 6.77. Calc. for $\text{C}_{19}\text{H}_{20}\text{N}_2\text{O}_3 \cdot \frac{1}{2}\text{H}_2\text{O}$: C, 68.46; H, 6.30%. Found for dehydrated substance: C, 70.42, 70.44; H, 6.13, 5.99. Calc. for $\text{C}_{19}\text{H}_{20}\text{N}_2\text{O}_3$: C, 70.37; H, 6.17%.)

Acetyl-strychninolone- ϵ . For the preparation of acetyl-strychninolone- ϵ , the directions given for the preparation of the acetyl derivative of strychninolone- α were followed. It was purified by recrystallization from methanol and ethanol. Needles, m.p. $214\text{--}215^{\circ}$. (Found: C, 69.17, 69.27; H, 5.99, 5.82. Calc. for $\text{C}_{21}\text{H}_{20}\text{N}_2\text{O}_4$: C, 69.23; H, 5.52%.)

Oxidation of Strychninolone-a with Chromic Acid: Formation of Strychninone. To 3 g. of strychninolone, dissolved in 200 c.c. of glacial acetic acid, 1.2 g. of chromic anhydride, dissolved in 100 c.c. of glacial acetic acid, were added little by little with constant stirring. The mixture was allowed to stand overnight and the glacial acetic acid was distilled under reduced pressure. The residue was dissolved in water and shaken with acetic ester. The acetic ester was separated and washed with water. After the removal of the solvent, the residue was treated with a small amount of methanol, and the methanol was evaporated until the odour of acetic acid almost vanished, when a crystalline substance separated out. It was dissolved in a small amount of methanol, filtered, and acetic ester was added to the solution, when crystals melting at 273° were obtained. They dissolve in dilute alkali in slight yellow colour and are reprecipitated with carbon dioxide. (Found: C, 71.39, 71.41; H, 5.37, 5.37. Calc. for $\text{C}_{19}\text{H}_{16}\text{N}_2\text{O}_3$: C, 71.25; H, 5.00%.)

Oxidation of Dihydrostrychninolone-a with Chromic Acid. To 2 g. of dihydrostrychninolone-a (m.p. 275°), dissolved in glacial acetic acid, 1.0 g. of chromic anhydride, dissolved in glacial acetic acid, was added drop by drop. The mixture was allowed to stand overnight and the solvent was distilled under reduced pressure. The residue was treated with water and shaken with acetic ester. The layer of acetic ester was separated, dried with anhydrous sodium sulphate, and when the solvent was distilled, crystals came out. They were recrystallized from acetic ester, m.p. 314° . They dissolve slowly in alkali. (Found: C, 71.25, 71.07; H, 5.61, 6.11. Calc. for $\text{C}_{19}\text{H}_{18}\text{N}_2\text{O}_3$: C, 70.80; H, 5.59%.)

INFLUENCES OF HYDROGEN-ACCEPTOR ON FUCOSE FERMENTATION BY *ASPERGILLUS ORYZAE*.

By Tetsutaro TADOKORO.

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On the mechanism of fucose fermentation, no experimental results have been hitherto reported. It has to be explained by reference to pentose fermentation which has been investigated by some authors. The mechanism of pentose fermentation by fungus is different from that by bacteria. In the latter case, CO₂, acetone, acetic, lactic, and succinic acids, and ethyl alcohol are found in the fermentation products. In the former case it was stated by Behren⁽¹⁾ that *Botrytis cinerea*, *Rhizopus nigricans*, and *Penicillium glaucum* utilized arabinose. It was also stated by Czapek⁽²⁾ that *Aspergillus niger* consumed xylose and arabinose, though the products are far different from those of fermentation by fungus. Niktinsky reported that *Aspergillus niger* easily utilized arabinose as a carbon source and that there is no difference from *d*-glucose. Peterson, Fred, and Schmidt⁽³⁾ stated that when pentose, i.e. arabinose, was fermented by *Aspergillus*, by *Penicillium*, or by *Mucor*, they could not find any alcohol nor volatile acid excepting CO₂. White and Willamen⁽⁴⁾ reported that *Fusarium* formed alcohol from arabinose. Amelung⁽⁵⁾ isolated citric acid from *Aspergillus* culture media containing arabinose. Butkewitsch⁽⁶⁾ stated that citric acid was formed from arabinose by *Citromyces* while only a trace was formed by *Aspergillus*. Accordingly the present author has explained the mechanism of arabinose fermentation as follows: arabinose would be broken down to C₃-compound at first and glucose might be changed to glucuronic acid then to saccharic acid and at last to citric acid. Jurist⁽⁷⁾ stated that the saccharic acid then changes to ketipinic acid and at last to citric acid while Franzen and Schmidt formed citric acid from ketipinic acid ester, treating with KOH. Tamiya⁽⁸⁾ found kojinic acid in the fermentation by *Aspergillus flavus*. Schreyer⁽⁹⁾ reported that *Aspergillus*

(1) Behren, *Centr. Bakt.*, II, **4** (1898), 514.

(2) Czapek, *Hofmeister's Beitrage*, **3** (1902), 62.

(3) Peterson, Fred, and Schmidt, *J. Biol. Chem.*, **60** (1924), 628.

(4) White and Willamen, *Biochem. J.*, **22** (1928), 583.

(5) Amelung, *Z. physiol. Chem.*, **166** (1927), 161.

(6) Butkewitsch, *Biochem. Z.*, **142** (1923), 195.

(7) Jurist, *J. Am. Chem. Soc.*, **44** (1925), 1136.

(8) Tamiya, *Acta Phytochim.*, **4** (1929), 227.

(9) Schreyer, *Biochem. Z.*, **202** (1928), 131.

formed fumaric acid from arabinose. There is only one report that methylpentose, i.e. isorhodeose, was fermented by *Aspergillus niger* to form tartaric acid.

Among the yeasts, it was reported by Lintner that *Schizosaccharomyces thermantitonus* ferments arabinose but other kinds of yeast do not. Many yeasts contain large quantities of methylpentosan, which is called yeast gummy substance and the nucleic acid of yeast contains ribose, a kind of pentose.

As to bacteria, it was reported by Schmidt and Peterson⁽¹⁰⁾ that the acetone fermentation bacteria formed butyl alcohol, acetone, volatile and non-volatile acids with CO₂ and by Bertrand⁽¹¹⁾ that in sorbose fermentation, *Bacterium xylinum* formed arabonic acid. Lafar⁽¹²⁾ stated that oxalic acid fermentation was caused by *B. aceti*, *B. acetogenum*, *B. ascendens*, *B. Kutzengianum*, *B. xylinum*, and by *Thermobacter aceti*. Grimbert⁽¹³⁾ proved that *Pneumococcus* formed lactic acid and acetic acid from arabinose, Further, Tollens⁽¹⁴⁾ proved that ethyl alcohol is formed by *B. ethaceticus* and by other putrefaction bacteria. Seiler⁽¹⁵⁾ stated that anhydropentose was changed to galactan, C₁₂H₂₀O₁₀, by *B. metarabinum* and by *B. persiae*.

Among the references on the influences of the hydrogen acceptor, i.e. oxygen, methyl blue, and quinone, in acetic acid fermentation, Tamiya and Tanaka⁽¹⁶⁾ stated that quinone is the most powerful reagent. Thus the dehydration due to the presence of these reagents in acetic acid fermentation is explained by the following chemical reaction: CH₃CH₂OH + Acc. = CH₃CHO + H₂Acc. or CH₃CH(OH)₂ + Acc. = CH₃COOH + H₂Acc. Also the same reaction was observed in the case of the formation of succinic acid from acetic acid, of fumaric acid and of succinic acid from alcohol and of fumaric acid from succinic acid. Fischer⁽¹⁷⁾ observed fumaric and maleic acid formation from Na-succinate of muscle in the presence of methyl blue. Also there is need of the hydrogen acceptor in the formation of propionic acid from lactic acid and formic acid decomposition to CO₂.

However, there is no report concerning the products of fucose fermentation by *Aspergillus oryzae* nor the differences in the fermentation products when cultured by the same fungus under different conditions of culture.

(10) Schmidt and Peterson, *J. Biol. Chem.*, **61** (1924), 163.

(11) Bertrand, *Compt. rend.*, **126** (1898), 762.

(12) Lafar, "Handbuch Tech. Mykolog.", Bd. 5, 588.

(13) Grimbert, *Ann. inst. Pasteur*, **9** (1895), 240.

(14) Tollens, *J. Landw.*, **49** (1901), 29.

(15) Seiler, *Centr. Bakt.*, II, **4** (1898), 514.

(16) Tamiya and Tanaka, *Acta Phytochim.*, **6** (1932), 1.

(17) Fischer, *Arch. Pharma.*, **257** (1919), 33.

The writer has had the opportunity of getting plentiful amounts of substances consisting principally of fucose in the experiments relating with chemical studies of *Iridaea laminarioides*.

Preparation of fucose. The air-dried samples of *Iridaea laminarioides*, upon extraction with 35% alcohol at 40°C., yielded a very small amount of viscous liquid containing colouring matters. The evaporated extract was mixed with acetone and the precipitate was freed from acetone and extracted again with alcohol to free it from chromoproteid. The residue was hydrolysed with 5% H_2SO_4 , neutralised with $\text{Ba}(\text{OH})_2$ and then filtered. The filtrate was evaporated and treated with alcohol to obtain the syrup of sugars. This syrup is made up of the hydrolytic products of the dilute alcohol soluble polysaccharides and the hydrolysed products are composed from fucose. *Aspergillus oryzae* was then cultured at 30°C. for a few days until the time of spore formation. The nutritional salts were prepared as follows: $\text{NaNO}_3 = 4$, $\text{KH}_2\text{PO}_4 = 2$, $\text{MgSO}_4 \cdot 7\text{H}_2\text{O} = 1$, $\text{FeCl}_3 = 1$ drop in 100 c.c. of water.

Separation and detection of the fermentation products. The fungus membrane of the surface of the fermented liquid was taken away, the liquid was filtered, and freed from volatile matters by steam distillation. The distillate was used as samples for the detection of acetaldehyde, acetone, alcohol, acetic acid, and formic acid.

The residual liquid was neutralised with NaOH, Cu-acetate was added to precipitate kojinic acid, the liquid filtered, and the filtrate was acidified with acetic acid and then precipitated with Pb-acetate. The Pb-precipitate may contain oxalic, citric, fumaric, tartaric, and allied acids, and when the filtrate is made alkaline with ammonia, the precipitate which is formed by Pb-acetate may contain glycolic acid, and its filtrate, lactic acid. The Pb-precipitate, containing oxalic, citric, and allied acids, was treated with H_2S and reprecipitated with Pb-acetate in 50% alcohol solution in the presence of ammonia. The oxalic acid fraction was insoluble and the citric acid fraction became soluble. The Pb-precipitate, containing citric and tartaric acid fraction was treated with H_2S ; then the filtrate was concentrated and mixed with two volumes of 95% alcohol, some K-acetate was added. Then the precipitate was found to be composed of tartaric and the filtrate was citric acid.

For the detection of acetaldehyde, the silver mirror reaction, the phenylhydrazine reaction and the *p*-bromo-phenylhydrazine reaction were employed. For the detection of acetone, Gablisen's Na-nitroprusside reaction was used with ammonia. For the detection of alcohol, the iodine and K-iodide reactions were carried out with KOH. For the detection of acetic acid, the formation of the hexa-acetate of ferri-salt was used, and also the distillation test of

Ca-acetate and the silver acetate crystals with AgCO_3 . For the detection of formic acid, the precipitate by Pb-acetate in ammoniacal solution, the colour reaction with FeCl_3 and with resorcinol and H_2SO_4 , and the detection of methyl blue with K-bisulphite were employed. For the detection of kojinic acid use was made of the colour reaction with FeCl_3 , the reducing test with Fehling's solution, the diazo-reaction with diazobenzenesulphonic acid, and determination of the melting point. For the detection of lactic acid, the guaiacol reaction with H_2SO_4 , the acetaldehyde formation, treatment with K-permanganate and the crystallisation of Zn-lactate were used. For the detection of glycolic acid, the *p*-cresol reaction with acetic acid and H_2SO_4 , Bülow's hydrazine reaction with FeCl_3 and H_2SO_4 , and the crystals and the melting point of the phenylhydrazide were examined. For the detection of citric acid, the formation of Hg-HgSO_4 , acetone-dicarboxylic acid salt by Denigès's reagent, Stahre's reaction with K-permanganate, and Na-nitroprusside reaction were tested. For the detection of tartaric acid, Fenton's dihydroxymaleic acid reaction, the colour reactions with resorcinol, with α -naphthol and with ammonium molybdate were employed. For the detection of fumaric acid, the melting point of free acid and Ca-fumarate was examined. For the detection of oxalic acid, the colour reaction with FeCl_3 , with resorcinol and H_2SO_4 , and the Ca-Ag-oxalate were examined. For the detection of glycerinaldehyde, the orcinol and the phloroglucinol reaction, the reduction of Fehling's solution, and the phenylosazone were examined. For the detection of carboxylic acid, the colour reactions of α -naphthol, of phloroglucinol, of orcinol, of resorcinol and of naphthoresorcinol were examined, and the osazone test was made.

Differences between fucose fermentation products by *Aspergillus oryzae* with and without methyl blue. The liquid resulting from fermentation of fucose by *Aspergillus oryzae* with and without methyl blue, was filtered, and distilled in steam. Both the distillates showed neither the acetaldehyde reactions, i.e. the phenylhydrazine or the silver mirror reaction, nor acetone reaction, i.e. reaction with Na-nitroprusside, acetic acid, and ammonia. The filtrate showed also no alcohol reaction, i.e. reaction with KI, iodine, and KOH, and no acetic acid reaction, i.e. with FeCl_3 . These results coincide with the results of tests of the distillate of arabinose fermentation which were reported in the Journal of Agr. Chemical Society of Japan.⁽¹⁸⁾

As to the detection of formic acid by means of Pb-acetate, and FeCl_3 , and by resorcinol and H_2SO_4 , the reactions were faint, and in the presence of methyl blue, these reactions were not observed at all, while as to the arabinose fermentation, pretty noticeable reactions were observed.

(18) Tadokoro, *J. Agr. Chem. Soc. Japan*, **11** (1935), 167.

The distillation residue was neutralized with NaOH and a precipitate was formed, Cu-acetate added, the liquid filtered, the filtrate was freed from Cu-salts, and the Pb-precipitate was formed by Pb-acetate after acidification with acetic acid. In the detection of kojinic acid obtained from H_2S decomposition of Cu-precipitates, the $FeCl_3$ reaction, the reduction of Fehling's solution, and the diazo-reaction, were positive, although, when it was extracted with ether, no crystals could be obtained; but when methyl blue was used, no reaction could be observed.

The Pb-precipitate which corresponds to the oxalic and citric acid fraction, was obtained as stated above by the treatment with Pb-acetate and acetic acid. From the filtrate, after making it alkaline with ammonia, the Pb-precipitate was obtained, which corresponds to the glycolic acid fraction. After the separation of this precipitate, the filtrate contained also Pb-salts which correspond to the lactic acid fraction.

The Pb-precipitate of the oxalic acid and citric acid fraction was decomposed with H_2S , and after being concentrated, Pb-acetate and ammonia were added in the presence of 50% alcohol. Therefore the oxalic acid fraction comes out as precipitate while the citric acid fraction remains in the filtrate. All these Pb-salts were decomposed with H_2S , filtered, the filtrate was concentrated and the various reactions were examined.

For the detection of glycolic acid, the concentrated solution was treated with ether. After the ether extract was freed from ether, the following reactions were tested. The cresol reaction with glacial acetic acid and H_2SO_4 showed greenish blue and the guaiacol reaction showed violet colour. Bülow's reaction⁽¹⁹⁾ with $FeCl_3$ and H_2SO_4 in the presence of phenylhydrazine showed reddish violet. The phenylhydrazone was formed, treated with phenylhydrazine on the water bath, freed from the excess of phenylhydrazine, extracted with ether, and white crystals of the phenylhydrazide were obtained which melted at $118^\circ C$. after purification with acetic acid. But in the case of using methyl blue, these colour reactions were not observed at all.

For the detection of lactic acid and maleic acid, after the concentrated solution was treated with ether, examination was made of the following reaction.

As to the formation of acetaldehyde, upon heating the solution with K-permanganate it was detected. The rose colour was also observed after treating with H_2SO_4 and guaiactincture, and bright yellow was seen with $FeCl_3$. A large quantity of the liquid was boiled with $ZnCO_3$, and crystals of Zn-lactate were obtained. When the ZnO content was determined by the ordinary method, it was found to correspond to 28.02%. But in the case of

(19) Bülow, *Ann.*, **236** (1886), 195.

using methyl blue, these reactions were not observed and naphthoresorcinol reaction only was seen. Further for the detection of maleic acid, Denigès's reaction⁽²⁰⁾ and diazo-reaction were observed, but Kleeman's reaction could not be observed. From these results in the case of using methyl blue, maleic acid is apparently formed instead of lactic acid.

For the detection of oxalic acid, the precipitate with CaCl_2 in ammoniacal solution which is insoluble in acetic acid was formed. The resorcinol H_2SO_4 reaction showed green blue, the FeCl_3 reaction showed greenish yellow. But Cu-oxalate with Cu-acetate, and Ag-oxalate with AgNO_3 were formed in small quantities in the presence of HNO_3 , so the liquid does not seem to contain large quantities of oxalic acid.

In the detection of citric acid, the white precipitate with Denigès's reagent and the characteristic colour with Na-nitroprusside were not observed, so the presence of citric acid is questionable. For the detection of tartaric acid, Fenton's reaction with FeSO_4 and H_2O_2 and the ammonium molybdate reaction with H_2O_2 were negative. Therefore the presence of tartaric acid is also uncertain. The resorcinol H_2SO_4 and the α -naphthol- H_2SO_4 reactions which are common to this acid and succinic acid were observed. But the pyrrole-reaction of succinic acid was very faint, and in the FeCl_3 reaction no precipitate was formed, but the material showed only a clear red colour. From these results it may be stated that the presence of succinic acid is questionable while that of oxocarboxylic acid is more probable. Furthermore in the phloroglucinol-HCl and in the orcinol-HCl reactions, the red colour was indicated in amyl alcohol, and the reddish violet colour was indicated in ether in the naphthoresorcinol-HCl reaction. The oxocarboxylic acid not precipitated by Cu-acetate, did not give the diazo-reaction and did not reduce Fehling's solution; those points are distinguished from kojinic acid. This acid formed osazone with phenylhydrazine and acetic acid, it is soluble in ether and melts at $155-158^\circ$, so it is near to the melting point of glucuronic acid. In the case of using methyl blue, it gave a strong diazo-reaction, so it is probable that maleic acid is formed in the fermented liquid.

The lactic acid fraction was extracted with ether, and the extract freed from ether. It showed red colour when tested with orcinol, with phloroglucinol and H_2SO_4 , and also with resorcinol and HCl, so it seems to contain glyceraldehyde.

Differences in chemical mechanism of fucose fermentations with and without methyl blue. Recently Peterson and Fred⁽²¹⁾ observed the formation of lactic and acetic acids in the heterogeneous lactic acid fermentation of

(20) Denigès, *Compt. rend.*, **130** (1900), 32.

(21) Peterson and Fred, *J. Biol. Chem.*, **64** (1925), 643.

xylose by *Lactobacillus pentaaceticus* and also of arabinose by *Pneumococcus* as stated above. As it has already been stated by Virtanen⁽²²⁾ that the preform of lactic acid is methylglyoxal hydrate in sugar fermentation by *B. coli*, this mechanism will be assumed in the following methylpentose fermentation. Years ago Tate⁽²³⁾ stated that lactic acid formation was observed in the fermentation of rhamnose by *Friedlander's bacillus*, and the other report stated also that isorhodeose was fermented by certain micro-organisms. In the case of methylpentose fermentation, the glycolic acid formation was observed always remarkably, so the chemical mechanism of other acid formation may be communicated to this acid. For example, it was stated by Challenger that formic acid was formed from glycolic acid in oxidative fermentation by *Aspergillus niger*.

Butkewitsch⁽²⁴⁾ stated that citric acid is formed always from glycolic acid by condensation. Fedorff proved the formic acid and the acetaldehyde formation from methylglyoxal by bacteria, and Sakaguchi proved that citric acid is formed easily from acetaldehyde by *Aspergillus* as had already been stated by Neuberg. Tamiya⁽¹⁶⁾ stated that citric acid is formed from two mols of acetic acid and one mol of formic acid.

The acetaldehyde might be formed from methylglyoxal by the dehydration process. In the condensation of acetaldehyde, oxalacetic acid is formed at first, and then maleic acid might be formed also. The maleic acid formation in hexose fermentation was proved by Nishikawa, with cultured *Aspergillus*. Aubel⁽²⁵⁾ stated following Astel's explanation that by oxidation, propionic, acetic, and formic acid are formed while by dehydration, fumaric, maleic, and lactic acids are formed from succinic acid in sugar fermentation.

Sumiki⁽²⁶⁾ proved that the maleic acid formation with other organic acids occurs in the hexose fermentation by *Aspergillus glaucus*.

In the fucose fermentation, the presence of glycerinaldehyde was proved in the experiment as the intermediate product, so kojinic acid was assumed to be formed from glycerinaldehyde by the oxidative synthesis as stated by Tamiya, and the citric acid is formed by the condensation of glycerinaldehyde as stated by Sakaguchi.

The presence of oxocarboxylic acid in the sugar fermentation liquid was reported by Butkewitsch who stated that bacteria formed glucuronic acid from

(22) Virtanen, *Ann. acad. sci. Fennicae*, **29** (1927), No. 26.

(23) Tate, Czapek's "Biochem. d. Pflanzen", I, 1913, 316.

(24) Butkewitsch, *Biochem. Z.*, **142** (1923), 195.

(25) Aubel, *Ergebnisse d. Enzymforschung*, **4** (1935), 251.

(26) Sumiki, *J. Agr. Chem. Soc. Japan*, **6** (1930), 1153; **7** (1931), 819.

gluconic acid. According to Sumiki the latter is proved in the oxidative fermentation of hexose by *Aspergillus*. In the same way, it was stated by Tamiya that arabonic acid is formed in arabinose fermentation by *Aspergillus flavus*, and also by Bertrand that the same acid formation is caused by *Bacterium xylinum*. Next, Sumiki⁽²⁶⁾ proved 2-hydroxymethylfurane-5-carboxylic acid formation in the hexose fermentation by *Aspergillus glaucus* and gluconic acid formation by other *Aspergillus*. Further Sakaguchi proved gluconic acid formation from glycerine by *Aspergillus*, so it shows that the gluconic acid formation is not only a result of the simple oxidation of glucose but it is caused by the oxidative synthesis from the substances with smaller molecules. Therefore, it is probably formed from pentose and methylpentose and also from their cleavage products. The author found glycerinaldehyde which comes easily from glycerine by dehydration in the fucose fermented liquid, and it is more likely that glycerinaldehyde forms gluconic acid and then oxocarboxylic acid.

Anyhow, the important fact of chemism in the cleavage of pentose molecule is the formation of C₃- and C₂-compound as stated by Lek⁽²⁷⁾ that in butyl alcohol fermentation by bacteria, the first cleavage of pentose molecule occurs to form an equimolecular mixture of methylglyoxal and glycoaldehyde.

In the above explanation, the author intended to consider the influences of the hydrogen acceptor in the light of the experimental results reported in the above section.

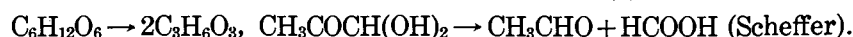
As described in the above section, the influences of methyl blue on acetic acid fermentation caused acetaldehyde to be formed from ethyleneglycol, etc. In muscle there is formed also maleic acid from succinic acid, etc. And it is known that the dehydration reaction of yeast⁽²⁸⁾ is greatly retarded in the presence of methyl blue and their cleavage mechanism is prevented, so much quantities of acetaldehyde were found instead of alcohol, caused by delay in the dismutation of acetaldehyde to alcohol. For the same reason, the action of yeast on methylglyoxal and on pyroracemic acid is always delayed. It is known that various changes were wrought upon chemism of fermentation by the presence of sulphite such as the accumulation of acetaldehyde in alcohol fermentation and in butyric acid fermentation, and such as that of pyroracemic acid in propionic acid fermentation of glucose.

In fucose fermentation with methyl blue, the formic acid formation was delayed, and this change of chemical mechanism is caused by the prevention of the oxidation and of the dehydration of these acid forming substances. So the prevention of the following chemical mechanisms happens as stated by

(27) Lek, Diss. Delft, 1930.

(28) Sonderhoff, *Ergebnisse d. Enzymforschung*, **3** (1934), 183.

many authors in the different cases of fermentation, for instance, by Harden, by Grey, by Neuberg and by Scheffer in hexose fermentation by *B. coli*:



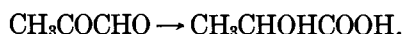
The last reaction is also stated to occur in hexose fermentation by *B. Aerogenes*. Brinkmann stated the following reaction in anaerobic culture of lower fungus:



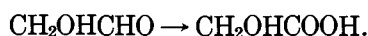
By Challenger the following reaction was stated in the culture media of *Aspergillus niger*: $CH_2OHCO_2H \rightarrow HCO_2H + H_2O + CO_2$.

Thus the formation of CO_2 and H_2 from formic acid is caused by dehydration, and these reactions must be delayed also as less CO_2 -formation was observed in the experimental results.

Aubel stated that in the oxidative fermentation of hexose by *Aspergillus*, propionic, acetic, and formic acids were formed, while in the case of the prevention of oxidation, fumaric, maleic, and lactic acids were formed by dehydration and also maleic acid formation was observed from lactic acid. So in the experiment of the fucose fermentation, using methyl blue, maleic acid would be observed instead of formic acid which is formed in the case of fermentation without methyl blue. The following lactic acid formation is also prevented by using methyl blue in the fucose fermentation:



Glycolic acid is a normal product in the fucose fermentation by *Aspergillus oryzae* but it could not be detected under the influence of the addition of methyl blue, so the following reaction would be prevented:



NEW COMPOUNDS OF UREA-FORMALDEHYDE CONDENSATION PRODUCTS.

By Hiroaki KADOWAKI.

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Although many reports concerning urea-formaldehyde condensation products have been published by many investigators since Hölzer⁽¹⁾, of these condensation products, there are only two whose constitutional formulae have been accounted for to this day. They are namely, monomethylol-urea⁽²⁾ ($\text{H}_2\text{N}-\text{CO}-\text{NH}-\text{CH}_2\text{OH}$) and dimethylol-urea⁽³⁾ ($\text{HOCH}_2-\text{NH}-\text{CO}-\text{NH}-\text{CH}_2\text{OH}$). They are soluble crystalline compounds. It has been observed that urea-formaldehyde condensation products contain, besides crystalline compounds, insoluble amorphous compounds and resinous compounds. Of these, resinous compound is so-called urea resin, and is also termed "organic glass,"⁽⁴⁾ being one of the important synthetic resins. The present author⁽⁵⁾ has, for the past few years, been investigating methods of manufacture of this resin, and especially, most recently, investigated the chemical constitution and the mechanism of formation of this resin and fortunately succeeded in obtaining the expected results.

In this paper the author wishes to report on the thirty new compounds (given in Table 1) out of the condensation products of urea or urea derivatives with formaldehyde, which the author succeeded in synthesizing in the course of his research.

Methylenediurea (I, Table 1) was obtained, in the presence of acid, by the action of 1 mol of formaldehyde on 8 mol of urea. In the past, in the production of urea-formaldehyde condensation products, we had some instances in which formaldehyde was used as (raw) material considerably in excess. However, in the case of urea, 1.33 mol of urea on 1 mol of formaldehyde, as used by Dixon⁽⁶⁾, was the maximum, and the use of any greater excess has never been reported. But the present author succeeded in obtaining methylenediurea as the result of experiment with a great excess of urea as (raw) material. Generally speaking, when urea is reacted upon formaldehyde in

(1) Hölzer, *Ber.*, **17** (1884), 659.

(2) (3) Einhorn and Hamburger, *Ber.*, **41** (1908), 21.

(4) There are other names besides "organic glass."

(5) Kadowaki, *Repts. Imp. Ind. Research Laboratory, Osaka, Japan*, **7** (1926), No. 6; **13** (1932), No. 3, No. 6; **14** (1933), No. 6; **14** (1934), No. 11; **16** (1935), No. 6.

(6) Dixon, *J. Chem. Soc.*, **113** (1918), 233.

Table 1.

No.	Name	Constitutional formula	Properties	Photo-gram
I	Methylene-diurea	$\begin{array}{c} \text{NH-CO-NH}_2 \\ \text{H}_2\text{C} \diagup \quad \diagdown \\ \text{NH-CO-NH}_2 \end{array}$	Needle-crystals m.p. 218°C. (effervesces)	Fig. 1 500×
II	Trimethylene-tetraurea	$\begin{array}{c} \text{NH-CO-NH}_2 \\ \text{H}_2\text{C} \diagup \quad \diagdown \\ \text{NH-CO-NH} \diagup \text{CH}_2 \\ \text{H}_2\text{C} \diagdown \quad \diagup \\ \text{NH-CO-NH} \diagdown \text{CH}_2 \\ \text{NH-CO-NH}_2 \end{array}$	White powder, at 230°C. turns yellow.	Fig. 2 500×
III	Penta-methylene-hexaurea	$\begin{array}{c} \text{NH-CO-NH}_2 \\ \text{H}_2\text{C} \diagup \quad \diagdown \\ \text{NH-CO-NH} \diagup \text{CH}_2 \\ \text{H}_2\text{C} \diagdown \quad \diagup \\ \text{NH-CO-NH} \diagdown \text{CH}_2 \\ \text{H}_2\text{C} \diagup \quad \diagdown \\ \text{NH-CO-NH} \diagup \text{CH}_2 \\ \text{H}_2\text{C} \diagdown \quad \diagup \\ \text{NH-CO-NH} \diagdown \text{CH}_2 \\ \text{NH-CO-NH}_2 \end{array}$	White powder, at 236°C. turns yellow.	Fig. 3 500×
IV	Methylol-methylene-diurea	$\begin{array}{c} \text{NH}_2\text{-CO-NH}_2 \\ \text{H}_2\text{C} \diagup \quad \diagdown \\ \text{NH-CO-NH-CH}_2\text{OH} \end{array}$	White powder.	Fig. 4 500×
V	Methylenebis-methylolurea	$\begin{array}{c} \text{NH-CO-NH-CH}_2\text{OH} \\ \text{H}_2\text{C} \diagup \quad \diagdown \\ \text{NH-CO-NH-CH}_2\text{OH} \end{array}$	White powder m.p. 223°C. (effervesces)	Fig. 5 500×
VI	Methylenebis-acetylurea	$\begin{array}{c} \text{NH-CO-NH-COCH}_3 \\ \text{H}_2\text{C} \diagup \quad \diagdown \\ \text{NH-CO-NH-COCH}_3 \end{array}$	Needle-crystals m.p. 156°C.	Fig. 6 20×
VII	Methylenebis-methylurea	$\begin{array}{c} \text{NH-CO-NH-CH}_3 \\ \text{H}_2\text{C} \diagup \quad \diagdown \\ \text{NH-CO-NH-CH}_3 \end{array}$	Prism-crystals m.p. 184°C.	Fig. 7 20×
VIII	Mono-methylolurea-methylether	$\begin{array}{c} \text{NH-CH}_2\text{-OCH}_3 \\ \text{OC} \diagup \quad \diagdown \\ \text{NH}_2 \end{array}$	Plate-crystals m.p. 91°C.	Fig. 8 16×
IX	Mono-methylolurea-ethylether	$\begin{array}{c} \text{NH-CH}_2\text{-OC}_2\text{H}_5 \\ \text{OC} \diagup \quad \diagdown \\ \text{NH}_2 \end{array}$	Needle-crystals m.p. 111°C.	Fig. 9 40×
X	Dimethylolurea-dimethylether	$\begin{array}{c} \text{NH-CH}_2\text{-OCH}_3 \\ \text{OC} \diagup \quad \diagdown \\ \text{NH-CH}_2\text{-OCH}_3 \end{array}$	Needle-crystals m.p. 101°C.	Fig. 10 40×
XI	Dimethylolurea-diethylether	$\begin{array}{c} \text{NH-CH}_2\text{-OC}_2\text{H}_5 \\ \text{OC} \diagup \quad \diagdown \\ \text{NH-CH}_2\text{-OC}_2\text{H}_5 \end{array}$	Plate-crystals m.p. 124°C.	Fig. 11 40×

Table 1. (Continued)

No.	Name	Constitutional formula	Properties	Photogram
XII	Dimethylolurea-di- <i>n</i> -propylether	$\text{OC} \begin{cases} \text{NH-CH}_2\text{-OC}_3\text{H}_7 \\ \text{NH-CH}_2\text{-OC}_3\text{H}_7 \end{cases}$	Prism-crystals m.p. 95°C.	Fig. 12 57.5×
XIII	Dimethylolurea-di- <i>n</i> -butylether	$\text{OC} \begin{cases} \text{NH-CH}_2\text{-OC}_4\text{H}_9 \\ \text{NH-CH}_2\text{-OC}_4\text{H}_9 \end{cases}$	Needle-crystals m.p. 93°C.	Fig. 13 40×
XIV	Dimethylolurea-di- <i>n</i> -amylether	$\text{OC} \begin{cases} \text{NH-CH}_2\text{-OC}_5\text{H}_{11} \\ \text{NH-CH}_2\text{-OC}_5\text{H}_{11} \end{cases}$	Plate-crystals m.p. 84°C.	Fig. 14 80×
XV	Dimethylolurea-dibenzylether	$\text{OC} \begin{cases} \text{NH-CH}_2\text{-OCH}_2\text{C}_6\text{H}_5 \\ \text{NH-CH}_2\text{-OCH}_2\text{C}_6\text{H}_5 \end{cases}$	Needle-crystals m.p. 112°C.	Fig. 15 57.5×
XVI	Dimethylolurea-diethylthioether	$\text{OC} \begin{cases} \text{NH-CH}_2\text{-SC}_2\text{H}_5 \\ \text{NH-CH}_2\text{-SC}_2\text{H}_5 \end{cases}$	Pillar-crystals m.p. 108.5°C.	Fig. 16 30×
XVII	Methylenebis-methylolurea-methylether	$\text{H}_2\text{C} \begin{cases} \text{NH-CO-NH-CH}_2\text{-OCH}_3 \\ \text{NH-CO-NH-CH}_2\text{-OCH}_3 \end{cases}$	Plate-crystals, at 240°C. turns yellow.	Fig. 17 30×
XVIII	Dimethyloltri-methylene-tetraurea-dimethylether	$\begin{array}{c} \text{H}_2\text{C} \begin{cases} \text{NH-CO-NH-CH}_2\text{-OCH}_3 \\ \text{NH-CO-NH} \end{cases} \\ \text{H}_2\text{C} \begin{cases} \text{NH-CO-NH} \\ \text{NH-CO-NH-CH}_2\text{-OCH}_3 \end{cases} \end{array} \text{CH}_2$	White powder.	
XIX	Monomethylol-urea peroxide	$\text{OC} \begin{cases} \text{NH-CH}_2\text{-O-OH} \\ \text{NH}_2 \end{cases}$	Needle-crystals m.p. 153°C.	
XX	Hexamethylol-triurea peroxide	$\begin{array}{c} \text{HO-O-CH}_2\text{-NH-CO-NH-CH}_2\text{-O} \\ \text{O-CH}_2\text{-NH-CO-NH-CH}_2\text{-O} \\ \text{O-CH}_2\text{-NH-CO-NH-CH}_2\text{-O-OH} \end{array}$	Amorphous powder.	
XXI	<i>N,N'</i> -Dimethylol-urondimethyl-ether	$\begin{array}{c} \text{CO} \\ \text{CH}_3\text{O-CH}_2\text{-N} \quad \text{N-CH}_2\text{-OCH}_3 \\ \text{H}_2\text{C} \quad \text{CH}_2 \\ \text{O} \end{array}$	Colourless transparent liquid, b.p. 82-83°C. (0.1 mm.)	
XXII	<i>N,N'</i> -Dimethylol-urondiethyl-thioether	$\begin{array}{c} \text{CO} \\ \text{C}_2\text{H}_5\text{S-CH}_2\text{-N} \quad \text{N-CH}_2\text{-SC}_2\text{H}_5 \\ \text{H}_2\text{C} \quad \text{CH}_2 \\ \text{O} \end{array}$	Pillar-crystals m.p. 59°C.	Fig. 19 20×

Table 1. (Concluded)

No.	Name	Constitutional formula	Properties	Photogram
XXIII	<i>N</i> -Methyl- <i>N'</i> -methyloluron-methylether		Colourless transparent liquid, b.p. 89-90°C. (0.2 mm.)	
XXIV	<i>N</i> -Methyl- <i>N'</i> -methyloluron-ethylthioether		Colourless transparent liquid, b.p. 122-125°C. (1.0 mm.)	
XXV	<i>N</i> -Ethyl <i>N'</i> -methyloluron-methylether		Colourless transparent liquid, b.p. 91-93°C. (1.0 mm)	
XXVI	<i>N</i> -Ethyl- <i>N'</i> -methyloluron-ethylthioether		Needle-crystals m.p. 15.5°C.	
XXVII	<i>N,N'</i> -Dimethyluron		Prism-crystals m.p. 38.5°C.	
XXVIII	Tetramethyl-dimethylene-diureid		Needle-crystals m.p. 258°C.	Fig. 20 40×
XXIX	<i>N,N</i> -Dimethyl- <i>N'</i> -methylolurea-methylether		Prism-crystals m.p. 65°C.	
XXX	Methylenebis-methyloluron-methylether		Colourless transparent sticky substance.	



Fig. 1.

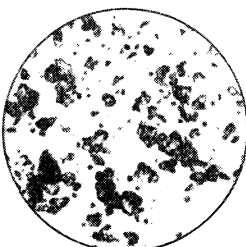


Fig. 2.

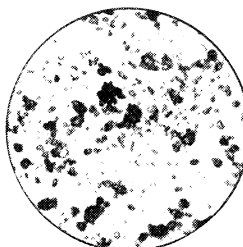


Fig. 3.

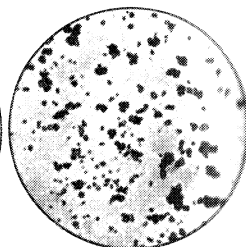


Fig. 4.

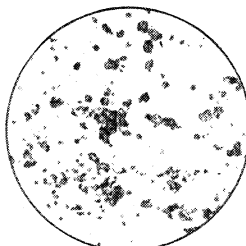


Fig. 5.

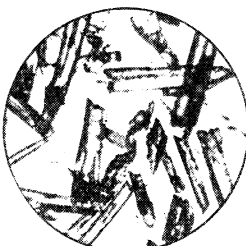


Fig. 6.

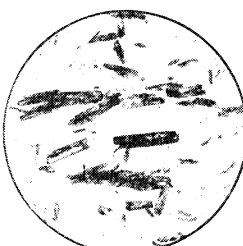


Fig. 7.

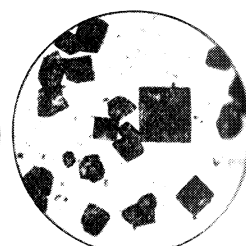


Fig. 8.

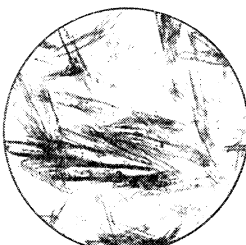


Fig. 9.

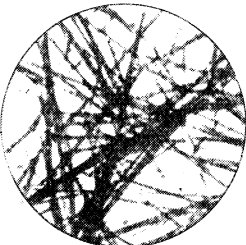


Fig. 10.



Fig. 11.



Fig. 12.



Fig. 13.

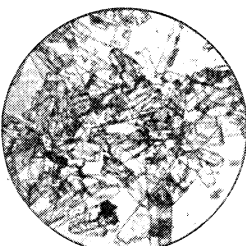


Fig. 14.

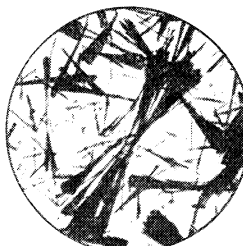


Fig. 15.

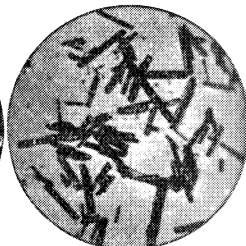


Fig. 16.

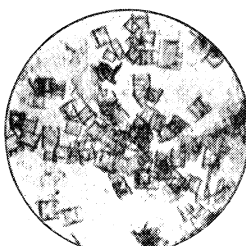


Fig. 17.



Fig. 18.

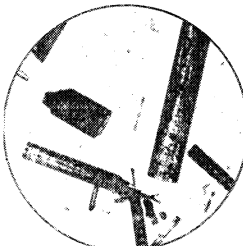


Fig. 19.



Fig. 20.

the presence of acid, there is a strong tendency to form polymer, and as the existence of acid is necessary for the formation of methyleneurea in water solution, if lower methyleneurea alone is desired to be obtained, special conditions of experiment must be prepared. According to the author's observation, insoluble methyleneurea⁽⁷⁾ heretofore known, should be regarded as the mixture of higher methyleneurea.

It is noteworthy that such a soluble crystalline methyleneurea as methylenediurea was obtained, while methyleneurea heretofore known is insoluble. The author, by taking advantage of the solubility of methylenediurea, was enabled to know the nature and the formation characteristics⁽⁸⁾ of methyleneurea, and consequently was able to know also the formation characteristics⁽⁹⁾ of methylolurea. This new knowledge of the formation characteristics of methyleneurea and methylolurea would surely be most useful in the manufacture of resin.

In the next place trimethylenetetraurea (II) and pentamethylenehexaurea (III) were obtained in the following method: The precipitate which was formed by the addition of a small quantity of acid to the aqueous solution of methylenediurea, was subjected to a fractional extraction by means of hot water and boiling water, and each was obtained as the precipitate from the extract. These are interesting compounds for the purpose of observation of the constitution of the higher methyleneurea.

Methylolmethylenediurea (IV) and methylenebismethylolurea (V) were obtained, by the action of formaldehyde, in the presence of alkali, upon methylenediurea. Of these, compound V yields colourless, transparent, hard resin when it is heated under pressure. This resin is highly water-proof, and does not crack even when it is soaked in boiling water for several hours. Since, up to this time, the defect of urea-resin for practical use has been its lack of water-proof quality, it is noteworthy that a kind of resin with water-proof quality in a high degree, was obtained.

Methylenebisacetylurea (VI) was obtained by acetylation of methylenediurea, using acetic anhydride.

Methylenebismethylurea (VII) was obtained by the action of 1 mol of formaldehyde on 2 mol of methylurea (in the presence of acid). Since, in the

(7) Hölzer, *Ber.*, **17** (1884), 659; **18** (1885), 3302 (Anm.). Lüdy, *Monatsh.*, **10** (1889), 297. Hemmelmayer, *Monatsh.*, **12** (1891), 94. Tollens, *Ber.*, **29** (1896), 2751. Dixon, *J. Chem. Soc.*, **113** (1918), 233. Scheibler, Trostler und Scholz, *Z. angew. Chem.*, **41** (1928), 1305.

(8) Kadowaki, *Repts. Imp. Ind. Research Laboratory, Osaka, Japan*, **13** (1932), No. 6, 15-41.

(9) Kadowaki, *ibid.*, **14** (1933), No. 6, 16-29.

case of methylurea, one of the hydrogen atoms of amido-radical of urea has been replaced by a methyl-radical, condensation products formed by the reaction with formaldehyde is considerably simpler, compared with the case of urea.

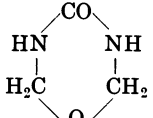
Monomethylolureamethylether (VIII) was obtained by making methyl alcohol act upon monomethylolurea, in the presence of acid. Again, this compound can be obtained simply by heating monomethylolurea with methyl alcohol somewhat longer. So far as the present author knows no research has been made concerning the reaction of alcohol upon monomethylolurea and dimethylolurea. The author experimented upon the reaction of monomethylolurea, dimethylolurea and methylenebismethylolurea on alcohol or mercaptane, for the purpose of investigating the character of methylolurea, and by using the similar method as used in obtaining the compound VIII, succeeded to obtain compounds from IX to XVII. Of these, compounds formed by the reaction of dimethylolurea upon alcohol yields, on heating, colourless, transparent, hard resin. Above all, resins obtained from XIII, XIV, and XV have been observed to possess a greater degree of water-proof quality.

Next, dimethyloltrimethylenetetraureadimethylether (XVIII) was obtained as precipitate by the action of 8 mol of formalin, in the presence of acid, on 1 mol of urea at about -5°C . On this occasion, the formation of methylether was due to the reaction of methyl alcohol contained in formalin.

Monomethylolurea peroxide (XIX) and hexamethyloltriurea peroxide (XX) were obtained by the reaction of hydrogen peroxide (slightly acidic to litmus) on monomethylolurea and dimethylolurea. Moreover, the author obtained a liquid peroxide by using hydrogen peroxide which was neutralized beforehand. The author also obtained an insoluble crystalline peroxide $(\text{C}_3\text{H}_6\text{N}_2\text{O}_3)_n$ (Fig. 18) by adding acid to the mixture of dimethylolurea and hydrogen peroxide. The above-mentioned crystalline peroxide is different in its process of preparation from those which have been formerly obtained, but as its characteristics and analytical results are alike, it must be related to them.⁽¹⁰⁾

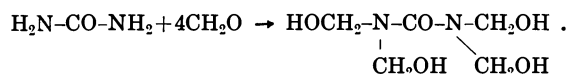
N,N'-Dimethylolurondimethylether (XXI) was obtained, first by the action of 1 mol of urea on 4 mol of formaldehyde, by heating in the presence of alkali (or by the reaction through concentration at room temperature), and then, by the action of methyl alcohol in the presence of acid. This compound contains, in its constitution, one dimethyleneetherurea-ring. Although this ring is an important one, frequently appearing in urea-formaldehyde condensation products, it is an unknown ring. Therefore, the author gave the name

(10) Girsewald and Siegens, *Ber.*, **47** (1914), 2464. Bois de Chesne, *Kolloid Beihefte*, **36** (1932), 418.

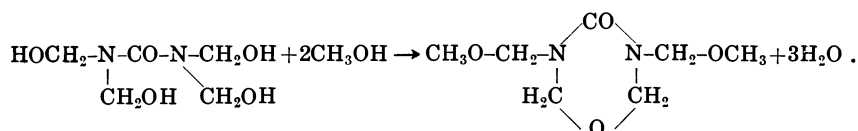
of "uron" to the normal constitution of this ring . This uron

ring is a stable ring and does not easily decompose when it is acted on by dilute acid.

That which is formed by the reaction of urea on formaldehyde by heating, first in the presence of alkali, in the process of manufacture of compound XXI is undoubtedly tetramethylolurea :



That the compound XXI was formed in the treatment with methyl alcohol in the presence of acid, could be considered due to the process that, out of the two methylol-radical which were united with each urea amido-radical, one first reacting upon methyl alcohol, formed methylether, and then the other, mutually reacting, formed uron ring :



N-Methyl-*N'*-methyloluronmethylether (XXIII), *N*-ethyl-*N'*-methyloluronmethylether (XXV), *N,N'*-dimethyluron (XXVII)⁽¹¹⁾, tetramethyldimethylenediureid (XXVIII)⁽¹²⁾, *N,N'*-dimethyl-*N'*-methylolureamethylether (XXIX) and methylenebismethyloluronmethylether (XXX) were obtained by the similar method as used in obtaining compound XXI, by the use of methylurea, ethylurea, *N,N'*-dimethylurea, *N,N*-dimethylurea and methylenediurea, in place of urea. All these are compounds whose three or four hydrogen atoms of urea-amidoradical are replaced by methylene-radical or alkyl-radical, and they have a very important place in our observation of the conditions of the union of urea with formaldehyde.

N,N'-Dimethylurondiethylthioether (XXII) was obtained by the action of ethylmercaptane in the presence of acid on compound XXI. *N*-Methyl-*N'*-methyloluronethylthioether (XXIV) and *N*-ethyl-*N'*-methyloluronethylthioether (XXVI) were obtained by the action of ethylmercaptane, in the presence of acid, on compound XXIII and compound XXV.

(11) (12) *N,N'*-Dimethyluron and tetramethyldimethylenediureid can also be obtained simply by the reaction of *N,N'*-dimethylurea and formaldehyde through heating in the presence of acid.

Experimental.

(1) **Methylenediurea** $C_3H_3N_4O_2$. Urea (1540 g.) was dissolved in the equal weight of water. When 22.5 c.c. of conc. hydrochloric acid and 250 c.c. of 38.37% formalin were added some white turbidity appeared in a few minutes. After leaving the mixture to stand for two days, it was neutralized with potassium hydroxide, and the precipitate from it was scooped out. The precipitate was treated with alcohol, and after urea contained in it was removed, it was recrystallised from water. (Yield: 279.6 g. Found: C, 26.89; H, 6.21; N, 41.98%; mol. wt., 117.6; CH_2O , 23.24%. Calculated for $C_3H_3N_4O_2$: C, 27.25; H, 6.12; N, 42.42%; mol. wt., 132. Calculated for $CH_2O/C_3H_3N_4O_2$: CH_2O , 22.73%.)

(2) **Trimethylenetetraurea** $C_7H_{16}N_8O_4$ and **Pentamethylenhexaurea** $C_{11}H_{24}N_{12}O_6$. Methylenediurea (10 g.) was dissolved in 200 c.c. of water, and when one drop of conc. hydrochloric acid was added to the solution, white turbidity appeared after a few minutes. After leaving the solution to stand for one day, the precipitate was scooped out and was thoroughly washed with water, and then was heated together with 1 l. of water at $95^\circ C$., and the solution was filtered while still warm, and when the filtrate was cooled, precipitate was separated. (Yield: 2.97 g. Found: C, 30.52; H, 6.00; N, 40.72; CH_2O , 31.78. Calculated for $C_7H_{16}N_8O_4$: C, 30.41; H, 5.84; N, 40.59. Calculated for $3CH_2O/C_7H_{16}N_8O_4$: CH_2O , 32.61%.) Then, the residue, together with 1 l. of water, was boiled, and was filtered while still warm, and when the filtrate was cooled, precipitate separated out. (Yield: 0.71 g. Found: C, 31.26; H, 5.90; N, 40.11; CH_2O , 34.17. Calculated for $C_{11}H_{24}N_{12}O_6$: C, 31.41; H, 5.76; N, 40.00. Calculated for $5CH_2O/C_{11}H_{24}N_{12}O_6$: CH_2O , 35.71%.)

(3) **Methylolmethylenediurea** $C_4H_{10}N_4O_3$. Methylenediurea (5 g.) was dissolved in 150 c.c. of water, and 0.1 g. of barium hydroxide and 2.96 g. of 38.37% formalin were added to the solution, and after leaving it to stand for 55 minutes, it was neutralized by passing a current of carbon dioxide and was filtered. The filtrate was evaporated and dried. The dried substance was extracted by heating with 60% alcohol. Then, this extract separated out a precipitate when it was cooled. This precipitate contains a small quantity of methylenebismethylolurea. (Yield: 0.58 g. Found: C, 30.57; H, 6.30; N, 32.72. Calculated for $C_4H_{10}N_4O_3$: C, 29.63; H, 6.22; N, 34.59%.)

(4) **Methylenebismethylolurea** $C_5H_{12}N_4O_4$. Methylenediurea (10 g.) was dissolved in 200 c.c. of water and 0.4 g. of barium hydroxide and 11.9 g. of 38.37% formalin were added, and the solution was left to stand for ten minutes, and then, it was neutralized by passing a current of carbon dioxide, and filtered. The filtrate was evaporated and dried. This dried substance was heated with 60% alcohol. The extract separated out precipitate when it was left to cool. (Yield: 2.9 g. Found: C, 31.79; H, 6.25; N, 30.10. Calculated for $C_5H_{12}N_4O_4$: C, 31.23; H, 6.30; N, 29.17%.)

(5) **Methylenebisacetylurea** $C_7H_{12}N_4O_4$. To 6 g. of methylenediurea 20 c.c. of acetic acid, 70 c.c. of acetic anhydride, and 1.5 c.c. of conc. sulphuric acid were added, and when the solution was left to cool after it was boiled for ten minutes, crystals were separated out. The crystals were scooped out, and were recrystallized from water. (Yield: crude 2.4 g. Found: CH_3CO , 59.3. Calculated for $CH_3CO_2H/C_7H_{12}N_4O_4$: CH_3CO , 55.5%.)

(6) **Methylenebismethylurea** $C_5H_{12}N_4O_2$. Methylurea (5.64 g.) was dissolved in 3 c.c. of 37.57% formalin and when one drop of conc. hydrochloric acid was added, the solution generated intense heat, and its temperature rose. When left to cool, crystals were separated out. These crystals were scooped out, and were recrystallized from alcohol. (Yield: crude 4.55 g. Found: N, 35.16. Calculated for $C_5H_{12}N_4O_2$: N, 35.00%.)

(7) **Monomethylolureamethylether** $C_3H_8N_2O_2$. Methyl alcohol (5 g.) and one drop of 5 N hydrochloric acid were added to 0.85 g. of monomethylolurea and were dissolved, and after allowing the solution to stand for one minute, it was neutralized with silver carbonate, and was filtered, and when the filtrate was evaporated, there remained crystals. These crystals were recrystallized from methyl alcohol. (Yield: crude 0.96 g. Found: C, 34.75; H, 7.58; N, 26.94. Calculated for $C_3H_8N_2O_2$: C, 34.58; H, 7.76; N, 26.91%.)

(8) **Monomethylolureaethylether** $C_4H_{10}N_2O_2$. Ethyl alcohol (15 g.) and 3 drops of 5 N hydrochloric acid were added to 1.9 g. of monomethylolurea and were dissolved. After leaving the solution to stand for 7 minutes, it was neutralized with silver carbonate, and was filtered. When this filtrate was concentrated, crystals separated out. These crystals were recrystallized from alcohol. (Yield: crude 1.37 g. Found: N, 23.84. Calculated for $C_4H_{10}N_2O_2$: N, 23.72%.)

(9) **Dimethylolureadimethylether** $C_5H_{12}N_2O_3$. Methyl alcohol (100 c.c.) and one drop of 5 N hydrochloric acid were added to 10 g. of dimethylolurea, and were dissolved, and the solution was left to stand for 5 minutes, and then, it was neutralized with silver carbonate, and was filtered. When the filtrate was concentrated, crystals separated out. The crystals were scooped out and were recrystallized from methyl alcohol. (Yield: 10.6 g. Found: C, 40.36; H, 8.33; N, 19.13%; mol. wt., 138; CH_2O , 40.61%. Calculated for $C_5H_{12}N_2O_3$: C, 40.51; H, 8.17; N, 18.91%; mol. wt., 148. Calculated for $2CH_2O/C_5H_{12}N_2O_3$: CH_2O , 40.54%.)

(10) **Dimethylolureadiethylether** $C_7H_{16}N_2O_3$. Ethyl alcohol (100 c.c.) and one drop of 5 N hydrochloric acid were added to 10 g. of dimethylolurea, and were dissolved. After allowing the solution to stand for 7 minutes, it was neutralized with silver carbonate and was filtered. When the filtrate was evaporated crystals remained. These crystals were recrystallized from alcohol. (Yield: crude 11.9 g. Found: N, 15.96; CH_2O , 34.83. Calculated for $C_7H_{16}N_2O_3$: N, 15.90. Calculated for $2CH_2O/C_7H_{16}N_2O_3$: CH_2O , 34.83%.)

(11) **Dimethylolureadi-*n*-propylether** $C_9H_{20}N_2O_3$. Dimethylolurea (1 g.) was dissolved by the addition of 5 g. of *n*-propyl alcohol and one drop of N hydrochloric acid. After leaving the solution to stand for 10 minutes, it was neutralized with silver carbonate, and was filtered. Through the concentration of the filtrate, crystals separated out. The crystals were scooped out and were recrystallized from ether. (Yield: crude 1.45 g. Found: N, 13.92. Calculated for $C_9H_{20}N_2O_3$: N, 13.72%.)

(12) **Dimethylolureadi-*n*-butylether** $C_{11}H_{24}N_2O_3$. Dimethylolurea (1 g.) was dissolved by the addition of 5 g. of *n*-butyl alcohol and one drop of N hydrochloric acid. After the solution was left to stand for 20 minutes, it was neutralized with silver carbonate, and was filtered. The filtrate was strongly cooled, and then crystals separated out. The crystals were scooped out and were recrystallized from ether. (Yield: crude 1.06 g. Found: N, 12.08. Calculated for $C_{11}H_{24}N_2O_3$: N, 12.07%.)

(13) **Dimethylolurea-*n*-amylether** $C_{13}H_{28}N_2O_3$. *n*-Amyl alcohol (5 g.) and one drop of 5 N hydrochloric acid were added to 1 g. of dimethylolurea and were dissolved. After allowing the solution to stand for 20 minutes, it was neutralized with silver carbonate, and was filtered. The filtrate was evaporated and dried. The dried substance was heated and extracted with ether. When the extract was cooled, crystals separated out. The crystals were scooped out and were recrystallized from ether. (Yield: crude 1.0 g. Found: N, 10.80. Calculated for $C_{13}H_{28}N_2O_3$: N, 10.76%.)

(14) **Dimethylolureadibenzylether** $C_{17}H_{20}N_2O_3$. Dimethylolurea (1 g.) was dissolved by adding 5 g. of benzyl alcohol and one drop of 5 N hydrochloric acid. After the solution was allowed to stand for 5 minutes, it was neutralized with silver carbonate and was filtered. When the filtrate was strongly cooled, crystals separated out. The crystals were scooped out and were dissolved in benzene. On adding ether to this solution, crystals separated out. (Yield: 1.0 g. Found: N, 9.24, Calculated for $C_{17}H_{20}N_2O_3$: N, 9.33%.)

(15) **Dimethylolureadiethylthioether** $C_7H_{16}N_2S_2O$. When 5 g. of dimethylolurea was added to 13 g. of ethylmercaptane, to which 10 drops of 5 N hydrochloric acid had been added beforehand, a soft lump was produced. After washing it thoroughly with water, it was heated with alcohol and dissolved. When the solution was cooled, crystals separated out. The crystals were scooped out and were recrystallized from alcohol. (Yield: 5.5 g. Found: C, 41.84; H, 7.78; N, 13.25; S, 30.76. Calculated for $C_7H_{16}N_2S_2O$: C, 40.33; H, 7.74; N, 13.45; S, 30.78%.)

(16) **Methylenebismethylolureadimethylether** $C_7H_{16}N_4O_4$. Methyl alcohol (100 c.c.) and 0.5 c.c. of 5 N hydrochloric acid were added to 3.77 g. of methylenebismethylolurea, and after allowing it to stand for 10 minutes, it was neutralized with silver carbonate, and was heated at 60°C., and was filtered. When the filtrate was cooled, crystals separated out. The crystals were scooped out and were recrystallized from methyl alcohol. (Yield: 2.71 g. Found: C, 37.88; H, 7.34; N, 25.76%; mol. wt., 223.9; CH_2O , 41.13%. Calculated for $C_7H_{16}N_4O_4$: C, 38.15; H, 7.33; N, 25.45; mol. wt., 220.2. Calculated for $3CH_2O/C_7H_{16}N_4O_4$: CH_2O , 40.90%.)

(17) **Dimethyloltrimethylenetetraureadimethylether** $C_{11}H_{24}N_8O_6$. Urea (95 g.) was dissolved in 1000 c.c. of 38% formalin, and the solution was filtered. Then the filtrate was cooled to -6.5°C., and when 10 c.c. of conc. hydrochloric acid was added, in 10 minutes, it yielded white turbidity. Leaving it to stand for one hour the precipitate was scooped out and was washed with alcohol. (Yield: 39.4 g. Found: C, 36.09; H, 6.63; N, 30.68; CH_2O , 43.45. Calculated for $C_{11}H_{24}N_8O_6$: C, 36.25; H, 6.60; N, 30.75. Calculated for $5CH_2O/C_{11}H_{24}N_8O_6$: CH_2O , 41.20%.)

(18) **Monomethylolurea peroxide** $C_2H_6N_2O_3$. Monomethylolurea (2.2 g.) was dissolved in 66 c.c. of 3% hydrogen peroxide (slightly acidic to litmus). The solution was dried by evaporation. This dried substance was dissolved in a small quantity of water by heating. When this solution was cooled, crystals separated out. The crystals were scooped out and were recrystallized from 50% alcohol. (Yield: 1.92 g. Found: C, 22.33; N, 26.63%; mol. wt., 98.8; avail. O, 15.30%. Calculated for $C_2H_6N_2O_3$: C, 22.64; N, 26.42%; mol. wt., 106.0. Calculated for $O/C_2H_6N_2O_3$: avail. O, 15.09%.)

(19) **Hexamethyloltriurea peroxide** $C_9H_{20}N_6O_{11}$, **Crystalline peroxide** $(C_3H_6N_2O_3)_n$ and **Liquid peroxide**. (A) *Hexamethyloltriurea peroxide*. Dimethylolurea (20 g.) was dissolved

in 500 c.c. of 3% hydrogen peroxide (slightly acidic to litmus), and when the solution was evaporated, there remained liquid. This was washed with carbon tetrachloride and ether, and then was dissolved in alcohol. Next, when a portion of insoluble substance was removed, and the solution was evaporated, solid remained. This solid was again dissolved in alcohol, ether was added to the solution, and precipitate separated out. (Yield: crude 5 g. Found: N, 21.30%; mol. wt., 383.2. Calculated for $C_9H_{20}N_6O_{11}$: N, 21.60%; mol. wt., 388.2.)

(B) *Crystalline peroxide*. When 2.5 g. of dimethylolurea was dissolved in 50 c.c. of 3% hydrogen peroxide, and 0.5 c.c. of 5N hydrochloric acid was added to it, crystals separated out. (Yield: 2.06 g. Found: C, 30.48; H, 5.29; N, 23.65; avail. O, 13.73. Calculated for $C_3H_6N_2O_3$: C, 30.49; H, 5.12; N, 23.73. Calculated for $O/C_3H_6N_2O_3$: avail. O, 13.55%.)

(C) *Liquid peroxide*. Dimethylolurea (12 g.) was dissolved in 500 c.c. of 3% hydrogen peroxide which had been neutralized with barium hydroxide, and when the solution was evaporated, there remained liquid. This liquid was dissolved in alcohol, and a small quantity of the insoluble substance was removed, and the solution was evaporated, and liquid was obtained. When this liquid was poured into ether, it became slightly turbid. The turbidity was filtered, and then the filtrate was evaporated, there remained liquid.

(20) *N,N'-Dimethylolurondimethylether* $C_7H_{14}N_2O_4$. Barium hydroxide (5 g.) and 60 g. of urea were dissolved in 320 c.c. of 38% formalin, and when the solution was heated in boiling water for 10 minutes, and was evaporated, there remained slightly sticky liquid. This was dissolved in the mixture of 1 l. of methyl alcohol and 6 c.c. of conc. hydrochloric acid, and after leaving the solution to stand for 15 minutes, it was neutralized with barium hydroxide, and was filtered. A slightly fluid liquid remained when the filtrate was evaporated. After the inorganic salt was removed by treating it with chloroform, and dimethylolurondimethylether also was removed by treating it with ether, it was subjected to vacuum distillation for refining. (Yield: crude 126 g. Found: C, 43.86; H, 7.73; N, 14.74%; mol. wt., 188.5; CH_2O , 59.32%. Calculated for $C_7H_{14}N_2O_4$: C, 44.19; H, 7.42; N, 14.72%; mol. wt., 190.1. Calculated for $4CH_2O/C_7H_{14}N_2O_4$: CH_2O , 63.16%.)

(21) *N,N'-Dimethylolurondiethylthioether* $C_9H_{18}N_2S_2O_2$. *N,N'*-Dimethylolurondi-methylether (10 g.) was dissolved in 14 g. of ethylmercaptane, and when 3 drops of conc. hydrochloric acid were added thereto, heat generated, and the temperature of the solution rose. After cooling, it was neutralized with barium hydroxide, and inorganic salt was removed by the treatment with ether, and when it was evaporated, there remained transparent liquid. When this liquid was subjected to vacuum distillation, the greater part distilled at 125–134°C. (0.1 mm.), and when left to stand, it crystallized. The crystals were dissolved in a small quantity of alcohol, and crystals were separated out by adding water to the solution. (Yield: crude 14.8 g. Found: C, 43.19; H, 7.37; N, 11.16; S, 25.33%; mol. wt., 240.6. Calculated for $C_9H_{18}N_2S_2O_2$: C, 43.15; H, 7.25; N, 11.19; S, 25.62%; mol. wt., 250.3.)

(22) *N-Methyl-N'-methyloluronmethylether* $C_6H_{12}N_2O_3$. Barium hydroxide (3 g.) and 10 g. of methylurea were dissolved in 42.7 c.c. of 38% formalin, and after the solution was heated in boiling water for 10 minutes, it was evaporated. Then, a slightly sticky liquid remained. This was dissolved in the mixture of 100 c.c. of methyl alcohol and 2.5 c.c. of conc. hydrochloric acid. After leaving it to stand for 15 minutes, it was

neutralized with barium hydroxide, and was filtered. When the filtrate was evaporated, there remained slightly fluid liquid. This was treated with chloroform in order to remove inorganic salt, and then, was subjected to vacuum distillation for refinement. (Yield: crude 15.0 g. Found: C, 44.28; H, 7.93; N, 17.43%; mol. wt., 162.5; CH_2O , 53.27%. Calculated for $\text{C}_6\text{H}_{12}\text{N}_2\text{O}_3$: C, 44.97; H, 7.56; N, 17.50%; mol. wt., 160.1. Calculated for $3\text{CH}_2\text{O}/\text{C}_6\text{H}_{12}\text{N}_2\text{O}_3$: CH_2O , 56.25%.)

(23) *N*-Methyl-*N'*-methyloluronethylthioether $\text{C}_7\text{H}_{14}\text{N}_2\text{SO}_2$. *N*-Methyl-*N'*-methyloluronmethylether (6.2 g.) was dissolved in 12.4 g. of ethylmercaptane, and when 3 drops of conc. hydrochloric acid were added thereto, the temperature of the solution rose, heat being generated. After cooling, it was neutralized with barium hydroxide, and again was treated with ether to remove inorganic salt. On evaporation, a transparent liquid remained. This liquid was washed with water, and was refined through vacuum distillation. (Yield: crude 5.8 g. Found: C, 43.91; H, 7.65; N, 14.52%; mol. wt., 186.4. Calculated for $\text{C}_7\text{H}_{14}\text{N}_2\text{SO}_2$: C, 44.16; H, 7.42; N, 14.73%; mol. wt., 190.2.)

(24) *N*-Ethyl-*N'*-methyloluronmethylether $\text{C}_7\text{H}_{14}\text{N}_2\text{O}_3$. Barium hydroxide (4 g.) and 22.5 g. of ethylurea were dissolved in 81 c.c. of 38% formalin, and the solution was heated in boiling water for 10 minutes. After evaporation, there remained a slightly sticky liquid. This liquid was dissolved in the mixture of 200 c.c. of methyl alcohol and 5 c.c. of conc. hydrochloric acid. After leaving it to stand for 15 minutes, it was neutralized with barium hydroxide, and was filtered. The filtrate was evaporated, and then slightly fluid liquid remained. This liquid was treated with chloroform in order to remove inorganic salt contained in it. Then, it was refined by vacuum distillation. (Yield: crude 41 g. Found: C, 47.72; H, 8.44; N, 16.23%; mol. wt., 174.1; CH_2O , 46.77%. Calculated for $\text{C}_7\text{H}_{14}\text{N}_2\text{O}_3$: C, 48.24; H, 8.10; N, 16.09%; mol. wt., 174.1. Calculated for $3\text{CH}_2\text{O}/\text{C}_7\text{H}_{14}\text{N}_2\text{O}_3$: CH_2O , 51.72%.)

(25) *N*-Ethyl-*N'*-methyloluronethylthioether $\text{C}_8\text{H}_{16}\text{N}_2\text{SO}_2$. *N*-Ethyl-*N'*-methyloluronmethylether (6.6 g.) was dissolved in 12.4 g. of ethylmercaptane. On adding 3 drops of conc. hydrochloric acid to the solution, it generated heat, and its temperature rose. After it was left to cool, it was neutralized with barium hydroxide and was again treated with ether to remove the inorganic salt contained therein. There remained slightly fluid liquid when it was evaporated. Washing it with water, it was subjected to vacuum distillation. It distilled mostly at 110–113°C. (1.0 mm.) and when the distillate was cooled strongly, crystals separated out. (Yield: crude 7.7 g. Found: C, 46.82; H, 8.32; N, 13.62%; mol. wt., 204.6. Calculated for $\text{C}_8\text{H}_{16}\text{N}_2\text{SO}_2$: C, 47.01; H, 7.90; N, 13.72%; mol. wt., 204.2.)

(26) *N,N'*-Dimethyluron $\text{C}_5\text{H}_{10}\text{N}_2\text{O}_2$ and Tetramethyldimethylenediureid $\text{C}_8\text{H}_{16}\text{N}_4\text{O}_2$. Barium hydroxide (1.5 g.) and 8.8 g. of *N,N'*-dimethylurea were dissolved in 24 c.c. of 38% formalin, and after heating the solution in boiling water for 5 minutes, it was evaporated. Then, a slightly sticky liquid remained. This liquid was dissolved in the mixture of 150 c.c. of methyl alcohol and 1.5 c.c. of conc. hydrochloric acid. Leaving it to stand for 15 minutes, it was neutralized with barium hydroxide, and was filtered. Through evaporation of the filtrate, there remained a slightly fluid liquid. Removing the inorganic salt contained therein by treatment with chloroform, it was subjected to vacuum distillation. Then, the greater part distilled, leaving crystals. The crystals were recrystallized from alcohol. (Yield: 1.3 g. Found: C, 47.78; H, 8.43; N, 28.00%;

mol. wt., 190.4; CH_2O , 30.07%. Calculated for $\text{C}_8\text{H}_{16}\text{N}_4\text{O}_2$: C, 47.95; H, 8.08; N, 27.99%; mol. wt., 200.2. Calculated for $2\text{CH}_2\text{O}/\text{C}_8\text{H}_{16}\text{N}_4\text{O}_2$: CH_2O , 29.99%.)

The distillate was refined by the treatment with the mixture of ethylmercaptane and hydrochloric acid, and was subjected to vacuum distillation. The best part distilled at 64°C . (0.1 mm.). When the distillate was strongly cooled, it formed crystals. These were recrystallized from ether. (Yield: crude 3.5 g. Found: C, 46.96; H, 7.83; N, 21.63%; mol. wt., 131.5; CH_2O , 46.21%. Calculated for $\text{C}_5\text{H}_{10}\text{N}_2\text{O}_2$: C, 46.12; H, 7.75; N, 21.53; mol. wt., 130.1. Calculated for $2\text{CH}_2\text{O}/\text{C}_5\text{H}_{10}\text{N}_2\text{O}_2$: CH_2O , 46.14%.)

(27) *N,N*-Dimethyl-*N'*-methylolureamethylether $\text{C}_5\text{H}_{12}\text{N}_2\text{O}_2$. Barium hydroxide (4 g.) and 8.8 g. of *N,N*-dimethylurea were dissolved in 24 c.c. of 38% formalin, and when the solution was heated in boiling water for 10 minutes, and was evaporated, a slightly sticky liquid remained. This liquid was dissolved in the mixture of 100 c.c. of methyl alcohol and 2.8 c.c. of conc. hydrochloric acid, and leaving it to stand for 15 minutes it was neutralized with barium hydroxide, and was filtered. When the filtrate was evaporated a transparent liquid remained. Removing the inorganic salt contained in it by treating it with chloroform, it was left to stand at room temperature. Then, crystals separated out. The crystals were scooped out, and were recrystallized from ether. (Yield: 7 g. Found: C, 45.51; H, 9.29; N, 21.32%; mol. wt., 128.7; CH_2O , 22.78%. Calculated for $\text{C}_5\text{H}_{12}\text{N}_2\text{O}_2$: C, 45.42; H, 9.16; N, 21.21%; mol. wt., 132.1. Calculated for $\text{CH}_2\text{O}/\text{C}_5\text{H}_{12}\text{N}_2\text{O}_2$: CH_2O , 22.72%.)

(28) Methylenebismethyloluronmethylether $\text{C}_{11}\text{H}_{20}\text{N}_4\text{O}_6$. Barium hydroxide (1 g.) and 13.2 g. of methylenediurea were dissolved in 50 c.c. of 38% formalin, and when the solution was heated in boiling water for 10 minutes, and was evaporated, colourless, transparent sticky substance remained. This was dissolved in the mixture of 200 c.c. of methyl alcohol and 1 c.c. of conc. hydrochloric acid. Leaving it to stand for 15 minutes, it was neutralized with barium hydroxide and was evaporated. Then, sticky liquid remained. Removing inorganic salt contained therein by the treatment of chloroform, it was refined with ether. (Yield: crude 27.0 g. Found: C, 42.67; H, 7.84; N, 18.92%; mol. wt., 273.3; CH_2O , 63.73%. Calculated for $\text{C}_{11}\text{H}_{20}\text{N}_4\text{O}_6$: C, 43.39; H, 6.63; N, 18.42%; mol. wt., 304.2. Calculated for $7\text{CH}_2\text{O}/\text{C}_{11}\text{H}_{20}\text{N}_4\text{O}_6$: CH_2O , 69.03%.)

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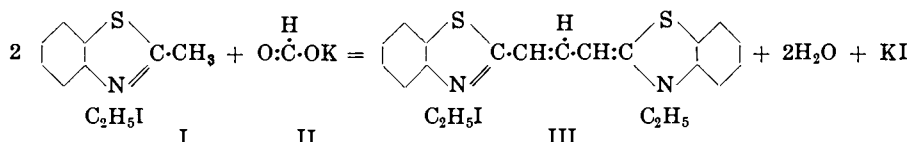
ÜBER CYANINFARBSTOFFE. VIII. EINE NEUE SYNTHESE VON 8-METHYL-TRIMETHINTHIOCYANIN-DERIVATEN UND ÜBER DIE REAKTIONSFÄHIGKEIT DER 8-METHYLGRUPPE.

Von Terutaro OGATA.

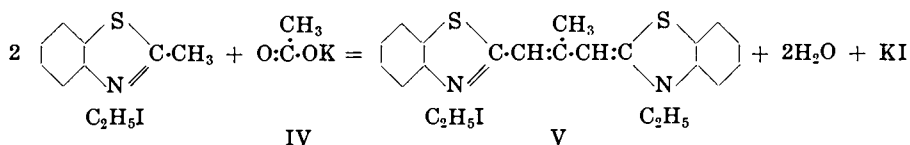
Eingegangen am 14. November 1935. Ausgegeben am 28. März 1936.

Zur Darstellung der für die Photographie wertvollen 8-Methylthiocyanin-Derivate, beim mittelständigen C-Atom der Trimethinkette durch CH_3 -substituiert, sind in letzter Zeit 2 Verfahren ausgearbeitet worden. Hamer⁽¹⁾ hat durch Einwirkung des Orthoessigsäureäthylesters auf einer Lösung von μ -Methylbenzothiazoläthyljodid (I) in Pyridin oder Essigsäureanhydrid 8-Methylfarbstoffe erhalten. Kürzlich haben dann Brooker und White⁽²⁾ nach interessanten Versuchen die quartären Salze der μ -Methylbenzothiazol-Derivate durch Erhitzen mit Pyridin bei Gegenwart von Triäthylamin in 8-Methylfarbstoffe überzuführen vermocht.

Vor einigen Jahren habe ich aus Jodäthylat (I) durch Einwirkung von K-formiat (II) in Gegenwart von Essigsäureanhydrid 20% iger Ausbeute Trimethinthiocyanin (III) erhalten.



Bald danach habe ich durch Anwendung von K-acetat (IV) statt des K-formiats, als Quelle des zentralen Äthylenradikals des Farbstoffmoleküls, einen kupferroten Farbstoff gewonnen (man konnte hierbei Bildung von 8-Methylthiocyanin (V) erwarten). Die Reaktion kann in folgender Gleichung ausgedrückt werden:

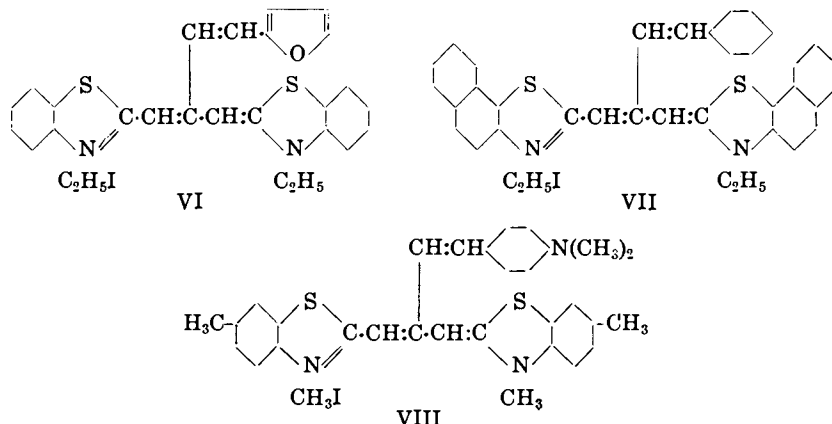


Der oben erwähnte 8-Methylfarbstoff (V) hat mit dem Trimethinthiocyanin (III) charakteristische Eigenschaften gemeinsam, nur ist er wesentlich wirksamer, vor allem gegen Aldehyd, mit dem er kondensiert wird. Unter

(1) F. M. Hamer, *J. Chem. Soc.*, **1928**, 160.

(2) L. G. S. Brooker und F. L. White, *J. Am. Chem. Soc.*, **57** (1935), 547.

Einwirkung eines Aldehyds (z.B. des Furfurols) auf dem 8-Methylfarbstoff in Gegenwart von Piperidin entstand ein Furfur-vinylfarbstoff (VI), der analytisch bestimmt wurde.



Versuche, aus dem 1,1',4,4',8-Pentamethyl-trimethinthiocyanin (3)⁽³⁾ und dem 1,1'-Diäthyl-8-methyl-dibenzo-trimethinthiocyanin (4)⁽³⁾ mittels eines Aldehyds (z.B. des Benzaldehyds oder des *p*-Dimethylaminobenzaldehyds) Vinylfarbstoffe (z.B. VII, VIII) darzustellen, waren auch erfolgreich. Die neuen Vinylfarbstoffe sind gut wirkende Sensibilisatoren für photographische Emulsionen (nach der Orientalischen Photographischen Industriellen Akt.-Ges., Tokio). Spektroskopisch ist eine erhebliche Verschiebung des Absorptionsbandes nach dem Gebiet der längeren Wellen hin bemerkenswert.

Beschreibung der Versuche.

Trimethinthiocyanin aus μ -Methylbenzothiazoläthyljodid und K-formiat. (1) 1,1'-Diäthyl-trimethinthiocyaninjodid (III) wird aus 0.6 g. μ -Methyl-benzothiazoläthyljodid (I) und 0.6 g. K-formiat (II) in Gegenwart von 1 c.c. Essigsäureanhydrid durch 30 Minuten langes Erhitzen bei 150° dargestellt. Das Rohprodukt wurde mit Äther und dann mit Wasser gewaschen. Aus Methylalkohol kristallisiert es in hellblauen Säulen vom Schmp. 269° (unter Zersetzung), der mit einem nach der Dianil-Methode⁽⁴⁾ gewonnenen Präparat durch den Misch-schmp. festgestellt wurde. Abs.-max. 560 m μ , Sens.-max. 590 m μ . (Gef.: I, 26.11; S, 12.53. Ber. für $\text{C}_{21}\text{H}_{21}\text{N}_2\text{IS}_2$: I, 25.78; S, 13.03%.)

8-Methylfarbstoffe aus Alkyljodiden und K-acetat. (2) 1,1'-Diäthyl-8-methyl-trimethinthiocyaninjodid (V). Ein Gemisch von 0.6 g. (2 Mol) μ -Methylbenzothiazoläthyljodid (I), 0.1 g. (1 Mol) K-acetat und 0.4 c.c. Essigsäureanhydrid wurde 60 Minuten lang bei 165° erhitzt. Durch Waschen zuerst mit Äther, dann mit Wasser und Alkohol konnte der Farbstoff fast rein erhalten werden. Das Rohprodukt (0.21 g.) wird aus 60 c.c. Methylalkohol umkristallisiert und er gibt kupferrote Kristalle (doch manchmal stahlblaue

(3) Siehe die Beschreibung der Versuche.

(4) T. Ogata, *Proc. Imp. Acad. Japan*, **9** (1953), 604.

Nadeln), die bei 286° schmelzen (Zers.); Ausbeute 0.15 g. (30%). Abs.-max. $540\text{ m}\mu$, Sens.-max. $580\text{ m}\mu$. (Gef.: I, 25.45; S, 12.50. Ber. für $\text{C}_{22}\text{H}_2\text{N}_2\text{IS}_2$: I, 25.07; S, 12.67%.)

(3) 1,1',4,4',8-Pentamethyl-trimethinthiocyaninjodid bildete sich durch halbstündiges Erhitzen (bei 165°) einer Lösung von 0.3 g. 2,5-Dimethylbenzothiazolmethyljodid und 0.05 g. K-acetat in 0.2 c.c. Essigsäureanhydrid. Stahlblaue Kristalle aus Methylalkohol. Schmp. 279° (Zers.); Ausbeute 20%. Abs.-max. $540\text{ m}\mu$, Sens.-max. $580\text{ m}\mu$. (Gef.: I, 25.09; S, 12.27. Ber. für $\text{C}_{22}\text{H}_{25}\text{N}_2\text{IS}_2$: I, 25.07; S, 12.67%.)

(4) 1,1'-Diäthyl-8-methyl-3,4,3',4'-dibenzo-trimethinthiocyaninjodid wird aus μ -Methyl- β -naphtothiazoläthyljodid und K-acetat wie Farbstoff (2) hergestellt. Grün glänzende Nadelchen aus Methylalkohol. Schmp. 293° (Zers.); Ausbeute 7%. Abs.-max. $590\text{ m}\mu$, Sens.-max. $600\text{ m}\mu$. (Gef.: I, 20.65; S, 10.34. Ber. für $\text{C}_{30}\text{H}_{27}\text{N}_2\text{IS}_2$: I, 20.93; S, 10.58%.)

Einwirkung von Aldehyden auf 8-Methylfarbstoffe. (5) 1,1'-Diäthyl-8-furfur-vinyl-trimethinthiocyaninjodid (VI) wird aus 0.25 g. 8-Methyl-trimethincyanin (2), 0.5 c.c. Furfurol und 2 c.c. Alkohol in Gegenwart von 15 Tropfen Piperidin durch etwa 30 Minuten langes Erhitzen bei 90° dargestellt. Die rote Farbe der Lösung schlägt dann in violett um. Das Rohprodukt wird nach dem Erkalten abgesaugt. Schöne, grün glänzende Kristalle aus Methylalkohol. Schmp. 277° (Zers.); Ausbeute 0.09 g. Abs.-max. $560\text{ m}\mu$. (Gef.: I, 22.85. Ber. für $\text{C}_{27}\text{H}_{25}\text{ON}_2\text{IS}_2$: I, 22.99%.)

(6) 1,1'-Diäthyl-8-phenyl-vinyl-trimethinthiocyaninjodid. 0.25 g. 8-Methyltrimethinthiocyanin (2) wurde mit 0.1 c.c. Benzaldehyd in 1 c.c. Alkohol und 5 Tropfen Piperidin 15 Minuten lang bei 90° erwärmt. Nach dem Waschen mit Alkohol wurde der Rückstand aus Methylalkohol umkristallisiert. Stahlblaue Kristalle vom Schmp. 266° (Zers.); Ausbeute 0.17 g. Abs.-max. $560\text{ m}\mu$, Sens.-max. $600\text{ m}\mu$. (Gef.: I, 21.26; S, 10.76. Ber. für $\text{C}_{29}\text{H}_{27}\text{N}_2\text{IS}_2$: I, 21.36; S, 10.80%.)

(7) 1,1'-Diäthyl-8-phenyl-vinyl-3,4,3',4'-dibenzo-trimethinthiocyaninjodid (VII) wurde aus 0.18 g. 8-Methylfarbstoff (4) durch $3/4$ stündiges Erhitzen bei 90° mit 0.06 c.c. Benzaldehyd in 1 c.c. Alkohol und 8 Tropfen Piperidin gewonnen. Grün glänzende Kristalle aus Methylalkohol. Schmp. 265° (Zers.); Ausbeute 0.12 g. Abs.-max. $610\text{ m}\mu$. (Gef.: I, 18.58; S, 8.91. Ber. für $\text{C}_{37}\text{H}_{31}\text{N}_2\text{IS}_2$: I, 18.28; S, 9.24%.)

(8) 1,1'-Diäthyl-8-*p*-dimethylaminophenyl-vinyl-trimethinthiocyaninjodid. 0.5 g. 8-Methyl-trimethinthiocyanin (2) wurde mit 0.2 g. *p*-Dimethylaminobenzaldehyd in 3 c.c. Alkohol und 15 Tropfen Piperidin 25 Minuten lang bei 90° erhitzt. Grüne glänzende Kristalle. Schmp. 252° (Zers.); Ausbeute 0.22 g. Abs.-max. $560\text{ m}\mu$, Sens.-max. $600\text{ m}\mu$. (Gef.: I, 20.05; S, 9.76. Ber. für $\text{C}_{31}\text{H}_{25}\text{N}_3\text{IS}_2$: I, 19.92; S, 10.07%.)

(9) 1,1',4,4'-Tetramethyl-8-*p*-dimethylaminophenyl-vinyl-trimethinthiocyaninjodid (VIII) wurde aus 0.2 g. 8-Methylfarbstoff (3) und 0.08 g. *p*-Dimethylaminobenzaldehyd wie Farbstoff (8) dargestellt. Man reinigte es durch Umkristallisation aus Methylalkohol (750 c.c. per 1 g.). Grüne Kristalle vom Schmp. 292° (Zers.); Ausbeute 0.07 g. Abs.-max. $570\text{ m}\mu$. (Gef.: I, 20.23; S, 9.75. Ber. für $\text{C}_{31}\text{H}_{32}\text{N}_3\text{IS}_2$: I, 19.92; S, 10.07%.)

(10) 1,1'-Diäthyl-8-*p*-dimethylaminophenyl-vinyl-3,4,3',4'-dibenzotrimethinthiocyaninjodid entsteht aus 0.3 g. Farbstoff (4) und 0.1 g. *p*-Dimethylaminobenzaldehyd auf ähnliche Weise wie Farbstoff (9). Grüne, metallisch glänzende Kristalle. Schmp. 288° ; Ausbeute 0.1 g. Abs.-max. $610\text{ m}\mu$. (Gef.: I, 17.17; S, 8.74. Ber. für $\text{C}_{39}\text{H}_{36}\text{N}_3\text{IS}_2$: I, 17.22; S, 8.60%.)

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THE CONSTITUTION OF AWOBANIN AND AWOBANOL,
THE COLOURING MATTER OF AWOBANA⁽¹⁾
AND ITS CO-PIGMENT.

By Miss Chika KURODA.

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Flowers of "Tsuyukusa", *Commelina communis*, are beautiful azure blue and the extracted flower juice colours fabrics blue, hence the name "Tsukikusa" or "Awobana", meaning a paint grass or a blue flower. The colouring matter is one of the most well known and the oldest of its kind in Japan and the usage has a historical interest. Though no longer in practical use as a dye, as the colour can be easily washed away, it is still employed for drawing patterns in the art of "Yuzen" silk print and "Shiborizome" (tied dyeing). In some regions, therefore, the plant is especially cultivated for the production of "Awobana paper" which is painstakingly prepared by painting the flower juice on sheets of paper and drying them in the sun. No record of the chemical study on this pigment has been found.

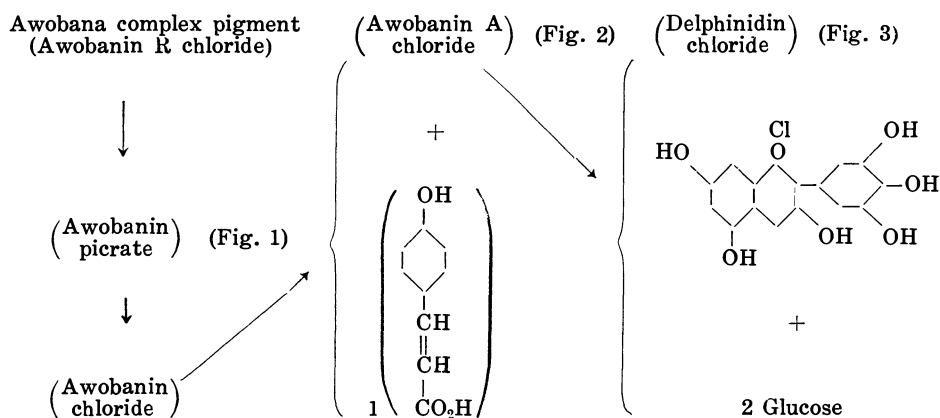
The present author was attracted to the study of this pigment, which she desired first, to obtain in a pure crystalline state, though it was difficult. However, beautiful blue coloured precipitate, like ultramarine, was finally isolated on adding methyl alcohol to its aqueous solution prepared from the Awobana paper. The blue powder thus obtained remarkably kept the colour unchanged in dry state (even in aqueous solution the colour was preserved considerably). In this respect the pigment seemed unusually stable for an anthocyanin; furthermore by decomposition with alkali, *p*-hydroxy-acetophenone which is not usually derived from anthocyanin was produced along with *p*-coumaric acid. Therefore, the constitution of this pigment was considered to belong to a special series and not to anthocyanin, and the study was followed accordingly.

However, after several investigations, it was shown that the main bright colour of this pigment is due to an anthocyanin awobanin named by the author in presence of a co-pigment awobanol also named by the author and metals which were detected in ashes after combustion (K, Mg, Al, SO₄, PO₄, etc.).

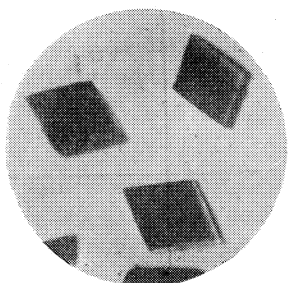
(1) "Awobana" is the local name for the flower of *Commelina communis* var. *hortensis* Makino used in Shiga, where the commercial Awobana paper is produced. It may not be synonymous with the so-called "Awobana" or "Tsuyukusa" (*Commelina communis*).

The above results were already reported in short notes.⁽²⁾ Now, to summarise details of the above study and to report some new results, the present communication is made.

Notwithstanding difficulties in the separation of awobanin from awobanol because of their properties which resemble each other in many respects, the two were finally separated and the constitution of awobanin was successfully confirmed as follows. Awobana paper was steeped in water, to the solution, an aqueous lead acetate solution was added to precipitate the lead salt of the pigment. On treating the lead salt with $\text{CH}_3\text{OH-HCl}$, it was converted into the chloride (red) in methyl alcoholic solution. The chloride of the colouring matter was precipitated by the addition of ether several times, then a red powdery pigment was obtained as chloride. The isolation of pure anthocyanin from the above chloride was exceedingly difficult, however, after careful treatments, a new crystalline glucoside of the pigment awobanin was obtained as picrate (Fig. 1), and finally as chloride. Awobanin was confirmed to be a compound of another anthocyanin (delphinidin 3,5-diglucoside, awobanin A named by the author) and *p*-coumaric acid by the following procedures. Analytical results of the picrate and the chloride agreed with delphinidin picrate + 2 glucose + *p*-coumaric acid + $5\text{H}_2\text{O}$ and delphinidin chloride + 2 glucose + *p*-coumaric acid + $5\text{H}_2\text{O}$, respectively. When awobanin was treated with cold alkali in H_2 gas, *p*-coumaric acid as one of the above component was isolated quantitatively. As another component, crystalline glucoside awobanin A finally separated slowly, when awobanin was specially treated with 20% aqueous HCl at room temperature and left for several days. The identification of awobanin A thus obtained is shown below.

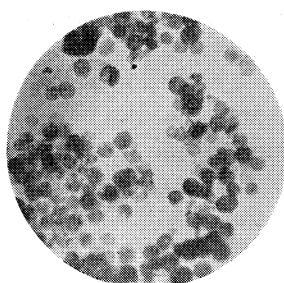


(2) Kuroda, *Proc. Imp. Acad. Japan*, **7** (1931), 61. Kuroda, *ibid.*, **9** (1933), 94. Kuroda, *ibid.*, **11** (1935), 238.



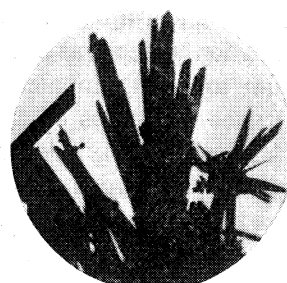
Awobanin picrate

Fig. 1.



Awobanin A chloride

Fig. 2.



Awobanin aglucone

Fig. 3.

Upon recrystallization, needle crystals were obtained from methyl alcohol and prisms from $\text{CH}_3\text{OH-HCl}$ (Fig. 2). On analysis, both forms were found to agree with diglucoside of delphinidin chloride $\text{C}_{27}\text{H}_{31}\text{O}_{17}\text{Cl} + 3\text{H}_2\text{O}$. The estimation of sugar was carried out by Pavy's method, the result being in agreement. When hydrolyzed with HCl , 1 mol of aglucone and 2 mols of sugar were produced. From the sugar, glucosazone was formed, agreeing in the properties and the melting point. The aglucone (Fig. 3) crystallized out in prisms from $\text{CH}_3\text{OH-HCl}$, and it gave all the reactions of delphinidin.

The analysis showed the compound to be delphinin chloride $\text{C}_{15}\text{H}_{11}\text{O}_7\text{Cl} + 3\text{H}_2\text{O}$. Alkali fusion was applied to the aglucone and the glucoside. Phloroglucinol which was confirmed by the reactions and the analytical results, and also an acid which was precipitated with lead acetate were formed. The latter seems to be gallic acid by qualitative tests, etc., and was converted into trimethyl ether with dimethyl sulphate, which melted at 168° (gallic acid trimethyl ether melts at 168°). Micro-Zeisel estimation proved the absence of methoxyl groups in the aglucone.

Now the position of the glucose was confirmed to be "3" and "5" by Karrer's perhydrol method.⁽³⁾ Furthermore colour reactions with Na_2CO_3 and with buffered solution were exactly in agreement with "delphinin chloride", 3,5-diglucoside of delphinidin chloride in literature.⁽⁴⁾ Absorption spectrum was observed to be similar to the diglucoside of delphinidin chloride. The yield of the diglucoside was considerable. Delphinidin monoglucoside was also noticed.

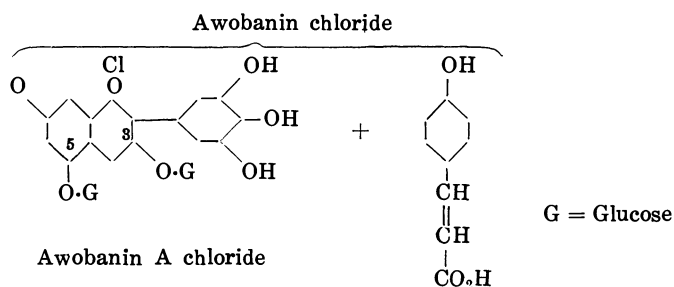
A crystalline co-pigment awobanol was obtained from the blue aqueous solution prepared from the Awobana powder, or Awobana paper, when it was heated with HCl . This compound seemed to be closely related to the chief

(3) *Helv. Chim. Acta*, **15** (1932), 1212.

(4) Reynolds, Robinson, and Scott-Moncrieff, *J. Chem. Soc.*, **1934**, 1235.

pigment because of the comparatively large yield, and because of the red colouration which was shown on reduction either with Mg and HCl or with sodium amalgam in alcohol. The following studies were made upon this substance: analyses of awobanol (needles or plates) and its acetyl derivative (crystalline); acetyl determination and estimation of CH_3O -group. Alkali fusion gave *p*-hydroxy-benzoic acid and a small quantity of a product which shows the phloroglucinol reaction. Alkali decomposition also gave the above phenol, however, *p*-hydroxy-acetophenone was produced in a considerable quantity. Consequently it was assumed that awobanol is not directly related to the chief Awobana pigment and rather a co-pigment.

In concluding, the pigment in Awobana is considered to be the anthocyanin combined with *p*-coumaric acid and co-pigment awobanol.



The further study of the positions of *p*-coumaric acid, the co-pigment and the relations of the ashes with Awobana pigment is in progress.

Experimental.

Isolation of Awobanin. The commercial Awobana paper (800 g.) was extracted with cold water, to the resulting blue coloured solution, an aqueous lead acetate solution was added to precipitate the lead compound of the pigment; the precipitate was sucked, and dried on a tile (blue powder 100 g.). On treating the lead salt with CH_3OH -HCl (2%) it was converted into chloride in CH_3OH solution. From the resulting red solution chloride of pigment was precipitated by the addition of ether (yield 25 g.). The chloride was dissolved in absolute CH_3OH , from which the pigment was precipitated as a red powdery substance on addition of ether. Though the process was repeated several times, the pigment seemed to contain some quantity of awobanol and other impurity. Furthermore as the chloride was very easily soluble in water or CH_3OH , the isolation of the crystalline pigment from the substance was extremely difficult. The chloride was named awobanin chloride (R) by the author.

However it was finally successfully obtained in crystalline state after several experiments and especially by using the material prepared from fresh flowers, instead of Awobana paper. However, as it was generally difficult to have the material of the

Awobana pigment directly, from the fresh flowers, the author has usually studied with the material which was prepared from Awobana paper, except the above one occasion.

The fresh flowers were extracted with $\text{CH}_3\text{OH-HCl}$ (2%) in cold; from the resulting red solution the lead salt of pigment was precipitated, and was converted into its chloride, and was purified in the usual way as mentioned above. To the solution of the chloride (R) thus obtained (7 g.) dissolved in hot H_2O (30 c.c.), picric acid (3 g.) was added, heated on the water bath, and left for one day, then an oily matter separated. When the oily matter was carefully treated with dilute aqueous picric acid on the water bath, picrate of the pigment crystallized out in reddish brown lustrous plates (2 g.). (Found for air dried material: C, 46.00, 46.06; H, 4.64, 4.68; N, 3.84, 3.93. Calculated for $\text{C}_{42}\text{H}_{39}\text{O}_{26}\text{N}_3 + 5\text{H}_2\text{O}$: C, 46.19; H, 4.49; N, 3.85%.) This was recrystallized from picric acid + CH_3OH (Fig. 1). The picrate was converted into chloride, when ether was added to the picrate dissolved in 2% $\text{CH}_3\text{OH-HCl}$, then the chloride crystallized out in red fine needles (decomposition over 200°). (Found for air dried material: C, 48.31, H, 5.54; Cl, 3.60. Calculated for $\text{C}_{36}\text{H}_{37}\text{O}_{19}\text{Cl} + 5\text{H}_2\text{O}$: C, 48.1; H, 5.23; Cl, 3.8%.) This substance was easily soluble in cold water or methyl alcohol, giving a purple red colour. With sodium carbonate it gave a pure blue colour fading to clear green.

Decomposition of Awobanin with Cold Alkali. Awobanin (0.1 g.) dissolved in water (2.5 c.c.) was treated with cold aqueous NaOH (5 c.c.) in H_2 for 2 hours. The product was acidified, extracted with ether. *p*-Coumaric acid (white crystals, m. p. 208° both alone and after admixture with an authentic specimen) was isolated from the ethereal solution. (Found for material dried on H_2SO_4 ; C, 65.8; H, 5.0. Calculated for $\text{C}_9\text{H}_8\text{O}_3$: C, 65.9; H, 4.9%.)

When awobanin R was decomposed with hot aqueous alkali in H_2 gas, *p*-coumaric acid and *p*-hydroxy-acetophenone were isolated.

Isolation of Awobanin A. The solution of awobanin chloride (R) (1 g.) dissolved in cold 20% aqueous HCl was left for few days at room temperature; dark purple substance gradually crystallized out (0.5 g.), it was washed with CH_3OH , then with 0.5% aqueous HCl (yield 0.25 g.). For analysis a specimen was recrystallized from CH_3OH (air dry). (Found: C, 45.43; H, 5.11; Cl, 4.77. Calculated for $\text{C}_{27}\text{H}_{31}\text{O}_{17}\text{Cl} + 3\text{H}_2\text{O}$: C, 45.25; H, 5.17; Cl, 4.60%.) This substance was purified under several conditions as follows: (1) From $\text{CH}_3\text{OH-HCl}$ (2%) it crystallized in needles; (2) When it was dissolved in minimum quantity of 0.5% hot aqueous HCl and an equal volume of 3% $\text{C}_2\text{H}_5\text{OH-HCl}$ was added, it crystallized out in plates (Fig. 2). However, analytical results were identical.

Direct Comparison of Colour Reactions of Awobanin A and Nasunin A Chloride. Both specimens were recrystallized in the same way with different results as follows. The compound was dissolved in a minimum quantity of 0.5% hot aqueous HCl and an equal volume of 3% $\text{C}_2\text{H}_5\text{OH-HCl}$ was added. After cooling, awobanin A chloride crystallized out in small hexagonal plates with golden lustre while the other separated in fine needles with golden lustre.

The colour reactions in buffered solution of the above two specimens recrystallized in the same way were compared. The colours given by the two pigments were almost identical except that awobanin A became red at a lower *pH* than nasunin A: (1) rose-pink, fading slowly; (2) rose-pink; (3) (4) the same, fading to very pale pink rapidly; (5) (6) bluish-pink, becoming colourless rapidly; (9) (10) blue-violet; (11) violet-red; (13) violet-blue; (14) violet; (15) deep blue.

Both specimens were very sparingly soluble (or insoluble) in cold water, alcohol, and dilute aqueous HCl but readily in hot dilute aqueous HCl. All the ordinary reactions, the colours with Na_2CO_3 (a bright pure blue) and with FeCl_3 in alcoholic solution (violet-blue) were observed identical.

Hydrolysis of Awobanin A with Hot Acid. (1) *Isolation of delphinidin chloride (aglucone) from awobanin A.* When awobanin A (0.1 g.) was boiled with 20% aqueous HCl for three minutes, chloride of aglucone separated. This was crystallized under the same conditions with nasunidin chloride. The aglucone crystallized out in plates with a green metallic lustre which was quite identical with delphinidin chloride from nasunin A. (Found: C, 45.75; H, 4.08. Calculated for $\text{C}_{15}\text{H}_{11}\text{O}_7\text{Cl} + 3\text{H}_2\text{O}$: C, 45.9; H, 4.33%.)

(2) *The colour reactions with buffered solution.* The both specimens, the aglucones from nasunin and awobanin chlorides gave quite identical results agreeing with those of delphinidin chloride in the literature: (1) red, pink in 30 seconds; (2) violet red, colourless in 30 seconds; (3) permanganate, colourless in 30 second; (4) similar to (3); (5) violet; (6) deep violet red; (9) blue violet; (10) similar to (9); (11) blue violet; (13) blue violet dichromic, pale yellow in $1\frac{1}{2}$ hours; (14) indigo blue, pale yellowish gray in $1\frac{1}{2}$ hours; (15) (16) similar to (14).

(3) *Estimation of sugar.* The above resulting 20% aqueous HCl solution (the filtrate from the aglucone) was neutralized with alkali and dried. The dry mass was treated under the same conditions with nasunin A and sugar was estimated by Pavy's method. (Found: sugar, 47.81. Calculated for $\text{C}_{27}\text{H}_{31}\text{O}_{17}\text{Cl} + 3\text{H}_2\text{O}$: sugar, 50.28%.)

(4) *The position of sugar.* Awobanin A chloride (0.3 g.) was treated with 30% H_2O_2 as in the case of kuromamin (see following paper) and glucosazone was separated from position 3; m.p. 205° , 0.04 g. The filtrate from the above osazone was heated with 15% aqueous HCl on the water bath for $1\frac{1}{2}$ hours, then filtered. The filtrate was neutralized with alkali and dried in vacuum. From the residue, glucosazone was isolated by aid of $\text{C}_6\text{H}_5\text{NH}\cdot\text{NH}_2\text{HCl}$ and sodium acetate as usual. After purifying, yield 0.06 g.; m.p. 203° alone and in mixed sample with an authentic specimen. Micro-Zeisel estimation proved the absence of methoxyl groups in the aglucone.

Alkali Fusion of Awobanidin (Aglucone of Awobanin). Awobanidin chloride (0.8 g.) was fused with NaOH (0.5 g.) and a small quantity of water at 203° , after cooling, the product was acidified with HCl, extracted with ether; the ether was evaporated, and from the ethereal residue dissolved in water, lead salt was precipitated by addition of lead acetate, the precipitate (yellowish brown) was filtered, (filtrate A). The precipitate was washed with water, then decomposed with dilute H_2SO_4 and extracted with ether; the ethereal residue dissolved in a small quantity of CH_3OH , was methylated with $(\text{CH}_3)_2\text{SO}_4$ and 50% aqueous KOH in H_2 gas; the reaction product was heated on the water bath to decompose the methyl ester and to evaporate CH_3OH , then was acidified, extracted with ether; the ethereal residue was again extracted with hot benzene. The benzene soluble part was crystallized from hot water, then gallic acid trimethyl ether, m.p. 165° , was isolated. The filtrate A was treated with dilute H_2SO_4 , and PbSO_4 was removed; when the filtrate was extracted with ether, phloroglucinol was isolated, m.p. 208° both alone and after admixture with the authentic specimen. (Found: C, 44.5; H, 6.2. Calculated for $\text{C}_6\text{H}_3(\text{OH})_3 + 2\text{H}_2\text{O}$: C, 44.45; H, 6.7%.)

Absorption Spectra of Awobanin A and Awobanidin Chloride. The substance in each case was dissolved in CH_3OH (N/10000), and iron arc was used as a light source. The photographs taken will be reproduced in another paper.

Preparation of Awobana Powder. Awobana paper was treated with water; to the resulting blue solution, CH_3OH was added, then a blue powder precipitated; this was sucked, and washed with CH_3OH well; the dry powder thus obtained was easily soluble in water giving a beautiful blue colour.

Isolation of Awobanol. The aqueous solution (or prepared directly from Awobana paper) of Awobana powder was heated with aqueous HCl (nearly 3%) for 1-2 hours, and was left. After a few days a red oily matter gradually separated and solidified. After filtering, the red powder was treated with CH_3OH , several times, then raw awobanol was obtained in pink needles. After purifying with hot CH_3OH it crystallized out in pale needles (m.p. 216°). This substance was soluble in hot CH_3OH , but insoluble in ether, and gave a brownish violet colour with FeCl_3 . (Found: C, 57.13; H, 4.54%.) When heated with water it was converted into another yellowish flat crystals (m.p. 256°).

Preparation of Acetyl Derivative of Awobanol. (1) With sodium acetate and acetic anhydride at 100°C . a crystalline product in white needles (m.p. $148-150^\circ$) was obtained. (Found: C, 55.99; H, 4.53%.) (2) With acetic anhydride and conc. H_2SO_4 at room temperature, a crystalline product in white needles (m.p. $148-156^\circ$) was obtained. (Found: C, 55.99; H, 4.53%.)

Decomposition of Awobanol with Alkali. Awobanol was fused with NaOH in the usual way, the product was acidified, extracted with ether, from the neutral part of the ethereal residue, *p*-hydroxy-acetophenone was isolated, white needles from hot water, m.p. 107° both alone and after admixture with the authentic specimen. (Found: C, 70.23; H, 5.9. Calculated for $\text{C}_8\text{H}_8\text{O}_2$: C, 70.59; H, 5.8%.)

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THE CONSTITUTION OF NATURAL COLOURING MATTERS, KUROMAMIN, SHISONIN, AND NASUNIN.

By Chika KURODA and Mizu WADA.

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“Kuromame”, “Shiso”, and “Nasu” are widely used vegetables in Japan, and as they are specially favoured for their bright colours, the chemical study of their colouring matters is of great importance as well as of much interest. However almost no literature has been found upon the subjects.

The authors were fortunately successful in isolating their main colouring matters in crystalline state, and after several investigations it was very curious to find that all three of these pigments are anthocyanin. Their short sketches have already been made⁽¹⁾, and now the following details will be recorded.

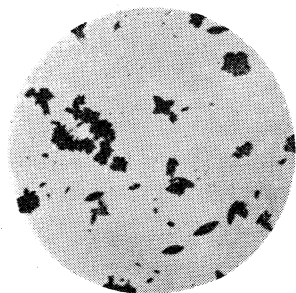
I. Kuromamin, The Colouring Matter of “Kuromame”.

“Kuromame”⁽²⁾ which belongs of *Glycine Soja Benth.*, is given the special name because of its delicacy of taste and of the specially deep bluish colour of the seed-coat. Not only used as common food it is specially served as one of happy symbolical sweets in the typical ceremonial menu of New Year. It is also favoured as medicinal matter especially recommended to vocalists. As results of preliminary tests the black pigment was treated as anthocyanin; however, the pigment seemed at first to be a mixture of a water soluble colouring matter and another water insoluble bluish matter. Therefore the treatment was carried out accordingly. From the reddish purple aqueous solution obtained by leaving the beans immersed in cold water, a bluish-green precipitate was formed on addition of aqueous lead acetate. The lead salt was converted into chloride in the usual manner. Isolation of pure pigment from the chloride was exceedingly difficult. However, after several experiments the pigment was successfully obtained by purifying the lead salt with cold acetic acid. The chloride, obtained from the lead salt thus purified, still contained impurities, but the latter dissolved in CH_3OH easily, therefore the isolation of crystalline pigment was finally successful after removing the impurities by special treatment. The glucoside crystallized in green

(1) Kuroda and Wada, *Proc. Imp. Acad. Japan*, **9** (1933), 101; **9** (1933), 517; **11** (1935), 189; **11** (1935), 28; **9** (1933), 51; **11** (1935), 235.

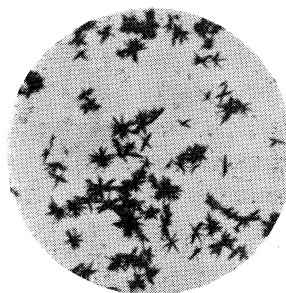
(2) “Kuro” means black and “Mame” bean in Japanese.

leaflets with metallic lustre. Its analytical results and decomposition products with boiling HCl proved to be monoglucoside of cyanidin chloride $C_{21}H_{21}O_{11}Cl + 1\frac{1}{2}H_2O$.



Kuromamin chloride from
water-soluble pigments
from "Kuromame" from Hokkaido

Fig. 1.



Kuromamidin chloride from
water-soluble pigments
from "Kuromame" from Hokkaido

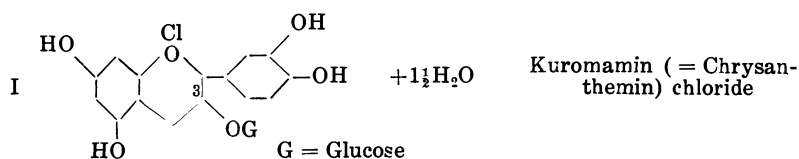
Fig. 2.

The dry seed-coat, after the removal of the above water-soluble colouring matter was treated with $CH_3OH-HCl$, and the pigment from the resulting red solution, was purified and isolated in crystalline state as chloride by using lead salt method as previously mentioned. The chloride was proved to be monoglucoside of cyanidin chloride $C_{21}H_{21}O_{11}Cl + 1\frac{1}{2}H_2O$ by analysis and by its decomposition products as well as by the water-soluble pigment.

By these experiments, the nature of the colouring matter of the seed-coat was shown to be identical whether derived from the water-soluble portion or otherwise. This observation was verified by treating the seed-coat directly with $CH_3OH-HCl$ instead of first treating it with water. The name kuromamin is given to the crystalline glucoside by the authors.

It was suggested that there may exist possible disagreement in the chemical structure of the colouring matter among different samples from unlike localities. Indeed there are amazingly numerous varieties of "Kuromame" on market, differing considerably in their appearances. Such a consideration led to our further studies to apply the above treatment to the beans from Manchuria (Mukden and Shing Tai Tzu). As the results, it was shown that the colouring matters of "Kuromame", regardless of the varieties and the localities, belong to the same kind of compound.

After several investigations, the above glucoside "kuromamin", in every respect, was found to be identical with chrysanthemin (I), namely cyanidin 3-monoglucoside.



The procedures will be pointed out as follows :

(1) The analytical result of kuromamin chloride agreed with that of chrysanthemin chloride $C_{21}H_{21}O_{11}Cl + 1\frac{1}{2}H_2O$ in literature⁽³⁾; and m.p. 182° of kuromamin picrate also agreed with that of chrysanthemin picrate.

(2) By characteristic colour reactions, the position of glucose was determined to be "3", namely kuromamin chloride turning violet with Na_2CO_3 ; blue with $NaOH$ or $FeCl_3$. In these respects they were exactly identical with chrysanthemin chloride⁽⁴⁾, but distinctly different from cyanenin (synthetic, 5-monoglucoside of cyanidin) chloride⁽⁵⁾ which is known to give bright bluish green colouration with Na_2CO_3 and to be oxidised rapidly with $FeCl_3$. Further confirmative colour reactions with buffered solution⁽⁶⁾ were observed. Then, the results with kuromamin chloride and natural specimen⁽⁷⁾ of chrysanthemin chloride were quite identical, and agreed with the report on synthetic⁽⁸⁾ chrysanthemin chloride, and were distinctly distinguished from those of cyanenin chloride⁽⁹⁾ and natural specimen of cyanin chloride (3,5-diglucoside of cyanidin), and mecocyanin chloride, (3-gentiobioside of cyanidin chloride⁽¹⁰⁾, natural and synthetic).

(3) Distribution number was determined by Willstätter's method; the results being 19 (1st) and 19.15 (2nd) in agreement with those of the literature (natural⁽¹¹⁾, 19 and 19.5; synthetic⁽¹²⁾, 19 and 19.1).

(4) As results of observations of absorption spectrum, kuromamin chloride and chrysanthemin chloride were also proved to be quite identical and were distinguished from those of cyanin chloride (natural, from dahlia and "shiso")⁽¹³⁾.

(3) Willstätter and Bolton, *Ann.*, **421** (1916), 146. S. Murakami, Robertson, and R. Robinson, *J. Chem. Soc.*, **1931**, 2670.

(4) S. Murakami, R. Robinson, and A. Robertson, *ibid.*, **1931**, 2668.

(5) Leon and Robinson, *ibid.*, **1932**, 2222.

(6) R. Robinson and A. Robertson, *Biochem. J.*, **23** (1929), 35.

(7) From flower of deep red *chrysanthemum indicum*.

(8) Murakami, Robertson, and Robinson, *J. Chem. Soc.*, **1931**, 2671.

(9) A. Leon and Robinson, *ibid.*, **1932**, 2222.

(10) Willstätter and Weil, *Ann.*, **412** (1916), 231. Grove, Inubuse, and Robinson, *J. Chem. Soc.*, **1934**, 1611.

(11) Willstätter and Bolton, *Ann.*, **412** (1916), 146.

(12) Murakami, Robinson, and Robertson, *J. Chem. Soc.*, **1931**, 2670.

(13) Kuroda and Wada, *Proc. Imp. Acad. Japan*, **11** (1935), 28.

(5) The aglucone of kuromamin was again verified exactly to be cyanidin, on comparing its properties (solubilities, colour reactions, and appearances, etc.) with those of our specimen of synthetic cyanidin chloride⁽¹⁴⁾ (for which the writers thank Miss Yashiro for her kind help in a part of this synthesis) and of the aglucone from "Shiso" pigment and was also identified by the absorption spectrum⁽¹³⁾.

(6) Upon the decomposition with acid, kuromamin yielded one mol each of cyanidin and glucose. The quantity of glucose was determined exactly by Pavy's method; the result was found to be in agreement (Found: 35. Calc.: 35%).

(7) Furthermore by Karrer's method⁽¹⁵⁾ the position of glucose was also proved to be "3", namely by action of perhydrol.

(8) Kuromamin chloride was compared with the report on idaein chloride, 3-monogalactoside of cyanidin chloride⁽¹⁶⁾ $C_{21}H_{21}O_{11}Cl + 2\frac{1}{2}H_2O$; then they were actually distinguished from each other in their solubilities, quantities of water of crystallisation, and in their osazones (glucosazone from kuromamin, m.p. 203° ; galactosazone, m.p. 186°).

Experimental.

Isolation of Kuromamin Chloride from Water-soluble Portion. When the beans (36 l.) from Hokkaido were immersed in cold water for several hours, a reddish purple aqueous solution was obtained. From the aqueous solution, bluish green precipitate was formed on addition of saturated aqueous lead acetate which was then filtered, dried on a tile quickly, powdered (yield, 0.5% of the beans) and triturated with cold glacial acetic acid. From the purple acetic acid solution thus obtained, a pure indigo blue lead salt of the pigment was precipitated upon the addition of several times its volume of ether (yield, 17 g.). When the above lead salt was treated by 2% $CH_3OH-HCl$, a red solution was obtained, and the chloride of the colouring substance was precipitated by addition of ether. And the chloride was triturated with a small quantity of absolute CH_3OH to remove easily soluble impurities. It crystallized out from dry $CH_3OH-HCl$ in leaflets with a metallic lustre (Fig. 1) (yield, 0.4 g.). On analysis, the result agreed with a monoglucoside of cyanidin chloride (Found: C, 49.38; H, 4.73. Calc. for $C_{21}H_{21}O_{11}Cl + 1\frac{1}{2}H_2O$: C, 49.30; H, 4.69%).

Hydrolysis of Kuromamin Chloride (from Water-soluble Portion) with Acid. The above kuromamin chloride (air dry, 0.1 g.) was dissolved in hot 0.1% aqueous HCl (6 c.c.), conc. HCl (6 c.c.) added, and the mixture was boiled for three minutes. On cooling, an aglucone (Fig. 2) crystallized out in reddish brown needles. Yield, 0.0642 g. (air dry, 64.2% calc. 65.3%). It showed all the qualitative reactions of cyanidin chloride. The aglucone was recrystallized from 2% $CH_3OH-HCl$ for analysis (Found: C, 52.79; H, 4.14. Calc. for

(14) A. Robertson and R. Robinson, *J. Chem. Soc.*, **1928**, 1526.

(15) Karrer and Meuron, *Helv. Chim. Acta*, **15** (1932), 1212.

(16) Willstätter and Mallison, *Ann.*, **408** (1915), 15.

cyanidin chloride $C_{15}H_{11}O_6Cl + H_2O$: C, 52.89; H, 3.82%). Micro-Zeissel estimation proved the absence of methoxyl groups in the aglucone.

Sugar. (1) *Estimation.* The above filtrate removed from the aglucone was neutralized with alkali carefully, evaporated on the water bath to dryness, then dissolved again in water, and filtered to remove completely any insoluble matter, and was dried on the water bath; the dry matter dissolved in H_2O (pale yellow solution), was made up to 100 c.c. of about 10% NH_3 with conc. NH_3 and the sugar estimated with Pavy's solution.

(2) *Osazone.* The resulting acid solution obtained upon decomposition of kuromamin chloride with 20% aqueous HCl was neutralized with alkali carefully and dried. The dry matter was dissolved in water and filtered. When the filtrate was heated with $C_6H_5NH-NH_2 \cdot HCl$ and sodium acetate, glucosazone was formed: washed with CH_3OH , and ether, m.p. 205° , both alone and after admixture with the authentic specimen.

Isolation of Kuromamin Chloride from Water-insoluble Portion. The dry seed-coat, after the removal of the water-soluble pigment, was treated with 0.5% $CH_3OH-HCl$ and to the resulting red solution, methyl alcohol solution of lead acetate was added drop by drop, and the bluish purple lead salt of the pigment was collected after removing the initial white precipitate of lead chloride. The purification of both the above lead salt and chloride of pigment was carried out as in the case of the water-soluble pigment. The chloride (0.5 g.) thus obtained was recrystallized from dry $CH_3OH-HCl$ twice. The kuromamin chloride separated in leaflets with green metallic lustre. (Found: C, 49.24; H, 4.43. Calc. for $C_{21}H_{21}O_{11}Cl + 1\frac{1}{2}H_2O$: C, 49.30; H, 4.69%.)

Hydrolysis with Acid. When the acid decomposition of the glucoside (from water-insoluble portion) (0.1 g.) was carried out as previously mentioned, cyanidin chloride (0.065 g.) separated in brown-red needles. Yield, 65%; calc. 65.3%. For analysis, the aglucone was recrystallized from 2% $CH_3OH-HCl$ (Found: C, 52.70; H, 3.62. Calc. for $C_{15}H_{11}O_6Cl + H_2O$: C, 52.86; H, 3.82%. Estimation of sugar: Found: 34.05. Calc.: 35.22%).

Direct Isolation of Kuromamin Chloride from "Kuromame" from Hokkaido. The seed-coats were separated from the beans by the help of an electric fan, grinding in a hand mill at room temperature. They were then immersed in 2% $CH_3OH-HCl$ for three hours, and into the resulting red solution, methyl alcohol solution of lead acetate was added drop by drop in order to precipitate the lead salt of pigment. On carrying out the subsequent treatment as already mentioned, the glucoside crystallized out; 1.5 g. of the crystalline chloride was derived from 8 l. of beans or 370 g. of seed-coat, showing a notable increase in the yield, hence the advantage of the present method (over the one employed formerly when beans were first immersed in water). (Found: C, 49.21; H, 4.79. Calc. for $C_{21}H_{21}O_{11}Cl + 1\frac{1}{2}H_2O$: C, 49.30; H, 4.60%.) The conversion of the glucoside led to a quantitative yield of crystalline aglucone (Found: C, 52.72; H, 3.62. Calc. for cyanidin chloride $C_{15}H_{11}O_6Cl + H_2O$: C, 52.92; H, 3.82%).

Isolation of Kuromamin Chloride from "Kuromame" from Mukden. The seed-coat (550 g.) of beans from Moukden was treated with 2% $CH_3OH-HCl$ directly and purified by the foregoing method. The glucoside obtained in crystals with a green metallic lustre was decomposed into one molecule each of cyanidin chloride and glucose, and analytical results of both the glucoside (Found: C, 49.02; H, 4.59. Calc.: C, 49.30; H, 4.69%) and the aglucone (Found: C, 52.51; H, 3.46. Calc.: C, 52.94; H, 3.82%)

agreed with cyanidin chloride-3-monoglucoside. 0.5 g. of the crystalline glucoside was derived from 550 g. of seed-coat.

Isolation of Kuromamin Chloride from "Kuromame" from Shing Tai Tzu. Seed-coat of beans from Shing Tai Tzu was treated under the same condition as that from Mukden with the same results: Analytical results of both the glucoside (Found: C, 48.98; H, 4.55%) and the aglucone (Found: C, 52.87; H, 3.97%) agreed with 3-monoglucoside of cyanidin chloride. 0.5 g. of kuromamin chloride was derived from 580 g. of seed-coat.

Kuromamin Picrate. Kuromamin chloride was dissolved in 0.05% aqueous HCl, and saturated aqueous picric acid was added. In every respect the picrate that separated as a deep brownish-red prisms with bronze glance in mass (decomposition point, 190–192°), was found to be identical with chrysanthemin (cyanidin-3-monoglucoside) picrate.

The Alkali Fusion of Kuromamin Chloride. Kuromamin chloride (1 g.) was fused with KOH (3 g.) and H₂O (small quantity) at 203°. After cooling, the product was dissolved in water, acidified with conc. HCl, extracted with ether, and was evaporated. From the ethereal residue, a lead salt was precipitated by the addition of lead acetate. The lead salt filtered was decomposed with dilute H₂SO₄ and extracted with ether; the ethereal solution was treated with animal charcoal, and evaporated. When the residue was purified with hot water, protocathechuic acid crystallized out in white needles; m.p. 193°, both alone and after admixture with an authentic specimen (the quantity was not enough for analysis). The filtrate from the lead precipitate was treated with dilute H₂SO₄; after removing PbSO₄, the filtrate was extracted with ether. From the ethereal solution, phloroglucinol was obtained in white long needles; m.p. 210°, both alone and after admixture with an authentic specimen (Found: C, 44.45; H, 6.26. Calc. for C₆H₆O₃+2H₂O: C, 44.44; H, 6.17%).

The Oxidation of Kuromamin Chloride with H₂O₂. To the chloride (1 g.) dissolved in 1% aqueous Na₂CO₃ (80 c.c.) 3% aqueous H₂O₂ (80 c.c.) was added and the mixture was left at room temperature for three hours, then acidified with H₂SO₄ and extracted with ether. From the ethereal extract protocathechuic acid was isolated in white needles; m.p. 193°, both alone and after admixture with the authentic specimen. (Found: C, 48.97; H, 4.75. Calc. for C₇H₆O₄+H₂O: C, 48.83; H, 4.65%.)

The Position of Sugar. Kuromamin chloride (0.3 g.) was dissolved in hot H₂O (3.5 c.c.) and after cooling, into the solution, 30% H₂O₂ (2.5 c.c.) was added and the mixture left at room temperature. When yellow coloured solution thus obtained, was neutralized with 2N NaOH very carefully, the excess of H₂O₂ was decomposed with Pt-black, and the whole was dried by distillation in vacuum. From the aqueous solution of the residue, glucosazone (m.p. 205°, both alone and after admixture with the authentic specimen) was obtained by heating with C₆H₅NH·NH₂·HCl and sodium acetate (yield, 0.05 g.). In this result, the position of glucose was proved to be "3". The filtrate from the above osazone was treated as in the case of shisonin (see following pages), however, no osazone from position "5" has been formed.

Preparation of Chrysanthemin Chloride from Chrysanthemum. The fresh dark red flowers were treated with 2% CH₃OH-HCl and from the resulting red solution, a lead salt was precipitated by the addition of lead acetate. The lead salt was also converted into chloride as usual; the raw chloride dissolved in 0.05% aqueous HCl was converted into picrate as previously mentioned. And the picrate was reconverted into chloride by aid

of 2% $\text{CH}_3\text{OH-HCl}$, and was purified as in the case of kuromamin chloride, then chrysanthemin chloride crystallized out in leaflets with green metallic lustre and was found to be quite identical with kuromamin in every respect.

Experiments with Buffered Solution. Colour reactions in a range of buffered solution of graded pH were examined. The method of the Robertson and Robinson⁽¹⁴⁾ was applied and the numbers refer to solutions of pH from 3.2 (1) to 11.0 (14) and then to more alkaline solution of unknown pH. The chloride of kuromamin and natural chrysanthemin gave quite identical results as follows: (1) Salmon-red; (2) salmon-red, fading; (3) bluish-red, fading; (4) bluish salmon-red to pink fading; (5) pink; (6) brown-violet; (9) (10) (11) brown-violet-red (keeping considerably); (13) (14) brown-violet; (15) violet; (16) bluish-violet.

Distribution Number. Amyl alcohol for this experiment was purified as follows: commercial amyl alcohol was washed with 0.5% aqueous HCl several times, then washed with water to remove a trace of acid and distilled (b.p. over 110°). Kuromamin chloride (air dry, 0.01 g.) was dissolved in 0.5% aqueous HCl (50 c.c.) and was shaken with the above amyl alcohol. The operation was repeated twice. After standing the amyl alcoholic layer was kept for use. The preparation of standard solution: kuromamin chloride (0.0019 g., air dry) was dissolved in hot 2% $\text{CH}_3\text{OH-HCl}$ (2 c.c.), to the solution, amyl alcohol was added and the whole made up to 50 c.c. and was used as standard. The result of 1st operation; 0.0019 g. in amyl alcohol layer, distribution number 19; 2nd: 0.00155 g. in amyl alcohol layer, distribution number 19.15.

The Colour Reactions with Buffered Solutions. The three specimens, kuromamidin, shisonidin (17) and synthetic cyanidin chlorides gave the identical results. (1) Red, pink in 30 seconds; (2) bluish red, colourless in 30 seconds; (3) reddish violet, colourless in 30 seconds; (4) blue reddish violet, colourless in 30 seconds; (5) permanganate, colourless in 1 hour; (6) bluer than (5) permanganate in 30 seconds; (9) violet red, deep permanganate in 30 seconds.; (10) similar but a little bluer; (11) violet blue; (13) dark blue violet dichroic; (14) similar to (13); (15) dark blue violet; (16) blue, dark yellowish gray in 1 hour.

Absorption Spectra of Kuromamin, Chrysanthemin, Kuromamidin, and Synthetic Cyanidin Chloride. Photographs were taken for each substance dissolved in CH_3OH (N/10000), with iron arc as the light source. They were reproduced in another paper.⁽¹⁷⁾

The authors desire to thank the Imperial Academy for a grant, and Viscount Masatoshi Okochi, the President of the Institute, for his kindness for obtaining samples of the beans from Manchuria.

II. Shisonin, The Colouring Matter of "Shiso".

The pigment of "Shiso" leaves (*Perilla Ocimoides L. var Crispa Benth*)⁽¹⁸⁾ is extensively used for colouring "Umeboshi" which is a kind of plum pickle favoured throughout Japan. The chemical study on this pigment was made

(17) Kuroda and Wada, *Proc. Imp. Acad. Japan*, **11** (1935), 189.

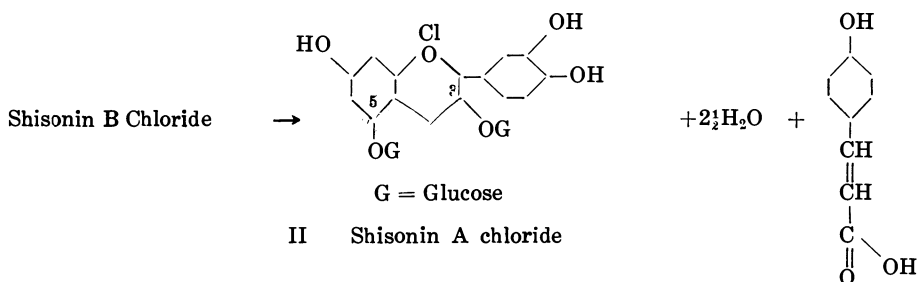
(18) Japanese special name "Chirimen Shiso".

by Dr. Kaoru Kondo,⁽¹⁹⁾ a crystalline pigment "perillanin" was isolated and considered to be delphinidin-mono-glucoside combined with protocatechuic acid.

The present authors have undertaken the study of the anthocyan pigment obtained from the leaves cultivated in Tokyo, and some interesting new observations were made.

From "Shiso" leaves, a pigment which was named shisonin by the authors, was isolated as chloride. After several investigations shisonin was shown to be a mixture of glucosides, shisonin A and another new glucoside shisonin B. Shisonin A was isolated in a crystalline state as its chloride from the shisonin chloride by use of a suitable solvent. Shisonin B chloride was confirmed to be a compound of shisonin A chloride and *p*-coumaric acid, because the above two components were isolated, when shisonin B chloride was treated with cold alkali in H₂ atmosphere.

Shisonin A chloride was identified to be cyanin chloride, 3,5-diglucoside of cyanidin (II) in every respect.



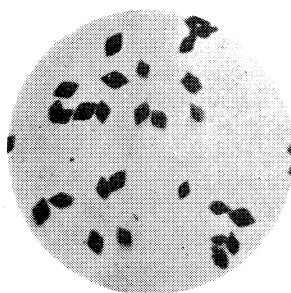
For the direct comparisons, cyanin chloride was prepared from dahlia.⁽²⁰⁾ Appearances of crystals obtained in both cases under similar conditions were quite identical rhombic plates (Fig. 3) or fine needles (Fig. 4), m.p. (d.p.) being 195° as cyanin chloride. Moreover all the colour reactions, solubilities (except that, it was almost insoluble in cold water, or in dilute aqueous HCl, differing in this respect from mecocyanin⁽²¹⁾), and the analytical results (C₂₇H₃₁O₁₆Cl + 2½H₂O)⁽²²⁾ were in agreement.

(19) *J. Pharm. Soc. Japan*, **51** (1931), 254.

(20) Kōzō Hayashi, *J. Bot. Japan*, **47** (1933), 396.

(21) Mecocyanin chloride, 3-bioside of cyanidin chloride C₂₇H₃₁O₁₆Cl·3H₂O: Willstätter and Weil, *Ann.*, **412** (1916), 231. A. Leon and R. Robinson *J. Chem. Soc.*, **1931**, 2737.

(22) Willstätter and Nolan, *Ann.*, **408** (1915), 1. Willstätter and Mallison, *Ann.*, **408** (1915), 147.



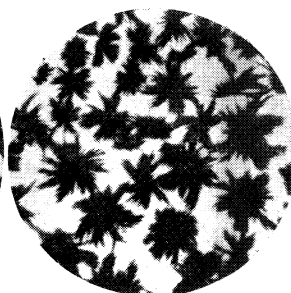
Shisonin A chloride
from "Shiso"

Fig. 3.



Shisonin A chloride
from "Shiso"

Fig. 4.



Shisonidin chloride
from "Shiso"

Fig. 5.

Upon the decomposition with acid, from shisonin A chloride (m.p. 195°), one molecule of cyanidin chloride and two molecules of glucose were yielded quantitatively as anticipated. The estimation of the glucose was carried out by Pavy's method, in which the result agreed. And the positions of the glucose were proved to be "3" and "5" by Karrer's method.

The aglucone (brown crystals, Fig 5) was exactly proved to be cyanidin chloride ($C_{15}H_{11}O_6Cl + H_2O$), by its properties, analysis, and by the following decomposition products. When fused with alkali, it gave phloroglucinol and protocathechuic acid. The protocathechuic acid was obtained, however, in a better yield when the aglucone was oxidized with H_2O_2 in a sodium carbonate solution.

More confirmative colour reactions with buffered solution⁽¹⁴⁾ were observed. The results with shisonin and cyanin chloride (from dahlia) were quite identical, and agreed with the report on synthetic cyanin chloride,⁽²³⁾ and were distinctly distinguished from those of chrysanthemin chloride, obtained from natural pigments, and also of cyanenin (synthetic, cyanidin 5-monoglucoside) chloride⁽⁹⁾ and mecocyanin chloride⁽⁸⁾ (natural).

As the results of estimation of distribution number and of observation of absorption spectrum, shisonin A was also proved to be quite identical with cyanin chloride.

In view of the above experimental results, the anthocyanin of "Shiso" is considered to be a mixture of shisonin A and shisonin B, the latter being a compound of *p*-coumaric acid and shisonin A; further study on the arrangement of *p*-coumaric acid in the interesting second glucoside shisonin B is progressing.

(23) R. Robinson and A. R. Todd, *J. Chem. Soc.*, **1932**, 2496.

Experimental.

Preparation of Shisonin Chloride. A dry powder, which was cautiously prepared from the leaves (obtained from the vegetable market in Tokyo) was soaked in cold petroleum ether to remove the yellow pigment. On separating the yellow solution, it was then extracted with 2% $\text{CH}_3\text{OH-HCl}$. On addition of ether to the above resulting red solution a heavy red flocculent crude chloride of the colouring matter was precipitated and then, by dissolving this in H_2O and adding lead acetate the pigment was purified as lead salt. The lead salt was reconverted into chloride by aid of $\text{CH}_3\text{OH-HCl}$ and ether by the similar method as previously mentioned for kuromamin chloride and purified.

The Isolation of Shisonin A Chloride. Amorphous shisonin chloride (2 g.) dissolved in water (50 c.c.) was treated with 4 N aqueous NaOH (50 c.c.) in H_2 and left for two hours at room temperature; then acidified with conc. HCl (calculated quantity) and extracted with ether. The residue (0.1 g.) of ethereal solution was washed with a small quantity of cold water, then was recrystallized from hot water by aid of animal charcoal twice. *p*-Coumaric acid, m.p. 207° , both alone and after admixture with the authentic specimen. (Found: C, 65.64; H, 5.06. Calc. for $\text{C}_9\text{H}_8\text{O}_3$: C, 65.64; H, 5.06%.)

When the above aqueous red solution, obtained free from *p*-coumaric acid, was left at room temperature, a dark brown coloured crystalline substance with metallic lustre gradually separated (the separation finished in 2 or 3 days); the dry matter (0.5 g.) thus obtained was washed with cold CH_3OH , was dissolved in hot 0.01% aqueous HCl (small quantity), to which an equal volume of 3% $\text{C}_2\text{H}_5\text{OH-HCl}$ was added and left. Shisonin A chloride (decomposition point 195°) crystallized out in small rhombic plates (Fig. 3) with metallic lustre. It was recrystallized three times for analysis. (Found: C, 47.03; H, 5.54. Calc. for $\text{C}_{27}\text{H}_{31}\text{O}_{16}\text{Cl} + 2\frac{1}{2}\text{H}_2\text{O}$: C, 46.86; H, 5.21%.)

The Decomposition of Shisonin A Chloride with Acid. Shisonin A chloride (0.1024 g., air dry) was boiled with 20% aqueous HCl (5 c.c.) on the sand bath for three minutes, then cooled with ice; an aglucone crystallized out in reddish brown needles. Yield, 0.05 g. (air dry, 48.81%, calc. 49.2%). It showed all the qualitative reactions of cyanidin chloride. For analysis, a specimen was recrystallized from 2% $\text{CH}_3\text{OH-HCl}$. (Found: C, 52.72; H, 4.06. Calc. for cyanidin chloride $\text{C}_{15}\text{H}_{11}\text{O}_6\text{Cl} + \text{H}_2\text{O}$: C, 52.86; H, 3.82%). Micro-Zeisel estimation proved the absence of methoxyl groups in the aglucone.

Sugar. (1) *Estimation.* Crystalline shisonin A chloride (0.0985 g.) was boiled with 20% aqueous HCl for 3 minutes. After cooling, the filtrate removed from the aglucone was treated as in the case of kuromamin and sugar was estimated by Pavy's method (Found: sugar, 50.44. Calc. for $\text{C}_{27}\text{H}_{31}\text{O}_{16}\text{Cl} + 2\frac{1}{2}\text{H}_2\text{O}$: 52.10%).

(2) *Osazone.* Glucosazone from the resulting acid solution obtained by acid hydrolysis of shisonin A chloride was formed in a similar method to the case kuromamin chloride.

(3) *The position of sugar.* Shisonin A chloride (0.3 g.) was treated with 30% H_2O_2 as in the case of kuromamin and glucosazone from position "3" was obtained, m.p. 205° , 0.04 g. The filtrate from the above osazone was heated with 15% aqueous HCl on the water bath for $1\frac{1}{2}$ hours, then filtered. The filtrate was neutralized with alkali and dried in vacuum. From the residue, glucosazone from position "5" was isolated by aid of $\text{C}_6\text{H}_5\text{NH-NH}_2\cdot\text{HCl}$ and sodium acetate as usual. After purifying, yield 0.06 g.; m.p. 203° , both alone and after admixture with the authentic specimen.

Isolation of Shisonin A Chloride by the Use of Solvent. When amorphous shisonin chloride (5 g.) was warmed with absolute CH_3OH on the water bath and left for a few days, a pigment free from *p*-coumaric acid (microscopic crystals upon treatment with CH_3OH) was separated (dry matter 1.5 g.); this was sucked. This crystallized out in small rhombic plates (decomposition point 195°) with golden metallic lustre, when the dry matter was dissolved in hot 0.5% aqueous HCl and an equal volume of 3% $\text{C}_2\text{H}_5\text{OH}$ -HCl was added. Recrystallized twice for analysis (Found: C, 46.74; H, 5.42. Calc. for $\text{C}_{27}\text{H}_{31}\text{O}_{16}\text{Cl} + 2\frac{1}{2}\text{H}_2\text{O}$: C, 46.86; H, 5.21%.) From the compound, an aglucone was produced. (Found: C, 52.84; H, 4.06. Calc. for $\text{C}_{15}\text{H}_{11}\text{O}_6\text{Cl} + \text{H}_2\text{O}$: C, 52.86; H, 3.82%.)

Alkali Fusion of Shisonin A Chloride. Shisonin chloride (0.7 g.) was fused with KOH (2.1 g.); from the product, phloroglucinol (m.p. 207°) and protocatechuic acid (m.p. 196° , both alone and after admixture with the authentic specimen) were obtained.

The Oxidation of Shisonin A Chloride with H_2O_2 . The oxidation with 3% H_2O_2 was similarly carried out as in the case of kuromamin; protocatechuic acid was isolated in good yield, m.p. 196° . (Found: C, 48.90; H, 4.55. Calc. for $\text{C}_7\text{H}_6\text{O}_4 + \text{H}_2\text{O}$: C, 48.83; H, 4.65%.)

Cyanin Chloride from Dahlia. The dark coloured flowers of dahlia ("Chishima", "Ubatama", "Black diamond" about 100 g.) was immersed in 2% CH_3OH -HCl (160 c.c.) in cold for three hours. When the resulting red solution was concentrated at 35° under reduced pressure and left, the pigment crystallized out in needles. It was filtered, dried, and to the solution of the dry matter dissolved in 0.01% hot aqueous HCl (1 part), 3% $\text{C}_2\text{H}_5\text{OH}$ -HCl (1 part) was added. Cyanin chloride crystallized in small rhombic plates with golden lustre (decomposition point 195°). To remove a trace of monoglucoside, the above chloride was dissolved in 0.5% aqueous HCl saturated previously with *n*-butyl alcohol and was shaken with butyl alcohol, saturated with 0.5% aqueous HCl twice, and then with isoamyl alcohol. Now, the aqueous layer was warmed and 3% $\text{C}_2\text{H}_5\text{OH}$ -HCl was added. Pure cyanin chloride was isolated from the solution.

Another Comparison of Shisonin A and Cyanin Chloride. All the apparent characters of the specimens were identical and they furnished solutions (aqueous and alcoholic) having the same colour and behaviour under all conditions. All the ordinary reactions, the colours with Na_2CO_3 (blue) and aqueous FeCl_3 (violet) were observed identical.

The colour reactions in a range of buffered solutions were investigated and the same results were obtained as follows: (1) Rose, fading; (2) (3) bluish rose, colourless in 30 seconds; (4) cherry red, fading; (5) permanganate fading less rapidly; (9) more intense and more stable; (9) (10) (11) reddish-violet; (13) violet, fading; (14) blue violet, fading; (15) (16) blue, fading rapidly.

Comparison of Distribution. Shisonin A chloride (10 mg.) was dissolved in 0.5% aqueous HCl (50 c.c.) previously saturated with *n*-butyl alcohol. A similar solution of cyanin chloride (from dahlia) was prepared and both solutions were shaken twice with *n*-butyl alcohol (50 c.c. each time) previously saturated with 0.5% aqueous HCl. Each butyl alcohol layer was matched colorimetrically and was found to be identical.

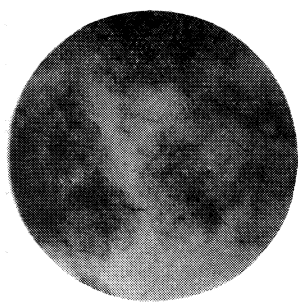
Absorption Spectra of Shisonin A, Cyanin (from Dahlia) and Shisonidin Chloride. Photographs were taken for each substance dissolved in CH_3OH (N/10000), with iron arc as a light source. They were reproduced in another paper.⁽²⁻⁴⁾

(24) Kuroda and Wada, *Proc. Imp. Acad. Japan*, **11** (1935), 189.

III. Nasunin, Colouring Matter of "Nasu".⁽²⁵⁾

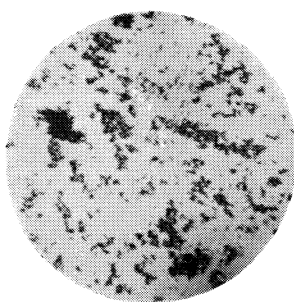
The vegetable fruit of egg-plant (*Solanum Melongena L. var erculentum* Ness) is not only a popular and useful vegetable food material from summer to autumn Japan, but the colour of its epidermis is noted for the beautiful dark purple which is taken as a standard, in dyeing from the olden time, being called as "Nasu blue." As cares are taken even in cooking to preserve this colour unaffected, the authors have been attracted to the study of the pigment. As the colour was extremely delicate and changeable it called for absolutely tedious methods with a special precautions to isolate the pigment. After preliminary tests, as the bright colouring matter of "Nasu" was shown to belong to an anthocyanin, the treatments were carried out by using the lead salt method accordingly.

The isolation of "Nasu" pigment in a crystalline state, was extraordinarily difficult; however, after several experiments, a new crystalline glucoside which was named nasunin by the authors was successfully obtained as picrate (Fig. 6), and finally as chloride.



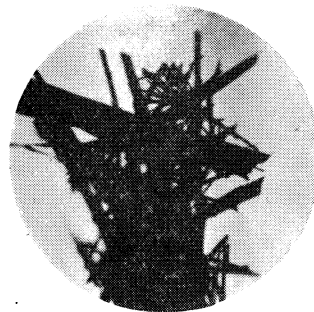
Nasunin Picrate
from "Nasu"

Fig. 6.



Nasunin A chloride
from "Nasu"

Fig. 7.



Nasunidin chloride
from "Nasu"

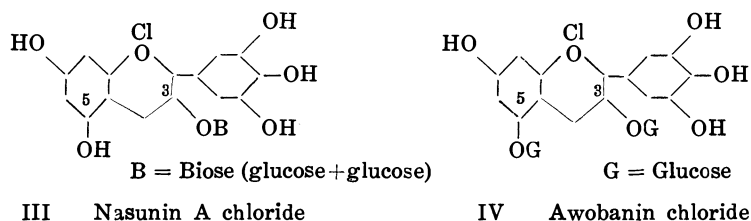
Fig. 8.

Then, as the results of careful investigations, nasunin was confirmed to be a compound of *p*-coumaric acid (1 mol) and a new glucoside which was named nasunin A by the authors was isolated as chloride, and was shown to be 3-bio-di-glucoside of delphinidin. The procedures are as follows: (1) Analytical results of nasunin chloride and picrate agreed with $C_{36}H_{37}O_{19}Cl + 10H_2O$, $C_{42}H_{49}O_{26}N_3 + 4H_2O$, respectively. (2) The one component *p*-coumaric acid in nasunin was isolated quantitatively, when nasunin chloride was carefully treated with cold dilute aqueous NaOH in H_2 . From the same glucoside, the above acidic component was also obtained by action of fused alkali. (3) On

(25) "Nasu" is the Japanese name of egg-plant.

partial hydrolysis of nasunin chloride with cold 20% aqueous HCl, nasunin A as the another component in nasunin was isolated in crystalline state as chloride (Fig. 7). The analytical result ($C_{27}H_{31}O_{17}Cl + 3H_2O$) was in agreement with diglucoside of delphinidin chloride. Decomposition of the glucoside with boiling HCl gave 1 mol of delphinidin chloride (Fig. 8) and 2 mols of glucose quantitatively.

Now one of the positions of glucose in nasunin was proved to be "3" by applying Karrer's⁽¹⁵⁾ perhydrol method to nasunin chloride. Accordingly, the two formulae as di-glucoside are possible as indicated below:



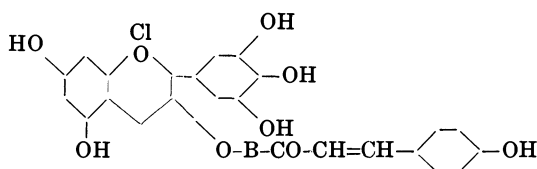
IV was obtained from "Awobana".⁽²⁶⁾ Although nasunin A in question corresponds well to the sample of IV from "Awobana" in almost every respect (absorption spectrum, appearance, and the results of analyses), there are some disagreements as follows: (1) Notwithstanding the fact that the glucoside of "Awobana" is confirmed to be 3,5-diglucoside by Karrer's perhydrol method, in the case of egg-plant, there are some experimental evidences against the glucose linkage "5". (2) Comparing the two substances in reactions in buffered solutions at 15 grades of pH⁽¹⁴⁾, "Awobana" gives slightly more pink colouration than the other. (3) Solubilities of the two, in CH_3OH , H_2O , and HCl are also somewhat different, "Awobana" being less soluble. The decomposition point was a little different from that of "Awobana".

With such experimental facts in consideration, of the two proposed formulæ, III seems more probable.

Now, as to the manner of combination of one mol of *p*-coumaric acid, it may be linked as an ester to the biase at "3". A favourable example of such a view is violanin⁽²⁷⁾ (VI). Considering this example with the previously mentioned nasunin A which seemed to be 3-bioside of delphinidin, for the formula of nasunin chloride, V may be much more probable. Further studies will be made to confirm the present consideration.

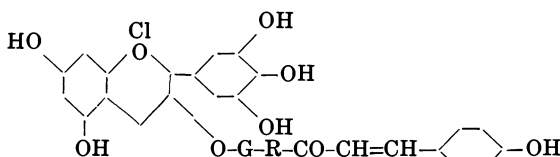
(26) See the foregoing paper.

(27) Karrer and Meuron, *Helv. Chim. Acta*, **16** (1933), 292.



V Nasunin chloride

B = Biose (glucose + glucose)



VI Violanin chloride

G = Glucose R = Rhamnose

Experimental.

Isolation of "Nasu" Pigment. The skins which were quickly peeled off from the fresh fruits were immediately immersed in 3% $\text{CH}_3\text{OH-HCl}$. Then in a few hours, the solution which turned bright red was taken out, and to this, a methyl alcohol solution of lead acetate was added drop by drop; the resulting white precipitate, lead chloride, was previously removed, then the indigo blue salt of the pigment was sucked, washed well with cold water, dried on a tile quickly, and powdered (150 fruits yielded 15 g. of the lead compound). The lead salt thus obtained was converted into a chloride solution by treating again with 2% $\text{CH}_3\text{OH-HCl}$. From the solution, the chloride of the colouring matter was precipitated upon the addition of several times its volume of ether, as the reddish purple and crystalline powder (150 fruits yielded about 1.5 g. of the chloride).

From this material dissolved in methyl alcohol, the colouring matter was precipitated by the addition of ether, this process being repeated for the purification.

Nasunin Picrate. To the solution of amorphous nasunin chloride (5 g.) in hot 1% HCl , powdered picric acid (3 g.) was added, warmed on the water bath for a few minutes, and left at room temperature for few days, then a reddish picrate gradually crystallized out (5 g.). The picrate thus obtained was dried, powdered, triturated with ether carefully to remove picric acid, and then was recrystallized twice from hot aqueous solution of picric acid saturated in cold (yield 2.5 g.). The picrate separated in beautiful red slender needles (copper-red mass in dry state, Fig. 6); for analysis, the specimen was purified several times (Found: C, 46.85; H, 4.82. Calc. for $\text{C}_{42}\text{H}_{39}\text{O}_{26}\text{N}_3 + 4\text{H}_2\text{O}$: C, 46.96; H, 4.37%). It agreed with picrate of delphinidin diglucoside combined with 1 mol of *p*-coumaric acid.

Nasunin Chloride. To the solution of the above pure picrate (2 g.) in 2% $\text{CH}_3\text{OH-HCl}$, ether was added, then reddish purple coloured nasunin chloride was isolated. The quantity of picric acid obtained from the above mother liquor (mixture of CH_3OH and ether) was determined (Found: picric acid, 0.38 g. or 38%. Calc. for $\text{C}_{42}\text{H}_{39}\text{O}_{26}\text{N}_2 + 4\text{H}_2\text{O}$: 0.38 g. or 38%).

The chloride was purified several times from $\text{CH}_3\text{OH-HCl}$ or dilute aqueous HCl ; the appearance of the chloride was similar to the picrate. (Found: C, 44.03; H, 5.7; Cl, 3.33. Calc. for $\text{C}_{36}\text{H}_{77}\text{O}_{19}\text{Cl}+10\text{H}_2\text{O}$: C, 43.73; H, 5.7; Cl, 3.31%.)

The Decomposition of Nasunin Chloride with Cold Alkali. Nasunin chloride (0.1 g.) dissolved in water (2.5 c.c.) was treated with cold 16% aqueous NaOH (5 c.c.) and kept for $2\frac{1}{2}$ hours at room temperature in H_2 . The product was acidified, extracted with ether. From the ethereal solution, *p*-coumaric acid (white crystal, m.p. 207°) was isolated quantitatively (Found: 0.015 g. or 15%. Calc. for $\text{C}_{36}\text{H}_{37}\text{O}_{19}\text{Cl}+10\text{H}_2\text{O}$: 16.6%. Found: C, 65.61; H, 4.64. Calc. for $\text{C}_9\text{H}_8\text{O}_3$: C, 65.85; H, 4.87%).

Alkali Fusion of Nasunin Chloride. Nasunin chloride (1 g.) was fused with KOH (2 g.) (compare, fusion of nasunidin). When the ethereal extract of the product was triturated with minimum quantity of water, *p*-coumaric acid was obtained from the water-insoluble part, purified from hot water; the acid was obtained in white needles, m.p. 208° (Found: C, 65.54; H, 5.15. Calc. for $\text{C}_9\text{H}_8\text{O}_3$: C, 65.85; H, 4.88%). Other phenolic products obtained from delphinidin were also found.

Decomposition of Nasunin Chloride with Acid. When nasunin chloride (0.1275 g.) was boiled with 20% aqueous HCl for three minutes, and was cooled, delphinidin chloride separated out in an amorphous state as in the acid hydrolysis of nasunin A. The filtrate obtained free from the above aglucone was extracted with ether to remove *p*-coumaric acid, and the sugar content in the acid solution was determined by Pavy's method (Found: sugar, 0.05083 g. or 39.47. Calc. for $\text{C}_{36}\text{H}_{37}\text{O}_{19}\text{Cl}+10\text{H}_2\text{O}$: 36.44%).

Nasunin A Chloride. The solution of nasunin chloride (1 g.) dissolved in cold 20% aqueous HCl was left for a few days at room temperature. A bluish purple precipitate gradually separated (0.3 g.), which was washed with 0.5% HCl , and dried; this was dissolved in a minimum quantity of 0.5% hot aqueous HCl and an equal volume of 3% $\text{CH}_3\text{OH-HCl}$ was added. On leaving for some time, nasunin A chloride crystallized out in golden lustrous fine needles (Fig. 7). It was recrystallized twice (decomposition point 197°) for analysis (Found: C, 44.90; H, 5.30; Cl, 4.45. Calc. for $\text{C}_{27}\text{H}_{31}\text{O}_{17}\text{Cl}+3\text{H}_2\text{O}$: C, 45.25; H, 5.17; Cl, 4.6%).

Hydrolysis of Nasunin A Chloride with Acid. To the purified nasunin A chloride (0.1 g.) dissolved in hot dilute aqueous HCl an equal volume of conc. HCl was added and the mixture boiled for two minutes. On cooling in contact with ice, an aglucone separated out as an apparently amorphous, nearly black precipitate. It was filtered, washed well with 20% HCl , and dried. The amorphous product was dissolved in hot dry CH_3OH , touched with dry HCl , then an aglucone crystallized out in plates with green metallic lustre (Fig. 8) and was dried in the air. It showed all the qualitative reactions of delphinidin (Found: C, 46.09; H, 4.57. Calc. for delphinidin chloride $\text{C}_{15}\text{H}_{11}\text{O}_7+3\text{H}_2\text{O}$: C, 45.91; H, 4.57%).

Micro-Zeisel estimation proved the absence of methoxyl groups in the aglucone. A delphinidin chloride hydrate of this composition has not previously been isolated, but it was already observed that the quantity of water of crystallization in such a substance depends on the conditions of crystallization.

Sugar. (1) *Estimation.* The above filtrate removed from the aglucone was neutralized with alkali, dried on the water bath, then the sugar was determined by Pavy's method as previously mentioned (Found: sugar, 0.0502 g. or 50.2%. Calc. for $\text{C}_{27}\text{H}_{31}\text{O}_{17}\text{Cl}+3\text{H}_2\text{O}$: 50.28%).

(2) *Osazone*. Glucosazone from the resulting acid solution obtained upon decomposition of nasunin A chloride was formed in the similar method as in the case of kuromamin chloride.

(3) *The position of sugar*. Nasunin A chloride (0.3 g.) was treated with 30% H_2O_2 as in the case of kuromamin, and glucosazone from position "3" was obtained in a considerable quantity, m.p. 205° . The filtrate from the above osazone was treated as in the case of shisonin, however, osazone from the position "5" was not found distinctly.

Alkali Fusion of Nasunidin (Aglucone of Nasunin). Nasunidin chloride (0.8 g.) was fused with NaOH (2.5 g.) and a small quantity of water at 203° . After cooling, the product was acidified with HCl, extracted with ether, and was evaporated. From the ethereal residue dissolved in water, a yellowish brown lead salt was precipitated by addition of lead acetate. The lead salt was filtered (filtrate A), washed with water, decomposed with dilute H_2SO_4 , and extracted with ether. The ethereal residue dissolved in small quantity of CH_3OH was methylated with $(CH_3)_2SO_4$ and 50% aqueous KOH in H_2 ; the reaction product was heated on the water bath to decompose the ester and to evaporate CH_3OH , then acidified, extracted with ether, evaporated, and the residue was again extracted with hot benzene. The benzene-soluble part was crystallized from hot water, then gallic acid trimethyl ether (m.p. 165° , both alone and after admixture with the authentic specimen) was isolated. From filtrate A treated with dilute H_2SO_4 , phloroglucinol was isolated (m.p. 208° , both alone and after admixture with the authentic specimen). No *p*-coumaric acid was found in this decomposition.

Direct Comparison of Nasunin A and Awobanin A Chloride. Both specimens were recrystallized in the same way with a different result as follows: The compound was dissolved in a minimum quantity of 0.5% hot aqueous HCl and an equal volume of 3% $C_2H_5OH-HCl$ was added. After cooling, nasunin A chloride crystallized out in fine needles with golden lustre, while the other separated in small hexagonal plates with golden lustre.

The colour reactions of the above two specimens in buffered solutions were compared. The colours given by the two pigments were almost identical except that nasunin A became blue at a lower pH than awobanin A. (1) Rose-pink, fading rapidly; (3) (5) bluer, fading rapidly; (4) bluish-pink, fading to colourless rapidly; (9) (10) blue-violet; (11) violet; (13) violet-blue; (15) deep blue.

Both specimens were very sparingly soluble (or insoluble) in cold water, alcohol, and dilute aqueous HCl but readily in hot dilute aqueous HCl. All the ordinary reactions, the colours with Na_2CO_3 (a bright pure blue) and alcoholic $FeCl_3$ (violet-blue) were observed identical.

In buffered solution the colour reactions of both specimens, namely the aglucones from nasunin and awobanin chlorides, gave quite identical results agreeing with those of delphinidin chloride in the literature. (1) red, pink in 80 seconds; (2) violet red, colourless in 30 seconds; (3) permanganate, colourless in 30 seconds; (4) similar to (3); (5) violet; (6) deep violet red; (9) blue violet; (10) similar to (9); (11) blue violet; (13) blue violet dichroic, pale yellow in $1\frac{1}{2}$ hours; (14) indigo blue, pale yellowish gray in $1\frac{1}{2}$ hours; (15) (16) similar to (14).

The authors desire to thank Professor R. Majima for the kindest advice throughout this work, the Imperial Academy for a grant, and Miss Sumi Matsumoto for a part of micro-analyses.

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Physical and Chemical Research.*

ÜBER EIN UMLAGERUNGSPRODUKT DES FUKUGETINS (FUKUGENETIN).

Von Masuo MURAKAMI und Tôsi IRIE.

Eingegangen am 19. November 1935. Ausgegeben am 28. März 1936.

Fukugetin ist ein Farbstoff, der in der Rinde von *Garcinia spicata* oder *Xanthocymus ovalifolia* aufgefunden wird. Wir⁽¹⁾ untersuchten seit längerem die chemische Konstitution (I) dieses Farbstoffes und konnten sie mit ziemlicher Sicherheit festlegen. Da Fukugetin in seinem Molekül eine aktive Gruppe, $-\text{COCH}-\text{CH}-$ enthält, wird es durch Alkalien oder Säuren



leicht isomerisiert. Fukugenetin ist eines von seinen Isomeren. Über die Natur dieses Isomers stellten wir einige Untersuchungen an.

Beim Erhitzen des Fukugetins mit 50%iger Kalilauge erhielt J. Shinoda⁽²⁾ zuerst Fukugenetin und stellte einige Derivate her. Für diese Isomerisierung ist Erhitzen mit 30%iger Kalilauge geeignet. Wir gewannen dabei in ziemlich guter Ausbeute ein saures Produkt, welches Roh-Fukugenetin genannt wurde und aus zwei Isomeren besteht, die aber nicht direkt voneinander getrennt werden konnten. Bei seinem Methylderivat konnte aber die zwei Isomeren gefasst werden. Das eine Produkt (A) schmilzt bei 208° und wird durch Methylierung⁽³⁾ des reinen Fukugenetins auch gewonnen. Das andere (B) vom Schmp. 199–200° wird auch bei Methylierung aus dem später erwähnten Anhydro-isofukugenetin oder Triacetyl-anhydro-isofukugenetin erhalten. Nach der Zeiselschen Methoxylbestimmung scheint dieses Isomer 5 Methoxylgruppen zu enthalten, während aber die Imidomethylbestimmung die Existenz einer weiteren Methoxylgruppe zeigt. Wir stellten andererseits ein Methylderivat vom Schmp. 178.5–9° her, dessen Zeiselsche Bestimmung zu dem für 5 Methoxylgruppen berechneten Wert führte. Dieses Pentamethylderivat hat einen aktiven Wasserstoff und geht bei Methylierung in das obige Isomer B unter Verschwinden des aktiven Wasserstoffes über. Aus diesen Gründen müssen 6 Methoxylgruppen im B-Isomer⁽⁴⁾ vorhanden sein. Beim Verseifen mit 10%igem alkoholischem Kali liefert es Tetramethylderivat vom Schmp. 258–260°, das eine Carbonsäure ist, also muss ein Methylester der Carbonsäure vorliegen.

(1) M. Murakami, *Proc. Imp. Acad. Japan*, **8** (1932), 500. M. Murakami und T. Irie, *ibid.*, **10** (1934), 568.

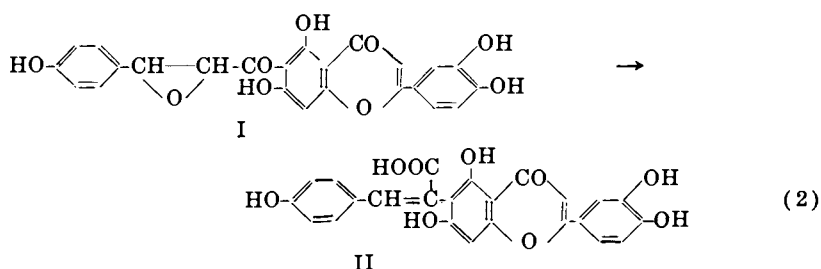
(2) (3) J. Shinoda, *J. Pharm. Soc. Japan*, **52** (1932), 1009.

(4) J. Shinoda gab das Isomer als Pentamethylderivat an.

In der zweiten Mitteilung⁽⁵⁾ berichteten wir die Umlagerung des Pentamethylfukugetins mit 5%igem alkoholischem Kali und erklärten sie mit der Reaktion (1).



Während die schwache Kalilauge zur Bildung der enolischen Hydroxylgruppe führt, verursacht die starke die Bildung der Carboxylgruppe. Da diese Umlagerungen den Keto-oxidoumlagerungen⁽⁶⁾ sehr ähnlich sind, erklären wir sie mit Reaktion (2).

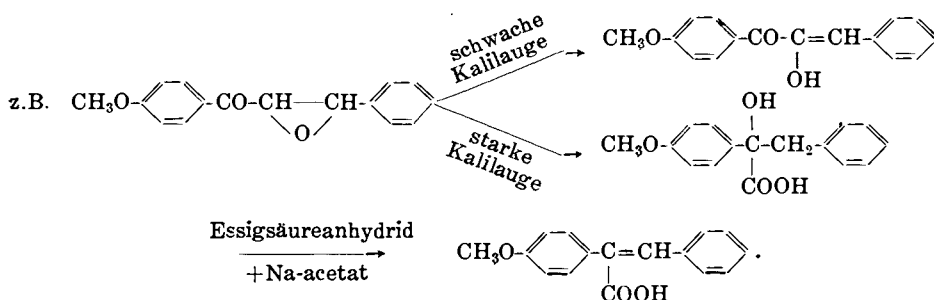


Mit Konstitution II lassen sich die obigen Eigenschaften des B-Isomers deutlich erklären. Methylderivat A hat eine mit B gleiche Molekularformel, also ist es wahrscheinlich eine Stereoisomer von B in Bezug auf die aufs neue gebildete Doppelbindung. Das rohe Fukugenetin enthält daher zweifellos neben dem von J. Shinoda isolierten Fukugenetin ein Isomer (Is-fukugenetin), welcher das Methylderivat B gibt.

Isofukugenetin kann nicht aus dem rohen Fukugenetin isoliert werden, aber beim Erhitzen mit verd. Schwefelsäure verwandelt es sich in Anhydro-

(5) M. Murakami und T. Irie, *loc. cit.*

(6) O. Widman, *Ber.*, **49** (1916), 477. Jörlander, *Ber.*, **50** (1917), 406, 1458. M. Murakami und T. Irie, *loc. cit.*



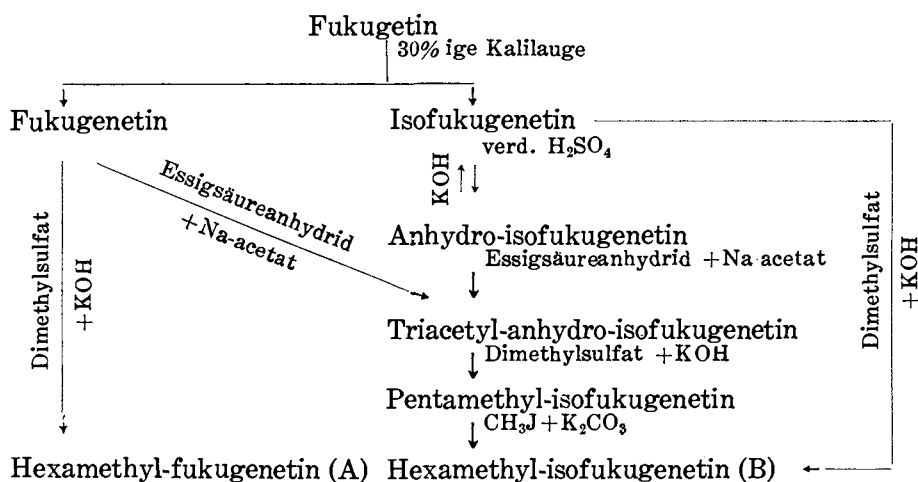
isofukugenetin⁽⁷⁾, aus dem beim Behandeln mit verd. Kalilauge wieder Isofukugenetin rückgebildet werden kann, während Fukugenetin unverändert bleibt.

Da das Anhydro-isofukugenetin schon die saure Natur verliert, und bei der Acetylierung merkwürdigerweise nur Triacetyl-anhydro-isofukugenetin liefert, muss es noch dazu einen aktiven Wasserstoff unabhängig von der Laktonbildung verlieren.

Fukugenetin wird durch Erhitzen mit Essigsäureanhydrid und Natriumacetat in Anhydro-isofukugenetin verändert, während aber aus der Isofukugenetinreihe eine Rückveränderung bisher nicht möglich war.

In Tabelle 1 werden diese Veränderungen schematisch dargestellt.

Tabelle 1.



Versuche.

Roh-Fukugenetin. 5 g. Fukugetin wurden mit 50 g. 30%iger Kalilauge im Wasserstoffstrom 30 Minuten lang gekocht. Nach dem Ansäuern mit Salzsäure wurden die Produkte in Äther aufgenommen und die ätherische Lösung mit wässriger Bicarbonatlösung geschüttelt. Aus der ätherischen Lösung wurde Fukugetin in kleiner Menge (0.2 g.) zurückgewonnen. Sein Pentamethylderivat schmolz bei 203–4°. Aus der Bicarbonatlösung wurde nach dem Ansäuern mit Salzsäure das rohe Fukugenetin erhalten. Ausbeute 2.1 g.

Acetylierung des rohen Fukugenetins. (Triacetyl-anhydro-isofukugenetin). 2 g. rohes Fukugenetin wurden mit 20 c.c. Essigsäureanhydrid und 3 g. Natriumacetat 2 Stunden lang gekocht. Dabei schieden sich gelbe Kristalle aus, die allmählich zu einem Kristall-

(7) Das Anhydro-fukugenetin von J. Shinoda.

brei erstarrten. Das Produkt wurde filtriert, zuerst mit Alkohol, dann mit Wasser gewaschen und aus Eisessig umkristallisiert. Schmp. 267°. Ausbeute 2 g.⁽⁸⁾ Die alkoholische Lösung zeigte mit Eisenchlorid keine Färbung. (Gefunden: Acetyl, 23.13, 23.96, 23.98. Berechnet für $C_{24}H_{11}O_5(OCOCH_3)_3$: 23.28%. Gefunden: C, 64.89; H, 3.87. Berechnet für $C_{30}H_{20}O_{11}$: C, 64.73; H, 3.62%.)

Die Substanz wurde auch aus Anhydro-isofukugenetin gewonnen.

Darstellung des Anhydro-isofukugenetins aus rohem Fukugenetin. 3.5 g. rohes Fukugenetin wurden in 35 c.c. Äthanol gelöst, mit 20 c.c. verd. Schwefelsäure versetzt und 3 Stunden lang gekocht. Das enthaltene Isofukugenetin wurden dabei als Anhydro-isofukugenetin ausgeschieden. Es kristallisierte aus Pyridin in orangegelben Nadeln, die bei 380° noch nicht schmolzen. (Gefunden: C, 66.41, 66.67; H, 3.72, 3.54. Berechnet für $C_{24}H_{14}O_8$: C, 66.96; H, 3.28%.)

Isofukugenetin aus Anhydro-isofukugenetin. Wenn man eine rote Lösung von 0.1 g. Anhydro-isofukugenetin mit 5 c.c. 10%iger Kalilauge bei gewöhnlicher Temperatur eine Weile stehen lässt, so schlägt die Farbe in gelb um. Beim Einleiten eines CO_2 -Stroms schied sich aus der gelben Lösung ein gelber Niederschlag ab, der das Kaliumsalz der Carbonsäure war. Nach Ansäuern und Umkristallisieren wurde es in gelben, nadelförmigen Kristallen erhalten, die bei 380° noch nicht schmolzen. (Gefunden: C, 63.82; H, 3.77. Berechnet für $C_{24}H_{16}O_9$: C, 64.27; H, 3.60%.)

Methylierung des rohen Fukugenetins. 2.2 g. rohes Fukugenetin wurden in 40 c.c. Methanol und 40 g. Dimethylsulfat gelöst und allmählich mit Kalilauge (32 g. in 64 c.c. Wasser) versetzt. Das rohe Methylderivat, das aus zwei Isomeren besteht, wurde dabei ausgeschieden. Seine alkoholische Lösung zeigte mit Eisenchlorid keine Färbung. Die Trennung der beiden Isomeren wird in Tabelle 2 entworfen.

Kristalle A, B, und C waren identisch, und wurden auch bei der Methylierung des Fukugenetins erhalten (Hexamethyl-fukugenetin). (Gefunden: C, 67.93, 67.52; H, 5.64, 5.68. Berechnet für $C_{30}H_{28}O_9$: C, 67.64; H, 5.33%.)

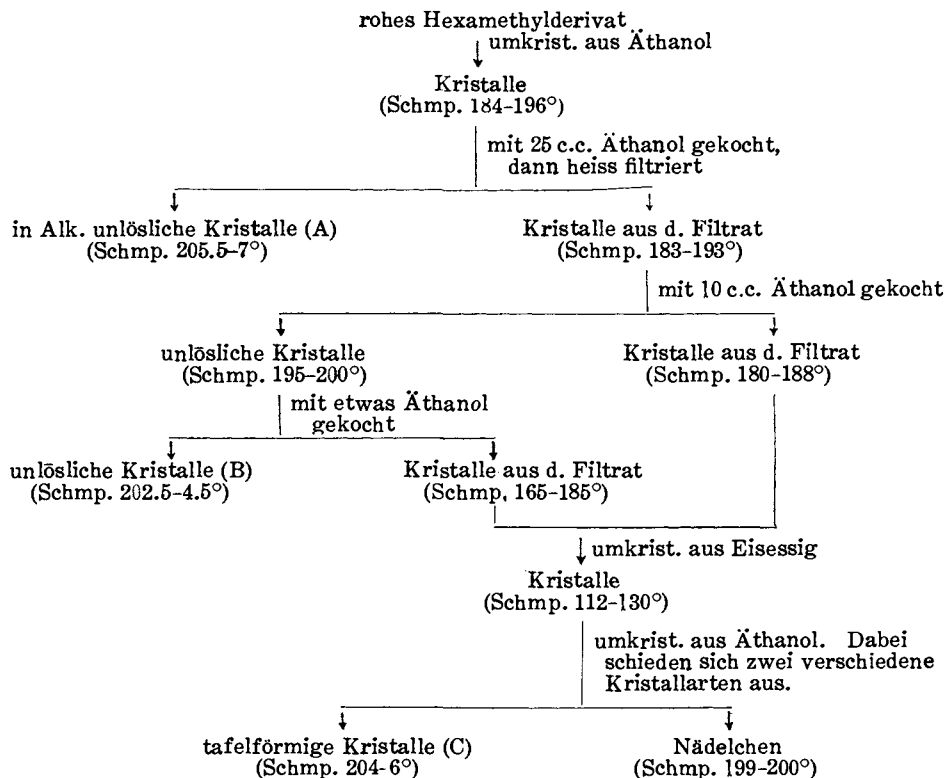
Nadelförmige Kristalle vom Schmp. 199–200° wurden auch bei der Methylierung des Anhydro-isofukugenetins und des Triacetyl-anhydro-isofukugenetins erhalten (Hexamethyl-isofukugenetin). (Gefunden: C, 67.40, 67.70; H, 5.60, 5.63. Berechnet für $C_{30}H_{28}O_9$: C, 67.64; H, 5.33%. Gefunden als gesamte Werte bei Zeiselsche Methode und Imidomethyl-Bestimmung: OCH_3 , 33.85. Berechnet für $C_{24}H_{10}O_3(OCH_3)_6$: 34.9%.)

Pentamethyl-isofukugenetin aus Triacetyl-anhydro-isofukugenetin. Die Methylierungsmethode war die gleiche wie bei rohem Fukugenetin. Wenn die Kalilauge in der Kälte sehr langsam hinzugefügt wurde, so wurde Hexamethyl-isofukugenetin (Schmp. 198°) gewonnen. Wenn die Kalilauge aber in der Wärme hinzugefügt wurde, so wurde Pentamethyl-isofukugenetin erhalten, das nach dem Umlösen aus Äthanol oder Essigsäureanhydrid bei 178.5–179° schmolz. (Gefunden: OCH_3 , 30.86. Berechnet für $C_{24}H_{11}O_4(OCH_3)_5$: 29.94%. Gefunden für 0.2042 g. Subst.: CH_4 , 8.0 c.c. Berechnet für $C_{24}H_{10}O_3(OCH_3)_5OH$: CH_4 , 8.8 c.c. Gefunden: C, 67.03; H, 5.26. Berechnet für $C_{29}H_{26}O_9$: C, 67.16; H, 5.06%.)

Bei der Methylierung nach der Claisenschen Methode lieferte die Substanz Hexamethyl-isofukugenetin.

(8) Da sich alles Fukugenetin, das in dem rohen Fukugenetin enthalten ist, unter den gleichen Bedingung in Isofukugenetin umwandelte, wurde solch eine gute Ausbeute erzielt.

Tabelle 2.



ÜBER DIE STEREOISOMERIE DES 6-METHYL-DEKAHYDRO-CHINOLINS. (Vorläufige Mitteilung.)

Von Shin-ichiro FUJISE und Mitsuo IWAKIRI.

Eingegangen am 20. November 1935. Ausgegeben am 28. März 1936.

Die Stereochemie der hydrierten hetero-bicyclischen Verbindungen hat, seit der Entdeckung von *cis*- und *trans*-Dekahydrochinolin bzw. -isochinolin, beträchtliche Fortschritte gemacht⁽¹⁾. H. Finger und W. Breiwieser⁽²⁾ stellten 6-Methyl-dekahydrochinolin durch Reduktion von α -Cyan-6-methyl-chinolin mittels Natrium und Alkohol dar. Sie erhielten eine perhydrierte Base vom Schmp. 44°. Später gewann S. Yamaguchi⁽³⁾ 6-Methyl-dekahydrochinolin von Schmp. 67° durch Reduktion von Benz-tetrahydrochinolin mit Natrium und Alkohol.

Die kristallisierten 6-Methyl-dekahydrochinoline, die die obigen Forscher erhalten hatten, zeigten verschiedene Schmelzpunkte. Im allgemein müssen monosubstituierte Dekahydrochinoline modellgemäss in je vier Racemformen auftreten; im Falle des 8-Oxy-dekahydrochinolins hat der eine von uns (F.) drei Racemformen isoliert⁽⁴⁾. Nun konnte man im Zweifel sein, ob bei den zwei oben beschriebenen 6-Methyl-dekahydrochinolinen der Fall einer Stereoisomerie vorlagte oder die niedrig schmelzenden Kristalle von einer unreinigten Base herrühren können; da die stereochemische Untersuchung des 6-Methyl-dekahydrochinolins noch nicht ausgeführt ist, möchten die Verfasser hier die Resultate ihrer Versuche berichten.

Durch Hydrierung von 6-Methyl-chinolin in Eisessig bei 50° mit Platin-oxyd und Wasserstoff, gewannen wir die vollständig hydrierte Base in fast quantitativer Ausbeute. Sie siedet bei 213–215° und das Destillat erstarrt bei guter Kühlung zu etwa dreisiebentel. Die Kristalle zeigten nach Umlösen in Petroläther einen Schmp. von 68–69°. Die flüssige Base wurde mit Bromwasserstoff-salz gereinigt und siedet nach Regeneration der freien Base bei 212–212.5°. Ganz allgemein ergaben der feste bzw. der flüssige Anteil zwei Reihen von Derivaten und die physikalischen Konstanten zeigten, dass die flüssige Base wie im Falle des Dekahydrochinolins, die *cis*-, feste die *trans*-Form sein muss.

(1) G. Wittig, „Stereochemie,“ S. 148 (Leipzig, 1930). S. Fujise, *Sci. Rep. Phys. Chem. Research, Japan*, **8** (1928), 161, 185; **9** (1929), 91.

(2) *J. prakt. Chem.*, **79** (1909), 445.

(3) *J. Pharm. Soc. Japan*, **43** (1923), 53.

(4) Vgl. dazu Fussnot (1).

	Siedp.(°C.)	d_4^{74}	n_D^{74}	EM_D
<i>trans</i> -6-Methyl-dekahydrochinolin (fest)	211.5-212	0.8694	1.46005	+0.69
<i>cis</i> -6-Methyl-dekahydrochinolin (flüssig)	212-212.5	0.8843	1.46514	+0.33

Schmelzpunkte der Derivate (°C.).

	Fest	Flüssig
Hydrochlorid	265	263-264
Hydrobromid	244-245	252-253
Goldchloriddoppelsalz	117-119	152-153
Platinchloriddoppelsalz	171.5-172.5	230 (zersetz.)
<i>p</i> -Nitrobenzoylverbindung	124.5-125	138-139
Benzoylverbindung	95-99	nicht kristallisiert

Das feste *trans*-6-Methyl-dekahydrochinolin wurde mit *d*-Bromcampher-sulfonsäure in die optisch aktiven Formen gespalten und zwar erhielten wir *d*-Form in reinem Zustand; sie schmolz bei 92-93°. $[\alpha]_D^{14.5} = +4.8^\circ$ (in Alkohol). Der Drehungswert ist nahezu gleich mit dem des *trans-d*-Dekahydrochinolins.

Das perhydrierte 6-Methyl-chinolin von Schmp. 44°, das H. Finger und W. Breiwieser isolierten, dürfte nach unserer Meinung unreine *trans*-Base gewesen sein.

Auf die experimentellen Einzelheiten soll später eingegangen werden.

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ÜBER DIE FARBSTOFFE IM HOLZTEILE DES "HINOKI"- BAUMES. I. HINOKITIN UND HINOKITIOL.

(Vorläufige Mitteilung.)

Von Tetsuo NOZOE.

Eingegangen am 20. November 1935. Ausgegeben am 28. März 1936.

Über die ätherischen Öle im Holze des "Hinoki"-baumes (*Chamaecyparis obtusa*, Sieb. et Zucc.), einem der wichtigsten Baumaterialien in Japan, insbesondere in Formosa, wurden bisher ziemlich eingehende Untersuchungen durchgeführt, während über die in demselben Holze enthaltenen Farbstoffe kaum Berichte vorliegen. Hirao⁽¹⁾ isolierte aus dem sauren Teile des ätherischen Öles des Formosanischen "Hinoki"-holzes eine ungesättigte Fettsäure, Chamaensäure von der Formel $C_{10}H_{16}O_2$. Bei der Oxydation dieser Säure mit Ferrichlorid erhielt er Hinokitin, einen roten Farbstoff vom Schmelzpunkt $250-1^\circ$, für den die Molekularformel $C_{30}H_{34}O_{10}$ angenommen wurde. Er schrieb übrigens die Farbe des "Hinoki"-öles, so wie des "Hinoki"-holzes diesem Farbstoff zu, wofür aber die Bestätigung noch gänzlich fehlt.

Früher als Hirao isolierten Tsuchihashi und Tasaki⁽²⁾ aus dem Formosanischen "Hinoki"-öl eine Säure $C_9H_{16}O_2$ und ein Phenol $C_{10}H_{14}O_2$. Da die physikalischen Konstanten dieser Säure ganz verschieden von denen der Chamaensäure sind, untersuchten Kafuku und der Verfasser dieser Arbeit⁽³⁾ den sauren Teil des ätherischen Öles im Holze, sowie in den Blättern und Wurzeln des "Hinoki"-baumes, um über diese Diskrepanz der physikalischen Konstanten sichere Daten zu gewinnen. Unsere Ergebnisse stimmten aber im wesentlichen mit den von Tsuchihashi und Tasaki⁽²⁾ überein, und liessen überdies erkennen, dass die so genannte Chamaensäure und die von uns erhaltene phenolische Substanz die gleichen physikalischen Konstanten miteinander gemein haben.

Der nach der üblichen Weise abgetrennte und anfangs als rein angenommene saure und phenolische Teil zeigt jeweils eine identische Farbenreaktion mit Ferrichlorid, aber nach den näheren Untersuchungen hat die Säure selbst nichts mit der betreffenden Farbenreaktion zu tun, sondern nur die phenolische Substanz färbt sich unter Bildung des Hinokitins rot.

(1) *J. Chem. Soc. Japan*, **47** (1926), 666, 743.

(2) *Report of Govern. Research Inst. Formosa*, **1** (1920).

(3) Dieses Bulletin, **6** (1931), 40. Zum Teil noch unpubliziert.

Der unter Bildung von Hinokitin völlig vom phenolischen abgetrennte saure Teil weist in seinen physikalischen Konstanten keinen grossen Unterschied von demselben vor der Behandlung auf, zeigt aber im Gegensatz zu dem letzteren die Farbenreaktion nicht, und die eingehenden Untersuchungen lassen erkennen, dass die Säure 1-Rhodinsäure $C_{10}H_{18}O_2$ ist.

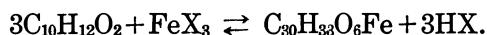
Die Hauptfraktion des phenolischen Teiles entspricht nach Elementaranalyse und Titration einem einwertigen Phenol von der Formel $C_{10}H_{12}O_2$ oder $C_{10}H_{14}O_2$. Um die Funktion des zweiten Sauerstoffatoms des Phenols zu erklären, wurde die Substanz mit Alkohol- bzw. Keton-reagenzien behandelt. Sie reagierte sämtlich damit, aber die Reaktionsprodukte konnten nie kristallinisch erhalten werden. Die phenolische Substanz enthält auch keine Methoxylgruppe.

Wenn man die phenolische Substanz in der Anwesenheit von Natriumacetat mit einer Ferrichloridlösung behandelt, so kann man sehr leicht in guter Ausbeute Kristalle des oben erwähnten Hinokitins darstellen. Da es von grossen Vorteil schien, zur Aufklärung der Konstitution jener phenolischen Substanz das Hinokitin Prüfung zu unterziehen, wurde zuerst eine genauere Untersuchung darüber in Angriff genommen.

Hinokitin löst sich in Wasser, Pyridin, heissem Aceton, Chloroform und Benzol und ist in sonstigen gewöhnlichen Lösungsmitteln schwer löslich. Es bildet prachtvolle dunkelrote Kristalle vom Schmelzpunkt 251° , sublimiert im Hochvakuum schönen Nadeln und lässt sich allem Anschein nach fast unzersetzt destillieren. Selbst in einer sehr verdünnten Lösung ist es ziemlich intensiv rot gefärbt und hat zwei Absorptionsmaxima bei 584 und $540\text{ m}\mu$ im sichtbaren Gebiet des Spektrums. Nach der Analyse ist seiner Formel nicht $C_{30}H_{34}O_{10}$, sondern $C_{30}H_{33}O_6Fe$, d.h. es enthält entgegen allen Annahmen Eisen.

Wenn man aus dem Hinokitin das Eisen entfernt, so erhält man wieder ein flüchtiges Öl, das der Formel $C_{10}H_{12}O_2$ entspricht und in seinen physikalischen, aber auch übrigen Eigenschaften mit der ursprünglichen phenolischen Substanz ziemlich gut übereinstimmt. Beim Behandeln dieses Öles mit Ferrichlorid erhält man quantitativ wieder das Hinokitin.

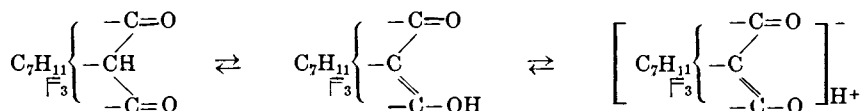
Das auf diese Weise mit dem Hinokitin in Beziehung stehende Öl wurde Hinokitiol genannt. Das Hinokitin ist also kein Oxydationsprodukt des Hinokitiols, sondern ein inneres Komplexsalz, Eisen (III)-Hinokitiolat. Die von uns abgetrennte und zuerst als rein angenommene phenolische Substanz war ebenso wie die Chamaensäure Hiraos⁽¹⁾ etwas 1-Rhodinsäure enthaltendes Hinokitiol. Die Beziehung zwischen dem Hinokitiol und Hinokitin ist also folgendermassen anzunehmen:



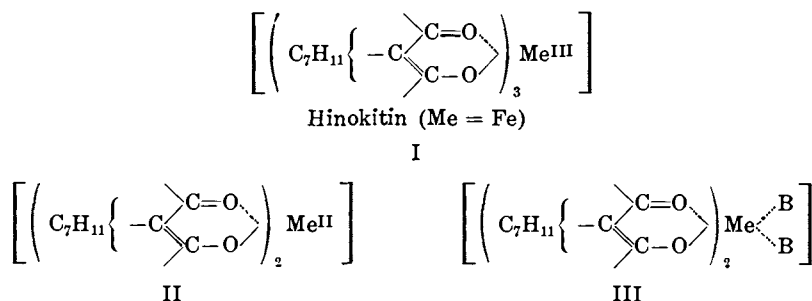
Über die Konstitution des über Hinokitin rein dargestellten Hinokitiols ist die Untersuchung noch im Gange. Mittels Alkohol-bzw. Keton-reagenzien erhaltene Derivate des Hinokitiols sind noch nicht kristallinisch erhalten worden. Immerhin konnten innere Komplexsalze desselben mit mehreren Metallen in gut kristallisiertem Zustand leicht hergestellt werden, worunter alle ausser denen der Alkalimetalle in Wasser unlösliche, in organischen Lösungsmitteln lösliche bzw. leicht lösliche neutrale Substanzen sind und allgemeine Eigenschaften eines neutralen inneren Komplexsalzes zeigen. Die inneren Komplexsalze des Hinokitiols mit zwei wertige Metallen bilden im allgemeinen mit zwei Mol organischen Basen kristallinische Verbindungen von konstantem Schmelzpunkt. Einige wichtige Metallkomplexsalze des Hinokitiols seien im folgenden angegeben :

Metalle	Schmp.	Pyridin-deriv.	Chinolin-deriv.	Anilin-deriv.
Cr ⁺⁺⁺	230°	—	—	—
Fe ⁺⁺⁺	251°	—	—	—
Co ⁺⁺⁺	208°	—	—	—
Cu ⁺⁺	177°	107°	96°	89°
Ni ⁺⁺	242°	210°	—	162°
Co ⁺⁺	210°	209°	—	113°
Mn ⁺⁺	>300°	>300°	—	—
Cd ⁺⁺	>300°	>300°	—	—
Zn ⁺⁺	—	164°	—	—
Mg ⁺⁺	>300°	>300°	—	—

Das Hinokitiol absorbiert bei katalytischer Reduktion 3-4 Mol Wasserstoff, die so erhaltene Substanz bildet im Gegenteil zum Hinokitiol nicht mehr innere Metallkomplexsalze, woraus folgt, dass das Hinokitiol eine ungesättigte 1,2- oder 1,3-Oxyoxo- oder Dioxoverbindung sein sollte. Die vergleichenden Studien zeigten aber, dass das Hinokitiol ein zwei Doppelbindungen enthaltendes monocyclisches 1,3-Diketon – wahrscheinlich mit einem Fünfring – ist, und folgendes Gleichgewicht vorliegen dürfte :



Zusammenfassend haben also Hinokitin und Metall-hinokitiol-Komplexsalze im allgemeinen folgende Formel I bzw. II und demnach die Verbindungen der Komplexsalze mit organischen Basen Formel III :



Der Verfasser hat festgestellt, dass die rote Färbung des "Hinoki"-öles hauptsächlich dem Hinokitin zuzuschreiben ist; es ist aber gut möglich, dass das im "Hinoki"-öle gefundene Hinokitin aus dem im Öle vorkommenden Hinokitiol a posteriori, also z.B. aus dem Hinokitiol und dem Eisen des gebrauchten eisernen Gefäßes, gebildet wurde. Da aber das Hinokitiol, eine mit Metallen ausserordentlich leicht Komplexsalze bildende Substanz, im "Hinoki"-holze vorkommt, ist es ganz leicht möglich, dass Metallhinokitiolate wie Hinokitin auch als eigentliche Farbstoffe des "Hinoki"-holzes selbst vorliegen. In dieser Hinsicht sind jetzt Versuche, die Farbstoffe des Hinokiholzes direkt zu trennen und rein zu erhalten, im Gange.

Es scheint noch nicht bekannt zu sein, dass eine fast farblose Substanz wie das Hinokitiol mit einem Metall unter Bildung eines Komplexsalzes schon als Farbstoff in der Natur vorkommt; das Hinokitin dürfte also zu einem neuen Typus der natürlichen Farbstoffe gehören.

Der Verfasser hat noch mikroskopisch festgestellt, dass auch im ätherischen Öle des "Benihi"-baumes (*Chamaecyparis formosensis*, Matsum.) das Hinokitiol vorkommt, und ist mit Rücksicht darauf, dass Hinokitiol, Hinokitin und mit ihnen verwandte Verbindungen in der Natur weitverbreitet sein dürften, augenblicklich mit Arbeiten weitere derartige Verbindungen aufzufinden beschäftigt.

Herren Prof. K. Kafuku ist der Verfasser für seine Leitung und den Herren Prof. R. Majima von der Universität zu Osaka und Prof. Y. Nakatsuka für die ihm gewährten Erleichterungen bei dieser Arbeit zu herzlichem Dank verpflichtet. Der Kaiserlichen Akademie spricht er auch seinen Dank für die finanzielle Unterstützung dieser Arbeit aus.

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ÜBER DIE LACCASE DES JAPANISCHEN LACKS. II. ÜBER
DIE REAGIERBARKEIT DER LACCASE GEGEN
POLYPHENOLE UND DIAMINE.⁽¹⁾

Von Kunihiko SUMINOKURA.

Eingegangen am 26. November 1935. Ausgegeben am 28. März 1936.

Von den Polyphenole und Diamine oxydieren durch molekularen Sauerstoff bei Anwesenheit von Laccase nur diejenigen leicht, bei welchen die OH- oder NH₂-Gruppen in Ortho- oder Para-Stellung stehen, während dies die Meta-Verbindungen nur schwer tun, was früher bereits Bertrand⁽²⁾ mitgeteilt hat und später von verschiedenen Autoren als richtig bestätigt wurde.

Ich behandelte 48 Phenole und Amine mit der Laccase des japanischen Lacks und Sauerstoffgas. Die bei meinen Versuchen gewonnenen Resultate finden sich in Tabelle 1. Am leichtesten oxydieren bei Anwesenheit der Laccase die *p*-Phenylendiamine (Dimethyl-*p*-phenylendiamin, *p*-Phenylendiamin), dann kommen die *o*-Dioxyphenole (Urushiol, Oxyhydrochinon, Brenzcatechin), die *o*-Phenylendiamine (*o*-Phenylendiamin, Adrenalin, Diamidophenol) und die Benzole mit einer Hydroxyl- plus einer Methoxyl-Gruppe. Die Meta-Verbindungen (Resorcin, Orcin, Phloroglucin, *m*-Phenylendiamin), die Benzole mit zwei Äthoxylgruppen (Hydrochinondiäthyläther) und die Benzole mit einer Hydroxyl- plus verschiedenen anderen Gruppen (Tyrosin, Tyramin, Thymol, Salicylaldehyd) oxydieren nicht. Obgleich Alizarin, Protocatechusäure und Dioxyphenylalanin Ortho-Dihydroxyl besitzen, oxydieren diese Verbindungen doch nicht. Hydrourushiol oxydiert nur schwer. Ebenso oxydieren das Methylenoxyd des Safrols und die aliphatischen Diamine gar nicht. Merkwürdig sind die Kresole; die, obgleich sie nur eine Hydroxyl-Gruppe besitzen, oxydieren sie doch etwas bei Anwesenheit der Laccase. Hier auch oxydieren nur Ortho- und Meta-Kresole, aber die Para-Verbindung nicht.

(1) I. Mitteilung, *Biochem. Z.*, **224** (1930), 292-321.

(2) G. Bertrand, *Compt. rend.*, **122** (1896), 1132.

Tabelle 1.

Substanz	Konstitution	Oxyd. mit Laccase
Ortho-Verbindungen		
Brenzcatechin	$\text{C}_6\text{H}_4 \begin{cases} \text{OH (1)} \\ \text{OH (2)} \end{cases}$	+
Pyrogallol	$\text{C}_6\text{H}_3 \begin{cases} \text{OH (1)} \\ \text{OH (2)} \\ \text{OH (3)} \end{cases}$	+
Urushiol	$\text{C}_6\text{H}_3 \begin{cases} \text{OH (1)} \\ \text{OH (2)} \\ \text{C}_{15}\text{H}_{27} \text{ (3)} \end{cases}$	+
Hydrourushiol	$\text{C}_6\text{H}_3 \begin{cases} \text{OH (1)} \\ \text{OH (2)} \\ \text{C}_{15}\text{H}_{31} \text{ (3)} \end{cases}$	+ (wenig)
Guajacol	$\text{C}_6\text{H}_4 \begin{cases} \text{OH (1)} \\ \text{OCH}_3 \text{ (2)} \end{cases}$	+
Eugenol	$\text{C}_6\text{H}_3 \begin{cases} \text{OH (1)} \\ \text{OCH}_3 \text{ (2)} \\ \text{CH}_2\text{CH:CH}_2 \text{ (4)} \end{cases}$	+
Adrenalin	$\text{C}_6\text{H}_3 \begin{cases} \text{CH(OH)CH}_2\text{NHCH}_3 \text{ (1)} \\ \text{OH (3)} \\ \text{OH (4)} \end{cases}$	+
o-Kresol	$\text{C}_6\text{H}_4 \begin{cases} \text{OH (1)} \\ \text{CH}_3 \text{ (2)} \end{cases}$	+ (wenig)
o-Phenylendiamin	$\text{C}_6\text{H}_4 \begin{cases} \text{NH}_2 \text{ (1)} \\ \text{NH}_2 \text{ (2)} \end{cases}$	+
3-Methoxy-4-oxy-phenyläthyl-methyl-ke-ton		+
„ -octenyl-ke-ton		+
„ -heptenyl-ke-ton		+ (wenig)
„ -pentadecyl-ke-ton		—
„ -nonyl-ke-ton		—
„ -octyl-ke-ton		—
„ -heptyl-ke-ton		—
„ -hexyl-ke-ton		—
Protocatechusäure	$\text{C}_6\text{H}_3 \begin{cases} \text{COOH (1)} \\ \text{OH (3)} \\ \text{OH (4)} \end{cases}$	—

Tabelle 1. (Fortsetzung.)

Substanz	Konstitution	Oxyd. mit Laccase
Dioxyphenylalanin	$\begin{array}{c} \text{CH}_2\text{CH}(\text{NH}_2)\text{COOH} \text{ (1)} \\ \text{C}_6\text{H}_3 \begin{array}{l} \diagup \text{OH} \text{ (3)} \\ \diagdown \text{OH} \text{ (4)} \end{array} \end{array}$	—
Alizarin	$\begin{array}{c} \text{CO} \\ \text{C}_6\text{H}_4 \begin{array}{l} \diagup \text{CO} \\ \diagdown \text{CO} \end{array} \text{C}_6\text{H}_2 \begin{array}{l} \diagup \text{OH} \text{ (1)} \\ \diagdown \text{OH} \text{ (2)} \end{array} \end{array}$	—
Veratrol	$\text{C}_6\text{H}_4 \begin{array}{l} \diagup \text{OCH}_3 \text{ (1)} \\ \diagdown \text{OCH}_3 \text{ (2)} \end{array}$	—
Thymol	$\text{C}_6\text{H}_4 \begin{array}{l} \diagup \text{OH} \text{ (1)} \\ \diagdown \text{CH}(\text{CH}_3)_2 \text{ (2)} \end{array}$	—
Salicylaldehyd	$\text{C}_6\text{H}_4 \begin{array}{l} \diagup \text{OH} \text{ (1)} \\ \diagdown \text{CHO} \text{ (2)} \end{array}$	—
Saligenin	$\text{C}_6\text{H}_4 \begin{array}{l} \diagup \text{OH} \text{ (1)} \\ \diagdown \text{CH}_2\text{OH} \text{ (2)} \end{array}$	—
Meta-Verbindungen		
Resorcin	$\text{C}_6\text{H}_4 \begin{array}{l} \diagup \text{OH} \text{ (1)} \\ \diagdown \text{OH} \text{ (3)} \end{array}$	—
Orcin	$\text{C}_6\text{H}_3 \begin{array}{l} \diagup \text{OH} \text{ (1)} \\ \diagdown \text{OH} \text{ (3)} \\ \text{CH}_3 \text{ (5)} \end{array}$	—
Phloroglucin	$\text{C}_6\text{H}_3 \begin{array}{l} \diagup \text{OH} \text{ (1)} \\ \diagdown \text{OH} \text{ (3)} \\ \text{OH} \text{ (5)} \end{array}$	—
Dioxybenzoesäure	$\text{C}_6\text{H}_3 \begin{array}{l} \diagup \text{COOH} \text{ (1)} \\ \diagdown \text{OH} \text{ (2)} \\ \text{OH} \text{ (4)} \end{array}$	—
Dioxybenzaldehyd	$\text{C}_6\text{H}_3 \begin{array}{l} \diagup \text{CHO} \text{ (1)} \\ \diagdown \text{OH} \text{ (2)} \\ \text{OH} \text{ (4)} \end{array}$	—
<i>m</i> -Phenylendiamin	$\text{C}_6\text{H}_4 \begin{array}{l} \diagup \text{NH}_2 \text{ (1)} \\ \diagdown \text{NH}_2 \text{ (3)} \end{array}$	—
Xylenol	$\text{C}_6\text{H}_3 \begin{array}{l} \diagup \text{OH} \text{ (1)} \\ \diagdown \text{CH}_3 \text{ (3)} \\ \text{CH}_3 \text{ (4)} \end{array}$	—
<i>m</i> -Kresol	$\text{C}_6\text{H}_4 \begin{array}{l} \diagup \text{OH} \text{ (1)} \\ \diagdown \text{CH}_3 \text{ (3)} \end{array}$	+ (wenig)

Tabelle 1. (Fortsetzung.)

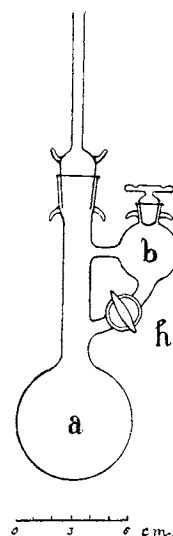
Substanz	Konstitution	Oxyd. mit Laccase
Para-Verbindungen		
Hydrochinon	$\text{C}_6\text{H}_4 \begin{cases} \text{OH} (1) \\ \text{OH} (4) \end{cases}$	+
Oxyhydrochinon-triacetat	$\text{C}_6\text{H}_3 \begin{cases} \text{OOCCH}_3 (1) \\ \text{OOCCH}_3 (2) \\ \text{OOCCH}_3 (4) \end{cases}$	+
Hydrochinonmonomethyläther	$\text{C}_6\text{H}_4 \begin{cases} \text{OH} (1) \\ \text{OCH}_3 (4) \end{cases}$	+
Hydrochinondimethyläther	$\text{C}_6\text{H}_4 \begin{cases} \text{OCH}_3 (1) \\ \text{OCH}_3 (4) \end{cases}$	—
Hydrochinondiäthyläther	$\text{C}_6\text{H}_4 \begin{cases} \text{OC}_2\text{H}_5 (1) \\ \text{OC}_2\text{H}_5 (4) \end{cases}$	—
Diamidophenol-hydrochlorid	$\text{C}_6\text{H}_3 \begin{cases} \text{OH} (1) \\ \text{NH}_2\text{-HCl} (2) \\ \text{NH}_2\text{-HCl} (4) \end{cases}$	+
<i>p</i> -Phenylendiamin	$\text{C}_6\text{H}_4 \begin{cases} \text{NH}_2 (1) \\ \text{NH}_2 (4) \end{cases}$	+
Dimethyl- <i>p</i> -phenylendiamin	$\text{C}_6\text{H}_4 \begin{cases} \text{NH}_2 (1) \\ \text{N}(\text{CH}_3)_2 (4) \end{cases}$	+
„ -hydrochlorid	$\text{C}_6\text{H}_4 \begin{cases} \text{NH}_2\text{-HCl} (1) \\ \text{N}(\text{CH}_3)_2 (4) \end{cases}$	—
<i>p</i> -Kresol	$\text{C}_6\text{H}_4 \begin{cases} \text{OH} (1) \\ \text{CH}_3 (4) \end{cases}$	—
Tyrosin	$\text{C}_6\text{H}_4 \begin{cases} \text{OH} (1) \\ \text{CH}_2\text{CH}(\text{NH}_2)\text{COOH} (4) \end{cases}$	—
Tyramin	$\text{C}_6\text{H}_4 \begin{cases} \text{OH} (1) \\ \text{CH}_2\text{CH}_2\text{NH}_2 (4) \end{cases}$	—
Methylenoxyd-Verbindung		
Safrol	$\text{CH}_2 \begin{matrix} \diagup \text{O} \diagdown \\ \diagdown \text{O} \diagup \end{matrix} \text{C}_6\text{H}_3\text{CH}_2\text{CH}:\text{CH}_2$	—
Aliphatische Amine		
Äthylendiamin	$\text{NH}_2(\text{CH}_2)_2\text{NH}_2$	—
Putrescin-dihydrochlorid	$\text{NH}_2(\text{CH}_2)_4\text{NH}_2\text{-2HCl}$	—
Cadaverin-dihydrochlorid	$\text{NH}_2(\text{CH}_2)_5\text{NH}_2\text{-2HCl}$	—

Experimenteller Teil.

Nachdem Phenole bzw. Amine in einen Reaktionskolben (Abb. 1, a) aufgenommen worden, wurden einige c.c. Wasser oder Alkohol und 10 c.c. 1/3 Mol Phosphat-Puffer von pH 6.0 hinzugefügt. In der Kugel b wurde bei geschlossenem Hahn h eine Laccase-Lösung gebracht. Darauf wurde der Reaktionskolben mit der Gasbürette verbunden und in einen Thermostaten von 20.0°C. getaucht. Nachdem er evakuiert und darauf mit Sauerstoff gefüllt wurde, wurde der Hahn h geöffnet und der Reaktionskolben geschüttelt. Damit die Versuche unter konstantem Druck verlief, benützte ich die Petterson'sche Bürette.

Die meisten Substrate wurden in der Menge von 5/10000 g. Mol. verwendet, nur die Methoxylhydroxyl Ketone (Diese Ketone verdanke ich der Liebenswürdigkeit von Prof. Dr. H. Nomura.) der von 2/10000 g. Mol. Um die Reaktionsgeschwindigkeiten miteinander vergleichen zu können, wurde stets dasselbe aus dem japanischen Lack („Kiurushi“ aus Saji, Tottori) hergestellte Laccasepräparat benützt.

Die Resultate, die sich bei den gegen Laccase indifferenten Substraten ergaben, sind hier nicht mitgeteilt.



Versuch 1. Substrat: Brenzcatechin 5/10000 g. Mol. Laccase: 50 mg. Barometrischer Druck: 770.5 mm. Abb. 1. Reaktionskolben.

Tabelle 2.

Reaktionsdauer	O ₂ absorbiert	Reaktionsdauer	O ₂ absorbiert
1 Min.	1.293 mg.	90 Min.	8.508 mg.
3	1.939	115	9.259
5	2.401	180	11.502
10	3.245	240	12.728
17	4.036	300	13.546
30	4.986	420	14.404
60	7.083	495	14.694
77	8.006	ca. 22 Stdn. (nicht geschüttelt)	15.947

Versuch 2. Substrat: Guajakol 5/10000 g. Mol. Laccase: 50 mg. Barometrischer Druck: 767.4 mm.

Tabelle 3.

Reaktionsdauer	O ₂ absorbiert	Reaktionsdauer	O ₂ absorbiert
1 Min.	0.407 mg.	120 Min.	4.624 mg.
3	0.499	180	5.885
5	0.578	240	6.726
10	0.801	270	6.858
15	1.077	360	7.173
30	1.760	480	7.751
60	2.890	540	7.974
90	3.849	ca. 23 Stdn. (nicht geschüttelt)	9.511
105	4.190		

Versuch 3. Substrat: Eugenol 5/10000 g. Mol. Laccase: 50 mg. Barometrischer Druck: 767.6 mm.

Tabelle 4.

Reaktionsdauer	O ₂ absorbiert	Reaktionsdauer	O ₂ absorbiert
1 Min.	0.486 mg.	120 Min.	6.833 mg.
3	0.644	190	7.227
5	0.854	244	7.332
10	1.406	300	7.503
15	1.879	422	7.858
30	3.403	476	7.989
35	3.916	481	8.002
60	5.519	508	8.160
90	6.504	ca. 23 Stdn. (nicht geschüttelt)	11.813

Versuch 4. Substrat: Hydrochinon 5/10000 g. Mol. Laccase: 50 mg. Barometrischer Druck: 761.8 mm.

Tabelle 5.

Reaktionsdauer	O ₂ absorbiert	Reaktionsdauer	O ₂ absorbiert
1 Min.	0.547 mg.	64 Min.	7.987 mg.
3	0.912	80	8.417
5	1.290	290	8.548
10	2.046	410	8.808
25	4.222	530	8.834
30	4.886	ca. 23 Stdn. (nicht geschüttelt)	13.095
60	7.792		

Versuch 5. Substrat: Adrenalin 5/10000 g. Mol. Laccase: 50 mg. Barometrischer Druck: 759.8 mm.

Tabelle 6.

Reaktionsdauer	O ₂ absorbiert	Reaktionsdauer	O ₂ absorbiert
5 Min.	1.261 mg.	180 Min.	15.854 mg.
15	2.378	240	17.673
30	3.704	360	19.194
60	6.121	480	20.129
84	7.914	570	20.818
120	10.630	ca. 23 Std. (nicht geschüttelt)	22.481
135	11.838		

Versuch 6. Substrat: Urushiol (destilliert) 5/10000 g. Mol. Laccase: 50 mg. Barometrischer Druck: 765.0 mm.

Tabelle 7.

Reaktionsdauer	O ₂ absorbiert	Reaktionsdauer	O ₂ absorbiert
3 Min.	2.395 mg.	180 Min.	13.190 mg.
9	5.587	240	13.464
17	8.767	300	13.752
30	11.292	360	13.936
45	11.881	420	14.145
60	12.195	ca. 21 Std. (nicht geschüttelt)	18.254
120	12.836		

Versuch 7. Substrat: Hydrourushiol 5/10000 g. Mol. Laccase: 50 mg. Barometrischer Druck: 767.5 mm.

Tabelle 8.

Reaktionsdauer	O ₂ absorbiert	Reaktionsdauer	O ₂ absorbiert
1 Min.	0.197 mg.	240 Min.	1.603 mg.
4	0.263	300	2.299
13	0.328	390	2.639
30	0.394	ca. 25 Std. (nicht geschüttelt)	3.143
60	0.736	30 Std. (von 25 bis 30 Std. geschüttelt)	4.452
120	1.051		

Versuch 8. Substrat: *o*-Phenylendiamin 5/10000 g. Mol. Laccase: 50 mg. Barometrischer Druck: 760.8 mm.

Tabelle 9.

Reaktionsdauer	O ₂ absorbiert	Reaktionsdauer	O ₂ absorbiert
1 Min.	0.547 mg.	88 Min.	8.015 mg.
3	0.859	120	9.343
6	1.236	182	10.904
10	1.757	240	11.594
15	2.342	300	12.140
30	3.956	425	12.635
45	5.296	540	12.856
60	6.454	ca. 23 Stdn. (nicht geschüttelt)	14.639

Versuch 9. Substrat: *o*-Kresol 5/10000 g. Mol. Laccase: 50 mg. Barometrischer Druck: 766.8 mm.

Tabelle 10.

Reaktionsdauer	O ₂ absorbiert	Reaktionsdauer	O ₂ absorbiert
2 Min.	0.446 mg.	330 Min.	0.801 mg.
30	0.459	420	1.076
120	0.512	540	1.273
240	0.761		

Versuch 10. Substrat: *o*-Kresol 5/10000 g. Mol. Laccase: 200 mg. Barometrischer Druck: 765.9 mm.

Tabelle 11.

Reaktionsdauer	O ₂ absorbiert	Reaktionsdauer	O ₂ absorbiert
1 Min.	0.432 mg.	240 Min.	1.965 mg.
10	0.642	330	2.279
60	1.114	420	2.764
120	1.376	540	3.249

Versuch 11. Substrat: 3-Methoxy-4-hydroxy-phenyläthyl-methyl-keton 2/10000 g. Mol.
Laccase: 30 mg. Barometrischer Druck: 763.5 mm.

Tabelle 12.

Reaktionsdauer	O ₂ absorbiert	Reaktionsdauer	O ₂ absorbiert
1 Min.	0.326 mg.	60 Min.	2.455 mg.
10	0.744	120	3.199
15	0.901	150	3.265
31	1.750	330	3.435

Versuch 12. Substrat: 3-Methoxy-4-hydroxy-phenyläthyl-octenyl-keton 2/10000 g. Mol.
Laccase: 10 mg. Barometrischer Druck: 766.0 mm.

Tabelle 13.

Reaktionsdauer	O ₂ absorbiert	Reaktionsdauer	O ₂ absorbiert
1 Min.	0.472 mg.	120 Min.	1.547 mg.
5	0.642	240	1.927
15	0.905	300	2.045
30	0.957	360	2.596
62	1.010	420	2.570

Versuch 13. Substrat: Pyrogallol 5/10000 g. Mol. Laccase: 10 mg. Barometrischer Druck: 761.2 mm. Nur bei diesem Versuch wurde neben dem Reaktionskolben noch ein kleiner Kolben mit KOH verwendet, um das sich entwickelnde CO₂-Gas⁽³⁾ zu absorbieren.

Tabelle 14.

Reaktionsdauer	O ₂ absorbiert	Reaktionsdauer	O ₂ absorbiert
8 Min.	0.260 mg.	302 Min.	8.970 mg.
15	1.263	360	9.452
30	2.005	472	10.715
60	4.062	555	11.665
120	6.067	ca. 23 Stdn. (nicht geschüttelt)	16.443
225	8.020		

(3) R. Willstätter und H. Heiss, *Ann.*, **433** (1923), 17.

Versuch 14. Substrat: *m*-Kresol 5/10000 g. Mol. Laccase : 50 mg. Barometrischer Druck : 772.3 mm.

Tabelle 15.

Reaktionsdauer	O ₂ absorbiert	Reaktionsdauer	O ₂ absorbiert
10 Min.	0.132 mg.	180 Min.	0.397 mg.
30	0.159	300	0.568
60	0.278	420	0.648
90	0.304	540	0.833
120	0.264		

Versuch 15. Substrat: Oxyhydrochinon-triacetat 5/10000 g. Mol. Laccase : 50 mg. Barometrischer Druck : 761.6 mm.

Tabelle 16.

Reaktionsdauer	O ₂ absorbiert	Reaktionsdauer	O ₂ absorbiert
3 Min.	2.709 mg.	180 Min.	10.199 mg.
9	4.403	240	10.499
15	5.575	300	10.773
30	7.581	360	10.799
60	8.949	420	11.137
90	9.522	480	11.228
120	9.861	525	11.359

Versuch 16. Substrat: Hydrochinon-monomethyläther 5/10000 g. Mol. Laccase : 50 mg. Barometrischer Druck : 763.0 mm.

Tabelle 17.

Reaktionsdauer	O ₂ absorbiert	Reaktionsdauer	O ₂ absorbiert
15 Min.	1.853 mg.	123 Min.	6.917 mg.
31	3.184	305	7.269
47	4.463	420	7.308
61	5.129	515	7.373

Versuch 17. Substrat: Diamidophenol-hydrochlorid 5/10000 g. Mol. Laccase: 50 mg. Barometrischer Druck: 763.9 mm.

Tabelle 18.

Reaktionsdauer	O ₂ absorbiert	Reaktionsdauer	O ₂ absorbiert
3 Min.	0.483 mg.	132 Min.	7.970 mg.
9	1.163	180	9.002
15	1.803	245	9.995
30	3.214	300	10.557
45	4.416	360	11.197
60	5.278	480	12.124
120	7.669	600	12.751

Versuch 18. Substrat: *p*-Phenylendiamin 5/10000 g. Mol. Laccase: 30 mg. Barometrischer Druck: 766.4 mm.

Tabelle 19.

Reaktionsdauer	O ₂ absorbiert	Reaktionsdauer	O ₂ absorbiert
1 Min.	2.086 mg.	20 Min.	8.698 mg.
2	3.831	60	8.777
5	6.796	180	8.973
8	8.134	360	9.039
15	8.632	480	9.078

Versuch 19. Substrat: Dimethyl-*p*-phenylendiamin 5/10000 g. Mol. Laccase: 50 mg. Barometrischer Druck: 762.2 mm.

Tabelle 20.

Reaktionsdauer	O ₂ absorbiert	Reaktionsdauer	O ₂ absorbiert
2 Min.	5.006 mg.	123 Min.	11.146 mg.
5	7.717	180	11.602
7	8.108	210	12.410
10	8.473	300	13.349
30	9.151	420	14.366
60	9.660	540	14.809

Zum Schluss möchte ich den Herren T. Oshida und S. Yamane für ihre Hilfe, sowie der Keimeikai für ihre finanzielle Unterstützung bei Ausführung dieser Arbeit meinen herzlichen Dank ausdrücken.

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THE EXCHANGE REACTIONS BETWEEN HEAVY WATER AND HYDROGEN COMPOUNDS.

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I. Introduction. It was shown by many authors that hydrogen of polar radicals, such as $-\text{NH}_2$, $[\text{NH}_4]^+$, $-\text{COOH}$, undergoes an exchange with its isotope when dissolved in water containing heavy water. The author investigated these exchange reactions to study the differences of the exchangeabilities of these polar radicals quantitatively.

II. The Methods of the Experiment. Water containing 0.490 mol HDO (assuming that ordinary water contains 0.020 mol HDO), was prepared by electrolysis. Soluble hydrogen compounds were dissolved in this water (20–30 c.c.) and after the equilibrium attained, all the water was separated by distillation. Concentration of HDO was determined by measuring its specific gravity by the float method. The float, made of pyrex glass, has thin wall, which is crooked by a slight change of pressure. The measuring tube containing the float and water (about 15 c.c.) was immersed in Dewar vessel containing ice, and the pressure in the tube was regulated by the height of water column. Sensibility of the float is 1×10^{-6} . As water is separated by distillation, it is a fault of this experiment that the deviation of the equilibrium may take place due to the change in concentration during distillation.

III. The Order of the Exchange Reactions. In these experiments concentration of HDO is 0.490 mol. And it is assumed that only one of the hydrogen of polar radicals in one molecule will exchange when suitably great concentration of hydrogen compounds is used, although it is doubtful that in these isotopic exchange reactions the reaction proceeds strictly step by step.

For instance, in fructose the equilibrium constant of the reaction $5\text{C}_6\text{H}_{12}\text{O}_6 + 5\text{HDO} = 5\text{C}_6\text{H}_{11}\text{DO}_6 + 5\text{H}_2\text{O}$ is

$$K = \frac{[\text{C}_6\text{H}_{11}\text{DO}_6]^5 [\text{H}_2\text{O}]^5}{[\text{C}_6\text{H}_{12}\text{O}_6]^5 [\text{HDO}]^5}.$$

If it is assumed that the exchangeabilities of five OH-radicals are the same, then the equilibrium constant of the exchange reaction of each OH-radical must be expressed as follows:

$$K_{m_i} = \frac{[\text{C}_6\text{H}_{11}\text{O}_6\text{D}][\text{H}_2\text{O}]}{[\text{C}_6\text{H}_{12}\text{O}_6][\text{HOD}]} \quad (i = 1, 2, 3, 4, 5).$$

K_m is called the mean equilibrium constant. In this expression the concentration of $\text{C}_6\text{H}_{11}\text{O}_6\text{D}$ corresponds to 1/5 of the measured decrease of HDO concentration.⁽¹⁾ Then

$$K = K_{m_1}, K_{m_2}, K_{m_3}, K_{m_4}, K_{m_5}.$$

Generally, when, although each mean equilibrium constant is not the same, the differences are not so large, K_m approximately equals

$$\sqrt[n]{K_{m_1}K_{m_2} \cdots K_{m_n}} = \sqrt[n]{K}.$$

The results of the exchange reactions by 0.490 mol and 2.15 mols HDO are shown in Table 1.

Table 1.

Compound	Concentration (molarity)	Concentration of HDO (mol)	Decrease of conc. of HDO (mol)	Conc. of H_2O (mol)	K_m	Condition
Fructose	1.110	0.490	0.070	55.089	8.91	boiling 2 hrs.
„	1.00	2.15	0.28	53.64	12.	„ 3 hrs.
NH_4Cl	8.149	0.490	0.115	55.134	2.10	„ 2 hrs.
„	2.00	2.15	0.20	53.56	3.0	„ 3 hrs.

K_m are the equilibrium constants when the bimolecular reactions, such as $\text{C}_6\text{H}_{12}\text{O}_6 + \text{HDO} = \text{C}_6\text{H}_{11}\text{DO}_6 + \text{H}_2\text{O}$ and $\text{NH}_4\text{Cl} + \text{HDO} = \text{NH}_3\text{DCl} + \text{H}_2\text{O}$, are assumed. The separation of water is carried out by distillation, K_m must be somewhat larger than real values. Temperature range is 100°–120°C. Temperature regulation is not performed strictly as the temperature coefficients of the exchange are not large.

(1) The author made a mistake in the calculation of the equilibrium constant of the bimolecular exchange reaction in the previously published paper (*J. Chem. Soc. Japan*, **56** (1935), 1180.), and corrected in this paper as above by the kind advice of Mr. Masao Harada, Shiomi Institute, Osaka.

The value of K_m at 2.15 mols HDO is slightly larger indicating that the order of the reaction by 2.15 mols HDO tends to increase. However all the following results are deduced under the assumption that the exchange reaction at 0.490 mol HDO proceeds always bimolecularly.

IV. The Discussion of the So-called "Mean Equilibrium Constant."

It may be pointed out in these experiments that the so-called equilibrium constants are somewhat larger owing to the deviation of the equilibrium according to change of concentration during distillation. The following experiments indicate to what extent this influence must be considered

Urea. Urea is precipitated with $\text{Hg}(\text{NO}_3)_2$ as $\text{CO}(\text{NH}_2)_2 \cdot 2\text{Hg}(\text{NO}_3)_2$ which transforms into $\text{CO}(\text{NH})_2 2\text{HgNO}_3$ liberating HNO_3 . If a calculated quantity of $\text{Hg}(\text{NO}_3)_2$ is added to urea solution, all the urea is removed at once from the reaction system and the equilibrium constant in this case gives true one. The following results have been obtained at 22°, 80°, and 100°C.; at 22°C. the amount of HNO_3 liberated was very small, but with rising temperature its amount gradually increases. HNO_3 was neutralized with Na_2CO_3 and liberated H_2O was calculated as 0.020 mol HDO.

Table 2.

Temperature (°C.)	Concentration (molarity)	Concentration of HDO (mol)	Decrease in conc. of HDO (mol)	Conc. of H_2O (mol)	K_m	Condition
100	2.000	0.455	0.008	55.062	0.12	heating 3 hrs.
80	2.000	0.454	0.015	55.070	0.24	„ 3 hrs.
22	2.000	0.463	0.047	55.093	0.79	„ 1 day

K_m values decrease with rising temperature. Therefore it will be concluded that D content of HNO_3 liberated must be considerably large. K_m values obtained by distillation under reduced pressure at 50°C. and 100°C. are 0.71 and 0.50 respectively as indicated in Table 3. The value obtained by extrapolation to 22°C. from these values is 0.92 which is about 15% larger than the true equilibrium constant, namely, 0.79.

Ammonium Chloride. As the concentration of the solute in saturated solution is constant during distillation. The equilibrium constant obtained from saturated solution must be a nearly true constant when it is assumed that NH_4Cl in solid phase does not take part in the reaction. The constant at 100°C. becomes 0.47₇ which is about 10% larger than 0.52₆ for unsaturated solution. In general it is assumed that the so-called equilibrium constants are about 10-16% larger than the true ones.

Table 3.

Compound	Temp.	Conc. of compounds (molarity)	HDO conc. (mol)	Decrease in HDO conc. (mol)	H ₂ O conc. (mol)	<i>K_m</i>
H ₂ NOH·HCl	100°	3.741	0.490	0.065	55.084	0.57
„	100°	3.623	„	0.065	55.084	0.59
IClO ₄	100°	1.931	0.401	0.030	53.208	0.75
H ₂ SO ₄	100°	8.590	0.479	0.118	46.635	0.45
H ₃ BO ₃	100°	5.662	0.490	0.060	55.079	0.46
H ₃ PO ₄	100°	9.199	0.415	0.061	55.155	0.34
NaOH	100°	17.498	0.490	0.064	55.083	0.21
NH ₄ Cl	100°	8.149	„	0.115	55.134	0.52 ₆
„	100°	14.449 (sat.)	„	0.162	55.181	0.47 ₇
„	70°	11.263 (sat.)	„	0.133	55.152	0.46 ₁
CO(NH ₂) ₂	100°	8.326	„	0.109	55.128	0.48
„	100°	8.326	„	0.117	55.136	0.52
„	50°	8.326	„	0.146	55.165	0.71
C ₆ H ₁₂ O ₆ (fructose)	100°	1.110	„	0.063	55.082	1.55
„	50°	1.122	„	0.051	55.070	1.19
COOH COOH	100°	4.899	0.407	0.034	55.136	0.51
„	50°	3.470	0.431	0.031	55.109	0.62
CH ₂ COOH CH ₂ COOH	100°	6.353	0.490	0.043	55.062	0.42
CH ₂ —CH ₂ —COOH CH ₂ —COOH	100°	2.117	„	0.015	55.034	0.41
CH ₂ —CH ₂ —COOH CH ₂ —CH ₂ —COOH	100°	0.684	„	0.007	55.026	0.5
COONa COOH	100°	3.180	0.423	0.021	55.107	0.91
CH ₂ —COONa CH ₂ —COOH	100°	2.952	0.471	0.011	55.049	0.4 ₅
CHCOOH HOOCCH	100°	0.689	0.490	0.008	55.028	0.6 ₅
CHCOOH CHCOOH	100°	2.154	„	0.024	55.043	0.66
HOCHCOOH CH ₂ COOH	100°	2.000	„	0.021	55.040	0.41

Table 3. (Concluded)

Compound	Temp.	Conc. of compounds (molarity)	HDO conc. (mol)	Decrease in HDO conc. (mol)	H ₂ O conc. (mol)	K_m
HOCHCOOH HOCHCOOH	100°	2.000	0.490	0.030	55.049	0.45
„ CH ₂ -COOH HOC-COOH CH ₂ -COOH	50°	6.004	„	0.095	55.114	0.56
„ H ₂ NCH ₂ COOH	100°	3.388	0.461	0.043	55.091	0.42
„ H ₂ O ₂	50°	3.949	0.456	0.053	55.107	0.46
„ C ₆ H ₁₂ O ₆ (glucose)	100°	2.256	0.490	0.034	55.053	0.62
„	100°	3.331	„	0.046	55.065	0.58
„	50°	2.691	„	0.057	55.076	0.92
„	50°	3.331	„	0.064	55.083	0.84
„	50°	5.524	0.284	0.034	55.259	0.68
„	100°	1.110	0.498	0.031	55.042	0.67
„	100°	1.110	0.396	0.028	55.141	0.77
„	50°	1.092	0.396	0.045	55.158	1.35
CH ₂ OH CHOH CH ₂ OH	100°	4.978	0.362	0.049	55.196	0.59

V. The Relation between the Equilibrium Constants and Temperature. *Ammonium Chloride.* The equilibrium constant of the saturated solution is 0.47₇ at 100° and 0.46₁ at 70°C as indicated in Table 3. The relation between the equilibrium constant of the reaction $\text{NH}_4\text{Cl} + \text{HDO} = \text{NH}_3\text{DCl} + \text{H}_2\text{O}$ and temperature may be expressed by the following equation :

$$\log K_m = -\frac{300}{4.57T} - 0.146 .$$

The heat quantity 300 cal., that is the zero point energy difference between reacting components, indicates that this reaction is endothermic. The zero point energy difference between HDO and H₂O is 1700 cal., therefore the difference between NH₄Cl and NH₃DCl is 1400 cal.

Fructose. The so-called equilibrium constant is 1.55 at 100° and 1.19 at 50°C. From the expression

$$\log K_m = -\frac{1200}{4.57T} + 0.895$$

it follows that the reaction $\text{C}_6\text{H}_{12}\text{O}_6 + \text{HDO} = \text{C}_6\text{H}_{11}\text{DO}_6 + \text{H}_2\text{O}$ is endothermic.

The zero point energy difference between $\text{C}_6\text{H}_{12}\text{O}_6$ and $\text{C}_6\text{H}_{11}\text{DO}_6$ is 500 cal.

Oxalic Acid. The following expression was obtained from the so-called equilibrium constants at 100° and 50°C ., the dissociation of oxalic acid being neglected :

$$\log K_m = \frac{900}{4.57T} - 0.815 .$$

The reaction $\text{H}_2\text{C}_2\text{O}_4 + \text{HDO} = \text{HDC}_2\text{O}_4 + \text{H}_2\text{O}$ is exothermic. The zero point energy difference between $\text{H}_2\text{C}_2\text{O}_4$ and HDC_2O_4 is 2600 cal.

Urea. The so-called equilibrium constant is 0.52 at 100° and 0.71 at 50°C . The zero point energy difference between $\text{CO}(\text{NH}_2)_2$ and $\text{CO}(\text{NH}_2)(\text{NHD})$ was obtained as 3400 cal. from the following relations :

$$\log K_m = \frac{1700}{4.57T} - 1.296 .$$

VI. The Relation between the Mean Equilibrium Constants and Chemical Constitutions. Table 3 summarizes the results of exchange reactions between several hydrogen compounds and water containing 0.490 mol HDO. In these experiments almost all the water distilled over within 10 minutes under reduced pressure.

Now, for instance, in fructose, if each of five OH-radicals have the same chance of exchange independently, so the equilibrium constants 1.55 at 100°C and 1.19 at 50°C , can be regarded as the changeabilities.

However, as these calculations are based upon the assumption that the exchangeability is a function of each OH-group only, and independent of the structure of the molecule, these values are all approximate. In the case of glycocoll which has different polar radicals, $-\text{NH}_2$ and $-\text{COOH}$, in one molecule, it was assumed that the chances of exchange of $-\text{NH}_2$ and $-\text{COOH}$ are the same.

Hydroxylamine Hydrochloride. The mean value of the mean equilibrium constant at 100°C . is 0.58. If the constitution $\text{H}_3\text{N}=\text{O}^+\text{HCl}^-$ is assumed, there are two exchangeable radicals $\text{H}_3\text{N}=\text{}$ and $=\text{OH}^+$. If the exchangeability of $\text{NH}\equiv$ is assumed as 0.52 at 100°C . from the results of NH_4Cl , the exchangeability of $=\text{OH}^+$ becomes 0.80.

Strong Acids. Perchloric Acid. Assuming that perfect dissociation takes place and all the H becomes H_3O^+ in solution, the mean equilibrium constant 0.75 can be regarded as the exchangeability of $=\text{OH}^+$ which coincides with 0.80 for hydroxylamine hydrochloride. *Sulphuric Acid.* Assuming that the primary dissociation is perfect and the secondary dissociation can be neglected, and taking the value 0.75 as the exchangeability of $=\text{OH}^+$, 0.1 was obtained as the exchangeability of HSO_4^- .

Weak Acids. Boric Acid. The mean equilibrium constant is 0.46, so the exchangeability of OH combined with B is 0.46 at 100°C . *Phosphoric Acid.* The mean equilibrium constant is 0.34, so the exchangeability of OH combined with P is 0.34 at 100°C .

Strong Base. Sodium Hydroxide. The value of K_m is 0.21. The exchangeability of OH^- is 0.21, assuming perfect dissociation.

Ammonium Chloride. The value of K_m is 0.52 in unsaturated solution. The exchangeability of $\equiv\text{NH}^+$ is 0.52 at 100° and 0.45 at 50°C .

Urea. The constitution of urea in neutral solution was assumed as $\text{OC} \begin{smallmatrix} \text{NH}_2 \\ \text{NH}_2 \end{smallmatrix}$. The mean value of K_m is 0.50. The exchangeability of $=\text{NH}$ combined with C is 0.50 at 100° and 0.71 at 50°C .

Fructose. The value of K_m is 1.55 at 100° and 1.19 at 50°C ., so the exchangeability of $-\text{OH}$ combined with C is 1.55 at 100° and 1.19 at 50°C .

Glucose. The value of K_m is 0.77 or 0.67 at 100° and 1.35 at 50°C . The values 1.55 and 1.19 for fructose are too large compared with other exchangeabilities. 0.72 is regarded as the exchangeability of $-\text{OH}$ at 100°C . for this time.

Glycerine. The purity of glycerine used was 83.55%. K_m at 100°C . was 0.59.

Saturated Dicarboxylic Acids. Table 3 summarizes the results for oxalic acid, succinic acid, glutaric acid, and adipic acid. Malonic acid was excluded owing to its unstableness. The value of adipic acid is not so credible due to its low solubility.

If it is assumed that these values are in parallel with the strength of hydrogen bond in $-\text{COOH}$, it is concluded that the binding force of H in $-\text{COOH}$ increases when the number of carbon atoms is increased from two to four, but does not change from four to five. The binding force is not influenced whether the number of carbon atoms in the chain is odd or even. If it is assumed that two carboxyl-groups in the molecule have the same

chance of exchange, the exchangeability of the carboxyl-group is obtained as 0.51 for oxalic acid and 0.42 for succinic acid. When Na is substituted for H of one of the carboxyl-groups in oxalic acid and succinic acid the exchangeability of H of the other -COOH becomes 0.91 for oxalic acid and 0.45 for succinic acid. The influence based upon the so-called "electron shift" due to highly ionisable character of Na-oxalate or Na-succinate can not be recognized obviously.

Unsaturated Dicarboxylic Acids. Fumaric Acid. The equilibrium constant was obtained as 0.65, although it can not be so credible a value because of the low solubility of the acid.

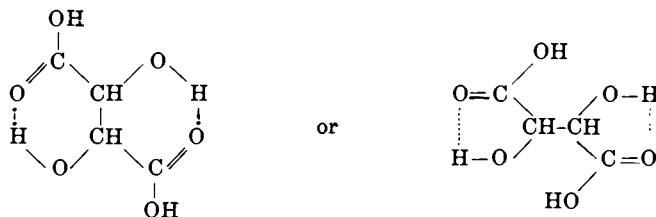
Maleic Acid. The mean equilibrium constant was obtained as 0.66 which is fairly high when compared with 0.42 for succinic acid. This behaviour is probably due to the existence of the double bond between two carbon atoms. The parallelism of the difference of properties between fumaric acid and maleic acid did not appear in this experiment.

Hydroxycarboxylic Acids. Malic Acid. The mean equilibrium constant is 0.41. If exchangeabilities of two carboxyl-groups are taken as 0.42 from succinic acid and the exchangeability of hydroxyl-group is taken as 1.55 from fructose, the calculated exchangeability of malic acid becomes $\sqrt[3]{0.42^2 \times 1.55} = 0.64$. When the exchangeability 0.72 for glucose is used, then $\sqrt[3]{0.42^2 \times 0.72} = 0.50$.

Tartaric Acid. The experimental value of the equilibrium constant at 100°C . is 0.45, the calculated value being $\sqrt[4]{0.42^2 \times 1.55^2} = 0.80$. The value of K_m at 50°C . is 0.56. The exchangeability of the carboxyl-groups at 50°C . may be estimated as 0.52 in connection with the exchangeability of oxalic acid and succinic acid at 100°C . The calculated value is $\sqrt[4]{0.52^2 \times 1.19^2} = 0.79$. When 0.72 is used for OH, then $\sqrt[4]{0.72^2 \times 0.42^2} = 0.55$ at 100°C .

Citric Acid. The experimental equilibrium constant is 0.42 at 100°C , the calculated value being $\sqrt[4]{1.55 \times 0.42^3} = 0.57$ or $\sqrt[4]{0.72 \times 0.42^3} = 0.48$. The equilibrium constant is 0.46 at 50°C , the calculated value being $\sqrt[4]{1.19^2 \times 0.52^2} = 0.64$. The specific rotation of *d*-tartaric acid decreases gradually with increasing concentration. Lowry and Austin⁽²⁾ suggested that hydrogen atoms of hydroxyl-groups are co-ordinated with oxygen atoms of carboxyl-groups and assumed the existence of the following molecules in solution :

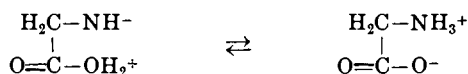
(2) Lowry and Auslin, *Nature*, **114** (1924), 431.



But the exchangeability of hydrogen in such a co-ordinated constitution must be lower than the hydrogen of free hydroxyl-radical. The results mentioned above do not favour this assumption.

Amino Acid. Glycocoll. The mean value of the experimental equilibrium constants is 0.59 at 100°C. and 0.88 at 50°C. The calculated value at 100°C. is $\sqrt[3]{0.50^2 \times 0.51} = 0.50$, if it is assumed that the exchangeabilities of -COOH and =NH are 0.51 from oxalic acid and 0.50 from urea, respectively. The calculated value of the exchangeability at 50°C. is $\sqrt[3]{0.71^2 \times 0.62} = 0.68$ in the same manner. These values do not coincide with the experimental

ones. If glycocoll forms an intramolecular salt such as $\begin{array}{c} \text{H}_2\text{C-NH}_3^+ \\ | \\ \text{O=C-O}^- \end{array}$, the calculated exchangeability of glycocoll becomes 0.52 at 100°C. from the value of NH_4Cl , while the calculated value 0.45 which is extrapolated from the values of NH_4Cl at 100°C. and 70°C. is by far smaller. Now if it is assumed that glycocoll can exist in two intramolecular salts:



and at 50°C. the left form is more probable, then calculated exchangeability becomes close to the experimental value. Namely, if the exchangeability of =OH^+ is taken as 0.80 at 100°C. as in hydroxylamine hydrochloride which may be slightly larger at 50°C., then the calculated value is $\sqrt[3]{0.71 \times 0.80^2} = 0.77$.

Hydrogen Peroxide. The mean equilibrium constant is 0.68 at 50°C. The exchangeability of -OH of water is assumed 1.00. If the constitution of H_2O_2 is assumed as H-O-O-H , the value of K_m is 1.00, and if the constitution $\begin{array}{c} \text{O-H} \quad \quad \text{O} \\ || \quad \text{or} \quad || \\ \text{O-H} \quad \quad \text{H-O-H} \end{array}$ is assumed, the exchangeability of =OH is the same as =OH^+ from hydroxylamine hydrochloride, and then the exchangeability

becomes 0.80. When the co-ordinated formula such as $\begin{array}{c} \text{O} \\ \diagup \quad \diagdown \\ \text{H}-\text{O}-\text{H} \end{array}$ is assumed, the exchangeability of co-ordinated hydrogen must be smaller, therefore in this connection the above formula is very probable for H_2O_2 .

VII. The Comparison of the Exchangeabilities. Table 4 summarizes the exchangeabilities of the different radicals. The exchangeability of each

Table 4.

Radical	Temperature	
	100°C.	50°C
—OH (alcoholic)	1.55 or 0.72	1.19
—OH (water)	1.00	
=OH ⁺ (hydroxylamine hydrochloride)	0.80	
—OH (boric acid)	0.46	
—OH (phosphoric acid)	0.34	
≡NH ⁺ (ammonium chloride)	0.52	0.45
=NH (urea)	0.50	0.71
—COOH (oxalic acid)	0.51	0.62
—COOH (succinic acid)	0.42	
—COOH (maleic acid)	0.66	
—COOH (Na oxalate)	0.91	
—COOH (Na-succinate)	0.4 ₅	
HSO ₄ ⁻ (sulphuric acid)	0.1	
OH ⁻ (sodium hydroxide)	0.2	

radical depends upon the differences of zero point energies between H-substituted radical and D-substituted radical, for instance, —OH and —OD. The greater the difference of zero point energies, the smaller the above-mentioned exchangeability. The exchangeability is a measure of the strength of the chemical bindings. The exchangeability depends upon not only the element with which hydrogen is combined, but also the kind and the valency state of the element to which the radical is connected. Namely among the exchangeabilities of —OH⁻, =NH and —COOH, combined with the carbon atom, that of —OH is the largest and that of —COOH the smallest.

When the element with which the radicals are combined differ, the exchangeabilities are as follows: H—OH 1.00, C—OH 0.72, B—OH 0.46, P—OH 0.34. And further the experiments upon the exchangeability of saturated dicarboxylic acids and unsaturated dicarboxylic acids show that the influence of the length of the chain upon the exchangeabilities of

-COOH disappears when the number of carbon atom is increased to four and the double bond increases the exchangeability slightly.

The influence of "electron shift" due to dissociation is obviously recognized in the cases of HSO_4^- and OH^- . In this connection the polarities of the radicals must have some influences upon their exchangeabilities. The parallelism between exchangeability and polarity or Raman frequency cannot be discussed perfectly owing to the lack of suitable data.

VIII. Applications. In the exchange reactions between soluble hydrogen compounds and water containing 0.490 mol HDO, the second order reaction being assumed, the exchangeabilities of polar radicals have been found quantitatively. These exchangeabilities are the measure of the differences of the zero point energies or chemical binding forces. By using these values, the exchangeability of any substance of the known constitution may be found and moreover the determination of the kind or the number of polar radicals of an unknown substance may be possible. The interchange of isotopes does not affect the valency state at all, so it is a most trustworthy way to apply these data to the determination of the constitution, as shown in the cases of hydroxycarboxylic acids, glyccoll, and H_2O_2 . Further, these data also suggest the possible method of the isolation of other isotopes.

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STUDIES OF THE RAMAN EFFECT OF ORGANIC SUBSTANCES. V. RAMAN EFFECT OF HOMO-CYCLIC COMPOUNDS.

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Introduction.

Of the Raman spectra of homo-cyclic compounds, several investigations have been carried out on the monocyclic compounds, such as benzene cyclohexane and their derivatives⁽¹⁾, but comparatively few papers on the condensed ring compounds have been published. Naphthalene and its halogen and alkyl substitution products have been studied by Ziemecki⁽²⁾ and by Gockel⁽³⁾, and some hydrogenated derivatives by Bonino and Cella⁽⁴⁾, and by Mukerji⁽⁵⁾. The experimental data of indene have been reported recently by Bonino and Ansidei⁽⁶⁾. In the present investigation, the studies of the Raman spectra of benzene, cyclohexane, indene, naphthalene, tetrahydro-naphthalene, and decahydro-naphthalene have been repeated and the studies have been now extended to the condensed tri-cyclic and tetra-cyclic compounds, such as tetrahydro-acenaphthene, decahydro-acenaphthene, decahydro-pyrene and perhydro-pyrene, which have not been reported hitherto.

Experimental.

Most of the substances used were kindly supplied by Dr. Kageyama of the Fuel Research Institute of Navy in Tokuyama, excepting naphthalene and indene. Commercial pure naphthalene (Merck's) was repurified by means of recrystallization (from alcohol) and sublimation. The alcohol solution (4/100 mol) and benzene solution (ca. 5/100 mol) of naphthalene were used in the experiments of the Raman spectra. As to indene, the chemically pure substance, made by Takeda, was fractionated over metallic sodium.

(1) Kohlrausch, "Smekal-Raman-Effekt", p. 223, 328. Dadiou, Kohlrausch, and Pongratz, *Manatsh.*, **60** (1932), 253; **61** (1932), 426; **63** (1933), 427; **64** (1934), 361, 374; **65** (1934), 6. Murray and Andrews, *J. Chem. Physics*, **1** (1933), 400; **2** (1934), 119.

(2) S. Ziemecki, *Z. Physik*, **78** (1932), 126.

(3) H. Gockel, *Z. physik. Chem.*, B, **29** (1935), 79.

(4) G. B. Bonino and P. Cella, *Atti accad. Lincei*, **13** (1931), 784; **15** (1932), 572.

(5) S. K. Mukerji, *Nature*, **134** (1934), 811.

(6) *Memoria dei Prof. G. B. Bonino e Dott. M. Ansidei letta alla R. Accademia delle Scienze dell' Istituto di Bologna*, 1934.

All the substances were redistilled over metallic sodium before use. The distillation being carried out in vacuum except in the cases of benzene and cyclohexane. The physical constants measured by Dr. Kageyama and the boiling point observed in our laboratory are tabulated in Table 1. The Raman spectra were photographed with a spectrograph of three prisms⁽⁷⁾. About 12 c.c. of each substance was used. The Raman spectra of decahydro-pyrene and perhydro-pyrene could hardly be obtained without the use of the filter solution. The data for them seem to be incomplete on account of their strong back ground of the plate, which can not be removed even under the filtered mercury light. The experimental results are shown in Tables 3-14. The numbers of the Raman lines (n), the number of the plate, and the conditions under which the spectra were taken, are indicated in Table 2.

Table 1. Physical Constants of the Substances.

Substance	B.p. °C./mm. (Hg)*		n_D^{25}	d_4^{25}
Benzene	80.5/760	80.5/760	1.4992	0.8728
Cyclohexane	80.7/760	80.7/760	1.4250	0.7734
Phenyl-cyclohexane	92/5	80-82/3.5	1.5225	0.9339
Di-cyclohexyl	94/10	92.5-94.5/9.7	1.4820	0.8853
Tetrahydro-naphthalene	71-72/6	75-76/6.8	1.5410	0.9666
Decahydro-naphthalene	63/9	68/14.2	1.4770	0.8847
Tetrahydro-acenaphthene	98/5	97.5-99.5/3.6	1.5582	1.0115
Decahydro-acenaphthene	80/5	93-100/9.7	1.5016	0.9456
Decahydro-pyrene	160/5	162-163/5.4	1.5782	1.0553
Perhydro-pyrene	164/10	138-140/5.5	1.5225	0.9875
Indene	62/10		1.5755	0.9813

* Boiling points shown in the first column were observed in our laboratory.

Table 2.

Substance	No. of table	n	No. of plate	Width of slit (10 ⁻² mm.)	Temp. (°C.)	Time of exposure (hours)
Benzene	3	45	135	90	24	7
			160	70	15	7
			273	64	25	12
			274	70	25	10

(7) This Bulletin, 9 (1934), 328.

Table 2. (*Concluded*)

Substance	No. of table	<i>n</i>	No. of plate	Width of slit (10 ⁻² mm.)	Temp. (°C.)	Time of exposure (hours)
Cyclohexane	4	66	130	90	24	6
			131	100	24	4
			150	80	13	5
			151	90	14	6
			277	64	23	15
			278	70	23	40
Phenyl-cyclohexane	5	79	118	80	25	4
			155	90	15	7
			157	76	15	5
			279	70	20	10
			280	64	24	7
			281	70	24	7
Dicyclohexyl	6	58	152	80	13	7
			153	80	14	5
Indene	7	65	275	70	25	8
			276	76	26	18
Naphthalene (in Alcohol)	8 (a)	14	141	90	22	14
			142	96	22	15
			177	64	19	15
Naphthalene (in Benzene)	8 (b)	14	181	70	18	15
Tetrahydro-naphthalene	9	87	159	70	15	6
			161	64	15	7
			217	62	30	15*
Decahydro-naphthalene	10	69	154	90	14	7
			156	80	15	6
Tetrahydro-acenaphthene	11	79	163	60	15	7
			164	60	15	10
Decahydro-acenaphthene	12	68	158	76	15	8
			162	60	14	10
Decahydro-pyrene	13	32	166	60	15	10
			167	70	15	8
Perhydro-pyrene	14	42	235	76	15	12
			236	70	28	16*

* A solution of sodium nitrite was used as the filter.

Table 3. Benzene.

No.	ν	I	$\nu_0 - \Delta\nu$	No.	ν	I	$\nu_0 - \Delta\nu$
1	24440	3	q-2948	24	22253	$1/2$	e- 685(k-2452)
2	24406	2	p-2947	25	22158	$1/2$	e- 780(k-2547)
3	24338	5	q-3050(o-2955)	26	22139	$1/2$	f- 856
4	24304	1	k- 401(p-3049)	27	22087	5	e- 851
5	24289	4	p-3064	28	22054	$1/2$	g- 985
6	24225	4	q-3163(o-3068)	29	22047	$1/2$	g- 992
7	24203	3	q-3185	30	22003	1	f- 992
8	24165	1	p-3188	31	21958	2	e- 980
9	24101	5	k- 604	32	21945	10	e- 993
10	23931	2	(e+ 992)	33	21758	8	e-1180(k-2947)
11	23910	1	i- 606(k-795)	34	21654	6	k-3051
12	23857	4(b)	k- 848	35	21641	8(d)	k-3064
13	23724	2	k- 981	36	21567	$1/2$	i-2949
14	23712	10	k- 993	37	21539	2(b)	k-3166(e-1399)
15	23676	$1/2$	i- 840(k-1029)	38	21519	3	k-3186
16	23531	5	k-1174(i-985)	39	21463	3	i-3053
17	23524	8	i- 992	40	21452	5	i-3063
18	23339	2(d)	i-1177	41	21352	6	e-1586(i-3164)
19	23302	2	k-1403	42	21332	5	e-1606(i-3184)
20	23121	6	k-1584	43	19988	3	e-2950
21	23101	5	k-1604	44	19887	3	e-3051
22	22534	$1/2$ (d)	e -404	45	19874	5	e-3064
23	22333	8	e -605				

$\Delta\nu$: 404 ($1/2$ d); 605 (8); (685) ($1/2$); (780) ($1/2$); 849 (5); (981) (2); 993 (10); (1029) ($1/2$); 1176 (5); 1401 (2); 1585 (6); 1605 (5); (2452) ($1/2$); (2547) ($1/2$); 2948 (6); 3051 (6); 3064 (8d); 3166 (2b); 3186 (3).

Table 4. Cyclohexane.

No.	ν	I	$\nu_0 - \Delta\nu$	No.	ν	I	$\nu_0 - \Delta\nu$
1	24535	5	q-2853	5	24438	3(b)	o-2855
2	24500	3	p-2853(q-2888)	6	24430	3	p-2923
3	24464	4	q-2924(p-2889)	7	24414	3	p-2939
4	24450	4	q-2938	8	24367	3	o-2926

Table 4. (Concluded)

No.	ν	I	$\nu_0 - \Delta\nu$	No.	ν	I	$\nu_0 - \Delta\nu$
9	24351	3	o-2942	38	22016	1(d)	g-1023
10	24325	0	k- 380	39	22008	3	k-2697
11	24278	1	k- 427	40	21969	$\frac{1}{2}$	f-1026
12	23904	8	k- 801	41	21943	0	k-2762
13	23739	1	e- 801	42	21912	8	e-1026
14	23714	3	i- 802	43	22855	10	k-2850
15	23677	6(d)	k-1028	44	22838	2	f-1158
16	23550	3	k-1155	45	22820	5(b)	k-2885
17	23489	1(d)	i-1027	46	22785	8	e-1153(k-2920)
18	23442	8	k-1263	47	22768	8	k-2937
19	23362	2(d)	k-1343(i-1154)	48	22673	8	e-1265(i-2843)
20	23298?	0(d)	(e+424)	49	22629	1(d)	i-2887
21	23279	$\frac{1}{2}$	k-1407	50	22596	6	e-1342(i-2920)
22	23261	8(d)	k-1426	51	21579	5	i-2937
23	22240	$\frac{1}{2}$	k-1444(i-1255)	52	21553	$\frac{1}{2}$	f-1442
24	23222	0	k-1465	53	21534?	0	e-1404
25	23073	2	k-1483	54	21514	$\frac{1}{2}$	e-1424
26	22736	$\frac{1}{2}$	i-1443	55	21495	10	e-1443
27	22555	3(d)	e- 202	56	21474	$\frac{1}{2}$	e-1464
28	22514	4	e- 383	57	21452	$\frac{1}{2}$	e-1486
29	22356	$\frac{1}{2}$ (b,d)	e- 424(k-2349)	58	20592	$\frac{1}{2}$ (d)	e-2346
30	22239	2(b,d)	k-2349	59	20477	$\frac{1}{2}$	e-2461(Hg)
31	22195	1	k-2466(e-699)	60	20312	1	e-2626
32	22171	$\frac{1}{2}$	f- 800	61	20277	2	e-2661
33	22154	1	e- 767(k-2534)?	62	20241	1	e-2697
34	22136	10	e- 784(k-2552)?	63	20088	8	e-2850
35	22105	$\frac{1}{2}$ (d)	e- 802	64	20054	3	e-2884(f-2941)
36	22076	2	e- 833(k-2600)	65	20017	6	e-2921
37	22041	5(d)	k-2629	66	20001	6	e-2937
			k-2664				

$\overline{\Delta\nu}$: 202 ($\frac{1}{2}$); 382 (3d); 425 (4); (699) (2b,d); (767) ($\frac{1}{2}$): (784) (1); 802 (10); (833) ($\frac{1}{2}$ d); 1026 (8); 1154 (4); 1264 (8); 1342 (3); 1405 (0); 1425 ($\frac{1}{2}$); 1444 (10d); 1465 ($\frac{1}{2}$); 1485 ($\frac{1}{2}$); 2347 ($\frac{1}{2}$ d); 2463 ($\frac{1}{2}$); (2534) ($\frac{1}{2}$); (2552) (1); 2600 ($\frac{1}{2}$ d); 2628 (2); 2663 (5d); 2697 (3); (2762) (0); 2850 (10); 2885 (3); 2920 (8); 2937 (8).

Table 5. Phenyl-cyclohexane.

No.	ν	I	$\nu_0 - \Delta\nu$	No.	ν	I	$\nu_0 - \Delta\nu$
1	24604	2(d)	k- 101	38	22700	$1/2$ (d)	e- 238
2	24459	2(bb,d)	q-2929	39	22661	6	e- 277
3	24429	3	k- 276	40	22578?	0(b,d)	e- 360
4	24345?	$1/2$ (d)	k- 360	41	22556?	0(b,d)	e- 382
5	24327	$1/2$	k- 378	42	22529	$1/2$	e- 409
6	24292	1	k- 413(p-3061)	43	22502	2	e- 436
7	24268?	0	k- 437	44	22478	2	e- 460
8	24239	$1/2$ (d)	k- 466(i-277)	45	22317	6	e- 621
9	24083	2	k- 622	46	22245?	0	f- 752
10	23965	$1/2$	k- 740	47	22197	1(d)	e- 741
11	23933	2	k- 772	48	22165	5	e- 773
12	23878	2	k- 827	49	22130?	0	f- 865
13	23868	1	k- 837	50	22111	3	e- 827
14	23842	1	k- 863	51	22097	1(d)	e- 841
15	23811	$1/2$	k- 894	52	22077	3	e- 861
16	23710	4	k- 995	53	22044	2(d)	e- 894
17	23702	4	k-1003	54	22013	$1/2$	e- 925(k-2692)
18	23674	4	k-1031	55	21943	10	e- 995
19	23658	2(d)	k-1047	56	21937	10	e-1001
20	23626	1(b,d)	k-1079	57	21909	6	e-1029
21	23587?	0	k-1118	58	21889	4	e-1049
22	23573?	0	k-1132	59	21854	8(b,d)	k-2851(e-1084)
23	23549	2	k-1156	60	21814	3(b,d)	e-1124
24	23528	2	k-1177	61	21807		e-1131
25	23506	3(d)	k-1199	62	21785	6(d)	e-1153
26	23476	1(d)	k-1229	63	21773	5(d)	k-2932
27	23443	2	k-1262	64	21764	4	e-1174
28	23426	4	k-1279	65	21740	5	e-1198
29	23408	$1/2$	k-1297	66	21710	4	e-1228
30	23377?	$1/2$ (d)	k-1328	67	21676	4(b)	e-1262
31	23354?	0(d)	k-1351	68	21656	6	e-1282
32	23264	5(d)	k-1441	69	21641	4	k-3064(e-1297)
33	23216	2	e+ 278	70	21610	1(d)	e-1328
34	23102	5(b,d)	k-1603	71	21591	1(d)	e-1347
35	22827?	2(bb,d)	e- 111	72	21498	5	e-1440
36	22797	$1/2$	e- 141	73	21364	1(b)	e-1574
37	22781	$1/2$ (d)	e- 157	74	21357		e-1581

Table 5. (*Concluded*)

No.	ν	I	$\nu_0 - \Delta\nu$	No.	ν	I	$\nu_0 - \Delta\nu$
75	21341	6	e-1597	78	20006	4(bd)	e-2932
76	21330	5	e-1608	79	19878	$1/2$	e-3060
77	20086	4	e-2852				

$\overline{\Delta\nu}$: 106 (2b,d)?; (141) ($1/2$ d)?; (157) ($1/2$ d)?; 238 ($1/2$ d); 277 (6); 360 ($1/2$ d)?; 380 ($1/2$); 411 ($1/2$); 437 (2); 460 (2); 621 (6); 741 (1d); 773 (5); 827 (3); 839 (1d); 862 (3); 894 (2d); (925) ($1/2$)?; 995 (10); 1002 (10); 1030 (6); 1048 (4); 1082 (3b,d); $\left(\begin{smallmatrix} 1121 \\ 1132 \end{smallmatrix}\right)$ (3b,d); 1155 (6d); 1175 (4); 1193 (5); 1229 (4); 1262 (4); 1281 (6); 1297 (1); 1328 (1d); 1349 (1d); 1440 (5); $\left(\begin{smallmatrix} 1574 \\ 1581 \end{smallmatrix}\right)$ (1b); 1597 (6); 1608 (5); (2692) ($1/2$)?; 2852 (4); 2932 (4); 3062 (3).

Table 6. Di-cyclohexyl.

No.	ν	I	$\nu_0 - \Delta\nu$	No.	ν	I	$\nu_0 - \Delta\nu$
1	24458	4(bb,d)	k- 247(q-2930)	22	23260	6(d)	k-1445
2	24435	4(d)	p-2918(o-2858)	23	23212	1(d)	k-1493
3	24345	2(b,d)	k- 260	24	23166	$1/2$ (d)	i-1350
4	24268	1	k- 437	25	22836	1(d)	e- 102
5	24244	2	k- 461	26	22799	1(d)	e- 139
6	24219	2	k- 486	27	22767	$1/2$ (d)	e- 171
7	23938	4	k- 767	28	22692	1	e- 246
8	23920	3	k- 785	29	22620	3(b)	e- 318
9	23903	1	k- 802	30	22574	1(d)	e- 364
10	23859	4	k- 846	31	22554	$1/2$ (d)	e- 384
11	23746	1	k- 959(i-770)	32	22504	1	e- 434(f-486)
12	23728?	$1/2$	i- 788	33	22479	2	e- 459
13	23702	1(d)	k-1003	34	22454	2	e- 484
14	23668	5(b,d)	k-1037	35	22426	1	e- 512
15	23622	2	k-1083	36	22173	4	e- 765
16	23590	2	k-1115	37	22151	3	e- 787
17	23543	2	k-1162	38	22137	1	e- 801
18	23508	1(d)	k-1197	39	22092	5	e- 846
19	23463	0	k-1242	40	22044	1(b,d)	k-2661
20	23441	4(b)	k-1264	41	21980	1	e- 958
21	23356	3	k-1349(i-1160)	42	21936	2	e-1002

Table 6. (*Concluded*)

No.	ν	I	$\nu_0 - \Delta\nu$	No.	ν	I	$\nu_0 - \Delta\nu$
43	21899	5(b,d)	e-1039	51	21586	4	e-1352
44	21854	10	e-1084(k-2851)	52	21495	8(d)	e-1443
45	21817	3(d)	e-1121(k-2888)	53	21448	0	e-1490
46	21781	8(d)	e-1157(k-2924)	54	20273	1	e-2665
47	21768	8(d)	k-2937	55	20082	5	e-2856
48	21738	2(b)	e-1200	56	20-45	2	e-2893
49	21698	2	e-1240	57	20020	5(b)	e-2918
50	21669	6(d)	e-1269	58	19998		e-2940

$\Delta\nu$: 102 (1d)?; 139 (1d ?); 171 ($1/2$ d)?; 246 (1); 318 (3b); 364 (1d); 384 ($1/2$)?; 435 (1); 460 (2); 485 (2); (512) (1); 766 (4); 787 (3); 801 (1); 846 (5); 958 (1); 1002 (2); 1038 (5b,d); 1083 (5); 1118 (3d); 1160 (3d); 1199 (2b); 1240 (2); 1267 (6d); 1351 (4); 1444 (8d); 1493 (1d); 2663 (1); 2853 (5); 2890 (2); ($\frac{2921}{2939}$)(8b,d).

Table 7. Indene.

No.	ν	I	$\nu_0 - \Delta\nu$	No.	ν	I	$\nu_0 - \Delta\nu$
1	24463	$1/2$	p-2890	19	23392	2	k-1313
2	24315	$1/2$ (d)	(k- 390(i-201) (q-3073)	20	23345	8	k-1360
3	24280	1(b,d)	p-3073	21	23312	6	k-1393(i-1204)
4	24171	3	k- 534	22	23302	$1/2$?	i-1214
5	24114	3(d)	k- 591	23	23248	8	k-1457
6	23975	6	k- 730	24	23155	10(b)	k-1550(i-1361)
7	23941	1	k- 764	25	23118	4	k-1587(i-1398)
8	23876	3(d)	k- 829	26	23096	10	k-1609
9	23844	3	k- 861	27	22734	3(d)	e- 204
10	23783	$1/2$ (d)	k- 922(i-733)	28	22559	2	e- 379
11	23760	2(b)	k- 945	29	22547	2	e- 391
12	23686	8	k-1019(i-830)	30	22404	8	e- 534(f-591)
13	23638	5	k-1067	31	22347	6(d)	e- 591
14	23592	6(b,d)	k-1113	32	22208	10	e- 730
15	23554	2(d)	k-1151	33	22177	3(d)	e- 761
16	23499	10	k-1206(i-1017)	34	22108	5(d)	e- 830
17	23478	6(d)	d-1227	35	22097	2	e- 841
18	23421	2	k-1284	36	22078	5	e- 860

Table 7. (*Concluded*)

No.	ν	I	$\nu_0 - \Delta\nu$	No.	ν	I	$\nu_0 - \Delta\nu$
37	22026	1(d)	e-912	52	21631	6(b)	e-1307(k-3074)
38	22013	1(d)	e-925	53	21603	1(d)	f-1392
39	21994	5(b,b)	e-944	54	21592	2(d)	k-3113
40	21969	1(b,d)	f-1026	55	21579	10	e-1359
41	21921	10	e-1017	56	21544	8(d)	e-1394(f-1451)
42	21870	6	e-1068	57	21481	10	e-1457
43	21832	6(b,d)	e-1106	58	21448	2	e-1490(f-1547)
44	21820	5(b,d)	k-2885	59	21408	1	i-1587
45	21797	$1/2$ (d)	f-1198	60	21388	10	e-1550(f-1607)
46	21785	3(d)	e-1153	61	21351	5	e-1587
47	21773	1(d)	f-1222	62	21329	10	e-1609
48	21735	10	e-1203	63	20048	4(b)	e-2890
49	21714	6(d)	e-1224(f-1281)	64	19872	3(b,d)	e-3066
50	21669	7(d,b)	k-3036	65	19825	2(d)	e-3113
51	21651	5	e-1287				

$\bar{\nu}$: 204 (3d); (379) (2); 391 (2); 532 (8); 591 (6d); 730 (10); 762 (3d); 830 (5d); (841) (2); 860 (5); (912) (1d); 923 (1d); 944 (5b,b); 1018 (10); 1067 (6); 1110 (6b,d); 1152 (3d); 1204 (10); 1225 (6d); 1285 (5); 1310 (5b); 1359 (10); 1394 (8d); 1457 (10); (1490) (2); 1560 (10); 1587 (5); 1609 (10); 2890 (4); (3036) (2b,d); 3066 (3b,d); 3113 (2d),..

Table 8(a). Naphthalene (in Alcohol).

No.	ν	I	$\nu_0 - \Delta\nu$	No.	ν	I	$\nu_0 - \Delta\nu$
1	24458	5(b,d)	q-2930	23	22177	5	e-761
2	24428	5(b,d)	p-2925	24	22055	6(d)	e-883
3	24416	5(b,d)	q-2972	25	21989	$1/2$	k-2716
4	24380	2(d)	p-2973	26	21943	$1/2$	f-1052
5	24364	2(d)	o-2929	27	21912	3	e-1026
6	24227	$1/2$	o-3066	28	21889	3(d)	e-1049(k-2818)
7	24193	3	k-612	29	21840	5(b,d)	e-1098
8	23942	4	k-763	30	21823	5(b,d)	k-2882(e-1115)
9	23821	5(d)	k-884	31	21776	8(b,d)	k-2929(e-1162)
10	23676	3	k-1029	32	21733	6(d)	e-1276
11	23654	3(d)	k-1051	33	21662	4(d)	e-1381
12	23607	2(d)	k-1098	34	21632	5(d)	k-3073
13	23542	1	k-1163	35	21585	2	i-2931
14	23432	3(d)	k-1273	36	21557	10	e-1381
15	23324	8	k-1381	37	21488	6(b,d)	e-1450
16	23252	5(d)	k-1453	38	21475	6(b,d)	e-1463
17	23242	5(d)	k-1463(f-1274)	39	21460	1	e-1478
18	23137	3	i-1379	40	21356	3	e-1582
19	23126	3	k-1579	41	20056	5(b,d)	e-2882
20	22514	2(d)	e-424	42	20011	6(b,d)	e-2927
21	22492	$1/2$ (d)	e-446	43	19964	6(b,d)	e-2974
22	22424	5	e-514	44	19870	1	e-3068

$\bar{\nu}$: (Alcohol) 424 (2d); 446 ($1/2$ d); 883 (6d); 1050 (3d); 1098 (5b,d); (1115) (1); 1162 (2); 1275 (4d); 1451 (6b,d); (1478) (1); (2716) ($1/2$); 2818 (3d); 2882 (5d); 2928 (8b,d); 2973 (6d).

$\bar{\nu}$: (Naphthalene) 513 (5); 762 (5); 1027 (3); 1381 (10); 1463 (5d); 1581 (3); 3070 (5d).

Table 8 (b). Naphthalene (in Benzene).

No.	ν	I	$\nu_0 - \nu$	No.	ν	I	$\nu_0 - \nu$
1	24440	2(d)	q-2948	23	22161	1	e-777
2	24321	4	q-3067	24	22087	3	e-851
3	24286	4	p-3067	25	22003	1(d)	f-992
4	24225	4	o-3068	26	21958	1	e-980
5	24191	5	k-514	27	21945	10	e-993
6	24101	5	k-604	28	21910	4	e-1028
7	23941	6	k-764	29	21788	1	e-1150
8	23926	2	k-779	30	21763	5(d)	e-1175
9	23857	1(d)	k-848	31	21654	6	k-3051
10	23724	2	k-981	32	21641	8(d)	e-1297(k-3064)
11	23712	8	k-993	33	21555	8	e-1383
12	23677	3	k-1028	34	21539	1	k-3166
13	23566	$\frac{1}{2}$	k-1149	35	21519	2	k-3186
14	23527	5	k-1178	36	21474	4(b, d)	e-1464
15	23323	8	k-1382	37	21449	3	e-1489
16	23241	5	k-1464	38	21419	$\frac{1}{2}$	f-1576
17	23129	k(b, d)	k-1576	39	21360	4(b, d)	e-1578
18	23121		k-1584	40	21354	4(b, d)	e-1584
19	23101	2	k-1604	41	21332	3	e-1606
20	22424	6	k-514	42	19990	3	e-2948
21	22328	6	e-610	43	19887	3	e-3051
22	22174	6	e-764	44	19874	6	e-3064

ν : (Benzene) 607 (6); 778 (1); 849 (3); 980 (1); 993 (10); 1176 (5d); 1584 (4b); 1605 (3); 2948 (3); 3051 (6); 3064 (8d); 3166 (1); 3816 (2).

ν : (Naphthalene) 514 (6); 764 (6); 778 (1)?; 1028 (4); 1382 (8); 1464 (4); 1577 (4); (3064) (8).

Table 9. Tetrahydro-naphthalene.

No.	ν	I	$\nu_0 - \nu$	No.	ν	I	$\nu_0 - \nu$
1	24590	3(d)	k-115	10	24193	2(b)	k-512
2	24540	4(d)	k-165	11	24118	3	k-587
3	24466	1	p-2887	12	24000	2	k-705(i-516)
4	24441	4(d)	k-264(q-2947)	13	23977	5	k-728
5	24404	3	p-2949	14	23960	$\frac{1}{2}$	k-745
6	24346	2(b, d)	i-170(q-3042)	15	23938	1	k-767
7	24305	2(d)	p-3048	16	23897	2	k-808
8	24268	3	k-437	17	23881	3	k-824
9	24247	2	k-456(i-269)	18	23832	1	k-873

Table 9. (Concluded)

No.	ν	I	$\nu_0 - \Delta\nu$	No.	ν	I	$\nu_0 - \Delta\nu$
19	23782	2	i- 734	54	22031	2(b, d)	e- 907(k-2674)
20	23714	2	i- 802	55	21987	2(d)	e- 941(k-2713)
21	23691	$1/2$	i- 825	56	21948	3	f-1047
22	23664	8	k-1041	57	21927	1	f-1068
23	23634	3(b, d)	k-1071	58	21898	10	e-1040
24	23589	$1/2$ (d)	k-1116	59	21867	8	e-1071
25	23541	4(d)	k-1164	60	21839	6	k-2866(f-1156)
26	23498	6	k-1207	61	21819	6	k-2886(e-1119)
27	23473	2(d)	k-1232(i-1043)	62	21792	6(b)	k-2913(f-1203)
28	23415	3	k-1290	63	21773	6(b)	e-1165
29	23402	3	k-1303	64	21757	6(b)	k-2948(f-1238)
30	23358	5	k-1347	65	21734	8	e-1204
31	23344	3	k-1361	66	21700	3	e-1238
32	23320	6	k-1385	67	21678	3	k-3027
33	23269	6	k-1436	68	21660	5	k-3045(f-1335)
34	23251	3	k-1454	69	21640	4	e-1298(f-1355)
35	23240	3(d)	k-1465	70	21626	$1/2$ (d)	i-2890
36	23194	2(d)	e+ 256	71	21595	4	e-1343
37	23121	3(d)	k-1584	72	21579	4	e-1359
38	23103	6(d)	k-1602	73	21553	5	e-1385
39	22819	5(d)	e- 119	74	21505	6	e-1433
40	22774	6(b, d)	e- 164	75	21488	3	e-1450
41	22669	4(d)	e- 269	76	21476	3	e-1462
42	22620	1(d)	e- 318	77	21442	$1/2$ (b, d)	e-1496
43	22503	6	e- 435	78	21355	4	e-1583
44	22480	4	e- 458(f-515)	79	21335	6	e-1603
45	22428	4(b)	e- 510	80	20073	4	e-2865
46	22354	6	e- 584	81	20053	4	e-2885
47	22234	3	e- 704(f-761)	82	20023	3(d)	e-2915(Hg)
48	22210	8	e- 728	83	19998	5	e-2940
49	22191	1	e- 747(f-804)	84	19958	$1/2$ (d)	f-3037
50	22173	3	e- 765(f-822)	85	19937	$1/2$	f-3058
51	22130	3	e- 808	86	19907	3(d)	e-3031
52	22117	4(d)	e- 821	87	19895	4	e-3043
53	22066	3	e- 872				

$\Delta\nu$: 117 (5d); 164 (6b, d); 267 (4d); (318) ($1/2$ d); 436 (6); 457 (4); 511 (4b); 585 (6); 704 (3); 728 (8); 746 (1); 766 (3); 808 (3); 822 (4d); 872 (3); (907) (2b, d); (941) (2d); 1040 (10); 1071 (4); 1117 ($1/2$ d); 1164 (6b); 1205 (8); 1235 (3); 1284 (3); 1301 (3); 1345 (4); 1360 (4); 1385 (5); 1435 (6); 1452 (3); 1463 (3); (1496) ($1/2$ b, d); 1583 (4); 1602 (6); (2674) (2b, d); (2713) (2d); 2866 (6); 2885 (6); 2914 (3d)?; 2994 (6b); 3029 (3d); 3044 (5).

Table 10. Decahydro-naphthalene.

No.	ν	I	$\nu_0 - \Delta\nu$	No.	ν	I	$\nu_0 - \Delta\nu$
1	24533	3(bb, d)	k- 172(q-2855)	36	22445	4	e- 493
2	24490	3(d)	q-2898(p-2863)	37	22337	4	e- 601
3	24466	3(bb, d)	q-2922	38	22233	$1/2$	f- 762
4	24416	3(bb, d)	p-2937(k-289)	39	22199	$1/2$	f- 796
5	24374	2(d)	k- 331	40	22187	6	e- 751
6	24352	2(d)	k- 353(i-164)	41	22178	3(d)	e- 760
7	24296	3	k- 409	42	22136	3	e- 802
8	24217	3	k- 488	43	22082	5	e- 856
9	24104	3	k- 601(i-412)	44	22062	3	e- 876
10	23954	3	k- 751	45	22041	3(d)	k-2664
11	23947	1	k- 758	46	22008	1(d)	e- 930(f-987)
12	23902	$1/2$	k- 803	47	21960	3(b, d)	e- 978
13	23848	3	k- 857	48	21949		e- 989(f-1046)
14	23828	$1/2$	k- 877	49	21919	3	e-1019
15	23771	$1/2$	k- 934	50	21891	4	e-1047
16	23715	2(b, d)	k- 990(i-801)	51	21877	3(b, d)	e-1061
17	23685	1	k-1020	52	21847	8(b, d)	k-2858(f-1148)
18	23658	4	k-1047(i-858)	53	21809	4	k-2896
19	23645	3	k-1060(i-871)	54	21788	8	k-2917(e-1150)
20	23555	$1/2$	k-1150	55	21770	8(b, d)	k-2935(e-1168)
21	23533	2(d)	k-1172(e+595)	56	21762	8(b, d)	e-1176
22	23455	3	k-1250(i-1061)	57	21711	$1/2$	f-1284
23	23446	3	k-1259	58	21702	$1/2$	e-1236 ?
24	23432	3	k-1273(e+494)	59	21690	4	e-1248
25	23350	1	k-1355(e+412)	60	21678	4	e-1260
26	23335	3	k-1370	61	21661	4	e-1277(i-2855)
27	23251	4(d)	k-1454(i-1265)	62	21587	4(d)	e-1351(i-2925)
28	22786	1(b, d)	e- 152	63	21570	4(d)	e-1368
29	22766	1(b, d)	e- 172	64	21487	6(b, d)	e-1451
30	22641?	0	e- 297	65	20280	0	e-2658
31	22610	2(d)	e- 328	66	20082	6	e-2856
32	22579	2	e- 359	67	20041	3	e-2897
33	22557	2	e- 381	68	20022	6(b)	e-2916
34	22530	5	e- 408	69	20002		e-2936
35	22496?	$1/2$ (d)	e- 442				

$\bar{\Delta\nu}$: 152-172 (1bb, d); 297 (0); 329 (2d); 356 (2); (381) (2); 408 (5); (442) ($1/2$ d); 491 (4); 601 (4); 751 (6); 759 (3d); 802 (3); 856 (5); 876 (3); 932 (1d); 990 (3b, d); 1020 (3); 1047 (4); 1060 (3b, d); 1150 (1); 1170 (2); (1236) ($1/2$); 1249 (4); 1260 (4); 1275 (4); 1353 (4d); 1369 (4d); 1452 (6b, d); 2661 (3d); 2857 (8b, d); 2896 (4); (2916) (8b, d); 2936 (8b, d).

Table 11. Tetrahydro-acenaphthene.

No.	ν	I	$\nu_0 - \Delta\nu$	No.	ν	I	$\nu_0 - \Delta\nu$
1	24575	1(d)	k-130	38	22690	4(d)	e-248
2	24548	2(d)	k-157(q-2840)	39	22557	4	e-381
3	24485	$1/2$ (d)	k-220	40	22536	2	e-402(f-459)
4	24453	3(b, d)	k-252(q-2935)	41	22497	1	f-498
5	24302	$1/2$ (d)	k-403	42	22481	7	e-457
6	24251	3	k-454	43	22431	4(d)	e-507(f-564)
7	24199	2(d)	k-506	44	22370	8	e-568
8	24136	5(b)	k-569	45	22348	5	e-590(f-647)
9	24113	2	k-592(i-403)	46	22331	0	e-607
10	24099	$1/2$	k-606	47	22288	10	e-650
11	24056	6	k-649	48	22215	$1/2$ (d)	e-723(k-2490)
12	23944	1(d)	k-761	49	22172	2	e-766
13	23908	3	k-797	50	22138	6	e-800
14	23866	$1/2$	i-650	51	22112	1	e-826(k-2593)
15	23847	$1/2$	k-858	52	22080	2	e-858
16	23764	1	k-941	53	22066	1	e-872(k-2639)
17	23750	1	k-955	54	22037	3(b, d)	k-2668(f-958)
18	23676	6	k-1029	55	22001	3	e-937
19	23644	5	k-1061	56	21987	3	e-951
20	23610	$1/2$	k-1095	57	21963?	$1/2$	f-1032
21	23578	2	k-1127(i-938)	58	21908	8	e-1030
22	23550	2	k-1155	59	21877	6	e-1061(f-1118)
23	23525	0	k-1183	60	21865	7(b)	k-2840
24	23498	$1/2$	i-1018	61	21843	4	e-1095(k-2862)
25	23483	6	k-1222	62	21822	3	e-1116
26	23453	2	k-1252(i-1063)	63	21808	3	e-1130(f-1187)
27	23429	2(b, d)	k-1276	64	21779	3	e-1159
28	23384	2	i-1132	65	21764	4	k-2941
29	23369	4(b, d)	k-1336	66	21752	3	e-1186
30	23358	5(b, d)	i-1158	67	21716	8	e-1222(f-1279)
31	23276	6	k-1429	68	21689	3	e-1249
32	23254	4	k-1451	69	21659	5(d)	{e-1279(k-3046) (f-1336)}
33	23154	4(d)	e+216	70	21599	6(b, d)	e-1339
34	23097	6(d)	k-1608	71	21504	8	e-1434
35	22808	3	e-130	72	21486	6	e-1452
36	22773	6(b, d)	e-165	73	21328	7(d)	e-1610
37	22718	6	e-220	74	20273	1	e-2665

Table 11. (Concluded)

No.	ν	I	$\nu_0 - \Delta\nu$	No.	ν	I	$\nu_0 - \Delta\nu$
75	20099	3(d)	e-2839	78	19899	1(d)	e-3039
76	20088	1	e-2850	79	19869?	$1/2$ (d)	e-3069
77	20000	5(b, d)	e-2938				

$\Delta\nu$: 130 (3); 161 (6b, d); 220 (6); 250 (4d); 381 (4); 402 (2); 456 (7); 507 (4d); 568 (8); 591 (5); 607 ($1/2$)?; 650 (10); (723) ($1/2$ d)?; 764 (2); 799 (3); (826) (1)?; 858 (2); (872) (1); 939 (1); 953 (3); 1030 (5); 1061 (6); 1095 (4); (1116) (3); 1128 (3); 1157 (3); 1185 (3); 1222 (6d); 1250 (3); 1278 (5d); 1338 (5d); 1432 (8); 1452 (6); 1609 (7d); (2490) ($1/2$ d)?; (2593) (1)?; (2639) (1)?; 2666 (3b, d); 2840 (7b); 2856 (2); 2940 (5b, d); 3043 (5d); (3069) ($1/2$ d)?.

Table 12. Decahydro-acenaphthene.

No.	ν	I	$\nu_0 - \Delta\nu$	No.	ν	I	$\nu_0 - \Delta\nu$
1	24454	2(b, d)	q-2934	26	22610	1	e- 328
2	24422	1(b, d)	p-2931	27	22580	$1/2$	e- 358
3	24404	$1/2$ (d)	p-2949	28	22566	2(d)	e- 372
4	24380	$1/2$ (d)	k- 325	29	22506	2	e- 432
5	24351	1(d)	k- 354	30	22488	1(d)	f- 507
6	24274	$1/2$	k- 431	31	22443	3(d)	e- 495
7	24203	$1/2$ (d)	k- 502	32	22423	$1/2$ (d)	e- 515
8	24159	$1/2$	k- 546	33	22390	4	e- 548
9	24084	1	k- 621	34	22373?	$1/2$	f- 622
10	23984	3	k- 721	35	22343	1	e- 595
11	23954	1	k- 751	36	22318	3	e- 620
12	23851	1	k- 854	37	22215	6	e- 723
13	23755	2	k- 950	38	22182	4	e- 756
14	23681	1	k-1024	39	22150	$1/2$	f- 845
15	23637	1(d)	k-1068	40	22129	1	e- 809
16	23607	$1/2$	k-1098	41	22105	1	k-2600
17	23587	0	i-1028	42	22084	3(d)	e- 854
18	23548	0	k-1157	43	22042	3(d)	k-2663
19	23469	$1/2$	k-1236	44	22028	2(d)	e- 910(k-2677)
20	23416	1(d)	k-1289	45	22011	2	k-2694
21	23333	1(d)	k-1372	46	21988	4	e- 950
22	23255	4(d)	k-1450	47	21957	2(d)	k-2748
23	23226	1	k-1479	48	21913	4	e-1025
24	22832	1(d)	e- 106	49	21894	2(b, d)	k-2761(f-1101)
25	22761	2(d)	e- 177	50	21870	8(b, d)	e-1068

Table 12. (*Concluded*)

No.	ν	I	$\nu_0 - \Delta\nu$	No.	ν	I	$\nu_0 - \Delta\nu$
51	21842	6(b, d)	e-1096	60	21567	5(b, d)	e-1371
52	21812	4	k-2893	61	21493	8(d)	e-1445
53	21773	8(b, d)	e-1165(k-2932)	62	21456	4(d)	e-1482
54	21756	6(b, d)	k-2949	63	20276	$\frac{1}{2}$ (d)	e-2662
55	21726	1	e-1212 ?	64	20238	1(d)	e-2700
56	21702	2	e-1236	65	20087	4(b)	e-2851
57	21691	1	i-2934	66	20045	2	e-2893
58	21649	5(b, d)	e-1289	67	20013	6(b, d)	e-2925
59	21617	4(d)	f-1378	68	19996	6(b, d)	e-2942

$\Delta\nu$: (106) (1d) ?; (177) (2d); 326 (1); 356 ($\frac{1}{2}$); (372) (2d); 432 (2); 498 (3d); (515) ($\frac{1}{2}$ d); 547 (4); (595) (1); 620 (3); 722 (6); 754 (4); (809) (1); 854 (3d); (910) (2); 950 (4); 1025 (4); 1068 (8b, d); 1096 (6b, d); 1161 (0); (1212) (1) ?; 1236 (2); 1289 (5b, d); 1371 (5b, d); 1448 (8d); 1481 (4d); (2600) (1); 2663 (3d); (2677) (2) ?; 2697 (2); (2748) (2d); (2761) (2d) ?; 2851 (4b); 2893 (4); 2925 (6b, d); 2942 (6b, d).

Table 13. Decahydro-pyrene.

No.	ν	I	$\nu_0 - \Delta\nu$	No.	ν	I	$\nu_0 - \Delta\nu$
1	23484	$\frac{1}{2}$	k-1221	17	21877	6(b, d)	e-1061(k-2828)
2	23421	0	k-1284	18	21841	6(d)	k-2864(e-1097)
3	23344?	$\frac{1}{2}$	k-1361	19	21773	8(b, d)	k-2932
4	23252	$\frac{1}{2}$	k-1453	20	21717	5	k-1221
5	23100	2	k-1605	21	21660	0	e-1278
6	22758	2(b, d)	e- 158	22	21623	2	k-3082(e-1315)
7	22620?	$\frac{1}{2}$ (d)	e- 318	23	21599	1	e-1339
8	22549	2(b, d)	e- 389	24	21577	3(d)	e-1361
9	22526?	$\frac{1}{2}$ (d)	e- 412	25	21503	6(b, d)	e-1434
10	22413	2	e- 525	26	21490	6(d)	e-1448
11	22381	1	e- 557	27	21359	$\frac{1}{2}$ (d)	e-1579
12	22352	2(b)	e- 586	28	21335	3(d)	e-1603
13	22324	1	e- 614	29	20114	4	e-2824
14	22296?	0(d)	e- 642	30	20081	2	e-2857
15	22128?	0	e- 810	31	20004	5(b, d)	e-2934
16	22047	4	e- 891	32	19850	$\frac{1}{2}$	e-3088

$\Delta\nu$: (158) (2b, d); (318) ($\frac{1}{2}$ d) ?; (389) (2b, d); (412) (0d) ?; (525) (2); (557) (1); 587 (2b); (614) (1); (642) (0d) ?; (810) (0) ?; (891) (4); (1061) (6b, d); (1097) (6d); 1221 (5); 1281 (0); (1315) (2); (1339) (1); 1361 (3d); (1435) (6b, d); (1579) ($\frac{1}{2}$ d); 1604 (3d); 2826 (4); 2961 (2bb, d); 2934 (5bb, d); 3085 (3). 1450 (6d)

Table 14. Perhydro-pyrene.

No.	ν	I	$\nu_0 - \Delta\nu$	No.	ν	I	$\nu_0 - \Delta\nu$
1	23402	$1/2$	e+ 464	22	22105	2	e- 833
2	23360	1(d)	k-1345	23	22076	2	e- 862
3	23349?	$1/2$	k-1356	24	21969	$1/2$	e- 969
4	23302?	1(b, d)	e+ 364	25	21929	$1/2$	e-1009
5	23263?	$1/2$	k-1442	26	21906	$1/2$	e-1032
6	23168	1	i-1447	27	21882	4	k-2823(e-1056)
7	22677	1(d)	e- 261(f-318)	28	21846	3	k-2859(e-1092)
8	22644	1	e- 294(f-351)	29	21790	4(b, d)	k-2915(e-1148)
9	22616	2	e- 322	30	21779	3(b, d)	k-2926(e-1159)
10	22587	3	e- 351	31	21721	1	e-1217
11	22566	2(d)	e- 372(f-429)	32	21709	4(d)	e-1229
12	22518	4(b, d)	e- 420	33	21690	3(d)	e-1248
13	22512	4(b, d)	e- 426	34	21647	$1/2$ (b, d)	e-1291
14	22474	4(b)	e- 464	35	21611	0	e-1327
15	22448	1	e- 490	36	21590	1	e-1348
16	22406	1	e- 532	37	21581	4(b, d)	e-1357
17	22375	3	e- 563	38	21492	4(d)	e-1446
18	22304	1(b, d)	e- 634	39	20120	3	e-2818
19	22240	1(d)	e- 698	40	20093	3	e-2846
20	22195	4	e- 743	41	20028	5(b)	e-2910
21	22148	2	e- 790	42	20007	4(b)	e-2931

$\Delta\nu$: 261 (1d); 294 (1); 322 (2); 351 (3); 372 (2d); 420 (4b, d); 426 (4b, d); 464 (4b); 490 (1); 532 (1); 563 (3); 634 (1b, d); 698 (1d); 743 (4); 790 (2); 833 (2); 862 (2); (969) ($1/2$)?; 1009 ($1/2$); 1032 ($1/2$); (1056) (4); (1092) (3); (1148) (4b, d); (1159) (3b, d); 1217 ($1/2$); 1229 (4d); 1248 (3d); 1291 (1b, d); 1327 (0); 1348 (1); 1357 (4b, d); 1444 (4d); 2820 (3); 2853 (3); 2912 (4b); 2938 (4b).

Discussion.

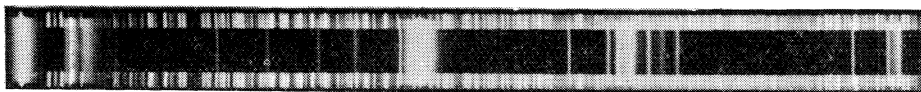
The Raman spectra of benzene and cyclohexane have been studied by several authors⁽¹⁾, especially by Wood and Collins⁽⁸⁾ with the improved arrangement. The so-called "complete Raman spectrum of benzene" has been published by Grassman and Weiler⁽⁹⁾. In the present experiments the long exposure of 40 hours has been tried with cyclohexane in order to obtain a complete Raman spectrum of the substance. The result is compared with

(8) R. Wood and G. Collins, *Phys. Rev.*, **42** (1932), 386.

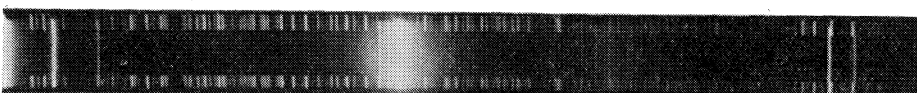
(9) P. Grassman and J. Weiler, *Z. Physik*, **86** (1933), 321.



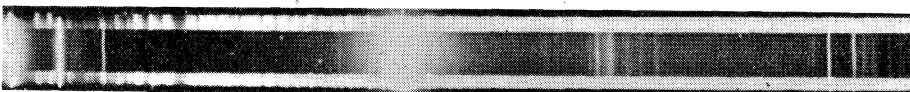
(1) Benzene



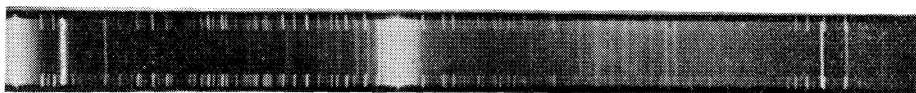
(2) Cyclohexane



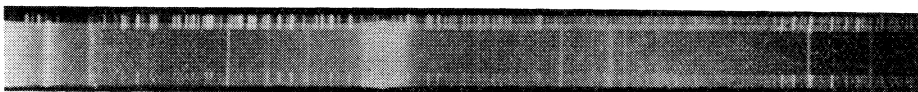
(3) Phenyl-cyclohexane



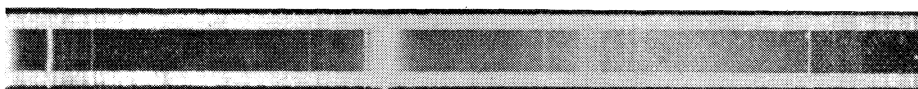
(4) Di-cyclohexyl



(5) Indene



(6a) Naphthalene (in benzene)



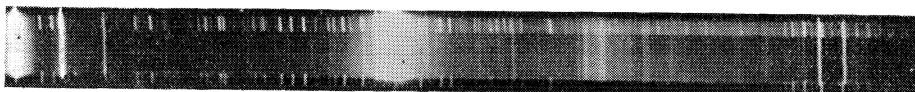
(6b) Naphthalene (in alcohol)



(7) Tetrahydro-naphthalene



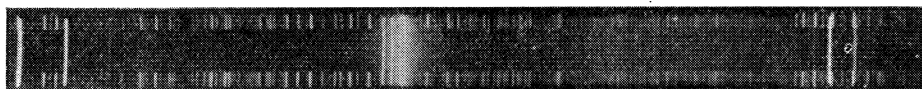
(8) Decahydro-naphthalene



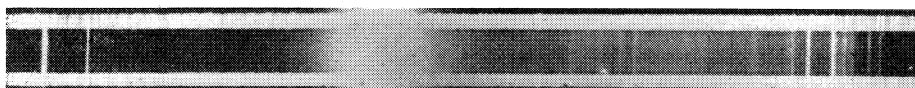
(9) Tetrahydro-acenaphthene



(10) Decahydro-acenaphthene



(11) Decahydro-pyrene



(12) Perhydro-pyrene

those obtained by Krishnamurti⁽¹⁰⁾, and Wood and Collins⁽⁸⁾ as shown in Table 15. Four new lines corresponding to $\Delta\nu$ 1405, 1425, 1465, and 1485 cm^{-1} are found to be accompanied with the deformation frequency of the CH_2 -group. These lines are very weak and appear in the equal intervals of about 20 cm^{-1} . As shown in Table 4 and Table 15, some other new lines of $\Delta\nu$ 22171, 22154

Table 15. Comparison of the Results with Cyclohexane.

Krishnamurti	Wood, Collins	Matsuno, Han	Krishnamurti	Wood, Collins	Matsuno, Han
—	—	202 ($1/2$)	—	—	1464 ($1/2$)
381 ($1/2$)	380 (2)	382 (3d)	—	—	1485 ($1/2$)
425 (1)	422 (3)	425 (4)	2351 (0)	—	2347 ($1/2$ d)
695 (0)	—	(699) (2b,d)?	2462 (0)	—	2463 ($1/2$)
—	—	(767) ($1/2$)?	—	—	(2534) ($1/2$)?
—	—	(784) ($1/2$)?	—	—	(2552) (1)?
802 (10)	801 (10)	802 (10)	—	—	(2600) ($5/2$ d)?
—	—	(833) ($1/2$ d)?	2630 (0)	2626 (0)	2628 (3)
992 (0)?	—	—	2662 (1)	2661 (1)	2663 (5d)
1028	1026 (8)	1026 (8)	2696 ($1/2$)	2693 (0)	2697 (3)
1156 (1)	1154 (4)	1154 (4)	—	2750 (0)	(2762) (0)?
1266 (5)	1264 (8)	1264 (8)	2852 (8)	2849 (10)	2850 (10)
1344 ($1/2$)	1342 (2)	1342 (3)	2889 (1)	2880 (1)	2885 (2)
—	—	1404 (0)	2922 (8)	2920 (10)	2920 (8)
—	—	1424 ($1/2$)	2938 (8)	2934 (10)	2937 (8)
1444 (5)	1442 (10)	1444 (10d)			

(10) P. Krishnamurti, *Indian J. Physics*, **6** (1931), 543.

and 22105 cm.^{-1} are observed also very weak. These lines may correspond to the shifts of $\Delta\nu$ 767, 784 and 833 cm.^{-1} respectively, when they are assumed to have been excited by the 22938 cm.^{-1} mercury line. These lines coincide, however, with the shifts of $\Delta\nu$ 2534, 2552 and 2600 cm.^{-1} respectively, when they are assumed to have been excited by the 24705 cm.^{-1} mercury line. The assignments of these new lines will be given by the experiments done by the longer exposure and by using the filter. The other intense Raman lines of $\Delta\nu$ 382, 425, 802, 1026, 1154, 1264, 1342, 1444, 2628, 2663, 2697, 2850, 2920, and 2937 cm.^{-1} in cyclohexane have been observed by nearly all investigators.

If we ascribe most of the intense lines of these Raman shifts, i.e., $\omega_1 = 382(3)$, $\omega_2 = 425(4)$, $\omega_3 = 802(10)$, $\omega_4 = 1026(8)$, $\omega_5 = 1154(4)$, $\omega_6 = 1264(8)$, $\omega_7 = 1342(3)$, $\omega_8 = 2444(10)$, $\omega_9 = 2850(10)$, $\omega_{10} = 2920(8)$, $\omega_{11} = 2937(8)$, to the Raman-active fundamentals, most of the other weak lines may be probably associated with the harmonic or the combination frequencies of these fundamentals, as shown in Table 16.

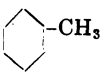
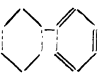
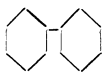
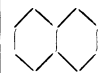
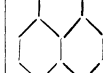
Table 16.

$\omega_{\text{cal.}}$	$\omega_{\text{obs.}}$	$\omega_{\text{cal.}}$	$\omega_{\text{obs.}}$
$2\omega_1 = 764$	(767)	$2\omega_6 = 2528$	(2534)
$2\omega_2 = 850$	(833)	$2\omega_7 = 2684$	2697
$2\omega_5 = 2308$	2347	$2\omega_8 = 2888$	2885
$\omega_4 - \omega_3 = 224$	202	$\omega_9 - \omega_1 = 2468$	2466
$\omega_3 - \omega_1 = 420$	425 ($= \omega_2$)	$\omega_{10} - \omega_1 = 2538$	(2534)
$\omega_8 - \omega_4 = 418$		$\omega_{11} - \omega_1 = 2555$	(2552)
$\omega_5 - \omega_1 = 772$	(784)	$\omega_6 + \omega_7 = 2606$	(2600)
$\omega_6 - \omega_2 = 839$	(833)	$\omega_6 + \omega_8 = 2708$	2697
$\omega_9 - \omega_8 = 1406$	1405		
$\omega_1 + \omega_4 = 1408$			

In Table 17, Raman frequencies of cyclohexane, methyl- and phenyl-cyclohexane, di-cyclohexyl, decahydro- and tetrahydro-naphthalene, tetrahydro- and decahydro-acenaphthene are tabulated. The shifts associated with the benzene ring are excluded from this table. Data of methyl-cyclohexane, observed by Godchot⁽¹¹⁾, are cited for comparison.

(11) Godchot, Canals, and Cauquil, *Compt. rend.*, **194** (1932), 176.

Table 17. Raman Frequencies associated with the Cyclohexane Ring.

								
ω_1	382	392	360 380	364 384	356 (381)	—	381	356 (372)
ω_2	425	444 775	411 437 460 741 773	435 460 766 787	408 751 759	436 457 704 728 746 766	402 456 764	432 722 754
ω	802	845 896 971	827 839 862 894 (925)	801 846 958	802 856 876 (932) 890	808 822 872 (907) (941)	799 (826) 858 (872) 939 953	(809) 854 (910) 950
ω_4	1023	1038	1048	1038	1047	1040	1030	1025
ω_5	1154	1167	1155 1175	1160	1150 1170	1164	1157	1161
ω_6	1264	1266	1262	1267	1249 1260 1275	1235 1284	1250 1278	1236 1289
ω_7	1342	1352	1349	1351	1353 1369	1345 1360 1385	1338	1371
ω_8	1444	1446	1440	1444	1452	1435 1452 1463	1432 1451	1448

All the fundamental frequencies in cyclohexane appear also in its mono-substitution products, viz., methyl-, phenyl-cyclohexane, and di cyclohexyl, as shown in Table 17. It is of interest, however, to note that some of these fundamentals, such as those of ca. $\Delta\nu$ 440, 845 and 1037 cm^{-1} , which appear in the mono-substitution products, have higher values than in cyclohexane itself. This seems to indicate that the introduction of the aromatic or the aliphatic radicals has the effect of raising the force constants, or of sharpening the valency angle. Further, when we take tetrahydro- and decahydro-naphthalene as the ortho-di-substitution products of cyclohexane, we find that most of the frequencies appear equal among these two substances, except the shift denoting ω_1 , which disappears in the case of tetraphydro-

naphthalene. The frequencies corresponding to the fundamentals of the cyclohexane ring appear also in tetrahydro- and decahydro-acenaphthene which may lead to the consideration that they are 1,2,3-tri-substitution products of cyclohexane.

The displacement or the spalling of the fundamental frequencies, ω_2 and ω_3 , and the decrease of the intensity of ω_3 in phenyl-cyclohexane and dicyclohexyl may be attributable to the disturbance of the symmetry of the cyclohexane ring by the adjacent benzene or cyclohexane ring, while the displacement or the spalling of ω_3 , ω_6 and ω_7 in tetrahydro- and decahydro-naphthalene may be possibly attributable to the existence of the isomers, besides to the cause explained above.

In the previous paper⁽¹²⁾, we ascribed the frequencies of $\Delta\nu$ 733-780, and 915-965 cm^{-1} to the valency frequencies of the $\begin{array}{c} \text{C} \\ \diagup \quad \diagdown \\ \text{C}-\text{CH} \end{array}$ or $\begin{array}{c} \text{C} \\ | \\ \text{C}-\text{C}-\text{C} \\ | \\ \text{C} \end{array}$ linkage.

The fact that the frequencies in these regions are also observed in phenyl-cyclohexane, dicyclohexyl, tetrahydro- and decahydro-naphthalene, tetra-

hydro- and decahydro-acenaphthene which have the linkage of $\begin{array}{c} \text{C} \\ \diagup \\ \text{C}-\text{C} \\ \diagdown \\ \text{C} \end{array}$ seems to offer another verification for it (Table 17).

We may consider phenyl-cyclohexane as mono-derivative, indene, naphthalene and tetrahydro-naphthalene as di-derivatives (ortho), tetrahydro-acenaphthene as tri-derivative (1:2:3), and decahydro-pyrene as tetra-derivative (1:2:3:4), of benzene. In the case of phenyl-cyclohexane, the frequencies of $\Delta\nu$ 621, 1002, 1030, 1175-1198, 1597-1608 and 3062 cm^{-1} are taken as the characteristic lines of the mono-derivatives of benzene, corresponding to $\alpha = 616$, $\beta = (849)$, $\gamma = 1000$, $\xi = 1026$, $\delta = 1166$, and $\epsilon = 1595$, as denoted by Dadiou, Pongratz and Kohlrausch⁽¹³⁾. These frequencies correspond also to those at $\Delta\nu$ 611, 833, 994, 1022, 1191, 1589-1609 and 3047 cm^{-1} in diphenyl which have been observed by Dadiou and Kohlrausch and by Wood⁽¹⁴⁾. The lower values of the Raman frequencies in diphenyl than in phenyl-cyclohexane may be attributable to the mutual effect of the benzene ring.

Dadiou, Pongratz, and Kohlrausch have reported that in the di-derivatives of benzene (ortho), only the frequencies of $\Delta\nu$ 3060 and 1595 cm^{-1} appear

(12) This Bulletin, **10** (1935), 220.

(13) Dadiou, Pongratz, and Kohlrausch, *Monatsh.*, **60** (1932), 253.

(14) Kohlrausch, "Smekal-Raman-Effekt", 1931, p. 332.

constantly, while $\Delta\nu$ 616 and 1166 cm^{-1} disappear occasionally. They have concluded also that the Raman line corresponding to $\xi = \text{ca. } 1040 \text{ cm}^{-1}$ appears intensely and that corresponding to $\gamma = 1000$ disappears in the ortho-di-derivatives of benzene. We have also reported that the frequencies of $\Delta\nu$ 1000 and 615 cm^{-1} disappear in the cases of ortho-di-derivatives, such as phthalates, salicylates, and *o*-cresyl acetate⁽¹⁵⁾. It is interesting that in the cases of indene, naphthalene, tetrahydro- and dihydro-naphthalene⁽¹⁶⁾, the disappearance of the frequencies of 616 and 1000 cm^{-1} would indicate that these substances have the characteristic Raman spectra of the ortho-di-substitution products of benzene. The appearance of the intense line corresponding to $\Delta\nu$ 1040 cm^{-1} in tetrahydro-naphthalene, 1047 in dihydro-naphthalene, 1017 in indene, and 1026 in naphthalene indicates also the character of the ortho-di-substitution products of benzene.

In tetrahydro-acenaphthene the disappearance of $\Delta\nu$ 1000 and the appearance of $\Delta\nu$ 607, 650, 1157, 1609 and 3043 cm^{-1} may correspond to $\Delta\nu$ 615, 668, (1154), (1596), and 3036 cm^{-1} in xylol (1 : 2 : 3)⁽¹⁴⁾ and 611, 671, (1161), 1582 and 3050 cm^{-1} in xylidine (1 : 2 : 3)⁽¹⁴⁾. The appearance of the intense lines corresponding to 650 in tetrahydro-acenaphthene, 654 in 1,2,3-trimethylbenzene⁽¹⁷⁾, 668 in xylol and 671 in xylidine seems to characterise the tri-(1 : 2 : 3)-substitution products of benzene.

Thus, in the case of phenyl-cyclohexane which can be considered as a mono-substitution product of benzene on one hand, and as that of cyclohexane on the other from the chemical constitution, the Raman frequencies can be classified into groups, one due to the benzene ring, viz., $\Delta\nu$ 411, 621, 839, 995, 1002, 1030, 1198, 1574–1608 cm^{-1} , etc., another due to the cyclohexane ring, viz., 380, 437, 827, 862, 1048, 1155, 1262, 1349 and 1440 cm^{-1} and the rest due to the combination frequencies, such as 277, 741, 773, 894, 1082, etc. As to the frequencies above 2850 cm^{-1} , it is well known that the frequencies $\Delta\nu$ 2852 and 2932 cm^{-1} are attributable to the valency frequencies of the aliphatic C–H bond and 3062 cm^{-1} to the aromatic C–H bond.

In Fig. 1 and Fig. 2, α , β , γ , ξ , δ and ϵ denote the frequencies associated with the benzene ring, ω_1 , ω_2 , ω_3 , ω_4 , ω_5 , ω_6 , ω_7 , and ω_8 those associated with the cyclohexane ring. As will be obvious from the figures, some of the frequencies in the region of ca. $\Delta\nu$ 850 and 1040 cm^{-1} can be considered due to the benzene ring as well as to the cyclohexane ring.

(15) This Bulletin, **9** (1934), 87.

(16) Bonino and Cella, *Atti accad. Lincei*, **15** (1932), 572.

(17) Kohlrausch and Pongratz, *Monatsh.*, **65** (1934), 6.

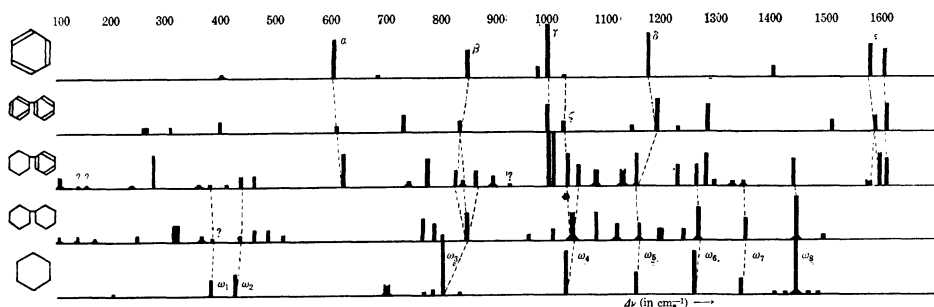


Fig. 1.

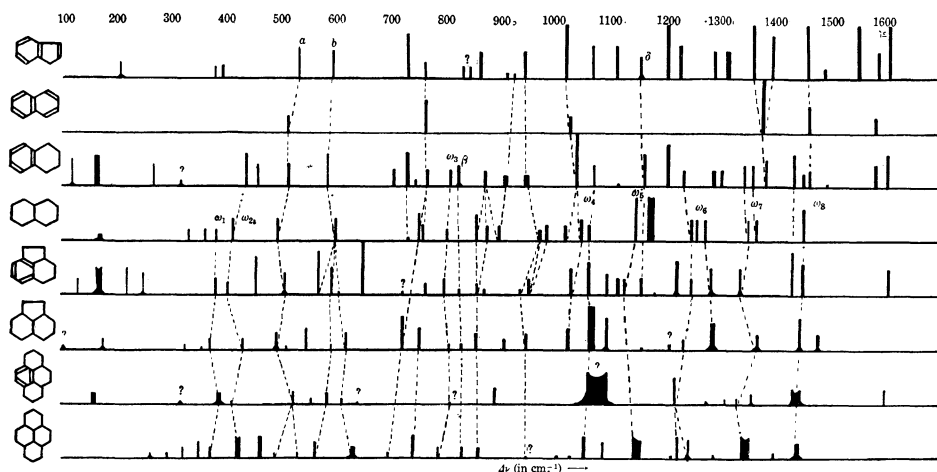


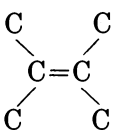
Fig. 2.

In the same way, we may consider tetrahydro-naphthalene, tetrahydro-acenaphthene and decahydro-pyrene as the substitution products of benzene as well as cyclohexane, as mentioned above. In these cases, the possible effect of the condensed ring may be the displacement or disappearance or spalting of the lines.

It is to be noted that the frequency of ca. $\Delta\nu$ 491 cm^{-1} appears in decahydro-naphthalene, decahydro-acenaphthene, and perhydro-pyrene which have the

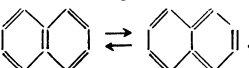
linkage of $\begin{array}{c} \text{C} & & \text{C} \\ & \diagdown & / \\ & \text{C}-\text{C} \\ & / & \diagdown \\ \text{C} & & \text{C} \end{array}$, while $\Delta\nu$ 532 cm^{-1} appears in indene and ca. 514 cm^{-1}

in naphthalene, tetrahydro-naphthalene and tetrahydro-acenaphthene which

have a linkage of  in the ring. A line at ca. $\Delta\nu$ 590 cm^{-1} is observ-

ed also in all the condensed ring compounds, except naphthalene. The frequency of $\Delta\nu$ 1435 cm^{-1} appears in the case of dihydro-naphthalene, tetrahydro-naphthalene, tetrahydro-acenaphthene and decahydro-pyrene.

The fact that the more complicated Raman spectrum is obtained in the case of indene than that of naphthalene may be explained by the reasons that naphthalene has the higher degree of symmetry than indene and that naphthalene has been observed in solution while indene in liquid state. It is interesting that the doublet at $\Delta\nu$ 1583 and 1605 cm^{-1} appear in benzene, and 1576 and 1615 cm^{-1} in cyclohexadiene $-(1, 3)^{(18)}$ while only a line at $\Delta\nu$ 1577 cm^{-1} appears in naphthalene which may be considered as the resonance between

the two forms, that is: . Bright Wilson⁽¹⁹⁾ has explained

the doublet of $\Delta\nu$ 1587 and 1605 cm^{-1} in the Raman spectrum of benzene on the basis of quantum mechanical resonance between $\nu_8(1587-1605)$ and $\nu_1(991) + \nu_6(605)$. In the case of naphthalene, the disappearance of one of the doublet in benzene, mentioned above, may be reasonable, for $\nu_1(991)$ and $\nu_6(605)$ do not occur in naphthalene. It is remarkable that, besides the frequencies of $\Delta\nu$ 1587 and 1609 cm^{-1} , a very intense line corresponding to 1550 cm^{-1} appears in indene. From the fact that only the line at 1500 cm^{-1} appears in the case of cyclopentadiene⁽²⁰⁾ in place of 1494 cm^{-1} in furane⁽²¹⁾, we may consider that the frequency of 1550 cm^{-1} in indene may correspond to that of $\Delta\nu$ 1500 cm^{-1} in cyclopentadiene, and the existence of the other two lines, viz., $\Delta\nu$ 1587 and 1609 cm^{-1} , is associated with the benzene ring. Consequently, the molecule of indene can be considered as the derivatives of benzene as well as of cyclopentadiene, which corresponds to the normal ex-

pression of the chemical formula: . It has to be assumed, however,

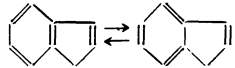
in this case that the frequencies of $\Delta\nu$ 1584 cm^{-1} which is associated with the benzene ring is little influenced by the condensed ring as in the case of naphthalene and tetrahydro-naphthalene, while that of $\Delta\nu$ 1500 cm^{-1} which is associated with the cyclopentadiene ring is considerably influenced by the condensed ring. Since the frequencies of $\Delta\nu$ 1585 and 1615 cm^{-1} have been

(18) J. W. Murray, *J. Chem. Physics*, **3** (1935), 59.

(19) E. Bright Wilson, *Phys. Rev.*, **46** (1934), 146.

(20) R. Truchet and J. Chapron, *Compt. rend.*, **198** (1934), 1934.

(21) L. Médard, *Bull. soc. chim.*, (5), **1** (1934), 934.

also observed in cyclopentene⁽²²⁾, it seems reasonable to consider the molecule of indene as a derivative of benzene as well as of cyclopentene, that is, the existence of the form of  can also be considered. Consequently, the existence of the two forms is more probable, that is , as in the case of naphthalene.

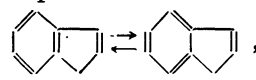
Summary.

1. The Raman spectra of the following substances have been measured : benzene, cyclohexane, phenyl-cyclohexane, di-cyclohexyl, indene, naphthalene, tetrahydro-naphthalene, decahydro-naphthalene, tetrahydro-acenaphthene, decahydro-acenaphthene, decahydro-pyrene, and perhydro-pyrene.

2. A complete Raman spectrum of cyclohexane has been obtained.

3. Considering phenyl-cyclohexane, tetrahydro-naphthalene, tetrahydro-acenaphthene, and decahydro-pyrene as the substitution products of benzene as well as of cyclohexane, the Raman frequencies of these substances have been classified into three groups, i. e., the first due to the benzene ring, the second due to the cyclohexane ring, and the third due to the combination of the two.

4. The disappearance of $\Delta\nu$ 616 and 1000 cm.^{-1} in the di-derivatives (ortho) of benzene has been confirmed even in the case of the condensed ring compounds, such as indene, naphthalene, and tetrahydro-naphthalene.

5. The oscillation of the two forms of indene, i. e. , has been explained.

In conclusion, the authors wish to express their thanks to Dr. Kageyama for his supply of the samples. The authors express their indebtedness to Ass. Prof. T. Nozoe for his kind advices. A part of expenses of this experiment was defrayed from a grant given by the Nippon Gakujutsu-Shinkokwai, to which thanks are due.

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(22) L. Piaux, *Compt. rend.*, **198** (1934), 1496.

THE NORMAL FREQUENCIES OF VIBRATION OF BENZENE COMPOUNDS IN THE ULTRAVIOLET ABSORPTION.

By Kôiti MASAKI.

Received February 8th, 1936. Published April 28th, 1936.

Introduction. Although some investigations have been made on the ultraviolet absorption spectra of benzene and its derivatives in vapour state, little progress has however been made in this direction, since these results rest always on an assumption, that (0.0)-band is the most intense, applying the intensity distribution of Frank-Condon principle to vibration bands in excited state. However, certain spectroscopic data (Raman and infrared) may be identified with the normal frequencies of vibration, by which the above-mentioned assumption may be proved experimentally, provided that (1.0)-bands on the ultraviolet absorption are known. Unfortunately these data are not yet obtained for reason of complications of bands and the feeble intensity, the band of wave number 500 cm.^{-1} at room temperature being less intense than (0.0)-band by an amount of 10% from calculation by Maxwell-Boltzmann's energy distribution law. Author's attempts have however been made with considerable success, obviating this difficulty by purification of the sample, and by comparison of a number of plates which were taken in good experimental conditions.

This paper contains the results of the spectroscopic investigation of vapour of the following mono-substituted substances: toluene, chlorobenzene, bromobenzene, phenol, aniline, benzaldehyde, and benzonitrile.

Experimental. The samples, supplied as "purest" by Kahlbaum, were repurified by several fractional distillations under reduced pressure until the distillation temperature became constant with accuracy higher than $\pm 0.05^\circ\text{C}$. The absorption vessels were cylindrical glass tubes 15-60 cm. long with quartz windows cemented on. The apparatus, in which the sample was cooled with liquid air, was first evacuated by an oil pump, and then by opening a cock it was filled with vapour of the sample to a suitable pressure which was measured by a mercury manometer. A water-cooled hydrogen discharge tube constructed to have a powerful intensity was employed as a source of the ultraviolet radiation. An exposure of 30 minutes or of one hour was found sufficient, the slit-width being 0.02 mm. The spectra were photographed on a Hilger E_2 and also on E_1 spectrograph. The iron arc was used as comparison.

Results. In Table 1-7, the experimental data are given with the wave number shifts⁽¹⁾ in Raman. The figures in brackets give the relative intensities of the spectra, d indicating diffuse band.

Discussion of these results will be given in another place.

Table 1. Toluene ($C_6H_5CH_3$)

Wave length in air ($\text{\AA}$)	Wave number in vacuo (cm.^{-1})	Frequency separation	Wave number shifts in Raman
27274-43 (d)	36654-96	781	786 (4)
27126-45	36854	623	622 (2)
27048-66	36960-36	517	520 (2)
26915	37143	334	333 (2)
26675	37477-60	0	

Table 2. Chlorobenzene (C_6H_5Cl)

27501	36353	701	704 (8)
27437	36436	618	615 (6)
27286	36638	416	418 (8)
26980	37054	0	

Table 3. Bromobenzene (C_6H_5Br)

27519	36328	668	670
27472	36390	606	608
27253	36682	315	314
27231	36712	285	—
27187	36771	226	—
27021	36996	0	

Table 4. Phenol (C_6H_5OH)

28134	35534	820	813 (3b)
27962	35752	604	614
27903	35828	528	526 (2)
27671	36128	228	235 (2)
27498	36356	0	

(1) Kohlrausch, "Der Smekal-Raman-Effekt," 1931.

Table 5. Aniline ($\text{C}_6\text{H}_5\text{NH}_2$)

Wave length in air ($\text{\AA}$)	Wave number in vacuo (cm^{-1})	Frequency separation	Wave number shifts in Raman
30292	33002	1032	1028 (5)
30255	33043	991	993 (10)
30100	33213	821	813 (5b)
29838	33505	529	530 (3)
29742	33613	421	—
29575	33803	231	233 (3)
29374	34034	0	

Table 6. Benzaldehyde ($\text{C}_6\text{H}_5\text{CHO}$)

29242	34187	1007	1001 (8)
29122	34323	866	827 (3)
29030	34437	757	752 (0)
28940	34544	650	648 (1)
28911	34579	615	615 (3)
28747-85 (d)	34776-30	418-464	439 (4)
28588-601 (d)	34970-54	224-240	239 (1b)
28478	35105	89	
28406	35194	0	

Table 7. Benzonitrile ($\text{C}_6\text{H}_5\text{CN}$)

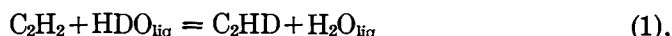
28155 (d)	35507	1009	998 (5)
27846	35901	616	619 (1)
27793	35970	547	545 (1)
27758 (d)	36015	501	—
27726 (d)	36057	459	460 (1/2)
27377	36516	0	

INTERCHANGE EQUILIBRIUM BETWEEN ACETYLENE AND HEAVY WATER.

By KOZO HIROTA and GO OKAMOTO.

Received March 16th, 1936. Published April 28th, 1936.

The interchange equilibrium of the reaction,



has recently been studied experimentally by Gillespie and Reyerson^{(1) (2)}. We calculated the equilibrium constant K_1 from existing spectroscopic data and found an excellent agreement with the experimental value.

K_g of the gas reaction, $\text{C}_2\text{H}_2 + \text{HDO}_{\text{gas}} = \text{C}_2\text{HD} + \text{H}_2\text{O}_{\text{gas}}$, can be expressed in term of molecular constants. Assuming that the rotational degree of freedom is fully excited and, according to Urey⁽³⁾, that the interatomic potential energy is not affected by isotopic replacement, we have

$$\log K_g = -\frac{\Sigma \epsilon_0}{kT} + \frac{3}{2} \log \frac{M_{\text{C}_2\text{HD}} M_{\text{H}_2\text{O}}}{M_{\text{C}_2\text{H}_2} M_{\text{HDO}}} + \log \frac{I_{\text{C}_2\text{HD}} \left(\frac{I_{\text{H}_2\text{O}}}{I_{\text{HDO}}} \right)^{\frac{3}{2}}}{I_{\text{C}_2\text{H}_2}} + \log \frac{Q_{\text{C}_2\text{HD}} \cdot Q_{\text{H}_2\text{O}}}{Q_{\text{C}_2\text{H}_2} \cdot Q_{\text{HDO}}} \quad (2),$$

where
$$\Sigma \epsilon_0 = \sum_{\text{C}_2\text{HD}}^{3n-5} \frac{h\nu_0}{2} + \sum_{\text{H}_2\text{O}}^{3n-6} \frac{h\nu_0}{2} - \sum_{\text{C}_2\text{H}_2}^{3n-5} \frac{h\nu_0}{2} - \sum_{\text{HDO}}^{3n-6} \frac{h\nu_0}{2},$$

$$\frac{1}{2} \sum^{3n-5(6)} \nu_0 = \frac{1}{2} \sum^{3n-5(6)} \nu_e + \frac{1}{4} \sum_i^{3n-5(6)} \sum_j^{3n-5(6)} x_{ij},$$

ν_e is harmonic frequency, x_{ij} anharmonicity constant, $I = \sqrt[3]{I_A I_B I_C}$ mean moment of inertia, $Q = \frac{3n-5}{II} (1 - e^{-\frac{h\nu_0}{kT}})^{-1}$ for acetylene, and $Q = \frac{3n-6}{II} (1 - e^{-\frac{h\nu_0}{kT}})^{-1}$ for water molecule. The present calculation was based on the following spectroscopic data:

(1) Reyerson and Gillespie, *J. Am. Chem. Soc.*, **57** (1935), 2250.

(2) Reyerson and Gillespie, *Ibid.*, **58** (1936), 282.

(3) Urey and Rittenberg, *J. Chem. Physics*, **1** (1933), 137. Urey and Greiff, *J. Am. Chem. Soc.*, **57** (1935), 321.

	C ₂ H ₂	C ₂ HD	H ₂ O	HDO
Moment of inertia	$23.50 \times 10^{-40}(4)$	$27.90 \times 10^{-40}(8)$	I_A $1.03 \times 10^{-40}(7)$ I_B 2.07 I_C 3.10	$1.18 \times 10^{-40}(7)$ 3.74 4.92
Fundamental frequency (cm. ⁻¹)	ν_{8_2} 3372 ⁽⁴⁾ ν_{8_1} 1974 ν_a 3288 δ_a 729* δ_s 618*	3350 ⁽⁵⁾ 1860 2550 541 ^{(6)*} 679*	ν_1 3654 ⁽⁷⁾ ν_2 3756 ν_8 1596	2720 ⁽⁷⁾ 3750 1403

* Twofold degenerated.

Anharmonicity constants x_{ij} were taken from Mecke's analysis⁽⁹⁾ for H₂O and from Herzberg's for C₂H₂⁽⁴⁾⁽¹⁰⁾; x_{ij} for HDO and C₂HD were computed by assuming the proportionality, $x_{ij} \propto \nu_i \nu_j$; $\frac{1}{2} \Sigma \nu_e$, $\frac{1}{4} \Sigma x_{ij}$, and $\frac{1}{2} \Sigma \nu_0$ calculated from the original data are given below :

	C ₂ H ₂	C ₂ HD	H ₂ O	HDO
$\frac{1}{2} \Sigma \nu_e$	5773 cm. ⁻¹	5195 cm. ⁻¹	4603 cm. ⁻¹	4008 cm. ⁻¹
$\frac{1}{4} \Sigma x_{ij}$	52	45	35	26
$\frac{1}{2} \Sigma \nu_0$	5825	5240	4638	4034

We obtain therefore from expression (1)

$$\log K_g = -\frac{54}{0.434RT} - 0.524 + \frac{1}{0.434} \log \frac{Q_{C_2HD} \cdot Q_{H_2O}}{Q_{C_2H_2} \cdot Q_{HDO}} \quad (3)$$

with $K_g = 0.62$ at 25°C.

(4) Herzberg and Spinks, *Z. Physik*, **91** (1934), 386.

(5) Sutherland, *Nature*, **134** (1934), 775.

(6) Randall and Sleator, *Phys. Rev.*, **45** (1934), 124.

(7) Barker and Sleator, *J. Chem. Physics*, **3** (1935), 660.

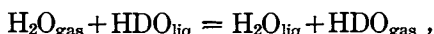
(8) Herzberg, Patat and Spinks, *Nature*, **133** (1934), 951.

(9) Macke, *Z. Phys.*, **81** (1933), 445, 465.

(10) Herzberg and Funke, *Phys. Rev.*, **49** (1936), 100.

The last term of the expression gives a small correction arising from the small deformation frequencies of acetylene molecule.

K_1 for the equilibrium (1) can readily be calculated by combining (3) and the constant K_w of the equilibrium,



determined by one of the authors⁽¹¹⁾. We have finally,

$$K_1 = K_g K_w = 0.59 \text{ at } 25^\circ\text{C.}, \text{ where } K_w = 0.96 \text{ at } 25^\circ\text{C.}$$

The agreement with the recent experimental data $K_1 = 0.599^{(2)}$ at 25°C. is satisfactory.

One could also use other sets of frequencies due to different authors as given below :

Fundamental freq.		Harmonic freq. ⁽¹³⁾	
$\text{C}_2\text{H}_2^{(12)}$		H_2O	HDO
ν_{s_2}	3370	ν_1 3895	3844
ν_{s_1}	1975	ν_2 3803	2848
ν_a	3277	ν_8 1635	1424
δ_a	729 *		
δ_s	600 *		

* Twofold degenerated.

The result is nearly unaltered by replacing ν_0 's of water with those due to Clusius and Bartholomé ($K_{1,25^\circ\text{C.}} = 0.62$) whereas one obtains $K_{1,25^\circ\text{C.}} = 0.66$, if Mecke's value for acetylene were used instead of Herzberg's. Assignment of δ_s has been frequently under discussion⁽¹⁴⁾, the discrepancy of the frequency between these authors being the chief cause of the above difference in theoretical values. Our result is in favour of the assignment $\delta_s = 618 \text{ cm.}^{-1}$ rather than $\delta_s = 600 \text{ cm.}^{-1}$ in agreement with Morino's theoretical results.

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(11) Horiuti and Okamoto, this Bulletin, **10** (1935), 282.

(12) Mecke, *Z. physik. Chem.*, B, **17** (1932), 1.

(13) Farkas and Farkas, *Trans. Faraday Soc.*, **30** (1934), 1071. Clusius and Bartholomé, *Z. Elektrochem.*, **40** (1934), 529. Teller, *Det Kg. Danske Vidensk. Selskab*, (1934).

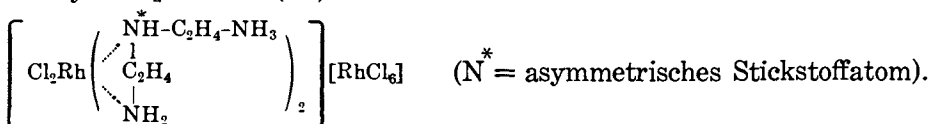
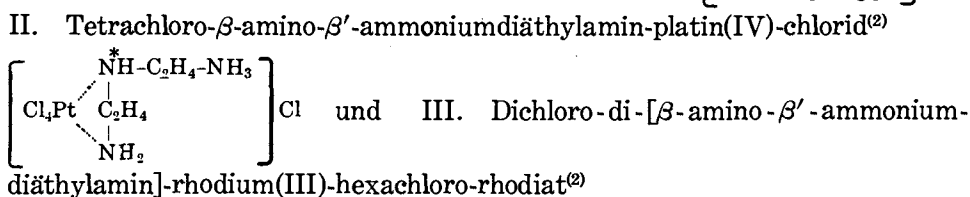
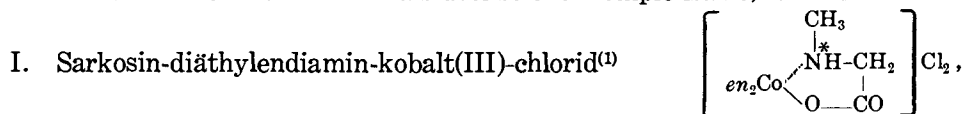
(14) Morino, *Sci. Pap. Inst. Phys. Chem. Research, Japan*, **26** (1934), 1; see also Morino and Mizushima, *Physik. Z.*, **18** (1935), 600.

VERSUCHE ZUR AKTIVIERUNG VON KOMPLEXSALZEN, DIE EIN DURCH BINDUNG AN DAS ZENTRALATOM ENTSTANDENES ASYMMETRISCHES STICK- STOFFATOM ENTHALTEN.

Von Yuichi NAKATSUKA und Hiroshi IINUMA.

Eingegangen am 16. Dezember 1935. Ausgegeben am 28. Mai 1936.

Wenn das sekundäre Amin der allgemeinen Formel NHRR' , worin R und R' zwei verschiedene Kohlenwasserstoffreste bedeuten, durch Verknüpfen seines Stickstoffs mit einem Metallatom ein Komplexion bildet, so ist der Stickstoff asymmetrisch, und das betreffende Komplexsalz kann mittels einer optisch aktiven Säure bzw. Base in die Antipoden gespalten werden. Wir kennen bisher noch nicht mehr als drei solche Komplexsalze, nämlich



Das Salz I ist zweifach asymmetrisch, und zwar findet sich ausser der Stickstoffasymmetrie noch die Molekularasymmetrie oder in diesem Falle die sogenannte Kobaltasymmetrie. Tatsächlich wurde das Komplexradikal mit Hilfe von Bromcamphersulfonsäure zweifach aktiviert. Die Aktivität, die auf die Kobaltasymmetrie zurückzuführen ist, ist beständig, wogegen die, die auf der Stickstoffasymmetrie beruht, sehr unbeständig ist, indem sich das aktive Bromcamphersulfonat der Reihe in der Lösung selbst rasch razemisiert. Man kann überhaupt kein aktives Salz in Bezug auf die Stickstoffasymmetrie erhalten, dessen negativer Bestandteil inaktiv ist.

(1) Meisenheimer, *Ann.*, **438** (1924), 261.

(2) Mann, *J. Chem. Soc.*, **1934**, 466.

Negativ verlief dagegen der Versuch, das Salz II zu aktivieren, und aus dem Salze III konnte man überhaupt kein Salz gewinnen, das irgendeinen optisch aktiven Säurerest enthält.

Wir⁽³⁾ haben schon mehrere Verbindungen der allgemeinen Formel $[\text{CoA}_2(\text{DH})_2]\text{X}$ dargestellt, worin A Ammoniak bzw. koordinativ einwertiges primäres Amin, DH einen einwertigen Dimethylglyoximrest und X einen einwertigen Säurerest bedeutet. Wir haben damals auch gezeigt, dass 2 DH sehr fest plan konfiguriert sind und infolgedessen 2A trans-Stellungen besetzen müssen. Es ist noch zu bemerken, dass als A Anilin und seine Homologen leicht und beständig am Zentralkobaltatom koordinierbar sind. In allen bisher gewonnenen Salzen der Reihe sind aber 2A immer primäre Amine oder Pyridin, und ein als A sekundäres bzw. tertiäres Amin enthaltendes Salz ist noch nicht bekannt.

In der vorliegenden Arbeit wurde versucht, Methylanilin als A mit dem Kobaltatom zu verknüpfen und das so erhaltene, kein asymmetrisches Kobaltatom enthaltende Salz in Bezug auf die Stickstoffasymmetrie in die optisch aktiven Komponenten zu zerlegen.

Es soll aber als allgemeine Regel betrachtet werden, dass unter dem primären, sekundären, und tertiären Amin das erste am leichtesten und das letzte am schwersten koordinierbar ist. Dimethylanilin als tertiäres Amin scheint sich ganz schwer zu koordinieren, und wir konnten tatsächlich weder $[\text{Co}\{\text{C}_6\text{H}_5\text{N}(\text{CH}_3)_2\}_2(\text{DH})_2]\text{X}$ noch $[\text{Co}\{\text{C}_6\text{H}_5\text{N}(\text{CH}_3)_2\}(\text{DH})_2]\text{X}$ gewinnen. Methylanilin als sekundäres Amin verknüpft sich leichter als Dimethylanilin, und es gelang uns $[\text{Co}(\text{C}_6\text{H}_5\text{NHCH}_3)(\text{DH})_2]\text{Cl}$ herzustellen, obwohl in diesem Falle das echte Salz $[\text{Co}(\text{C}_6\text{H}_5\text{NHCH}_3)_2(\text{DH})_2]\text{X}$ noch keineswegs erhalten wurde. Wenn das zuletzt beschriebene echte Salz überhaupt erhalten würde, so wäre es doch sehr bemerkenswert, da zwei austauschbare asymmetrische Zentren darin vorliegen, genau wie es bei Weinsäure der Fall ist.

Wir haben daraufhin noch weiter versucht, ob das Salz $[\text{CoAA}'(\text{DH})_2]\text{X}$, worin A Methylanilin und A' irgendein primäres Amin bedeutet, herstellbar ist oder nicht. Falls man als A' Ammoniak bzw. Anilin anwendet, kann man auch kein solches Salz erhalten, sondern nur das Salz $[\text{CoA}'(\text{DH})_2]\text{X}$ d.h. das kein Methylanilin, also kein asymmetrisches Stickstoffatom enthaltende Salz. Dagegen fungiert α - bzw. β -Naphthylamin recht gut als A' um das Salz $[\text{CoAA}'(\text{DH})_2]\text{X}$ zu bilden.

Zu einer alkoholischen Lösung von Kobaltchlorid und Dimethylglyoxim (1 Mol : 2 Mole) fügt man Methylanilin im Überschuss. Wird die Lösung mit Luft oxydiert, so entsteht $[\text{Co}(\text{C}_6\text{H}_5\text{NHCH}_3)(\text{DH})_2]\text{Cl}$. Beim Eintragen von α -

(3) Dieses Bulletin, 11 (1936), 48.

bzw. β -Naphthylamin (1 Mol) scheidet sich das Salz $[\text{Co}(\text{C}_6\text{H}_5\text{NHCH}_3)(\text{C}_{10}\text{H}_7\text{NH}_2)(\text{DH})_2]\text{Cl}$ aus.

Um das oben erwähnte α -Naphthylamin enthaltende Radikal in die optisch aktiven Komponenten zu zerlegen, wurden das d -Camphersulfonat, d - α -Brom- π -camphersulfonat, d -Tartrat und d -Camphernitronat⁽⁴⁾ hergestellt, und alle diese Salze der fraktionierten Kristallisation unterworfen.

Wegen der intensiven Farbe der Lösung war es aber fast unmöglich bei einer Konzentration über 0.05% Drehwerte zu beobachten⁽⁵⁾. Im Falle vom Camphernitronat erschwerte die geringe Löslichkeit und die Unbeständigkeit in der Lösung die Fraktionierung noch mehr.

Das Drehungsvermögen der 0.05%igen Lösung z.B. des Camphersulfonates von jeder Fraktion betrug lediglich $\alpha_D = +0.003^\circ$, und das des Bromcamphersulfonates $\alpha_D = +0.015^\circ$. Die beiden Drehungen stimmten gut überein, jede für sich mit der des Camphersulfonat- und Bromcamphersulfonatradi-kals selbst, woraus folgt, dass kein Beweis für die Aktivierung des Komplexradikals erhalten wurde.

Wenn man auch aus der alkoholischen Lösung fraktioniert und in demselben Lösungsmittel die Drehung beobachtet, kann man zu keinen besonderen Ergebnissen kommen.

Von β -Naphthylamin enthaltenden Salzen mit aktiven Säuren wurden d -Camphersulfonat und d -Camphernitronat hergestellt. Die Farbe dieser Salzreihe ist viel heller als die der α -Salzreihe, aber die Produkte sind viel schwerer löslich; wir konnten auch in diesem Falle keine Aktivierung des Komplexradikals beobachten.

Wie aus der Darstellungsweise der betreffenden Komplexsalze ersichtlich ist, kettet sich Methylanilin aller Wahrscheinlichkeit nach nicht fest genug an das Zentralkobaltatom. Ferner liegt das asymmetrische Stickstoffatom in unserm Falle nicht als Ringglied im Gegenteil zu dem des schon erwähnten Meisenheimerschen bzw. Mannschen Salzes vor; dieser Umstand wirkt immer noch nachteilig auf die Festigkeit der Bindung zwischen Kobalt und dem betreffenden Stickstoff. Auf diese verhältnismässig lockere Verkettung des Methylanilins und auch auf die Anwesenheit des mit dem asymmetrischen Stickstoff direkt gebundenen Wasserstoffatoms muss wohl die recht grosse Razemisierungsgeschwindigkeit zurückzuführen sein, und infolgedessen

(4) Wir haben die Pseudosäure Nitrocampher besonders darum angewandt, weil Werner, *Ber.*, **45** (1912), 865, sonst nicht spaltbares Triäthylendiaminchromsalz und neulich Neogi u. Mukherjee, *J. Indian Chem. Soc.*, **11** (1934), 225, 681, auch sonst unspaltbares Triäthylendiamincadmium- und -zinksalz erfolgreich in die optisch aktiven Komponenten zerlegten.

(5) Beobachtet wurde stets im 1 dm. Rohr bei gewöhnlicher Temperatur.

gelang auch nicht die Spaltung in die optisch aktiven Komponenten. Dass das Sarkosin-diäthylendiamin-kobalt(III)-salz von Meisenheimer in Bezug auf die Stickstoffasymmetrie aktiviert werden konnte, lässt sich dadurch erklären, dass die betreffende Aktivität von der Kobaltaktivität unterstützt wurde.

Beschreibung der Komplexsalze.

Didimethylglyoxim- α -naphthylamin-methylanilin-kobalt(III)-salze. *Das Chlorid.* Man fügt zu einer Lösung von 0.8 g. kristallisiertem Kobaltchlorid und 0.8 g. Dimethylglyoxim in 20 c.c. Alkohol 1.2 g. Methylanilin, dann unter Durchblasen von Luft 0.5 g. in wenig Alkohol gelösten α -Naphthylamins, und setzt die Durchleitung des Luftstroms längere Zeit fort. Das Chlorid scheidet sich in rotbraunen Tafeln aus. Dasselbe Chlorid ist auch aus einer konzentrierten Lösung des unten beschriebenen Acetats oder Camphersulfonats der Reihe beim Zusatz von Natriumchlorid im Überschuss zu erhalten. Nicht gut löslich in Wasser, leicht löslich in Alkohol. (Gef.: Co, 9.20; N, 12.99; H₂O, 11.00. Ber. für [Co(C₆H₅NHCH₃)(C₁₀H₇NH₂)(DH)₂]Cl·4H₂O: Co, 9.12; N, 13.00; H₂O, 11.13%.)

Das Acetat. In eine Lösung von 1.0 g. Dimethylglyoxim und 1.0 g. kristallisiertem Kobaltchlorid in 20 c.c. Alkohol trägt man 1.4 g. Methylanilin und dann unter Einleiten von Luft langsam 0.6 g. in wenig Alkohol gelösten α -Naphthylamins ein. Die so erhaltene dunkelbraune Flüssigkeit wird im Vakuum bei gewöhnlicher Temperatur fast zur Trockne eingengt, und mit Äther völlig ausgewaschen um das überschüssige Methylanilin wegzunehmen. Der Rückstand wird in etwa 40 c.c. Wasser aufgenommen, filtriert und in das Filtrat Ammoniumacetat im Überschuss eingetragen. Rotbraune Kristalle; gut löslich in Wasser und Alkohol. (Gef.: Co, 8.42; N, 12.00. Ber. für [Co(C₆H₅NHCH₃)(C₁₀H₇NH₂)(DH)₂]O₂CCH₃·6H₂O: Co, 8.35; N, 11.90%). Beim Erhitzen auf 110° zersetzt; verliert im Vakuum über konzentrierter Schwefelsäure nur 3H₂O.

Das d-Camphersulfonat. Zu einer warmen Lösung von 1.3 g. Kobaltcamphersulfonathexahydrat⁽⁶⁾ in 15 c.c. Wasser fügt man 15 c.c. Alkohol und 0.5 g. Dimethylglyoxim, und erwärmt um das Dimethylglyoxim in Lösung zu bringen. Während die Lösung noch warm ist, trägt man 0.7 g. Methylanilin und dann unter Durchblasen von Luft 0.3 g. in wenig Alkohol gelösten α -Naphthylamins ein. Die so erhaltene dunkelbraune Flüssigkeit wird im Vakuum bei gewöhnlicher Temperatur etwa bis zum halben Volum eingengt. Nach Schütteln mit Äther wird die verbleibende wässrige Flüssigkeit stehen gelassen. Das Camphersulfonat kristallisiert in gelborangen Tafeln aus. Dasselbe Salz ist auch leicht erhältlich aus einer konzentrierten Lösung des Acetates der Reihe beim Zusatz von Ammoniumcamphersulfonat im Überschuss. Ziemlich gut löslich in Wasser, leicht löslich in Alkohol. (Gef.: Co, 6.94; N, 9.91; H₂O, 8.83. Ber. für [Co(C₆H₅NHCH₃)(C₁₀H₇NH₂)(DH)₂]O₂SC₁₀H₁₅O·4H₂O: Co, 7.00; N, 9.96; H₂O, 8.54%.)

Das d- α -Brom- π -camphersulfonat. Leicht erhältlich aus einer wässrigen Lösung des Camphersulfonates der Reihe beim Zusatz von Ammoniumbromcamphersulfonat. Orangefarbene Nadeln, wenig löslich in Wasser, gut löslich in Alkohol. (Gef.: Co, 6.36; N, 9.45;

(6) Hergestellt aus Kobaltchlorid und Camphersulfonsäure.

H₂O, 6.00. Ber. für [Co(C₆H₅NHCH₃)(C₁₀H₇NH₂)(DH)₂]O₃SC₁₀H₁₄OBr·3H₂O: Co, 6.55; N, 9.29; H₂O, 5.97%.)

Das d-Tartrat. Leicht erhältlich aus einer konzentrierten Lösung des Acetates der Reihe beim Zusatz von Seignettesalz im Überschuss. Orangebraune Nadeln; schlecht löslich in Wasser, leicht löslich in Alkohol. (Gef.: Co, 8.35; N, 11.98; H₂O, 13.98. Ber. für [Co(C₆H₅NHCH₃)(C₁₀H₇NH₂)(DH)₂]C₄H₄O₆·10H₂O: Co, 8.39; N, 11.95; H₂O, 12.80%.)

Das d-Camphernitronat. Erhältlich aus einer Lösung vom / cetat oder Camphersulfonat der Reihe beim Zusatz von Natriumcamphernitronat⁽⁷⁾. Orangefarbene Kriställchen; schwer löslich in Wasser, leicht löslich in Alkohol. (Gef.: Co, 7.46; N, 12.40; H₂O, 6.84. Ber. für [Co(C₆H₅NHCH₃)(C₁₀H₇NH₂)(DH)₂]NO₂C₁₀H₁₄O·3H₂O: Co, 7.46; N, 12.46; H₂O, 6.46%.)

Didimethylglyoxim-β-naphthylamin-methylanilin-kobalt (III)-salze. *Das Acetat.* Die Darstellung entspricht ganz der des α-Salzes. Braune säulenförmige Kristalle; gut löslich in Wasser und Alkohol. (Gef.: Co, 8.37; N, 11.90. Ber. für [Co(C₆H₅NHCH₃)(C₁₀H₇NH₂)(DH)₂]O₂CCH₃·6H₂O: Co, 8.35; N, 11.90%.) Beim Erhitzen auf 110° zersetzlich, verliert im Vakuum über konzentrierter Schwefelsäure kein Gewicht.

Das d-Camphersulfonat. Erhältlich genau wie das entsprechende α-Salz. Gelbe nadelförmige Kristalle; nicht gut löslich in Wasser. (Gef.: Co, 16.74; N, 9.55. Ber. für [Co(C₆H₅NHCH₃)(C₁₀H₇NH₂)(DH)₂]O₂SC₁₀H₁₅O·6H₂O: Co, 6.71; N, 9.54%.) Beim Erhitzen im Vakuum auf 110° verliert das Salz nur 3H₂O.

Das d-Camphernitronat. Die Darstellungsvorschrift dieses Salzes entspricht ganz der des α-Salzes. Gelbes kristallinisches Pulver; sehr wenig löslich in Wasser. (Gef.: Co, 7.18; N, 12.05. Ber. für [Co(C₆H₅NHCH₃)(C₁₀H₇NH₂)(DH)₂]O₂NC₁₀H₁₄O·4H₂O: Co, N, 7.30; 12.12%.) Beim Erhitzen im Vakuum auf 110° verliert das Salz nur 2H₂O.

Herrn S. Murayama sind wir für seine Hilfe bei dieser Arbeit zu Dank verpflichtet.

*Chemisches Laboratorium der
Universität, Taihoku.*

(7) Dargestellt nach Lowry, *J. Chem. Soc.*, **73** (1898), 995.

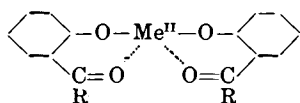
BEITRÄGE ZUR KENNTNIS DER KOMPLEXCHEMISCHEN RINGSYSTEME MIT PARA-BINDUNG.

I. *p*-OXYBENZALDEHYD-*o*-PHENYLENDIIMIN- UND VANILLIN-*o*-PHENYLENDIIMIN-KUPFER.⁽¹⁾

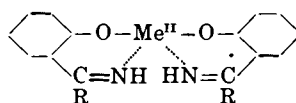
Von Yuichi NAKATSUKA und Hiroshi IINUMA.

Eingegangen am 16. Dezember 1935. Ausgegeben am 28. Mai 1936.

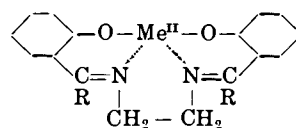
Komplexchemische Fünfer- und Sechseringe, die durch Verknüpfen von *o*-Disubstitutionsprodukten des Benzols mit einem Metallatom gebildet werden, sind vielerlei bekannt. Einige mit der vorliegenden Arbeit in Zusammenhang stehende Verbindungstypen⁽²⁾ seien im folgenden angegeben:



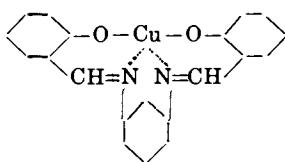
I



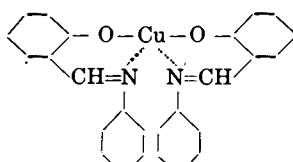
II



III



IV



V

Me'': Cu, Ni, Co, Cd usw.

R: H, Alkyl.

Verbindung IV ist gleichzeitig ein Beispiel einer komplexchemischen Verbindung mit Meta-Bindung. Es scheint noch keine Verbindung sicher bekannt zu sein, die einen durch Verknüpfung von *p*-Stellungen des Benzols mit einem Metallatom gebildeten Ring enthält. Wenn die eben angegebene Verbindung V sich überhaupt als solche betrachten lässt, so dürfte sie wohl als die bisher einzige ihrer Art angenommen werden. In Anbetracht des Valenzwinkels kann man sich vorstellen, dass solche Verbindungen sehr schwer darstellbar sein müssen. Wenn man jedoch die entsprechenden *p*-Derivate des Benzols anstatt der an das Metallatom leicht komplexcyclisch verknüpfbaren *o*-Derivate anwendet, ist die Darstellungsmöglichkeit solcher Verbindungen anscheinend doch nicht ganz ausgeschlossen.

(1) Vorgetragen am 4. April 1935 auf der Hauptversammlung der Japanischen Chemischen Gesellschaft.

(2) Pfeiffer und Mitarbeiter, *J. prak. Chem.*, [2], **129** (1931), 163; *Ann.*, **503** (1933), 84.

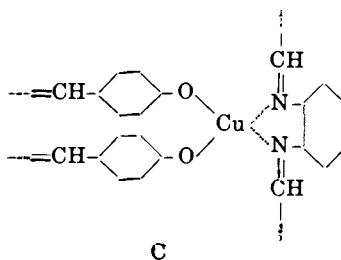
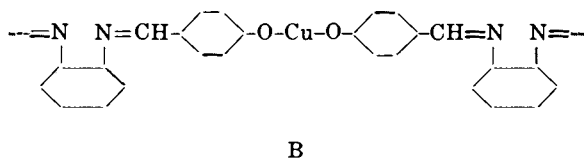
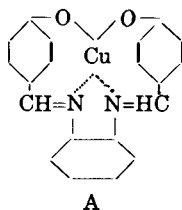
Wie eben erwähnt, verknüpfen sich nach Pfeiffer und Mitarbeitern *o*-Oxyaldehyde bzw. *o*-Oxyketone komplexcyclisch sehr leicht mit dem zweiwertigen Metallatom, und die so erhaltenen Verbindungen kondensieren primäre Amine auch sehr leicht. Um daher komplexcyclische Verbindungen mit Para-Bindung zu gewinnen, haben wir die entsprechenden *p*-Derivate und zwar *p*-Oxybenzaldehyd und Vanillin, und zum komplexchemischen Ringschluss als Metall Kupfer angewandt.

Wir konnten aber weder *p*-Oxybenzaldehyd- bzw. *p*-Oxybenzaldimin-kupfer, noch die entsprechenden Vanillinverbindungen irgendwie darstellen. Aus dem Modell ist es freilich auch leicht zu ersehen, dass in diesen Fällen die Carbonyl- bzw. Iminogruppe vom Zentralkupferatom zu weit entfernt ist um eine Verbindung miteinander zu gestatten.

Bildet *p*-Oxybenzaldehyd-*o*-phenylendiimin mit Kupfer überhaupt ein inneres Komplexsalz, so kommen zwei Stickstoffatome davon, wie ersichtlich, sehr nahe an das Kupferatom, und daher ist es möglich, eine erwünschte Verbindung mit Para-Bindung zu gewinnen. Es gelang uns tatsächlich das Komplexsalz, *p*-Oxybenzaldehyd-*o*-phenylendiimin-kupfer, darzustellen, obwohl dieses *p,o*-Salz selbstverständlich ungleich schwerer zu erhalten ist als das entsprechende *o,o*-Salz.

Das Salz enthält zwei Mole Kristallwasser, löst sich sehr wenig in Methanol und praktisch in fast allen anderen Lösungsmitteln unlöslich. Aus einer grossen Menge Methanol umkristallisiert lässt sich das Salz in Nadeln wasserfrei gewinnen.

Das Molekulargewicht des Salzes konnte nicht bestimmt werden, da es kein geeignetes Lösungsmittel gibt. In Bezug auf die Konstitutionsfrage kommen demnach folgende drei Formeln in Betracht:

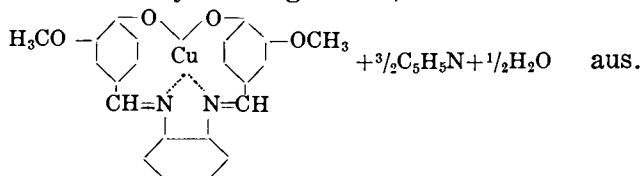


Zuerst ist zu bemerken, dass aus der *p*-Oxybenzaldehyd-imin-kupferreihe nur das *p*-Oxybenzaldehyd-*o*-phenylendiimin-kupfer dargestellt wurde. Alle Versuche, *p*-Oxybenzaldehyd-*o*-phenylendiimin-kupfer (a), *p*-Oxybenzaldehyd-phenylimin-kupfer (b), -*m*-phenylendiimin-kupfer (c) und -*p*-phenylendiimin-kupfer (d) zu gewinnen, verliefen dagegen negativ.

Wenn die Konstitution B richtig wäre, könnten die Salze a, b, c und d ebenfalls alle dargestellt werden; wäre die Formel C richtig, so müssten die Salze a und b auch darstellbar sein.

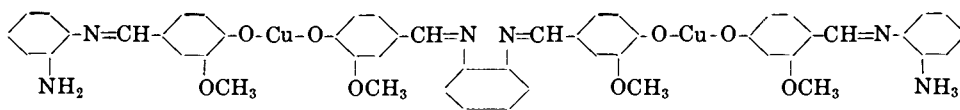
Überdies wird das betreffende Salz, wie oben beschrieben, in gut ausgebildeten Kristallen erhalten; dies lässt den Schluss zu, dass das Molekül des Salzes nicht so sehr gross sein dürfte. Hätte das Salz die Formel B oder C, so müsste das Molekulargewicht sehr gross sein. Mithin kommt die Formel B bzw. C nicht in Frage, und als die einzige richtige bleibt demnach die Formel A mit Para-Bindung.

Die der oben beschriebenen entsprechende Vanillinverbindung, Vanillin-*o*-phenylendiimin-kupfer, konnte auch erst nach mehrmaligen erfolglosen Versuchen erhalten werden. Das Salz ist noch schwerer herstellbar als das oben erwähnte *p,o*-Salz; dies kommt vermutlich daher, dass das Sauerstoffatom des zur Hydroxylgruppe *o*-ständigen Methoxyls des Vanillins durch Ausübung einer Nebenvalenzkraft störend wirkt. Bei der Herstellung dieses Salzes wird Pyridin angewandt, und das Salz kristallisiert als

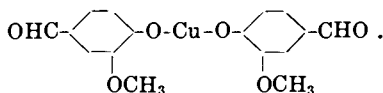


Ausser diesen zwei Para-Bindungen enthaltenden Verbindungen haben wir noch folgende hergestellt:

(1) Vanillin-*o*-phenylendiimin-di-[vanillin-*o*-aminophenylimin]-dikupfer,

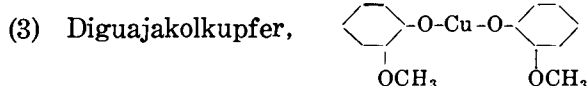


(2) Divanillinkupfer,



Zwei Verbindungen derselben Zusammensetzung wurden gewonnen, die eine in rotorangenen Tafeln und die andere in gelben Nadeln kristallisiert. Ob diese Erscheinung einer Isomerie oder Polymerie zugeschrieben werden muss,

ist nicht klar, da es bisher keine geeigneten Lösungsmittel gibt, womit die Molekülgrösse ermittelt werden kann.



Experimenteller Teil.

***p*-Oxybenzaldehyd-*o*-phenylendiimin-kupfer.** Fügt man zu einer warmen Lösung von 0.8 g. Kupferacetathydrat und 1.0 g. *p*-Oxybenzaldehyd in 30 c.c. Wasser 0.6 g. *o*-Phenylendiamin, so entsteht eine gelbgrüne Trübung. Beim vorsichtigen Erwärmen scheiden sich feine orangefarbene Kriställchen in reichlichen Mengen aus, die noch warm abfiltriert und mit warmem Wasser und Alkohol nachgewaschen werden. (Gef.: Cu, 15.48; N, 6.83; H₂O, 8.56. Ber. für CuC₂₀H₁₄O₂N₂·2H₂O: Cu, 15.37; N, 6.77; H₂O, 8.70%.) Aus Methanol umkristallisiert erhält man das Salz ohne Kristallwasser in orangefarbenen Säulen. (Gef.: N, 7.49. Ber. für CuC₂₀H₁₄O₂N₂: N, 7.41%.)

Vanillin-*o*-phenylendiimin-kupfer. Man löst 1.0 g. Vanillin und 0.4 g. *o*-Phenylendiamin in 20 c.c. 50%igem Alkohol. Fügt man zu dieser einige Zeit erwärmten Lösung eine Lösung von 0.6 g. Kupferacetathydrat und 2 g. Pyridin in 30 c.c. Wasser, so scheiden sich feine nadelförmige orangefarbene Kriställchen aus, die nach gelindem Erwärmen abfiltriert werden. Das Salz löst sich kaum in gewöhnlichen Lösungsmitteln. (Gef.: Cu, 11.28; N, 8.51; C₅H₅N+H₂O, 15.58. Ber. für CuC₂₀H₁₈O₄N₂·³/₂C₅H₅N·¹/₂H₂O: Cu, 11.25; N, 8.68; C₅H₅N+H₂O, 15.60%.)

Vanillin-*o*-phenylendiimin-di-[vanillin-*o*-aminophenylimin]-dikupfer. Man fügt zu einer Lösung von 0.6 g. Phenylendiamin in 30 c.c. 50%igem Alkohol 0.8 g. Vanillin und erwärmt gelinde. Versetzt man mit einer Lösung von 1.0 g. Kupferacetathydrat und 3.6 c.c. 5%igem Ammoniak in 30 c.c. Wasser, so entsteht eine dunkelgrüne Trübung. Beim vorsichtigen Erwärmen auf dem Wasserbade erhält man einen gelbbraunen Niederschlag, der abfiltriert und mit warmem Wasser und Alkohol nachgewaschen wird. Feine körnige Kriställchen, gut löslich in Pyridin, aber kaum löslich in sonstigen gewöhnlichen Lösungsmitteln. (Gef.: Cu, 11.68; N, 7.70; H₂O, 8.43. Ber. für Cu₂C₅₀H₄₄O₈N₆·5H₂O: Cu, 11.82; N, 7.82; H₂O, 8.43%.)

Divanillin-kupfer. Man löst 1.0 g. Kupferacetathydrat in 40 c.c. Wasser, und fügt nach dem Erwärmen über 90° 1.6 g. Vanillin hinzu. Wenn man 3.0 c.c. 5%iges Ammoniak unter Umrühren hineinfließen lässt, so scheiden sich sofort rotorange gefärbte viereckige Tafeln ab, die rasch abfiltriert und mit warmem Wasser und Alkohol nachgewaschen werden. Unlöslich in Wasser, Alkohol und Chloroform, ziemlich gut löslich in Pyridin; leicht zersetzbar durch verdünnte Säuren oder Alkalien. (Gef.: Cu, 17.47. Ber. für CuC₁₆H₁₄O₆: Cu, 17.50%.) Obwohl zur Darstellung Ammoniak verwendet wird, enthält das Salz nach der Analyse keinen Stickstoff.

Wenn man die oben geschilderte Reaktion bei gewöhnlicher Temperatur verlaufen lässt, so erhält man gelbe Nadeln der gleichen Zusammensetzung (Gef.: Cu, 17.63). Dieselben erhält man auch aus der oben beschriebenen rotbraunen Verbindung. In

Methanol löst sich die rotbraune Verbindung ziemlich gut, aber daraus scheidet sich sofort die gelbe Verbindung ab. (Gef.: Cu, 17.45.) Unlöslich in Wasser und Alkohol, schwer löslich in Methanol.

Diguajakol-kupfer. Man löst 0.7 g. Kupferacetathydration in wenig Wasser, trägt 1.0 g. Guajakol ein und erwärmt auf dem Wasserbade. Wenn man 2.7 c c. 5%iges Ammoniak hineinfließen lässt, so fällt ein in gewöhnlichen Lösungsmitteln unlösliches Pulver in reichlichen Mengen aus. (Gef.: Cu, 20.47. Ber. für $\text{CuC}_{14}\text{H}_{14}\text{O}_4$: Cu, 20.54%.) Die Verbindung enthält nach der Analyse keinen Stickstoff.

Herrn S. Murayama sprechen wir unsern wärmsten Dank für seine Hilfe aus.

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SYNTHESE EINIGER BRÜCKENDERIVATE DER WEINSÄURE
DURCH ACETALISIERUNG IHRER ESTER MIT ACETON,
ACETALDEHYD UND FORMALDEHYD.

Von Yojiro TSUZUKI.

Eingegangen an 26. Dezember 1935. Ausgegeben am 28. Mai 1936.

Über die Acetonierung des Weinsäurediäthylesters ist bereits berichtet worden.⁽¹⁾ In dieser Mitteilung wird über die Synthese anderer dergleichen Brückenderivate der Weinsäureester beschrieben und ihre Bedeutung für das Studium über optische Drehung und chemische Konstitution hingewiesen. Nach der bekannten Versuchen von der T. M. Lowry'schen Schule über die Rotationsdispersion der Weinsäurederivate kann man von diesen Brückenderivaten erwarten, dass sie einfache Dispersion zeigen, da in diesen Verbindungen durch Cyclisierung die freie Drehbarkeit der zwei asymmetrischen Zentren um die Zentralbindung völlig behindert ist. Und zwar in solchen Verbindungen könnte man hoffen, irgendwelche Regelmässigkeit in ihrer Molekularrotation, wenn es gelinge, aufzufinden, wie die, die man in den Verbindungen der Zuckergruppe erkennt, wo man der Regelmässigkeit vielleicht in den Verbindungen begegnet, deren Rotationsdispersion einfach ist. In solcher Absicht liefert diese Arbeit vorläufig einige Materiale, die sich hoffentlich zum Verständnis der

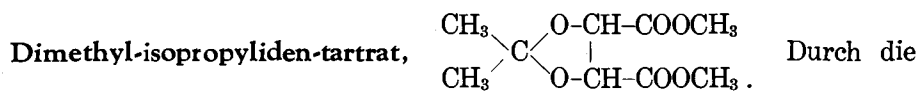
(1) Y. Tsuzuki, dieses Bulletin, **10** (1935), 255.

optischen Aktivität dieser Säure dienen, die uns wegen ihrer verwickelter Natur keine bedeutsame stoichiometrische Betrachtung darüber eine Zeitlang von beinahe einem Jahrhundert seit der Entdeckung ihrer Rotation anstellen gelassen hat. Zur Übersicht werden die physikalische Konstanten tabellarisch zusammengestellt.

Die physikalische Konstanten der Brückenderivate der Weinsäureester.

	Siedep.	d_4^{20}	n_D^{20}	M_D		$[\alpha]_D^{20}$	$[M]_D^{20}$
				Gef.	Ber.		
Diäthyl-isopropyliden-tartrat ⁽²⁾	150°(19 mm.)	1.1175'	1.4334	57.29	57.15	-51.19°(15°)	-125.9(15°)
Dimethyl-isopropyliden-tartrat	139°(16 mm.)	1.1900	1.4372	48.04	47.92	-53.13°	-115.9°
Diäthyl-äthyliden-tartrat	151°(19 mm.)	1.1456	1.4350	52.87	52.54	-74.67°	-173.3° -158.8°*
Dimethyl-äthyliden-tartrat	142°(18 mm.)	1.2382	1.4409	43.51	43.30	-82.17°	-167.7° -151.8°*
Diäthyl-methylen-tartrat	153-4°(19 mm.)	1.1958	1.4400	48.07	47.92	-78.54°	-171.3° -160.3°*
Dimethyl-methylen-tartrat	145°(17 mm.)	1.3073 (untergekühlt)					-156.3°*

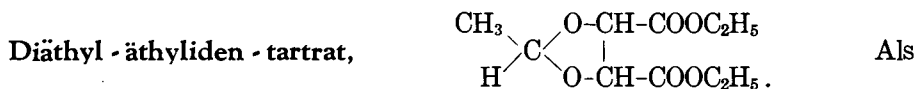
* Die Zahl mit Asterisk zeigt den Wert in Cyclohexan.



Acetonierung des Dimethyltartrats in fast gleicher Weise wie bei Diäthylester⁽¹⁾ synthetisiert. Ausbeute an reinem Ester 47% der Theorie. Die Synthese ist etwas schwerer als bei Diäthylester. Für die Rotationsmessung ist das Produkt besonders sorgfältig gereinigt, weil die Verunreinigung durch kleinste Menge des Ausgangsmaterials, dessen Rotation nach recht ist, stark die Linksdrehung der gebildeten Acetonverbindung herabsetzt. Zu diesem Zwecke wurde die Ätherlösung der Acetonverbindung mit Boraxlösung (wo der Weinsäureester reichlich gelöst wird) und dann mit Wasser mehrmals

(2) Wiederbeschreibung aus der früheren Mitteilung, Y. Tsuzuki, *loc. cit.*

geschüttelt, und durch wiederholte Fraktionierung in Vakuum gereinigt. Farblose Flüssigkeit. Siedep. 139° (16 mm., korr.), d_4^{20} 1.1900, n_D^{20} 1.4372, M_D 48.04 (47.92), $[\alpha]_D^{20}$ -53.13° , $[M]_D^{20}$ -115.9° . Gefunden: C, 49.73; H, 6.60; Aceton (nach Riiper), 26.26. Berechnet für $C_9H_{14}O_6$ (218.11): C, 49.51; H, 6.47; Aceton, 26.61%.



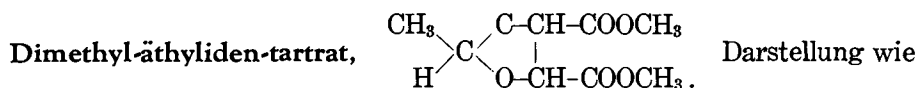
Acetaldehyd - acetal der Weinsäure ist bisher nur eine Diacetal⁽³⁾ bekannt, die durch 2-stündigem Erhitzen von Weinsäure mit Paraldehyd, Chloroform und wasserfreiem Natriumsulfat im Rohr auf 150° erhalten worden ist. Aber um die Verbindung zu gewinnen, die den gleichen Acetaldehydrest an den beiden alkoholischen Hydroxylen trägt, suchte ich den Ester zu acetalisieren. Obgleich die obige Arbeitsmethode bei freier Säure sehr bequem ist,⁽⁴⁾ verläuft beim Ester das Acetalisierungsprozess nicht so glatt. Wenn man den Ester mit ungeeignetem Kondensationsmittel acetalisiert, wird er während der Reaktion verseift und dadurch wird die Ausbeute schlechter. Die bequemste Methode, die ich versuchte, ist eine solche, die als Kondensationsmittel Phosphorpentoxyd zu benutzen.⁽⁵⁾

Zu der Mischung von 20 g. Diäthyltartrat und 10 g. Paraldehyd wurden 14 g. Phosphorpentoxyd in portionsweise während 30 Minuten gegeben. Durch die Reaktionswärme steigt die Temperatur auf $50-60^{\circ}$. Nach 1-stündigem Stehenlassen wurde die schwarzbraun gefärbte Reaktionsmasse mit Äther extrahiert. Die Ätherlösung wurde mit Natriumbikarbonat versetzt (um etwa Phosphorsäure zu neutralisieren), mit Boraxlösung dreimal geschüttelt, mit Natriumsulfat getrocknet. Nach Abdampfen des Äthers wurde der Rückstand in Vakuum fraktioniert. Ausbeute 9 g. Zur völligen Reinigung wurde die Ätherlösung der gereinigten Substanz nochmal mit Wasser geschüttelt, Äther verdampft, und der Rückstand in Vakuum wiederholt fraktioniert. Flüssigkeit. Siedep. 151° (19 mm., korr.), d_4^{20} 1.1456, n_D^{20} 1.4350, M_D 52.87 (52.54). $[\alpha]_D^{20}$ -74.67° , $[M]_D^{20}$ -173.3° , $[M]_D^{20}$ -158.8° (in Cyclohexan). Gefunden: C, 51.66, H, 7.00. Berechnet für $C_{10}H_{16}O_6$ (232.16): C, 51.70, H, 6.95%.

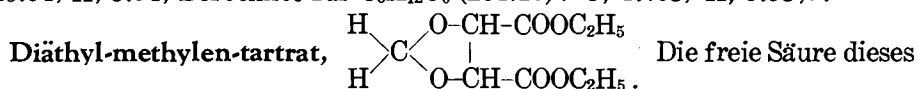
(3) Lobry de Bruyn und van Ekenstein, *Rec. trav. chim.*, **20** (1901), 342.

(4) Mit dieser Methode haben M. H. Palomma und Mitarbeiter neuerdings bei verschiedenen Oxy Säuren (Milch-, Oxybutter-, Methyläthylglykol-, und Diäthylglykolsäure) die entsprechenden Äthylenverbindungen mit guter Ausbeute gewonnen, *Ber.*, **68** (1935), 609.

(5) Vgl. van Ekenstein und Blanksma, *Rec. trav. chim.*, **25** (1906), 162.

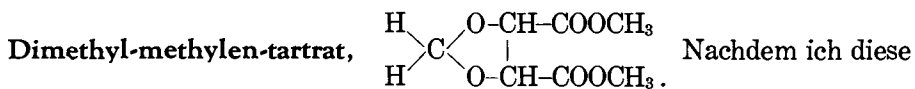


bei Diäthylester, aber bei etwas niedrigerer Temperatur. Die Reinigung ist schwerer, und die Ausbeute geringer. Bessere Ausbeute (20% d. Th.) erhält man durch 4-stündigen Erhitzen von 10 g. Dimethyltartrat mit 6 g. Paraldehyd, 10 g. wasserfreiem Natriumsulfat und 0.5 g. Zinkchlorid im Rohr bei 140°. Flüssigkeit. Siedep. 142° (18 mm., korr.), d_4^{20} 1.2382, n_D^{20} 1.4409, M_D 43.51 (43.30), $[\alpha]_D^{20}$ -82.17°, $[M]_D^{20}$ -167.7°, $[M]_D^{20}$ -151.8° (in Cyclohexan). Gefunden: C, 46.94, H, 5.94, Berechnet für $C_6H_{12}O_6$ (204.10): C, 47.03, H, 5.93%.



Esters, Monomethylen-Weinsäure⁽⁶⁾ ist aus Weinsäure und Polyoxymethylen mittels konzentrierter Schwefelsäure erhalten worden und diente sich zu der wichtigen Beobachtung über die Rotationsdispersion der Weinsäure.⁽⁷⁾ Bei der Acetalisierung des Diäthyltartrats wirkt aber dieser Kondensationsmittel zu heftig und auch beschwert die Reinigung des Produktes. Ich habe darum in folgender Weise gearbeitet, wenn auch nicht ganz bequem.

In 10 g. Diäthyltartrat wurden 4 g. Polyoxymethylen bei 150° gelöst, und dazu 4 g. Zinkchlorid bei 140° hinzugefügt. Nach 30 Minuten Erhitzen bei derselben Temperatur wurde der Ätherauszug aus der klaren schwachgefärbten Schmelze zweimal mit Wasser (aber nicht mit Boraxlösung) geschüttelt, und in üblicher Weise bearbeitet. Ausbeute an reiner Substanz 2.5 g. Eine gleiche Ausbeute erhält man durch die Einwirkung von Phosphorpentoxyd auf dem Gemisch von Ester und Polyoxymethylen. Farblose Flüssigkeit. Siedep. 153-4° (19 mm., korr.), d_4^{20} 1.1958, n_D^{20} 1.4400, M_D 48.07 (47.92), $[\alpha]_D^{20}$ -78.54°, $[M]_D^{20}$ -171.3°, $[M]_D^{20}$ -160.3° (in Cyclohexan). Gefunden: C, 49.35, H, 6.43. Berechnet für $C_9H_{14}O_6$ (218.11): C, 49.51, H, 6.47%.



Verbindung wie beim Äthylester erhalten habe, gelangte mir eine Veröffentlichung von Rule und Cunningham⁽⁸⁾, die dieselbe Verbindung durch Esterifizierung der freien Säure erhalten hatte. Da sie nur eine physikalische Konstante (Schmp. 31.5°) ausser der Molekularrotation ($[M]_{5461}$ in verschiedenen Medien) beschrieben, möchte ich die folgenden Konstanten hinzufügen. Siedep. 145° (17 mm., korr.), $[\alpha]_D^{20}$ -83.3° (in Cyclohexan, 1%), $[M]_D^{20}$ -156.3° (in Cyclohexan), $[\alpha]_D^{33.5}$ -93.4° (in Methanol, 4%).

(6) Lobry de Bryun und van Ekenstein, *Rec. trav. chim.*, **21** (1902), 313.

(7) Austin und Carpenter, *J. Chem. Soc.*, **125** (1924), 1943.

(8) *J. Chem. Soc.*, **1935**, 1038.

Über die obigen Versuchsergebnisse ist zusammenfassend zu bemerken, dass bei Methylestern die Synthese im allgemeinen merklich schwerer und die Ausbeute schlechter ist als bei Äthylestern. Dieser Unterschied kommt daraus, dass Dimethyltartrat leichter hydrolysierbar ist und, dass seine Reaktionsprodukte nicht so schwer löslich in Wasser und nicht so beständig sind wie die Äthyl-derivate, wodurch die Reinigung beträchtlich erschwert wird. Bei der Reinigung erweist sich die Methode im allgemeinen vorteilhaft, welche die Ätherlösung mit Boraxlösung schüttelt, um den unveränderten Ester herauszulösen, aber im Falle der Methylenverbindungen ist diese Methode vielmehr schädlich, weil die Methyl-derivate selbst beträchtlich in dieser Lösung gelöst werden.

Die hier gewonnenen Brückenderivate der Weinsäure sind alle flüssig und folglich wurde die Rotation im homogenen Medium beobachtet, während die von der Lowry'schen Schule erhaltenen befinden sich alle bei gewöhnlicher Temperatur im festen Zustand, so ist die Drehung nur in Lösung beobachtet worden. Man kann erwarten, dass bei diesen polaren Verbindungen der homogene Zustand zwar eine besondere Bedeutung für das Studium der Einflüsse der Lösungsmittel haben möge, obgleich es für den Vergleich der Molekularrotation keine begünstigte Bedingung ist, wenn man bedenkt die experimentellen Versuche von Rule⁽⁹⁾ über die Relation der Rotationsgrösse mit der Polarität der Lösungsmittel sowie die neue Theorie von Boys⁽¹⁰⁾ über die optische Aktivität (des einfachen asymmetrischen Moleküls), die zeigt, dass die Radien der vier Radikale ausserordentlich wirksame Faktoren der Rotationsgrösse sind.

Die hier synthetisierten Verbindungen sind noch in geringer Zahl, so dass sie uns noch nicht etwa theoretische Betrachtung über die Molekularrotation anstellen lassen. Nur sei bemerkt, dass der Äthylester immer stark linksdrehbar ist als der entsprechende Methylester und dass eine Neigung über die Rotationsgrösse: Methylen- > Äthyliden- > Isopropylidenverbindung beobachtet wird. Aber später nach Vermehrung der Tatsachenmateriale möchte ich über die Rotationsgrössen erörtern, die in homogenen sowie in verschiedenen Medien beobachtet werden, und auch über den Einfluss der Lösungsmittel. Über die Rotationsdispersion dieser Brückenderivate wird demnächst veröffentlicht.

*Musashi Hochschule,
Tokio-Nakaarai.*

(9) Seit 1931 (*J. Chem. Soc.*, **1931**, 674) zahlreiche Mitteilungen. Siehe *J. Chem. Soc.*, **1935**, 1038.

(10) *Proc. Roy. Soc., A.*, **144** (1934), 655.

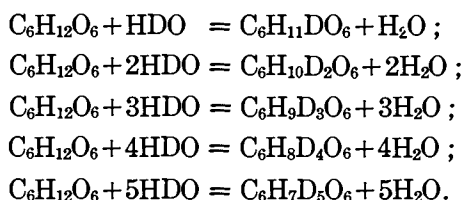
THE EXCHANGE REACTIONS BETWEEN HEAVY WATER AND AMINO ACIDS AND CARBOHYDRATES.

By Eijiro OGAWA.

Received December 26th, 1935. Published May 28th, 1936.

I. The Mechanism of the Exchange Reactions. The electronic structures of the H-substituted compounds and D-substituted compounds are the same. The two compounds only differ in the zero point energy content. It is doubtful that the exchange of H and D in one molecule occurs strictly step by step. The author considered following two assumptions.

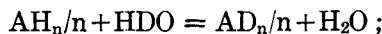
(a) It is assumed that the exchange occurs perfectly at random. Then the following reactions must be considered in the case of glucose for instance.



The concentrations of $\text{C}_6\text{H}_{11}\text{DO}_6$, $\text{C}_6\text{H}_{10}\text{D}_2\text{O}_6$, $\text{C}_6\text{H}_9\text{D}_3\text{O}_6$, $\text{C}_6\text{H}_8\text{D}_4\text{O}_6$, and $\text{C}_6\text{H}_7\text{D}_5\text{O}_6$ can not be obtained from the experiments. But the above hypothesis equals to the assumption that the exchangeable radicals can react quite independently. The equilibrium constant of the reaction $\text{OH} + \text{HDO} = \text{OD} + \text{H}_2\text{O}$ is

$$K_a = \frac{[\text{OD}][\text{H}_2\text{O}]}{[\text{OH}][\text{HDO}]} .$$

Generally on the molecule AH_n which contains n different exchangeable radicals, it becomes as follows :



$$K_m = \frac{[\text{AD}_n/n][\text{H}_2\text{O}]}{[\text{AH}_n/n][\text{HDO}]} .$$

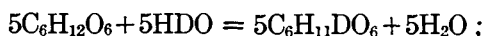
K_m is called the mean equilibrium constant. If the equilibrium constants of each radicals $K_1, K_2, \dots, K_n$ are known, then

$$K_m = (K_1 + K_2 + \dots + K_n)/n .$$

(b) If it is assumed that the exchange reactions proceed strictly step by step as in the ordinary chemical reactions, only one of H-atoms of the exchangeable radicals in one molecule is substituted at first. For instance in the case of glucose the equilibrium constant of the reaction $C_6H_{12}O_6 + HDO = C_6H_{11}DO_6 + H_2O$ is

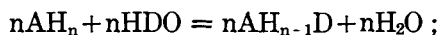
$$K_b = \frac{[C_6H_{11}DO_6][H_2O]}{[C_6H_{12}O_6][HDO]} ; \text{ and } K_b \neq K_a .$$

For five OH-radicals :



$$K = \frac{[C_6H_{11}DO_6]^5 [H_2O]^5}{[C_6H_{12}O_6]^5 [HDO]^5} ; \text{ and } K = K_b^5 .$$

If one molecule contains n different exchangeable radicals, then



$$K_n = \frac{[AH_{n-1}D]^n [H_2O]^n}{[AH_n]^n [HDO]^n} .$$

If $K_{b_1}, K_{b_2}, \dots, K_{b_n}$ are the equilibrium constants of each radical, then

$$\sqrt[n]{K_{b_1} K_{b_2} \dots K_{b_n}} = K_{mb} .$$

K_{mb} is called mean equilibrium constant. The concentration of D-substituted compounds in K_{mb} is expressed approximately by $1/n$ of the decrease in concentration of HDO, when the differences between $K_{b_1}, K_{b_2}, \dots, K_{b_n}$ are not large. The author considered that the mechanism of the exchange reaction is expressed by the assumption (a) approximately and calculated the mean equilibrium constant K_m in the following experiments. Since the concentration of D_2O can not be obtained, it is assumed that all the D in water are in the state of HDO.

II. The Velocity of the Exchange Reactions. Urea was dissolved at $16^\circ C$. in water containing hydrogen isotope and after 5 minutes precipitated perfectly as $CO(NH_2)_2 \cdot 2Hg(NO_3)_2$ with the calculated quantity of $Hg(NO_3)_2 \cdot H_2O$. The results were compared with the value at $22^\circ C$. at equilibrium in the previously published papers (Table 1).

Table 1.

Temperature	Concentration (molarity)	Concentration of HDO	Decrease of concentration of HDO
22°C.	2.000	0.463	0.047
16°C.	2.000	0.458	0.030

Namely the exchange has already reached at 60% of the equilibrium value.

III. The Influence of Catalyser on the Exchange Reactions. In the previously published papers it was reported that the D-content of nitric acid isolated when $\text{CO}(\text{NH}_2)_2 \cdot 2\text{Hg}(\text{NO}_3)_2$ slowly transforms into $\text{CO}(\text{NH})_2 \cdot 2\text{HgNO}_3$ is considerably high. It is probably due to the catalytic action of Hg-salt in solid phase, and DNO_3 , which has lower energy of formation, is first formed.

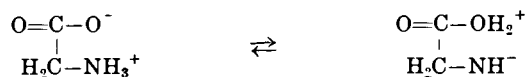
In this paper, in the exchange reaction of glucose the influence of platinum black was examined. The results are shown in Table 2.

Table 2.

Temperature	Pt-black	Conc. of glucose (molarity)	Conc. of HDO (mol)	Decrease in conc. of HDO (mol)	Conc. of H_2O (mol)	K_m
100°C.	0.23 g.	1.110	0.490	0.035	55.054	0.78
100°C.	0	1.459	0.396	0.036	55.149	0.77

K_m values are perfectly coincident, and this indicates that the equilibrium value obtained in the absence of catalyser is the true equilibrium constant.

IV. The Exchange Reactions of Amino Acids. In the previously published paper, in the molecule of glycocoll, it was assumed that COOH and NH_2 in α -position forms internal salt and the following two forms can be in equilibrium :



In this paper the results of glutamic acid and asparagine were examined (Table 3).

Table 3.

Substance	Tem. (°C.)	Conc. (molarity)	Conc. of HDO (mol)	Decrease in conc. of HDO	Conc. of H ₂ O	K _m
Glutamic acid (Kahlbaum)	100	0.647	0.490	0.014	55.033	0.64
Asparagine (Kahlbaum)	100	1.560	0.490	0.040	55.059	0.64

The constitution of glutamic acid and asparagine are $\text{HOOC}\cdot\text{CH}_2\cdot\text{CH}_2\cdot\text{CH}(\text{NH}_2)\cdot\text{COOH}$ and $\text{H}_2\text{NOC}\cdot\text{CH}_2\cdot\text{CH}(\text{NH}_2)\cdot\text{COOH}$ respectively. The exchangeabilities of $=\text{NH}$ and $-\text{COOH}$ were taken as 0.50 and 0.41, respectively, and then the calculated value of K_m is 0.45 for glutamic acid and 0.48 for

asparagine. If the constitution $\begin{array}{c} \text{O}=\text{C}-\text{O}^- \\ | \\ \text{H}-\text{C}-\text{NH}_3^+ \end{array}$ is assumed, then the calculated values become 0.48 for glutamic acid and 0.50 for asparagine using 0.50 for

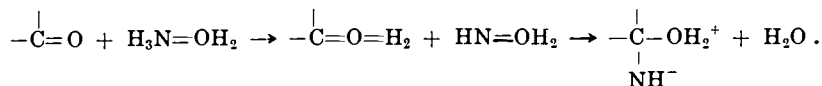
$=\text{NH}$.⁺ If the constitution $\begin{array}{c} \text{O}=\text{C}-\text{OH}_2^+ \\ | \\ \text{H}-\text{C}-\text{NH}^- \end{array}$ is assumed, and the value 0.80 is

taken for the exchangeability of $=\text{OH}^+$ from hydroxylamine hydrochloride, then the calculated values become 0.63 for glutamic acid and 0.62 for asparagine. Both values almost coincide with experimental values.

The electronic structure of N-atom and O-atom are $(1s)^2 (2s)^2 (2p)^3$ and $(1s)^2 (2s)^2 (2p)^4$, respectively. When the above-mentioned structure $\begin{array}{c} \text{O}=\text{C}-\text{OH}_2^+ \\ | \\ \text{H}-\text{C}-\text{NH}^- \end{array}$ is ac-

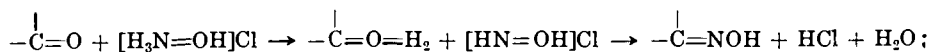
cepted, it follows that two of electrons of 2p level in oxygen atom become valence electrons before two of electrons of 2s level in nitrogen atom do.

The reactions of aldehyde and ketone furnish several illustrations of reactions of this type. For example, in the case of the reaction of aldehyde or ketone with ammonia in water, it follows

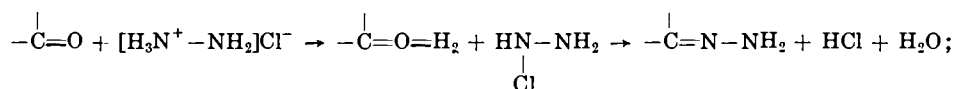


(The structure of ammonium hydroxide was considered as $\text{H}_3\text{N}=\text{OH}_2$ owing to its low dissociation constant, instead of $[\text{NH}_4]\text{OH}$.)

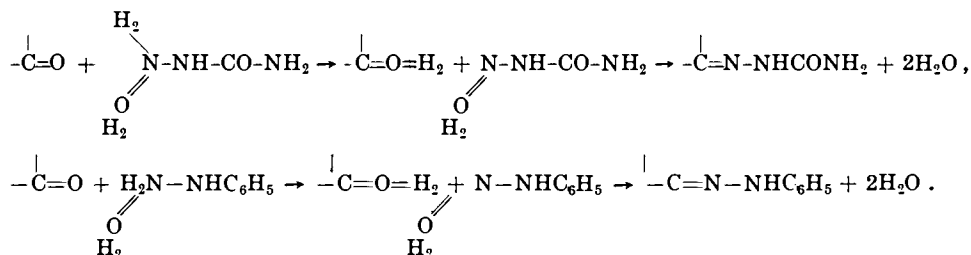
The reaction between aldehyde or ketone and hydroxylamine hydrochloride :



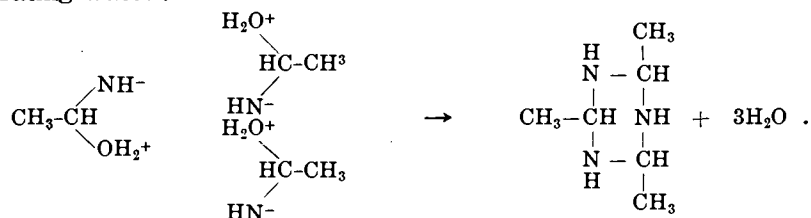
and the reaction between aldehyde or ketone and hydrazine hydrochloride :



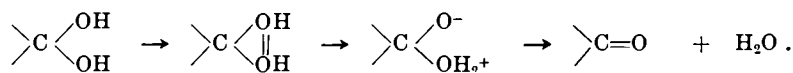
and the reaction between aldehyde or ketone and semicarbazide or phenylhydrazine in water :



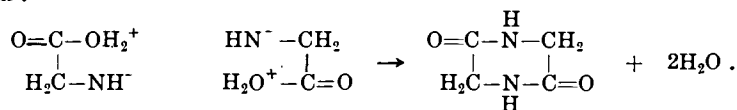
The compound of the constitution of $=\text{OH}_2$ easily loses water, so $\text{H}_3\text{N}=\text{OH}_2$ decomposes into NH_3 and H_2O and aldehyde ammonia easily polymerizes separating water :



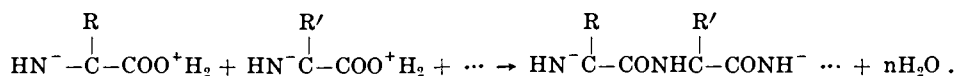
Generally in these examples the oxygen atom takes oxonium structure at first and then separates out as water. This course is probably the actual mechanism of dehydration. For example from two hydroxyl groups one molecule of water separate out in the following manner :



Then the dehydration of amino-acids can be considered easily, assuming the structure of $\begin{array}{c} \text{O}=\text{C}-\text{OH}_2^+ \\ | \\ -\text{C}-\text{NH}^- \end{array}$. From two molecules of glycocoll diketopiperazine is obtained :



Or from several molecules of amino-acids polypeptide is obtained :



V. The Exchange Reactions of the Carbohydrates. The exchangeabilities of fructose, glucose, galactose, maltose, lactose, starch, and inulin were measured. Glucose, galactose, maltose, lactose, and inulin used were the manufactures of Kahlbaum. Starch was a so-called soluble starch. Glucose and galactose were nearly anhydrous. Maltose, lactose, starch, and inulin lost water of 5.0, 1.5, 20.3, and 10.5% of their weights, respectively, when heated at 110°C. for 15 minutes. Glycerin used was 84.73%. D-content of these waters was calculated as 0.020 mol HDO and assumed that this water is miscible completely when solved.

In the case of glycerine the mean value of K_m at 100°C. was 0.46 and at 50°C. 0.64, which correspond to a 40% increase compared with 0.46. The value of fructose was too large compared with other K_m -values. This is probable due to its change of constitution in solution.

Generally the exchangeabilities depend upon polarities, kind and valency states of elements to which exchangeable radicals attach, or molecular structures. In these experiments the constitution of compounds are similar and the exchangeable radical is OH only, so the exchangeability of each OH can be regarded as constant. It becomes more reliable to apply the results of exchangeabilities to the determination of the constitution of these compounds.

K_m -values of glucose and galactose at 100°C. were 0.73 and 0.67, respectively, assuming that hexose has 5 OH; at 50°C. 0.83 and 0.65, respectively. The values of glucose are somewhat higher, but the values of 100°C. and 50°C. are very near in both cases. In the case of glycerin K_m -values at 100°C. and 50°C. indicate that the exchange reaction of hydroxyl radical is exothermic. K_m -value at 50°C. is about 40% larger than the value at 100°C. It is very natural to assume that the exchange reactions of hydroxyl radicals in glucose and galactose are also exothermic. If assumed that the value at 50°C. in glucose and galactose are about 40% larger than those at 100°C., there is no way but to consider the unclosed structure 100°C. If assumed that glucose and galactose have 7 OH at 100°C., K_m becomes 0.58 for glucose and 0.52 for galactose. In these calculations it was assumed that water attached to hexoses contains H_2O and HDO in the same molecular ratio in the solution. The author considers that aldehyde radical of aldose in water solution at 100°C. has the structure such as $\text{>C} \begin{matrix} \text{OH} \\ \text{OH} \end{matrix}$ in large amount and,

Table 4.

Substance	Temp. °C.	Conc.	Conc. of HDO	Decrease in conc. of HDO	Conc. of H ₂ O	K_m
Glycerin	100	6.582	0.355	0.053	55.207	0.49
	100	5.637	0.361	0.042	55.190	0.44
	50	6.146	0.357	0.062	55.214	0.63
	50	4.346	0.369	0.049	55.189	0.65
Fructose	100	1.110	0.490	0.048	55.067	1.08
	50	1.122	0.490	0.051	55.070	1.15
Glucose	100	1.110	0.396	0.028	55.141	0.76 0.60(7OH)
	100	1.110	0.498	0.031	55.032	0.66 0.55(7OH)
	100	1.459	0.396	0.036	55.149	0.76 0.60(7OH)
	50	2.776	0.396	0.067	55.180	0.83
Galactose	100	2.776	0.396	0.057	55.168	0.67 0.52(7OH)
	50	2.776	0.396	0.056	55.169	0.65
Maltose	100	1.354	0.387	0.035	55.157	0.50
	100	0.550	0.485	0.019	55.043	0.51
	100	0.936	0.390	0.025	55.134	0.50
	50	0.550	0.485	0.030	55.054	0.83
Lactose	100	1.357	0.393	0.044	55.160	0.64
	100	1.428	0.393	0.049	55.165	0.69
	50	0.717	0.394	0.031	55.146	0.82
Starch	100		0.361	0.028	55.176	
Inulin	100		0.377	0.032	55.164	

when aldose crystallises, it forms a ring structure containing one molecule of water as water of crystallization.

Maltose is composed from two molecules of glucose losing one molecule of water and lactose is composed from one molecule of galactose and one molecule of glucose. Each molecule has eight hydroxyl radicals. K_m -value of maltose were 0.50 at 100°C. as a mean value and 0.83 at 50°C. K_m -values of lactose were 0.66 at 100°C. as a mean value and 0.82 at 50°C. In these cases the values at 50°C. indicate clearly that the exchange reaction of hydroxyl group are exothermic. There is no need of considering the unclosed structures of disaccharides.

From these values it is concluded that the exchangeabilities of hydroxyl radicals of carbohydrates are about 0.6 at 100°C. and 0.8 at 50°C. Slightly different values are possibly due to the different degrees of dehydration of the

compounds used. The exchangeabilities of the carbohydrates are somewhat higher than that of the aliphatic hydroxyl compounds, namely, glycerin. This is probably due to the ring-form structure of the carbohydrates.

Starch is considered to be composed from anhydrides of maltose. Assuming that at 100°C. the molecule is hydrated such that there are 4 OH for each six of carbon atoms, K_m becomes 0.56. If 5 OH assumed for each six of carbon atoms, K_m becomes 0.46.

Inulin is considered to be composed from anhydride of fructose. If assumed that at 100°C. there are 4 OH for each six carbon atoms, then K_m becomes 0.55. If 5 OH assumed, then K_m becomes 0.44.

From these results it must be concluded that starch molecules in water at 100°C. are hydrated to the state of the constitution very near to those of maltose molecules. Similarly, inulin molecules are hydrated to the state of disaccharide instead of the fructose constitution. It is supposed that in the polysaccharide molecules the molecules of disaccharides become the unit of these structures and have the specially firmly combined constitutions.

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ELECTROLYTIC REDUCTION OF PYRROLE.

By Buhei SAKURAI.

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Reduction of pyrrole which is expected to produce pyrroline or pyrrolidine according to the strength of reduction, has been undertaken by many authors⁽¹⁾ both chemically and electrolytically. The results of their experiments show that the complete reduction is attainable only when some catalysers,⁽²⁾ such as reduced nickel, platinum oxide, palladium oxide or ferric chloride are used in reduction. As to the electrolytical reduction, there is a

(1) Ciamician and Dennstedt, *Ber.*, **16** (1883), 1536; Knorr and Rabe, *Ber.*, **34** (1901), 3491; M. Padoa, *Gazz. chim. ital.*, **36**, II (1906), 317; N. J. Putochin, *Ber.*, **55B** (1922), 2742; Adams, *Chem. Zentr.*, **95** (1924), I, 281; Meta de Jong and J. P. Wibout, *Rec. trav. chim.*, **49** (1930), 237; Zelinsky and Jurjew, *Chem. Zentr.*, **100** (1929), II, 3012; *Ber.*, **64** (1931), 101.

(2) N. J. Putochin, *J. Russ. Chem. Soc.*, **62** (1930), 2216.

German patent by Dennstedt⁽³⁾ who reduced pyrrole in a dilute sulphuric acid solution with a lead cathode and a current density of 1 amp. per sq. cm. and obtained pyrroline. From the results of the researches mentioned above, it seems that the complete reduction of pyrrole is possible only when some catalyser is present, no matter whether the reduction is undertaken chemically or electrolytically.

In the experiments here reported the present writer first tried to reduce pyrrole electrolytically by using zinc amalgam as the cathode. But as it failed to reduce pyrrole completely to pyrrolidine, electrolytic reduction in the presence of reduced nickel and platinum black was next tried. The reduction was carried out in the solution consisting of the mixture of 10% sulphuric acid and alcohol in equal volume and containing the catalyser in suspension. By this process pyrrole was for the first time completely reduced to pyrrolidine which was produced in a 15.6% yield. In this reduction a cathode having high over-voltage is not necessary. Copper gives equally satisfactory results. There was no appreciable difference between nickel and platinum, and strange to say the yield of the reduction product could not be increased above a certain limit by merely increasing the time of electrolysis.

Experiments. The catalyser was prepared in the following way. Nickel sulphate repeatedly recrystallized was dissolved in water, and nickel hydroxide was precipitated from it with sodium hydroxide. The precipitate, after having been filtered and washed with water till no reaction of sulphate appeared in the filtrate, was dried, ignited, and reduced in a combustion tube through which purified hydrogen gas was caused to flow at a temperature of 320-330°. The nickel thus reduced was cooled in the hydrogen gas and kept in absolute alcohol. Platinum black was made from platinum chloride by adding potassium hydroxide solution.

The conditions of the electrolysis were as follows. Cathode: spiral lead tube having surface area of 50 sq. cm.; cathodic solution: mixture of 50 c.c. of 10% sulphuric acid and 50 c.c. of alcohol, to which 2 g. of pyrrole and 0.2 g. of reduced nickel were added; anode: lead plate; anodic solution: 10% sulphuric acid; temperature: 30-34°; current density: 12 amp. per 100 sq. cm.; current quantity: 45 F. per mol.

Pyrrole dissolved in sulphuric acid gradually changes into an insoluble substance of reddish-brown colour on standing. This tendency increases when the density of sulphuric acid increases and the temperature rises. So electrolysis must be carried out with a dilute solution of sulphuric acid at low temperature. As sulphuric acid solution foams vigorously during electrolysis, it is convenient to add some alcohol to the electrolytic solution.

(3) Dennstedt, D. R. P. 127086 (1901).

The whole apparatus was kept in water and through the cathode tube water was caused to flow so as to cool it both from inside and outside, while the cathodic solution was kept stirred all through the electrolysis. As the electrolysis proceeds, the smell of pyrrole decreased gradually and at last completely faded out. After six hours' electrolysis the current was cut. The cathodic solution was taken out, and filtered, and the filtrate was evaporated on the water bath in order to drive off alcohol. The solution was now made alkaline with sodium hydroxide solution, and subjected to steam distillation. The distillate smelling of ammonia was introduced into dilute hydrochloric acid solution, and evaporated to dryness, when 0.5 g. of colourless crystalline material remained as the residue. To separate pyrroline from pyrrolidine as nitrosopyrroline the residue was again dissolved in 15% hydrochloric acid, previously cooled with ice, and 25% potassium nitrate solution was added. After a day it was extracted with ether, but no trace of nitrosopyrroline was obtained. The remaining solution was again made alkaline with sodium hydroxide solution and subjected to steam distillation, and the hydrochloric acid salt of pyrrolidine was isolated from it. Its gold double salt melting at 205° was analysed with the following results: 0.1900 g. of the salt left on ignition 0.0912 g. of gold (Found: Au, 48.10. Cal. for $C_4H_{10}NAuCl_4$: Au, 47.96%).

With a copper tube cathode pyrrolidine was also obtained in nearly the same yield. Even though the electrolysis was continued two or four times longer, the yield of pyrrolidine never increased. The higher current density was unfavourable as it caused a rise of temperature.

When platinum black was used as the catalyser 0.55 g. (corresponding to 17.6%) of hydrochloric acid salt of pyrrolidine was obtained under the same conditions.

The writer expresses his sincere thanks to Dr. Motooki Matsui, President of the Imperial University of Kyoto, at whose suggestion this work was accomplished.

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ZUR KENNTNIS DER FLUORESSENZ VON JAPANISCHEN HYALITEN IM ULTRAVIOLETTEN LICHT.

II. MITTEILUNG.

Von Ei-ichi IWASE.

Eingegangen am 11. April 1936. Ausgegeben am 28. Mai 1936.

Die unter obigem Titel berichteten Tatsachen, dass man die durch Filter-
Ultraviolett erregte Fluoreszenz des Hyalits nur an dem in radioaktivem
Bezirk gesammelten bemerkte, sowie dass dieses Fluoreszenzspektrum gleich
dem des Autunits und dem der Uranylphosphat-Phosphorsalzperle war,
führten mich zur Auffassung, dass der Träger der Fluoreszenz vom Hyalit
das darin enthaltene Uransalz ist.⁽¹⁾

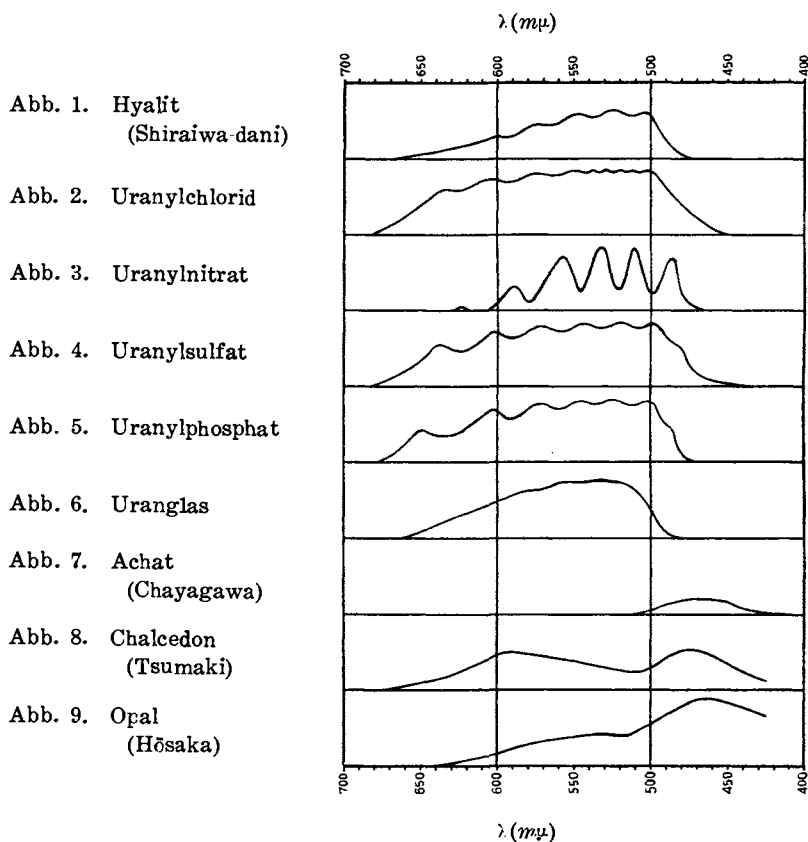
Seit kurzem ist Shiraiwadani bei Kido-mura in Shiga Präfektur als
Lagerstätte bekannt, wo radioaktive Mineralien wie Allanit, Fergusonit,
Gadolinit, Xenotim und radioaktiver Zirkon aufgefunden sind. Herr K.
Masutomi hatte die Güte, mir einige Stücke des Hyalits aus oben erwähnten
Orte zur Untersuchung zu überlassen. In der höchsten Erwartung, dass ich
an diesen Stücken auch die von dem spurenweise beigemengten Uransalze
herrührende Fluoreszenz wahrnehmen könnte, suchte ich sie mit dem durch
Woodsches Glas filtrierten Quecksilberbogenlicht zu beleuchten. Wie in Abb.
1 ersichtlich, ergaben sie wirklich eine Reihe von ziemlich scharfen Fluoreszenz-
banden zwischen 476 und 667 $m\mu$, mit Maxima bei etwa 491, 503, 524, 547, 575
und auch etwa 599 $m\mu$. In den Lagen stimmten diese Fluoreszenzbanden mit
den der schon untersuchten Hyalite aus Naegi und Tanokami überein. Also
konnte ich noch einen anderen fluoreszierenden Hyalit bekommen, dessen
Fluoreszenzfähigkeit zwar auf das darin enthaltene Uransalz zurückzuführen
ist.

Die früheren Beobachtungen, dass das Fluoreszenzspektrum des Hyalits
dem der synthetisch hergestellten Uranylphosphat-Phosphorsalzperle sowie
dem des Autunits identisch ist, ermöglichten mir zu schliessen, dass sich der
Träger der Fluoreszenz im Hyalite, d.h. Uranylsalz vermutlich als Phosphat
vorfindet. Während die Fluoreszenz der Uranylsalze schon von E. L. Nichols
und H. L. Howes unter Zusammenwirken mit E. Merritt, D. T. Wilber und
F. G. Wick⁽²⁾ eingehend und systematisch untersucht worden war, wurden die

(1) E. Iwase, *Sci. Pap. Inst. Phys. Chem. Research, Japan*, **26** (1935), 42.

(2) E. L. Nichols und H. L. Howes, "Fluorescence of the Uranyl Salts," Washington
(1919).

Fluoreszenzspektren einiger Uranylsalze wie Chlorid, Nitrat, Sulfat und Phosphat, zum Vergleich mit meinen gerade geschilderten Resultaten, unter meinen Versuchsbedingungen aufgenommen. Aus den in Abb. 2-5 dargestellten Messergebnissen geht hervor, dass nebst Phosphat noch Sulfat in den Lagen der Fluoreszenzbanden grosse Ähnlichkeit mit den Hyaliten hat.



Ferner zeigte das Uranglas, das ich Herrn S. Ito, Tokio Electric Company, verdankte, weiter verwaschene Fluoreszenzbanden im Gebiete von 480 bis 662 $m\mu$, mit Maxima bei etwa 518, 534, 557 und etwa 579 $m\mu$ (Abb. 6).

Schliesslich wurden einige mit Hyalite verwandte Mineralien untersucht, nämlich schmal milchweiss gestreifte, blass braune Stücke Achat aus Chayagawa bei Osamambe-mura in Hokkaidō, hellbraune Stücke Chalcedon aus Tsumaki bei Mitsukawa-mura in Niigata Präfektur und milchweiss getrübbte Stücke Opal aus Hōsaka in Fukushima Präfektur. Der Achat aus Chayagawa weist eine Bande zwischen etwa 420 und 507 $m\mu$ auf, deren Intensität bei

etwa $470\text{ m}\mu$ am grössten war (Abb. 7). Der Chalcedon aus Tsumaki ergab nun 2 Fluoreszenzbanden. Bei 593 und $470\text{--}475\text{ m}\mu$ bemerkte man ihre Maxima, deren Helligkeit fast gleich war (Abb. 8). Weiterhin bestand die Fluoreszenz des Opal aus Hōsaka aus einer, sehr hellen blauen Bande, ihr Maximum bei $463\text{ m}\mu$ besitzend, und einer mehr verwaschenen grünen, deren Lage sich kaum von der blauen Bande unterschied (Abb. 9). Es ist schon bekannt, dass der Torbenit bei Ultravioletterregung nicht leuchtet. Dies ist auch der Fall mit dem Torbernit aus Yanai in Yamaguchi Präfektur, den mir Herr Prof. K. Kimura an der kaiserlichen Universität zu Tokio freundlichst zur Verfügung stellte.

Zusammenfassung.

Auch aus Shiraiwadani, Shiga Präfektur, einem neulich bekannt gewordenen Produktionsgebiete einiger radioaktiven Mineralien, ist es mir gelungen noch einen fluoreszierenden Hyalit aufzufinden, in Übereinstimmung mit meiner schon veröffentlichten Ansicht, dass dessen Fluoreszenzfähigkeit auf das darin enthaltene Uransalz zurückzuführen ist. Vergleicht man das Fluoreszenzspektrum des Hyalits mit dem der verschiedenen Uranyl-salze, so kann man daraus schliessen, dass sich der Träger der Fluoreszenz vielleicht in Form von Phosphat oder Sulfat vorfindet.

Sowohl Uranglas als auch eine Reihe der Hyalit-ähnlichen Mineralien, z. B. Achat, Chalcedon und Opal, zeigen ganz andere Fluoreszenzspektren als Hyalit. Mit grosser Wahrscheinlichkeit ist zu vermuten, dass in der Lagerstätte fluoreszierenden Hyalits auch radioaktive Mineralien vorkommen.

Herrn Dr. S. Iimori möchte ich an dieser Stelle für sein stets förderndes Interesse meinen wärmsten Dank aussprechen.

*Forschungsanstalt für Physik und Chemie,
Tokio.*

Nachtrag (17. Mai 1936). Ende April dieses Jahrs bekam ich von Herrn Dr. H. Haberlandt in Wien einen Sonderabdruck seiner neuesten Arbeit über "Lumineszenzuntersuchungen an Fluoriten und anderen Mineralien" (*Mitt. d. Inst. f. Ra-Forschung*, Nr. 374; *Wiener Ber.*, IIa, **144** (1935), 665), in dem die Anwesenheit von Uran auch bei einem amerikanischen Hyalit und zwei mexikanischen Hyaliten durch Fluoreszenzspektrum sichergestellt wurde.

THE ACTION OF WEAK ALKALIES UPON GLUCOSE. I⁽¹⁾.

By Ryuzaburo NODZU and Ryoza GOTO.

Received January 25th, 1936. Published June 28th, 1936.

It has been frequently recorded in the literature that by the action of various alkaline reagents, glucose and certain other hexoses can be decomposed into methylglyoxal. Even in the distillation of the sugars with dilute soda solution, A. Fernbach and M. Schoen⁽²⁾, and especially F. Fischler⁽³⁾ have postulated the appearance of methylglyoxal in the distillate. In analogous experiments, however, O. Baudisch and H. J. Deuel⁽⁴⁾ have made plausible the presence of acetol, instead of methylglyoxal, in the distillate, by converting it into 3-hydroxyquinoline which was recognized by its intense colouration. Such a divergency in the results may be due to a slight difference in the experimental conditions. This divergency may, however, also be due to the formation of methylglyoxalphenylosazone (on whose formation the argumentation of most of the previous investigators seems to be mainly based), which can be formed from acetol as well as from methylglyoxal.

It was found in our previous work⁽⁵⁾ that when acetol and methylglyoxal coexist in a solution, they can be respectively identified by converting them into their well known semicarbazones which have quite different solubilities in water. In the present investigation, this principle was applied to the distillate which had been obtained, following Fischler, from a mixture of glucose and $\frac{1}{25}$ mol solution of sodium carbonate (alone or with sodium sulphite). This distillate was warmed on a water bath with an excess of semicarbazide hydrochloride and sodium acetate. And from the reaction product, acetolsemicarbazone in the main and a little diacetyl-bis-semicarbazone were isolated, but no methylglyoxal-bis-semicarbazone was obtained though carefully searched for. The distillate naturally gave methylglyoxalphenylosazone and diacetylphenylosazone when it was treated with phenylhydrazine.

(1) A paper under the same title was read before the 57th annual meeting of the Chemical Society of Japan (April 1935).

(2) A. Fernbach and M. Schoen, *Compt. rend.*, **158** (1914), 976.

(3) F. Fischler, *Z. physiol. Chem.*, **157** (1926), 1; **165** (1927), 53; **175** (1928), 237.

(4) O. Baudisch, *Biochem. Z.*, **89** (1918), 279; O. Baudisch and H. J. Deuel, *J. Am. Chem. Soc.*, **44** (1922), 1585.

(5) R. Nodzu, this Bulletin, **10** (1935), 122.

On the other hand, L. Marchlewski and his co-workers⁽⁶⁾ have found that the absorption spectrum of Fischler's distillate (with Na_2SO_3) is quite different from that of a solution of synthetic methylglyoxal. The cause of this disagreement has been left unexplained.

Now we traced Marchlewski's spectrographic experiments and arrived at results identical with his. As seen in the diagram (Fig. 1) which is prepared in the ordinary way, the absorption curve (Curve I) for Fischler's distillate (0.036% as methylglyoxal, 0.03% as acetol) has its maximum at 2673Å and minimum at 2301Å, figures that agree well with the values (max. 2665Å, min. 2260Å) of Marchlewski. For a solution (0.014%) of synthetic methylglyoxal, however, we found (Curve III₁ for pH 2.7 and III₂ for pH 7.0) the maxima at 2778Å (pH 2.7) and 2832Å (pH 7.0), which is in good agreement with the data of C. Neuberg and Schou (2780Å)⁽⁷⁾, Marchlewski (2765Å, pH 2.7; 2870Å, pH 11), and F. Fischler (2842Å for a neutral solution)⁽⁸⁾.

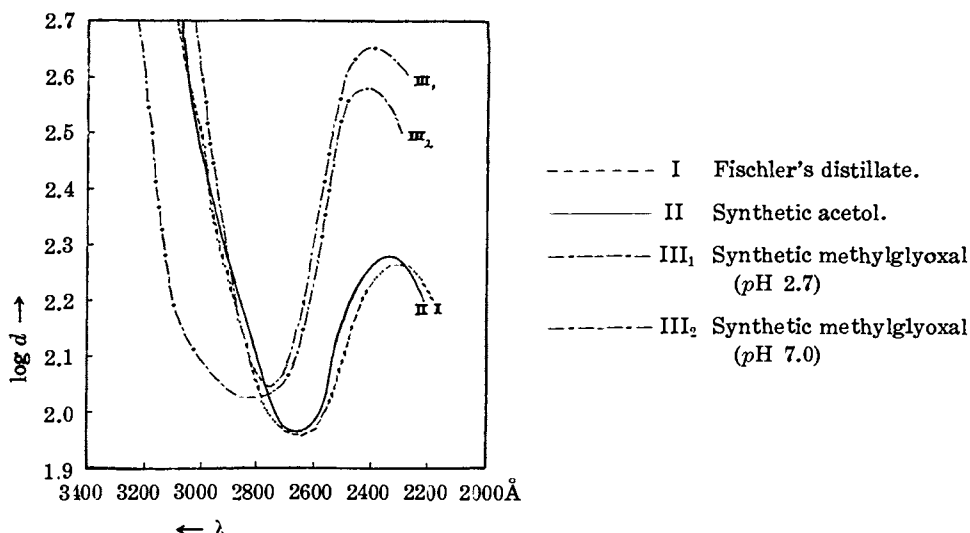


Fig. 1.

Thus we find a wide difference in the characteristics of the absorption curves between the distillate and a methylglyoxal solution.

On the other hand, a solution (0.04%) of synthetic acetol gave an absorption curve (Curve II) which has its maximum at 2680Å and minimum at

(6) L. Kwiecinski and L. Marchlewski, *Bull. Soc. Chim.*, **45** (1929), 610; L. Marchlewski, J. Pizlo, and W. Urbańczyk, *Biochem. Z.*, **264** (1933), 437.

(7) C. Neuberg and S. A. Schou, *Biochem. Z.*, **191** (1927), 469.

(8) F. Fischler, H. Hauss, and K. Täufel, *Biochem. Z.*, **227**, (1930), 161.

2344Å, and closely resembles that of Fischler's distillate (Curve I). A certain quantitative disagreement between the two curves may be partly due to an inaccuracy in the iodometric estimation of acetol⁽⁹⁾ and partly to the presence of some slight impurities, e.g. diacetyl, in the distillate.

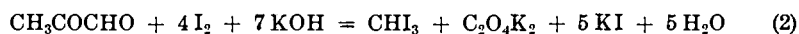
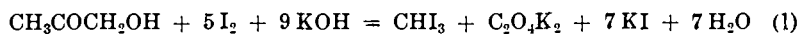
From the above evidence, it can no longer be doubted that it is not methylglyoxal but acetol that gave the methylglyoxalosazone in the distillate. This conclusion is also supported by the fact, which will be reported in a subsequent paper, that synthetic methylglyoxal did not distil over as such in a similar distillation experiment.

Moreover, glucose gives acetol on distillation with solid potassium hydroxide,⁽¹⁰⁾ alkali phosphates (M_2HPO_4) solution⁽¹¹⁾ or zinc carbonate⁽¹²⁾ in water. It seems quite likely, therefore, that acetol rather than methylglyoxal distils over when glucose is distilled with different alkaline reagents.

Experimental Part.

Distillation. $1/25$ Mol sodium carbonate solution was gently distilled, alone or with sodium sulphite, a glucose solution, and after its exhaustion distilled water being supplied drop by drop. The distillate was neutral to litmus paper and reduced Fehling's solution in the cold and gave a marked iodoform reaction.

Estimation of Methylglyoxal and Acetol.⁽¹³⁾ The content of the iodine-consuming substance in the distillate was determined as methylglyoxal by the iodometry of Fischler⁽¹⁴⁾. The value for acetol was obtained from that for methylglyoxal by computation, assuming the equation (1) for acetol instead of Fischler's (2) for methylglyoxal.



Semicarbazones. The distillate was warmed on a boiling water-bath for half an hour with a quantity of semicarbazide hydrochloride and sodium acetate equal to five equivalents to the methylglyoxal content. After letting the reaction product stand overnight, the white precipitate deposited was filtered. In the course of evaporation of the filtrate under reduced pressure to a small volume, a further precipitation occurred and the precipitate was filtered. These precipitates melted above 275°. The filtrate was concentrated over concentrated sulphuric acid in a vacuum desiccator to a syrup from which a brownish yellow solid mass was isolated. This mass was fractionally crystallized from water into a less soluble part (m.p. 245-257°), and a more soluble part (m.p. 194-196°) in major quantity. After recrystallization of these three substances from hot or

(9) See the experimental part.

(10) A. Emmerling and G. Loges, *Ber.*, **14** (1881), 1005; **16** (1883), 837.

(11) Recorded in a hitherto unpublished paper of ours.

(12) W. Löb, *Biochem. Z.*, **12** (1908), 78.

(13) See also this Bulletin, **10** (1935), 124.

(14) F. Fischler and R. Boettner, *Z. anal. Chem.*, **74** (1928), 28.

boiling water, they were identified as diacetyl-bis-semicarbazone (m.p. 279–230°), hydrazodicarbonamide (m.p. 257–258°) — a condensation product of semicarbazide itself — and acetolsemicarbazone (m.p. 198–200°), respectively, by determination of the mixed melting point and elementary analysis: Diacetyl-bis-semicarbazone (Found: C, 36.1; H, 5.8; N, 42. Calc. for $C_6H_{12}O_2N_6$: C, 36; H, 6; N, 42%), hydrazodicarbonamide (Found: N, 47.6. Calc. for $C_6H_6O_2N_4$: N, 47.5%), acetolsemicarbazone (Found: C, 36.6; H, 6.6; N, 31.9. Calc. for $C_4H_6O_2N_3$: C, 36.6; H, 6.9; N, 32%). In spite of careful search, methylglyoxal-bis-semicarbazone could not be isolated from the reaction product. Some experimental results are cited in Table 1.

Table 1.

No.	Glucose (g.)	Na_2CO_3 ($\frac{1}{25}$ mol soln.) (c.c.)	Na_2SO_3 (g.)	Distillate (c.c.)	Iodine consuming substance as acetol. (g.)	Semicarbazone (g.)		
						m.p. 275°	m.p. 245°	m.p. 194°
1	5	250	—	700	0.097	0.01	0.05	0.10
2	5	250	—	700	0.097	0.01	0.04	0.10
3	5	250	15	600	0.114	0.01	0.03	0.11
4	5	250	15	850	0.167	0.02	0.04	0.16
5	5	250	15	250	0.075	0.01	0.04	0.07

Phenylosazone. When the distillate was warmed with phenylhydrazine and acetic acid on a boiling water-bath for an hour, a brownish yellow precipitate was obtained. The insoluble part in hot 60% alcohol of the precipitate was recrystallized from boiling benzene into diacetylphenylosazone; m.p. 241–242°. (Found: N, 23.6. Calc. for $C_{16}H_{18}N_4$: N, 21.1%). By recrystallisation of the soluble part from aqueous alcohol, methylglyoxal-phenylosazone was obtained in a pure state; m.p. 149°. (Found: N, 22.8. Calc. for $C_{15}H_{16}N_4$: N, 22.2%). Neither of the osazones showed any lowering of melting point on admixing with its respective authentic specimen. The data of roughly quantitative experiments are cited in Table 2.

Table 2.

No.	Glucose (g.)	Na_2CO_3 ($\frac{1}{25}$ mol soln.) (c.c.)	Na_2SO_3 (g.)	Distillate (c.c.)	Iodine consuming substance as methylglyoxal. (g.)	Phenylosazone (g.)	
						m.p. 241°	m.p. 149°
1	5	250	15	750	0.168	0.015	0.028
2	5	250	—	750	0.150	0.008	0.024

Methylglyoxal and Acetol. A dilute methylglyoxal solution was prepared by oxidation of glycerol by means of hydrogen peroxide, following C. Neuberg and E. Hofmann's

directions⁽¹⁵⁾. It was acidic (pH 2.7) as already observed by Marchlewski and his collaborator. Acetol ($n_D^{20}=1.4222$, $D_{20}^{20}=1.0850$, b.p.=53-54°/18 mm.) was synthesised from monobromoacetone following A. Levene and A. Walti⁽¹⁶⁾.

The semicarbazones of acetol and methylglyoxal were prepared in a mixed solution, and easily separated from each other, by taking advantage of their difference of solubility in hot water — methylglyoxal-bis-semicarbazone is sparingly soluble, while acetol-semicarbazone easily soluble. It was also observed that the iodometric titration of acetol solution gave a far lower value than the actual one, i.e., 62-65% fluctuating with its concentration (0.2-0.02%). Hence, the iodometric titration does not appear to obey equation (1) merely.

Spectroscopy. For the spectroscopic investigation, Hilger's spectrograph E₂, a Geisler hydrogen tube as the light source and Eastman's panchromatic film were used. The experimental results are graphically shown according to Hartley (Fig. 1). A distillate (0.036% as methylglyoxal, 0.03% as acetol) obtained under the same experimental conditions as No. 5, Table 1, gave an absorption spectrum which is shown as Curve I in Fig. 1. The absorption curves for 0.014% solution of methylglyoxal at pH. 2.7 and pH. 7.0 (after neutralization with Na₂CO₃) are Curves III₁ and III₂, respectively. Curve II is for an acetol solution (0.04%). The acetol and methylglyoxal contents of solutions examined were all determined by iodometry.

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(15) C. Neuberg and E. Hofmann, *Biochem. Z.*, **224** (1930), 491.

(16) A. Levene and A. Walti, "Organic Syntheses", Vol. 10, 1930, p. 1.

ACTION OF LIQUID AMMONIA UPON ACETONE-
COMPOUNDS OF α -HYDROXY-ACIDS⁽¹⁾.

By Haruomi ÔEDA.

Received February 5th, 1936. Published June 28th, 1936.

In a previous communication⁽²⁾ it was reported that acetone-compounds of α -hydroxy-acids were hydrogenated into α -glycols in the presence of a catalyzer generally used in reducing esters into alcohols. In the present communication it will be reported that the acetone-compounds react with ammonia similarly as esters do, giving rise to acid amides.

(1) Studies on Hydroxy-acids and their Derivatives. IV.

(2) This Bulletin, **10** (1935), 531.

The general method for the preparation of acid amides from esters is to pass gaseous ammonia into alcoholic solutions of esters. This method is unfavourable for the present compounds owing to their small solubilities in cold alcohol. The procedure adopted here consists in keeping the acetone-compounds in contact with an excess of liquid ammonia, reaction temperature being varied to find out the best condition for producing acid amides.

In all experiments at elevated temperature (100°) for shorter duration and at room temperature for longer duration it was found that acid amides were readily formed and the following four compounds were prepared from corresponding acetone-compounds.

Amide of <i>dl</i> -lactic acid	$\text{CH}_3\cdot\text{CHOH}\cdot\text{CONH}_2$	m.p. $78.5\text{--}79.0^{\circ}$
Amide of <i>l</i> -leucic acid	$(\text{CH}_3)_2\text{CH}\cdot\text{CH}_2\cdot\text{CHOH}\cdot\text{CONH}_2$	m.p. $84\text{--}85^{\circ}$
Amide of <i>dl</i> -mandelic acid	$\text{C}_6\text{H}_5\cdot\text{CHOH}\cdot\text{CONH}_2$	m.p. $133\text{--}134^{\circ}$
Amide of <i>l</i> -phenyl-lactic acid	$\text{C}_6\text{H}_5\cdot\text{CH}_2\cdot\text{CHOH}\cdot\text{CONH}_2$	m.p. $112.5\text{--}113.5^{\circ}$

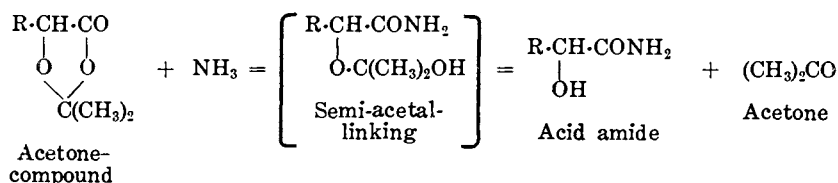
In all cases, the yield in the reaction at room temperature is better than that at elevated temperature and the samples obtained at both conditions are always contaminated with a considerable amount of deeply coloured tarry matter.

Recently Glattfeld and Macmillan⁽³⁾ pointed out the fact that an inequality of reactivity towards ammonia exists between various types of lactones, namely, at the boiling point of liquid ammonia under ordinary pressure, lactones of sugar acid type yielded acid amides, while other lactones such as γ -butyro-lactone failed. At the same condition of temperature, an attempt to obtain acid amides from acetone-compounds was tried.

In the reaction at lower temperature for shorter duration, the procedure was essentially to dissolve the acetone-compound in liquid ammonia kept in a Dewar vessel and to allow the solution to stand overnight. During the reaction ammonia freely evaporated and the temperature in the reaction vessel settled nearly down to -33° , the boiling point of liquid ammonia under ordinary pressure. The amides obtained in these cases were most satisfactory both in purity and in yield (amounting to 85-95%). The same procedure was again tried with ethyl esters of two of these hydroxy-acids. From these esters, amides obtained were but in poor yields (2 and 25%) and larger parts of esters were recovered unattacked. It can be said that here too an inequality of reactivity was observed and acetone-compounds of α -hydroxy-acids are far more reactive to ammonia than the corresponding esters.

The reaction mentioned above can be expressed as the formation of acid amides along with regeneration of acetone:

(3) *J. Am. Chem. Soc.*, **56** (1934), 2481.



Besides the main products, diacetoneamine $(\text{CH}_3)_2\text{C}(\text{NH}_2) \cdot \text{CH}_2 \cdot \text{CO} \cdot \text{CH}_3$, formed by the reaction of ammonia with acetone, was identified.

Experimental Part.

The acetone-compounds were prepared from hydroxy-acids and acetone by dehydration with conc. sulphuric acid⁽⁴⁾. They have the following constants:

Acetone- <i>dl</i> -lactic acid	b.p. 58-59° under 18 mm.
Acetone- <i>l</i> -leucic acid	b.p. 85-86° under 14 mm.
Acetone- <i>dl</i> -mandelic acid	m.p. 46-47°
Acetone- <i>l</i> -phenyl-lactic acid	m.p. 63-64°
Ethyl <i>dl</i> -lactate (Takeda)	b.p. 58° under 19 mm.
Ethyl <i>dl</i> -mandelate ⁽⁵⁾	b.p. 132-133° under 13 mm.

I. Reaction at Elevated Temperature. Twenty to twenty-five grams of acetone-compounds (0.10-0.15 mol) and 20-25 c.c. of dry liquid ammonia (representing 6-7 mols of ammonia to 1 mol of acetone-compound) were put into an autoclave (capacity 250 c.c.), kept below -35° by cooling with solid carbon dioxide and acetone. After closing, the autoclave was maintained at 100° for five hours by immersing it into boiling water.

II. Reaction at Room Temperature. Acetone compound and ammonia (just in the same amount and the same ratio as above) were put into an autoclave (300 c.c.), which was allowed to stand for two weeks at room temperature.

III. Reaction at Lower Temperature. Five to six grams of acetone compounds or esters (0.03-0.04 mol) together with 25-30 c.c. of liquid ammonia (25-30 mols to 1 mol of acetone-compound or ester) were put into a silvered Dewar vessel (capacity 100 c.c.) provided with soda-lime tube and allowed to stand overnight. Though the acetone-compounds seem to be fairly soluble in liquid ammonia, it was necessary to use such a large excess of ammonia so as to cover the whole mass of solid acetone-compound with the liquid.

After the lapse of time mentioned above, the gas-outlet of the autoclave was opened and the remaining ammonia was freely evaporated. The contents of the vessel were in a state of viscous liquid (mandelamide was found as crystalline cake), which were poured into an open dish placed on a water bath. By blowing over the surface of the liquid the evaporation of ammonia was quickened. In general, the amide crystallized as soon as the ammonia was completely removed. The vessels here used were all rinsed with hot alcohol, and the small amount of the amide obtained from the washings was combined with the main crop.

(4) H. Ōeda, this Bulletin, **10** (1935), 187.

(5) Prepared from *dl*-mandelic acid (Merck) and ethyl alcohol by dehydration with conc. sulphuric acid.

The crude amide thus separated was washed with a definite amount of benzene (when cold, it does not dissolve the amide) to remove the tarry matter. The solvent and a little moisture⁽⁶⁾ adhering the amides were completely removed in vacuum. The yields of crude amides⁽⁷⁾ and the analytical results of recrystallized samples are shown in Tables 1 and 2.

Table 1.

Starting material	Acetone-compound			Ester
Reaction temperature	100°	room temp.	ca. -33°	ca. -33°
Lactamide	47%	—	85%	less than 2.5%
Leucic acid amide	49%	79%	90%	—
Mandelamide	70%	92%	95%	25%
Phenyl-lactamide	55%	88%	90%	—

Table 2.

Substance	Solvent of recrystallisation	Analytical results	
		Found	Calculated
Amide of <i>dl</i> -lactic acid ⁽⁸⁾ m.p. 78.5-79°.0 (corr.)	benzene-alcohol (3 : 1)	N, 15.76	C ₃ H ₇ ON : N, 15.74%
Amide of <i>l</i> -leucic acid ⁽⁹⁾ m.p. 84-85° (corr.)	benzene-alcohol (10 : 1)	N, 10.77	C ₆ H ₁₃ ON : N, 10.69%
Amide of <i>dl</i> -mandelic acid ⁽¹⁰⁾ m.p. 133-134° (corr.)	absolute alcohol	N, 9.34	C ₈ H ₉ ON : N, 9.27%
Amide of <i>l</i> -phenyl-lactic acid ⁽¹¹⁾ m.p. 112.5-113.5° (corr.)	benzene-alcohol (2 : 1)	N, 8.46	C ₉ H ₁₁ ON : N, 8.48%
Acid oxalate of diacetoneamine ⁽¹²⁾ m.p. 124-125° (corr.) (hydrate)	95% alcohol	N, 6.49 H ₂ O, 8.22	C ₆ H ₁₃ ON·C ₂ H ₂ O ₄ ·H ₂ O : N, 6.27% H ₂ O, 8.07%

(6) During evaporation of ammonia, owing to considerable cooling condensation of water was unavoidable.

(7) The reaction at lower temperature was tried in a smaller scale corresponding to a quarter of the other reactions. Hence the yields in these experiments are shown by numbers rounded up to every 5 mol %. (Accuracy of weighing was 0.1 g. It corresponds to 2-3 mol % in yields of amides.)

(8) M.p. 74° given by Wislicenus, *Ann.*, **133** (1865), 261.

(9) Amide of active acid is unknown. That of *dl*-acid melts at 51-52°, Nicolle, *Bull. soc. chim.*, [4], **39** (1926), 60.

(10) The same m.p. is given by McKenzie and Wren, *J. Chem. Soc.*, **93** (1908), 311.

(11) M.p. 112-113° given by McKenzie, Martin, and Rule, *ibid.*, **105** (1914), 1588.

(12) M.p. 126-127° given by Everest, *ibid.*, **115** (1919), 591.

In every case, unreacted acetone-compound was never obtained, while in the experiments with esters, 4.1 g. out of 5.3 g. of ethyl lactate and 4.3 g. out of 7.2 g. of ethyl mandelate were recovered from the reaction products by vacuum distillation and amides were isolated from the residue of distillation.

The combined benzene solution obtained from four sets of experiments with acetone-compounds at lower temperature was evaporated to a small bulk, to which a saturated solution of oxalic acid in 95% alcohol was added. The whole mass turned to a crystalline oxalate and it was collected by suction. The oxalate obtained was extracted with a large bulk of boiling 95% alcohol. The unextracted portion was found to be ammonium oxalate by converting it into platinic double chloride (Found: Pt, 43.85. Calc. for $(\text{NH}_4)_2\text{PtCl}_6$: 43.94%). The diluted alcoholic extract was cooled and a little ammonium oxalate again precipitated. After filtration the solution was evaporated to a small bulk, from which an oxalate was isolated. It was found to be acid oxalate of diacetonamine (Table 2).

The tarry matter obtained from the reactions at higher and room temperatures gave also oxalates. But, after removal of the oxalates, there remained a considerable amount of resin, that means the tar comprised a part which did not form oxalate. It did not distil in acidic nor alkaline state even in vacuum, no further study of this resin has been made.

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 his constant encouragements during this study.

ÜBER DIE IN DEN BLÄTTERN VON *FICUS CARICA* ENTHALTENEN BESTANDTEILE.

Von Kunio OKAHARA.

Eingegangen am 17. Februar 1936. Ausgegeben am 28. Juni 1936.

Aus den Blättern von *Ficus Carica* habe ich durch das Ausziehen mit warmem Wasser einen neuen Stoff gewonnen. Dieser Stoff krystallisiert in farblosen Nadeln oder Scheiben vom Schmelzpunkt 161–162°. Seine empirische Zusammensetzung ist $C_{11}H_6O_3$. Diesen Stoff habe ich Ficusin genannt.

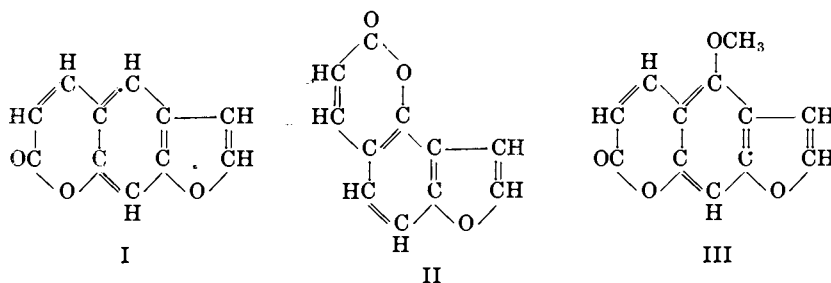
Ficusin besitzt einen bitteren Geschmack, weiter einen schwachen, eigentümlichen Geruch. In kaltem Alkohol löst es sich schwer, leichter in heissem Alkohol, Aceton, Chloroform, Benzol und Essigsäure. Einigermassen löst es sich in warmem Wasser und stellt saure Reaktion dar, doch in kaltem Wasser

ist es kaum löslich. Auch klein ist seine Löslichkeit in kalter Alkalilösung, aber in erwärmter Alkalilösung löst es sich ganz leicht und da kommt gelbe Flüssigkeit vor. Diese alkalische Ficusin-lösung scheidet durch das Ansäuern mit Salzsäure die Ficusinkrystalle wieder ab. Diese Tatsachen lassen vermuten, dass Ficusin einen Laktonkern enthält.

Ficusin lässt sich gegen seinen Schmelzpunkt verflüchtigen. Es besitzt keine Hydroxyl- und Methoxylgruppe, auch keine Carbonylgruppe, denn Phenylhydrazin hat keine Wirkung darauf. Diese Tatsache führt zu der Vermutung, dass zwei von drei Sauerstoffatomen in Ficusin zum Laktonkern und das dritte zu einem ätherischen Sauerstoffatom gehörig sind.

Das Behandeln von Ficusin mit Alkali und Dimethylsulfat liefert Methylficusinsäure $C_{11}H_7O_3(OCH_3)$, Schmp. $161.5-162^\circ$. Bei der katalytischen Reduktion mittels Palladiumschwarzes nimmt Ficusin in alkoholischer Lösung vier Wasserstoffatome auf und dann tritt Tetrahydroficusin $C_{11}H_{10}O_3$ vom Schmp. 154° auf. Also es ist nicht daran zu zweifeln, dass Ficusin zwei Doppelbindungen enthält. Die Oxydation alkalischer Ficusinlösung mit Wasserstoffsuperoxyd ergibt Furan-2,3-dicarbonsäure $C_6H_4O_5$. Daraus lässt sich der Schluss ziehen, dass Ficusin in seinem Molekül einen Furankern enthält.

Die Nitrierung von Ficusin mit Eisessig und konzentrierter Salpetersäure liefert Mononitroficusin $C_{11}H_5O_3(NO_2)$, gelbe Krystalle vom Schmelzpunkt 254° (unter Zers.). Weiter durch die Kalischmelzen lässt sich 4,6-dioxybenzol-1,3-dicarbonsäure (α -Resodicarbonsäure)⁽¹⁾ gewinnen. Der Zusammenfassung aller obengenannten Experimentalsresultaten soll die Konstitutionsformel von Ficusin (I) entsprechen.



Hier die Formel II erweist sich identisch mit derjenigen von Angelicin $C_{11}H_6O_3$ (Schmp. $138-139.5^\circ$), welches neuerdings von E. Späth⁽²⁾ aus *Angelica Archangelica* gewonnen wurde. Ficusin ist also ein Isomer von Angelicin, und im chemischen Aufbau haben die beiden Substanzen starke Ähnlichkeit untereinander.

(1) F. v. Hemmelmayer, *Monatsh.*, **38** (1911), 82; E. Späth, *Ber.*, **64** (1931), 2203.

(2) E. Späth, *Ber.*, **67** (1934), 852.

Weiter aus dem Acetonextrakt der Ficusblätter habe ich nebst Ficusin eine geringe Menge eines anderen Stoffs vom Schmp. 188–189° bekommen; seine Zusammensetzung erweist sich als $C_{12}H_8O_4$. Diese Substanz ist mit Ficusin darin nahe verwandt, dass sie einen Laktonkern enthält, dass in ihr Hydroxylgruppe fehlt, dass sie auf Phenylhydrazin keine Wirkung hat und dass zwischen beiden Verbindungen, hinsichtlich der Löslichkeit in verschiedenen organischen Lösungsmitteln, keinen nennenswerten Unterschied zu bemerken ist. Aber sie lässt sich durch folgendes von Ficusin unterscheiden, nämlich dass sie eine Methoxylgruppe besitzt. Das Behandeln dieser Substanz mit Natriumhydroxyd und Dimethylsulfat ergibt einen Stoff mit der empirischen Zusammensetzung $C_{14}H_{12}O_6$. Schmp. 138°. Die Resultate dieser Experimente zeigen, dass der obengenannte Stoff vom Schmelzpunkt 188–189° mit Bergapten⁽³⁾ identisch sei. Also seine Konstitutionsformel lässt sich mit III darstellen.

Die Experimente.

Die Abtrennung von Ficusin. Der durch das Behandeln von 28 kg. frischer zerquetschter Ficusblätter mit 170 Liter von Wasser während zwölf Stunden bei 90–100° gewonnene Extrakt wurde warm filtriert. Das gelbbraune Filtrat liess sich in Vakuum auf etwa 950 c.c. konzentrieren. Der zurückbleibende Sirup wurde mit 4 Liter von 95 proz. Alkohol, durch 6-stündige Umrühren auf dem Wasserbad ausgezogen. Die Vakuumdestillation dieses Alkoholextrakts scheidet zuerst etwa 2.8 g. von Kaliumnitratkrystallen ab. Bei der Eindampfung lieferte das Filtrat von Kaliumnitratkrystalle, nach der Entfernung von wenigem Chlorophyll und gelbem Farbstoffe mit Tierkohle, Ficusin als farblose Krystallnadeln. Ausbeute 15.6 g. Oder der kondensierte Alkoholextrakt ergab beim Wasserzusatz Ficusin als sehr kleine farblose Krystalle. Aus dem vom grössten Teile von Ficusin abgetrennten Filtrat konnte ich mit einer grossen Menge Äther ungefähr 1.2 g. von dieselben Substanz ausziehen. Also die gesamte Ausbeute von Ficusin erreichte etwa 16.8 g. Zur Umkrystallisierung wandte ich 95-proz. Alkohol an, weil Ficusin in warmem Alkohol leicht löslich und in kaltem Alkohol schwer löslich ist. Dadurch gewann ich etwa 12.2 g. reine Ficusinkrystalle.

Die Ficusinmenge in Ficusblättern ist je nach der Jahreszeit verschieden. Im Juli und August ist diese Menge ziemlich gross, aber nach dem Oktober wird sie viel geringer oder fehlt sogar fast völlig.

Ficusin, $C_{11}H_6O_3$. Ficusin krystallisiert in farblosen Nadeln oder Scheiben vom Schmp. 161–162°, und besteht aus Kohlenstoff, Wasserstoff und Sauerstoff. Die empirische Zusammensetzung erweist sich als $C_{11}H_6O_3$. Es löst sich in kaltem Alkohol schwer, leichter in heissem Alkohol, Aceton, Benzol, Chloroform und Essigsäure. Die Löslichkeit ist darunter in Aceton am grössten. In heissem Wasser löst es sich etwas, aber in kaltem Wasser gar nicht. Es löst sich in wässriger Lösung von Natrium- oder Kaliumhydroxyd. (Gefunden: Molekulargewicht in Campher, 190; C, 70.99; H, 3.29. Berechnet für $C_{11}H_6O_3$: Molekulargewicht, 186; C, 70.95; H, 3.25%.)

(3) C. Pomeranz, *Monatsh.*, **12** (1891), 379; **14** (1893), 28; H. Thoms, *Ber.*, **44** (1911), 3325; **45** (1912), 3705.

Wenig löst Ficusin sich in kalter Lösung von Natrium- oder Kaliumhydroxyd, viel leichter nach der Erwärmung dieser Lösung und ergibt eine gelbe Flüssigkeit. Diese alkalische Lösung scheidet durch das Ansäuern mit Salzsäure Ficusinkristalle wieder ab.

Methylficusinsäure, $C_{10}H_6 \begin{cases} COOH \\ OCH_3 \end{cases}$. 0.3 g. Ficusin wurden in wässriger Lösung von NaOH gelöst und mit Dimethylsulfat und überschüssigem NaOH behandelt. Durch das Ansäuern der Lösung mit Salzsäure wurden farblose Krystallnadeln abgeschieden. Diese Krystalle wurden von der Mutterlauge getrennt, mit Wasser völlig ausgerieben und aus 95-proz. Alkohol umkrystallisiert. Schmp. 161.5–162°. Ausbeute 0.25 g.

Ich habe das Molekulargewicht der Methylficusinsäure durch Titrieren bestimmt. 44.65 mg. der Substanz wurden in 10 c.c. von N/10 Natriumhydroxyd bis zur Auflösung gekocht, dann liess sich diese Lösung nach dem Erkalten mit N/10 Salzsäure neutralisieren (Phenolphthalein als Indikator). Die dafür verbrauchte Salzsäuremenge war 7.944 c.c. (Gefunden: 217.28. Berechnet für $C_{12}H_{10}O_4$, 218.08). (Gefunden: C, 66.02; H, 4.62; CH_3O , 13.91. Berechnet: C, 66.03; H, 4.62; CH_3O , 14.23%.)

Tetrahydroficusin, $C_{11}H_{10}O_3$. 0.4 g. Ficusin werden in 60 c.c. 95-proz. Alkohol gelöst und unter Zusatz von Palladiumschwarz in Wasserstoffatmosphäre geschüttelt. Durch dieses Behandeln bekam Ficusin vier Wasserstoffatome und ergab farblose Krystallprismen, die an der Wand des Apparates anhaftend vorlagen. Die ganze Lösung wird erwärmt um die ausgeschiedenen Krystalle zu lösen und zu filtrieren. Beim Erkalten des Filtrates scheiden sich 0.35 g. Krystalle aus, welche bei 154° schmelzen. (Gefunden: C, 69.76; H, 5.49. Berechnet für $C_{11}H_{10}O_3$: C, 69.44; H, 5.30%.)

Mononitroficusin, $C_{11}H_5O_3(NO_2)$. Die gelbfärbige Lösung, die durch kurzzeitige Erwärmung von 0.5 g. Ficusin mit 2.5 g. Eisessig und 1.5 g. Salpetersäure (Spez. Gewicht 1.4) gewonnen wurde, lieferte durch rasches Giessen auf die Eisstückchen gelben Niederschlag. Dieser Niederschlag wird mit kaltem Wasser völlig durchgerieben und aus 95-proz. Alkohol umkrystallisiert, wobei sich Mononitroficusin in gelben Nadeln ausscheidet. Schmp. 254° (unter Zersetz.). (Gefunden: C, 56.83; H, 2.48; N, 5.70. Berechnet für $C_{11}H_5O_5N$: C, 57.13; H, 2.18; N, 6.06%.)

Die Oxydation von Ficusin mit Wasserstoffsuperoxyd. 0.8 g. Ficusin werden in 80 c.c. 4-proz. methylalkolischer KOH gelöst, stundenlang bei Zimmertemperatur stehen gelassen, Methylalkohol wird in Vakuum ausgetrieben, mit 80 c.c. von 8-proz. Wasserstoffsuperoxyd versetzt und wieder 24 Stunden stehen gelassen. Dann erwärmt man dies während 6 Stunden bei 60°, nach dem Erkalten säuert man es mit Salzsäure an, und dann versetzt man es weiter mit Ammoniak bis zur alkalischen Reaktion und beseitigt die Oxalsäure durch das Zusetzen von überschüssigem Calciumacetat. Dann konzentriert man das Filtrat in Vakuum, extrahiert mit einer grossen Menge von Äther und nach der Abdampfung von Äther zieht man mit Alkohol aus dem Rückstand aus. Die gesamte Ausbeute, die durch die fraktionierte Destillation dieses Auszugs auf Ölbad (80–190°/0.013 mm. Hg) gewonnen wurde, war 88 mg.

Fraktion	I	Sip.	80–100°	ölige
„	II	„	100–150°	farblose Krystalle
„	III	„	150–190°	„ „

Da die Menge der bei 80–150° gewonnenen Substanz sehr klein war, so konnte ich davon eingehende Forschung nicht machen. 35 mg. von bei 150–190° gewonnene Substanz werden wieder im Luftbad (160–170°/0.007 mm. Hg) sublimiert. Ausbeute 28.5 mg.

Diese verflüchtigende Substanz krystallisierte sich aus Eisessig in farblosen Prismen vom Schmelzpunkt 220° (unter Zers.). Ausbeute 20.3 mg. Die Mischprobe mit einem authentischen Präparat von Furan-2,3-dicarbonsäure zeigt keine Schmelzpunktsdepression (Gefunden: C, 46.18; H, 2.78. Berechnet für $C_6H_4O_5$: C, 46.14; H, 2.58%).

Die Kalischmelzen von Ficusin. 1.5 g. Ficusin wurden in wenig Wasser gelöst, mit 15 g. Kaliumhydroxyd bis zum schmelzen erhitzt (bei $208-210^{\circ}$ eine Stunde behalten). Danach wurde das erkaltete Reaktionsprodukt in wenig Wasser gelöst und nach dem Ansäuern mit Schwefelsäure, mit ungefähr sechsmaler Menge von Äther geschüttelt. Der Abdampfungsrückstand dieser ätherischen Lösung wurde in wenig Alkohol gelöst, mit Tierkohle entfärbt und filtriert. Das Filtrat wird auf dem Wasserbad konzentriert, mit Wasser verdünnt (dabei ist das Auftreten des Niederschlags zu vermeiden), und dann im Trockenapparat gelegt. Dadurch gewinnt man farblose Krystalscheiben. Ausbeute 0.16 g. Zur Umkrystallisation war Alkohol anzuwenden. Schmp. 299° (unter Zers.). Ausbeute 0.10 g. In kaltem Wasser lösen sie sich nicht, in warmem Wasser etwas. Am leichtesten lösen sie sich in Äther und Alkohol. Bei Ferrichlorid-Reaktion tritt lebhaft rote Färbung auf. (Gefunden: C, 48.77; H, 3.38. Berechnet für $C_8H_6O_8$: C, 48.47; H, 3.05%.)

Durch das Behandeln mit Diazomethan, die Sublimation im Hochvakuum bei $130-140^{\circ}$ und dann die Umkrystallisierung aus Alkohol, lieferte die durch Kalischmelzen gewonnene Substanz (50 mg.) vom Schmp. 299° (unter Zers.) farblose Krystallnadeln vom Schmp. $147-148^{\circ}$. Ausbeute 35 mg. Die Mischprobe dieser Krystalle mit 4,6-dimethoxybenzol-1,3-dicarbonsäuredimethylester, welcher nach der Methode von F. v. Hemmelmayer und E. Späth dargestellt worden ist, zeigt keine Schmelzpunktsdepression. Also die durch Kalischmelzen gewonnene Substanz ist 4,6-dioxybenzol-1,3-dicarbonsäure (α -Resodicarbonsäure).

Die Abtrennung von Bergapten. Ficusblättern (1875 g.) werden mit Aceten zwei Tage extrahiert und der Extrakt wird durch Destillation eingengt bis die farblosen Krystalle sich an der Kolbenwand auszukrystallisieren beginnen. Der Destillationsrückstand wurde nach der Entfärbung mit Hilfe von aktiver Kohle filtriert und wieder konzentriert. Nach dem Erkalten ergab die Lösung durch Zusatz von Wasser nebst farblosen Krystallen eine gelbbraune harzartige Substanz. Bei der Erwärmung des Gemisches beider Stoffe auf dem Wasserbad mit 10%-igem Natriumhydroxyd lösten sich die farblosen Krystalle auf, aber die gelbbraune harzartige Substanz löste sich gar nicht. Das Filtrat trennte durch das Ansäuern mit Salzsäure wieder farblose Krystalle ab. Ausbeute etwa 5.7 g. Bei der Destillation dieser Krystalle im Hochvakuum mittels des Kempf'schen Sublimationsapparates (im Luftbad von $120-140^{\circ}$), kam das Sublimat an zwei Stellen, d. h. an vorderen und hinteren Teile des Apparates. Durch die mehrmalige Vakuumsublimation beider Teile gewann ich von dem vorderen Teil den Stoff vom Schmp. $161-162^{\circ}$, der nach Mischprobe sich mit Ficusin identisch erwies. Ausbeute ungefähr 3.5 g. Vom hinteren Teil gewann ich den Stoff vom Schmp. $188-189^{\circ}$. Ausbeute etwa 85 mg. Aus der Zusammenfassung folgender experimentaler Resultate lässt sich schließen, dass der Stoff vom Schmp. $188-189^{\circ}$ Bergapten sei (Gefunden: Molekulargewicht in Campher, 203; C, 66.93; H, 3.71; CH_3O , 13.44. Berechnet für $C_{12}H_8O_4$: Molekulargewicht, 216; C, 66.65; H, 3.73; CH_3O , 13.90%).

Methylbergaptensäure, $C_{14}H_{12}O_6$. 20 mg. Bergapten werden in wässrigem NaOH gelöst und mit überschüssigem Dimethylsulfat und Natriumhydroxyd behandelt. Durch das Ansäuern der alkalischen Lösung mit Schwefelsäure wurde Methylbergaptensäure

abgeschieden. Diese wurde mit Äther extrahiert und der beim Abdampfen des Äthers gewonnene Rückstand wurde zweimal in Hochvakuum (Sublimationstemp. 125-130°) sublimiert. Schmp. 138°. Ausbeute 13.1 mg. 6.124 mg. der Substanz wurden in 3 c.c. von N/100 Natriumhydroxyd bis zur Auflösung erwärmt, dann liess sich die Lösung nach dem Erkalten mit 0.735 c.c. von N/100 Schwefelsäure neutralisieren (Phenolphthalein als Indikator). Also es bedarf 2.265 c.c. von N/100 Natriumhydroxyd um 6.124 mg. von Methylbergaptonsäure zu neutralisieren (Gefunden: Molekulargewicht, 270.38; C, 60.95; H, 4.49. Berechnet für $C_{14}H_{12}O_6$: Molekulargewicht, 276.09; C, 60.85; H, 4.38%).

Zum Schluss danke ich Herrn Prof. Dr. R. Majima für seine grosse Unterstützung bei den obenerwähnten Experimenten recht sehr, wie auch Herrn Prof. Dr. Y. Asahina, der mir freundlichst die für die Mischprobe benötigte Furan-2,3-dicarbonsäure zur Verfügung gestellt hat. Der Firma Shionogi & Co. danke ich für die Hilfe, die er mir bei der Ficusinauszüchtung erwiesen hat.

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ON THE OCCURRENCE OF MANY NEW CONSTITUENTS
IN THE UNSAPONIFIABLE MATTER OF
SPERM BLUBBER OIL.

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The occurrence of some new alcohols (C_8 - C_{14}), hydrocarbons and ethers in sperm blubber oil has already been pointed out by the authors⁽¹⁾, and Toyama and co-operators⁽²⁾ have found $C_{14}F_1$ and $C_{16}F_1$ alcohols in sperm blubber oil.

The present authors have made further investigation on the composition of the new constituents which they found in sperm blubber oil and undertaken the naming of these compounds.

A large amount of the unsaponifiable matters used in this investigation was prepared by the method reported in the preliminary report. The distillates which came out until the temperature of oil bath $200^{\circ}C$. under 70 mm., were further fractionally distilled under 15 mm. For the convenience

(1) *J. Soc. Chem. Ind., Japan*, **38** (1935), 608B; *J. Chem. Soc. Japan*, **56** (1935), 1145, 1146.

(2) *J. Chem. Soc. Japan*, **56** (1935), 920.

of the experimental course the distillates were divided into two parts. Part 1 distilled out until 160°C. and part 2 at 160–180°C. By the usual method by means of Na-alcoholate, hydrocarbons and alcohols were separated. The percentages of hydrocarbons and alcohols are as follows :

	Alcohols	Hydrocarbons
Part 1	43	57
Part 2	38	62

Separation of Saturated and Unsaturated Alcohols. Part 1. The mixed alcohols thus separated from hydrocarbons were subjected to the fractional distillation under 15 mm. and the results of the final distillation and characteristics of each fraction are given in Table 1.

Table 1.

Fraction	Temp. (°C.)	Yield (g.)	Iodine value (Wijs)	d_4^{30}	n_D^{30}
1	85–90	2.8	50.1	0.8191	1.4329
2	90–95	3.9	50.8	0.8191	1.4347
3	95–100	5.5	49.1	0.8231	1.4362
4	100–105	12.4	49.2	0.8239	1.4378
5	105–110	6.9	49.2	0.8261	1.4397
6	110–115	6.4	52.6	0.8265	1.4408
7	115–120	3.5	51.9	0.8292	1.4420
8	120–125	4.2	50.6	0.8298	1.4422
9	125–130	2.9	52.6	0.8335	1.4434

From the iodine values of these portions it will be easily seen that each fraction is a mixture of saturated and unsaturated alcohols. For the purpose of separating it into individual alcohols it was acetylated, and then dissolved in ether, and the solution was cooled with ice water and a little excess of bromine was gradually added with constant stirring and care. The ethereal solution was then washed with sodium thiosulphate solution and dehydrated with anhydrous sodium sulphate. The ether was evaporated off on a water bath and the residual liquid was then distilled under 10 mm. The residual bromine was debrominated by usual method and the substance was saponified with alcoholic KOH solution. Free alcohol thus obtained was distilled once more. The results of separation of each fraction are given in Table 2.

Table 2.

	Weight of sample (g.)	Yield (g.)	B. p. (°C.)	d_4^{25}	n_D^{25}	Iodine value (Wijs)
Fraction 3	5.2	{sat. 2.1 unsat. 0.7	88-92/14mm. 95-98/15mm.	0.8249 0.8260	1.4301 1.4413	17.4 111.1
" 4	3.8	{sat. 1.2 unsat. 0.8	104/15mm. 80/15mm.	0.8235 0.8230	1.4330 1.4417	16.7 67.4
" 7	5.5	{sat. 2.0 unsat. 1.0	111/27mm. 105/15mm.	0.8219 0.8443	1.4346 1.4414	15.6 80.4

From the results of the above experiment it seemed possible to complete the separation of saturated and unsaturated alcohols, though a remarkable decrease of yield was unavoidable. The samples were so small in quantity that no further separation by the method has been carried out.

Part 2. The mixed alcohols freed from hydrocarbons were separated in the same way as in part 1. The experimental results are shown in Table 3 and Table 4.

Table 3. Saturated Alcohols.

Fraction	B. p. (°C.)	Yield (g.)	d_4^{25}	n_D^{25}	Iodine value (Wijs)
10	-110	3.3	0.8304	1.4387	28.0
11	110-115	4.1	0.8307	1.4413	23.5
12	115-125	4.5	0.8300	1.4430	27.1
13	125-135	4.7	0.8205	1.4445	22.0
14	135-145	2.4	0.8237	1.4464	24.4
15	145-155	5.6	0.8301	1.4478	22.2
16	155-165	1.9	—	1.4479	13.2
17	165-170	3.0	—	1.4503	14.6
18	170-	0.6	—	—	16.2

Table 4. Unsaturated Alcohols.

Fraction	B. p. (°C.)	Yield (g.)	d_4^{25}	n_D^{25}	Iodine value (Wijs)
19	-145	0.4	—	1.4420	115.4
20	145-155	2.5	0.8325	1.4439	107.3
21	155-165	1.4	0.8341	1.4441	91.8
22	165-175	3.2	0.8406	1.4440	68.5
23	175-185	3.2	0.8592	1.4436	58.2
24	-185/8mm.	5.9	0.8583	1.4435	14.6

Detection of Saturated Alcohols in Each Fraction. (1) *Fractions 1 and 2.* It was recognized that these fragrant fractions contain a small amount of hydrocarbons. From 5.1 g. of the sample, 1.8 g. of the alcohol were taken. It was difficult to separate the saturated alcohol from the mixed alcohols owing to the small quantity, so that the alcohol was brominated immediately and was distilled with care. As the yield obtained in the distillation was only some drops, the authors could not determine boiling point and characteristics. (Found: C, 72.19; H, 13.92. Calculated for $C_7H_{16}O$: C, 72.33; H, 13.89%.) The results of elementary analysis exactly corresponded to heptanol. Though the reaction product of this alcohol with phenyl isocyanate was a liquid, that with 4-iodo-biphenyl-4'-isocyanate was crystals melting at $150.5^\circ C$. From the experimental results it is assumed that the alcohol corresponds to heptanol-(1), but it can not be confirmed because the oxidation product of this alcohol was not investigated.

(2) *Fraction 3.* The sample (2 g.) was fractionated under 17 mm. as follows: fraction A distilling below 95° ; B at $95-97^\circ$; and C over 97° . Fraction B was the main distillate, and A and C were very small in quantity. (d_4^{25} 0.8249, n_D^{25} 1.4302. Found: C, 73.53; H, 13.96%; molecular refraction, 40.77. Calculated for $C_8H_{18}O$: C, 73.77; H, 13.94%; molecular refraction, 40.67.) Phenylurethane and α -naphthylurethane of this alcohol melted at 74° and 65° respectively, and no depression was observed in mixed melting points with corresponding urethanes of octanol-(1) (74° and 65°). (Found for phenylurethane: N, 5.32. Calculated for $C_{15}H_{23}NO_2$: N, 5.62%. Found for α -naphthylurethane: N, 4.50. Calculated for $C_{19}H_{25}NO_2$: N, 4.53%.) The acid amide prepared from this alcohol melted at 97° , and it was identified with caprylamide by mixed melting point (97.5°) with an authentic specimen (Found: N, 9.58. Calculated for $C_8H_{17}NO$: N, 9.78%).

(3) *Fraction 4.* After saturated alcohol was separated from this portion, redistillation was carried out under 15 mm. (Table 5).

Table 5.

Fraction	B. p. ($^\circ C$.)	Yield (g.)	d_4^{25}	n_D^{25}
A	-102	0.9	0.8277	1.4322
B	102-105	2.1	0.8285	1.4330
C	105-	0.8	0.8286	1.4330

Fraction B (Found: C, 74.80; H, 14.11. Calculated for $C_9H_{20}O$: C, 74.91; H, 13.98%) was subjected to the oxidation with dil. HCl and chromic acid

and the product was transformed into acid amide, m.p. 97°C. (Found: N, 8.77. Calculated for $C_9H_{19}NO$: N, 8.91%). There seemed to exist an alcohol having the molecular formula $C_9H_{20}O$, but the occurrence of C_8 - and C_{10} -alcohols has not been determined. A further investigation on this problem will be published in later communication.

(4) *Fractions 5 and 6.* The saturated alcohols (6.1 g.) separated from the unsaturated were distilled under 15 mm. (Table 6).

Table 6.

Fraction	B. p. (°C.)	Yield (g.)	d_4^{25}	n_D^{25}
A	-100	2.1	0.8277	1.4319
B	100-105	1.3	0.8281	1.4329
C	105-110	0.4	0.8285	1.4331
D	110-	0.7	0.8286	1.4333
Residue		0.9	—	—

M. p. of phenylurethane from fraction A	72°
„ „ from octanol(1)	72°
„ „ from fraction B	60.5°
„ 4-iodo-biphenylurethane from fraction B	145°
„ phenylurethane from fraction D	71.5°

It was shown fractions B and D were still impure.

(5) *Fraction 7.* Saturated alcohols (4.8 g.) were fractionally distilled under 15 mm. (Table 7).

Table 7.

Fraction	B. p. (°C.)	Yield (g.)	d_4^{25}	n_D^{25}
A	-115	0.3	0.8290	1.4339
B	115-120	3.0	0.8292	1.4344
C	120-	0.8	0.8294	1.4346

Further fractional distillation of fraction B was carried out under 15 mm. (Table 8).

Table 8.

Fraction	B. p. (°C.)	Yield (g.)	d_4^{25}	n_D^{25}
a	-117	1.4	0.8292	1.4342
b	117-120	1.1	0.8292	1.4345

Fractions a and b were identified with decanol-(1) and the authors propose a name "cachalotyl alcohol" for this alcohol. (Found for fraction b: C, 75.80; H, 14.09%; molecular refraction, 49.84. Calculated for $C_{10}H_{22}O$: C, 75.86; H, 14.02%; molecular refraction, 49.90.) Phenylurethane, m.p. 72.5° (Found: N, 4.88. Calculated for $C_{17}H_{27}NO_2$: N, 5.05%). α -Naphthylurethane, m.p. 66.0° (Found: N, 4.12. Calculated for $C_{21}H_{29}NO_2$: N, 4.15%). Oxidation product of fraction a, m.p. 29°. Acid amide from fraction a, m.p. 106.5° (Found: N, 8.12. Calculated for $C_{10}H_{21}NO$: N, 8.18%).

(6) *Fractions 10, 11, and 12.* Hydrocarbons were completely separated from these fractions in the same way as described above.

(7) *Fraction 13.* After the separation of hydrocarbons the residual alcohol was redistilled under 15 mm.: fraction A (2.0 g.) distilling below 140°, and B (1.4 g.) at 140-150°. Fraction B was combined with next fractions.

(8) *Fractions 14 and 15.* These fractions (7.1 g.) were fractionated under 15 mm.: fraction A (0.4 g.) distilling below 140°, B (6.3 g.) at 140-150°. Fraction B was again distilled under 15 mm. (Table 9).

Table 9.

Fraction	B. p. (°C.)	Yield (g.)	d_4^{25}	n_D^{25}
a	140-142	1.9	0.8300	1.4426
b	142-145	2.5	0.8312	1.4440
c	145-150	1.0	0.8322	1.4457

(Found for fraction b: C, 77.36; H, 14.05; molecular refraction, 59.50. Calculated for $C_{12}H_{26}O$: C, 77.33; H, 14.07; molecular refraction, 59.14.) Phenylurethane, m.p. 68° (Found: N, 4.49. Calculated for $C_{19}H_{31}NO_2$: N, 4.59%). α -Naphthylurethane, m.p. 74° (Found: N, 3.69. Calculated for $C_{23}H_{33}NO_2$: N, 3.83%).

The analytical results correspond to $C_{12}H_{26}O$, and the lower melting point of the phenylurethane from b compared with that of lauryl alcohol is due to the presence of two different saturated alcohols. Phenylurethane obtained by the recrystallisation from methyl alcohol showed m.p. $71^{\circ}C$., while that obtained from the mother liquor melted at $69.5^{\circ}C$. (Found for phenylurethane melting at 71° : C, 66.77; H, 10.41. Calculated for $C_{19}H_{31}NO_2$: C, 66.83; H, 10.24%. Found for phenylurethane melting at $69.5^{\circ}C$.: C, 66.71; H, 10.45. Calculated for $C_{19}H_{31}NO_2$: C, 66.83; H, 10.24%). The authors propose to call these alcohols "catadontidaeyl alcohol" and "isocatadontidaeyl alcohol", respectively.

(9) *Fraction 16.* This fraction is under experiment.

(10) *Water-soluble material.* The sample used in this investigation was collected in the case of distillation of the unsaponifiable matter. The alcohol in this sample was extracted with ether, and transformed into phenylurethane melting at $70^{\circ}C$. The experiments with the acid amide melting at $95-96^{\circ}C$. also showed that this water-soluble material mainly contains octanol-(1).

Detection of Unsaturated Alcohols. The authors could not determine the constituents because of minute amounts of the samples compared with saturated alcohols. The results of analyses are given below.

(1) *Fraction 3.* The characteristics and the results of analysis are as follows: B.p. $94-95^{\circ}C./15$ mm., d_4^{25} 0.8261, n_D^{25} 1.4414. (Found: C, 75.07; H, 12.77%; molecular refraction, 40.99. Calculated for $C_8H_{16}O$: C, 74.92; H, 12.59%; molecular refraction, 40.20.) The authors propose for this alcohol a name "agorophyl alcohol".

(2) *Fraction 4.* Characteristics: B.p. $100-102^{\circ}C./15$ mm., d_4^{25} 0.8340, n_D^{25} 1.4417. (Found: C, 76.71; H, 13.09. Calculated for $C_{10}H_{20}O$: C, 76.84; H, 12.91%.) For the alcohol the authors propose a name "macrocephalyl alcohol".

(3) *Fraction 20.* Characteristics: B.p. $140-141^{\circ}C./17$ mm., d_4^{25} 0.8361, n_D^{25} 1.4433. (Found: C, 77.74; H, 13.27%; molecular refraction, 53.99. Calculated for $C_{11}H_{22}O$: C, 77.75; H, 13.03%; molecular refraction, 53.06.)

By the oxidation with 5% ozone in chloroform solution, a pale yellow ozonide was obtained. The ozonide was decomposed with chromic acid in dilute acid solution and an acidic substance was obtained. It was extracted with ether, and on distilling off the ether an oily substance remained, which was separated into hardly soluble and soluble parts by shaking with water. The melting point of the acid amide obtained from the hardly soluble part through acid chloride, corresponds to peralgonic acid amide. From the soluble part the formation of oxalic acid was recognised. Though the authors

could not identify it with certainty owing to the small quantity of the sample the constitution may be assumed to be as follows: $\text{CH}_3 \cdot (\text{CH}_2)_7 \cdot \text{CH}=\text{CH} \cdot \text{CH}_2\text{OH}$.

(4) *Fraction 2.* Characteristics: B.p. 156–158°C./17 mm., d_4^{25} 0.8405, n_D^{25} 1.4440. (Found: C, 78.25; H, 13.37%; molecular refraction, 58.21. Calculated for $\text{C}_{12}\text{H}_{24}\text{O}$: C, 78.18; H, 13.13%; molecular refraction, 58.67.) The name "odontocetyl alcohol" is proposed.

Hydrocarbons and Ethers. The mixtures of hydrocarbons and ethers obtained by separating alcohols from part 1 and part 2 were fractionally distilled under 70 mm. (Tables 10 and 11).

Table 10. Part 1.

Fraction	B. p. (°C.)	Yield (g.)	d_4^{25}	n_D^{25}	Iodine value (Wijs)
1	100-105	3.5	0.8193	1.4390	90.5
2	105-112	2.6	0.8195	1.4410	97.7
3	112-114	3.5	0.8237	1.4452	95.9
4	114-118	2.9	0.8245	1.4470	96.4
5	118-120	8.0	0.8242	1.4523	98.3
6	120-130	4.6	0.8155	1.4550	105.0
7	130-135	3.4	0.8149	1.4542	105.8
8	135-145	2.7	0.8053	1.4520	
Residue and loss		3.7			

Table 11. Part 2.

Fraction	B. p. (°C.)	Yield (g.)	d_4^{25}	n_D^{25}	Iodine value (Wijs)
9	112-115	1.0	0.8651	1.4762	100.3
10	115-120	2.4	0.8651	1.4741	91.3
11	120-125	2.2	0.8592	1.4708	85.4
12	125-130	3.0	0.8584	1.4680	75.2
13	130-135	2.2	0.8450	1.4657	75.5
14	135-140	4.0	0.8348	1.4600	75.4
15	140-145	2.9	0.8318	1.4600	79.1
16	145-150	8.6	0.8285	1.4600	85.9
17	150-155	5.0	0.8248	1.4593	85.7
18	155-160	9.5	0.8220	1.4581	82.1
19	160-165	5.8	0.8189	1.4568	86.8
20	165-170	7.3	0.8132	1.4552	93.5
21	-140/4mm.	5.3	0.8266	1.4532	83.9

The lower fractions have very sweet odour. With the lapse of time they gradually changed from orange to brown in colour. When these fractions were distilled under atmospheric pressure polymeric substances having high melting points were produced.

Colour Reactions of the Fractions Distilling below 120°/70 mm. The fractions distilling below 120°/70 mm. gave the following colour reactions : (1) On the addition of bromine the colour changed from pink to dark purple through purple. (2) On dropping conc. HCl-alcoholic solution and conc. potassium nitrite solution in the sample and cooling with ice, it gets green colour and the solution showed orange colour on adding to ether. (3) In Denigé's reaction light yellow precipitate was obtained.

The Results of Analyses of the Above-mentioned Fractions (Table 12).

Table 12.

Fraction	Found		Fraction	Found	
	C	H		C	H
3 b.p. 112-114°/70mm. d_4^{20} 0.8200 n_D^{20} 1.4511 iodine value (Wijs) 40.8	81.15	12.64	18	85.40	13.39
	81.43	12.51		85.79	13.00
16	83.39	15.20	20	90.19	9.39
	83.40	15.09		88.89	9.30

Examination of the Fractions below 120°/70 mm.; Detection of a Tertiary Alcohol. The existence of a tertiary alcohol in this fraction was recognised by Denigé's reaction, but separation of it from unsaturated hydrocarbon was very difficult. A further investigation of this problem will be continued.

Ethers. A substance which seemed to be ethers was obtained from the fraction distilling below 120°C./70 mm. by separating alcohols, (Found : C, 81.36, 81.21 ; H, 12.70, 12.91. Calculated for $C_{18}H_{34}O$: C, 81.12 ; H, 12.87%). The absence of tertiary alcohols in this fraction was shown by the negative result of Denigé's reaction. Also the existence of OH-group was not recognised by Tschugajeff-Zerewitinoff's reaction. Accordingly the authors assumed that the oxygen detected by analysis was ethereal oxygen, and gave a general name "sperm oil ethers" and the naming of the individuals is preserved for next report.

The tetrahydro-compound obtained by hydrogenation in the presence of Adams Pt-black catalyst under high pressure (100 atm.) was distilled. The distillate gave the following characteristics: b.p. 223–224°C./75 mm., d_4^{20} 0.8191, n_D^{20} 1.4463 (Found: C, 79.88; H, 14.33%; molecular refraction, 86.64. Calculated for $C_{18}H_{38}O$: C, 79.92; H, 14.16; molecular refraction, 86.03).

The reaction product obtained by heating the tetrahydro-compound (4.2 g.) with HI (sp. gr. 1.7, 10 g.) in a sealed tube 6 hrs, 160°C.), was extracted with ether, washed with water, and fractionally distilled under 15 mm.: A –100°C., 0.2 g.; B 100°C.–, 0.3 g.; C residue, 2.2 g. Crystals obtained from fraction B and 4-iodo-biphenyl-4'-isocyanate melted at 145°C. corresponding to decanol-(1). From fraction A crystals could not be expected. Though the authors could not give a determinate constitution for this hydrogenated ether, they assumed the following: $C_{10}H_{21}-O-C_6H_{17}$.

In the same way as mentioned above ethers were separated from fraction 6, yield 0.2 g., b.p. 126°C./70 mm. (Found: C, 81.82; H, 13.40. Calculated for $C_{20}H_{38}O$: C, 81.55; H, 13.02%).

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ERZEUGUNG DES LEICHTEN WASSERS UND BESTIMMUNG
DER DEUTERIUM-KONZENTRATION IM
NORMALEN WASSER⁽¹⁾.

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Inhaltsübersicht. Es wurde leichtes Wasser durch die fraktionierte Elektrolyse von gewöhnlichem Wasser hergestellt, und der Sauerstoff des so gewonnenen leichten Wassers wurde durch den des gewöhnlichen Wassers ersetzt. Das spezifische Gewicht dieses leichten Wassers, das praktisch von Deuterium frei war, aber dessen Sauerstoff genau dieselbe Isotopenzusammensetzung wie der des gewöhnlichen Wassers besass, erwies sich bei 9.5°C. um $18.7 \pm 0.5 \gamma$ kleiner als das des Osaka-Leitungswassers. Daraus folgte,

(1) Vorläufig mitgeteilt in diesem Bulletin, **10** (1935), 257.

dass das D/H Verhältnis im letzteren 1 : 5600 ist. Daran anschliessend wurden die bisher veröffentlichten Daten von anderen Autoren kritisch durchgesehen, besonders betreffs der Isotopenzusammensetzung des Sauerstoffs, der von ihnen benutzt wurde.

Einleitung. Die Bestimmung von Deuterium-Konzentration in gewöhnlichem Wasser wurde schon von vielen Forschern auf verschiedenen Wegen durchgeführt. Die dabei verwendeten Methoden kann man nach ihren Prinzipien etwa in vier Gruppen einteilen.

(1) *Die spektroskopische Methode.* Anschliessend an die Entdeckung von Deuterium, schätzten Urey, Brickwedde und Murphy⁽²⁾ das D/H Verhältnis in gewöhnlichem Wasserstoff nach der Intensität der Balmerlinien von H und D. Dadurch fanden sie, dass $D : H = 1 : 4000$ ist.

(2) *Die massenspektroskopische Methode.* Die genauen Daten über das D/H Verhältnis in gewöhnlichem Wasser wurden zuerst von Bleakney und Gould⁽³⁾ durch massenspektroskopische Studien gewonnen. Sie zersetzten Regenwasser vollständig mittels erhitzter Eisenspäne und unterwarfen den dadurch erhaltenen Wasserstoff einer massenspektroskopischen Untersuchung. Bei diesem Versuche fanden sie, dass in gewöhnlichem Wasser $D : H = 1 : 5000$ ist. Dieser Wert ist bisher am allgemeinsten aufgenommen worden.

(3) *Die Methode, bei der die Geschwindigkeit der Anreicherung von Deuterium bei der Elektrolyse des Wassers benutzt wird.* Lewis und Macdonald⁽⁴⁾ schätzten das D/H Verhältnis in gewöhnlichem Wasser nach der Geschwindigkeit der Anreicherung von Deuterium bei der Herstellung des schweren Wassers durch die Elektrolyse des Wassers und fanden, dass $D : H = 1 : 6500$ ist. Auf einem ähnlichen Prinzip beruhte auch die Methode, die von Edwards, Bell und Wolfenden⁽⁵⁾ zur Bestimmung des Deuterium-Gehalts des gewöhnlichen Wassers benutzt wurde. Der von ihnen gefundene Wert war $D : H = 1 : 6220$.

(4) *Die Methode, die auf der Erzeugung des leichten Wassers beruht.* Eine andere zuverlässige Methode, die uns die Konzentration des Deuteriums in gewöhnlichem Wasser bestimmen lässt, besteht darin, dass man das Wasser auf irgendeine Weise von Deuterium befreit und das spezifische Gewicht des so erzeugten leichten Wassers im Verhältnis zu dem des gewöhnlichen Wassers bestimmt. Die Erzeugung des leichten Wassers kann man am zweckmässigsten durch die fraktionierte Elektrolyse des Wassers ausführen. Diese

(2) H. C. Urey, F. G. Brickwedde und G. M. Murphy, *Bull. Am. Phys. Soc.*, **6** (1931), 17; *Phys. Rev.*, **39** (1932), 164, 864; *ibid*, **40** (1932), 1.

(3) W. Bleakney und A. J. Gould, *Phys. Rev.*, **44** (1933), 265.

(4) G. N. Lewis und R. T. Macdonald, *J. Chem. Physics*, **1** (1933), 341.

(5) A. J. Edwards, R. P. Bell und J. H. Wolfenden, *Nature*, **135** (1935), 793.

Methode ist vielleicht am häufigsten im Vergleich mit den anderen zur Bestimmung des Deuterium-Gehalts von gewöhnlichem Wasser benutzt worden. Aber merkwürdigerweise gehen die dadurch erhaltenen Daten manchmal sehr weit auseinander, wie später gezeigt wird.

Wir wollten auch nach Methode 4 den Deuterium-Gehalt des Osaka-Leitungswassers bestimmen. Aber inzwischen haben wir gefunden, wie wir schon vorläufig mitteilten⁽⁶⁾, dass der Sauerstoff in der Luft spezifisch um 7 γ schwerer ist als der Sauerstoff, der in Wasser chemisch verbunden ist. Es ist ohne weiteres klar, dass dieser Unterschied auf das Resultat des Experiments, wenn man nach Methode 4 den Deuterium-Gehalt von Wasser bestimmen will, einen merklichen Einfluss ausüben kann. Wegen dieser Sachlage haben wir in der vorliegenden Arbeit besonders auf die Isotopenzusammensetzung des verwendeten Sauerstoffs achtgegeben.

Versuch A. Das leichte Wasser wurde zuerst, wie gebräuchlich, durch sukzessive Elektrolyse des gewöhnlichen Wassers hergestellt. Dem Osaka-Leitungswasser wurde NaOH 0.5 N zugesetzt und zwischen Nickel-Elektroden elektrolysiert. Der Knallgasstrom aus dem Elektrolysiergefäß wurde sorgfältig getrocknet, und ebensogut getrocknete Luft zugesetzt. Das so bereitete Gasgemisch wurde dann über das, bis auf 300°C. erhitzte Kupferoxyd geleitet und dort katalytisch zu Wasser rekombiniert. Auf der ersten Stufe der Elektrolyse wurde nur 1/10 Volumen des originalen Wassers zersetzt und rekombiniert. Dem dadurch entstandenen Wasser wurde wieder NaOH zugesetzt, und es wurde der zweiten Stufe der Elektrolyse unterworfen. Aber auf dieser Stufe wurde bis zu 1/2 Volumen des Elektrolysiervassers 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 bei der zweiten Stufe durchgeführt. Nach jeder Stufe der Elektrolyse wurde das rekombinierte Wasser sorgfältig gereinigt und dessen spezifisches Gewicht im Verhältnis mit dem des ebensogut gereinigten Osaka-Leitungswassers bei 18.9°C. bestimmt. Die Dichtemessung führten wir mittels eines Quarzschwimmers⁽⁷⁾ durch. Die Messgenauigkeit dürfe $\pm 0.5 \gamma$ sein. Wir haben zwei Reihen von fraktionierten Elektrolysen durchgeführt. Bei der ersten, ausgegangen von 10 l. Leitungswasser, wiederholten wir die Elektrolyse dreimal, und bei der anderen, ausgegangen von 5 l. originalem Wasser, wurden die sukzessiven Elektrolysen fünfmal

(6) N. Morita und T. Titani, dies Bulletin, **11** (1936), 36. In der vorläufigen Arbeit haben wir gefunden, dass der Dichteunterschied $8 \pm 2 \gamma$ ist. Aber aus dem genaueren Versuch ergab sich, dass er $7 \pm 1 \gamma$ ist. (Vgl. die nächste Mitteilung.)

(7) Der Schwimmer wurde von Dr. Harada in unserem Laboratorium konstruiert.

nacheinander ausgeführt. Die dadurch erhaltenen Ergebnisse gibt Tabelle 1 wieder.

Tabelle 1. Versuch A.

Stufe der Elektrolyse		1	2	3	4	5
Δs in γ	I. Reihe	14.9	18.3	19.4	—	—
	II. Reihe	14.2	18.4	19.2	19.2	19.2

Die Zahlen geben die Abnahme im spezifischen Gewicht des rekombinierten Wasser in γ Einheiten im Vergleich zu dem des originalen Wassers.

Aus Tabelle 1 ersieht man, dass das spezifische Gewicht des rekombinierten Wassers nach der dritten Stufe der Elektrolyse unabhängig von der Zahl der Elektrolysen konstant geworden ist. Dies kann auch aus der Trennungsfähigkeit der Elektrolyse wohl zu erwarten sein, angenommen, dass die Abnahme des spezifischen Gewichts allein von der Befreiung von Deuterium herkäme. Aber, wie schon von vielen Autoren darauf hingewiesen wurde, sollen auch die Sauerstoffisotopen durch die Elektrolysen mehr oder weniger getrennt worden sein. Es wurde von Johnston⁽⁸⁾ in seinem Versuche zur Erzeugung des leichten Wassers gefunden, dass das spezifische Gewicht des rekombinierten Wassers immer wieder abnahm, sogar nach vermuteter vollkommenen Befreiung von Deuterium. Dies führte er auf die elektrolytische Trennung der Sauerstoffisotope zurück. In unserem vorliegenden Experiment konnten wir keine solche stetige Abnahme des spezifischen Gewichts des rekombinierten Wassers finden. Diese Differenz kann man natürlich auf Verschiedenheit der Rekombinationsanordnung zurückführen. Johnston hat das Knallgas aus dem Elektrolysiergefäß ohne weiteres katalytisch rekombiniert. Dagegen wurde in unserem Fall dem Knallgasstrom zuerst Luft zugesetzt und dann liessen wir ihn katalytisch reagieren. Aber weil Luftsauerstoff spezifisch schwerer als Wassersauerstoff ist, konnte die Abnahme des spezifischen Gewichts wegen der elektrolytischen Abtrennung der schweren Sauerstoffisotope bis zu einem gewissen Grade durch die Zunahme des spezifischen Gewichts durch die Zumischung von Luftsauerstoff kompensiert werden. Auf jeden Fall muss man sicherheitshalber den Sauerstoff des oben hergestellten leichten Wassers durch den des gewöhnlichen Wassers ersetzen. Dies gelang uns dadurch, dass wir das leichte Wasser elektrolytisch zersetzten

(8) H. L. Johnston, *J. Am. Chem. Soc.*, **57** (1935), 484, 2737; *Nature*, **135** (1935), 842.

und den dadurch erhaltenen Wasserstoff mit dem Sauerstoff, der durch die vollständige Elektrolyse des gewöhnlichen Wassers gewonnen wurde, katalytisch rekombinieren liessen. Aber weil die Menge des leichten Wassers, das im vorliegenden Versuch hergestellt wurde, nicht ganz ausreichte, um damit weiter zu arbeiten, stellten wir von neuem grössere Mengen von leichtem Wasser her und normalisierten seinen Sauerstoff auf dem genannten Wege. Diesen zweiten Versuch nennen wir Versuch B gegen den vorliegenden Versuch A.

Versuch B. Zunächst wurden vier Sorten von leichtem Wasser entsprechend je der ersten bis vierten Stufe der Elektrolyse im Versuch A dargestellt. Die Arbeitsweise war genau dieselbe wie im Versuch A, ausgenommen die Elektroden, die im Versuch B aus Eisenblech bestanden. Die dadurch gewonnenen vier Sorten von leichtem Wasser, deren Volumen je 100 c.c. betrugen, wurden je mit 10 g. KOH versetzt und in einer grossen U-Röhre zwischen Nickel-Elektroden elektrolysiert. Der dadurch entwickelte Wasserstoffstrom wurde von wenig zugemischtem Sauerstoff sowie von Feuchtigkeit befreit, indem wir den Gasstrom zunächst über, bis auf ca. 300°C. erhitzten Platinasbest und dann durch das mit Kohlensäureschnee abgekühlte Glasrohr leiteten. Der mit diesem Wasserstoff zu kombinierende Sauerstoff wurde ebenfalls durch die Elektrolyse von 15 c.c. gewöhnlichem Wasser, das mit 3 g. KOH versetzt war, in einer kleinen U-Röhre erzeugt, und ebensogut von Wasserstoff und Feuchtigkeit befreit. Die so erzeugten beiden Ströme von Wasserstoff und Sauerstoff wurden dann miteinander vermischt und über dem, bis zur Rotglut elektrisch erhitzten Platinspiraldraht katalytisch rekombiniert. Dabei regulierten wir die Entwicklungsgeschwindigkeit von Wasserstoff so, dass sie ein wenig grösser als die doppelte des Sauerstoffs blieb. Durch diese Massnahme konnte man den Sauerstoff ohne Gefahr für die Änderung der Isotopenzusammensetzung restlos reagieren lassen. Das dadurch erzeugte Wasser wurde durch die Abkühlung mittels Kohlensäureschnee-Gemisch vollständig kondensiert aufgefangen. Während des Experiments wurde dem Sauerstoff-entwickelnden Elektrolyt von Zeit zu Zeit gewöhnliches Wasser zugesetzt, um das Volumen des Elektrolyts annähernd konstant zu halten. Und erst dann, als 15 c.c. Wasser ihm hinzugefügt worden waren, wurde er bis auf 3 c.c. herabelektrolysiert. Aber weil am Anfang noch 15 c.c. Wasser im Elektrolysiergefäss vorhanden war, wurden insgesamt 27 c.c. gewöhnliches Wasser elektrolytisch zersetzt. Der dadurch erzeugte Sauerstoff wurde wie oben gesagt restlos in Wasser verwandelt. Dabei wurde im Ganzen nur 1/2 Volumen vom leichten Wasser, das den Wasserstoff entwickelte, zur Elektrolyse verbraucht.

Auf diese Weise ersetzten wir den Sauerstoff der vier Sorten von leichtem Wasser, die je den vier Stufen der Elektrolysen im Versuch A entsprachen, vollständig mit dem Sauerstoff von gewöhnlichem Wasser. Sie wurden dann separat sorgfältig gereinigt und deren spezifisches Gewicht mittels eines Quarzschwimmers mit dem des gewöhnlichen Wassers bei 9.5°C. verglichen. Tabelle 2 gibt die Messresultate wieder.

Tabelle 2. Versuch B.

Sorte des verwendeten leichten Wassers	1	2	3	4
Δ in γ	16.9	18.6	18.7	18.7

Diese Resultate bedeuten: als wir z. B. das leichte Wasser aus der ersten Stufe der Elektrolyse im Versuch A dem Versuch B unterwarfen, erwies sich das spezifische Gewicht des dadurch erhaltenen Wassers um 16.9 γ kleiner als das des gewöhnlichen Wassers u. s. w. Die so gefundene Abnahme des spezifischen Gewichts ist offenbar nach der dritten Stufe konstant geworden. Aber um aus diesen Daten den Deuterium-Gehalt von gewöhnlichem Wasser auszurechnen, muss man noch zwei Faktoren in Rechnung ziehen.

(1) Das leichte Wasser, das zur Entwicklung von leichtem Wasserstoff verwendet wurde, enthielt noch das Deuterium, das aus zugesetztem KOH stammte.

(2) Die Isotopenzusammensetzung des von uns verwendeten Sauerstoffs wird wohl noch von der des gewöhnlichen Wassers insofern abweichen, als wir nur 90% des gesamten Wassers elektrolytisch zersetzten.

Die Einflüsse dieser beiden Faktoren wirkten auf das spezifische Gewicht des erzeugten leichten Wassers offenbar gegeneinander. Aus einer Rechnung haben wir gefunden, dass der Faktor 1 das spezifische Gewicht des erzeugten leichten Wassers wohl um ca. 0.2 γ erhöht⁽⁹⁾, dass dagegen der Faktor 2 es um ca. 0.4 γ herabsetzt⁽¹⁰⁾. Deshalb lag die Grösse der anzubringenden Korrek-

(9) Die zu 100 c.c. leichtem Wasser zugesetzten 10 g. KOH enthielten, den chemisch verbundenen Wasserstoff eingerechnet, 2 bis 3 g. Wasser. Dies erhöhte das spezifische Gewicht des leichten Wassers um ca. 0.5 γ . Deshalb sollte der Wasserstoff, der durch die Elektrolyse von 1/2 Volumen dieses Wassers erzeugt wurde, um 0.2 γ schwerer als reines Protium sein, angenommen, dass der Trennfaktor $\alpha = 4$ wäre.

(10) 15 c.c. gewöhnliches Wasser wurde zuerst bei konstantem Volumen (durch dauernden Zusatz von gewöhnlichem Wasser) elektrolysiert. Erst dann, als insgesamt noch 15 c.c. Wasser eingegossen worden waren, wurde der Elektrolyt bis auf 3 c.c. herab-elektrolysiert. Für die Annahme, dass der Trennfaktor für Sauerstoffisotope $\alpha = 1.008$ ist, (vgl. Fussnoten (8)), ergab sich, dass der dadurch erzeugte Sauerstoff um 0.4 γ leichter als der des gewöhnlichen Wassers sein musste.

tion, die offenbar die Differenz der eben genannten beiden Grössen ist, schon innerhalb des Messfehlers und die Resultate in Tabelle 2 können ohne weiteres zum Ausrechnen des Deuterium-Gehalts von gewöhnlichem Wasser benutzt werden.

Resultate. Falls das spezifische Gewicht des leichten Wassers, das von Deuterium frei ist, um Δs kleiner als das des gewöhnlichen Wassers ist, dann kann man das D/H Verhältnis im letzteren durch die Gleichung

$$\frac{D}{H} = \frac{\Delta s}{\left(\frac{\partial s}{\partial x}\right)_{x=0}} \quad (1)$$

berechnen. Der Nenner dieser Gleichung stellt die Änderung des spezifischen Gewichts s des schweren Wassers mit dessen Gehalt (Mol-Bruch) x an Deuterium bei $x = 0$ dar.

Die Beziehung zwischen dem spezifischen Gewicht des schweren Wassers und dessen Gehalt an Deuterium wurde von Lewis und Luten⁽¹¹⁾ abgeleitet. Modifiziert man die von ihnen gegebenen Formel mittels des neuesten Daten von Tronstad und seinen Mitarbeitern⁽¹²⁾ für das spezifische Gewicht des reinen schweren Wassers, dann erhält man

$$x = 9.419 (\Delta s) - 1.01 (\Delta s)^2,$$

wo Δs den Unterschied zwischen dem spezifischen Gewicht von schwerem und gewöhnlichem Wasser darstellt. Daraus folgt, dass

$$\left(\frac{\partial s}{\partial x}\right)_{x=0} = 0.1062 \quad \text{bei } 25^\circ\text{C.}$$

ist. Andererseits ergibt sich aus Tabelle 2, dass $\Delta s = 18.7 \pm 0.5 \gamma$ bei 9.5°C. ⁽¹³⁾ ist. Rechnet man diesen Wert mittels der bekannten Daten über die thermische Ausdehnung von schwerem Wasser auf 25°C. um⁽¹⁴⁾, dann erhält man

$$\Delta s = 18.9 \pm 0.5 \gamma \quad \text{bei } 25^\circ\text{C.}$$

Bringt man diese beiden Werte von $\left(\frac{\partial s}{\partial x}\right)_{x=0}$ sowie Δs in die Gleichung

(11) G. N. Lewis und D. B. Luten, Jr., *J. Am. Chem. Soc.*, **55** (1933), 5061.

(12) L. Tronstad, J. Nordhagen und J. Brun, *Nature*, **136** (1935), 515.

(13) Der Deuterium-Gehalt dieses leichten Wassers dürfte schätzungsweise kleiner als 5×10^{-6} sein.

(14) Bei dieser Umrechnung wurde angenommen, dass $\left(\frac{\partial s}{\partial x}\right)_{x=0} \propto (s_{\text{D}_2\text{O}} - 1)$, wobei $s_{\text{D}_2\text{O}}$ das spezifische Gewicht des reinen schweren Wassers ist.

(1), dann ergibt sich, dass das D/H Verhältnis in Osaka-Leitungswasser $D : H = 1 : 5600 \pm 200$ ist.

Diskussion. Die vorliegende Methode, die wir in der Einleitung Methode 4 genannt haben, ist auch von einigen anderen Autoren zur Bestimmung des Deuterium-Gehalts von gewöhnlichem Wasser benutzt worden. Aber merkwürdigerweise erhielten einige Autoren dabei sehr abweichende Resultate im Vergleich mit den anderen, wie aus den nebenstehenden beiden Tabelle ersichtlich ist. Tabelle 3 stellt die bisher veröffentlichten Daten über das D/H Verhältnis in gewöhnlichem Wasser, die nach Methode 4 bestimmt wurden, und Tabelle 4 die nach den anderen Methoden gefundenen zusammen.

Tabelle 3. D-Gehalt von gewöhnlichem Wasser, der nach Methode 4 bestimmt wurde.

Nr.	Beobachter	Probewasser	Δs	D : H
1	Johnston ⁽⁸⁾	Columbuser Leitungswasser	18.3 γ	1 : 5850
2	Webster, Wahl und Urey ⁽¹⁵⁾	Princeton Water	21. γ	1 : 5200
3	Tronstad, Nordhagen und Brun ⁽¹³⁾	Rjukaner Wasser	18.5 γ	1 : 6000
4	Ingold, Ingold, Whitaker und Whytlaw-Gray ⁽¹⁶⁾	Londoner Wasser	12. γ	1 : 9000
5	Christiansen, Crabtree und Laby ⁽¹⁷⁾	Melbournier Regenwasser	12.7 γ	1 : 8500
6	Vorliegende Arbeit	Osakaer Leitungswasser	18.9 γ	1 : 5600

Tabelle 4. D-Gehalt von gewöhnlichem Wasser, der nach verschiedenen Methoden bestimmt wurde.

Nr.	Beobachter	Methode ⁽¹⁸⁾	D : H
7	Urey, Brickwedde und Murphy ⁽²⁾	1	1 : 4000
8	Bleakney und Gould ⁽³⁾	2	1 : 5000
9	Lewis und Macdonald ⁽⁴⁾	3	1 : 6500
10	Edwards, Bell und Wolfenden ⁽⁵⁾	3	1 : 6200

(15) L. A. Webster, M. H. Wahl und H. C. Urey, *J. Chem. Physics*, **3** (1 35), 129.

(16) E. H. Ingold, C. K. Ingold, H. Whitaker, und R. Whytlaw-Gray, *Nature*, **134** (1934), 661.

(17) W. N. Christiansen, R. W. Crabtree und T. H. Laby, *Nature*, **135** (1935), 870.

(18) Über die Bedeutung dieser Ziffern vgl. die Einleitung.

Der in der vorliegenden Arbeit gefundene Wert (Nr. 6) stimmt gut mit dem von Johnston bestimmten (Nr. 1) überein und ist von derselben Grössenordnung wie die anderen bisher mitgeteilten Daten, ausgenommen die Nr. 4 und 5. Diese beiden Daten sind viel zu klein im Vergleich nicht nur mit denen, die nach derselben Methode 4 bestimmt wurden, sondern auch mit den auf anderem Wege gefundenen. Der Unterschied beträgt sogar 30 bis 50%. Dementsprechend ist die Dichteabnahme Δs des leichten Wassers, die von den betreffenden Autoren beobachtet wurde, durchschnittlich um 7γ kleiner als die von anderen Forschern gefundene. Aber solch ein merklicher Unterschied im Deuterium-Gehalt von gewöhnlichem Wasser auf verschiedenen Erdoberflächen ist kaum zu erwarten. Davon kann man sich leicht überzeugen, wenn man z.B. das spezifische Gewicht des Krystallisationswassers ein und desselben Minerals, das im Vergleich mit dem des gewöhnlichen Wassers an verschiedenen Orten bestimmt wurde, zum Vergleich heranzieht. Tabelle 5 gibt einige solche Beispiele wieder.

Tabelle 5. Sp. Gew. des Krystallisationswassers von einigen Mineralien.

Mineral	Δs	Vergleichswasser (Leitungswasser von)
Tincal aus Kalifornien ($\text{Na}_2\text{B}_4\text{O}_7 \cdot 10\text{H}_2\text{O}$)	$\pm 0\gamma$	Washington ⁽¹⁹⁾
	$+ 3\gamma$	London ⁽²⁰⁾
	$+ 2\gamma$	Osaka ⁽²¹⁾
Rasorit aus Kalifornien ($\text{Na}_2\text{B}_4\text{O}_7 \cdot 4\text{H}_2\text{O}$)	$+ 7\gamma$	Washington ⁽¹⁹⁾
	$+ 6\gamma$	London ⁽²⁰⁾
	$+ 4\gamma$	Osaka ⁽²¹⁾
Carnallit aus Stassfurt	$+ 3\gamma$	London ⁽²⁰⁾
	$+ 2\gamma$	Osaka ⁽²¹⁾

Aus der Zusammenstellung in Tabelle 5 darf man wohl schliessen, dass das spezifische Gewicht von gewöhnlichem Wassers von verschiedenen Orten der Erdoberfläche kaum mehr als 3γ von einander verschieden sein kann,

(19) E. W. Washburn und E. R. Smith, *Bur. Standards J. Research*, **12** (1934), 305.

(20) H. J. Emeléus, F. W. James, A. King, T. G. Pearson, R. H. Purcell und H. V. A. Briscoe, *J. Chem. Soc.*, **1934**, 1207, 1948.

(21) K. Okabe und T. Titani, noch nicht veröffentlicht. Weil die zu diesem Versuch bezogene Probe von Tincal und Rasorit ein intimes Gemisch aus kleinen Krystallen von beiden Mineralien und Gestein war und weil jede Probe mit der Hand daraus ausgewählt wurde, war es wahrscheinlich, dass die ausgewählten Krystalle mit der anderen Art von Krystallen mehr oder weniger vermengt waren.

abgesehen von der zeitlichen Veränderung an demselben Ort. Aber diese kann auch keine bedeutende Wirkung ausüben, mindestens insofern es sich um Leitungswasser handelt. Davon soll später die Rede sein. Nach dieser Sachlage muss man die Ursache für die oben genannte Diskrepanz vielmehr in der Arbeitsmethode suchen.

Das leichte Wasser, das nach Methode 4 zu verwenden ist, soll natürlich möglichst von Deuterium frei sein, aber zugleich soll der Sauerstoff dieses leichten Wassers genau dieselbe Isotopenzusammensetzung wie der des gewöhnlichen Wassers besitzen. Wir haben keinen Zweifel, dass in allen Fällen geeignete Massnahmen für die Normalisierung des Sauerstoffs des verwendeten leichten Wassers getroffen wurden. Aber es kommt jetzt in Frage, ob die Isotopenzusammensetzung des Sauerstoffs, der zur Erzeugung des leichten Wassers benutzt wurde, wirklich dieselbe, wie die des damit zu vergleichenden gewöhnlichen Wassers war. Denn wir haben gefunden, wie schon erwähnt, dass der Sauerstoff in Luft spezifisch schwerer ist als der Sauerstoff, der in Wasser chemisch verbunden ist. Aus unserem Versuch⁽⁶⁾ ergab sich, dass das spezifische Gewicht des Wassers, das durch die Verbindung von leichtem Wasserstoff mit dem Luftsauerstoff erzeugt wurde, um 7γ grösser war als das des Wassers, das aus demselben leichten Wasserstoff aber mit dem Wassersauerstoff hergestellt wurde. Dieser Unterschied ist gerade von derselben Grösse, wie die Diskrepanz, die sich innerhalb des spezifischen Gewichts des leichten Wassers findet, wie aus Tabelle 3 ersichtlich ist. Deshalb liegt nun die Vermutung nahe, dass die Autoren von Nr. 4 und 5 zur Verbrennung von leichtem Wasserstoff den Sauerstoff aus Luft verwendet haben dürften, obgleich wir darüber keine genauen Angaben in ihren Veröffentlichungen finden können. Vermehrt man nach dieser Vermutung die von diesen Autoren mitgeteilten Dichteabnahmen von leichtem Wasser je noch um 7γ , dann erhalten wir aus dem Versuch von Ingold und seinen Mitarbeitern $D:H = 1:5700$, und aus dem von Christiansen und seinen Mitarbeitern $D:H = 1:5500$. Diese Werte stehen offenbar im Rahmen der von anderen Autoren beobachteten.

Nimmt man die Mitte der Daten in Tabelle 3 und 4 ohne Berücksichtigung der Genauigkeit des einzelnen Wertes und ausgenommen die beiden Nr. 4 und 5 sowie Nr. 7, dann finden wir, dass in gewöhnlichem Wasser durchschnittlich $D:H = 1:5800 \pm 500$ ist. Die Abweichung des einzelnen Wertes von diesem Mittelwert darf man wohl auf die Verschiedenheit der Messmethoden sowie des verwendeten Probewassers zurückführen. Bei dieser Gelegenheit möchten wir noch darauf hinweisen, dass Regenwasser, das von einigen Autoren zur D/H-Bestimmung benutzt wurde, keine besonderen Vorzüge gegenüber Boden- oder Flusswasser besitzen dürfte. Denn es wurde

von einem von uns (T) und Harada⁽²²⁾ gefunden, dass das spezifische Gewicht von Regenwasser ziemlich merklich von den Bedingungen beim Sammeln abhängt. Am Anfang eines Regenfalls ist Regenwasser spezifisch ein wenig schwerer als gewöhnliches Wasser, aber gegen Ende wird es allmählich leichter. Dagegen scheint das spezifische Gewicht von Leitungswasser fast unabhängig von der Zeit konstant zu bleiben, wie Briscoe und seine Mitarbeiter⁽²⁰⁾ beim Londoner Leitungswasser experimentell gefunden haben. Das zur vorliegenden Arbeit herangezogene Osaka-Leitungswasser stammt vom grossen Biwa-See. Aber nach unseren bisherigen Erfahrungen konnten wir keine merklichen Schwankungen in seinem spezifischen Gewicht innerhalb des Messfehlers finden.

Der Nippon Gakujutsu-Shinkohkai (der Gesellschaft zur Förderung der japanischen Wissenschaft) sowie der Hattori-Hohkohkai (der Hattori-Stiftung) sind wir für ihre finanzielle Unterstützung zum herzlichsten Dank verpflichtet. Herrn Dr. Harada, der uns zur Bestimmung des spezifischen Gewichts behilflich gewesen ist, möchten wir auch unseren Dank aussprechen.

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(22) M. Harada und T. Titani, dieses Bulletin, **10** (1935), 206, 263.

ÜBER DEN UNTERSCHIED IN DER ISOTOPENZUSAMMEN-
SETZUNG VON LUFT- UND WASSERSAUERSTOFF UND
DEN ELEKTROLYTISCHEN TRENNFAKTOR
VON SAUERSTOFFISOTOPE.⁽¹⁾

Von Noriyoshi MORITA und Toshizo TITANI.

Eingegangen am 27. Februar 1936. Ausgegeben am 28. Juni 1936.

Einleitung. Beim Vergleich von zahlreichen Versuchsergebnissen über den Deuterium-Gehalt von gewöhnlichen Wasser sowie die elektrolytische Trennung von Sauerstoffisotope, kam uns die Vermutung, dass der Sauerstoff in Luft, den wir weiter unten Luftsauerstoff nennen wollen, spezifisch schwerer sei, als der Wassersauerstoff, der im Wasser chemisch verbunden ist. Um diese Vermutung näher zu prüfen, haben wir ein Experiment durchgeführt. Daraus ergab sich, wie erwartet, dass der Luftsauerstoff um 7 γ schwerer als der Wassersauerstoff ist. In demselben Experiment haben wir auch gefunden, dass der elektrolytische Trennfaktor der Sauerstoffisotope $\alpha = 1.01$ ist.

Versuch A. Zunächst wurde leichtes Wasser oder Deuterium-armes Wasser auf die übliche Weise durch die fraktionierte Elektrolyse von gewöhnlichem Wasser hergestellt. Durch nochmalige Elektrolyse dieses leichten Wassers konnten wir den leichten Wasserstoff, dessen D-Gehalt schätzungsweise kleiner als 1 Atom in 30,000 war,⁽²⁾ sich entwickeln lassen. Den so erhaltenen leichten Wasserstoff haben wir separat mit dem Luft- und Wassersauerstoff zu Wasser rekombiniert und das spezifische Gewicht des jeweils entstehenden Wassers miteinander verglichen. Dazu verwendeten wir die folgenden drei Sorten von Sauerstoff:

Sauerstoff I war Luftsauerstoff. In der Praxis verwendeten wir atmosphärische Luft, die im voraus gut getrocknet wurde, indem wir sie zunächst über Chlorcalcium und dann durch das mit Kohlensäureschnee-Gemisch abgekühlte Glasrohr leiteten.

Sauerstoff II war Wassersauerstoff, der durch teilweise Elektrolyse aus gewöhnlichen Wasser gewonnen wurde. In diesem Sauerstoff II kann man

(1) Die vorliegende Arbeit wurde von einem von uns bei der Tagung der japanischen chemischen Gesellschaft zu Tokio am 12. Oktober 1935 und zu Osaka am 22. November in demselben Jahr vorgetragen und vorläufig mitgeteilt in diesem Bulletin, **11** (1936), 36.

(2) Siehe weiter unten.

die extreme Verschiebung der Isotopenzusammensetzung infolge der elektrolytischen Trennung erwarten, weil nur weniger als 5% vom gesamten Elektrolysierwasser zersetzt worden waren.

Sauerstoff III war ebenfalls durch Elektrolyse erhaltener Wassersauerstoff. Aber in diesem Fall wurde die Elektrolyse fast bis zum Ende durchgeführt, d.h. mehr als 95% vom gesamten Volumen elektrolytisch zersetzt. Deshalb kann angenommen werden, dass Sauerstoff III dieselbe Isotopenzusammensetzung wie der im Wasser chemisch verbundene Sauerstoff besitzt.⁽³⁾

Der durch Elektrolyse gewonnene Sauerstoff wurde immer von beigemischtem Wasserstoff und Feuchtigkeit sorgfältig befreit, indem wir den Sauerstoffstrom zunächst über erhitztem Platinasbest und dann durch das mit Kohlensäureschnee-Gemisch abgekühlte Glasrohr leiteten. Der damit zu reagierende leichte Wasserstoff wurde ebenfalls durch ähnliche Massnahmen gereinigt und getrocknet. Die Rekombination der so hergestellten drei Sorten von Sauerstoff und leichtem Wasserstoff führten wir über dem auf 300° bis 350°C. erhitzten Kupferkatalysator durch, der aus Kupferoxyd durch die Reduktion mittels reinen Wasserstoffs hergestellt worden war. Wir verwendeten immer den Wasserstoff in grossem Überschuss, um den Sauerstoff vollständig reagieren zu lassen. Dabei funktionierte der Kupferkatalysator auch als ein sehr effektives Reservoir für den Sauerstoff. Nach dem Experiment wurde der leichte Wasserstoff noch lange Zeit über den erhitzten Katalysator geleitet, um ihn vollständig vom gebundenen Sauerstoff zu befreien und den verwendeten Sauerstoff restlos in Wasser zu verwandeln. Auf diese Weise wurden drei Sorten von Wasser I, II und III, je aus den drei Sorten von Sauerstoff I, II und III und dem leichten Wasserstoff hergestellt. Die so gewonnenen Arten von Wasser wurden alle sorgfältig gereinigt, und ihr spezifisches Gewicht wurde je mit dem des ebenso gut gereinigten Osaka-Leitungswassers bei 9.5°C. mittels eines Quarzschwimmers verglichen. Die Versuchsergebnisse sind in Tabelle 1 zusammengestellt.

Tabelle 1. Versuch A.

Wassersorten	verwendeter Sauerstoff	Δs in γ	Mittel
I	Luftsauerstoff	- 7.3 -- 6.7	- 7 $\pm$ 1
II	Wassersauerstoff aus teilweiser Elektrolyse	-16.0 -17.7	-17 $\pm$ 1
III	Wassersauerstoff aus vollkommener Elektrolyse	-14.2 -14.7 -15.3	-15 $\pm$ 1

(3) Der Unterschied im sp. Gew. ist schätzungsweise kleiner als 0.3 γ .

Vor der Diskussion über diese Ergebnisse wollen wir noch zwei andere Versuche beschreiben.

Versuch B. In diesem Versuch haben wir das Wasser I dadurch hergestellt, dass wir den leichten Wasserstoff in getrockneter Luft mit freier Flamme verbrannten. Das spezifische Gewicht des so dargestellten Wassers erwies sich um 7.8γ kleiner als das des gewöhnlichen Wassers. Obwohl in dieser Versuchsanordnung die isotopische Trennung von Sauerstoff nicht ganz ausgeschlossen war, stimmt der Betrag der gefundenen Dichteabnahme innerhalb des Messfehlerbereichs mit dem im Versuch A für Wasser I gefundenen gut überein. (Vgl. Tabelle 1, Reihe I). Daraus ersieht man, dass die katalytische Methode im Versuch A mit keiner merklichen Fehlerquelle behaftet war.

Versuch C. Weil der im Versuch A verwendete leichte Wasserstoff noch 1 Atom D in 30,000 Atomen H enthielt, wiederholten wir dasselbe Verfahren unter Verwendung von praktisch reinem, leichten Wasserstoff, dessen D-Gehalt schätzungsweise 1 in 200,000 war.⁽²⁾ Die sonstige Arbeitsweise war im grossen Ganzen dieselbe wie beim Versuch A, aber das ganze Verfahren wurde mit erhöhter Sorgfältigkeit durchgeführt. Die Versuchsergebnisse gibt Tabelle 2 wieder.

Tabelle 2. Versuch C.

Wassersorten	verwendeter Sauerstoff	Δs in γ
I	Luftsauerstoff	-11.4 ± 0.5
II	Wassersauerstoff aus teilweiser Elektrolyse	-20.0 ± 0.5
III	Wassersauerstoff aus vollkommener Elektrolyse	-18.1 ± 0.5

Folgerungen. Aus der Versuchsanordnung, die in Versuch A und C verwendet wurde, ist ohne weiteres klar, dass dort die isotopische Trennung von Sauerstoff bei der Wasserbildung ganz ausgeschlossen war. Nur eine solche von Wasserstoff könnte man annehmen, weil wir ihn bei der katalytischen Rekombination immer in grossem Überschuss verwendet haben. Aber wir haben in einer früheren Arbeit über die Erzeugung des leichten Wassers⁽⁴⁾ gefunden, dass das Wasser, das durch die Verbindung von reinem leichten Wasserstoff mit Wassersauerstoff entstand, um 18.7γ leichter als gewöhnliches Wasser war. Vergleicht man diesen Wert mit der Dichte-

(4) N. Morita und T. Titani, dieses Bulletin, 11 (1936), 403.

abnahme von Wasser III in Versuch A ($\Delta s = -15 \gamma$, vgl. Tabelle 1) bzw. C ($\Delta s = -18.1 \gamma$, vgl. Tabelle 2), dann ersieht man sofort, dass eine eventuell auftretende minimale Trennung von Wasserstoffisotopen beim Verbrennen auf jeden Fall, besonders in Versuch C, keinen merklichen Einfluss auf die Endresultate ausüben konnte. Deshalb kann man den Unterschied, der in beiden Versuchen A und C zwischen den spezifischen Gewichten der drei Arten von Wasser gefunden wurde, ausschliesslich auf die Verschiedenheit des spezifischen Gewichts der drei Arten von Sauerstoff zurückführen.

(1) Erstens erwies sich aus Tabelle 1 und 2, dass Wasser III, das den ganzen Sauerstoff von gewöhnlichen Wasser enthält, durchschnittlich um $2 \pm 2 \gamma$ schwerer als Wasser II war, das aus dem durch teilweise Elektrolyse des Wassers hergestellten Sauerstoff entsteht. Diesen Unterschied kann man offenbar auf die elektrolytische Trennung von Sauerstoffisotope zurückführen. Aus dem gefundenen Dichteunterschied 2γ folgt sofort, dass der Trennfaktor von Sauerstoffisotope unter den von uns verwendeten Versuchsbedingungen, d.h. bei der Elektrolyse von $2N$ NaOH zwischen Nickel-Elektroden, $\alpha(O^{16}/O^{18}) = 1.01 \pm 0.01$ ist. Dieser Wert stimmt mit den von Johnston⁽⁵⁾ sowie von Taylor und seinen Mitarbeitern⁽⁶⁾ gefundenen sehr gut überein. Die weitere Diskussion hiervon soll in der nächsten Mitteilung veröffentlicht werden.

(2) Der zweite und wichtigere Schluss folgt aus dem Vergleich des spezifischen Gewichts des Wassers I mit dem des Wassers III. (Vgl. Tabellen 1 und 2). Wasser I, das aus dem Luftsauerstoff hergestellt wurde, erwies sich immer schwerer als Wasser III, das aus dem kompletten Wassersauerstoff dargestellt wurde. Der Dichteunterschied zwischen beiden Arten von Wasser beträgt $8 \pm 2 \gamma$ in Versuch A (Tabelle 1) und $7 \pm 1 \gamma$ in Versuch C (Tabelle 2). Legt man grössers Gewicht auf den besseren Versuch C, erhält man den Mittelwert von $7 \pm 1 \gamma$. Daher kann man sagen, dass Luftsauerstoff um $7 \pm 1 \gamma$ bzw. 0.0007% schwerer als Wassersauerstoff ist. Dieser Unterschied im spezifischen Gewicht übt offenbar schon auf die vierte Dezimalstelle des Atomgewichts von Sauerstoff Einfluss aus.

Auf die Frage nach der Ursache dieses merklichen Unterschieds zwischen dem spezifischen Gewicht von Luft- und Wassersauerstoff kann man natürlich nicht sofort antworten. Aber es scheint uns interessant, das eben gefundene Resultat mit dem Verteilungsquotienten von O^{18} zwischen Sauerstoff und Wasser bzw. Wasserdampf, der von Urey und Greiff⁽⁷⁾ aus spektroskopischen Daten errechnet wurde, zu vergleichen. Die beiden Autoren fanden, dass

(5) H.L. Johnston, *J. Am. Chem. Soc.*, **57** (1935), 484.

(6) P.W. Selwood, H.S. Taylor, J.A. Hipple, Jr. und W. Bleakney, *J. Am. Chem. Soc.*, **57** (1935), 642.

(7) H.C. Urey und L.J. Greiff, *J. Am. Chem. Soc.*, **57** (1935), 321.

der Verteilungsquotient zwischen Sauerstoff/Wasser bei 25°C. = 1.006, dagegen der zwischen Sauerstoff/Wasserdampf = 1.02 ist. Auf Grund dieses Ergebnisses deuteten die genannten Autoren darauf hin, dass das Atomgewicht von Sauerstoff durch die Wahl der Reaktion für seine Bestimmung schon auf der vierten Dezimalstelle beeinflusst werden kann. Bei der Folgerung von Urey und Greiff handelt es sich natürlich um das Austauschgleichgewicht, und es ist nicht ohne weiteres klar, ob man es auch in unserem Fall damit zu tun hat. Aber wenn man vorläufig den Quotienten von O^{18} -Konzentration in Luft- und Wassersauerstoff berechnet, findet man, dass der Quotient zwischen Luft/Wasser = 1.035 ± 0.005 ist.⁽⁸⁾ Dieser Wert steht bemerkenswerterweise nicht dem Verteilungsquotienten von O^{18} zwischen Sauerstoff/Wasser (= 1.006) sondern vielmehr dem zwischen Sauerstoff/Wasserdampf (= 1.02) nahe.

Auf jeden Fall muss bei genaueren Versuchen die eben gefundene Tatsache in Betracht gezogen werden, dass es einen ziemlich merklichen Unterschied in der Isotopenzusammensetzung zwischen Sauerstoff in Luft und Wasser, den zwei wichtigsten Behältern von Sauerstoff, gibt. Die bisher manchmal beobachteten Diskrepanzen zwischen den von vielen Forschern veröffentlichten Daten über den Trennfaktor von Sauerstoffisotope, das Vorkommenverhältnis von Wasserstoffisotope und dergleichen scheinen uns mindestens teilweise durch die eben gefundene Tatsache befriedigend erklärt werden zu können. Näheres darüber soll in der nächsten Mitteilung erörtert werden.⁽⁹⁾

Zum Schluss möchten wir der Nippon Gakujutsu-shinkohkai (der Gesellschaft zur Förderung der japanischen Wissenschaft) sowie der Hattori-Hohkoku (der Hattori-Stiftung) für ihre finanzielle Unterstützung unseren herzlichsten Dank aussprechen. Herrn Dr. Harada, der uns bei der Dichtemessung behilflich gewesen ist, sind wir auch zum besten Dank verpflichtet.

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(8) Es wurde dabei angenommen, dass der Dichteunterschied allein von O^{18} herrührte und $O^{18} : O^{16} = 1 : 500$ ist.

(9) Nach dem Abschluss der vorliegenden Arbeit haben wir die Mitteilung von M. Dole (*J. Am. Chem. Soc.*, **57** (1935), 2731, Dezember) gefunden. Der von ihm gefundene Dichteunterschied ist aber 4.6γ d.h. kleiner als der von uns gefundene.

Anmerkung bei der Korrektur (24. Juni): In *J. Chem. Physics*, **4** (1936), 268, April, wurde die Mitteilung von M. Dole über die genauere Untersuchung veröffentlicht. In diesem Versuch wurde gefunden, dass der Unterschied $6.0 \pm 0.6 \gamma$ ist. Dieser Wert stimmt innerhalb der Messfehlergrenzen mit dem von uns gefundenen $7 \pm 1 \gamma$ sehr gut überein.

ÜBER DEN EINFLUSS DES DICHTUNTERSCHIEDS ZWISCHEN LUFT- UND WASSERSAUERSTOFF AUF DIE VERSUCHSERGEB- NISSE VON SAUERSTOFF- UND WASSERSTOFFISOTOPE.

Von Noriyoshi MORITA und Toshizo TITANI.

Eingegangen am 27. Februar 1936. Ausgegeben am 28. Juni 1936.

Einleitung. Es wurde von uns gefunden,⁽¹⁾ dass Sauerstoff in Luft, Luft-sauerstoff, um $7 \pm 1 \gamma$ schwerer ist als Wassersauerstoff, der in Wasser chemisch verbunden ist. In der vorliegenden Mitteilung wollen wir den Einfluss erörtern, der diese Tatsache auf die Versuchsergebnisse über den elektrolytischen Trennfaktor von Sauerstoffisotope und das Vorkommenverhältnis von H und D ausübt.

Elektrolytischer Trennfaktor von Sauerstoffisotope. Betreffend die elektrolytische Anreicherung von schwerem Sauerstoff, wurde der Trennfaktor zwischen leichtem und schwerem Sauerstoff schon von manchen Autoren untersucht. Tabelle 1 stellt die bisher veröffentlichten Daten zusammen.

Tabelle 1. Trennfaktor von Sauerstoffisotope.

Nr.	Beobachter	Elektrolyt	Elektroden	α_{18}^{16}
1	Johnston ⁽²⁾	0.5 N KOH	Eisen	1.008
2	Selwood, Taylor, Hipple, Jr. und Bleakney ⁽³⁾	0.5 N NaOH	Nickel	1.01
3	Morita und Titani ⁽¹⁾	2 N NaOH	Nickel	1.01
4	Greene und Voskuyl ⁽⁴⁾	1.25 N NaOH	Nickel	1.01
5	Hall und Johnston ⁽⁵⁾	konz. KOH	Eisen	<1.02
6	Smith und Wojciechowski ⁽⁶⁾	5 N NaOH	vernickeltes Gusseisen	1.05
7	Ogden ⁽⁷⁾	1.25 N NaOH	Nickel	1.13

(1) Dieses Bulletin, **11** (1936), 36, 414.

(2) H. L. Johnston, *J. Am. Chem. Soc.*, **57** (1935), 484.

(3) P. W. Selwood, H. S. Taylor, J. A. Hipple, Jr. und W. Bleakney, *J. Am. Chem. Soc.*, **57** (1935), 642.

(4) C. H. Greene und R. J. Voskuyl, *J. Am. Chem. Soc.*, **56** (1934), 1649.

(5) W. H. Hall und H. L. Johnston, *J. Am. Chem. Soc.*, **57** (1935), 1515.

(6) E. R. Smith und M. Wojciechowski, *J. Research Nat. Bur. Standards*, **15** (1935), 187; vgl. auch E. W. Washburn, E. R. Smith und F. A. Smith, *ibid.*, **13** (1934), 599.

(7) G. Ogden, *Nature*, **136** (1935), 913.

Die Daten Nr. 1 bis 4 wurden aus dem Versuch über die Elektrolyse von Wasser, dagegen die beiden Nr. 5 und 6 aus der isotopischen Analyse von industriellem Elektrolysierwasser gefunden. Die Versuchsmethode von Nr. 7 ist nicht ganz klar.

Betreffend Nr. 4 ist zu beachten, dass der in Tabelle 1 gegebene Wert aus dem Versuchsergebnis von Greene und Voskuyl von uns ausgerechnet wurde. Die beiden Autoren elektrolysierten 5% NaOH Lösung zwischen Nickelelektroden und verglichen das spezifische Gewicht des Wassers, das durch die Verbrennung des daraus entwickelten Sauerstoffs in gereinigtem Wasserstoff hergestellt wurde, mit dem des Wassers, das durch die Verbrennung von Luft in demselben Wasserstoff gewonnen wurde. Dabei fanden sie, dass das Wasser aus dem elektrolytischen Sauerstoff um 7.7γ leichter, dagegen das Wasser aus Luft um 1.1γ schwerer als das Cambridger Leitungswasser war. Falls man, wie früher getan wurde, direkt aus diesen Versuchsergebnissen den Trennfaktor von Sauerstoffisotope errechnet, dann folgt, dass $\alpha = 1.04$ ist. Die Diskrepanz zwischen diesem und den bis damals veröffentlichten anderen Daten (Nr. 1 und 2) ist schwer begreiflich gewesen.⁽³⁾ Aber wenn man den von uns gefundenen Dichteunterschied 7γ zwischen Luft- und Wassersauerstoff in Rechnung bringt, dann vermindert sich der Dichteunterschied zwischen beiden Arten von Wasser, die von Greene und Voskuyl dargestellt wurden, bis auf 1.8γ . Daraus folgt, dass der ihren Versuch beherrschende Trennfaktor $\alpha = 1.01$ gewesen ist.

Die isotopische Analyse von industriellem Elektrolysierwasser bei Nr. 5 wurde von Hall und Johnston dadurch ausgeführt, dass sie den elektrolytisch angereicherten Sauerstoff durch die Einleitung von CO_2 austrieben. Das dazu benutzte CO_2 befand sich in Austauschgleichgewicht mit gewöhnlichem Wasser. Durch diese Behandlung verminderte sich das spezifische Gewicht des industriellen Elektrolysierwassers um 3.4γ . Daraus folgt offenbar, dass $\alpha = 1.02$ ist. Dieses Resultat ist, nach den genannten Autoren, in befriedigender Übereinstimmung mit dem von Johnston⁽²⁾ früher gefundenen, dass der Trennfaktor zwischen O^{16} und O^{18} allein $\alpha = 1.01$ ist. Hall und Johnston fanden in demselben Versuch auch, dass das Wasser, das durch die Verbrennung von Sauerstoff aus Wasser in überschüssigem Wasserstoff dargestellt wurde, um 4 bis 5γ leichter war als das Wasser, das durch die Verbrennung von Wasserstoff in Luft gewonnen wurde. Die beiden Autoren führten diesen Dichteunterschied zwischen beiden Arten von Wasser auf die isotopische Trennung von Wasserstoff durch fraktionierte Verbrennung zurück. Aber nach unserer Ansicht muss der gefundene Unterschied im spezifischen Gewicht zum grössten Teil von demselben zwischen Luft- und Wassersauerstoff herrühren.

Die von Smith und seinen Mitarbeitern in Versuch Nr. 6 verwendete Methode beruhte auf demselben Prinzip wie oben Nr. 5. Sie trieben den angereicherten Wasserstoff in industriellem Elektrolysierwasser mittels Ammoniak aus. Das so behandelte Elektrolysierwasser erwies sich zunächst um 31 γ schwerer als gewöhnliches Wasser. Daraus folgte, dass $\alpha = 1.15$ ist. Aber nach der Späteren Untersuchung verminderte sich die Dichtezunahme bis zu 11 γ , und daraus schlossen sie, dass $\alpha = 1.05$ ist. Dieser Wert ist jedoch noch viel grösser als die von anderen Autoren gefundenen. Auf die Frage nach diesem Unterschied kann man natürlich nicht sofort antworten. Aber aus der eben geschilderten Geschichte des Experiments kann man wohl vermuten, dass die Reinigung des Probewassers nicht sehr leicht auszuführen war. Nach unserer eigenen Erfahrung haben wir gefunden, dass das Wasser, das im voraus mit Ammoniak behandelt worden war, äusserst schwer vollständig zu reinigen war. Besonders, ohne Gefahr für die Änderung der Isotopenzusammensetzung zu verfahren, erwies sich als fast unmöglich.

Der grösste Wert des Trennfaktors, der bis jetzt gefunden wurde, ist der letzte, Nr. 7, der kürzlich von Ogden veröffentlicht wurde. Dieses Ergebnis interessiert uns insofern, als es im grossen Ganzen unter ähnlichen Versuchsbedingungen wie die von No. 4, d.h. durch die Elektrolyse von 1.25 N NaOH Lösung mittels Nickelelektroden, gewonnen wurde. Aber leider können wir keine weiteren genaueren Angaben über die Arbeitsweise in der veröffentlichten Mitteilung finden.

Zusammenfassend kann man sagen, dass aus den meisten Versuchen, die von vielen Forschern unter verschiedenen Versuchsbedingungen und durch verschiedene Versuchsmethoden ausgeführt wurden, sich ergibt, dass der elektrolytische Trennfaktor von Sauerstoffisotope sehr nahe bei 1.01 liegt, falls man den Dichteunterschied zwischen Luft- und Wassersauerstoff in Betracht zieht.

Vorkommenverhältnis von H und D. Über den möglichen Einfluss, den der Dichteunterschied zwischen Luft- und Wassersauerstoff auf die Versuchsergebnisse über das D/H-Verhältnis in gewöhnlichem Wasser ausüben kann, haben wir schon an anderem Orte ausführlich gesprochen.⁽⁸⁾ Dort haben wir mitgeteilt, dass der D-Gehalt von gewöhnlichem Wasser durchschnittlich 0.017 Atomprozent ist. Aber es wurde von vielen Autoren gefunden, dass in der Natur vorkommende Wasserstoffverbindungen manchmal einen grösseren oder eventuell kleineren D-Gehalt besitzten. Dieser Schluss wurde aber dadurch gezogen, dass das Wasser, das durch die Verbrennung

(8) N. Morita und T. Titani, dieses Bulletin, **11** (1936), 403.

der betreffenden Verbindung in Luft bzw. Sauerstoff gewonnen wurde, ein grösseres oder kleineres spezifische Gewicht als das gewöhnliche Wasser besass. Auf diese Weise wurden z.B. Kohlen, Petroleum, natürliche Gase, viele Arten von pflanzlichen sowie tierischen Substanzen auf ihren D-Gehalt hin untersucht. Da die betreffenden Daten schon äusserst zahlreich sind, geben wir in Tabelle 2 nur wenige ausgewählte Beispiele wieder.

Tabelle 2. Dichtezunahme des Wassers aus verschiedenen Substanzen.

Nr.	Substanzen	zum Verbrennen verwendet	Δs in γ	Referat
1	natürliches Propan aus U.S.A.	käuflicher Sauerstoff	0	(9)
2	natürliches Butan aus Oklahoma	Linde-Sauerstoff	+6	(10)
3	natürliche Gase aus Northern Pennsylvania	Luft	+6	(11)
4	Kerosin aus Oklahoma	„	+7	(12)
5	Benzol aus Mallinckrodt	elektrolytischer Sauerstoff	0	(12)
6	Gasolin aus Machach-Kala in U.S.S.R.	Linde Sauerstoff	+10	(13)
7	Anthrazit aus U.S.A.	käuflicher Sauerstoff	0	(9)
8	Weidenholz	käuflicher Sauerstoff	+3	(9)
9	„	Luft	+3	(14)
10	Zedernholz	„	+5	(15)
11	Baumwolle	„	+6	(15)
12	Zucker	„	+8~9	(14)
13	„	„	+8	(16)
14	viele Arten von Kohlenhydraten	„	+4~7	(16)
15	Bambussprossling, Schale	„	+4	(15)
16	ditto Presssaft	(nicht verbrannt)	+1	(15)
17	Honig	Luft	+4	(12)
18	Maisöl	„	+5	(11)
19	Fuselöl	„	+4	(14)
20	Tomaten	„	+3~4	(14)
21	„	„	+2	(17)

(9) E. W. Washburn und E. R. Smith, *Bur. Standards J. Research*, **12** (1934), 305; *Science*, **79** (1934), 188; vgl. auch E. R. Smith, *ibid.*, 454.

(10) R. D. Snow und H. L. Johnston, *Science*, **80** (1934) 210.

(11) C. H. Greene und R. J. Voskuyl, *J. Am. Chem. Soc.*, **56** (1934), 1649.

(12) M. Dole, *J. Am. Chem. Soc.*, **56** (1934), 999; *J. Chem. Physics*, **2** (1934), 337, 548.

(13) N. S. Filippova, *J. Chem. Physics*, **3** (1935), 316.

(14) H. J. Emeléus, F. W. James, A. King, T. G. Pearson, R. H. Purcell und H. V. A. Briscoe, *J. Chem. Soc.*, **1934**, 1207, 1948.

(15) K. Okabe und T. Titani, dieses Bulletin, **10** (1935), 465.

(16) T. Titani und M. Harada, dieses Bulletin, **10** (1935), 205, 261.

(17) Aus einer unveröffentlichten Arbeit in unserem Laboratorium.

Falls die oben gezeigte Dichtezunahme ausschliesslich von der Anreicherung der schweren Isotope des Wasserstoffs herrührt, erreicht ihr Betrag oft mehr als 30% vom gesamten Gehalt an Deuterium. Aber es ist ohne weiteres klar, dass in den Fällen, wo die Substanzen in Luft verbrannt wurden, der Dichteüberschuss von Luftsauerstoff auf die Versuchsergebnisse einen wichtigen Einfluss ausübte. Besonders bei solchen Substanzen, die keinen oder wenig Sauerstoff in sich selbst enthalten, kann die gefundene Dichtezunahme ausschliesslich vom verwendeten Luftsauerstoff herrühren. Diese Sachlage ist sehr deutlich aus den Daten von Nr. 1 bis 7 erkennbar, wo zum Verbrennen von einigen ähnlichen Substanzen in einem Fall Luft bzw. Linde-Sauerstoff aber im anderen elektrolytischer bzw. käuflicher (vermutlich elektrolytischer) Sauerstoff benutzt wurde.

Für die Substanzen wie z.B. Nr. 8 bis 21, die den zum Verbrennen nötigen Sauerstoff teilweise oder manchmal genügend in sich selbst enthalten, kann man die tatsächliche Anreicherung von schwerer Isotope von Wasserstoff nicht von vornherein ausschliessen. Aber mindestens in den Fällen von Nr. 10 (Zedernholz), Nr. 11 (Baumwolle) und Nr. 13 (Zucker) ist es sicher, dass es sich um keine Anreicherung von Deuterium handelt. Denn es ist durch unseren Versuch, worüber wir später in diesem Bulletin ausführlich mitteilen wollen, gefunden worden, dass nach dem Ersetzen des Sauerstoffs des Probewassers durch den des gewöhnlichen Wassers der in Tabelle 2 zitierte Dichteüberschuss in jedem Fall restlos verschwunden ist.

Es gibt noch eine Frage in Bezug auf die Versuchsergebnisse über die Dichte des natürlichen Wassers oder die des Wassers, durch Verbrennung gewonnen wurde. Es wurde nämlich von vielen Forschern zur Reinigung des Probewassers Kupferoxyd benutzt. Diese Verbindung erwies sich als ein sehr wirksames Mittel, um letzte und oft sehr hartnäckige Verunreinigungen aus dem Probewasser zu beseitigen. Das Verfahren besteht darin, dass man das zu reinigende Wasser in Dampfform über, bis auf Rotglut oder manchmal zu noch höherer Temperatur erhitztes Kupferoxyd leitet. Deshalb haben wir dabei die Gefahr einer Änderung der Isotopenzusammensetzung des Sauerstoffs des Probewassers wegen der Austauschreaktion zwischen ihm und Kupferoxyd bzw. Luft zu bedenken. Aber aus dem Versuch von Dr. Harada in unserem Laboratorium⁽¹⁸⁾ sowie aus dem von uns ausgeführten ergab sich, dass mindestens bis zur Rotgluttemperatur dies nicht der Fall ist. Harada

(18) M. Harada, *J. Chem. Soc. Japan*, **56** (1935), 811.

leitete ein gegebenes Volumen gereinigten Leitungswassers in Dampfform über, bis auf Rotglut erhitztes Kupferoxyd und verglich das spezifische Gewicht des so behandelten Wassers mit des Anfangswassers. Aber die beiden stimmten immer innerhalb des Messfehlerbereichs ($\pm 0.5\gamma$) miteinander sehr gut überein. In unserem Versuch haben wir das Wasser, dessen Gehalt an schweren Sauerstoffisotope schätzungsweise fast um 10% vermehrt worden war, in Dampfform mit elektrolytischem Sauerstoff aus gewöhnlichem Wasser im Volumenverhältnis 1 : 4 vermischt und langsam über, auf 300°C. erhitztes Kupferoxyd geleitet. Das Durchströmen des Gasgemisches durch das Kupferoxydrohr dauerte etwa 1 Minute. Durch diese Behandlung konnten wir jedoch keine messbare Änderung im spezifischen Gewicht des Probewassers finden.

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THE MECHANISM OF THE ISOTOPIC EXCHANGE REACTIONS.

By Eijiro OGAWA.

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The total energy of a molecule can be expressed by $E_e + E_v + E_r$, where E_v and E_r represent the vibrational and rotational energies, respectively, and E_e is the electronic energy, which is, of course, of a greater order of magnitude than E_v and E_r ($E_e \gg E_v \gg E_r$). Consequently there will be three different possible manifestations of the isotopic effect.

The electronic isotopic effect, which has not been worked out even for the simplest of diatomic molecules, must be very small (Jeppesen,⁽¹⁾ Beutler and Mie, and Johnston⁽²⁾) have observed rather unexpected isotopic effect, i.e. 135 cm.^{-1} in H_2 and 20 cm.^{-1} in OH). For all present purposes, this will be possibly ignored. The vibrational isotopic effect, which is much larger, has been much more important in the isotopic exchange reactions.⁽³⁾ The rotational isotopic effect is small compared with the vibrational effect.

The apparent energy differences of isotope molecules can be interpreted as the difference of the zero point energies, assuming that the total energies of isotopic molecules are the same. For present purposes it will be sufficient only to consider the difference of the zero point vibrational energies.

The energy of vibration will be expressed in the usual way as

$$E_v = h_c \omega_e \left(v + \frac{1}{2} \right) - x_e \omega_e \left(v + \frac{1}{2} \right)^2 + \dots,$$

where ω_e is the frequency of vibration and is expressed by

$$\omega_e = \frac{1}{2\pi} \sqrt{\frac{K}{\mu}}.$$

K is the so-called restoring force, i.e. the force acting upon the nuclei when their distance is increased by one unit from its equilibrium value. μ is the reduced mass expressed by $\frac{1}{\mu} = \frac{1}{m_1} + \frac{1}{m_2}$, where m_1 and m_2 are the masses of both nuclei. K corresponds to the binding force between two nuclei.

(1) *Phys. Rev.*, **45** (1934), 480.

(2) *Naturwissenschaften*, **21** (1933), 495.

(3) Urey and Rittenberg, *J. Chem. Physics*, **1** (1933), 137; Rittenberg, Bleakney, and Urey, *J. Chem. Physics*, **2** (1934), 48; I. Farkas and A. Farkas, *Trans. Faraday Soc.*, **30** (1934), 1071.

If it is assumed that the distances between two nuclei are the same,⁽⁴⁾ the binding force, that depends only upon the charges of the constituent nuclei and electrons, is the same in both kinds of molecules. While the reduced mass of the molecule of the heavier isotope is larger than that of the lighter one, the vibration frequency ω_e and consequently the zero point energy of vibration will be smaller in the former. If ω_{eI} is the wave number of the vibrational band of the heavier molecular isotope I, then the corresponding band for the molecular isotope II will be displaced by an amount which can be calculated from

$$\frac{\omega_{eI}}{\omega_{eII}} = \frac{\mu_I^{-\frac{1}{2}}}{\mu_{II}^{-\frac{1}{2}}}.$$

The quantity $\frac{\mu_I^{-\frac{1}{2}}}{\mu_{II}^{-\frac{1}{2}}}$ is usually denoted ρ .

For instance, the molecule HCl^{37} , vibrating by reason of its increased mass a little slower than HCl^{35} , would have its vibrational band displaced towards smaller frequencies. And conversely in the isotopic molecules Cl^{35}M Cl^{37}M , when M is substituted by a heavier element, the vibration frequencies of chlorine atom and consequently the frequency differences of two molecular isotopes must increase. These isotopic effect has been actually observed in diatomic spectra.⁽⁵⁾ The differences of the zero point energies of vibration of $\text{Cl}^{35}\text{M}_1\text{--Cl}^{37}\text{M}_1$ and $\text{Cl}^{35}\text{M}_2\text{--Cl}^{37}\text{M}_2$ are not the same, and when $\text{M}_2 > \text{M}_1$, the difference is larger for the latter. This effect has been pointed out heretofore. Let us call this effect "effect A".

The author has investigated the equilibrium of the exchange reactions between heavy water and various hydrogen compounds⁽⁶⁾ and found that the equilibrium constants depend upon the polarities of molecules. For instance, in the reaction between hydrogen ion and water ($=\text{OH}^+$) + ($-\text{OD}$) = ($=\text{OD}^+$) + ($-\text{OH}$), the equilibrium constant is 1.60; on the other hand the equilibrium constant of the reaction between hydroxyl ion and water (OH^-) + ($-\text{OD}$) = (OD^-) + ($-\text{OH}$) is 0.42. In these cases the isotopic effect due to "effect A" can not be considered. In general, the larger the zero point energy differences between molecular isotopes, the greater the equilibrium constant.

Bernal and Tamm⁽⁷⁾ considered following isotopic effect. They said, "the marked differences between the physical properties of H_2O and D_2O and

(4) Anderson and Yost, *J. Chem. Physics*, **3** (1935), 242; van Cleave and Mass, *Can. J. Research*, **12** (1935), 57; Amdur, *J. Am. Chem. Soc.*, **57** (1935), 588.

(5) Aston, "Mass Spectra and Isotopes," p. 209.

(6) *Tech. Repts Kyushu Imp. Univ.*, **10** (1935), 272.

(7) *Nature*, **135** (1935), 229.

of all polar compounds of H and D can not be due to intramolecular differences, which are far too small, but must be connected with differences of effective intermolecular forces. It is possible to account for these differences in a quantitative way by taking into consideration the differences in the frequency of angular vibration or libration of a molecule in the field of its neighbours ''.

These considerations are very interesting in connection with the author's experimental results. But according to the author's opinion it is not absolutely necessary to assume the isotopic effect of the so-called angular vibration or libration of polar compounds. It is very natural to consider that the fundamental vibration of =OH^+ , -OH , and OH^- are not the same and therefore the frequency differences of vibration or zero point energy differences of $\text{OH}^+\text{-OD}^+$, $(\text{-OH})\text{-(OD)}$, or $\text{OH}^-\text{-OD}^-$ are also not the same. From these results it is possible to say that the isotopic effect will be greatest in the positively changed molecular ions. These results must be based upon the differences of the deformation of atoms or the differences of electronic binding forces in the different states of polarisation. This theory can also be applied to neutral molecules.

The equilibrium constant of the reaction $\text{H}_2\text{O} + \text{HD} = \text{HDO} + \text{H}_2$ is about 3 at 20°C .⁽⁸⁾ In this case hydrogen atom of water is positively polarised. According to the author's theory the zero point energy difference between -OH and -OD will exceed the difference between HH and HD by reason of the electropositeness of hydrogen atom of hydroxyl bond. The author has investigated the isotopic shift of oxygen by sulphuric acid⁽⁹⁾ and observed that O^{18} in H_2O^{18} can be removed by the flow of air. In this case oxygen atom of water is negatively polarised. The zero point energy difference between $\text{O}^{16}\text{O}^{16}$ and $\text{O}^{16}\text{O}^{18}$ will exceed that of O^{16}H and O^{18}H by reason of the electronegateness of oxygen atom of hydroxyl bond. These isotopic effects due to polarisation of atom will probably play the most important rôle in the isotopic exchange reactions. Let us call this "effect B". According to effect B it is concluded that the element is rich in heavier isotope when it is in the more positively polarised state. Various methods of separation of isotopes by the application of effects A and B will be considered.

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(8) Bonhoeffer and Rummel, *Naturwissenschaften*, **22** (1934), 45; A. Farkas and L. Farkas, *Proc. Roy. Soc. (London)*, A, **144** (1934), 467; *Trans. Faraday Soc.*, **30** (1934), 1071.

(9) *Tech. Repts Kyushu Imp. Univ.*, **11** (1936), 25.

THE ISOTOPIC SEPARATION OF OXYGEN, CHLORINE, BROMINE, AND NITROGEN BY THE CHEMICAL METHODS.

By Eijiro OGAWA.

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The author has pointed out two effects in the isotopic exchange reactions.⁽¹⁾ According to effect B which the author has considered first, the following theory has been presented; that is, the element is rich in heavier isotope when it is in the more positively polarised state. Effect B will be more important in the isotopic separation of the element by the chemical methods.

The Chemical Separation of Oxygen Isotopes. *The Separation by Sulphuric Acid.*⁽²⁾ The isotopic shifts of hydrogen and oxygen isotopes due to effect B will be expected in the exchange reaction between hydroxyl radical and hydrated hydrogen ion: $(=O^{16}H^+) + (-O^{18}D) = (=O^{18}D^+) + (-O^{16}H)$. Two mols of water was added to 1 mol of sulphuric acid, and water was divided into two portions by distillation. Two mols of water of the latter fraction was added to 1 mol of sulphuric acid now used and fractionated into two portions. This treatment was repeated 6 times. The density increase compared with ordinary water was 1.6×10^{-6} after the 2nd treatment, 3.1×10^{-6} after the 4th treatment, and 8.2×10^{-6} after the 6th treatment. When dried CO_2 was passed, the density increase went down to 5.8×10^{-6} . Similarly the density increase went down to 4.9×10^{-6} by dried air. The density decrease due to air can be attributed to the following exchange reaction: $(-O^{18}H) + O^{16}O^{16} = (-O^{16}H) + O^{16}O^{18}$.

The Separation by Sodium Hydroxide. One half of 80 g. of water was converted into hydrogen and NaOH by sodium. In this case the density of water must increase due to effect B. The isotopic shift of hydrogen by the evolution of hydrogen by sodium can be calculated as 3.3×10^{-6} , assuming that the separation coefficient in this case is 2. The equilibrium constant of exchange reaction between OH^- and $-OH$ is 0.42.⁽³⁾ The isotopic shift of hydrogen due to this reaction can be calculated as 3.6×10^{-6} . The density increase actually observed was 9.5×10^{-6} . From these results the density

(1) This Bulletin, **11** (1936), 425; *Tech. Repts Kyushu Imp. Univ.*, **11** (1936), No. 2.

(2) *Tech. Repts Kyushu Imp. Univ.*, **11** (1936), 1.

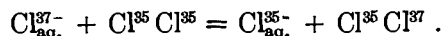
(3) This Bulletin, **11** (1936), 425; *Tech. Repts Kyushu Imp. Univ.*, **10** (1935), No. 6.

increase due to O^{18} is calculated as 2.6×10^{-6} . The separation coefficient of oxygen is 1.02.

The Separation by Potassium Nitrate. The density increase of water must be expected to be due to the following exchange reaction: $(=NO^{18-}) + (-O^{16}H) = (=NO^{16-}) + (-O^{18}H)$. The density increase of water of 2.57 mols KNO_3 solution is 1.2×10^{-6} . The equilibrium constant in this case is 1.006.

The Chemical Separation of Chlorine Isotopes.⁽⁴⁾ Chlorine is a mixture of Cl^{35} and Cl^{37} . The packing fractions are -4.8 and -5.2, respectively. The abundance ratio is 3.0~3.1 : 1. The chemical atomic weight is 35.457.

In the exchange reaction between chlorine ion hydrate and chlorine molecule, the isotopic shift of Cl^{37} in Cl_2 can be expected to be due to effects A and B.



HCl was oxidized to Cl_2 with HNO_3 and $KMnO_4$ in the existence of H_2SO_4 . The amount of HCl was decreased to 1/9.5 by this process (Table 1, B). Another portion of HCl was decreased to 1/19.7 by converting to Cl_2 with $KMnO_4$ alone in the existence of H_2SO_4 (Table 1, C). HCl was converted to NaCl and the latter recrystallized 3 times. Exactly equal weights of NaCl were taken and each precipitated with accurately the same volume of $AgNO_3$ solution, in slight excess. After precipitation the excess of $AgNO_3$ was determined nephelometrically (Table 1).

Table 1.

	NaCl(g.)	AgNO ₃ (g.)	Atomic weight of Cl
A(Kahlbaum's NaCl, recryst.)	6.0025	17.4463	35.453
B	6.0025	17.4463	35.453
B	6.0025	17.4506	35.439
C	6.0025	17.4576	35.416

The separation coefficients are 0.980 from the result of B, 0.964 from the result of C.

The Chemical Separation of Bromine Isotopes.⁽⁴⁾ Bromine is a mixture of two isotopes Br^{79} and Br^{81} . The packing fractions are -9.0 and -8.6, respectively. The abundance ratio is 1 : 1. The chemical atomic weight is 79.916.

In the exchange reaction between bromine ion hydrate and bromine molecule, the isotopic shift of Br^{81} in bromine can be expected to be due to effect A and B. Bromine (500 g.) in complete solution was converted into Br^- , BrO^- , and BrO_3^- by the action of NaOH, 1/19.2 of the total amount

(4) *Tech. Repts Kyushu Imp. Univ.*, **11** (1936), No. 2.

being left unchanged. The exchange reaction proceeds completely. Bromine was converted into NaBr and recrystallized 3 times and determined in the same way as chlorine (Table 2, B).

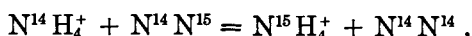
Table 2.

	NaBr(g.)	AgNO ₃ (g.)	Atomic weight of Br
A(Merck's NaBr, recryst. 2 times)	5.7077	9.4228	79.911
"	6.1752	10.1947	79.908
B	5.3249	8.7813	80.023

The separation coefficient is 1.076.

The Chemical Separation of Nitrogen Isotopes. Nitrogen is a mixture of two isotopes of N¹⁴ and N¹⁵. The packing fractions are 6.0 and 2.0. The abundance ratio is 99.86 : 0.14. The chemical atomic weight is 14.008.

In the exchange reaction between ammonium ion and nitrogen molecule :



ammonium ion will be rich in N¹⁴ according to effect A alone, and contrarily rich in N¹⁵ according to effect B alone.

Ammonium chloride (720 g.) was dissolved in 5 litres of water containing an excess of bromine. Into this solution concentrated NaOH solution was added drop by drop with constant stirring. The amount of NH₄Cl was decreased to 1/3.54 (Table 3, B) and 1/11.26 (C). Ammonia was driven off by NaOH and absorbed in HCl. NH₄Cl was recrystallized 2 times and determined in the same way as chlorine (Table 3).

Table 3.

	NH ₄ Cl(g.)	AgNO ₃ (g.)	Atomic weight of N
A(ord. NH ₄ Cl, recryst. 3 times)	9.0116	28.6216	14.002
B	9.0116	28.6205	14.004
C	9.0116	28.6189	14.007

Ammonium ion is rich in N¹⁵. Assuming that the atomic weight of nitrogen of NH₄Cl-A is 14.009, the atomic weights of nitrogen of NH₄Cl-B and -C are 14.011 and 14.014, respectively. Percentages of N¹⁵ are 0.31 in NH₄Cl-B and 0.61 in NH₄Cl-C. The separation coefficients are 2.7 from the result of B and 2.6 from the result of C. It is not so difficult to separate N¹⁴ and N¹⁵ completely by the chemical methods. From these results it can be concluded that effect B is the decisive factor in the isotopic exchange reactions.

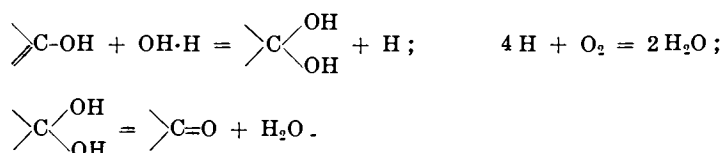
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ÜBER DIE KATALYTISCHE OXYDATIONSWIRKUNG DER METALLKOMPLEXVERBINDUNGEN XI. KATALYTISCHE OXYDATION IN SCHWEREM WASSER⁽¹⁾.

Von Kazuo YAMASAKI.

Eingegangen am 1. Juni 1936. Ausgegeben am 28. Juni 1936.

Mit den Untersuchungen über die katalytische Oxydationswirkung der Metallkomplexsalze haben sich Prof. Keita Shibata, Prof. Yuji Shibata und ihre Mitarbeiter schon lange beschäftigt⁽²⁾. Als Substrate dieser Oxydationswirkung wurden immer Polyphenole, aromatische Phenolamine, Polyamine, und andere Substanzen gewählt. Der Reaktionsmechanismus der katalytischen Wirkung der Metallkomplexsalze wird von den Autoren kurz folgendermassen erläutert: die sich in den labilen Komplexborn locker einlagernden Wassermoleküle werden so aktiviert, dass deren OH-Radikale auf die Substratmoleküle oxydierend einwirken, und die so frei gemachte Wasserstoffatome alsbald vom molekularen Sauerstoff aufgenommen werden. Schematisch wird diese Reaktion folgendermassen dargestellt:



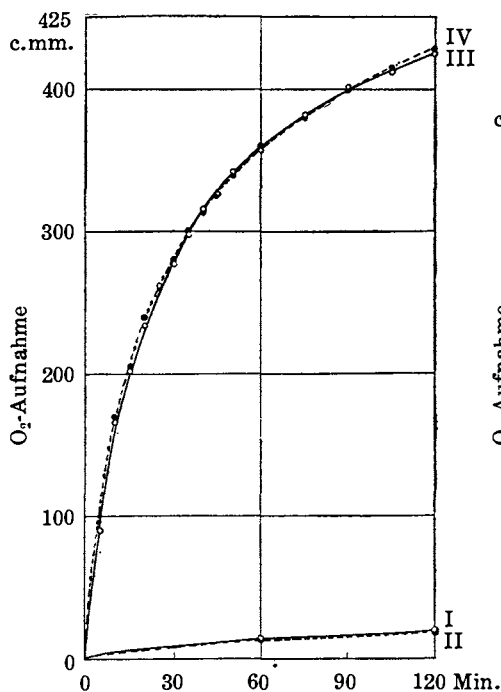
Da also das Wassermolekül eine ausschlaggebende Rolle in diesem Reaktionsmechanismus spielt, ist es zu erwarten, dass die Geschwindigkeit der genannten Reaktion in schwerem Wasser eine gewisse Verschiedenheit im Vergleich mit der in gewöhnlichem Wasser anzeigen wird. Tatsächlich wurde es in vorliegendem Versuch konstatiert, dass die katalytische Oxydation von Pyrogallol durch einige Kobaltkomplexsalze in schwerem Wasser bedeutend verzögert wird.

Methodisches und Versuchsergebnisse. Die Oxydation von Pyrogallol wurde durch die Messung von Sauerstoffverbrauch mittels des Warburgschen Manometers bei 25°C. verfolgt. Das zum Versuche in Verwendung gebrachte schwere Wasser wurde durch wiederholte Destillation in vacuo gereinigt.

(1) X. Mitteilung: Y. Shibata und K. Sakai, *J. Chem. Soc. Japan*, **55** (1934), 841.

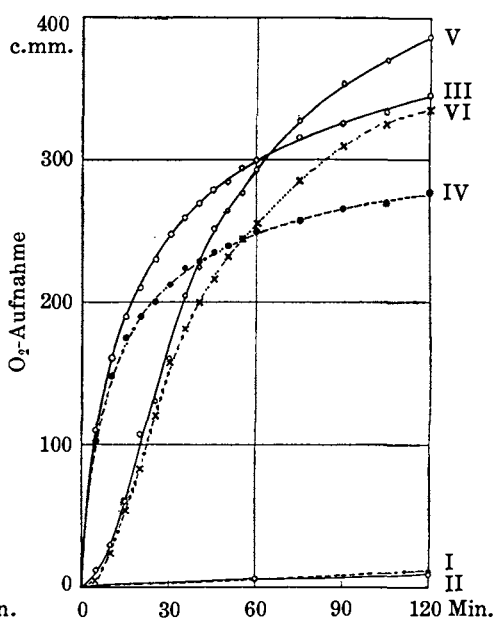
(2) Näheres vergleicht man: K. Shibata und Y. Shibata, „Katalytische Wirkungen der Metallkomplexverbindungen“, Tokyo, 1936.

(a) *Oxydation in verdünnter D₂O-Lösung von der Konzentration 9.42%⁽³⁾.*
 Das Reaktionsgemisch bestand aus: 2.5 mg. Pyrogallol in 2 c.c. schwerem bzw. gewöhnlichem Wasser in Hauptraum des Gefäßes und 1 c.c. 30%ige Kalilauge in Einsatzrohr; 0.5 mg. $[\text{Co}(\text{NH}_3)_5\text{Cl}]\text{Cl}_2$ in 2 c.c. schwerem bzw. gewöhnlichem Wasser in Ansatzbirne. Das Versuchsergebnis zeigt, dass kein messbarer Unterschied zwischen der Oxydationsgeschwindigkeit in so verdünnter D₂O-Lösung wie 9.42% und der in gewöhnlichem Wasser beobachtet wird (Abb. 1).



- I. Pyrogallol in gewöhnlichem Wasser.
 II. „ in schwerem Wasser (9.42%).
 III. Pyrogallol und $[\text{Co}(\text{NH}_3)_5\text{Cl}]\text{Cl}_2$ in gewöhnlichem Wasser.
 IV. Pyrogallol und $[\text{Co}(\text{NH}_3)_5\text{Cl}]\text{Cl}_2$ in schwerem Wasser (9.42%).

Abb. 1.



- I. Pyrogallol in H₂O
 II. „ in D₂O
 III. Pyrogallol und $[\text{Co}(\text{NH}_3)_5\text{Cl}]\text{Cl}_2$ in H₂O
 IV. „ „ in D₂O
 V. Pyrogallol und $[\text{Co}(\text{NH}_3)_4\text{CO}_3]\text{Cl}$ in H₂O
 VI. „ „ in D₂O

Abb. 2.

(3) Die Dichtemessung wurde von Herrn Dr. N. Morita durchgeführt. Ihm und auch Herrn Dr. M. Harada für seine Ratschläge bei der Reinigung des Wassers spreche ich meinen besten Dank aus.

(b) *Oxydation in schwerem Wasser von der Konzentration 99.6%*. Das Reaktionsgemisch bestand aus: 2.0 mg. Pyrogallol in 1 c.c. D_2O bzw. H_2O in Hauptraum des Gefäßes und 1 c.c. 30%ige Kalilauge in Einsatzrohr; 0.5 mg. Komplexsalz in 1 c.c. D_2O bzw. H_2O in Ansatzbirne. Die dazu verwendeten Komplexsalze sind $[Co(NH_3)_5Cl]Cl_2$ und $[Co(NH_3)_4CO_3]Cl$. Zum Vergleich wurde jedesmal ein entsprechender Versuch ohne Komplexsalzzusatz angestellt (Kontrollversuch) (Abb. 2).

Wie man aus Abb. 2 ersieht, verläuft die katalytische Oxydation von Pyrogallol in reinem schwerem Wasser bedeutend langsamer als in gewöhnlichem Wasser, während die an sich kleine Autoxydationsgeschwindigkeit von Pyrogallol in beiden Fällen keinen Unterschied zeigt. Die Farbe des Reaktionsgemisches beginnt nach 20 Sek. bei $[Co(NH_3)_5Cl]Cl_2$ und bei $[Co(NH_3)_4CO_3]Cl$ nach 7 Min. sich ins Braun umzuschlagen.

Zur Erklärung der hierbei gefundenen Verlangsamung der katalytischen Oxydation von Pyrogallol in schwerem Wasser könnten vielleicht verschiedene Umstände, wie z.B. geringere Löslichkeit von Sauerstoff in schwerem Wasser, grössere Viskosität des letzteren u. a. in Betracht gezogen werden, aber die wesentlichste Ursache dafür muss, unseres Erachtens, in der Reaktionsträgheit des sich an Oxydationsmechanismus beteiligenden D_2O -Moleküls bestehen. Die neulich von Champetier⁽⁴⁾ gefundenen Tatsache, dass die Hydratation des wasserfreien $CrCl_3$ in schwerem Wasser etwa dreimal so langsam vor sich geht wie in gewöhnlichem Wasser, scheint gerade unsere Annahme zu unterstützen.

Zusammenfassung.

Die Geschwindigkeit der katalytischen Oxydation von Pyrogallol durch Kobaltkomplexsalze in schwerem Wasser (99.6%) wurde bestimmt. Sie verläuft in D_2O bedeutend langsamer als in H_2O .

Es sei mir gestattet, Herrn Prof. Yuji Shibata für seine freundliche Anleitung und Ratschläge bei der Ausführung dieser Arbeit meinen herzlichsten Dank auszusprechen. Ferner Herren Prof. Y. Hori und Prof. T. Titani, welche mir die Proben des schweren Wassers zur Verfügung gestellt haben, bin ich zu grossem Dank verpflichtet.

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(4) G. Champetier, *Compt. rend.*, **201** (1935), 1118.

THE FORMATION OF CHOLESTANEDIONE-(3,6) FROM
CHOLESTENONE DIBROMIDE AND FROM
 Δ^4 - AND Δ^5 -CHOLESTENONES.

By Yoshiyuki URUSHIBARA and Toshio ANDO.

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On April 3rd of this year, on the occasion of the 58th annual meeting of the Chemical Society of Japan at Sendai, one of the authors (Ando) read a paper entitled "some compounds obtained from cholesterol dibromide" before Section II, and reported that cholestenone dibromide isolated in crystalline state from the oxidation product of cholesterol dibromide, on heating in absolute alcohol, was transformed into cholestanedione-(3,6) first prepared by A. Windaus⁽¹⁾. Then no mention was made of the mechanism of this transformation, because there was no experimental evidence to prove the intermediate course from cholestenone dibromide to cholestanedione. Nevertheless the fact that bromine was set free in the first stage of the reaction and the final product was a saturated 3,6-diketone made it very probable that Δ^5 -cholestenone was the first intermediate of the transformation, although Δ^5 -cholestenone was then unknown. On the appearance of the work by A. Butenandt and J. Schmidt-Thomé⁽²⁾ furnishing a method of preparing Δ^5 -cholestenone by the debromination of cholestenone dibromide with zinc and alcohol, the present authors heated Δ^5 -cholestenone with an equivalent quantity of bromine in absolute alcohol, when the same cholestanedione was obtained. But the matter proved not to be so simple as expected, because the same diketone was also obtained in a good yield by a similar treatment of Δ^4 -cholestenone. None of these specimens of the diketone has yet been compared with cholestanedione produced by the methods of A. Windaus, but the specimen obtained directly from cholestenone dibromide was identified with cholestanedione-(3,6) by the melting point, elementary analysis, preparation of dioxime and dibromo-substitution product, and the colour reaction of the latter.

On heating cholesterol dibromide in absolute alcohol cholesterol was regenerated in a good yield.

The authors are much interested in the recent work by H. H. Inhoffen⁽³⁾ dealing with a similar treatment of 4-bromocholestenone dibromide.

(1) *Ber.*, **36** (1903), 3755; **39** (1906), 2253.

(2) *Ber.*, **69** (1936), 832.

(3) *Ber.*, **69** (1936), 1134.

Experimental.

Cholestenone Dibromide, $C_{27}H_{44}OBr_2$. The benzene solution of cholestenone dibromide obtained by the oxidation of cholesterol dibromide, $C_{27}H_{46}OBr_2$, according to the directions of L. Ruzicka, H. Brüngger, E. Eichenberger, and J. Meyer⁽⁴⁾ was evaporated by blowing with an electric fan. The residue, on rubbing with a small amount of absolute alcohol, yielded colourless fine needles, which were washed with cold absolute alcohol (decomposition point $67-70^\circ$). Recrystallized carefully from acetone or aqueous acetone, the substance was obtained in fine long plates, decomposition point $65-66^\circ$ (Found: Br, 29.70. Calculated for $C_{27}H_{44}OBr_2$: Br, 29.40%). Cholestenone dibromide thus isolated in crystalline state is very unstable, and becomes gradually orange-red and then greyish yellow at ordinary temperature. The decomposition is naturally quicker at higher temperature or under diminished pressure. It is transformed into Δ^4 -cholestenone (m.p. $79-80^\circ$, decomposition point of semicarbazone 232° , corr.) by debromination with sodium iodide in alcohol⁽⁵⁾. Inhoffen⁽³⁾ gives decomposition point $68-69^\circ$ for cholestenone dibromide, and the properties described by him coincide with those observed by the present authors.

Cholestanedione-(3,6), $C_{27}H_{44}O_2$, from Cholestenone Dibromide. When crude cholestenone dibromide was warmed with alcohol, the resulting solution became reddish brown. Alcohol was evaporated off under diminished pressure, and the remaining dark brown mass was recrystallized repeatedly from acetone or aqueous acetone, when colourless prisms melting at $172-174^\circ$ (corr.) were obtained. No bromine was detected in this substance and no change was observed on boiling it with acetic anhydride. It was identified with cholestanedione-(3,6) by the examination of its properties, results of analysis (Found: C, 81.0, 80.7, 80.5; H, 10.9, 11.3, 11.2. Calculated for $C_{27}H_{44}O_2$: C, 80.91; H, 11.08%), and preparation of its derivatives. Windaus gives melting point $170-171^\circ$.

Pure cholestenone dibromide gave the same compound on heating with absolute alcohol.

Cholestanedione-(3,6)-dioxime. Prepared according to Windaus⁽⁶⁾. Colourless silky crystals, decomposition point $205-207^\circ$ (uncorr.) or $209-211^\circ$ (corr.) (Found: C, 75.34; H, 10.73; N, 6.95. Calculated for $C_{27}H_{44}(NOH)_2$: C, 75.26; H, 10.77; N, 6.51%).

Dibromocholestanedione-(3,6). Prepared according to Windaus⁽⁷⁾. Colourless small prisms, decomposition point $169-170^\circ$ (uncorr.) or $172-173^\circ$ (corr.) with evolution of gas (Found: C, 57.92; H, 7.82; Br, 29.70. Calculated for $C_{27}H_{42}O_2Br_2$: C, 58.03; H, 7.58; Br, 28.63%). The substance gave the characteristic colour reaction of dibromocholestanedione:⁽⁸⁾ An alcoholic solution of a minute quantity of this substance gave deep red colouration on adding one drop of aqueous potassium hydroxide, turning colourless on acidifying.

Cholestanedione-(3,6) from Δ^6 -Cholestenone. Crude Δ^6 -cholestenone prepared by the method of A. Butenandt and J. Schmidt-Thomé⁽²⁾ from pure cholestenone dibromide was boiled with an equivalent amount of bromine in absolute alcohol. The dark brown

(4) *Helv. Chim. Acta*, **17** (1934), 1413.

(5) R. Schoenheimer, *J. Biol. Chem.*, **110** (1935), 461.

(6) *Ber.*, **36** (1903), 3756. Windaus gives decomposition point about 205° .

(7) *Ber.*, **37** (1904) 2031. Windaus gives decomposition point about 165° with evolution of gas.

(8) *Ber.*, **37** (1904), 2032.

resinous matter remaining after the evaporation of alcohol was dissolved in warm acetone and the solution was cooled to crystallization. By repeated recrystallization from aqueous acetone cholestanedione was obtained in colourless fine needles, m.p. 170-172° (corr.) alone or in admixture with the specimen obtained directly from cholestenone dibromide.

Cholestanedione-(3,6) from Δ^4 -Cholestenone. Δ^4 -Cholestenone (m.p. 79-80°) prepared by the method of R. Schoenheimer⁽⁶⁾ was treated similarly with bromine and alcohol. In this case the product seemed to be a mixture. By repeated recrystallization cholestanedione-(3,6) was separated in colourless fine needles, m.p. 171-172.5° (corr.), no depression of the melting point (171-173°, corr.) when mixed with the specimen obtained from cholestenone dibromide.

Debromination of Cholesterol Dibromide with Alcohol. Cholesterol dibromide was boiled with absolute alcohol. The dark brown resinous matter obtained on distilling off alcohol was dissolved in warm acetone, and the solution was cooled to crystallization. Repeated recrystallization from aqueous acetone and acetone (with use of charcoal) yielded cholesterol in colourless small prisms, m.p. 149° (corr.). A mixture with an authentic specimen of cholesterol (m.p. 148-149°, corr.) melted at the same point 148-149° (corr.).

In conclusion the authors express their hearty thanks to Mr. Yasohachi Yamaguchi of Teikokusha Co. for his generous support of this work.

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Added in Proof (June 18th): The three specimens of cholestanedione-(3,6) melted at 172-3° (corr.), at 171-3° (corr.), and at 172-3° (corr.), respectively in order of the above description, in admixture with the cholestanedione, m.p. 173-4° (corr.), prepared by the reduction of Δ^4 -cholestenedione-(3,6), m.p. 123.5-124° (corr.), according to the directions of A. Windaus, *Ber.*, **39** (1906), 2249.

ON THE OCCURRENCE OF NEW HIGHLY UNSATURATED FATTY ACIDS, $C_{26}H_{40}O_2$ AND $C_{26}H_{42}O_2$, IN TUNNY OIL.

By Sei-ichi UENO and Chizuo YONESE.

Received February 28th, 1936. Published July 28th, 1936.

Tunny oil is obtained from the tunny fish, *Thynnus thynnus*. This fish is known under the Japanese names "Maguro", "Shibi", and "Oyio". The fish is most likely indigene to Japan and considerable number of the fish are caught there. The taste of the fish is very favourable and the fish is used chiefly for edible purpose, the oil, therefore, is scarcely prepared in this country. Concerning the composition of tunny oil, excepting the report on the chemical and physical properties by M. Tsujimoto, it has not been investigated hitherto. Recently, S. Ueno and M. Iwai⁽¹⁾ showed the presence of a highly unsaturated acid $C_{24}H_{38}O_2$ named scoliodonic acid in the liver oil of *scoliodon laticandus*. A little later than this, also Y. Toyama and T. Tsuchiya⁽²⁾ found a highly unsaturated acid $C_{24}H_{36}O_2$ (nisinic acid) from herring oil, cod-liver oil, pilot whale oil, sardine oil, squalus-suelii-liver oil with scoliodonic acid.

After further investigation on the highly unsaturated acids, the present authors have separated a new highly unsaturated acid in a tunny oil having the formula $C_{26}H_{40}O_2$ ($\bar{F}_6$) and also detected the occurrence of a new acid $C_{26}H_{42}O_2$ ($\bar{F}_5$), besides scoliodonic acid, nisinic acid, and clupanodonic acid. It has been found that both of these two highly unsaturated fatty acids are new acids and the authors have suggested the names "thynnic" acid for $C_{26}H_{40}O_2$, and "shibic acid" for $C_{26}H_{42}O_2$.

Experimental.

I. Properties of the Sample Oil. The tunny oil used in this investigation had the following properties: specific gravity d_4^{20} 0.9264; refractive index n_D^{20} 1.4820; acid value 4.2; iodine value 190.1; saponification value 183.4.

II. Separation of the Liquid Fatty Acids. The mixed fatty acids prepared by the usual method were separated from the solid fatty acids by means of the cooling method with cold water and ice water. Yield of the liquid acids 22.7%; sample oil 4 kg; liquid fatty acids 910 g. The liquid fatty acids thus obtained had the following properties: refractive index n_D^{20} 1.4770; iodine value (Wijs) 225.9; neut. value 180.9.

(1) *J. Soc. Chem. Ind., Japan*, **37** (1934), 251 B.

(2) *J. Soc. Chem. Ind., Japan*, **37** (1934), 530 B.

III. Fractional Distillation of Methyl Esters of the Liquid Acids. The liquid fatty acids were esterified with methyl alcohol containing 2% conc. sulphuric acid and then fractionated under a diminished pressure of 4 mm. The results of the fractional distillation are given in Table 1.

Table 1.

Fraction	B.p. (°C./4 mm.)	Yield (g.)
1	-180	49.5
2	180-188	66.0
3	188-200	48.0
4	200-203	56.0
5	203-210	63.0
6	210-215	63.5
7	215-225	55.0
8	225-227	31.0
9	residue and loss	41.0

For convenience of the experimental course, these distillates were classified into two parts and each part was repeatedly fractionated under a diminished pressure of 4 mm. The results of the final distillation and characteristics of each fraction are given in Tables 2, 3, and 4.

Table 2. Redistillation of Fractions -200°C./4 mm. (Sample 184 g.)

Fraction	B.p. (°C./4 mm.)	Yield (g.)	n_D^{20}
1	130-170	4.5	1.4478
2	170-176	15.5	1.4470
3	176-182	27.0	1.4471
4	182-185	24.0	1.4505
5	185-190	25.2	1.4531
6	190-195	30.5	1.4569
7	195-200	20.0	1.4610
8	200-210	19.5	1.4691
9	210-215	10.0	1.4780

Table 3. Redistillation of Fractions 200-225°C./4 mm. (Sample 234 g.)

Fraction	B.p. (°C./4 mm.)	Yield (g.)	n_D^{20}
1	—200	24.5	—
2	200—210	26.5	1.4660
3	210—215	60.2	1.4761
4	210—215	42.5	1.4761
5	215—220	33.4	1.4828
6	220—225	28.5	1.4872
7	225—226	9.0	1.4898

Table 4.

Fraction	B.p. (°C./4mm.)	Yield (g.)	n_D^{20}	Iodine value (Wijs)	Sap. value	Colour
1	130—170	4.5	1.4478	75.1	—	pale yellow
2	170—176	15.5	1.4470	37.8	—	"
3	176—182	27.0	1.4471	84.0	—	"
4	182—185	24.0	1.4505	95.8	—	"
5	185—190	25.2	1.4531	109.3	—	"
6	190—195	30.5	1.4569	131.9	—	"
7	195—200	20.0	1.4610	150.0	—	"
8	200—210	46.0	1.4660	163.0	—	"
9	210—215	112.7	1.4761	259.2	176.5	"
10	215—220	33.4	1.4828	271.3	180.6	"
11	220—225	28.5	1.4871	331.6	169.9	yellow
12	225—227	9.0	1.4898	319.5	166.3	"
13	225—227	31.0				

IV. Separation of Highly Unsaturated Fatty Acids. (1) *Separation from Fractions 12 and 13.* The mixed acids (30 g.) obtained from methyl esters by the usual method, were freed from unsaponifiable matter and then treated by sodium-salt-acetone-method:

	Yield (g.)	Colour
Fatty acid from soluble part	15	orange-red
Fatty acid from insoluble part	6	yellow

The highly unsaturated fatty acid prepared from these fractions had the following properties: d_4^{20} 0.9443; n_D^{20} 1.5042, n_D^{15} 1.5062; iodine value (Wijs) 372.1; neut. value 148.1. Bromine content of the ether insoluble polybromide: 71.27, 71.22% (calculated for $C_{26}H_{40}O_2Br_{12}$: 71.41; $C_{26}H_{42}O_2Br_{10}$: 67.42%). The calculation gives the following numbers:

	Neut. value	Iodine value
$C_{24}H_{38}O_2$ ($\overline{F}_5$)	156.7	354.2
$C_{24}H_{36}O_2$ ($\overline{F}_6$)	157.8	427.5
$C_{26}H_{42}O_2$ ($\overline{F}_5$)	145.4	328.8
$C_{26}H_{40}O_2$ ($\overline{F}_6$)	146.2	396.7

The isolated highly unsaturated acid was exhaustively hydrogenated at room temperature in the presence of Adams platinum catalyst. The hydrogenation product, after being decolorized with active charcoal and recrystallised from ether, formed shining plates, melting point 76–77°C., which were identified as pure cerotic acid ($C_{26}H_{52}O_2$) (pure cerotic acid melts at 77.8°C.). (Found: C, 78.20; H, 13.40. Calculated for $C_{26}H_{52}O_2$: C, 78.8; H, 13.1%.)

As stated above, the neutralisation value of the highly unsaturated acid obtained from these fractions corresponds to that of the C_{26} -series, the iodine value lies between the calculated values for $C_{26}H_{40}O_2$ and $C_{25}H_{42}O_2$, and bromine percentage of the bromide closely agrees with the calculated value for $C_{26}H_{40}O_2Br_{12}$. Accordingly, it may be considered to consist chiefly of $C_{26}H_{40}O_2$ ($\overline{F}_6$) and include a new acid $C_{26}H_{42}O_2$ ($\overline{F}_5$).

As these acids are not found in the literatures, the present authors propose the names "thynnic acid" for the acid $C_{26}H_{40}O_2$ ($\overline{F}_6$) and "shibic acid" for the acid $C_{26}H_{42}O_2$ ($\overline{F}_5$), after the fish names already described.

(2) *Separation from Fraction 11.* The mixed acids (24 g.) obtained from methyl esters (26.5 g.) were separated into soluble and insoluble parts by sodium-salt-acetone-method:

	Yield (g.)	Colour
Fatty acids from soluble part	17	orange-red
Fatty acids from insoluble part	4	yellow

The characteristics of the fatty acids from the soluble part: n_D^{20} 1.5007; iodine value (Wijs) 367.0; neut. value 155.0. The liquid fatty acids prepared above were further treated by means of lithium-salt-acetone-method and the acids from the soluble part had the following properties: n_D^{15} 1.5046, n_D^{20} 1.5018; d_4^{20} 0.9419; iodine value (Wijs) 369.1 (calculated for $C_{24}H_{38}O_2$ ($\overline{F}_5$) and $C_{24}H_{36}O_2$ ($\overline{F}_6$): neut. value, 156.7 and 157.8; iodine value, 354.2 and 427.5, respectively). Bromine content of ether insoluble polybromide: 72.13% (calculated for $C_{24}H_{36}O_2Br_{12}$ and $C_{24}H_{38}O_2Br_{10}$: 72.91 and 69.05% respectively).

The experimental results described above show that the highly unsaturated acid obtained from this fraction corresponds to the C_{24} -series and it is a mixture of scoliodonic acid $C_{24}H_{38}O_2$ ($\overline{F}_5$) and nisinic acid $C_{24}H_{36}O_2$ ($\overline{F}_6$).

(3) *Separation from Fraction 10.* The mixed acids (28 g.) obtained from methyl esters (32 g.) were separated into soluble and insoluble parts by means of sodium salt-acetone-method.

	Yield (g.)	Colour
Fatty acids from soluble part	20	orange-red
Fatty acids from insoluble part	4	yellow

The properties of the liquid acids from soluble part: n_D^{20} 1.4958, n_D^{15} 1.4978; d_4^{20} 0.9365; iodine value (Wijs) 333.4; neut. value 166.3 (calculated for $C_{22}H_{36}O_2$ (F_4) and $C_{22}H_{34}O_2$ (F_5): neut. value, 168.9 and 170.0; iodine value 305.6 and 384.3, respectively). The clupanodonic acid of M. Tsujimoto had the following properties: d_4^{15} 0.9385; d_4^{20} 0.9356; n_D^{20} 1.5020; b.p. 236°C./5 mm.; methyl ester b.p. 222°C./5 mm. By the experimental results it was shown that the highly unsaturated fatty acids prepared from this fraction correspond to the C_{22} -series, consisting of clupanodonic acid $C_{22}H_{34}O_2$ and an acid $C_{22}H_{36}O_2$.

(4) *Separation from Fraction 9.* The mixed acids (86 g.) obtained from methyl esters by the usual method were separated into the acetone soluble and insoluble parts:

	Yield (g.)	Colour
Fatty acids from soluble part	62.0	orange-red
Fatty acids from insoluble part	11.0	pale-yellow

The liquid acids from soluble part had the following properties: n_D^{20} 1.4855; iodine value (Wijs) 278.5. The highly unsaturated acids which were further separated by means of lithium-salt-acetone-method from the liquid acids prepared above had the following properties: n_D^{15} 1.4952, n_D^{20} 1.4936; d_4^{20} 0.9363; neut. value 166.2; iodine value (Wijs) 332.9. Bromine content of ether insoluble polybromide: 70.01 (calculated for $C_{22}H_{34}O_2Br_{10}$ and $C_{22}H_{36}O_2Br_8$: 70.01 and 65.80%, respectively). The characteristics and the analytical results showed that the properties of the highly unsaturated acid from this fraction agreed with that of the liquid acids from fraction 10 and clupanodonic acid is the main constituent of the highly unsaturated acid obtained from fractions 10 and 9. Accordingly, it was confirmed that clupanodonic acid exists in a large amount in tunny oil as in the cases of other fish oils.

(5) *Separation from Fractions 7 and 8.* The mixed acids (45 g.) obtained from methyl esters (64 g.) were separated by means of sodium-salt-acetone-method:

	Yield (g.)	Colour
Fatty acids from soluble part	33	orange-red
Fatty acids from insoluble part	4	yellow

The liquid fatty acids prepared in the same way had the following properties: n_D^{20} 1.4789, n_D^{25} 1.4791; neut. value 170.6; iodine value (Wijs) 220.9. From the properties described above, it was assumed that the liquid acids correspond to the C_{20} -series consisting of the acids of the $C_n H_{4n-4} O_2$ and the $C_n H_{2n-6} O_2$ series.

(6) *Separation from Fraction 6.* The mixed acids (27 g.) obtained from methyl esters (28 g.) were separated:

	Yield (g.)	Colour
Fatty acids from soluble part	7	yellow
Fatty acids from insoluble part	12	white

The properties of the fatty acids from soluble part: n_D^{20} 1.4712; neut. value 194.9; iodine value (Wijs) 185.0. From the properties, the authors assumed that the liquid acids from this fraction correspond to the lower unsaturated acids of the C_{18} -series.

(7) *Separation from Fractions 1, 2, 3, 4, and 5.* The liquid part from these fractions has not yielded highly unsaturated fatty acids.

Summary.

The mixed liquid acids obtained from the sample oil by cooling were converted into methyl esters which were fractionally distilled under a diminished pressure of 4 mm. From the highest boiling fraction, the authors separated a new highly unsaturated acid $C_{26}H_{40}O_2$ (Γ_6) and also detected the occurrence of another new acid $C_{26}H_{42}O_2$ (Γ_5) besides scoliodonic acid ($C_{24}H_{38}O$), nisinic acid ($C_{24}H_{36}O_2$) and clupanodonic acid ($C_{22}H_{34}O_2$). The present authors propose the names "thynnic acid" for the acid $C_{26}H_{40}O_2$ and "shibic acid" for the acid $C_{26}H_{42}O_2$.

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ÜBER DIE KOLLOIDSYNTHESE DURCH DAMPFEXPLOSIONEN UND DIE KOLLOIDCHEMISCHEN UNTERSUCHUNGEN DER DURCH DIESE METHODE HERGESTELLTEN DISPERSEN SYSTEME.

Von Naoyasu SATA,

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Einleitung.

Auf die Kolloiddispersion einer Substanz, die durch die Kondensation des Dampfes dieser Substanz im Innern des Dispersionsmittels geschieht, ist schon seit 1906 von P. P. von Weimarn⁽¹⁾ hingewiesen worden, als ein besonders interessanter Fall der Kolloidsynthese sowie von theoretischer als auch von experimenteller Seite.

Wegen der technologischen Schwierigkeiten wurde diese Methode experimentell lange nicht erreicht. Im Jahre 1925 hat A. Gutbier⁽²⁾ das erste Mal eine Möglichkeit dieser Methode zur Kolloidsynthese gezeigt, indem er den Dampf dispergierender Substanz im Innern des Dispersionsmittels durchleitet und kolloiddisperse Phase kondensieren lässt. Da er aber nur den Dampf von 1 Atm.-Druck angewendet hat, war der Mechanismus beim Moment der Dampfkondensation noch weit entfernt von der theoretisch verlangten idealen Bedingung, auf die ich später noch näher eingehen werde.

Durch Hineinexplodierenlassen des hocherhitzten, hochgespannten Dampfes einer dispergierenden Substanzen von einer geschlossenen Röhre in das Innere des Dispersionsmittels konnte ich zum ersten Mal fast die theoretisch verlangte ideal-ähnliche Dampfdispersion verwirklichen. Die so hergestellte Sole war viel feiner dispergiert und beständiger und wies vom kolloidchemischen Standpunkt aus weit interessantere Eigenschaften auf.

Im folgenden gebe ich eine ausführliche Darstellung dieser neuen Methode der Kolloidsynthese sowie der kolloidchemischen Untersuchungen an den so hergestellten dispersen Systemen.

(1) P. P. von Weimarn, „Die Allgemeinheit des Kolloidzustandes“, 471, Dresden und Leipzig (1923).

(2) A. Gutbier, *Z. anorg. allgem. Chem.*, **152** (1926), 163; **155** (1926), 199; **158** (1926), 99.

Theoretischer Teil.

Nach der Theorie "Die Allgemeinheit des Kolloidzustandes", die, wie wohlbekannt, von P. P. von Weimarn theoretisch sowie experimentell entwickelt worden ist, ist es jetzt für uns eine Selbstverständlichkeit, dass ein Kolloid nicht eine spezielle Gruppe der Substanz ist, sondern ein allgemeiner Zustand aller Substanzen, den man durch geeignete Bedingungen immer erreichen kann.

Einige wichtige Gleichungen dieser Theorie, die meine neue Methode der Kolloidsynthese betreffen, wurden hier wiedergegeben.

Die Teilchengrösse G der dispersen Phase eines dispersen Systems wurde von v. Weimarn wie folgt ausgedrückt:

$$G = f\{(Q-L)/L, v, t\}^{(3)},$$

wobei G : Teilchengrösse; Q : Konzentration vor dem Erscheinen des Teilchens; L : Löslichkeit; v : Volum des Systems; $(Q-L)/L$: relative Übersättigung; t : Temperatur, darstellt.

Daraus, bei konstanter Temperatur und Volumen, reduzierte er die Gleichung: $G \cdot (Q-L)/L = K$, d.h. es gibt eine hyperbole Beziehung zwischen Teilchengrösse und der relativen Übersättigung, die er für verschiedenartigste Fälle experimentell bestätigt hatte. Von dieser Gleichung kann man also konstatieren, dass man G willkürlich ändern kann, je nach der Wahl der Werte der Übersättigung $(Q-L)/L$; wodurch mit anderen Worten "Die Allgemeinheit des Kolloidzustandes" ausgedrückt werden kann. Die so ausgeschiedenen Teilchen bleiben selbstverständlich nicht immer in anfänglichen Dimensionen, sondern mit der Zeit wachsen sie weiter oder verschwinden sie wieder, je nach den äusseren Bedingungen. Die Geschwindigkeit des Wachstum disperser Phase wurde von v. Weimarn nach zwei Stufen geteilt; unter der ersten versteht man die Wachstumsgeschwindigkeit der molekularen Keime bis zur ultramikroskopischen bzw. kolloiden Dimension, und die zweite ist die Geschwindigkeit weiteren Wachstum der Kolloiddimension. Die Geschwindigkeit der ersten Stufe (W) wird nach v. Weimarn definiert:

$$W = K \cdot \frac{\text{Kristallisations(Kondensations)druck}}{\text{Kristallisations(Kondensations)widerstand}}^{(3)}$$

(3) P. P. v. Weimarn, „Theory of colloid state of matter“ [J. Alexander, „Colloid Chemistry“, Bd. I. S. 28, (New York, 1926)].

Er hat weiter abgeleitet die Gleichung $W = k \cdot \frac{(Q-L)}{L}$ d.h. die Geschwindigkeit (W) ist der relativen Übersättigung $[(Q-L)/L]$ proportional, unter Annahme, dass der Kristallisationsdruck der Konzentration vor dem Ausscheiden des Teilchens (Q) proportional ist und der Kristallisationswiderstand der Löslichkeit (L) proportional ist. Die Geschwindigkeit der zweiten Stufe ist die Kristallisationsgeschwindigkeit in gewöhnlichem Sinne und nach Noyes und Whitney⁽⁴⁾ folgendermassen abgeleitet:

$$V = \frac{D}{\delta} \cdot O \cdot (C-L), \quad (1)$$

wobei D : Diffusionskonstante; O : Kristalloberfläche; δ : Länge diffuser Schicht; C : Konzentration in der Nähe der Kriställchen. (In unserem Fall gleich Q); L : Löslichkeit, bedeutet.

Also die Kriställchen haben die Neigung proportional $(Q-L)$ zu wachsen. Daraus ergibt sich, dass man, um ein disperses System beständig zu halten, Bedingungen auswählen muss, diese Geschwindigkeit (V) möglichst hemmen.

Noch ein Faktor, der das Entstehen und die Stabilität kolloiddisperser Systeme bedingt, ist die Dispersität einzelner Teilchen. Wie bekannt, findet die Erhöhung des Dampfdruckes bzw. der Löslichkeit im System mit kleinen Teilchen statt, die durch folgende Gleichung angegeben wird:

$$\frac{RT}{M} \ln \frac{L_2}{L_1} = \frac{2\sigma}{\rho} \left(\frac{1}{r_2} - \frac{1}{r_1} \right)^{(5)}, \quad (2)$$

wobei L_1, L_2 : Der Dampfdruck bzw. die Löslichkeit der Teilchen r_1, r_2 ; r_1, r_2 : Teilchenradius; ρ : spezifisches Gewicht der Teilchen; σ : Oberflächenspannung der Flüssigkeit; M : Molargewicht der Teilchen als Dampf; R : Gaskonstant; T : Temperatur, bedeutet.

Wenn man in erster Näherung $\ln \frac{L_2}{L_1} = \frac{L_2-L_1}{L_1}$ setzt, erhält man aus (1) und (2)

$$V = \frac{D}{\delta} \cdot O \cdot \frac{2\sigma}{\rho} \left(\frac{1}{r_2} - \frac{1}{r_1} \right) L_1 \frac{M}{RT}, \quad (3)$$

oder

$$V = \kappa \cdot D \cdot \frac{\sigma L_1}{T} \left(\frac{1}{r_2} - \frac{1}{r_1} \right); \quad \kappa = \text{Konst.}$$

Also wird V umso kleiner je kleiner L_1 ist und V wird gleich 0 wenn $r_1 = r_2$ ist. Darunter versteht man, als den Stabilitätsbedingungen eines dispersen

(4) *Z. physik. Chem.*, **23** (1897), 698.

(5) H. Freundlich, „Kapillarchemie“, Bd. I, 54; Bd. II, 100, Leipzig (1930).

Systems, erstens, eine möglichst kleine Löslichkeit dispergierender Substanz, zweitens, die Monodispersität disperser Phase. Es entspricht auch der Tatsache, dass von gewöhnlichen kolloiden Lösungen wie z.B. von Metallen, Metalloxyden, Metallsulfiden u.s.w., disperse Substanzen in gewöhnlichem Sinne fast ganz und gar unlöslich sind; wie schwer ist auch eine Kolloidlösung mit der Stabilität von einigen Jahren herzustellen, da es kaum möglich ist, die absolute Monodispersität experimentell zu verwirklichen bei kolloider Dimension. Hier kommt in der Kolloidchemie eine dritte Substanz in Frage, nämlich der Stabilisator, welcher in erster Linie die Geschwindigkeit des Kristallwachstums hemmt und die Teilchen durch elektrokinetisches Gleichgewicht suspendieren lässt, ganz gleichgültig, ob es im Sinne von Weimarnschem dispersoidem Parasitismus oder Symbiose⁽⁶⁾ oder im Sinne von Freundlich-Paulischen⁽⁷⁾ stabilisierenden Hüllen von Ionen oder Ionenkomplexen.

Aus oben ausgeführten Erörterungen können wir zusammenfassend die drei folgenden Faktoren nennen, die hauptsächlich in wichtigster Abhängigkeit stehen von den Bedingungen der Kolloidsynthese und von der Stabilität entstandener disperser Systeme:

(1) Kristallisationsgeschwindigkeit von molekulardisperssem System bis zum kolloiddisperssem Gebiet, nämlich die Geschwindigkeit W .

(2) Kristallisationsgeschwindigkeit vom kolloiddispersen Gebiet bis zur grobdispersen Dimension, nämlich die Geschwindigkeit V .

(3) Dispersität einzelner Teilchen, d.h. Feststellung, ob die disperse Phase monodispers oder polydispers ist.

Durch den Vergleich dieser Faktoren mit vorhergehender theoretischer Erörterung, merkt man sofort, dass die Übersättigung $(Q-L)$ bzw. die relative Übersättigung $(Q-L)/L$ ⁽⁸⁾ bei diesen Faktoren die wichtigste Rolle spielt.

Also, um ein stabiles kolloiddisperses System zu erhalten, ist zuerst möglichst grosse W , d.h. grosse $(Q-L)/L$ nötig, und weiterhin, wenn die disperse Phase bis zur Kolloiddimension gewachsen ist, ist ein plötzliches Sinken des weiteren Kristallwachstums, d.h., möglichst kleine V erforderlich; ausserdem muss dazu eine solche Bedingung ausgewählt werden, die die disperse Phase möglichst monodispers ausscheidet. Alle bisherigen Methoden der Kolloidsynthese könnte man auf diesen Punkt reduzieren. Die von v. Weimarn gefundene Methode, wie z.B. die Kolloidsynthese durch Wechseln des Lösungsmittels⁽⁹⁾, oder die durch mechanisches

(6) P. P. von Weimarn, *Kolloid-Z.*, **4** (1909), 127; **37** (1925), 151; *Kolloid-Beihfte*, **1** (1910), 105; „Kristalloides u. kolloides Lösen u. Niederschlagen“, Bd. II, 541-638, Kyoto (1921).

(7) H. Freundlich, „Kapillarchemie“, Bd. II, 89 (1932).

(8) P. P. von Weimarn, *Kolloid-Beihfte*, **1** (1910), 331; E. Heymann, *Kolloid-Z.*, **48** (1929), 195.

(9) „Die Allgemeinheit des Kolloidzustandes“, S. 202; *Kolloid-Z.*, **8** (1911), 216.

Zerreiben⁽¹⁰⁾ fassen auf diesem Prinzip. Meine neue Methode der Kolloidsynthese durch Dampfexplosion, die bereits von v. Weimarn theoretisch besonders interessant festgelegt wurde⁽¹¹⁾, experimentell aber, der technischen Schwierigkeit wegen, bis jetzt noch nicht vollkommen ausgeführt worden war, kommt noch hier dazu.

A. Gutbier⁽¹²⁾ war der Erste, der diese Meinung von v. Weimarn zu verwirklichen versuchte. Da er aber einen offenen Apparat angewendet hatte, war, beim Moment des Kontaktes von Dampf mit Dispersionsmittel, dieser Dampf schon ziemlich abgekühlt und lag in der Nähe des Kondensationspunktes. Daraus kann man ersehen, dass dieser Versuch weit entfernt von der theoretisch verlangten Bedingung war. Dagegen habe ich einen geschlossenen Apparat benutzt, aus dem der hochoverhitzte Dampf mit einem Dampfdruck von wenigstens einigen Atmosphären explosionsartig in das Dispersionsmittel hineinstürzte und mit demselben augenblicklich in Kontakt kam, und zwar mit sehr grossem Wert der relativen Übersättigung $(Q-L)/L$. Daraus kann man auf viele ideal-ähnliche Fälle schliessen, sowie viele interessante Resultate erwarten, die auch wirklich eingetroffen sind, wie in folgenden Kapiteln ausführlich berichtet wurde.

Experimenteller Teil.

I. Allgemeines. A. Wahl und Reinheitsgrad der Versuchsmateriale. Die dispergierende Substanz habe ich vorläufig nur auf Quecksilber, Schwefel und Selen beschränkt, wie A. Gutbier, da sie unter hoher Temperatur und Druck verhältnismässig beständig sind. Ihre sehr kleine Löslichkeit im Wasser erfüllt auch die theoretisch nötige Bedingung.

Als Dispersionsmittel wurde destilliertes Wasser benutzt. Der Reinheitsgrad dieser Versuchsmateriale ist folgender :

Quecksilber⁽¹³⁾: Geliefert von der Firma Tyôsyôkô (Osaka, Japan); es ist speziell gereinigt durch monatelanges Behandeln mit Salpetersäure, Wasser und Vakuum-Destillation, zum Gebrauch wissenschaftlicher Quarzlampen. Nach chemischer Analyse konnte man gar keine Verunreinigung nachweisen. Spektroskopisch⁽¹⁴⁾ wurde eine winzigste Spur von Pb nachgewiesen, wobei aber nicht ganz klar ist, ob es sich um die Verunreinigung von Quecksilber handelt, oder ob sie während der Spektroskopie hineingekommen ist. Ausser Blei wurde die gewöhnliche hartnäckige Verunreinigung wie z. B. Cd oder Zn nicht nachgewiesen. Schwefel: Sublimiertes Präparat nach J.A.B. Selen: E. Merck, schwarz, in Stangen. Destilliertes Wasser: Durch Luftstrom, frei von CO₂, NH₃, zweimal destilliertes Leitfähigkeitswasser nach Bourdillon.

(10) „Die Allgemeinheit des Kolloidzustandes“, S. 268; S. Utzino, *Japan. J. Chem.*, **2** (1923), 21; *Kolloid-Z.*, **32** (1923), 149.

(11) *Kolloid-Z.*, **66** (1933), 4; Fussnote (13), (14).

(12) A. Gutbier, *Z. anorg. allgem. Chem.*, **152** (1926), 163; **155** (1926), 199; **158** (1926), 99.

(13) N. Sata, *Kolloid-Z.*, **71** (1935), 49.

(14) Spektroskopie wurde ausgeführt von Herrn Prof. Asada, Physikal. Inst. d. Osaka Univers., für dessen Liebenswürdigkeit ich an dieser Stelle herzlich danken möchte.

B. Methodik und Apparate. Das Hauptprinzip der Methodik liegt darin, dass die Kolloiddispersion einer Substanz durch Explodieren überhitzter, hochgespannter Dämpfe oder Flüssigkeiten, die auch im Moment der Explosion sofort verdampfen, vor sich geht, sodass man im Moment der Explosion einen enorm grossen Wert der Übersättigung erwarten kann, den man sonst auf keine Weise erreichen könnte. Bei der experimentellen Ausführung kann man sich die Methodik bzw. die Apparate in den verschiedenartigsten Fällen denken, je nach der Natur der dispergierenden Substanzen sowie der Dispersionsmittel. Ganz übersichtliche, grundlegende Variationen der Ausführung sind schematisch in Abb. 1 wiedergegeben. Ausser oben

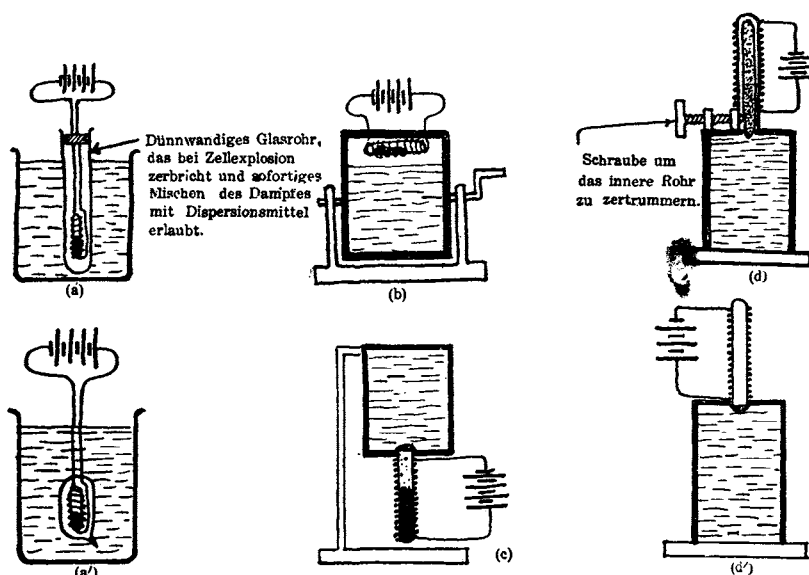


Abb. 1.

gezeigten Fällen wurden noch andere neue Möglichkeiten ausführlich untersucht.

(a) Nach nebenstehendem Apparat, aus Abb. 2 ersichtlich, habe ich mit Hg ein undurchsichtiges, graues, disperses System erhalten. Die Stabilität hängt nur von dem Vorhandensein der stabilisierenden Substanzen ab, wie nachher noch eingehend erwähnt wird. Mit S und Se ist die Kolloidsynthese mit diesem Apparat sehr schwer. Die Hauptursache liegt darin, dass der Temperaturkoeffizient ihres Dampfdruckes viel weniger als Hg ist. Deshalb muss man S auf beinahe 1000°C . erhitzen und Se auf noch höhere Temperatur bringen, um genü-

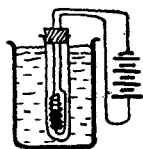


Abb. 2.

genden Dampfdruck zu erhalten, die innere und äussere Zelle und das Schutzrohr zu brechen. Erfahrungsgemäss ist jedenfalls 1 Atm. oder mehr zu einer solchen Explosion nötig, wenn man die Zelle und das Rohr aus dünnstem Glas herstellen würde. Da aber bei dieser Temperatur kein Glas druckfest ist, kann man dazu nur Quarz benutzen, trotzdem es damit noch schwerer ist, Zellen mit gleichmässigen Wänden herzustellen. Wenn die Zellwand nicht gleichmässig ist, bricht sie an dem schwächsten Teil bei verhältnismässig niedrigem Dampfdruck, und der Dampf stürzt heraus, ohne die Kraft zu haben, die äussere Zelle zu brechen und weiter in das Dispersionsmittel zu dispergieren.

In Wirklichkeit konnte ich durch Anwendung der Quarzzelle mit S nur unstabile grobe Suspension erhalten, und bei Se ist es überhaupt nicht zur richtigen Explosion bis zum Aussenrohr gekommen. Es wurde das Quarz auch lokal über 1000°C. an den Kontaktstellen mit Heizungsdraht erhitzt (natürlich nur Pt- oder Wo- oder Ta-Draht brauchbar), wobei es an den Stellen, die mit Heizungsdraht in Berührung kamen, weich wurde; und hier findet schon ein Aufblasen und Auspusten des Zellinhaltes statt, wie es z.B. beim Kuchenbacken der Fall ist.

(b) Umkehr-Apparat (Schüttel-Apparat). Dieses Prinzip habe ich (nach Abb. 3) nicht nur durch einfaches Umdrehen, sondern gleichzeitig auch durch

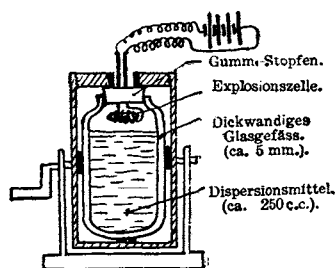


Abb. 3.

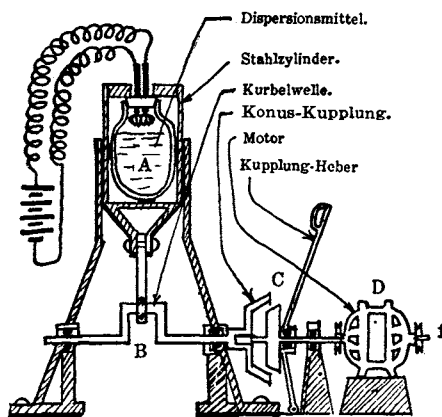


Abb. 4.

starkes Schütteln verwirklicht. Der Apparat ist nämlich mittels einer Kurbelwelle durch eine Kupplung mit einem Motor verbunden, und durch Einschalten der Kupplung wird er stark geschüttelt. Der Apparat ist schematisch aus Abb. 4 ersichtlich. In einem Stahlzylinder befindet sich ein dickwandiges (5 mm. stark) Glasgefäss A mit Zelle und Dispersionsmittel. Der

Zylinder wurde durch eine Kurbelwelle B mit dem Motor D verbunden, zwischen denen sich eine Konuskupplung C befindet, wodurch man Gefäß A mit Motor D schütteln und isolieren kann. Zuerst schaltet man die Heizung ein, und wenn der Zellinhalt genügend Dampfdruck erhalten hat, 'schaltet' man die Kupplung ein, wodurch das Gefäß A plötzlich stark geschüttelt wird. Natürlich zerbricht die Zelle im ersten Moment durch Berühren mit dem kalten Dispersionsmittel, und hochohitzter Dampf mischt sich explosionsartig mit demselben. Der Vorteil dieses Apparates liegt darin, dass man die Temperatur bei der Explosion einigermaßen kontrollieren kann, wenn man mit bekannter Elektrizitätsmenge arbeitet, und dass man auch durch plötzliches starkes Mischen die Erhöhung der relativen Übersättigung beschleunigen kann. Mit dieser Apparatur, wie Abb. 4 zeigt, erhält man mit Hg immer schöne Resultate. Bei den Versuchen mit dem Apparat waren die Explosionen manchmal so stark, dass die 5 mm. dicke Glasflasche zerbrochen wurde. Trotzdem ist das erhaltene Sol nicht so stabil. Diese Tatsache wird durch den Mangel am Stabilisator erklärt, auf den ich später noch zurückkommen werde. Die Ursache der starken Explosion bei Hg liegt nicht am Apparat selbst, sondern an Hg, welches schon bei 500°C. 8 Atm. Dampfdruck erzeugt, und dessen Temperaturkoeffizient enorm gross ist⁽¹⁵⁾. Mit S konnte ich in manchen Fällen die schöne, bläuliche kolloide Lösung erhalten, die eine sehr kurze Lebensdauer hat, und zwar konnte man sehr gut den Koagulationsübergang beobachten (worüber an anderer Stelle oft berichtet wurde⁽¹⁶⁾), der aus Tabelle 1 ersichtlich ist:

Tabelle 1.

Gleich nach der Explosion	Die Flüssigkeit ist ganz klar, auf ihrer Oberfläche schwimmen die groben S-Flocken.
Nach 5 Minuten	Die Flüssigkeit wird schön bläulich-opaleszierend.
Nach 5-10 Minuten	Die Flüssigkeit ändert sich von bläulich-opaleszierend zu bläulich-weisstrübe opaleszierend mit zunehmender weisser Trübung.
Nach 10 Minuten	Die Flüssigkeit fängt an, weisstrübe zu koagulieren.
Nach 1 Tag	Die Flüssigkeit ist ganz klar, vollständig koaguliert.

Bei Se wurde zuerst mit Glaszelle untersucht, und zwar erhitzt man sie vorsichtig bis zu dem Moment, wo das Glas anfängt aufzublasen, und schaltet dabei die Kupplung ein. Die erhitzte Glaszelle zerbricht dabei explosionsartig,

(15) „Landolt-Börnstein Tabellen,“ 5. Aufl., II, S. 1334.

(16) R. Auerbach, *Kolloid-Z.*, **27** (1920), 223, u. a.

aber da die Temperatur selbst nicht hoch genug ist, um genügende Dampfspannung von Selen zu erzeugen, ist hier ein Teil von Selen, welcher vielleicht nur in geschmolzenem Zustand vorhanden war, kondensiert und schwimmt als Selenanflug auf der Flüssigkeitsoberfläche. Eine ganz kleine Menge dispergiert als grobdisperse rote Suspension, die sehr schnell absetzt. Mit Quarz- zelle erhält man auch fast dasselbe Resultat wie mit Glas, oder ein noch schlechteres, weil das Glas beim Berühren mit kaltem Dispersionsmittel explosionsartig zerbricht, während das Quarz ohne Schaden bleibt. Das Quarz wurde aufgeblasen, wobei die lokal stark erhitzte Kontaktstelle mit Pt-Draht und das erhaltene disperse System noch verdünnter ist als mit einer Glaszelle, weil das Glas in kleine Stücke springt, und zwar nicht durch den Innendruck von Selen-Dampf, sondern durch den Kontakt mit dem kalten Dispersionsmittel. Jedenfalls wurde der sich in der Zelle befindende Dampf (kann sehr wenig sein) mit dem Dispersionsmittel gemischt, und dieses ergibt ein disperses System. Dagegen scheinen bei der Quarzzelle fast alle Dämpfe in der Zelle wieder zu kondensieren, ohne sich mit dem Dispersionsmittel zu mischen, weil Quarz durch den Kontakt mit kaltem Dispersionsmittel nicht zerbricht. Jedenfalls dürfte diese Einrichtung eine grosse Anwendungsmöglichkeit finden, besonders in der Technik, weil man sie leicht und einfach kontrollieren kann. Nur vorläufig fehlt uns eine geeignete Zellen-Material und Heiz-Quelle, um einen genügenden Dampfdruck zur dispergierenden Substanz zu erzielen.

(c) Methode der Explosion von unten oder von oben. Die Explosion nach dem Prinzip von (c) bzw. (d) (Abb. 1), Einspritzen von oben oder unten, wurde bis jetzt als die beste befunden, und ist auch deren Ausführung am bequemsten.

Es war mir zuerst gelungen mit allen drei Versuchsmaterialien, d. h. mit Quecksilber, Schwefel und Selen, die stabilen dispersen Systeme durch dieses Prinzip zu erhalten und zwar wie aus Abb. 5 schematisch zu ersehen ist. Nach eingehenden, bis jetzt ausgeführten, Untersuchungen wurden noch viele Fehler gefunden und die Apparatur in vielen Punkten verbessert. Anfangs konnte man noch nicht immer reproduzierbare Resultate erhalten, d. h. die erhaltenen Sole waren manchmal stabil und manchmal unstabil. Nachher ist es allmählich aufgeklärt worden, dass der Fehler im Apparat lag, in dem die Explosion von unten geschah. Gewöhnlich fiel bei der Explosion das Quarzrohr wegen des Explosionsrückstosses ab, wobei die Flüssigkeit über Asbestplatte, Nichromdraht und Quarzrohr strömte und sich in die unten befindliche Schale ergoss wie Abb. 5 zeigt. So ist es sehr leicht verständlich, dass die löslichen Substanzen auf oben genannte Weise aus ungereinigten Versuchsmitteln extrahiert, sich in den Solen vermischen, die manchmal als Stabilisator, manchmal

als Koagulator wirken, wodurch nichtreproduzierbare Resultate verursacht werden. Diese Vermutung wurde auch wirklich durch folgenden Versuch, wie in Abb. 6 dargestellt, bestätigt.

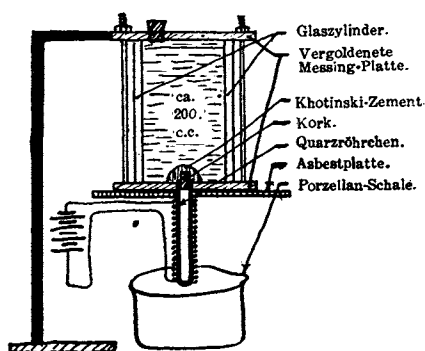


Abb. 5.

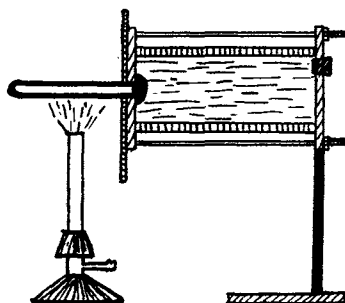


Abb. 6.

Jetzt wird der ganze Apparat um 90° gedreht und horizontal gehalten, damit man nach der Explosion die Flüssigkeit immer rein halten kann. Natürlich fliegt in den meisten Fällen bei der Explosion das Quarzrohr infolge des Gegenstosses wie eine Gewehrkuugel zurück, und die obere Hälfte des Inhaltes fließt heraus.

So sind die Versuche in Wirklichkeit in der Weise ausgeführt, wie aus Abb. 7 ersichtlich ist. Es wurde jetzt als Explosionsrohr ein dickwandiges Quarzrohr mit geschliffenem Quarzstopfen angewendet.

Nach der Explosion wurden die dispersen Systeme durch Wegfliegen des Quarzrohres in zwei Teile geteilt (A und B). Natürlich endet die Dispergation augenblicklich vor dem Aufschwimmen der Flüssigkeit; A ist das disperse System, das ganz rein und ohne Berührung mit dem äusseren Teil im Gefäß bleibt, B ist der Teil, der ausgeströmt ist, wobei durch Berühren der Asbestplatte usw. eine unreine Beimengung möglich ist. Bei diesen beiden Proben wurden Sedimentationsvorgänge beobachtet. Das zusammenfassende Resultat ist folgendes: Wenn die Flüssigkeit keine oder eine nicht geeignete Menge Stabilisator enthält, dann setzt Fraktion A ab, und sedimentiert schon in 1–2 Tagen ganz klar. Dagegen ist bei B die Sedimentation ganz unbestimmt, einmal schnell, einmal langsam, ein anderes Mal sehr stabil, genau wie die Resultate bei den anfänglichen Versuchen, die in Abb. 5 ausgeführt wurden, zeigen, wo sich die Flüssigkeit in der unteren Schale sammelt. Dadurch dürfte die Nichtreproduzierbarkeit der genannten Untersuchung, die durch zufällige Beimengung verursacht ist, konstatiert sein.

Der Apparat wurde, wie Abb. 8 zeigt, noch verbessert, um diese ausströmenden Verluste zu vermeiden. Dazu wurde ein automatischer Schluss angesetzt. Damit bleibt die ganze Flüssigkeit, trotz des Wegfalls des Quarzrohres durch Explosionsstoss, in dem Gefäss.

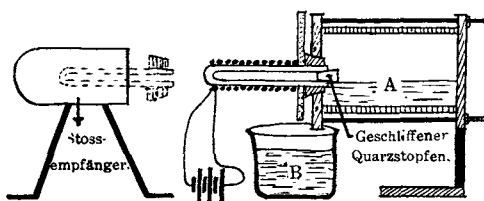


Abb. 7.

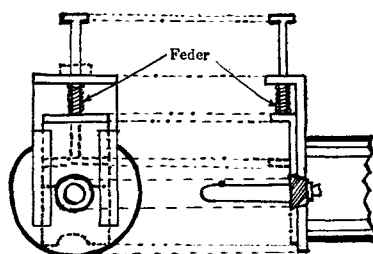


Abb. 8.

Noch eine Verbesserung in der Ausführung ist dadurch erzielt worden, dass man möglichst viele Dämpfe vom Explosionsrohr ohne Verlust in das Gefäss einspritzen kann. Es ist nämlich, besonders beim gefärbten Dampf gebenden System, wie z.B. dem Fall Se, bemerkt worden, dass bei der Explosion fast der grösste Teil des erzeugten Dampfes aus dem Gefäss wegfiegt, weil der Gegenstoss durch die Explosion so gross ist, und dass durch die grosse Geschwindigkeit des Zurückfliegens die Dämpfe keine Zeit haben, vor dem Zuschliessen des automatischen Schlusses in die Flüssigkeit hineinzustürzen. Dieses merkt man daran, dass rote Se-Dämpfe bei der Explosion

aufsteigen. Dieser Fehler wurde dadurch beseitigt, dass man das Explosionsrohr von hinten mit einer Asbestplatte leise stützt, wie auf folgender Abb. 9 gezeigt ist. Dabei merkt man gleich, dass dadurch viel weniger Dämpfe hinaussteigen, als wie dieses ohne Stütze der Fall war, und dass man auch viel konzentrierteres Sol erhalten kann.

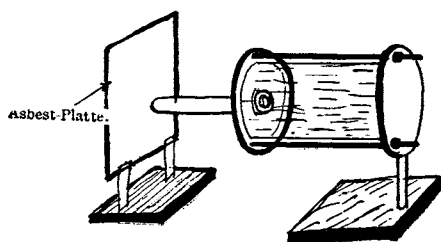


Abb. 9.

C. Über die Stabilität der Sole. Wie schon darauf hingewiesen wurde, hängt die Stabilität der Sole erstens von dem Apparat ab, mit welchem sie hängestellt werden, und zweitens von der Natur der dispergierenden Substanzen und natürlich auch vom Vorhandensein der Stabilisatoren.

Den Zusammenhang der Stabilität mit den Apparaten habe ich in vorhergehendem Kapitel ziemlich genau beschrieben. Ausserdem kann man auch leicht erwarten, dass man durch die Explosion höheren Dampfdrucks ein Sol höherer Stabilität erhält als durch die Explosion niedrigeren Dampfdrucks. Die Stabilität der Sole hängt auch mit der Natur der dispergierenden Substanzen zusammen. Es ist selbstverständlich, dass man mit einer Substanz von niedrigem Siedepunkt leichter einen höheren Dampfdruck erzeugen kann, als mit einer solchen von hohem Siedepunkt. Aus diesem Grunde war es schwer, mit schwerem siedenden Schwefel bzw. Selen ein hoch-disperses Sol zu erhalten, wohingegen wir mit leichtem siedenden Quecksilber fast immer gute Resultate erzielen konnten. Das Verhalten der Stabilisatoren ist durch die Ursache der Nichtreproduzierbarkeit bei unseren vorhergegangenen Versuchen im vorigen Kapitel erklärt worden. Nämlich, in diesem Fall wurden die Sole durch die von unten her stattgefundene Explosion hergestellt und sammelten sich unten in einer Porzellanschale. Dabei kommt die Flüssigkeit selbstverständlich mit Explosionsrohr, Asbestplatte und Korken in Berührung (die vielleicht teilweise verbrannt sind, wobei möglicherweise stabilisierend-wirkende Humusstoffe usw. entstehen können). Bei allen diesen Stoffen kann man nicht garantieren, dass sie chemisch rein sind. Deshalb ist es sehr leicht verständlich, dass sie manchmal stabilisierend-wirkende Substanzen zur Sole zugeben würden und ein anderes Mal koagulierend-wirkende. Dann ist es ohne weiteres möglich, dass die Resultate nicht reproduzierbar sind. Diese Störungen wurden ganz einfach durch den Gebrauch eines horizontalen Apparates mit automatischem Schluss beseitigt, wie schon genau erklärt wurde. Im folgenden Kapitel habe ich mich mit der Untersuchung der Sol-Stabilität im Zusammenhang mit dem Vorhandensein der Stabilisatoren und anderer Verunreinigungen beschäftigt.

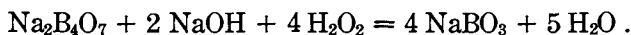
(Fortsetzung folgt.)

THE ELECTROLYTIC FORMATION OF SODIUM PERBORATE. Part I.

By Ryoichi MATSUDA.

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Sodium perborate is readily obtained when a saturated solution of borax containing an equivalent quantity of sodium hydroxide is treated with an excess of hydrogen peroxide⁽¹⁾:



S. M. Tanatar⁽²⁾ states that perborates are produced at the anode by the electrolysis of concentrated solutions of sodium orthoborate, but E. J. Constam and J. C. Bennette⁽³⁾ could not confirm Tanatar's results.

Sodium perborate is an industrial product and is manufactured chemically as well as electrochemically. In the electrochemical process the presence of sodium carbonate is necessarily requisite for the production of perborate, while it is not so in the chemical one. Accordingly two distinct views have been proposed as to the significance of the presence of sodium carbonate in the electrolytic formation of perborate; one counting the carbonate as nothing essential to do with the anodic reaction, and the other considering that it plays a part therein.

Tanatar⁽⁴⁾ assumes that borate is oxidised by hydrogen peroxide formed at the anode, and K. Arndt⁽⁵⁾ considers that the active oxygen produced at the anode as a result of OH-ion discharge is responsible for perborate formation. Both of these investigators are alike representatives of the former view. F. Foerster,⁽⁶⁾ on the other hand, states that percarbonate is primarily produced at the anode, and the hydrogen peroxide which results from the hydrolysis of the former is responsible for the oxidation in question. The present author is inclined to consider, according to the results of following experiments, that the electrolytic formation of perborate is rendered possible only through the intermediate production of percarbonate.

(1) S. M. Tanatar, *Z. physik. Chem.*, **26** (1898), 132; *ibid.*, **29** (1899), 162; B. Bruhat and H. Dubois, *Compt. rend.*, **140** (1905), 506.

(2) *Loc. cit.*

(3) *Z. anorg. Chem.*, **25** (1900), 265.

(4) *Loc. cit.*

(5) *Z. Elektrochem.*, **28** (1922) 263.

(6) "Elektrochemie wässriger Lösungen," 4th Ed. (1923).

In addition to the study of the mechanism of the anodic reaction a comparison of electrolysis using diaphragm with that without it is made, as well as a study of the effects of adding several foreign substances from a practical point of view.

Experimental and Discussion.

For the purpose of electrolyses with diaphragm a spiral of Pt-wire of 0.5 mm. diameter is used as the anode, rotating at the centre of a porous cylinder which, standing at the centre of a beaker, makes the anode chamber. The anode is thoroughly ignited immediately before electrolysis. The cathode is also a spiral of Pt-wire placed against the inner wall of the beaker. The anolyte which is 120 c.c. at the commencement of electrolysis and suffers little decrease in volume at the end of it is kept at 15°C. by cold water circulating through a spiral of glass tubing immersed in the cylinder, and is stirred at the same time by the rotation of the anode. The catholyte is N-sodium hydroxide solution in all cases. The same amount of electricity, 1020 coulombs, is supplied in each electrolysis, unless otherwise mentioned.

For the purpose of electrolyses without diaphragm the same anode is employed as above, rotating at the centre of the electrolytic vessel, a stout test-tube, which is surrounded by cold water to keep the anolyte at 15°C. The cathode is a Pt-wire spirally wound against the wall of the vessel. In these cases also, the same amount of electricity, 1020 coulombs, is supplied, unless otherwise mentioned. The electrolyte which is 100 c.c. at the beginning, in this case, is not less than 99.5 c.c. at the end of electrolysis.

The analysis of the electrolyte is performed as follows: When there is no solid in the electrolysed solution, which is the case in most instances, duplicate portions of 30.0 c.c. are treated with sulphuric acid and subsequently titrated with N/10 potassium permanganate. When there is a considerable amount of solid in the solution, the latter together with the former is treated, as a whole, in the way mentioned above. It is assumed that the peroxidic product which reacts with permanganate is sodium percarbonate when the original solution contains merely sodium carbonate, but sodium perborate when the solution contains borate.

Electrolyses with Diaphragm. Three solutions are electrolysed as anolyte to see the effect of current density on the current efficiency which is varied 5–50 amp./dm.² Table 1 and Fig. 1 show the results.

Table 1.

Solution \ Current density (amp./dm. ²)	5	10	20	30	40	50
(1) 0.5 mol Na ₂ CO ₃ +0.1 mol Na ₂ B ₄ O ₇ per liter	30.7	37.2	42.5	46.7	47.3	47.8
(2) 1.0 mol „ +0.1 mol „ „ „	38.1	43.8	49.8	52.4	51.9	52.7
(3) 1.5 mols „ +0.1 mol „ „ „	41.1	47.9	54.5	56.1	58.6	59.3

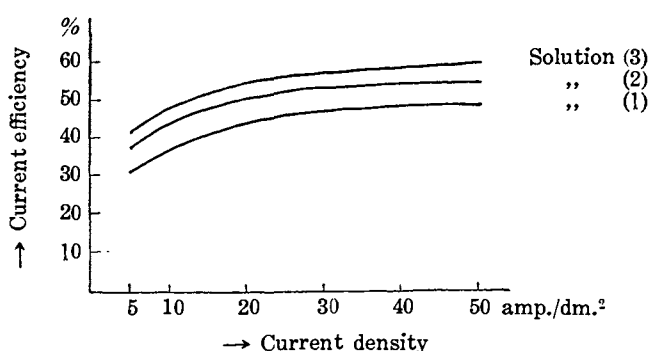


Fig. 1.

As illustrated in Table 1 and Fig. 1, the increase of sodium carbonate concentration in these cases is favourable to the current efficiency of perborate production. Increase of current density is also favourable to the same and its effect is more remarkable when the current density is comparatively smaller than when it is greater.

Perborate, as can be seen from following experiments, is hardly formed by the electrolysis of borate by itself and sodium carbonate is, at least from the practical point of view, indispensable for its electrolytic production. According to P. C. Alsgaard⁽⁷⁾ an addition of sodium carbonate causes some decrease in the solubility of perborate, yet sodium carbonate is not likely to affect the present electrolyses in this respect, since crystallisation of perborate does not take place in any of above experiments. The fact, however, that the increase of sodium carbonate increases the current efficiency seems to be in favour of the view that carbonate plays some part or other in the present electrochemical reaction.

(7) *Trans. Am. Electrochem. Soc.*, **40** (1921), 139.

Change of Current Efficiency with Time. The four solutions are electrolysed, as anolyte, with the current density of 10 amp./dm.², the results of which are shown in Table 2.

Table 2.

Solution \ Time (min.)	15	30	45	60	90
(2) see Table 1	67.7	61.9	57.8	51.3	46.4
(3) „	68.6	66.4	61.8	53.3	50.1
(4) 1.0 mol Na ₂ CO ₃ solution saturated with borax	69.3	60.9	56.0	55.7	43.0
(4) 1.0 mol Na ₂ CO ₃ solution only	56.5	51.7	41.7	37.5	28.2

Current efficiency steadily decreases with time in each case. Although the total content of perborate or percarbonate in the respective solution increases with time, the current efficiency decreases. That is to say that the rate of the increase of the peroxidic product is decreasing.

Electrolyses of Metaborate Solutions. In order to examine the possibility of perborate formation from metaborate the solutions shown in Table 3, as anolyte, are electrolysed.

Table 3.

Solution \ Current density (amp./dm. ²)	5	10	20	40
(6) 0.4 mol sodium metaborate per liter	2 drops	1	0.5	0
(7) 0.8 mol „ „	3	6	3	1
(8) 1.2 mols „ „	3	7	3	—
(9) 0.4 mol metaborate + 0.8 mol NaOH per liter	—	0	0	—
(10) 0.4 mol metaborate + 0.8 mol KOH „	0	0	0	—

Numbers of drops in Table 3 refer to titers of N/10 potassium permanganate for 30.0 c.c. portions of electrolysed anolytes, and a rough idea of current efficiency can be obtained from the following example, viz., 7 drops of permanganate solution correspond to 1.2% current efficiency. When the anolyte contains free alkali besides metaborate in these experiments, no

peroxidic product is formed at all, but it is formed, although in a small amount, when the anolyte consists of metaborate only.

As it seems interesting to the author to make out the reason why the production of the peroxidic compound is so scanty, if any in these cases—either because it is immediately decomposed after its formation, or because its production is initially small—the following experiments are made.

Rate of Decomposition of Peroxidic Compounds. Solutions (2), (5), and (7), after being electrolysed as anolyte with the current density of 20 amp./dm.² (0.566 amp., half an hour), are examined as to their content of peroxidic oxygen; a 25.0 c.c. portion of each solution is titrated with N/10 permanganate after standing for the under-mentioned period (Table 4).

Table 4.

Temp. (°C.)	Time (min.) Solu- tion	0	15	30	45	60	90	120
50	(2)	12.5 c.c.	—	8.05	—	5.85	—	3.90
	(5)	6.50	—	1.50	—	0.70	0.40	0.30
	(7)	3 drops	3 drops	3 drops	—	—	—	—
80	(2)	12.6 c.c.	2.75	1.65	0.60	0.45	—	—
	(5)	6.1	0.75	0.35	0.10	—	0	—

Assuming that the peroxidic compound contained in Solution (2) is perborate and that contained in Solution (5) percarbonate, it is clear from the above experiments that the former peroxidic compound is much more stable than the latter. Although the electrolytic formation of perborate from borate by itself is hardly possible from the practical point of view, it will be so if percarbonate which is easily producible by electrolysis and, at the same time, is liable to decompose can be transformed, by some process or other, into perborate which is more stable than the former. And above facts show that such is likely to be the mechanism by which perborate is electrolytically produced in the presence of carbonate.

Stability of perborate in metaborate and carbonate solutions is now examined. Solutions containing 0.8 mol metaborate and 1.0 mol sodium carbonate per liter respectively are saturated with sodium perborate crystals and then treated in the same way as in the previous experiment. The results are shown in Table 5, where numbers of c.c. refer to the titres of N/10 permanganate.

Table 5.

	Time- (min.) Temp. (°C.)	0	15	30	60	90
Solution (7) sat. with perborate	50	15.0 c.c.	13.4	12.1	9.1	9.1
Solution (5) sat. with perborate	50 80	15.0 14.8	13.5	8.3 0	3.6	2.2

Further, an electrolysis of Solution (7) saturated with perborate is undertaken to see to what extent perborate is decomposed during electrolysis. The current density is 20 amp./dm.² (0.566 amp., half an hour) and the N/10 permanganate titres of 25.0 c.c. portions of the original solution, the one immediately after above electrolysis, and the original solution after standing for half an hour at the same temperature as in the electrolysis, i.e., 15°C., are 15.0, 9.1, and 14.9 c.c. respectively. These results show that the decomposition of perborate during electrolysis is not to such an extent as exhausting. Conditions under which perborate exists in these cases may not be quite identical with those of electrolyses of metaborate solutions, still it is evident from above facts that perborate is much more stable in the metaborate solution than in the carbonate one. It is probable, therefore, that the small current efficiencies as regard to perborate production in electrolyses of metaborate solutions are due to its initial production itself being minute, but not to the fact that perborate which is once formed in a greater amount is mostly decomposed in subsequent instances.

Electrolyses without Diaphragm. The following solutions are electrolysed for the purpose of observing the effects of disusing diaphragm and also of adding foreign substances :

- (11) 0.5 mol Na₂CO₃ + 0.1 mol Na₂B₄O₇ + 1.0 g. K₂CrO₄ per liter,
- (12) 1.0 mol „ + 0.1 mol „ + 1.0 g. „ „ ,
- (13) 1.5 mols „ + 0.1 mol „ + 1.0 g. „ „ ,
- (14) 1.0 mol „ + 30 g. „ + 0.1 g. „ „ ,
- (15) 1.0 mol „ + 30 g. „ + 0 g. „ „ ,
- (16) 1.0 mol „ + 30 g. „ + 0.1 g. K₂SO₄ „ „ ,
- (17) 1.0 mol „ + 30 g. „ + 0.5 g. „ „ ,
- (18) 1.0 mol „ + 30 g. „ + 0.1 g. KCl „ „ .

Their current efficiencies are shown in Table 6, and some of them represented graphically in Fig. 2. Current densities are varied just as in the case

of electrolyses with diaphragm, the amount of electricity supplied being the same, 1020 coulombs, in all cases.

Current efficiency is increased by the increase of current density for the same amount of electricity. Solutions (11), (12), and (13), which respectively differ from Solutions (1), (2), and (3) which are electrolysed with diaphragm in containing 1.0 g. K_2CrO_4 in addition per liter, are inferior to the latter three with respect to current efficiency.

Table 6.

Solution \ Current density (amp./dm. ²)	5	10	20	30	40	50
(11)	9.6%	19.6	23.2	26.0	25.5	23.7
(12)	19.6	27.8	34.3	37.1	36.4	39.6
(13)	21.4	29.8	36.4	39.2	41.0	41.7
(14)	30.3	42.1	51.4	54.4	59.6	57.2
(15)	30.1	38.9	49.3	51.4	55.6	56.0
(16)	30.0	39.2	47.8	50.3	53.9	54.9
(17)	23.2	34.6	45.3	49.9	52.4	52.8
(18)	27.8	40.7	48.5	52.8	55.3	58.5

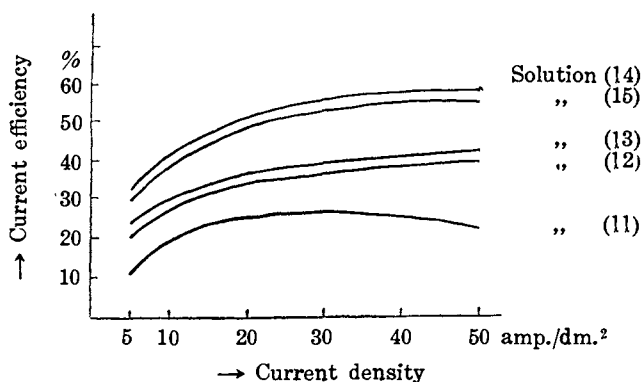


Fig. 2.

Potassium chromate consumes part of the peroxidic oxygen when the solution is treated with sulphuric acid for the sake of titration. And when it is contained as much as 1.0 g. per liter in the solution, its negative effect on current efficiency is probably more than compensated by the positive one which may have occurred during the course of electrolysis. When potassium

chromate is contained in a very small amount, e.g. 0.1 g. per liter as in Solution (14), its presence is so advantageous that the current efficiency is decidedly greater than that of any of Solutions (11), (12), and (13) and is nearly equal to that of Solution (3) in spite of its smaller content of borax.

It is rather striking that the current efficiency of Solution (15) which contains no foreign substance is equal to those of Solutions (2) and (14), because the presence of potassium chromate in the electrolyte was generally considered to be advantageous to perborate production. Solutions containing sulphate tend to decrease their current efficiencies and this tendency is the greater, the more sulphate is contained. This is because the persulphate which is produced at the anode side by side with perborate decreases the apparent current efficiency, being incapable of reacting with permanganate. The presence of sulphate in a small amount is not specially favourable. Solution (18) containing 0.1 g. of potassium chloride gives a good current efficiency, yet there is an unavoidable disadvantage, in this case, that the Pt-anode is attacked by its presence.

Change of Current Efficiency with Time at Constant Current Density. Solution (15) which contains sodium carbonate and borax but no other foreign substance is electrolysed with the current density of 20 amp./dm.² The current efficiency, as shown in Table 7, gradually decreases as time goes on to 120 minutes.

Table 7.

Time (min.)	15	30	45	60	90	120
Current efficiency (%)	55.8	49.3	41.2	35.7	28.5	22.9

Now, what will be the results of supplying the materials which are being consumed during electrolysis? As the first step, 0.5 g. of borax which is the calculated amount to recover the same consumed for the perborate production is added in five equal portions at 15, 30, 45, 60, and 90 minutes after the beginning of electrolysis. The current efficiency of 120 minutes' electrolysis is then 25.4%, being a small improvement of the original value.

Secondly, besides addition of borax, carbon dioxide is supplied which is assumed to be lost during electrolysis. When the gas is kept passing up in the electrolyte, coming out of a tube at the bottom of the cell, the inner diameter of which tube is 3.5 mm., at the rate of about 50 bubbles per minute, the current efficiency is 18.6% for the electrolysis of the same period as above. When carbon dioxide is passed in, the other conditions remaining

the same as before, for every other 15 minutes, the current efficiency is 24.5%. Among several other results, the highest current efficiency, 27.3%, is obtained by supplying the gas into the solution so as just check its coming out of the tube for 5 minutes each half an hour. The current efficiency of 5 hours' electrolysis under the same conditions as last-mentioned is 12.0%.

Summary.

(1) It is shown that under certain conditions there is no distinction between electrolysis with diaphragm and that without it as regard to the current efficiency of perborate production and it is possible to disuse diaphragm without affecting the current efficiency.

(2) The presence of a comparatively large amount of potassium chromate is harmful to the perborate production. When present in a small amount, however, it is not harmful but, then, advantage owing to its presence is not so considerable as was generally accepted.

(3) Effects of adding potassium sulphate and potassium chloride are studied.

(4) Current efficiency is increased, when a solution containing sodium carbonate and borax is electrolysed, by replenishing borax and carbon dioxide.

(5) Electrolyses of metaborate solutions, rates of thermal decomposition of percarbonate and perborate solutions as well as stability of perborate in the course of electrolysis are studied and consequently it is concluded that perborate is probably, in the electrochemical process, a secondary product of the anodic reaction, the primary one being percarbonate.

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ISOTOPENAUSTAUSCH ZWISCHEN WASSER UND EINIGEN ORGANISCHEN VERBINDUNGEN.⁽¹⁾

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Inhaltsübersicht. Die Austauschreaktion von D-Atomen zwischen Wasser und einigen organischen Verbindungen wurde untersucht. Mit CHCl_3 , $\text{C}_2\text{H}_5\text{OC}_2\text{H}_5$ und $\text{C}_6\text{H}_5\text{CHO}$ konnten wir keinen Austausch finden. Dagegen mit $\text{C}_6\text{H}_5\text{NH}_2$, $\text{C}_6\text{H}_5\text{OH}$, $\text{C}_4\text{H}_4\text{NH}$, $\text{C}_6\text{H}_5\text{COOH}$ und $\text{C}_6\text{H}_5\text{CH}_2\text{OH}$, wo eine Austauschreaktion gefunden wurde, bestimmten wir die Gleichgewichtskonstante K sowie den Verteilungsquotienten k der D-Atome zwischen ihnen und Wasser bei Zimmertemperatur. Die beiden Konstanten K und k änderten sich nicht, nicht einmal bei langer Erwärmung der Verbindungen mit Wasser. Daher vermuten wir, dass nur solche H-Atome, die mit O oder N verbunden sind, mit D-Atomen des Wassers ausgetauscht wurden.

Die Beziehung zwischen dem Verteilungsquotienten k und der Dissoziationskonstante der Verbindung, die ionisierbare H-Atome enthält, wurde theoretisch überlegt und an Hand der vorliegenden Experimentalresultate geprüft.

Einleitung. Eine der interessantesten Anwendungen von Deuterium liegt darin, dass man D-Atome beim Versuche von Austausch der H-Atome als eine Art von Indikatoren verwenden kann. Wenn man z.B. eine H-haltige Verbindung in schwerem Wasser löst, oder, falls sie nicht löslich ist, damit vermischt und schüttelt, findet ein Austausch von H- bzw. D-Atomen zwischen beiden Substanzen statt. Diese Austauschreaktion wird dadurch nachgewiesen, dass die Dichte des verwendeten schweren Wassers während des Versuchs abnimmt, und eventuell zum Schluss ein Gleichgewichtszustand, Austausch- oder Isotopengleichgewicht erreicht wird. Aus solch einem Versuch kann man über die Austauschbarkeit der H-Atome in den betreffenden Substanzen Schlüsse ziehen. Auf diesem Wege hat man einige interessante Ergebnisse über den Austausch von H-Atomen zwischen Wasser und organischen Verbindungen, hauptsächlich dank den Arbeiten von Bonhoeffer und seinen Mitarbeitern,⁽²⁾ erhalten. Es wurde nämlich gefunden, dass nur solche H-Atome, die an O oder N gebunden sind, durch blosses Lösen oder Vermischen direkt mit H-Atomen von Wasser ausgetauscht werden. Dagegen

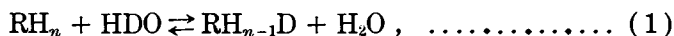
(1) Vorläufig mitgeteilt in diesem Bulletin, **10** (1935), 554.

(2) Vgl. z.B. K. F. Bonhoeffer, *Z. Elektrochem.*, **40** (1934), 469.

sind die an C gebundenen H-Atome ohne Katalysator allgemein nicht austauschbar. Diesen Umstand kann man eventuell dazu benutzen, um die Anzahl von Hydroxyl oder Aminoradikalen in einem gegebenen Molekül zu ermitteln. Aber dabei muss man noch folgende zwei Tatsachen in Betracht ziehen, worauf Bonhoeffer auch schon hingewiesen hat.

(1). Erstens wird die Sachlage etwas komplizierter, wenn die betreffende Substanz in der wässerigen Lösung irgendeine desmotropische Umwandlung erleidet. Ein gutes Beispiel dafür wurde bekanntlich an Azeton von Bonhoeffer und Klar und anderen Forschern⁽³⁾ nachgewiesen. Trotzdem alle H-Atome in dieser Verbindung direkt mit C verbunden zu sein scheinen, werden sie allmählich, besonders deutlich in der alkalischen Lösung, mit denen des Wassers ausgetauscht. Dieses Resultat wurde durch die Keto-Enol-desmotropische Umwandlung von Azeton erklärt. Später wurden noch viele ähnliche Fälle gefunden.

(2). Zweitens zeigen die D-Atome oft die Neigung, aus dem Wasser in die organischen Verbindungen mehr oder weniger absorbiert oder akkumuliert zu werden. Ein merkwürdiger Fall wurde z. B. von Bown⁽⁴⁾ mit Äthylalkohol nachgewiesen. Aber nicht selten gibt es auch den entgegen gesetzten Fall, wie an einem Beispiel weiter unten gezeigt wird. Diese Neigung zur Akkumulation der D-Atome kann man bekanntlich entweder durch den Verteilungsquotienten der D-Atome zwischen beiden Substanzen oder durch die Gleichgewichtskonstante der betreffenden Austauschreaktion quantitativ ermitteln. Falls die D-Konzentration nicht zu gross ist, kann man die Austauschreaktion zwischen einem organischen Molekül RH_n , das n austauschbare H-Atome von gleicher Natur enthält, und schwerem Wasser durch die folgende Gleichung darstellen:



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:

$$K = \frac{[RH_{n-1}D][H_2O]}{[RH_n][HDO]}, \dots\dots\dots (2)$$

und der Verteilungsquotient k der D-Atome wird durch die folgende Formel definiert:

(3) K. F. Bonhoeffer und R. Klar, *Naturwissenschaften*, **22** (1934), 45; R. Klar, *Z. physik. Chem.*, B, **26** (1934), 335; K. Schwarz und H. Steiner, *ibid.*, B, **25** (1934), 153; J. O. Halford, L. C. Anderson und J. R. Bates, *J. Am. Chem. Soc.*, **56** (1934), 491.

(4) Vgl. M. Polanyi, *Nature*, **135** (1935), 20.

$$k = \frac{\text{(Atomare Konz. von D in den gesamten austauschbaren H der organischen Substanz)}}{\text{(Atomare Konz. von D in den gesamten H des Wassers)}} \cdot \dots (3)$$

Die so definierten Konstanten K und k stellen beide für eine gegebene Verbindung eine charakteristische Konstante dar, und es gibt eine einfache Beziehung:

$$K = \frac{n}{2} k, \dots (4)$$

so lange als die D-Konzentration genügend klein bleibt. Für den praktischen Zweck ist der Verteilungsquotient 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.

Um die oben geschilderten zwei Möglichkeiten an Hand von einigen organischen Verbindungen näher zu untersuchen, haben wir das vorliegende Experiment durchgeführt, dessen Ergebnisse schon vorläufig in diesem Bulletin mitgeteilt wurden.⁽¹⁾

Versuche. Die zum Versuch benutzten Substanzen waren eine Reihe von aromatischen Verbindungen: Anilin, Phenol, Pyrrol, Benzaldehyd, Benzoesäure und Benzylalkohol. Weil sie fast alle in Wasser schwer löslich waren, wurden sie mit verdünntem schweren Wasser verschieden lange geschüttelt und davon durch blosse Abhebung getrennt. Der Verteilungsquotient k wurde dann entweder aus der Abnahme der D-Konzentration in der Wasserphase oder der Zunahme in der organischen Substanz errechnet. Aber um solch ein Experiment durchzuführen ist zuerst erforderlich, von der Geschwindigkeit der betreffenden Reaktionen, nämlich der desmotropischen Umwandlung und dem Isotopenaustausch, Kenntnis zu haben. Betreffs der ersten darf man wohl annehmen, dass sie nicht sehr gross ist. Dagegen von der Austauschreaktion kann man von vornherein erwarten, dass sie der Kategorie der schnellen Reaktion angehört. Wir haben in einem anderen Experiment gefunden,⁽⁵⁾ dass das Austauschgleichgewicht zwischen Zucker und Wasser sehr schnell erreicht wird. Wenn dies auch bei anderen Verbindungen der Fall wäre, dann brauchte man die organische Verbindung nicht so lange mit schwerem Wasser zusammen zu bringen. Vielmehr muss man auf die Versuchsbedingungen bei der Trennung von beiden Substanzen besonders achten. Dagegen vom Standpunkt der Möglichkeit einer Nebenreaktion, der desmotropischen Umwandlung, ist es wünschenswert, die be-

(5) M. Harada und T. Titani, dieses Bulletin, 11 (1936), 55.

treffende Substanz möglichst lange mit schwerem Wasser zu erwärmen. Infolgendessen sind wir in der Praxis wie folgt verfahren.

Durchschnittlich wurden 2 c.c. von 1 bis 2 prozentigem schweren Wasser mit einer geeigneten Menge von organischer Verbindung in einem Glasröhrchen eingeschmolzen. Es wurde dann gut evakuiert und bei erhöhter Temperatur verschieden lange geschüttelt. Die Menge der verwendeten organischen Verbindung wurde so gewählt, dass sie im Vergleich mit 2 c.c. Wasser die äquivalente Anzahl von austauschbar zu erwartenden H-Atomen enthielt. Nach einer bestimmten Zeit wurden das Wasser und die organische Substanz von einander abgetrennt. Dies geschah meistens bei Zimmertemperatur durch blosse Abhebung, weil die von uns verwendeten Substanzen fast alle in Wasser schwer löslich waren. Aber weil das abgetrennte Wasser noch eine Menge von organischer Substanz enthielt, wurde es mit einem geeigneten Lösungsmittel, wie z. B. Äther oder Chloroform, einige Male gut ausgewaschen. Das so ausgewaschene Wasser wurde im Vakuum mit Pumpenöl nebeneinander aber mit gemeinsamer Gasphase stehen gelassen.⁽⁶⁾ Durch diese Behandlung wurde das im Wasser wenig eingelöste Lösungsmittel vollständig durch das Pumpenöl absorbiert und weggenommen. Das wie oben behandelte Wasser wurde dann sorgfältig gereinigt und dessen Dichte durch die Schwebemethode mittels eines kleinen Quarzschwimmers genau bestimmt, die wir mit d_w bezeichnen wollen. Die Reinigung des Wassers führten wir auf folgende Weise durch. Zunächst wurde es in Dampfform über, bis auf Rotglut erhitztes Kupferoxyd geleitet. Es wurde dann unter Zusatz von Kaliumpermanganat und Ätznatron destilliert und zum Schluss im Vakuum zweimal destilliert. Die vom Wasser abgetrennte feuchte organische Substanz wurde zunächst durch Zusammenschütteln mit geeignetem anorganischen Salz wie z. B. Natriumsulfat oder Natriumkarbonat entwässert, und dann im Vakuum über Chlormalcium gut getrocknet. Die getrocknete Substanz wurde dann im Luftstrom mittels erhitzten Kupferoxyds vollständig verbrannt. Das dabei abdestillierte Wasser wurde ebenfalls gut gereinigt und dessen Dichte genau bestimmt, die wir mit d_o bezeichnen. Durch die eben geschilderten Methoden konnten wir die Gefahr für die Verschiebung des Austauschgleichgewichts beim Abtrennen in hohem Masse vermindern. Denn mindestens bei verdünntem schweren Wasser wurde bestätigt, erstens, dass die Löslichkeit des leichten und schweren Wassers in Äther oder desgleichen gleich ist,⁽⁷⁾ und zweitens, dass die Verteilung von Deuterium zwischen dem Krystallisationswasser und der Mutterlauge bei den

(6) J. Horiuti und K. Koyano, noch nicht veröffentlichte Mitteilung.

(7) H. Erlenmeyer und H. Gärtner, *Helv. Chim. Acta*, **17** (1934), 970; *Nature*, **134** (1934), 327.

anorganischen Salzen wie Natriumsulfat oder Natriumkarbonat gleichmässig ist.⁽⁸⁾ Der Verlust an Proben während dieser Behandlung betrug durchschnittlich 2 bis 3% der Anfangsmenge. Diesen Verlust konnten wir durch Vergleich der oben bestimmten zwei Dichten d_w und d_o mit der Anfangsdichte d_a des verwendeten schweren Wassers ermitteln.

Aus den so erhaltenen drei Daten von Dichten d_a , d_w und d_o wurden der Verteilungsquotient k bzw. die Gleichgewichtskonstante K ausgerechnet und zwar durch die Kombination von je zwei aus drei Dichtebestimmungen. Den Wert von k aus d_a und d_w bezeichnen wir mit k_1 , den aus d_w und d_o mit k_2 und den aus d_o und d_a mit k_3 . Dann sollten natürlich k_1 , k_2 und k_3 theoretisch identisch sein. Aber in der Praxis rechneten wir womöglich immer diese drei aus, erstens wegen der Sicherheit und zweitens um durch deren Vergleich über den Verlust an Proben Kenntnis zu gewinnen. Dadurch ergab sich, dass dieser Verlust meistens in der organischen Substanz eintritt. Dieser Sachlage trugen wir beim Ausrechnen des Mittelwerts von k aus k_1 , k_2 und k_3 Rechnung. Die Gleichgewichtskonstante K wurde dann mittels der Gleichung (4) aus k leicht ausgerechnet. Die so ermittelten Daten an k und K sind in der folgenden Tabelle 1 zusammengestellt, wo die fettgedruckten Buchstaben **H** in der zweiten Vertikalreihe die als austauschbar betrachteten H-Atome darstellen.

Tabelle 1. Versuchsergebnisse.

Substanz	Formel	Verteilungsquot. k	Gleichgewichtskonst. K
Chloroform	CHCl_3	(kein Austausch)	
Äthyläther	$\text{C}_2\text{H}_5\text{OC}_2\text{H}_5$	(kein Austausch)	
Anilin	$\text{C}_6\text{H}_5\text{NH}_2$	1.11	1.11
Phenol	$\text{C}_6\text{H}_5\text{OH}$	1.07	0.54
Pyrrol	$\text{C}_4\text{H}_4\text{NH}$	0.88	0.44
Benzaldehyd	$\text{C}_6\text{H}_5\text{CHO}$	(kein Austausch)	
Benzoessäure	$\text{C}_6\text{H}_5\text{COOH}$	1.0	0.5
Benzylalkohol	$\text{C}_6\text{H}_5\text{CH}_2\text{OH}$	1.10	0.55

Jedes dieser Resultate ist der Durchschnitt aus zwei bis fünf unabhängig von einander ausgeführten Messungen und die Genauigkeit dürfte durchschnittlich $\pm 5\%$ sein, ausgenommen den Fall von Benzoessäure. Wie man

(8) A. Güntherschulze und F. Keller, *Z. Elektrochem.*, **40** (1934), 182; K. Okabe, M. Harada und T. Titani, dieses Bulletin, **9** (1934), 460; H. Erlenmeyer und H. Gärtner, *Helv. Chim. Acta*, **17** (1934), 970; J. N. Friend, *Nature*, **134** (1934), 463; J. N. E. Day, E. D. Hughes, C. K. Ingold und C. L. Wilson, *J. Chem. Soc.*, **1934**, 1593.

leicht aus der Tabelle ersieht, ist der Verteilungsquotient k in jedem Fall nicht viel von eins verschieden.

Experiment. Die Versuchsmethodik an der einzelnen Substanz ist im folgenden einfach zusammengestellt.

Chloroform und Äthyläther. Diese beiden Substanzen wurden zunächst untersucht, weil sie als Waschflüssigkeit in anderen Experimenten benützt wurden. Aus einigen Versuchen ergab sich, dass bei Äther mindestens innerhalb einer Stunde und bei Chloroform innerhalb von 25 Stunden bei Zimmertemperatur kein Austausch von H-Atomen mit Wasser eintrat.

Anilin. Drei Versuche wurden durchgeführt: in (1) wurden 0.110 Mol Anilin bei 40°C., in (2) 0.055 Mol bei 0°C. und in (3) ebenfalls 0.055 Mol bei 110°C. je mit 0.111 Mol 0.7 prozentigem schweren Wasser 24 Stunden lang geschüttelt. Die Trennung von Anilin und Wasser geschah in jedem Fall durch blosse Abhebung, und zwar in (1) bei Zimmertemperatur, in (2) bei 0°C. im abgekühlten Zimmer und in (3) bei 60°C. Das Wasser wurde dann mit Chloroform ausgewaschen und mit Pumpenöl nach der in der Einleitung geschilderten Methode behandelt. Das feuchte Anilin wurde zunächst mit Kaliumkarbonat entwässert, dann über Chlorcalcium getrocknet, und schliesslich durch Verbrennung in Wasser verwandelt. Der Verteilungsquotient k wurde dann auf die schon oben erwähnte Weise aus drei Dichtebestimmungen, d. h. aus der des verwendeten schweren Wasser vor und nach dem Experiment sowie der des aus Anilin erhaltenen Wassers ausgerechnet. Dabei wurde angenommen, dass nur zwei H im NH_2 -Radikal direkt austauschbar sind. Die so errechneten Werte von k sind in der folgenden Tabelle 2 zusammengestellt, wobei die Bedeutungen von k_1 , k_2 und k_3 gleich wie die schon oben erklärten sind.

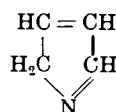
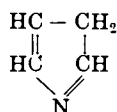
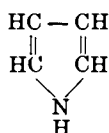
Tabelle 2. Verteilungsquotient für Anilin.

Versuchsnr.	k_1	k_2	k_3	
1	1.11	1.21	1.12	Mittel: $k = 1.11$
2	1.10	1.10	1.10	
3	1.13	1.07	1.04	

Aus diesen Resultaten ersieht man sofort, dass die Temperatur beim Abtrennen, mindestens innerhalb 0° und 60°C., keinen merklichen Einfluss auf die Grösse von k ausübt. Deshalb führten wir die Abtrennung in den folgenden Experimenten meistens bei Zimmertemperatur aus.

Phenol. Weil bei dieser Verbindung die Möglichkeit für eine Keto-Enol-desmotropische Umwandlung besteht,⁽⁹⁾ führten wir fünf Experimente unter verschiedenen Bedingungen durch. Wir erwärmten 0.06 bis 0.17 Mol Phenol je mit 0.11 Mol 2 prozentigem schweren Wasser bei verschiedenen Temperaturen und verschieden lange. Z. B. in einem Experiment dauerte die Erwärmung nur 3 Stunden bei 50°C. aber im anderen extremen Fall dauerte sie 100 Stunden bei Temperaturen zwischen 200° und 300°C. Aber wider Erwarten stimmten die k -Werte aus allen Versuchen untereinander gut überein, angenommen dass nur ein H-Atom im OH-Radikal austauschbar ist. Der grösste gefundene Wert von k war 1.14, der kleinste 1.03 und als Mittelwert aus fünf Versuchen erwies sich $k = 1.07$. Jedoch darf man keine grosse Genauigkeit verlangen, weil k nur aus der Phenolphase errechnet wurde. Wir zogen das Phenol, das in Wasser gelöst vorhanden war, mit Tetrachlorkohlenstoff aus und trockneten die so erhaltene Lösung in CCl_4 mit Na_2SO_4 . Das Phenol wurde aus dieser Lösung durch die fraktionierte Destillation gewonnen und nachdem wir uns seiner Reinheit durch die Schmelzpunkt-Bestimmung versichert hatten, wurde es schliesslich zu Wasser verbrannt.

Pyrrol. Diese Verbindung besitzt auch die Möglichkeit der desmotropischen Umwandlung wie die folgenden drei möglichen Strukturformeln zeigen:⁽¹⁰⁾



Aber aus drei unabhängig durchgeführten Versuchen ergab sich, dass k , das unter Annahme von nur einem einzigen austauschbaren H-Atom berechnet wurde, nicht viel von eins verschieden, sogar etwas kleiner als eins war. Bei den Versuchen wurden 0.071 Mol Pyrrol mit 0.11 Mol 0.7 bis 2 prozentigem schweren Wasser bei 50°C. 5 bis 50 Stunden lang geschüttelt. Sonst arbeiteten wir ähnlich wie beim Anilin. Zum Auswaschen des wenig eingelösten Pyrrols aus dem durch Abhebung davon getrennten Wasser verwendeten wir Äther. Das abgetrennte Pyrrol wurde mit Natriumkarbonat entwässert, über Chlorcalcium getrocknet und dann zu Wasser verbrannt. Das Ausrechnen der k -Werte führten wir auch genau so wie beim Anilin durch und erhielten als Mittelwert $k = 0.88$.

Benzaldehyd. Diese Substanz wurde besonders lang mit schwerem Wasser unter Erwärmung geschüttelt, um einen eventuell zu erwartenden

(9) Vgl. „Beilsteins Handbuch der org. Chem.“, 4. Aufl., S. 107.

(10) Vgl. H. Fischer und H. Orth, „Die Chemie des Pyrrols“, Bd. I, Leipzig (1934).

Austausch⁽¹¹⁾ näher zu prüfen. In einem Experiment wurden 0.20 Mol Benzaldehyd mit 0.11 Mol 0.7 prozentigem schweren Wasser bei 60°C. 20 Stunden lang und im anderen dieselbe Menge bei derselben Temperatur 100 Stunden lang geschüttelt. Aber in keinem Fall konnten wir irgendein Anzeichen für den Isotopenaustausch finden. Wir gaben besonders darauf acht, die Reaktionsgefäße vor dem Experiment gut zu evakuieren. Sonst würde das Benzaldehyd während der Schüttelung allmählich oxydiert und das Experimentalresultat erwies sich als undeutlich.

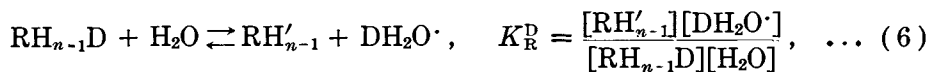
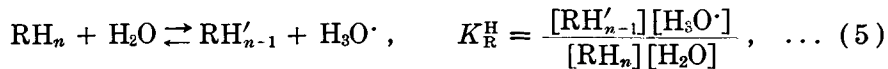
Benzoessäure. Wir führten damit, alles zusammen, vier Versuchen aus. Durchschnittlich 0.05 Mol Benzoessäure wurden mit 0.11 Mol 0.7 bis 2 prozentigem schweren Wasser bei 90°C. bis 130°C. von 16 bis 170 Stunden lang erwärmt. Säure und Wasser wurden dann durch die Destillation im Vakuum abgetrennt. Die abgetrennte Säure wurde zu Wasser verbrannt. Das Ausrechnen von k wurde genau wie beim Anilin auf drei Wegen durchgeführt. Unter der Annahme, dass nur ein H-Atom austauschbar ist, ergab sich der Mittelwert von $k = 1.04$. Aber dieser Wert mag um einige Prozent zu gross sein, weil die Abtrennung durch die Destillation ausgeführt wurde.

Benzylalkohol. Diese Verbindung interessiert uns vom Standpunkt der Akkumulation der D-Atome.⁽⁴⁾ Je 0.096 Mol (10 c.c.) Benzylalkohol wurden mit 0.11 Mol (2 c.c.) 2 prozentigem schweren Wasser im Vakuum auf 60°C. erwärmt. Die Erwärmung dauerte je 4, 5 und 16 Stunden. Nach der Beendigung der Erwärmung wurde das Reaktionsrohr bis zur Zimmertemperatur abgekühlt. Dadurch schieden sich die beiden Substanzen in zwei Phasen und wurden durch Abhebung voneinander getrennt. Der Alkohol wurde dann mit Kaliumkarbonat entwässert, über Chlorcalcium getrocknet und zu Wasser verbrannt. Die Wasserphase wurde zunächst mit Äther ausgewaschen und dann mit Pumpenöl behandelt. Das Ausrechnen von k geschah auf drei Wegen wie beim Anilin. Der Mittelwert von k , der unter der Annahme von einem einzigen austauschbaren H-Atom berechnet wurde, erwies sich als 1.10.

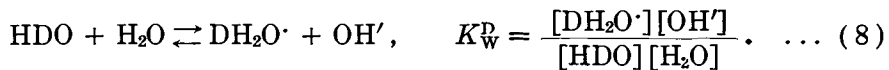
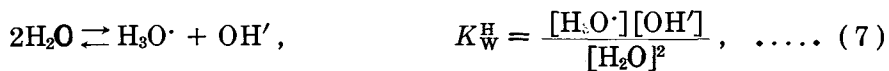
Diskussion. Wie man aus Tabelle 1 ersieht, ist der Verteilungsquotient k in jedem Fall nicht viel von eins verschieden. Jedoch kann man einen kleinen aber unverkennbaren Unterschied zwischen den einzelnen k -Werten bemerken. Diesen Unterschied kann man vielleicht auf die verschiedene Bindungskraft der austauschbaren H-Atome zurückführen. Weil die direkt austauschbaren H-Atome allgemein ionisierbar sind, kann man die Verbindung, die sie enthält, als eine Art von Säure betrachten. Der Einfachheit halber nehmen wir an, dass die Verbindung n austauschbare H-Atome von

(11) Es wurde von Klar (*Z. physik. Chem.*, B, **26** (1934), 335) der Austausch beim Acetaldehyd und Formaldehyd beobachtet.

gleicher Natur enthält und ihre Molekel mit RH_n ausgedrückt werden. Dann kann man für die Dissoziation dieser Verbindung in verdünntem schweren Wasser folgende Gleichgewichte annehmen:



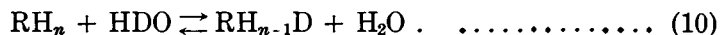
wobei die zweimal ausgetauschten Molekel $\text{RH}_{n-2}\text{D}_2$ u.s.f. wegen der Kleinheit der D-Konzentration vernachlässigt werden. Ebenfalls denken wir uns für leichtes und schweres Wasser folgende zwei Dissoziationsgleichgewichte:



Aus diesen vier Gleichungen (5), (6), (7) und (8) erhalten wir die Beziehung:

$$\frac{K_{\text{R}}^{\text{H}} / K_{\text{R}}^{\text{D}}}{K_{\text{W}}^{\text{H}} / K_{\text{W}}^{\text{D}}} = \frac{[\text{RH}_{n-1}\text{D}][\text{H}_2\text{O}]}{[\text{RH}_n][\text{HDO}]} = K. \quad \dots (9)$$

Die rechte Seite dieser Gleichung (9) ist nichts anderes als die Gleichgewichtskonstante K der Austauschreaktion:



Diese Gleichung (10) ist natürlich dieselbe wie Gleichung (1) in der Einleitung. Dort haben wir zwischen der Gleichgewichtskonstante K und dem Verteilungsquotienten k die folgende Beziehung aufgestellt:

$$K = \frac{n}{2}k. \quad \dots (11)$$

Bringt man diese Beziehung (11) in die Gleichung (9), dann folgt:

$$k = \frac{1/n(K_{\text{R}}^{\text{H}} / K_{\text{R}}^{\text{D}})}{1/2(K_{\text{W}}^{\text{H}} / K_{\text{W}}^{\text{D}})}. \quad \dots (12)$$

Aus dieser Gleichung (12) ersieht man, dass der Verteilungsquotient k für die Austauschreaktion (10) mit dem Verhältnis $1/n(K_{\text{R}}^{\text{H}} / K_{\text{R}}^{\text{D}})$ zunimmt, weil das Verhältnis der Dissoziationskonstanten der beiden Arten von Wasser $K_{\text{W}}^{\text{H}} / K_{\text{W}}^{\text{D}}$ konstant bleibt. Aber weil die Grösse $1/n K_{\text{R}}^{\text{H}}$ offenbar die auf ein bestimmtes H-Atom von RH_n -Molekel bezogene Dissoziationskonstante darstellt, ist die Grösse $1/n(K_{\text{R}}^{\text{H}} / K_{\text{R}}^{\text{D}})$ nichts anderes als das Verhältnis der

Dissoziationskonstanten von beiden monobasischen Säuren $\text{RH}_{n-1}\text{-H}$ und $\text{RH}_{n-1}\text{-D}$. Dieses Verhältnis soll aber nach der Überlegung von Halpern⁽¹²⁾ grösser werden, je schwächer die betreffende Säure wird. Infolgedessen, können wir für die Beziehung zwischen dem Verteilungsquotienten und der Dissoziationskonstante einer Verbindung folgende Schlüsse ziehen: Der Verteilungsquotient k von D-Atomen zwischen der Verbindung RH_n und Wasser nimmt zu, je schwächer die betreffende Verbindung als monobasische Säure wirkt und vice versa. Diese Folgerung scheint durch die vorliegenden Versuchsergebnisse bestätigt zu werden. Denn für k haben wir die folgende Reihenfolge:

$$k(\text{Benzoesäure}, 1.0) < k(\text{Phenol}, 1.07) < k(\text{Benzylalkohol}, 1.10) \\ \geq k(\text{Zucker}, 1.1)^{(13)}.$$

Dieselbe Reihenfolge, aber gerade in entgegengesetzter Richtung, stimmt mit der des Dissoziationsgrades der H-Atome von einzelnen Verbindungen überein.

Eine ähnliche Überlegung kann man auch mit Basen ausführen, wenn man diese als Protonakzeptor ansieht und statt der üblichen Dissoziation des OH-Radikals die des aufgenommenen H-Atoms in Betracht zieht. Dann folgt, dass der Verteilungsquotient zunimmt, je stärker die Base wird, weil das aufgenommene H-Atom desto stärker gebunden wird. In dem vorliegenden Versuch haben wir nur zwei Beispiele dafür, nämlich Anilin und Pyrol. Aber mindestens für diese beiden ist die Reihenfolge von k gerade wie erwartet, nämlich:

$$k(\text{Anilin}, 1.11) > k(\text{Pyrrol}, 0.88).$$

Zum Schluss sprechen wir Herrn Dr. Morita in unserem Laboratorium für seine Freundlichkeit ein Teil des nötigen schweren Wassers uns zur Verfügung gestellt zu haben, unseren herzlichen Dank aus. Der Nippon Gakujutsu-Shinkokai (der Gesellschaft zur Förderung der japanischen Wissenschaft) und der Hattori-Hohkokhai (der Hattori-Stiftung) sind wir auch für ihre finanzielle Unterstützung zum besten Dank verpflichtet.

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Schiomi Institut für physikalische
und chemische Forschungen.*

(12) O. Halpern, *J. Chem. Physics*, **3** (1935), 456.

(13) M. Harada und T. Titani, noch nicht veröffentlichte Arbeit.

ÜBER DIE VERTEILUNG DES LUMINESZENZTRÄGERS IM GIPSKRISTALL.

Von Ei-ichi IWASE.

Eingegangen am 17. April 1936. Ausgegeben am 28. Juli 1936.

Die eigentümliche Gestalt der zwei durch Kontaktwirkung erzeugten Mineralien, Chiasolit⁽¹⁾ und Cerasit,⁽²⁾ fesselte seit langem die Aufmerksamkeit der Mineralogen. Mit ihrer Ausnahme ist die Verfärbung des natürlichen Kristalls bzw. das Vorhandensein winziger Fremdstoffe in natürlichen Mineralien meistens schichten- oder zonenweise parallel zu einer gewissen Fläche gestuft, z.B. bei Steinsalz,⁽³⁾ Quarz,⁽⁴⁾ Fluorit⁽⁵⁾ u.s.w. Eine weitere Ausnahmestellung nimmt auch Gips ein. R. Tomaschek⁽⁶⁾ beobachtete an Gips von Leimen (bei Heidelberg) sehr helle Phosphoreszenz nach Erregung mit Zinkfunken, wobei die phosphoreszenzfähigen Teile nicht gleichmässig über den ganzen Kristall, sondern in Sanduhrform auftraten. Diese Erscheinung fand auch A. Josten⁽⁷⁾ an Gips von verschiedenen Fundorten im ultravioletten Lichte.

Zufällig hatte ich Gelegenheit, die Beobachtung an 10 Gipskristallen von Gánt (Ungarn) auszuführen. Ihr Verhalten in dem durch Woodsches Glas filtrierten Lichte einer Quarz-Quecksilberbogenlampe wurde unter Benutzung von Riken Ultrazin Filter Nr. 2 aufgenommen. Unter ihnen gaben drei Kristalle ihre Sanduhrstruktur auf die prachtvollste Weise durch Fluoreszenzkund, wie man in den Abb. 1–3 ansehen wird. Der Spitzenwinkel der Leuchtkegel beträgt 80° oder 90° bei den in Abb. 1 und 2 dargestellten Kristallen. Obgleich der Kristall in Abb. 3 nach dem Aussehen aus zwei sich zusammengefügt zu bestehen scheint, zeigt er doch nur eine Sanduhr mit Spitzenwinkeln von 70° und 100°. Während die hier untersuchten Kristalle von Gánt fast immer scharfwinklige Leuchtkegel zeigten, ergab ein prächtig ausgebildeter Gipskristall von Wiesloch (bei Baden), den Herr Prof. J. Harada in der kaiserlichen Universität zu Hokkaido freundlichst zur Verfügung

(1) C. Hintze, „Handbuch der Mineralogie“, Zweiter Band, 133, Leipzig (1897).

(2) C. Hintze, *ebenda*, 931; Y. Kikuchi, *J. Fac. Sci. Imp. Univ. Tokyo*, **3** (1890), 314–34; K. Masutomi, „Mineralien von Geschmack“ (japanisch), **2** (1930), Nr. 11.

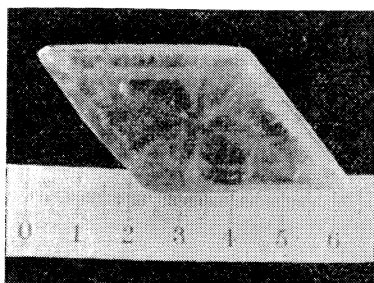
(3) K. Przibram, *Sitzber. Akad. Wiss. Wien, Math.-naturw. Klasse. Abt. II a*, **143** (1934), 489.

(4) S. Ito, *Tokyo Electric Review*, **7** (1932), 87.

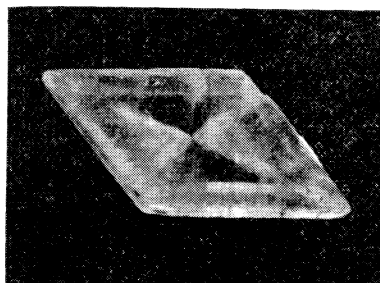
(5) H. Steinmetz, *Z. Krist.*, **61** (1925), 380; O. Mügge, *Nachr. Ges. Wiss. Göttingen. Geschäft. Mitt., Math.-physik. Klasse*, (1923), 1.

(6) W. Wien und F. Harms, „Handbuch der Experimentalphysik“, **23**, 451 (1928).

(7) A. Josten, *Centr. Mineral. Geol.*, **A**, (1930), 432–435.

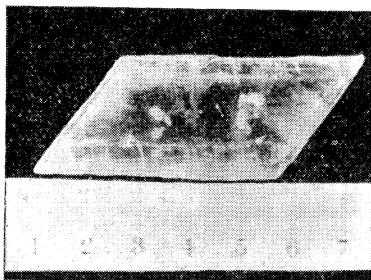


Im Tageslichte.
(Mit Zentimeter-Längenmaße.)

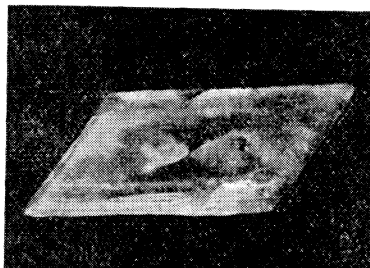


Im ultravioletten Lichte.

Abb. 1. Probe : Gips aus Gánt.

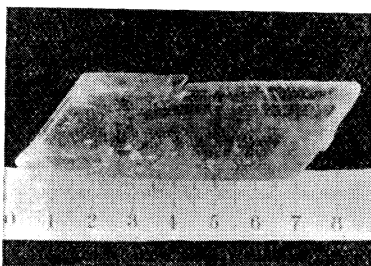


Im Tageslichte.

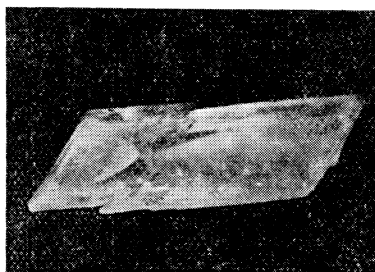


Im ultravioletten Lichte.

Abb. 2. Probe : Gips aus Gánt.



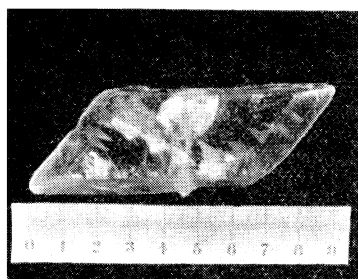
Im Tageslichte.



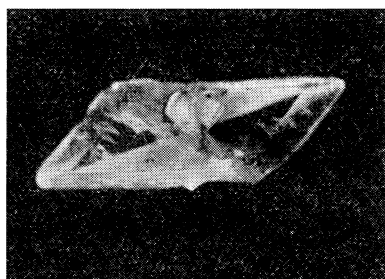
Im ultravioletten Lichte.

Abb. 3. Probe : Gips aus Gánt.

stellte, Fluoreszenzkegel mit stumpfen Winkeln von 120° und 130° , deren Winkel fast mit den von Tomaschek⁽⁶⁾ untersuchten gleich sind. Die Resultate gibt Abb. 4 wieder. Weiterhin wurden Versuche an Gips der folgenden japanischen Vorkommen angestellt, um solche Sanduhrstruktur nachzuweisen: Hanaoka in Akita Präfektur, Hakone in Kanagawa Präf., Ogasawara-Insel in Tokio Präf., Nojiri-See in Nagano Präf., Ikuno in Hiogo Präf., Udo in Shimane Präf., Okinazawa in Iwate Präf., Aizu in Fukushima Präf.,

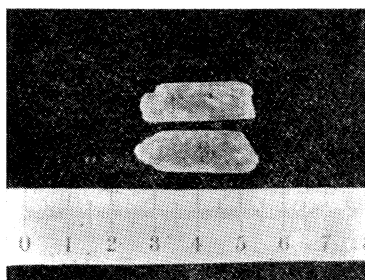


Im Tageslichte.

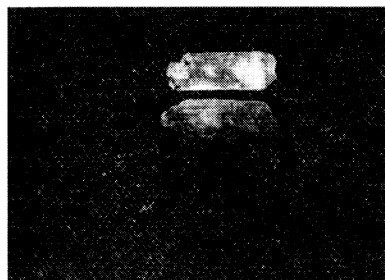


Im ultravioletten Lichte.

Abb. 4. Probe: Gips aus Wiesloch.



Im Tageslichte.



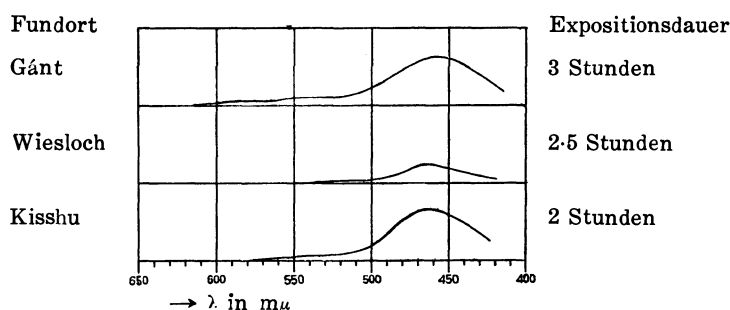
Im ultravioletten Lichte.

Abb. 5. Probe: Gips aus Kisshu.

Yogozawa in Yamanashi Präf., Kune in Shizuoka Präf. und Kisshu bei Kankiohokudo in Korea. Nur beim letzteren Vorkommen konnte ich die Erscheinung unvollkommen wahrnehmen, wie aus Abb. 5 ersichtlich ist. Alle anderen Kristallstücke zeigten keine Fluoreszenz. Dem Entgegenkommen der Herren N. Katayama, O. Nagashima und K. Sakurai verdanke ich die Möglichkeit, die Untersuchung an so vielen japanischen Kristallen auszuführen.

Überblickt man die oben erwähnten Ergebnisse vom kristallographischen Gesichtspunkte, so kommt man zum beachtenswerten Schlusse, dass zwar der Spitzenwinkel des Leuchtkegels von sehr verschiedener Grösse ist, aber dass stets nur die Anwachspyramide auf der Fläche (111) fluoreszierte, dagegen die auf (110), abgesehen von einigen Reflexen, vollkommen dunkel blieb. Diese Tatsache stimmte überraschenderweise mit der von Josten⁽⁷⁾ berichteten überein. Die Struktur des Gipskristalls ist durch röntgenographische Untersuchungen ziemlich eingehend erforscht. Nach der von E. Onorato⁽⁸⁾ für Gips ermittelten atomischen Anordnung beträgt der mittlere Abstand zwischen dem Kalziumatome und einem bestimmten Sauerstoffatome des Sulfations 1.8 Å, der also um 30% kleiner ist gegenüber dem normalen Abstände. Die Richtung, in der sich diese Zwang erfahrenden Atome einlagern, ist ungefähr senkrecht zur Fläche (101). Zur Unterstützung dafür kann ich die Angabe von L. A. Coromilas⁽⁹⁾ anführen, dass die Richtung des minimalen Dehnungsmodulus durch den stumpfen Winkel β geht und zur C-Achse etwa um 13.5° geneigt ist.

Nimmt man an, dass diese Fluoreszenz von winzigen Mengen von Verunreinigungen herrührt und weiter dass das Wachstum des Kristalls von der Spitze des Leuchtkegels an eintritt, so könnte man die gesetzmässige Sanduhrstruktur, die der Kristall im ultravioletten Lichte aufweist, erklären wie folgt: Die Fluoreszenz bewirkende Fremdschubstanz wird während des Wachstums des Gipskristalls in der Anwachspyramide auf (110) d.h. in der standhaft wachsenden Richtung, nicht eingelagert, sondern sie sammelt sich nur in der Anwachspyramide auf (111), d.h. in der Zwang erleidenden Richtung.



Schematische Darstellung des Fluoreszenzspektrums von Gips.

Abb. 6.

(8) R. W. G. Wyckoff, „The Structure of Crystals,“ 2. Aufl. (1931), 308; E. Onorato, *Z. Krist.*, **66** (1928), 504.

(9) L. A. Coromilas, *Z. Krist.*, **1** (1877), 409.

Welche Beimengung als Lumineszenzträger an dieser Leuchterscheinung teilnimmt, ist noch nicht festzustellen. Alle fluoreszierenden Stücke von Gánt, Wiesloch und Kisshu ergaben immer dieselbe breite verwaschene Fluoreszenzbande mit Maximum bei etwa $460\text{ m}\mu$, deren Einzelheiten aus Abb. 6 erkennbar sind. Deshalb kann man aus diesen spektrographischen Ergebnissen leicht schliessen, dass der Lumineszenzträger für Gips von verschiedenen Fundorten der gleiche ist. An dieser Stelle möchte ich auf den interessanten radiochemischen Versuch von O. Hahn, H. Käding und R. Mumbrauer⁽¹⁰⁾ über verschiedene Arten der Abscheidung kleiner Substanzmengen in Rubidiumsulfatkristallen hinweisen, welcher in sehr enger Beziehung mit dem Leuchtverhalten des Gipskristalls im ultravioletten Lichte steht.

Zusammenfassung.

An Gips von Gánt in Ungarn, von Wiesloch in Deutschland sowie von mehreren Orten in Japan wurde untersucht, welche Teile des Kristalls fluoreszieren, wenn er dem durch Woodsches Glas filtrierten Quarz-Quecksilberbogenlichte ausgesetzt wird. Ihre Fluoreszenzspektren werden miteinander verglichen. Meiner Meinung nach dürfte die regelmässige Verteilung des Lumineszenzträgers im Innern des Gipskristalls in engem Zusammenhang mit der durch röntgenoskopische Untersuchungen klargestellten Struktur des Kristalls gesetzt werden.

Zum Schluss ist es mir ein grosses Vergnügen, Herrn Dr. S. Iimori für sein freundliches Interesse an dieser Arbeit zu danken.

*Forschungsanstalt für Physik und Chemie,
Tokio.*

(10) O. Hahn, H. Käding und R. Mumbrauer, *Z. Krist.*, **87** (1934), 387.

ÜBER DIE KOLLOIDSYNTHESE DURCH DAMPFEXPLOSIONEN UND DIE KOLLOIDCHEMISCHEN UNTERSUCHUNGEN DER DURCH DIESE METHODE HERGESTELLTEN DISPERSEN SYSTEME.

(Fortsetzung*.)

Von Naoyasu SATA.

Eingegangen am 20. März 1936. Ausgegeben am 28. August 1936.

II. Spezielles. A. Quecksilber. Von dem Quecksilber-Hydrosol als ein Gegenstand der kolloid-chemischen Untersuchung hat man schon oft gehört; es hat auch als Arzneimittel zu therapeutischen Zwecken eine wichtige Bedeutung. Die Herstellungsmethodik hat sich bis vor kurzem fast nur auf den chemischen und elektrischen Weg beschränkt⁽¹⁷⁾; letzteren kann man eher als eine Art chemischen Weges betrachten, da er unter Anwendung derartig hoher Spannungen bzw. Stromstärke mit der rein mechanischen Dispergation nur wenig zu tun hat. Es ist noch nicht lange her, dass die rein mechanische Dispergation von I. Nordlund⁽¹⁸⁾ und dann von A. Gutbier⁽¹⁹⁾ untersucht wurde, und zwar untersuchte Nordlund die Verschiedenheit der Dispergationsmethodik und Gutbier entwickelte die Abhängigkeit der Stabilisatoren⁽²⁰⁾, während A. Feick die Polychromie des Quecksilbersols von verschiedener Beschaffenheit⁽²¹⁾ vergleichend untersucht hat. Im folgenden habe ich die Abhängigkeit des Stabilisierens erstens vom Gesichtspunkt zufälliger Verunreinigungen aus und zweitens, durch absichtliches Hinzufügen reiner stabilisierendwirkenden Substanzen, systematisch untersucht.

(a) **Einfluss zufälliger Verunreinigungen.** Den Staub muss man zuerst als wahrscheinlichste Verunreinigung ansehen. Der Stadtstaub, der hauptsächlich aus feinsten Russkohlenteilchen von verschiedenem Rauch besteht, kann nicht nur reine Kohle, sondern auch Humusstoffe und andere hochmole-

* Fortsetzung aus S. 455 dieses Bandes.

(17) The Svedberg, „Herstellung kolloider Lösungen anorganischer Stoffe“, Dresden und Leipzig (1922).

(18) I. Nordlund, *Kolloid-Z.*, **26** (1920), 128; Diss. Upsala (1918).

(19) A. Gutbier, *Z. anorg. allgem. Chem.*, **152** (1926), 163; **155** (1926), 199; **158** (1926), 99.

(20) A. Gutbier, I. Huber u. E. Kuhn, *Kolloid-Z.*, **19** (1916), 33; A. Gutbier u. A. Wagner, *Kolloid-Z.*, **19** (1916), 291.

(21) R. Feick, *Kolloid-Z.*, **37** (1925), 257.

kulare, teerartige organische Substanzen enthalten, die durch unvollständige Verbrennung entstanden sind. Alle diese Substanzen können stabilisierend wirken. Um den Einfluss des Staubes auf die Stabilität zu demonstrieren, habe ich die Kolloidsynthese in Staubextrakt ausgeführt.

Einige Uhrgläser, die zufälligerweise auf den Chemikalienschränken im Laboratorium mehrere Monate gestanden und sich mit Staub überzogen hatten, wurden mit Wasser gespült und das Spülwasser filtriert. Von dieser schwach schwarzen Flüssigkeit habe ich zuerst die qualitative anorganische Analyse ausgeführt. Das Resultat ist aus Tabelle 2 ersichtlich.

Tabelle 2.

Ionen	Cl	SO ₄ u. SO ₃	NH ₃
	Spuren	deutlich	deutlich
Bemerkung: Ausserdem gibt NH ₄ OH ganz wenigen Niederschlag von Hydroxyden.			

Von den gefundenen Ionen ist nur Ammonium-Ion stabilisierend (oder wenigstens neutral) wirkend, worauf Bull und Söllner hingewiesen haben⁽²²⁾. Sonstige Ionen wirken alle koagulierend. Als Dispersionsmittel habe ich etwa 20 mal verdünnte Lösungen von dieser Flüssigkeit benutzt. Das Sol ist gleich nach der Explosion fast schwarzgrau und ganz undurchsichtig. Es wurde ein Teil mit doppeltem Filtrierpapier von Schleicher und Schüll Nr. 602 (extra hart) filtriert, und ein anderer Teil wurde unfiltriert in die Probierrgläser von 20–25 mm. Durchmesser und 200 mm. Länge mit geschliffenem Glasstöpsel aus garantiertem Hartglas gefüllt und beobachtet⁽²³⁾. Bis zu einer Woche zeigten beide gar keinen Unterschied und blieben undurchsichtig wie anfangs. Nach 5–8 Tagen setzte sich der undurchsichtigste Teil ab und liess eine schön bläulich opaleszierende, bei Durchsicht gelbe Flüssigkeit, zurück. Merkwürdigerweise vollzog sich dieser Vorgang bei dem filtrierten Präparat viel langsamer als bei dem unfiltrierten, und das Sol war auch bei ersterem viel konzentrierter. Daraus konnte man vermuten, dass im Filtrierpapier etwaige stabilisierend wirkende Substanzen vorhanden waren, die sehr wahrscheinlich auch Staub sein konnten. Den Einfluss des Filtrierens auf die Stabilität hat

(22) H. Bull u. K. Söllner, *Kolloid-Z.*, **60** (1930), 264.

(23) Wenn nicht besonders erwähnt, wurden während meiner ganzen Versuche Probierrgläser von dieser Grösse benutzt. Betreffend ihre Glasqualität und Reinigung, siehe N. Sata, *Kolloid-Z.*, **71** (1935), 49.

schon H. Gessner⁽²⁴⁾ an V_2O_5 -Sol untersucht und gefunden, dass die Behandlung einen, in der Ordnung der elektrischen Leitfähigkeit erkennbaren Einfluss ausübt, welcher für die Stabilität der Kolloide manchmal genügende Größenordnung ist. Ausserdem darf man die Wirkung nichtleitender Substanzen, wie Staub, organische Substanzen usw. nicht ausser acht lassen. Diesen Vorgang erkennt man deutlich an Abb. 10. Diese Sole sind bis zu

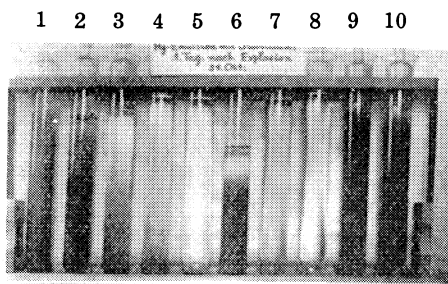


Abb. 10.

1. Kork-Extrakt (filtriert)
 2. Kork-Extrakt (unfiltriert)
 3. Teil B (ausgeströmter Teil)
 4. Na_2SO_3 (filtriert)
 5. Na_2SO_3 (unfiltriert)
 6. Na_2SO_3 (Teil B)
 7. Pikrinsäure, Spur (filtriert)
 8. Pikrinsäure, Spur (unfiltriert)
 9. Staub-Extrakt (filtriert)
 10. Staub-Extrakt (unfiltriert)
- } 0.01 Mol/l.

einem Jahr ohne Veränderung geblieben. Nach 1.5 Jahren hat das unfiltrierte Sol ganz klar (Tyndall-Kegel ist aber noch sehr stark) abgesetzt, wohingegen das filtrierte 1/5 von oben ganz klar und 4/5 von unten noch schön bläulich opaleszierend geblieben ist. Daraus sieht man, dass Staub, obwohl er koagulierende Ionen enthält, sehr stark stabilisierend wirkt. Seine Hauptbestandteile sollen, wie schon bemerkt, Humusstoffe und andere teerartige hochmolekulare Verbindungen sein, von denen wir noch nichts Genaueres wissen.. Jedenfalls möchte ich darauf aufmerksam machen, dass man bei der Kolloidsynthese auf die Reinigung der Apparate usw. besondere Sorgfalt verwenden muss.

Zweitens ist die Wirkung angebrannten Korks als zufällige Verunreinigung zu bezeichnen. Durch oben ausgeführten Versuch ist es bestätigt, dass die Hauptbestandteile der stabilisierend wirkenden Substanzen von Staubextrakt, von Kohle und anderen unvollständigverkohlten Substanzen stammten. So war es für mich zunächst nötig, die Wirkung der Kohle, die aus Kork entstanden ist, zu untersuchen, da dies auch eine wichtige Verunreinigung in meiner Untersuchung bedeutete. Zu diesem Zwecke stellte ich folgenden Versuch an.

Es wurde ein Apparat ohne automatischen Verschluss benutzt. Nach der Explosion sprang natürlich das Explosionsrohr mit dem halbverbrannten Kork

(24) H. Gessner, *Kolloid-Beihfte*, **19** (1924), 226.

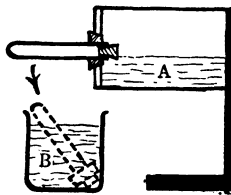


Abb. 11.

weg, und die Hälfte der Flüssigkeit strömte aus. Diese wurde, wie Abb. 11 schematisch zeigt, mit einem Becher aufgefangen. In dem Gefäss blieb noch unberührtes, reines Sol A. Ein Teil davon wurde filtriert, und dieser wurde ebenso wie der unfiltrierte und herausgeströmte Teil B wie gewöhnlich in den Probiergläsern beobachtet. Der Sedimentationsvorgang ist in Tabelle 3 zusammengestellt.

Tabelle 3.

	Im Gefäss gebliebener Teil A		Herausgeströmter und mit gebranntem Kork berührter Teil B
	unfiltriert	filtriert	
Anfangs alle gleich grauschwarz undurchsichtig			
Nach 1 Tag*	20 mm. von oben ganz klar, unten weisslichgrau	5 mm. von oben bläulich klar, unten undurchsichtig	
Nach 3 Tagen	alles ganz klar abgesetzt. Tyndallkegel stark	Nach 14 Tagen setzt sich der undurchsichtige Teil ab, und es bleibt schön bläulich opaleszierendes, homogenes Sol zurück.	
Nach 1.5 Monaten	ganz klar optisch leer	Einige mm. von oben fängt es an ganz klar abzusetzen.	keine Änderung
Nach 7 Monaten	—	ganz klar abgesetzt	keine Änderung
Nach 1 Jahr u. 1 Monat	—	—	1/5 ganz klar 4/5 bläulich grau

* Siehe auch Abb. 10.

Hierdurch wurde erstens die stabilisierende Wirkung von Filtrierpapier wieder bestätigt und zweitens, dass angebrannter Kork, wie wir vermuteten, stabilisierende Substanzen enthält. So ist es erklärt, dass die stabilen Sole in meinem vorläufigen Versuch hauptsächlich durch angebrannten Kork stabilisiert worden waren, und auch, dass mit dem Apparat mit automatischem Schluss ohne Zusatz eines Stabilisators keinesfalls stabile Sole zu erhalten sind, worauf ich nachher wieder zurückkomme. Hierbei möchte ich nochmals darauf aufmerksam machen, dass bei der Kolloidsynthese sehr oft die Verunreinigungen nicht nur koagulierend (was sofort bemerkbar ist) wirken, sondern auch stabilisierend, wie in diesem Fall, wobei man von der Wirkung des Stabilisators oft enttäuscht wird.

(b) **Reine anorganische Stabilisatoren.** (1) *Allgemeines.* Nach der Theorie⁽²⁵⁾ von v. Weimarn über die Dispergation und über den dispersoiden Parasitismus besitzt die Stabilitätskurve einer Reihe disperser Systeme mit verschiedenen Stabilisator-Konzentrationen in allen Fällen ein Maximum, wenn nicht andere Variablen, die einen Einfluss auf die zeitliche Existenz disperser Systeme ausüben, dies verhindern. Diese Tatsache ist schon oft von ihm selbst und seinen Mitarbeitern⁽²⁶⁾ bestätigt worden.

Mit den Fortschritten auf dem Gebiet der Präzisionsuntersuchungen der Feinstruktur der Kolloidteilchen, besonders dank den Arbeiten von Wo. Pauli und seinen Mitarbeitern⁽²⁷⁾, ist es uns allmählich klar geworden, dass die Kolloidteilchen durch Ionenkomplexe stabilisiert werden, die durch Adsorption oder lockere chemische Bindungen an den Kolloidteilchen adsorbiert oder verbunden sind, die durch chemische Oberflächen-Reaktion⁽²⁸⁾ zwischen disperser Phase und Dispersionsmittel entstanden sind. Die Schwierigkeit des Studiums liegt darin, dass diese Ionenkomplexe nur in adsorbiertem Zustand stabil sind, und dass es uns noch nicht möglich ist, sie in freiem Zustand zu isolieren.

Ich habe gerade festgestellt, dass Staub, angebrannter Kork usw., deren genaue chemische Zusammensetzung wir nicht wissen, bei dieser Kolloidsynthese durch Explosion stabilisierend wirken, und die Sole aus reinem Dispersionsmittel und reiner disperser Phase, in diesem Fall Quecksilber und Wasser, keinesfalls beständig bleiben. Bei weiterem Verfolgen des Stabilisierungsvorganges muss man noch einfachere Stabilisatoren verwenden, deren chemische Zusammensetzungen unbekannt sind. Als solche von den einfachen anorganischen Verbindungen habe ich ausgewählt: Natriumsulfit, Natriumsulfid und Natriumjodid. Sie sind alle an sich schon nicht stabile Verbindungen, und es ist zu erwarten, dass sie mit Quecksilber in kolloiden Dimensionen leicht in verschiedene Oberflächenkomplexe übergehen. Da E. Saur und D. Steiner⁽²⁹⁾ das Entstehen von Quecksilbersulfid, durch Mischen kolloiden Quecksilbers mit kolloidem Schwefel, experimentell bestätigen konnten, kann man auch bei der Reaktion kolloider Quecksilber und obengenannter Verbindungen interessante Resultate erwarten. Der Versuch wurde folgendermassen ausgeführt.

(25) P. P. von Weimarn, *Kolloid-Z.*, **4** (1909), 127; *Kolloid-Beihefte*, **1** (1910), 105; *Kolloid-Z.*, **37** (1925), 151; „Kolloides und kristalloides Lösen und Niederschlagen“ Bd. 2, S. 541-638, Kyoto (1921).

(26) E. Iwase, *Kolloid-Z.*, **45** (1928), 31; P. P. von Weimarn u. S. Utzino, *Memoires Coll. Sc. Kyoto Imp. Univ.*, **8** (1925), 291.

(27) Wo. Pauli, „Elektrochemie der Kolloide“, Wien (1929); „Kolloid-Elektrolyt“, *Trans. Faraday Soc.*, **31** (1935), 1.

(28) „Kapillarchemie“, Bd. II, S. 223.

(29) *Kolloid-Z.*, **73** (1935), 45.

Zuerst habe ich eine 0.1 mol Lösung hergestellt, und durch Verdünnen wurden die Lösungen bis 0.000001 mol vorbereitet. Das Synthesen-Gefäss wurde mit den Lösungen gefüllt, und eine Explosion angestellt. Nach derselben wurden die Sole für etwa 30 Minuten stehen gelassen, um gröbere Teilchen sich absetzen zu lassen, ca. 50 c.c. davon wurden in ein Probierglas gegossen und beobachtet. Weil vorher festgestellt wurde, dass das Filtrieren stabilisierend wirkt, habe ich in folgenden Versuchen die Stabilität der Sole ohne Filtrieren untersucht.

(2) *Natriumsulfit* (E. Merck, rein trocken). 0.1 mol Lösung: Anfangs undurchsichtig grau-schwarz. Nach einem Tag wird es fast klar und nach 2 Tagen ganz klar abgesetzt, bis kein Tyndall-Kegel mehr zu merken ist. 0.01 mol Lösung: Anfangs undurchsichtig. Nach 1 Std. halbdurchsichtig, Durchsichtsfarbe gelblich-braun. Nach 1 Tag aber setzt es fast ganz klar, bleibend Spuren von bläulicher Färbung, ab. Nach 2 Tagen ist es ganz klar, und die Spuren bläulicher Färbung bleiben noch einige Tage. 0.0001 mol Lösung: Wie oben, aber noch unstabiler. 0.000001 mol Lösung: Wie oben, aber nach 2 Tagen bleibt zwar noch wenig, aber doch merkliche Trübung, die einige Monate anhält, aber vielleicht durch irgendwelche andere Verunreinigungen verursacht wird.

Zusammenfassend könnte man von der Wirkung des Natriumsulfits darauf schliessen, dass es bei allen Konzentrationen keine stabilisierende Wirkung hat, sondern sogar koagulierend wirkt, weil bei manchen Versuchen anfangs die gelbbraune Durchsichtsfarbe, das Zeichen kolloider Dispersität, bemerkt worden ist, trotzdem nach 2 Tagen schon praktisch alles abgesetzt war. Bei einigen Proben von dieser Reihe mit Natriumsulfit habe ich auch feststellen können, dass Filtrieren und gebranntes Kork die koagulierende Kraft von dieser Verbindung überwiegt, und das Sol stabilisiert (Abb. 10). Dieselbe Aufnahme zeigt noch einen Versuch mit Pikrinsäure, da diese auf die Kohle-Dispergation stabilisierend wirkt⁽³⁰⁾ und man daher in meinem Fall auch derartige Wirkungen erwarten konnte, aber das Resultat ergab im Gegenteil ganz und gar koagulierende Wirkungen.

(3) *Natriumsulfid* (Kahlbaum, zur Analyse und Reagens D. A. B. 6). 0.1 mol Lösung: Anfangs schwarz-grau, ganz undurchsichtig. Nach 1 Tag aber setzt es fast ganz klar ab und nach 4 Tagen ist bereits kein Tyndall-Kegel mehr zu merken. 0.01 mol Lösung: Anfangs wie oben, schwarzgrau undurchsichtig. Nach 5 Tagen wird es halbdurchsichtig mit orange-roter Durchsichtsfarbe. Aufsichtsfarbe ist noch schwarzgrau, es erhält aber einen bräunlichen Ton. Nach etwa 3–4 Monaten wurde es weisslich-grau mit bläu-

(30) Wo. Ostwald, *Kolloid-Z.*, **43** (1927), 227.

licher Opaleszenz und blieb so stabil bis zu 10 Monaten. Nach 10 Monaten fängt es allmählich an, sich abzusetzen und setzt bis zu einem Jahr fast ganz klar ab. 0.001 mol Lösung: Anfangs ist sie wie immer schwarzgrau undurchsichtig. Sedimentationsvorgang ist in diesem Fall mehrfarbig. Der undurchsichtige Teil erhält nach 4 Tagen einen gelblich-braunen Ton und ändert sich allmählich zu orange-gelb und wird endlich nach 10 Tagen schön goldgelb. Nach etwa 2 Monaten verschwindet dieser Ton und es bleibt eine schöne bläulich-opaleszierende Flüssigkeit. Das Sol fängt etwa nach 6 Monaten an, von oben her ganz klar abzusetzen, bis nach 11–12 Monaten alles ganz klar wird. 0.0001 mol Lösung: Anfangs wie oben, nach 1 Tag weisslich-grau, halbdurchsichtig. Nach 2 Tagen oben 10 mm. bläulich-opaleszierend-durchsichtig, unten bräunlich-grau, halbdurchsichtig. Nach 1.5 Monaten fängt es an, klar abzusetzen und nach 2 Monaten setzt es ganz klar ab. 0.00001 mol Lösung: Das Sol ist sehr unstabil, und zwar wird es nach 1 Tag ganz klar und nach 10 Tagen ist kein Tyndall-Kegel mehr zu merken.

Die Ergebnisse sind auf Abb. 12 graphisch dargestellt; Lebensdauer sind als Ordinate und Stabilisatorkonzentrationen als Abzissen gezeichnet. Die Kurve zeigt ein ausgesprochenes Maximum bei der Stabilisatorkonzentration von etwa 0.01 mol. Der Sedimentationsvorgang ist auf Abb. 13–15 erkennbar, und zwar, zeigen Abb. 13 u. 14 auch dabei den Einfluss des Filtrierens, das ausgesprochen stabilisierend wirkt, und Abb. 15 stellt den Einfluss der Verunreinigung dar; man sieht darauf Teil A (siehe Abb. 11), welcher ganz rein im Gefäss geblieben ist und Teil B, der aus dem Gefäss ausgeströmt ist und dabei verunreinigt wurde, was zugleich stabilisierend wirkte.

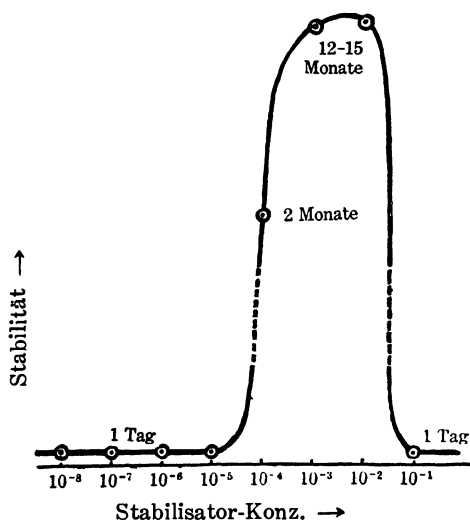


Abb. 12.

Kurz zusammenfassend konnte ich von der Wirkung des Natriumsulfids auf Folgendes schliessen: Durchschnittlich erhält man mit der Natriumsulfid-Lösung als Dispersionsmittel gleich nach der Explosion schwarz-graues Sol. Im bestimmten Bereich der Salzkonzentrationen merkt man nach dem Absetzen eines schwarz-grauen Teiles, dass das System einen schönen gold-gelben Ton zeigt. Das Stabilitätsoptimum liegt auch in dieser Gegend. Daraus kann man schliessen, dass das Natriumsulfid mit Quecksilber durch

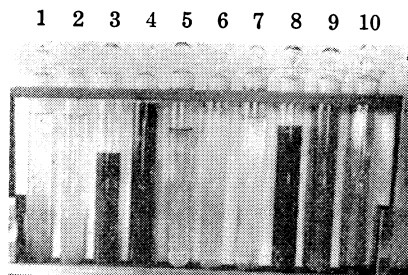


Abb. 13.

(Na₂S-Lösung: 5 Std. nach der Explosion.)

Na ₂ S-Konzentration (Mol/l.)									
1	2	3	4	5	6	7	8	9	10
10 ⁻⁸	10 ⁻⁶	10 ⁻⁴	10 ⁻²	10 ⁻¹	10 ⁻⁸	10 ⁻⁶	10 ⁻⁴	10 ⁻²	10 ⁻¹
unfiltriert					filtriert				

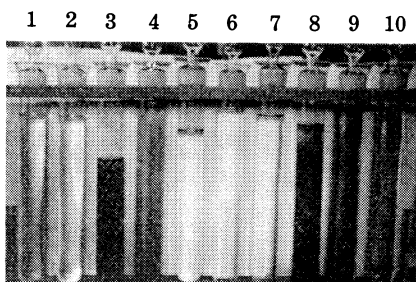


Abb. 14.

(Wie oben: Nach 2 Tagen.)

Na ₂ S-Konzentration (Mol/l.)									
1	2	3	4	5	6	7	8	9	10
10 ⁻⁸	10 ⁻⁶	10 ⁻⁴	10 ⁻²	10 ⁻¹	10 ⁻⁸	10 ⁻⁶	10 ⁻⁴	10 ⁻²	10 ⁻¹
unfiltriert					filtriert				

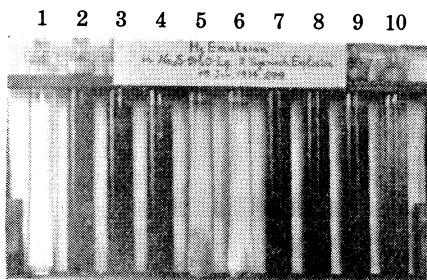


Abb. 15.

Na ₂ S-Konzentration (Mol/l.)									
1	2	3	4	5	6	7	8	9	10
10 ⁻¹	10 ⁻²	10 ⁻³	10 ⁻⁴	10 ⁻⁵	10 ⁻¹	10 ⁻²	10 ⁻³	10 ⁻⁴	10 ⁻⁵
Teil A					Teil B				

Oberflächenreaktionen ca. 2 Sorten von Komplexen liefert, nämlich schwärzliche und goldgelbliche, die stabilisierend oder koagulierend wirken, je nach den Konzentrationen. Vom Standpunkt reiner anorganischer Chemie aus, sind mögliche Verbindungen zwischen Quecksilber und Natriumsulfid, Hg₂S und HgS, und zwar ist Hg₂S⁽³¹⁾ die unstabilere Form, die gewöhnlich schwarz

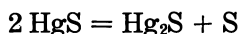
(31) Gmelin-Krauts, „Handbuch d. anorg. Chem.“, Bd. V (II), S. 570, Heidelberg (1914).

oder bräunlich-schwarz ist und sich durch Wärme oder Licht⁽³²⁾ leicht in HgS und Hg zersetzt. Ausserdem hat C. Baskerville⁽³³⁾ gezeigt, dass Hg₂S, mit Luft in geschlossenem Rohr erhitzt, eine kontinuierliche Farbänderung von weiss-gelb → orange-gelb → braun → schwarz aufweist.

Bei meinem Versuch habe ich auch bemerkt, dass die Sole, die in 0.01–0.001 mol Na₂S-Lösung hergestellt waren, folgende Farbänderung ergaben; nämlich anfangs schwarzgraues, undurchsichtiges Sol, nach 4 Tagen wurde es bräunlichgelb bis orangegelb und von 10 Tagen ab schön goldgelb, bis sich nach 2 Monaten alles absetzte. Aus dieser Tatsache kann man ersehen, dass wenigstens eine Sorte von Mercuro- oder Mercuri-Sulfiden hier in meinem Fall entstanden sind. Weil HgS eine beständigere Form ist, könnte man vermuten, dass bei Explosion von Quecksilber in die Na₂S-Lösung, im ersten Moment, durch Oberflächenreaktion auf kolloiddisperses Hg-Teilchen, ein Gemisch von Hg₂S und HgS entstanden wäre. Hier findet die stufenweise Zersetzung etwa wie folgende Formel zeigt, statt:



Ein Teil von HgS bleibt in der Lösung und wirkt als Koagulator bzw. Stabilisator, je nach der Konzentration, weil HgS in Na₂S-Lösung ziemlich löslich ist⁽³⁴⁾. Nach Alsberg⁽³⁵⁾ scheint diese Reaktion auch umkehrbar zu verlaufen, besonders in alkalischer Lösung:



Daraus muss man schliessen, dass in unserem Fall bei der Explosion komplizierte, chemische Vorgänge bei geeigneten Na₂S-Konzentrationen vor sich gehen, wie man es durch die Vielfarbigkeit des Systems vermuten kann. Dagegen entsteht aber, bei extrem konzentrierten oder verdünnten Salzkonzentrationen, in den Systemen Hg₂S oder HgS, aber nur in schwarzen Modifikationen. Wenn aber Hg₂S entsteht, ist es sehr möglich, dass sich rotes HgS durch seine Zersetzung⁽³⁶⁾ abscheidet und die Färbung des Systems verursacht. Da wir in den Konzentrationen beider extremen Fälle keine Farbänderung gemerkt hatten, könnte man vielleicht sagen, dass sich dort nur HgS in schwarzer Modifikation gebildet hätte.

(32) J. W. Mellor, „A Comprehensive Treatise on Inorg. and Theoret. Chem.“, Bd. IV, S. 944, London (1923); U. Antonny, *Gazz. chim. ital.*, **1** (1894), 194.

(33) Mellor, *loc. cit.*, Bd. IV, S. 944; *J. Am. Chem. Soc.*, **25** (1903), 799.

(34) Gmelin-Krauts, *loc. cit.*, V (II), S. 584.

(35) Alsberg, *Chem. News*, **23** (1871), 73; Pascal, „Traite de chim. min.“ VIII, S. 902.

(36) Gmelin-Krauts, *loc. cit.*, S. 570.

Anschliessend möchte ich darauf aufmerksam machen, dass das freie metallische Quecksilber doch mit Natriumsulfid bei gewöhnlicher Temperatur reagiert, was man in gewöhnlichem Zustande niemals erwarten konnte, ausser wenn die Reaktion in kolloidem Zustand geschieht, wie in unserem Fall. Es ist aber selbstverständlich, wenn man sich vergegenwärtigt, dass schon zwischen kolloidem Quecksilber und Schwefe keine chemische Reaktion vor sich geht, wie von E. Sauer und D. Steiner⁽³⁷⁾ nachgewiesen wurde. Die Reaktionsprodukte, deren chemische Zusammensetzung wir noch nicht genau wissen, scheinen als adsorbierter Zustand eine stabilisierende Wirkung bei geeigneter Konzentration auszuüben.

(4) *Natriumjodid* (E. Merck, reinst. D.A.B. 6). 0.1 mol Lösung: Sehr unstabil und nach 5 Stunden schon ganz klar abgesetzt, obwohl sie anfangs schwarzgrau undurchsichtig war. 0.01 mol. Lösung: bleibt 1/2 Tag undurchsichtig, schwarzgrau; dann fängt sie an abzusetzen. Nach 2 Tagen, während welchen 1/3 ganz klar abgesetzt und 2/3 noch grau undurchsichtig sind, geschieht plötzlich in dem undurchsichtigen Teil eine schön grüngraue Färbung, wie japanisches Teepulver. Dieser setzt am 4. Tag ganz klar ab und hinterlässt auf dem Boden des Probierglases einen grünen Niederschlag. 0.001 mol Lösung: Grüne Färbung kommt schon bei 3.5 stündigem Stehen nach der Explosion vor, wo das Sol noch ganz undurchsichtig ist. Nach 1/2 Tag fängt es an abzusetzen, und nach einer Woche ist das Sol ganz klar geworden. In diesem Fall bleibt auch grüner Bodensatz wie beim vorherigen Versuch. 0.0001 mol Lösung: Grau-silbernes Sol fängt vom 1. Tag an abzusetzen, aber hier bleibt der obere Teil halbdurchsichtig, schwach grau, bläulich opaleszierend. Nach 10 Tagen ist die ganze Flüssigkeit homogen bläulich-grau, mit schöner bläulicher Opaleszenz und so stabilisiert, bleibt sie ohne Veränderung bis zu 4 Monaten und fängt dann allmählich an abzusetzen, bis sie nach 11 Monaten fast ganz klar wird. 0.00001 mol Lösung: Ein graues, undurchsichtiges Sol fängt sofort an abzusetzen, welches nach 3 Tagen ganz klar wird.

Die Ergebnisse sind auf Abb. 16 und 17 dargestellt. Auf Abb. 17 sieht man wieder, dass der herausgeströmte Teil B durch irgendeine Verunreinigung stabilisiert ist.

Durch umstehend ausgeführte Untersuchungen wurde bestätigt, dass das Quecksilber auch mit Natriumjodid bei der Reaktion kolloiddispersen Systems reagiert, die bei gewöhnlicher Temperatur nicht stattfindet. Die entstandene Verbindung besitzt eine schöne, grüne Farbe. Das Entstehen dieser Verbindung macht sich erst einige Stunden nach der Reaktion (Explosion), durch Farbänderung des Systems von grau zu grün, bemerkbar. Es ist mir noch

(37) *Kolloid-Z.*, **73** (1935), 45.

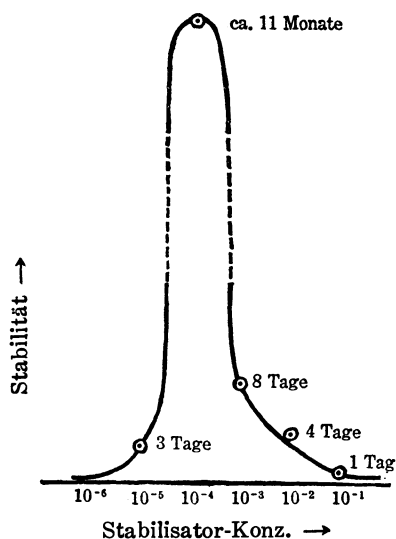


Abb. 16.

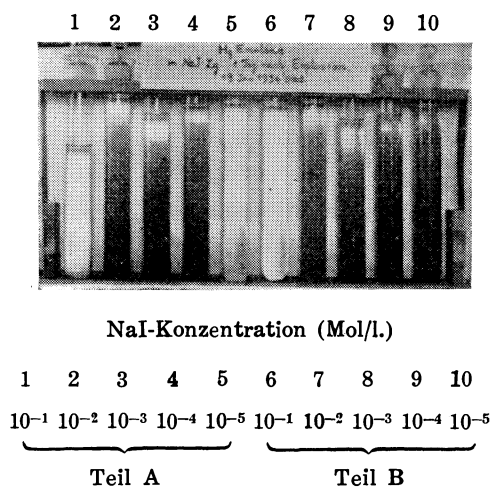


Abb. 17.

unbekannt, ob diese grüne Verbindung erst nach einigen Stunden entsteht, oder ob die grüne Farbe erst einige Stunden nach dem Absetzen größerer grauer Quecksilberteile zu sehen ist; und zwar scheint es, dass sie koagulierend wirkt, da das grüne Sol schon nach einigen Tagen absetzt. Dagegen liegt das Stabilitätsoptimum bei etwa 0.0001 molarer NaI-Konzentration. Daraus könnte man schließen, dass diese grüne Verbindung bei sehr kleiner Konzentration auch stabilisierend wirkt. Aber es ist in diesem Fall beachtenswert, dass hier das stabile Bereich sehr schmal ist, und zwar nur in der Nähe der Salzkonzentration von 0.0001 mol liegt, im Vergleich zu dem Fall mit Natriumsulfid, wo sich das stabile Bereich der Salzkonzentrationen von 0.01 mol. bis 0.001 und noch weiter erstreckte (Siehe Abb. 2).

Ich möchte jetzt über die Natur dieser grünen Verbindung bemerken. Zwischen Quecksilber und Jod sind zwei richtige Verbindungen bekannt, nämlich Quecksilberjodid (HgI_2) und Quecksilbersubjodid (HgI). Wegen der wohlbekannten, interessanten Umlagerung durch Wärme von gelb zu roter Modifikation, ist Quecksilberjodid (HgI_2) sehr eingehend studiert worden, aber über die grüne Modifikation oder die Entstehung der grünen Farbe wurde noch niemals berichtet⁽³⁸⁾. Das Quecksilbersubjodid (HgI) hingegen wurde bisher weniger studiert; bei ihm hat man jedoch von Anfang an auf die grüne Modifikation aufmerksam gemacht⁽³⁹⁾, die nämlich nach den genaueren

(38) Gmelin-Krauts, *loc. cit.*, Bd. V (II), S. 766; Mellor, *loc. cit.*, Bd. IV, S. 895.

(39) Mellor, *loc. cit.*, Bd. IV, S. 897; R. Varet, *Ann. chim. physiq.*, (7), **8** (1896), 92; *Compt. rend.*, **120** (1895), 1504, 1114.

Untersuchungen von M. François⁽⁴⁰⁾ ganz anders erklärt worden waren. Nach M. François gibt es nämlich nur eine Modifikation, und zwar ist sie rein gelb wie Bleichromat. Er hat experimentell bestätigt, dass dieses gelbe Subjodid seine Farbe von gelbgrün zu grün durch Mischen mit feinverteiltem Quecksilber, wenn feinverteiltes Quecksilber zusammen vorhanden ist, ändert. Das Verhalten unseres dispersen Systems stimmt darin vollkommen mit der Ansicht von M. François überein. Nämlich gleich nach der Explosion sieht man keine grüne Farbe, weil vielleicht zuviel disperses Quecksilber in diesem System vorhanden ist, und einige Stunden nach dem Absetzen dieses Quecksilbers lässt sich erst die grüne Farbe feststellen. Also konnte ich konstatieren, dass durch die Explosion das Subjodid entsteht, das an der Oberfläche kolloiden Quecksilbers adsorbiert und stabilisierend wirkt als Ionenkomplex, wie bei dem Prinzip, das Wo. Pauli⁽⁴¹⁾ behauptet. Nach E. Beckmann und A. Stock⁽⁴²⁾ entsteht das grüne Produkt bei gewöhnlicher Temperatur nur aus metallischem Quecksilber und Jodlösungen in organischen Lösungsmitteln und aus den wässrigen Lösungen erhält man nur ein braunrotes Produkt. Ausserdem beträgt die Löslichkeit⁽⁴³⁾ von Mercurojodid in Wasser etwa 0.042 g. / 100 c.c. Der Wert ist nicht sehr gross in gewöhnlichem Sinne, aber vom Standpunkt der Kolloidchemie aus, ist er insofern beachtlich⁽⁴⁴⁾, als er koagulierend oder stabilisierend wirken kann, je nach den Konzentrationen, wie aus Abb. 16 ersichtlich ist. Hiervon hat man wiederum ein Beispiel, dass bei der Kolloid-Dimension eine chemische Reaktion stattfindet, die unter gewöhnlichen Bedingungen nicht geschieht.

(c) **Einfluss des Lichtes (Ultraviolettstrahlen) auf die Stabilität.** Wie schon oft erwähnt⁽⁴⁵⁾, sind Natriumsulfide und Natriumjodide sowie auch Sulfide und Jodide von Quecksilber in grossem und kleinerem Masse lichtempfindlich, d. h. die erwähnten, chemischen Vorgänge können durch Belichtung beeinflusst werden. Deshalb kann man leicht annehmen, dass die Wirkungen dieser Verbindungen auf die Stabilität der dispersen Systeme von Quecksilber auch durch Licht beeinflusst werden. Um diese Verhalten klarzumachen, habe ich noch folgenden Reihe von Untersuchungen angestellt. Nach den Explosionen wurden die Sole in zwei Probiergläser gefüllt, wovon das eine in

(40) Mellor, *loc. cit.*, S. 897; M. François, *Compt. rend.*, **122** (1896), 193.

(41) Wo. Pauli, „Elektrochemie der Kolloide“, Wien (1929); *Trans. Faraday Soc.*, **31** (1935), 1.

(42) E. Beckmann u. A. Stock, *Z. physik. Chem.*, **17** (1895), 107; auch Mellor, *loc. cit.*, S. 896.

(43) Gmelin-Krauts, *loc. cit.*, V (II).

(44) H. Gessner, *Kolloid-Beihfte*, **19** (1924), 226.

(45) Mellor, *loc. cit.*, IV, S. 899.

einen dunklen Schrank gestellt und das andere den Ultraviolettstrahlen einer Quarzlampe⁽⁴⁶⁾ ausgesetzt wurde. Der Sedimentationsvorgang ist wie bei den vorigen Versuchen beobachtet worden und zeigte folgende Ergebnisse.

(1) *Versuche mit Natriumjodid-Lösungen.* Die Sole wurden für einige Tage nur während der Tageszeit, etwa 8 bis 9 Stunden, belichtet. Wenn kein Unterschied im Vergleich zu den unbelichteten bemerkt wurde, wurde die Belichtung ausgeschaltet, und die Sole im Tageslicht aufbewahrt. Wenn aber die belichteten Sole sich merklich von den unbelichteten unterschieden, wurden sie weiter belichtet, bis sich keine Änderung mehr zeigte.

0.1 mol Lösung: Belichtet und unbelichtet, beide Teile setzen schon in 10 Stunden ganz klar ab. 0.01 mol Lösung: Hier sieht man einen sehr merklichen Unterschied zwischen dem belichteten Sol und dem unbelichteten. Ersteres erhält nämlich nach 5 Stunden eine grünliche Färbung und setzt nach einem Tag ganz klar ab. Der unbelichtete Teil dagegen bleibt einen ganzen Tag grau undurchsichtig, ohne grüne Färbtönung. Vom 2. Tag ab beginnt er abzusetzen, bis er nach 6 Tagen ganz klar wird. Es ist merkwürdig, dass man in diesem Fall einen grünen Bodensatz bemerkt, obwohl man während des Absetzens keine grüne Färbung sah (es könnte auch möglich sein, dass der Vorgang sich während der Nachtzeit vollzog). 0.001 mol Lösung: Das Belichten lässt deutlich seinen Einfluss merken, und zwar fängt der belichtete Teil, der anfangs grau undurchsichtig war, nach 2 stündigem Belichten, an grünlich zu werden. Die grüne Färbung nimmt immer mehr zu und erreicht ihr Maximum nach etwa 3 Stunden und nimmt dann wieder ab, wobei sich ein grau undurchsichtiger Teil absetzt. Das System wird nach 2 Tagen fast ganz klar mit Spuren grünlich blauer Trübung, die nach 10 Tagen ganz verschwindet. Der unbelichtete Teil zeigt dagegen erst nach 1 Tag eine schwach grüne Färbung, während das System schon halbdurchsichtig ist. Die grüne Farbe verschwindet an demselben Tag, und das System wird allmählich klarer, bis es nach 10 Tagen ganz klar ist. 0.0001 mol Lösung: Ein Teil wurde für 1 Tag belichtet, zeigt aber keinen Unterschied von dem unbelichteten. Beide bleiben wie bei dem vorhergehenden Versuch sehr stabil, und nur zuletzt setzt der belichtete Teil nach 11.5 Monaten ab, wohingegen der unbelichtete nach 12.5 Monaten ganz klar absetzt. 0.00001 mol Lösung: Beide gleich sehr unstabil, setzen nach 1 Tag ganz klar ab.

Die Ergebnisse obiger Versuche sind in Abb. 18 und 19 dargestellt.

(46) Quecksilberquarzlampe ist mir von Herrn Prof. Asada, aus dem physikalischen Institut der Osaka-Universität zur Verfügung gestellt worden, dem ich in dieser Stelle herzlichst danken möchte.

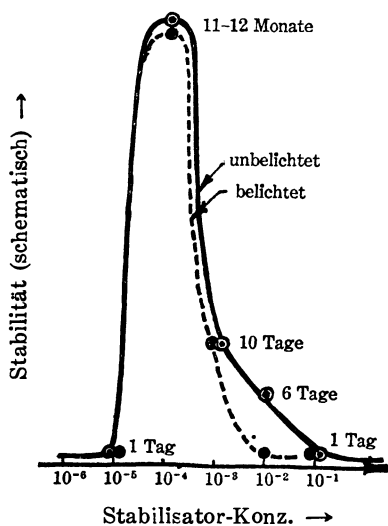


Abb. 18.

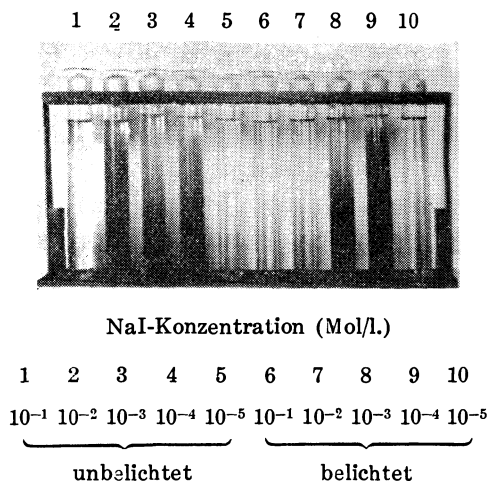


Abb. 19.

(1 Tag nach der Explosion)

Über die Versuchsergebnisse möchte ich folgendes bemerken; belichtetes Sol setzt durchschnittlich etwas schneller ab als unbelichtetes, aber der Unterschied ist nicht so gross. Der Unterschied könnte auch noch, ausser durch die ultraviolettstrahlen, durch Wärmestrahlen verursacht werden, worauf ich nachher noch zurückkomme. Beim Versuch mit 0.01 mol Lösung, wobei die Konzentration grüner Verbindungen das Maximum erreicht, lässt sich ein merklicher Unterschied beweisen; das belichtete Sol setzt nämlich bereits in einem Tag ab, wozu das unbelichtete 6 Tage braucht.

(2) *Versuche mit Natriumsulfid-Lösungen.* 0.1 mol Lösung: Belichtet und unbelichtet, unstabil. Nach 7 Stunden sind sie fast abgesetzt, und nach 1 Tag ganz klar. 0.01 mol Lösung: Bei dieser Konzentration scheint die Stabilität ihr Maximum zu erreichen, und der Lichteffect lässt sich auch nicht in zu grossem Masse bemerken. Nach 10 Tagen werden die belichtete sowie die unbelichtete Flüssigkeit fast gleich bläulich-grau, halbdurchsichtig, mit gelbbrauner Durchsichtsfarbe, trotz 10 tägiger Belichtung (natürlich jeden Tag ca. 7-8 Stunden während der Tageszeit). So bleiben sie 3 Monate stabil und setzen allmählich ab, und nach 5 Monaten werden sie klar lila-blau, und bleiben bis zu mehr als 1 Jahr stabil. Der unbelichtete Teil zeigt fast dieselben Vorgänge und dieselbe Stabilität. Es ist hier zu bemerken, dass die Stabilität durch das Belichten fast nicht beeinflusst wird. 0.001 mol Lösung: Hier überzeugt man sich wieder sehr deutlich vom Lichteffect. Das belichtete Sol bleibt einen Tag ganz undurchsichtig, ebenso wie das unbelichtete. Am

zweiten Tag aber wird ersteres halbdurchsichtig mit gelbbraunlicher Durchsichtsfarbe, und nach dem 3. Tag hat es ganz klar abgesetzt. Das unbelichtete Sol fängt nach 1 Tag an, von oben her ganz allmählich abzusetzen, und es bleibt eine bläulich opaleszierende Flüssigkeit mit orange-gelber Durchsichtsfarbe zurück. Nach 3 Monaten verliert es die opaleszierende Trübung und wird lila-blau; so bleibt es bis zu 10.5 Monaten und von diesem Zeitpunkt an wird es ganz klar. Hier in diesem Versuch hat man keine gold-gelben Farbtöne bemerkt wie in vorherigem Versuch. Man könnte es so verstehen, dass vielleicht die Bedingungen beim Moment der Explosionen nicht die gleichen sind, obwohl dasselbe Quecksilber und dieselbe Salzkonzentration benutzt wurde, aber vielleicht differierte etwa der Dampfdruck oder die Erhitzungstemperatur sowie die Menge kolloiddispersen sowie grobdispersen Quecksilbers, alles Bedingungen, die wir noch nicht kontrollieren können. Da aber die Absetzungsvorgänge und die Stabilität immer übereinstimmen, so muss man daraus schliessen, dass die Farberscheinung hauptsächlich mit den kolloid-unabhängigen, groben Teilen des Systems überdeckt worden war.

0.0001 mol Lösung: Das belichtete Sol fängt sehr schnell an, abzusetzen, und zwar wird es nach 1 Tag ganz klar; das unbelichtete Sol dagegen setzt sehr langsam ab, und es bleibt eine bläulich durchsichtige Flüssigkeit zurück. Nach 7 Tagen ist es fast homogen bläulich, nur 10 mm. von unten her bleibt es noch ganz bräunlich-grau, undurchsichtig. Nach 10 Tagen fängt es von oben her an, ganz klar abzusetzen, bis es schliesslich nach 1 Monat ganz klar wird.

0.00001 mol Lösung: Beide sehr unstabil, setzen sie nach einem Tag ganz klar ab.

Es wurde noch eine Serie von Versuchen mit Natriumsulfid zur Kontrolle ausgeführt, weil in diesem Fall manchmal grosse Lichteefekte bemerkt worden waren; und ich erhielt auch sehr gute, mit vorhergehenden Versuchen übereinstimmende Resultate (Stabilitätsmaximum bei 0.01 mol lichtempfindlich 0.001–0.0001 mol usw.). Bei Natriumsulfidlösungen ist der Lichteefekt besonders bei verhältnismässig kleinen Konzentrationen von 0.0001–0.001 mol bemerkbar wie in Abb. 20 dargestellt wurde.

In diesem Fall ist besonders zu beachten, dass der Lichteefekt auf einen viel grösseren Bereich, nämlich von 0.0001–0.001 mol einwirkt, wohingegen bei Na-

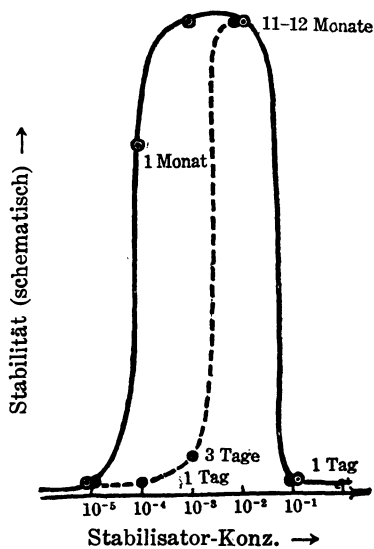


Abb. 20.

triumjodidlösungen nur auf einen kleineren Bereich, in der Nähe von 0.01 mol Konzentration, seinen Einfluss geltend machte.

(3) *Zusammenfassende Diskussion über den Lichteffect.* Durch die vorher ausgeführten Versuche ist es bestätigt, dass die Wirkungen des Lichtes, nämlich der Ultraviolettstrahlen, sich bei der Kolloidsynthese durch Explosion in Lösungen von Natriumsulfid bzw. Natriumjodid bemerkbar machen, wie man es erwartet hatte. Diese Wirkungen lassen sich nach zwei Seiten hin nachweisen, nämlich durch die Stabilität der Sole und durch ihr Verhalten während der Sedimentation.

Die Stabilität nimmt durch Bestrahlen immer mehr ab.

Man beachte die Tatsache, dass sich die Wirkung des Lichtes gerade deutlich bemerkbar macht durch die Buntfarbigkeit des Systems bei der Sedimentation. Diesen Umstand kann man sich erklären, wenn man bedenkt, dass durch Lichtwirkungen verschiedene photochemische Reaktionen vor sich gehen, die durch Ausscheidung verschiedener Modifikationen die Buntfarbigkeit verursachen dürften.

Nur ein merklicher Unterschied liegt bei der Wirkungsstelle. Nämlich bei Natriumsulfidlösungen liegt das Maximum des Lichteffectes bei einer grösseren Salzkonzentration als das Maximum der Stabilität, während sich in Natriumjodidlösung das Lichteffect-Maximum bei einer verdünnteren Salzkonzentration befindet als das Stabilitäts-Maximum, wie man auf Abb. 18 und 20 sieht. Die Ursache des Verhaltens liegt vielleicht darin, dass die Löslichkeit bei den Sulfiden und Jodiden verschieden ist, was auch bei der Stabilität eine wichtige Rolle spielt.

Nun möchte ich in bezug auf den Einfluss der Wärmestrahlen noch auf etwas kurz hinweisen. Ich stellte die Sole in Reagenzgläsern vor eine Quarzlampe in einer Entfernung von 30 cm., was natürlich eine Erhöhung der Temperatur bewirkte. Die Lufttemperatur betrug an dieser Stelle etwa 25–30°C., während die Zimmertemperatur etwa 10–15°C. war, eine Tatsache, die man bezüglich der Wirkung auf die Stabilität auch nicht übersehen darf. Aber ich habe nachher erfahren, dass die stabilen Sole im Hochsommer bei einer Zimmertemperatur von 30–35°C. ganz stabil, ohne Veränderung geblieben waren, und erst im November bis Dezember angefangen hatten, abzusetzen. Daraus können wir schliessen, dass die Hauptursache doch auf die Ultraviolettstrahlen zurückzuführen sein wird, obwohl sie durch Glas-Probiergläser grösstenteils absorbiert wurden und nur wenige die Sole erreichen konnten.

B. Selen. Das Selen mit thermischer Methode zu dispergieren, ist schon von A. Gutbier⁽⁴⁷⁾ zusammen mit Quecksilber und Schwefel versucht worden, und er berichtet, dass durch Einblasen von hochoverhitztem Selen-Dampf in Wasser, ein rotes Sol erhalten werden kann, und dass gelbrotes Sol unstabiler als rosafarbiges ist. Aber die Stabilität und deren Bedingungen hat er nicht weiter untersucht. Durch die Dampfexplosionsmethode habe ich durch einen vorläufigen Versuch mit genau derselben Einrichtung wie für Quecksilber (Siehe Abb. 5) schon sehr stabiles, orangegelbes Sol erhalten, aber auch sehr oft ziegelrotes Sol, welches viel unstabiler als das vorgenannte ist. Ausführliche Untersuchung der Stabilitätsbedingungen und des Verhaltens des gewonnenen Se-Sols sind im Folgenden behandelt.

(a) **Über die Methodik.** Hier traten Schwierigkeiten auf, wegen der im Vergleich zu Quecksilber und Schwefel viel schwereren Verdampfung von Selen (Siedepunkt 688°C.). Aber nach vielen Versuchen kann ich jetzt mit demselben Apparat mit automatischem Schluss, den ich auch bei Quecksilber angewandt habe, auch bei Selen gute Resultate erzielen. Als Stopfen für das Quarzexplosionsrohr habe ich anfangs ebenso wie beim Versuch mit Quecksilber einen geschliffenen Quarzstopfen benutzt. Weil aber bei Selen der Dampfdruck nicht so schnell hochsteigt wie bei Quecksilber, bleibt der Stopfen bis zum Moment der Explosion nicht ganz dicht, sondern der Dampf entweicht durch ganz feine Risse im Schliff. Im anderen Fall zwingt sich das geschmolzene Selen zwischen Stopfen und Quarzrohr und hält den Stopfen so fest, dass man nur durch Zerschneiden des Rohres den Stopfen herausziehen konnte. So habe ich ganz einfach wie anfangs Korkstopfen angewendet und zwar dieselben sehr fest hineingedrückt und darauf mit Khotinski-Wachs zugeschmolzen, wie in Abb. 20 ersichtlich ist. Zuerst habe ich wie früher vor den

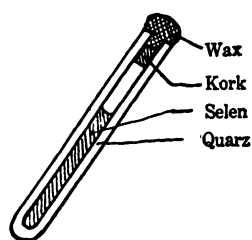


Abb. 21.

Kork etwas Asbest-Watte (E. Merck, für Gooch'sche Tiegel) gesteckt, aber als ich nachher fand, dass der Kork ohne Schaden herausgesprengt wird, auch ohne Asbest, habe ich die Asbestwatte weggelassen. Das Selen, und zwar das reine Selen in Stangenform von E. Merck, ist diesmal in das Explosionsrohr nicht in Form feiner Pulver eingeführt worden, sondern wurde in geschmolzenem Zustand hineingegossen, ungefähr 1.00 → 1.50 g., bis zu 1/3 → 1/2 Volumen des ganzen Rohres. Die Erhitzungsdauer bis zur

Explosion betrug durchschnittlich 2–3 Minuten. Dann erfolgte die Explosion immer ausgezeichnet, weil das Quarzrohr dickwandig genug (2–3 mm.) war,

(47) *Z. anorg. allgem. Chem.*, **155** (1926), 199.

und man dasselbe ohne Gefahr stark erhitzen konnte, mittels 2 oder 3 Teklu-Brennern. Die ganze Selen-Masse verteilte sich in Form wattiger Flocken und die Flüssigkeit wurde im Moment undurchsichtig. Nach einigen Minuten sanken fast alle Selenflocken auf den Boden, und nur ein Teil schwamm noch auf der Oberfläche der Flüssigkeit (er bedeckte dieselbe in ganz feinen lamellen Formen und war sehr schwer abzunehmen). Die Flüssigkeit hatte also jetzt eine schwach getrübbte, orangegelbe Farbe mit ziegelrotem Schimmer, der nach einigen Tagen verschwand. (Diesmal wurde auch das unfiltrierte Sol beobachtet, weil man vorher schon öfters bemerkt hatte, dass die Filtration die eigentliche Stabilität meistens veränderte.) (Abb. 10).

(b) **Über die Einflüsse auf die Stabilität und Konzentration der Sole.**

(1) *Mittels Rühren.* Dieses wie oben erwähnter Weise erhaltene Sol wurde nach einigen Tagen fast ganz klar, hatte aber noch Spuren von gelblicher Trübung, mit sehr starkem gelblich-weißen Tyndall-Kegel; dieser blieb sehr lange (mehr als 1 Jahr), während die Trübung nach einigen Tagen verschwand. Weil es mir nicht möglich war durch eine einmalige Explosion eine grössere Konzentration zu erreichen, habe ich zuerst im Gefäss einen Rührer eingerichtet, wie Abb. 22 zeigt, mit der Absicht, die relative Übersättigung

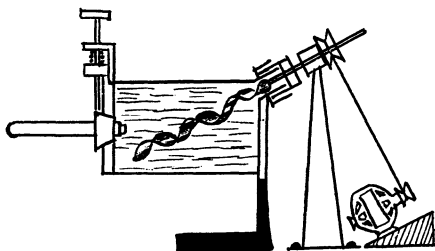


Abb. 22.

dadurch eventuell etwas erhöhen zu können. Das Resultat war natürlich negativ, weil die Kristallisationsgeschwindigkeit, die in diesem Fall sehr gross ist, die Rührgeschwindigkeit bei Weitem übertraf. Ausserdem habe ich versucht, die Explosion in demselben Dispersionsmittel zu wiederholen, mit dem Erfolg, dass das Sol durch die wiederholten Explosionen immer konzentrierter wurde, bis nach 4-5 Explosio-

sionen die Solkonzentration ihren Grenzwert erreichte. Aber die Trübung verschwand nach etwa 1.5 Monaten, und nur eine Spur derselben blieb sehr lange ohne Veränderung (bis zum 7. Monat beobachtet). Dann habe ich als Stabilisator Gelatine verwendet, wie es schon A. Gutbier⁽⁴⁸⁾ versucht hatte. Die Gelatine-Konzentration von 0.1–0.00001% konnte zwar etwas länger die Trübung halten, aber sie zeigte keinen allzu grossen Unterschied zu reinem Wasser. Mit Gummi-arabicum als Stabilisator habe ich auch ungefähr dasselbe Resultat wie mit Gelatine erhalten; es wirkt also nicht so stark als Stabilisator wie für andere hydrophobe Kolloide. Da hier zwei kräftige

(48) A. Gutbier, *Kolloid-Z.*, **31** (1924), 33.

Schutzkolloide ihre Wirkung versagt haben, musste ich noch andere, stabilisierend-wirkende Möglichkeiten untersuchen.

(2) *Mittels Schütteln.* Inzwischen hatte ich mich bei der Kolloid-Dispergation von Quecksilber unter Anwendung einiger Stabilisatoren von neuem davon überzeugt, dass das Schütteln der Flüssigkeit eine grosse Rolle spielt⁽⁴⁹⁾, was hauptsächlich durch die Wirkung gelöster Gase in dem Dispersionsmittel bestätigt wurde, d.h. kurz ausgedrückt, Durchblasen oder Durchspritzen von Hg ruft weniger Dispergation hervor als starkes Hand- oder Maschineschütteln, und auch das Strahlen von U. S. W.⁽⁵⁰⁾ mit einer Frequenz von 450,000 hat keinen grösseren Dispergations-Effekt als einfaches Schütteln. Es ist auch erklärt worden, dass der Sauerstoff der Luft vom chemischen Standpunkt aus dabei eine Hauptrolle spielt. Über den Stabilitätseinfluss anwesender Gase (Stickstoff, Sauerstoff, Luft und Kohlensäure) bei Selenol wurden von K. Juna⁽⁵¹⁾ Untersuchungen angestellt. Diese Versuche, bei denen das Sol nicht durch die thermische Methode sondern durch Wechseln des Lösungsmittels hergestellt worden war, zeigen uns, dass man den Einfluss anwesender Gase nicht ganz ausser acht lassen darf.

Ich habe schon zu anfangs, bei meinen vorläufigen Versuchen (Abb. 5) bemerkt, dass das disperse System mit dieser Methode, durch seinen unangenehmen Geruch ein Vorhandensein von Selenwasserstoff (SeH_2) aufweist, welcher sich bei Berührung mit Sauerstoff aus der Luft allmählich in Selen und Wasser zersetzt ($2 \text{SeH}_2 + \text{O}_2 = 2 \text{H}_2\text{O} + 2 \text{Se}$), und so ausgeschiedenes Selen kann auch kolloid-dispergierend sein. Da nun das Selen nach Pélabon⁽⁵²⁾ eine grosse Menge SeH_2 zu adsorbieren vermag, so ist es möglich eine Erklärung für die Stabilität Selen-Sole zu finden, und zwar wäre diese zurückzuführen auf „dispersoiden Parasitismus“ von Selenteilchen auf Kosten von SeH_2 und verwandte Selenverbindungen, welche bei der Explosion entstanden sind.

Nun habe ich auch versucht, ob man das gewonnene Sol durch Schütteln stabilisieren kann, was auch erfolgreich gelungen ist. Durch 1 bis 2 Explosionen erhaltenes, fast wasserklares Sol wird deutlich gelbtrübe nach 1/2 -1 stündigem Schütteln und ist viel konzentrierter als das vorhergehende, durch 4 Explosionen, ohne Schütteln, gewonnenes Sol. Nach einem Monat ergab es eine fast klare Flüssigkeit mit Spuren von gelber Trübung, und so blieb es sehr lange ohne Veränderung. Die genauere Untersuchung über die Abhängigkeit der Stabilität vom Schütteln, wurde wie folgt ausgeführt: Zuerst habe ich die Anzahl der Explosionen festgestellt, die die optimale Sol-Konzen-

(49) N. Sata, *Kolloid-Z.*, **71** (1935), 48.

(50) Verkürzung von Ultraschallwellen.

(51) K. Juna, dieses Bulletin, **6** (1931), 24.

(52) Pélabon, *Compt. rend.*, **116** (1893), 1292.

tration hervorruft. Ich stellte in dem Gefäß mit der Flüssigkeit eine Explosion an und schüttelte sie darauf 10 Minuten; dabei verschwand der anfangs sich sehr stark bemerkbar machende Selenwasserstoff-Geruch. Dann füllte ich von der Flüssigkeit 20 c.c. in ein Probierglas. Dieses Experiment wiederholte ich noch dreimal, wobei das System immer konzentrierter wurde. Bei der dritten und vierten Explosionsprobe stellte ich fast das gleiche Aussehen fest, nämlich halbdurchsichtig mit weiss-gelber Trübung und orange-gelber Durchsichtsfarbe, und in diesem Fall war fast kein ziegelroter Schimmer bemerkbar. Die stabilisierende Wirkung von Gelatine und Gummi-arabicum ist auch bereits untersucht worden, die, wie Gutbier schon festgestellt hat, fast keine Wirkung zeigte⁽⁵³⁾. Nachdem die 4 Explosionen ausgeführt waren, wurde das Schütteln fortgesetzt bis zu 14 Stunden, und stündlich davon eine Probe von 20 c.c. genommen und beobachtet. Dabei wurde festgestellt, dass das Sol bei 2-3 stündigem Schütteln einen konstanten Wert der Konzentration erreicht, und zwar eine fast undurchsichtige, orange-gelbe Flüssigkeit mit orange-rötlicher Durchsichtsfarbe ergibt.

(3) *Mittels Durchleiten von Luft.* Weil der Sauerstoff der Luft prinzipiell stabilisierend wirkt, wie schon an anderer Stelle⁽⁵⁴⁾ mit Quecksilber bestätigt wurde, könnte man in diesem Fall mit Selen auch dasselbe Resultat erwarten. So habe ich einen Versuch angestellt, um die stabilisierende Wirkung durch Durchleiten von Luft zu untersuchen. Es wurde durch ein durch 4 Explosionen hergestelltes Sol ein starker Strom von Luft geleitet, wie Abb. 23 zeigt. Der Luftstrom war so stark, dass die Se-Flocken nicht am

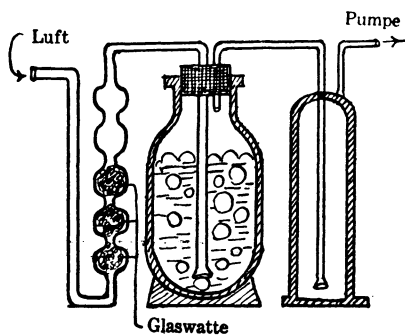


Abb. 23.

Boden der Flasche blieben, sodass man dadurch also praktisch dieselbe Wirkung wie mit mechanischem Schütteln erreichte⁽⁵⁵⁾. Durch das Durchleiten von Luft über Nacht (ca. 14 Stunden) erhielt man genau dasselbe Resultat, wie im anderen Fall durch mechanisches Schütteln von 3-4 Stunden. Weiter wurde das Sol noch 9 Stunden mit einer Maschine geschüttelt, wodurch aber keine Vermehrung der Konzentration zu merken war.

(53) A. Gutbier, *Z. anorg. allgem. Chem.*, **158** (1926), 101.

(54) *Kolloid-Z.*, **71** (1935), 48.

(55) Einen ebensolchen Versuch hat schon Nordlund ausgeführt mit Hg, wobei das Hg. durch welches Luft geleitet wurde, Blasen bildete, durch deren Platzen auch die kolloide Dispergation verursacht wurde, die aber kein besseres Resultat gezeigt hat als beim einfachen, mechanischen Schütteln (*Kolloid-Z.*, **26** (1920), 128).

C. Schwefel. Da Schwefel bei ca. 445°C. siedet, ist es nicht so schwer wie bei Selen, einen Dampfdruck von einigen Atmosphären zu erreichen, und somit die für meine Methode nötige Dampfexplosion zu erzeugen. Dass die Stabilität, soweit das System durch mechanische Methode hergestellt ist, wegen der grösseren Löslichkeit von Schwefel im Vergleich mit Quecksilber bzw. Selen, auf keinen Fall gross ist, wurde sowohl theoretisch als auch experimentell bestätigt⁽⁵⁶⁾. Ich konnte aber durch genannte Verbesserungen an der Apparatur und wiederholte Explosionen eine viel konzentriertere Suspension erhalten, deren Sedimentationsvorgang sowie kolloidchemische Natur

Tabelle 4.

Explosionen	1	2	3	4	5
Menge S (g.)	0.40	0.45	0.45	0.45	0.40
Gleich nach Explosion (Abb. 24)	halbdurchsichtige Milch mit gelbgrünlichen Tönen	fast undurchsichtig	ganz undurchsichtige Milch mit gelbgrünlichen Tönen, die nach 10-15 Minuten verschwinden		
Nach 7 Stunden (Abb. 25)	halbdurchsichtig, rein weisse Milch	5 mm. von oben orange-gelb durchsichtig, unten fast undurchsichtig	5 mm. von oben orangegelb durchsichtig, unten ganz undurchsichtig		
Nach 1 Tag (Abb. 26)	1/4 von oben ganz klar, 3/4 halbdurchsichtig	5 mm. von oben ganz klar, dann lilarote Schicht und unten fast undurchsichtig	ganz undurchsichtig		
Nach 2 Tagen (Abb. 27)	homogen schwach getrübt	1/4 von oben halbdurchsichtig und unten mehr getrübt	noch mehr getrübt	fast undurchsichtig	
Nach 3 Tagen	20 mm. von oben ganz klar, unten bleibt noch schwache Trübung	5 mm. von oben ganz klar, unten halbdurchsichtig bis fast undurchsichtig			
Nach 10 Tagen (Abb. 30)	ganz klar abgesetzt	bleibt noch schwache Trübung mit bläulichen Tönen		noch mehr getrübt	
Nach 14 Tagen	—	ganz klar abgesetzt		noch eine Spur getrübt	
Nach 16 Tagen	—	—		ganz klar abgesetzt	

(56) P. P. von Weimarn, *Kolloid-Z.*, 8 (1910), 214, 216.

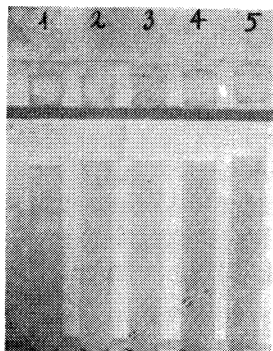


Abb. 24.

Gleich nach den Explosionen.

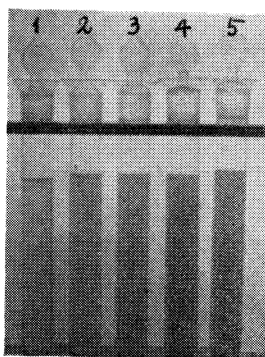


Abb. 25.

Nach 5 Stunden.

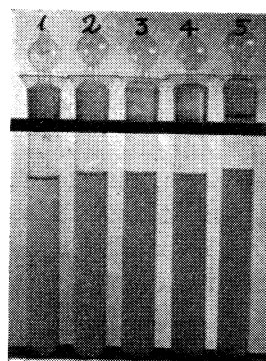


Abb. 26.

Nach 1 Tag.

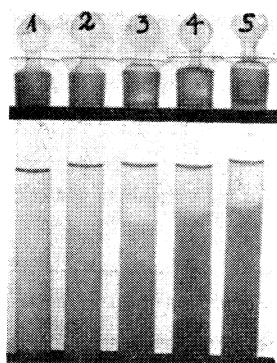


Abb. 27.

Nach 2 Tagen.

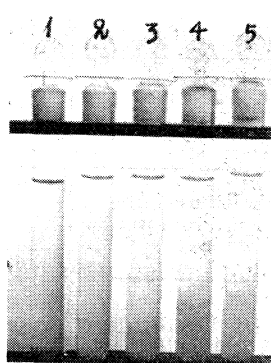


Abb. 28.

Nach 4 Tagen.

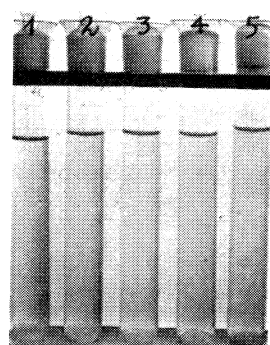


Abb. 29.

Nach 8 Tagen.

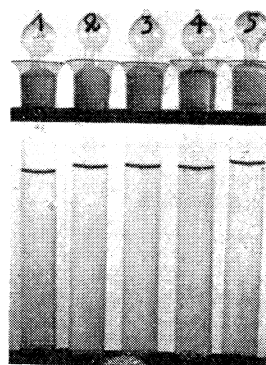


Abb. 30.

Nach 10 Tagen.

ich untersuchen konnte. Der benutzte Schwefel war ein sublimiertes, pulverisiertes Präparat nach dem Japanischen Arznei-Buch, und zwar wurde für jede Explosion 0.4 bis 0.5 g. gebraucht. Versuchsergebnisse sind in Tabelle 4 und Abb. 24-30 zusammengestellt.

Zusammenfassend möchte ich auf Folgendes hinweisen: Mit Schwefel als dispergierende Substanz konnte ich ebenfalls keine stabilen Sole erhalten, was hauptsächlich auf die grosse Löslichkeit von Schwefel in Wasser zurückzuführen ist. Anfangs hatten wir genügend Merkmale von Kolloid-Dispergation durch ihre Farberscheinung, Filtrierbarkeit usw. Aber dann begannen sie schon sehr schnell zu koagulieren und nach etwa 5-8 Tagen, haben sie praktisch vollkommen abgesetzt. Die Konzentration nahm mit der Wiederholung der Explosionen zu, wie in dem Falle mit Selen, das auch nach 4-5 Explosionen sein Maximum erreicht. Nun möchte ich darauf aufmerksam machen, dass die Schwefel-Sole anfangs nicht rein-weiss-trübe, sondern gelblichgrüne Töne zeigen, die nach 5-10 Minuten verschwinden und eine rein-weiße Milch ergeben. Da die Dispersität anfangs ziemlich gross ist, und es unmöglich ist, diese gelbe Farbe mit der eigentlichen Schwefelfarbe zu verursachen, möchte ich annehmen, dass bei der Explosion einige Schwefelverbindungen durch Oberflächenreaktion entstanden sind, die den Solen die gelb-grünen Töne gegeben haben, sich aber durch die Koagulation gleich zersetzten. Der starke Geruch von Schwefelwasserstoff, der sich nach jeder Explosion bemerkbar machte, beweist auch, dass einige chemische Reaktionen bei der Explosion stattgefunden haben.

(Fortsetzung folgt.)

ON THE CHANGES OF WEIGHT OF THE ELECTRODES OF THE LEAD-ACID STORAGE CELL IN THE COURSE OF DISCHARGE.

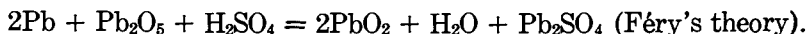
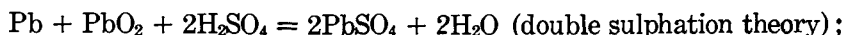
By Kyôji KINOSHITA.

Received May 4th, 1936. Published August 28th, 1936.

Introduction. More than seventy years have elapsed since Gaston Planté made the first lead storage cell in 1859. Many authors studied this cell, yet there remains some ambiguity in the chemical change involved in the charge and discharge of the cell. It may be considered to be rather complicated matters.

The double sulphation theory was proposed by Gladstone and Tribe⁽¹⁾ for the fundamental chemical reaction of the cell, which then was supported by many investigators. Dolezalek⁽²⁾ made an important contribution to the theory, by treating it thermodynamically and applying the Gibbs-Helmholz equation to this problem. On the other hand Féry⁽³⁾ held a different opinion against the double sulphation theory, which is usually called Féry's theory. Chéneveau⁽⁴⁾ measured the changes of weight of the electrodes of the storage cell and obtained the results in favour of Féry's theory, while Denina's results of the similar experiment supported the double sulphation theory.⁽⁵⁾

These two theories can be expressed by the following chemical equations:



Changes of weight of the positive and negative electrodes calculated from these theories are given in Table 1. This table shows the increases of weight of the electrodes in the discharge of 1 ampere hour of the electricity.

(1) Vinal, "Storage Batteries," (1930), 152.

(2) Dolezalek, "Die Theorie des Bleiaccumulators," (1901).

(3) Féry, *Bull. soc. chim.*, **25** (1919), 223.

(4) Féry and Chéneveau, *Bull. soc. franç. élec.*, (1926), 13-32.

(5) Denina, *Giorn. chim. ind. applicata*, **12** (1930), 67; c.f. Jumau, *Rev. gén. élec.*, **28** (1930), 311.

Table 1.

	Double sulphation theory	Féry's theory
Positive electrode	+ 1.196 g.	- 0.294 g.
Negative electrode	+ 1.791 g.	+ 1.791 g.

In the case of positive plate it is expected that the weight increases in discharge from the double sulphation theory, while decreases from Féry's theory. The change of weight of the negative plate is expected to be the same for both of these theories. The present author has made some experiments on this subject and the results are described in this paper.

Experimental Procedures. A small pasted type electrode of the lead-acid cell, being dipped in dilute sulphuric acid, was hung from one of the arms of a thermobalance by a hook made of a glass capillary. The cell was placed in a thermostat maintained at 25°C. The thermobalance is provided with a small mirror at the top of its arm and the inclination of the arm can be observed by means of a telescope and a scale. Besides the mirror, it possesses a pointer and a scale as in the ordinary chemical balance. Both of these devices have been used in the present experiments. The sensibility of the balance was lessened by the damping effect due to the immersion of the electrode in the solution of the cell, and was about 0.02 g.

The electrodes used in the experiments were made by Nippon Tikudenti K. K. The dimensions of the plates were about 20 mm. $\times$ 96 mm. $\times$ 3 mm., and their capacity was about 1 ampere hour. The discharge current was maintained to 250 milli-amperes throughout the experiments, and the change of weight was measured every 1/4 a.h. of discharge. A glass vessel of about 800 c.c. was used as the container of the solution. By using such a large vessel the variation of the density of the solution before and after the discharge was only 0.001 in specific gravity. The volumes of the electrodes used for the experiments were found to be about 4-5 c.c., accordingly the variations of buoyancy due to the change of the density of solution do not need to be taken into consideration.

Results of the Experiments. (1) **The Positive Plate.** The measurements of the positive plate were made first. In this case the change of weight

accompanied in the process of discharge must have the opposite signs according to the two theories cited above. Ten cycles of charge and discharge were made, and the results of measurements are given in Table 2 and Table 3. The weight always increases in the course of discharge.

Table 2. Increases of Weight of the Positive Plate (g.).

Cycle	Discharge capacity			
	1/4 a.h.	1/2 a.h.	3/4 a.h.	1 a.h.
1	—	0.44	—	0.54
2	—	—	—	0.55
3	—	—	—	0.55
4	0.13	0.29	0.44	0.54
5	—	0.31	—	0.61
6	0.13	0.30	0.45	0.55
7	0.14	0.30	0.45	0.55
8	0.13	0.29	0.43	0.53
9	0.13	0.29	0.44	0.55
10	0.13	0.30	0.46	0.55
mean	0.13	0.32	0.45	0.55

Table 3. Increases of Weight of the Positive Plate per 1/4 a.h. of Discharge (g.).

Cycle	Discharge capacity			
	1/4 a.h.	1/2 a.h.	3/4 a.h.	1 a.h.
4	0.13	0.16	0.15	0.10
6	0.13	0.17	0.15	0.10
7	0.14	0.16	0.15	0.10
8	0.13	0.16	0.14	0.10
9	0.13	0.16	0.15	0.11
10	0.13	0.17	0.16	0.09
mean	0.13	0.16	0.15	0.10

Table 2 gives the changes of weight due to the discharge of 1/4 a.h., 1/2 a.h., 3/4 a.h., and 1 a.h., while Table 3, changes of weight per 1/4 a.h. of discharge. From Table 2, we can see that the changes of weight by discharge of 1/4 a.h., 1/2 a.h., 3/4 a.h., and 1 a.h. give well reproducible values. In Table 6 changes of weight per 1 a.h. of discharges measured by the author are compared with the values observed by Chéneveau.⁽⁴⁾ It is remarkable that Chéneveau's values are always a little larger than author's values. It is noticeable, from Table 3, that the weight increases per 1/4 a.h. discharge at different stages are not equal, the initial and the final being smaller than the middle. The increases of weight corresponding to the first, second, third, and final discharge of 1/4 a.h. are 0.13 g., 0.16 g., 0.15 g., and 0.10 g., respectively. Such an inequality of the weight change is probably due to some secondary reaction, the occurrence of which being considered from the evolution of gas bubbles especially at the beginning and at the final stages of discharge.

(2) **The Negative Plate.** Five cycles of discharge were made in the experiment. The specific gravity of the electrolyte solution was taken to be 1.262 (at 27.5°C.). Experimental results are tabulated in Table 4 and Table 5.

Table 4. Increases of Weight of the Negative Plate (g.).

Cycle	Discharge capacity			
	1/4 a.h.	1/2 a.h.	3/4 a.h.	1 a.h.
1	0.29	0.56	0.81	1.08
2	0.29	0.58	0.85	1.13
3	0.30	0.59	0.87	1.14
4	0.29	0.59	0.87	1.16
5	0.30	0.60	0.89	1.16
mean	0.29	0.58	0.86	1.13

Table 5. Increases of Weight of the Negative Plate per 1/4 a.h. of Discharge (g.).

Cycle	Discharge capacity			
	1/4 a.h.	1/2 a.h.	3/4 a.h.	1 a.h.
1	0.29	0.27	0.25	0.27
2	0.29	0.29	0.27	0.28
3	0.30	0.29	0.28	0.27
4	0.29	0.30	0.29	0.29
5	0.30	0.30	0.29	0.27
mean	0.29	0.29	0.28	0.27

Thus the changes of weight of the negative electrode give fairly well reproducible values. In Table 7 author's results of the changes of weight per 1 a.h. of discharge are compared with Chéneveau's values, the former being a little smaller than the latter.

Discussion of the Results. In Table 6 and Table 7 author's results are compared with Chéneveau's data and with the theoretical values calculated from both of the two theories cited above.

Table 6. Comparison of Observed Values with Theoretical Values (g.) (Positive Plate).

Observed values		Theoretical values	
Kinoshita	Chéneveau	D. S. theory	Féry's theory
0.54	0.69	1.196	-0.294
0.55	0.73		
0.54	0.73		
0.61	0.63		
0.55	0.78		
0.55	0.51		
0.53			
0.55			
0.55			

Table 7. Comparison of Observed Values with Theoretical Values (g.) (Negative Plate).

Observed values		Theoretical values	
Kinoshita	Chéneveau	D. S. theory	Féry's theory
1.08	1.26	1.791	1.791
1.13	1.47		
1.14	1.37		
1.16	1.27		
1.16	1.23		
	1.35		

From these tables we see that the weight changes of the electrodes during the course of discharge do not agree well with the theoretical values calculated

from the double sulphation theory or Fèry's theory. The weight increase is actually observed both by the present author and Chèneveau in the case of positive plate, while the weight decrease must be expected from Fèry's theory. As the explanation for the discrepancy of Chèneveau's measurements from the theory, Fèry assumed the existence of a side reaction which takes place at the negative electrode side by side with the formation of Pb_2SO_4 , and the migration of Pb-ion from negative to positive electrode.⁽⁴⁾

On the other hand observed values for both positive and negative electrodes were found to be smaller than the values calculated from the double sulphation theory, being about 51–46% for the positive, and 65–57% for the negative electrode. These experimental results give no decisive conclusion for the two theories mentioned above. The present data, however, are rather coincident with Chèneveau's values, and show very good constancy among themselves.

As already stated, the effect of buoyancy change due to the variation of the specific gravity of sulphuric acid is very small, and the principal causes of error may be the effect of gas bubbles in the pores of the electrodes. Further investigations have been undertaken on this point.

Experiments on the Different Conditions of Cell. Now the conditions of the cells such as the concentration, temperature and the viscosity of the electrolyte are altered and the effect on the weight change is studied.

To determine the viscosity and the specific gravity, a small amount of the electrolyte solution was taken out into an Ostwald pycnometer or a viscosimeter, respectively. In discharging the cell, current was maintained to 250 milli-amperes throughout the experiments, and change of weight was measured every 1/4 a.h. of the discharge.

(1) **Experiments with the Very Dilute Sulphuric Acid.** At first the specific gravity of the sulphuric acid in the cell was reduced to 1.111 by dilution with water. Owing to the dilution of the electrolyte the capacity of the cell diminished to about 1/2 a.h. Accordingly measurements were made only for the discharge capacities of 1/4 a.h. and 1/2 a.h. The results obtained for the positive electrode are tabulated in Table 8 and Table 9.

The discharges from the first to the 9th cycle were made at room temperature (about 15°C.), and from the 10th to the 16th cycle at 30°C., the cell being kept in a water thermostat.

In Table 8 and Table 9 we notice that there are no remarkable effects of the dilution of the solution, though slightly smaller values were obtained in the case of dilute electrolyte solution. Moreover, increase of the values was noticed at the temperature raised to 30°C.

Table 8. Increases of Weight of the Positive Plate (g.).

Cycle	Discharge capacity		Temperature (°C.)
	1/4 a.h.	1/2 a.h.	
1	0.19	0.38	
2	0.13	0.30	
3	0.11	0.26	
4	0.13	0.29	
5	0.11	0.23	
6	0.12	0.25	
7	0.13	0.25	
8	0.12	0.25	
9	0.11	0.24	
10	0.17	0.34	30
11	0.15	0.33	30
12	0.14	0.32	30
13	0.14	0.30	30
14	0.13	0.27	30
15	0.15	0.29	30
16	0.20	0.40	30
mean	0.14	0.29	

Table 9. Increases of Weight of the Positive Plate per 1/4 a.h. of Discharge (g.).

Cycle	Discharge capacity		Temperature (°C.)
	1/4 a.h.	1/2 a.h.	
1	0.19	0.19	
2	0.13	0.17	
3	0.11	0.15	
4	0.13	0.16	
5	0.11	0.12	
6	0.12	0.13	
7	0.13	0.12	
8	0.12	0.13	
9	0.11	0.13	
10	0.17	0.17	30
11	0.15	0.18	30
12	0.14	0.18	30
13	0.14	0.16	30
14	0.13	0.14	30
15	0.15	0.14	30
16	0.20	0.20	30
mean	0.14	0.15	

(2) **Experiments with the Concentrated Sulphuric Acid.** Concentration of the electrolyte was increased to the specific gravity of 1.540. In this case the active materials of the plate fell out of the grid in the initial charge, so the experiments could not be continued.

(3) **Experiments with the Viscous Electrolyte Solution.** Viscosity of the electrolyte solution may be one of the most important factors which affect the existence of the gas bubbles in the pores of the electrode. The viscosity of the liquid will prevent the escaping of the gas bubbles from the pores.

In order to increase the viscosity gelatin and glycerin were added to the solution. The viscosity was measured by the Ostwald viscosimeter. The solution of the cell was made by dissolving 2 grams of gelatin in 1000 c.c. of the sulphuric acid of the specific gravity 1.240. The change of weight of the positive electrode was measured with this cell. The experimental results are tabulated in Table 10 and Table 11.

Table 10. Increases of Weight of the Positive Plate (g.).

Cycle	Discharge capacity		Relative viscosity
	1/4 a.h.	1/2 a.h.	
1	0.13	0.47	1.962/25°C.
2	0.13	0.30	
3	0.16	0.30	

Table 11. Increases of Weight of the Positive Plate per 1/4 a.h. of Discharge (g.).

Cycle	Discharge capacity		Relative viscosity
	1/4 a.h.	1/2 a.h.	
1	0.13	0.24	1.962/25°C.
2	0.13	0.17	
3	0.16	0.14	

The capacity of the cell decreased to about one half of the normal value by the increase of viscosity of the electrolyte solution. The measurements were only made at 1/4 a.h. and 1/2 a.h. of discharge. The weight increases at 1/4 a.h. and 1/2 a.h. are tabulated in Table 10 and those for every 1/4 a.h. of discharge are tabulated in Table 11.

Next, the viscosity was increased by the addition of glycerin. Thus 260 c.c. of glycerin was added to 1000 c.c. of sulphuric acid (specific gravity of 1.240). The specific gravity of this mixture was found to be 1.2461 at 25°C. and its relative viscosity was 3.143/25°C. By using such solution the capacity of the cell decreased seriously, probably by the lack of supply of the electrolyte to the active material, and the cell could scarcely stand a discharge of 250 milli-amperes during a few minutes.

Experimental results obtained with the negative electrode were tabulated in Table 12 and Table 13.

Table 12. Increases of Weight of the Negative Plate (g.).

Cycle	Discharge capacity		Relative viscosity
	1/4 a.h.	1/2 a.h.	
1	0.38	0.66	2.034/25°C.
2	0.30	0.59	
3	0.31	0.61	
4	0.28	0.57	
5	0.28	0.60	
6	0.28	0.51	
7	0.28	0.57	
8	0.27	0.56	
9	0.27	0.55	
mean	0.29	0.58	

Table 13. Increases of Weight of the Negative Plate per 1/4 a.h. of Discharge (g.).

Cycle	Discharge capacity		Relative viscosity
	1/4 a.h.	1/2 a.h.	
1	0.38	0.28	2.034/25°C.
2	0.30	0.29	
3	0.31	0.30	
4	0.28	0.29	
5	0.28	0.32	
6	0.28	0.23	
7	0.28	0.29	
8	0.27	0.29	
9	0.27	0.28	
mean	0.29	0.29	

A solution made from 10 g. of gelatin and 1000 c.c. of sulphuric acid (specific gravity of 1.240) was used in this experiment. The discharge capacity of the electrode also diminished to about one half of the normal value.

Conclusion. From the results described above the changes of weight of the electrodes during the course of discharge do not agree well with the calculated values from both double sulphation theory and Féry's theory. The changes of weight of the electrodes show no remarkable differences by the alteration of conditions such as the concentration or the viscosity of the electrolyte solution. On the other hand the capacities of the electrodes, both positive and negative, were affected seriously by the alterations of such conditions, especially by adding glycerin to the solution. In this case the terminal voltage of the cell fell to about 1.0 volt for a several minutes of discharge. These may lead to the considerations that the effect of gas bubbles in the pores of the electrodes are considered to be rather small. The active materials of the both positive and negative electrodes are submitted to the chemical change during the course of discharge, and therefore there occurs the volume change of these materials. So that Jumau⁽⁶⁾ and Tomii⁽⁷⁾ proposed the necessity of the correction for the buoyancy change of the electrode before and after the discharge. Such a correction was made to author's results. The densities of the active materials assumed in Féry's theory, i.e. Pb_2O_5 and Pb_2SO_4 , are not known, so the corrections of the buoyancies cannot be done in this case. The densities and the molecular volumes of lead, lead peroxide, and lead sulphate are shown in Table 14. The required amounts of Pb and PbO_2 for the discharge of 1 a.h. are 3.866 g. and 4.463 g., respectively.

Table 14.

	Density	Mean density	Molecular volume	Difference of molecular volume
Lead	11.37	11.37	18.2 c.c.	30.4 c.c.
Lead sulphate	6.23	6.23	48.6 c.c.	
Lead peroxide	8.91-9.50	9.21	26.0 c.c.	22.6 c.c.

It follows that the volume changes of the electrodes for the discharge of 1 a.h. are $(30.4 \times 3.866 / 207.2) = 0.567$ c.c. for the negative plate and $(22.6 \times 4.463 / 239.2) = 0.422$ c.c. for the positive plate. Assuming that the

(6) Jumau, *Rev. gén. élec.*, **20** (1926), 235.

(7) Tomii, *J. Soc. Chem. Ind., Japan*, **34** (1931), 59 C.

density of the solution does not change throughout the course of discharge and is 1.261, the corrections for the buoyancy change for the discharge of 1 a.h. are 0.71 g. for the negative plate and 0.53 g. for the positive plate. These correction values are added to author's results described already, and the corrected values are compared with Chéneveau's values, which are also corrected (Table 15).

Table 15.

Increases of Weight per 1 a.h. of Discharge (g.) (Negative plate).			Increases of Weight per 1 a.h. of Discharge (g.) (Positive plate).		
Observed values (corrected)		Theoretical value from D.S. theory	Observed values (corrected)		Theoretical value from D.S. theory
Kinoshita	Chéneveau		Kinoshita	Chéneveau	
1.79	1.97	1.791	1.07	1.22	1.196
1.84	2.18		1.08	1.26	
1.85	2.08		1.07	1.26	
1.87	1.98		1.14	1.16	
	1.94		1.08	1.31	
	2.06		1.08	1.04	
			1.06		
			1.08		
			1.08		

As seen from Table 15 the corrected values are somewhat larger for the negative plates and about 10% smaller for the positive plates than the calculated values. In spite of these discrepancies, the results obtained in the present experiments are in favour of the double sulphation theory.

In conclusion the author wishes to express his hearty thanks to Prof. Sameshima of the Tokyo Imperial University for his kind advice throughout this experiments.

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ZUR LUMINESZENZ DES CALCITS. I.
DAS FLUORESZENZSPEKTRUM JAPANISCHEN CALCITS
IM ULTRAVIOLETTEN LICHT.

Von Ei-ichi IWASE und Takehiro KURONUMA.

Eingegangen am 7. Mai 1936. Ausgegeben am 28. August 1936.

Seit langem haben sich viele Forscher mit der Fluoreszenz des Calcits befasst.⁽¹⁾ Ein neuerer Versuch von W. Witteborg⁽²⁾ zeigte, dass bei den Calciten aus dem Elberfelder Kalkstein, die durch ultraviolettes Licht hervorgerufene Fluoreszenzfarbe im Zusammenhang mit Tracht sowie minerogentischem Alter steht. Dagegen schlossen A. Köhler und H. Leitmeier⁽³⁾ aus ihren Beobachtungen über Fluoreszenz von etwa 300 Stufen von Calciten, dass solche Altersunterschiede im allgemeinen auf Grund der Fluoreszenz allein nicht erkannt werden konnten. Kurz und bündig berichtete auch St. Kreutz⁽⁴⁾ über die Abhängigkeit der Fluoreszenz polnischer Calcite von ihrer Genesis. Genauere umfassende spektroskopische Untersuchungen über die durch ultraviolettes Licht erregte Fluoreszenz des Calcits scheinen uns bis jetzt nicht angestellt worden zu sein. So haben wir im folgenden die Fluoreszenzspektren von 76 Stufen von japanischen Calciten aufgenommen. Die Lagen der Fundorte dieser Calcite kann man in Abb. 1 sehen. Ferner haben wir die Bestimmungen einiger Spurenbestandteile an den 23 Stufen durchgeführt, um den Zusammenhang mit ihren Fluoreszenzspektren aufzufinden.

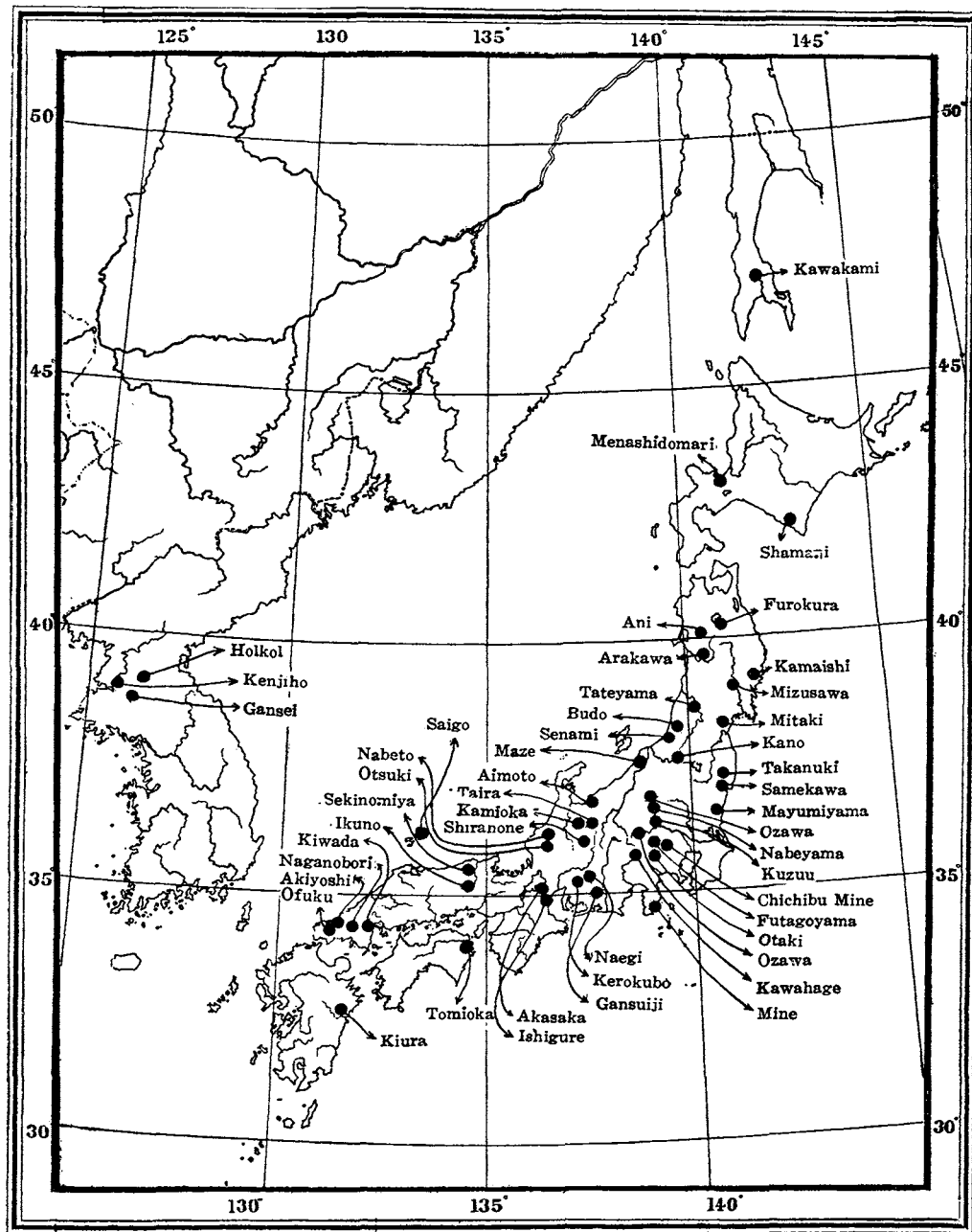
Zur Erregung der Fluoreszenz diente das durch Woodsches Glas filtrierte Quecksilberbogenlicht (Hg-Linien zwischen 4047 und 2804 Å) aus einer Hewitt Quarz-Quecksilberlampe, die mit 3 A. und 100 V. betrieben war. Die Aufnahme des Fluoreszenzspektrums wurde mittelst eines lichtstarken Flüssigkeitsprisma-Spektrographen von Kipp und Zonen durch 2 stündige Exposition gemacht. Unmittelbar vor dem Spalt des Spektrographen befand sich das zu untersuchende Kristallstück, auf das die durch Quarzlinse gesammelte Erregungsstrahlen von einer Seite geworfen wurden. Für die ganze Untersuchung wurden immer Wratten und Wainwright „Hypersensitive Panchromatic“ Platten verwendet. Die Versuchsergebnisse findet man in Tabelle 1 zusammengestellt, in der auch Kristalltracht, Paragenesis und sonstige Beschaffenheit der Stufen enthalten sind.

(1) Z.B. J. Schincaglia, *J. Nuovo Cimento Pisa*, IV, **10** (1899), 212; A. Pochettino, *Atti Acc.*, **13** II, (1904), 301.

(2) W. Witteborg, *Centr. Mineral. Geol.*, **A**, (1932) 364.

(3) A. Köhler und H. Leitmeier, *Centr. Mineral. Geol.*, **A**, (1933), 401.

(4) S. Kreutz, *Comptes rend. mens. d. séances math. nat. clas, Acad. Polonais*, Nr. 7 (1932), 5.



1 : 16 000 000

Abb. 1. Fundorte der hier untersuchten Calcite.

Tabelle 1.

Nr.	Fundort	Mineral-Beschreibung	Schematische Darstellung des Fluoreszenzspektrums			
			λ (m μ)			
			700	600	500	400
1	Aimoto, Toyama Präf.	blass grünlichweißer kristallini- scher Kalkstein, in Kontaktzone vorkommend				
2	Akasaka, Gifu Präf.	farbloße oder lichtgelbe durchsich- tige skalenoeiderische Kristalle aus Lücken von Kalkstein				
3	"	weisses, klein nadliges Kristall- aggregat				
4	"	farbloße durchscheinende Kristall- masse mit Überkrustung rot- erdigen Kalksinters				
5	Akiyoshi, Yama- guchi Präf.	erdiger. zonaren Aufbau zeigender Tropfstein				
6	"	weisser Marmor				
7	Ani, Akita Präf.	blass bläuliches durchscheinendes Kristallaggregat auf Kupferkies				
8	"	blass gelbe durchscheinende flache Rhomboeder mit Kupferkies				
9	Arakawa, Akita Präf.	blass gelbe durchsichtige hexa- gonalsäulige Kristalle				
10	Ashio, Tochigi Präf.	farbloße durchscheinende flache Rhomboeder, begleitet von Kup- ferkies und Liparit				
11	"	farbloße durchscheinende flache Rhomboeder				
12	"	blass weingelbe durchscheinende Kristallstücke				
13	"	blass-violett weisser Papierspat mit Kupferkies				
14	"	weisse säulige Kristalle				
15	"	weisse flache Rhomboeder				
16	"	weisse flache Rhomboeder mit aufsitzenden farbloßen spitzen durchsichtigen facet- tierten Skalenoeidern. begleitet von Kupferkies				
17	Budo, Niigata Präf.	weisses skalenoeiderisches Kristall- aggregat mit Sphalerit und Dolo- mit				
18	Chichibu Mine, Saitama Präf.	blass gelbe Kristalle aufweissem Marmor, in Kontaktzone vor- kommend				

Tabelle 1. (Fortsetzung)

Nr.	Fundort	Mineral-Beschreibung	Schematische Darstellung des Fluoreszenzspektrums			
			λ (m μ)			
			700	600	500	400
19	Furokura, Akita Präf.	weisse Skalenoeder, im Kupfererz- gang vorkommend				
20	Futagoyama, Saitama Präf.	blass gelbe durchscheinende Spalt- stücke				
21	„	farblose durchsichtige Spaltstücke				
22	„	farblose spätige Stufe, eine Kom- bination von (2131) und (1011)				
23	Gansei, Kōkaido, Korea.	braun gefleckte weisse Grundrhom- boeder				
24	Gansuiji, Shizu- oka Präf.	blass gelbe etwas getrübte Röhr- chen (Stalaktit)				
25	Holkol, Korea	blass braungelber Marmor, der in Kontakt- lagerstätte vorkommt, von Brucit und Ludwigit begleitend				
26	Ikuno, Hiogo Präf.	blass rötlich, weisse Kristalle mit Fluorit, die sich im Gold-, Silber- und Kupfer-erzgang vorfinden				
27	„	farblose durchsichtige flache Rhom- boeder				
28	Ishigure, Mi-e Präf.	blass gelbe Kristallmasse, in Peg- matit-Druse				
29	„	blass weingelbe durchscheinende Kristalle				
30	Kamaishi, Iwate Präf.	weiss getrübte Kristallmasse mit Magnetit, in Eisenkontaktzone vorkommend				
31	Kamioka, Gifu Präf.	weisse auf Zinkkontaktlagerstätte vorkommende Spaltstücke mit Quarz und Salit				
32	„	farblose durchscheinende flache Rhomboider mit Sphalerit und Bleiglanz				
33	Kano, Fukushi- ma Präf.	blass gelbe beinahe würfelförmige Kristalle mit Anhydrit vorkom- mend				
34	Kawahage, Na- gano Präf.	sehr wenig opaleszierende Spalt- stücke				
35	„	farblose flache Rhomboider, in Kontaktzone, von Bergkristall begleitet				
36	Kawakami, Sachalin.	blass gelbe Kristalle, in Am- moniten				

Tabelle 1. (Fortsetzung)

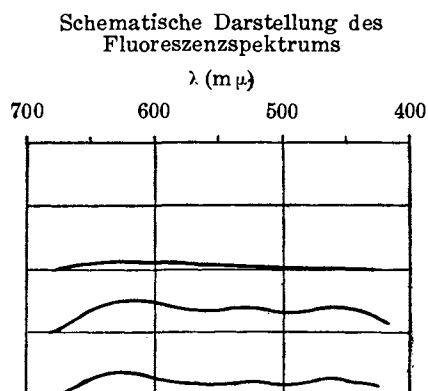
Nr.	Fundort	Mineral-Beschreibung	Schematische Darstellung des Fluoreszenzspektrums			
			λ (m μ)			
			700	600	500	400
37	Kawakami, Sachalin.	blass weingelbe Kristalle, in Ammoniten				
38	Kenjiho, Korea	weisse mit gelber Kruste übergezogene Spaltstücke, in Eisenerzstätte				
39	Kerokubo, Gifu Präf.	blass gelbe Kristalle, in Druse von Granite				
40	„	gelblich braune durchsichtige Kristallmasse				
41	Kiura, Ōita Präf.	milchweiss getrübbte Spaltstücke, auf Zinnkontaktzone				
42	„	blass violette durchscheinende Spaltstücke				
43	„	dunkelbraune undurchsichtige Kristallstücke				
44	Kiwada, Yamaguchi Präf.	weisse Kristallmasse, mit Kassiterit Einschluss, in Kontaktlagerstätte				
45	Kuzuu, Tochigi Präf.	braun gefleckte derbe Kristallmasse gebildet aus Kalkstein				
46	„	farblose durchsichtige Spaltstücke				
47	(Mandschurei)	„				
48	Mayumiyama Ibaragi Präf.	weisser Marmor				
49	Maze, Niigata Präf.	blass weingelbe Rhomboeder, auf Basalt				
50	„	blass weingelbe durchscheinende Kristalle begleitet von Analzim und Natrolith				
51	„	braungelbe Kristalle mit Analzim				
52	„	farblose durchsichtige säulige Kristalle begleitet von Analzim				
53	Menashidomari, bei Otaru, Hokkaido	kleine weisse prismatische Kristalle, in Andesit, von Chabazit und Laumontit begleitet				
54	Mine, Shizuoka Präf.	gelblich braune faserige Kristallgruppe (kristalline dicke Zapfen)				

Tabelle 1. (Fortsetzung)

Nr.	Fundort	Mineral-Beschreibung	Schematische Darstellung des Fluoreszenzspektrums			
			λ (m μ)			
			700	600	500	400
55	Mitaki, bei Sendai, Miyagi Präf.	farblose säulige kleine Kristalle, in Andesit Hohlraum				
56	Mizusawa, Iwate Präf.	hellblaue durchscheinende Kristallstücke				
57	„	blass gelbliche durchsichtige kleine Prisma, im Kupfererzgang				
58	Nabeto, Ishikawa Präf.	blass weingelbe Spaltstücke				
59	Nabeyama, Tochigi Präf.	kleiner traubiger Stalaktit				
60	Naegi, Gifu Präf.	blass gelbe Kristallstücke				
61	Naganobori, Yamaguchi Präf.	weisse Spaltstücke, auf Kupferkontaktlagerstätte				
62	Ofuku, Yamaguchi Präf.	blass weingelber damastartig glänzender Faserkalk, in Kupferkontaktlagerstätte				
63	Otaki, Saitama Präf.	farblose durchsichtige Spaltstücke, in Kalkstein Hohlräumen				
64	Otsuki, Fukui Präf.	grauer kristallisierter Kalkstein mit Graphit				
65	Ozawa, Gumma Präf.	halbdurchscheinende Kristallmasse				
66	Saigo, Shimane Präf.	blass gelbe durchscheinende Kristalle, in Schiefertön Lücken				
67	Samekawa, Fukushima Präf.	bläulich weisse Kristallstücke				
68	Sekinomiya, Hiogo Präf.	blumenkohlartige Kristalle von $-\frac{1}{2}$ R, auf Quarz mit Antimonglanz sitzend				
69	Senami, Niigata Präf.	schneeweiße rhomboederische Kristallaggregate (Zapfen)				
70	Shamani, Hokkaido	weisse derbe Kristallmasse, in Tonschiefer				
71	Shirahone, Nagano Präf.	blass gelblich weisse derbe Kristallmasse				
72	Taira, Nagano Präf.	blass rosenrote kleine kugelförmige Kristalle, aus heisser Quelle (Teufelskonfekte)				

Tabelle 1. (Fortsetzung)

Nr.	Fundort	Mineral-Beschreibung
73	Takanuki, Fukushima Präf.	grauer körniger Kalkstein, der Sulfiderz enthält
74	Tateyama, Yamagata Präf.	graue schlammartige Masse
75	Tomioka, Fukushima Präf.	farblose durchscheinende säulige Kristallaggregate, in Kalkstein Hohlraum
76	Yorii, Saitama Präf.	weisser Marmor



Wie Tabelle 1 zeigt, gibt es ziemlich viele Stufen, die ganz und gar nicht fluoreszieren: nämlich 21 Stufen, 28% der hier untersuchten. Immer weist jeder fluoreszenzfähiger Calcit sicher eine Fluoreszenzbande auf, deren maximale Schwärzung photographischer Platte bei 625–635 m μ liegt. Beachtenswert ist, dass die Lage dieser Bande mit der von S. Iimori⁽⁵⁾ sowie H. Steinmetz⁽⁶⁾ schon gemessenen Thermolumineszenzbande des Calcits übereinstimmt. Nun emittieren 25 Stufen vornehmlich solche rötlich orange Fluoreszenzbande, das sind 33% im ganzen.

In folgenden Proben ist nebst oben erwähntem Schwärzungsschwerpunkt eine andere schwache Schwärzung zu beobachten, deren Maximum bei 460–470 m μ liegt: Nr. 7, Nr. 11, Nr. 14, Nr. 19, Nr. 53, Nr. 56 usw. Nach S. Hoshijima⁽⁷⁾ ergab das Phosphoreszenzspektrum des Calcits von Tochigi Präfektur 2 Banden, die sich in den Gebieten von 674 bis 532 m μ und von 532 bis 430 m μ erstrecken. Auch teilte J. Yoshimura⁽⁸⁾ mit, dass der Stalaktit aus Kiura in Ōita Präfektur bei durch Kathodenstrahlen erregter Lumineszenz 2 Banden aufweist, die sich in den Gebieten von 640 bis 550 m μ und von 490 bis 400 m μ befinden. Es ist beachtenswert, dass unsere in Rede stehenden 2 Fluoreszenzbanden mit den von Hoshijima und Yoshimura wahrgenommenen 2 Banden übereinstimmen.

Ferner zeigen Proben Nr. 10, Nr. 52, Nr. 66 und Nr. 72 noch eine Schwärzung mit Maximum bei 515–520 m μ . Betrachtet man die Aufnahme der Fluoreszenzspektren der Proben Nr. 9, Nr. 20 und Nr. 28, so gewahrt man ein

(5) S. Iimori, *Sci. Papers Inst. Phys. Chem. Research* (Tokyo), **20** (1933), 274.

(6) H. Steinmetz, *Centr. Mineral. Geol.*, **A**, (1934), 209.

(7) S. Hoshijima, *Sci. Papers Inst. Phys. Chem. Research* (Tokyo), **21** (1933), 15.

(8) J. Yoshimura, *Sci. Papers Inst. Phys. Chem. Research* (Tokyo), **23** (1934), 241.

Schwärzungsmaximum auch bei 560–570 m μ . In solchen Fällen fügen sich die Fluoreszenzbanden meistens zusammen und nehmen fast das ganze sichtbare spektrale Gebiet ein. Wir hatten 20 weisslich fluoreszierende Stufen zum Versuche: 26% aller untersuchten Proben.

Sehr wesentlich hängt die Lumineszenzfarbe des Calcits vom stofflichen Gehalte der Ausgangslösung bzw. des Calcits selbst ab. Darum wurde die Menge von Spurenbestandteilen in Calciten auf analytischem Wege für 23 Stufen bestimmt, nämlich: I. Teil: Fe, Al und seltene Erden einschliessend und II. Teil: Mn, Zn, Cu usw. Tabellen 2, 3 und 4 geben je die Zusammenstellung der Messergebnisse an nichtfluoreszierenden, rötlich orange fluoreszierenden und weisslich fluoreszierenden Calciten.

Tabelle 2. Analyse nichtfluoreszierender Calcite.

I: % Fe, Al und seltene Erde als Oxyde.
II: % Mn, Zn, Cu usw. als Oxyde.

Nr. der Probe	I (%)	II (%)	I/II	I+II (%)
1	0.059	0.045	1.11	0.095
6	0.076	0.134	0.57	0.210
35	0.073	0.068	1.73	0.141
43	1.637	0.554	2.96	2.191
45	0.283	0.006	47.2	0.289
47	0.056	0.037	1.52	0.096
48	0.103	0.033	3.12	0.136

Tabelle 3. Analyse rötlich orange fluoreszierender Calcite.

Nr. der Probe	I (%)	II (%)	I/II	I+II (%)
13	0.239	0.256	0.93	0.495
15	0.549	0.103	5.33	0.652
17	0.994	0.530	1.88	1.524
22	0.024	0.145	0.17	0.169
30	0.227	0.206	1.10	0.433
31	0.032	0.175	0.18	0.207
32	0.884	0.425	2.40	1.309
38	0.349	0.451	0.77	0.800
41	0.272	0.273	1.00	0.545
69	0.228	0.149	1.56	0.377
				Mittel (0.65 ₁)

Tabelle 4. Analyse weisslich fluoreszierender Calcite.

Nr. der Probe	I (%)	II (%)	I/II	I+II (%)
9	0.364	0.646	0.56	1.010
20	0.026	0.675	0.04	0.701
49	0.038	0.004	9.50	0.042
50	0.134	0.015	8.93	0.149
71	0.166	0.008	20.8	0.174
75	0.047	0.042	1.20	0.089
				Mittel (0.36 ₁)

Man sieht, dass rötlich orange fluoreszierender Calcit metallische Beimengungen enthält maximal 1.52%, minimal 0.21% : durchschnittlich 0.65%; bei weisslich fluoreszierendem sind die Zahlen : max. 1.01%, min. 0.04%: durchschnittlich 0.36%.

Zu bemerken ist, dass die zur Erzlagerstätten gehörenden Calcite fast immer rötlich orange fluoreszieren. Und man findet weisslich fluoreszierende Calcite öfters in den durch Umkristallisation aus Kalken entstandenen. Darum sind die metallischen Beimengungen in ersteren grösser als in letzteren.

Stellen wir aus den Tabellen solche Calcite zusammen, die für das Verhältnis I/II annähernd den Wert 1 haben, so erhalten wir fünf Stufen, wie in Tabelle 5.

Tabelle 5. Calcite mit gleichem Wert 1 für das Verhältnis I/II.

Nr. der Probe	Fluoreszenz	I/II	I+II (%)
1	nein	1.1	0.095
13	rötlich orange	0.9	0.495
30	„	1.1	0.433
41	„	1.0	0.545
75	weisslich	1.2	0.089

In den drei rötlich orange fluoreszierenden Calciten ist die Menge der metallischen Beimengung beinahe gleich. Dagegen hat der weisslich fluoreszierende und der nichtfluoreszierende Calcit beträchtlich kleinere Menge solcher Beimengung. Trotzdem diese beiden ziemlich gleiche Mengen der

Beimengung enthalten, zeigen sie in der Fluoreszenz-bedeutenden Unterschied, der vielleicht von verschiedenem relativem Gehalt an Eisen, Aluminum, seltenen Erden usw. herrührt.⁽⁹⁾

Zusammenfassung.

(1) Es wurde die durch ultraviolettes Licht hervorgerufenen Fluoreszenzspektren an 76 Stufen japanischer Calcite aufgenommen.

(2) Im ganzen betrachtet, ergaben Calcite verschiedener Fundorte nicht mehr als 4 Fluoreszenzbanden, deren maximale Helligkeit bei 625–635 m μ , 460–470 m μ , 515–520 m μ und 560–570 m μ liegt. Die erste Bande bemerkt man an jedem fluoreszenzfähigen Calcit.

(3) Von den untersuchten Calciten fluoreszierten 21 Stufen gar nicht, etwa 25 Stufen deutlich rötlich orange und 20 Stufen stark weisslich.

(4) Durch Analyse wurden einige Spurenbestandteile der aufs Geratewohl gewählten 23 Stufen ermittelt.

(5) Die durch Sinterbildung entstehenden Calcite fluoreszierten weisslich, die den Erzlagerstätten angehörenden dagegen meistens rötlich orange.

Einige Stücke Calcit stellten uns Herr Prof. Z. Harada, sowie Herren O. Nagashima und K. Sakurai in liebenswürdiger Weise zur Verfügung, wofür wir ihnen vielmals danken.

Eine besondere Freude ist es uns, Herrn Dr. S. Iimori für eine Reihe wertvoller Hinweise herzlich zu danken.

*Forschungsanstalt für Physik und Chemie,
Tokio.*

(9) Vgl. S. Hata, *Sci. Papers Inst. Phys. Chem. Research* (Tokyo) **20** (1933), 168. Er versuchte, Thermolumineszenzfähigkeit des Calcits in Zusammenhang mit dem Gehalt der Beimengung zu setzen.

ZUR LUMINESZENZ DES CALCITS. II. THERMOLUMINESZENZSPEKTREN JAPANISCHER CALCITE.

Von Ei-ichi IWASE.

Eingegangen am 7. Mai 1936. Ausgegeben am 28. August 1936.

Über die spektrale Zusammensetzung der natürlichen Thermolumineszenz von Calciten sind vor kurzem Messungen vom Nabeto⁽¹⁾ und die vom Andreasberger⁽²⁾ Vorkommen vorgelegt. Da sich die Bande der Thermolumineszenz vom Calcit mit der bei der Verbrennung von Calcium-Metall deckt, so kam Dr. Iimori zu der Auffassung, dass das Ausleuchten vom Calcit als eine Art hochverdünnter Calcium-Flamme im Kristalle betrachtet werden kann und das spektrale Gebiete, in dem sich die Lumineszenz aufweist, von der Grundsubstanz wesentlich abhängen dürfte, wenn auch wohl die Intensitätsverteilung und die Einzelheiten des Spektrums von den in geringer Konzentration beigemengten „Aktivatoren“ bedingt sind.

Mit Hilfe des lichtstarken Flüssigkeitsprisma-Spektrographen von Kipp und Zonen und photographischer Platten abgestufter Farbempfindlichkeit im weniger brechbaren spektralen Teile wurden die Thermolumineszenzspektren einer Anzahl von japanischen Calciten systematisch aufgenommen, um ihre spektrale Zusammensetzung aufzuklären. In Tabellen 1–3 zeigte ich die Ergebnisse meiner Untersuchungen.

Wenn die Thermolumineszenz mit Ilford „Special Rapid Panchromatic“ Platte festgehalten wird, so erkennt man an all den untersuchten Stufen aus Nabeto, Naegi, Ishigure, Ashio, Kerokubo und Futagoyama keine Unterschiede, sondern stets nur eine verwaschene breite Schwärzung, deren Schwerpunkt bei etwa $600\text{ m}\mu$ liegt (Tabelle 1). Wenn man grössere Mengen der Stufe zur Untersuchung verwendet, dehnt sich zwar die Schwärzung auf der Platte weiter nach den beiden Seiten aus, aber der Schwerpunkt bleibt immer bei etwa $600\text{ m}\mu$, wie der Versuch an der Stufe aus Futagoyama zeigt. Nun zog ich auch die Fluoreszenz bei Beleuchtung mit durch Woodsches Glas filtrierten Quecksilberbogenlicht in Betracht und wählte unter stark thermolumineszenzfähigen Calciten drei aus: die Stufen aus Kerokubo, Futagoyama und Nabeto. Die Stufe aus Kerokubo zeigt rötlich orange Fluoreszenz, die aus Futagoyama starke grünlich weisse Fluoreszenz und Nachleuchten, dagegen fluoresziert die aus Nabeto ganz und gar nicht.

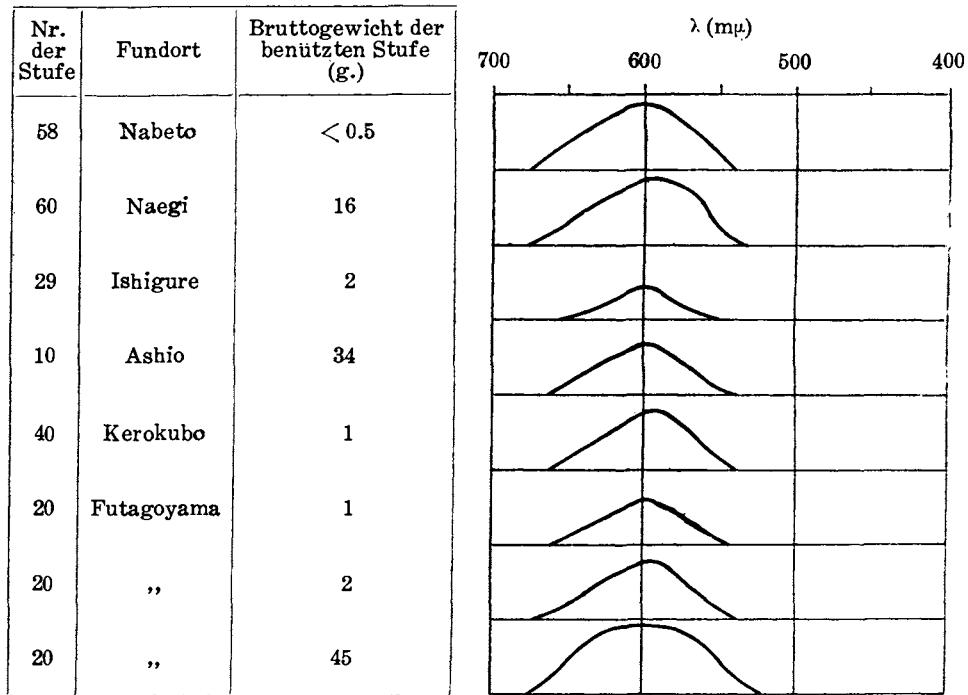
(1) S. Iimori, *Sci. Papers Inst. Phys. Chem. Research* (Tokyo), **20** (1933), 274.

(2) H. Steinmetz, *Centr. Mineral. Geol.*, **A**, (1934), 209.

Tabelle 1. Schematische Darstellung der Mikrophotometerkurve vom Thermolumineszenzspektrum.

Plattensorte: Ilford „Special Rapid Panchromatic“ Platte.

Relative Spaltbreite: 50.



Bei Verwendung der noch mehr farbempfindlichen, Ilford „Hypersensitive Panchromatic“ Platte, zeigen diese drei Stufen einige bemerkenswerten Unterschiede (Tabelle 2). Die Thermolumineszenz der Stufe aus Nabeto ergibt zwei Schwärzungsmaxima: bei 605 m μ und noch bei 635 m μ . In der Mikrophotometerkurve ist das erste Maximum höher als das letzte. Auch ergeben die Stufen aus Futagoyama und Kerokubo auf dieser Platte zwei Schwärzungsschwerpunkte, die aber bei etwa 600 m μ und 625–630 m μ liegen und in beinahe demselben Schwärzungsgrad auftreten.

Ferner verwendete ich Wratten und Wainwright „Hypersensitive Panchromatic“ Platte für Calcite aus Futagoyama und Nabeto (Tabelle 3). Die Exposition zur Platte wird 1, 2 und 3 Male wiederholt, jedesmal unter Benutzung von 0.5 g. der Stufe. Im Falle der Stufe aus Futagoyama kommt das Maximum der Schwärzung bei etwa 625 m μ vor, und durch wiederholte

Tabelle 2. Schematische Darstellung der Mikrophotometerkurve vom Thermolumineszenzspektrum.

Plattensorte: Ilford „Hypersensitive Panchromatic“ Platte.

Relative Spaltbreite: 50.

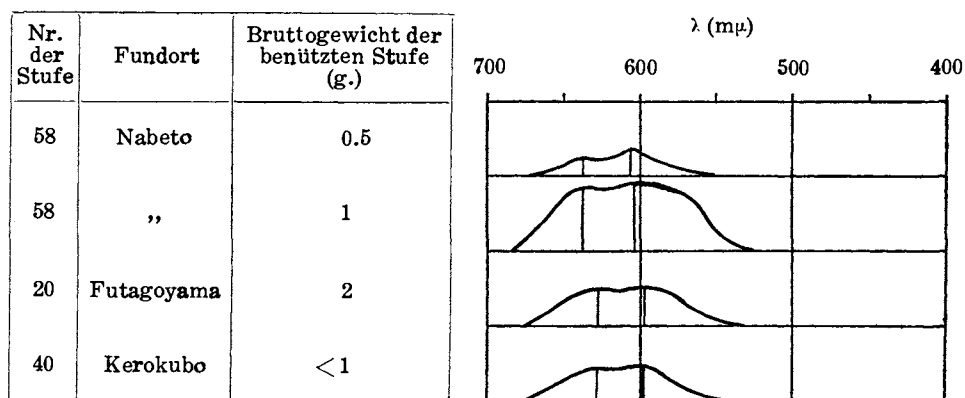
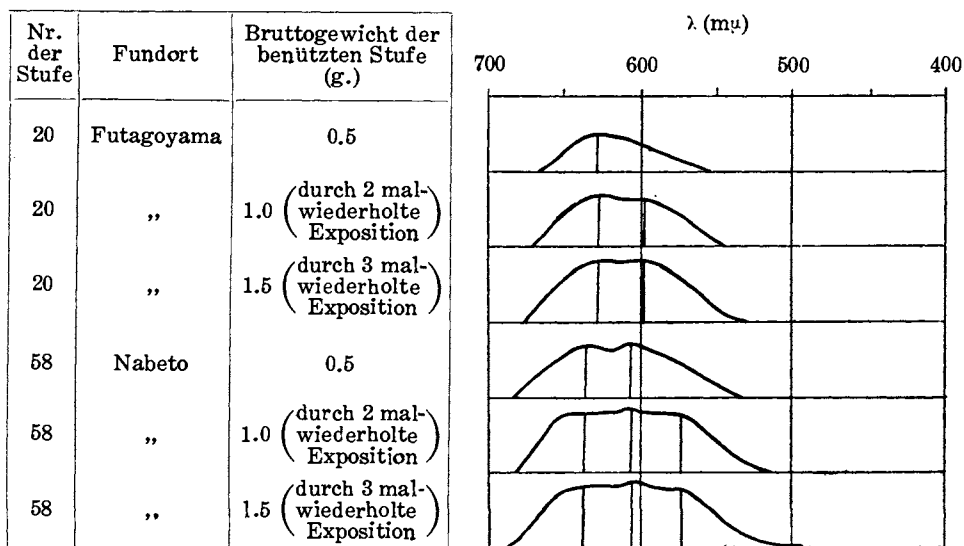


Tabelle 3. Schematische Darstellung der Mikrophotometerkurve vom Thermolumineszenzspektrum.

Plattensorte: Wratten und Wainwright „Hypersensitive Panchromatic“ Platte.

Relative Spaltbreite: 100.



Expositionen wird auch die Schwärzung gegen etwa $600\text{ m}\mu$ stark. Bei der Stufe aus Nabeto zeigt sich das Maximum bei $635\text{--}640\text{ m}\mu$ niedriger als das Maximum bei $605\text{ m}\mu$, und dabei ist noch ein anderes Maximum bei etwa $570\text{--}575\text{ m}\mu$ zu sehen.⁽³⁾

In einem mit Mangan aktivierten Calciumoxyd-Phosphor wird nach E. L. Nichols⁽⁴⁾ die für das Mangan charakteristische gelblichrote verwaschene Emissionsbande durch die linienartigen engen Banden des Samariums oder Thuliums ersetzt, das in noch geringer Konzentration dem Phosphor zugesetzt wird. All diese einzelnen Unterschiede des Thermolumineszenzlichtes von japanischen Calciten mögen wohl auch in solcher verdrängenden Wirkung der Metalle begründet sein.

Ausser spektraler Zusammensetzung der Thermolumineszenz und Fluoreszenz in ultravioletten Strahlen ist der Calcit aus Nabeto noch verschieden von den aus Futagoyama: Bei Erwärmung zeigt die Stufe aus Futagoyama Ausleuchten während relativ kurzer Zeit, doch die aus Nabeto gibt mehr als 7 Minuten lang dauernde Thermolumineszenz, die nicht ganz vergeht. Im natürlichen Zustande lumineszieren die Stufen aus Arakawa und Kawahage bei Erwärmung fast oder gar nicht. Erwärmt man sie aber nach vorausgegangener Röntgenbestrahlung, so lumineszieren sie schwach. Solche Thermolumineszenzbande kommt in derjenigen Lage vor, welche die natürliche Thermolumineszenzbande von anderen oben erwähnten Calciten einnimmt.

Aus der Tabelle 4 ersieht man, dass sich stark thermolumineszenzfähige Calcite gegen ultraviolette Strahlen sehr verschieden verhalten, nämlich dass sie grünlich weiss, rötlich orange, rosa, oder gar nicht fluoreszieren. In Fluoreszenz und Nachleuchten verhält sich ferner die Stufe aus Arakawa ähnlich der aus Futagoyama, sie zeigt aber keine natürliche Thermolumineszenz. Wie weiter oben schon bemerkt worden ist, ergeben die Stufen aus Arakawa und Kawahage eine Thermolumineszenzbande im oben öfters erwähnten orangen Gebiete des Spektrums, wenn sie nach Röntgenbestrahlung erwärmt werden. In ultravioletten Strahlen fluoresziert die erste Stufe sehr stark grünlich weiss, doch die letzte gar nicht.

Kurz, man findet durchaus keinen einfachen Zusammenhang zwischen Thermolumineszenz und Fluoreszenz des Calcits.

(3) Vgl. auch die neue Angabe von H. Haberlandt, *Sitzber. Akad. Wiss. Wien, Math.-naturw. Klasse*, Abt. II a, **144** (1935), 664. Von den zahlreichen Calciten, deren Thermolumineszenzspektren der Verfasser untersuchte, zeigte nur eine gelblich gefärbte Stufe aus Altenberg (bei Igau in Mähren) die seltenen Erdlinien neben einer öfters bemerkbaren gelbroten Thermolumineszenzbande.

(4) E. L. Nichols, *J. Opt. Soc. Am.*, **13** (1926), 573.

Tabelle 4.

Nr. der Stufe*	Fundort	Bemerkung	Fluoreszenz	Thermolumineszenz
58	Nabeto, Ishikawa Präf.	blass weingelbe durchsichtige Spaltstücke	nein	sehr stark
60	Naegi, Gifu Präf.	blass gelbe durchsichtige Kristallstücke	nein	stark
2)	Ishigure, Mi-e Präf.	blass weingelbe durchscheinende Kristalle	sehr schwach (rosa)	sehr stark
10	Ashio, Tochigi Präf.	farblose durchscheinende flache Rhomb.	schwach (rosa)	schwach
40	Kerokubo, Gifu Präf.	gelblich braune durchsichtige Kristallmasse	stark (rötlich orange)	sehr stark
20	Futagoyama, Saitama Präf.	blass gelbe durchscheinende Spaltstücke	stark (grünlich weiss, Nachleuchten)	sehr stark
9	Arakawa, Akita Präf.	blass gelbe durchsichtige hexagonalsäulige Kristalle	stark (grünlich weiss, Nachleuchten)	nein
35	Kawahage, Nagano Präf.	farblose flache Rhomb.	nein	nein

* Vgl. I. Mitteilung.

Zusammenfassung.

(1) Die Zusammensetzung des Thermolumineszenzlichtes von japanischen Calciten wurde eingehend untersucht unter Verwendung des lichtstarken Flüssigkeitsprisma-Spektrographen von Kipp und Zonen und dreier Sorten photographischer Platten mit abgestufter Farbempfindlichkeit.

(2) Die Verwendung von Ilford „Special Rapid Panchromatic“ Platte ergab stets nur eine breite verwaschene Schwärzung bei Aufnahme der Thermolumineszenz für alle hier in Betracht kommende Stufen. Dagegen waren einige Unterschiede der Schwärzung auf Ilford „Hypersensitive Panchromatic“ Platte und Wratten und Wainwright „Hypersensitive Panchromatic“ Platte bemerkbar. Die komplizierteste Thermolumineszenz mit drei Schwärzungsschwerpunkten zeigte die Stufe aus Nabeto, wenn man Wratten und Wainwright „Hypersensitive Panchromatic“ Platte verwandte.

(3) An solchen Calciten, denen eigentliche natürliche Thermolumineszenzfähigkeit fehlt, wurden die Spektren der nach vorheriger Röntgenbestrahlung erst erzielten Thermolumineszenz aufgenommen.

(4) Beim Versuche, sowohl die Fluoreszenz unter Filterultraviolett als auch das Nachleuchten der Calcite mit ihrem Thermolumineszenzverhalten in

Verbindung zu bringen, konnte man kaum einfache Gesetzmässigkeit auffinden.

Einige Stücke der hier benützten Calcite stellten mir die Herren O. Nagashima und K. Sakurai in liebenswürdiger Weise zur Verfügung, wofür ich ihnen vielmals danke. Eine besondere Freude ist es mir, Herrn Dr. S. Iimori für eine Reihe wertvoller Hinweise herzlich zu danken.

*Forschungsanstalt für Physik und Chemie,
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**ZUR LUMINESZENZ DES CALCITS. III.
ÄNDERUNG DER FLUORESZENZSPEKTREN VON CALCITEN
DURCH VORHERIGES ERHITZEN.**

Von Ei-ichi IWASE.

Eingegangen am 9. Mai 1936. Ausgegeben am 28. August 1936.

Der Einfluss vorheriger Erhitzung auf die durch ultraviolette Strahlen erregte Fluoreszenz gewisser Mineralien ist nur in letzter Zeit aufgefallen. E. L. Nichols, H. L. Howes und D. T. Wilber bemerkten nämlich,⁽¹⁾ dass vorheriges starkes Glühen einen schwach weisslich fluoreszierenden Calcit in einem rötlich fluoreszierenden verwandelt. Die Verstärkung der Phosphoreszenz nach mässigem Erwärmen und völligem Wiedererkalten beobachtete ich an einem intensiv lumineszenzfähigen Fluorite japanischen Vorkommens.⁽²⁾ Auch fanden H. Haberlandt und K. Przibram,⁽³⁾ dass vorsichtiges Erwärmen vor der ultravioletten Belichtung die Fluoreszenzfähigkeit mancher Fluorite verstärkt. Dass bei Calciten, Baryten, Cölestin usw., nebst Verstärkung der Fluoreszenz auch eine Änderung der Fluoreszenzfarbe nach Erhitzen eintreten kann, wurde dann von A. Köhler und H. Leitmeier berichtet.⁽⁴⁾

Bei der Fortsetzung meiner Versuche über die Lumineszenz japanischer Calcite wurde auch die nach Erwärmen hervorgebrachte Änderung des

(1) E. L. Nichols, H. L. Howes und D. T. Wilber, „Cathodo-luminescence and cathodoluminescence“, (1928), 25.

(2) E. Iwase, *Bull. Inst. Phys. Chem. Research* (Tokyo), **11** (1931), 923.

(3) H. Haberlandt und K. Przibram, *Mitt. d. Inst. f. Ra-Forsch.*, Nr. 313; *Sitzber. Akad. Wiss. Wien, Math.-naturw. Klasse, Abt. II a*, **142** (1933), 236.

(4) A. Köhler und H. Leitmeier, *Centr. Mineral. Geol.*, A, (1933), 409.

Fluoreszenzspektrums an einiger Anzahl Stufen systematisch untersucht. Im folgenden möchte ich die Ergebnisse meiner Untersuchungen zusammenfassen und mitteilen.

In einem elektrischen Ofen wurde die Erwärmung des Calcits meistens bis zu 6–7 stündigem Glühen über 700°C. abgestuft. Die Fluoreszenzaufnahme erfolgte nach völligem Abkühlen. Erregung der Fluoreszenz und Aufnahme des Fluoreszenzspektrums wurden ausgeführt wie in der ersten Mitteilung. Hierbei wurden Wratten und Wainwright „Hypersensitive Panchromatic“ Platten verwendet.

(1) **Blass gelbe Spaltstücke aus Futagoyama, Saitama Präfektur (Stufe Nr. 20⁽⁵⁾).** Ohne Vorbehandlung ergibt er 3 Fluoreszenzbanden im spektralen Gebiete von Orangegelb, Grün und Blau, deren Maxima bei 584–615, 523 und 462–471 $m\mu$ liegen und deren Helligkeiten auf der Platte fast gleich sind (Abb. 2a). Nach Erhitzen auf 180°C. verstärken die Banden sich im langwelligen Teile und auch bei 564 $m\mu$ (Abb. 2b). Die Fluoreszenzhelligkeit erreicht ihren höchsten Grad nach Erhitzen auf 345°C., wobei ziemlich helle Maxima auch bei 480 und 447 $m\mu$ bemerkbar sind (Abb. 2c). Bei Erhitzung auf 450°C. erfolgt nun eine geringe Schwächung der Helligkeit im ganzen, besonders merklich im kurzwelligen Teile (Abb. 2d). Im kurzwelligen Teile verschwächt sich die Fluoreszenz der auf 550°C. erhitzten Probe noch beträchtlicher (Abb. 2e). Hierbei zeigt sich das Maximum bei 493 $m\mu$ nur wenig, während das bei 531 $m\mu$ sich deutlich vorfindet. Nach Erhitzen auf 640°C. bemerkt man eine breite Fluoreszenzbande mit Maximum nur bei 637 $m\mu$ (Abb. 2f). Diese Bande ist ziemlich temperaturbeständig: nach Ausglühen bis zu 730°C. wird sie schwächer aber sie ist immer noch zu bemerken (Abb. 2g).

Es hat sich gezeigt am Calcite aus Futagoyama, dass vorausgegangene Erhitzung die Intensität der Banden über das ganze Gebiet gleichmässig verstärkt, soweit die Erhitzungstemperatur nicht zu hoch ist, und dass durch Erhitzen auf 345–450°C. die Fluoreszenz zur maximalen Helligkeit verstärkt wird, weiter nach Erhitzen auf etwa 450°C. Schwächung der Banden vom kurzwelligen Teile an eintritt, und noch während Veränderung der Bandenhelligkeit die scharfen Maxima bei 453, 447, 480, 490, 493, 497, 524 und 531 $m\mu$ zu beobachten sind. Auch ist zu bemerken, dass die Wellenlänge des Maximums von der orangen Fluoreszenzbande desto länger wird, je höher die vorherige Erhitzungstemperatur des Calcits ist.

(2) **Blass blaue Kristallstücke aus Mizusawa, Iwate Präfektur (Stufe Nr. 56).** Das Fluoreszenzspektrum dieser Stufe besteht im natürlichen

(5) Für Stufe Nr. vgl. I. Mitteilung.

Zustande aus 4 verschiedenen hellen Banden : die blauen Banden mit Maxima bei 473 und 462 $m\mu$ sind stark, die grüne Bande mit Maximum bei 520 $m\mu$ stärker und die orange Bande mit Maximum bei 617 $m\mu$ am stärksten (Abb. 4a). Nach Erhitzen auf 345°C. erfolgt die Verstärkung der Banden, und die 2 Maxima der blauen Banden verschmelzen. Jedoch verändern sich die Helligkeiten der Maxima von den Banden beinahe nicht, wenn man ihre relativen Verhältnisse betrachtet (Abb. 4b). Die Intensität bei 611 $m\mu$ erhöht sich, so dass die Photometerkurve von 611 bis 631 $m\mu$ flach wird. Die auf 540°C. erhitzte Probe zeigt die stärkste Fluoreszenzhelligkeit, dabei verstärkt die Bande ihre Helligkeit auch etwa bei 571 $m\mu$ (Abb. 4c). Nach Ausglühen auf 725°C. verschwächen sich die Banden im kurzwelligen Teile sehr merklich, während die langwelligen Banden temperaturbeständig sind (Abb. 4d).

(3) **Blass weingelbe Kristallstücke aus Ashio, Tochigi Präfektur (Stufe Nr. 12).** Diese Stufe ergibt Fluoreszenzbanden in 3 Teilen des Spektrums : Orange, Grün und Blau (Abb. 6a). Im ersten schliessen sich 2 Banden zusammen. Nach Erhitzen auf 380°C. verstärken die Banden ihre Helligkeit merklich und schliessen sich zu einer Verwaschenen zusammen (Abb. 6b). Erhitzt man die Stufe auf 570°C., so schwächen sich ihre kurzwelligen Fluoreszenzbanden, aber die Helligkeit ihrer langwelligen Banden sinkt nicht ab, wobei Maxima bei 528, 496 und 461 $m\mu$ zu bemerken sind (Abb. 6c). Die Fluoreszenz der auf 635°C. erhitzten Stufe wird schwächer über das ganze spektrale Gebiet (Abb. 6d). Die Banden im kurzwelligen Teile schwächen sich merklich und Maxima treten bei 528 und 501 $m\mu$ auf.

(4) **Blass gelbe Kristalle aus Saigo, Shimane Präfektur (Stufe Nr. 66).** Ohne vorausgegangenes Erhitzen zeigt diese Stufe 3 Banden mit Maxima bei 623, 524 und 476 $m\mu$ (Abb. 8a). Die Helligkeit der Fluoreszenz wird am stärksten nach Erhitzen auf 345°C. (Abb. 8b). Durch Erhitzen auf 550°C. verkleinern die Banden im kurzwelligen Teile ihre Helligkeit beträchtlich, während die im langwelligen Teile temperaturbeständiger sind (Abb. 8c). Man sieht hier ziemlich scharfe linienartige Banden bei 525, 533 und 492 $m\mu$.

(5) **Blass gelbe hexagonalsäulige Kristalle aus Arakawa, Akita Präfektur (Stufe Nr. 9).** 5 Helligkeitsmaxima ergeben sich im natürlichen Fluoreszenzspektrum. Je kürzer die Wellenlänge der Bande ist, desto stärker ist die Helligkeit (Abb. 10a). Nach Erhitzen auf 380°C. verstärken sich die Banden und wird die Photometerkurve über das ganze spektrale Gebiet beinahe eben (Abb. 10b). Nach Erhitzen auf etwa 555°C. geht die maximale Helligkeit der Fluoreszenz schon vorüber, denn im kurzwelligen Teile beginnt Schwächung einzutreten (Abb. 10c). Man sieht dabei ziemlich scharfe Bandenmaxima bei 458 und 436 $m\mu$. Die Helligkeit der Fluoreszenz wird nach Ausheizen auf

630°C. schwächer, besonders deutlich im kurzwelligen Teile; auch zeigt sich eine Anzahl von schmalen linienartigen Banden (Abb. 10d). Solche schmale Fluoreszenzbanden sind auf Abb. 11 wiedergegeben, sie waren durch verschiedene Exposition der Platte aufgenommen.

2 mg. seltene Erden wurden aus 200 g. dieser Stufe ausgezogen. Den Röntgenemissionspektren nach, die Herr S. Shinoda liebenswürdigerweise aufgenommen hat, werden Ce, Nd, La, Pr, Sm, Dy und Gd nachgewiesen, wobei sich Ce am meisten und Gd am wenigsten vorfindet. Beim Vergleich mit S. Fagerbergs Ergebnissen⁽⁶⁾ über die Kathodenphosphoreszenz der seltenen Erden in Kalziumoxyd, könnten die schmalen Fluoreszenzbanden am auf 630°C. erhitzten Calcite aus Arakawa meistens den oben erwähnten seltenen Erden zugeschrieben werden, wie aus Tabelle 1 ersichtlich.

Tabelle 1. Schmale Fluoreszenzbanden des Calcits aus Arakawa nach Erhitzen auf 630°C.

Banden- Wellenlänge beobachtet m μ	Elemente identifiziert nach Fagerbergs Daten. λ (Å)
636	Pr (6334.7)
614	Pr (6191.0; 6068.9) Sm (6149.1)
586	Sm (5864.3) Dy (5861.6; 5850.5)
574	Sm (5760.1) Dy (5754.3; 5733.3)
560	Pr (5570.2)
545	?
523	?
520	Pr (5174.0)
512	?
494	Pr (4928.5)
483	Pr (4865.5; 4857.9)
460	Nd (4591.0)

Alle bisher erwähnten Calcite fluoreszieren weisslich. Rötlich orange fluoreszierende Calcite, z.B. weisse Kristallmasse aus Kiwada in Yamaguchi Präfektur (Stufe Nr. 44) und blass rötlich weisse Kristalle aus Ikuno in Hiogo Präfektur (Stufe Nr. 26) zersprangen während des Erhitzens; sie behielten

(6) Sven Fagerberg, *Nova Acta Regiae Societatis Scientiarum Upsaliensis*, Ser. IV, Vol. 7. No. 6 (1931).

die gleiche Fluoreszenzfarbe bei und zeigten keine Verstärkung der Fluoreszenzintensität. Auch fand man an nichtfluoreszierenden Calciten—z.B. farblose Spaltstücke aus Futagoyama in Saitama Präfektur (Stufe Nr. 21), blass bläulich weisse Kristallmasse aus Samekawa in Fukushima Präfektur (Stufe Nr. 67), weisse rhomboedrische Kristalle mit braun gefleckten Oberflächen aus Gansei in Korea (Stufe Nr. 23) und farblose Spaltstücke aus Mandschurei (Stufe Nr. 47)—nach Erhitzen keinen bedeutenden Effekt.

Aus der kurzen Darstellung ist folgendes hervorzuheben. Das Fluoreszenzspektrum des weisslich fluoreszierenden Calcits besteht aus breiten und schmalen Banden, im natürlichen Zustande decken sich die beiden. Durch vorausgegangene Erhitzung nehmen die Fluoreszenzbanden zuerst an Helligkeit zu, dann nach Anwendung noch höherer Temperatur ab, und unter geeigneten Bedingungen schwächen sich nur die breiten Fluoreszenzbanden relativ schnell, während die schmalen Banden hell und deutlich zurückbleiben. In Tabelle 2 sind solche schmalen Fluoreszenzbanden angegeben.

Tabelle 2. Relativ schmale Fluoreszenzbanden nach Erhitzen.

(Hier sind kürzwelligere Banden als etwa 530 m μ angegeben)

Fundort	Maximale Lage der Banden (m μ)					
Futagoyama	524			480	453	447
„	532		497	490		
„	531		493			
Ashio	528		496		461	
„	528		501			
Saigo	533	525		492		
Arakawa	530	520	512	494	483	460
„	525				458	436

Im allgemeinen sind die Fluoreszenzbanden im kurzwelligen Gebiete mehr temperaturempfindlich als die im langwelligen und das vorausgegangene Erhitzen macht manchmal die schmalen linienartigen Banden, die von den breiten Banden verborgen sind, sichtbar.

Dies ist nicht der Fall bei den Calciten, welche entweder rötlich orange oder gar nicht fluoreszieren.

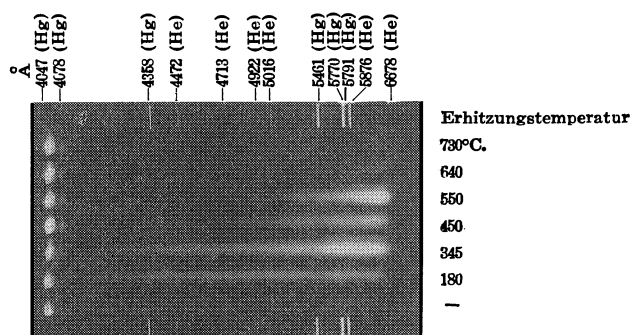


Abb. 1. Änderung des Fluoreszenzspektrums durch vorheriges Erhitzen.
Fundort: Futagoyama. Expositionsdauer: 20 Minuten.

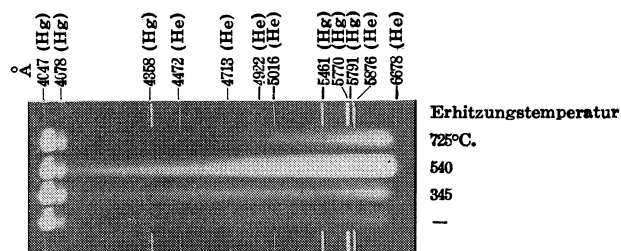


Abb. 3. Änderung des Fluoreszenzspektrums durch vorheriges Erhitzen.
Fundort: Mizusawa. Expositionsdauer: 40 Minuten.

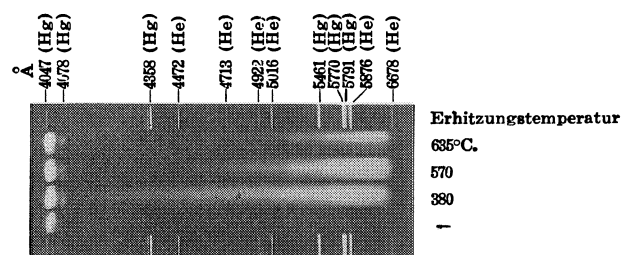


Abb. 5. Änderung des Fluoreszenzspektrums durch vorheriges Erhitzen.
Fundort: Ashio (Stufe Nr. 12). Expositionsdauer: 20 Minuten.

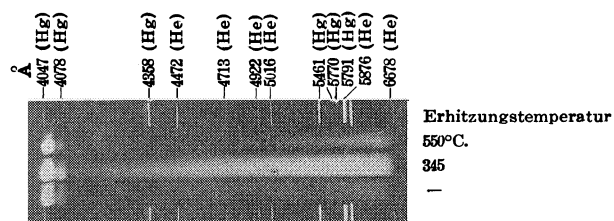


Abb. 7. Änderung des Fluoreszenzspektrums durch vorheriges Erhitzen.
Fundort: Saigo. Expositionsdauer: 20 Minuten.

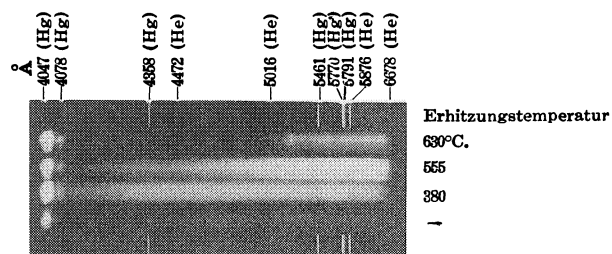


Abb. 9. Änderung des Fluoreszenzspektrums durch vorheriges Erhitzen.
Fundort: Arakawa. Expositionsdauer: 10 Minuten.

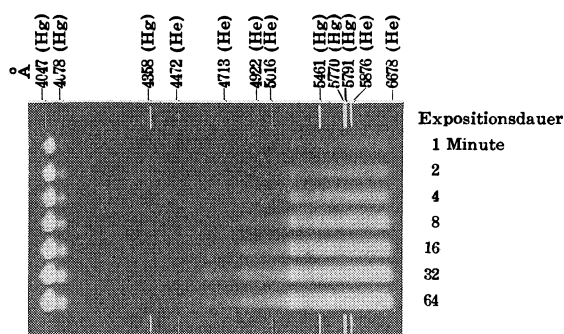


Abb. 11. Nach Erhitzen auftretende schmale Fluoreszenzbanden.
Fundort: Arakawa. Temperatur vorheriger Erhitzung: 630°C.

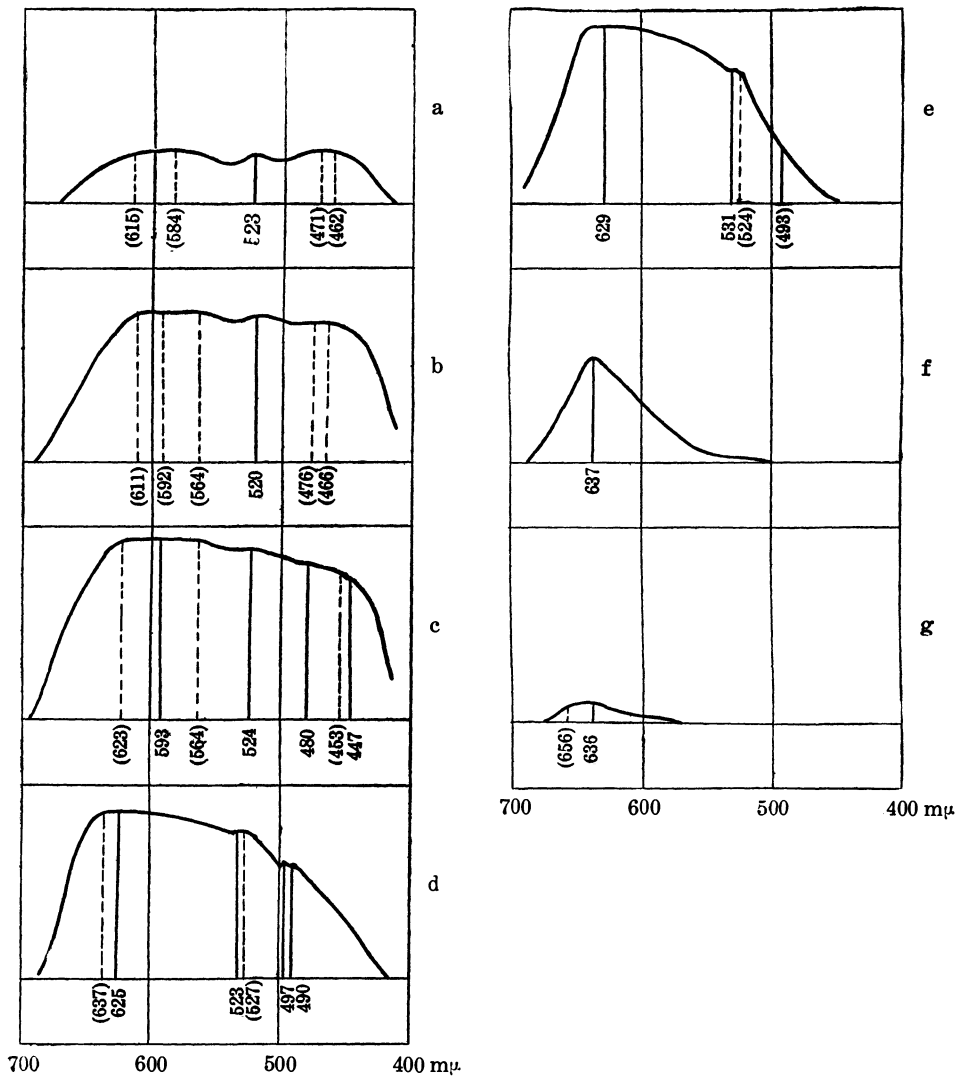


Abb. 2. Schematische Darstellung der Mikrophotometerkurve vom Fluoreszenzspektrum des Calcits aus Futagoyama.

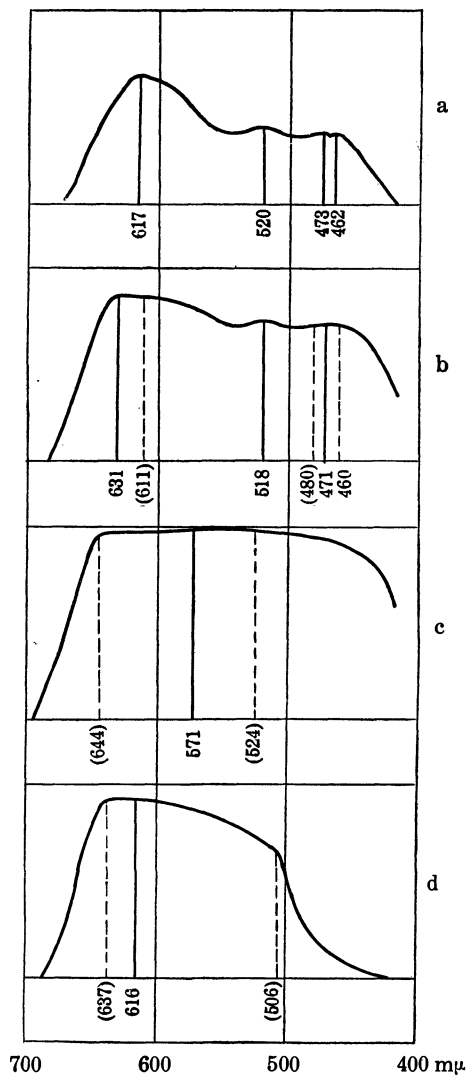


Abb. 4. Schematische Darstellung
der Mikrophotometerkurve vom
Fluoreszenzspektrum des
Calcits aus Mizusawa.

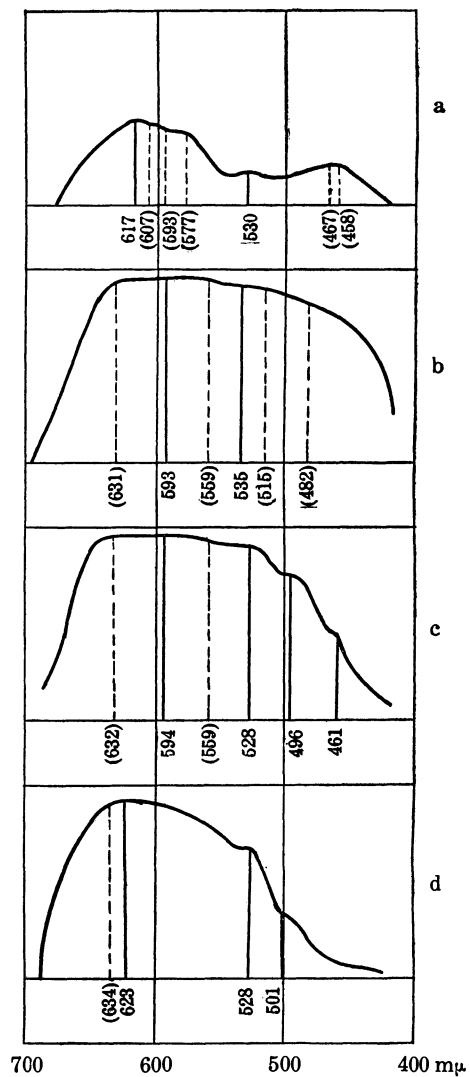
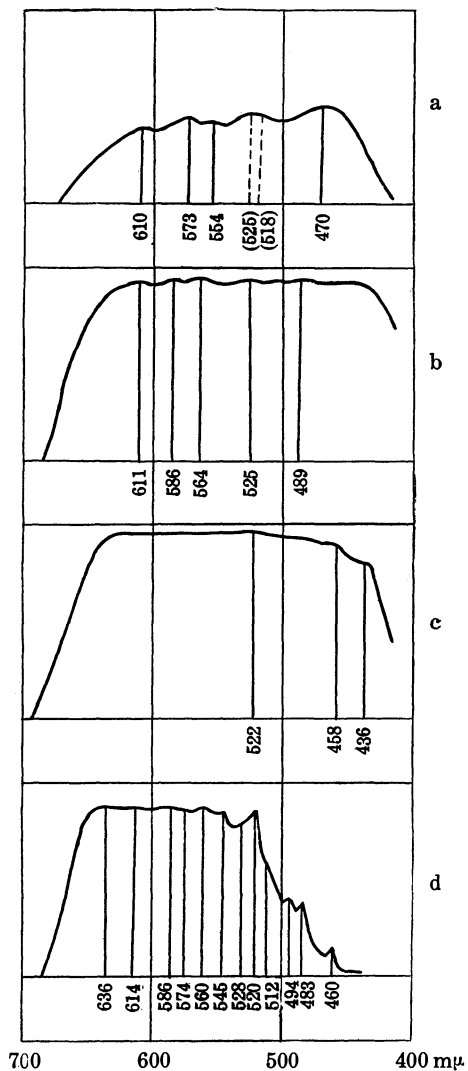
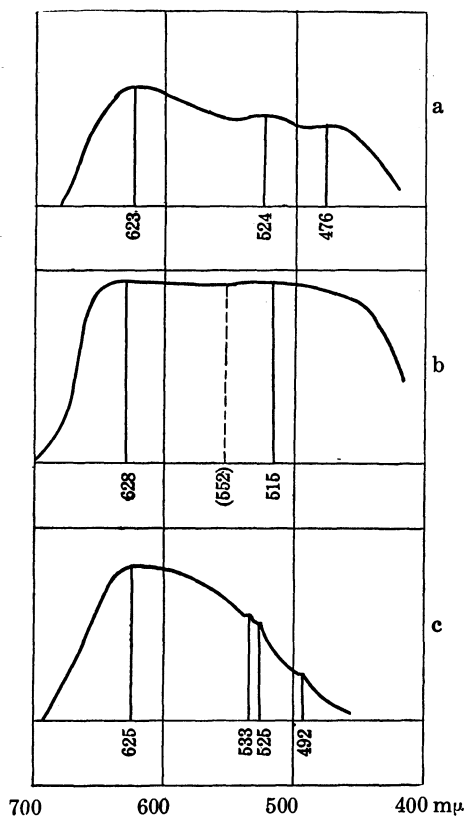


Abb. 6. Schematische Darstellung
der Mikrophotometerkurve vom
Fluoreszenzspektrum des
Calcits aus Ashio.



Zusammenfassung.

(1) Veränderungen der Fluoreszenz unter ultravioletten Strahlen durch vorherige Erhitzung wurden an einer Gruppe von japanischen Calciten spektrographisch näher untersucht.

(2) Zur Untersuchung kamen: blass gelbe Spaltstücke sowie farblose aus Futagoyama, Saitama Präf., blass blaue Kristallstücke aus Mizusawa, Iwate Präf., blass weingelbe Kristallstücke aus Ashio, Tochigi Präf., blass gelbe Kristalle aus Saigo, Shimane Präf., blass gelbe hexagonalsäulige Kristalle aus Arakawa, Akita Präf., weisse Kristallmasse aus Kiwada, Yamaguchi Präf., blass rötlich weisse Kristalle aus Ikuno, Hiogo Präf., blass bläulich weisse Kristallmasse aus Samekawa, Fukushima Präf., weisse rhomboedrische Kristalle mit braun gefleckter Oberfläche aus Gansei, Korea und farblose Spaltstücke aus Mandschurei.

(3) Die Fluoreszenz-Farbe und -Helligkeit der im natürlichen Zustande weisslich fluoreszierenden Calcite zeigte stets starke Abhängigkeit von vorheriger Erhitzung, während die der eigentlich orange fluoreszierenden sowie der nichtfluoreszierenden gegen vorherige Erhitzung unempfindlich blieben.

(4) Mit Erhöhung der Erhitzungstemperatur nahm die bei gewöhnlicher Temperatur und im ultravioletten Lichte beobachtete Helligkeit der Fluoreszenz natürlich weisslich fluoreszierender Calcite zunächst zu, zeigte ein Maximum, um dann wieder abzunehmen. Der Grad der Erwärmung, welcher die maximale Fluoreszenzhelligkeit hervorbringt, ist für einzelne Kristalle verschieden.

(5) Weisslich fluoreszierende Calcite besaßen zuweilen nach mässigem Erhitzen die beachtenswerte Eigenschaft, eine Anzahl von schmalen Fluoreszenzbanden aufzuweisen, die sonst von den breiten verwaschenen Banden ganz verborgen wurden.

(6) Bei der Stufe aus Arakawa konnte man solche schmalen Fluoreszenzbanden auf die seltenen Erden zurückführen, derer Gegenwart nach der Röntgenemissionsmethode festgestellt wurde.

Zum Schluss halte ich es für meine angenehme Pflicht, Herrn Dr. S. Iimori für sein reges Interesse an dieser Arbeit herzlich zu danken.

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STUDIES OF MONOMOLECULAR FILMS BY THE RIPPLE METHOD. I.

By Jitsusaburo SAMESHIMA and Tsunetaka SASAKI.

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They say that the navigator, in former times, used to drop some oil into the sea from ship side to subside the breakers in the case of stormy weather.⁽¹⁾ The vegetable oil, such as linseed oil, is said to be most effective in this action. We undertook to study this phenomena.

At first, we made the wave by blowing the surface of water in a basin by an air blower. Then a small quantity of oil was dropped on the water surface, but the wave did not subside.

Next, we put the water basin on a thin wooden plate with a small electric motor side to side. Thus the vibration accompanied by the rotation of motor made fine stationary waves on the water surface of the basin. Now the surface is touched with a glass rod which is varnished with the oil, for example, oleic acid, then the wave subsides at once. This is a good lecture demonstration. If the initial water surface is contaminated with some dirty matter, then the experiment does not result well. The wave surface must sufficiently be clean and free from oily matter. It is advisable to sweep the water surface with a paraffined glass rod before the experiment is done.

Thirdly, we have made the ripple by means of a tuning fork, which is kept in contact with the surface of the water. The results obtained by this method is described in the following lines.

The action of the oil film on the ripple was first studied by Miss Pockels in 1891.⁽²⁾ Recently, Gorter and Seeder have developed this method and experimented on palmitic acid, lauric acid, casein and zein.⁽³⁾ We followed the method of Gorter and Seeder in our measurement.

Ripple was made by electrically-maintained tuning forks, whose vibrational numbers were 50, 100 and 200 per second respectively. The height of the wave was measured by means of the reflection of light on the waved surface. Fig. 1 is the schematic view of the measuring apparatus.

(1) Marcellin, *Kolloid-Beiheft*, **38** (1933), 185.

(2) Miss Pockels, *Nature*, **43** (1891), 437.

(3) Gorter and Seeder, *Kolloid-Z.*, **58** (1932), 257.

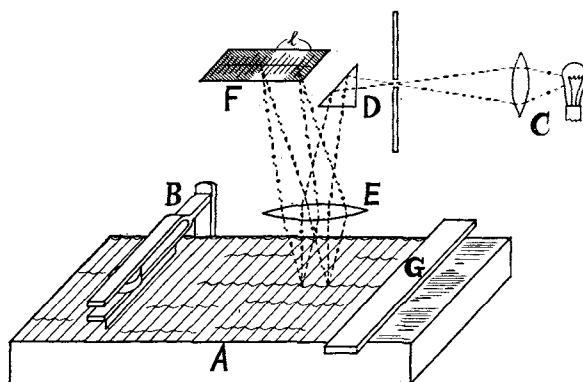


Fig. 1.

A is the water tray, the inner side of which is painted with paraffin. The wave is made by the tuning fork B. C, D, E shows the optical system by which a parallel light comes vertically on the water surface. The diffuse light reflected by the wave surface is now focused by the lens E on the scale F as a band of light. The width of the band, l , on the scale is nearly proportional to the amplitude of the wave, provided the amplitude is small compared with the wave length. G is a glass plate painted with paraffin and is used to change the surface area of water covered with oil film.

The "thickness" of the oil film, or the area of the single oil molecule is changed by two methods. The first method is as follows: A small quantity of the benzene solution of oil is put on the water and after the solvent has evaporated the wave is made and measured. Then the thickness of oil is changed by adding more and more oil (dissolved in benzene) successively and the measurements are done at every time. The area of the water surface is kept constant throughout. A tray of the size $14 \times 20 \text{ cm.}^2$ was used in this case. We shall call this method "the method of constant surface area".

Then the second method is as follows: A small quantity of the benzene solution of oil is put on the water surface, and after the benzene has evaporated the area of the oily surface is changed by glass slide G. A tray of $14 \times 50 \text{ cm.}^2$ was used in this case. We shall call this method "the method of constant oil quantity".

The area occupied by the single oil molecule, α , is calculated as usual, by dividing the area of water surface with the number of molecules of the spread oil. The width, l , of the band of reflected light on the scale E changes with the molecular area of oil, α . The relations between these two quantities have been measured.

The underlying water in the tray was sometimes alkaline and sometimes acidic according to the solubility of the oil in the water. The tap water of $pH=8$ is used as the alkaline water and the hydrochloric acid of 0.04 N as the acidic one.

Table 1 shows the observed data for palmitic acid spread on the alkaline water ($pH=8$) at 14°C ., the constant surface area method being used. The vibrational frequency of the tuning fork was 100 per second. The area of the tray was $14 \times 20\text{ cm}^2$.

Table 1.

Quantity of palmitic acid (mg.)	Area per molecule α ($\text{\AA}^2$)	Width of the band l (cm.)	Quantity of pa.mitic acid (mg.)	Area per molecule α ($\text{\AA}^2$)	Width of the band l (cm.)
0		4.2	0.0348	34.0	3.45
0.0132	89.7	3.95	0.0375	31.6	2.9
0.0158	74.7	3.8	0.0400	29.6	1.0
0.0205	57.8	3.95	0.0436	27.2	0.5
0.0230	51.5	3.95	0.0463	25.6	0.3
0.0256	46.2	4.0	0.0478	24.8	0.34
0.0282	42.0	3.95	0.0504	23.5	0.32
0.0309	38.3	3.95	0.0543	21.8	0.30
0.0329	36.0	3.7	0.0582	20.3	0.30

Fig. 2 shows the curve of α against l . The value of α at the minimum point of l is $25.6\text{ \AA}^2$. We shall denote this point with α_m .

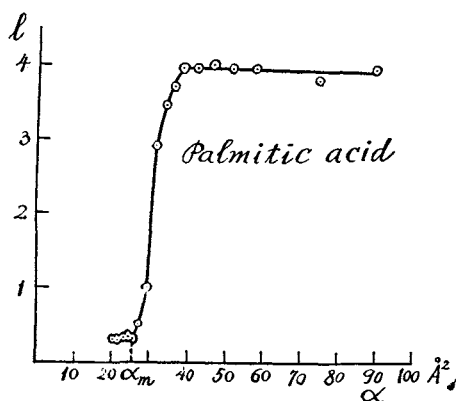


Fig. 2.

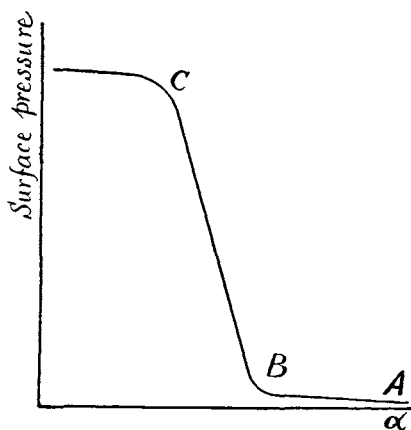


Fig. 3.

Now we shall consider the reason of the subsiding action of oil film on the water surface. The curve in Fig. 3 shows the general relation between the molecular area and the surface pressure of oil on water. In this curve the region AB corresponds to the gaseous film and BC the condensed film. In the portion AB the surface pressure is very small or the surface tension is nearly equal to that of the pure water. At point B the surface tension begins to show sharp decrease which continues until C .

It is probable that the subsiding action of wave is caused by the change of surface tension. In Fig. 4 the line ace shows the level of the water surface, and $abcde$ the waved surface. The surface $abcde$ is, of course, larger

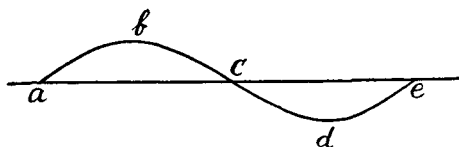


Fig. 4.

than the surface ace , so the oil film on the waved surface is thinner than that on the plane one. The surface tension of the waved surface is, therefore, larger than the plane one, and accordingly, the surface force will act to suppress the wave. Thus the decrease of the surface tension acts as the counter-force against the wave making action.

In the region AB in Fig. 3, the surface tension is almost independent of the molecular area, so the wave height does not differ from that of the clean water surface. If, however, the molecular area is smaller than the point B , the decrease of surface tension becomes significant and accordingly the wave will subside.

From the above consideration, we know that the point B in Fig. 3 corresponds to the point a_m in Fig. 2. The sectional area of the oil molecule is calculated, generally, by the surface pressure curve, assuming that the point B expresses the close packed monomolecular oil film. By the ripple method, therefore, the value of a_m will be the cross section of the oil molecule, for palmitic acid this being $25.6 \text{ \AA}^2$.

The curves of l against a obtained on stearic acid, myristic acid, oleic acid, tetradecyl alcohol and palmitonitrile are given in Fig. 5, Fig. 6 and Fig. 7.

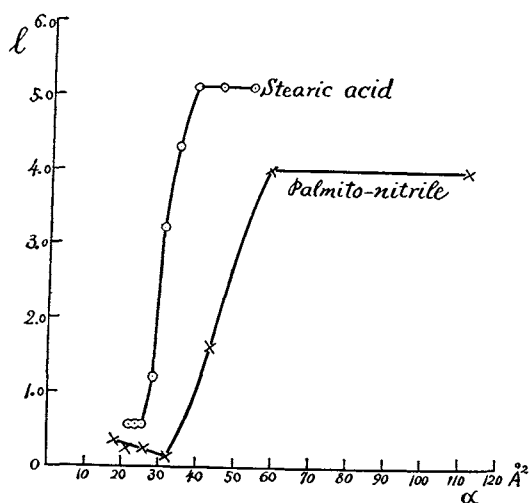


Fig. 5.

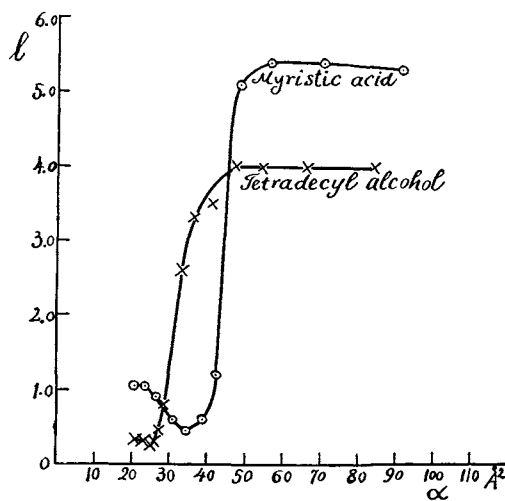


Fig. 6.

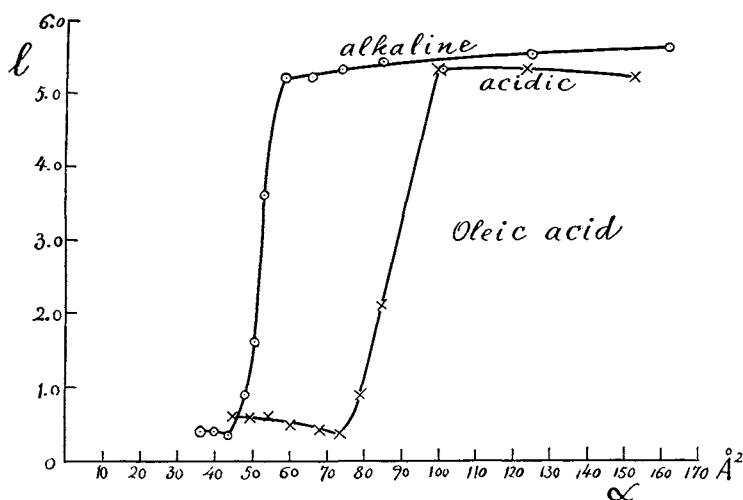


Fig. 7.

These curves have been obtained by the constant surface area method and the tuning fork of 100 vibrations. The results are summarised in Table 2. This table shows the film substances, temperatures, properties of the underlying water and the values of α_m obtained. Moreover, in the last column, the values of the cross sectional areas of the molecules are given which were calculated from the surface pressure curves by other authors.

Table 2.

Substance	Temperature (°C.)	Underlying water	α_m (Å ²)	Molecular area (Å ²)	Author
Palmitic acid	14	alkaline (pH=8)	25.6	21	Langmuir ⁽⁴⁾
Stearic acid	14	alkaline (pH=8)	25.8	22	Langmuir
Myristic acid	5	alkaline (pH=8)	34.6	21 (condensed film) 40.6 (expanded film)	Adam ⁽⁵⁾
Oleic acid	14	alkaline (pH=8)	43.7	46	Langmuir
Oleic acid	13	acidic (0.04 N HCl)	74.0		
Tetradecyl alcohol	17	alkaline (pH=8)	25.1	21.6	Adam
Palmitonitrile	12	alkaline (pH=8)	32.9	27.7	Adam

From this table we see that the values of α_m are nearly equal to the values of molecular area obtained by Langmuir and Adam, excepting the oleic acid film on the acidic water. The molecules of the acidic substances have less affinity with the acidic underlying water than the alkaline one. So the oil molecules may be in active motion, or float in inclined state instead of vertical position. The value of α_m , therefore, becomes larger in this case than the case of alkaline underlying water. This fact will be discussed further in the second paper of the present investigation.

We shall now study the effect of the vibrational number of the tuning fork. According to the theory of hydrodynamics there is the following equation.

$$v^2 = \frac{g\lambda}{2\pi} + \frac{2\pi\gamma}{\rho\lambda}$$

where v denotes the velocity of propagation of the wave, g the gravity constant, λ the wave length, γ the surface tension and ρ the density of liquid. The first term of the light side of this equation gives the effect of gravitational force and the second term that of the surface tension.

In the present experiment, if the vibrational number of the tuning fork is large the wave length λ will be small and the first term of the equation becomes negligible. In such a case the height of the wave is mainly governed

(4) Langmuir, *J. Am. Chem. Soc.*, **39** (1917), 1848.

(5) Adam, *Proc. Roy. Soc., A*, **101** (1922), 452; **103** (1923), 687; Adam and Dyer, *Proc. Roy. Soc., A*, **106** (1924), 694.

by the surface tension, and the wave will be subsided by the change of surface tension. If, however, the vibrational number of the tuning fork is small, the wave will not be subsided by the surface action only, but will have a residual wave of considerable height at the point α_m . We have tested the relations between the damping effect of film and the wave length by using the tuning forks of 50, 100 and 200 vibrations per second. Table 3 gives the percentage ratios of the height of the residual wave to that of the undamped one.

Table 3.

Vibration number of tuning fork per second	50	100	200
Palmitic acid	27%	7.5%	3.7%
Myristic acid	38	8.4	3.3
Oleic acid	23	7.4	3.3
Palmitonitrile	19	5.0	4.2

From Table 1 and Fig. 2, for example, the readings of the widths of the band l , for palmitic acid in using 100 vibration fork are taken. In this case, the value of l of damped wave (at α_m) and that of undamped one are 3 mm. and 40 mm. respectively, being given as 7.5% in Table 3. We see, from this table, that the height of the residual wave decreases with the increase of vibrational number. Thus the larger the vibrational frequency, the more predominant the capillary wave.

Now we shall consider the subsiding action of oil for the breaker in the ocean. The high wave in the ocean is not, of course, the capillary one, so the action of oil may not, directly, be explained by the mechanism described above. But we may understand the damping action of the oil for breakers in ocean in the following manner.

The high wave is produced, mainly, by the action of wind. If there is no ripple in the water surface, then the wind will pass along the surface without any appreciable resistance. If, however, the water surface is not smooth but full of ripples, then the resistance between the water surface and the air current will be large and, accordingly, the breakers will appear. Thus the ripple is considered to be the cause of the breaker. The oil film has the subsiding action on the ripples as has been described in this paper. So the oil film will decrease the resistance between the wind and the surface, and consequently, the breaker will no more appear.

The present experiment has been done by the fund of Nippon Gakujutsu Shinkokwai (Foundation for the Promotion of Scientific and Industrial Research of Japan) for which the authors' sincere thanks are due. Some of the substances used in the experiment were synthesized by Professor Kubota and other members in the organic laboratory of our institute to whom the authors express their gratitude.

Summary.

(1) The change of height of the capillary wave by the oil film has been measured, "the constant surface area method" being used. The substances tested are palmitic acid, stearic acid, myristic acid, oleic acid, tetradecyl alcohol, and palmitonitrile.

(2) The area per molecule of oil has been calculated for which the capillary wave subsides, and this has been compared with the cross sectional area of molecules obtained by other authors.

(3) The effect of the change of vibrational number on the subsiding action of wave has been studied.

(4) The mechanisms of the subsiding action of oil film on the capillary wave and the breaker have been described.

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STUDIES OF MONOMOLECULAR FILMS BY THE RIPPLE METHOD. II.

By Tsunetaka SASAKI and Jitsusaburo SAMESHIMA.

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In the preceding paper we have described the results obtained by the "method of constant surface area".⁽¹⁾ In the present report, the experiments are described on the "method of constant oil quantity".

The total area of the water tray is 14×50 cm.², and the effective area can be changed by moving a glass strip (Fig. 1 in the preceding paper). The wave is made by an electrically maintained tuning fork of 100 vibrations per second. Known quantity of oil (dissolved in benzene) is put on the water surface and the wave height is measured as was described in the preceding paper. Now the surface area is changed by moving the glass strip, the oil film being compressed or expanded, and the wave height is measured every time.

Fig. 1 shows the general type of the curves of the molecular area, a , against the wave height, l . The curve acd corresponds to the compression

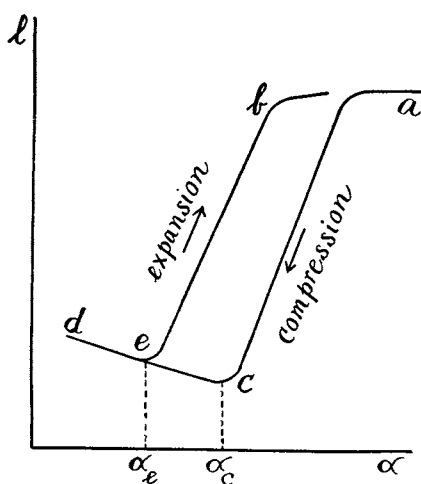


Fig. 1.

of the film, starting from a , passing a minimum point c and reaching d . The curve deb corresponds to the expansion of the film. At the point e the wave begins to appear and its height increases to b . Thus there occurs a hysteresis phenomena.

Table 1 shows the data obtained on the oleic acid. The quantity of the oleic acid dispersed on the surface is 0.0000292 gram. The temperature is 15°C., the underlying water is acidic (0.05 N HCl) and the vibration frequency of the tuning fork is 100 per second. The data are plotted in Fig. 2.

(1) Sameshima and Sasaki, this Bulletin, **11** (1936), 539.

Table 1.

Compression			Expansion		
Surface area (cm. ²)	Area per molecule α (Å ²)	Width of the band l (cm.)	Surface area (cm. ²)	Area per molecule α (Å ²)	Width of the band l (cm.)
560	89.4	5.0	238	38.0	0.8
532	84.9	4.8	252	40.2	0.75
504	80.4	4.5	266	42.4	0.75
476	76.0	4.0	280	44.7	0.70
448	71.5	3.1	294	46.9	0.65
392	62.6	1.1	308	49.2	0.65
378	60.3	0.7	322	51.4	0.95
364	58.1	0.4	336	53.6	1.4
350	55.9	0.45	350	55.9	2.4
336	53.6	0.55	364	58.1	3.1
322	51.4	0.7	392	62.6	3.3
308	49.2	0.7	448	71.5	4.7
294	46.9	0.72	476	76.0	5.2
280	44.7	0.70	504	80.4	5.3
266	42.4	0.75	532	84.9	5.3
252	40.2	0.75			
238	38.0	0.8			
224	35.7	0.9			

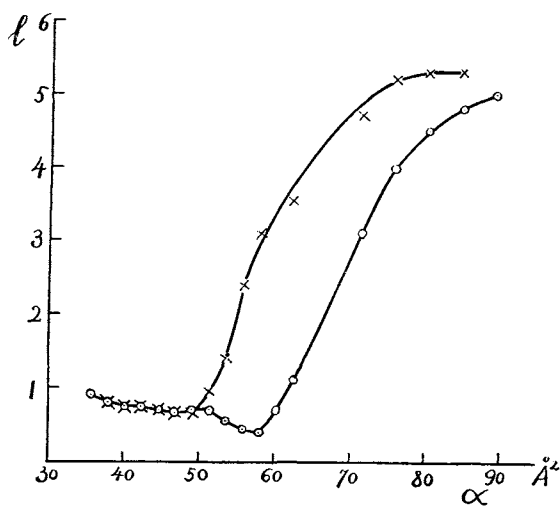


Fig. 2.

Similar results have been obtained on palmitic acid, myristic acid, tetradecyl alcohol and palmitonitrile. The hysteresis phenomena were observed by Langmuir in the measurement of surface pressure.⁽²⁾

We shall consider the meaning of the curves of Fig. 1. In the film the polar group in the oil molecule is attracted by the underlying water, and therefore, the oil molecule is considered to stand vertically at the surface of the water. The affinity, however, between the acid oil and the water is smaller in the case of the acidic water than in the case of alkaline one. So when the underlying water is acidic and the surface area is sufficiently large, some of the molecules may be in the inclined state, instead of vertical. The surface film of such a state is now compressed until the oil molecules are in contact with one another, forming a monomolecular film. This state corresponds to the point *c* in Fig. 1 and is pictured schematically in Fig. 3A. The capillary



Fig. 3.

wave subsides at this point. On further compression the oil molecule will stand up gradually until all in vertical position as shown in Fig. 3B, and then follows the usual compression behavior of the monomolecular film.

Now we enlarge the surface of water by moving the barrier in the opposite direction, and let the film expand. At the point *e* in Fig. 1 the wave begins to appear and its height increases gradually until the point *b*. The point *e* corresponds to the state of Fig. 3B, i.e. the monomolecular film of the uncompressed state. All the oil molecules are in vertical position at this point. The point *e*, therefore, corresponds to the point α_m in Fig. 2 of the preceding paper.

The values of the area of a single molecule α at the kink point *e* in the expansion curve and *c* in the compression one are given in Table 2. The vibrational frequency of the tuning fork is 100 per second.

Table 2.

Film substance	Underlying water	Temperature (°C.)	Values of α at the kink point of the curve of	
			compression α_c (Å ²)	expansion α_e (Å ²)
Oleic acid	acidic (0.05 N HCl)	15	58	49
Palmitic acid	acidic (0.05 N HCl)	11	29	25
Myristic acid	acidic (0.05 N HCl)	12.5	57	52
Tetradecyl alcohol	alkaline (pH=8)	17	35	23
Palmitonitrile	acidic (0.05 N HCl)	11	39	32

(2) Langmuir, *J. Am. Chem. Soc.*, **39** (1917), 1874.

The values of α_e at the kink point of the curve of expansion are thus nearly identical with the values of α_m obtained from the "method of constant surface area", given in Table 2 in the preceding paper.

In the case of myristic acid the value of α_e is $52 \text{ \AA}^2$ at 12.5°C ., while α_m is $34.6 \text{ \AA}^2$ at 5°C . The myristic acid forms an expanded film at 12.5°C ., but a half condensed film at 5°C ., so the molecular area differs in these two temperatures. When the underlying water is alkaline, the film dissolves into the water and the definite kink point is not obtained.

The compression curve has not been drawn for the substances shown in Table 3. The expansion curves have been measured, and therefore, only the values of α_e are given in the table.

Table 3

Film substance	Underlying water	Temperature ($^\circ\text{C}$.)	Molecular area from the expansion curve α_e ($\text{\AA}^2$)
Lauric acid	acidic (0.05 N HCl)	14	47
Tripalmitin	acidic (0.05 N HCl)	13	71
Triolein	acidic (0.05 N HCl)	12	138
Ricinoleic acid	acidic (0.05 N HCl)	12	91
Ethyl palmitate	acidic (0.05 N HCl)	12	65

The above are the results of measurements on the substances of known molecular weight. In these cases, thus, we can know a sectional area of the molecule by the ripple method. If, however, a substance of unknown molecular weight is used, the approximate magnitude of its molecular weight may be calculated. The experiment has been done on mastic.

The selected sample of mastic is dissolved in ethyl alcohol, filtered and then diluted with benzene. The solution thus obtained is put on the water surface of the tray. The solution spreads and the alcohol and benzene soon evaporate, the film of mastic remaining on the surface. The quantity of mastic dissolved in the solution is determined by evaporating the solvents at 110°C . and weighing the residue. Table 4 and Fig. 4 show the results of measurements on mastic.

Table 4.

Weight of mastic (g.)	Area of the film (cm. ²)	Width of the band l (cm.)	Weight of mastic (g.)	Area of the film (cm. ²)	Width of the band l (cm.)
6.25×10^{-5}	280	0.4	6.54×10^{-5}	280	0.3
	294	0.4		294	0.3
	308	0.3		308	0.3
	322	0.25		322	0.3
	336	0.3		336	0.3
	350	1.2		350	0.1
	364	3.2		364	0.2
	378	4.2		378	0.9
	392	4.6		392	2.6
	420	5.0		406	3.6
				420	4.1
				448	4.6
				476	4.7

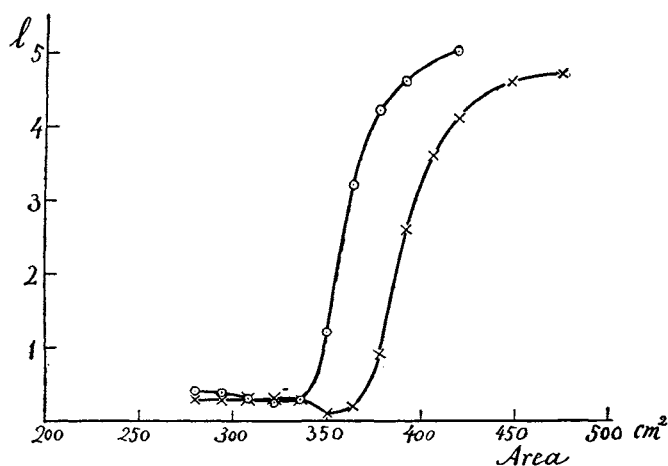


Fig. 4.

From Fig. 4 we see that the wave subsides at the film area of 330 cm.² in the first experiment, and 350 cm.² in the second one.

The molecular weight of mastic is not known, so the area per molecule cannot be calculated. We shall assume that the mastic molecule has the cubic form, and calculate its molecular weight.

Let us denote with g the weight of mastic spread on the water surface, and s the area of film where the wave subsides, and d the density of mastic, then the thickness of the film will be expressed by g/sd . The diameter of the single molecule is assumed to be equal to the thickness of the film, and the

volume of single molecule is $(g/sd)^3$. The molecular weight is expressed by,

$$M = \left(\frac{g}{sd} \right)^3 Nd = \frac{Ng^3}{s^3d^2}$$

where N denotes the Avogadro number.

In the present experiment, the density of the mastic has been found to be $d = 1.058$. The value of the molecular weight calculated from the results of the first experiment is as follows :

$$M = \frac{6.06 \times 10^{23} \times (6.25 \times 10^{-5})^3}{330^3 \times 1.058^2} = 3678.$$

The same from the second experiment is :

$$M = \frac{6.06 \times 10^{23} \times (6.54 \times 10^{-5})^3}{350^3 \times 1.058^2} = 3532.$$

Taking the means, we have the value 3605. Thus the molecular weight of mastic has been found to be about 3600.

The present experiment has been done by the fund of Nippon Gakujutsu Shinkokwai (Foundation for the Promotion of Scientific and Industrial Research of Japan) for which the authors' sincere thanks are due. Some of the substances used in the experiment were synthesized by Professor Kubota and other members in the organic laboratory of our institute to whom the authors express their gratitude.

Summary.

(1) The change of height of the capillary wave by the oil film has been measured, "the constant oil quantity method" being used. The substances tested are oleic acid, palmitic acid, myristic acid, tetradecyl alcohol, palmitonitrile, lauric acid, tripalmitin, triolein, ricinoleic acid, and ethyl palmitate.

(2) It has been found that there occurs some hysteresis phenomena in the subsiding action of the capillary wave by compression and expansion of the film.

(3) The areas per molecule of oils have been calculated from the kink point in the expansion curve of the film.

(4) Experiments have been done on mastic, the molecular weight of which being estimated at about 3600.

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RAMANSPEKTRUM VON DEUTEROÄTHANOL.

Von San-ichiro MIZUSHIMA, Yonezo MORINO und Go OKAMOTO.

Eingegangen am 16. Juli 1936. Ausgegeben am 28. August 1936.

Deuteroäthanol C_2H_5OD (ca. 3 c.c.) wurde durch die Zersetzung von Natriumäthylat mit schwerem Wasser (99.6%) hergestellt und sein Ramanspektrum mit demjenigen des Äthanol verglichen. Für die von uns beobachteten Äthanollinien⁽¹⁾

434(3b), 884(10), 1050(4), 1093(3), 1273(2b), 1452(6), 1483(2b),
2716(2), 2877(8b), 2928(10b), 2971(9b), 3370 ± 80 ,

ist die Existenz entsprechender Deuteroäthanollinien sichergestellt. Anstatt der Bande 3370 ± 80 von C_2H_5OH haben wir bei C_2H_5OD eine Bande viel kleinerer Frequenz 2510 ± 50 gefunden, wodurch ihre Deutung als OH- bzw. OD- Valenzschwingung bestätigt wird (wie aus der Berechnung als Zweimassen-Modell folgt). Sonst haben wir keinen grossen Isotopieeffekt gefunden, obwohl das Auftreten der Deformationsschwingung des Hydroxylwasserstoffes mit einer ähnlich grossen Verschiebung zu erwarten ist⁽²⁾. Kleinere Isotopieverschiebung kann man natürlich bei anderen Linien erwarten und nach unserer Berechnung an den Kettenfrequenzen 434, 884, 1050 von $CH_3 \cdot CH_2 \cdot OH$ beträgt die Verschiebung -6 , -3 , -8 cm^{-1} . Für die scharfe und intensive Linie 884 von C_2H_5OH haben wir bei C_2H_5OD eine entsprechende Linie tieferer Frequenz 876 gefunden.

Wir danken Herren Prof. M. Katayama (Tokyo) und Prof. J. Horiuti (Sapporo) für ihre Ratschläge zu dieser Arbeit. Ferner danken wir dem Hattori-Hokokai, das die zur Durchführung notwendigen Mittel zur Verfügung gestellt hat.

*Chemisches Institut der kaiserlichen Universität
zu Tokyo und zu Sapporo.*

(1) Bezüglich der früheren Beobachtungen an C_2H_5OH sei auf die zusammenfassenden Berichte von Hibben (*Chem. Rev.*, **18** (1936), 1) verwiesen.

(2) Vgl. auch Redlich u. Pordes (CH_3OD): *Sitzber. Akad. Wiss. Wien, Math.-naturw. Klasse, Abt. IIb*, **145** (1936), 67.

**DER ISOTOPENAUSTAUSCH ZWISCHEN ANILIN-
CHLORHYDRAT UND SCHWEREM WASSER.
(Vorläufige Mitteilung.)**

Von Masao HARADA und Toshizo TITANI.

Eingegangen am 27. Juli 1936. Ausgegeben am 28. August 1936.

Die Austauschreaktion der H-Atome zwischen Anilinchlorhydrat $C_6H_5NH_3Cl$ und schwerem Wasser wurde unter zwei verschiedenen Versuchsbedingungen untersucht. Dabei ergab sich, dass nicht nur drei H-Atome im NH_3Cl -Radikal, sondern unter Umständen auch einige (höchstwahrscheinlich drei) H-Atome im Benzolkern austauschbar werden.

Versuch I. Eine abgewogene Menge von Anilinchlorhydrat wurde in einer ebenfalls abgewogenen Menge von verdünntem (1 bis 3 prozentigem) schwerem Wasser von der bekannten D-Konzentration bei 50°C. aufgelöst. Nachdem die Lösung in einem zugeschmolzenen Glasrohr verschieden lange auf verschiedenen Temperaturen gehalten worden, wurde das Wasser vom Anilinchlorhydrat durch die Vakuumdestillation bei 50°C. möglichst vollständig abgetrennt und der „scheinbare“ Verteilungsquotient (V. Q.) k' der D-Atome in der üblichen Weise berechnet. Dabei wurde zuerst angenommen, dass sich nur drei H-Atome im NH_3Cl -Radikal an der Austauschreaktion beteiligten. Die so berechneten Werte von k' haben wir in der dritten Reihe der Tabelle 1 wiedergegeben.

Tabelle 1.

Erwärmungs- temperatur (°C.)	Erwärmungsdauer in Stdn.	k'	n
(ohne Erwärmung)		$1.10 \pm 0.01^{(1)}$	0
60	0 ⁽²⁾	1.20	0.3
„	1	1.17	0.2
„	3	1.21	0.3
80	0 ⁽²⁾	1.16	0.2
„	1	1.63	1.7
„	3	2.10	3.1
„	120	1.99	2.9

(1) Der Mittelwert aus drei unabhängig ausgeführten Versuchen.

(2) Das Anilinchlorhydrat wurde bei 60° bzw. 80°C. in schwerem Wasser gelöst und sofort durch die Vakuumdestillation bei 50°C. davon abgetrennt.

Auf Grund dieser Versuchsergebnisse nahmen wir an, dass nicht nur drei H-Atome im NH_3Cl -Radikal, sondern auch einige H-Atome in C_6H_5 durch die Erwärmung der Lösung mit denen des Wassers allmählich ausgetauscht wurden. Unter dieser Annahme berechneten wir die Anzahl n dieser H-Atome in C_6H_5 . Die so berechneten Werte von n finden sich in der letzten Reihe der Tabelle 1. Bei dieser Berechnung wurde aber vorausgesetzt, dass der V. Q. der D-Atome zwischen dem NH_3Cl -Radikal und H_2O $k' = 1.1$ und der zwischen C_6H_5 und H_2O gleich dem zwischen Benzol und Wasser, d.h. $k = 0.95$,⁽³⁾ ist. Was den kleinen Bruch von n bei 60°C . anbetrifft, so wissen wir nicht, ob es sich dabei um die wirkliche Zunahme der austauschbaren H-Atome oder bloss um Experimentalfehler handelt. Aber bei 80°C . kann man mit Gewissheit sagen, dass drei H-Atome in C_6H_5 durch die Erwärmung der Lösung allmählich mit denen des Wassers ausgetauscht wurden und es innerhalb einiger Stunden zum Austauschgleichgewicht kam. Über den Mechanismus der Reaktion wissen wir noch nichts Sicheres.

Versuch II. Der zweite Versuch, der wir mit Anilinchlorhydratkristallen ausführten, ist vielleicht interessanter als der erste. Beim Versuch II wurde das Anilinchlorhydrat zuerst in eine gegebene Menge des schweren Wassers bei 50°C . aufgelöst. Die beiden Substanzen wurden dann sofort durch die Vakuumdestillation bei 50°C . voneinander getrennt und separat aufbewahrt. Das so behandelte Anilinchlorhydrat und Wasser wollen wir mit A_1 bzw. W_1 bezeichnen. Berechnet man aus diesem Versuch den V. Q. zwischen dem NH_3Cl -Radikal und H_2O , so findet man für diesen stets 1.1 ± 0.1 , welcher Wert mit dem beim Versuch I ohne Erwärmung der Lösung gefundenen gut übereinstimmt. (Vgl. Tabelle 1, die zweite Horizontalreihe.) Dies überzeugte uns davon, dass das Austauschgleichgewicht zwischen dem NH_3Cl -Radikal und H_2O durch diese Behandlung erreicht wurde. Das so behandelte Anilinchlorhydrat A_1 wurde dann, nachdem es auf einer Tonplatte in einem Exsikkator gut getrocknet worden, in einem zugeschmolzenen Glasrohr verschieden lange auf verschiedenen Temperaturen gehalten. Erst nach der Abkühlung wurde A_1 wieder in dem Wasser W_1 gelöst, mit dem die H-Atome im NH_3Cl -Radikal von A_1 im Austauschgleichgewicht gewesen waren. Das aus dieser Lösung durch die Vakuumdestillation bei 50°C . abgetrennte Wasser nennen wir W_2 . Dieser Versuch zeigte uns, dass die D-konzentration von W_2 kleiner als die von W_1 war. In der dritten Reihe der Tabelle 2 findet sich die relative Abnahme $\Delta\%$ der D-Konzentration von W_2 im Vergleich mit der von W_1 , die sich aber auf den idealen Fall, wo 2 Mole Anilinchlorhydrat gegen 3 Mole Wasser verwendet wurden, bezieht.

(3) J. Horiuti und M. Polanyi, *Nature*, **134** (1934), 377; *Trans. Faraday Soc.*, **30** (1934), 1164.

Tabelle 2.

Vorwärmung der Kristalle		Δ %	n
Temperatur (°C.)	Dauer in Stdn.		
(ohne Vorwärmung)		6.7 ⁽⁴⁾	0.5
60	1	4.8	0.3
100	1	5.6	0.4
130	1	5.3	0.4
160	1	24.9	3.1
180	1	23.8	2.9
195	2	25.8	3.4
220	3	23.2	2.9

Diese Ergebnisse legen uns die Vermutung nahe, dass durch die Erwärmung der Anilinchlorhydratkristalle über 160°C. in diesen bzw. in den Molekülen derselben eine sozusagen tautomerische Umwandlung stattfand und dadurch ein Teil der D-Atome im NH_2Cl -Radikal, die durch die Austauschreaktion mit schwerem Wasser W_1 aufgenommen worden waren, in den Benzolkern derselben Substanz übergingen, so dass beim wiedermaligen Auflösen dieser Kristalle A_1 im Wasser W_1 eine Menge der D-Atome aus W_1 in das NH_2Cl -Radikal des A_1 aufgenommen wurde. Unter dieser Annahme berechneten wir die Anzahl n der H-Atome in C_6H_5 , die sich an dieser intramolekularen Austauschreaktion beteiligten. Die so gefundenen Werte von n sind in der letzten Reihe der Tabelle 2 wiedergegeben. Auf Grund dieser Werte ist es ziemlich sicher, dass die tautomerische Umwandlung zwischen 130° und 160°C. stattfindet und dabei höchstwahrscheinlich drei H-Atome im Benzolkern teilnehmen, obwohl wir über Stellung im Benzolkern sowie den kleinen Bruchteil von n , der bei Temperaturen von unter 130°C. gefunden wurde, zurzeit noch nichts Sicheres wissen. Vielleicht erhalten wir hierüber Aufklärung, wenn wir anstatt des Anilinchlorhydrats seine mit CH_3 substituierten Derivate, wie Toluidin- bzw. Mesidinchlorhydrat, verwenden. Diese Versuche sind jetzt im Gang.

Der Nippon Gakujutsu-Shinkohkai (der Gesellschaft zur Förderung der japanischen Wissenschaft) sowie der Hattori-Hohkoku (der Hattori-Stiftung) sind wir für ihre finanzielle Unterstützung zu herzlichstem Dank verpflichtet.

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(4) Der Mittelwert aus vier Versuchen, die parallel mit den Versuchen mit Vorwärmung durchgeführt wurden.

THE NITRILE-ESTERS OF 2-METHYLPROPENE-1,1,3,3-TETRACARBOXYLIC ACID.

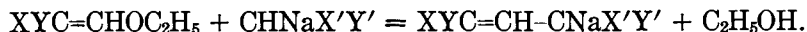
By Yoshiyuki URUSHIBARA and Matsuji TAKEBAYASHI.

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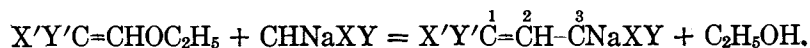
Introduction. One of the authors revealed the true nature of the so-called diethyl dicyano-glutaconate,⁽¹⁾ and then carried out a series of condensations to synthesize other nitrile-esters of propene-1,1,3,3-tetracarboxylic acid (α,γ -dicarboxy-glutaconic acid).⁽²⁾ The introduction to the present paper must be begun with summarizing these previous studies.

The sodium derivative of diethyl 1,3-dicyano-propene-1,3-dicarboxylate (diethyl α,γ -dicyano-glutaconate) (VI or $C_{11}H_{11}O_4N_2Na$) is formed by the reaction of ethyl cyanacetate, chloroform, and sodium ethylate, or by the condensation of ethyl ethoxymethylene-cyanacetate $C_2H_5OCO(CN)C=CHOC_2H_5$ and ethyl sodio-cyanacetate $CHNa(CN)COOC_2H_5$, and it crystallizes in needles (colourless when pure) with two molecules of water of crystallization. It is transformed into a yellow crystalline substance on acidifying its aqueous solution. The latter had been long considered diethyl dicyano-glutaconate (H for Na in VI or $C_{11}H_{12}O_4N_2$) corresponding to the sodium compound, but it is really a more complicated compound with formula XV or $(C_{11}H_{12}O_4N_2)_2 \cdot H_2O$.

Nine cases are possible for the condensation of the ethoxymethylene compound $XYC=CHOC_2H_5$ with the sodium derivative of the methylene compound $CH_2X'Y'$, where X, Y, X', and Y' represent independently either cyano-group CN or carbethoxy-group $COOC_2H_5$, and the products of the nine cases would be different from one another, including all the possible nitrile-esters (in the form of the sodium derivatives) of propene-1,1,3,3-tetracarboxylic acid $(HOOC)_2C=CH-CH(COOH)_2$, if the condensation could be expressed simply by the following equation:



Nevertheless, if the condensation is carried out in alcoholic solution, the product of the reaction to be represented by the above equation is the same as that of the reaction to be represented by the following equation:



(1) Y. Urushibara, this Bulletin, **2** (1927), 26, 236.

(2) Y. Urushibara, this Bulletin, **2** (1927), 278; **3** (1928), 219; **5** (1930), 1.

(If $X = X'$ and $Y = Y'$, the two equations are identical, but this is of course not meant here.) The common product of the two different reactions is one of the two required by the above equations, and the one that possesses more carbethoxy-groups in carbon atom 3 than in carbon atom 1. There are three of such pairs among the nine cases, and, therefore, only six compounds, namely I, III, V, VI, VIII, and IX, can be obtained. In the cases where the above equations require the products II, IV, and VII, they are supplanted by III, V, and VIII respectively.

- (I) $(C_2H_5OCO)_2C=CH-CN a(COOC_2H_5)_2$
- (II) $(C_2H_5OCO)_2C=CH-CN a(CN)COOC_2H_5$
- (III) $C_2H_5OCO(CN)C=CH-CN a(COOC_2H_5)_2$
- (IV) $(C_2H_5OCO)_2C=CH-CN a(CN)_2$
- (V) $(CN)_2C=CH-CN a(COOC_2H_5)_2$
- (VI) $C_2H_5OCO(CN)C=CH-CN a(CN)COOC_2H_5$
- (VII) $C_2H_5OCO(CN)C=CH-CN a(CN)_2$
- (VIII) $(CN)_2C=CH-CN a(CN)COOC_2H_5$
- (IX) $(CN)_2C=CH-CN a(CN)_2$

No ambiguity is involved in the formulation of compounds I, VI, and IX⁽³⁾ with cyano- and carbethoxy-groups arranged symmetrically. Sodium compound I and the corresponding free ester (X) give a colouration (blue) with ferric chloride in alcoholic solution, while VI and IX not. Thus it is shown that only the compound in which carbon atom 3 possesses two carbethoxy-groups can exist in the enolic form and gives the colour reaction with ferric chloride. The common product of the condensation of ethoxymethylene-malonitrile with diethyl sodio-malonate and the condensation of diethyl ethoxymethylene-malonate with sodio-malonitrile is V and not IV, because it gives a violet colouration with ferric chloride. The sodium derivative of triethyl cyano-propene-tricarboxylate obtained by the condensation of ethyl ethoxymethylene-cyanacetate with diethyl sodio-malonate and by the condensation of diethyl ethoxymethylene-malonate with ethyl sodio-cyanacetate gives a violet colouration with ferric chloride and formula III can thus be ascertained. The above two examples suggest that carbon atom 3 generally retains more carbethoxy-groups than carbon atom 1. For this reason the constitution of ethyl sodio-tricyano-propene-carboxylate can be assumed to be VIII.

Now, if the condensation of the ethoxymethylene compound $XYC=CHOC_2H_5$ and the sodium derivative of the methylene compound $CHNaX'Y'$ is carried out in ether where the reaction is heterogeneous, four compounds,

(3) It is not considered here in what manner the sodium atom is combined.

$\text{XYC}=\text{CH}-\text{CNaX}'\text{Y}'$, $\text{X}'\text{Y}'\text{C}=\text{CH}-\text{CNaXY}$, $\text{X}'\text{Y}'\text{C}=\text{CH}-\text{CNaX}'\text{Y}'$, and $\text{XYC}=\text{CH}-\text{CNaXY}$, may be found side by side in the reaction products. This was deduced by gathering the results of all the cases of condensation except those satisfying the conditions $\text{X} = \text{X}'$ and $\text{Y} = \text{Y}'$, where the four compounds are the same. By the condensation in ether the sodium derivative of 3,3-dicyanopropene-1,1-dicarboxylate (IV), which could not be obtained by the condensation in alcoholic solution, was isolated besides its isomeride (V) from the reaction products of diethyl ethoxymethylene-malonate $(\text{C}_2\text{H}_5\text{OCO})_2\text{C}=\text{CHOC}_2\text{H}_5$ and sodio-malonitrile $\text{CHNa}(\text{CN})_2$. The theory stated above in general formulæ means that in this case of condensation I and IX also might have been found in the products, although it was not the case. To give another example, III, I, and VI were isolated from the products of condensation of ethyl ethoxymethylene-cyanacetate and diethyl sodio-malonate in ether. Compounds II and VII have not yet been obtained even by the reactions in ether.

These sodium compounds behave differently towards acids. The sodium derivative of tetraethyl propene-1,1,3,3-tetracarboxylate (I) gives the corresponding free ester (X), a colourless oily substance insoluble in water. Triethyl 1-cyano-propene-1,3,3-tricarboxylate (XI) is obtained as an oily substance on acidifying the aqueous solution of its sodium derivative (III). It crystallizes gradually on keeping in the desiccator. It has a stronger acid character, but seems to be more easily changeable, than tetraethyl propene-tetracarboxylate (X). The sodium compound (III) forms hygroscopic crystals.

The sodium derivative of diethyl 3,3-dicyano-propene-1,1-dicarboxylate (IV) crystallizes in colourless needles and behaves very similarly to the tetracyano-compound (IX). On acidifying its aqueous solution no apparent change is observed. The sodium derivative of diethyl 1,1-dicyano-propene-3,3-dicarboxylate (V), forming nearly colourless crystals with half a molecule of water of crystallization, gives an oily substance on acidifying its aqueous solution. The oily substance can be collected as such by quick extraction with ether followed by also quick dehydration and evaporation of the extract. It is supposed to be diethyl 1,1-dicyano-propene-3,3-dicarboxylate (XII). It gives a bluish-violet colouration with ferric chloride. If the oily substance precipitated is left in the mother liquor, soon it goes again into solution and a colourless crystalline compound separates out. This is diethyl 1,1-dicarbamyl-propene-3,3-dicarboxylate (XIII), and melts at $139-140^\circ$, solidifying then and decomposing at higher temperature. When the oily substance is dissolved in alcohol, it is transformed into another crystalline compound, diethyl 1-cyano-1-carbamyl-propene-3,3-dicarboxylate (XIV), melting at 212° .

As mentioned above, the sodium derivative of diethyl 1,3-dicyanopropene-1,3-dicarboxylate (VI) crystallizes with two molecules of water of

crystallization and gives a yellow crystalline compound with the formula $(C_{11}H_{12}O_4N_3)_2 \cdot H_2O$ on acidifying its aqueous solution. The yellow compound melts at 183° and its constitution is supposed to be XV. The sodium derivative of ethyl 1,1,3-tricyano-propene-3-carboxylate (VIII or $C_9H_6O_2N_3Na$), forming colourless crystals with a molecule of water of crystallization, gives a similar compound $(C_9H_7O_2N_3)_2 \cdot H_2O$, yellow crystals melting at 190° .

The sodium derivative of 1,1,3,3-tetracyano-propene (IX) forms colourless fine needles with a molecule of water of crystallization. On adding hydrochloric acid to its aqueous solution no apparent change is observed. The unchanged sodium compound (with a molecule of water of crystallization) can be crystallized out from the aqueous solution acidified with hydrochloric acid. But, if the aqueous solution acidified with hydrochloric acid is extracted with ether several times, the aqueous layer leaves sodium chloride alone on evaporation. If the ethereal extract is dried and evaporated in vacuum, a colourless crystalline substance remains, but it decomposes quickly into a brown amorphous mass. The unstable crystalline substance is supposed to be 1,1,3,3-tetracyano-propene (XVI). An aqueous solution can be obtained by evaporating the ethereal extract on water. The substance is stable in solution and behaves as a very strong acid. The electrolytic dissociation of this compound will be dealt with in a separate paper.

- (X) $(C_2H_5OCO)_2C=CH-CH(COOC_2H_5)_2$
- (XI) $C_2H_5OCO(CN)C=CH-CH(COOC_2H_5)_2$
- (XII) $(CN)_2C=CH-CH(COOC_2H_5)_2$
- (XIII) $(H_2NCO)_2C=CH-CH(COOC_2H_5)_2$
- (XIV) $H_2NCO(CN)C=CH-CH(COOC_2H_5)_2$
- (XV) $(C_{10}H_{12}O_4N)-CO-NH-C(NH)-(C_{10}H_{12}O_4N)$
- (XVI) $(CN)_2C=CH-CH(CN)_2$

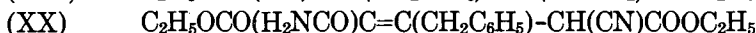
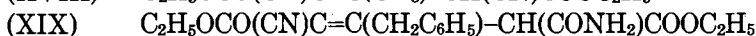
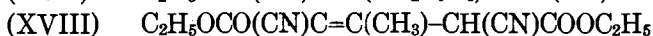
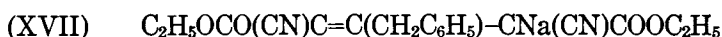
Thus the nature and the arrangement of the four groups, X, Y, X', and Y', exert a great influence on the behaviour of the sodium compound of the propene derivative $XYC=CH-CHX'Y'$.

Now, ethyl ethoxyethylidene-cyanacetate (ethyl α -cyano- β -ethoxy-crotonate) $C_2H_5OCO(CN)C=C(CH_3)OC_2H_5$ reacts with the sodium derivative of ethyl cyanacetate in the same way as ethyl ethoxymethylene-cyanacetate, yielding the sodium derivative of diethyl 1,3-dicyano-2-methylpropene-1,3-dicarboxylate (diethyl α,γ -dicyano- β -methyl-glutaconate) (XXVI).⁽⁴⁾ In the same way ethyl α -cyano- β -ethoxy- γ -phenyl-crotonate $C_2H_5OCO(CN)C=C(CH_2C_6H_5)OC_2H_5$ and the sodium derivative of ethyl cyanacetate condense to produce the sodium

(4) Y. Urushibara, this Bulletin, 3 (1928), 102; also compare *ibid.*, 3 (1928), 261.

derivative of diethyl 1,3-dicyano-2-benzylpropene-1,3-dicarboxylate (diethyl α, γ -dicyano- β -benzyl-glutaconate) (XVII).⁽⁵⁾ Thus it is shown that $\text{XYC}=\text{CROC}_2\text{H}_5$ and $\text{CHNaX}'\text{Y}'$ condense in the same way whether R is hydrogen or an alkyl or a similar group.

Sodium compound XXVI⁽⁶⁾ gives an oily substance on acidifying its aqueous solution. This oily substance is supposed to be diethyl 1,3-dicyano-2-methylpropene-1,3-dicarboxylate (XVIII), but it is so unstable that it soon changes into a red crystalline mass. Sodium compound XVII gives also an oily substance, which is quickly transformed into a colourless crystalline compound. The latter has the composition of diethyl 1(or 3)-cyano-3(or 1)-carbamyl-2-benzylpropene-1,3-dicarboxylate (XIX or XX).



The present paper is concerned with other cases of the condensation of the ethoxyethylidene compound $\text{XYC}=\text{C}(\text{CH}_3)\text{OC}_2\text{H}_5$ and the sodium derivative of the methylene compound $\text{CHNaX}'\text{Y}'$, and the comparison of the properties of the produced nitrile-esters of 2-methylpropene-1,1,3,3-tetracarboxylic acid $(\text{HOOC})_2\text{C}=\text{C}(\text{CH}_3)-\text{CH}(\text{COOH})_2$ or their sodium derivatives with those of the corresponding compounds of the propene-1,1,3,3-tetracarboxylic acid series.

The Preparation of Ethoxyethylidene Compounds as the Materials of the Condensation. Among three ethoxyethylidene compounds only ethyl ethoxyethylidene-cyanacetate $\text{C}_2\text{H}_5\text{OCO}(\text{CN})\text{C}=\text{C}(\text{CH}_3)\text{OC}_2\text{H}_5$ is known, and it is obtained by the condensation of triethyl orthoacetate with ethyl cyanacetate by means of acetic anhydride.⁽⁷⁾ Ethoxyethylidene-malonitrile $(\text{CN})_2\text{C}=\text{C}(\text{CH}_3)\text{OC}_2\text{H}_5$ has been obtained by a similar method, malonitrile being used instead of ethyl cyanacetate in the above-mentioned condensation. Ethoxyethylidene-malonitrile forms colourless crystals melting at 91° . In spite of several attempts of synthesis including the condensation of diethyl malonate with triethyl orthoacetate, diethyl ethoxyethylidene-malonate $(\text{C}_2\text{H}_5\text{OCO})_2\text{C}=\text{C}(\text{CH}_3)\text{OC}_2\text{H}_5$ has not yet been obtained.

The Condensations of the Ethoxyethylidene Compounds and the Sodium Derivatives of the Methylene Compounds and the Investigation of the Products. Nine cases are also possible for the condensation of the ethoxy-

(5) Y. Urushibara, this Bulletin, 3 (1928), 316.

(6) It has not yet been crystallized from water; from alcohol it crystallizes without solvent of crystallization.

(7) Y. Urushibara, this Bulletin, 3 (1928), 103.

ethylidene compound $\text{XYC}=\text{C}(\text{CH}_3)\text{OC}_2\text{H}_5$ and the sodium derivative of the methylene compound $\text{CHNaX}'\text{Y}'$, X, Y, X', and Y' representing independently either cyano-group CN or carbethoxy-group COOC_2H_5 . And, if the reaction proceeded simply to yield the normal product $\text{XYC}=\text{C}(\text{CH}_3)\text{-CNaX}'\text{Y}'$, nine compounds XXI-XXIX, the sodium derivatives of all the possible nitrile-esters of 2-methylpropene-1,1,3,3-tetracarboxylic acid, would be obtained. But from the examples of the propene-1,1,3,3-tetracarboxylic acid series it can be naturally expected that compounds XXII, XXIV, and XXVII, which have more cyano-groups in carbon atom 3 than in carbon atom 1, will not be obtained by the condensation in alcoholic solution, compounds XXIII, XXV, and XXVIII appearing as the substitutes respectively.

As diethyl ethoxyethylidene-malonate is not obtainable, three cases of condensation out of the nine can not be realized. The condensation of ethyl ethoxyethylidene-cyanacetate and ethyl sodio-cyanacetate producing compound XXVI has been already described by one of the authors as mentioned above. The remaining five cases have now been studied, all the reactions being carried out in alcoholic solution. If they were carried out in ether, four compounds might be expected from each reaction, that is to say, the condensation of $\text{XYC}=\text{C}(\text{CH}_3)\text{OC}_2\text{H}_5$ and $\text{CHNaX}'\text{Y}'$ would give $\text{XYC}=\text{C}(\text{CH}_3)\text{-CNaX}'\text{Y}'$, $\text{X}'\text{Y}'\text{C}=\text{C}(\text{CH}_3)\text{-CNaXY}$, $\text{X}'\text{Y}'\text{C}=\text{C}(\text{CH}_3)\text{-CNaX}'\text{Y}'$, and $\text{XYC}=\text{C}(\text{CH}_3)\text{-CNaXY}$.

From the comparison of VI, XVII, and XXVI, it appeared that the compound represented by the general formula $\text{XYC}=\text{CR-CNaX}'\text{Y}'$ might behave differently according to the nature of the group R even if the arrangement of the four negative groups was the same, but, so far as the compounds described below are concerned, there is no difference in the chemical behaviour between the propene series ($\text{R} = \text{H}$) and the 2-methylpropene series ($\text{R} = \text{CH}_3$).

- (XXI) $(\text{C}_2\text{H}_5\text{OCO})_2\text{C}=\text{C}(\text{CH}_3)\text{-CNa}(\text{COOC}_2\text{H}_5)_2$
- (XXII) $(\text{C}_2\text{H}_5\text{OCO})_2\text{C}=\text{C}(\text{CH}_3)\text{-CNa}(\text{CN})\text{COOC}_2\text{H}_5$
- (XXIII) $\text{C}_2\text{H}_5\text{OCO}(\text{CN})\text{C}=\text{C}(\text{CH}_3)\text{-CNa}(\text{COOC}_2\text{H}_5)_2$
- (XXIV) $(\text{C}_2\text{H}_5\text{OCO})_2\text{C}=\text{C}(\text{CH}_3)\text{-CNa}(\text{CN})_2$
- (XXV) $(\text{CN})_2\text{C}=\text{C}(\text{CH}_3)\text{-CNa}(\text{COOC}_2\text{H}_5)_2$
- (XXVI) $\text{C}_2\text{H}_5\text{OCO}(\text{CN})\text{C}=\text{C}(\text{CH}_3)\text{-CNa}(\text{CN})\text{COOC}_2\text{H}_5$
- (XXVII) $\text{C}_2\text{H}_5\text{OCO}(\text{CN})\text{C}=\text{C}(\text{CH}_3)\text{-CNa}(\text{CN})_2$
- (XXVIII) $(\text{CN})_2\text{C}=\text{C}(\text{CH}_3)\text{-CNa}(\text{CN})\text{COOC}_2\text{H}_5$
- (XXIX) $(\text{CN})_2\text{C}=\text{C}(\text{CH}_3)\text{-CNa}(\text{CN})_2$

(1) *Condensation of Ethyl Ethoxyethylidene-cyanacetate* $\text{C}_2\text{H}_5\text{OCO}(\text{CN})\text{C}=\text{C}(\text{CH}_3)\text{OC}_2\text{H}_5$ and *Diethyl Sodio-malonate* $\text{CHNa}(\text{COOC}_2\text{H}_5)_2$. The product is expected to be the sodium derivative of triethyl 1-cyano-2-methylpropene-1,3,3-tricarboxylate (XXIII). It is obtained

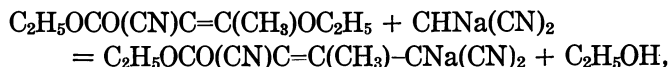
as hygroscopic crystals. It gives a dark-red colouration with ferric chloride in accordance with the assumed structure (XXIII). On acidifying its aqueous solution the corresponding free ester, triethyl 1-cyano-2-methylpropene-1,3,3-tricarboxylate (XXX), is precipitated as an oily substance. When the oil is collected and kept in the desiccator, it crystallizes slowly. The substance is insoluble in water, but soluble in ether and in alcohol. It dissolves in the aqueous solution of sodium carbonate or hydroxide, and on acidifying the solution it is precipitated. Thus XXIII and XXX manifest behaviours analogous to those of III and XI respectively, and this fact supports the assigned formulæ.

(2) *Condensation of Ethoxyethylidene-malonitrile* $(\text{CN})_2\text{C}=\text{C}(\text{CH}_3)\text{OC}_2\text{H}_5$ and *Diethyl Sodio-malonate* $\text{CHNa}(\text{COOC}_2\text{H}_5)_2$. The product is expected to be the sodium derivative of diethyl 1,1-dicyano-2-methylpropene-3,3-dicarboxylate (XXV). From water it crystallizes in light-yellow needles with half a molecule of water of crystallization. It is easily soluble in water and in alcohol. It gives a dark-red colouration with ferric chloride in accordance with the assumed structure (XXV). On acidifying the aqueous solution of this sodium compound an oily substance is formed, which is supposed to be diethyl 1,1-dicyano-2-methylpropene-3,3-dicarboxylate (XXXI or $\text{C}_{12}\text{H}_{14}\text{O}_4\text{N}_2$). The oily substance is easily transformed into two crystalline compounds, one melting at 232° and the other at 164° . Both are insoluble in water and in ether. The compound melting at 232° has the composition $\text{C}_{12}\text{H}_{14}\text{O}_4\text{N}_2 \cdot \text{H}_2\text{O}$ and formula XXXII may be given to it in analogy to compound XIV. The compound melting at 164° possesses the composition $\text{C}_{12}\text{H}_{14}\text{O}_4\text{N}_2 \cdot 2\text{H}_2\text{O}$, and formula XXXIII may be given to it in analogy to compound XIII. These compounds may be called respectively diethyl 1-cyano-1-carbamyl-2-methylpropene-3,3-dicarboxylate and diethyl 1,1-dicarbamyl-2-methylpropene-3,3-dicarboxylate. The fact that the difference in the melting points between XIV [212°] and XXXII [232°] is nearly equal to the difference between XIII [140°] and XXXIII [164°] justifies the assigned relationship of analogy and homology. Here again exists a perfect parallelism of behaviours between the compounds of the propene series and the compounds of the 2-methylpropene series: the sodium compounds (V and XXV) crystallize with half a molecule of water, and the free compounds (XII and XXXI) are easily combined with a molecule of water (giving XIV and XXXII respectively) and also with two molecules of water (giving XIII and XXXIII respectively). These circumstances reciprocally strengthen the grounds for assigning formulæ XXV, XXXI, XXXII, and XXXIII respectively corresponding to formulæ V, XII, XIV, and XIII, which have been established on a stronger basis by the synthesis of compound IV.

- (XXX) $\text{C}_2\text{H}_5\text{OCO}(\text{CN})\text{C}=\text{C}(\text{CH}_3)-\text{CH}(\text{COOC}_2\text{H}_5)_2$
 (XXXI) $(\text{CN})_2\text{C}=\text{C}(\text{CH}_3)-\text{CH}(\text{COOC}_2\text{H}_5)_2$
 (XXXII) $\text{H}_2\text{NCO}(\text{CN})\text{C}=\text{C}(\text{CH}_3)-\text{CH}(\text{COOC}_2\text{H}_5)_2$
 (XXXIII) $(\text{H}_2\text{NCO})_2\text{C}=\text{C}(\text{CH}_3)-\text{CH}(\text{COOC}_2\text{H}_5)_2$

(3) *Condensation of Ethoxyethylidene-malonitrile* $(\text{CN})_2\text{C}=\text{C}(\text{CH}_3)\text{OC}_2\text{H}_5$ and *Ethyl Sodio-cyanacetate* $\text{CHNa}(\text{CN})\text{COOC}_2\text{H}_5$. The product is expected to be the sodium derivative of ethyl 1,1,3-tricyano-2-methylpropene-3-carboxylate (XXVIII), because this structure not only corresponds to the normal product of the condensation, but also possesses more carbethoxy-groups in carbon atom 3 than in carbon atom 1. Further, its behaviour, being very similar to that of compound VIII, are in accordance with the assumed structure: The sodium compound crystallizes in colourless needles with a molecule of water of crystallization ($\text{C}_{10}\text{H}_9\text{O}_2\text{N}_3\text{Na}\cdot\text{H}_2\text{O}$). On acidifying its aqueous solution a nearly colourless crystalline substance separates out gradually. It is insoluble in water and in ether, but soluble in alcohol, from which it can be recrystallized in colourless crystals. It melts at $212-213^\circ$ with decomposition, and has the composition $\text{C}_{10}\text{H}_9\text{O}_2\text{N}_3\cdot\frac{1}{2}\text{H}_2\text{O}$ or $(\text{C}_{10}\text{H}_9\text{O}_2\text{N}_3)_2\cdot\text{H}_2\text{O}$.

(4) *Condensation of Ethyl Ethoxyethylidene-cyanacetate* $\text{C}_2\text{H}_5\text{OCO}(\text{CN})\text{C}=\text{C}(\text{CH}_3)\text{OC}_2\text{H}_5$ and *Sodio-malonitrile* $\text{CHNa}(\text{CN})_2$. If the reaction proceeded as follows:



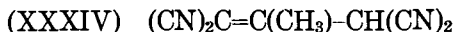
a product with formula XXVII would be formed. But the sodium compound produced behaves unlike the 3,3-dicyano-compounds, VII, IX, and XXIX (see below), and manifests the same properties as XXVIII obtained by the condensation of ethoxyethylidene-malonitrile and ethyl sodio-cyanacetate: The present sodium compound crystallizes in colourless needles with a molecule of water of crystallization ($\text{C}_{10}\text{H}_9\text{O}_2\text{N}_3\text{Na}\cdot\text{H}_2\text{O}$), and, on acidifying its aqueous solution, yields a light-yellow crystalline compound. The latter is insoluble in water and in ether, but can be recrystallized in colourless crystals from alcohol, melts at $227-228^\circ$ with decomposition, and gives analytical results corresponding to formula $\text{C}_{10}\text{H}_9\text{O}_2\text{N}_3\cdot\frac{1}{2}\text{H}_2\text{O}$ or $(\text{C}_{10}\text{H}_9\text{O}_2\text{N}_3)_2\cdot\text{H}_2\text{O}$. Therefore, in spite of a small difference in the melting points of the two specimens of the crystalline derivative, it is very probable that the product of the present condensation is the sodium derivative of ethyl 1,1,3-tricyano-2-methylpropene-3-carboxylate (XXVIII), the same as obtained by the preceding condensation.

There exist analogies in all respects between the propene series and the 2-methylpropene series: by the condensation in alcoholic solution the 1,1,3-tricyano-3-carbethoxy-compounds, VIII and XXVIII, are exclusively formed,

even when the 1, 3, 3-tricyano-1-carbethoxy-compounds, VII and XXVII respectively, may be expected as the normal products; the sodium compounds obtained, VIII and XXVIII, crystallize with a molecule of water, and, on acidifying their aqueous solutions, yield the crystalline compounds with similar compositions, $(C_9H_7O_2N_3)_2 \cdot H_2O$ and $(C_{10}H_9O_2N_3)_2 \cdot H_2O$ respectively.

Nevertheless, there is one point of disagreement: the compound $(C_9H_7O_2N_3)_2 \cdot H_2O$ is yellow, while the compound $(C_{10}H_9O_2N_3)_2 \cdot H_2O$ is colourless. It has been repeatedly experienced that the sodium derivatives of the nitrile-esters of dicarboxy-glutaconic acid appear often coloured (mostly yellow), the same compound sometimes being tinged with different colours,⁽⁸⁾ while it is very probable that they must be all colourless when pure, because most of them have been really obtained in colourless state. The colouring, and even the colourless, impurities of the sodium compounds may affect the colour of the compounds derived from them.⁽⁹⁾ Thus it is not impossible that the colour of such derivatives may not be essential. But, without any further investigations, there may be no saying what is the fact with the compounds in question.

(5) *Condensation of Ethoxyethylidene-malonitrile* $(CN)_2C=C(CH_3)OC_2H_5$ and *Sodio-malonitrile* $CHNa(CN)_2$. The sodium derivative of 1,1,3,3-tetracyano-2-methylpropene (XXIX) separates out in light-yellow crystals from the alcoholic reaction mixture without evaporation. It is recrystallized from water in colourless silky crystals with a molecule of water $(C_8H_3N_4Na \cdot H_2O)$. When its aqueous solution is acidified with hydrochloric acid nothing separates out. On evaporating the acidified solution over sulphuric acid in vacuum, the sodium compound is recovered unchanged. But, if the acidified solution is shaken repeatedly with ether, and the combined ethereal extract is dried with calcium chloride and evaporated in vacuum, colourless silky crystals remain. This crystalline compound is supposed to be 1,1,3,3-tetracyano-2-methylpropene (XXXIV), but it is very unstable and decomposes quickly into a dark-red amorphous substance. It is, however, stable in solution. Its aqueous solution behaves as a very strong acid; it dissolves zinc and magnesium with the evolution of hydrogen gas. The electrolytic dissociation of this compound will be dealt with in a separate paper.



Thus XXIX and XXXIV behave so much similarly to IX and XVI respectively, that the two series can not be distinguished from each other except by the analytical results. The parallelism goes farther: A sodium-free by-product

(8) Y. Urushibara, this Bulletin, 2 (1927), 28, 238, 284.

(9) Y. Urushibara, this Bulletin, 2 (1927), 284.

is formed by the condensation of ethoxymethylene-malonitrile and sodio-malonitrile, and is obtained from the mother liquor of the sodium derivative of 1,1,3,3-tetracyano-propene C_7HN_4Na . It has the composition $C_7H_2N_4 \cdot C_2H_5OH$ and melts at $211-212^\circ$ without decomposition.⁽¹⁰⁾ Similarly from the mother liquor of the sodium derivative of 1,1,3,3-tetracyano-2-methylpropene $C_8H_3N_4Na$, a compound with formula $C_8H_4N_4 \cdot C_2H_5OH$ and melting point 226° is obtained.

If the reaction of ethoxyethylidene-malonitrile and sodio-malonitrile is carried out without cooling, the yield of the sodium-free by-product $C_8H_4N_4 \cdot C_2H_5OH$ increases at the cost of the sodium compound $C_8H_3N_4Na$, and the reaction mixture or the mother liquor of the sodium compound shows a stronger alkaline reaction than when the yield of the by-product is smaller.

Experimental Part.

Preparation of the Ethoxyethylidene Compounds. (1) *Ethoxyethylidene-malonitrile*.

A mixture of triethyl orthoacetate (1 mol), malonitrile (1 mol), and acetic anhydride (2 mols) was heated in a flask with an upright condenser, the cooling water being stopped from running. Ethyl acetate formed was collected through a bent tube attached at the top of the condenser. When it reached the required amount, the mixture in the flask was distilled, under the ordinary pressure until the temperature reached 140° , and then under diminished pressure. Ethoxyethylidene-malonitrile distilled constantly at 120° under 2 mm. Melting point 91° . Easily soluble in alcohol, difficultly soluble in ether, and insoluble in water. (Found: N, 20.68. Calculated for $C_7H_5ON_2$: N, 20.59%.)

(2) *Attempted Preparation of Diethyl Ethoxyethylidene-malonate*. Following reactions were attempted all in vain: (a) Condensation of triethyl orthoacetate and diethyl malonate by means of acetic anhydride. (b) The same with the addition of zinc chloride. (c) Diethyl acetyl-malonate prepared according to the directions of H. Lund⁽¹¹⁾ was transformed into its silver derivative through the sodium derivative, and the silver compound and ethyl iodide were heated in alcohol. (d) The same reaction in ether instead of alcohol. (e) Action of ethyl iodide on the potassium derivative of diethyl acetyl-malonate. (f) Hydrolysis of ethyl ethoxyethylidene-cyanacetate by sulphuric acid in alcohol. (g) Transformation of the cyano-group of ethyl ethoxyethylidene-cyanacetate into a carbethoxy-group through $-C(NH)OC_2H_5$ and $-C(OC_2H_5)_3$. (h) Action of diazomethane on diethyl acetyl-malonate in ether.

Condensations of Ethoxyethylidene Compounds and the Sodium Derivatives of Methylene Compounds. Sodium (1 mol) was dissolved in absolute alcohol, the methylene compound (1 mol) was added to the alcoholic sodium ethylate, and the ethoxyethylidene compound (1 mol) was introduced gradually under cooling. The reaction liquor was evaporated to crystallization over sulphuric acid in vacuum at the ordinary temperature.

(10) Y. Urushibara, this Bulletin, **2** (1927), 286.

(11) *Ber.*, **67** (1934), 935.

(1) *Condensation of Ethyl Ethoxyethylidene-cyanacetate and Diethyl Sodio-malonate.* The product (XXIII) was obtained as a crystalline mass by evaporating the reaction liquor over sulphuric acid in vacuum and washing the residue with ether. The substance obtained was very hygroscopic, so that it was not recrystallized. It gave a dark-red colouration with ferric chloride. The crude substance was dissolved in water and the solution was acidified with dilute hydrochloric acid, when an oily substance separated out. The oily substance was extracted with ether, the ethereal solution was shaken with aqueous sodium carbonate, the aqueous solution was acidified, and the oil was collected by extraction with ether followed by evaporation of the solvent in vacuum. The oily substance thus obtained was orange-coloured, and when it was kept in a sulphuric acid desiccator, crystals appeared slowly. After dried in vacuum, the substance was analysed (Found: C, 56.33; H, 6.81; N, 5.02. Calculated for XXX or $C_{14}H_{19}O_6N$: C, 56.97; H, 6.40; N, 4.71%).

(2) *Condensation of Ethoxyethylidene-malonitrile and Diethyl Sodio-malonate.* The product (XXV) was obtained as a crystalline mass by evaporating the reaction liquor. It was readily soluble in alcohol. It was recrystallized from water in light-yellow needles with half a molecule of water of crystallization (Found: H_2O , 3.02. Calculated for $C_{12}H_{13}O_4N_2Na \cdot \frac{1}{2}H_2O$: H_2O , 3.20%. Found for anhydrous substance: N, 10.02. Calculated for XXV or $C_{12}H_{13}O_4N_2Na$: N, 10.29%). The substance gave a dark-red colouration with ferric chloride.

On adding dilute hydrochloric acid to an aqueous solution of the sodium compound, an orange-red oily substance separated out immediately. The oil was extracted with ether, the ethereal solution was shaken with 10% aqueous sodium carbonate, and the aqueous solution was acidified and shaken with ether. A small amount of a crystalline substance soluble in neither the aqueous nor the ethereal layer was collected, washed with water and ether, and dried. It was obtained as colourless crystals melting at 232° (Found: C, 53.67; H, 6.28; N, 10.64. Calculated for XXXII or $C_{12}H_{14}O_4N_2 \cdot H_2O$: C, 53.73; H, 5.97; N, 10.44%). On evaporating the ethereal layer without drying, another colourless crystalline substance separated out, which did not dissolve again in ether. It was collected, washed with ether and water, and dried, melting point 164° (Found: C, 50.18; H, 6.66; N, 10.07. Calculated for XXXIII or $C_{12}H_{14}O_4N_2 \cdot 2H_2O$: C, 50.35; H, 6.29; N, 9.79%).

(3) *Condensation of Ethoxyethylidene-malonitrile and Ethyl Sodio-cyanacetate.* On evaporating the reaction liquor, the product (XXVIII) separated out in crystals. It was easily soluble in water, alcohol, and acetone. Recrystallized from water, it was obtained as colourless needles with a molecule of water of crystallization (Found: H_2O , 7.07. Calculated for $C_{10}H_8O_2N_3Na \cdot H_2O$: H_2O , 7.41%. Found for anhydrous substance: N, 18.48. Calculated for XXVIII or $C_{10}H_8O_2N_3Na$: N, 18.67%).

When an aqueous solution of the sodium compound was acidified with dilute hydrochloric acid, a crystalline substance separated out after a while. It was insoluble in water and in ether. It was recrystallized from alcohol, colourless crystals, melting point $212-213^\circ$ with decomposition (Found: C, 56.52; H, 4.73; N, 19.94. Calculated for $(C_{10}H_8O_2N_3)_2 \cdot H_2O$: C, 56.60; H, 4.72; N, 19.81%).

(4) *Condensation of Ethyl Ethoxyethylidene-cyanacetate and Sodio-malonitrile.* The product crystallized out on evaporating the reaction liquor in vacuum. By repeated recrystallization from water it was obtained as colourless needles (Found: H_2O , 7.66. Calculated for $C_{10}H_8O_2N_3Na \cdot H_2O$: H_2O , 7.41%. Found for anhydrous substance: N, 18.90. Calculated for $C_{10}H_8O_2N_3Na$: N, 18.67%).

On adding dilute hydrochloric acid to an aqueous solution of the sodium compound a light-yellow crystalline substance separated out slowly. It was insoluble in water and in ether. It was recrystallized from alcohol, colourless crystals, melting point $227-228^{\circ}$ with decomposition (Found: C, 56.81; H, 4.99; N, 19.90. Calculated for $(C_{10}H_9O_2N_3)_2 \cdot H_2O$: C, 56.60; H, 4.72; N, 19.81%).

(5) *Condensation of Ethoxyethylidene-malonitrile and Sodio-malonitrile.* The product (XXIX) crystallized out without evaporation. It was recrystallized from water, colourless silky crystals with a molecule of water of crystallization (Found: H_2O , 8.87. Calculated for $C_8H_3N_4Na \cdot H_2O$: H_2O , 9.18%. Found for anhydrous substance: N, 31.54. Calculated for XXIX or $C_8H_3N_4Na$: N, 31.46%).

On acidifying an aqueous solution of the sodium compound with hydrochloric acid nothing separated out. When the acidified solution was evaporated over sulphuric acid in a vacuum desiccator, the original sodium compound remained, the desiccator being filled with the fume of hydrogen chloride. An acidified aqueous solution of the sodium compound was shaken with ether several times, and the ethereal solution was dried with calcium chloride and evaporated by suction, when colourless silky crystals appeared and immediately decomposed into an amorphous substance coloured like red phosphorus.

The mother liquor of the sodium compound was evaporated over sulphuric acid in the vacuum desiccator. The remaining yellow crystalline mass contained light-yellow crystals insoluble in water. They were collected and recrystallized from alcohol. Thus a colourless crystalline compound melting at 226° was obtained (Found: C, 59.27; H, 5.22; N, 27.89. Calculated for $C_8H_4N_4 \cdot C_2H_5OH$: C, 59.41; H, 4.95; N, 27.72%).

When the condensation was carried out without cooling, the reaction mixture was coloured intensely, and the sodium compound (XXIX) did not crystallize out. The crystalline mass obtained by evaporating the reaction liquor consisted mainly of the sodium-free by-product $C_8H_4N_4 \cdot C_2H_5OH$.

Summary.

The sodium derivatives of the nitrile-esters of 2-methylpropene-1,1,3,3-tetracarboxylic acid $(HOOC)_2C=C(CH_3)-CH(COOH)_2$ have been synthesized, and their properties have been compared with those of the corresponding compounds of the propene-1,1,3,3-tetracarboxylic acid series synthesized previously. It has been observed that, with one exceptional case of the 1,3-dicyano-1,3-dicarbethoxy-compounds, there exist analogies in all respects between the 2-methylpropene-tetracarboxylic acid series and the propene-tetracarboxylic acid series.

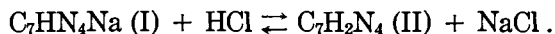
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THE ELECTROLYTIC DISSOCIATION OF 1,1,3,3-TETRA-CYANO-PROPENE AND 1,1,3,3-TETRACYANO-2-METHYLPROPENE.*

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Introduction. The sodium derivative of 1,1,3,3-tetracyano-propene (I) is obtained by the condensation of ethoxymethylene-malonitrile $(\text{CN})_2\text{C}=\text{CHOC}_2\text{H}_5$ and sodiomalonitrile $\text{CHNa}(\text{CN})_2$.⁽¹⁾ When recrystallized from water, it forms colourless fine needles with a molecule of water of crystallization. When the aqueous solution of this sodium compound is acidified with hydrochloric acid, no apparent change is observed. The unchanged sodium compound (with a molecule of water of crystallization) can be crystallized out from the aqueous solution acidified with hydrochloric acid, by cooling when a comparatively large amount of this compound has been dissolved by heating, or by evaporating over sulphuric acid in vacuum when the concentration is smaller. But, if the acidified solution is shaken repeatedly with ether, the aqueous layer leaves sodium chloride alone on evaporation, and on evaporating the dried ethereal extract in vacuum, the free compound, 1,1,3,3-tetracyano-propene (II), remains in colourless crystals. The free compound, isolated in this way, is extremely unstable, and decomposes quickly into a brown amorphous mass. It is, however, stable in solution. If the ethereal solution of the free compound and the aqueous solution of the equivalent amount of sodium chloride are evaporated up together in vacuum, the sodium compound (I) remains, while hydrogen chloride is driven off. These experimental facts show the strong acid character of the compound II, and the well-defined reversibility of the reaction :



The sodium derivative of 1,1,3,3-tetracyano-2-methylpropene (III) is obtained analogously by the condensation of ethoxyethylidene-malonitrile $(\text{CN})_2\text{C}=\text{C}(\text{CH}_3)\text{OC}_2\text{H}_5$ and sodio-malonitrile $\text{CHNa}(\text{CN})_2$.⁽²⁾ As mentioned in the preceding paper,⁽²⁾ this sodium compound and the corresponding free com-

* Read before Section II at the 58th Annual Meeting of the Chemical Society of Japan at Sendai (April 3rd, 1936).

(1) Y. Urushibara, this Bulletin, 2 (1927), 285.

(2) See p. 565 of this volume.

pound, 1,1,3,3-tetracyano-2-methylpropene (IV), behave so much similarly to I and II respectively, that the two groups can not be distinguished from each other except by analysis.

The present paper deals with the determination of the degrees of the electrolytic dissociation, and some investigations on the salts, of 1,1,3,3-tetracyano-propene (II) and 1,1,3,3-tetracyano-2-methylpropene (IV), which behave as strong acids even though they possess no carboxyl-group.

- (I) $(\text{CN})_2\text{C}=\text{CH}-\text{CNa}(\text{CN})_2$
- (II) $(\text{CN})_2\text{C}=\text{CH}-\text{CH}(\text{CN})_2$
- (III) $(\text{CN})_2\text{C}=\text{C}(\text{CH}_3)-\text{CNa}(\text{CN})_2$
- (IV) $(\text{CN})_2\text{C}=\text{C}(\text{CH}_3)-\text{CH}(\text{CN})_2$

The Preparation of the Aqueous Solutions of 1,1,3,3-Tetracyano-propene and 1,1,3,3-Tetracyano-2-methylpropene. As mentioned above, 1,1,3,3-tetracyano-propene (II) and 1,1,3,3-tetracyano-2-methylpropene (IV) are extremely unstable when isolated, so that their aqueous solutions were prepared from the sodium derivatives as follows: The recrystallized sodium compound ($\text{C}_7\text{HN}_4\text{Na}\cdot\text{H}_2\text{O}$ or $\text{C}_8\text{H}_3\text{N}_4\text{Na}\cdot\text{H}_2\text{O}$) (1/160 mol) was dissolved in a little amount of water and aqueous potassium bisulphate was added in excess. The resulting solution was extracted with pure ether several times. The ethereal solution was dried with anhydrous sodium sulphate, filtered into a flask, and evaporated in vacuum to some extent. After the addition of purified water in an amount (70–80 c.c.) a little smaller than the calculated for 1/16 N, the ether was driven off in vacuum completely. The aqueous solution obtained in this way was colourless and gave no precipitate nor turbidity on adding barium chloride. Then the aqueous solution was titrated with barium hydroxide (1/20 N), and by adding the required amount of purified water, the solution was made up to 1/16 N, the titer being confirmed by titration after dilution.

The Determination of the Degrees of the Electrolytic Dissociation by Measuring the Molecular Conductivities. The 1/16 N solution (20 c.c.) was taken in a conductivity vessel. The conductivity was measured at 25.0° by the method of Wheatstone bridge. Then the concentration of the solution in the vessel was made one half by taking out half the volume of the solution and adding the same volume of pure water, and the conductivity was measured again. By repeating the same procedure the conductivities of the solutions in the concentrations down to 1/512 N were measured. The molecular conductivities were plotted against the concentrations, and the value for the infinite dilution was obtained by extrapolation of the concentration-molecular conductivity curve. Three series of measurements were carried out and the

mean value of the molecular conductivity was obtained for each concentration. The degree of dissociation was calculated by dividing the molecular conductivity for each concentration by the value for the infinite dilution. From the degree of dissociation the concentration of the hydrogen ions and pH were calculated. The results of experiments are shown in Table 1 and Table 2. Table 3 shows the degrees of dissociation of hydrochloric acid calculated similarly from the molecular conductivities.⁽³⁾ 1,1,3,3-Tetracyano-propene and 1,1,3,3-tetracyano-2-methylpropene manifest high degrees of electrolytic dissociation, comparable with those of hydrochloric acid.

Table 1. Electrolytic Dissociation of 1,1,3,3-Tetracyano-propene at 25.0°.

Concentration (N)	Molecular conductivity				Degree of dissociation	Concentration of hydrogen ions (N)	pH
	1	2	3	mean			
1/16	355.2	354.8	352.9	354.3	0.881	0.0551	1.26
1/32	376.2	371.2	370.4	372.6	0.926	0.0289	1.54
1/64	388.4	385.2	384.5	386.0	0.960	0.0150	1.82
1/128	399.5	396.5	395.7	397.2	0.987	0.00771	2.11
1/256	400.7	400.5	399.9	400.4	0.995	0.00389	2.41
1/512	401.3	400.5	400.4	400.7	0.996	0.00195	2.71
0	403	402	402	402.3			

Table 2. Electrolytic Dissociation of 1,1,3,3-Tetracyano-2-methylpropene at 25.0°.

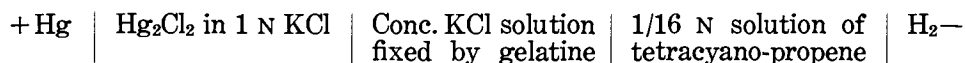
Concentration (N)	Molecular conductivity				Degree of dissociation	Concentration of hydrogen ions (N)	pH
	1	2	3	mean			
1/16	350.1	353.9	351.1	351.7	0.879	0.0548	1.26
1/32	370.0	371.6	372.2	371.3	0.928	0.0290	1.54
1/64	380.5	383.2	382.2	382.0	0.955	0.0149	1.83
1/128	391.2	392.3	389.6	391.0	0.978	0.00764	2.12
1/256	391.4	395.3	392.9	393.2	0.983	0.00384	2.42
1/512	397.2	398.0	398.0	398.4	0.996	0.00195	2.71
0	400	400	400	400			

(3) W. Ostwald, "Lehrbuch der allgemeinen Chemie," 1893, Vol. II, p. 1.

Table 3. The Degree of the Electrolytic Dissociation of Hydrogen Chloride at 25°.

Concentration (N)	1/8	1/16	1/32	1/64	1/128	1/256	0
Molecular conductivity ⁽³⁾	378	386	393	399	401	403	407
Degree of dissociation	0.928	0.948	0.965	0.980	0.985	0.990	

The Determination of the Hydrogen Ion Concentration by Measuring the Electromotive Force. The following cell was constructed by combining a calomel electrode and a hydrogen electrode containing the 1/16 N solution of 1,1,3,3-tetracyano-propene by means of a concentrated solution of potassium chloride fixed by gelatine:



pH is obtained from the following equation:

$$pH = \frac{E - 0.284}{0.0001986 T},$$

where *E* is the electromotive force of the cell, and *T* the absolute temperature. The electromotive force was measured at 15°C. From the value of *pH* the concentration of hydrogen ions and the degree of dissociation were calculated. The results are shown in Table 4. For comparison *pH* of the 1/16 N hydrochloric acid was determined similarly, Table 5.

Table 4. *pH* of the 1/16 N Solution of 1,1,3,3-Tetracyano-propene at 15°C.

No. of exp.	<i>E</i> (volt)	<i>pH</i>	Concentration of hydrogen ions (N)	Degree of dissociation
1 2 3	0.3575 0.3595 0.3580	1.29 1.33 1.30 } mean 1.30	0.050	0.80

Table 5. *pH* of 1/16 N Hydrochloric Acid at 15°C.

No. of exp.	<i>E</i> (volt)	<i>pH</i>	Concentration of hydrogen ions (N)	Degree of dissociation
1 2	0.3555 0.3550	1.25 1.24 } mean 1.25	0.057	0.90

Chemical Properties of 1,1,3,3-Tetracyano-propene and 1,1,3,3-Tetracyano-2-methylpropene, and the Solubilities of their Salts. The aqueous solution of 1,1,3,3-tetracyano-propene decomposes carbonates, and dissolves zinc, magnesium, and tin at the ordinary temperature with the evolution of hydrogen gas. On adding silver nitrate to the solution of the sodium salt (I) acidified with nitric acid, the silver salt of 1,1,3,3-tetracyano-propene is precipitated. The mercurous salt is also insoluble in water. The salts of other metals are soluble in water. Thus the salts of 1,1,3,3-tetracyano-propene resemble chlorides in solubilities in water. Silver and lead salts are more easily soluble in water than silver and lead chlorides respectively.

1,1,3,3-Tetracyano-2-methylpropene shows quite similar properties. Its salts are generally less soluble, and more easily crystallizable, than the salts of 1,1,3,3-tetracyano-propene, except the silver salts.

The degrees of ionization of the sodium salts (I and III) and the solubilities of the silver salts are described below.

The Degrees of the Electrolytic Dissociation of the Sodium Derivatives of 1,1,3,3-Tetracyano-propene and 1,1,3,3-Tetracyano-2-methylpropene. The molecular conductivities of the aqueous solutions of these sodium compounds in various concentrations were measured at 25.0°. The value for the infinite dilution was obtained also by extrapolating the concentration-molecular conductivity curve. The degree of dissociation was calculated by dividing the molecular conductivity for each concentration by the value for the infinite dilution. The results are shown in Table 6 and Table 7. In the 1/10 N solution the sodium derivative of 1,1,3,3-tetracyano-propene shows the degree of dissociation 0.70, while the sodium derivative of 1,1,3,3-tetracyano-2-methylpropene 0.67.

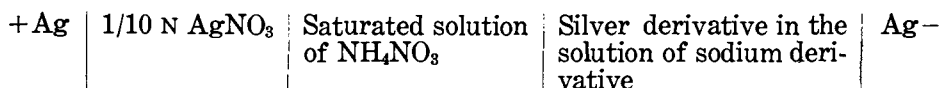
Table 6. The Electrolytic Dissociation of the Sodium Derivative of 1,1,3,3-Tetracyano-propene at 25.0°.

Concentration (N)	Molecular conductivity	Degree of dissociation
1/10	67.7	0.70
1/20	74.8	0.78
1/40	79.5	0.82
1/80	83.6	0.87
1/160	87.8	0.92
1/320	90.9	0.95
1/640	91.8	0.97
0	95.0	

Table 7. The Electrolytic Dissociation of the Sodium Derivative of 1,1,3,3-Tetracyano-2-methylpropene at 25.0°.

Concentration (N)	Molecular conductivity	Degree of dissociation
1/10	66.2	0.67
1/16	72.1	0.73
1/32	77.8	0.79
1/64	80.9	0.82
1/128	86.0	0.83
1/256	88.9	0.91
1/512	92.2	0.95
0	96.0	

The Solubilities of the Silver Derivatives of 1,1,3,3-Tetracyano-propene and 1,1,3,3-Tetracyano-2-methylpropene. The following concentration cell was constructed :



For the determination of the solubility of the silver derivative of 1,1,3,3-tetracyano-propene C₇HN₄Ag three measurements of the electromotive force were carried out at 18° with the cathode solutions prepared by adding one or two drops of a silver nitrate solution to the 1/10 N, 1/80 N, and 1/160 N solutions of the sodium derivative (I). For the silver derivative of 1,1,3,3-tetracyano-2-methylpropene C₈H₃N₄Ag only one measurement was made at 23° with the 1/10 N solution of the sodium compound (III). The concentration of the silver ions in the cathode solution (x) was calculated from the electromotive force (E) by the following equation :

$$E = 0.058 \log \frac{0.081}{x} .$$

The solubility product was obtained by multiplying the concentration of the silver ions (x) by the concentration of the anion obtained from Table 6 and Table 7 (the value for 25°), and the solubility of the silver compound (g./l.) by multiplying the square root of the solubility product by the molecular weight of the silver compound. The results are shown in Table 8 and Table 9. The solubilities of the silver derivatives of 1,1,3,3-tetracyano-propene and 1,1,3,3-tetracyano-2-methylpropene are greater than the solubility of silver chloride (about 1.5×10^{-3} g./l.), but it takes a long time (about 2 weeks) to decompose these silver derivatives with dilute hydrochloric acid at room temperature.

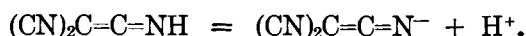
Table 8. The Solubility of the Silver Derivative of 1,1,3,3-Tetracyano-propene at 18°.

No. of exp.	E (volt)	x (N)	Concentration of the anion (N)	Solubility (g./l.)
1	0.2609	2.573×10^{-6}	0.070	$\left. \begin{array}{l} 0.1056 \\ 0.1023 \\ 0.0921 \end{array} \right\} \begin{array}{l} \text{mean} \\ 0.1000 \end{array}$
2	0.2156	1.554×10^{-5}	0.011	
3	0.2046	2.407×10^{-5}	0.0058	

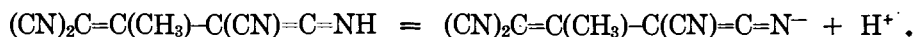
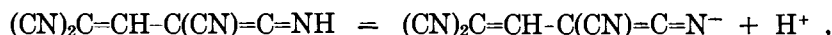
Table 9. The Solubility of the Silver Derivative of 1,1,3,3-Tetracyano-2-methylpropene at 23°.

E (volt)	x (N)	Concentration of the anion (N)	Solubility (g./l.)
0.2431	3.315×10^{-5}	0.067	0.388

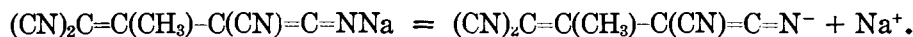
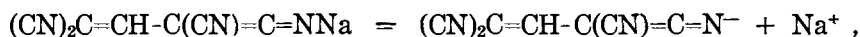
The Constitutions of 1,1,3,3-Tetracyano-propene and 1,1,3,3-Tetracyano-2-methylpropene and the Mode of Ionization. According to Hantzsch and Osswald,⁽⁴⁾ cyanoform $\text{CH}(\text{CN})_3$ behaves as a strong acid, showing the degree of dissociation 0.92 at 25° in the concentration 1/32 N. Further, like 1,1,3,3-tetracyano-propene and 1,1,3,3-tetracyano-2-methylpropene, cyanoform is very unstable when isolated, polymerizing rapidly, but it is stable in aqueous solution. Cyanoform is considered to exist in the form $(\text{CN})_2\text{C}=\text{C}=\text{NH}$ in aqueous solution and to ionize as follows : ⁽⁵⁾



This form of cyanoform has been confirmed by F. Arndt, H. Scholz, and E. Frobel,⁽⁶⁾ who call it the ketene-imide-form or briefly the enamide-form. It may be considered that 1,1,3,3-tetracyano-propene and 1,1,3,3-tetracyano-2-methylpropene exist also in the enamide-form and dissociate in the same way :



In the salts the imide hydrogen is replaced by a metal atom, the electrolytic dissociation taking place in the same way :



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(4) *Ber.*, **32** (1899), 641.

(5) Hantzsch and Osswald, *loc. cit.*; also compare Baker, "Tautomerism," 1934, p. 121.

(6) *Ann.*, **521** (1935), 105.

STUDIES ON THE RAMAN EFFECT OF ORGANIC SUBSTANCES.
VI. RAMAN EFFECT OF SESQUICHAMENE
AND SOME OTHER TERPENES.

By Kichimatsu MATSUNO and Kwan HAN.

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Introduction. In the present paper, the Raman spectra of sesquichamene, $C_{15}H_{24}$, *d*- α -pinene, *d*-sabinene, *d*-verbenol, *d,l*- Δ^1 -terpinenol-(4), menthyl acetate and isobornyl acetate are reported. The constitution of sesquichamene has not been thoroughly determined. Kafuku and Nozoe⁽¹⁾ suggested that sesquichamene is a sesquiterpene of tricyclic class like cedrene, the Raman spectrum of which has been studied by the present authors⁽²⁾. α -Pinene⁽³⁾⁽⁹⁾⁽¹⁰⁾⁽¹¹⁾ and sabinene have been investigated by several authors, our results could be compared with theirs.

Experimental. Most of the substances used were kindly supplied by Ass. Prof. T. Nozoe and his co-workers.

Sesquichamene $C_{15}H_{24}$ was obtained from the essential oil of the leaves of "Arisan-hinoki" or *Chamaecyparis obtusa*, Sieb. et Zucc. f. *formosana*, Hayata.⁽⁴⁾ The physical properties of the sample used were as below: b. p. 120–123°/12 mm., d_4^{24} 0.92386, n_D^{24} 1.4883, $[\alpha]_D - 86.31^\circ$.

d-Sabinene was obtained from the essential oil of the leaves of "Arisan-hinoki"⁽³⁾ (b.p. 162° or 80–82°/50 mm., $d_4^{17.5}$ 0.8442, n_D^{20} 1.4681, $[\alpha]_D + 72^\circ$).

d- α -Pinene was obtained from the oil of the roots of "hinoki" or *Chamaecyparis obtusa*, Sieb. et Zucc. f. *formosana*, Hayata (b.p. 155–156°, n_D^{20} 1.4671, d_4^{20} 0.8585, $[\alpha]_D + 45.25^\circ$).

d-Verbenol was obtained by the autoxidation of *d*- α -pinene.

d,l- Δ^1 -Terpinenol-(4) was obtained from the leaves of *Liquidambar formosana*, Hance⁽⁴⁾ (b.p. 123°/50 mm., n_D^{20} 1.4751, $[\alpha]_D - 0.04^\circ$).

Menthyl acetate was obtained by heating *l*-menthol with acetic anhydride at 150° (b.p. 108°/15 mm., d_4^{20} 0.9185, n_D^{20} 1.4468).

Isobornyl acetate⁽⁵⁾ was prepared by heating camphene⁽⁶⁾ (m.p. 51–52°) with glacial acetic acid (b.p. 106.5–107.5°/15 mm., d_4^{15} 0.9866, n_D^{15} 1.4651).

(1) K. Kafuku and T. Nozoe, this Bulletin, **6** (1931), 111.

(2) This Bulletin, **10** (1935), 220.

(3) K. Kafuku, T. Nozoe and C. Hata, this Bulletin, **6** (1931), 40.

(4) K. Kafuku, T. Nozoe and C. Hata, *J. Chem. Soc. Japan*, **55** (1934), 244.

(5) J. B. Cohen, "Practical Organic Chemistry," (1926), p. 293.

(6) Camphene was synthesized from pinene hydrochloride (m.p. 119–120°), J. B. Cohen, *ibid.*, p. 292.

All the substances were redistilled in vacuum before use. In the case of *d*-verbenol, about 3 c.c. of the sample was used. The observation of its Raman lines was difficult on account of the strong background. The Raman spectra were taken by means of spectrograph of three prisms⁽⁷⁾. The results are summarized in Table 1. The numbers of the Raman lines(*n*), the number of the plates and the conditions under which the spectra were taken, are summarized in Table 2. The results on α -pinene obtained by the authors are compared with those obtained by Bonino-Cella⁽⁸⁾, Dupont-Daure-Allard⁽⁹⁾, Venkateswaran-Bhagavantam⁽¹⁰⁾, and Daure⁽¹¹⁾ in Table 3. Our results are in good agreement with those obtained by Daure.

Table 1. The Values of $\Delta\nu$ for Sesquichamene and Some Other Terpenes.

(1) Sesquichamene

91 (3b, d); 132 (3b, d); 254 (3d); 280 (3); (302) (2d); (336) (2d); 360 (5d); 386 (5d); (407) (1); 434 (4); 496 (3); 539 (3); 572 (3); 590 (8); 604 (4); (684) (1/2); 770 (6); 814 (5); 843 (1d); 882 (4bb); 907 (4d); 926 (1d); 934 (2); 954 (4); 964 (4); 988 (1d); 1006 (4); 1022 (1d); (1042) (2); 1058 (2); 1100 (3b, d); 1119 (3b, d); 1155 (6b, d); (1186) (1); 1192 (4); 1208 (1); 1263 (4); 1296 (4); (1322) (2b); (1346) (2); 1375 (4); 1398 (4); 1434 (5); 1453 (4d); 1471 (4); 1647 (1); 1680 (10); 2844 (4b, d); 2869 (3bb, d); 2908 (6b, d); 2966 (2b, d); 3006 (5bb); 3084 (1); 3167 (4).

(2) *d*-Sabinene

(120) (3b, d); (169) (2b, d); (214) (1); 306 (3); 333 (1); 362 (3d); (373) (1/2); 441 (3); 491 (1d); 509 (3); 566 (2); 634 (3d); 655 (5); 785 (5); 808 (4d); 866 (4b, d); 882 (2d); 915 (6d); 930 (1); 954 (6bb); 989 (3); 1031 (5); 1067 (4); 1103 (6b, d); 1145 (4d); 1170 (3d); 1197 (6); 1214 (1d); 1270 (4b, d); 1308 (4bb); 1379 (3d); 1415 (8); 1438 (4d); 1447 (5d); 1468 (4d); 1656 (10b, d); 2830 (4); 2913 (2); 2940 (2); 2964 (6); 2996 (4b, d); 3070 (4b).

(3) *d*- α -Pinene

134 (3b, d); (208) (2b, d); 261 (3d); 306 (2d); (333) (0); 388 (3b, d); (426) (2); (465) (2); (488) (3); 564 (4); 620 (3); 667 (6); 774 (4); 822 (2); 844 (5); 885 (1); 905 (3); 930 (1); 953 (3b, d); (998) (0); 1015 (1d); 1042 (3d); 1085 (3); 1125 (2); 1163 (4); 1183 (3b, d); 1223 (3b, d); 1264 (4b, d); 1308 (2); 1328 (3b, d); 1374 (3d); 1433 (5d); 1444 (3b, d); 1468 (2); 1660 (6); 2833 (4d); 2874 (4b, d); 2912-2925 (5bb, d); 2951 (3b, d); 2988 (5d); 3031 (4b, d).

(7) This Bulletin, **9** (1934), 327.

(8) G. B. Bonino and P. Cella, *Mem. accad. Italia, Biol; Chim; Fis; Mat.*, **2** (1931), 5.

(9) G. Dupont, P. Daure and J. Allard, *Bull. soc. chim.*, **49** (1931), 1401.

(10) S. Venkateswaran and S. Bhagavantam, *Indian J. Physics*, **7** (1933), 585.

(11) P. Daure, *Compt. rend.*, **198** (1934), 725.

Table 1. (*Concluded*)(4) *d*-Verbenol

141 (4); (204) (3); (313) (2); 402 (2); (470) (1); 517 (1); 577 (2); 614 (2); 651 (1); (689) (1/2); 731 (2); 777 (3); (799) (1); 843 (2d); (925) (3d); 946 (1b, d); 973 (2d); (1007) (1/2); (1037) (1b, d); 1092 (3d); 1150 (5bb, d); (1185) (3b); 1216 (3); 1258 (3); (1312) (1/2); (1338) (1); 1376 (3); (1395) (1d); 1446 (5d); 1593 (6); 1657 (5); 2860 (3); 2908 (3b, d); 2972 (3).

(5) *d,l*- Δ^1 -Terpinenol-(4)

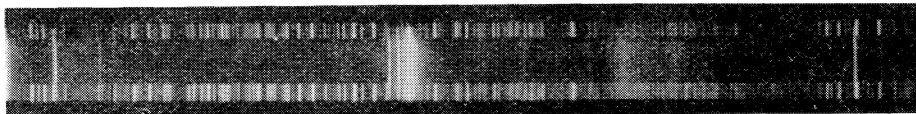
194 (1bb, d); 323 (3d); 434 (4); 455 (1/2d); 495 (1/2d); 518 (3); 546 (1/2); 568 (1/2d); 651 (3); 683 (3); 732 (8); 765 (4b, d); 802 (4b, d); 839 (1d); 864 (3d); 890 (5); 928 (2); 951 (5); 962 (1d); (996) (2); 1027 (2b); 1051 (2); 1073 (6); 1096 (1/2); 1131 (8b, d); 1163 (6d); 1250 (5d); 1312 (6bb, d); 1371 (6d); 1428 (6); 1449 (6); 1468 (4); 1682 (8); 2832 (2d); 2349 (6b); 2879 (6bb, d); 2910 (6bb, d); 2932 (6); 2966 (3); 3020 (1/2).

(6) Menthyl acetate

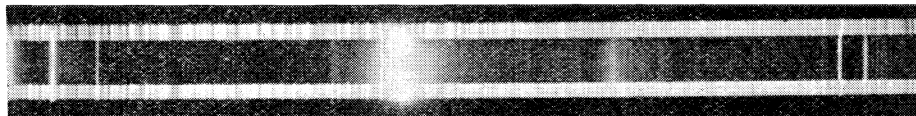
230 (1/2); 293 (3); 318 (3); (409) (3); (424) (0); 465 (2); 504 (3); 544 (4d); 596 (2); 651 (3); (717) (1/2)?; 768 (5); 776 (6); 809 (4); 846 (2); 875 (5); (905) (2); (924) (1); 930 (1); (954) (3); 975 (3); 1042 (4); (1062) (1/2); 1081 (6b, d); 1150 (6bb, d); 1163 (6bb, d); 1184 (6d); 1242 (5); 1271 (4); 1347 (3); 1381 (3d); 1443 (5); 1462 (6d); 1737 (2d); 2848 (6b, d); 2870 (6bb, d); 2930 (4d); 2966 (6d).

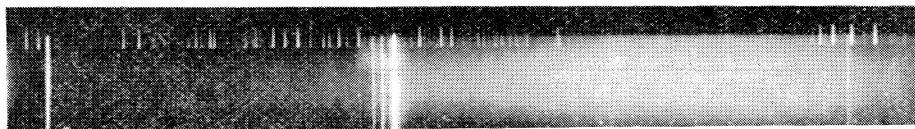
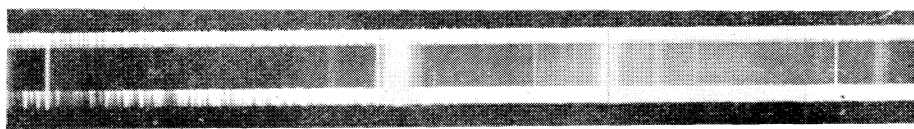
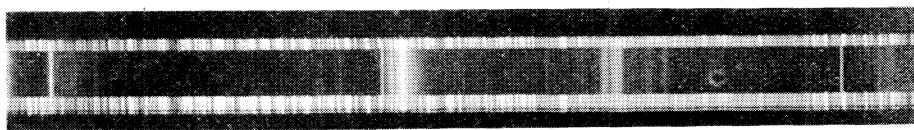
(7) Isobornyl acetate

231 (1); 260 (1); 315 (1/2); 345 (1); 387 (2b); 526 (3); 586 (1/2); 621 (5); 655 (3); 747 (2d); 803 (1d); 859 (4); 897 (2); 942 (3); 987 (2); 1022 (3); 1077 (1); 1104 (4); 1131 (2); 1164 (8); 1246 (3); 1323 (2b); 1376 (3b); 1440 (4b, d); 1473 (1/2); 1735 (3); 2874 (2); 2932-2968 (8b).

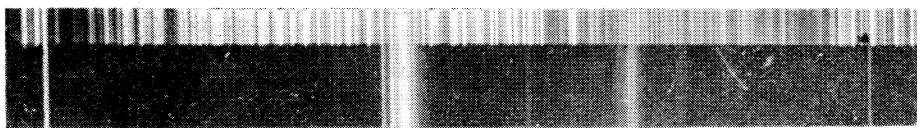


(1) Sesquichamene

(2) *d*-Sabinene(3) *d*- α -Pinene

(4) *d*-Verbenol(5) *d,l*- Δ^1 -Terpinenol-(4)

(6) Menthyl acetate



(7) Isobornyl acetate

Table 2.

Substance	<i>n</i>	No. of plates	Width of slit (10 ⁻² mm.)	Temp. (C.)	Time of expo- sure (hours)
Sesquichamene	104	258	76	24°	6
		259	76	25	14
		260	64	24	8
		261	64	23	12
<i>d</i> -Sabinene	83	176	64	19	10
<i>d</i> - α -Pinene	85	174	70	19	10
		175	64	19	10
<i>d</i> -Verbenol	54	145	90	21	12
<i>d,l</i> - Δ^1 -Terpinenol-(4)	70	172	70	19	6
		173	60	19	10
Menthyl acetate	64	266	70	23	6
		267	64	23	12
Isobornyl acetate	41	184	70	19	14

Table 3. Comparison of the Results on α -Pinene.

Bonino -Cella ⁽⁸⁾	Venkateswaran -Bhagavantam ⁽⁹⁾	Dupont etc. ⁽¹⁰⁾	Daure ⁽¹¹⁾	Nevgi-Jatkar ⁽¹²⁾	The authors
123	134		139	139	134
213	213	222	207	204	208
266	261	278	258	259	261
308	306	308	307	308	306
			335		333?
392	388	391	389	390	388
			394		
	428		424	421	426
478	476	477	467	474	465
			483		(488)
565	564	573	565	568	564
619		623	613	620	620
			623		
	647				
673	666	672	668	662	667
778	774	776	771	774	774
			789		
	816		820		822
847	844	840	845	840	844
	878		889		885
	904		908	901	905
	931		930		930
			940		
953	949	962	952	949	953
	994		1000		998
			1018		1015
1045	1042	1048	1047	1038	1042
			1070		
1086	1087	1091	1085	1081	1085
1127	1131	1134	1124	1121	1125
1174	1175	1177	1166	1167	1163
			1184		1183
			1205		
1218	1224	1234	1223	1217	1223
1268	1270	1271	1269	1262	1264
	1305	1299	1309		1308

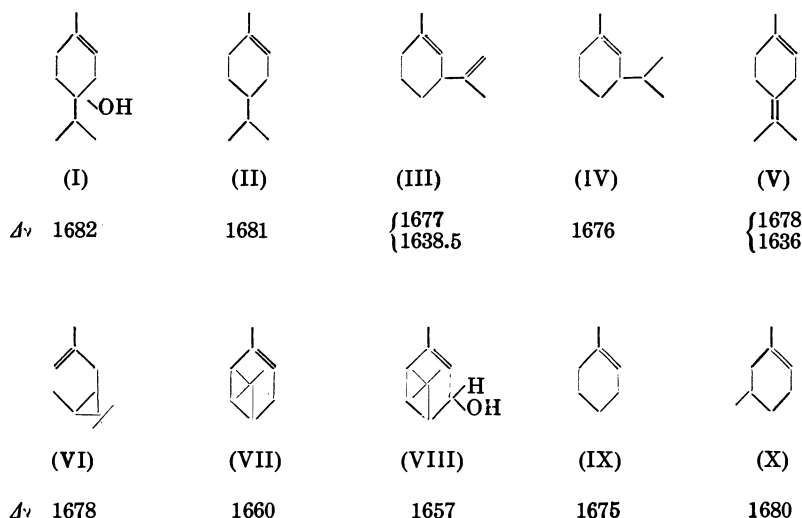
(12) G. V. Nevgi and S. K. Kulkarin Jatkar, *J. Indian Inst. Sci.*, **17A** (1934), 189.

Table 3. (*Concluded*)

Bonino -Cella	Venkateswara -Bhagavantam	Dupont etc.	Daure	Nevgi-Jatkar	The authors
1328	1332	1332	1330 1339	1324	1328
1378	1375 1436	1383 1430	1377 1437	1376	1374 1433
1449			1448 1457	1445	1444
		1490	1476		1468
1656	1661 2833	1672	1659	1653	1660 2833
2863	2876			2876	2874
2923	2917			2914	2912
					2925
	2948				2951
2987	2989			2988	2988
3034	3029			3025	3031
3110					
3157					

Discussion. From the point of view of organic chemists, sesquichamene as well as cedrene is a tricyclic sesquiterpene. As shown in Table 4, most of the Raman lines in sesquichamene agree well with those in cedrene. The remarkable difference is that the intense lines corresponding to $\Delta\nu$ 733, 656 and 630 cm^{-1} in cedrene, disappear in sesquichamene, and that the Raman frequency associated with the C:C linkage is found at $\Delta\nu$ 1682 cm^{-1} in sesquichamene, while at 1666 cm^{-1} in cedrene. This seems to lead to the consideration that sesquichamene may have the chemical constitution similar to that of cedrene, excepting the ring containing the C:C linkage. In the previous paper⁽²⁾, we summarized the Raman frequencies associated with the C:C linkage, and concluded that -CH₃ has the frequency of $\Delta\nu$ 1660 cm^{-1} , while -CH₃ has that of $\Delta\nu$ 1675 cm^{-1} . In the case of sesquichamene, the fact that the corresponding frequency is found at $\Delta\nu$ 1682 cm^{-1} , seems to suggest that sesquichamene may have a 1-methyl-cyclohexene-(1) ring if cedrene has a linkage of 1-methyl-cyclopentene-(1), as suggested by the

organic chemist.⁽¹³⁾ The fact that the corresponding frequencies are found at $\Delta\nu$ 1682 cm^{-1} in *d,l*- Δ^1 -terpinenol-(4) (I), 1681 cm^{-1} in carvomenthene (II)⁽¹⁰⁾ 1677 and 1638.5 cm^{-1} in sylvestrene (III)⁽¹⁴⁾, 1675.5 cm^{-1} in Δ^1 -*m*-menthene (IV)⁽¹⁴⁾, 1681 and 1668 cm^{-1} in terpinolene (V)⁽¹⁴⁾, 1636 and 1678 cm^{-1} in Δ^3 -carene (VI)⁽¹⁵⁾, 1660 cm^{-1} in α -pinene (VII), 1657 cm^{-1} in *d*-verbenol (VIII), 1675 cm^{-1} in 1-methyl-cyclohexene (IX)⁽¹⁶⁾ and 1680 cm^{-1} in 1,4-dimethyl-cyclohexene-(1)⁽¹⁶⁾, as shown below seems to give a confirmation for it.



When we take the frequencies of 1638.5 and 1636 cm^{-1} as due to the ethylene linkage of the side chain, in the case of III and V respectively, we may conclude that the frequency associated with the ethylene linkage in the

ring, is found at $\Delta\nu$ 1680 cm^{-1} in the case of or type, and $\Delta\nu$ 1660 cm^{-1} in the case of . It is possible to consider that sesquichamene

has a 1-methyl-cyclohexene ring in its molecule if there is not any remarkable spanning effect due to the tricyclic bond upon the C:C linkage.

(13) K. Káfuku, *J. Chem. Soc. Japan*, **55** (1934), 1235.

(14) G. Dupont, P. Daure and J. Lévy, *Bull. Soc. Chim.*, **51** (1932), 921.

(15) G. Dupont and R. Gachard, *ibid.*, **51** (1932), 1579.

(16) M. Godehot, E. Canales and G. Cauquil, *Compt. rend.*, **197** (1933), 1407.

Table 4.

Sesqui- chamene	Cedrene	Sabinene	α -Pinene	<i>d</i> - Verbenol	<i>dl</i> - <i>dl</i> - terpinenol (4)	Menthyl acetate	Isobornyl acetate
91	(87)						
132	(124)	(120)?	134	141			
	144				194		
	189	(169)	(208)	(204)		230	260
	237	(214)					
254	260		261			293	315
280	(288)				329	318	
(302)	308	306	306	(313)			345
	317		(333)?			(409)	337
336	340	333				(424)	
360	(364)	362			434	465	
386	389	(373)	388	402			
(407)	410		426				
434	437	441		(470)?	455		
	454		465		495		
496	491	491	488		518	504	526
		509		517	546	544	
539	532	566	564	577	568	596	596
572	571						
590	587						
604	611			614			
	630	634	620				
	656	655	667	651	651	651	655
(684)	698			(689)	683		
	733			730	732	(717)?	747
770	780	785	774	777	765	768	
						776	
	802	808		(799)	802	809	803
814	819		822				
843	(833)		844	843	839	846	859
	850	866			864	875	
882	(873)	882	885		890		897
907	915	915	905			(905)	
926							
934	938	930	930	(925)	928	(924)?	
						930	942
954	965	954	953	946	951	(954)	

Table 4. (*Concluded*)

Sesqui- chamene	Cedrene	Sabinene	α -Pinene	<i>d</i> - Verbenol	<i>dl</i> - <i>dl</i> - Terpinenol-(4)	Menthyl acetate	Isobornyl acetate
964					962	975	
988	986	989	998	973	(996)		987
1000	1001		1015	(1007)	1027		1022
1022	1024					1042	
(1042)	1038	1031	1042	(1037)	1051	(1062)	
1058	1066	1067			1073	1081	1077
	(1087)		1085	1092	1096		
1100	1105	1109					1104
1119	1127		1125		1131		1131
	1143	1145		1150		1150	
1155	1167	1170	1163		1163	1163	1164
(1186)		1183	1183	(1185)		1184	
1192	1201	1197					
1208	1219			1216			
	1237	1214	1223			1242	1246
1263	1275	1270	1264	1258	1250	1271	
1296	1297	1308	1308	(1312)	1312		1323
(1322)	1325		1328	(1338)			
(1346)	1350					1347	
1375	1375	1379	1374	1376	1371	1381	1376
1398		1415		1395			
1443	1434	1438	1433		1428		
1453	1452	1447	1444	1446	1449	1443	1440
1471	1475	1468	1468	(1469)	1468	1462	1473
(1595)							
1647	(1646)?			1593			
1680	1666	1656	1660	1657	1682	1737	1735
2844	2830	2830	2833		2832		
					2849		
2869	2875		2874	2860	2879	2848	2874
2908	2916	2913	2912	2908	2910	2870	
	2937	2940	2925		2932	2930	2932
2966	2967	2964	2951	2972	2966	2966	(2968)
3006		2996	2988				
3084	3030	3070	3031		3020		
3167							

The Raman frequencies of sesquichamene, cedrene, *d*-sabinene, *d*- α -pinene, *d*-verbenol, *d,l*- Δ^1 -terpinenol-(4), menthyl acetate and isobornyl acetate are tabulated in Table 4 for comparison. A glance at Table 4 enables us to notice that cedrene and sesquichamene have the most complicated Raman spectra. The frequencies of ca. $\Delta\nu$ 496–532 and 572 cm^{-1} are found in all the substances in the present investigation. These may correspond to 491–514 and 590 cm^{-1}

in the condensed ring compounds which have the linkage $\begin{array}{c} \text{C} \quad \text{C} \\ \diagdown \quad \diagup \\ \text{C}-\text{C} \\ \diagup \quad \diagdown \\ \text{C} \quad \text{C} \end{array}$, as shown in

one of our previous papers.⁽¹⁷⁾ The Raman lines in the region of $\Delta\nu$ 1453 cm^{-1} , which are associated with the CH_2 group, are observed in the following six substances at the nearly equal intervals, as shown in Table 5.

Table 5.

Sesquichamene	Cedrene	Sabinene	α -Pinene	<i>d</i> -Verbenol	<i>d,l</i> - Δ^1 -Terpinenol-(4)
1398 (4)		1415 (8)		1395 (1d)	
1434 (5)	1434 (8)	1438 (4d)	1433 (5d)		1428 (6)
1453 (4d)	1452 (8)	1447 (5d)	1444 (3b, d)	1446 (5d)	1449 (6)
1471 (4)	1475 (6b, d)	1468 (4d)	1468 (2)	1469 (6)	1468 (4)

The frequency of $\Delta\nu$ 1464 cm^{-1} is found also in naphthalene, which has not any CH_2 group. The further discussion will be reported after studying the Raman spectra of other terpenes, which are in the course of experiments.

Summary.

(1) The Raman spectra of the following substances have been measured : Sesquichamene, *d*-sabinene, *d*- α -pinene, *d*-verbenol, *d,l*- Δ^1 -terpinenol-(4), menthyl acetate, and isobornyl acetate.

(2) The occurrence of the intense line at $\Delta\nu$ 1682 cm^{-1} seems to suggest that sesquichamene may have a linkage of 1-methyl-cyclohexene-(1) if cedrene has a linkage of 1-methyl-cyclopentene-(1).

(17) This Bulletin, **11** (1936), 321.

In conclusion, the authors wish to express their thanks to Ass. Prof. T. Nozoe and his co-workers, for the supply of the samples. A part of expenses of this experiment was paid from a grant given by the Nippon Gakujutu Sinko Kwai, to which thanks are due.

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OPTICAL ROTATORY DISPERSION OF SOME BRIDGED DERIVATIVES OF ALKYL TARTRATES.*

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In marked contrast to tartaric acid and its esters whose rotatory dispersion is anomalous⁽¹⁾, many of the bridged derivatives of tartaric acid are known to exhibit simple rotatory dispersion⁽²⁾, i. e. the dispersion in the transparent region can be expressed by a single term of Drude's equation, $\alpha = k / (\lambda^2 - \lambda_0)$, which was first demonstrated by Austin and Carpenter⁽³⁾ in the cases of dimethylene tartrate, in which the bridging takes place between the hydroxyl and carboxyl groups (type A) and of monomethylene tartaric acid, where the two alcoholic hydroxyl groups are linked together (type B), and then by Austin and Parker⁽⁴⁾ in the case of diacetyl tartaric anhydride, in which the bridging is performed between the two carboxyl groups (type C). Of the B type, two more bridged derivatives were added on the list later by Brynmor Jones⁽⁵⁾, namely dimethyl and diethyl benzylidene-tartrates.

Recently the author obtained some bridged derivatives of alkyltartrates of the B type such as diethyl isopropylidene-tartrate (I)⁽⁶⁾, dimethyl isopropyl-

* Studies on the synthesis of bridged derivatives of tartaric acid and their optical activity. Paper III.

(1) Lowry and Austin, *Trans. Roy. Soc. (London)*, **222 A** (1922), 293; Lowry and Cutter, *J. Chem. Soc.*, **121** (1922), 532; Bruhat, *Trans. Faraday Soc.*, **26** (1930), 400.

(2) Lowry and Dickson, *Trans. Faraday Soc.*, **10** (1914), 96.

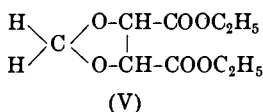
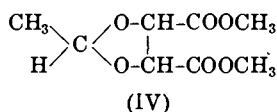
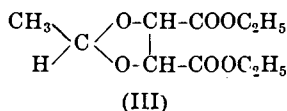
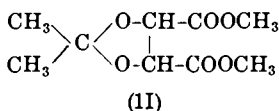
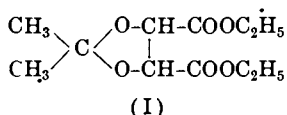
(3) *J. Chem. Soc.*, **125** (1924), 1939.

(4) *J. Chem. Soc.*, **127** (1925), 1926.

(5) *J. Chem. Soc.*, **1933**, 788.

(6) Tsuzuki, this Bulletin, **10** (1935), 255.

lidene-tartrate (II), diethyl ethylidene-tartrate (III), dimethyl ethylidene-tartrate (IV) and diethyl methylene-tartrate (V)⁽⁷⁾.



These compounds are all liquid substances, in contrast to the hitherto examined compounds which are all in the solid state and whose rotatory dispersion was necessarily observed in solution, which induces the author to take interest in examining the rotatory dispersion of these compounds whether the dispersion is really simple or complex, especially when the following fact is recalled that ethyl tartrate in pure liquid state shows the characteristics of anomalous dispersion in the visible region, i. e. inflection maximum and reversal of sign in the curve of the $\alpha-\lambda$ diagram. And if the dispersion be actually shown to be simple, it may be of no small interest further to inquire into the characteristic wave length λ_0 by comparing its value with those of similar compounds. As already recognized, the anomalous rotatory dispersion of tartaric acid and its esters mentioned above is considered to be due to two partial rotations with opposite signs, and actually the dispersion has been proved to conform to two terms of Drude's equation: $\alpha = k_1/(\lambda^2 - \lambda_1^2) - k_2/(\lambda^2 - \lambda_2^2)$. This is attributed, on the other hand, to the free rotation of the two halves of the molecule about the central bond, since it has been observed that simple rotatory dispersion is associated with ring formation⁽⁸⁾, by which process the free rotation must be impeded⁽⁹⁾. It may therefore be admitted that with ring formation one of the two terms of Drude's equation appears to become negligibly small, thus leaving in the derivative of the type A only a negative term and in those of the type B as well as C a positive term. These considerations direct us to an interesting problem about the relation between the chemical structure and the optical activity or optically active absorption band, particularly about "identity of structure" and

(7) Tsuzuki, this Bulletin, **11** (1936), 362.

(8) Austin, *J. Chem. Soc.*, **125** (1924), 1941; **127** (1925), 1926; *Trans. Faraday Soc.*, **26** (1930), 415.

(9) The impedance of free rotation may also be caused by the introduction of bulky substituents as in diacetyl-tartaric acid which exhibits simple dispersion. Austin, *J. Chem. Soc.*, **1928**, 1828.

“persistence of absorption”. The present paper aims also to deal with this problem.

The experimental results are shown in Tables 1-5.

Table 1. Rotatory Dispersion of Diethyl Isopropylidenetartrate (I).

$$\alpha = \frac{-17.775}{\lambda^2 - 0.03110}, \quad [\alpha]^{20} = 0.8948 \alpha,$$

$$d^{20} = 1.1175, \quad t = 20^\circ, \quad l = 1 \text{ dm.}$$

λ	$\alpha_{\text{obs.}}$	$\alpha_{\text{calc.}}$	Difference
6362	— 47.49°	— 47.56°	+ 0.07°
6234	— 49.76	— 49.71	— 0.05
5893	— 56.23	— 56.23	±
5461	— 66.43	— 66.54	+ 0.11
5219	— 73.66	— 73.68	+ 0.02
5086	— 78.28	— 78.12	— 0.16
4916	— 84.33	— 84.41	+ 0.08
4680	— 94.64	— 94.58	— 0.06
4358	— 111.70	— 111.90	+ 0.20

Table 2. Rotatory Dispersion of Dimethyl Isopropylidenetartrate (II).

$$\alpha = \frac{-19.847}{\lambda^2 - 0.03012}, \quad [\alpha]^{20} = 0.8025 \alpha,$$

$$d^{20} = 1.1900, \quad t = 20^\circ, \quad l = 1 \text{ dm.}$$

λ	$\alpha_{\text{obs.}}$	$\alpha_{\text{calc.}}$	Difference
6708	— 47.40°	— 47.27°	— 0.13°
6438	— 51.74	— 51.63	— 0.11
6234	— 55.24	— 55.36	+ 0.12
5893	— 62.68	— 62.59	— 0.09
5461	— 74.06	— 74.06	±
5218	— 81.78	— 81.95	+ 0.17
5086	— 86.70	— 86.84	— 0.14
4916	— 93.85	— 93.85	±
4799	— 99.17	— 99.10	— 0.07
4358	— 124.0	— 124.2	+ 0.2

Table 3. Rotatory Dispersion of Diethyl Ethylidenetartrate (III).

$$\alpha = \frac{-25.150}{\lambda^2 - 0.04400}, \quad t = 16^\circ, \quad l = 1 \text{ dm.}$$

$$d^{16} = 1.1520, \quad [\alpha]^{16} = 0.8680 \alpha$$

λ	$\alpha_{\text{obs.}}$	$\alpha_{\text{calc.}}$	Difference
6708	- 61.72°	- 61.95°	+ 0.23°
6438	- 67.55	- 67.87	+ 0.32
6234	- 72.95	- 72.97	+ 0.02
5893	- 83.20	- 82.94	- 0.26
5461	- 98.75	- 98.94	+ 0.19
5218	-110.45	-110.17	- 0.28
5086	-117.00	-117.17	+ 0.17
4916	-127.08	-127.23	+ 0.15
4799	-134.89	-134.94	+ 0.05
4358	-172.45	-172.32	- 0.13

Table 4. Rotatory Dispersion of Dimethyl Ethylidenetartrate (IV).

$$\alpha = \frac{-15.427}{\lambda^2 - 0.04324}, \quad t = 16^\circ, \quad l = 0.5 \text{ dm.}$$

$$d^{16} = 1.2450, \quad [\alpha]^{16} = 1.6065 \alpha$$

λ	$\alpha_{\text{obs.}}$	$\alpha_{\text{calc.}}$	Difference
6708	- 37.79°	- 37.93°	+ 0.14°
6438	- 41.60	- 41.55	- 0.05
6234	- 44.65	- 44.65	±
5893	- 50.65	- 50.75	+ 0.10
5461	- 60.52	- 60.52	±
5218	- 67.61	- 67.35	- 0.26
5086	- 71.50	- 71.61	+ 0.11
4916	- 77.73	- 77.75	+ 0.02
4799	- 82.61	- 82.43	- 0.18
4358	-105.05	-105.16	+ 0.11

Table 5. Rotatory Dispersion of Diethyl Methylenetartrate (V).

$$\alpha = \frac{-13.748}{\lambda^2 - 0.04585}, \quad t = 20^\circ, \quad l = 0.5 \text{ dm.}$$

$$d^{20} = 1.1958, \quad [\alpha]^{20} = 1.6725 \alpha.$$

λ	$\alpha_{\text{obs.}}$	$\alpha_{\text{calc.}}$	Difference
6708	— 33.93°	— 34.02°	+ 0.09°
6438	— 37.21	— 37.29	+ 0.08
6234	— 40.25	— 40.11	— 0.14
5893	— 45.90	— 45.62	— 0.28
5461	— 54.48	— 54.49	+ 0.01
5218	— 60.83	— 60.71	— 0.12
5086	— 64.62	— 64.62	±
4916	— 70.18	— 70.21	+ 0.03
4799	— 74.52	— 74.50	— 0.02
4358	— 95.25	— 95.41	+ 0.16

As shown in the tables, the rotatory dispersions of these compounds can be expressed by a one-term Drude equation, so they are apparently simple in the visible region, which may be further confirmed by the dispersion ratio and the optically active absorption band calculated from the dispersion constant λ_0^2 (Table 6).

Table 6. Dispersion Ratio and Absorption Band of Bridged Derivatives of Tartaric Acid.

Bridged derivative	Dispersion ratio $\alpha_{4358} / \alpha_{5461}$	λ_0 (Å)
Diethyl isopropylidenetartrate (I)	1.681	1763
Dimethyl isopropylidenetartrate (II)	1.674	1735
Diethyl ethylidenetartrate (III)	1.742	2102
Dimethyl ethylidenetartrate (IV)	1.736	2080
Diethyl methylenetartrate (V)	1.748	2141

The values of the dispersion ratio and the absorption band are those which may be expected to occur in those compounds whose rotatory dispersions are simple. It may therefore be safely concluded that the rotatory dispersions of these compounds are not only normal, but very probably simple.

From Table 6 it is also noticed that a perceptible difference exists between the characteristic wave length of the derivatives formed by the condensation of aldehydes (III, IV, V) and that of those obtained from acetone (I, II): viz. the former compounds possess the characteristic frequency at about 2100 Å, while those of the latter are located at about 1750 Å.

For the comparison, the values of the dispersion ratio and the characteristic wave length of several saturated aliphatic compounds (including some with aromatic radical) exhibiting simple rotatory dispersion is cited, (Table 7).

Table 7. Dispersion Ratio and Characteristic Wave Length of Aliphatic Compounds.

	Dispersion ratio $\alpha_{4358} / \alpha_{5461}$	Characteristic wave length (Å)	Author
Primary amyl alcohol	1.700	1880	} Lowry and Dickson ⁽¹⁰⁾
Isovaleric acid	1.710	1940	
Ethyl isovalerate	—	1710	
Methylene-tartaric acid (in water)	1.740	2100	Levene, Rothen and Marker ⁽¹¹⁾
Dimethyl benzylidene- tartrate (in ethyl- acetate)	1.739	2087	} Austin and Carpenter ⁽³⁾
Diethyl benzylidene- tartrate (in methyl- alcohol)	1.739	2087	
			} Jones ⁽⁵⁾

It is clearly seen from Table 7 that all the bridged derivatives of tartaric acid formed by the condensation of aldehydes possess the characteristic wave length at about 2100 Å, but the compounds derived from acetone (Table 6) considerably shorter wave lengths which are just coincident with that of carboxylic ester, but are somewhat shorter than those of free carboxylic acid as well as of primary amyl alcohol. Although it is a tempting task to elucidate the relation between the absorption band and the chemical structure, it is still a doubtful question whether this latter wave length (1750 Å) corresponds with the absorption band of saturated aliphatic carboxylic ester, for the rotatory dispersion of pure ethyl tartrate can be expressed by the equation

$$[\alpha] = 25.005 / (\lambda^2 - 0.03) - 20.678 / (\lambda^2 - 0.056),^{(12)}$$

which possesses the two characteristic wave lengths λ_1 and λ_2 at 1730 Å and 2370 Å respectively, and the former wave length (1730 Å) has practically the

(10) *J. Chem. Soc.*, **103** (1913), 1067.

(11) *J. Chem. Physics*, **1** (1933), 662.

(12) Lowry and Cutter, *J. Chem. Soc.*, **121** (1922), 532.

same numerical value as the characteristic wave length of the compounds from acetone, but of opposite sign, and the latter negative term of this equation will presumably be attributed to the carboxyl group.⁽¹³⁾

Finally it will be remarked that the above-mentioned characteristic frequency of the bridged derivatives from aldehydes (2100 Å) can neither be identified with that of the positive nor that of the negative term of the rotatory dispersion of ethyl tartrate (and of tartaric acid⁽¹³⁾). To interpret this may be quite difficult. But it will be permitted to suppose that in the present case the absorption maximum may be displaced to a more or less extent through the bridging of the hydroxyl groups by means of chromophoric molecules, although the optically active absorption band of a substituent may generally be retained in the derivatives. The author wishes to further the studies of the rotatory dispersion of similar compounds touching this point.

The measurements of the rotatory dispersion have been enabled by the kindness of Dr. T. Higashi and Dr. H. Shiba of the Institute of Physical and Chemical Research, Tokyo, to whom the author wishes to express his grateful acknowledgements.

Summary.

(1) Rotatory dispersions in the region from 6708 Å to 4358 Å of diethyl and dimethyl isopropylidene-tartrates, diethyl and dimethyl ethylidene-tartrates and diethyl methylene-tartrate, bridged derivatives of alkyl-tartrates, in which both the hydroxyls are linked with the rest of the carbonyl compounds have been measured, all with no solvent, and shown to be expressed by one term of Drude's equation.

(2) It is pointed out that the absorption bands of the condensation products from ketone are located at about 1750 Å, whereas those of the compounds derived from aldehydes at about 2100 Å, and the relation between these values and the chemical constitution is discussed.

(3) Considering the fact that the dispersion ratio $\alpha_{4358}/\alpha_{5461}$ and the characteristic wave length λ_0 range from 1.674 to 1.748 and from 1735 Å to 2141 Å respectively, the rotatory dispersion of these compounds is concluded to be very probably simple.

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(13) It will be noted also that Bruhat has located the two characteristic frequencies of the anomalous rotatory dispersion of aqueous solutions of tartaric acid at 1750 Å and 2330 Å, *Trans. Faraday Soc.*, **26** (1930), 400.

ÜBER DEN GEHALT DES SALZWASSERS AUS PETROLEUM-QUELLEN AN SCHWEREM WASSER. I.⁽¹⁾

Von Toshizo TITANI und Kenzo OKABE.

Eingegangen am 12. Juni 1936. Ausgegeben am 28. September 1936.

Inhaltsübersicht. Wir bestimmten mit Hilfe des spezifischen Gewichts den Gehalt des Salzwassers von zehn japanischen Petroleumquellen an schwerem Wasser. Dabei fanden wir, dass dieser nicht nur von der Tiefe, aus der das Wasser stammt, sondern hauptsächlich von der Erdbeschaffenheit um die Ölquellen herum beeinflusst wird.

Einleitung. Viele Autoren haben festgestellt, dass das Wasser verschiedenen natürlichen Herkommens oft ein grösseres bzw. kleineres spezifische Gewicht als gewöhnliches Wasser (meistens Leitungswasser) besitzt, was sie auf die Zu- bzw. Abnahme des Gehalts an schwerem Wasser⁽²⁾ zurückführten. Unter anderen wurde das Meerwasser in dieser Hinsicht von vielen Forschern besonders eingehend untersucht und durchschnittlich um 2γ schwerer als gewöhnliches Wasser gefunden. Gleichzeitig aber zeigten hauptsächlich die umfangreichen Untersuchungen von Wirth, Thompson und Utterback,⁽³⁾ dass dieser Dichteüberschuss des Meerwassers nicht genau konstant ist, sondern sich mit dem Ort und der Meerestiefe ein wenig, doch deutlich verändert. Besonders interessant ist die Abhängigkeit des spezifischen Gewichts des Meerwassers von der Meerestiefe. Den Untersuchungen von Wirth und seinen Mitarbeitern nach nimmt das spezifische Gewicht des Meerwassers nicht, wie man zuerst erwartete, mit zunehmender Tiefe gleichmässig zu, sondern die Veränderung der Dichte des Meerwassers mit der Tiefe scheint irgendeinem ganz anderen Gesetze zu folgen. Das Wasser, das aus 2,000 m. Tiefe stammte, war z.B. keineswegs schwerer als das oberflächliche, ja das erstere erwies sich sogar als ein wenig leichter als das letztere. Leider ist man sich über die Ursache bzw. Ursachen dieser hochinteressanten Untersuchungsergebnisse noch völlig im Dunkeln.

(1) Vorläufig mitgeteilt in diesem Bulletin, **10** (1935), 259. Auszug aus der japanischen Mitteilung im *Nippon Sekiyu Gijutsu Kyokai Shi* (*Journal der japanischen Assoziation der Petroleum-Techniker*), **4** (1936), 1.

(2) Unter dem Wort „schweres Wasser“ verstehen wir hier nicht nur D₂O, sondern auch alle Arten von Wasser, die schwere Isotope von Wasserstoff und Sauerstoff enthalten.

(3) H.E. Wirth, T.G. Thompson und C.L. Utterback, *J. Am. Chem. Soc.*, **57** (1935), 400; *Nature*, **135** (1935), 662.

Was das tief unter der Erde befindliche Wasser anbetrifft, so haben einige Forscher bis heute hauptsächlich das Wasser aus Petroleumquellen, das oft Salzwasser genannt wird, untersucht, so A.F. Scott⁽⁴⁾ das Salzwasser aus zwei amerikanischen Ölbohrlöchern von je 5,000 Fuss Tiefe. Aber er fand dabei zwischen dem gereinigten Salzwasser und gewöhnlichem Wasser keinen Unterschied im spezifischen Gewicht. Doch war die Genauigkeit seiner Messung ($\pm 2\gamma$) nicht sehr gross. Später untersuchten Briscoe⁽⁵⁾ und seine Mitarbeiter das Wasser vom persischen Ölfeld und fanden es um 1.9γ schwerer als Londoner Leitungswasser. Auch wir haben vor kurzem das Salzwasser von zehn verschiedenen japanischen Petroleumquellen auf seinen Gehalt an schwerem Wasser untersucht. Die zum Versuch notwendigen Wasserproben erhielten wir durch die freundliche Vermittlung von Dr. Y. Chitani im Kaiserlichen geologischen Forschungsbüro von der Nippon Sekiyu Kaisha (Nippon Petroleum Co.) und der Nippon Kogyo Kaisha (Nippon Bergbau Co.), wofür wir an dieser Stelle allen unseren herzlichsten Dank aussprechen möchten.

Untersuchung. Wir bestimmten den Gehalt der Wasserproben an schwerem Wasser mit Hilfe des spezifischen Gewichts dieser Proben. Weil aber das direkt vom Ölfeld bezogene Salzwasser stets ziemlich stark durch Öl und verschiedene anorganische Substanzen verunreinigt war, musste es zunächst vollständig gereinigt werden. Zu diesem Zweck wurde das Probewasser in Dampfform über bis zu Rotglut erhitztes Kupferoxyd geleitet. Dies wurde zwei bis dreimal wiederholt, bis alle flüchtigen Verunreinigungen dadurch oxydiert waren. Das so behandelte Wasser wurde dann mit Natron und Kaliumpermanganat versetzt und langsam destilliert. Nötigenfalls wurde diese Destillation zweimal nacheinander durchgeführt. Das so erhaltene Destillat wurde zum Schluss durch drei aufeinander folgende Destillationen im kohlenstofffreien Luftstrom gereinigt. Die erste Destillation führten wir unter Zusatz von Phosphorperoxyd, die zweite von Bariumoxyd und die letzte ohne Zusatz aber unter Verwendung des Quarzkühlers aus.

Das spezifische Gewicht des so gereinigten Wassers verglichen wir mittels eines Quarzschwimmers nach der Schwebemethode mit dem ebensogut gereinigten Osaka-Leitungswasser. Die Messgenauigkeit dürfte $\pm 0.5\gamma$ betragen. Nach Beendigung der ersten Dichtemessung wurde das Probewasser nochmals genau nach der obenangegebenen Methode gereinigt und einer zweiten Dichtemessung unterworfen. Dieses Verfahren, in einer Reinigung und der sich anschliessenden Dichtemessung bestehend, wiederholten wir zwei- bis dreimal und berechneten aus den einzelnen Messresultaten den Mittelwert.

(4) A.F. Scott, *Science*, **79** (1934), 565.

(5) H.J. Emeléus, F.W. James, A. King, T.G. Pearson, R.H. Purcell und H.V.A. Briscoe, *J. Chem. Soc.*, **1934**, 1948.

Die so erhaltenen Mittelwerte des Dichteunterschiedes Δs sind in der letzten Reihe der Tabelle wiedergegeben, wo im Vergleich mit dem spezifischen Gewicht des Osaka-Leitungswassers die Zahl mit dem + Zeichen die Zunahme und die mit dem — Zeichen die Abnahme des spezifischen Gewichte des Probewassers bedeutet.

Untersuchungsergebnisse

Gruppe	Nr.	Ölquelle	Tiefe der Bohrung in m.	Δs in γ
I	1	Kashiwasaki, Nr. 69	1,100	+0.4
	2	„ Nr. 81	1,150	+0.4
	3	„ Nr. 87	1,155	± 0.0
	4	„ Warimati	1,405	+0.4
	5	„ Takamati, Nr. 2	1,300	—0.1
	6	„ „ Nr. 3	1,460	—0.4
II	7	Akita, Asahigawa	410	± 0.0
	8	„ Katte	833	+1.6
	9	„ Kinshohjisan	754	+1.7
III	10	Akita, Omonogawa	31	—1.5

Die untersuchten Proben kann man zweckmässig in drei Gruppen einteilen. Die I. Gruppe besteht aus sechs Proben, Nr. 1 bis 6, die alle vom Etigo-Ölfeld stammen, die II. Gruppe aus drei Proben vom Akita-Ölfeld und die III. Gruppe nur aus Probe Nr. 10 vom Omonogawa im Akita-Ölfeld. Aus diesen Untersuchungsergebnissen ersieht man sofort, dass zwischen dem spezifischen Gewicht des Salzwassers und der Tiefe des Bohrloches keine einfache Beziehung besteht. Obwohl die Bohrlöcher bei der Gruppe I viel tiefer als die der anderen zwei Gruppen sind, besitzt das Wasser der Gruppe I innerhalb des Messfehlers ($\pm 0.5 \gamma$) doch dasselbe spezifische Gewicht wie gewöhnliches Wasser. Dagegen ist das Wasser der Proben Nr. 8 und 9 der Gruppe II, das aus Bohrlöchern stammt, die viel weniger tief als die der Gruppe I sind, deutlich schwerer als gewöhnliches Wasser sowie das der Proben der Gruppe I. Ausserdem haben wir einen Fall, nämlich Nr. 10, wo das Probewasser sogar leichter als gewöhnliches Wasser ist.

Diskussion. Die obigen Untersuchungsergebnisse legen die Vermutung nahe, dass bei dem Gehalt des Salzwassers an schwerem Wasser nicht bloss die Tiefe des Bohrloches, sondern noch mehr die Erdbeschaffenheit um die Ölquellen herum eine wichtige Rolle spielt. Über die Entstehung des Salz-

wassers in den Petroleumquellen stimmen die Ansichten nicht ganz überein. Was aber das Ölfeldwasser der Gruppen I und II (d.h. von Nr. 1 bis 9) anbetrifft, so herrscht die Meinung, dass dieses Wasser ursprünglich Meerwasser war, sich aber mit der Zeit mehr oder weniger mit Zirkulationswasser bzw. Bodenwasser gemischt hat. Sollte dies der Fall sein, so ist anzunehmen, dass das Wasser in diesen Ölfeldern ähnlich wie das Meerwasser von heute ursprünglich schwerer als das Bodenwasser war. Aber diese höhere Dichte hat später durch das Hinzutreten des Bodenwassers, welches Hinzutreten natürlich von der Erdbeschaffenheit um die Ölbehälter herum beeinflusst wird, mehr oder weniger abgenommen, bis sie endlich, wenn die Erdschichten in der Umgebung des Bohrloches für Wasser durchlässig waren, im Laufe langer Zeit durch die Beimischung von reichlichen Mengen Bodenwasser fast ganz verschwand. Dagegen behielt das Salzwasser eines Ölbehälters in einer sehr dichten Erdschicht seine eigentliche Isotopenzusammensetzung ohne merkliche Veränderung bei und ist heute noch schwerer als das Bodenwasser. Von diesem Gesichtspunkt aus wollen wir die vorliegenden bei den Proben Nr. 1 bis 9 gewonnenen Untersuchungsergebnisse diskutieren.

Die Ölbehälter der Proben Nr. 1 bis 6 der Gruppe I befinden sich alle im oberen Teil der Teradomari-Schicht des Miozäns.⁽⁶⁾ Obwohl diese Schicht, deren Dicke durchschnittlich 1,000 m. beträgt, hauptsächlich aus schwarzem Schieferthon besteht, enthält sie doch beträchtliche Mengen von rauhem vulkanischen Tuff. Auf dieser Schicht lagern noch einige Schichten, bei denen es sich entweder ebenfalls um rauhen sandartigen Schieferthon oder um Wechsellagerungen von Sandstein und Schieferthon handelt. Zuletzt finden sich Sand und Ton aus der Quartärperiode. Es ist auch bekannt, dass diese Gegend reich an Verwerfungen ist. Dieser geologische Befund um die Ölquellen herum legt die Vermutung sehr nahe, dass grosse Mengen von Bodenwasser in die Ölbehälter diffundiert sind, wodurch der Dichteüberschuss des darin befindlichen Salzwassers in hohem Masse abnahm. Für die Richtigkeit dieser Vermutung spricht, dass wir bei den Proben der Gruppe I fast dasselbe spezifische Gewicht wie das des gewöhnlichen Wassers fanden.

Die Ölbehälter, denen die Proben Nr. 7 bis 9 der Gruppe II entstammen, befinden sich in der Funakawa-Schicht des Miozäns.⁽⁶⁾ Bei Nr. 9 lagert auf dieser Schicht noch die Kitaura-Schicht, während bei Nr. 7 und 8 auf der Funakawa-Schicht bis zur Erdoberfläche keine Schichten mehr liegen. Die ölhaltende Funakawa-Schicht, deren Dicke durchschnittlich 700 m. beträgt, besteht aus schwarzem Schieferthon und die darunter liegende 400 m. dicke Onnagawa-Schicht aus kieselartigem Schieferthon. Da alle diese Schichten sehr dicht sind, muss das Eindringen des Bodenwassers in den darin befind-

(6) I. Ohmura, „Erdölgeologie“, 1932 (japanisch).

lichen Ölbehälter sehr schwer vor sich gegangen sein, so dass sich die höhere Dichte des Salzwassers in diesen Ölbehältern bis heutigentages fast nicht verändert hat, wofür die Tatsache spricht, dass die Proben Nr. 8 und 9 je um 1.6γ bzw. 1.7γ schwerer als gewöhnliches Wasser waren. Nur bei der Probe Nr. 7 lag die Abweichung des spezifischen Gewichts von dem des gewöhnlichen Wassers innerhalb der Messfehlergrenzen. Aber dies dürfte von irgendeiner lokalen Ursache, z.B. von einer Spalte oder dergleichen, herrühren.

Das Wasser von Probe Nr. 10 verdankt seine Entstehung ganz anderen geologischen bzw. geographischen Verhältnissen als das der anderen Proben. Das Bohrloch von Probe 10 befindet sich auf dem Flussbett des Omonogawa (Omonofluss), welches letzteres dadurch entstand, dass ein Teil der Kitaura-Schicht verwitterte und fortgerissen wurde und an dessen Stelle Sand und Ton der Quartärperiode sedimentierte. Der Ölbehälter von Nr. 10 befindet sich gerade in dieser Schicht von Sand und Ton über der Kitaura-Schicht. Deshalb muss das Wasser dieses Bohrloches eine reichliche Menge von Flusswasser, das in den Ölbehälter hineindiffundierte, enthalten, oder der grösste Teil des Wassers von Probe Nr. 10 muss Flusswasser sein. Daher war auch der Rückstand bei der Destillation dieser Probe kleiner als der bei der Destillation der anderen Proben. Damit lässt sich zwar erklären, dass sich Probe Nr. 10 hinsichtlich ihres spezifischen Gewichts ganz anders als die anderen Proben verhält, nicht aber, dass sie eine noch geringere Dichte als gewöhnliches Wasser besass. Zur Erklärung dieser Eigentümlichkeit liesse sich vielleicht heranziehen, dass das Flusswasser des Omonogawa in Juni, wo diese Probe aufgenommen wurde, oder noch einige Monate früher viel Schneewasser enthielt und dieses besonders von frisch gefallenem Schnee durchschnittlich um 2γ leichter als gewöhnliches Wasser ist.⁽⁷⁾

Auf Grund der obigen Untersuchungsergebnisse darf man wohl sagen, dass das spezifische Gewicht des Salzwassers aus Petroleumquellen nicht bloss von der Tiefe des Bohrloches, sondern noch viel mehr von der Erdbeschaffenheit um die Ölbehälter herum beeinflusst wird. Wir werden demnächst noch weitere Proben auf ihr spezifisches Gewicht untersuchen.

Zum Schluss möchten wir der Nippon Gakujutsu Shinkohkai (der Gesellschaft zur Förderung der japanischen Wissenschaft) sowie der Hattori-Hohkai (der Hattori-Stiftung) für ihre finanzielle Unterstützung bei Ausführung dieser Untersuchung unseren besten Dank aussprechen.

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(7) M. Harada und T. Titani, dieses Bulletin, **10** (1935), 206, 263.

**ÜBER DIE KOLLOIDSYNTHESE DURCH DAMPFEXPLOSIONEN
UND DIE KOLLOIDCHEMISCHEN UNTERSUCHUNGEN
DER DURCH DIESE METHODE HERGESTELLTEN
DISPERSEN SYSTEME.
(Fortsetzung und Schluss.*)**

Von Naoyasu SATA.

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III. Kolloidchemische Untersuchungen. Wie bekannt, gibt es verschiedene Möglichkeiten für die Herstellung gleicher Substanzen in kolloiden Lösungen, je nach der Verschiedenheit der Dispergationstechnik und auch dem Vorhandensein verschiedener Stabilisatoren. Daraus kann man schließen, dass diese Sole auch in ihren kolloidchemischen Eigenschaften verschieden voneinander sind.

Ich habe in dieser Abhandlung eine neue Möglichkeit der Kolloidsynthese, nämlich die Kolloid-Dispergation durch Dampfexplosion untersucht und in ihr die erfolgreichste Herstellungsmethode der Kolloidsysteme gefunden. Weiterhin habe ich festgestellt, dass sich die gewonnenen Sole ziemlich konzentriert und sehr stabil unter Anwendung geeigneter Stabilisatoren halten. Es ist selbstverständlich notwendig und auch sehr interessant, die Sole, auf ihre kolloid-chemischen Eigenschaften hin, noch weiter zu untersuchen. Dieses Thema habe ich in den folgenden Kapiteln behandelt.

A. Herstellung der Vorrats-Sole und Bestimmung ihrer Konzentrationen. Geeignete Konzentrationen von Stabilisatoren, die die höchste Stabilität ergeben, habe ich bereits untersucht und festgestellt. Zu weiteren Untersuchungen stellte ich zuerst aus einem Dispersionsmittel mit einer Stabilisator-Konzentration von höchster Stabilität, 1 Liter Vorrats-Sole her. Nachdem ich sie einige Monate stehen gelassen und das Sol ziemlich homogen stabilisiert hatte, habe ich die Konzentration gemessen und weitere Versuche angestellt.

(a) **Quecksilber-Sol.** Nach oben ausgeführtem Versuch ist bei Quecksilbersolen festgestellt worden, dass deren Stabilitäts-Maximum bei den Konzentrationen von 0.0001 mol für Natriumjodid und zwischen 0.001 mol und 0.01 mol für Natriumsulfid zu erkennen ist. Also habe ich die Vorrats-Sole mit diesen Stabilisator-Konzentrationen hergestellt und in Flaschen von

* Fortsetzung aus S. 503 dieses Bandes.

ca. 10 cm. Durchmesser mit geschliffenen Stöpseln im Dunkeln stehen lassen. Der Vorgang des Absetzens bis das Sol homogen und stabil wurde, was etwa 3 Monate gedauert hat, ist in Tabelle 5 dargestellt.

Tabelle 5.

Sol-Nr.	Hg-4	Hg-3	Hg-2
Stabilisator-Konzentration	Natriumjodid	Natriumsulfid	
	0.0001 mol/l.	0.001 mol/l.	0.01 mol/l.
Gleich nach Explosion	Grau undurchsichtig.	Grau-schwarz undurchsichtig	Grau-bläulich undurchsichtig.
Nach 3 Tagen (15. März)	2/3 von oben gelblich-braun, halbdurchsichtig. Unten undurchsichtig.	12 mm. von oben bläulich durchsichtig. Durchsichtsfarbe rot. Unten undurchsichtig.	Homogen bläulich-grau, undurchsichtig.
Nach 8 Tagen (20. März)	Homogen gelblich grau durchsichtig. Durchsichtsfarbe orange-rot.	Setzt der undurchsichtige Teil mehr ab. Die Farbtöne sind dieselben.	Homogen halbdurchsichtig. Durchsichtsfarbe rot.
Nach 18 Tagen (30. März)	Keine Änderung.	1/4 von oben bräunlich-grau, halbdurchsichtig. Durchsichtsfarbe orange-gelb.	Setzt etwas mehr ab, Durchsichtsfarbe orange-gelb.
Nach 38 Tagen (20. April)	Halbdurchsichtig mit bläulicher Opaleszenz. Durchsichtsfarbe gelb.	Ganze Flüssigkeit homogen. Die Farbtöne wie oben.	Wie Hg-3, aber viel konzentrierter.
Nach 1.5 Monaten (1. Juni)	Mehr bläulich durchsichtig mit schöner Opaleszenz.	Schön gelblich-grün, Durchsichtsfarbe gelblich-orange.	Bräunlich-gelb halbdurchsichtig. Durchsichtsfarbe gelb.
Nach 6 Monaten (16. Nov.)	Aufsichtsfarbe weisslich blau mit Opaleszenz. Durchsichtsfarbe gelb.	Aufsichtsfarbe bräunlich grau. Durchsichtsfarbe gelb.	Aufsichtsfarbe bläulich-grau. Durchsichtsfarbe rötlich braun.

N.B. Hier muss man beachten, dass die Stabilität durch die Hochsommertemperatur von 30°C. kaum beeinflusst worden war. Es ist auch zu bemerken, dass die Farbintensität nach dem Sommer wieder zunehmende Neigung aufweist, die einmal durch die Sommerhitze abgenommen hatte.

Die Konzentrationen der Sole sind nach dem Stabilisieren der Sole, welches durch Stehenlassen von etwa 2 Monaten erreicht wurde, bestimmt worden. Also genau am 61. Tag nach der Explosion wurden von jeder Sole ca. 50 c.c. abpipettiert und durch doppelten Filter von Schleicher und Schüll (Nr. 602 extrahart) filtriert und 10 c.c. der Filtrate in den Quarztiegel genommen. Da Quecksilber flüchtig ist, wurde das Eindampfen in einem Schwefelsäure-Exik-

kator mit vermindertem Druck bei Zimmertemperatur ausgeführt (dazu wurde die Schwefelsäure von E. Merck „Zur Analyse“ verwendet). Die flüssige Masse verschwand nach etwa 3 bis 4 Tagen, und das Gewicht wurde nach 5–7 Tagen konstant. Von dem Gewicht fester Substanzen wurde das Gewicht der Stabilisator abgerechnet und die Sol-Konzentrationen, festgestellt (Tabelle 6).

Tabelle 6.

	Hg-4	Hg-3	Hg-2
Stabilisator	Natriumjodid	Natriumsulfid	
Mol im Liter	0.0001	0.001	0.01
Totalmenge (g.)	9.9775	9.9797	9.9694
Quecksilber (g.)	0.00145	0.00292	0.0096
Konzentration (%)	0.0145	0.0292	0.096

Also liegen die Konzentrationen zwischen 0.015–0.1%, je nach dem Stabilisator und seinen Konzentrationen. A. Gutbier⁽⁵⁷⁾ teilte mit, dass er die Konzentration um 2.5% erhöhen konnte. Aber diese Konzentration wurde an frischem Sol bestimmt, und ausserdem war es nur ein für 1 oder 2 Wochen stabiles Präparat, welches man mit meinem jahrelang stabilen Sol nicht direkt vergleichen kann.

(b) **Selen-Sol.** Das Selen-Vorratssol wurde nach der oben erwähnten Weise, wie folgt, hergestellt. Etwa 900 c.c. disperse Systeme wurden durch je 4 malige Explosionen vorbereitet. Die ganze Masse, die Flüssigkeit und die Selen-Flocken wurden, wie erwähnt, solange geschüttelt, bis die Trübung konstant blieb, was etwa 6–9 Stunden dauerte. Nach 1 monatigem Stehenlassen wurden von dem stabilisierten Teil vorsichtig ca. 500 c.c. abpipettiert und zu weiteren Untersuchungen verwendet. Dieses schwach getrübbte, rot-bräunliche, in Aufsicht und Durchsicht schön orangefarbige Sol blieb für ein Jahr mit nur sehr wenigem Sediment am Boden ohne Veränderung. Die Konzentration betrug nach 1 Monat 0.006%. Da ich jetzt das Sol nicht filtrierte, aber einen Monat lang stehen gelassen habe, scheint dieser Wert ein Maximum für das durch diese Methode hergestellte Sol zu sein.

(c) **Schwefel-Sol.** Weil man mit Schwefel keine stabilen Vorrats-Sole herstellen kann, muss man mit frisch hergestellten Solen während ihrer

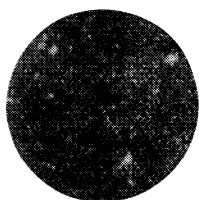
(57) *Z. anorg. allgem. Chem.*, **158** (1926), 99.

Lebensdauer von 5–10 Tagen arbeiten. Trotzdem habe ich die Konzentrationen solcher Sole gemessen. Also gleich nach 5 Explosionen und nach dem Absetzenlassen von gröberen Teilchen für 10 Minuten, erhielt man die Konzentration von 0.094%, und dasselbe Sol, sofort filtriert, betrug 0.0098%. Letzteres hat etwa 10 mal weniger Wert ergeben als das Erstere, obwohl das Aussehen beider Sole, d.h. Trübung, Farbton usw., nicht sehr verschieden waren. Diese Tatsache möchte ich auf die Polydispersität des Sols zurückführen. Nämlich zuerst strömten Teilchen bis zu Maschengröße durch den Filter, da aber die Teilchen polydispers waren, wurde der Filter immer mehr verstopft, sodass endlich die Maschen kleiner wurden, und das anfangs sehr trübe und schnell tropfende Filtrat mit der Zeit immer klarer wurde und endlich ein fast ganz klares, sehr langsam tropfendes Filtrat ergab.

B. Mikro- und ultramikroskopische Untersuchung. Von den kolloid-chemischen Untersuchungen an diesen Solen wurden zuerst mikro- und ultramikroskopische Versuche ausgeführt. Zu diesem Zweck wurde das Zeiss-Mikroskop mit Kombinationen von Okularen (K. 12/15 x; Kompens-Okular 6) und Objektiven (Apochromat 2 mm.; 8 mm. „n.A. = 0.65“; 16 mm. „n.A. = 0.30“) und Zeiss'schem Wechselkondensor nach Siedentopf verwendet.

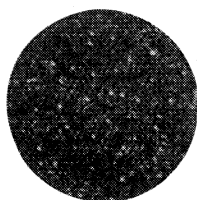
Als Küvette habe ich die „Leitz'sche Kammer für Dunkelfeldbeobachtung und Ultramikroskopie“ benutzt. Zur Aufnahme wurde die Leitz'sche Mikro-Aufsatzkamera „Makam“ angewendet.

(a) **Quecksilber-Sol.** Die vorher erwähnten, stabilen Quecksilber-Sole (Hg-2, Hg-3, Hg-4) zeigten 9 Monate nach der Herstellung unter dem Ultramikroskop sehr viele Teilchen, die eine blass-grüne oder genauer grünlich-weiße Farbe hatten, in lebhafter Brown'scher Bewegung, wie auf Abb. 31, 32 und 33 zu sehen ist.



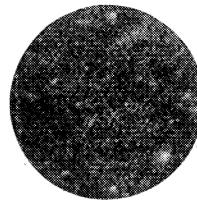
Hg-2

Abb. 31.



Hg-3

Abb. 32.



Hg-4

Abb. 33.

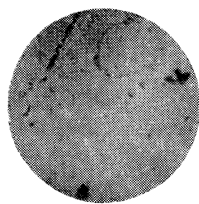
Die Teilchen waren in frisch hergestellten dispersen Systemen in allen Fällen stark polydispers. Auf den Abbildungen sehen die Konzentrationen umgekehrt aus, nämlich Hg-4 ist am konzentriertesten und Hg-2 am ver-

dünntesten. In Wirklichkeit waren zwischen den photographierten Teilchen noch volle, feinere Teilchen zu erkennen, nur sind sie nicht abgebildet worden, da sie zu klein waren. Hg-4 dagegen enthielt hauptsächlich gröbere Teilchen, die fast alle auf den Aufnahmen abgebildet wurden. Daraus kann man schliessen, dass die Dispersität in Natriumsulfid-Lösungen (Hg-2, Hg-3) viel grösser ist als in Natriumjodid-Lösungen (Hg-4). Man merkte auch noch, dass sie ziemlich monodispers geworden waren, nachdem man sie einige Monate hatte stehen lassen.

Nun wäre noch etwas über das Verhalten des Koagulums zu bemerken. Das Koagulum des Hg-Sols von den vorläufigen Versuchen, die ich wie Abb. 5 ausgeführt habe, besteht aus massiven metallischen Hg-Teilchen verschiedener Grösse und aus Hg-Flocken, welche aus winzigen Hg-Tröpfchen zusammengesetzt sind. Besonders interessant ist eine solche Flocke, die nicht zu stark gealtert ist, da sich die ultramikroskopischen Hg-Tröpfchen darin in deutlicher Brown'scher Bewegung befinden. Die Hg-Niederschläge, welche aus solchen Flocken bestehen, kann man durch Schütteln mit Wasser zu dispersen Lösungen dispergieren, die in der Durchsicht bläulich-gelb sind; solche sekundäre, disperse Systeme sind jedoch instabil. Aber das Koagulum aus Na_2S bzw. NaI mit stabilisierten dispersen Systemen sieht ganz anders aus. Es ist besonders zu bemerken, dass darin fast gar keine Hg-Tröpfchen mikro- bzw. ultramikroskopischer Grösse zu erkennen sind wie im vorhergehenden Fall, sondern das Koagulum besteht aus undurchsichtiger, grauer, sandiger Masse, bei der keine Kristallform zu unterscheiden ist. Wenn man diese Masse durch Drücken mit dem Deckglas zerreibt, wird sie zu ultramikroskopischen Teilchen aufgelöst, die sofort lebhaft Brown'sche Bewegung anfangen. Daraus muss man konstatieren, dass das Koagulum in diesem Fall ein Aggregat ultramikroskopischer Teilchen ist. Hier darf man nicht den gründlichen Unterschied bei dem Koagulum der dispersen Systeme mit und ohne Vorhandensein des Stabilisators übersehen. In dem vorläufigen Versuch habe ich keine besonderen Stabilisatoren benutzt, woraus man schliessen könnte, dass das Koagulum hauptsächlich aus metallischen Quecksilbertropfen verschiedener Grösse bestanden hat. Dagegen sieht man, in dem Versuch mit dem Stabilisator, im Koagulum keine Quecksilbertropfen, sondern nur Aggregate sehr feiner Teilchen, die man wieder dispergieren kann. Diese Tatsache stimmt mit der Vermutung überein, dass das fein dispergierte Quecksilber beim Vorhandensein von Stabilisatoren, sofort mit chemischen Verbindungen bedeckt wurde, die zwischen ihnen durch Oberflächenreaktion entstanden sind. Man kann diese Erscheinung leicht erklären, wenn man bedenkt, dass dieses Häutchen die Teilchen stört, sich zu Tropfen zu vereinigen.

Soweit über das allgemeine Verhalten der drei von mir hergestellten Sole, sonstige mikrostrukturelle Unterschiede zwischen ihnen, ausser dem Unterschied in bezug auf ihre Konzentration, konnte ich nicht bemerken.

(b) **Selen-Sol.** Die ultramikroskopische Untersuchung hat gezeigt, dass dieses Sol auch stark polydispers ist. Die überwiegende Zahl der ultramikroskopischen Teilchen hat eine grünliche Farbe, diese Teilchen sind von kleinsten Dimensionen und befinden sich in lebhafter Brown'scher Bewegung. Andere Teilchen haben eine orange Farbe, und nur wenige Teilchen sehen rot aus. Die rötlichen Teilchen haben die grössten Dimensionen und zeigen weniger lebhaft Brown'sche Bewegung als die grünlichen. Die orange-farbenen Teilchen haben mittlere Dimensionen, zwischen grünlich und rötlich. Hier möchte ich darauf aufmerksam machen, dass sie in ihrer Brown'schen Bewegung im Gegensatz zu den Quecksilbersol-Teilchen, die ziemlich gleichmässig glänzten, unregelmässig schillernd glänzten. Daraus könnte man vielleicht vermuten, dass die Teilchen entweder stäbchenförmig oder plättchenförmig sind, wenigstens keine Kugelform besitzen. Abb. 34 u. 35 sind einige vergleichende Dunkel- und Hellfeld-Photographien. Zum Zwecke deutlicheren Vergleichs wurde besonders die Stelle im mikroskopischen Feld ausgewählt, an der grobe Teilchen sichtbar waren. Das Koagulum von Selen-Solen bestand aus rotem, sandigem Aggregat feiner Teilchen, die keinen Rückschluss auf Kristallform gestatten und ausserdem noch aus grob amorpher Selen-Masse von rötlicher bis tiefroter Farbe. Es war aber nicht möglich dieses Aggregat im Gegensatz zum Quecksilber-Aggregat wieder zu dispergieren, z.B. durch Drücken mit dem Deckgläschen.



(Hellfeld)

Abb. 34.



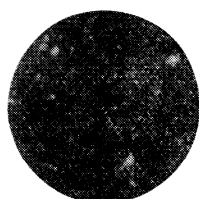
(Dunkelfeld)

Abb. 35.

(c) **Schwefel-Sol.** Mikro- und ultramikroskopische Untersuchungen von frisch gebildetem Schwefel-Niederschlag hatten folgendes Ergebnis: Die Hauptmasse des Niederschlags bestand aus kugelförmigen Körnern und Aggregaten. Die Körner hatten ganz verschiedene Grösse, von groben mikroskopischen bis zu ultramikroskopischen Dimensionen. Grössere kugelförmige Körner waren von ganz verschiedener Beschaffenheit: (1) Keine

Struktur (ganz klare, unterkühlte Schwefeltropfen); (2) sphärolitische, radiale Struktur; (3) körnige Struktur. In kleiner Zahl fand man in S-Niederschlag sehr schöne Mikrokriställchen mit rhombischen Umrissen. Flocken aus kugeligen Teilchen befanden sich sehr viele im Niederschlag. Ein Teil der grossen kugeligen S-Teilchen hatte sich aller Wahrscheinlichkeit nach durch mechanische Dispergation bei explosivem Aufkochen des flüssigen Schwefels gebildet.

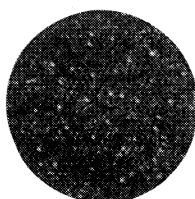
Es werden hier die mikro- und ultramikroskopischen Aufnahmen der Sole gezeigt, die ich 4 Stunden nach der Explosion aufgenommen habe (Abb. 36, 37 u. 38).



(Hellfeld)

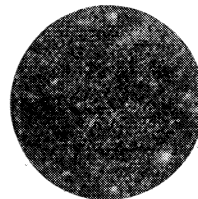
Unfiltriertes Sol.

Abb. 36.



(Dunkelfeld)

Abb. 37.



(Dunkelfeld)

Filtriertes Sol.

Abb. 38.

C. Die Viskosität der Sole. Um die mechanischen Eigenschaften dieser Sole zu untersuchen, habe ich zuerst ihre Viskosität gemessen. Dieselbe wurde mit Ostwald'schem Viskosimeter im Thermostat von 25°C. bestimmt. Die Versuchsergebnisse sind in Tabelle 7 dargestellt.

Tabelle 7.

	Hg-2	Hg-3	Hg-4	Se-Sol	Reines Wasser
d	0.99843	0.99770	0.99726	0.99745	0.99707
η	0.00905	0.00903	0.00898	0.00894	0.00893

Hier sieht man kaum einen Unterschied bezüglich der Viskosität dieser Sole im Vergleich mit reinem Wasser, eine winzige Abweichung besteht nur in der Viskositätserhöhung bei den Solen Hg-2 und Hg-3, die man hauptsächlich auf das Vorhandensein der Salze zurückführen könnte. In diesem

Punkt stimmt das Resultat mit demjenigen von A. Gutbier⁽⁵⁸⁾ überein, was man auch von der Hydrophobität dieser Sole leicht vermuten kann.

D. Die Oberflächenspannung der Sole. Die Oberflächenspannungen der Sole wurden parallel der Viskosität mit dem Stalagmometer gemessen, und zwar haben sie folgende Zahlen ergeben (Tabelle 8).

Tabelle 8. (Zimmertemperatur 23–25°C.).

	Wasser	Hg-2	Hg-3	Hg-4	Se-Sol
dyn./cm.	71.78	73.36	72.44	71.86	72.88

Durchschnittlich zeigten die Oberflächenspannungen eine geringe Erhöhung, was man durch die Wirkung anorganischer Salze erklären kann. Eine verhältnismässig grosse Erhöhung bei Se-Sol, obwohl kein Salz zugegeben wurde, ist noch nicht zu erklären. Jedenfalls, den obenerwähnten, geringen Verschiedenheiten der Viskosität entsprechend, weisen die Oberflächenspannungen der Sole auch kaum einen merklichen Unterschied gegen reines Dispersionsmittel auf, eine Tatsache, die auch auf die hydrophoben Eigenschaften der Sole zurückzuführen ist.

E. Die elektrophoretischen Eigenschaften der Sole. Vor den Koagulationsversuchen habe ich die Sole auf die elektrische Ladung ihrer Teilchen hin geprüft, nämlich elektrophoretische Untersuchungen angestellt. Da diese Sole ziemlich empfindlich gegen langwierige Messungen mit Cohen'schem U-Rohrapparat⁽⁵⁹⁾ sind, und es auch sehr schwierig ist, die sich verschiebende Sol-Grenze im U-Rohr zu beobachten, weil alle diese Sole nicht so stark wie die Sole von Gold bzw. Eisenoxyd usw. gefärbt sind, habe ich die elektrophoretischen Untersuchungen direkt unter dem Mikroskop unter Anwendung des Kardioid-Kondensors ausgeführt. Zur Elektrode wurde KCl-haltiger Agar-Agar benutzt⁽⁶⁰⁾. Die kataphoretische Wanderungsgeschwindigkeit zwischen den Teilstrichen im Okular-Mikrometer von 0.235 mm. ist in folgender Tabelle 9 zusammengestellt. Zur Kontrolle wurden an dem Goldsol (nach Zsigmondy—Weimarn) und an dem Eisenoxydsol (durch Hydrolyse von Eisenchloridlösung), von denen das erste negativ und das zweite positiv geladene Teilchen enthielt, dieselben Messungen ausgeführt.

(58) *Z. anorg. allgem. Chem.*, **158** (1926), 100.

(59) H. Freundlich, „Kapillarchemie“, Bd. I, 335.

(60) *Ibid.*; N. Schönfeld, *Z. Elektrochem.*, **39** (1933), 103.

Tabelle 9.

	Eisenoxydsol	Goldsol	Hg-2	Hg-3	Hg-4	Se-Sol
Teilchenladung	+	—	—	—	—	—
Geschwindigkeit 0.235 mm./48 v.	—	2→2.5''	4→5''	3''	2→3''	2→2.5''
Geschwindigkeit 0.235 mm./96 v.	2''	1→1.5''	2→3''	2→2.5''	1→1.5''	1→1.5''

Die Zahlenwerte in dieser Tabelle dürften nur halb-quantitativ angenommen werden, weil ich diesen Versuch nur zur Bestimmung des Ladungssinnes der Teilchen ausgeführt habe. Es musste für die genaue Bestimmung der Teilchenwanderungsgeschwindigkeit eine spezielle Einrichtung angewandt werden, unter besonderer Berücksichtigung der Empfindlichkeit der Sole gegen den elektrischen Strom und den Konvektionseinfluss, der durch das Laden der Kontaktfläche, Glas-Wasser usw., hervorgerufen wird. Daraus sieht man, dass alle diese Sole negativ geladene Teilchen enthalten. Die Geschwindigkeit von den Solen Hg-3, Hg-4 und Se-Sol ist ziemlich schnell und hat eine ähnliche Grössenordnung wie die Geschwindigkeit bei Goldsol bzw. Eisenoxydsol, dagegen enthält nur das Hg-2 viel langsamer wandernde Teilchen.

F. Die Koagulationsversuche. (a) **Elektrolytkoagulation von Quecksilber-Sol.** Durch die oben ausgeführten Untersuchungen weist man darauf hin, dass diese Sole negativ geladene Teilchen enthalten und typische hydrophobe Eigenschaften zeigen, und es bleibt mir zuletzt die interessante Aufgabe über die Koagulation, die ich zuerst an den Hg-Solen untersucht habe, zu berichten. Die Koagulationsversuche wurden wie gewöhnlich in den Probiergläsern von 22–25 mm. Durchmesser, unter Anwendung von 5–10 c.c. Sol und derselben Menge Salzlösung⁽⁶¹⁾, ausgeführt. Durch diesen Versuch wurden nicht nur die Koagulationswerte bestimmt, sondern sind auch die zeitlichen Änderungen der Koagulationsvorgänge bei verschiedenen Salzkonzentrationen verfolgt worden. Von der Natur der Negativität und Hydrophobität der Sole habe ich zuerst die Wirkung der Wertigkeit der Kationen untersucht. Die

(61) Wo. Ostwald, „Kleines Praktikum d. Kolloidchemie“, S. 127, Dresden u. Leipzig (1926).

Ergebnisse der Koagulationsversuche mit Natrium-, Kalzium- und Aluminiumchlorid sind in folgenden Tabellen 10, 11, 12 und Abb. 39 dargestellt. Die benutzten Salze sind alle Kahlbaum'sche Präparate „zur Analyse“.

Tabelle 10. NaCl-Koagulation.

NaCl millimol/l.	Hg-2	Hg-3	Hg-4
	Stabilisator und seine Konzentrationen		
	0.01 mol Na ₂ S	0.001 mol Na ₂ S	0.0001 mol NaI
5	—	—	Bläulich weisse Trübung wird nach 12 Tagen ganz klar.
10	Schwach bläulich trübes Sol wird nach 8 Monaten bläulich klar und nach 11-12 Monaten ganz klar.	Schön bläulich opaleszierendes Sol setzt allmählich ab u. wird nach 60-75 Tagen ganz klar.	—
15	—	—	Wie 5 Millimol, aber nach 13 Tagen ganz klar.
20	Wie oben, aber nach 30 Tagen blau klar u. nach 80 Tagen ganz klar.	Wie oben, aber nach 75 Tagen ganz klar.	—
25		Wie oben, aber nach 30 Tagen ganz klar.	Wie oben, aber nach 2 Tagen ganz klar.
40	Wie oben, aber nach 40 Tagen ganz klar.	Wie oben, aber nach 10 Tagen ganz klar.	Nach 1 Tag ganz klar.
50	Tritt starke Trübung ein u. nach 1/2 Tag ganz klar.	Es tritt sofort starke Trübung ein u. ist nach 5 Tagen ganz klar.	Nach 1 Tag ganz klar.
60 80	—	Wie oben, aber nach 1 Tag ganz klar.	—
100 150 200	Ganz klar nach 1 Tag.	Nach 1 Tag ganz klar.	Nach 1 Tag ganz klar.

Tabelle 11. CaCl_2 —Koagulation.

CaCl_2 millimol/l.	Hg-2	Hg-3	Hg-4
	Stabilisator und seine Konzentrationen		
	0.01 mol Na_2S	0.001 mol Na_2S	0.0001 mol NaI
0.15	Wie ohne Salzzusatz bis zu 1.5 Jahren und länger keine Veränderung.	Schwach getrübbtes Sol wird nach 5 Tagen bläulich klar u. nach 30 Tagen ganz klar.	Nach 12 Tagen ganz klar.
0.20	Bläulich opaleszierende Trübung verschwindet nach 5 Monaten u. wird ganz klar nach 7-8 Monaten.	—	Nach 6 Tagen ganz klar.
	—	Nach 25 Tagen ganz klar.	—
0.30	Es fängt nach 5 Tagen an zu trüben und wird nach 5 Monaten ganz klar.	Nach 10 Tagen ganz klar.	—
0.40	Die bläuliche Trübung verschwindet allmählich u. wird es nach 30 Tagen ganz klar.	Sofort trübt es sich u. ist nach 4 Tagen ganz klar.	Grünlich graue Trübung tritt sofort ein u. nach 4 Tagen wird es ganz klar.
0.50	Wie oben u. nach 10 Tagen ganz klar.	Wie oben u. nach 3 Tagen ganz klar.	Wie oben u. nach 4 Tagen ganz klar.
0.60	Wie oben u. nach 3 Tagen ganz klar.	Nach 2 Tagen ganz klar.	Nach 4 Tagen ganz klar.
0.80	Nach 1 Tag ganz klar.	Nach 1 Tag ganz klar.	Nach 3 Tagen ganz klar.
1.00	—		
2.00	—	—	Nach 1 Tag ganz klar.

Tabelle 12. AlCl_3 —Koagulation.

AlCl_3 millimol/l.	Hg-2	Hg-3	Hg-4
	Stabilisator und seine Konzentrationen		
	0.01 mol Na_2S	0.001 mol N_2S	0.0001 mol NaI
0.025	Bei diesen Konzentrationen wird das Sol durch Salzzusatz nicht beeinflusst und verschwindet die Trübung ganz allmählich, aber bis nach 1.5 Jahren bleibt es noch schwach bläulich opaleszierend.	Die Trübung verschwindet allmählich, aber es ist bis jetzt noch bläulich nach 1–1.5 Jahren.	Nach 13 Tagen ganz klar
0.035		Nach 13 Tagen g. klar	
0.040		Nach 9 Tagen g. klar	
0.050		Nach 12 Tagen g. klar	Nach 5 Tagen g. klar
0.060		Nach 5 Tagen g. klar	Nach 3 Tagen g. klar
0.080		Nach 2 Tagen g. klar	—
0.100			Nach 2 Tagen g. klar
0.12			—
0.15		Nach 1 Tag ganz klar	Nach 1 Tag g. klar
0.16			—
0.18			—
0.20			—
0.25		—	Nach 1 Tag g. klar
0.50	—	—	Nach 1 Tag g. klar
0.75	—	—	Nach 1 Tag g. klar
1.00	—	—	Nach 1 Tag g. klar
1.50	Nach 15 Tagen g. klar		
1.60	Nach 6 Tagen g. klar		
1.80			
2.00	Nach 1 Tag ganz klar		
5.00			
10.00			
20.00			

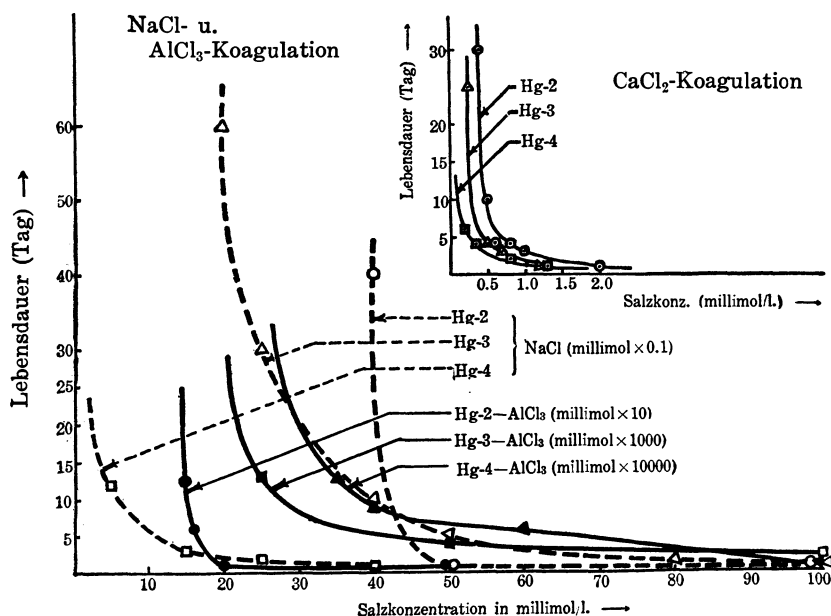


Abb. 39.

Nachdem man die Koagulation verschiedener Kathionen, nämlich Na⁺, Ca²⁺, und Al³⁺, gemessen hatte, schien es mir wünschenswert, den Einfluss der Halogen-Ionen zu untersuchen, was J. Doolan⁽⁶²⁾ an hydrophobem Selen-Sol getan hatte. Nun habe ich die Koagulationsversuche mit Bariumchlorid, Bariumbromid und Bariumjodid angestellt. BaCl₂ war Kahlbaum'sches Präparat „zur Analyse“ und BaBr₂ war de Haen'sches Präparat, umkristallisiert. BaI₂ habe ich selbst aus reiner Jodwasserstoffsäure von E. Merck und Natriumkarbonat hergestellt. Die Koagulationsversuche wurden wie in vorhergehendem Fall ausgeführt. Die Ergebnisse sind in folgenden Tabellen 13–16 und Abb. 40–42 dargestellt.

Tabelle 13. Koagulation von Hg-2 (Stabilisator = 0.01 mol Na₂S).

Salz-Konz. millimol/l.	BaCl ₂	BaBr ₂	BaI ₂
0.25	Scheidet sofort nach dem Salzzusatz goldgelben Niederschlag aus, welcher sich nach 1/2–1 Stunde absetzt. Die Flüssigkeit bleibt nach dem Absetzen des Niederschlags fast ohne Veränderung bräunlich-grau mit bläulicher Opaleszenz wie anfangs. Dieses Sol setzt ganz allmählich ab und ist bis nach 8 Monaten noch eine Spur bläulich.		—
0.50			
0.75			
1.00			
1.25			
1.50			

(62) J. Doolan, *J. Phys. Chem.*, **29** (1925), 178.

Tabelle 13.—(Fortsetzung)

Salz-Konz. millimol/l.	BaCl ₂	BaBr ₂	BaI ₂
2.00	Verlauf wie oben, aber nach 50 Tagen ist es ganz klar.	Verlauf wie oben, aber nach 66 Tagen ist es ganz klar.	Ohne Abscheidung des Niederschlags wie bei BaCl ₂ bzw. BaBr ₂ , setzt es allmählich stark getrübbes Sol nach 54 Tagen ganz klar ab.
3.00	Verlauf wie oben, aber nach 25 Tagen ganz klar.	Verlauf wie oben, aber nach 38 Tagen ganz klar.	Verlauf wie oben, aber nach 54 Tagen ganz klar.
4.00	Beim Salzzusatz tritt nur Trübung ein und zwar ohne Niederschlag.		Wie oben, jedoch nach 30 Tagen ganz klar.
	Nach 5 Tagen ganz klar.	Nach 19 Tagen ganz klar.	
4.50	—	Wie oben, aber nach 12 Tagen ganz klar.	Wie oben, aber nach 19 Tagen ganz klar.
5.00	Wie oben, aber nach 1 Tag ganz klar.	Wie oben, aber nach 1 Tag ganz klar.	Wie oben, aber nach 5 Tagen ganz klar.
6.00	Wie oben, aber nach 1 Tag ganz klar.	Wie oben, aber nach 1 Tag ganz klar.	Wie oben, aber nach 1 Tag ganz klar.

Tabelle 14. Koagulation von Hg-3 (Stabilisator = 0.001 mol Na₂S).

Salz-Konz. milli- mol/l.	BaCl ₂		BaBr ₂		BaI ₂	
0.25	Sofort nach d. Salz- zusatz scheidet Niederschlag aus, die restlichen bläulich grauen Sole werden ganz klar nach folgen- den Tagen,	60	Wie bei BaCl ₂ , aber ganz klar nach folgenden Tagen,	—	Hier scheidet keinen Nieder- schlag aus, nur die Trübung wird etwas vermehrt. Sie sind ganz klar nach folgenden Tagen,	—
0.50		15		18		20
0.75		3		6		8
1.00		3		4		6
1.25		1		2		5
1.50		1		1.5		3
2.00	Tritt starke Trübung ein u. nach 1 Tag ganz klar.		Tritt starke Trübung ein u. nach 1 Tag ganz klar.			1
3.00	Nach 1 Tag ganz klar.		Nach 1 Tag ganz klar.			1
4.00	Nach 1 Tag ganz klar.		Nach 1 Tag ganz klar.			

Tabelle 15. Koagulation von Hg-4 (Stabilisator = 0.0001 mol NaI).

Salz-Konz. milli- mol/l.	BaCl ₂		BaBr ₂		BaI ₂	
0.25	Koagulation ver- läuft auf einmal. Die Sole sind ganz klar nach folgen- den Tagen,	27	Koagulation ver- läuft auf einmal. Die Sole sind ganz klar nach folgen- den Tagen,	—	Scheidet sofort schöne grüne Flocken aus, die nach folgenden Stunden ganz klar absetzen,	8
0.50		5		5		8
0.75		2		3		8
1.00		2		3		4
1.25		1		2		4
1.50		0.5		1		4
2.00		0.5		0.5		4
4.00		0.5		0.5		4

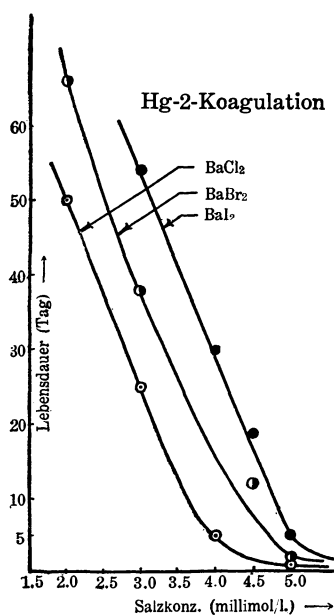


Abb. 40.

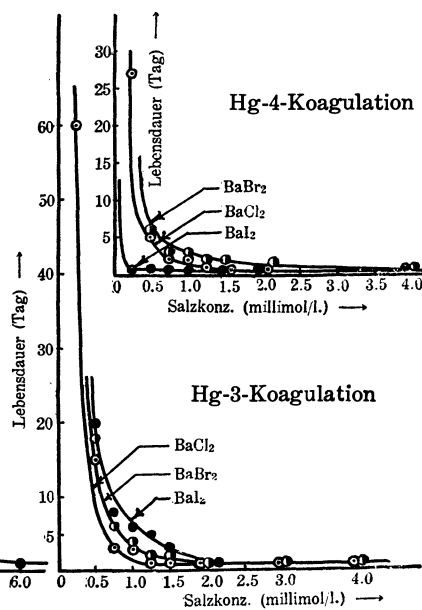


Abb. 42.

Von den ausgeführten Versuchen wurden für meine Hg-Sole die Koagulationswerte γ für vollständige Koagulation in einem Tag auf Tabelle 16 zusammengestellt.

Tabelle 16. Koagulationswerte γ der Hg-Sole in Millimol im Liter.

Sol-Nr.	Hg-2	Hg-3	Hg-4
Stabilisator und seine Konzentration	0.01 mol Na ₂ S	0.001 mol Na ₂ S	0.0001 mol NaI
NaCl	50.0	75.0	35.0
CaCl ₂	2.0	1.5	1.0
AlCl ₃	2.0	0.08	0.05
BaCl ₂	5.0	1.5	1.25
BaBr ₂	5.0	2.0	2.00
BaI ₂	6.0	2.5	0.25

Obwohl, wie schon erwähnt, die Hg-Sole auf ihre Herstellungsweise, bzw. auf ihre Eigenschaften hin, schon sehr oft untersucht worden sind, fehlen uns nur noch die Koagulationsversuche. A. Gutbier⁽⁶³⁾ teilte nur mit, dass er seine Hg-Sole mit etwa 0.1 N Elektrolytlösungen zum Koagulieren bringen konnte.

Bei meinen Versuchsergebnissen merkt man zuerst, dass die Empfindlichkeit der Sole durchschnittlich

$$\begin{array}{ccccc} \text{Hg-2} & < & \text{Hg-3} & < & \text{Hg-4} \\ \text{Stabilisator: } 0.01 \text{ mol Na}_2\text{S} & & 0.001 \text{ mol Na}_2\text{S} & & 0.0001 \text{ mol NaI} \end{array}$$

ist, was man durch die in ihnen schon vorher als Stabilisator vorhandenen Salzkonzentrationen leicht erwarten kann. Die Abhängigkeit zwischen Kathion-Wertigkeit und Koagulationswerten ist von H. Schulze⁽⁶⁴⁾, W.C.D. Whetham⁽⁶⁵⁾, T.B. Robertson⁽⁶⁶⁾ und anderen experimentell sowie theoretisch eingeleitet und bestätigt worden und zwar folgendermassen ausgedrückt:

$$\frac{1}{C_1} : \frac{1}{C_2} : \frac{1}{C_3} : \dots = 1 : X : X^2 : \dots,$$

wobei C_n : Koagulationswert n -wertiger Elektrolyte
 X : ein Konstant

(63) *Z. anorg. allgem. Chem.*, **155** (1926), 101.

(64) *J. prakt. Chem.*, **25** (1882), 431; S. Linder u. H. Picton, *J. Chem. Soc.*, **67** (1895), 63.

(65) *Phil. Mag.*, (5), **48** (1899), 474; W. B. Hardy, *Am. J. Phys. Chem.*, **4** (1900), 235; Wo. Ostwald, *Kolloid-Z.*, **26** (1920), 28; **73** (1935), 30.

(66) „Physikal. Chemie d. Proteine“, S. 94, Dresden (1912).

darstellt. Setzt man den Koagulationswert von Hg-3 und Hg-4 aus Tabelle 16, so erhält man folgende Zahlen:

$$1/C_{\text{NaCl}} : 1/C_{\text{CaCl}_2} : 1/C_{\text{AlCl}_3} = 0.0133 : 0.666 : 12.5 \quad \text{für Hg-3}$$

$$1/C_{\text{NaCl}} : 1/C_{\text{CaCl}_2} : 1/C_{\text{AlCl}_3} = 0.0144 : 0.500 : 11.0 \quad \text{für Hg-4.}$$

Also, die Zahlenwerte für zwei, ganz verschieden stabilisierte, Sole muss man als sehr befriedigende Übereinstimmung wahrnehmen, obwohl sich die Werte mit der obenerwähnten Formel ($1 : X : X^2$) nicht vollkommen decken. Hierzu möchte ich nur bemerken, dass diese Tatsache nicht nur das genannte Gesetz unterstützt, da diese Regel bis jetzt nur bei speziellen Solen gültig bestätigt wurde, sondern, dass diese Sole die typischen schwach solvatisierten hydrophoben Suspensoide sind, und die Koagulation nur durch Neutralisation⁽⁶⁷⁾ der Ladung erreicht wurde. Das Sol, Hg-2, dagegen zeigt eine ganz deutliche Anomalie in seinen Koagulationswerten auch auf der Koagulationskurve. Es koaguliert durchschnittlich bei viel grösseren Salzkonzentrationen im Vergleich mit den Solen Hg-3 bzw. Hg-4. In diesem Fall muss man zuerst bedenken, dass Hg-2 einen ziemlich konzentrierten Stabilisator enthält. Daraus dürfte man vielleicht vermuten, dass es schon hydrophile Eigenschaften an sich aufweist gegen das typische hydrophobe Hg-3 bzw. Hg-4; ähnliche Zusammenhänge bestehen zwischen dem v. Weimarn'schen hydrophoben Schwefelsol und dem hydrophilen Odén'schen Sol⁽⁶⁸⁾.

Über die Feinstruktur einzelner Teilchen, worauf H. Freundlich beim Odén'schen Sol hingewiesen hatte, kann ich bei Hg-2 noch nichts sagen; aber wie ich schon im Kapitel „Stabilität der Sole“ berichtet habe, ist es durch seine Farbänderung bei Sedimentation ziemlich sicher, dass das Sol ausser metallischem Quecksilber auch Quecksilber-Schwefel-Verbindungen enthält, dessen genaue Zusammensetzungen auch noch unbekannt sind. Nach Winsinger⁽⁶⁹⁾ und H. Freundlich⁽⁷⁰⁾ ist das schwarze mit H₂S gefallene Quecksilbersulfid durch Schütteln mit H₂S-haltigem Wasser leicht zu einer kolloiden Lösung peptisierbar. So erhaltenes Sol ist schwarz-braun, ölig in konzentriertem Zustand und grau-braun mit grünlicher Opaleszenz in verdünntem Zustand. Die Farbtöne sind denjenigen von meinem mit Natriumsulfid stabilisierten Hg-2-Sol sehr ähnlich. Freundlich hat bei diesem Sol folgende Koagulationswerte gefunden. (Tabelle 17).

(67) „Kapillarchemie“, II. 367.

(68) H. Freundlich u. P. Scholz, *Kolloid-Beihfte*, **16** (1922), 234.

(69) Winssinger, *Bull. acad. roy. méd. Belg.*, (3), **15** (1888), 390.

(70) H. Freundlich, *Z. physik. Chem.*, **85** (1913), 643; The Svedberg, „Herstellung kolloider Lösungen anorganischer Stoffe“, S. 40, Dresden (1922).

Tabelle 17. Koagulationswerte (millimol/l.) von HgS-Sol nach Freundlich⁽⁷¹⁾.

NaCl	13.0	SrCl ₂	0.88	$\frac{1}{2} \cdot \text{Al}_2(\text{SO}_4)_3$	0.044
KCl	10.0	BaBr ₂	0.68	YCl ₃	0.073
NH ₄ Cl	10.0	HgCl ₂	0.11	Ce(NO ₃) ₃	0.056

Koagulationswerte von Hg-2 (Na₂S stabilisiertes Hg-Sol).

NaCl	50.0	CaCl ₂	2.0	AlCl ₃	2.0
		BaCl ₂	5.0		
		BaBr ₂	5.0		
		BaI ₂	6.0		

Zum Vergleich sind die Koagulationswerte meines Hg-2-Sols angegeben, die eine starke Abweichung aufweisen. Diese Abweichung scheint mir die Tatsache zu bestätigen, dass die Teilchen von meinem Hg-2 nur oberflächlich mit HgS bedeckt und damit stabilisiert worden sind und innerlich Kerne aus metallischem Quecksilber entstanden sind, obwohl die Farberscheinung sehr ähnlich mit reinem HgS-Sol ist. Hier darf man nicht vergessen, dass mein Hg-2-Sol einen gründlichen Unterschied in seiner Stabilität aufweist, und zwar hält sich mein Hg-2-Sol über 1 Jahr sehr beständig, dagegen weist HgS-Sol nur eine Lebensdauer von 10–15 Tagen auf⁽⁷²⁾. Um den Unterschied dieser ähnlichen Sole klar zu machen, habe ich noch einen Versuch angestellt, und zwar wollte ich analytisch nachweisen, dass die disperse Phase meines Hg-2-Sols doch hauptsächlich aus Hg entstanden ist. Zu diesem Zwecke versuchte ich, nachdem ich mein Hg-2 in dem H₂SO₄-Exikator zur Trockene gebracht hatte, an der zurückgebliebenen Masse durch chemische Analyse den Gehalt an freiem Quecksilber zu bestimmen, was mir aber nicht möglich war, da die Quantität der Masse nicht ausreichte.

Aber auf folgende Weise konnte ich mich von dem deutlichen Unterschied zwischen meinem Na₂S-stabilisierten Hg-Sol (Hg-2) und dem reinen HgS-Sol überzeugen.

(71) *Z. physik. Chem.*, **85** (1913), 646.

(72) Nach meinem eigenen Versuch u. auch nach Freundlich, *Z. physik. Chem.*, **85** (1913), 646.

Nach M. C. Méhu⁽⁷³⁾ löst sich HgS weder in NaOH noch in Na₂S, jedoch in einem Gemisch von beidem. Wenn dies wirklich der Fall ist, so müssen sich die HgS-Teilchen in alkalischer Na₂S-Lösung sofort auflösen, während die Teilchen des Hg-2, die entweder aus reinen Hg-Tröpfchen oder, von HgS umhüllten, Hg-Tröpfchen bestanden, sich gar nicht oder nur teilweise auflösen. Ich hatte von frisch hergestelltem HgS-Sol durch Verdünnen ein bläulich-weiss opaleszierendes Sol, welches man dem Aussehen nach von meinem Hg-2 kaum unterscheiden konnte, vorbereitet. Es wurde nun die Zeitdauer des AuflöSENS beider Sole, HgS-Sol und Hg-2, durch Verschwinden des Tyndall-Kegels erkennbar, gemessen. Die Resultate sind in Tabelle 18 angegeben.

Tabelle 18.

	Hg-2	HgS	Hg-2	HgS	Hg-2	HgS	Hg-2	HgS
c.c. Sol	2.5	2.5	2.5	2.5	4.0	4.0	4.0	4.0
c.c. 0.1 N KOH	1.25	1.25	5.0	5.0	—	—	—	—
c.c. 0.1 N Na ₂ S	1.25	1.25	5.0	5.0	—	—	—	—
c.c. 1.0 N KOH	—	—	—	—	0.5	0.5	1.3	1.3
c.c. 1.0 N Na ₂ S	—	—	—	—	0.5	0.5	1.3	1.3
Tyndall Kegel schwach nach	14'	5'	5.5'	2'	1'	20''	30''	3-5''
Fast kein Tyn- dall Kegel nach	27'	15'	8'	3'	3→4'	60''	1→2'	10''

Daraus ersieht man, dass mein Hg-2-Sol viel längere Zeit braucht als HgS-Sol, um molekular zu lösen, ein Nachweis, dass beide Sole doch voneinander verschieden sind, trotz sehr ähnlichem Aussehen. Die Tatsache, dass das Hg-2, obwohl man vermutete, dass darin vorhandene Teilchen aus Hg-Tröpfchen bestehen, sich im Gemisch KOH und Na₂S löst, möchte ich folgendermassen erklären. Es ist wohlbekannt, dass Natriumsulfid⁽⁷⁴⁾ (gewöhnlich nicht in Form von Na₂S, sondern Na₂S·9H₂O) sehr hygroskopisch ist und durch Hydrolyse Alkali ausscheidet bei Aufnehmen der Luftfeuchtigkeit. Vom Hg-2-Sol, in welchem die kolloiddispersen Hg-Tröpfchen mit 0.01 mol Na₂S-Lösung in Berührung sind, könnte man erwarten, dass sich diese Hg-

(73) Gmelin-Krauts, V (II), S. 583.

(74) P. Pascal, „Traite de chimie minerale“, VI, S. 488, Paris (1934).

Tröpfchen nach monatelangem Stehen, schon zu einer, im KOH-Na₂S-Gemisch löslichen, Form verändert hätten, obwohl sich der Lösevorgang viel langsamer vollzog als bei reinem HgS.

Nach H. Freundlich ist HgS-Sol dafür bekannt, dass es eine unregelmässige Reihe bei der Koagulation mit AgNO₃⁽⁷⁵⁾ zeigt. Es ist auch sehr wohl möglich, dass mein Hg-Sol, das vielleicht mit HgS umhüllt stabilisiert ist, in etwaigem Zusammenhang mit der Erscheinung der unregelmässigen Reihe steht, worüber man weitere Untersuchungen abwarten muss. Jedenfalls werden uns diese beiden Sole ein sehr interessanter Gegenstand für die kolloidchemische Untersuchung bleiben.

Was den Einfluss von Anionen betrifft, den ich mit BaCl₂, BaBr₂ und BaI₂ untersucht habe, so verhalten sich alle drei Sole normal, worauf J. Doolan⁽⁷⁶⁾ schon hingewiesen hat, nämlich der Koagulationswert γ nimmt mit dem Atomgewicht der Anionen ab, d.h.

$$\gamma \text{ Chlorid} < \gamma \text{ Bromid} < \gamma \text{ Jodid} .$$

Aber dieser Einfluss ist in meinem Fall sehr klein. Er ist erst nur in den Kurven zeitlicher Absetzung bemerkbar und bei den Koagulationswerten selbst kaum zu erkennen, wie man auf den Abb. 42, 43 und 44 sieht. Dieses Resultat könnte auch dadurch verursacht werden, dass ich zufälligerweise als Koagulator Bariumsalze angewendet habe. Wie Tabellen 13, 14 und 15 zeigen, entsteht bei den Koagulationsversuchen mit BaCl₂, BaBr₂ und BaI₂ beim Fall Hg-2 und Hg-3 (d.h. Na₂S-stabilisierte Sole) sofort nach dem Salzzusatz der goldgelbe bis weisse Niederschlag, was dagegen bei NaI-stabilisiertem Hg-4 nicht der Fall ist. Wenn man sich erinnert, dass Na₂S durch Hydrolyse NaOH ausscheidet, dann ist es sehr wahrscheinlich, dass dieses NaOH im Zusammensein mit löslichen Bariumsalzen (BaCl₂, BaBr₂, BaI₂) durch Doppelreaktion unlösliche Bariumsalze (z.B. BaO₂, BaCO₃ aus Ba(OH)₂) niederschlägt⁽⁷⁷⁾, die natürlich in kleinem oder grossem Masse über die Koagulation Einflüsse ausüben könnten. Noch eine interessante Anomalie stellt das mit NaI-stabilisierte Hg-4 bei der BaI₂-Koagulation dar, wie auf Abb. 44, und zwar sind seine Gründe auf das Vorhandensein gemeinsamer Jod-Ionen zurückzuführen. Die Wirkung gemeinsamer Ionen ist schon von v. Weimarn⁽²⁵⁾⁽²⁶⁾

(75) *Z. physik. Chem.*, **85** (1913), 647; „Kapillarchemie“, Bd. II, 137.

(76) *J. Phys. Chem.*, **20** (1925), 178.

(77) Beim Hinzufügen von BaCl₂, BaBr₂ und BaI₂ zu reiner wässriger Na₂S-Lösung, konnte ich tatsächlich das Ausscheiden weissen Niederschlags nachweisen.

theoretisch als auch experimentell oft erörtert worden. Ausserdem habe ich schon bestätigt, dass die Lebensdauer-Stabilisatorkonzentrations-Kurve von Hg-4⁽⁷⁸⁾, welches mit NaI als Stabilisator hergestellt ist, ein viel kleineres Maximumgebiet der Stabilität aufweist, als das mit Na₂S stabilisierte Hg-2 bzw. Hg-3⁽⁷⁹⁾. Daraus könnte man ersehen, dass das Hg-4 für NaI besonders empfindlich ist, da es mit sehr kleinem Überschuss an Jod-Ionen schon in unstabiles Gebiet übergehen würde.

Im Allgemeinen möchte ich bei der Koagulation von Hg-Solen darauf hinweisen, dass sie eine typisch hydrophobe Natur besitzen, wenn die zugefügte Stabilisator-Konzentration nicht zu gross ist, und in diesem Fall (Hg-3 u. Hg-4) die Teilchen durch adsorbierte Ionenkomplexe stabilisiert werden, welcher Meinung auch Wo. Pauli ist⁽⁸⁰⁾. Wenn dagegen die Stabilisator-Konzentration ziemlich gross ist, scheinen die Teilchen schon vollkommen mit irgendwelchen Verbindungen umhüllt und weisen eine recht komplizierte hydrophile Natur auf, wie es bei Hg-2 der Fall ist.

(b) **Elektrolytkoagulation von Selen-Sol.** Das Selen-Sol ist schon oft Gegenstand⁽⁸¹⁾ eingehender Untersuchung der von Smolukowski entwickelten Theorie der Koagulation gewesen, da es, unabhängig von der Darstellungsweise, ein typisch hydrophobes Suspensoid ist. Ich habe die Koagulationsversuche vorgenommen, um den Einfluss verschiedener Salze zu beobachten, wie J. Doolan ausgeführt hat. Da das Selen kein so grosses spezifisches Gewicht wie Quecksilber hat, geschieht es sehr oft, dass die koagulierten Teilchen oder Flocken bei kritischen Salzkonzentrationen in kurzer Zeit nicht ganz klar absetzen, sondern dass die Sole oft sehr lange Spuren von Trübung haben, die vielleicht durch Wiedermischen der Flüssigkeit, wegen der Wärmekonvektion, verursacht wurden. Die Unterscheidung zwischen koagulierten und nicht-koagulierten Solen ist aber sehr einfach, wenn man ihre Tyndall-Kegel beobachtet, und zwar sieht man bei ihnen, dass die koagulierten feine, ausgeflockte Teilchen haben, wohingegen die nicht-koagulierten ganz homogene, orangegelbe Tyndall-Kegel aufweisen. Die Versuchsergebnisse sind in Tabellen 19 u. 20 und Abb. 43 u. 44 dargestellt.

(78) Siehe Abb. 16.

(79) Siehe Abb. 12.

(80) *Loc. cit.*, „Elektrochemie der Kolloide“.

(81) H. Krøyt u. E. Arkel, *Kolloid-Z.*, **32** (1923), 29; *Rec. trav. chim.*, **39** (1920), 656; **40** (1921), 169; E. Arkel, Diss. Utrecht, 1920; J. Doolan, *J. Phys. Chem.*, **29** (1925), 178; K. Juna, dieses Bulletin, **6** (1931), 24.

Tabelle 19. Koagulation von Se-Sol.

C: Salzkonzentration in Millimol im Liter.

<i>C</i>	NaCl	<i>C</i>	CaCl ₂	<i>C</i>	AlCl ₃
250	22 Tage	3.0	3 Monate	0.015	Mehr als 7 Monate
375	12 Tage	4.0	75 Tage	0.020	15 Tage
375	13 Tage	5.0	46 Tage	0.025	5 Tage
500	11 Tage	7.0	21 Tage	0.030	1 Tag
500	9 Tage	8.0	10 Tage	0.036	1 Tag
500	9 Tage	10.0	10 Tage	0.040	
550	8 Tage	12.5	6 Tage	0.050	
750	4 Tage	15.0	6 Tage	0.075	
1000	2 Tage	17.5	4 Tage	0.100	
1250	2 Tage	20.0	3 Tage	0.150	
1500	2 Tage	30.0	2 Tage	0.200	
		50.0	2 Tage	0.300	

Tabelle 20. Koagulation von Se-Sol.

C: Salzkonzentration in Millimol im Liter.

<i>C</i>	BaCl ₂	BaBr ₂	BaI ₂
0.25	7 Monate	44 Tage	Mehr als 7 Monate
0.50	4 Monate	23 Tage	20 Tage
0.75	11 Tage	15 Tage	18 Tage
10.0	6 Tage	9 Tage	9 Tage
12.5	5 Tage	—	8 Tage
15.0	4 Tage	5 Tage	6 Tage
20.0	2 Tage	3 Tage	3 Tage
30.0	2 Tage	2 Tage	1 Tag
40.0	2 Tage	2 Tage	1 Tag
50.0	2 Tage	2 Tage	1 Tag

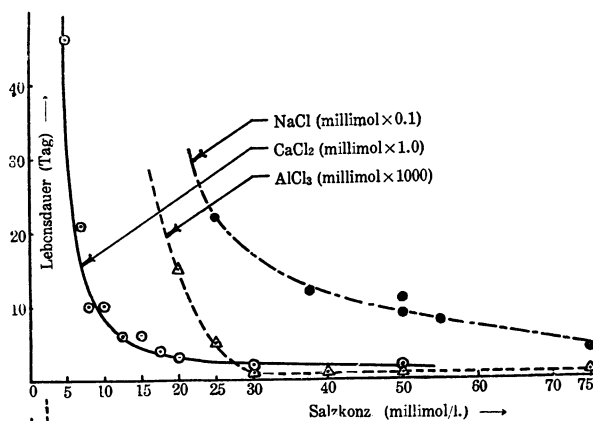


Abb. 43.

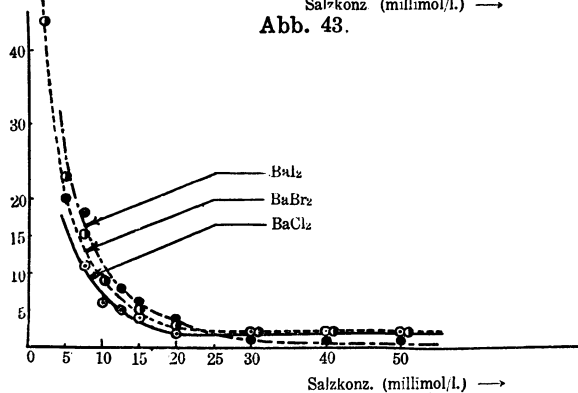


Abb. 44.

Die Versuchsergebnisse über die Koagulationswerte γ für Se-Sol sind in Tabelle 21 zusammengestellt.

Tabelle 21. Koagulationswerte des Se-Sols in Millimol im Liter.

Salz	NaCl	CaCl ₂	AlCl ₃	BaCl ₂	BaBr ₂	BaI ₂	
Sata	875	25.0	0.0275	17.5	22.5	22.5	
J. Doolan ⁽⁸²⁾	NaCl	CaCl ₂	Al ₂ (SO ₄) ₃	BaCl ₂	KCl	KBr	KI
	40	0.3	0.04	0.3	35	35	60

Im Vergleich mit den Ergebnissen anderer Autoren merkt man hier eine enorme Abweichung. Als Grund dafür muss man zuerst an die Verschieden-

(82) *J. Phys. Chem.*, **29** (1925), 183.

heit in der Herstellungsmethodik denken, da mein Sol durch rein mechanische Dispergation hergestellt ist, dagegen die anderen durch chemische Reduktion zubereitet sind. In Anbetracht dieser Verschiedenheit müsste mein Sol eigentlich viel empfindlicher gegen Elektrolyte sein, da praktisch keine stabilisierenden Beimengungen vorhanden sind. Aber in Wirklichkeit ist das Gegenteil der Fall, und zwar sind bei meinem Sol die Koagulationswerte etwa 50–100 mal grösser als bei den anderen. Ich möchte deshalb die grossen Abweichungen in diesem Fall hauptsächlich auf die Verschiedenheit der Sol-Konzentrationen und des Alters zurückführen. Wie bekannt, kann man zu dem, die Koagulation bestimmenden Faktor, ausser den Eigenschaften der Kolloidteilchen selbst, noch die Sol-Konzentration und das Alter der Sole zählen. Der Zusammenhang zwischen Koagulation und Sol-Konzentration wurde schon oft untersucht, aber von den Autoren, wie z.B. Freundlich⁽⁸³⁾, Kruyt⁽⁸⁴⁾, Burton und Bishop⁽⁸⁵⁾ sowie S. Gosch und N. Dhar⁽⁸⁶⁾, sind immer noch voneinander verschiedene Resultate erhalten worden und verschiedene Erklärungen gegeben. Daraus muss man schliessen, dass diese Abhängigkeit sich nicht auf eine einheitliche, einfache Regel bringen lässt und nach der Natur des Sols und der Kolloidteilchen in jedem einzelnen Fall besondere Erklärungen gefunden werden müssen.

Meinen Fall möchte ich einfach so erklären, dass die Teilchen vielleicht in Form von Folien suspendieren, wie die ultramikroskopische Untersuchung annehmen lässt, und ausserdem ist die Konzentration so klein im Vergleich mit anderen, chemisch hergestellten Solen, dass sich die kritische Koagulations-Konzentration erst bei viel grösseren Werten sicher feststellen lässt. Dazu darf man auch nicht den Einfluss der Wärme-Konvektion ausser acht lassen, die immer Schwierigkeiten beim Beobachten kritischer Koagulationskonzentrationen bringt. Die Koagulationsabhängigkeit von dem Alter der Sole wurde von S. Gosch und N. Dhar⁽⁸⁷⁾ untersucht. Es ist ganz klar, dass etwaige Abhängigkeit zwischen ihnen vorhanden ist. Und es ist selbstverständlich nicht möglich, alle Fälle einheitlich zu behandeln, denn so scheint es sich z.B. bei As_2S_3 -Sol im Alter nur um die Grenzflächenbedingungen zu handeln, wohingegen bei den Solen der Metallhydroxyde, wie z.B. Eisenhydroxydsol, die Kolloidteilchen selbst den Einfluss des Alters zu erleiden scheinen⁽⁸⁸⁾. Von der Tatsache aus, dass mein Se-Sol, obwohl es keine Zusatz-

(83) H. Freundlich, *Z. physik. Chem.*, **44** (1903), 129.

(84) H. Kruyt u. V. Spek, *Kolloid-Z.*, **25** (1919), 11.

(85) Burton u. Bishop, *J. Phys. Chem.*, **24** (1920), 701; **25** (1921), 517.

(86) S. Gosch u. N. Dhar, *Kolloid-Z.*, **36** (1925), 137 (Zusammenfassung).

(87) *Kolloid-Z.*, **36** (1925), 134; *J. Phys. Chem.*, **30** (1926), 1564.

(88) H. Weiser u. W. Milligan, *J. Phys. Chem.*, **39** (1935), 26; J. Böhm, *Z. anorg. allgem. Chem.*, **149** (1925), 210; *Kolloid-Z.*, **42** (1927), 276.

Substanz enthält, vom Altern kaum beeinflusst wird, was seine Beständigkeit in Farbtönen und der sehr geringe Bodensatz usw. beweisen, möchte ich die Koagulationsanomalie wohl hauptsächlich auf die Konzentration und die Struktur der Se-Teilchen selbst zurückführen. Zusammenfassend möchte ich bei Se-Sol darauf hinweisen, dass dasselbe, obwohl es hydrophob ist, nicht nur von sich selbst aus ohne besonderen Stabilisator beständig ist, sondern dass es auch gegen Elektrolyte sehr unempfindlich ist. Hierbei darf man nicht vergessen, dass mein Se-Sol durch Schütteln beständig und auch konzentrierter geworden ist, was sonst umgekehrt d.h. koagulierend wirkt⁽⁸⁹⁾. Daraus kann man vermuten, dass das Selen mit Selenwasserstoff, der bei der Explosion entstanden ist, und mit in Wasser gelöst vorhandenen Gasen, wie z.B. Sauerstoff, etwaige stabilisierend wirkende, chemische Verbindungen ergeben hätte.

Die Untersuchung der Feinstruktur der Kolloidteilchen dieses Sols wird uns eine interessante Aufgabe bleiben.

(c) **Elektrolytkoagulation von Schwefel-Sol.** Obwohl die S-Sole, durch unsere Methode hergestellt, ziemlich unbeständig waren, und zwar nur eine Lebensdauer von 8–15 Tagen hatten, wurden die Koagulationsversuche mit frisch hergestellten Solen, durch 5 mal wiederholte Explosionen, ausgeführt. Für die vollständige Koagulation, die 1/2 bis 1 Tag dauerte, wurden die folgenden Koagulationswerte erhalten.

Tabelle 22.

	NaCl	CaCl ₂	AlCl ₃	BaCl ₂	BaBr ₂	BaI ₂	CeCl ₃
Sata	17.5	2.25	0.045	2.25	2.30	2.30	—
Freundlich ⁽⁹⁰⁾	34.0	3.8	—	3.6–2.6	—	—	0.1–0.2

Zum Vergleich wurden die Koagulationswerte, die von H. Freundlich an v. Weimarn'schem S-Sol festgestellt sind, angegeben. Er weist darauf hin, dass die Differenz der Koagulationswerte von der Schwefel-Konzentration als auch von der Alkoholmenge nicht viel ausmacht. Die Koagulationswerte meines Sols für alle Elektrolyte verschiedener Wertigkeiten sind etwa zweimal kleiner als die der v. Weimarn'schen. Daraus könnte man vermuten, dass dieses Sol viel mehr hydrophobe Eigenschaften aufweist als das v. Weimarn'sche. Ob für deren Ursache entweder der Umstand, dass Schwefel in viel

(89) „Kapillarchemie“, Bd. II, S. 154.

(90) *Kolloid-Beihfte*, **16** (1925), 238.

reinerem Zustand im Wasser dispergiert worden ist, oder dass Schwefel, von starkem Erhitzen unter Druck und plötzlichem Abkühlen, in anderer Modifikation als der von v. Weimarn'schen sich befindet, verantwortlich ist, kann man nicht sicher sagen. Das Eintreten grünlich-gelber Farbtöne in den ersten 5–10 Minuten nach der Explosion dürfte diese Vermutung unterstützen.

Schlusswort.

Bei den umstehend ausgeführten, kolloidsynthetischen Untersuchungen durch die neue Methode der Kolloidsynthese mittels Dampfexplosion, habe ich mich mit den am leichtesten dispergierbaren Substanzen, wie Quecksilber, Schwefel und Selen beschäftigt, insbesondere mit der Anwendbarkeit, den Ausführungseinrichtungen und Eigenschaften so hergestellter, disperser Systeme. Durch eine nur kleine Verbesserung an den Einrichtungen, die immer noch keine besonderen Geräte, als nur gewöhnliche Laboratoriumsmittel verlangen, konnte ich die Anwendbarkeit dieser Methode bei Quecksilber vom Siedepunkt 357°C . bis auf das Selen mit einem Siedepunkt von 688°C . erhöhen, dessen Kolloiddispersion ich mit einer provisorischen Einrichtung noch nicht erfolgreich ausführen konnte. Diese Tatsache zeigt uns das zukünftige Entwicklungsbereich dieser Methode, durch die man nur durch die Erhöhung des Dampfdrucks die Kolloiddispersion verschiedener Substanzen erreichen kann. Dass der wichtigste Punkt dieser Methode, deren Theorie schon früher bekannt war, auf der Verwirklichung derselben in der Praxis beruht, habe ich schon erwähnt. Ausserdem ist es auch durch meinen Versuch bestätigt, dass noch ein anderer wichtiger Punkt, besonders aus praktischen Gründen, die Reinheit der, durch diese Methode hergestellten Sole ist. Von den nicht immer reproduzierbaren Resultaten dieser Methode, die ich anfangs bei den vorläufigen Versuchen noch nicht erklären konnte, war ich bei weiteren Versuchen imstande festzustellen, dass sie durch zufällige Verunreinigungen verursacht wurden. Ausserdem erhielt man dabei noch die Bestätigung, dass keine dispersen Systeme ohne Stabilisator stabil bleiben können, ganz gleichgültig, ob er besonders hinzugefügt oder während der Dispersion entstanden ist. Da es bei der bisherigen Dispersionsmethodik, unabhängig davon, ob die chemisch, elektrisch oder mechanisch ist, fast unmöglich ist, die Verunreinigungen ganz und gar auszuschalten, weiss man noch nichts Genaueres über die Stabilisatorwirkung und ihren Mechanismus. Meine neue Dampfexplosionsmethode weist in diesem Punkt einen grossen Vorteil auf, unter der Voraussetzung, dass die dispergierende Substanz die Hitze und den Druck einiger Atmosphären ertragen kann, wie Quecksilber usw. Dann ist beim Moment der Explosion, obwohl der hochehitze Dampf mit dem Dispersionsmittel in

Kontakt kam, eine Zersetzung oder das Entstehen neuer Verbindungen durch diesen Kontakt kaum möglich, weil die Menge kalten Dispersionsmittels unendlich grösser ist, als der hochehitze Dampf, und die Dampfcondensation sich fast momentan vollzieht, sodass währenddessen eine chemische Verbindung der Hitze wegen nicht möglich ist; natürlich ist es eine andere Frage, ob hier eine Oberflächenreaktion zwischen kondensiertem Dampf und Dispersionsmittel stattfindet. Hierbei konnte man annehmen, dass eine ideale Dispergation einer reinen dispergierenden Substanz in reinem Dispersionsmittel geschehen ist. Also konnte man durch diese Methode hoffen, den Mechanismus des Stabilisierens zu studieren. Einige Versuche, die ich mit Quecksilber disperser Systeme und mit Natriumsulfid bzw. Natriumjodid als Stabilisator ausgeführt habe, dürften eine Richtung dieses Studiums zeigen.

Was die Eigenschaften der, durch diese Methode hergestellten, Sole betrifft, so möchte ich zuerst darauf hinweisen, dass es typisch hydrophob sind. Die Sole, die eine verhältnismässig kleine Menge von Stabilisatoren enthalten, wie Hg-3 oder Hg-4, stellen besonders diese Tatsache dar, im Hinblick auf die Gültigkeit der Theorie von Whetham. Das bringt uns die Vermutung nahe, dass diese Sole durch die Adsorption von Komplex-Ionen stabilisiert worden sind, die bei der Explosion durch Oberflächenreaktion zwischen dispergierender Substanz und vorhandenem Stabilisator entstanden sind.

Hg-2, welches mit konzentrierterem Stabilisator hergestellt ist, weist besondere Eigenschaften auf. Nämlich erstens, zeigt es eine viel merklichere hydrophile Natur als die anderen Sole; zweitens ähnelt es stark dem Sol, das aus einer, als reiner Stabilisator zu betrachtenden, Substanz entstanden ist, in diesem Fall ist es nämlich mein mit Na_2S stabilisiertes Hg-2 (wirklich stabilisierende Substanz ist natürlich HgS) und reines HgS-Sol nach Wissinger, wie ich im anderen Kapitel schon erwähnt habe. Daraus schliesst man, dass dieses Hg-2-Sol schon vollkommen mit HgS an der Oberfläche umhüllt ist. Hier hat man es mit drei interessanten Sorten von Solen zu tun, nämlich

- (1) Hg-3 : Hg-Sol mit adsorbierten Hg-Sulfiden stabilisiert,
- (2) Hg-2 : Hg-Sol mit Hg-Sulfiden umhüllt stabilisiert,
- (3) HgS-Sol: Nach Wissinger aus reinem HgS entstanden.

Die vergleichende Untersuchung dieser drei Arten von Solen gibt uns einen interessanten Versuchsgegenstand, um den Stabilisator-Mechanismus aufzuklären, dessen Weg man nur durch meine neue Dampfexplosionsmethode finden kann.

Unser Selen-Sol weist auch merkwürdige Eigenschaften auf, nämlich erstens lässt es sich nicht besonders gut stabilisieren durch Zusatz gewöhnlicher, hydrophiler Schutzkolloide, wie z.B. Gelatine, „Gum-Acacia Merck“

usw., wie die anderen Sole⁽⁹¹⁾, und zweitens ist es sehr beständig gegen Elektrolyte, obwohl kein besonderer Stabilisator zugesetzt wurde, sondern nur durch Schütteln stabilisiert wurde. Da wir durch diese Methode wegen der unvollkommenen Einrichtungen noch nicht genug konzentriertes Sol erhalten konnten, habe ich diese Anomalie einfach mit der, durch Wärmekonvektion verursachten Unklarheit des Koagulationsendpunktes, erklärt. Und es ist auch sehr leicht möglich, wenn man bedenkt, dass das Selen ein spezifisches Gewicht von 4.5 besitzt, im Vergleich mit dem 13.59 von Quecksilber. Aber ich möchte noch darauf aufmerksam machen, dass das Selen-Sol in nicht so grossen sichtbaren Flocken wie die Hg-Sole, sondern in sehr feinen, mikroskopischen Flocken abgesetzt war. Es ist wohlbekannt, dass die Koagulation im Allgemeinen in zwei Stufen vor sich geht, nämlich durch langsame und durch rasche Koagulation⁽⁹²⁾, von denen erstere als ein viel komplizierterer Vorgang zu bezeichnen ist, als die letztere. Da die langsame Koagulation mit der elektrischen Entladung der Kolloid-Teilchen und dem darauffolgenden wirksamen Zusammenstoss zu tun hat, woraus Teilchen bestimmter Grösse erwachsen, die von der Erdbeschleunigung abgesetzt werden, muss man die Koagulationsanomalie unserer Se-Sole auch als eine Art verwickelter Koagulation betrachten. So möchte ich konstatieren, dass dieses Se-Sol ein sehr grosses Gebiet der langsamen Koagulation aufweist, worüber man, zwecks näherer Erklärung, noch weitere Forschungen anstellen muss.

Zusammenfassung.

(1) Eine neue Methode der Kolloidsynthese, nämlich die Dampfexplosionsmethode, die die Kolloiddispersion durch die Explosion der Dämpfe dispergierender Substanzen im Innern der Dispersionsmittel gestattet, ist ausführlich untersucht worden.

(2) Die kolloiddispersen Systeme von Quecksilber, Schwefel und Selen wurden auf diese Art und Weise hergestellt.

(3) Die Bedingungen, um stabile, konzentrierte, disperse Systeme zu erhalten, wurden auf folgende Gesichtspunkte hin untersucht :

- (a) Apparate und Einrichtungen,
- (b) zur Explosion nötige Menge der dispergierenden Substanzen,
- (c) Abhängigkeit der Sol-Konzentrationen von der Zahl der Explosionen,
- (d) Vorhandensein des Stabilisators und andere Verunreinigungen,
- (e) Einfluss von Licht auf die Stabilität.

(91) A. Gutbier, *Kolloid-Z.*, **31** (1922), 33; **32** (1923), 255; **33** (1924), 35, 334.

(92) R. Zsigmondy, *Nachr. kgl. Ges. Wiss. Göttingen*, **1**, a (1917); „Kapillarchemie“ Bd. II, S. 140.

(4) Bei Quecksilber wurde es bestätigt, dass es ohne Stabilisator unmöglich ist, ein stabiles, disperses System zu erhalten.

(5) Natriumsulfid und Natriumjodid wurden als stabilisierend wirkend gefunden; deren Wirksamkeit weist ein Maximum zwischen bestimmten Konzentrationsgebieten auf, wie es die Theorie von v. Weimarn verlangt; dagegen war die Wirkung von Natriumsulfit nicht nur stabilisierend, sondern auch koagulierend.

(6) Es wurde ferner bestätigt, dass es unmöglich ist, Schwefel in rein hydrophobem Zustand in stabilem, kolloiddispersen System zu dispergieren, wie durch andere Methoden auch gezeigt wurde.

(7) Bei Selen wurde gefunden, dass man durch einfaches Maschine-Schütteln ein stabiles, disperses System erhalten kann.

(8) Die kolloidchemischen Eigenschaften der erhaltenen dispersen Systeme wurden untersucht, und zwar wurden:

- (a) Mikro- und ultramikroskopische Untersuchungen angestellt,
- (b) die Viskosität und die Oberflächenspannung studiert,
- (c) die elektrophoretische Untersuchungen und Koagulationsversuche ausgeführt.

(9) Durch vorher genannte Untersuchungen wurde bestätigt, dass diese dispersen Systeme durchschnittlich typisch hydrophob sind.

(10) Nur mit 0.01 mol Na_2S stabilisiertes Hg-Sol weist mehr hydrophile Eigenschaften auf. Und durch seine grossen Koagulationswerte und durch die Ähnlichkeit von diesem Sol mit HgS-Sol in seiner Farberscheinung wurde festgestellt, dass das Sol vielleicht mit HgS umhüllte Teilchen enthält.

(11) Das Selen-Sol weist auch eine Anomalie in seiner Unempfindlichkeit gegen Elektrolyte auf, obwohl es keinen besonderen Stabilisator enthält und es wurde vermutet, dass deren Ursache mit der Sol-Konzentration und dem Alter der Sole im Zusammenhang steht.

(12) Zum Schluss wurde darauf aufmerksam gemacht, dass diese Methode, die die reine Dispergation in reinem Dispersionsmittel gestattet, zur Untersuchung des Mechanismus des Stabilisierens eine neue Richtung zeigt.

An dieser Stelle möchte ich Herrn Prof. Dr. P. P. von Weimarn (geb. 1879, gest. 1935) in Verehrung und Dankbarkeit gedenken, da er in seinen letzten fünf Lebensjahren mir nicht nur bei vorliegender Arbeit, sondern auch bei allen meinen kolloidwissenschaftlichen Studien, in lebenswürdiger Weise mit Rat und Tat zur Seite stand. Ich werde dem grossen Forscher stets treue ehrende Erinnerung bewahren und kann nicht umhin, meinem Bedauern Ausdruck zu verleihen, dass es mir nicht vergönnt war, ihm dieses Werk persönlich vorlegen zu können.

Herrn Professor Dr. J. Sameshima danke ich herzlichst für sein reges Interesse und seine freundliche Unterstützung bei dieser Arbeit.

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ISOTOPIC INTERCHANGE REACTION BETWEEN CHLOROFORM AND WATER.

By J. HORIUTI and Y. SAKAMOTO.

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It is well known that chloroform decomposes when heated with alkaline solution in air. It was found now that in vacuum the isotopic interchange reaction between chloroform and heavy alkaline solution proceeds quicker than the decomposition.

Twenty c.c. of usually purified chloroform was sealed air-free in a reaction vessel of 80 c.c. capacity together with 0.5 c.c. of heavy alkaline, neutral or acidic solution. The reaction vessel was heated in a boiling water bath for a few days, opened and then the contents were separated from one another for analysis. The water of the solution or from the chloroform, which was burnt by a special furnace, was determined in density by means of a micro-pycnometer.⁽¹⁾ Part of the solution was tested for free chlorine ion by means of N/100 AgNO₃ solution in order to follow the decomposition of chloroform.

Solution	Time <i>t</i> (hours)	D-content in solution		D-content in chloroform after the reaction	<i>k_i</i> (hr ⁻¹) × 10 ⁴	<i>k_d</i> (hr ⁻¹) × 10 ⁴
		init. <i>D</i> ₀	fin. <i>D</i> _{<i>t</i>}			
N/10 KOH	21	4.02	3.72	—	8	—
	72	„	3.03	0.26	9	0.1
	60	„	2.79	—	14	0.1
	48	„	3.20	0.16	10	0.1
Pure water	85	3.14	3.18	—	0.4	—
N/100 H ₂ SO ₄	15	2.91	2.86	—	3	—

(1) Okamoto and Shindo, *J. Chem. Soc. Japan*, **57** (1936), 669. The original method by Gilfillan and Polanyi, *Z. physik. Chem., A*, **166**, 254 (1933), has since been essentially improved by these authors.

D-contents are given in terms of atomic percentage of deuterium. It is obvious from the table that the interchange reaction takes place with alkaline solution, which was confirmed by analysing both of the reactants. Interchange reaction with neutral or with acidic solution, if any, is far slower than that with alkaline solution.

Assuming the approximate chemical equivalence of H and D, the first order rate of interchange, $k_i \left(= \frac{2n_w}{n_{ch}} \frac{1}{t} \ln \frac{D_0}{D_t} \right)$, was calculated for chloroform from the decrease of D-content in the solution and this was compared with the rate of decomposition, $k_d \left(= \frac{n_{Cl'}}{3n_{ch}} \cdot \frac{1}{t} \right)$. n_w , n_{ch} and $n_{Cl'}$ are number of gram mols or gram ions of the water, the chloroform and free chlorine ions respectively. k_i or k_d is, therefore, the fraction of total quantity of chloroform which undergoes interchange (including the replacement of H atom of $CHCl_3$ by other H atoms from water or decomposition per unit time). We see from the figures in the table that a chloroform molecule is quickly interchanging its H atom with water before decomposition.

Detailed description of the experimental procedure and the discussion of the mechanism will be given later.

*Chemical Department, Faculty of Science,
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ÜBER KOBALTAMMINE, DIE QUARTÄRE AMMONIUM-BASEN KOORDINIEREN.⁽¹⁾

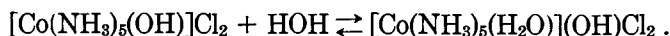
Von Yuichi NAKATSUKA.

Eingegangen am 1. Juli 1936. Ausgegeben am 28. Oktober 1936.

Während meines Studium über Aquokobaltiammine habe ich gefunden, dass das Absorptionsspektrum des Aquopentamminkobaltichlorids in einer ammoniakalischen Lösung ganz verschieden ist von der wässrigen Lösung des Hydroxopentamminsalzes mit demselben Kobaltgehalt.

In der vorliegenden Arbeit habe ich einige Untersuchungen über aminhaltige Lösungen von Aquokobaltiamminen im allgemeinen durchgeführt, und dadurch bin ich auf den Schluss angekommen, dass in solchen Lösungen sich diejenigen Salze noch unbekannter Reihe bilden, bei denen statt koordinativ gebundener Wassermoleküle quartäre Ammoniumhydroxyde sich am Kobaltatom koordinieren.

Absorptionskurven wässriger bzw. aminhaltiger Lösungen von Aquokobaltiamminen und verwandter Salze. $[\text{Co}(\text{NH}_3)_5(\text{OH})]\text{Cl}_2$ reagiert in wässriger Lösung alkalisch; das beruht, wie allgemein angenommen, auf folgendem:⁽²⁾



Wenn man deswegen eine Lösung von $[\text{Co}(\text{NH}_3)_5(\text{OH})]\text{Cl}_2$ mit einer Säure abstumpft, bildet sich das $[\text{Co}(\text{NH}_3)_5(\text{H}_2\text{O})]$ -Salz.

Ebenfalls ist die saure Reaktion der Lösung von $[\text{Co}(\text{NH}_3)_5(\text{H}_2\text{O})]\text{Cl}_3$ durch das folgende Gleichgewicht bedingt:



Daraus ist folgendes gleicherweise leicht vorstellbar: Werden zu einer Lösung von $[\text{Co}(\text{NH}_3)_5(\text{H}_2\text{O})]\text{Cl}_3$ OH-Ionen zugesetzt, so wird sich das Hydroxosalz bilden. Dieses geht tatsächlich vor sich, wenn man eine alkalische Substanz, wie NaOH bzw. Na_2CO_3 , als OH-Ionenquelle nimmt. Eine wässrige Lösung von $[\text{Co}(\text{NH}_3)_5(\text{OH})]\text{Cl}_2$ und eine gemischte Lösung von

(1) Die meisten Teile dieser Arbeit wurden 1927 in Japanisch veröffentlicht: *J. Chem. Soc. Japan*, **48** (1927), 66.

(2) Vgl. Werner-Pfeiffer, „Neuere Anschauungen auf dem Gebiete der anorganischen Chemie“. 5. Aufl., S. 251, Braunschweig 1923.

$[\text{Co}(\text{NH}_3)_5(\text{H}_2\text{O})]\text{Cl}_3$ und NaOH bzw. Na_2CO_3 von demselben Kobaltgehalt geben beide dasselbe Absorptionsspektrum. Abb. 1 zeigt Absorptionskurven folgender Lösungen :

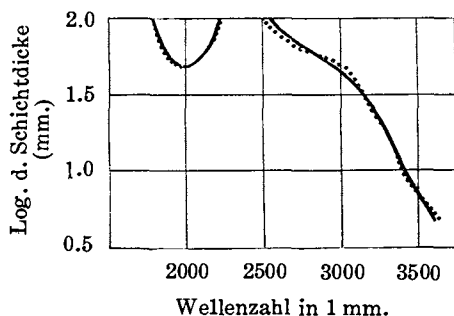


Abb. 1. — Lösung A
 Lösung B

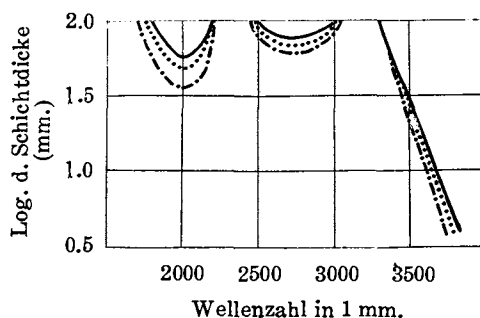
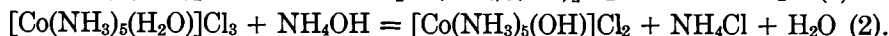
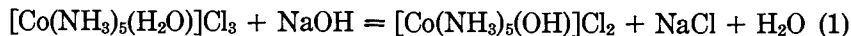


Abb. 2. — Lösung C
 Lösung D
 - · - · - Lösung E

Lösung A : $[\text{Co}(\text{NH}_3)_5(\text{OH})]\text{Cl}_2^{(3)}$ 0.01 norm.⁽⁴⁾ wässrige Lösung,

Lösung B : $[\text{Co}(\text{NH}_3)_5(\text{H}_2\text{O})]\text{Cl}_3$ 0.01 norm. in 0.1 norm. Na_2CO_3 -Lösung.⁽⁵⁾

Wenn aber statt NaOH bzw. Na_2CO_3 NH_3 -Lösung verwendet wird, findet man eine Absorptionskurve ganz verschiedener Art im ultravioletten Gebiet (siehe Abb. 2). Nun wurde bisher doch allgemein angenommen, dass solche Lösungen stets $[\text{Co}(\text{NH}_3)_5(\text{OH})]$ -Salz geben, wie folgende Gleichungen zeigen :



Die Ursache des eben angegebenen Unterschieds der Absorption kann man verschieden deuten, jedoch kann die zutreffende Erklärung nur folgende sein, was weiter unten näher begründet wird : Wenn man zu einer Lösung von $[\text{Co}(\text{NH}_3)_5(\text{H}_2\text{O})]\text{Cl}_3$ NH_3 zusetzt, so bildet sich nicht $[\text{Co}(\text{NH}_3)_5(\text{OH})]\text{Cl}_2$ (wenigstens hauptreaktionsweise nicht), sondern eine noch unbekannte Art Ammin. Also die oben angegebene Gleichung (2) entspricht nicht dem tatsächlichen Reaktionsverlauf. In Abb. 2 sind Absorptionskurven folgender Lösungen dargestellt (die Absorptionskurve desselben Chlorids in der wässrigen Lösung wird in Abb. 3 wiedergegeben) :

(3) Dieses Salz hat gewöhnlich ein Mol. Kristallwasser. In der vorliegenden Arbeit wird es aber Einfachheit halber stets ohne Kristallwasser angegeben.

(4) Normalität der Kobaltiammine bezieht sich stets auf Kobaltatom, also z.B. 0.01 norm. $[\text{Co}(\text{NH}_3)_5(\text{H}_2\text{O})]_2(\text{SO}_4)_3$ -Lösung ist 0.005 molar.

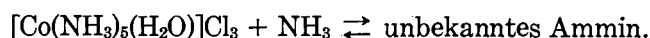
(5) Die NaOH -Lösung des Kobaltiammins ist nicht sehr beständig, und deswegen wurde Na_2CO_3 fast immer statt NaOH verwendet.

Lösung C: $[\text{Co}(\text{NH}_3)_5(\text{H}_2\text{O})]\text{Cl}_3$ 0.01 norm. in 0.01 norm. NH_3 -Lösung,

Lösung D: $[\text{Co}(\text{NH}_3)_5(\text{H}_2\text{O})]\text{Cl}_3$ 0.01 norm. in 0.1 norm. NH_3 -Lösung,

Lösung E: $[\text{Co}(\text{NH}_3)_5(\text{H}_2\text{O})]\text{Cl}_3$ 0.01 norm. in 1.0 norm. NH_3 -Lösung.

Daraus lässt sich deutlich erkennen, dass die Absorptionsbanden um so tiefer werden, je konzentrierter NH_3 in der Lösung ist. Dieselbe Vertiefung wird auch festgestellt, wenn man die Lösung während der Aufnahme des Spektrums mit Eis kühlt. Durch das oben beschriebene wird man sich leicht überzeugen, dass in einer ammoniakalischen Lösung von $[\text{Co}(\text{NH}_3)_5(\text{H}_2\text{O})]\text{Cl}_3$ folgendes Gleichgewicht stattfindet:



Das Gleichgewicht verschiebt sich nach rechts mit der Zunahme der NH_3 -Konzentration und auch mit der Abnahme der Temperatur.

Andere Aquopentamminsalze, wie das Sulfat, Nitrat und Oxalat reagieren auch mit NH_3 -Lösung ganz genau wie das Chlorid. Nur die Endabsorption des Nitrats zeigt eine geringe Abweichung, aber als Ganzes können dennoch alle diese Kurven mit denen des Chlorids als identisch angesehen werden. Die Bildung des betreffenden Ammins beruht also lediglich auf der Reaktion von NH_4OH mit dem $[\text{Co}(\text{NH}_3)_5(\text{H}_2\text{O})]$ -Radikal. Säurereste der Salze spielen dabei keine Rolle.

Zum Vergleich seien hier noch Absorptionskurven folgender Lösungen in Abb. 3 angegeben:

Lösung F: $[\text{Co}(\text{NH}_3)_5(\text{H}_2\text{O})]\text{Cl}_3$ 0.01 norm. wässrige Lösung,

Lösung G: $[\text{Co}(\text{NH}_3)_5\text{Cl}]\text{Cl}_2$ 0.01 norm. wässrige Lösung.

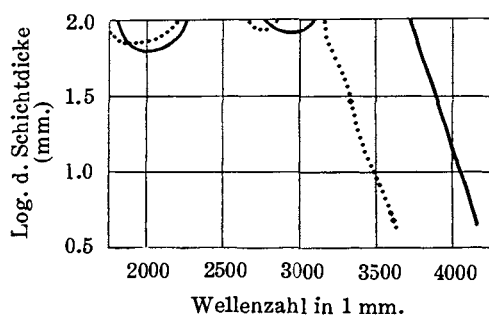


Abb. 3. — Lösung F
..... Lösung G

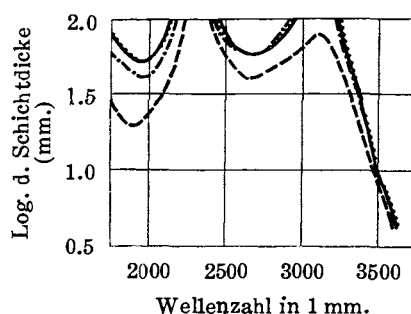


Abb. 4. — Lösung H
..... Lösung I
- · - · - Lösung K
- - - - Lösung L

Es ist doch nun sehr wahrscheinlich, dass das koordinativ gebundene Wassermolekül vom $[\text{Co}(\text{NH}_3)_5(\text{H}_2\text{O})]$ -Radikal bei der Bildung des betreffenden Ammins eine grosse Rolle spielt. Um diese Ansicht zu klären, wurden folgende Ammine, die kein koordinatives Wasser in den Komplexradikalen enthalten, daraufhin untersucht, ob sie auch mit NH_4OH ähnliche Reaktion geben können oder nicht: (1) $[\text{Co}(\text{NH}_3)_5\text{Cl}]\text{Cl}_2$, (2) $[\text{Co}(\text{NH}_3)_5(\text{OH})]\text{Cl}_2$, (3) $[\text{Co}(\text{NH}_3)_6](\text{NO}_3)_3$, (4) $[\text{Co}(\text{NH}_3)_5(\text{NCS})]\text{SO}_4$, (5) $[\text{Co}(\text{NH}_3)_5(\text{NO}_2)]\text{Cl}_2$, (6) $[\text{Co}(\text{NH}_3)_4(\text{CO}_3)]_2\text{SO}_4$, (7) $[\text{Co}(\text{NH}_3)_2(\text{NO}_2)_4]\text{NH}_4$. Es ergab sich, dass alle diese Ammine, ausser $[\text{Co}(\text{NH}_3)_5\text{Cl}]\text{Cl}_2$, nicht mit NH_4OH reagieren. Die ammoniakalische Lösung von $[\text{Co}(\text{NH}_3)_5\text{Cl}]\text{Cl}_2$ zeigte dagegen dieselbe Absorptionskurve wie die ammoniakalische $[\text{Co}(\text{NH}_3)_5(\text{H}_2\text{O})]\text{Cl}_3$ -Lösung. Diese Tatsache braucht jedoch deshalb nicht besonders berücksichtigt zu werden, da $[\text{Co}(\text{NH}_3)_5\text{Cl}]\text{Cl}_2$ in alkalischer Lösung glatt in $[\text{Co}(\text{NH}_3)_5(\text{H}_2\text{O})]\text{Cl}_3$ übergeht und infolgedessen dessen Absorptionskurve ergeben muss. Wenn also ein Ammin kein Wassermolekül koordinativ gebunden enthält, oder wenn ein anderes koordinatives Atom bzw. eine Atomgruppe von einem Kobaltiammin in der alkalischen Lösung fest gebunden ist und durch Wasser nicht substituiert wird, dann entsteht die betreffende neue Art des Ammins nicht.

Wenn man einerseits zu der betreffenden Ammin-Lösung d.h. der ammoniakalischen Lösung von $[\text{Co}(\text{NH}_3)_5(\text{H}_2\text{O})]\text{Cl}_3$ Alkohol fügt, so zersetzt sich dieses Ammin und es fällt $[\text{Co}(\text{NH}_3)_5(\text{OH})]\text{Cl}_2$ aus;⁽⁶⁾ dies zeigt, dass sich $[\text{Co}(\text{NH}_3)_5(\text{OH})]\text{Cl}_2$ nur bei der Fällung bildet. Wird die Lösung andererseits in der Kälte mit HCl neutralisiert, so entsteht, wie allgemein bekannt, $[\text{Co}(\text{NH}_3)_5(\text{H}_2\text{O})]\text{Cl}_3$ wieder. Durch diese beiden Reaktionen lässt sich erklären, dass das zentrale Kobaltatom des betreffenden Ammins, wie das Mutteraquosalz, fünf Moleküle NH_3 koordiniert, dass aber an der sechsten Koordinationsstelle eine mit einem Sauerstoffatom gebundene Atomgruppe steht nach folgendem Schema: $[(\text{NH}_3)_5\text{Co}(\text{OX})]$, wo X noch unbekannt ist.

Im folgenden werden nun die Reaktionen von $[\text{Co}(\text{NH}_3)_5(\text{H}_2\text{O})]$ -Salz mit Aminen bzw. Aminverbindungen anstelle von Ammoniak beschrieben. Folgende Verbindungen wurden dazu verwendet: (1) Äthylendiamin $\text{NH}_2\cdot\text{CH}_2\cdot\text{CH}_2\cdot\text{NH}_2$, (2) Methylamin $\text{CH}_3\cdot\text{NH}_2$, (3) Diäthylamin $(\text{C}_2\text{H}_5)_2\text{NH}$, (4) Trimethylamin $(\text{CH}_3)_3\text{N}$, (5) Tetramethylammoniumhydroxyd $(\text{CH}_3)_4\text{NOH}$, (6) Piperidin $\text{C}_5\text{H}_{11}\text{N}$, (7) Pyridin $\text{C}_5\text{H}_5\text{N}$, (8) Harnstoff $\text{CO}(\text{NH}_2)_2$, (9) Urethan $\text{NH}_2\cdot\text{COOC}_2\text{H}_5$. Die beiden letzten, Harnstoff und Urethan, geben keine Reaktion mit $[\text{Co}(\text{NH}_3)_5(\text{H}_2\text{O})]$ -Salz; alle anderen Amine reagieren jedoch, und zwar geben die Amine von (1) bis (6) genau dieselben Absorptionskurven wie in dem Falle, wo Ammoniak verwendet wurde. Bei Pyridin greift die Absorption desselben auf die des Ammins über und deswegen kann

(6) A. Werner, *Ber.* **40** (1907), 4106.

man die Endabsorption nicht bemerken, aber man findet noch die zwei charakteristischen Banden des betreffenden Ammins. Diese Banden sind jedoch bei Pyridin nicht so tief wie bei den anderen. Dies ist durch die Unvollständigkeit der Reaktion bedingt, welche darauf zu beruhen scheint, dass Pyridin als Base nicht stark genug reagiert; seine Ionisationskonstante liegt in der Grössenordnung 10^{-9} , während alle anderen reagierbaren Amine viel stärker sind und Dissoziationskonstanten von der Ordnung 10^{-5} haben. Über diese Beziehung wird nachher nochmals die Rede sein.

Ich habe aus dem oben beobachteten den Schluss bezogen, dass das koordinative Wassermolekül eine grosse Rolle spielt, wenn $[\text{Co}(\text{NH}_3)_5(\text{H}_2\text{O})]$ -Salz mit Aminen reagiert. Ganz gleicherweise finden solche Reaktionen auch bei $[\text{Co}(\text{NH}_3)_4(\text{H}_2\text{O})_2]$ - und $[\text{Co}(\text{NH}_3)_3(\text{H}_2\text{O})_3]$ -Salzen statt. Diese beiden Arten Ammine geben in der Aminlösung überhaupt sehr ähnliche Absorptionen mit $[\text{Co}(\text{NH}_3)_5(\text{H}_2\text{O})]$ -Salz.

Absorptionskurven folgender Lösungen sind in Abb. 4 angegeben (vgl. Abb. 2):

Lösung H: $[\text{Co}(\text{NH}_3)_4(\text{H}_2\text{O})_2]\text{Cl}_3$ 0.01 norm. in 0.1 norm. NH_3 -Lösung,

Lösung I: $[\text{Co}(\text{NH}_3)_4(\text{H}_2\text{O})_2]_2(\text{SO}_4)_3$ 0.01 norm. in 0.1 norm.
 $\text{NH}_2\cdot\text{CH}_2\cdot\text{CH}_2\cdot\text{NH}_2$ -Lösung,

Lösung K: $[\text{Co}(\text{NH}_3)_4(\text{H}_2\text{O})_2]\text{Cl}_3$ 0.01 norm. in 1.0 norm. NH_3 -Lösung,

Lösung L: $[\text{Co}(\text{NH}_3)_3(\text{H}_2\text{O})_3]\text{Cl}_3$ 0.01 norm. in 1.0 norm. NH_3 -Lösung.

Alle diese Kurven sind mit denen der $[\text{Co}(\text{NH}_3)_5(\text{H}_2\text{O})]$ -Salze in der Aminlösung ganz analog, aber im Vergleich zu diesen hat eine Verschiebung der beiden Absorptionsmaxima nach Rot und eine Erhöhung der ultravioletten Absorption stattgefunden, was in um so grösserem Masse der Fall ist, je mehr H_2O -Moleküle in den Mutterkomplexradikalen vorhanden sind.

Die ammoniakalische Lösung von $[\text{Co}(\text{NH}_3)_5(\text{H}_2\text{O})]\text{Cl}_3$ ist beständig und lange Zeit haltbar, dagegen ist eine gleiche Lösung von $[\text{Co}(\text{NH}_3)_4(\text{H}_2\text{O})_2]\text{Cl}_3$ viel unbeständiger und trübt sich nach kurzer Zeit, wenn man keinen Überschuss an Ammoniak nimmt. Das System $[\text{Co}(\text{NH}_3)_3(\text{H}_2\text{O})_3]\text{Cl}_3 - \text{NH}_3$ ist noch unbeständiger, und man muss daher einen sehr grossen Überschuss an Ammoniak anwenden, damit keine Trübung entsteht. Deswegen ist es fast unmöglich eine Aufnahme des Spektrums der 0.01 norm. $[\text{Co}(\text{NH}_3)_3(\text{H}_2\text{O})_3]\text{Cl}_3$ -Lösung in 0.1 norm. NH_4OH zu machen (siehe Lösung L oben).

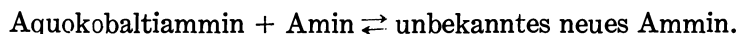
Eine ammoniakalische Lösung von $[\text{Co}(\text{NH}_3)_4(\text{H}_2\text{O})\text{Cl}]\text{Cl}_2$ bzw. $[\text{Co}(\text{NH}_3)_4\text{Cl}_2]\text{Cl}^{(7)}$ gibt identische Absorption mit der von $[\text{Co}(\text{NH}_3)_4(\text{H}_2\text{O})_2]\text{Cl}_3$. Ebenso verhalten sich in dieser Beziehung gleich ammoniakalische Lösungen

(7) Beide 1, 2- und 1, 6-Dichlorosalze gehen in Lösung in dasselbe Diaquosalz über.

von $[\text{Co}(\text{NH}_3)_3(\text{H}_2\text{O})\text{Cl}_2]\text{Cl}$ und $[\text{Co}(\text{NH}_3)_3(\text{H}_2\text{O})_3]\text{Cl}_3$, wie es bei den ammoniakalischen Lösungen von $[\text{Co}(\text{NH}_3)_5(\text{H}_2\text{O})]\text{Cl}_3$ und $[\text{Co}(\text{NH}_3)_5\text{Cl}]\text{Cl}_2$ der Fall ist.

Aus allen oben angegebenen Tatsachen kann man folgern, dass Aquokobaltiammine im allgemeinen mit Aminen in der Lösung eine Reihe neuer Ammine geben. Diese Ammine haben ähnliche Konstitution, gleichgültig, ob sie aus Mono-, Di- oder Triaquosalzen gebildet werden. Die Komplexradikale kann man demnach folgendermassen schreiben: $[(\text{NH}_3)_5\text{Co}(\text{OX})]$ aus Monoaquopentamminsalz, $[(\text{NH}_3)_4\text{Co}(\text{OX})_2]$ aus Diaquotetramminsalz und $[(\text{NH}_3)_3\text{Co}(\text{OX})_3]$ aus Triaquotriamminsalz.

Im folgenden seien nun alle denkbaren Reaktionsweisen zwischen Aquokobaltiamminen und Aminen näher erörtert, um schliesslich festzustellen, dass folgendes die einzige Erklärung für die angeführten Beobachtungen sein muss:



(1) Wenn die oben auf S. 630 angegebene Gleichung (2), die sich auf die Reaktion zwischen $[\text{Co}(\text{NH}_3)_5(\text{H}_2\text{O})]\text{Cl}_3$ und NH_4OH bezieht, richtig wäre, müsste sich NH_4Cl bilden. Kann nun der Unterschied der Absorption der wässrigen Lösung des $[\text{Co}(\text{NH}_3)_5(\text{OH})]\text{Cl}_2$ einerseits und der ammoniakalischen Lösung des $[\text{Co}(\text{NH}_3)_5(\text{H}_2\text{O})]\text{Cl}_2$ andererseits durch das nach obiger Gleichung gebildete NH_4Cl bedingt sein? Es ist von vornherein sehr unwahrscheinlich, dass NH_4Cl einen solchen Einfluss haben könnte. Sicherheitshalber aber habe ich ein Absorptionsspektrum der gemischten Lösung von $[\text{Co}(\text{NH}_3)_5(\text{OH})]\text{Cl}_2$ und NH_4Cl aufgenommen. Die Lösung zeigte nur dieselbe Absorption wie eine $[\text{Co}(\text{NH}_3)_5(\text{OH})]\text{Cl}_2$ -Lösung und eine ganz andere als die der ammoniakalischen Lösung von $[\text{Co}(\text{NH}_3)_5(\text{H}_2\text{O})]\text{Cl}_3$. Das heisst, bei der Reaktion zwischen Aquokobaltiamminen und Aminen bilden sich keine Hydroxosalze und die Gleichung (2) entspricht nicht dem wirklichen Reaktionsverlauf.

(2) Aus $[\text{Co}(\text{NH}_3)_5(\text{H}_2\text{O})]\text{Cl}_3$ und NH_4OH kann sich $[\text{Co}(\text{NH}_3)_6]\text{Cl}_3$ bilden, aber, wie allgemein bekannt, geht diese Reaktion bei Zimmertemperatur und bei solch einer kleinen Konzentration nicht vor sich. Zudem ist die Farbe dieser ammoniakalischen Lösung auch verschieden von der des $[\text{Co}(\text{NH}_3)_6]\text{Cl}_3$. Überdies kann man sich noch durch folgendes davon überzeugen, dass sich $[\text{Co}(\text{NH}_3)_6]\text{Cl}_3$ dabei nicht bildet: Fügt man nämlich zur ammoniakalischen Lösung von $[\text{Co}(\text{NH}_3)_5(\text{H}_2\text{O})]\text{Cl}_3$ in der Kälte HCl , so entsteht $[\text{Co}(\text{NH}_3)_6]\text{Cl}_3$ nicht hingegen $[\text{Co}(\text{NH}_3)_5(\text{H}_2\text{O})]\text{Cl}_3$ wieder. Ferner kann man keine denkbare Gleichung für die Reaktion zwischen $[\text{Co}(\text{NH}_3)_5(\text{H}_2\text{O})]\text{Cl}_3$ und $(\text{CH}_3)_4\text{NOH}$ angeben, um damit zu einem Salz vom Hexammintypus zu kommen, obgleich $(\text{CH}_3)_4\text{NOH}$ genau wie NH_4OH reagiert (siehe oben). Wenn sich überdies $[\text{Co}(\text{NH}_3)_6]\text{Cl}_3$ aus $[\text{Co}(\text{NH}_3)_5(\text{H}_2\text{O})]\text{Cl}_3$ und NH_4OH in solch einer verdünnten

Lösung bilden würde, sollten sowohl $[\text{Co}(\text{NH}_3)_4(\text{H}_2\text{O})_2]\text{Cl}_3$ als auch $[\text{Co}(\text{NH}_3)_3(\text{H}_2\text{O})_3]\text{Cl}_3$ dasselbe Salz $[\text{Co}(\text{NH}_3)_6]\text{Cl}_3$ geben. Aber das ist nicht der Fall, wie Absorptionskurven zeigen (siehe Abb. 2 und 4). Mithin kommt die Bildung von $[\text{Co}(\text{NH}_3)_6]$ -Salz nicht in Frage.

(3) Es wäre weiterhin denkbar, dass ein Teil des $[\text{Co}(\text{NH}_3)_5(\text{H}_2\text{O})]\text{Cl}_3$ unter der Wirkung von NH_4OH in $[\text{Co}(\text{NH}_3)_5(\text{OH})]\text{Cl}_2$ übergehen könnte. Die ammoniakalische Lösung von $[\text{Co}(\text{NH}_3)_5(\text{H}_2\text{O})]\text{Cl}_3$ müsste demnach $[\text{Co}(\text{NH}_3)_5(\text{H}_2\text{O})]\text{Cl}_3$ und $[\text{Co}(\text{NH}_3)_5(\text{OH})]\text{Cl}_2$ enthalten. Wenn dies der Fall wäre, sollte sich mehr $[\text{Co}(\text{NH}_3)_5(\text{OH})]\text{Cl}_2$ bilden, falls die NH_3 -Konzentration grösser wird. Aber wie schon in Abb. 2 gezeigt, nähert sich die Absorptionskurve der ammoniakalischen Lösung von $[\text{Co}(\text{NH}_3)_5(\text{H}_2\text{O})]\text{Cl}_3$ der von $[\text{Co}(\text{NH}_3)_5(\text{OH})]\text{Cl}_2$ nicht. Dass in der Lösung noch viel $[\text{Co}(\text{NH}_3)_5(\text{H}_2\text{O})]\text{Cl}_3$ unangegriffen bleibt, kann auch nicht angenommen werden, da auch ein schwaches Alkali wie Na_2CO_3 schon praktisch vollständig $[\text{Co}(\text{NH}_3)_5(\text{OH})]\text{Cl}_2$ aus $[\text{Co}(\text{NH}_3)_5(\text{H}_2\text{O})]\text{Cl}_3$ gibt (siehe Abb. 1), usw. usw. Als die einzige richtige Erklärung bleibt demnach die oben angeführte übrig.

Ermittlung des Reaktionsverhältnisses zwischen Aquokobaltiammin und Amin in der Lösung mittels spektrographischer Methode. Ich habe oben mitgeteilt, dass Aquokobaltiammin mit Amin im allgemeinen in der Lösung unter Bildung einer neuen Art Ammin an der Stelle des koordinativen Wassers reagiert. Um nun das Reaktionsverhältnis beider Verbindungen festzustellen, habe ich zunächst die von Shibata angegebene spektrographische Methode⁽⁸⁾ gebraucht. An Hand von folgendem Lösungspaar sei die Methode kurz erklärt:

Lösungspaar I $\begin{cases} \text{A } [\text{Co}(\text{NH}_3)_5(\text{H}_2\text{O})]\text{Cl}_3 & 0.01 \text{ norm.} \\ \text{B } \text{NH}_3 & 0.01 \text{ norm.} \end{cases}$ (Schichtdicke 100 mm.)

Man stellt zunächst z.B. folgende Reihe der gemischten Lösungen her:

(1) Lösung A (kein B dabei),	(9) 2 Vol. A + 3 Vol. B,
(2) 5 Vol. A + 1 Vol. B,	(10) 1 Vol. A + 2 Vol. B,
(3) 4 Vol. A + 1 Vol. B,	(11) 3 Vol. A + 7 Vol. B,
(4) 3 Vol. A + 1 Vol. B,	(12) 1 Vol. A + 3 Vol. B,
(5) 7 Vol. A + 3 Vol. B,	(13) 1 Vol. A + 4 Vol. B,
(6) 2 Vol. A + 1 Vol. B,	(14) 1 Vol. A + 5 Vol. B,
(7) 3 Vol. A + 2 Vol. B,	(15) Lösung B (kein A dabei).
(8) 1 Vol. A + 1 Vol. B,	

(8) Y. Shibata. T. Inoue u. Y. Nakatsuka, *Japan. J. Chem.*, **1** (1922), 1.

Nun photographiert man die Absorptionsspektren dieser gemischten Lösungen eins nach dem andern nebeneinander auf einer Platte, wobei die Schichtdicke und alle anderen Bedingungen stets konstant gehalten werden.

Wie aus dem oben angegebenen zu ersehen ist (siehe Abb. 2 und 3), verschiebt sich die Endabsorption vom betreffenden Ammin nach rot, und deshalb muss die Konzentration des betreffenden Ammins am grössten sein in derjenigen Lösung, welche das Maximum der Endabsorption gibt. Da ferner alle oben angegebenen Lösungsgemische identische Gesamtkonzentration haben, d. h. alle 0.01 norm. sind, muss die Konzentration des entstehenden Ammins am grössten sein in derjenigen gemischten Lösung, in welcher das Volumverhältnis der beiden Urlösungen A und B dasselbe wie das Reaktionsverhältnis der beiden Substanzen ist. Diese Beziehung kann sehr leicht mathematisch hergeleitet werden.⁽⁹⁾ Abb. 5 zeigt die Resultate, die mit dem oben angegebenen Lösungspaar I und dem folgenden Paar II erhalten wurden :

Lösungspaar II $\left\{ \begin{array}{l} \text{A} \quad [\text{Co}(\text{NH}_3)_5(\text{H}_2\text{O})]\text{Cl}_3 \\ \text{B} \quad \text{NH}_3 \end{array} \right. \begin{array}{l} 0.1 \text{ norm.} \\ 0.1 \text{ norm.} \end{array} \text{ (Schichtdicke 10mm.)}$

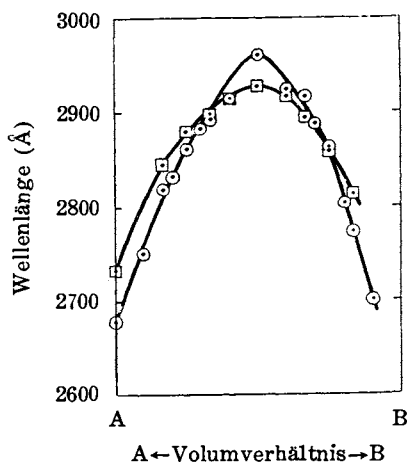


Abb. 5. $\circ-\circ-\circ$ Lösungspaar I
 $\square-\square-\square$ Lösungspaar II

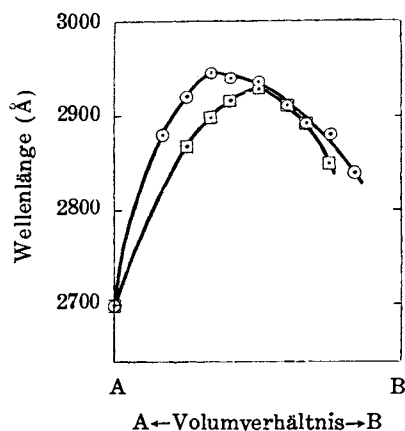


Abb. 6. $\circ-\circ-\circ$ Lösungspaar III
 $\square-\square-\square$ Lösungspaar IV

Als Abszisse ist das Volumverhältnis beider Lösungen A und B, und als Ordinate die Wellenlänge des Absorptionsendes in Å.E. aufgetragen. Die Schichtdicke der einzelnen gemischten Lösung betrug immer 100 mm. bzw. 10 mm. Das Maximum der Endabsorption liegt bei der gemischten Lösung

(9) T. Inoue, *Japan. J. Chem.*, **3** (1928), 132.

(1 Vol. A + 1 Vol. B), d.h. ein Mol. $[\text{Co}(\text{NH}_3)_5(\text{H}_2\text{O})]\text{Cl}_3$ reagiert mit einem Mol NH_3 . Mit dem Sulfat der Reihe erhält man gleichfalls eine Kurve, die bei der gemischten Lösung 1 : 1 das Maximum hat.

Andere Amine als NH_3 reagieren ebenso wie dieses. In Abb. 6 sind die Resultate angegeben, die mit folgenden Lösungspaaren erhalten wurden :

Lösungspaar III	A	$[\text{Co}(\text{NH}_3)_5(\text{H}_2\text{O})]_2(\text{SO}_4)_3$	0.01 norm.	(Schichtdicke 100 mm.)
	B	$\text{NH}_2\text{-CH}_2\text{-CH}_2\text{-NH}_2$	0.02 norm.	
Lösungspaar IV	A	$[\text{Co}(\text{NH}_3)_5(\text{H}_2\text{O})]_2(\text{SO}_4)_3$	0.01 norm.	(Schichtdicke 100 mm.)
	B	$(\text{C}_2\text{H}_5)_2\text{NH}$	0.01 norm.	

Beim Lösungspaar III findet man das Maximum an der Stelle, an der das Volumverhältnis 2 : 1 ist. Dies ist deswegen selbstverständlich, da die Konzentration des Amins als Base hier doppelt so gross ist wie in den anderen Fällen.

Ferner wurden noch folgende Lösungspaare untersucht :

Lösungspaar V	A	$[\text{Co}(\text{NH}_3)_4(\text{H}_2\text{O})_2]_2(\text{SO}_4)_3$	0.01 norm.	(Schichtdicke 100 mm.)
	B	$\text{NH}_2\text{-CH}_2\text{-CH}_2\text{-NH}_2$	0.02 norm.	
Lösungspaar VI	A	$[\text{Co en}_2(\text{H}_2\text{O})_2]\text{Cl}_3$	0.01 norm.	(Schichtdicke 100 mm.)
	B	$\text{NH}_2\text{-CH}_2\text{-CH}_2\text{-NH}_2$	0.02 norm.	

Abb. 7 und 8 geben die mit diesen beiden Lösungspaaren erhaltenen Ergebnisse an.

Die ammoniakalische Lösung von $[\text{Co}(\text{NH}_3)_3(\text{H}_2\text{O})_3]\text{Cl}_3$ ist sehr unbeständig und trübt sich sogleich nach der Herstellung. Daher kann man mittels dieser Methode das Reaktionsverhältnis nicht ermitteln, aber infolge der Regelmässigkeit der Absorptionskurven der aminhaltigen Lösungen der Mono-, Di- und Triaquokobaltiammine, die schon oben beschrieben wurde, kann man ohne Zweifel schliessen, dass das Triaquoradikal auch ganz ähnlich reagieren wird.

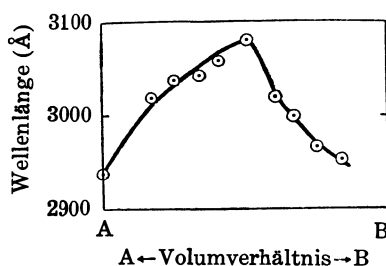


Abb. 7. Lösungspaar V

Alle bis eben beschriebenen Tatsachen zeigen also folgendes : Aquokobaltiammine reagieren mit Ammoniak bzw. Aminen im allgemeinen in der Lösung unter Bildung einer neuen Reihe Ammine, und zwar in solchem Verhältnisse, dass auf ein koordinatives Wassermolekül ein basisches Stickstoffatom von Ammoniak bzw. Amin kommt.

Zum Vergleich sind die Resultate von folgenden Systemen in Abb. 9 und 10 angegeben :

Lösungspaar VII $\left\{ \begin{array}{l} \text{A } [\text{Co}(\text{NH}_3)_5(\text{OH})]\text{Cl}_2 \\ \text{B } \text{NH}_3 \end{array} \right.$ 0.01 norm. (Schichtdicke 100 mm.)
0.01 norm.

Lösungspaar VIII $\left\{ \begin{array}{l} \text{A } [\text{Co}(\text{NH}_3)_5(\text{H}_2\text{O})]\text{Cl}_3 \\ \text{B } \text{Na}_2\text{CO}_3 \end{array} \right.$ 0.01 norm. (Schichtdicke 100 mm.)
0.01 norm.

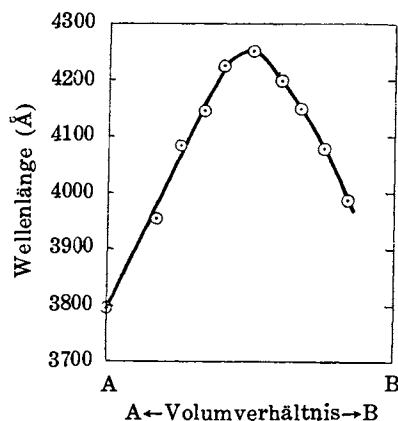


Abb. 8. Lösungspaar VI

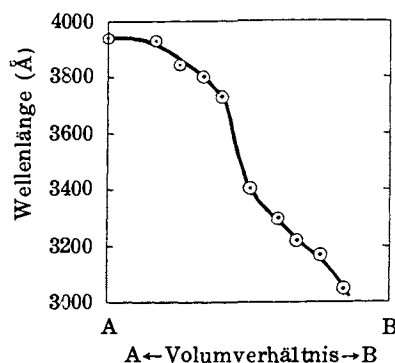


Abb. 9. Lösungspaar VII

Das Lösungspaar VII gibt natürlich kein Maximum, wogegen VIII ein deutliches Maximum zeigt, da sich in diesem Falle $[\text{Co}(\text{NH}_3)_5(\text{OH})]\text{Cl}_2$ bildet (vgl. Abb. 1).

Ermittlung des Reaktionsverhältnisses mittels Viskositätsmessungen.
Die Viskosität ist bekanntlich keine einfach festzulegende Grösse, insbesondere wenn es sich um Elektrolytlösungen handelt. Im allgemeinen verlaufen die Viskositäts-Konzentrations-Kurven von Elektrolyten konvex

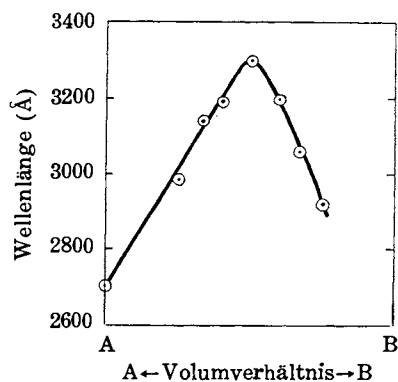


Abb. 10. Lösungspaar VIII

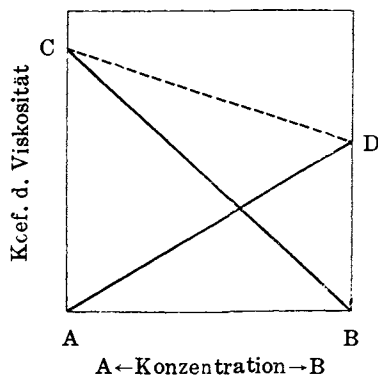


Abb. 11.

gegen die Konzentrationachse; falls man aber den Konzentrationsbereich zwischen 0—0.1 norm. wählt, können die Kurven als gerade Stück betrachtet werden.⁽¹⁰⁾ Wenn deshalb A und B in der Lösung nicht miteinander reagieren, oder beide, keinen merklichen Einfluss aufeinander bzw. auf ihren molekularen Zustand haben, dann sind die Beziehungen zwischen Viskosität und Konzentration wie in Abb. 11 angegeben. Die gerade Linie CB zeigt die von A, DA die von B, und CD die von (A + B). Ich habe diese Beziehung mit folgenden Lösungspaaren geprüft, bei denen A und B nicht miteinander reagieren:

Lösungspaar 1	{ A $[\text{Co}(\text{NH}_3)_5]\text{Cl}_3$	0.1 norm.	(Temp. 25.0°)
	{ B NH_3	0.1 norm.	
Lösungspaar 2	{ A $[\text{Co}(\text{NH}_3)_5(\text{H}_2\text{O})]_2(\text{SO}_4)_3$	0.1 norm.	(Temp. 25.0°)
	{ B $\text{H}_2\text{N}\cdot\text{COOC}_2\text{H}_5$	0.1 norm.	
Lösungspaar 3	{ A $[\text{Co}(\text{NH}_3)_5(\text{H}_2\text{O})]\text{Cl}_3$	0.1 norm.	(Temp. 25.0°)
	{ B $\text{CO}(\text{NH}_2)_2$	0.1 norm.	

Nun reagiert aber beispielsweise $[\text{Co}(\text{NH}_3)_5(\text{H}_2\text{O})]\text{Cl}_3$ in Lösung mit NH_3 , weshalb die Viskositätskurve dieses Lösungspaares von der oben angegebenen Linie CD abweichen kann. Als Reaktionsprodukt von $[\text{Co}(\text{NH}_3)_5(\text{H}_2\text{O})]\text{Cl}_3$ und NH_3 in der Lösung kann ferner sehr wahrscheinlich $[\text{Co}(\text{NH}_3)_5(\text{HONH}_4)]\text{Cl}_3$ angesehen werden. Wenn aber dieses Ammin gebildet wird, nimmt die gesamte Zahl der Moleküle in der gemischten Lösung ab. Die Viskosität der in verschiedenem Verhältnisse gemischten Lösung kann daher vielleicht etwas kleiner sein als die Linie CD zeigt. Und wenn es überhaupt eine maximale Abweichung der Viskosität gibt, werden $[\text{Co}(\text{NH}_3)_5(\text{H}_2\text{O})]\text{Cl}_3$ und NH_3 in demjenigen Verhältnisse reagieren, welches der Stelle der maximalen Abweichung entspricht. Dieses geht bei diesem Lösungspaar wirklich vor sich, wie Abb. 12 zeigt:

Lösungspaar 4	{ A $[\text{Co}(\text{NH}_3)_5(\text{H}_2\text{O})]\text{Cl}_3$	0.1 norm.	(Temp. 25.0°)
	{ B NH_3	0.1 norm.	

Das Abweichungsmaximum liegt an der Stelle, an der das Volumverhältnis beider Lösungen 1:1 ist, also ein Mol $[\text{Co}(\text{NH}_3)_5(\text{H}_2\text{O})]\text{Cl}_3$ reagiert mit einem Mol NH_3 in der Lösung. Dieses Ergebnis stimmt mit dem durch die spektrophische Methode erhaltenen vollkommen überein.

Ich habe auch die Viskosität des folgenden Lösungspaares gemessen:

Lösungspaar 5	{ A $[\text{Co}(\text{NH}_3)_5(\text{H}_2\text{O})]\text{Cl}_3$	0.1 norm.	(Temp. 25.0°)
	{ B Na_2CO_3	0.1 norm.	

(10) Vgl. Landolt-Boernstein, „Physikalisch-chemische Tabellen“.

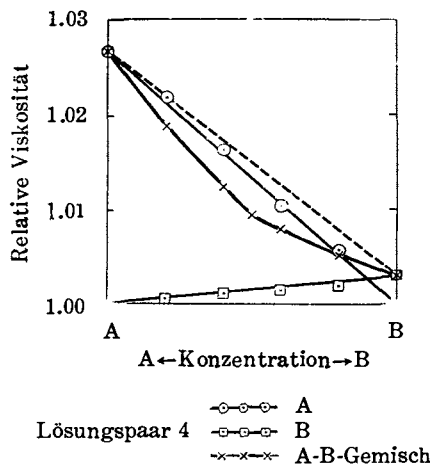


Abb. 12.

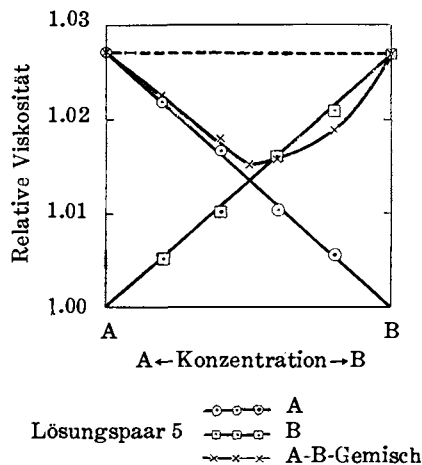


Abb. 13.

Auch dieses Paar gibt das Abweichungsmaximum beim Verhältnisse 1:1 (siehe Abb. 13), aber das Reaktionsprodukt ist in diesem Falle das Salz $[\text{Co}(\text{NH}_3)_5(\text{OH})]\text{Cl}_2$, wie schon beschrieben worden.

Gefrierpunktserniedrigung der gemischten Lösungen von Aquopentaminkobaltisalzen und Ammoniak bzw. Äthylendiamin. Wie schon oben beschrieben wurde, besteht in der ammoniakalischen Lösung von $[\text{Co}(\text{NH}_3)_5(\text{H}_2\text{O})]$ -Salz mit grösster Wahrscheinlichkeit folgendes Gleichgewicht:



Ich habe ferner schon festgestellt, dass das Gleichgewicht sich weitgehend nach rechts verschiebt, wenn man die Lösung mit Eis erkalten lässt. Wenn nun $[\text{Co}(\text{NH}_3)_5(\text{H}_2\text{O})]\text{X}_3$ und $[\text{Co}(\text{NH}_3)_5(\text{HONH}_4)]\text{X}_3$ in der verdünnten Lösung vollständig oder gleichermassen ionisieren, und die oben genannte Reaktion zu Ende verläuft, nimmt die gesamte Zahl von Molekülen bzw. Ionen ab. Daher muss die Gefrierpunktserniedrigung einer solchen Lösung in demjenigen Masse kleiner werden wie die Summe der Erniedrigungen der beiden Lösungen, $[\text{Co}(\text{NH}_3)_5(\text{H}_2\text{O})]$ -Salz und NH_3 , was sich aus der Molekularerniedrigung berechnen lässt. Ich habe zuerst das System $[\text{Co}(\text{NH}_3)_5(\text{H}_2\text{O})]_2(\text{SO}_4)_3 - \text{NH}_3$ studiert. Die Gefrierpunktserniedrigungen sind folgende:

$[\text{Co}(\text{NH}_3)_5(\text{H}_2\text{O})]_2(\text{SO}_4)_3$ -Lösung	0.02 norm. (0.01 molar)	0.076° (1)
NH_3 -Lösung	0.02 norm.	0.044° (2)
Gemischte Lösung, worin die Konzentration vom Ammin und NH_3 dieselbe wie oben		0.088° (3)

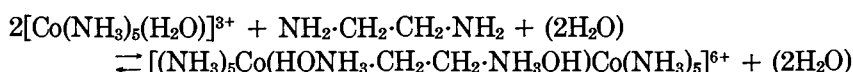
Vergleicht man die Summe (1) + (2) d.h. 0.120° , mit (3), so findet man (3) viel kleiner und zwar in dem Masse, dass die Differenz (0.032°) fast genau der theoretischen Erniedrigung der 0.02 molaren wässrigen Lösung (0.034°) entspricht. Man kann daher sagen, dass die oben angegebene Reaktion bei 0° fast vollständig nach rechts abläuft, und der grösste Teil des Ammoniaks in der Lösung als $[\text{Co}(\text{NH}_3)_5(\text{HONH}_4)]$ -Salz vorliegt.

Ich habe weiter Äthylendiamin statt Ammoniak angewandt, wobei sich folgende Erniedrigungswerte ergaben:

$[\text{Co}(\text{NH}_3)_5(\text{H}_2\text{O})]_2(\text{SO}_4)_3$ -Lösung wie oben im Versuch mit Ammoniak
 $\text{NH}_2\cdot\text{CH}_2\cdot\text{CH}_2\cdot\text{NH}_2$ -Lösung 0.02 norm. (0.01 molar) 0.019°

Gemischte Lösung: die Konzentration der beiden gelösten Stoffe wie oben mit Ammoniak 0.073° .

In diesem Falle ist die Reaktionsgleichung wie folgt:

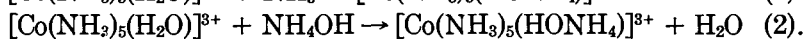
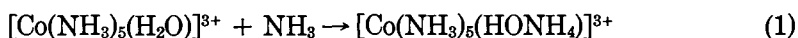


Es bildet sich also hier ein sechswertiges positives Radikal. Dieses Radikal ist von ganz besonderem Typus; die beiden Kobaltatome sind durch Äthylendiammoniumhydroxyd als Brückenglied mittels Nebenvalenzbindung verknüpft.

Wenn $[\text{Co}(\text{NH}_3)_5(\text{H}_2\text{O})]_2(\text{SO}_4)_3$ und $\text{NH}_2\cdot\text{CH}_2\cdot\text{CH}_2\cdot\text{NH}_2$ gänzlich miteinander reagierten, würde die Erniedrigung der gemischten Lösung noch viel kleiner sein als die beobachtete. Die gefundene, etwas grössere Erniedrigung als die theoretische, ist der Unvollkommenheit der Reaktion zuzuschreiben, d.h. das oben angegebene Gleichgewicht verschiebt sich nicht genug nach rechts. Die Bildung des $[\text{Co}(\text{NH}_3)_5(\text{HONH}_4)]$ -Radikals folgt nach dem Zusammentreffen eines $[\text{Co}(\text{NH}_3)_5(\text{H}_2\text{O})]$ -Radikals mit einem Molekül NH_3 ; dagegen bildet sich das $[(\text{H}_3\text{N})_5\text{Co}(\text{HONH}_3\cdot\text{CH}_2\cdot\text{CH}_2\cdot\text{NH}_3\text{OH})\text{Co}(\text{NH}_3)_5]$ -Radikal aus zwei $[\text{Co}(\text{NH}_3)_5(\text{H}_2\text{O})]$ -Radikalen und einem Molekül $\text{NH}_2\cdot\text{CH}_2\cdot\text{CH}_2\cdot\text{NH}_2$. Es ist aber einzusehen, dass das erstere Zusammentreffen viel häufiger vor sich gehen kann, und daher ist es sehr natürlich, dass die letztere Reaktion unvollkommener ist als die erstere.

Zusammenfassend kann man also feststellen: In einer gemischten Lösung von Aquokobaltiammin und Ammoniak bzw. Amin entsteht eine neue Art Ammin, welches quartäres Ammoniumhydroxyd anstelle eines Wassermoleküls des Mutteraquoammins am Kobaltatom koordiniert enthält.

Der Mechanismus der Bildung des neuen Ammins. Für die Bildung von $[\text{Co}(\text{NH}_3)_5(\text{HONH}_4)]$ -Salzen aus $[\text{Co}(\text{NH}_3)_5(\text{H}_2\text{O})]$ -Salzen und NH_3 in Lösung können folgende zwei Reaktionsweisen angegeben werden:



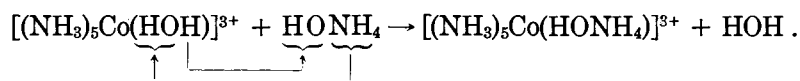
Wie schon gezeigt, reagiert $(\text{CH}_3)_4\text{NOH}$ ganz genau wie NH_3 , sodass für diesen Fall nur die Gleichung vom Typus (2) gültig sein kann, also :



Deshalb ist es viel wahrscheinlicher, dass Amine sich nicht als solche mit Aquokobaltiamminen vereinigen, sondern im allgemeinen als quartäre Ammoniumbasen unter Abspaltung von Wasser reagieren.

Diese Reaktionsweise wird auch einigermaßen durch folgende Tatsache gestützt: Pyridin, eine schwächere Base als Ammoniak bzw. Alkylamine, reagiert viel unvollkommener, wie schon gezeigt. Da die Stärke des Amins als Base in erster Linie vom Wasseradditionsvermögen abhängig ist, und Pyridin Pyridiniumhydroxyd in viel geringerem Masse als Ammoniak Ammoniumhydroxyd bildet, reagiert Pyridin viel schwächer.

Der Mechanismus der Bildung muss also wie folgt sein :



Zusammenfassung.

(1) Aus dem Absorptionsspektrum wurde gefunden, dass Aquokobaltiammin und Ammoniak bzw. Amin in Lösung ein entsprechendes Hydroxosalz nicht bilden, sondern eine neue Art Ammin.

(2) Dass in der ammoniak- bzw. aminhaltigen Lösung von Aquokobaltiammin sich kein Hydroxosalz bildet, wurde auch durch die Gefrierpunktserniedrigung solcher Lösungen bewiesen.

(3) Spektrographische Untersuchungen und auch Viskositätsmessungen zeigten, dass Aquokobaltiammin mit Ammoniak bzw. Amin in solchem Verhältnisse reagiert, dass einem koordinativen Wassermolekül ein basisches Stickstoffatom entspricht.

(4) Die neue Art Ammin enthält quartäres Ammoniumhydroxyd an derjenigen Koordinationsstelle gebunden, welche vom Wassermolekül des Mutteraquokobaltiammins besetzt war.

Die meisten Teile der spektrographischen Arbeit wurden 1924 im Laboratorium von Herrn Prof. Y. Shibata der Universität zu Tokio durchgeführt. Für diese Liebenswürdigkeit und sein Interesse an dieser Arbeit sage ich hier meinen herzlichsten Dank. Zu Dank bin ich auch Herrn Y. Ishigaki für seine Hilfe bei dieser Arbeit verpflichtet.

*Chemisches Laboratorium der Universität
zu Taihoku.*

ON THE OIL OF HOKKE (*Pleurogrammus monoptygius*, Pallas),
WITH SPECIAL REFERENCE TO THE OCCURRENCE
OF NEW HIGHLY UNSATURATED
C₂₈-FATTY ACIDS.

By Sei-ichi UENO and Masayoshi IWAI.

Received July 7th, 1936. Published October 28th, 1936.

"Hokke" (*Pleurogrammus monoptygius*, Pallas) is a fish widely distributed in the sea of the northern part of Honshu and Hokkaido, Japan. According to the growth of the fish, it is classified into kinds of the following names; "Taraba-hokke" (about 420 mm. in length), "Chuhokke" (about 350 mm. in length) and "Rosoku-hokke" (about 300 mm. in length), etc. These fishes contain much quantities of oil, but their flesh is disagreeable to our taste. Hitherto, the Hokke oil has scarcely appeared in the market and the properties of the oil have not been investigated.

A sample of oil (probably of "Taraba-hokke") from Matsumae Hokkaido, had the following properties: acid value, 19.0; n_D^{20} , 1.4714; d_4^{15} , 0.9153; saponification value, 183.3; iodine value (Wijs), 92.1; oxidised acid, 0.10%; unsaponifiable substances, about 1.5%. The oil was a liquid having a reddish orange colour and separated much solid fat in winter season.

The fatty acids freed from unsaponifiable matters showed the following properties: n_D^{20} , 1.4623; neutralisation value, 184.2; iodine value (Wijs), 96.04; ether insoluble polybromide, 9.77%; Br of polybromide, 68.48%:

The solid acids obtained by the lead-salts-alcohol method showed a comparatively high percentage of unsaturated acids: solid acids: yield, 29.2%; iodine value, 20.9; neutralisation value, 190.0; m.p. 41.8-44.7°C. and liquid acids: yield, 70.8%; iodine value, 114.7; neutralisation value, 170.6. As the solid acids are undoubtedly composed mainly of cetoleic acid C₂₂H₄₂O₂, the following results can be obtained by calculation: saturated acids: 11.3%; Neutralisation value, 205.0; unsaturated acids: 88.7%.

The results of the fractional distillation of methyl esters of mixed fatty acids freed from unsaponifiable matters are given in Table 1 and shown diagrammatically in Fig. 1.

Table 1.

Fraction	Distillation temperature (°C./5 mm.)	Saponification value	Iodine value	n_D^{25}	Yield (g.)
1	145–150	204.8	26.1	1.4478	47.5
2	150–155	216.7	27.7	1.4451	31.4
3	155–160	220.2	32.8	1.4451	33.7
4	160–165	219.7	35.7	1.4453	36.5
5	165–170	216.0	39.5	1.4461	33.3
6	170–175	215.2	50.4	1.4488	54.9
7	175–180	207.5	58.0	1.4498	79.0
8	180–185	208.2	67.3	1.4518	84.0
9	185–190	197.3	82.7	1.4546	126.1
10	190–195	190.8	94.8	1.4578	73.1
11	195–200	186.3	105.4	1.4598	67.5
12	200–205	182.4	113.1	1.4608	100.5
13	205–210	178.6	115.6	1.4626	104.0
14	210–215	175.3	114.5	1.4638	30.6
15	215–220	174.1	117.7	1.4640	35.5
16	220–225	171.5	118.5	1.4643	51.3
17	225–230	168.8	122.7	1.4651	97.9
18	230–235	162.8	124.3	1.4668	68.1
19	235–240	157.2	129.5	1.4708	7.2
20	240–243	152.0	135.9	1.4788	6.2
Residue	—	145.2	117.7	1.4833	33.8

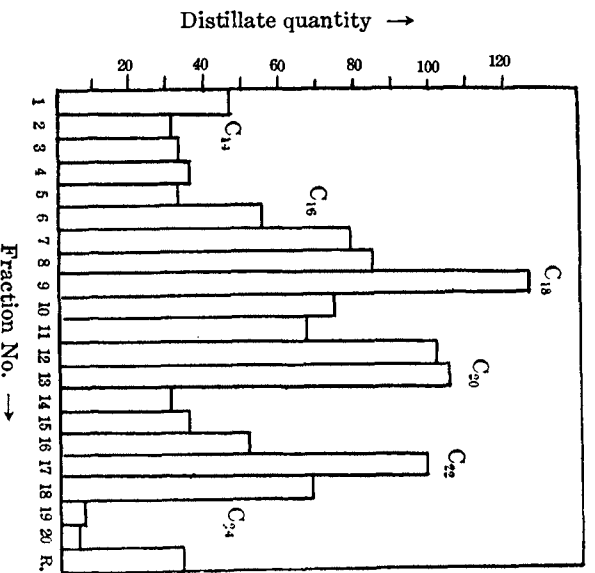


Fig. 1. Diagrammatic representation of the result of fractional distillation of methyl esters.

By comparison with many examples of distillation of methyl esters of such kinds of oils, it will be easily seen that the distillates seem most likely to consist of methyl esters of following fatty acids: (1) Lower fractions 1-8: palmitic acid $C_{16}H_{32}O_2$ (chief component), myristic acid $C_{14}H_{28}O_2$, $C_{16}H_{30}O_2$, etc. (2) Main fractions 9, 10, and 11: oleic acid $C_{18}H_{34}O_2$ (chief component), stearic acid $C_{18}H_{36}O_2$, highly unsaturated fatty acids of C_{18} and C_{20} , etc. (3) Fractions 13 and 14: $C_{20}H_{38}O_2$, $C_{20}H_{32}O_2$, $C_{20}H_{30}O_2$, $C_{20}H_{40}O_2$ arachidic acid, etc. (4) Fractions 17 and 18: clupanodonic acid $C_{22}H_{34}O_2$, behenic acid $C_{22}H_{44}O_2$, etc. (5) Higher fractions and residue: fatty acid of C_{24} , etc.

Detection of Highly Unsaturated Fatty Acids of High Molecular Weight. A sample oil (3500 g.) was methylated by Haller's method and the methyl esters were distilled in vacuo up to $215^\circ C/5$ mm. From the distillation residue (450 g.) unsaponifiable substances were removed by means of repeated extraction with ether, and after changing again the acids into methyl esters, they were fractionally distilled. Properties of final distillates are given in Table 2.

Table 2.

Fraction	Distillation temperature ($^\circ C/3$ mm.)	Saponification value	Iodine value	n_D^{15}	Yield (g.)
1	210-215	165.3	125.0	1.4628	31.1
2	215-220	162.3	117.9	1.4630	12.1
3	220-225	159.9	118.8	1.4640	38.3
4	225-230	153.2	126.9	1.4660	17.8
Residue	—	150.0	151.5	—	28.7

Highly unsaturated fatty acids were separated from these fractions as lithium salts which are soluble in 94% acetone. The properties of these fatty acids and their bromides are given in Table 3.

Table 3.

	Yield (g.)	Neutra- lisation value	Iodine value	n_D^{15}	Yield of ether-in- soluble poly- bromide (%)	Decomposi- tion temp. of poly- bromide	Bromine content of polybromide (%)
Fraction 1	5.3	157.3	318.2	1.5003	98.0	about 220°	72.10
Fraction 3	4.0	142.1	286.5	1.5010	74.4	„ 213	70.94
Fraction 4	2.6	132.2	267.7	1.5074	50.3	„ 215	65.35
Residue	3.2	133.4	239.0	1.5120	28.4	„ 225	71.28

If only the neutralisation values be considered, the highly unsaturated fatty acid from fraction 1 may be almost identified with C_{24} -acids, and the bromine content of the polybromide (72.10%) corresponds to the value between $C_{24}H_{38}O_2$ and $C_{24}H_{36}O_2$ as shown in Table 4.

Table 4.

	Neutralisation value	Iodine value	Br % of bromide
Found	157.3	318.2	72.10
$C_{24}H_{36}O_2$ (Nisinic acid) ⁽¹⁾ ($\bar{F}_6$)	157.8	427.5	72.91
$C_{24}H_{38}O_2$ (Scoliodonic acid) ⁽²⁾ ($\bar{F}_5$)	156.7	354.2	69.05

The unsaturated fatty acid from fraction 3 is similarly identified with C_{26} -acids and the bromine content (70.94%) of the bromide corresponds to a mixture of $C_{26}H_{40}O_2Br_{12}$, and $C_{26}H_{42}O_2Br_{10}$ as shown in Table 5.

Table 5.

	Neutralisation value	Iodine value	Br % of bromide
Found	142.1	286.5	70.94
$C_{26}H_{40}O_2$ (Thynnic acid) ⁽³⁾ ($\bar{F}_6$)	146.2	396.7	71.39
$C_{26}H_{42}O_2$ (Sibic acid) ⁽⁴⁾ ($\bar{F}_5$)	145.4	328.8	67.41

The saturated acid which was obtained by the hydrogenation of the fatty acid from fraction 2 melted at 70.3–71.5°C and the determination of neutralisation value and ultimate analysis were made. (Found: C, 78.56; H, 13.06; neutralisation value, 138.9. Calculated for $C_{26}H_{52}O_2$: C, 78.8; H, 13.1; neutralisation value, 141.5).

Neutralisation values of fraction 4 and the residue correspond to C_{23} -acids. The bromine percentages of the bromides precipitated from the ether solutions of the acids (65.35 and 71.28) nearly agreed respectively with that of $C_{28}H_{46}O_2Br_{10}$ and with that of a mixture $C_{28}\bar{F}_7$ -, $C_{23}\bar{F}_6$ -, $C_{28}\bar{F}_5$ -, $C_{28}\bar{F}_4$ -acids, etc. as seen from Table 6.

(1) Toyama and Tsuchiya, this Bulletin, **11** (1935), 543.

(2) S. Ueno and M. Iwai, *J. Soc. Chem. Ind.*, Japan, **37** (1934), 251 B.

(3) S. Ueno and C. Yonese, *J. Chem. Soc. Japan*, **57** (1936), 182.

(4) S. Ueno and C. Yonese, *J. Chem. Soc. Japan*, **57** (1936), 182.

Table 6.

Calculated for	Neutralisation value	Iodine value	Br % of bromide
$C_{28}H_{42}O_2$ (F_7)	136.7	433.1	73.16
$C_{28}H_{44}O_2$ (F_6)	136.1	369.4	69.94
$C_{28}H_{46}O_2$ (F_5)	135.4	306.3	65.86
$C_{28}H_{48}O_2$ (F_4)	134.7	243.4	60.56

The saturated acid (m.p. 72.0–73.5°C.) obtained from the mixture of fraction 4 and the residue corresponds to $C_{28}H_{56}O_2$ in the results of ultimate analysis and neutralisation value. (Found: C, 79.12; H, 13.69; neutralisation value, 134.7. Calculated for $C_{28}H_{56}O_2$: C, 79.20; H, 13.10; neutralisation value, 132.2).

Detection of Cetoleic Acid $C_{22}H_{42}O_2$. The saponification values of fractions 1,2,3, etc. (Table 2) are respectively higher than those of the corresponding methyl esters of highly unsaturated acids in the literatures. This is explained if lower acids of lower unsaturation are present. The authors have isolated an acid $C_{22}H_{42}O_2$ (m.p. 33.0–33.7°) from the lithium salt of the fractions 2 and 3 (Table 2) insoluble in 94% acetone (Found: C, 77.76; H, 12.51; neutralisation value, 166.0; iodine value, 75.1. Calculated for $C_{22}H_{42}O_2$: C, 78.03; H, 12.51; neutralisation value, 165.8; iodine value, 75.0). By means of the mixed melting point the acid has been identified with cetoleic acid (m.p. 33–34°): mixed m.p. with erucic acid (m.p. 33–34°) from rape seed oil, 26.7–27.3°; mixed m.p. with cetoleic acid (m.p. 32.0–32.5°) from Menuke-fish oil⁽⁵⁾, 32.0–32.9°.

Investigation of the Unsaponifiable Constituents. The unsaponifiable matter is a reddish brown mass having many crystals of cholesterol (35.4%). The sample (20.2 g.) was subjected to fractional crystallisation from methanol as follows: Fraction 1: m.p. 142.3–144.0°, yield 6.7 g. Fraction 2: m.p. 139.5–140.1°, yield 1.5 g. Residue: liquid, yield 10.1 g.

The crystalline fractions were recrystallised several times from 95% alcohol and a substance with a melting point 146–147°C was obtained, which was identified with cholesterol $C_{27}H_{46}O$. The liquid portion, which still contained a small quantity of cholesterol, was acetylated, and the product was distilled in vacuo as given in Table 7.

(5) S. Ueno and M. Iwai, *J. Soc. Chem. Ind., Japan*, **37** (1934), 52 B.

Table 7.

Fraction	Distillation temperature (°C / 8 mm.)	Saponification value	Iodine value	Yield (g.)	Color
1	135-160	51.8	29.6	0.9	Pale yellow liquid
2	160-180	142.7	57.2	0.8	" " " (with some crystals)
3	180-200	183.3	92.6	1.4	Orange
4	200-230	159.9	104.7	1.8	"
5	230-245	136.8	103.6	2.4	"
Residue				1.5	Black

Acetyl derivative of	Formula	Saponification value	Iodine value
Cholesterol	$C_{27}H_{45}O \cdot COCH_3$	131.0	59.2
Oleyl alcohol	$C_{18}H_{33}O \cdot COCH_3$	182.0	82.3

From these results, the liquid unsaponifiable matter seems to consist chiefly of oleyl alcohol $C_{18}H_{33}OH$.

Summary.

The chemical and physical characteristics of a sample of the oil of "Hokke" (*Pleurogrammus monopterygius*, Pallas) have been determined. In the investigation of higher fractions and distillation residue, the authors have recognised the probable existence of highly unsaturated fatty acids of higher molecules such as nisinic acid $C_{24}H_{36}O_2$ ($\bar{F}_6$), scoliodonic acid $C_{24}H_{38}O_2$ ($\bar{F}_5$), thynnic acid $C_{26}H_{40}O_2$ ($\bar{F}_6$), sibic acid $C_{26}H_{42}O_2$ ($\bar{F}_5$), and highly unsaturated fatty C_{28} -acid such as $C_{28}H_{46}O_2$ ($\bar{F}_5$), etc. In addition to these compounds, it appears also to contain $C_{23}H_{42}O_2$ ($\bar{F}_7$), $C_{28}H_{44}O_2$ ($\bar{F}_6$), etc. Highly unsaturated C_{28} -fatty acids have not yet been reported as occurring in any other oils.

Since the authors found shortly before scoliodonic acid $C_{24}H_{38}O_2$ ($\bar{F}_5$) in a shark liver oil (*Scoliodon laticaudus* Müller and Henle), the research of these kinds of highly unsaturated fatty acids of higher molecules became to arouse interest in our country. Thus, Y. Toyama and T. Tsuchiya⁽⁶⁾ found nisinic acid $C_{24}H_{36}O_2$ and scoliodonic acid $C_{24}H_{38}O_2$ in herring oil, sardine oil and other

(6) Y. Toyama and T. Tsuchiya, *J. Soc. Chem. Ind., Japan*, **37** (1934), 530 B.

fish oils, S. Ueno and C. Yonese⁽⁷⁾ detected not only these new acids, but also thynnic acid $C_{23}H_{40}O_2$, sibic acid $C_{26}H_{42}O_2$, etc.

In consideration of the distribution of constituent acids in several kinds of fish oils, the general distribution curves of fatty acid shown in Fig. 2 can

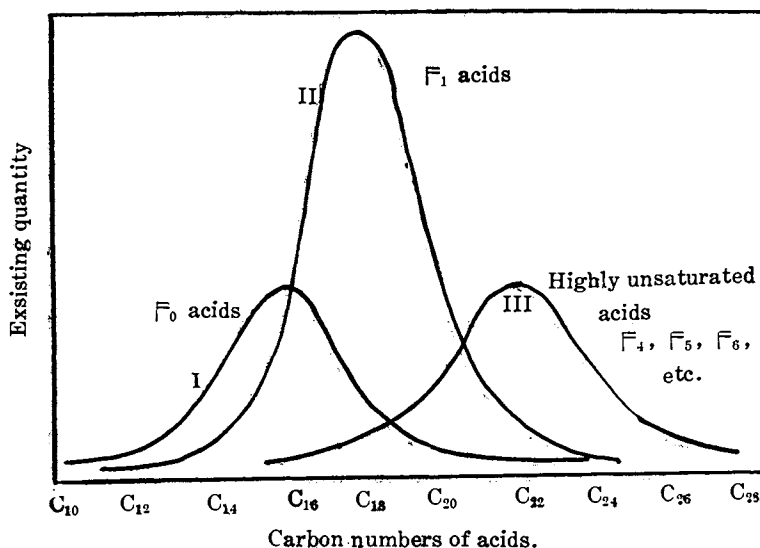


Fig. 2. General distribution curves of fatty acids in fish oil.

be assumed. From curve III, it is evident that the highly unsaturated C_{28} -acids have a possible existence. Nevertheless, to our vexation in the present experiment, these compounds have not been isolated in a pure state, but their occurrence could only be suggested by the bromine contents of bromides.

Unsaponifiable substances contain 35.4% of cholesterol $C_{27}H_{46}O$, and the remainder, which is in liquid state, seems to be composed chiefly of oleyl alcohol $C_{18}H_{38}OH$.

It is a characteristic of this oil that it contains comparatively large quantities of higher molecular C_{20} - and C_{22} -acids, among which the authors have isolated an acid $C_{22}H_{42}O_2$, undoubtedly cetoleic acid.

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(7) S. Ueno and C. Yonese, *J. Chem. Soc. Japan*, **57** (1936), 322.

THE ELECTROLYTIC FORMATION OF PERSULPHATE. PART II.

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It was proposed in the previous report⁽¹⁾ of the present investigation that persulphuric acid is produced when sulphuric acid is oxidised by the hydroxyl ions discharged at the anode. The present paper is to confirm the above view. The electrolyses in the present case are performed without diaphragm in contrast with those in Part I⁽¹⁾ in which a porcelain cylinder was employed as such. The anode, in the present case, consists of a spiral of platinum wire of 0.5 mm. diameter, its total surface available to electrolysis being 3.25 cm.² It is thoroughly ignited, unless otherwise mentioned, immediately before use and is kept rotating at the center of the electrolytic vessel. The cathode is also a platinum wire as thick as the anode and is spirally wound against the inner wall of the vessel, and its total surface is 14.14 cm.² The electrolyte is contained in the vessel, a glass beaker, and kept at 15°C. by cooling with cold water from outside. The same methods are employed for the analysis of the electrolysed solutions as stated in Part I.

Experiment 1. Electrolyses of 7 N Sulphate Solutions with the Anode Unignited. The following five solutions are electrolysed by means of the anode without previous ignition. The volume of the electrolyte is 150 c.c. and the same amount of electricity, 1170 coulombs, is supplied in each case.

Solution	(0 : 7):	no	(NH ₄) ₂ SO ₄ ,	7 N	H ₂ SO ₄ ;
„	(1 : 6):	N	„	, 6 N	„ ;
„	(3 : 4):	3 N	„	, 4 N	„ ;
„	(5 : 2):	5 N	„	, 2 N	„ ;
„	(7 : 0):	7 N	„	, no	„ .

The current efficiencies with two different anodic current densities are shown in Table 1 and Fig. 1.

(1) This Bulletin, **11** (1936), 1.

Table 1.

C.D. ⁽²⁾ (amp./dm. ²)	Caro's acid C.E. ⁽²⁾ (%)		The total C.E. ⁽²⁾ (%)	
	40	80	40	80
Solution (0:7)	0.18	0.18	0.68	0.80
„ (1:6)	0.13	0.13	0.77	3.40
„ (3:4)	0.34	0.34	5.90	23.60
„ (5:2)	1.36	1.70	25.20	33.00
„ (7:0)	0.46	0.45	41.90	45.90

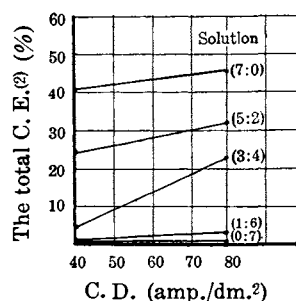


Fig. 1.

As can be seen in Table 1, the more concentrated the solution with respect to ammonium sulphate, the greater the current efficiency; hence Solution (7:0) gives the highest C.E.⁽²⁾ Since this solution contains no free H_2SO_4 , it becomes ammoniacal by electrolysis. According to Elbs⁽³⁾ HSO_4 -ions, being discharged at the anode, are responsible for $\text{H}_2\text{S}_2\text{O}_8$ -formation. But these ions can by no means exist either in a neutral sulphate solution or in an ammoniacal one as in the present case. Therefore Elbs' view does not seem valid, but the present authors' one that OH -ions play an important part in $\text{H}_2\text{S}_2\text{O}_8$ -formation is again capable of accounting for these facts: the more concentrated the solution with respect to OH -ions, the better the C.E. in spite of shortage of HSO_4 '-concentration. The C.E. as to Caro's acid is less than 2% in each case, so that nothing conclusive can be deduced therefrom.

Experiment 2. Electrolyses of 7 N Sulphate Solutions with the Anode Ignited. The same kinds of solutions are electrolysed as in Experiment 1; the anode is thoroughly ignited, in this case, immediately before electrolysis. The C.E.'s are shown in Table 2 and Fig. 2.

Table 2.

C.D. (amp./dm. ²)	Caro's acid C.E. (%)		The total C.E. (%)			
	40	80	30	40	60	80
Solution (0:7)	—	—	0.43	0.65	—	0.99
„ (1:6)	1.42	1.7	16.7	19.4	24.2	34.7
„ (3:4)	—	—	42.7	46.4	53.6	61.8
„ (5:2)	—	—	53.2	59.0	72.8	73.0
„ (7:0)	—	—	54.6	65.1	—	67.1

(2) Current efficiency and current density are abbreviated as C.E. and C.D. respectively.

(3) *Z. Elektrochem.*, **1** (1894), 417.

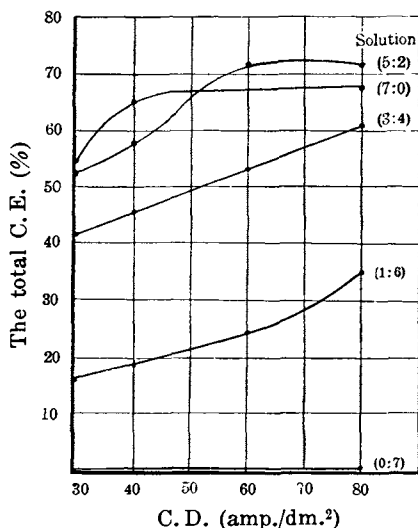


Fig. 2.

concentrations being 0.2555 and 0.2167 amp./100 c.c. at the anodic C.D.⁽²⁾ 10 amp./dm.², respectively in the former and latter cases. The other experimental conditions, e.g. the temperature, the nature of electrodes, etc., are the same. Solution (2:5) was electrolysed in Part I, but not in the present case. Assuming that the C.E. of Solution (2:5) would come between those of Solutions (1:6) and (3:4), (see Fig. 2) it might never be inferior to that of the same solution in Part I which was electrolysed with diaphragm. Similar comparison of Solution (5:2) with Solution (5:1) in Part I can be made, when the difference of their concentrations is taken into consideration, to see that the C.E. of the former solution would not be inferior to that of the latter. Then it can be inferred that electrolysis without diaphragm is not inferior in C.E. to that with it when the solution contains ammonium sulphate. However, it is not the case when the solution contains merely free H_2SO_4 , but no sulphate. Since $\text{H}_2\text{S}_2\text{O}_8$ was formed in a considerable amount when Solution (0:7) was electrolysed with diaphragm, as shown in Part I, the fact that the yield of $\text{H}_2\text{S}_2\text{O}_8$ by the same solution is so scanty in the present case, is probably due to that $\text{H}_2\text{S}_2\text{O}_8$ which once formed is mostly reduced by the cathodic hydrogen whose reducing action is, in this solution, most powerful of the five.

Experiment 3. Electrolyses of 15 N Sulphate Solutions. The electrodes, the temperature and the amount of electricity supplied are the same as in Experiment 2. The volume of the electrolyte is 130 c.c., unlike the previous cases, and the current concentration is accordingly 0.2500 amp./100 c.c.

The effect of igniting the Pt-anode on C.E. is decidedly favourable in all the four solutions containing ammonium sulphate, but it is scarcely perceptible in the case of Solution (0:7) which contains no above sulphate. Now let the writers compare some of the electrolyses of 7 N solutions in Part I with the result of the present experiment in order to elucidate such a difference of C.E. In the former case a diaphragm of porous cylinder was used to keep the anolyte free from the cathodic influence, but no such is used in the latter. The amount of electricity supplied and current concentrations are not identical but not very different from each other: 828 and 1170 coulombs are supplied, accordingly the current concen-

when the C.D. is 10 amp./dm.². This value is nearly the same as that in Part I which was 0.2555 amp./100 c.c. in the corresponding case.

Table 3.

	C.D. (amp./dm. ²)	5	10	20	30	40	60	80
Caro's acid C.E. (%)	Solution (0:15)	20.0	24.1	24.1	23.5	24.8	25.5	24.1
	„ (1:14)	21.1	21.0	18.1	14.3	13.2	10.4	10.1
	„ (3:12)	9.0	7.2	5.2	5.9	5.3	3.6	2.5
	„ (5:10)	4.6	4.2	2.1	1.9	3.0	3.2	2.9
The total C.E. (%)	Solution (0:15)	25.5	40.0	58.7	67.3	71.7	74.0	66.0
	„ (1:14)	37.5	46.3	61.4	72.9	74.7	79.2	75.3
	„ (3:12)	45.0	54.4	63.1	74.0	74.8	80.2	77.0
	„ (5:10)	48.1	58.0	66.1	72.1	78.2	83.0	78.6

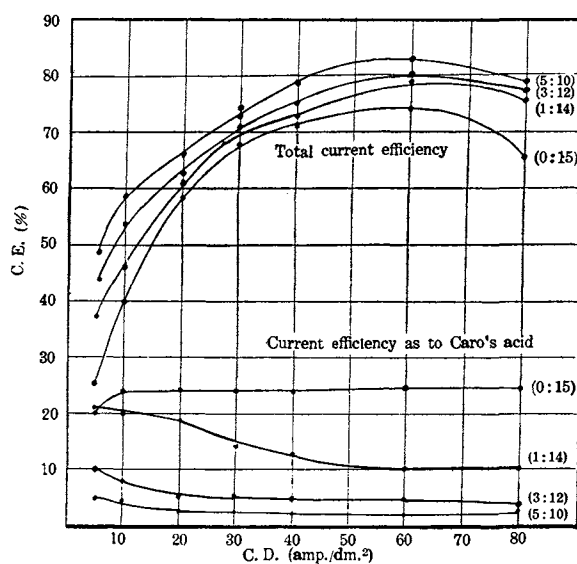
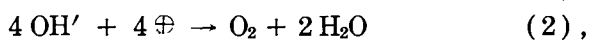
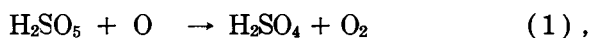
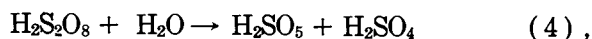
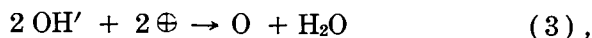


Fig. 3.

The anodic phenomena, as written in Foerster's book, are formulated as following:





where $\text{H}_2\text{S}_2\text{O}_8$, the present authors consider, is formed by the oxidation of H_2SO_4 with the anodic oxygen in contrast with Foerster's view that HSO_4' is oxidised to $\text{H}_2\text{S}_2\text{O}_8$.

Among the four 15 N solutions (see Table 3 and Fig. 3) Solution (0:15) has the smallest C.E. of the total peroxidic oxygen, mainly because its OH' -concentration is the least of the four. Its total C.E. increases with C.D. while the latter is comparatively small, but it begins to decrease at a certain C.D., therefore there is a maximum C.E. At the C.D., 5 amp./dm.², the proportion of Caro's acid C.E. to the total one is the greatest in the present experiment, because this solution, being the most concentrated with respect to free H_2SO_4 , is the most favourable for $\text{H}_2\text{S}_2\text{O}_8$ to be transformed to H_2SO_5 according to the reaction (4). Though the total C.E. continues to increase with C.D., the Caro's acid one soon ceases to do so and remains almost constant from 10 amp./dm.² on, therefore the proportion of the Caro's acid C.E. to the total one steadily decreases with C.D. This is because the higher the C.D., to the greater extent the reaction (3) occurs to form the atomic oxygen which is needful to the reaction (1); in consequence more H_2SO_5 is decomposed according to the latter reaction, and the quantities of H_2SO_5 formed and decomposed are balanced.

All the other three solutions containing ammonium sulphate excel Solution (0:15) in the total C.E., which, in each case, increases with C.D. to a maximum value, and which is the higher, the more concentrated the solution with regard to the sulphate. The difference of C.E.'s of these four solutions can thus be explained mainly by the difference of OH' -concentrations just as in Part I. The Caro's acid C.E.'s of the latter three solutions decrease with C.D. and the more concentrated the solution with respect to the sulphate, the smaller the C.E. and, consequently, the proportion of the Caro's acid C.E. to the total one as well.

Solution	(0:15)	(1:14)	(3:12)	(5:10)
The proportion of the Caro's acid C.E. to the total C.E. (at 5 amp./dm. ²)	0.784	0.563	0.200	0.096
Viscosity	5.323	5.438	5.532	5.856

The viscosity of the solution may have something to do with lessening the Caro's acid C.E. When $\text{H}_2\text{S}_2\text{O}_8$ is hydrolysed to H_2SO_5 in the neighbourhood of the anode, it has to get out of the reach of the anodic oxygen in order to avoid the decomposition, and the greater the viscosity of the solution, the less easy for the H_2SO_5 to move away, hence the more H_2SO_5 to be decomposed. From the viscosities of the four solutions it is gathered that the viscosity tends to lessen the Caro's acid C.E. to the greater extent, the more concentrated the solution with respect to the sulphate. The Caro's acid C.E.'s are controlled by the concentration of free H_2SO_4 as well as by the viscosity. And the results are as shown in Table 3 and Fig. 3. Hydrogen peroxide is detectable in all cases of this experiment.

Experiment 4. Electrolyses of 20 N Sulphate Solutions. The results are shown in Table 4 and Fig. 4.

Table 4.

	C.D. (amp./dm. ²)	5	10	20	30	40	60	80
Caro's acid C.E. (%)	Solution (0:20)	38.5	46.5	51.2	53.4	51.2	48.2	43.8
	„ (1:19)	43.5	50.9	53.3	51.0	47.4	40.5	36.1
	„ (3:17)	48.9	48.9	48.9	44.2	36.1	27.7	25.6
The total C.E. (%)	Solution (0:20)	39.3	55.2	62.1	60.2	59.9	58.0	54.4
	„ (1:19)	47.2	57.2	66.3	67.2	65.1	61.0	56.5
	„ (3:17)	57.3	67.4	72.0	73.8	67.8	62.3	58.4

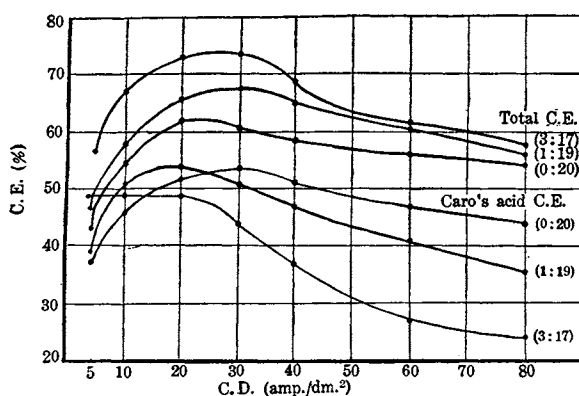


Fig. 4.

Three solutions (0:20), (1:19), and (3:17) are electrolysed. Although the difference of OH' -concentration between these solutions may not be so marked as between those which are less concentrated than the present ones, nevertheless the total C.E. is the greater in the present case also, the more concentrated the solution as to the sulphate. And it is confirmed that OH' -ions discharged at the anode play an important rôle in the electrolysis under investigation. C.E.'s at the C.D., 5 amp./dm.², are greater in the present case than the corresponding values in Experiment 3, which fact is attributed to the greater concentration of solutions in the present case. The maximum values of C.E. are smaller and are reached at smaller C.D.'s than in Experiment 3. The latter of the two facts is also due to the greater concentrations of the present solutions. The cause that the maximum C.E.'s are smaller in this case has connexion with the behaviour of H_2SO_5 which is described as following.

Solution	(0 : 20)	(1 : 19)	(3 : 17)
The proportion of the Caro's acid C.E. to the total C.E. (at 5 amp./dm. ²)	0.980	0.922	0.853
Viscosity	11.28	11.40	13.73

Much greater proportions of Caro's acid C.E. to the total one in this case is remarkable, compared with the previous ones. Of the three solutions, (0:20) maintains the highest proportion of Caro's acid throughout the whole range of C.D. here concerned. The Caro's acid C.E. curves have maximum points, from whence they begin to descend, except Solution (3:17), in which case the C.E. remains constant at smaller C.D. These maximum points are situated at smaller C.D.'s than, or at least at the same ones as, those corresponding to those of the total C.E. If that be so, it can be inferred that the decrease of the total C.E. is caused by that of Caro's acid. The more concentrated the solution with respect to H_2SO_4 , and the greater the C.D., the more liable H_2SO_5 to be decomposed. So that the Caro's acid C.E. of Solution (3:17) is the greatest and that of Solution (0:20) the smallest at 5 amp./dm.², and vice versa at 80 amp./dm.². Generally speaking, the total C.E. of the 20 N solutions is greater at lower C.D., and that of the 15 N ones is so at higher C.D. The greater the viscosity of a solution, the greater its influence to lessen the Caro's acid C.E., as in the previous experiment. Hydrogen peroxide is also detectable in all cases of this experiment.

Experiment 5. Change of C.E. with Time at a Constant C.D. The results are shown in Table 5 and Fig. 5. Solution (0:15) is electrolysed at a constant C.D., 30 Amp./dm.², the other conditions being the same as in the previous case.

Table 5. Electrolysis of Solution (0:15) with the C.D., 30 amp./dm.².

	Time	5 min.	10	20	30	40	50	1 hr.
C.E. (%)	Caro's acid	10.2	16.3	23.5	24.7	28.2	32.6	33.6
	The total	67.7	64.8	67.3	66.6	66.4	65.4	62.7
Number of mol × 1000	Caro's acid		0.49	1.42	2.24	3.41	4.98	6.11
	The total peroxidic oxygen		1.97	4.08	6.06	8.01	9.91	11.4

	Time	1½ hrs.	3	4	5	7	10	15
C.E. (%)	Caro's acid	35.6	27.5	23.8	20.0	15.9	9.47	6.96
	The total	61.3	43.3	37.0	28.6	20.9	14.8	9.65
Number of mol × 1000	Caro's acid	9.72	15.0	17.3	18.2	20.2	17.2	19.0
	The total peroxidic oxygen	16.7	23.6	26.9	26.5	26.6	26.9	26.3

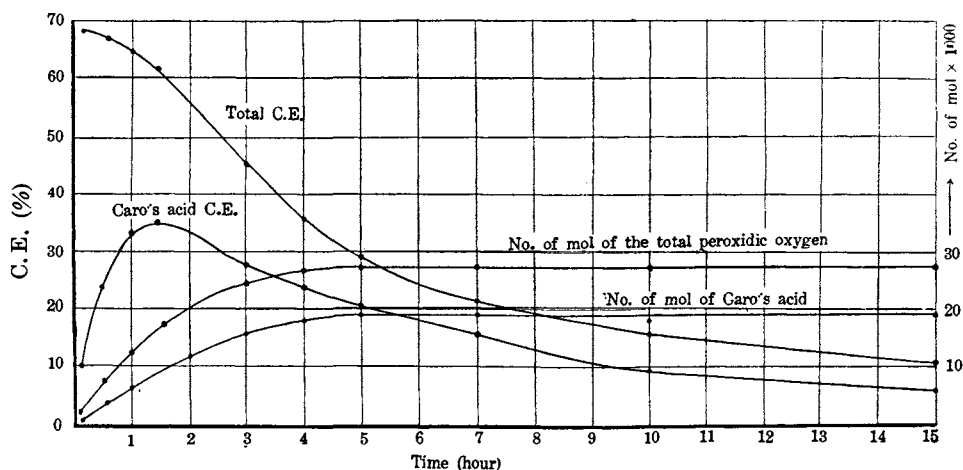


Fig. 5.

The total C.E. keeps decreasing from the beginning but the Caro's acid one increases at first and then decreases after reaching a maximum value. The numbers of mol of both H_2SO_5 and the total peroxidic oxygen increase for the first few hours and thereafter are kept almost constant. The very gradual decrease of both C.E.'s (Fig. 5) is noticeable, because in those experiments where diaphragm was used C.E. decreased quite steadily (see Foerster's book). When the peroxidic compounds are free to come into touch with the cathodic hydrogen as in the present case, it is rather expected that their yield might be smaller than otherwise, but actually it is not the case.

Summary.

(1) Experiment 1. 7 N sulphate solutions are electrolysed with an unignited Pt-anode, diaphragm being disused. The highest C.E.⁽²⁾ is obtained in the case of 7 N ammonium sulphate containing no free H_2SO_4 , which fact the present authors' view is able to account for, but not Elbs'.

(2) Experiment 2. The same kinds of solutions are electrolysed without diaphragm as in the previous experiment and the favourable effect of using the ignited Pt-anode is clearly observed in the case of solutions containing ammonium sulphate. The C.E. in the present case, in general, does not seem inferior to that of electrolysis with diaphragm. 7 N H_2SO_4 solution containing no ammonium sulphate, however, has a very poor C.E. which is attributed to the vigorous cathodic reduction, in this solution, of the anodic products.

(3) Experiment 3. Four 15 N sulphate solutions are electrolysed. Caro's acid, being formed in an appreciable amount, is proved to be helpful in explaining the mechanism of the anodic reactions from the view-point of OH' -concentration. It is suggested in this case that the viscosity of the solution has more or less effect on the C.E.

(4) Experiment 4. Three 20 N sulphate solutions are electrolysed, in which the total C.E.'s are smaller and Caro's acid ones greater than the corresponding values in the 15 N solutions. As in the previous cases, the more concentrated the solution with respect to ammonium sulphate, the greater the total C.E. The behaviour of Caro's acid and the viscosity of the solution are discussed in connexion with the C.E.

(5) Experiment 5. Change of the C.E. with time is traced to 15 hours, when 15 N H_2SO_4 solution is electrolysed at a constant C.D.⁽²⁾ And it is found that electrolysis without diaphragm is, again, not inferior, but rather superior, to that with it with regard to C.E.

(6) The present authors' view about the mechanism of electrolytic formation of persulphate comes into line with that proposed by one of them (R.M.)⁽⁴⁾ for Kolbe's reaction. Thus it is shown that electrolytic oxidation of both inorganic and organic compounds is explicable by one and the same theory.

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(4) This Bulletin, **7** (1932), 18; *ibid.*, **7** (1932), 297.

STUDIES ON THE OILINESS OF LIQUIDS. I. MEASUREMENTS OF THE STATIC FRICTION COEFFICIENTS.

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When two solid surfaces are brought into contact and made to slide the one on the other, the friction force comes into play. The friction is generally lessened by the presence of a liquid film between the solid surfaces. This effect is expressed by the term "oiliness" of the liquid and is the subject of the present series of investigations.

Now if a solid body of weight W is made just to slide on a horizontal surface by means of a force F whose direction is parallel to the surface, then $\frac{F}{W}$ is known as the coefficient of friction. Thus,

$$\frac{\text{Frictional resistance}}{\text{Normal weight}} = \frac{F}{W} = \mu.$$

The coefficient of friction may differ according to whether motion is imparted to the body at rest or whether the force F is required to keep the body in motion. In the former case the coefficient is known as the static coefficient of friction while in the latter as the kinetic coefficient of friction.

Although a large number of investigators have published data bearing on the subject of lubrication, most of them conducted their experiments on the standpoint of the practical application.⁽¹⁾ Moreover, the variations in their

(1) For example: Wilson and Barnard, *Ind. Eng. Chem.*, **14** (1922), 682, 683; Hersey, *J. Franklin Inst.*, **219** (1935), 677; **220** (1935), 93, 187; Archbutt and Deeley, "Lubrication and Lubricants," (London); Nash and Bowen, "The Principles and Practice of Lubrication," (London).

operating conditions and the indefiniteness of the chemical nature of the liquids used thus prevented any correlation of their results.

In practice, there are two types of lubrication, complete or film lubrication in which the solid faces are completely separated by a thick film of an oil, and incomplete or boundary lubrication in which the faces are separated by a very thin film which may be sometimes only one molecule thick. The theory of complete lubrication is a problem in hydrodynamics, and outside the scope of the present investigation.

The friction coefficients of some chemically definite substances have been measured by W. B. Hardy and his collaborators.⁽²⁾ It seems necessary, however, to test their results and to extend the measurements to a larger number of substances, with the hope of finding relations between oiliness and other properties, especially molecular constitutions of the liquid.

We measure the boundary lubrications of chemically pure substances as well as mixtures of known compositions. The static and the kinetic coefficients of friction are measured by using several different methods, which have been designed in our laboratory. In the present paper one of the methods for measuring the static coefficient of friction is described.

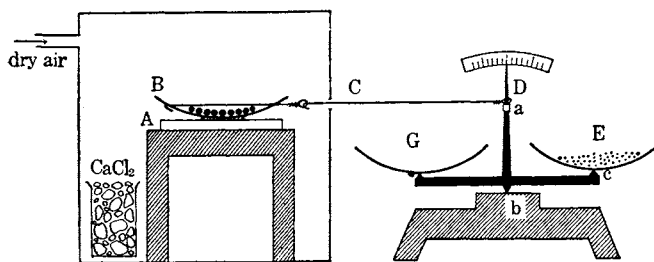


Fig. 1.

Experimental Procedure. The apparatus is shown in Fig. 1. A is an optical glass plate of plane surface which is settled on a suitable stand. B is a slider made of a watch glass, and its weight is adjusted by putting lead shots in it. C is a thin copper wire, one end of which is hitched to the cutting of the watch glass B. The other end of C is connected with the middle part of the pointer D of a prescription balance.

(2) W. B. and J. K. Hardy, *Phil. Mag.*, **38** (1919), 32; W. B. Hardy, *Phil. Mag.*, **40** (1920), 201; *J. Chem. Soc.*, **127** (1925), 1207; Hardy and Doubleday, *Proc. Roy. Soc. (London)*, A, **100** (1922), 550; **101** (1922), 487; **104** (1923), 25; Doubleday, *J. Chem. Soc.*, **121** (1922), 2875; *Proc. Roy. Soc. (London)*, A, **106** (1924), 341; Hardy and Bircumshaw, *Proc. Roy. Soc. (London)*, A, **108** (1925), 1; "Collected Scientific Papers of Sir William Bate Hardy," (Cambridge, 1936).

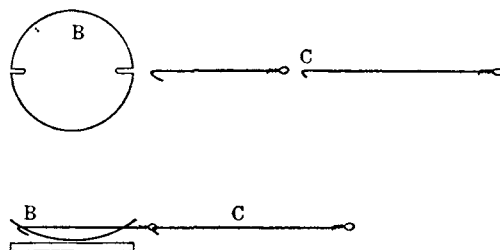


Fig. 2.

Fig. 2 shows the upper and the side views of B and C. C is made of two pieces of wire, short and long, each having a small hook at one end and a small ring at the other. The short piece is hitched to a cutting on the rim of the watch glass, and stretched out through another cutting opposite to the first one. The long piece is hooked to the ring of the short piece and to the pointer of the balance.

A and B are put in a glass case, provided with a vessel containing calcium chloride. A current of dry air is passed through the case during the observation to prevent the effect of moisture on the surfaces and the lubricating liquid. The lubricating liquid is poured on A and then the slider B is put on it. The position of the slider is adjusted so that the pointer D takes the upright position, the right and the left pans being balanced.

Now, fine sand is poured in a thin stream from a reservoir to the right pan E. The quantity of sand gradually increases until finally the right pan goes downward, the pointer inclines to right side, and the slider A moves rightward. Then C is detached from D and the weight of the sand on the right pan E is measured by putting balance weights on the left pan G.

Let the weight of the sand be s , the length between a and b be l , and the distance between b and c be l' , then the force acting on the slider is expressed by the following equation :

$$F = s \frac{l'}{l}.$$

So the coefficient of friction μ is obtained by

$$\mu = \frac{F}{W},$$

where W denotes the weight of the slider, i. e. the sum of the weight of watch glass, lead shots, and one half of the wire C.

It is one of the most important conditions that the sliding surfaces are sufficiently clean and free from any greasy matter. The glass plate and the slider are cleaned in the following manner before each observation. They are boiled for half an hour with a chromic acid solution, washed and rubbed with the finger tip under the running tap water, and finally rinsed with distilled water. They are dried in a desiccator containing calcium chloride, a current of dry air being passed. No grease is applied on the ground part of the desiccator, to avoid the contamination of the sliding surfaces.

Measurement. The purest samples available were used in the experiments. Most of the substances were distilled before the tests.

It is already known that the coefficient of friction is not seriously affected by the change of temperature.⁽³⁾ We conducted, therefore, our experiments at room temperature without special adjustment of the temperature. The temperature was between 17°C. and 24°C. For the measurement, we took the readings of s several times for a definite value of W , and then took their average. The value of l'/l was 1.23 for the balance used in the present measurements, so we get $F = 1.23 s$. Some of the actual examples are shown in Table 1. The results are summarized in Table 2.

Table 1.

Lubricant	W (g.)	Value of s (g.)		F (g.) (1.23 s)	μ (F/W)
		reading	average		
Ethyl alcohol	33.90	20.00	19.78	24.33	0.72
		19.50			
		19.15			
		19.30			
		20.20			
		20.50			
Glycol	22.00	8.10	8.31	10.22	0.46
		8.25			
		9.30			
		7.20			
		8.70			

(3) Hardy and Doubleday, *Proc. Roy. Soc. (London)*, A, **101** (1922), 487.

Table 2. - (Continued)

Lubricant	W (g.)	F (g.)	μ	Lubricant	W (g.)	F (g.)	μ
Acetic acid CH_3COOH	18.35	12.41	(0.68)	Caproic acid $\text{CH}_3(\text{CH}_2)_4\text{COOH}$	17.6	11.77	(0.67)
	21.5	12.80	0.60		23.7	13.70	0.58
	22.8	13.97	0.61		26.3	15.13	0.58
	26.7	15.14	0.57		30.0	18.39	0.61
	32.7	19.03	0.58		33.0	19.46	0.59
	34.2	20.50	0.60		40.0	23.09	0.58
	39.8	23.99	0.60		45.4	27.05	0.60
		Mean 0.59				Mean 0.59	
Propionic acid $\text{CH}_3\text{CH}_2\text{COOH}$	7.60	5.72	(0.75)	Heptylic acid $\text{CH}_3(\text{CH}_2)_5\text{COOH}$	14.2	9.94	(0.70)
	11.95	7.92	(0.66)		17.9	11.93	(0.67)
	15.30	9.57	(0.63)		23.3	14.15	0.61
	23.15	13.57	0.59		27.75	17.71	0.64
	23.60	13.46	0.57		32.95	20.78	0.63
	27.7	16.17	0.58		34.9	20.49	0.59
	30.65	16.84	0.55		41.5	24.81	0.60
	37.1	21.39	0.58		46.95	30.48	0.64
		Mean 0.58				Mean 0.62	
Butyric acid $\text{CH}_3(\text{CH}_2)_2\text{COOH}$	17.6	12.72	(0.73)	Caprylic acid $\text{CH}_3(\text{CH}_2)_6\text{COOH}$	19.8	10.47	0.53
	18.95	12.49	(0.66)		22.25	11.54	0.52
	24.1	14.24	0.59		24.05	12.45	0.52
	26.15	15.22	0.58		27.85	15.48	0.56
	27.8	15.94	0.57		30.0	15.26	0.51
	35.5	21.14	0.60		33.05	18.00	0.54
	40.0	24.08	0.60		35.7	19.09	0.53
		Mean 0.59			40.4	22.73	0.56
Valeric acid $\text{CH}_3(\text{CH}_2)_3\text{COOH}$	20.90	13.60	(0.65)		40.8	19.94	0.49
	22.95	13.64	0.59	Nonylic acid $\text{CH}_3(\text{CH}_2)_7\text{COOH}$	22.25	2.50	0.56
	26.85	16.64	0.62		22.5	12.20	0.54
	31.1	18.04	0.58		28.8	16.49	0.57
	36.6	22.68	0.62		29.7	17.54	0.59
	40.75	24.6	0.60		37.3	21.40	0.57
	43.95	27.52	0.63		41.25	23.61	0.57
		Mean 0.61				Mean 0.57	

Table 2.—(Concluded)

Lubricant	<i>W</i> (g.)	<i>F</i> (g.)	μ	Lubricant	<i>W</i> (g.)	<i>F</i> (g.)	μ
<i>n</i> -Hexane C_6H_{14}	17.55	12.18	0.69	Toluene $C_6H_5CH_3$	24.7	19.71	0.80
	21.7	14.59	0.67		24.9	18.45	0.74
	24.55	17.00	0.69		25.7	20.01	0.78
	25.1	17.17	0.68		28.1	22.65	0.81
	34.7	22.3	0.64		33.3	24.7	0.74
	34.7	23.99	0.69		34.7	26.41	0.76
	37.6	25.78	0.69		35.1	25.83	0.74
		Mean 0.68			38.1	29.26	0.77
<i>n</i> -Heptane C_7H_{16}	21.7	15.72	0.72		44.7	32.95	0.74
	22.3	14.93	0.67		Mean 0.76		
	32.6	20.32	0.62	Liquid paraffine	21.9	15.12	(0.69)
	34.7	25.40	0.73		37.1	20.66	0.56
	41.7	30.18	0.72		40.2	22.13	0.55
	43.5	30.77	0.71		45.5	25.70	0.56
		Mean 0.69			48.3	26.71	0.55
<i>n</i> -Octane C_8H_{18}	22.9	14.49	0.63		57.3	29.01	0.51
	27.0	16.41	0.61		Mean 0.55		
	38.0	24.27	0.64	Glycol $(CH_2OH)_2$	15.2	7.81	(0.51)
	42.1	25.45	0.60		22.0	10.22	0.46
		Mean 0.62			34.0	15.74	0.46
<i>n</i> -Nonane C_9H_{20}	23.3	13.82	0.60		41.3	14.75	0.45
	28.0	18.27	0.65		49.2	22.23	0.45
	33.5	21.34	0.64		Mean 0.46		
	37.4	23.94	0.64	Ethyl acetate $CH_3COOC_2H_5$	19.7	13.76	0.70
	41.9	27.62	0.66		26.2	18.92	0.72
		Mean 0.64			27.7	18.95	0.68
Benzene C_6H_6	15.8	12.29	0.78		36.2	24.89	0.69
	22.0	16.64	0.76		Mean 0.70		
	23.3	19.33	0.83	Oleic acid $C_{17}H_{33}COOH$	23.1	7.55	(0.33)
	26.8	21.37	0.80		24.3	6.46	0.27
	33.1	25.0	0.76		32.3	9.52	0.29
	34.0	27.19	0.80		40.7	11.36	0.28
	41.4	31.15	0.75		51.1	15.30	0.30
		Mean 0.78			Mean 0.29		
Lubricant oil "Planet-RM medium"	37.4	8.55	0.23		37.4	8.55	0.23
	49.1	10.18	0.21		49.1	10.18	0.21
		Mean 0.22				Mean 0.22	

The values of μ in parentheses are excluded in the calculation of mean values. The tangential force required to move the slider is proportional to the normal force between the surfaces or, in our notation, μ is independent of W . This fact is designated by the name "Amontons's or Coulomb's law." In the region, however, where the value of W is too small, this law does not hold, giving large value of μ . The data in parentheses in Table 2 correspond to this region. Fig. 3 and Fig. 4 show the relations between μ and the number of carbon atoms in the molecule of the substance. Further discussion will be given in later papers.

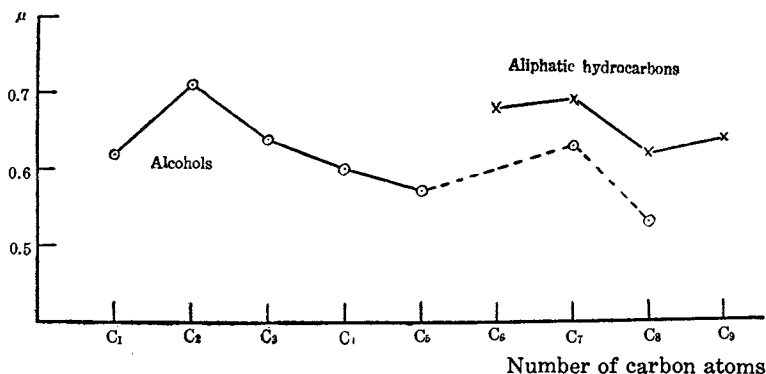


Fig. 3.

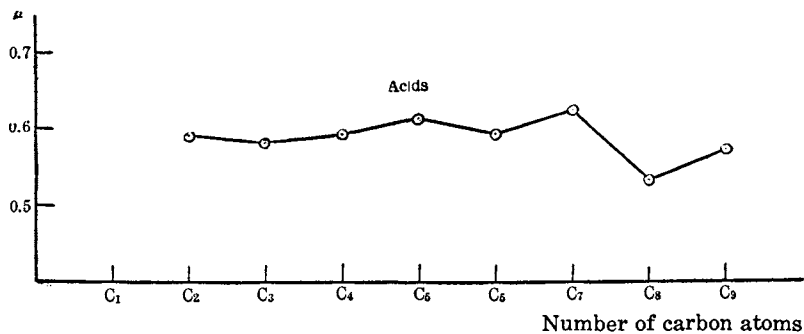


Fig. 4.

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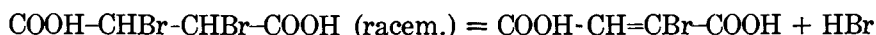
ÜBER DIE HETEROGENE REAKTIONSKINETIK DER UMWANDLUNG VON DIBROMBERNSTEINSÄURE IN MONOBROMFUMARSÄURE.

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Einleitung. Kruyt⁽¹⁾ hat auf der 34. Hauptversammlung der Deutschen Bunsen-Gesellschaft in seinem Vortrag „Molekulare Orientierung in der Adsorptionsschicht und heterogene Katalyse“ eine anregende Betrachtung über den Mechanismus der heterogenen Katalyse dargelegt, dass die Reaktionsfähigkeit eines adsorbierten Moleküls von seiner Orientierung in der Adsorptionsschicht beeinflusst sei. Diese Betrachtung wurde aber von Freundlich⁽²⁾ mit einigen Bedenken in seinem Buch referiert. Es sollte allerdings näher geprüft werden, ob die Reaktionsbeschleunigung bzw. Reaktionsverlangsamung der Orientierung von Molekülen allein zugeschrieben werden kann. Dazu erscheint es wünschenswert, die Versuche von Kruyt und van Duin⁽³⁾ zu wiederholen und zwar bei verschiedenen Temperaturen und mit verschiedenen Adsorbentien, worauf Kruyt selbst damals hingedeutet hat.

Gelegentlich haben wir nun die Kinetik der von van Duin zur Prüfung des Kruytschen Gedankenganges verwendeten monomolekularen Reaktion:



einmal im homogenen System und ein anderes Mal im heterogenen System im Vorhandensein von (1) Silica-gel (2) Zuckerkohle (3) Häminzuckerkohle untersucht, um das Charakteristische der Erscheinung eingehender betrachten zu können. Dabei wurden die Adsorptionsverhältnisse von Reaktionsteilnehmern berücksichtigt, die bei Kruyt und van Duin beiseite gelassen wurden, die aber möglicherweise mit der Beschleunigung bzw. Verlangsamung der Reaktion in enger Beziehung stehen müssen. Die gewonnenen Erfahrungen führten uns zu einer Auffassung, die—unabhängig davon, wie man die Kruytsche Hypothese deuten würde—zur Erklärung der Erscheinung notwendig zu sein scheint.

Versuche der Reaktionskinetik. Bevor wir auf die Ergebnisse der Versuche eingehen, soll kurz die Methodik beschrieben werden. Der Ausgangs-

(1) H. R. Kruyt, *Z. Elektrochem.*, **35** (1929), 539.

(2) H. Freundlich, „Kapillarchemie“, Bd. I, 447, Leipzig (1930).

(3) H. R. Kruyt und C. F. van Duin, *Rec. trav. chim.*, **40** (1922), 249; **47** (1928), 715.

stoff, Dibrombernsteinsäure, wurde nach der Methode von McKenzie⁽⁴⁾ dargestellt, indem man Maleinsäure in ätherischer Lösung mit Brom reagieren liess. Die Reinheit des bereiteten Präparates wurde mit Säure-Titration geprüft; nämlich, eine eingewogene Menge 0.2769 g. Dibrombernsteinsäure in 20 c.c. Flüssigkeit verbrauchte 23.82 c.c. von 0.0845 N NaOH, die 0.2775 g. von der Säure entsprechen. Sein Schmelzpunkt wurde gemessen mit dem Ergebnis: 168–169°C.

Die zu den Versuchen verwendeten Adsorbentien wurden folgenderweise hergestellt: (1) Silica-Gel, aus Natriumsilikat (Präparat Merck) nach der Methode von Patrick⁽⁵⁾, (2) Zuckerkohle, aus reinstem Rohrzucker nach der Methode von O. Warburg⁽⁶⁾, (3) Häminzuckerkohle, nach der Methode von Warburg und Brefeld⁽⁷⁾, indem man 20 g. Rohrzucker und 0.4 g. Hämin mit 5 g. Kaliumcarbonat verkohlte. Das Hämin hat man aus Rinderblut nach der Pilotyscher Methode⁽⁸⁾ dargestellt.

Die hier untersuchte Reaktion im homogenen System ist bekanntlich bei gewöhnlichen Temperaturen eine äusserst langsam verlaufende Reaktion⁽⁹⁾. Wir untersuchten die Kinetik der Reaktion bei Temperaturen 30°, 40°, und 50°C., wobei wir die Reaktion längstens etwa 100 Stunden und wenigstens etwa 6 Stunden lang verfolgen mussten.

In ein Reaktionsgefäss wurde eine eingewogene Menge etwa 1.35 g. von Dibrombernsteinsäure mit 200 c.c. destilliertem Wasser gebracht, hierzu dann 2 g. Adsorbens hinzugefügt. Das Gefäss befand sich in einem Thermostaten und das Reaktionsgemisch wurde von Zeit zu Zeit, insbesondere vor der jeweiligen Probeentnahme geschüttelt. Zu den Einzelproben wurden je 20 c.c. von dem Reaktionsgemisch genommen, die man in 40 c.c. kaltes Wasser einlaufen liess, wodurch die Reaktion praktisch zum Stillstand gebracht werden konnte. Das Gemisch wurde dann vom Adsorbens mittels Glasfilter befreit (bei Silica-Gel wurde das Gemisch stehen gelassen bis die Sedimentation beendet war), und je 10 c.c. von der klaren Flüssigkeit wurden zur Titration angewandt.

Den Reaktionsfortschritt hat man durch die Titration des Bromions nach der Volhardschen Methode und gleichzeitig durch die Titration der sich vermehrenden Säuremenge mit Standard-Baryt ermittelt.

Da man immer einige Zeit warten musste, bis die Temperatur des Reaktionsgemisches derjenigen vom Thermostaten gleich wurde, fing man die

(4) Alex. McKenzie, *Chem. Zentr.*, **83** (1912), II, 1101.

(5) O. Ruff und P. Mautner, *Z. angew. Chem.*, **40** (1927), 428.

(6) O. Warburg, *Biochem. Z.*, **136** (1923), 266.

(7) O. Warburg und W. Brefeld, *Biochem. Z.*, **145** (1924), 461.

(8) Piloty, *Ann.*, **377** (1910), 358.

(9) van't Hoff, „Studies in Chemical Dynamics“, London (1896).

Probe erst 20 Minuten nach der Einsetzung des Reaktionsgefäßes in den Thermostaten an, und die bis dahin umgesetzte Menge von Dibrombernsteinsäure wurde bei jeder Konzentrationsbestimmung als Korrektur abgerechnet. Die Anfangskonzentration wurde einfach aus dem zuerst eingewogenen Wert von Dibrombernsteinsäure ermittelt, weil die Reaktionsendwärtsbestimmung durch die mehrfache Umsetzung der Dibrombernsteinsäure bei Erhitzung erschwert ist. Die Ergebnisse sind in Tabellen 1-4 zusammengestellt.

Tabelle 1. Homogene Reaktionskinetik.

t (Min.)	x_1	$a-x_1$	k_1	x_2	$a-x_2$	k_2
<u>30.4°C.</u>						
0	0	24.89		0	24.89	
371	1.82	23.07	0.000204	1.78	23.11	0.000206
727	3.54	21.35	0.000211	3.23	21.66	0.000193
1445	6.63	18.26	0.000214	6.26	18.63	0.000200
2160	8.81	16.08	0.000203	8.69	16.20	0.000198
2880	10.69	14.20	0.000195	11.06	13.73	0.000206
4320	14.00	10.89	0.000194	14.19	10.70	0.000195
5760	16.72	8.17	0.000193	16.81	8.08	0.000195
			Mittelwert 0.000202			Mittelwert 0.000199
<u>39.9°C.</u>						
0	0	24.80		0	24.80	
120	2.03	22.77	0.000713	1.98	22.82	0.000694
240	3.91	20.89	0.000715	3.95	20.85	0.000722
482	7.30	17.50	0.000722	7.14	17.66	0.000704
720	9.63	15.17	0.000683	9.78	15.02	0.000694
960	12.26	12.34	0.000710	12.11	12.69	0.000697
1380	15.34	9.46	0.000699	15.15	9.65	0.000683
1760	17.52	7.28	0.000685	17.18	7.62	0.000669
			Mittelwert 0.000704			Mittelwert 0.000696
<u>49.9°C.</u>						
0	0	24.30		0	24.30	
20	1.21	23.09	0.00255	1.14	23.16	0.00238
40	2.35	21.95	0.00253	2.26	22.04	0.00238
80	4.56	19.74	0.00259	4.44	19.86	0.00257
160	8.20	16.10	0.00255	8.03	16.27	0.00251
240	11.20	13.10	0.00255	10.77	13.53	0.00248
320	13.07	11.23	0.00241	13.22	11.08	0.00245
			Mittelwert 0.00253			0.00246

Tabelle 2. Heterogene Reaktionskinetik an Silica-Gel.

t (Min.)	x_1	$a-x_1$	k_1	x_2	$a-x_2$	k_2
<u>30.4°C.</u>						
0	0	24.89		0	24.89	
360	1.88	23.01	0.000217	1.41	23.48	0.000162
720	3.43	21.43	0.000211	2.58	22.31	0.000152
1445	6.33	18.56	0.000203	5.05	19.83	0.000154
2160	8.89	16.00	0.000205	7.32	17.57	0.000161
2880	11.45	13.44	0.000213	9.54	15.35	0.000168
4320	14.46	10.43	0.000201	12.68	12.21	0.000164
5760	16.94	7.95	0.000198	15.60	9.29	0.000170
			Mittelwert 0.000207			Mittelwert 0.000163
<u>39.9°C.</u>						
0	0	24.46		0	24.46	
120	1.71	22.75	0.000637	1.31	23.15	0.000458
239	3.64	20.82	0.000669	2.02	22.44	0.000359
483	7.35	17.11	0.000741	5.67	18.79	0.000540
720	10.75	13.71	0.000784	7.95	16.51	0.000510
961	12.32	12.14	0.000727	10.14	14.32	0.000556
1380	15.38	9.08	0.000718	12.82	11.64	0.000483
1680	17.09	7.37	0.000713	14.79	9.67	0.000552
			Mittelwert 0.000713			Mittelwert 0.000518
<u>50.0°C.</u>						
0	0	24.92		0	24.92	
20	1.26	23.66	0.00248	0.73	24.19	(0.00143)
40	2.74	22.18	0.00255	1.68	23.24	0.00188
82	4.75	20.17	0.00255	2.52	22.40	0.00129
160	9.05	15.87	0.00276	6.72	18.20	0.00193
240	11.50	13.42	0.00255	9.01	15.91	0.00186
310	13.35	11.57	0.00246	11.47	13.45	0.00197
			Mittelwert 0.00256			Mittelwert 0.00174

Tabelle 3. Heterogene Reaktionskinetik an Zuckerkohle.

t (Min.)	x_1	$a-x_1$	k_1	x_2	$a-x_2$	k_2
<u>30.4°C.</u>						
0	0	24.89		0	24.89	
360	1.50	23.39	0.000166	0	24.89	—
720	2.86	22.03	0.000169	0.61	24.28	(0.000035)
1440	5.72	19.17	0.000181	2.52	22.37	0.000073
2800	9.86	15.03	0.000175	4.49	20.40	0.000069
4320	13.40	11.49	0.000179	6.26	18.63	0.000067
5760	15.66	9.23	0.000172	8.99	15.90	0.000078
			Mittelwert 0.000175			Mittelwert 0.000072
<u>39.9°C.</u>						
0	0	24.51		0	24.51	
120	1.49	23.02	0.000518	1.27	23.24	0.000439
240	3.19	21.32	0.000586	2.58	21.93	0.000462
483	6.24	18.27	0.000561	4.66	19.85	0.000435
721	8.99	15.52	0.000633	5.78	18.73	0.000373
961	11.59	12.92	0.000665	7.35	17.16	0.000370
1383	14.71	9.80	0.000666	9.02	15.49	0.000331
1665	16.20	8.81	0.000649	10.64	13.87	0.000340
			Mittelwert 0.000609			Mittelwert 0.000393
<u>50.0°C.</u>						
0	0	25.10		0	25.10	
21	1.24	23.86	0.00230	1.06	24.04	0.00212
41	2.24	22.86	0.00216	2.40	22.70	0.00230
81	4.18	20.92	0.00225	3.74	21.36	0.00196
166	7.02	18.08	0.00197	5.92	19.18	0.00161
242	8.96	16.14	0.00183	6.38	18.72	0.00121
327	11.35	13.75	0.00182	7.50	17.60	0.00109
			Mittelwert 0.00205			Mittelwert 0.00171

Tabelle 4. Heterogene Reaktionskinetik an Häminzuckerkohle.

t (Min.)	x_1	$a-x_1$	k_1	x_2	$a-x_2$	k_2
<u>30.4°C.</u>						
0	0	24.89		0	24.89	
360	1.36	23.53	(0.000156)	—	—	—
720	3.24	21.65	0.000193	—	—	—
1440	5.87	19.02	0.000188	1.46	23.43	0.000042
2160	8.66	16.23	0.000198	1.67	23.22	0.000032
2880	11.15	13.74	0.000206	3.03	21.86	0.000045
4320	14.67	10.22	0.000204	4.65	20.24	0.000046
5760	17.99	6.90	0.000222	6.61	17.28	0.000063
			Mittelwert 0.000202			Mittelwert 0.000045
<u>39.9°C.</u>						
0	0	24.48		0	24.48	
121	1.34	23.14	(0.000465)	0.51	23.97	0.000174
240	3.42	21.06	0.000626	1.11	23.37	0.000193
480	6.54	17.94	0.000646	2.58	21.90	0.000232
720	9.52	14.96	0.000683	3.95	20.53	0.000244
961	11.82	12.66	0.000685	4.56	19.92	0.000215
1380	15.38	9.10	0.000715	5.57	18.91	0.000187
1680	17.39	7.09	0.000736	6.28	18.20	0.000176
			Mittelwert 0.000682			Mittelwert 0.000203
<u>49.9°C.</u>						
0	0	25.10		0	25.10	
20	0.74	24.36	(0.00159)	0.73	24.37	0.00147
41	2.15	22.95	0.00217	1.40	23.70	0.00139
81	4.53	20.57	0.00246	2.20	22.86	0.00115
161	7.42	17.61	0.00217	4.00	21.10	0.00108
241	10.76	14.34	0.00250	5.82	19.28	0.00109
311	13.43	11.67	0.00246	6.66	18.44	0.00099
			Mittelwert 0.00223			Mittelwert 0.00117

In diesen Tabellen stellt x_1 die durch Brom-Titration ermittelte umgesetzte Dibrombernsteinsäure, x_2 die durch Säure-Titration ermittelte umgesetzte Dibrombernsteinsäure dar, während $a - x_1$ bzw. $a - x_2$ die noch nicht umgesetzte Dibrombernsteinsäure darstellt. Die Geschwindigkeitskonstante k_1 bzw. k_2 wurde nach der Gleichung:

$$k = \frac{2.3}{t} \log \frac{a}{a-x}$$

berechnet. Im homogenen System verläuft die hier betrachtete Reaktion bekanntlich monomolekular, und zwar stimmen die beiden gewonnenen Reaktionskonstanten k_1 und k_2 miteinander gut überein, im heterogenen System dagegen ist die Sachlage nicht immer die Gleiche und soll von Fall zu Fall näher betrachtet werden. Es sei jedoch bemerkt, dass sich die Reaktion im heterogenen System nicht in der Grenzflächenschicht allein, sondern teilweise noch in homogener Flüssigkeit vollziehen kann.

(1) An Silica-Gel: Die Reaktion verläuft in diesem Fall annähernd monomolekular. Der Mittelwert der Geschwindigkeitskonstante k_1 ergab sich etwas grösser als die entsprechende Konstante der homogenen Reaktion, während k_2 kleiner als die entsprechende Konstante der homogenen Reaktion war. Man dürfte aber nicht aus dem kleineren Wert von k_2 auf die Reaktionsverlangsamung schliessen, denn man muss bedenken, dass die Säuren im Reaktionsgemisch durch Silica-Gel mehr oder weniger adsorbiert werden, sodass sich der Wert von der umgesetzten Menge x_2 scheinbar kleiner ergibt. Im Gegensatz dazu, könnte man wohl aus dem grösseren Wert von k_1 schliessen, dass die Reaktion an Silica-Gel im Vergleich mit der homogenen Reaktion etwas beschleunigt ist, indem man berücksichtigt, dass dabei die Bestimmung von umgesetzter Dibrombernsteinsäure wegen der unbedeutend kleinen Adsorption des Bromions kaum gestört wird.

(2) An Zuckerkohle: In diesem Falle ergaben sich die beiden ermittelten Geschwindigkeitskonstanten k_1 und k_2 kleiner als die entsprechenden Konstanten der homogenen Reaktion. Dass k_2 viel kleiner als k_1 ist, wird der möglichen starken Adsorption der entstandenen Monobromfumarsäure an dem Adsorbens zugeschrieben. Jedenfalls ist die Reaktion an Zuckerkohle im Vergleich mit der homogenen Reaktion bedeutend verlangsamt.

(3) An Häminzuckerkohle: Die Geschwindigkeitskonstante k_1 ist im Mittelwert ein wenig kleiner als die entsprechende homogene Konstante, während k_2 ausgesprochen kleiner als die entsprechende Konstante der homogenen Reaktion ist. Dies dürfte darauf hindeuten, dass die Reaktion an

Häminzuckerkohle im Ganzen nur ein wenig verlangsamt ist, ungeachtet der sich sehr klein ergebende Konstante k_2 , wofür die stärkere Adsorption der entstandenen Monobromfumarsäure durch das Adsorbens verantwortlich sein könnte.

Zusammenfassend sei gesagt, dass die Umwandlung der Dibrombernsteinsäure in Monobromfumarsäure an Silica-Gel etwas beschleunigt ist, dagegen ist sie an Zuckerkohle sowie an Häminzuckerkohle mehr oder weniger verlangsamt. Die Verlangsamung der Reaktion an Kohle könnte nun eine allgemeine Erscheinung sein, weil das Gleiche auch an technischer Kohle (Merckscher Blutkohle) von van Duin⁽⁸⁾ gefunden worden ist. Hier soll noch bemerkt werden, dass bei Kohle die Geschwindigkeitskonstante mit der Fortschreitung der Reaktion veränderlich ist, und zwar findet eine fast regelmässige Verminderung von k_2 statt, was bald weiter unten erläutert werden wird.

Versuche der Adsorption. Nach der oben angestellten Betrachtung ist es naturgemäss klar, dass zur weiteren Deutung der Resultaten der kinetischen Versuche einige Kenntnisse über die Adsorptionsverhältnisse der Reaktionsteilnehmer notwendig sind. Man konnte allerdings nicht die Adsorption jedes einzelnen Reaktionsteilnehmers aus dem Reaktionsgemisch bestimmen. Wohl aber war es möglich, gleichzeitig mit den Versuchen der Kinetik, die Adsorption der Säuremischung (Dibrombernsteinsäure und Monobromfumarsäure) annähernd zu ermitteln, in folgender Weise: Man hat nämlich bei jeder Probeentnahme die ganze Säuremenge (Dibrombernsteinsäure, Monobromfumarsäure und Bromwasserstoff) im Reaktionsgemisch durch Titration bestimmt und von dieser ganzen Säuremenge das Säure-Äquivalent des Bromions, das durch Brom-Titration bestimmt wurde, abgezogen, auf welchem Wege man die Konzentration der sich in der Flüssigkeit befindenen beiden Säuren (Dibrombernsteinsäure und Monobromfumarsäure) erhielt. Die letzte Konzentration, wenn sie von der Anfangskonzentration von Dibrombernsteinsäure reduziert wird, ergibt die adsorbierte Menge der beiden Säuren wie in Tabellen 5-7 wiedergegeben ist. In diesen Tabellen, bedeuten C die ganze Säuremenge in Lösung in Millimol in Liter, c' das Säure-Äquivalent des Bromions in Millimol i. L., c die sich in Lösung befindene Säuremischung in Millimol i. L. und a die adsorbierte Menge der Säuremischung in Millimol pro 10 g. Adsorbens. Hierbei wurde angenommen, dass die Adsorption vom Bromion an dem Adsorbens vernachlässigt werden kann, was sie auf Grund unserer anderweitigen Erfahrungen, die bei Versuchen mit Kaliumbromidlösung an den oben verwendeten Adsorbentien gewonnen wurden, als durchaus statthaft gezeigt hat.

Tabelle 5. Adsorption der Säuremischung (Dibrombernsteinsäure und Monobromfumarsäure) an Silica-Gel.

t (Min.)	C	c'	c	α
<u>30.4°C.</u>				
0	21.11	0	21.11	3.78
360	21.82	0.94	20.88	4.01
720	22.40	1.72	20.68	4.21
1445	23.64	3.17	20.47	4.42
2160	24.77	4.45	20.32	4.57
2880	25.88	5.73	20.16	4.73
4820	27.45	7.23	20.21	4.68
5760	28.91	8.47	20.44	4.45
<u>39.9°C.</u>				
0	21.00	0	21.00	3.46
120	21.66	0.86	20.80	3.66
239	22.01	1.82	20.19	4.27
483	23.84	3.68	20.16	4.30
720	24.98	5.38	19.60	4.86
961	26.07	6.16	19.91	4.55
1380	27.41	7.69	19.82	4.64
1680	28.40	8.55	19.85	4.61
<u>50.0°C.</u>				
0	21.97	0	21.97	2.95
20	22.34	0.63	21.71	3.21
40	22.81	1.37	21.44	3.47
81	23.23	2.38	20.85	4.07
162	25.33	4.53	20.80	4.12
240	26.48	5.75	20.73	4.19
320	27.17	6.68	21.03	3.89

Tabelle 6. Adsorption der Säuremischung (Dibrombernsteinsäure und Monobromfumarsäure) an Zuckerkohle.

t (Min.)	C	c'	c	α
<u>30.4°C.</u>				
0	23.86	0	23.86	1.03
360	23.86	0.75	23.11	1.78
720	24.17	1.43	22.74	2.15
1440	25.12	2.86	22.26	2.63
2880	26.11	4.93	21.18	3.71
4320	26.99	6.70	20.29	4.60
5760	28.26	7.80	20.43	4.43

Tabelle 6. (*Fortsetzung.*)

<i>t</i> (Min.)	<i>C</i>	<i>c'</i>	<i>c</i>	<i>a</i>
<u>39.9°C.</u>				
0	23.36	0	23.36	1.15
121	24.00	0.75	23.25	1.26
241	24.56	1.60	22.96	1.55
483	25.69	3.12	22.57	1.94
721	26.25	4.50	21.75	2.76
961	27.04	5.80	21.24	3.27
1383	27.87	7.36	20.51	4.00
1665	28.68	8.10	20.58	3.93
<u>50.0°C.</u>				
0	22.88	0	22.88	2.22
21	23.41	0.62	22.79	2.31
41	24.08	1.12	22.96	2.14
81	24.65	2.09	22.56	2.54
166	25.84	3.51	22.33	2.77
242	26.07	4.48	21.59	3.51
327	26.62	5.68	20.94	4.16

Tabelle 7. Adsorption der Säuremischung (Dibrombernsteinsäure und Monobromfumar säure) an Hainzuckerkohle.

<i>t</i> (Min.)	<i>C</i>	<i>c'</i>	<i>c</i>	<i>a</i>
<u>30.4°C.</u>				
0	22.62	0	22.62	2.27
360	22.44	0.68	21.76	3.13
720	22.47	1.62	20.85	4.04
1440	23.35	2.94	20.41	4.48
2160	23.46	4.33	19.13	5.76
2880	24.14	5.58	18.56	6.33
4320	24.65	7.34	17.31	7.58
5760	25.93	9.00	16.93	7.96
<u>39.9°C.</u>				
0	22.25	0	22.25	2.23
121	22.51	0.67	21.84	2.64
240	22.81	1.71	21.10	3.38
480	23.54	3.77	19.77	4.71
720	24.23	4.76	19.47	5.01
961	24.53	5.91	18.62	5.86
1380	25.04	7.69	17.35	7.13
1680	25.35	8.70	16.65	7.83
<u>49.9°C.</u>				
0	21.73	0	21.73	3.37
20	22.10	0.37	21.73	3.37
41	22.43	1.08	21.35	3.75
81	22.85	2.27	20.58	4.52
161	23.72	3.71	20.01	5.09
241	24.64	5.38	19.26	5.84
311	25.06	6.72	18.34	6.76

Man sieht in diesen Tabellen, dass die Adsorption der Säuremischung an Silica-Gel unabhängig von dem Reaktionsfortschritte beinahe konstant stattfindet, während sie sich an Zuckerkohle sowie an Häminzuckerkohle mit dem Fortschritte der Reaktion vermehrt. Der letzte Umstand kommt wahrscheinlich daher, dass die entstandene Monobromfumarsäure aus dem Reaktionsgemisch durch Kohle stärker adsorbiert wird als die reagierende Dibrombernsteinsäure. Diese Vermutung wurde ferner durch den folgenden Versuch unterstützt.

Man hat nämlich die Adsorption von Dibrombernsteinsäure und von Monobromfumarsäure einzeln in ihrer Lösung an den verwendeten Adsorbentien untersucht. Die dazu gebrauchte Monobromfumarsäure wurde aus der oben hergestellten Dibrombernsteinsäure nach der Methode von Michael⁽¹⁰⁾ dargestellt. Die Adsorption von Dibrombernsteinsäure wurde bei Zimmertemperatur 14°C. und in etwa 1-2 Stunden Arbeitszeit ausgeführt, wobei man sich davon überzeugte, dass man den aus dem Auftreten der Reaktion herrührenden Fehler umgehen kann. Die Adsorption von Monobromfumarsäure wurde auch unter gleichen Bedingungen gemessen. Die Ergebnisse sind in Tabellen 8-9 wiedergegeben. In der Tabellen bedeuten c die Gleichgewichtskonzentration in Millimol i. L. und a die adsorbierte Menge in Millimol pro Gramm Adsorbens. Die Berechnung erfolgte nach der bekannten Formel: $a = ac^{\frac{1}{n}}$. Abb. 1 enthält die Adsorptionsisothermen.

Table 8. Adsorption der Dibrombernsteinsäure bei 14°C.
(1 g. Adsorbens in 100 c.c. der Lösung)

	c	a beob.	a ber.
Silica-Gel $1/n = 0.018$ $\alpha = 0.320$	46.37	0.349	0.349
	21.95	0.346	0.345
	9.57	0.338	0.340
	3.44	0.333	0.334
Zuckerkohle $1/n = 0.495$ $\alpha = 0.029$	95.0	0.26	0.28
	44.8	0.20	0.19
	21.3	0.13	0.13
	9.9	0.09	0.09
Häminzuckerkohle $1/n = 0.296$ $\alpha = 0.102$	46.82	0.305	0.304
	22.99	0.241	0.247
	11.04	0.191	0.198
	5.12	0.165	0.158

(10) Michael, *J. prakt. Chem.*, **52** (1895), 289.

Tabelle 9. Adsorption der Monobromfumarsäure bei 14°C.
(1 g. Adsorbens in 100 c.c. der Lösung)

		c	α beob.	α ber.
Silica-Gel	$1/n = 0.052$ $\alpha = 0.288$	40.65	0.345	0.349
		18.50	0.334	0.335
		8.21	0.330	0.321
		2.70	0.302	0.303
Zuckerkohle	$1/n = 0.105$ $\alpha = 0.085$	21.31	0.118	0.118
		10.34	0.106	0.109
		4.74	0.101	0.100
Häminzuckerkohle	$1/n = 0.123$ $\alpha = 0.209$	41.08	0.305	0.330
		19.36	0.300	0.301
		8.66	0.273	0.272
		3.44	0.235	0.243

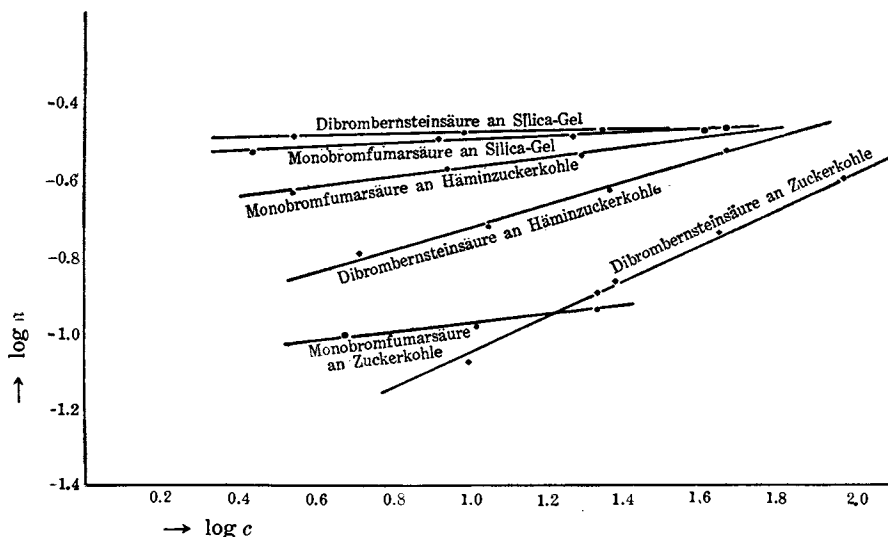


Abb. 1.

Hieraus ist ersichtlich, (1) dass an Silica-Gel die Adsorption der beiden betreffenden Säuren beinahe gleichmässig stattfindet, obwohl Monobromfumarsäure ein wenig geringer als Dibrombernsteinsäure adsorbiert ist. (2) An Kohlen, insbesondere an Häminzuckerkohle ist dagegen Monobromfumarsäure bedeutend stärker adsorbiert als Dibrombernsteinsäure. Durch diese Adsorptionsverhältnisse der beiden Säuren an den verschiedenen Adsorbentien wäre,

obgleich sie noch in dem Reaktionsgemisch möglicherweise modifiziert werden, die oben bemerkte Konstanz (bei Silica-Gel) bzw. Inkonstanz (bei Kohle) der Adsorption der Säuremischung mit dem Reaktionsfortschritte verständlich gemacht.

Der Typ der heterogenen Reaktion. Man kann nun aus dem Ergebnis der Reaktionskinetik, die oben untersuchten heterogenen Reaktionen – mit einem Ausgangsstoff – in einige Typen ordnen, nämlich :

(1) Die Reaktion an Silica-Gel gehört zu solchen Reaktionen, in denen die Hemmung von Reaktionsprodukten wegen ihrer verhältnismässig kleinen Adsorption an Adsorbens fehlt. Die Reaktion in der Adsorptionsschicht sollte dann einfach der adsorbierten Menge des Ausgangsstoffes proportional verlaufen, und zwar bei schwacher Adsorption des Ausgangsstoffes nach der folgenden Gleichung :

$$\frac{dx}{dt} = k(a-x) \quad , \quad (1)$$

welche tatsächlich bei der Reaktion an Silica-Gel gültig gefunden wurde.

(2) Im Gegensatz dazu ist die Reaktion an Zuckerkohle oder Häminzuckerkohle eine solche Reaktion, in der die Hemmung von Reaktionsprodukten auftritt. Das Reaktionsprodukt, Monobromfumarsäure, wurde ja als der Ausgangsstoff Dibrombernsteinsäure stärker adsorbiert, sodass es auf die Reaktion hemmend einwirken kann. Die Reaktionsgeschwindigkeit soll in diesem Fall etwa folgendermassen gegeben werden :

$$\frac{dx}{dt} = \frac{k(a-x)}{1+bx} \quad , \quad (2)$$

unter der Annahme, dass der Ausgangsstoff schwach und das Reaktionsprodukt mittelstark adsorbiert wird. Hier bedeuten $a-x$ die Konzentration des Ausgangsstoffes (Dibrombernsteinsäure) und x diejenige des Reaktionsproduktes (Monobromfumarsäure). Sowohl k auch b sind Konstanten. Um diese Gleichung zu prüfen, brauchte man die integrierte Gleichung :

$$k = \frac{1+ah}{t} \log \frac{a}{a-x} - \frac{bx}{t} \quad , \quad (3)$$

worin ferner gesetzt werden (nach Hinshelwood⁽¹¹⁾):

$$\frac{1}{t} \log \frac{a}{a-x} = k_m \quad \text{und} \quad \frac{x}{t} = v \quad .$$

(11) C. N. Hinshelwood, „The Kinetics of Chemical Change in Gaseous Systems“, 322, Oxford (1933).

Es muss also letzten Endes geprüft werden, ob k_m eine lineäre Funktion von v ist. Es hat sich in der Tat bei den Reaktionen an Kohle bestätigt, dass dieser Anspruch im Ganzen in ausgeprägtem Masse erfüllt ist (bei 30°C. treten mehr oder weniger Abweichungen auf), — wobei man versuchsweise für x bzw. $a-x$ den durch Säure-Titration ermittelten Wert x_2 bzw. $a-x_2$ einsetzt — wie in Tabellen 10–11 gezeigt ist.

Tabelle 10. Heterogene Reaktion an Zuckerkohle.

	t	x	v	k_m	$v+k/b$	$a+1/b$
39.9°C. $a=24.51$	120	1.49	0.0106	0.003439	0.0158	36.1
	240	3.19	0.0108	0.000462	0.0160	34.7
	483	6.24	0.0097	0.000435	0.0149	34.2
	721	8.99	0.0080	0.000373	0.0133	35.5
	961	11.59	0.0077	0.000370	0.0129	34.8
	1383	14.71	0.0065	0.000331	0.0118	35.5
	1665	16.20	0.0064	0.000340	0.0116	34.2
50.0°C. $a=25.10$	21	1.24	0.0505	0.00212	0.0572	27.0
	41	2.24	0.0585	0.00230	0.0652	28.3
	81	4.18	0.0462	0.00196	0.0529	27.0
	166	7.02	0.0357	0.00161	0.0424	26.3
	242	8.96	0.0264	0.00121	0.0331	27.4
	327	11.35	0.0229	0.00109	0.0296	27.2

Tabelle 11. Heterogene Reaktion an Häminzuckerkohle.

	t	x	v	k_m	$v+k/b$	$a+1/b$
39.9°C. $a=24.48$	720	9.52	0.0055	0.000244	0.0063	25.7
	961	11.82	0.0047	0.000215	0.0055	25.7
	1380	15.38	0.0040	0.000187	0.0048	25.8
	1680	17.39	0.0037	0.000176	0.0045	25.7
49.9°C. $a=25.10$	20	0.74	0.0365	0.00147	0.0406	27.6
	41	2.15	0.0339	0.00139	0.0380	27.3
	81	4.53	0.0277	0.00115	0.0318	27.7
	161	7.42	0.0248	0.00108	0.0289	26.8
	241	10.76	0.0242	0.00109	0.0281	26.6
	311	13.43	0.0214	0.00099	0.0255	25.8

Aktivierungswärme der Reaktion. Aus der Temperaturabhängigkeit der homogenen Reaktion kann man mittels der bekannten Arrheniusschen Gleichung⁽¹²⁾:

$$k = Z \cdot e^{-\frac{E}{RT}} \quad \text{oder} \quad \log k = H - \frac{E}{RT} \quad (4)$$

die Aktivierungswärme der Reaktion berechnen, wie in Tabelle 12 gezeigt ist. Dieselbe Gleichung soll auch für die heterogene Reaktion verwendet werden, sofern die Reaktionsgeschwindigkeitskonstante der betreffenden Reaktion durch einfache Potenzen des reagierenden Stoffes zu kennzeichnen ist. Tabelle 13 gibt die Resultaten der Berechnung für den Fall der Reaktion an Silica-Gel wieder, wobei sich die Reaktionsgeschwindigkeitskonstante einfach durch Gleichung (1) ausdrücken lässt. Zum anschaulichen Vergleich hat man die beiden Resultaten in Abb. 2 eingetragen.

Tabelle 12. Aktivierungswärme der homogenen Reaktion.

$E = 10925$

$H = 14.30$

t	T	$k_{\text{beob.}}$	$k_{\text{ber.}}$
30.4	303.4	0.000199	0.000200
39.9	312.9	0.000696	0.000693
50.0	323.0	0.00246	0.00246

Tabelle 13. Aktivierungswärme der Reaktion an Silica-Gel.

$E = 10280$

$H = 13.15$

t	T	$k_{\text{beob.}}$	$k_{\text{ber.}}$
30.4	303.4	0.000163	0.000163
39.9	312.9	0.000518	0.000523
49.9	322.9	0.00174	0.00170

Man könnte nun wohl annehmen, dass die hier untersuchte Reaktion im heterogenen System teilweise eine echte Grenzflächenschicht-Reaktion ist. Dann liesse sich die von Polanyi⁽¹³⁾ und Hinshelwood⁽¹⁴⁾ stammende Betrachtungsweise der Aktivierungswärme der heterogenen Reaktion hierauf übertragen. Die oben berechnete Aktivierungswärme der heterogenen Reaktion an Silica-Gel wird also nach Hinshelwood als eine scheinbare Aktivierungswärme definiert. Diese scheinbare Aktivierungswärme lässt sich ferner im Fall der Reaktion, in der keine Hemmung der Reaktionsprodukte auftritt, was bei Silica-Gel wirklich der Fall ist, ausdrücken wie folgt: $E = Q - \lambda$, wo Q die wahre Aktivierungswärme und λ die Adsorptionswärme des Ausgangsstoffes bedeutet. Die scheinbare Aktivierungswärme ist demnach in

(12) Hierbei ist gesetzt: $\log Z = H$.

(13) M. Polanyi, *Z. Elektrochem.*, **27** (1921), 143.

(14) C. N. Hinshelwood, *loc. cit.*

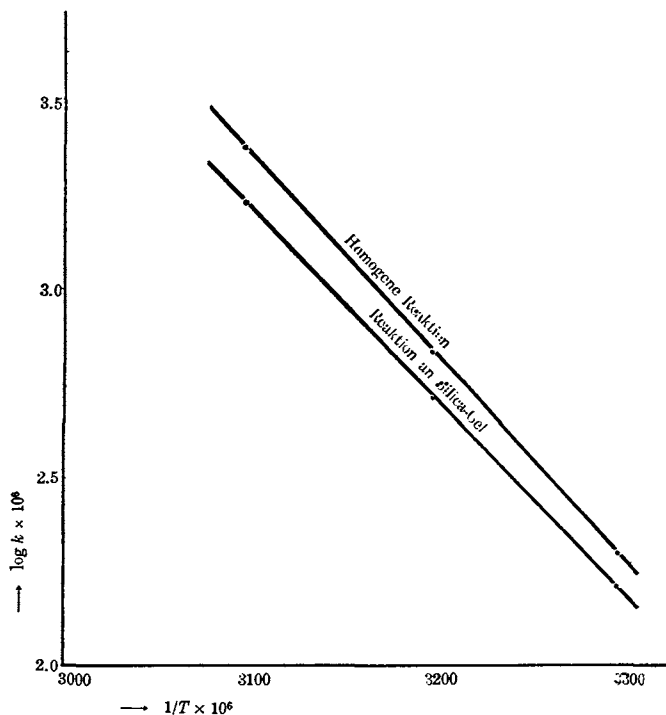


Abb. 2.

diesem Fall um die Adsorptionswärme des Ausgangsstoffes vermindert gegenüber der wahren. Die erhaltene scheinbare Aktivierungswärme der Reaktion an Silica-Gel ergab sich in der Tat kleiner als die Aktivierungswärme der homogenen Reaktion; man kann jedoch weiter nichts über die wahre Aktivierungswärme sagen, sofern die Adsorptionswärme λ nicht direkt fassbar ist.

Für die Reaktion an Kohle, in der die Reaktionsgeschwindigkeitskonstante nicht mehr durch einfache Potenzen des reagierenden Stoffes zu kennzeichnen ist, sondern sich etwa durch Gleichung (2) ausdrücken lässt, bestehen eine einfache Beziehung zwischen Temperaturkoeffizient und Aktivierungswärme nicht. Man hat aber versuchsweise hierbei auch mittels der Arrheniusschen Gleichung die Aktivierungswärme (sogenannte Brutto-Aktivierungswärme⁽¹⁵⁾) berechnet, deren Deutung hier noch offen bleiben soll. Tabellen 14-15 zeigt die Ergebnisse.

(15) G. M. Schwab, „Katalyse vom Standpunkt der chemischen Kinetik“, 167, Berlin (1931).

Tabelle 14. Aktivierungswärme der Reaktion an Zuckerkohle.

 $E = 16130$ $H = 22.48$

t	T	$k_{\text{beob.}}$	$k_{\text{ber.}}$
30.4	303.4	0.000078	0.000079
39.9	312.9	0.00050	0.00050
50.0	323.0	0.0032	0.0032

Tabelle 15. Aktivierungswärme der Reaktion an Häminzuckerkohle.

 $E = 10885$ $H = 14.18$

t	T	$k_{\text{beob.}}$	$k_{\text{ber.}}$
30.4	303.4	0.00017	0.00017
39.9	312.9	0.00066	0.00061
49.9	322.9	0.0021	0.0021

Man könnte doch hieraus folgendes erwähnen. Bei Zuckerkohle ergibt sich die Aktivierungswärme wahrscheinlich infolge deren Vermehrung um die Adsorptionswärme des Reaktionsproduktes scheinbar grösser, während sie sich bei Häminzuckerkohle trotz der stärkeren Adsorption des Reaktionsproduktes scheinbar kleiner ergibt, wodurch die Reaktion an Häminzuckerkohle ungeachtet der möglichen grösseren Hemmung des Reaktionsproduktes verhältnismässig wenig gestört ist.

Schlussbetrachtungen. Das Ergebnis, dass die oben untersuchte Reaktion an einem „carbophilen“⁽¹⁶⁾ Adsorbens wie Kohle verlangsamt wurde, während sie an einem „oxophilen“ Adsorbens wie Silica-Gel ungestört, ja sogar beschleunigt wurde, steht mit dem Kruytschen Gedankengang nicht im Widerspruch, denn die Orientierung von Molekülen in der Adsorptionsschicht kann an den oben genannten zwei Adsorbentien verschiedenartig stattfinden, infolgedessen kann die molekulare Orientierung auf die Reaktionsgeschwindigkeit an den zwei Adsorbentien eventuell entgegengesetzten Einfluss ausüben⁽¹⁷⁾.

Immerhin wird das gleiche Ergebnis durch die oben erhaltenen Adsorptionsverhältnisse der Reaktionsteilnehmer gedeutet werden, indem man berücksichtigt, dass die Reaktion an Kohle durch das Reaktionsprodukt infolge seiner stärkeren Adsorption gehemmt wird, aber an Silica-Gel findet diese Hemmung nicht statt. Es scheint demnach gerade bei dieser Reaktion an Kohle der Gedankengang wertvoll zu sein, dass die Reaktionsgeschwindigkeit von dem Reaktionsprodukte, welches möglicherweise auf den reagierenden Stoff verdrängend wirkt, stark beeinflusst wird.

(16) Terminologie nach L. Gurwitsch, *Kolloid-Z.*, **32** (1923), 80.

(17) An dem oben verwendeten Silica-Gel gilt die Traubesche Regel nicht, was wir durch Versuche mit einer Reihe der normalen Fettsäuren (von Ameisensäure bis Valeriansäure) bestätigt haben. Die Adsorption dieser Säuren fand im Konzentrationsbereich von 50 bis 500 Millimol i. L. beinahe in gleicher Weise statt—Ameisensäure wurde etwas stärker als die anderen Säuren adsorbiert—unabhängig von der Zahl der Kohlenstoffatome.

Es sei hier jedoch bemerkt, dass es sich im Fall der von uns untersuchten Reaktion nicht um die Reaktionsbeschleunigung bzw. Reaktionsverlangsamung handelt, die von der Verschiebung eines chemischen Gleichgewichtes hervorgerufen wird⁽¹⁸⁾, weil die untersuchte Reaktion unter den gegebenen Bedingungen nur in einer Richtung fortschreitet.

Die gefundenen Adsorptionsverhältnisse stehen auch mit den Daten von der Aktivierungswärme der Reaktion im Einklang, soweit die Aktivierungswärme der heterogenen Reaktion auf Grund der Theorie von Polanyi-Hinshelwood gedeutet werden kann. Ferner könnte man aus dem tatsächlichen Umstände, dass die Temperaturabhängigkeit der heterogenen Reaktion (an Kohle) von derjenigen der homogenen Reaktion unterschiedlich ist, wohl schliessen, dass die Verlangsamung der Reaktion im heterogenen System nicht einfach der Verringerung der Konzentration in der Flüssigkeit zuzuschreiben ist⁽¹⁹⁾.

Wir kommen nun zu einem anderen Effekt, nämlich zum Effekt der Haftintensität der adsorbierten Moleküle in der Grenzflächenschicht, der auf die Reaktion je nach dem verwendeten Adsorbens verschiedenartig wirken kann. Als wir auf diesen Gedanken gekommen waren, ist uns eine Arbeit von Lindau und Salomon⁽²⁰⁾ eingegangen, die in äusserst eleganter Weise das Problem der Haftfestigkeit bzw. der Wechselzahl der adsorbierten Moleküle in der Grenzflächenschicht experimentell behandelt. Dabei haben die genannten Autoren zur Bestimmung der Haftfestigkeit von der gleichen Adsorbierbarkeit optischer Antipoden Gebrauch gemacht.

Die Kenntnjs, welche mittels dieses Verfahrens gewonnen wird, dürfte nun für den Mechanismus der von uns untersuchten Katalyse nützlich sein. Wir führten also die Bestimmung der Haftfestigkeit adsorbierter Moleküle in der Grenzflächenschicht von den oben gebrauchten Adsorbentien durch, und zwar verwendeten wir dazu als Adsorptiv rechts- und links-Weinsäure, aber vorläufig nicht die hier direkt in Frage kommende Dibrombernsteinsäure. Immerhin könnte das Ergebnis mit Weinsäure ohne weitere Modifizierung für die vorliegende Diskussion verwendet werden.

Sowohl im System wässrige Weinsäurelösung (Gleichgewichtskonzentration 3.3 Millimol i. L.)-Zuckerkohle, als auch im System wässrige Weinsäurelösung (Gleichgewichtskonzentration 8.2 Millimol i. L.)-Häminzuckerkohle wurde gefunden, dass der Austausch der optisch antipoden Moleküle schon in der Schüttelzeit von etwa 30 Sekunden vollkommen vollzieht, — kein

(18) J. J. Thomson, „Application of Dynamics to Physics and Chemistry“, 236, London (1888); H. Freundlich und F. Juliusburger, *Z. physik. Chem.*, A, **146** (1930), 321; H. Freundlich und G. Salomon, *Z. physik. Chem.*, A, **166** (1933), 179; *Helv. Chim. Acta*, **17** (1934), 88.

(19) Vgl. H. Freundlich, „Kapillarchemie“, I, S. 448.

(20) G. Lindau und S. Salomon, *Ber.*, **67** (1934), 1296. Wir möchten hierbei Herrn Dr. G. Lindau (Dresden) für seine freundliche Anregung zur Arbeit durch die Übersendung der Sonderabdrücke wärmst danken.

merklicher Unterschied zwischen Zuckerkohle und Häminzuckerkohle — während im System wässrige Weinsäurelösung (Gleichgewichtskonzentration 9.4 Millimol i. L.)-Silica-Gel der Austausch in der Schüttelzeit von etwa 4 Minuten noch unvollkommen (etwa 66% Austausch) stattfindet. Hieraus könnte man wohl schliessen, dass an Kohle keine feste spezifische Bindung der adsorbierten Moleküle erfolgt, im Gegensatz dazu an Silica-Gel eine festere Bindung der adsorbierten Moleküle erfolgt. Die festere Bindung der adsorbierten Moleküle an dem Adsorbens möchte ein längeres Verweilen der Moleküle auf der Grenzflächenschicht⁽²¹⁾, demnach eine grössere Übergangswahrscheinlichkeit zum aktivierten Zustand bedingen. Auch diese Vorstellung steht mit der beobachteten Erscheinung im Einklang.

Demnach gibt es also einige verschiedenen Wege, auf denen die heterogene Katalyse hervortreten kann. Es mag daher fragwürdig erscheinen, ob es überhaupt gelingen wird, die Erscheinung einem möglichen Effekt allein zuzuschreiben. Wir halten es auf Grund der vorliegenden Versuche für sehr wahrscheinlich, dass einige oben vorgebrachten möglichen Vorstellungen tatsächlich der beobachteten Erscheinung entsprechen. Dennoch dürfte im allgemeinen der Versuch, einzelne Modelle der Katalyse wie die Kruytsche Orientierungstheorie durchzuarbeiten, eine grosse Bedeutung haben, weil wir die Erscheinung in diesem Gebiete vielleicht nur auf diese Weise weiter erklären können. Eine allgemeine Deutung des Kruytschen Gedankenganges in der heterogenen Katalyse im flüssigen Medium, besonderes in bezug auf die Enzymkatalyse, soll hier noch unter bleiben.

Zusammenfassung.

(1) Angeregt durch die Kruytschen Orientierungstheorie der heterogenen Katalyse wurde versucht, das Charakteristische der Erscheinung der heterogenen Katalyse im flüssigen Medium eingehender zu betrachten und zwar mit der verhältnismässig einfachen Reaktion:

racem. Dibrombernsteinsäure = Monobromfumarsäure + Bromwasserstoff.

(2) Diese Reaktion wurde einerseits im homogenen System und andererseits im heterogenen System im Vorhandensein von (1) Silica-Gel (2) Zuckerkohle (3) Häminzuckerkohle, bei Temperaturen 30°, 40°, und 50°C. kinetisch untersucht. Die Reaktion ist an Silica-Gel etwas beschleunigt, demgegenüber an Zuckerkohle sowie an Häminzuckerkohle mehr oder weniger verlangsamt im Vergleich der homogenen Reaktion.

(3) Gleichzeitig mit dem Versuch der Reaktionskinetik wurde die Adsorption der Säuremischung (Dibrombernsteinsäure und Monobromfumarsäure) aus dem Reaktionsgemisch an den verwendeten Adsorbentien annähe-

(21) Die theoretische Deutung des Verweilens der Moleküle in der Adsorptionsschicht in der heterogenen Katalyse bei Stossreaktion: Born und Weisskopf, *Z. physik. Chem.*, B, **12** (1931), 206.

rungsweise bestimmt. Aus der Veränderlichkeit dieser Adsorption der Säuremischung mit dem Fortschritte der Reaktion, konnte man die Adsorptionsverhältnisse der beiden Reaktionsteilnehmer — Dibrombernsteinsäure und Monobromfumarsäure — an dem gegebenen Adsorbens vorstellen. Es wurde ferner die Adsorption von Dibrombernsteinsäure und von Monobromfumarsäure einzeln in ihrer Lösung an den verwendeten Adsorbentien bei einer niedrigeren Temperatur 14°C. gemessen. Monobromfumarsäure (Reaktionsprodukt) wurde an Kohle stärker als Dibrombernsteinsäure (Ausgangsstoff) adsorbiert, während an Silica-Gel die beiden Säuren fast gleichmässig adsorbiert wurden.

(4) Die Verlangsamung der Reaktion an Kohle wird wohl durch die erhaltenen Adsorptionsverhältnisse der Reaktionsteilnehmer verstanden, indem man den möglichen hemmenden Einfluss des Reaktionsproduktes infolge seiner stärkeren Adsorbierbarkeit berücksichtigt. Je nachdem, ob die Hemmung durch das Reaktionsprodukt vorhanden oder nicht vorhanden ist, lässt sich die Reaktionsgeschwindigkeit der untersuchten heterogenen Reaktion durch die Gleichung:

$$\frac{dx}{dt} = k(a-x) \quad \text{oder} \quad \frac{dx}{dt} = \frac{k(a-x)}{1+bx}$$

ausdrücken, die experimentell bestätigt wurden. Darin bedeuten x die umgesetzte Menge von Ausgangsstoff, $a-x$ die gebliebene Menge von Ausgangsstoff, k und b Konstanten.

(5) Aus der Temperaturabhängigkeit der Reaktion wurde die Aktivierungswärme mittels der Arrheniusschen Gleichung ermittelt, mit dem Ergebnis: $E = 10925$ für die homogene Reaktion, $E = 10280$ für die Reaktion an Silica-Gel, $E = 16130$ für die Reaktion an Zuckerkohle, $E = 10885$ cal. für die Reaktion an Häminkohle. Die ermittelte Aktivierungswärme der heterogenen Reaktion nach der Polanyi-Hinshelwoodschen Betrachtungsweise in Übereinstimmung mit dem Ergebnis der Adsorptionsversuche klar gestellt.

(6) Auf Grund der vorliegenden Versuche wurde einige möglichen Vorstellungen zur Erklärung der Erscheinung vorgebracht, von denen auch die Kruytsche Orientierungstheorie eine Mögliche sein kann. Die Kenntnis über die Haftfestigkeit der adsorbierten Moleküle in der Grenzflächenschicht, die mittels des von Lindau und Salomon angegebenen Verfahrens gewonnen wurde, hat man günstigerweise für die vorliegende Diskussion verwendet. Eine mögliche festere Bindung des reagierenden Stoffes an Silica-Gel mag mit der Reaktionsbeschleunigung an diesem Adsorbens im Zusammenhang stehen.

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A THEORY OF THE NEGATIVE ADSORPTION OF DEBYE-HÜCKEL ELECTROLYTE.

By Kyozo ARIYAMA.

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I. Introduction. Since Heydweiller and his coworkers⁽¹⁾ discovered that the surface tension of the solution of inorganic salts in water increases as the solute is increased, various attempts have been made to explain the phenomena. Wagner⁽²⁾, for example, developed a very elaborate mathematical theory of surface tension, and attributed the effect to the 'image force' near the boundary between two dielectrics, e.g., water and air. Recently Onsager and Samaras⁽³⁾ tried to simplify the mathematical difficulty of Wagner's theory by introducing new simplifying assumptions. However, the mathematics involved is still very difficult. The present author derives an explicit formula for the negative adsorption by a very simple calculation assuming fundamentally nothing more than those assumed by the previous workers.

II. Special case. In order to simplify the discussion, let us consider a special case, that is, very dilute binary solutions of univalent ions. In accordance with the theory of Debye-Hückel for the dilute solution of strong electrolyte, we consider that each ion is surrounded by the ion atmosphere of the opposite charge in the statistical average. The potential energy of a positive ion of charge E due to the negative ion atmosphere surrounding it may be shown to be $-\frac{E^2 m}{D}$ where $m^2 = \frac{8\pi C_\infty E^2}{DkT}$. In the expression for m , C_∞ is the average concentration of the solution, and D the dielectric constant of the solution, T the absolute temperature. If we suppose that the charge $-E$ is distributed uniformly on the surface of the sphere of radius $1/m$, the potential at its center is given by $-Em/D$. Therefore as long as we are concerned with the potential energy of an ion due to its ion atmosphere, we shall be able to replace the ion atmosphere by a sphere of $1/m$ on whose surface the opposite charge is uniformly distributed. This simplifies the mathematics of our arguments a great deal without serious loss in accuracy. Then, a positive ion of charge E situated at a distance $r > \frac{1}{m} = a$ from the

(1) Heydweiller, *Ann. Physik*, (4), **33** (1910), 145.

(2) Wagner, *Physik. Z.*, **25** (1924), 474.

(3) Onsager and Samaras, *J. Chem. Physics*, **2** (1934), 529.

free surface of the solution will be completely surrounded by the negative ion atmosphere. However, if we consider an ion of $+E$ situated at a distance $r < \frac{1}{m}$ from the surface, the sphere that carries charge $-E$ surrounding the $+E$ ion will be cut by the free surface of the solution. The area of the sphere that lies above the surface of the solution will be equal to $2\pi a(a-r)$. The contribution of the potential energy by this area of the sphere on the positive ion at its center will be equal to $\frac{-E^2}{2Da} \left(1 - \frac{r}{a}\right)$. Since the positive ion at a distance $r < a$ has the potential energy much smaller than the positive ions at a distance $r > a$, it appears that this ion ($r < a$) is acted upon by a force directing into the solution from the surface. The potential energy of this force is given by $\frac{E^2}{2Da} \left(1 - \frac{r}{a}\right)$. We have so far considered the case for positive ions, but it is easy to see that each negative ion of charge E situated at a distance $r < a$ is acted upon by a force directing into the solution, and that the potential energy of this force is also equal to $\frac{E^2}{2Da} \left(1 - \frac{r}{a}\right)$.

According to the Maxwell-Boltzmann Statistics, the probability that an ion lies at a distance between r and $r + dr$ will be proportional to $e^{\frac{-E^2}{2aDkT} \left(1 - \frac{r}{a}\right)} dr$. If C_∞ is the average number of ions in 1 c.c. at a distance sufficiently far away from the surface, the number of ions C at a distance between r and $r + dr$ will be given by

$$C = C_\infty e^{\frac{-E^2}{2aDkT} \left(1 - \frac{r}{a}\right)} dr. \quad (1)$$

Therefore the number of ions adsorbed at the surface, α , will be given by

$$\begin{aligned} \alpha &= \int_0^a (C - C_\infty) dr = -C_\infty \int_0^a \left[1 - e^{\frac{-E^2}{2aDkT} \left(1 - \frac{r}{a}\right)} \right] dr \\ &= -C_\infty a \left[1 - \frac{2aDkT}{E^2} \left(1 - e^{\frac{-E^2}{2aDkT}} \right) \right] \end{aligned} \quad (2)$$

$$\therefore \alpha = -\frac{C_\infty}{kT} \frac{E^2}{4D}. \quad (3)$$

If we compare this equation with Gibbs's adsorption equation,

$$\alpha_1 = -\frac{C_\infty}{RT} \left(\frac{\partial \sigma}{\partial C} \right)_T, \quad (4)$$

where σ is the surface tension, we can immediately recognize that the equation (3) is essentially correct in form. In order that the equation (3) and (4) should be identical, the following equation should hold:

$$\left(\frac{\partial \sigma}{\partial C} \right)_T = \frac{E^2 N}{4D}. \quad (N: \text{Avogadro's number}) \quad (5)$$

Now the equation (5) can be subjected to experimental test. The equation (5) means that for a given concentration the increase in surface tension is the same for all univalent binary electrolytes, and that the change of the surface tension of the univalent binary electrolyte with the concentration of the solution is constant as long as the solution is sufficiently dilute. These theoretical conclusions were conclusively shown to hold in Schwenker's experiment.⁽⁴⁾

Table 1. Surface Tension for KCl Solution.

Concentration (mol/litre)	Diff. of surface tension of water and solution $\sigma - \sigma_0$ (mg./mm.)	$\frac{\sigma - \sigma_0}{C} \times 10^{-2}$ (σ in dyn./cm.)
0.015	0.0034	11.11
0.030	0.0066	10.91
0.050	0.0108	10.59
0.075	0.0156	10.20
0.100	0.0202	9.91
0.130	0.0245	9.24
0.160	0.0272	8.34

To show that the equation (5) holds quantitatively, we shall take, as an example, the case for KCl solutions given in Schwenker's paper. In Table 1 the experimental values for the increase of the surface tension with the concentration is shown in the third column. The values for $\frac{\sigma - \sigma_0}{C}$ decreases slightly as the concentration is increased, so that the constancy of the quantity demanded by our theory does not hold strictly. However, the theoretical

(4) Schwenker, *Ann. Physik*, (5), **11** (1931), 525.

account for this slight variation of the value for $\frac{\sigma - \sigma_0}{C}$ will be discussed later.

Now taking $E = 4.8 \times 10^{-10}$ e.s.u., and $D = 80$ for the solution, we get

$$\frac{E^2 N}{4D} = 4.36 \times 10^2 .$$

This value agrees with the experimental value in the order of magnitude. But for very dilute solutions discrepancy with the experimental value becomes quite large. However, generally speaking the agreement may be considered very satisfactory for such a simple theory as this one.

III. **Effect of concentration.** It may be possible that some force other than the one we have considered above may be acting upon the ions at the vicinity of the free surface. Therefore, taking into account of all possible effects there may be at the surface we may write the equation (5) as

$$\left(\frac{\partial \sigma}{\partial C} \right)_T = \gamma \frac{E^2 N}{4D} = \frac{E^2 N}{4D'} . \quad (6)$$

Where γ is a constant and D' takes this correction factor into account in D . Calculating D' for the most dilute concentration we get $D' = 31.5$.

Now according to the theory of Debye and Hückel⁽⁵⁾ for concentrated solutions of strong electrolyte, the potential energy of an ion due to its ion atmosphere is given by $-E^2 m/D (1 + md)$ where d is the diameter of ions. Therefore, the adsorption α is accordingly modified, and is given in the first approximation by

$$\alpha = -\frac{C_\infty}{kT} \frac{E^2}{4D(1 + md)} . \quad (7)$$

Taking into consideration of the equation (6) gives

$$\left(\frac{\partial \sigma}{\partial C} \right)_T = \frac{E^2 N}{4D'(1 + md)} . \quad (8)$$

The value of d for KCl is 3.76×10^{-8} cm. Using the value $D' = 31.5$, and calculating the values of the right hand side of the equation (8) for concentrations given in Table 1, we get the values that agrees quite well with the values in the table. This seems to support strongly the view that the decrease of $\partial \sigma / \partial C$ from the constant value as the concentration is increased is due to the relative decrease in the activity coefficient of the solution.

(5) See for example Falkenhagen, "Electrolyte," p. 250.

IV. **General case.** It is easy to extend the above theory to a more general case in which S kinds of ions are homogeneously distributed in the solution. Let us suppose that the valences for S kinds of ions are represented by $Z_1E, Z_2E, \dots, Z_sE$, and the concentrations by $C_1, C_2, \dots, C_s$ respectively. The potential energy of an i th ion species due to its ion atmosphere is $-(Z_iE)^2m/D$ where

$$m^2 = \frac{4\pi E^2}{DkT} \sum_{i=1}^s C_i Z_i^2$$

Therefore the adsorption α is expressed as

$$\alpha = \frac{-1}{4kTD} \sum_{i=1}^s C_i (Z_iE)^2. \quad (9)$$

In the case of binary solutions of univalent ions the adsorption layer is electrically neutral since there are as many positive ions as there are negative ions. In general, however, there will be a resultant electric charge in the adsorption layer because the number of adsorbed ions for the ions of the species is proportional to the square of the charge of the ions. The total net electric charge in the adsorption layer is given by

$$\begin{aligned} \text{total charge} &= -\frac{1}{4kTD} \sum_{i=1}^s (Z_iE)^2 C_i (Z_iE) \\ &= -\frac{1}{4kTD} \sum_{i=1}^s C_i (Z_iE)^3. \end{aligned} \quad (10)$$

For an example, the adsorption layer of the solution of Na_2SO_4 should be charged positively. Such electric unbalance will tend to retard the negative adsorption. It is extremely important to find out whether such an electric unbalance in the adsorption layer for solutions like Na_2SO_4 exists or not.

In conclusion, the author wishes to express his thanks to Professor H. Erickson for his kind encouragement.

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THE ADDITION OF HYDROGEN BROMIDE TO ALLYL BROMIDE IN THE PRESENCE OF VARIOUS SUBSTANCES. I.

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One of the authors (Urushibara) observed that in the absence of foreign substances hydrogen bromide adds to undecenoic acid $\text{CH}_2=\text{CH}-(\text{CH}_2)_8-\text{COOH}$ in toluene solution to give 10-bromo-undecenoic acid $\text{CH}_3-\text{CHBr}-(\text{CH}_2)_8-\text{COOH}$ mainly, while in the presence of a trace of something coming from air the product was nearly pure 11-bromo-undecenoic acid $\text{CH}_2\text{Br}-\text{CH}_2-(\text{CH}_2)_8-\text{COOH}$.⁽¹⁾ At that time the effect was attributed to the action of moisture. On the subsequent appearance of the paper of M. S. Kharasch and F. R. Mayo,⁽²⁾ Professor R. Robinson of Oxford (private communication) pointed out that further experiments were required before it could be decided whether the active catalyst was really moisture or, as hitherto unsuspected, the oxygen of the air. According to Kharasch and Mayo, in the absence of oxygen and peroxides or in the presence of an antioxidant such as diphenylamine hydrogen bromide adds slowly to allyl bromide $\text{CH}_2=\text{CH}-\text{CH}_2\text{Br}$ (in the dark at room temperature in the absence of solvents) to give mainly 1,2-dibromopropane $\text{CH}_3\text{CHBrCH}_2\text{Br}$ (the normal addition), while in the presence of oxygen or a peroxide such as benzoyl peroxide the addition is rapid and the product consists mainly of 1,3-dibromopropane $\text{CH}_2\text{BrCH}_2\text{CH}_2\text{Br}$ (the abnormal addition). The effect is called the peroxide effect. Subsequently R. Ashton and J. C. Smith⁽³⁾ found that the substance which came from air and influenced the direction of addition of hydrogen bromide to undecenoic acid was also oxygen. Several papers on the effect of oxygen and peroxides on the addition of hydrogen bromide to the ethylenic linkage have since been published.⁽⁴⁾

The experiments described in the present paper have been carried out to investigate the effects of various substances other than oxygen and peroxides

(1) Report of the discussion of the Chemical Society of London (March 2nd, 1933), *J. Soc. Chem. Ind.*, **52** (1933), 219.

(2) *J. Am. Chem. Soc.*, **55** (1933), 2468.

(3) *J. Chem. Soc.*, **1934**, 435.

(4) M. S. Kharasch and co-workers, *J. Am. Chem. Soc.*, **55** (1933), 2521, etc.; R. P. Linstead and H. N. Rydon, *J. Chem. Soc.*, **1934**, 2001; P. L. Harris and J. C. Smith, *J. Chem. Soc.*, **1935**, 1108, 1572.

on the direction of addition of hydrogen bromide to allyl bromide and on the yield of the products. The results are summarized in the accompanying table.

No. of experiment	Substance	Amount added (g.)	Specific susceptibility (χ)	Products			
				Yield (%)	Boiling point ($^{\circ}\text{C./mm.}$)	Composition (%)	
						1,3-Dibromopropane	1,2-Dibromopropane
1	None			20	40–41/18	7	93
2	Oxygen (air)	—	$+107.7 \times 10^{-6}$	35	57–61/18	93	7
3	Sulphur	0.03	-0.34×10^{-6}	15	40–42/17	17	83
4	Nitric oxide	—	$+0.48 \times 10^{-6}$	23	40–41/17	12	88
5	Reduced iron	3.4	ferro-magnetic	36	54–64/21	71	29
6 ⁽⁵⁾	„	3.4	„	37	54–64/21	73	27
7	Reduced nickel	3.5	„	36	52–67/24	68	32
8 ⁽⁵⁾	„	3.5	„	34	48–67/24	63	37
9	Platinum black	0.7	$+1.1 \times 10^{-6}$	34	44–45/20	12	88
10 ⁽⁵⁾	„	1.0	„	35	44–46/22	4	96
11	FeBr_2 (anhydrous)	2.0	—	20	44–45/21	7	93
12	MnSO_4 (anhydrous)	2.0	$+114 \times 10^{-6}$	15 ⁽⁶⁾	44–45/21	7	93

The experimental procedure, the treatment of the reaction products, and the method of the determination of the proportion of 1,2-dibromopropane and 1,3-dibromopropane were practically the same as described by Kharasch and Mayo. All the substances used as catalysts were carefully prepared. Just before use, reduced iron, reduced nickel, and platinum black, contained in the reaction tubes, were heated at 250° in vacuum for an hour and then washed with pure hydrogen bromide gas three times. Other solid substances were treated in vacuum at room temperature. Allyl bromide (24 g. or 0.2 mol) and hydrogen bromide (20 g. or 0.25 mol) were collected in air- and moisture-free state in the mixing tubes cooled in solid carbon dioxide and chloroform. The reaction tubes and the mixing tubes were then connected by fusion after filled with hydrogen bromide gas. The whole system was immediately evacuated, while the mixing tubes were cooled in liquid air, and then the contents of the mixing tubes were distilled into the reaction tubes by cooling the latter in liquid air. Nitric oxide, carefully prepared and freed from oxygen by solidification and evacuation, was passed into the mixture of allyl bromide and hydrogen bromide before distillation. When the distillation was over, the reaction tubes were sealed off without the entrance of air. In ex-

(5) The reaction tube was shaken during daytime.

(6) Fraction boiling over $100^{\circ}/21$ mm. : 3%.

periment 2 (see the table) air was allowed to enter the tube before sealing. The tubes were placed in a bomb-furnace, or shaken in an iron pipe during daytime, in the dark at room temperature for three days. Then the contents were treated according to the directions of Kharasch and Mayo, the composition of the addition products being determined by the refractive indices. The yields shown in the table were, however, calculated in percentages to the theoretical value from the weights of the products.

The reaction mixture dissolved sulphur totally, ferrous bromide partially, but not other solid substances. Iron and nickel seemed to be attacked slightly by hydrogen bromide, although no change was observed in appearance of the catalysts after the reaction.

Sulphur and nitric oxide show only a small influence, if any, on the direction of addition and on the yield of the products. A similar result with nitric oxide was obtained by Ashton and Smith in the addition of hydrogen bromide to undecenoic acid. Reduced iron, reduced nickel, and platinum black all increase the total yields of the products, but the ferro-magnetic metals influence the direction of addition to produce much more 1,3-dibromopropane than 1,2-dibromopropane like oxygen, their catalytic action being selective, while the para-magnetic platinum seems to accelerate both the normal and the abnormal additions. The fact that ferrous bromide influences neither the direction of addition nor the yield of the products affords an evidence for attributing the effect of the reduced iron to the action of the metallic iron itself and not to ferrous bromide which may be formed by the attack of hydrogen bromide. Kharasch and Mayo added hydrogen bromide to allyl bromide in the presence of iron wire in the experiments on the effect of iron salts, but the catalyst probably happened to be not sufficient in quantity and still less in the surface area for detecting the action of the metal. Manganous sulphate manifests practically no influence on the direction of addition.

The additions in the presence of the ferro-magnetic catalysts and diphenylamine have given results similar to those of the experiments with the same metals but without the antioxidant. The details will follow.

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ÜBER DEN GEHALT DER KOHLENHYDRATE AN SCHWEREM SAUERSTOFF.

(Vorläufige Mitteilung.)

Von Noriyoshi MORITA und Toshizo TITANI.

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Einige Autoren fanden bei ihren Versuchen das Wasser, das bei der Verbrennung verschiedener Arten von Kohlenhydrat bzw. kohlenhydrathaltigen Substanzen in Luft gebildet wurde, immer um 5 bis 8 γ dichter als gewöhnliches. Um nun zu sehen, ob es sich dabei in diesen Substanzen um die wirkliche Anreicherung der schweren Isotope des Wasserstoffes bzw. Sauerstoffes handelte, oder ob wie in anderen ähnlichen Fällen⁽¹⁾ die grössere Dichtigkeit des Luftsauerstoffes dem Sauerstoff in gewöhnlichem Wasser (Wassersauerstoff) gegenüber eine Rolle spielte, haben wir drei Versuche ausgeführt.

Im Versuch I haben wir die drei Arten Wasser, von denen das erste bei der Verbrennung von Rohrzucker, das zweite bei der von Baumwolle und das dritte bei der von Zedernholz in Luft gewonnen wurde und die dem gewöhnlichen Wasser gegenüber einen Dichteüberschuss von je 7.4, 5.7 und 4.5 γ besaßen,⁽²⁾ isotopisch analysiert. Die analytische Methode bestand darin, dass wir jedes Probewasser durch Elektrolyse vollständig spalteten und den dabei entstandenen Sauerstoff in überschüssigem Protiumgas, d.h. praktisch deuteriumfreiem Wasserstoff, katalytisch zu Wasser verbrannten. Die Dichte des so gewonnenen Wassers verglichen wir dann je mit dem originalen Probewasser sowie mit dem gewöhnlichen Protowasser, das aus gewöhnlichem Wasser auf ähnliche Weise wie oben hergestellt wurde. Bei diesem Versuch I fanden wir, dass der obenangegebene Dichteüberschuss des aus je Rohrzucker (7.4 γ), Baumwolle (5.7 γ) und Zedernholz (4.5 γ) gewonnenen Wassers fast restlos auf die Anreicherung der schweren Sauerstoffes in diesem Wasser zurückzuführen war, dagegen der Anteil des gefundenen Dichteüberschusses des Wassers, der von der Anreicherung des schweren Wasserstoffes in demselben herrührte, nicht grösser als 1 γ sein konnte. Weil aber, wie leicht zu ersehen ist, der Wasserstoff des gebildeten Wassers nichts anderes als der Wasserstoff der verbrannten Substanz selbst ist, so geht aus diesem letzteren Ergebnis hervor, dass der Wasserstoff im Kohlenhydrat, falls man ihn in Wasser verwandelt, um ca. 1 γ oder weniger schwerer als gewöhnliches

(1) Vgl. N. Morita und T. Titani, dieses Bulletin, **11** (1936), 419.

(2) T. Titani und M. Harada, dieses Bulletin, **10** (1935), 261; K. Okabe und T. Titani, *ibid.*, 465.

Wasser sein kann. Dagegen rührte nach dem ersteren Ergebnis der Dichteüberschuss des gebildeten Wassers fast ausschliesslich von der Anreicherung des schweren Sauerstoffes in demselben her. Doch können wir dabei nichts Bestimmtes über die Isotopenzusammensetzung des Sauerstoffes im Kohlenhydrat sagen, weil mindestens ein Teil des Sauerstoffes im gebildeten Wasser aus dem zur Verbrennung verwendeten Luftsauerstoff besteht, dieser aber bekanntlich $7 \pm 1 \gamma$ dichter als gewöhnlicher Wassersauerstoff ist.

Die Ergebnisse des Versuches I wurden durch den Versuch II bestätigt, wo wir denselben Rohrzucker wie im Versuch I statt in Luft im elektrolytischen Sauerstoff, dessen Dichte um $1.6 \gamma^{(3)}$ kleiner als gewöhnlicher Wassersauerstoff angenommen wurde, verbrannten. Das dabei gebildete Wasser erwies sich um ca. 1γ schwerer als gewöhnliches. Aber bei der isotopischen Analyse dieses Wassers fanden wir den Sauerstoff in demselben fast ebenso dicht wie gewöhnlicher Wassersauerstoff, weshalb der gefundene Dichteüberschuss von 1γ des Probewassers restlos auf die Anreicherung des schweren Wasserstoffes in demselben, folglich im verbrannten Zucker, zurückzuführen ist. Dieses letztere Resultat entspricht gut dem oben beim Versuch I angegebenen Schlusse. Dagegen weist das erste Resultat des Versuches II, dass nämlich das gebildete Wasser trotz der kleinen Dichtigkeit des zur Verbrennung verwendeten Sauerstoffes fast dieselbe Dichte wie gewöhnliches Wasser zeigte, ohne weiteres darauf hin, dass der Sauerstoff im Zucker selbst auch um einige γ schwerer als gewöhnlicher Wassersauerstoff sein muss. Dieses wurde durch den Versuch III direkt bewiesen, wo wir 150 g. Zucker der Trockendestillation im Wasserstoffstrom unterwarfen und dadurch vollständig zersetzten. Die Zersetzungsprodukte bestanden aus Kohle, einer öligen Flüssigkeit und Gas. Allen in diesen Zersetzungsprodukten enthaltenen Sauerstoff verwandelten wir in Wasser. Wir erhielten auf diese Weise insgesamt 63 g. reines Wasser, nämlich 73% des theoretisch berechneten, und bei der isotopischen Analyse dieses Wassers fanden wir, dass der Sauerstoff in demselben, folglich im Zucker selbst, um $4 \pm 1 \gamma$ schwerer als gewöhnlicher Wassersauerstoff ist.

Der Dichteüberschuss des Sauerstoffes im Kohlenhydrat dem gewöhnlichen Wassersauerstoff gegenüber wurde schon von Greene und Voskuyl⁽⁴⁾ erwartet und von ihnen theoretisch berechnet. Dabei nahmen sie an, dass atmosphärische Kohlensäure sich mit Wasser im Austauschgleichgewicht befindet, so dass der Sauerstoff in CO_2 um $10 \pm 1 \gamma$ schwerer als gewöhnlicher

(3) Diese sowie die anderen weiter unten zitierten Werte von Dichtezu- bzw. abnahme der verschiedenen Sauerstoffarten sind, wie sich bei der isotopischen Analyse direkt ergab, in der Tat die des aus dem betreffenden Sauerstoff und Protiumgas hergestellten Wassers dem gewöhnlichen Protowasser gegenüber.

(4) C. H. Greene und R. J. Voskuyl, *J. Am. Chem. Soc.*, **58** (1936), 693.

Wassersauerstoff ist. Weiter nahmen sie an, dass die Pflanzen bei der Assimilation zwei Atome von CO_2 -Sauerstoff und ein Atom von H_2O -Sauerstoff aufnehmen und daraus ein Molekül von Sauerstoff an die Atmosphäre zurückgeben, so dass das übriggebliebene eine Sauerstoffatom in der Pflanzensubstanz Verwertung findet. Unter diesen Annahmen ergab sich, dass sowohl der Sauerstoff im gebildeten Kohlenhydrat als auch der im abgegebenen O_2 schwerer als gewöhnlicher Wassersauerstoff sein müssen, und zwar um $7 \pm 1\gamma$. Diesen letzteren Wert benutzten die beiden Autoren dazu, um den Dichteunterschied von $7 \pm 1\gamma$ zwischen Luft- und Wassersauerstoff zu erklären. Die Diskrepanz zwischen diesem von Greene und Voskuyl berechneten (7γ) und dem von uns experimentell gefundenen Dichteüberschuss ($4 \pm 1\gamma$) des Sauerstoffes im Zucker dem gewöhnlichen Wassersauerstoff gegenüber kann von Versuchsfehlern herrühren. Schliesst man diese Möglichkeit aus, so lässt sich der Unterschied wie folgt erklären: Man könnte z.B. annehmen, dass bei der Assimilation nicht die sämtlichen O-Atome von CO_2 und H_2O , sondern nur die Hälfte der O-Atome aus CO_2 , dagegen alle O-Atome aus H_2O von den Pflanzen aufgenommen werden.⁽⁵⁾ Führt man nun unter sonst gleicher Annahme wie oben die Rechnung durch, so findet man ohne weiteres, dass der Sauerstoff im gebildeten Kohlenhydrat um $5 \pm 1\gamma$, dagegen der im abgegebenen O_2 um $8 \pm 1\gamma$ schwerer als gewöhnlicher Wassersauerstoff sein muss. Der erstere Wert stimmt offenbar mit dem für Zucker experimentell gefundenen und der letztere mit dem Dichteüberschuss des Luftsauerstoffes dem Wassersauerstoff gegenüber hinreichend gut überein. Bei der Verbrennung des Kohlenhydrats, der Gegenreaktion der Assimilation, treten vielleicht sämtliche O-Atome gleich in der Reaktion ein. Unter dieser Annahme muss der Sauerstoff des Wassers, das bei der Verbrennung von Zucker in Luft gebildet wird, um $6 \pm 1\gamma$ schwerer als gewöhnlicher Wassersauerstoff sein. Falls man dagegen zur Verbrennung den elektrolytischen Sauerstoff benutzt, dessen Dichte z.B. um 1.6γ kleiner als gewöhnlicher Wassersauerstoff ist, kann der Sauerstoff im gebildeten Wasser nur um 0.2γ dichter als gewöhnlicher Wassersauerstoff sein. Alle diese Werte stimmen mit den beim Versuch I und II experimentell gefundenen innerhalb des Messfehlerbereichs hinreichend gut überein. Die ausführliche Mitteilung der vorliegenden Arbeit folgt später in diesem Bulletin.

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(5) Ein diesem ähnliches Reaktionsschema wurde schon so früh wie 1870 von A. v. Baeyer (*Ber.*, **3** (1870), 63) angegeben.

RAMANSPEKTRUM VON DEUTEROMETHANOL.

Von San-ichiro MIZUSHIMA, Yonezo MORINO und Go OKAMOTO.

Eingegangen am 29. September 1936. Ausgegeben am 28. Oktober 1936.

Im Anschluss an unserer früheren Messung⁽¹⁾ des Isotopieeffektes in Ramanspektrum haben wir die Spektren von Methanol⁽²⁾ und Deuteromethanol CH₃OD untersucht. Die letzte Substanz (ca. 6 c.c.) wurde durch die Zersetzung von Natriummethylat mit schwerem Wasser (99.6%) hergestellt und sorgfältig gereinigt um die untergrundfreien Spektren zu gewinnen. Einige Aufnahmen⁽³⁾ wurden mit ungefiltertem und die anderen mit gefiltertem Licht (Chininsulfatlösung als Filter) gemacht. Die von uns gemessenen Ramanfrequenzen (in cm.⁻¹) und die in üblicher Weise geschätzten Intensitäten (in Klammern) sind in der Tabelle

CH ₃ OH	CH ₃ OD
(6) 1033 ± 2 (e, k, i)	(6) 1029 ± 2 (e, k, i)
(2) 1107 ± 5 (e, k)	(1) 955 ± 5 (e, k)
(1) 1165 ± 4 (e, k)	(1) 1163 ± 4 (e, k)
(5b) 1464 ± 3 (e, k)	(5b) 1463 ± 3 (e, k)
(10) 2835 ± 2 (e, k, i)	(10) 2834 ± 2 (e, k, i)
(1) 2911 ± 5 (e)	(1) 2905 ± 5 (e)
(9) 2940 ± 3 (e, k, i)	(9) 2943 ± 3 (e, k, i)
(3) 2993 ± 3 (e, k)	(3) 2992 ± 3 (e, k)
3270~3480 (e, k)	2420~2560 (e, k)

wiedergegeben. Bei einer Reihe von Frequenzen ist die Isotopieverschiebung Null oder fast Null. Das besagt, dass innerhalb der Fehlergrenzen das Wasserstoffatom an diesen Schwingungen nicht teilnimmt, dass diese vielmehr praktisch im CH₃O-Rest lokalisiert sind. In Übereinstimmung mit der Beobachtung von Redlich und Pordes⁽⁴⁾ haben wir bei der Bande

3270~3480 einen grossen Isotopieeffekt gefunden. Die Verschiebung zeigt, dass sich bei dieser Schwingung das Wasserstoffatom gegen den praktisch ruhenden Molekülrest bewegt (wie aus der Berechnung als Zweimassen-Modell folgt). Die andere auffallende Isotopieverschiebung, die den bisherigen Messungen fehlte, ist bei der Linie 1107 von CH₃OH (955 von CH₃OD)

(1) Mizushima, Morino u. Okamoto, dieses Bulletin, **11** (1936), 553 (Vgl. auch Morino u. Mizushima, *Phys. Z.*, **36** (1935), 600).

(2) Bezüglich der bisherigen Beobachtungen an CH₃OH sei auf die zusammenfassenden Berichte von Hibben (*Chem. Rev.*, **18** (1936), 1) verwiesen.

(3) Die Aufnahmen wurden mit einem lichtstarken Spektrograph eigener Konstruktion gemacht (Vgl. Mizushima, Morino u. Noziri, *Sci. Papers Inst. Phys. Chem. Research* (Tokyo), **29** (1936), 63).

(4) Redlich u. Pordes, *Sitzber. Akad. Wiss. Wien, Math.-naturw. Klasse, Abt. IIb*, **145** (1936), 67.

gefunden. Es liegt nahe diese Ramanfrequenz der Deformationsschwingung des Hydroxylwasserstoffes zuzuschreiben.

Bezüglich näherer Einzelheiten in experimenteller und theoretischer Hinsicht sei auf die demnächst erscheinende Mitteilung verwiesen.

Wir danken Herren Prof. M. Katayama (Tokyo) und Prof. J. Horiuti (Sapporo) für ihre Ratschläge zu dieser Arbeit. Ferner danken wir dem Nippon-Gakujutsushinkôkai, das die zur Durchführung notwendigen Mittel zur Verfügung gestellt hat.

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STUDIES ON THE RAMAN EFFECT OF ORGANIC SUBSTANCES. VII. RAMAN EFFECT OF FURANE DERIVATIVES.

By Kwan HAN.

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Introduction. In one of the previous papers⁽¹⁾, the Raman spectra of α -mono-derivatives of furane were reported. Nearly at the same time, some of the furane derivatives were also studied by Bonino and Ansidei⁽²⁾ and by Médard⁽³⁾. In the present investigation the Raman spectra of some α -mono-derivatives, α , α' -di-derivatives and α , β -di-derivatives, which have not been reported hitherto, have been studied in order to confirm the characteristic frequencies attributable to the furane ring and to study the constitutive influences exerted upon them. The more complete investigation will be reported after studying the other poly-substitution products of furane, which are now in the course of experiments.

Experimental. The substances used were synthesized by the following processes. α -Furfuryl methyl ether (I) (b. p. 134–136°) and α -furfuryl ethyl ether (II) (b. p. 148–150°) were prepared by Wissell-Tollens' method⁽⁴⁾, that is, by warming the mixtures of α -furfuryl alcohol, F-CH₂OH,⁽⁵⁾ and the corresponding alkyl iodides with potassium hydroxide. The ethers obtained were dried over calcium chloride and then fractionated over metallic sodium.

α -Furfuryl-acetone (III) (b. p. 101–102°/21 mm.) was obtained by reducing furfurylidene-acetone, F-CH:CH·CO·CH₃,⁽⁵⁾ with 2.5% sodium amalgam in acetic acid solution, according to Harries and Kaiser⁽⁶⁾.

α -Furyl-ethylene (IV) (b. p. 99°) was obtained by the decarboxylation of α -furfuracrylic acid, F-CH:CH·COOH⁽⁶⁾, at about 260°C. The substance obtained was washed with aqueous sodium carbonate and dried over anhydrous sodium sulphate⁽⁷⁾.

(1) This Bulletin, **9** (1934), 327.

(2) G. B. Bonino and R. Manzoni-Ansidei, *Z. physik. Chem.*, B, **25** (1934), 327.

(3) L. Médard, *Bull. soc. chim.*, (5), **1** (1934), 934.

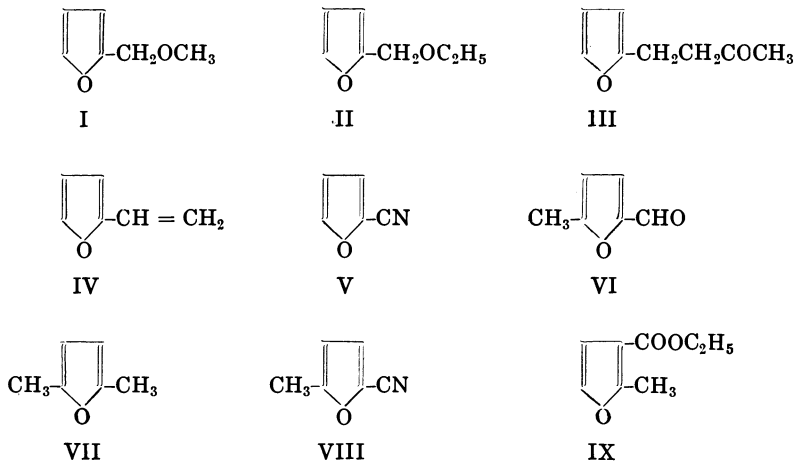
(4) L. von Wissell and V. Tollens, *Ann.*, **272** (1893), 297.

(5) F denotes α -furyl-group  in this paper.

(6) C. Harries and Friedrich Kaiser, *Ber.*, **32** (1893), 1323.

(7) C. Liebermann, *Ber.*, **27** (1894), 287.

α -Furyl cyanide (V) (b. p. 146–147°) was prepared by treating α -furfuraldoxime, F-CH : NOH, with acetic anhydride according to Pinner⁽⁸⁾.



2-Methyl-furfural-(5)⁽⁹⁾ (VI) (b. p. 83–85°/15 mm.) was prepared by reducing a mixture of hydrochloric acid (sp. gr. 1.173) and ordinary sugar with stannous chloride.

2,5-Dimethyl-furane (VII) (b. p. 93°) was prepared by dropping small pieces of potassium hydroxide into a mixture of 2-methyl furfural-(5), hydrazine hydrate and methyl alcohol under sufficient cooling (Wolff-Kischner's method)⁽¹⁰⁾. The substance obtained was washed with a saturated aqueous solution of calcium chloride and sodium bisulphite. It was, then, dehydrated over calcium chloride and redistilled over metallic sodium under normal pressure.

2-Methyl-furyl cyanide-(5)⁽¹¹⁾ (VIII) (b. p. 65°/10 mm.) was prepared from α -furfuryl chloride and aqueous potassium cyanide. α -Furfuryl chloride⁽¹²⁾ was obtained by treating α -furfuryl alcohol with thionyl chloride and pyridine in absolute ether.

Ethyl 2-methyl-furoate-(3)⁽¹³⁾ (IX) (b. p. 100–101°/25 mm.) was prepared by treating a mixture of 1,2-dichlorether (b. p. 140–145°) and ethyl acetoacetate with aqueous sodium hydroxide.

(8) A. Pinner, *Ber.*, **25** (1892), 1415.

(9) "Organic Syntheses", Vol. XIV, p. 62 (1934).

(10) This Bulletin, **9** (1934), 327.

(11) T. Reichstein, *Ber.*, **63** (1930), 749.

(12) W. R. Kirner, *J. Am. Chem. Soc.*, **50** (1928), 1955.

(13) H. Gilman and R. Robert, *Rec. trav. chim.*, **51** (1932), 408.

About 3–10 c.c. of each sample was used. The Raman spectra were taken by means of a spectrograph with three prisms⁽¹⁾. The results are shown in Table 1. The numbers of the Raman lines(*n*), the number of the plates, and the conditions under which the spectra were taken, are summarized in Table 2. 2,5-Dimethyl-furane has been studied by Bonino and Manzoni-Ansidei⁽²⁾. Their results are in good agreement with those reported in the present paper. On account of the colouration, the Raman spectrum of 2-methyl-furfural-(5) (VI) could not be observed completely, except some of the intense lines, viz., $\Delta\nu$ 1355, 1375, 1521, 1590, 1675 and 3122 cm^{-1} . The all data and the photograph of this substance are omitted in this paper.

Table 1. The $\Delta\nu$ Values of the Raman Spectra of Furane Derivatives.

(1) α -Furfuryl methyl ether (I).

140 (3b, d); 166 (3); 383 (3bb, d); (433) (0) ?; 466 (2); (604) ($1/2$); 627 (4d); 642 (3); (740) (1bb, d); (819) (1bb, d); 883 (5); 901 (4); 920 (4); 951 (5b, d); 1018 (4); 1077 (8); 1150 (5); 1224 (6d); (1291) (1); 1384 (8b); 1445 (3d); (1473) ($1/2$) ?; 1501 (10); 1593 (6d); 2819 (5); 2841 (0); 2894 ($1/2$); 2938 (1); 2985 ($1/2$); 3116 (6b, d); 3141 (2).

(2) α -Furfuryl ethyl ether (II).

(167) (1b, d); 351 (2); (384) (0); 627 (2); (640) (0); (807) (0d) ?; 840 (2); 887 (3); 923 (3); (971) (1d); 1018 (3d); 1078 (6d); 1150 (2); 1223 (5b, d); 1384 (6d); 1444 (3b, d); 1501 (10); 1594 (5d); 2930 (5); 2974 (4); 3115 (6b, d); 3145 (5).

(3) α -Furfuryl-acetone (III).

625 (0); 650 ($1/2$ d); 732 ($1/2$) ?; 748 (1); 807 (0) ?; 876 (1d); 938 (1d); 1020 ($1/2$); 1041 (2b, d); 1083 (5); 1150 (5bb, d); (1209) (1d); 1250 ($1/2$); 1292 ($1/2$) ?; 1388 (4d); 1412 ($1/2$); 1446 (1d); 1477 (2); 1509 (10); 1597 (6d); 1679 (2); 1721 (3); 2918 (3); 2974 ($1/2$); 3120 (4d); (3155) (4d).

(4) α -Furyl-ethylene (IV).

217 (6); (368) ($1/2$ b, d); 481 (5); 655 (5); 716 (2d); (736) ($1/2$ b, d); (811) (1d); 885 (3); 908 (1); 925 (4); 1002 (1); (1017) ($1/2$); 1027 (8); 1079 (4d); 1145 (3b, d); 1216 (5); 1255 (3); 1292 (8d); 1387 (8); 1491 (10); 1576 (4); 1642 (10); 3004 ($1/2$); 3125 (3); (3154).

(5) α -Furyl cyanide (V).

183 (8); (311) ($1/2$); 570 (8s); 591 (1s); 640 (5); 655 (4); 761 (1d); 837 (2d); 887 (6d); 928 (6); 938 (4b); 1020 (7); 1072 (8); 1151 (8); 1232 (6); 1379 (10); (1456) (2); 1471 (10b); 1566 (6); 2233 (10); 3133 (5d); 3156 (3).

(6) 2,5-Dimethyl-furane (VII).

266 (2d); 290 (1d); 396 (0); (445) ($1/2$); 610 (5); 689 (1); 781 (0); 923 ($1/2$); 991 (2); 1018 (3); 1086 (2b, d); 1217 (5d); (1269) (1); 1351 (2); 1379 (2); 1452 (4d); 1503 (1); 1573 (8); 2926 (6d); 2956 ($1/2$ d); 2975 ($1/2$); 3118 (3).

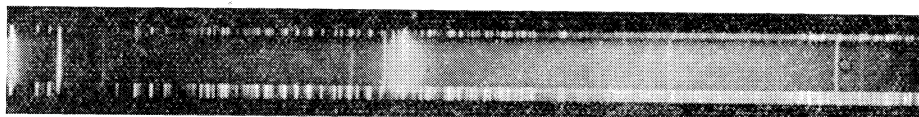
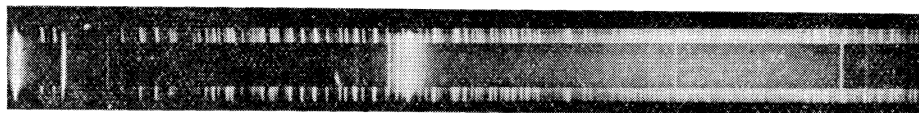
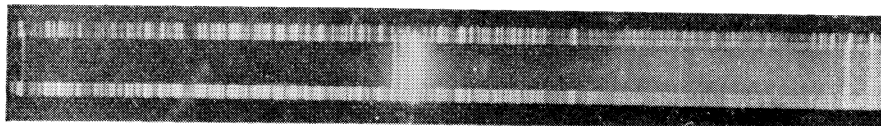
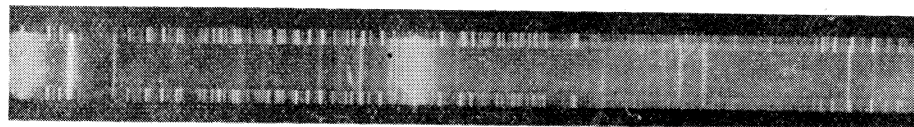
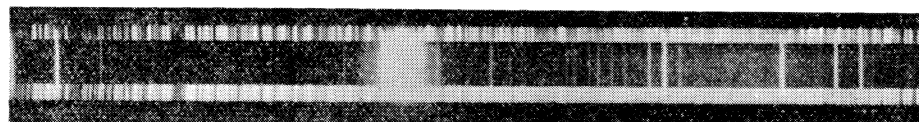
Table 1. (*Concluded*)

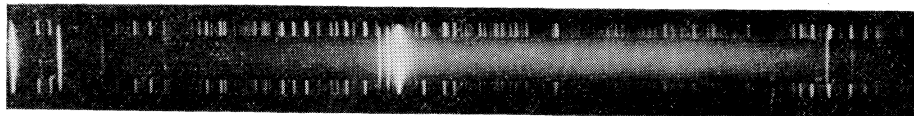
(7) 2-Methyl-furyl cyanide-(5) (VIII).

164 (4d); 260 (2d); 343 ($1\frac{1}{2}$ d); 386 (2d); 433 ($1\frac{1}{2}$); 493 ($1\frac{1}{2}$); 616 (1); 649 (3);
675 (0); 952 ($1\frac{1}{2}$); 999 (1); 1028 (5); 1202 (4); 1223 (2); 1356 (3d); 1388 (2); 1449 ($1\frac{1}{2}$);
1507 (2); 1523 (10); 1570 (0); 1600 (6); 2231 (8); 2932 (4); 2977 ($1\frac{1}{2}$); 3120 (3d).

(8) Ethyl 2-methyl-furoate-(3) (IX).

327 (1d); 359 (1d); 609 (2); 638 (3b); 684 (4b); 775 (2); 833 (1d); 869 (4d); 899 (6);
948 (2); 1013 (3d); 1041 (6); 1236 (2d); 1304 (6); 1345 (2); 1372 (2); 1396 (3); 1415 (3);
1453 (4b, d); 1522 (10); 1603 (6b, d); 1716 (6b, d); 2932 (8b, d); 2979 (3b, d);
(3120) (4d); 3157 ($1\frac{1}{2}$).

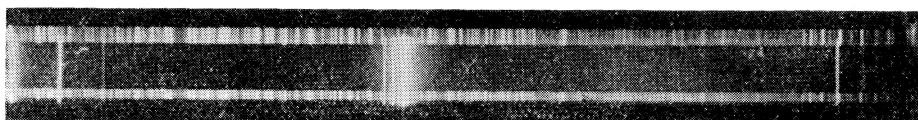
(1) α -Furfuryl methyl ether (I)(2) α -Furfuryl ethyl ether (II)(3) α -Furfuryl-acetone (III)(4) α -Furyl-ethylene (IV)(5) α -Furyl cyanide (V)



(6) 2, 5-Dimethyl-furane (VII)



(7) 2-Methyl-furyl cyanide-(5) (VIII)



(8) Ethyl 2-methyl-furoate-(3) (IX)

Table 2.

Substance	n	No. of plates	Width of slit (10^{-2} mm.)	Temp. (°C.)	t (hours)
α -Furfuryl methyl ether (I)	56	210	70	23	8
		211	64	23	10
α -Furfuryl ethyl ether (II)	44	221	70	30	8
		222	64	30	10
α -Furfuryl-acetone (III)	29	257	75	25	8
α -Furyl ethylene (IV)	53	231	70	23	6
α -Furyl cyanide (V)	44	225	70	30	8
		226	64	30	10
		290	75	24	5
		291	70	25	14
2,5-Dimethyl-furane (VII)	36	328	70	26	6
		329	70	25	8
2-Methyl-furyl cyanide-(5) (VIII)	39	229	70	28	6
		230	70	28	8
Ethyl 2-methyl-furoate-(3) (IX)	38	247	70	26	6
		248	64	26	8
		256	64	25	8

Discussion. The Raman lines corresponding to ω_1 626, ω_2 885, ω_3 923, ω_4 1018, ω_5 1083, ω_6 1150, ω_7 1223, ω_8 1384, ω_9 1505, ω_{10} 1602, ω_{11} 3117, and ω_{12} 3150 cm.^{-1} in α -furfuryl-acetone (III), α -furfuryl methyl ether (I), and α -furfuryl ethyl ether (II) are in good coincidence with those in α -methyl-furane, F-CH_3 , α -furfuryl alcohol, $\text{F-CH}_2\text{-OH}$, and α -furfuryl acetate, $\text{F-CH}_2\text{-O-CO-CH}_3$, which have been reported in Part III⁽¹⁾ (See Table 3). As to the other α -furyl- and furoyl-compounds, such as α -furyl-ethylene, α -furyl cyanide and alkyl furoates, these characteristic frequencies are also nearly constant, excepting ω_9 and ω_{10} (Table 4). The frequency of ca. 960 cm.^{-1} and those in the region of $\Delta\nu$ 810 and 740 cm.^{-1} appear also in most of the α -mono-derivatives of furane.

It is remarkable that the intense lines at ω_2 885, ω_6 1150 and ω_{12} 3150 cm.^{-1} in α -mono-derivatives, are not observed in the α , α' -di-derivatives of furane, such as 2,5-dimethyl-furane and 2-methyl-furyl cyanide-(5). The intense line corresponding to ω_5 1083 cm.^{-1} in α -mono-derivatives disappears in 2-methyl-furyl cyanide-(5) and appears weakly in 2,5-dimethyl-furane, while a new line corresponding to $\Delta\nu$ 1355 cm.^{-1} is observed in the α , α' -di-derivatives.

It is of interest to note that, in the case of α -mono-derivatives of furane, two frequencies, ω_9 and ω_{10} , in the region between 1460 and 1600 cm.^{-1} are slightly reduced by the constitutive influence of the unsaturated side chain attached to the furane ring. As shown below in Table 6, in passing from α -methyl-furane to α -furyl-ethylene and α -furyl cyanide, the corresponding frequencies, ω_9 and ω_{10} , are reduced about 20 in wave numbers.

The frequencies in question in other furane derivatives which have been observed hitherto, are summarized in Table 5. A glance at Table 5 will lead to the conclusion that, in α -furfuryl-compounds, $\text{F-CH}_2\text{-X}$, ω_9 and ω_{10} remain nearly constant, while in the furfuralidene-compounds, F-CH=CH-X , a slight decrease of ω_9 is found. The mean values of ω_9 and ω_{10} are taken as $\Delta\nu$ 1505 and 1600 cm.^{-1} for furfuryl, and $\Delta\nu$ 1480 and 1575 cm.^{-1} for furfuralidene- or furoyl-compounds, while the corresponding ones in furyl cyanide are $\Delta\nu$ 1471 and 1566 cm.^{-1}

Table 3. Raman Spectra of α -Furfuryl-compounds. (F: )

	F-CH ₃	F-CH ₂ -CH ₂ -COCH ₃	F-CH ₂ -OH	F-CH ₂ -O-CO-CH ₃	F-CH ₂ -OCH ₃	F-CH ₂ -OC ₂ H ₅
	253 343		177 421	172 193 315 332	140 166 383 469	167 351 384
ω_1	626 654	625 650	603 626	621 659	604 627 642	627 640
	718	732 748	741	745		
	796 (856)	807	816	835	819	796
ω_2	888	876	888	886	883	885
ω_3	917 (976)	938	922 959	924 964	901 920 951	923
ω_4	1018	1018	1018	1022	1017	1018
ω_5	1084	1083	1083	1083	1077	1078
ω_6	1147	1150	1154	1153	1150	1150
ω_7	1215	1209	1228	1231	1224	1223
ω_8	1376 (1389)	1390	1374 (1391)	1389	1384	1394
Δ	1453	1446 1477	1477	1450	1473	1453
ω_9	1510	1509	1507	1505	1501	1501
ω_{10}	1605	1597	1602	1604	1593	1594
	2745 2888 2928 2955 3000	2811 2976	2940	2946	2821 2841 2939	2930 2974
ω_{11}	3119	3117	3117	3130	3116	3115
ω_{12}	3153	3160	3154	3156	3141	3145

Table 4. Raman Frequencies of α -Furoyl- and α -Furyl-
compounds. (F : )

	F-CO·OCH ₃	F-CO·Cl	F-CO·H	F-CH : CH ₂	F-CH : CH·COOC ₂ H ₅	F-C : N
	170 233 335 395 493	191 336 427 552	162 213 302 503	 217 368 481	 462	183 (311) 570
ω_1	602 618		598 630	 655	 635	591 640 655
	770 798	785 824	749 775	716 (736) (811)	768 794 862	761 837
ω_2	888	887	882	885	887	887
ω_3	911 922	950	928 945	908 925	939	928 938
ω_4	1019	1025	1019	1002 1017 1027	1021	1020
ω_5	1081	1084	1080	1079	1081	1072
ω_6	1122 1172	1163	1151 1159	1145	1160	1151
ω_7	1236	1232	1207 1223	1216	1212	1232
	1307	1254 ?	(1275) ?	1256 1292	1265 1283	
ω_8	1390	1388	1368 1393	1387	1392	1379
			1441			1456
ω_9	1478	1460	1463 1475	1491	1479	1471
ω_{10}	1572 1583	1560	1483 1568	1576	1575	1566
	1726	1744 1777	1668 1688	1642	1640 1704	2233

Table 5. ω_9 and ω_{10} in α -Mono-derivatives of Furane. (F: )

F-H	1483 ⁽¹³⁾		F-CH:CH ₂	1491	1576
F-CH ₃	1510	1605	F-CH:CH-COOH	1483	1577
F-CH ₂ CH ₂ COCH ₃	1509	1597	F-CH:CH-COOC ₂ H ₅	1480	1575
F-CH ₂ OH	1507	1602	F-CO-OR	1478	1572
F-CH ₂ OCH ₃	1501	1593	F-CO-H	1463 1475	1568
F-CH ₂ OC ₂ H ₅	1501	1594	F-CO-Cl	1460	1560
F-CH ₂ OCOCH ₃	1505	1604	F-C:N	1471	1566

Table 6.

Molecule	ω_9	ω_{10}
α -Methyl-furane, F-CH ₃	1510	1605
α -Furyl-ethylene, F-CH:CH ₂	1491	1576
α -Furyl cyanide, F-C:N	1471	1566

Table 7.

Molecule	ω_9	ω_{10}	Molecule	ω_9	ω_{10}
VII	1503 (1)	1574 (8)	F-CH ₃	1510 (10)	1605 (6)
VI	1521 (10)	1590 (6)	F-CHO	1475 (10)	1568 (8)
VIII	1523 (10)	1600 (6)	V	1471 (10)	1566 (6)

As shown in Tables 6 and 7, by comparing ω_9 and ω_{10} in α -mono-derivatives of furane with those in the corresponding α , α' -di-derivatives, the following contrasts are pointed out:

(1) In contrast to the α -mono-derivatives mentioned above, two frequencies corresponding to ω_9 and ω_{10} , are argued in passing from 2, 5-dimethyl-furane to 2-methyl-furfural-(5) and 2-methyl-furyl cyanide-(5).

(2) The relation of the relative intensities of ω_9 and ω_{10} in α -methyl-furane contrasts that in α , α' -dimethyl-furane, while that of ω_9 and ω_{10} in α -furfural and α -furyl cyanide is similar to those in 2-methyl-furfural-(5) and 2-methyl-furyl cyanide-(5), respectively.

(13) G. B. Bonino and R. Manzoni-Ansidei, *Z. physik. Chem.*, B, **25** (1934), 327.

(3) The values of ω_9 and ω_{10} in α -methyl-furane are slightly higher than those in α , α' -dimethyl furane, while those in α -furfural and α -furyl cyanide are lower than those in 2-methyl-furfural-(5) and 2-methyl-furyl cyanide-(5) by about 50 cm.^{-1}

In the case of ethyl 2-methyl-furoate-(3), the Raman lines in question, are found at ω_9 1522 and ω_{10} 1608 cm.^{-1} , which may be compared with ω_9 1510 and ω_{10} 1605 in α -methyl-furane and ω_9 1478, ω_{10} 1572 cm.^{-1} in α -furoates. It leads to the conclusion that ω_9 and ω_{10} of 2-methyl-furoate-(3) approach nearer to the values of α -methyl-furane than to those of α -furoates, F-COOR.

In α -furyl-ethylene the Raman lines at $\Delta\nu$ 1642 and 1292 cm.^{-1} are associated with the ethylene linkage of the side chain. The latter may correspond to $\Delta\nu$ 1342 cm.^{-1} in ethylene. The weak lines at $\Delta\nu$ 1507 and 1570 cm.^{-1} in 2-methyl-furyl cyanide-(5) may be attributed to 2-furfuryl cyanide, which is possibly expected from the preparation of the sample from α -furfuryl chloride.

The intense lines at $\Delta\nu$ 183(8), 570(8s) and 2233(10) in α -furyl cyanide, may be associated with the structure of $\text{R-C}\equiv\text{N}$, corresponding to $\Delta\nu$ 170(8b), 549(5) and 2224(12b) in phenyl cyanide, and 376(4), 917(3) and 2250(6) in methyl cyanide.

$\text{R-C}\equiv\text{N}$	ω_1	ω_2	ω_3
$\text{CH}_3\text{-C}\equiv\text{N}$	2250 (6)	917 (3)	376 (4)
$\text{F-C}\equiv\text{N}$	2233 (10)	570 (8s)	183 (8)
$\text{C}_6\text{H}_5\text{-C}\equiv\text{N}$	2224 (12b)	549 (5)	170 (8b)

This estimation is made from the relation of the relative intensities and from the order of the mass of R, when we take R for furyl and phenyl in place of methyl radical.

Summary.

(1) The Raman spectra of the following substances have been measured : α -furfuryl methyl ether, α -furfuryl ethyl ether, α -furfuryl-acetone, α -furyl-ethylene, α -furyl cyanide, 2,5-dimethyl-furane, 2-methyl-furyl cyanide-(5) and ethyl 2-methyl-furoate-(3).

(2) The characteristic frequencies of the α -furfuryl-radical are confirmed. The difference of the Raman spectra of the mono- and di-derivatives of furane is established.

(3) The constitutive influences exerted on the Raman frequencies in the region between ν 1400 and 1600 cm^{-1} are observed.

(4) The Raman lines at 1642 and 1292 cm^{-1} in α -furyl-ethylene are associated with the structure of $\text{R}-\text{CH}:\text{CH}_2$, and those at 183, 570, and 2233 cm^{-1} in α -furyl cyanide with the structure of $\text{R}-\text{C}\equiv\text{N}$, when R is taken as furyl radical.

In conclusion, the author wishes to express his thanks to Prof. K. Matsuno for his kind guidance throughout the experiment. The author is indebted also to Ass. Prof. T. Nozoe for his valuable advice in the work of synthesis of the samples. The expense of this experiment was paid from a grant given by the Nippon Gakujutu Sinko Kwai, to which thanks are due.

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THE ABSORPTION SPECTRA OF NITROGLYCERINE.

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The absorption spectra of nitroglycerine have been studied with a view to a further study of the modes of photochemical decomposition.

In 1919, Harry Hepworth⁽¹⁾ obtained the absorption spectra of the nitric esters of glycerol to make clear that there is no evidence of chemical isomerism in solution, and that the labile and stable solid forms of nitroglycerine are to be regarded as physical isomerides. And therefore it has been only found that all of the nitric esters of glycerine showed end absorption almost linear between 40000 cm.^{-1} and 47000 cm.^{-1}

From the consideration of the some nitrocompounds and nitroesters, the selective absorption of nitroglycerine should appear from the concentration of N/10 in the ordinary thickness (from 1 mm. to 100 mm.) and therefore it could not be discovered by Hepworth, since the solubility in water used by him as a solvent prevented to obtain a concentration higher than N/20000.

The author's investigations have been done for a considerable range of concentration and thickness from 50 cm. of nitroglycerine in liquid to 1 mm. of N/1000 alcoholic solution. The results are in a good agreement with his prediction.

Experimental. The experiments were made with nitroglycerine prepared in the laboratory, washed with successive changes of distilled water, dried in vacuum over solid potassium hydroxide, and finally obtained as a clear, mobile, faint yellow oil which froze at 12.6°C. ; sp. gr. 1.5958 at 25°C.

The absorption of a column of nitroglycerine in liquid and in alcoholic solution for a suitable concentration and thickness of layer previously described was examined with Hilger E_2 spectrograph. A hydrogen discharge tube constructed by the author was used as a source of continuous light. Photographic plates employed were the Ilford soft gradation panchromatic plates and the Schumann plates for the short wave length. The time of exposure was five minutes. The results are given in Table 1 and the curve of the absorption is shown in Fig. 1.

(1) *J. Chem. Soc.*, **115** (1919), 840.

Table 1. Nitroglycerine.

Logarithms of thickness		Wave length λ ($\text{\AA}$)	Wave number ν (mm. ⁻¹)
	$\log D$		
Pure liquid ⁽²⁾	2.70	4227	2365
	2.23	3767	2654
	2.00	3586	2788
	1.00	3214	3115
1 N	2.00	3263	3061
	1.80	3225	3100
	1.60	3191	3133
	1.40	3161	3163
	1.20	3126	3198
	1.00	3117	3207
	2.00	3117	3207
	1.80	3076	3250
	1.60	3031	3298
	1.40	2973	3363
N/10	1.20	2907	3439
	1.00	2838	3523
	0.80	2748	3639
	0.70	2696	3708
	0.60	2612	3827
	0.50	2493	4010
	0.40	2449	4082
	0.20	2405	4167
	0.00	2374	4211
	2.00	2830	3533
N/100	1.90	2778	3599
	1.70	2695	3703
	1.50	2492	4012
	1.40	2471	4046
	1.20	2439	4116
	1.00	2385	4192
	0.70	2325	4300
	0.50	2282	4381
	0.20	2230	4483
	2.00	2384	4193
N/1000	1.95	2370	4218
	1.70	2285	4300
	1.50	2285	4375
	1.40	2272	4400
	1.20	2230	4483
	0.90	2178	4590
	0.50	2105	4749
	2.48	2384	4193
	2.43	2370	4218
	2.18	2285	4300

Alcoholic solution

- (2) Since the density of nitroglycerine is 1.60, pure liquid corresponds to 7.05 N.
- (3) For convenience of comparison of the spectra, the author took one gram mol divided by the number of NO₂ group for one gram mol; in the case of nitroglycerine it is equal to the molecular wt. divided by 3.

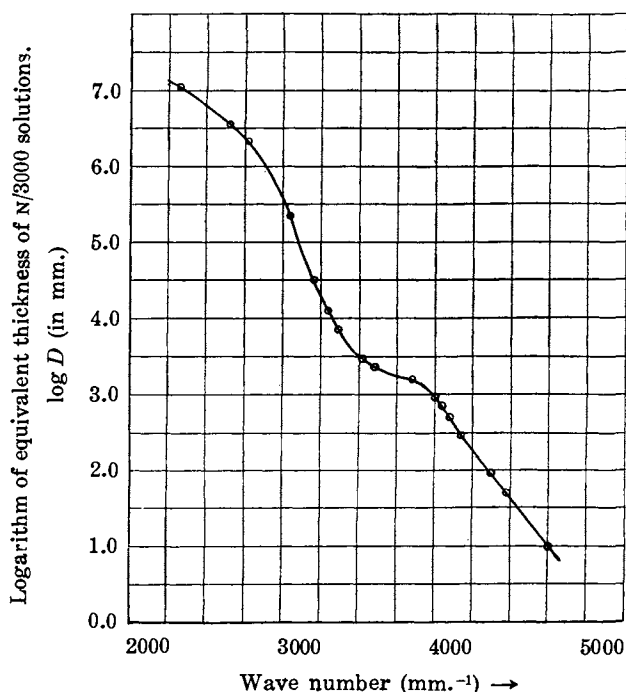


Fig. 1. The Absorption Spectra of Nitroglycerine.

Discussion. The first and probably the second absorption bands of nitroglycerine may be reasonably attributed to the NO_2 -groups in the molecule, since the absorption spectra of the simple nitrocompounds and also nitric esters lacking other special groups (except NO_2) which not only have an absorption at wave length greater than $2000 \text{ \AA}$, but also show irregularity of the band owing to the effect of an intense polarity, are quite similar in type. The absorption bands of these compounds, namely, nitromethane,⁽⁴⁾⁽⁵⁾⁽⁶⁾ nitroethane,⁽⁴⁾⁽⁶⁾⁽⁷⁾ nitropropane,⁽⁶⁾ 2-nitro-propane,⁽⁶⁾ nitrocyclohexane,⁽⁶⁾ 1-methyl-1-nitro-cyclopentane,⁽⁶⁾ nitric acid,⁽⁸⁾ ethyl nitrate,⁽⁷⁾ are almost the same at the wave lengths ca. $3200\text{--}2500 \text{ \AA}$ and less than $2500 \text{ \AA}$ and also similar in the intensity as Table 2 shows.

(4) Baly, *J. Chem. Soc.*, **93** (1908), 1747.

(5) Hedley, *Ber.*, **41** (1908), 1195.

(6) Zelinsky and Rosanoff, *Z. physik. Chem.*, **78** (1912), 629.

(7) J. W. Goodeve, *Trans. Faraday Soc.*, **30** (1934), 504.

(8) P. Bovis, *Ann. phys.*, **10** (1928); *Compt. rend.*, **178** (1924), 1964; *ibid.*, **185** (1928), 57.

Table 2. The 1st Absorption Bands of Nitrocompounds and Nitroesters.

Compound	Wave length (Å)	Max. (Å)	Intensity (log ϵ)*
Nitromethane	3000—2500	2700	1.2
Nitroethane	3300—2500	2760	1.1
Nitropropane	3100—2500	2760	1.0
2-Nitropropane	3100—2500	2740	1.1
Nitrocyclohexane	3200—2500	2780	1.1
1-Methyl-1-nitrocyclopentane	3200—2500	2810	1.2
Nitric acid	3100—2500	2700	1.0
Ethyl nitrate	3100—2500	2700	1.0
Nitroglycerine	3300—2500	—	1.0

* ϵ is the molecular extinction coefficient.

From the results, these two diffused bands common to the nitrocompounds and nitroesters may be attributed to the NO_2 -group in which the valency-electronic jumps accompanied by molecular vibration may be expected. The general discussion will be given in another paper.

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CHEMICAL STUDIES ON CANNED MEATS.
II. ON THE CONTENTS OF GASES AND METALS
IN STORED CANS.

By Yuzuru OKUDA and Kitaro KATAI.

Received August 20th, 1936. Published November 28th, 1936.

In the first paper⁽¹⁾ on some chemical changes of muscle proteins in canning, we described the changes of *pH*, of the forms of nitrogen and sulphur, of elementary composition, of the contents of arginine, histidine, lysine, cystine, cysteine, tyrosine, tryptophane and proline. The present communication deals with the contents of gases and metals in the cans which have endured long storage.

(1) This Bulletin, 9 (1934), 75.

As a means to know the changes of canned meats and the state of corrosion of can-materials, gases, such as carbon dioxide, hydrogen, oxygen and nitrogen, sometimes ammonia and hydrogen sulphide, together with metals, such as iron and tin, dissolved from cans were determined with the results shown in Tables 1, 2 and 3.

Table 1. Beef. + : present; — : absent

Age of cans (years)	15	7	5	1
No. of analysis	6	7	3	3
Blown cans	+	—	—	—
Corrosion of cans	+++	++	++	+
Putrid odor	—	—	—	—
Appearance of meat	Normal	Normal	Normal	Normal
Contents (g.)	156	159	450	459
Water (%)	61.0	60.5	60.2	59.7
Dry matter „	39.0	39.5	39.8	40.3
Gas (c.c.)	79.5	25.9	15.9	10.4
CO ₂ (%)	3.4	4.9	3.6	2.8
O ₂ „	1.3	1.8	3.0	4.7
H ₂ „	82.2	22.3	22.3	12.2
N ₂ „	13.2	71.0	71.2	80.4
Fe (mg. %)	191.5	15.6	14.2	13.7
Sn „	375.0	219.5	104.5	78.3
pH	5.8	5.6	5.8	5.8

Table 2. Crab.

Age of cans (years)	5	3	1
No. of analysis	6	4	6
Contents (g.)	231	221	224
Water (%)	79.2	78.5	80.0
Dry matter „	20.8	21.5	20.0
Gas (c.c.)	9.5	7.0	11.0
CO ₂ (%)	0.3	0.6	0.4
O ₂ „	9.6	7.2	10.1
H ₂ „	11.6	11.9	8.7
N ₂ „	78.5	80.4	80.8
Fe (mg. %)	10.6	11.3	9.7
Sn „	19.9	17.9	15.0
pH	6.9	6.9	7.0

Table 3. Salmon and Tunny.

Age of cans (years)	Salmon		Tunny	
	1	7	1	7
Contents (g.)	452	480	404	422
Water (%)	73.7	75.2	62.4	61.1
Dry matter „	26.3	24.8	37.6	38.9
Gas (c.c.)	1.5	5.0	21.5	102.0
CO ₂ (%)	0	1.8	13.1	5.5
O ₂ „	6.7	10.2	0.7	0.3
H ₂ „	35.3	25.0	20.8	73.8
N ₂ „	58.0	63.0	65.4	20.4
Fe (mg. %)	13.8	15.9	12.7	49.9
Sn „	24.2	108.7	87.0	214.8

The results of the experiments carried out with canned meats of different ages of storage, from 1 to 15 years, were as follows :

(1) Among gases contained in cans examined, the quantity of nitrogen was the largest in the majority of the cans, but in some old cans the amount of hydrogen was frequently more than that of nitrogen.

(2) The proportion of oxygen as compared to that of nitrogen was much smaller than it is in the air.

(3) The content of carbon dioxide in cans was larger than that in the air, but it did not increase appreciably during the storage of the cans.

(4) Free ammonia and hydrogen sulphide showed only traces.

(5) The concentration of hydrogen ion of the canned meats showed almost no change in storage.

(6) The contents of iron and tin in both canned beef and fish were nearly proportional to that of hydrogen in the cans which was produced by corrosion of can-materials. But in the case of crab meat packed in the cans which are covered inside with lacquer, almost no increase of the contents of iron, tin and hydrogen was observed.

(7) Unusual increase of hydrogen gas in some very long-stored beef-cans sometimes gave rise to the so-called "blown" cans, in which the ends become convex, and are apparently analogous to the spoiled cans dilated by the pressure of carbon dioxide produced by the action of bacteria upon the contents.

A part of the expense of this investigation was defrayed by a research grant from the "Hattori-Hokokwai", to whom our thanks are due.

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CHEMICAL STUDIES ON CANNED MEATS.

III. CARBON DIOXIDE AND HYDROGEN GASES PRODUCED AT CANNING AND IN STORAGE.

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For the purpose of knowing the changes of canned meat and the state of corrosion of can-materials, we determined oxygen, nitrogen, carbon dioxide and hydrogen gases in commercial cans as described in the preceding paper.⁽¹⁾ In the experiment recorded in the present paper, carbon dioxide was again determined as a means of knowing some chemical changes which occurred in canned meat, and hydrogen gas to know the state of the corrosion of can-material. But in the present case, instead of commercial cans, sealed glass tubes containing a certain meat, tin and iron powders, and solutions of different hydrogen ion concentrations were used for the sake of more exact comparison. The tubes were heated at 130° for different hours, to know the influence of heat and pressure upon canned meat and can-material at canning, and preserved at 50° for different periods to know the effect of storage.

The experiments were performed with three kinds of meats, but only the data with beef are described below, as the results with other meats were analogous.

Table 1. Carbon Dioxide (c.c.)

(a) Sulphuric acid was added.

Meat powder	Fresh meat				Somewhat spoiled meat			
pH, before and after heating	4.0—4.5				4.0—4.3			
Hours of heating	1			3	1			3
Days of storage	0	30	60	0	0	30	60	0
Fe added	2.1	2.6	2.1	3.1	2.2	2.1	1.8	2.7
Sn added	1.4	2.6	2.9	2.2	1.1	1.9	2.5	1.8
Fe and Sn added	2.2	2.2	1.9	3.1	2.0	2.1	1.5	2.8

(1) This Bulletin, 11 (1936), 715.

(b) Water was added.

Meat powder	Fresh meat				Somewhat spoiled meat			
pH, before and after heating	5.5—5.7				5.5—5.7			
Hours of heating	1			3	1			3
Days of storage	0	30	60	0	0	30	60	0
Fe added	1.7	1.2	0.8	2.6	1.7	1.1	1.2	2.5
Sn added	1.5	2.4	2.8	2.3	1.2	2.0	2.4	2.0
Fe and Sn added	1.5	0.5	0.9	2.4	1.4	0.8	0.8	2.4

(c) Sodium hydroxide was added.

Meat powder	Fresh meat				Somewhat spoiled meat			
pH, before and after heating	8.5—7.9				8.2—7.9			
Hours of heating	1			3	1			3
Days of storage	0	30	60	0	0	30	60	0
Fe added	0.9	0.5	0.2	1.8	1.1	0.3	0.2	2.0
Sn added	0.9	1.2	1.3	1.6	1.0	1.4	1.8	1.8
Fe and Sn added	0.9	0.3	0.2	1.4	1.2	0.5	0.2	2.0

Table 2. Hydrogen (c.c.)

(a) Sulphuric acid was added.

Meat powder	Fresh meat				Somewhat spoiled meat			
pH, before and after heating	4.0—4.5				4.0—4.3			
Hours of heating	1			3	1			3
Days of storage	0	30	60	0	0	30	60	0
Fe added	18.6	48.2	57.7	32.5	19.9	55.0	60.1	30.2
Sn added	0.3	0.2	0.2	0.3	0.3	0.3	0.1	0.3
Fe and Sn added	19.7	49.3	57.8	32.8	23.7	54.1	63.3	27.8

(b) Water was added.

Meat powder	Fresh meat				Somewhat spoiled meat			
pH, before and after heating	5.5—5.7				5.5—5.7			
Hours of heating	1			3	1			3
Days of storage	0	30	60	0	0	30	60	0
Fe added	5.2	32.1	36.0	7.4	5.9	34.9	41.1	8.1
Sn added	0.2	0.2	1.2	0.3	0.2	0.1	0.5	0.2
Fe and Sn added	5.2	33.4	33.0	8.7	5.6	40.0	41.6	9.6

(c) Sodium hydroxide was added.

Meat powder	Fresh meat				Somewhat spoiled meat			
pH, before and after heating	8.5—7.9				8.2—7.9			
Hours of heating	1			3	1			3
Days of storage	0	30	60	0	0	30	60	0
Fe added	0.5	16.4	21.5	1.2	1.8	22.9	27.1	5.2
Sn added	0.2	0.1	0	0.2	0	0	0.1	0.2
Fe and Sn added	0.9	17.2	21.2	0.8	1.4	22.1	27.8	5.1

The results of experiments performed with beef and fish were as follows :

(1) The production of carbon dioxide at canning increased a little more, as a rule, in the presence of iron than in the presence of tin alone. And also the longer the time of heating the more was the increase.

(2) The production of carbon dioxide during storage, gradually increased in the presence of tin alone, but decreased in the presence of iron. The decrease seem to be due to the fact that carbon dioxide produced by gradual oxidation acts on iron to make iron carbonate and hydrogen.

(3) The production of carbon dioxide seems to have some relation with the hydrogen ion concentration of meat juice and the kind of meats, but the relation with the freshness of the meat is not definite.

(4) The production of hydrogen is chiefly due to the presence of iron but only slightly to that of tin. In the presence of iron, the production had an

intimate relation with the hydrogen ion concentration of meat juice, the stronger being the concentration the more the production. The production increased proportionally to the length of time of heating at canning, and to the period of storage of cans.

(5) The kind and freshness of meats have more or less influence upon the production of hydrogen from can-material.

(6) The quantity of carbon dioxide produced was generally very small as compared to that of hydrogen.

In conclusion, the authors wish to express their thanks to the "Hattori-Hokokwai" for a research grant from which was defrayed a part of the cost of the investigation.

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SPECTROGRAPHIC METHODS OF STUDYING UNSTABLE
COMPOUNDS. II.⁽¹⁾ THE AQUOTIZATION OF TRANS-
DICHLORO-TETRAMMINE COBALTC CHLORIDE
IN AQUEOUS SOLUTIONS.

By Ryutaro TSUCHIDA.

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Introduction. It is well known that trans-dichloro-tetrammine cobaltic salt undergoes a marked colour change⁽²⁾ in aqueous solutions; its bright green colour fades rapidly away, passes a neutral tint and changes gradually to purple and finally to red. Quantitative measurement of light-absorption of this interesting compound, however, has scarcely been reported. R. Luther and A. Nikolopoulos⁽³⁾ have measured the absorption only in the visible region, and yet the authors themselves acknowledge the inaccuracy of their measurement owing to its instability. R. Samuel⁽⁴⁾ published an absorption curves as

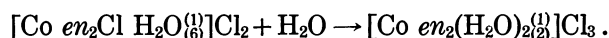
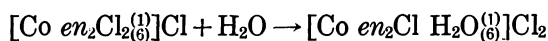
(1) R. Tsuchida, this Bulletin, **10** (1935), 27.

(2) Y. Shibata, "Spectrochemistry", Vol. I. (1935), 327; *J. Coll. Sci., Imp. Univ. Tokyo*, **37** (1915), Art. 2, 25.

(3) *Z. physik. Chem.*, **82** (1913), 367.

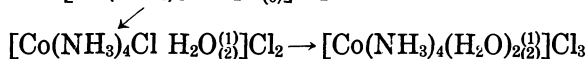
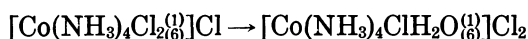
(4) *Z. Physik*, **70** (1931), 54.

that of $[\text{Co}(\text{NH}_3)_4\text{Cl}_2]\text{Cl}^{(6)}$, but the given absorption is almost identical with that of $[\text{Co}(\text{NH}_3)_4(\text{H}_2\text{O})\text{Cl}_{\frac{1}{2}}]\text{Cl}_2$, i.e., an aquotization product of both the isomers of dichloro-tetrammine cobaltic chloride. Because of its high reaction velocity, there has been hardly any quantitative investigation on the change of this salt in aqueous solutions, except that of Prof. K. Matsuno⁽⁶⁾, who showed the change in its valency effect on the coagulation of arsenious sulphide sol. The mechanism of the change, therefore, has been left to imagination from the analogy of this compound with trans-dichloro-diethylenediamine cobaltic chloride, which has also been investigated by Prof. K. Matsuno⁽⁷⁾ by means of his ingenious method of coagulation of arsenious sulphide sol. The change was concluded to be due to the following reactions.



The velocity constants have been given as 0.011 and 0.0031 referring to minute, i.e., 1.9×10^{-4} and 5.2×10^{-5} for second.

The reaction of $[\text{Co}(\text{NH}_3)_4\text{Cl}_2\frac{1}{2}]\text{Cl}$, however, is too rapid to follow quantitatively by means of the coagulation method or by measuring the electrolytic conductivity. Moreover, the aquotization takes place in the following scheme, as we shall see later.



It is obvious that the conductivity of the system is hardly affected by the second reaction and the valency of the ions remains the same during the isomeric change. Then both the conductivity measurement and the coagulation method would be inapplicable for this case. Spectrographic method could be more advantageously applied even for this rapid and complicated reaction. The present author photographed from time to time the absorption spectra of mixed solutions of the praseo-salt and its aquotization products as a whole, and analyzed the absorption at leisure in order to study the kinetics and at the same time to find the extinction coefficients which should belong to the praseo-salt.

Experimental. Trans-dichloro-tetrammine cobaltic chloride was prepared by the the method of S.M. Jörgensen⁽⁸⁾. A weighed portion of this salt was

(5) The configuration of the isomer used in the measurement has not been stated in the original.

(6) *J. Coll. Sci., Imp. Univ. Tokyo*, **41** (1921), Art. 11, 12.

(7) This Bulletin, **1** (1926), 133.

(8) *Z. anorg. Chem.*, **14** (1897), 416.

expeditiously dissolved in water to make a 0.0150 mol/l. solution, the moment of dissolution being taken as the starting point of the reaction. This solution was subject to spectrographic analysis by means of a spectrograph equipped with a sector-photometer. The first photographic recording was made 6 minutes after the time of dissolution with an aperture of the sector. Further recordings were made after successive intervals of 2, 4, 8, . . . minutes, i.e. after 8, 12, 20, . . . minutes from the starting point, the aperture of the sector being kept at the same angle as in the first recording. Next, with a freshly prepared solution of the same concentration, the absorption spectra were photographed after 6, 8, 12, 20, . . . minutes from the time of dissolution, the angle of the sector being kept constant throughout the second series of experiments, but different from that for the first. The process was repeated with many a portion, on the same conditions except the aperture of the sector which was varied for each portion. The room temperature was kept at about 17°C. throughout the experiment. The absorption of the mixed solutions were found by measuring the photographic plates, and a set of curves was obtained (Fig. 1).

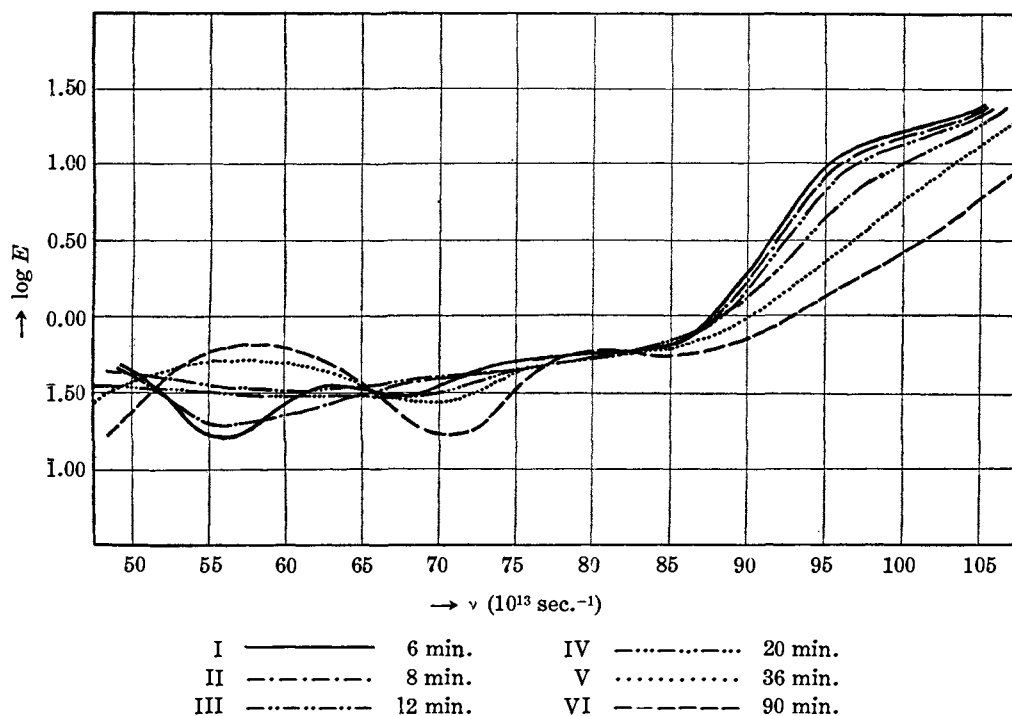


Fig. 1.

E represents $\Sigma \epsilon c$ in $I = I_0 \times 10^{-d \Sigma \epsilon c}$, where ϵ 's are molar extinction coefficients, C 's, concentrations and d , the thickness of layer. From these curves the following facts may be concluded.

(1) The curve VI, i.e., the absorption after 90 minutes, is almost identical with that of $[\text{Co}(\text{NH}_3)_4\text{ClH}_2\text{O}_{(2)}^{(1)}]\text{Cl}_2$ (Curve C⁽⁹⁾ in Fig. 5), but considerably different from that of $[\text{Co}(\text{N}_3\text{H})_4(\text{H}_2\text{O})_2]^{(1)}\text{Cl}_3$ (Curve D⁽⁹⁾ in Fig. 5). It can, therefore, be concluded that by this time the aquotization has so far proceeded that only one molecule of water has entered the complex radical and diaquotetrammine cobaltic chloride has not yet been produced in appreciable quantity.

(2) The praseo-salt and its aquotization products have equal molar extinction coefficients for two frequencies 66×10^{13} and 82.5×10^{13} .

(3) The bulges of the curves (I, II, III and IV) at about 96×10^{13} indicate the probable existence of an absorption band belonging to an unstable compound which changes gradually with the disappearance of the bulge.

Analysis and Discussion. Let X and Y be the compounds contained in mixed solutions and the molar extinction coefficients of X and Y for frequencies $\nu_1, \nu_2, \dots$ be $\epsilon_1^X, \epsilon_2^X, \epsilon_1^Y, \epsilon_2^Y, \dots$. Then the following relation exists among the concentrations of X in the mixed solutions, I, II, III, ...

$$\left| \begin{array}{cc} \epsilon_1^X & \epsilon_1^Y \\ \epsilon_2^X & \epsilon_2^Y \end{array} \right| = \frac{\left| \begin{array}{cc} E_1^I & \epsilon_1^Y \\ E_2^I & \epsilon_2^Y \end{array} \right|}{[\text{X}]_I} = \frac{\left| \begin{array}{cc} E_1^{II} & \epsilon_1^Y \\ E_2^{II} & \epsilon_2^Y \end{array} \right|}{[\text{X}]_{II}} = \frac{\left| \begin{array}{cc} E_1^{III} & \epsilon_1^Y \\ E_2^{III} & \epsilon_2^Y \end{array} \right|}{[\text{X}]_{III}} = \dots (1),$$

where E 's represent the measurable absorptions, the suffixes denoting the solutions and the frequencies. In our case two frequencies, 56×10^{13} ($= \nu_1$) and 82.5×10^{13} ($= \nu_2$) are chosen for practical analysis. For the former frequency, $[\text{Co}(\text{NH}_3)_4\text{ClH}_2\text{O}_{(2)}^{(1)}]\text{Cl}_3$ has an extinction coefficient nearly equal to the maximum value in its first band, while $[\text{Co}(\text{NH}_3)_4\text{Cl}_2]^{(1)}\text{Cl}$ and $[\text{Co}(\text{NH}_3)_4\text{ClH}_2\text{O}_{(6)}^{(1)}]\text{Cl}_2$ are supposed to have much smaller values approximately equal to each other. For the latter frequency, $[\text{Co}(\text{NH}_3)_4\text{Cl}_2]^{(1)}\text{Cl}$ and its aquotization products have equal coefficients. The analysis is as follows.

From (1)

$$\frac{E_1^I - E_2^I \frac{\epsilon_1^Y}{\epsilon_2^Y}}{[\text{X}]_I} = \frac{E_1^{II} - E_2^{II} \frac{\epsilon_1^Y}{\epsilon_2^Y}}{[\text{X}]_{II}} = \dots = \alpha \quad (2)$$

(9) These complex salts were prepared and studied by Messrs. K. Fukui, S. Seki and M. Kobayashi in this laboratory.

From Fig. 1 we have

$$E_2^I = E_2^{II} = E_2^{III} = \dots \dots \dots$$

Assuming $[\text{Co}(\text{NH}_3)_4\text{Cl H}_2\text{O}_{(2)}]\text{Cl}_2$ as Y, we have

from Fig. 5

$$\log \epsilon_1^Y = 1.60 \quad \text{and} \quad \log \epsilon_2^Y = 1.56,$$

and from Fig. 1, $E_2 = 1.78$.

Therefore we get

$$\alpha[X] = E_2 \frac{\epsilon_1^Y}{\epsilon_2^Y} - E_1 = 0.661 - E_1 \quad (3)$$

The values of $\log \alpha[X]_I, \log \alpha[X]_{II}, \dots$ were calculated by (3) and plotted against time resulting a convex curve (Fig. 2).

The curve thus obtained was extrapolated to t_0 , at which $[X]$ was 0.0150 mol/l. From $\log \alpha[X]_{t=0}$, we could estimate $[X]$'s for the solutions after 6, 8, 12, $\dots$ minutes from the time of dissolution.

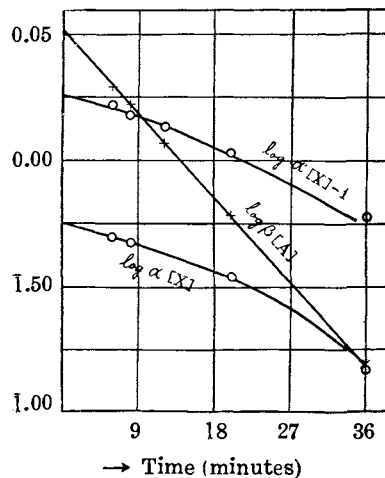


Fig. 2.

Table 1.

	Time (min.)	E_1	$\alpha[X]$	$\log \alpha[X]$	$[X]$
I	6	0.159	0.502	1.701	0.0134
II	8	0.187	0.474	1.676	0.0126
III	12	0.329	0.332	1.521	0.0088
IV	20	0.310	0.351	1.545	0.0093
V	36	0.513	0.148	1.170	0.0053
VI	90	0.617	0.004	2.643	0.0012
	0	extrapol.	0.563	1.750	0.0150

In order to confirm the results, another set of frequencies, $82.5 \times 10^{13} (= \nu_2)$ and $102 \times 10^{13} (= \nu_1)$ was taken for similar analysis. From Fig. 5 and Fig. 1,

$$\log \epsilon_1^Y = 2.16, \quad \log \epsilon_2^Y = 1.56 \quad \text{and} \quad \log E_2 = 1.78.$$

$$\text{Therefore } \alpha' [X] = E_1 - E_2 \frac{\epsilon_1^Y}{\epsilon_2^Y} = E_1 - 2.40 . \quad (3')$$

Log $\alpha' [X]$ plotted against time (Fig. 2) gives another convex curve quite similar to log $\alpha [X]$. Extrapolating the curve to t_0 , we obtained log $\alpha' [X]_{t=0}$ from which $[X]$ could be calculated (Table 2).

Table 2.

	Time (min.)	E_1	$\alpha[X]$	log $\alpha'[X]$	$[X]$
I	6	19.1	16.7	1.223	0.0141
II	8	17.4	15.0	1.176	0.0126
III	12	15.9	13.5	1.130	0.0114
IV	20	13.2	10.8	1.033	0.0091
V	36	8.32	5.9	0.771	0.0050
VI	90	2.64	2.2	0.301	0.0002
	0	extrapol.	17.8	1.250	0.0150

From $[X]$ the concentration of $[\text{Co}(\text{NH}_3)_4\text{Cl H}_2\text{O}_{(2)}^{(1)}]\text{Cl}_2$, $[C]$, can be found by $[C] = [A]_0 - [X]$.

Table 3.

The Concentration of $[\text{Co}(\text{NH}_3)_4\text{Cl H}_2\text{O}_{(2)}^{(1)}]\text{Cl}_2$.

	Time (min.)	From Table 1 (mol/l.)	From Table 2 (mol/l.)	Mean $[C]$ (mol/l.)
	0	0.0000	0.0000	0.0000
I	6	0.0016	0.0009	0.0014
II	8	0.0024	0.0024	0.0024
III	12	0.0062*	0.0036	0.0036
IV	20	0.0057	0.0059	0.0058
V	36	0.0097	0.0100	0.0099
VI	90	0.0138	0.0148	0.0143
* This value is excluded from further calculation because of its deviation.				

The concentration of $[\text{Co}(\text{NH}_3)_4\text{Cl H}_2\text{O}_{(2)}^{(1)}]\text{Cl}_2$ in each case being now known, the contribution of the salt to the light absorption of the reaction mixture

can be calculated from the concentration (Table 3) and its extinction coefficients (Curve C in Fig. 5), and is subtracted from the absorption of the corresponding mixed solution. The residual absorption, i.e., the absorption, due to compounds other than $[\text{Co}(\text{NH}_3)_4\text{Cl}_2]^{(1)}\text{Cl}_2$ is shown in Fig. 3, where $E - \epsilon^c[\text{C}]$ is represented by F .

It is evident from this set of curves that the solutions are still mixtures, as we can easily point out at least three different absorption bands, of which one with the frequency of 65×10^{13} and another of about 10×10^{14} gradually disappear as the reaction proceeds, while the band at 75×10^{13} becomes more and more distinct. If $[\text{Co}(\text{NH}_3)_4\text{Cl}_2]^{(1)}\text{Cl}$ and $[\text{Co}(\text{NH}_3)_4\text{Cl}_2]^{(1)}\text{Cl}_2$ were the only constituents of the mixed solutions, such gradual change of F would never be seen, but a set of curves with an identical shape and different heights should result after the analysis. Moreover, if the praseo-salt were to change directly to the cis-aquochloro-salt as a reaction of the first, or of the higher, order, the curves of $\log \alpha[\text{X}]$ and $\log \alpha'[\text{X}]$ should be straight, or concave upwards. We have, however, seen that the curves are convex upwards (Fig. 2). This feature of the curves may be explained, if we assume that the praseo-salt, A, changes first to an intermediate compound, B, and then to the cis-aquochloro-salt, C. Then $\log ([\text{A}] + [\text{B}])$ will give a curve convex upwards. Another fact also indicates that some compound must intervene between A and C; in spite that the colour of the praseo-salt had almost completely disappeared in 30 minutes, the absorption of the cis-aquochloro-salt alone was not seen till after 90 minutes. The absorption curves in Fig. 3, therefore, represent mixed solutions of $[\text{Co}(\text{NH}_3)_4\text{Cl}_2]^{(1)}\text{Cl}$ and the intermediate compound. Whatever the constitution of the latter may be, the analysis of the curves may be done as follows. For this purpose the extinction coefficients of at least one of the salts must be known, but we know none of them: B is an unknown substance and A is the compound whose extinction coefficients are searched for. For practical purpose, however, we may assume without much risk that after 36 minutes from the time of dissolution the praseosalt had completely disappeared, as was shown by the colour of the solution.

$$\text{Then} \quad F_1^V \simeq \epsilon^B[\text{B}] \quad . \quad (4)$$

Then frequencies $76 \times 10^{13} (= \nu_1)$ and $96 \times 10^{13} (= \nu_2)$ were chosen for analysis.

From (1)

$$\begin{vmatrix} \epsilon_1^A & \epsilon_1^B \\ \epsilon_2^A & \epsilon_2^B \end{vmatrix} = \frac{\begin{vmatrix} F_1^I & \epsilon_1^B \\ F_2^I & \epsilon_2^B \end{vmatrix}}{[\text{A}]_I} = \frac{\begin{vmatrix} F_1^{II} & \epsilon_1^B \\ F_2^{II} & \epsilon_2^B \end{vmatrix}}{[\text{A}]_{II}} = \dots\dots\dots (1')$$

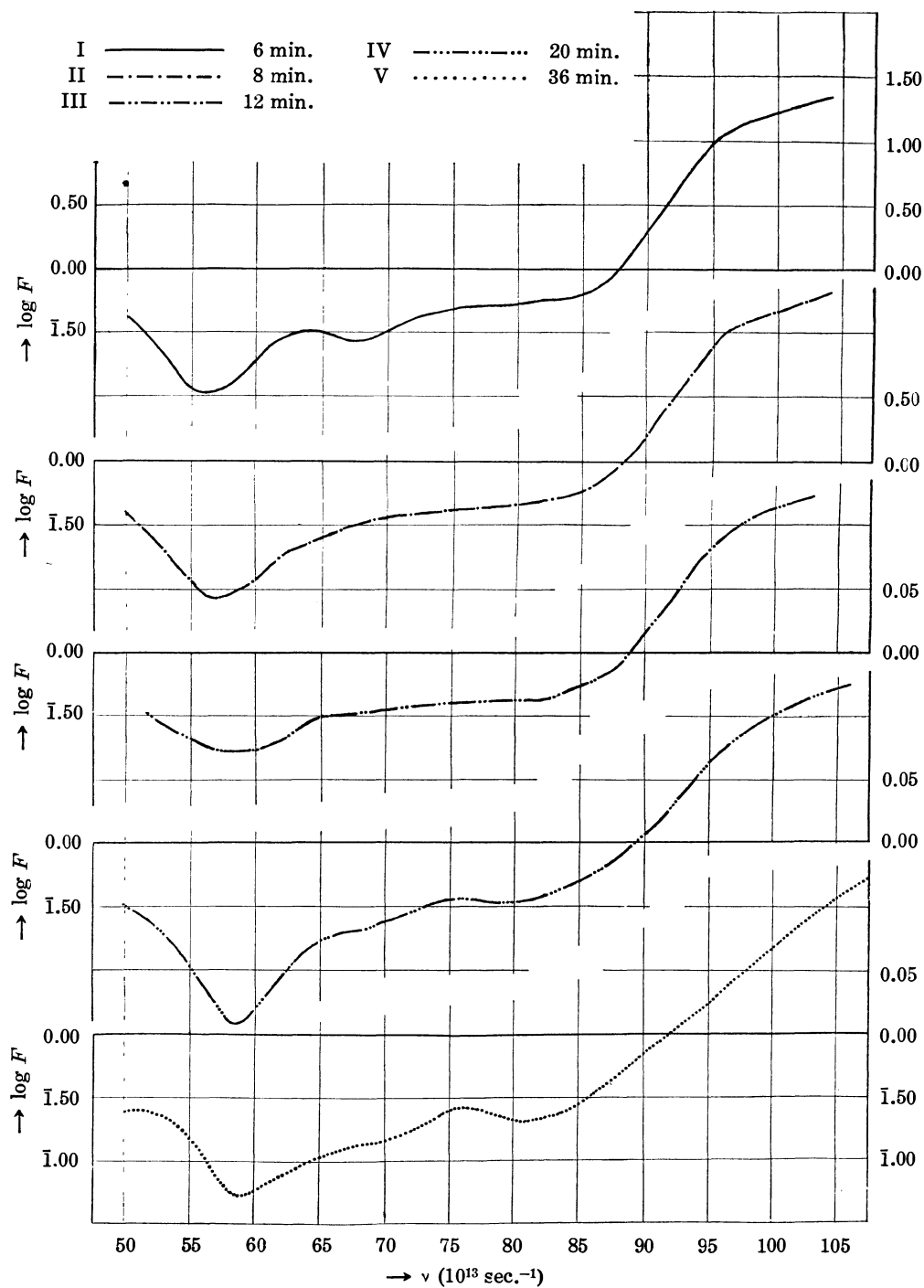


Fig. 3.

We get from (4) and Table 3,

$$F_1 \simeq 0.0051 \epsilon_1^B \quad \text{and} \quad F_2 \simeq 0.0051 \epsilon_2^B.$$

$$\therefore \beta = \frac{F_1^I F_2^V - F_2^I F_1^V}{[A]_I} = \frac{F_1^{II} F_2^V - F_2^{II} F_1^V}{[A]_{II}} = \dots\dots\dots (5)$$

When $\log \beta [A]$ thus calculated by (5) was plotted against time, a straight line was obtained (Fig. 2). This shows that the change of the praseo-salt into B is a reaction of the first order. Extrapolating this straight line, we obtain $\log \beta [A]_{t=0}$ which corresponds to the initial concentration of $[\text{Co}(\text{NH}_3)_4\text{Cl}_2^{(1)}]\text{Cl}$, i.e., 0.0150 mol/l. Hence $[A]$ in each of the mixed solutions can be calculated as in Table 4.

Table 4.

The Concentration of $[\text{Co}(\text{NH}_3)_4\text{Cl}_2^{(1)}]\text{Cl}$.

	Time (min.)	$\log F_1$	$\log F_2$	$F_1 F_2^V - F_2 F_1^V$	$\log \beta [B]$	$[A]$ (mol/l.)
I	6	1.698	1.057	1.92	0.283	0.0088
II	8	1.613	0.996	1.68	0.225	0.0077
III	12	1.600	0.902	1.21	0.082	0.0056
IV	20	1.547	0.724	0.61	1.785	0.0028
	0	extrapolated		3.27	0.515	0.0150
	36	,,		0.15	1.180	0.0007

The concentration of B can be found by $[B] = [A]_0 - [A] - [C]$, from Tables 3 and 4.

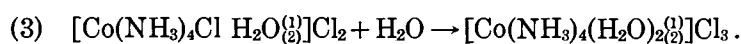
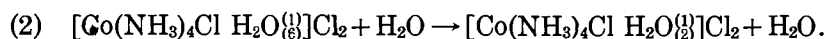
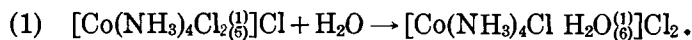
As to the constitution of the intermediate compound B, there are two possible cases to be considered.

A	B	C
(1) $[\text{Co}(\text{NH}_3)_4\text{Cl}_2^{(1)}]\text{Cl}$	$[\text{Co}(\text{NH}_3)_4\text{Cl}_2^{(2)}]\text{Cl}$	$[\text{Co}(\text{NH}_3)_4\text{Cl H}_2\text{O}^{(1)}]\text{Cl}_2$
(2) ,,	$[\text{Co}(\text{NH}_3)_4\text{Cl H}_2\text{O}^{(1)}]\text{Cl}_2$	,,

Prof. Matsuno's research⁽¹⁰⁾ on $[\text{Co en}_2\text{Cl}_2^{(1)}]\text{Cl}$ favours the second case, and as we shall see later, kinetic considerations and the absorption spectra also support the view.

(10) *Loc. cit.*

The aquotization reaction of trans-dichlorotetrammine cobaltic chloride, therefore, can be shown by the following formulæ.



As to the third reaction⁽¹¹⁾ it is not certain whether it proceeds in the sense of the arrow irreversibly or reversibly. Whichever the case may be, the above calculations are scarcely affected by the third reaction, because the two complex salts concerned in it have quite similar absorption curves (Fig. 5).

Kinetics. From the above calculations and discussions, the first and the second reactions may be expressed by the following equations.

$$\frac{d[\text{B}]}{dt} = k_1[\text{A}] \quad \text{and} \quad \frac{d[\text{C}]}{dt} = k_2[\text{B}].$$

$$\text{Hence} \quad [\text{A}] = [\text{A}]_0 e^{-k_1 t}, \quad (6)$$

$$[\text{B}] = \frac{k_1[\text{A}]_0}{k_1 - k_2} (e^{-k_1 t} + e^{-k_2 t}), \quad (7)$$

$$\text{and} \quad [\text{C}] = \frac{[\text{A}]_0}{k_1 - k_2} (k_2 e^{-k_1 t} - k_1 e^{-k_2 t}). \quad (8)$$

From [A] in Table 4, k_1 is calculated by means of (6) (Table 5).

Table 5.
The Velocity Constant k_1 .

Time (sec.)	[A] (mol/l.)	k_1 at 17°C.
6×60	0.0088	1.48×10^{-3}
8×,,	0.0077	$1.39 \times ,,$
12×,,	0.0053	$1.37 \times ,,$
20×,,	0.0028	$1.40 \times ,,$
36×,,	0.0007	$1.31 \times ,,$
	Mean value	1.39×10^{-3}

Table 6.
The Velocity Constant k_2 .

Time (sec.)	[B] (mol/l.)	k_2 at 17°C.
8×60	0.0049	8.1×10^{-4}
12×,,	0.0058	$10.5 \times ,,$
20×,,	0.0064	$9.3 \times ,,$
36×,,	0.0044	$8.3 \times ,,$
	Mean value	9.05×10^{-4}

(11) Y. Shibata, *J. Chem. Soc. Japan*, **36** (1915), 127; *ibid.*, **38** (1917), 696;
J. N. Brønsted, *Z. physik. Chem.*, **122** (1926), 392; *J. Am. Chem. Soc.*, **49** (1927), 439.

The velocity constant k_2 is calculated by means of (7), k_1 , $[A]$ and $[B]$ being now known (Tables 3, 4 and 5).

The concentrations of the three salts are calculated from (6), (7) and (8), substituting k_1 and k_2 thus found.

Table 7. Concentrations of the Compounds contained in the Mixed Solutions.

Time (min.)	$[\text{Co}(\text{NH}_3)_4\text{Cl}_2\text{H}_2\text{O}_{(6)}^{(1)}]\text{Cl}$ (mol/l.)		$[\text{Co}(\text{NH}_3)_4\text{Cl H}_2\text{O}_{(6)}^{(1)}]\text{Cl}_2$ (mol/l.)		$[\text{Co}(\text{NH}_3)_4\text{Cl H}_2\text{O}_{(2)}^{(1)}]\text{Cl}_2$ (mol/l.)	
	Found	Calc.	Found	Calc.	Found	Calc.
0	0.0150	0.0150	0.0000	0.0000	0.0000	0.0000
6	0.0088	0.0092	0.0048	0.0046	0.0014	0.0012
8	0.0077	0.0076	0.0049	0.0055	0.0024	0.0019
12	0.0056	0.0055	0.0058	0.0063	0.0036	0.0032
20	0.0028	0.0028	0.0064	0.0062	0.0058	0.0050
36	0.0007	0.0008	0.0044	0.0038	0.0099	0.0104
90	0.0000	0.0000	0.0007	0.0003	0.0143	0.0147

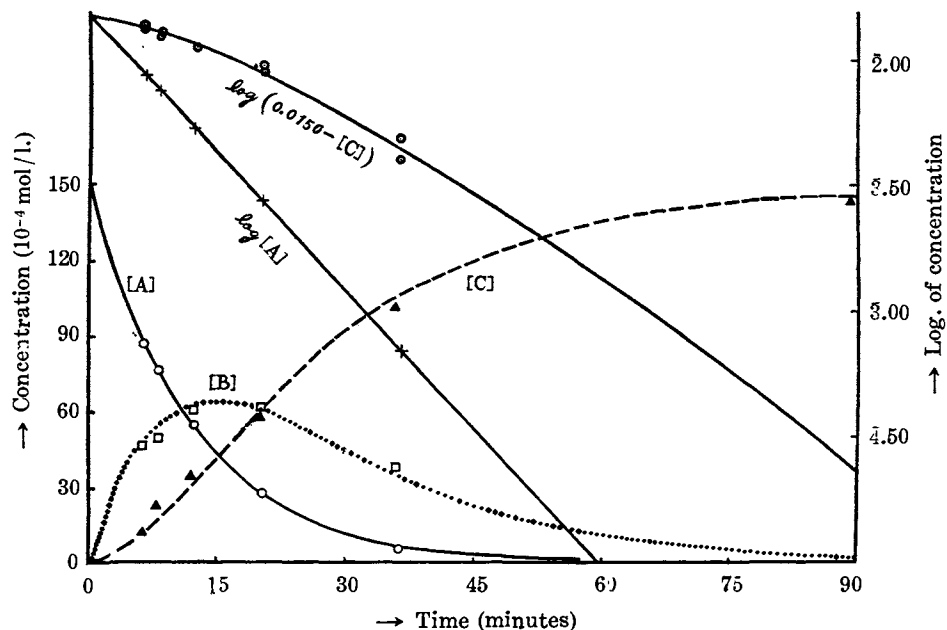


Fig. 4.

The results are summarized in Fig. 4 in which the smooth curves show the calculated values.

The maximum value of [B] is attained at

$$t_{\max.} = \frac{\ln k_1 - \ln k_2}{k_1 - k_2} . \quad (10)$$

The results of the analysis show that the maximum value is attained at a point between 12 and 20 minutes, while the calculation by (10) gives 15 minutes.

Absorption Curves of $[\text{Co}(\text{NH}_3)_4\text{Cl}_2]^{(1)}\text{Cl}$ and $[\text{Co}(\text{NH}_3)_4\text{Cl H}_2\text{O}]^{(1)}\text{Cl}_2$. Trans-aquochloro-tetrammine cobaltic salt has never been reported. Trans-dichloro-tetrammine cobaltic salt can never exist alone in aqueous solutions and consequently its absorption has never been observed without superposition of those of its aquotization products. In order to find molar extinction coefficients of these very unstable complex compounds, the curves I and V in Fig. 1 were again analysed making use of the calculated concentrations in Table 7. The results are shown in Fig. 5, together with the absorption curves of $[\text{Co}(\text{NH}_3)_4\text{Cl H}_2\text{O}]^{(1)}\text{Cl}_2$ and $[\text{Co}(\text{NH}_3)_4(\text{H}_2\text{O})_2]^{(1)}\text{Cl}_3$.

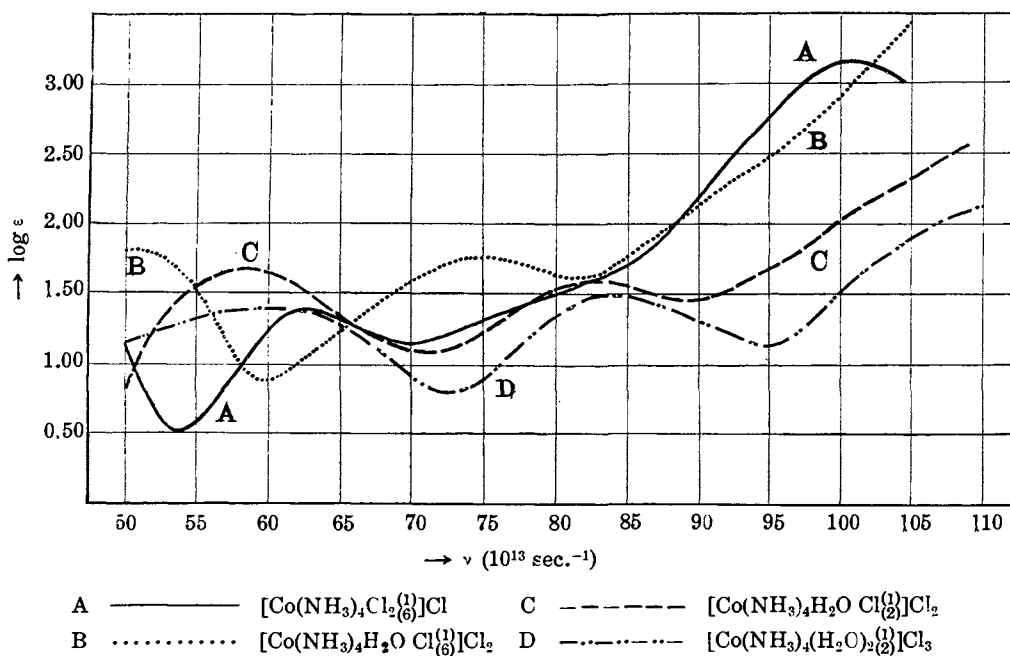


Fig. 5.

The selective absorption bands of these complex salts are given in Table 8.

Table 8.

	The first band		The second band		The third band	
	ν	$\log \epsilon$	ν	$\log \epsilon$	ν	$\log \epsilon$
$[\text{Co}(\text{NH}_3)_4\text{Cl}_2\frac{(1)}{(6)}]\text{Cl}$	$< 50 \times 10^{13}$	1.2	62.5×10^{13}	1.37	10×10^{14}	3.16
$[\text{Co}(\text{NH}_3)_4\text{Cl H}_2\text{O}\frac{(1)}{(6)}]\text{Cl}_2$	50 ,,	1.3	74.5 ,,	1.76	—	—
$[\text{Co}(\text{NH}_3)_4\text{Cl H}_2\text{O}\frac{(1)}{(2)}]\text{Cl}$	58.5 ,,	1.67	82.5 ,,	1.59	—	—
$[\text{Co}(\text{NH}_3)_4(\text{H}_2\text{O})_2\frac{(1)}{(2)}]\text{Cl}_3$	60 ,,	1.40	84 ,,	1.49	—	—

The first and the second band of $[\text{Co}(\text{NH}_3)_4\text{Cl H}_2\text{O}\frac{(1)}{(6)}]\text{Cl}_2$ is of higher frequency than the corresponding band of $[\text{Co}(\text{NH}_3)_4\text{Cl}_2\frac{(1)}{(6)}]\text{Cl}$. In other words, the substitution of the Cl ion in the co-ordination by H_2O molecule shows a hypsochromic effect. Similar effect is observed when Cl in $[\text{Co}(\text{NH}_3)_4\text{Cl H}_2\text{O}\frac{(1)}{(2)}]\text{Cl}_2$ is substituted by H_2O .

One of the most remarkable features of the absorption curve of the praseo-salt is that it has three absorption bands, of which the third is of interest. Generally speaking, most complex salts have two selective absorption bands in the visible and the near-ultraviolet regions and it has been known that only a few trans-dinitro-complex compounds such as $[\text{Co}(\text{NH}_3)_4(\text{NO}_2)_2\frac{(1)}{(6)}]\text{Cl}$ ⁽¹²⁾, $[\text{Co}(\text{NH}_3)_3(\text{NO}_2)_3]$ ⁽¹²⁾, $[\text{Co}(\text{NH}_3)_2(\text{NO}_2)_4]\text{NH}_4$ ⁽¹²⁾, $[\text{Co}(\text{NH}_3)_3(\text{NO}_2)_2\text{Cl}]$ ⁽¹³⁾ and $[\text{Co}(\text{NH}_3)_3(\text{NO}_2)_2\text{Br}]$ ⁽¹³⁾, and some rhodanatoammine complex salts⁽¹⁴⁾ show the third absorption bands. The author should like to predict that the third band is one of the general characteristics of those complex compounds which have at least one pair of ions co-ordinated in trans-position to each other. In order to confirm this view, Mr. S. Kashimoto⁽¹⁵⁾ in this laboratory has recently examined $[\text{Co}(\text{NH}_3)_4\text{NO}_2\text{Cl}]\text{Cl}$ and $\text{Na}_3[\text{Co}(\text{NO}_2)_6]$ and found that they have also the third absorption bands.

(12) Y. Shibata, *J. Chem. Soc. Japan*, **36** (1915), 1243.

(13) M. Kobayashi, A. Hagitani, and I. Mita, *ibid.*, **57** (1935), 500.

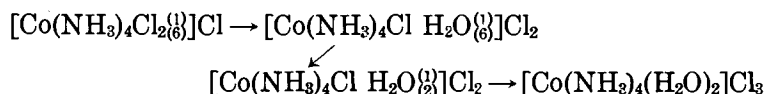
(14) Y. Shibata and K. Matsuno, *J. Coll. Sci., Imp. Univ. Tokyo*, **41** (1921), Art. 9.

(15) The results shall soon be published.

Summary.

(1) A new complex compound $[\text{Co}(\text{NH}_3)_4\text{Cl H}_2\text{O}_{(6)}^{(1)}]\text{Cl}_2$ was found by the spectrographic analysis.

(2) Trans-dichloro-tetrammine cobaltic chloride in aqueous solutions changes in the following scheme :



(3) The velocity constants of the first two reactions were found to be 1.39×10^{-3} and 9.05×10^{-4} respectively.

(4) The absorption curves were found for the unstable complex salts $[\text{Co}(\text{NH}_3)_4\text{Cl}_2]^{(1)}\text{Cl}$ and $[\text{Co}(\text{NH}_3)_4\text{Cl H}_2\text{O}_{(6)}^{(1)}]\text{Cl}_2$, both of which can never exist in aqueous solutions without contamination of related compounds.

(5) The praseo-salt shows a third absorption band of the same type as that of $[\text{Co}(\text{NH}_3)_4(\text{NO}_2)_2]^{(1)}\text{Cl}$.

(6) The third absorption band is supposed to be one of the general characteristics of those complex salt which have in the co-ordination at least one pair of ions in trans-positions to each other.

(7) Substitution of Cl in $[\text{Co}(\text{NH}_3)_4\text{Cl}_2]^{(1)}\text{Cl}$ or $[\text{Co}(\text{NH}_3)_4\text{Cl H}_2\text{O}_{(2)}^{(1)}]\text{Cl}_2$ by H_2O , has hypsochromic effect.

The author wishes to express thanks to Prof. Y. Shibata for his kind interest and to Messrs. M. Kobayashi and N. Shigematsu for their assistance in the experimental work.

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DIHYDROXYSTEARIC ACID IN CASTOR OIL.*

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The presence of a dihydroxystearic acid $C_{18}H_{36}O_4$ melting at $141-143^\circ$ as a minor constituent in castor oil was first pointed out by Juillard.⁽¹⁾ Since then Haller,⁽²⁾ Meyer,⁽³⁾ Eibner and Münzing,⁽⁴⁾ Myddleton, Berchem and Barrett,⁽⁵⁾ Panjutin and Rapoport,⁽⁶⁾ Heiduschka and Kirsten⁽⁷⁾ also found this acid in castor oil, but there has been lacking of investigation in detail on this acid, and its constitution remained quite unknown. Lewkowitsch⁽⁸⁾ stated in his classical work that this acid—being a natural product—is probably optically active, but this interesting account seemed to be overlooked by subsequent investigators, and there has been no work containing the optical rotation of this acid.

A few years ago we found that methyl or ethyl esters prepared by the methanolysis or ethanolysis of castor oil deposited a minor quantity of laminar crystals at the room temperature in winter, which were confirmed to consist mainly of methyl or ethyl ester of dihydroxystearic acid by examining their characteristics. Afterward we were supplied with a sufficient quantity of crystalline deposit which was separated from the methyl ester of castor oil by the courtesy of the Taisho Kagaku Kogyo K.K. From this crystalline deposit, dihydroxystearic acid was obtained in a pure state, and its properties were examined with a special reference to the constitution and the optical rotation. For the determination of the constitution of dihydroxystearic acid, it was oxidised with sodium bichromate and sulphuric acid, and *n*-nonoic acid $CH_3 \cdot (CH_2)_7 \cdot COOH$ and azelaic acid $HOOC \cdot (CH_2)_7 \cdot COOH$ were identified among the oxidation products. Hence the dihydroxystearic acid was found to be 9,10-dihydroxystearic acid having the formula $CH_3 \cdot (CH_2)_7 \cdot CHOH \cdot CHOH \cdot (CH_2)_7 \cdot COOH$. This formula was verified also in another way; methyl dihydroxystearate was converted into methyl dibromostearate by the action of

* Translated from the Japanese text published in *J. Chem. Soc. Japan*, **57** (1936), 976.

(1) *Bull. soc. chim.*, [3], **13** (1895), 238.

(2) *Compt. rend.*, **144** (1907), 462.

(3) *Arch. Pharm.*, **235** (1897), 184.

(4) *Chem. Umschau Fette, Öle, Wachse Harze*, **32** (1925), 153, 166.

(5) *J. Am. Chem. Soc.*, **49** (1927), 2264.

(6) *Chem. Umschau Fette, Öle, Wachse Harze*, **37** (1930), 130.

(7) *Pharm. Zentralhalle*, **71** (1930), 81.

(8) "Chemical Technology and Analysis of Oils, Fats and Waxes," 6th Edition, Vol. I, p. 226.

hydrogen bromide, the latter was debrominated, and the octadecenoic acids were liberated on saponification followed by acidulation of the debrominated product. The octadecenoic acids thus obtained were found to be a mixture of two geometrical isomerides (oleic and elaidic acids) of $\Delta^{9:10}$ -octadecenoic acids. The optical rotation of dihydroxystearic acid was examined in methanol or chloroform by using a 40 cm. tube, and the solutions were found to be slightly dextro-rotatory, but an accurate measurement was difficult due to an extremely small angle of rotation.⁽⁹⁾ Solutions of methyl dihydroxystearate showed also very small dextro-rotation, but the determination of the angle of rotation was difficult.

The acetylated product of methyl or ethyl ester of dihydroxystearic acid was a liquid at the ordinary temperature, and the specific rotation was measured without using solvent; $[\alpha]_D^{30} + 0.19^\circ$ for diacetyl ester of methyl dihydroxystearate and $[\alpha]_D^{30} + 0.31^\circ$ for diacetyl ester of ethyl dihydroxystearate.

It is thus confirmed by the foregoing results that dihydroxystearic acid in castor oil is *d*-9,10-dihydroxystearic acid. As for the racemic 9,10-dihydroxystearic acid derived from $\Delta^{9:10}$ -octadecenoic acids (oleic and elaidic acids), there are known two isomerides. The one melts at 130° and is obtained from oleic acid by Hazura's oxidation method; the other melts at 100° and is obtained from elaidic acid by Hazura's oxidation method. Resolution of these racemic acids into optically active isomerides has hitherto been studied by Freundler⁽¹⁰⁾ and Inoue and Suzuki.⁽¹¹⁾ Freundler resolved 9,10-dihydroxystearic acid of higher melting point into optically active isomerides by means of its strychnine salt. Ethyl ester of *d*-isomeride had m.p. $98-99^\circ$ and $[\alpha]_D + 1.6^\circ$, while ethyl ester of *l*-isomeride had m.p. $98-99^\circ$ and $[\alpha]_D - 2.1^\circ$. Since, however, the solubility of both isomerides was very small, the specific rotation was not measured accurately, and the above figures were stated to show only approximate values. Also Inoue and Suzuki resolved 9,10-dihydroxystearic acids derived from oleic and elaidic acids by means of strychnine salt. The specific rotation observed by these authors were as follows: $[\alpha]_D + 23.20^\circ$ and -23.60° for *d*- and *l*-isomerides obtained from 9,10-dihydroxystearic acid of m.p. 130° ; $[\alpha]_D + 27.60^\circ$ and -27.45° for *d*- and *l*-isomerides obtained from 9,10-dihydroxystearic acid of m.p. 100° . The melting points of optically active isomerides were not recorded in their paper.

(9) The angle of rotation greater than 0.25° was clearly discriminated by the polariscope used, but a 4% solution of dihydroxystearic acid in a 40 cm. tube showed an angle of rotation smaller than $+0.25^\circ$, and it was difficult to measure it accurately. Roughly speaking, the specific rotation of dihydroxystearic acid should not be greater than $+1.6^\circ$ ($0.25 \div 4 \div 0.04$).

(10) *Bull. soc. chim.*, [3], **13** (1895), 1052.

(11) *Proc. Imp. Acad.* (Tokyo), **7** (1931), 261.

In comparison of *d*-acid separated from castor oil in these experiments and *d*-acids obtained from racemic 9,10-dihydroxystearic acids by the above cited authors, *d*-acid obtained by Freundler has an appreciably lower melting point than *d*-acid of castor oil, while *d*-acids obtained by Inoue and Suzuki show exceedingly greater specific rotations than *d*-acid of castor oil. After it has been confirmed in these experiments that *d*-acid of castor oil is 9,10-dihydroxystearic acid and its specific rotation is very small (not exceeding $+1.6^\circ$), the discrepancy between the results of our experiments on *d*-acid of castor oil and those of above cited authors on *d*-acids obtained from racemic 9,10-dihydroxystearic acid is not explainable. In order to gain a fuller information regarding this point, we have prepared racemic 9,10-dihydroxystearic acid by oxidation of oleic acid and attempted to resolve it into optically active isomerides by means of its strychnine salt. For the preparation of the strychnine salt of dihydroxystearic acid, strychnine nitrate was added to an alcoholic solution of potassium dihydroxystearate following the method of Freundler with a modification that strychnine nitrate instead of sulphate was used in our experiment. In another experiment dihydroxystearic acid and free strychnine were heated in chloroform solution following the method of Inoue and Suzuki. It was, however, found that no substantial amount of strychnine and dihydroxystearic acid combined by these methods, and the products contained large amount of free strychnine and dihydroxystearic acid. Resolution of dihydroxystearic acid as its strychnine salt was not attained. It should also be noted here regarding the stability of *d*-acid separated from castor oil. According to Inoue and Suzuki the optically active isomerides obtained from racemic 9,10-dihydroxystearic acids had a strong tendency to undergo racemisation. When they were heated in alcoholic solutions for 30 minutes they were completely converted into racemic compounds. Aqueous solutions of their potassium salts were quite inactive. Similar facts were reported by Grün⁽¹²⁾ in the case of *d*-isomeride (m.p. 90°) obtained from racemic 9,12-dihydroxystearic acid. Its alcoholic solution became inactive on standing for some time; on heating at $130-140^\circ$ it became rapidly inactive. The *d*-acid of castor oil is, however, very stable. Even after prolonged heating of its alcoholic solution, the crystals separated on cooling showed the same melting point. After the elapse of several months the melting point of dihydroxystearic acid remained unaltered. Even when dihydroxystearic acid of castor oil was converted into its methyl or ethyl ester and then reconverted into free acid by saponification followed by acidification, there was no indication of racemisation. It is thus seen that contrary to the observations of previous investigators on the optically active isomerides obtained by the resolution of

(12) *Ber.*, **39** (1906), 4400.

racemic compounds, the *d*-acid of castor oil is quite stable and shows no tendency to undergo racemisation.⁽¹³⁾

Experimental.

1. **Separation of Dihydroxystearic Acid.** The starting material used in these experiments was supplied by the courtesy of the Taisho Kagaku Kogyo K.K. It was a crude deposit which was separated in a yield of ca. 3% from the methyl esters prepared by the methanolysis of castor oil on cooling at 0–5°. Since the removal of the liquid esters was incomplete, the crude deposit formed a pasty mass at the ordinary temperature. In these experiments 1 kg. of the crude deposit was first mixed with 1 l. of methanol and after heating on the water bath for a short time, a small amount of flocculent precipitate was removed by filtration. The clear solution was allowed to stand at the room temperature, and the crystalline deposit was filtered off. The filtrate formed a further quantity of crystalline deposit on ice-cooling. The crystalline deposits thus obtained were united and redissolved in 1 l. of methanol by warming. A small amount of flocculent precipitate was again removed by filtration, and the clear solution was ice-cooled to separate the crystalline deposit which was filtered and treated with methanol as before. After repeating the methanol treatment five times there were obtained finally 89 g. of methyl dihydroxystearate in lustrous laminar crystals which had m.p. 111–112°⁽¹⁴⁾ and saponification value 167.5 (calc. for methyl dihydroxystearate $C_{19}H_{38}O_4$: 170.9). The optical rotation of methyl dihydroxystearate was examined in a 4% solution in methanol by using a 40 cm. tube, but an accurate measurement was difficult due to an extremely small dextro-rotation (less than +0.25°).

On heating methyl dihydroxystearate with twice its weight of acetic anhydride at 140° for 2 hours and subsequently washing the product with boiling water, diacetyl ester $C_{19}H_{36}O_2(OCOCH_3)_2$ was obtained. It formed a colourless liquid and had the following constants: d_4^{15} 0.9826, n_D^{15} 1.4498, $[MR_L]_D$ 113.3 (calc. 113.4), $[\alpha]_D^{30}$ +0.19°, saponif. value 403.7 (calc. 408.2).

For the preparation of dihydroxystearic acid the methyl ester was saponified with alcoholic potash, the product was diluted with water and then acidulated with hydrochloric acid. The dihydroxystearic acid liberated was separated by filtration, washed with water and recrystallised from ether-alcohol (1:1), yielding laminar crystals; m.p. 142–143°, neutralisation value 177.5 (calc. for $C_{18}H_{36}O_4$: 177.4). A 1% solution in chloroform and a 4% solution in methanol showed only a very slight rotation in a 40 cm. tube, but the determination of specific rotation was difficult due to an extremely small angle of rotation.

Dihydroxystearic acid was dissolved in alcohol, and after addition of a small amount of sulphuric acid the solution was refluxed on the water bath in order to complete esterification. The product was taken up with ether, the ethereal solution was first washed with a solution of potassium carbonate in order to remove sulphuric acid and unchanged dihydroxy-

(13) S. Ishikawa and G. Maeda presented a paper at the 29th meeting of the Institute of Physical and Chemical Research held on May 22, 1936, in which the separation of methyl dihydroxystearate from commercial methyl ester of ricinoleic acid and the constitution of this dihydroxystearic acid were dealt with. According to these authors this acid seems not to be 9, 10-dihydroxystearic acid. The present investigation showed, however, that the dihydroxystearic acid of castor oil is *d*-9,10-dihydroxystearic acid, but the presence of any other dihydroxystearic acid was not ascertained.

(14) Juillard (*loc. cit.*) gave m.p. 104–106°. Haller (*loc. cit.*) gave m.p. 107–108°.

stearic acid as their potassium salts. The ethereal solution was then washed thoroughly with water, and after distilling off a portion of the solvent from the solution, it was allowed to cool when the crystals of ethyl dihydroxystearate $C_{20}H_{40}O_4$ separated; m.p. 104–105°, saponif. value 161.9 (calc. 162.9).

Diacyl ester of ethyl dihydroxystearate $C_{20}H_{38}O_2(OCOCH_3)_2$ was obtained by heating ethyl dihydroxystearate with acetic anhydride. It formed a colourless liquid having the following constants: d_4^{15} 0.9743, n_D^{15} 1.4485, $[MR_L]_D$ 117.8 (calc. 118.0), $[\alpha]_D^{80} +0.31^\circ$, saponif. value 392.6 (calc. 392.9).

2. Oxidation of Dihydroxystearic Acid. Fifteen grams of dihydroxystearic acid was mixed with 30 g. of sodium bichromate, 75 g. of sulphuric acid and 300 g. of water, and the mixture was heated in an oil bath, the temperature of which was kept at 110°, for 30 minutes and then subjected to steam distillation by which about 1 l. of distillate was collected. The distillate (a) consisted of a minor proportion of oily substances together with aqueous solution. The residue (b) from steam distillation was a dark green liquid. The distillate was saturated with sodium chloride and shaken with petroleum ether. The petroleum ether solution was separated, and after distilling off petroleum ether there remained 6.4 g. of colourless oil which had d_4^{15} 0.9038, n_D^{15} 1.4336, $[MR_L]_D$ 45.53 (calc. for $C_9H_{18}O_2$: 45.30), neutral. value 350.8 (calc. for $C_9H_{18}O_2$: 354.8). This oil was converted into the acid chloride by heating with thionyl chloride on the water bath. The acid chloride formed was dropped into ice-cooled ammonia and the precipitated acid amide was filtered and washed with water. It was dissolved in 50% alcohol, treated with active carbon and cooled down to separate the crystals which were identified with *n*-nonoic acid by its m.p. and mixed m.p. 98.5–99°.

The residue (b) from steam distillation was shaken with 2 l. of ether. The ethereal solution was separated and after washing with saturated brine the ether was distilled off leaving 4 g. of bluish-green coloured crystalline solid as residue. This was dissolved in boiling water, in which a small amount of green coloured substances remained insoluble. The clear solution was separated and cooled down to deposit laminar crystals which on recrystallisation from water gave pure azelaic acid; yield 2 g., m.p. 106–107°, neutr. value 593.0 (calc. for $C_9H_{16}O_4$: 596.5). It showed no depression of melting point when admixed with an authentic specimen of azelaic acid.⁽¹⁵⁾

3. Preparation of Oleic and Elaidic Acids from Methyl Dihydroxystearate. Ten grams of methyl dihydroxystearate was heated in a flask for 30 minutes by means of an oil bath, the temperature of which was kept at 140°. During heating a current of hydrogen bromide was passed through the melted mass. The methyl dibromostearate thus formed was a viscous oil. Ten c.c. of methanol and 13 g. of zinc powder were added to the product and the mixture was refluxed on the water bath. Ten c.c. of 5N hydrogen chloride in methanol was added in the course of 20 minutes, and the heating was continued for another 20 minutes, after which the product was taken up with ether. The ethereal solution was washed with water, the ether was distilled off, and the residue consisting of methyl octadecenoate was saponified with alcoholic potash. The soap solution was acidified with

(15) The specimen of azelaic acid used for the mixed melting point test was prepared by the ozonolysis of oleic acid and had m.p. 105–106°. Azelaic acid obtained in these experiments from dihydroxystearic acid in castor oil is believed to have a higher purity than the specimen from oleic acid.

hydrochloric acid, and the separated free acids were taken up with petroleum ether. The petroleum ether solution was washed with water, the solvent was distilled off, and there remained 8 g. of residue which had neutral. value 196.0, iodine value 84.1 and m.p. 35–36°. On cooling the solution of the residue in 80% alcohol, there was formed about 5 g. of crystalline solid which yielded on recrystallisation from 80% alcohol crystals having neutral. value 198.7 (calc. for $C_{18}H_{34}O_2$: 198.8), iodine value 87.6 (calc. for $C_{18}H_{34}O_2$: 89.9) and m.p. 44.5–45°. No depression of melting point was observed when this substance was added to an authentic specimen of elaidic acid.⁽¹⁶⁾ The mother liquor separated from crystals of elaidic acid contained a liquid fatty acid which deposited only a minute amount of solid after standing for several days at the room temperature. The liquid portion was found to consist of oleic acid, since it was converted into a solid mass by the action of nitrous acid and the latter yielded after purification elaidic acid having neutral. value 197.1, iodine value 88.3 and m.p. 44.5–45°.

4. Preparation of Dihydroxystearic Acid from Oleic Acid and Attempt to Resolve it into Optically Active Isomerides by Means of its Strychnine Salt. Fifteen grams of oleic acid prepared from tsubaki oil was mixed with 18 c.c. of potassium hydroxide solution (ca. 28%) and then diluted with 1 l. of water. To this solution of potassium oleate, 1 l. of potassium permanganate solution (1.5%) was gradually added with constant stirring, and then sulphur dioxide was passed through the solution until the excess of potassium permanganate and the insoluble oxides of manganese disappeared completely. Dihydroxystearic acid was separated by filtration, and after being washed with water it was recrystallised from 95% alcohol yielding 11.2 g. of crystals having m.p. 129.5–130°. By repetition of these operations a further quantity of dihydroxystearic acid was prepared.

Thirty-six grams of dihydroxystearic acid and 45 g. (ca. 20% in excess) of strychnine were refluxed on the water bath when a clear solution was obtained. After heating for 30 minutes, 2 l. of chloroform was added to the solution, and it was kept at the room temperature over a night. A large amount of crystals (27 g.) separated, but these were found to be unchanged dihydroxystearic acid by their neutr. value and melting point. This experiment was then discontinued.

Thirty-eight grams of dihydroxystearic acid was dissolved in 1.7 l. of alcohol and neutralised with alcoholic potash. Fifty grams of strychnine nitrate (in small excess) was added to the solution, and it was refluxed on the water bath for 1 hour. There was formed a considerable amount of precipitate which seemed to be potassium nitrate. The substances contained in the clear solution separated from the precipitate were subjected to fractional crystallisation, and there were obtained 4 fractions F_1 – F_4 . The first fraction F_1 was separated further into 8 fractions F_{1-1} – F_{1-8} by means of fractional crystallisation from chloroform. The fraction F_{1-6} , which was most abundant in quantity, was separated further into 5 fractions F_{1-6-1} – F_{1-6-5} from chloroform solution. The fraction F_4 obtained by the first fractional crystallisation was separated into 6 fractions F_{4-1} – F_{4-6} from chloroform solution. Fractions thus obtained were separately examined, but they were found to contain a considerable amount of strychnine and dihydroxystearic acid in free state, and to what extent dihydroxystearic acid was resolved into the optically active isomerides as their strychnine salts was difficult to know.

(16) The specimen of elaidic acid used for the mixed melting point test was prepared from oleic acid separated from tsubaki oil and had m.p. 43.5–44°.

Summary.

A dihydroxystearic acid, which is contained as a minor component in the fatty acids of castor oil, has been separated and proved to be identical with *d*-9,10-dihydroxystearic acid.

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THE HIGHLY UNSATURATED ACIDS IN SARDINE OIL. XII.
A FURTHER EXPERIMENT ON THE SEPARATION
OF OCTADECATRIENOIC ACID $C_{18}H_{30}O_2$.

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In the 1st report⁽¹⁾ of this series the highly unsaturated C_{16} - and C_{18} -acids of sardine oil were examined with the results that hiragonic acid $C_{16}H_{26}O_2$ and moroctic acid $C_{18}H_{28}O_2$ were isolated from C_{16} - and C_{18} -acids, respectively, and the presence of an octadecatrienoic acid $C_{18}H_{30}O_2$ was also indicated. The constitutions of hiragonic and moroctic acids were established in the 2nd and 3rd reports⁽²⁾ of this series.

The presence of an octadecatrienoic acid in sardine oil was first pointed out by Fahrion.⁽³⁾ He analysed a fraction of the bromides which was separated from the brominated products of the sardine oil fatty acids as the portion insoluble in petroleum ether, and he believed it to be a hexabromide derived from an octadecatrienoic acid which he named jecoric acid, but there is little doubt that the fraction of the bromides analysed by him is not really a single compound. Although the presence of an octadecatrienoic acid in various kinds of marine animal oils besides sardine oil has been also frequently reported, the evidence for the presence of this acid seems, in most cases, to rest on inadequate experimental results. However, Tsujimoto⁽⁴⁾ brought out a strong

(1) This Bulletin, **4** (1929), 83.

(2) This Bulletin, **10** (1935), 192, 232.

(3) *Chem. Ztg.*, **17** (1893), 521.

(4) *Rept Tokyo Imp. Ind. Research Lab.*, **6** (1911), 17; **12** (1917), 169.

evidence for the presence of an octadecatrienoic acid in carp oil and snapping-turtle oil by the finding that the bromine content of ether-insoluble bromides obtained from the fatty acids of these oils lay close to the calculated value for $C_{18}H_{30}O_2Br_6$. In a recent investigation on the oil from *Chanos chanos*, Kafuku and Hata⁽⁵⁾ reported the separation of bromides obtained from the liquid fatty acids and found that the fraction which was insoluble in ether but soluble in benzene consisted of a hexabromide which was identical with that derived from linolenic acid. These authors seem to be the first, so far as we know, who indicated the presence of linolenic acid in fish oils with certainty. In the following we describe the results of our further experiments on the separation of octadecatrienoic acid starting with 60 kg. of the ethyl esters of sardine oil fatty acids. In these experiments sufficient indications of the presence of octadecatrienoic acid were obtained, but the separation and the identification of octadecatrienoic acid were not attained. A fraction of octadecatrienoic acid was separated from the debrominated product obtained from the bromides which were insoluble in ether but soluble in benzene, but it could not be freed from the contamination of moroctic and hiragonic acids together with the products of intramolecular polymerisation of these acids. Judging from the results of these experiments, octadecatrienoic acid forms an extremely minor constituent of sardine oil fatty acids.

Experimental.

Sixty kg. of the mixed ethyl esters prepared by the ethanolic saponification of sardine oil were fractionated, and 28.5 kg. of a fraction boiling below $215^\circ/10$ mm. was collected. This fraction was saponified, the fatty acids liberated were dissolved in 85% methanol, and the solution was cooled. The crystalline deposit consisting chiefly of saturated acids was removed by filtration, and the filtrate was neutralised with aqueous solution of lithium hydroxide. The insoluble lithium soaps consisting mainly of the lithium soaps of saturated and mono-ethylenic acids were removed by filtration, and 7.5 kg. of fatty acids were recovered from the filtrate in the usual way. The fatty acids thus obtained were converted into the methyl esters, which were then fractionated yielding 5.9 kg. of a fraction boiling below $215^\circ/15$ mm. This fraction was brominated in ethereal solution, and the ether-insoluble bromides were separated and then treated with benzene yielding 1.5 kg. of the bromides soluble in benzene, from which 463 g. of the methyl esters were regenerated by debromination. The methyl esters were fractionated with the following results: (1) below $190^\circ/15$ mm. 98 g., (2) $190-205^\circ/15$ mm. 175 g., (3) $205-215^\circ/15$ mm. 120 g., (4) $215-221^\circ/15$ mm. 40 g., (5) residue 30 g. For the details of the above experiments the 2nd report⁽⁶⁾ of this series should be consulted, in which the fraction (1) was subjected to a further fractionation for the separation of methyl hiragonate. In the present experi-

(5) *J. Soc. Chem. Ind., Japan*, **38** (1935), 1414.

(6) *This Bulletin*, **10** (1935), 192.

ment the fraction (3) was fractionated repeatedly, and the following two fractions were collected separately.

Fraction	B.p./15 mm.	Saponif. v.	Iodine v. (Wijs)	Yield (g.)
(a)	205–210°	190.1	291.0	23
(b)	210–215°	190.9	292.4	28

Since the characteristics of the fractions (a) and (b) show no appreciable difference, they were united and subjected to the fractional precipitation of sodium soaps in acetone in the following manner: 45 g. of the fatty acids obtained from the united fractions were dissolved in 360 c.c. of acetone, neutralised with an approximately 4N alcoholic solution of sodium hydroxide, and alcohol was added until the total volume of the alcoholic solution of sodium hydroxide and the alcohol subsequently added measured 54 c.c. Then 36 c.c. of water and 450 c.c. of acetone were added to the solution, and after heating for a short time the insoluble sodium soaps were precipitated by cooling and filtered. The precipitate and the filtrate were worked up to separate the fatty acids in the usual way.

	Neutr. v.	Iodine v.	Yield (g.)
Fatty acids from the precipitate	201.7	293.8	30.5
Fatty acids from the filtrate	198.6	331.9	14.5

The fatty acids from the precipitate were again fractionated by the sodium-soap-acetone method in the following way: 30 g. of the fatty acids from the precipitate were dissolved in 240 c.c. of acetone, neutralised with an approximately 4N alcoholic solution of sodium hydroxide, and alcohol was added until the total volume of the 4N alcoholic sodium hydroxide solution required for neutralisation and the alcohol added measured 30 c.c. Then 30 c.c. of water and 300 c.c. of acetone were added, and after heating for a short time the solution was cooled down to separate the precipitate of insoluble sodium soaps which was filtered and decomposed with hydrochloric acid yielding 23 g. of fatty acids with neutr. value 202.2 and iodine value 284.2. These were fractionated as their methyl esters, (22 g.), and the following fractions were separated.

Fraction	B.p./15 mm.	d_4^{15}	n_D^{15}	Saponif. v.	Iodine v.	Yield (g.)
(1)	199–205°	—	—	—	—	0.4
(2)	205–208°	0.9143	1.4810	197.5	277.4	3.3
(3)	208–212°	0.9144	1.4815	195.4	274.7	4.5
(4)	212–215°	0.9159	1.4825	193.0	267.4	9.9
(5)	215–217°	—	—	—	—	0.6
Residue	—	—	—	—	—	3.3 (diff.)

While the specific gravity and the refractive index, as is seen from the above table, become higher as the boiling point becomes higher, the iodine value falls slightly as the boiling point becomes higher. This is possibly due to a contamination of polymerised methyl esters in the high boiling fractions. The fraction (4) has the characteristics which are close to the calculated values for methyl octadecatrienoate $C_{18}H_{29}O_2CH_3$ (saponif. value 192.0, iodine value 260.6), but it was found from the results of bromination to contain more highly unsaturated methyl esters together with some polymerised methyl esters besides methyl octadecatrienoate. On brominating 7.0 g. of the fraction (4), there were obtained 4.2 g. (60%) of ether-insoluble bromides. These were heated with 400 c.c. of benzene on the water bath under a reflux condenser and then cooled down to about 35° . The insoluble portion was filtered, and on distilling off benzene from the filtrate there remained benzene-soluble bromides with Br-content 65.28% which were higher in Br-content than $C_{18}H_{29}O_2CH_3Br_6$ (62.13% Br). The benzene-soluble bromides were again refluxed with 300 c.c. of benzene, and after cooling the solution to about 30° , a small amount of insoluble bromides was filtered. From the filtrate, 2.5 g. of benzene-soluble bromides were obtained, which had Br-content 64.78% and melted at 195° with slight darkening. The Br-content seems to indicate that the bromides thus obtained contain more highly unsaturated methyl esters besides $C_{18}H_{29}O_2CH_3Br_6$.

Summary.

After having found in a previous study that sardine oil contains an octadecatrienoic acid as a minor constituent of highly unsaturated C_{18} -acids, we have attempted in the present experiment to separate the octadecatrienoic acid starting with a large amount of sardine oil. The results of the present experiment seem to indicate that the octadecatrienoic acid giving an ether-insoluble bromide is contained only in far lesser proportion than presumed before.

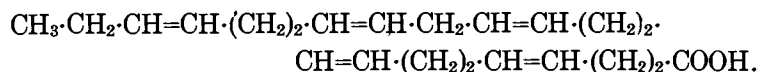
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THE HIGHLY UNSATURATED ACIDS IN SARDINE OIL. XIII.
OXIDATION OF METHYL CLUPANODONATE WITH
POTASSIUM PERMANGANATE IN
ACETONE SOLUTION.

By Yoshiyuki TOYAMA and Tomotaro TSUCHIYA.

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The constitution of clupanodonic acid, which forms an important constituent of the highly unsaturated acids in sardine oil, was dealt with in the 8th report⁽¹⁾ of this series. Amyl clupanodonate was subjected to ozonolysis, and propionic aldehyde, acetaldehyde, carbon dioxide, succinic acid and amyl hydrogen succinate were identified among the products of ozonolysis. Also the presence of lower acids, which were deemed to consist of propionic and acetic acids, was indicated. Of these compounds propionic aldehyde and propionic acid are derived from the group $\text{CH}_3\cdot\text{CH}_2\cdot\text{CH}=\text{}$, while acetaldehyde, acetic acid together with carbon dioxide are formed by a further degradation of the products of ozonolysis derived from the group $=\text{CH}\cdot\text{CH}_2\cdot\text{CH}=\text{}$. Succinic acid and amyl hydrogen succinate are evidently derived from the groups $=\text{CH}\cdot(\text{CH}_2)_2\cdot\text{CH}=\text{}$ and $=\text{CH}\cdot(\text{CH}_2)_2\cdot\text{COOC}_5\text{H}_{11}$ respectively. Hence the groups jointed by five ethylenic linkings in clupanodonic acid were found to be $\text{CH}_3\cdot\text{CH}_2\cdot\text{CH}=\text{}$, $=\text{CH}\cdot\text{CH}_2\cdot\text{CH}=\text{}$, three of $=\text{CH}\cdot(\text{CH}_2)_2\cdot\text{CH}=\text{}$ and $=\text{CH}\cdot(\text{CH}_2)_2\cdot\text{COOH}$. For the determination of the positions of the respective groups, we made use of the fact that the addition of bromine to the ethylenic linkings in clupanodonic acid proceeds selectively, and prepared dibromo-, tetrabromo- and hexabromo-derivatives of clupanodonic acid by the selective addition of bromine to the ethylenic linkings which lie more distant from the carboxyl group. The products of ozonolysis of these bromo-derivatives were examined, and the following formula of clupanodonic acid was established.

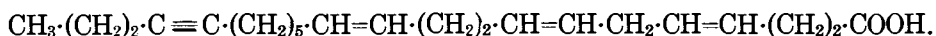


Before our experiment, Inoue and Sahashi⁽²⁾ oxidised the methyl ester of clupanodonic acid with potassium permanganate in acetone solution, and found

(1) This Bulletin, **10** (1935), 441.

(2) *Proc. Imp. Acad.* (Tokyo), **8** (1932), 371.

butyric, pimelic, succinic, adipic and oxalic acids among the oxidation products. Adipic and oxalic acids were thought by these authors to be formed by the secondary decomposition of pimelic and malonic acids, and consequently the oxidation products primarily derived from the groups jointed by unsaturated linkings in clupanodonic acid were found to be butyric, pimelic, succinic (2 mols), and malonic acids. For the determination of the positions of the respective groups, these authors subjected clupanodonic acid to partial hydrogenation and separated the product into the fractions of different degrees of saturation. The positions of the unsaturated linkings in each fraction were examined by the oxidation with potassium permanganate, and the following formula having one triple linking and three double linkings was proposed for clupanodonic acid.



While we used the ozonide method for the determination of the constitution of clupanodonic acid, Inoue and Sahashi used the permanganate method for the same purpose, but the difference of the oxidation method can not explain well the marked discrepancies between the results of our previous experiment and those obtained by Inoue and Sahashi. Leaving the positions of the respective groups jointed by unsaturated linkings undiscussed, it can hardly be accepted that the oxidation products obtained in our experiment on the amyl ester of clupanodonic acid by the ozonide method and those obtained by Inoue and Sahashi from the methyl ester of clupanodonic acid by the permanganate method resulted from the same single compound. It should, however, be noted that while the specimen of clupanodonic acid used for the determination of the constitution in our experiment was freed from C_{22} -acids of different degrees of unsaturation as far as possible and possessed high purity, the purities of specimens of clupanodonic acid which had been separated by several authors before our experiment are doubtful from the contamination of acids of different degrees of unsaturation. But such difference in the purity of clupanodonic acid alone can not explain the discrepancies between the results of our experiment and those obtained by Inoue and Sahashi. The following descriptions are the results of our experiment on the oxidation of methyl clupanodonate with potassium permanganate in acetone solution.

Among the products of oxidation of methyl clupanodonate with potassium permanganate in acetone solution, propionic acid, acetic acid, succinic acid and methyl hydrogen succinate were identified. Acetic acid is believed to be

formed by the secondary decomposition of malonic acid, and consequently the groups jointed by ethylenic linkings in clupanodonic acid were found to be $\text{CH}_3\cdot\text{CH}_2\cdot\text{CH}=\text{}$, $=\text{CH}\cdot(\text{CH}_2)_2\cdot\text{CH}=\text{}$, $=\text{CH}\cdot\text{CH}_2\cdot\text{CH}=\text{}$ and $=\text{CH}\cdot(\text{CH}_2)_2\cdot\text{COOH}$, of which three of the group $=\text{CH}\cdot(\text{CH}_2)_2\cdot\text{CH}=\text{}$ are present since clupanodonic acid has 22 carbon atoms in total. These results agree fully with those obtained by the ozonolysis of amyl clupanodonate in the previous experiment. Whilst the finding of the group $\text{CH}_3\cdot(\text{CH}_2)_2\cdot\text{CH}=\text{}$ by Inoue and Sahashi at the terminal opposite to the carboxyl group is based on the detection of butyric acid among the oxidation products, we could not find butyric acid, but we separated propionic acid which was identified as its *p*-bromophenacyl ester in pure state. Neither adipic acid nor pimelic acid could be found among the oxidation products in our experiment. In short, the oxidation products obtained in our experiment on methyl clupanodonate by means of potassium permanganate differ from those reported by Inoue and Sahashi, and the results of our experiment agree fully with those of the previous experiment of the ozonolysis of amyl clupanodonate. It is quite certain that clupanodonic acid has no triple linking but it has five ethylenic linkings. The structure is $\Delta^4:5, 8:9, 12:13, 15:16, 19:20$, docosapentenoic acid as has been established by the previous experiment.

Experimental.

1. Oxidation of Methyl Clupanodonate and Separation of Oxidation Products.

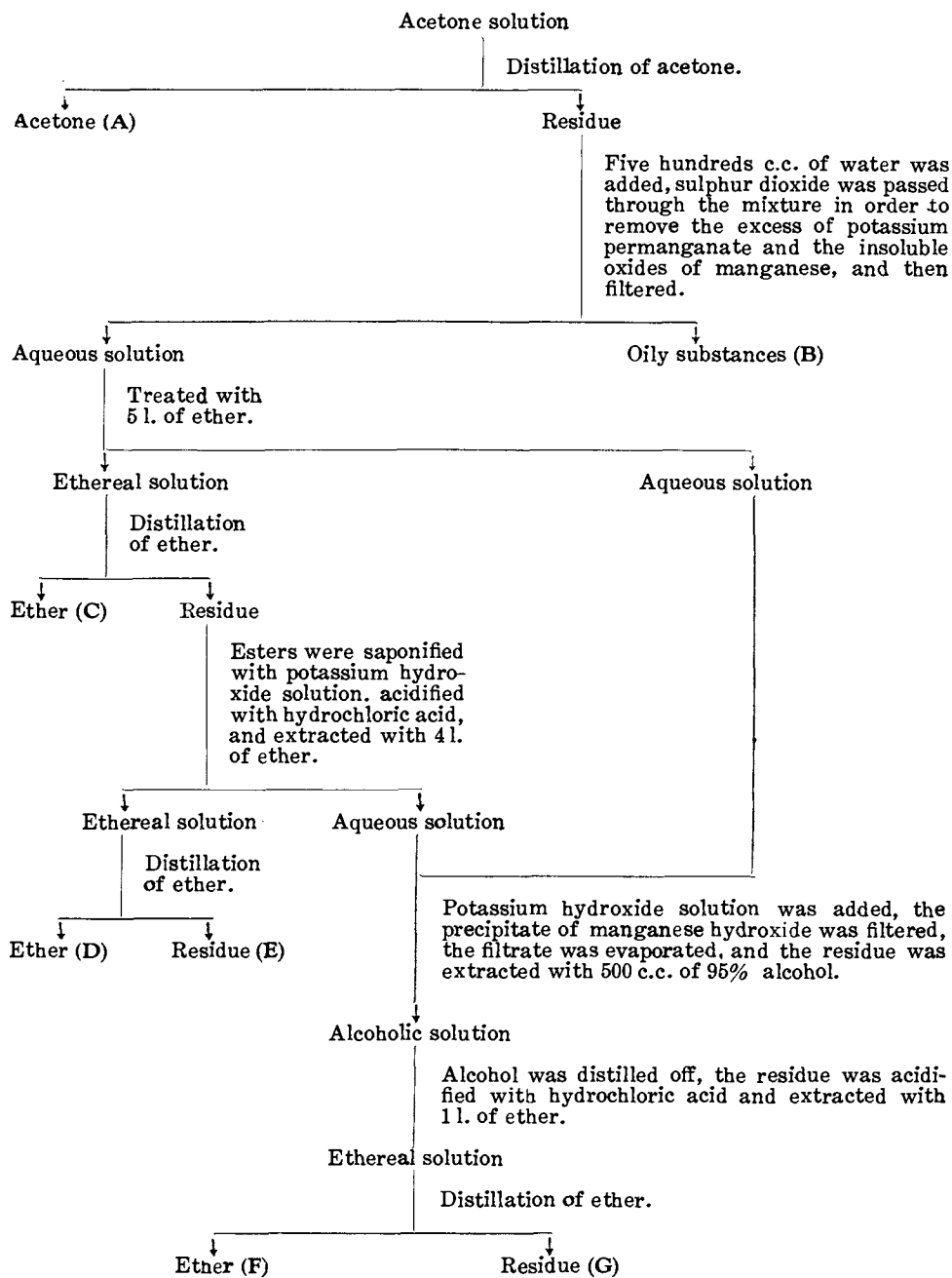
Methyl clupanodonate used in the present experiment was the same as described in the 7th report⁽³⁾ of this series, and had d_4^{15} 0.9240, n_D^{15} 1.4955, saponif. value 163.0 (calc. 163.0) and iodine value (Wijs) 368.0 (calc. 368.6). Amyl clupanodonate and free clupanodonic acid used for the experiment of ozonolysis described in the 8th report⁽⁴⁾ of this series were prepared from the same specimen of methyl clupanodonate.

Ten grams of methyl clupanodonate was dissolved in 200 c.c. of acetone, and 150 g. of potassium permanganate was added in small portions. In order to avoid a violent heat evolution, the solution was cooled at first and then potassium permanganate was added. After the heat evolution has ceased, the solution was heated on the water bath under a reflux condenser. Before the addition of a further quantity of potassium permanganate the solution was cooled, and then potassium permanganate was added. After the heat evolution has ceased, the solution was again heated. Repeating these operations the entire quantity of potassium permanganate was added in the course of 5 hours. The solution was refluxed for 5 hours more, and then the oxidation products were separated into several fractions as shown in Table 1.

(3) This Bulletin, **10** (1935), 433.

(4) This Bulletin, **10** (1935), 441.

Table 1.



2. **Oxidation Products Distilled off with the Solvents.** The acetone (A) and the ether (C, D, F), which were recovered in the separative operations shown in Table 1, showed acidic reaction. The acetone (A) was neutralised with potassium hydroxide, acetone was distilled off, and there remained the potassium salts. The ether (C, D, F) was shaken with potassium hydroxide solution by which the acidic substances were converted into the potassium salts and separated from the ethereal solution. The aqueous solution of potassium salts was evaporated to dryness and there remained the potassium salts as residue. The potassium salts thus obtained were united and treated with warm 95% alcohol in which potassium sulphite remained insoluble. The alcoholic solution was separated and evaporated. The residue was acidulated with dilute sulphuric acid and distilled. The distillate still contained sulphur dioxide. For the removal of last traces of sulphur dioxide, potassium permanganate was added to the distillate, and the solution was redistilled. The yield of final distillate was 43 g., and it had acid value 9.6, from which the total amount of acids contained in the distillate was calculated to be 0.44 g. as acetic acid. Thirty grams of distillate was nearly neutralised with N/10 alcoholic potash, and after addition of 1.4 g. of *p*-bromophenacyl bromide the solution was refluxed for 2 hours. A large amount of water was then added, and the separated solid was recrystallised from 60% alcohol. The crystals obtained melted at 84.5–85° both alone and after admixture with a pure specimen of *p*-bromophenacyl ester of acetic acid.

3. **Oxidation Products Dissolved in Water.** The residues (E) and (G) in Table 1 consisted of a mixture of crystalline solid and liquid. These were united and treated with petroleum ether (b. p. below 50°). The petroleum ether solution and the insoluble portion were separated.

(i) *Petroleum ether solution.* The solution was first heated on the water bath until the bulk of petroleum ether distilled over. It was then heated in an oil bath, and the distillate, which distilled over below 100° and was contaminated with a large proportion of petroleum ether, was collected and united with petroleum ether obtained before. The yield of distillate thus obtained was 154 g. It had acid value 4.3, from which the acidic substances contained in the distillate were calculated to be 0.71 g. as acetic acid. The *p*-bromophenacyl ester was prepared from the acidic substances contained in the distillate, and it was recrystallised from 60% alcohol yielding crystals which melted at 82–83° and showed no depression of melting point when admixed with a pure specimen of *p*-bromophenacyl ester of acetic acid (m. p. 84.5°) in various proportions. The portion which did not distil below 100° amounted to 1.9 g. It yielded two fractions on further heating: (1) b. p. 100–130°, 0.25 g.; (2) b. p. 130–140°, 0.8 g. Above 140° practically no distillate was obtained, and when the temperature of the oil bath reached 200° the residue began to show the indications of decomposition. The fraction (1) consisted mainly of propionic acid, and had n_D^{20} 1.3871 and neutr. value 763.2 (calc. 757.7). The *p*-bromophenacyl ester, when recrystallised from 70% alcohol, melted at 62.5–63° both alone and after admixture with a pure specimen of *p*-bromophenacyl ester of propionic acid. The final residue from distillation was a dark brownish viscous oil which was considered to be intermediate products which escaped a complete oxidation. It was subjected to a further oxidation by means of an alkaline solution of potassium permanganate, and the products were acidified and taken up with ether. On removal of ether from ethereal solution, there remained a crystalline solid (0.1 g.) which appeared to be impure succinic acid from its melting point 178–179°.

(ii) *The portion insoluble in petroleum ether.* This portion (7.5 g.) consisted of a mixture of reddish orange liquid and crystalline solid. It was washed with cold ether for

the removal of liquid portion, and the crystalline solid (a) was separated. The liquid portion obtained from the ethereal washing appeared to contain the substances which escaped a complete oxidation. It was subjected to a further oxidation with an alkaline solution of potassium permanganate. After acidification the products were taken up with ether, and on removal of ether there was obtained crystalline solid (b) which was still contaminated with a small proportion of oily substances. The crystalline solids (a) and (b) were united and recrystallised from ethyl acetate, yielding 1st crop of neutr. value 950.1 and m.p. 181-182° and 2nd crop of neutr. value 950.0 and m.p. 180-181°. Each crop showed no depression of melting point when admixed with a pure specimen of succinic acid (neutr. value calc. 950.6, m.p. 182-183°).

4. **Oily Substances.** Yield 3.6 g. These substances (B) contained some neutral substances which escaped oxidation. For the separation of acidic substances, the mixture was dissolved in ether and shaken with potassium hydroxide solution. The acidic substances were converted into the potassium salts and separated from ethereal solution. After the acidification of the aqueous solution of potassium salts with hydrochloric acid, the acidic substances liberated were taken up with ether. On distillation of ether, there were obtained 1.9 g. of acidic substances which showed neutr. value 432.1 and saponif. value 835.1 which are close to the calculated values for methyl hydrogen succinate (neutr. value 424.8, saponif. value 849.7). The free acid prepared from this acid ester by saponification followed by acidification melted at 179-180° after being washed with a little cold ether. The melting point was not lowered when the substance was admixed with succinic acid in various proportions.

Summary.

Methyl clupanodionate has been oxidised with potassium permanganate in acetone solution. Among the oxidation products propionic acid, acetic acid, succinic acid and methyl hydrogen succinate have been identified. Of these compounds acetic acid is believed to be formed by the secondary decomposition of malonic acid. Accordingly the presence of above-mentioned oxidation products gives an indication of the presence of the following groups in clupanodonic acid jointed by ethylenic linkings thus: $\text{CH}_3\cdot\text{CH}_2\cdot\text{CH}=\text{}$, $=\text{CH}\cdot\text{CH}_2\text{CH}=\text{}$, three of $=\text{CH}\cdot(\text{CH}_2)_2\cdot\text{CH}=\text{}$, and $=\text{CH}\cdot(\text{CH}_2)_2\cdot\text{COOH}$. These results agree fully with those obtained in a previous experiment of the ozonolysis of amyl clupanodionate.

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THE HIGHLY UNSATURATED ACIDS IN SARDINE OIL. XIV.
OXIDATION OF POTASSIUM CLUPANODONATE
WITH POTASSIUM PERMANGANATE IN
AQUEOUS SOLUTION.

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As described in the preceding report⁽¹⁾ of this series, the oxidation of methyl clupanodonate with potassium permanganate in acetone solution yielded propionic acid, acetic acid, succinic acid and methyl hydrogen succinate. Since acetic acid is believed to be formed by the secondary decomposition of malonic acid, the above results indicated that the respective groups jointed by the ethylenic linkings in clupanodonic acid consisted of $\text{CH}_3\cdot\text{CH}_2\cdot\text{CH}=\text{}$, $=\text{CH}\cdot\text{CH}_2\cdot\text{CH}=\text{}$, three of $=\text{CH}\cdot(\text{CH}_2)_2\cdot\text{CH}=\text{}$, and $=\text{CH}\cdot(\text{CH}_2)_2\cdot\text{COOH}$, and they agreed fully with the results derived from the ozonolysis of amyl clupanodonate in the 8th report⁽²⁾ of this series. The present paper deals with the results of the oxidation of potassium clupanodonate with potassium permanganate in aqueous solution. In the present experiment propionic acid, acetic acid and succinic acid were separated and identified from the oxidation products, and also the presence of malonic acid was indicated. Of these compounds acetic acid is considered to be formed by a further degradation of malonic acid which was formed primarily from the group $=\text{CH}\cdot\text{CH}_2\cdot\text{CH}=\text{}$. Accordingly the respective groups jointed by the ethylenic linkings in clupanodonic acid consist of $\text{CH}_3\cdot\text{CH}_2\cdot\text{CH}=\text{}$, $=\text{CH}\cdot\text{CH}_2\cdot\text{CH}=\text{}$, three of $=\text{CH}\cdot(\text{CH}_2)_2\cdot\text{CH}=\text{}$, and $=\text{CH}\cdot(\text{CH}_2)_2\cdot\text{COOH}$ assuming that the terminal group containing carboxyl group is $=\text{CH}\cdot(\text{CH}_2)_2\cdot\text{COOH}$. These results also agree fully with those derived from the ozonolysis of amyl clupanodonate and the permanganate oxidation of methyl clupanodonate in acetone.

Experimental.

1. Oxidation of Potassium Clupanodonate with Potassium Permanganate in Alkaline Aqueous Solution. Clupanodonic acid used in the present experiment is the same as that used in the previous experiment of ozonolysis, and had the following characteristics: d_4^{15} 0.9390, n_D^{15} 1.5035, neutr. value 170.4 (calc. 169.8), iodine value (Wijs) 383.2 (calc. 384.2).

(1) This Bulletin, **11** (1936), 745.

(2) This Bulletin, **10** (1935), 441.

Five grams of clupanodonic acid was mixed with 2 g. of potassium hydroxide and 500 c.c. of water giving a dilute alkaline solution of potassium clupanodonate. The solution was ice-cooled, and solutions of potassium permanganate were added gradually with constant stirring. Solutions of potassium permanganate consisted of 500 c.c. of a 2% solution, 400 c.c. of a 3% solution, 450 c.c. of a 4% solution and 400 c.c. of a 5% solution which were added successively in the course of 3 hours. After addition of the entire quantity of potassium permanganate, the solution was allowed to stand in an ice box for 17 hours, and then sulphur dioxide was passed through the solution in order to reduce the excess of potassium permanganate. The solution was then filtered with suction, and the precipitate of brown oxides of manganese was washed several times with hot water, using 300 c.c. each time. The filtrate and the washings were united, and after making the solution slightly alkaline, it was evaporated to dryness, and then acidulated with dilute sulphuric acid. The total volume of the solution was made up to about 100 c.c., and it was extracted with 5 l. of ether. The ether (a) was removed from ethereal solution by distillation, and there was obtained 7.3 g. of residue which was then extracted three times with petroleum ether using 100 c.c. each time. The petroleum ether solution and the insoluble portion (b) were separated. On distilling the petroleum ether solution, the distillate (c) boiling below 100° which consisted mainly of petroleum ether containing only a small proportion of other volatile substances was separated, and there remained 1.1 g. of residue (d).

2. **Oxidation Products Carried over with Solvents.** The ether (a) and the distillate (c) consisting largely of petroleum ether showed acidic reaction. These were shaken with potassium hydroxide solution, and the acidic substances were separated as the potassium salt solution. On acidification with sulphuric acid, the acidic substances were liberated, and after addition of a small amount of potassium permanganate, which oxidised sulphurous acid dissolved in the solution, it was distilled. The distillate amounted to 29 g. and had acid value 12.2, from which the acidic substances contained in the distillate is calculated to be 0.38 g. as acetic acid. The distillate was neutralised with alcoholic potash and refluxed with calculated amount of *p*-bromophenacyl bromide. The *p*-bromophenacyl ester formed was separated and recrystallised from 60% alcohol, giving crystals which melted at 84.5–85°, both alone and after admixture with a pure specimen of *p*-bromophenacyl ester of acetic acid.

3. **The Portion Soluble in Petroleum Ether.** The residue (d) obtained by removing the solvent from petroleum ether solution formed an orange yellow liquid. On distilling this portion the following two fractions were separated: (1) below 130°, 0.11 g.; (2) 130–140°, 0.22 g. The fraction (2) was converted into the *p*-bromophenacyl ester which on recrystallisation from 70% alcohol melted at 61.5–62°. The melting point was not lowered when the substance was admixed with *p*-bromophenacyl ester of propionic acid, m.p. 62.5–63°, in various proportions. The final residue from distillation was a dark brownish viscous liquid and appeared to contain intermediate oxidation products which escaped a complete oxidation. It was subjected to a further oxidation with an alkaline solution of potassium permanganate, and after acidification the product was taken up with ether. Removal of ether from ethereal solution left behind a mixture of crystalline solid and viscous liquid. The latter was removed by washing with a little cold ether, and there was obtained a crystalline solid which consisted of impure succinic acid melting at 178–179°.

4. **The Portion Insoluble in Petroleum Ether.** This portion (b) amounted to 5.8 g. It was washed with cold ether, and there remained 2.9 g. of crystalline solid (i). On removal of ether from the ethereal washing there remained a reddish orange liquid which was contaminated with a small proportion of crystalline solid and contained possibly substances of relatively high molecular weight which escaped a complete oxidation. For a further oxidation, it was oxidised by using 130 c.c. of an alkaline solution (5%) of potassium permanganate, and after treatment with sulphur dioxide, the product was taken up with ether. On removal of ether from ethereal solution there was obtained 2.6 g. of crystalline solid (ii) which was still contaminated with a small proportion of liquid substances. The crystalline solids (i) and (ii) were united and recrystallised from ethyl acetate, yielding succinic acid of neutr. value 950.1 (calc. 950.6) and m.p. 180-181°. On removal of ethyl acetate from the mother liquor from recrystallisation there remained a mixture of crystalline solid and viscous liquid, which was then extracted with a little water in which viscous liquid remained insoluble. The aqueous extract was saturated with sodium chloride and shaken with a large amount of ether. A crystalline substance was obtained after removal of ether from the ethereal solution. It had neutr. value 988.4 and decomposed when heated at 135°. On passing the volatile substances formed by the decomposition into a solution of barium hydroxide, it became turbid.

Summary.

Potassium clupanodotate has been oxidised with potassium permanganate in alkaline solution under cooling. Among the oxidation products, propionic, acetic and succinic acids have been separated. Also the presence of malonic acid is indicated. Of these compounds acetic acid is believed to be formed by a further degradation of malonic acid, and consequently the above results show that the respective groups jointed by the ethylenic linkings in clupanodonic acid are $\text{CH}_3\cdot\text{CH}_2\cdot\text{CH}=\text{}$, $=\text{CH}\cdot\text{CH}_2\cdot\text{CH}=\text{}$, three of $=\text{CH}\cdot(\text{CH}_2)_2\cdot\text{CH}=\text{}$, and $=\text{CH}\cdot(\text{CH}_2)_2\cdot\text{COOH}$, provided the terminal group containing the carboxyl group is assumed to be $=\text{CH}\cdot(\text{CH}_2)_2\cdot\text{COOH}$. The results of the present experiment agree fully with those obtained in the previous experiments of the ozonolysis of amyl clupanodotate and the permanganate oxidation of methyl clupanodotate in acetone solution.

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THE ADDITION OF HYDROGEN BROMIDE TO ALLYL BROMIDE
IN THE PRESENCE OF VARIOUS SUBSTANCES. II.
FURTHER EXPERIMENTS ON THE EFFECTS
OF FERRO-MAGNETIC CATALYSTS.

By Yoshiyuki URUSHIBARA and Matsuji TAKEBAYASHI.

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In the absence of oxygen and peroxides or in the presence of an anti-oxidant such as diphenylamine hydrogen bromide adds slowly to allyl bromide and the product consists mainly of 1,2-dibromopropane (the normal addition), while in the presence of oxygen or a peroxide such as benzoyl peroxide the addition is rapid and 1,3-dibromopropane is mainly produced (the abnormal addition).⁽¹⁾ As reported in the previous paper⁽²⁾ the authors found that the ferro-magnetic metals, iron and nickel, exert an influence similar to that of oxygen and peroxides on the addition of hydrogen bromide to allyl bromide, accelerating the abnormal addition. The experiments recorded in this paper have been carried out further to investigate the effects of ferro-magnetic substances on the addition of hydrogen bromide to allyl bromide. The experimental procedure and the conditions of addition were all the same as in the experiments recorded in the previous paper. The catalysts were heated at 250° in vacuum for an hour and then washed with pure hydrogen bromide gas. Each addition was carried out with 24 g. or 0.2 mol of allyl bromide and 20 g. or 0.25 mol of hydrogen bromide. The accompanying table shows the results of additions in the dark at room temperature in the absence of solvents and air, reaction time being three days.

Although, in the previous experiments on the effects of iron and nickel, peroxide-free allyl bromide was used and air was excluded, experiments were repeated with the addition of diphenylamine (0.5 g.), other conditions being unaltered. As shown in the table (experiments 1, 2, and 4), the results are quite similar to those obtained without the antioxidant (compare the table in the previous paper). Therefore, the effect observed in the experiments with the ferro-magnetic metals can be undoubtedly attributed to the metals, and the possibility of the participation of oxygen or peroxides which might have been present by any chance can be excluded.

(1) M.S. Kharasch and F.R. Mayo, *J. Am. Chem. Soc.*, **55** (1933), 2468.

(2) This Bulletin, **11** (1936), 692.

No. of exp.	Catalyst and amount added (g.)	Products				Remarks
		Yield (%)	Boiling point (°C./mm.)	Dibromo- propanes (%)		
				1,3-	1,2-	
1	Reduced iron 3.4	39	53-65/22	78	22	Diphenylamine 0.5 g. Shaken
2	„ „	33	48-62/18	71	29	Diphenylamine 0.5 g.
3	„ „	35	50-65/22	68	32	Magnetic field (5700 gausses) applied
4	Reduced nickel 3.5	32	45-58/16	58	42	Diphenylamine 0.5 g. Shaken
5	„ „	37	45-54/23	17	83	Nickel placed in air for 5 weeks after preparation Shaken
6	Reduced cobalt 3.5	42	38-43/16	7	93	Commercial cobalt Diphenylamine 0.5 g. Shaken
7	„ „	40	37-50/15	30	70	Freshly reduced cobalt Diphenylamine 0.5 g. Shaken
8	Iron-sand 4.6	47	45-48/24	12	88	Shaken
9	„ „	44	45-48/23	7	93	

All the additions recorded in the present and the previous papers took place in Pyrex glass tubes placed in a bomb-furnace or in an iron pipe, except experiment 3, where the Pyrex tube was placed in a magnetic field of about 5700 gauss, although the intensity of the field was far too small to expect any effect. The results are well within the range of the results obtained without the magnetic field.

If iron and nickel act as surface catalysts in the addition of hydrogen bromide to allyl bromide, their action must be governed by the conditions of the surface. In experiment 5, reduced nickel, which had been placed in air for five weeks after preparation and had taken a brown colour, was used. In this case, the effect of the metallic nickel on the direction of addition was far repressed. The good yield of the addition products may be attributed to the action of nickel oxide or bromide. In all other experiments with nickel the freshly reduced metal was used. In experiments with iron, the commercial reduced iron (Kahlbaum) was employed throughout. Thus it cannot be certain that the surface was clean from the oxide of iron. The oxide of iron would react with hydrogen bromide yielding ferric bromide. Ferric

chloride is known by Kharasch and Mayo to possess a tremendous accelerating effect upon the normal addition⁽³⁾. Therefore, if freshly reduced iron is used, effect of the metal may appear more conspicuous.

Cobalt was attacked by hydrogen bromide to a great extent, and a green solid substance was formed in the reaction mixtures, covering the metal. On this account, with commercial reduced cobalt (Kahlbaum) no effect (experiment 6), and even with freshly reduced cobalt but a slight effect (experiment 7), on the direction of addition were observed. The remarkable increasing effect on the yields of the products may be attributed to the action of the cobalt salt.

With a view to testing a strongly magnetic compound, iron-sand was used (experiments 8 and 9). The formation of a considerable amount of ferric bromide was shown by the intense brown colour of the reaction mixtures, and in accordance with it the yields of the reaction products were extremely increased without any marked influence on the composition of the products.

Further the authors have obtained some interesting results in the experiments with platinum black and oxygen or peroxides. The details will follow.

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(3) *Loc. cit.* see p. 2489.

THE FORMATION OF AN ISOMERIDE OF NEOERGOSTEROL BY THE PYROLYSIS OF ERGOPINACONE.

By Yoshiyuki URUSHIBARA and Toshio ANDO.

Received October 30th, 1936. Published November 28th, 1936.

Ergopinacone (14 g.) prepared from ergosterol (24 g.) according to the directions of H. H. Inhoffen⁽¹⁾ was subjected in portions of 1 g. to decomposition at 190° under the pressure of 0.15–0.25 mm. followed by the immediate distillation at 210–250° under 0.001–0.01 mm. Crystallization of the distillate from ethanol by adding water yielded crude neoergosterol (5.8 g.) melting at 129–134° (corr.). The crude neoergosterol (3 g.) was acetylated with acetic anhydride and the product was fractionally recrystallized from acetone. From the less soluble part pure neoergosteryl acetate (0.66 g.) was obtained in needles melting at 123.5–124° (corr.) (Found: C, 82.49, 81.90; H, 10.41, 10.36. Calculated for $C_{29}H_{42}O_2$: C, 82.41; H, 10.02%). Windaus⁽²⁾ and Inhoffen⁽¹⁾ give melting point 122–123°. From the more soluble part another substance (0.7 g.) forming fine prisms melting at 108–109° (corr.) was obtained. It gave the same analytical results as neoergosteryl acetate (Found: C, 82.33, 82.24; H, 9.96, 10.35. Calculated for $C_{29}H_{42}O_2$: C, 82.41; H, 10.02%). Its melting point did not rise on further recrystallization. The mixtures of this substance with neoergosteryl acetate melted at 105–108° (corr.) and at 106–115° (corr.) according as the portion of the latter was smaller and greater. Thus it was shown that the new substance is the acetate of an isomeride of neoergosterol, which the authors call "iso-neoergosterol." Hydrolysis of the acetate (100 mg.) melting at 108–109° with alcoholic potash and recrystallization of the product from methanol gave free iso-neoergosterol (58 mg.) in prisms melting at 138–139° (corr.) (Found: C, 84.63, 84.43; H, 10.47, 10.87. Calculated for $C_{27}H_{40}O$: C, 85.19; H, 10.60%).

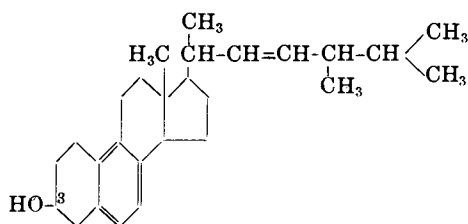
The crude neoergosterol (1 g.) was then recrystallized from ethanol. From the less soluble part pure neoergosterol (0.4 g.) was obtained, melting point 152–153° (corr.) (Found: C, 84.59, 84.65; H, 10.84, 11.06. Calculated for $C_{27}H_{40}O$: C, 85.19; H, 10.60%). Windaus and Inhoffen give melting point 151–152° (corr.). By the recrystallization of the more soluble part from methanol iso-neoergosterol (0.4) was obtained in prisms melting at 138–139°

(1) *Ann.*, **497** (1932), 130.

(2) Windaus and Borgeaud, *Ann.*, **460** (1928), 235.

(corr.) alone or in admixture with the specimen from the acetate (Found: C, 84.47; H, 10.99. Calculated for $C_{27}H_{40}O$: C, 85.19; H, 10.60%).

If iso-neoergosterol is demonstrated as the stereoisomeride of neoergosterol with regard to the carbon atom 3, it may be concluded that the carbon atom 3 takes part in the formation and the pyrolytic decomposition of ergopinacone and some light will be thrown on the yet unexplained chemical structure of the dimolecular derivative of ergosterol.



Neoergosterol

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STUDIES ON THE CONSTITUTION OF SHONANIC ACID, ONE
OF THE TWO CHARACTERISTIC VOLATILE ACIDS FROM
THE WOOD OF LIBOCEDRUS FORMOSANA, FLORIN.

I. THE ISOLATION OF SHONANIC ACID AND
ITS GENERAL PROPERTIES.

By Nobutoshi ICHIKAWA.

Received September 16th, 1936. Published December 28th, 1936.

Libocedrus formosana, Florin or "Shōnan-Boku" is a conifer indigenous to Formosa and its older growths are found along the northern part of the central mountain range at an altitude of 300–1200 m. above sea level. The heartwood is of somewhat light brown colour and bears a characteristic spicy odour and is highly resistant against the attack of the white ant, but as to the nature of its volatile constituents nothing had been known till Kinzō Kafuku and his collaborators studied the volatile oil of this wood from the standpoint of anti-white-ant materials. They distilled the wood chopped into small slices with steam and subsequently extracted the distillate with ether. The oil thus obtained had the following properties: d_{20}^{25} 1.0318; n_D^{25} 1.4956; $\alpha_D + 3.20^\circ$; acid value 295.8; ester value 5.4.

This oil was found to consist of 89% acidic, 6% phenolic, and 5% neutral, substances and the presence of a new acid of the formula $C_{10}H_{14}O_2$ melting at $103^\circ C$. was shown, but as to the nature of this acid nothing has been reported and the chemistry of the substance was left untouched for about 6 years ever since. The present author, with a view to studying the acid, extracted the sliced wood, about $3 \times 10 \times 15$ cm. in size, with a slight excess of sodium hydroxide solution and obtained a quantity of the material for examination. The yield of the volatile substances amounted nearly to 0.45% on the average and the product represented a reddish brown mobile fluid of the characteristic odour. The material was found to consist of 95% acidic and 5% phenolic substances and in the acidic portion there was shown the presence of at least three distinct crystalline substances, melting at $40-41^\circ$, $78-81^\circ$, and 103° , respectively.

The acid melting at 103° proved to be identical with the acid formerly obtained by Kafuku but its yield was not so rich as in the previous case. Thus the expectation of the present author to get a sufficient quantity of this acid for his investigation was not realized, but in its stead he could obtain a quantity of another acid melting at $40-41^\circ$, also an unknown substance of the

formula $C_{10}H_{14}O_2$, its amide melting at $116-117^\circ$ and anilide at $111-112^\circ$, respectively.

To this substance, which has never been described, the author gave the name "shonanic acid" and this paper deals with the chemistry of the new acid. The author, after a series of experiments, has at last succeeded in clearing up the structure of this acid, the detailed account of which will be reported in the following.

Shonanic acid $C_{10}H_{14}O_2$, when reduced catalytically with hydrogen and palladium on barium sulphate, absorbs 4 atoms of hydrogen giving rise to tetrahydroshonanic acid ($C_{10}H_{18}O_2$), but if alcohol and sodium (2 to 3 times of the required amount of sodium for the production of dihydroshonanic acid $C_{10}H_{16}O_2$ (1)) be used for reduction it gave dihydroshonanic acid $C_{10}H_{16}O_2$, showing that the two double bonds are conjugated. This dihydro-acid, on further reduction, can be transformed into tetrahydroshonanic acid $C_{10}H_{18}O_2$. The melting points of the amides of shonanic-, dihydroshonanic-, and tetrahydroshonanic acids are $116-117^\circ$, $130-131^\circ$, and $144-145^\circ$, respectively.

On consulting the literature, we find among the amides of saturated monocyclic acids of the formula $C_{10}H_{18}O_2$, dihydro- α -campholenic amide melting at $143-144^{(1)}$, which is very near that of tetrahydroshonanic amide.

In order to ascertain whether or not tetrahydroshonanic acid is identical with dihydro- α -campholenic acid, the latter was prepared from camphor (see the experimental part) and on examining the melting point of the mixture of their amides, it was found that they were quite different.

Although the formation of tetrahydroshonanic acid on catalytic reduction reveals the presence of two double bonds in shonanic acid, it absorbs but two atoms of bromine. This may be attributed to the conjugation of the two ethylene linkages, as seen from the behaviour of butadiene⁽²⁾, hexadiene-(2, 4)⁽³⁾, diphenyl-butadiene⁽⁴⁾, phellandrene⁽⁵⁾, sorbic acid⁽⁶⁾, cinnamylidene-malonic ester⁽⁷⁾, cinnamylidene-acetic acid⁽⁸⁾, crotonylidene-malonic ester⁽⁹⁾, and phenyl-cinnamenyl-acrylic acid⁽¹⁰⁾, which, though differing in the modes of addition, absorb only two atoms of bromine. The existence of the conjugated double bonds may further be confirmed by the molecular refraction of shonanic acid exhibiting an exaltation of +1.04. This is in accordance with the fact that the conjugation is consistently accompanied by an increase in refractivity.

(1) Mahla and Tiemann, *Ber.*, **33** (1900), 1931.

(2) Thiele, *Ann.*, **308** (1899), 339.

(3) Duden and Lemme, *Ber.*, **35** (1902), 1339.

(4) Straus, *Ber.*, **42** (1909), 2866.

(5) Semmler, *Ber.*, **36** (1903), 1753.

(6) (7) (8) (9) Houben, "Die Methoden der org. Chem.", Vol. II, 971.

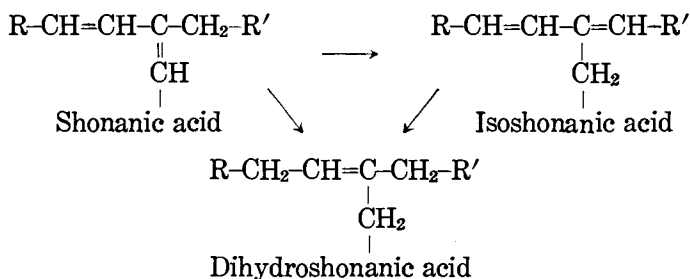
(10) Thiele and Rössner, *Ann.*, **306** (1899), 201.

Shonanic acid is isomerized to isoshonanic acid when heated with strong aqueous sodium hydroxide at about 110°C. Isoshonanic acid has the same formula $C_{10}H_{14}O_2$ as shonanic acid but melts at 45°C.

Though the melting point of iso-acid is near that of shonanic acid, they are distinctly different. Thus a mixture of both substances shows a depression of the melting point, and isoshonanic amide melts at 107–108° while shonanic amide at 116–117°, and, furthermore, isoshonanic acid can be recrystallized from 60% ethyl alcohol, while shonanic acid cannot.

Isoshonanic acid $C_{10}H_{14}O_2$, when reduced with sodium and ethyl alcohol, gives dihydroshonanic acid, while, if reduced catalytically, it absorbs 4 atoms of hydrogen to form tetrahydroshonanic acid. The isomeric change, therefore, should be regarded to be due to the shifting of the double bond and not to the change of ring system nor to the hydration at the double bond as in the cases of methylene-malonic acid⁽¹¹⁾, crotonic acid⁽¹²⁾, linolic acid⁽¹³⁾, and acrylic acid⁽¹⁴⁾. And it should also be noted that the isomerized acid boils higher by 13° than the original acid. Y. Fujita⁽¹⁵⁾, who arranged a number of examples of boiling points as regards isomeric substances with double bond at different positions, states that an elevation of 6–12° is observed only in the case of a shifting of the semicyclic double bond into the six-membered ring (table 4 of his report).

The presence of such a semicyclic double bond in the molecule of shonanic acid will be ascertained by further investigations. At any rate the relation between shonanic and isoshonanic acids, as regards their double bonds, may be represented as follows:



Thus to show the relation between shonanic, isoshonanic, dihydroshonanic, and tetrahydroshonanic acids:

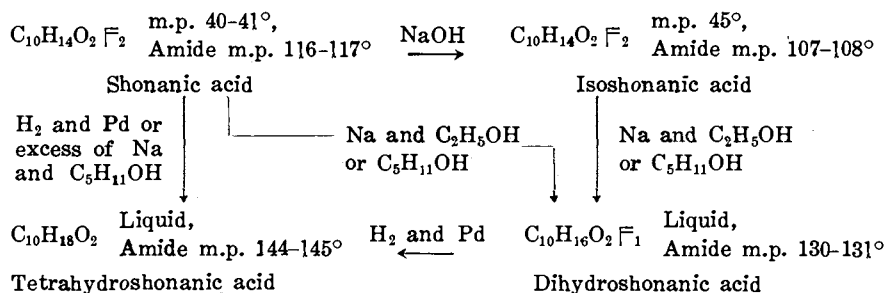
(11) Zelinsky, *Ber.*, **22** (1889), 3302.

(12) Stoemer and Stockmann, *Ber.*, **47** (1914), 1786.

(13) Schicht and Grün, D. R. P. 287660 (1915).

(14) Erlenmeyer, *Ann.*, **191** (1878), 281; Linnemann, *Ber.*, **8** (1875), 1095.

(15) Fujita, *J. Chem. Soc. Japan*, **52** (1931), 210.



Experimental.

I. **Extraction of Acids and Phenols from the Wood.** The wood chopped into small slices of about $10 \times 3 \times 15$ cm. in size was extracted with a slight excess of 5% sodium hydroxide solution for 3 days. The alkaline solution was decanted and the sliced wood washed thoroughly with water until reddish brown colour disappeared. The alkaline extract thus obtained was then acidified with dilute sulphuric acid when an insoluble organic matter separated which was extracted with ether and dried over anhydrous sodium sulphate. On distilling off the solvent there remained a tarry substance, which was then subjected to steam distillation to separate the volatile part from resinous matter.

The white, turbid distillate was neutralized with aqueous sodium carbonate and then the solution was concentrated to a smaller bulk and re-acidified to precipitate the acidic substance. The oily substance thus separated was taken in ether and then the ethereal solution was shaken with a solution of sodium bicarbonate to extract the organic acids free from phenolic substances.

This treatment was repeated twice when the yield of acidic and phenolic portions were as follows: wood taken 120 kg., acids 508 g. (0.42%), phenols 18 g. (0.015%). The acidic portion had the following properties: d_4^{30} 1.0450, n_D^{30} 1.4975, α_D^{22} -2.8° , acid value 306.8.

II. **Isolation of Shonanic Acid.** The acidic substance was fractionated 3 times under diminished pressure with Widmer's fractionating column and the fractions with the properties shown in Table 1 were obtained.

Table 1.

Fr. No.	B.p./6 mm.	n_D^{30}	d_4^{30}	α_D^{22}	Wt. (g.)	Wt. (%)
1	133-134	1.4905	1.0244	-2.72	74	14.92
2	134-135	1.4905	1.0233	-2.72	97	19.60
3	135-136	1.4912	1.0238	-3.56	92	18.55
4	136-137	1.4920	1.0244	-3.56	61	12.30
5	137-138	1.4935	1.0264	-4.20	36	7.25
6	138-139	1.4950	1.0290	-4.20	20	4.03

Table 1. (*Concluded*)

Fr. No.	B.p. /6 mm.	n_D^{30}	d^{30}	α_D^{22}	Wt. (g.)	Wt. (%)
7	139-140	1.4988	1.0320	-5.52	22	4.43
8	140-141	1.5011	1.0373	-5.80	18	3.69
9	141-142	1.5018	1.0371	-6.68	9	1.84
10	142-145	1.5085	1.0445	nil	9	1.84
11	145-148	1.5170	1.0577	-3.80	20	4.03
12	148-149	1.5179	1.0577	nil	11	2.22
13	149-152	1.5205	1.0645	nil	9	1.82
14	152-154/5mm.	1.5205	1.0797	+3.60	12	2.42
Residue					6	1.21

Fractions 1, 2 and 3, on standing at room temperature, deposited a small quantity of crystals and on shaking the vessel the whole of the contents coalesced at once into a crystalline mass. By nucleating fractions 4 and 5 with the crystals, they partly crystallized but fractions 6, 7, 8, and 9 remained liquid, while nearly half of fractions 10 and 11 were found to crystallize. From the residue of distillation some crystalline substance was obtained, the addition of which to fractions 14 and 13 resulted in partial solidification of both. The crystalline substances were then separated from the fluid ones by filtration (Table 2).

Table 2.

Fractions	Cryst. subst. (g.)	Liquid subst. (g.)
1-4	300	22
5	8	25
6-9	—	69
10-12	28	12
13	2	6
14 and residue	13	—

The crystalline substance from fractions 1-4 and 5 melted at 39-41° after repeated recrystallization from petroleum ether (b.p. 40-50°), while crystals from fractions 10-12 showed a melting point 78-81° after one recrystallization from 60% ethyl alcohol. The crystals from fraction 14 and from the residue were recrystallized twice from 85% ethyl alcohol when it showed a melting point

103°. The liquid portion from 1-4, 5, 6-9, 10-12, and 13 were separately fractionated once again and fractions boiling at 136-138°/6 mm. and 138-141°/6 mm. were obtained.

The former solidified to a crystalline mass melting at 40-41°, while the latter remained liquid. In this way the acidic substance was finally separated into four distinct portions shown in Table 3.

Table 3.

Portions	Wt. (g.)	Acid value	Bromine value	Ag % in Ag-salt	Proposed name
1 (m.p. 40-41°)	325	336.8	960.3	39.52	shonanic acid
2 (b.p. 139-141°/7mm.)	98	332.8	932.2	39.58	—
3 (m.p. 78-81°)	18	336.2	930.8	38.85	—
4 (m.p. 103°)	8	336.2	948.7	38.62	—

III. **The Properties of Shonanic acid.** Physical properties of the acid: b.p. 264°/754 mm., 134-134.5°/6 mm.; m.p. 40-41°; d_4^{46} 1.016; n_D^{46} 1.4842; $[\alpha]_D^{28}$ -0.75°; M.R. obs. as $C_{10}H_{14}O_2$ (n^2 -formula) 47.82, calc. for $C_{10}H_{14}O_2 F_2$ 46.78, exallation +1.04; acid value 336.8, calc. for $C_{10}H_{14}O_2$ 337.3; $[\alpha]_D^{18}$ -0.75° in alcohol (mean of 4 observations). (Found: C, 72.05, 72.40; H, 8.62, 8.47. Calculated for $C_{10}H_{14}O_2$: C, 72.3; H, 8.4%.)

The basicity of the acid was determined by the electrolytic conductivity method. The difference of the equivalent conductivities of N/32 and N/1024 sodium salt solutions was found 10×1.09 . From the value 1.09 shonanic acid must be monobasic.

The molecular formula was determined by analysis of silver shononate. The silver salt was prepared in the ordinary way which represented a white amorphous powder. It was dried in vacuo at 100°C. and then a weighed quantity was calcined (Found: Ag, 39.58, 39.55%). The results are in good accord with the supposed molecular formula $C_{10}H_{14}O_2$ for shonanic acid.

The theoretical values calculated for this formula agree completely with the corresponding experimental data except molecular refraction.

To determine the number of the double bond, 11.008 g. of sample dissolved in 50 c.c. absolute alcohol was catalytically hydrogenated at ordinary temperature with palladium on barium sulphate as catalyser and it was proved that the substance contains two double bonds in its molecule: H_2 gas absorbed, 3385 c.c. (30°C. 753.3 mm.) or 2895 c.c. (0°C., 760 mm.); calc. for $C_{10}H_{14}O_2 F_2$, 2970 c.c. (0°C., 769 mm.). Sample (0.2157 g.) absorbed 0.2019 g. bromine, while $C_{10}H_{14}O_2 F_2$ requires 0.4158 g. The amount of bromine absorbed corresponds to 1/2 of the theoretical, namely the acid absorbed only 2 atoms of bromine.

IV. **Some Derivatives of Shonanic Acid.** (1) *Acid Chloride.* The acid chloride was prepared as usual by heating a mixture of the acid and phosphorous trichloride. The product obtained was a colourless mobile fluid with a characteristic odour. The physical properties were as follows: b.p. 106-107°/20 mm., 215°/760 mm.; d_4^{20} 1.0577; n_D^{20} 1.4955.

(2) *Amide.* The amide was prepared by adding the acid chloride to cold concentrated aqueous ammonia. The amide obtained was collected, washed with cold water, and recrystallized from 50% ethyl alcohol. It melted at 116-117°C. By adding water to the filtrate another crop of the amide was obtained. (Found: N, 8.44, 8.32. Calc. for $C_{10}H_{16}ON$: N, 8.48%.)

(3) *Anilide*. The anilide was obtained by the interaction of aniline and the acid chloride in the cold. It melted at 111-112° after a recrystallization from 60% methyl alcohol. By further purification the melting point was not raised. (Found: N, 5.70. Calc. for $C_{10}H_{19}ON$: N, 5.8%.)

(4) *Methyl Ester*. The methyl ester was obtained by gentle heating of a mixture of methyl alcohol and the acid chloride on the water bath. The reaction product was poured into water when an oily substance separated out which was extracted with ether. The ethereal solution was washed with water, dried over anhydrous sodium sulphate, and then ether was distilled off. The remainder distilled at 113-114° under 20 mm. and showed the following properties: b.p. 222°/760 mm., 113-114°/20 mm.; n_D^{20} 1.4758; d_4^{20} 0.9848; α_D^{25} -2.84°; sap. value 313.1, calc. for $C_{11}H_{16}O_2$ 311.1.

(5) *Ethyl Ester*. The ethyl ester was prepared by heating a mixture of the acid (10 g.) with an excess of absolute alcohol containing 2.5% HCl on the boiling water bath for an hour. The reaction product, after distilling off the excess of ethyl alcohol, was dissolved in ether and the ethereal solution was shaken with water and sodium bicarbonate solution in order to remove traces of alcohol and acidic substances present and then fractionally distilled under diminished pressure. The amount of ethyl ester obtained was 9.3 g.; b.p. 228-229°/759 mm., 106-108°/7 mm.; d_4^{20} 0.9568; n_D^{20} 1.4674; α_D^{18} -4.24°; bromine value, 0.2739 g. absorbs 0.221 g. of bromine, $C_{12}H_{18}O_2$ requires 0.225 g.

(6) *Dihydroshonanic Acid*. Shonanic acid (15 g.) was dissolved in 150 c.c. of ethyl alcohol and 10 g. of metallic sodium (2.5 times of the theoretical amount) was added in small portions. The acidic product was isolated from the reaction product in the usual way and then distilled under reduced pressure. The rectified product showed the following properties: b.p. 142-143.5°/7 mm.; d_4^{20} 1.0333; n_D^{20} 1.4985; M. R. obs. 47.69, calc. for $C_{10}H_{16}O_2$ F_1 47.35; bromine value 879 (0.1131 g. absorbs 0.0995 g. of bromine), calc. for $C_{10}H_{16}O_2$ F_1 952. (Found: C, 71.47, 71.17; H, 9.31, 9.56. Calculated for $C_{10}H_{16}O_2$: C, 71.4; H, 9.5%. Analysis of the silver salt: Ag, 39.24, 39.37. Calculated for $C_{10}H_{16}O_2Ag$: Ag, 39.24%.)

The amide prepared by the interaction of aqueous ammonia and the acid chloride (b.p. 98.5°/16 mm., prepared as usual by using 1 g. PCl_3 for 1 g. acid) melted at 121-128° without any purification. The purified amide after twofold recrystallization from 20% ethyl alcohol, melted at 129-130°C.

(7) *Catalytic Hydrogenation of Dihydroshonanic Acid*. In order to determine the number of double bonds in the molecule of dihydroshonanic acid, it was hydrogenated catalytically with hydrogen and palladium and it was found to contain only one double bond: 2.32 g. of substance absorbed 359.0 c.c. (28°C., 758.0 mm.) or 312.6 c.c. (0°C., 760 mm.) of H_2 , $C_{10}H_{16}O_2$ F_2 requires 309.3 c.c. Physical properties of the hydrogenated acid (tetrahydroshonanic acid): b.p. 142-143°/7 mm.; d_4^{20} 0.9929; n_D^{20} 1.4704; M. R. obs. 47.73, calc. for $C_{10}H_{18}O_2$ 47.72; bromine value nil.

The amide was prepared from the acid chloride (b.p. 117°/20 mm.) and aqueous ammonia. It melted at 144°C. after one recrystallization from 60% ethyl alcohol and was proved to be identical by melting in admixture with the amide of tetrahydroshonanic acid obtained by catalytic hydrogenation of shonanic acid (see below).

(8) *Catalytic Reduction of Shonanic Acid*. Tetrahydroshonanic acid, the saturated acid, obtained by hydrogenation of shonanic acid with hydrogen and palladium on barium

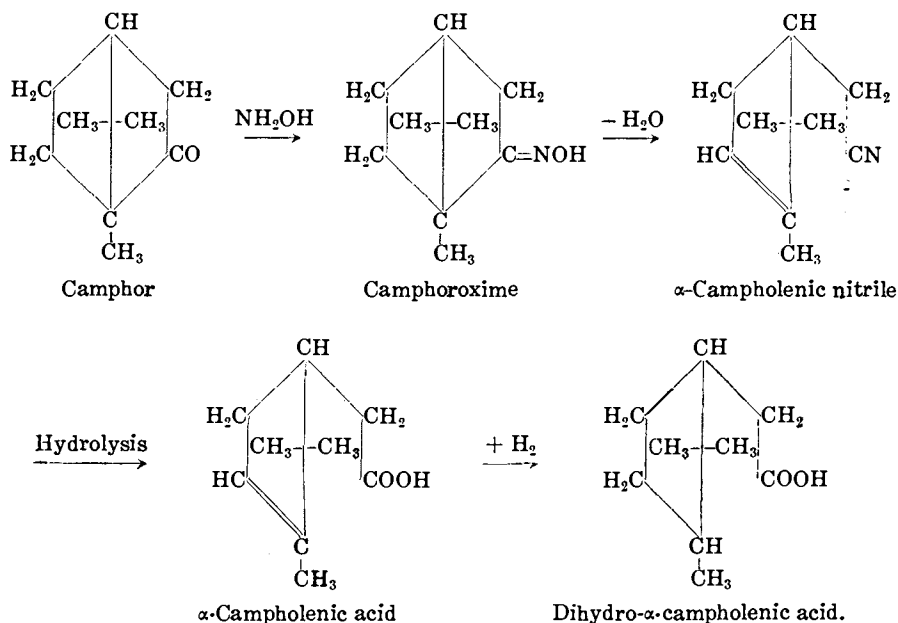
sulphate showed the properties: b.p. 140–141°/8 mm.; d_4^{27} 0.9950; n_D^{27} 1.4690; M.R. obs. 47.58, calc. for $C_{10}H_{18}O_2$ 47.72; bromine value nil. Analysis of the silver salt: Ag, 39.00. 39.02. Calculated for $C_{10}H_{17}O_2Ag$: 38.96%.

The acid was resistant against dilute permanganate solution in the cold showing that the substance was a saturated acid; this may also be recognized by the fact that the bromine value of the acid was proved to be nil as already mentioned.

The acid chloride prepared as usual by warming a mixture of the acid and phosphorous trichloride had the following properties: b.p. 115°/19 mm.; d_4^{30} 1.014; n_D^{30} 1.4704; M.R. obs. 51.64, calc. for $C_{10}H_{17}OCl$ 51.05.

The amide prepared from the acid chloride and aqueous ammonia was plates with pearly lustre and melted at 143° after once recrystallized from ethyl alcohol (Found: N, 8.31. Calculated for $C_{10}H_{19}ON$: N, 8.28%).

Among the known acids of formula $C_{10}H_{18}O_2$, we find dihydro- α -campholenic acid, the amide of which melts at 143–144°C. In order to ascertain whether or not tetrahydroshonanic acid is identical with dihydro- α -campholenic acid, the latter was prepared from camphor as shown below:



Camphoroxime was prepared according to the method described by Auwers⁽¹⁶⁾, m.p. 118–120°. α -Campholenic nitrile was prepared by dehydration of camphoroxime with 25% H_2SO_4 ⁽¹⁷⁾. The product being the mixture of α - and β -campholenic nitriles, was fractionally distilled 3 times under reduced pressure and the two following main fractions were obtained. Fraction 1: b.p. 220–225°; d_4^{30} 0.9063; n_D^{30} 1.4700; yield 20% of the product

(16) Auwers, *Ber.*, **22** (1889), 605.

(17) Tiemann, *Ber.*, **28** (1895), 1083.

(Found: N, 9.60. Calc. for $C_{10}H_{15}ON$: N, 9.4%). Fraction 2: b.p. 225–227°; d_4^{30} 0.9122; n_D^{30} 1.4648; yield 60% of the product (Found: N, 9.51. Calc. for $C_{10}H_{15}ON$: N, 9.4%).

Fraction 1 was found to represent β -campholenic nitrile by preparing β -campholenic amide melting at 84–86.5°⁽¹⁸⁾. The amide from fraction 2 showed melting point 124–125° agreeing with that of α -campholenic amide (m.p. 125°)⁽¹⁹⁾, $[\alpha]_D^{25} = -3.6^\circ$.

Fraction 2 was treated according to Wallach⁽²⁰⁾ with an excess of alcoholic potash and the product was fractionally distilled under ordinary pressure. Fraction (1): b.p. 224–249°; d_4^{30} 0.9766; n_D^{30} 1.4606; yield 18%. Fraction (2): b.p. 253–255°; d_4^{30} 0.9973; n_D^{30} 1.4664; yield 68%. The boiling point, density, and refractive index of fraction (2) correspond with those of α -campholenic acid (b.p. 256°, d 0.9920, n_D 1.4712)⁽²¹⁾ (Found: C, 71.23; H, 9.62. Calculated for $C_{10}H_{16}O_2$: C, 71.4; H, 9.5%). Although fraction (1) had the boiling point of β -campholenic acid (b.p. 247–248°), it showed no tendency of solidification probably owing to the presence of impurity such as campholene, the by-product produced by distillation of α - and β -campholenic acids.

Fraction (2) was dissolved in absolute alcohol, and hydrogenated catalytically with hydrogen and palladium on barium sulphate. 10.10 g. absorbed 1528 c.c. (30°, 753.6 mm.) or 1308 c.c. (0°, 760 mm.) H_2 . $C_{10}H_{16}O_2$ $\bar{F}_1$ requires 1348 c.c.

The acid here obtained, being saturated, does not absorb bromine and is stable to permanganate in the cold. The properties of the product were as follows: b.p. 259–261°/762 mm., 154–155/19 mm.; d_4^{27} 0.9736; n_D^{27} 1.4578; $\alpha_D^{27} +10.75^\circ$; acid value 331.0. Analysis of the silver salt: Ag, 38.94. Calc. for $C_{10}H_{17}O_2Ag$: 38.96%. The amide prepared from this acid in the usual way showed melting point 143–145°. On examining the melting point of a mixture of amides of tetrahydroshonanic and dihydro- α -campholenic acids, it softened at about 118° and melted at 139°, showing a depression of 6°. Thus it follows that they should be quite different substances. Tetrahydroshonanic acid ($C_{10}H_{18}O_2$), therefore, is a new substance.

V. Preparation of Isoшонanic Acid. Shonanic acid (5 g.) and 20 g. of 50% NaOH solution were heated to gentle boiling for about 4 hours, and then the product was fractionated under reduced pressure. The fraction distilling at 151–152°/7 mm. (b.p. 277–278°/756 mm.) solidified on cooling, and after recrystallization from 60% ethyl alcohol the substance melted at 45–46°, and in admixture with shonanic acid (m.p. 40–41°) melted at once, showing that they are quite different substances. Other evidence supporting this view are: shonanic acid cannot be recrystallized from 60% ethyl alcohol while iso-shonanic acid can be, and that the melting points of the amides are different, viz. 117° and 107°. Found: bromine value, 957. Calc. for $C_{10}H_{14}O_2$ $\bar{F}_2$: 963. Found: acid value, 335. Calc. for $C_{10}H_{14}O_2$: 337. Analysis of the silver salt: Ag, 39.41. Calc. for $C_{10}H_{13}O_2Ag$: Ag, 39.53%.

Acid Chloride. Obtained from 2 g. of the acid and 1.6 g. of PCl_3 . B.p. 107–108°/20 mm. n_D^{19} 1.5077.

(18) Tiemann, *Ber.*, **30** (1897), 245.

(19) Nägeli, *Ber.*, **17** (1884), 2071.

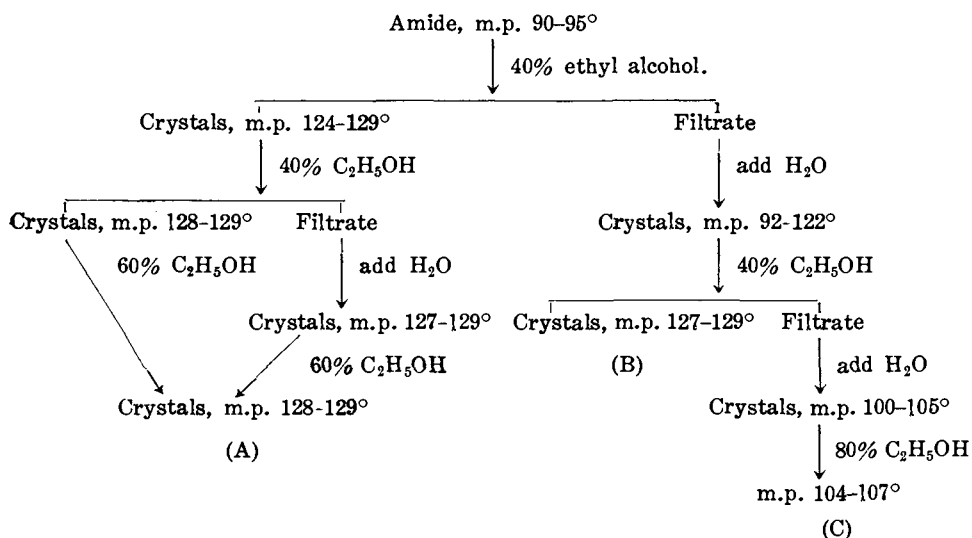
(20) Wallach, *Ann.*, 269 (1892), 336.

(21) Wallach, *Ann.*, **269** (1892), 338.

Amide. Prepared from acid chloride and aqueous ammonia. It melted at 102–106° without any purification, and at 107–108° after recrystallization from alcohol, the melting point rising no more on further purification. A mixture of shonanic amide (m.p. 116–117°) and this amide melted at 88–98°, showing that they are quite different substances.

VI. Preparation of Dihydroshonanic Acid from Isoshonanic Acid. Isoshonanic acid (3 g.) was dissolved in 100 c.c. of ethyl alcohol and reduced with 3 g. of metallic sodium. The product obtained showed the following properties: b.p. 144–148°/8 mm.; d_4^{20} 1.0290; n_D^{20} 1.4980; M.R. obs. 47.86, calc. for $C_{10}H_{16}O_2$ $\bar{F}_1$ 47.35; bromine value 943 (0.1379 g. absorbs 0.1300 g. Br), calc. for $C_{10}H_{16}O_2$ $\bar{F}_1$ 952.

Amide. The amide prepared from the acid chloride (b.p. 114/21 mm., d_4^{20} 1.0547, n_D^{20} 1.5002) and aqueous ammonia, melted at 90–95°, which was fractionally recrystallized as follows:



Crystals (A) and (B) were found to be dihydroshonanic amide by examination of the melting points of various mixtures, while crystals (C) was proved to be crude isoshonanic amide.

Summary.

(1) The existence of an unknown acid in the volatile part from the wood of *Libocedrus formosana*, Florin, or "Shōnan-Boku" is reported.

(2) Shonanic acid is an unsaturated monobasic acid with a monocyclic structure of the formula $C_{10}H_{14}O_2$, melting at 40–41°. Its amide melts at 116–117° and the anilide at 111–112°.

(3) Shonanic acid can be converted into tetrahydroshonanic acid by absorption of four atoms of hydrogen when reduced catalytically, while it absorbs only two atoms of bromine, and when reduced with sodium and ethyl alcohol an unsaturated acid, viz. dihydroshonanic acid ($C_{10}H_{16}O_2$), is obtained. These experimental facts together with the fact that the molecular refraction of shonanic acid exhibits an eminent exaltation lead to the conclusion that conjugated double bonds exist in its molecule.

(4) Though tetrahydroshonanic amide melts at 144° , it was proved that the acid is quite different from dihydro- α -campholenic acid ($C_{10}H_{18}O_2$, amide m.p. 144°).

(5) Shonanic acid isomerizes to isoshonanic acid by the action of hot strong alkali solution. Iso-acid melts at 45° and gives an amide melting at $107-108^\circ$.

(6) The isomerisation of shonanic acid to isoshonanic acid is accompanied by the elevation of the boiling point to the extent of $13^\circ C$. This phenomenon may probably be due to the migration of semicyclic double bond into the ring system of the acid, which must be ascertained by further investigations.

Thanks are due to Dr. Kinzô Kafuku for the helpful interest he has taken in this work.

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ÜBER DIE FARBSTOFFE DES GOLDRÖSCHENS, KERRIA JAPONICA, DC.

Von Takeo ITO, Harusada SUGINOME, Kiyoshi UENO
und Shigeto WATANABE.

Eingegangen am 24. Oktober 1936. Ausgegeben am 28. Dezember 1936.

Die Blüten des Goldröschens, *Kerria japonica*, DC., das in Japan einheimisch und in Gärten als Zierstrauch angepflanzt ist, zuweilen auch verwildert vorkommt, enthalten bekanntlich schönen, goldgelben Farbstoff. Dieser ist seit alten Zeiten in Japan ein typischer Farbtön gewesen. Obwohl schon früher Botaniker⁽¹⁾ diesen Farbstoff behandelten und zeigten, dass er ein Carotinoidfarbstoff sei, ist dessen Isolierung bisher noch nicht gelungen.

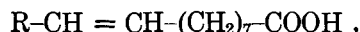
Nach Beschaffung einer ziemlich grossen Menge Ausgangsmaterials (17.6 kg. nach dem Trocknen bei 40°) haben wir neben Anthoxanthin den Hauptfarbstoff der Blüte in krystallisiertem Zustand isoliert. Es ist ein Farbwachs vom Schmelzpunkt 88–89°, das mit Helenien sowohl spektroskopisch als auch durch Mischprobe mit dem reinen, synthetischen völlig übereinzustimmen scheint. Verseift man das Farbwachs mit alkoholischem Kali, so entstehen Lutein und Fettsäure. Das Lutein ist ganz rein und schmilzt ohne weiteres bei 193–194° (korr.). Dagegen ist die Fettsäure unrein und schmilzt bei 47–48°. Der Schmelzpunkt lässt sich auch durch wiederholtes Umkrystallisieren nicht über 58° steigern. Bei kurzem Behandeln der Fettsäure mit Ozon erhielt man eine Säure vom Schmelzpunkt 61–62°, die als Palmitinsäure identifiziert werden kann. Verseift man dann das synthetische Helenien unter denselben Bedingungen wie beim natürlichen, so entstehen reines Lutein und reine Palmitinsäure, schmelzend bei 61–62°. Bei Anwendung der Blei-Alkohol-Methode auf die durch Verseifung erhaltene Fettsäure wurde die Palmitinsäure von der flüssigen Säure, die die Erniedrigung des Schmelzpunkts verursacht, befreit. Die letztere wurde dann in das Säureamid, schmelzend bei 75°, übergeführt und als Ölsäureamid identifiziert. Daraus folgt, dass das Farbwachs aus Blüten des Goldröschens neben dem Helenien, Luteindipalmitat, den Luteinester des Ölsäure enthält.

Überblickt man die Literatur über das Farbwachs, so entsteht der bestimmte Eindruck, dass Zeaxanthin und Lutein neben Palmitinsäure noch mit

(1) T. Tammes, *Flora*, **87** (1900), 205; A. Tschirch, *Ber. deut. botan. Ges.*, **22** (1904), 414; F. G. Kohl, *ibid.*, **24** (1906), 129, 222; van Wisselingh, *Flora*, **107** (1915), 371.

anderen Fettsäuren verestert sind. Kuhn⁽²⁾ und Zechmeister⁽³⁾ haben mit ihren Mitarbeitern gleichzeitig und unabhängig voneinander chemischpräparative Beweise dafür erbracht, dass Polyenalkohole sehr häufig mit Fettsäure verestert sind. Zunächst wurde gezeigt, dass das Physalien $C_{72}H_{116}O_4$ der Judenkirsche und des Bocksorns Dipalmitat des Zeaxanthins ist. Nachher haben Kuhn und Winterstein⁽⁴⁾ noch ein zweites Farbwachs, Helenien, Dipalmitat des Luteins, aus Blüten von *Helenium autumnale*, L. isoliert. Diesen Verfassern nach schmilzt das Helenien bei 92° . Aber darüber gibt es keine ausführliche Beschreibung. Ausser diesem liegen ziemlich viele Angaben⁽⁵⁾ über Farbwachse vor. Bemerkenswert ist, dass Kuhn und seine Mitarbeiter⁽⁶⁾ aus Blüten von *Tagetes gandifolium*, L. ein bei $84-85^\circ$ schmelzendes Farbwachs hergestellt haben. Diese Verfasser nahmen es als Helenien an, über Verunreinigungen war nichts angegeben. Sie haben durch Hydrolyse des Wachses niedrig schmelzende (50°) Palmitinsäure erhalten, und geschlossen, dass in der Tagetesblüte noch andere Fettsäuren vorkommen können und das Lutein sich vorzugsweise mit der Palmitinsäure zu verestern scheint.

Bei Ozonisierung von umkrystallisiertem Physalien erhielten Karrer und Pieper⁽⁷⁾ etwas Azelainsäure. Daraus schlossen sie, dass Physalien neben dem Zeaxanthindipalmitat den Zeaxanthinester einer Säure,



vermutlich Ölsäure, enthält.

Durch die Klärung der soeben angeführten Tatsachen ist das gemeinsame Vorkommen von verschiedenen Wachsen verständlicher geworden und das sogenannte Farbwachs ist in chemischer Beziehung nichts anders als das gewöhnliche Wachs. Demgemäss ist zu erwarten, dass verschiedene Wachse die durch Veresterung der Polyenalkohole mit Stearinsäure, Linolensäure usw., aber nicht mit Palmitinsäure, entstehen, in der Natur vorkommen werden.

Trotz wiederholter Umkrystallisation konnten wir ölsäurefreies Farbwachs nicht erhalten. Die Zerlegung des Farbwachsgemisches in seinen Komponenten wurde zuletzt durch Adsorption aus Benzin in einer Säule von

(2) R. Kuhn, A. Winterstein und W. Kaufmann, *Naturwissenschaften*, **18** (1930), 418; *Ber.*, **63** (1930), 1489.

(3) L. Zechmeister und L. v. Cholnoky, *Ann.*, **481** (1930), 42.

(4) R. Kuhn und A. Winterstein, *Naturwissenschaften*, **18** (1930), 754.

(5) R. Kuhn und A. Winterstein, *Ber.*, **64** (1931), 326; P. Karrer und H. Salomon, *Helv. Chim. Acta*, **13** (1930), 1063; R. Kuhn und E. Lederer, *Z. physiol. Chem.*, **200** (1931), 108.

(6) R. Kuhn, A. Winterstein, und E. Lederer, *Z. physiol. Chem.*, **197** (1931), 150.

(7) P. Karrer und B. Pieper, *Helv. Chim. Acta*, **14** (1931), 838.

Magnesiumoxyd ausprobiert. Dabei wurde eine kleine Menge von fremdem Farbstoff in der oberen Schicht zurückgehalten, das Farbwachs bildete in der unteren Schicht einen zweiten Farbring. Durch wiederholtes Nachgiessen von Benzin liess sich der Ring ausbreiten, aber er blieb einbändig. Unter denselben Bedingungen wurde die Fraktionierung durch Adsorption wiederholt. Dabei blieb das Wachs immer noch einbändig in der oberen Schicht zurück und nur eine untergeordnete Menge eines Nebenfarbstoffs, vielleicht Taraxanthin, verblieb in der unteren Schicht. Trotz vieler Bemühungen ist es nicht gelungen, weder das natürliche Farbwachsgemisch noch das künstliche durch chromatographische Analyse in Luteindipalmitat und Luteinölsäureester zu zerlegen.

Wenn man folglich die Reinheit eines Farbwachses prüfen will, so ist es nötig, dieselbe durch die bei der Verseifung entstandene Fettsäure zu prüfen.

Den grössten Teil der Blüten haben uns der Botanische Garten der Universität, Stadtleute aus Sapporo und zum Teil Dr. T. Hayashi, überlassen, denen wir an dieser Stelle nochmals bestens danken. Ebenso sind wir Hrn. Prof. T. Minoshima für die Überlassung eines Spektrographen zu aufrichtigem Dank verpflichtet.

Beschreibung der Versuche.

I. *Darstellung des Farbwachses aus Blüten.* Die Blüten, die von Stengel und Kelchen befreit und getrocknet waren, wurden fein vermahlen; 44.9 kg. frisches Ausgangsmaterial (127,000 Blüten) lieferten 6.85 kg. Trockenpulver. Man hat je 1000 g. davon mit Aceton bei Zimmertemperatur unter Stickstoff zweimal extrahiert. Die Auszüge (ca. 10 l.) wurden unter vermindertem Druck bei 40–50° eingeeengt. Nach vollständiger Entfernung des Lösungsmittels wurde das zurückbleibende rotbraune Öl mit Benzol behandelt und die unlöslichen Substanzen abgelassen. Die Lösung wurde unter vermindertem Druck zu 100 ml. eingedampft und langsam, unter Umrühren, mit 1000 ml. 95 proz. Alkohol versetzt, wobei das Farbwachs sich in einem rotbraunen, amorphen Zustand ausscheidet. Ausbeute 4–5 g. Das rohe Farbwachs wurde nochmals in 25–30 ml. Benzol gelöst und mit absolutem Alkohol gefällt, abgesaugt, dann mit demselben Lösungsmittel, nachdem es vorher je auf 30°, 40°, 50°, 60°, und 70° erwärmt war, gewaschen. Ausbeute 3.0–3.2 g.; Schmp. 85–86°. Das Präparat ist frei von farblosen Substanzen. Nach sechsmaliger Umkrystallisation aus Benzol-Alkohol wurde das Farbwachs zuletzt in Petroläther (Sdp. 40–60°) gelöst und mit absolutem Alkohol versetzt. Dabei scheidet sich der Farbstoff auf der Wand des Kolbens aus. Reibt man den amorphen Farbstoff mit dem Glasstab, so wandelt er sich in metallglänzende Krystalle um: Ausbeute 0.20 g.; Schmp. 88–89°. Die Substanz wurde bei 40–50° über P_2O_5 im Vakuum getrocknet und analysiert. (Gef.: C, 82.37; H, 11.15. Ber. für $C_{72}H_{116}O_4$: C, 82.68; H, 11.19%.)

Verseifung des Farbwachses. Eine Lösung von 0.15 g. Farbwachs, wie oben hergestellt, in 0.8 ml. Petroläther (Sdp. 40–60°) wurde mit 4.5 ml. 5-proz. äthylalkoholischem Kali über Nacht bei 30–35° unter Stickstoff stehen gelassen. Nach Zusatz einer grösseren Menge Wasser scheidet sich Lutein in orangerotfarbigem, krystallinischem Zustand aus;

es wird abgesaugt und mit Wasser gewaschen. Ausbeute 0.08 g.; es schmilzt ohne weiteres bei 193–194° (korr.). Das Lutein ist ganz rein und frei von farblosen Substanzen. Die Mutterlauge wurde, um das letzte Lutein zu entfernen, mit Äther behandelt. Nach dem Ansäuern mit Essigsäure extrahiert man die entstandene Fettsäure mit Äther. Die Säure war etwas gefärbt und fest, aber vermischte mit öligen Substanzen. Ausbeute 0.07 g. Nach der Umkrystallisation oder Destillation im Vakuum schmilzt die Säure konstant bei 58°. Diese wurde mit Thionylchlorid behandelt und das entstandene Säurechlorid mit Tribromanilin kondensiert. Das gereinigte Tribromanilid schmilzt bei 113–116°. Bei der Vermischung des Tribromanilids mit aus reiner Palmitinsäure hergestelltem, schmelzend bei 124°, beträgt der Schmp. 117–121°.

Synthese des Heleniens. Das Helenien wurde von Kuhn und Winterstein⁽⁸⁾ aus *Helennium autumnale*, L. zuerst isoliert, aber es scheint noch nicht synthetisiert zu sein⁽⁹⁾. 0.2 g. chromatographisch gereinigtes Lutein wurden in 4 ml. Pyridin gelöst und mit 0.8 g. Palmitinsäurechlorid versetzt. Nach 30 Minuten wurde das Reaktionsgemisch auf 50° für 30 Minuten erwärmt, und für weitere 30 Minuten bei Zimmertemperatur stehen gelassen. Beim Eingiessen des Reaktionsgemisches in eine grosse Menge Methanol scheidet sich das Farbwachs ab. Dies war in Äther aufgenommen, mit Bicarbonat gewaschen und zuletzt aus Chloroform-Alkohol umkrystallisiert worden. Ausbeute 0.31 g.; Schmp. 89°. (Gef.: C, 82.43; H, 11.12. Ber. für $C_{72}H_{116}O_4$: C, 82.68; H, 11.19%.) Bei der Vermischung des künstlichen Heleniens mit dem aus den Blüten des Goldröschens isolierten Farbwachs zeigt sich keine Depression; es schmilzt bei 88–89°.

Durch weitere Umkrystallisation aus Chloroform-Alkohol, Benzol-Alkohol oder Petroläther-Alkohol, konnten wir den Schmelzpunkt des künstlichen Heleniens über 88–89° steigern. Verseift man das synthetische Helenien, so entsteht reine, bei 61–62° schmelzende Palmitinsäure.

II. Trennung der Ölsäure von den aus Farbwachs erhaltenen Fettsäuren. Durch die Verseifung des wie oben gereinigten Farbwachses aus Goldröschchen bemerkten wir, dass die Palmitinsäure von anderen Fettsäuren begleitet ist. Um die Säure, die die Erniedrigung des Schmelzpunkts der Palmitinsäure verursacht, zu fassen, isolierten wir eine ziemlich grosse Menge der Säure aus den durch Verseifung entstandenen Fettsäuren. Dafür verwendeten wir das bei 85–86° schmelzende Farbwachs. Da das Farbwachs vom Schmp. 85–86° bei der Verseifung Lutein ergibt, das ohne weiteres bei 193–194° schmilzt, kann man erkennen, dass das Ausgangsmaterial genug rein ist. Aus 8.28 g. Farbwachs erhält man durch Verseifung 3.9 g. rohe Fettsäure. Wendet man auf diese Fettsäure die Blei-Alkohol-Methode an, so trennen sich 1.26 g. flüssige Säure von 2.60 g. fester Säure. Die feste Säure schmilzt bei 57–58°. Der Schmelzpunkt steigert sich weder durch Umkrystallisation noch durch Destillation unter vermindertem Druck. Endlich wurde die feste Säure für kurze Zeit mit Ozon behandelt und als Palmitinsäure, bei 61–62° schmelzend, nachgewiesen. Andererseits wurde die mit Lutein etwas gefärbte, flüssige Säure im Vakuum destilliert. Ausbeute 0.70 g. Diese wurde nach Hazzura weiter in Dibromstearinsäure übergeführt, wobei sehr wenige, in Eisessig und Petroläther unlösliche Bromverbindungen entstanden, welche nachgelassen waren. Man löst 0.91 g. Dibromverbindung in 4 ml. Methanol, versetzt sie mit 2 g. Zink, und kocht sie für 3–4 Stdn. auf dem Wasserbad. Nach dem Behandeln mit Lauge wurde das Methanol abdestilliert, mit Essigsäure angesäuert und ausgeäthert. Verdampft der Äther, so bleibt 0.40 g.

(8) *Loc. cit.*

(9) Vgl. P. Karrer und S. Ishikawa, *Helv. Chim. Acta*, **13** (1930), 1099.

flüssige Säure zurück. Sie wurde als Ölsäure identifiziert, indem die Säure in das Säureamid abgeleitet worden war. Dazu behandelt man die Säure mit Thionylchlorid, und das entstandene Säurechlorid wurde dann mit konz. NH_4OH amidiert. Ausbeute 0.2 g.; Schmp. 75–75.5° (aus verd. Alkohol). Es zeigte keine Depression bei Vermischung mit authentischem Präparat. (Gef.: N, 5.01. Ber. für $\text{C}_{18}\text{H}_{35}\text{NO}$: N, 4.98%.)

III. **Chromatographische Analyse von Farbwachsgemisch.** Die chromatographische Analyse von Tswett wurde von Kuhn und seinen Mitarbeitern⁽¹⁰⁾ mit Erfolg in die präparative Chemie der Carotinoide eingeführt. Es gibt aber kein Beispiel zu den Farbwachsen. Wir konnten das Farbwachsgemisch durch Adsorption an Magnesiumoxyd in Benzin (Sdp. 80–100°) zum Teil fraktionieren. Bemerkenswert ist, dass die Zerlegbarkeit des Farbwachsgemisches durch Adsorption nicht von den Säurekomponenten sondern von den Farbstoffkomponenten abhängig ist.

0.4 g. Farbwachs, Schmp. 85–86°, wurden in 40 ml. Benzin (80–100°) gelöst und durch eine Säule von lufttrocknem Magnesiumoxyd abgesaugt. Es wurde mit 240–250 ml. demselben Lösungsmittel nachgewaschen. Das obere, orangerote scharfe Band war abgelassen. Die untere orange-gelbe Schicht wurde abgehoben und mit Methanol oder Äthanol eluiert. Ausbeute 0.27 g. Diese wurde noch einmal wie zuerst chromatographiert. Dabei blieb das Farbwachs in der oberen, aber ein gelber Farbstoff in der unteren Schicht. Das Farbwachs wog nach Eluierung 0.20 g. Der Nebenfärbstoff gibt keine Farbenreaktion gegen 25proz. Salzsäure und hat die optischen Schwerpunkte 500, 469 $\text{m}\mu$ in CS_2 . Es scheint ein Taraxanthinester zu sein, aber zu wenig, um ihn genauer zu bestimmen. Dann wurde dreimal die Chromatographierung des Farbwachses unternommen, aber es war einbändig und nicht zerlegbar. Optische Schwerpunkte in CS_2 : 508, 475 $\text{m}\mu$.

Durch Verseifung aus 1.62 g. chromatographisch gereinigtem Farbwachs, Schmp. 86°, 0.89 g. reines Lutein und 0.73 g. Fettsäure. Diese Säure wurde durch die Blei-Alkohol-Methode in 0.51 g. Palmitinsäure und 0.22 g. Ölsäure zerlegt.

Es wurde dann die Fraktionierung des künstlichen Farbwachsgemisches durch Adsorption an Magnesiumoxyd ausprobiert. Dafür wurde auch Luteindioleat synthetisiert. Der Ester wurde wie beim Helenien mit 55–60proz. Ausbeute hergestellt. Als orangerotes Wachs aus Benzol-Alkohol gefällt. Schmp. 75–76°. Makroskopisch sieht man es kristallinisch, es besitzt die Konsistenz eines harten Wachses, und ist in gebräuchlichen Lösungsmitteln leichter löslich als der Palmitinsäureester. (Gef.: C, 83.08; H, 10.92. Ber. für $\text{C}_{76}\text{H}_{120}\text{O}_4$: C, 83.21; H, 10.94%.)

Chromatographische Analyse des künstlichen Gemisches von Lutein-dipalmitat und -dioleat. Man vermischt Dipalmitat mit Dioleat zu gleichen Teilen. 0.1 g. Farbwachsgemisch wurde in 10 ml. Benzin (Sdp. 80–100°) gelöst und durch eine Säule von MgO gesaugt. Es war nur einbändig und nicht zerlegbar. Fraktionierung durch Adsorption aus Benzin-Benzol (8:2) war ebenfalls erfolglos.

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(10) R. Kuhn und E. Lederer, *Naturwissenschaften*, **19** (1931), 306; *Ber.*, **64** (1931), 1349; R. Kuhn und H. Brockmann, *Z. physiol. Chem.*, **200** (1931), 255; A. Winterstein und G. Stein, *ibid.*, **220** (1933), 247, 263.

SYNTHETISCHE VERSUCHE IN DER SELENOPHEN-GRUPPE. II. NITRIERUNG UND SULFONIERUNG.

Von Sumio UMEZAWA.

Eingegangen am 24. Oktober 1936. Ausgegeben am 28. Dezember 1936.

Wie wir schon konstatierten⁽¹⁾, verhält sich das Selenophen weniger aromatisch als das Thiophen, dennoch haben das Selenophen und seine Derivate grosse Ähnlichkeit mit den Abkömmlingen des Benzols, besonders dem Thiophen. Um womöglich zu der dem Anilin oder Thiophenin korrespondierenden Base zu gelangen, habe ich sie zu nitrieren und zu sulfonieren versucht. In vorliegender Mitteilung möchte ich über die Darstellung der Nitro- und Sulfonsäure-derivate des Selenophens und des Halogenselenophens⁽²⁾ berichten.

Auf Selenophen selbst wirkt die konzentrierte oder rauchende Salpetersäure mit grosser Heftigkeit oxydierend; doch gelang die direkte Nitrierung bei der Verdünnung mit Essigsäureanhydrid und Eisessig bei tiefer Temperatur, allerdings in nur mässiger Ausbeute. Merkwürdig ist, dass bei diesem Verfahren das dabei entstandene 2-Nitroselenophen vom Schmelzp. 45-46° weiter nicht nitriert wird und das Reaktionsprodukt mit Methanol und Kalilauge keine Farbenreaktion⁽³⁾ zeigt (siehe später).

Obgleich das α -Nitroselenophen (I) ziemlich unbeständig ist und sich am Lichte sehr bald rot färbt, scheint es, dass die Einführung einer solchen negativen Gruppe in das Selenophen—auch bei den Halogenen wie später erwähnt wird—dasselbe gegenüber oxydierenden Reagenzien beständiger und der Nitrierung fähig macht⁽⁴⁾. Das α -Nitroselenophen lässt sich mit Nitriersäure zum 2,4-Dinitroselenophen vom Schmelzp. 77-79° (II) nitrieren. Bei dieser Überführung konnte kein Ortsisomer erhalten werden, der beim Thiophen⁽⁵⁾ gefunden wurde. In der Methanollösung zeigt das 2,4-Dinitroselenophen beim Versetzen der Kalilauge schöne Rotfärbung, die beim Mononitroselenophen nicht beobachtet wird.

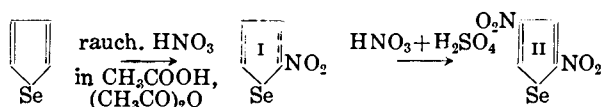
(1) Suginome u. Umezawa, dieses Bulletin, **11** (1936), 160.

(2) Suginome u. Umezawa, *loc. cit.*, **11** (1936), 162.

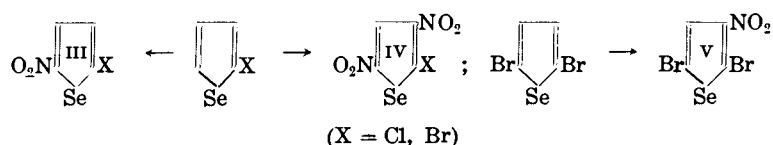
(3) Vgl. Steinkopf, *Ann.*, **513** (1934), 285; V. Meyer, „Die Thiophengruppe“, S. 100, Braunschweig (1888).

(4) Vergleich die Thiophenderivate. V. S. Babasinian, *J. Am. Chem. Soc.*, **50** (1928), 2751.

(5) Bei der Darstellung von Dinitrothiophen entsteht mindestens 20 Proz. Ortsisomeres. Siehe Steinkopf u. Höpner, *Ann.*, **501** (1933), 177.

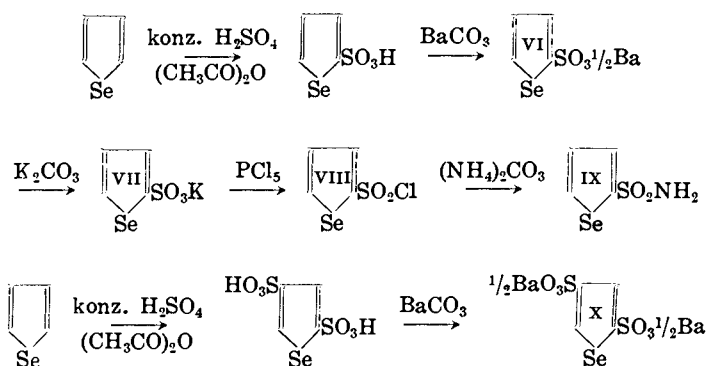


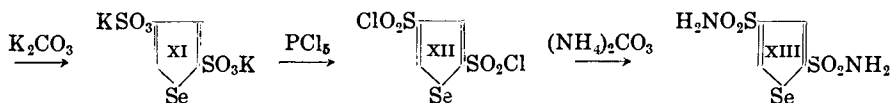
Das Nitrieren des halogenierten Selenophens verlief glatter als beim Selenophen selbst. Behandelt man 2-Bromselenophen in Essigsäureanhydrid mit rauchender Salpetersäure, so wird 2-Brom-5-nitroselenophen (III) erhalten, während bei der Reaktion ohne Lösungsmittel, infolge des weiteren Nitrierens 2-Chlor- oder 2-Brom-3,5-dinitroselenophen (IV) entstehen, die mit Methanol und Kalilauge ganz dem 2,4-Dinitroselenophen ähnliche, schöne Rotfärbung zeigen. Auch habe ich gelegentlich das 2,5-Dibrom-3-nitroselenophen (V) durch Einwirkung von rauchender Salpetersäure aus 2,5-Dibromselenophen erhalten.



Substituiertes α -Nitroselenophen wurde durch Halogenierung des α -Nitroselenophens nicht erhalten, da das letztere gegenüber Einwirkung von Halogenen unbeständig ist.

Auf Selenophen wirkt konzentrierte Schwefelsäure zersetzend unter Bildung einer unlöslichen, amorphen Masse. Wenn man aber das Selenophen in Essigsäureanhydrid mit der berechneten Menge konzentrierter Schwefelsäure bei tiefer Temperatur behandelt, so gelingt die Sulfonierung glatt. Die Selenophen-2-sulfonsäure und die Selenophen-2,4-disulfonsäure wurden in Sulfochloride und Sulfamide übergeführt, wie schematisch im folgenden dargestellt wird.





Wie bei der Nitrierung stellten sich Selenophen-disulfochlorid und disulfamid als scheinbar einheitlich dar. Die oben gegebenen Orientierungen der Nitro- und Sulfonsäure-gruppen werden in einer folgenden Mitteilung behandelt.

Es sei mir an dieser Stelle erlaubt, Herrn Prof. H. Sugimoto für die Überlassung dieser Arbeit, sowie für Anregungen und Ratschläge meinen verbindlichsten Dank auszusprechen. Gleichzeitig bin ich für Unterstützung der Kaiserlichen Akademie zu Dank verpflichtet.

Beschreibung der Versuche.

I. Nitrierung von Selenophen und seinen Halogenderivaten. α -Nitroselenophen (I). Zu einem Gemische von 3 c.c. Selenophen und 13 c.c. Essigsäureanhydrid lässt man eine Lösung von 20 c.c. Eisessig und 2 c.c. rauchender Salpetersäure im Laufe von etwa 30 Minuten unter Schütteln im Eiswasser zutropfen. Das Reaktionsgemisch färbt sich bald braun. Ist das ganze Nitriergemisch eingetragen, so lässt man es bei gleicher Temperatur noch etwa 10 Minuten stehen, giesst es dann in Eiswasser und lässt es zwecks Lösung des Essigsäureanhydrids in der Dunkelkammer einige Zeit stehen. Ein sich zu Boden setzendes, dunkles Öl wird vom wässrigen Anteil getrennt, mit sehr verdünnter Natriumkarbonatlösung gewaschen und mit Wasserdampf destilliert. Man erhält so das α -Nitroselenophen in Form einer gelben Krystallmasse, die auf Ton getrocknet wird. Ausbeute 0.9 g., etwa 15% der Theorie. Das Rohnitroselenophen, schmelzend bei etwa 38–42°, wird umkrystallisiert aus Petroläther (40–60°). Schwach-gelbe, schöne, prismatische Säulen. Schmp. 45–46°. (Gef.: N, 7.70; Se, 45.38. Ber. für $\text{C}_4\text{H}_3\text{O}_2\text{NSe}$: N, 7.95; Se, 44.89%.)

Am Lichte färbt sich das α -Nitroselenophen allmählich rot. Mit wässrigen Alkalien gekocht, die es in der Kälte nicht auflösen, löst es sich in braunroter Färbung auf. Die Methanollösung desselben zeigt keine Rotfärbung in verdünnter Kalilauge. Auch zeigt sich keine Indophenin-Reaktion. Es gelang mir nicht durch Behandeln mit konzentrierter Schwefelsäure—eine bei der Thiophenreihe⁽⁶⁾ glatt gehende Reaktion—die Nitroselenophensulfonsäure zu erhalten.

2,4-Dinitroselenophen (II). 0.2 g. α -Nitroselenophen werden mit der Nitriersäure (aus 2.5 c.c. konz. HNO_3 und 3 c.c. konz. H_2SO_4) nach und nach bei ungefähr -17° zur Lösung versetzt. Man lässt das klare Reaktionsgemisch bei gleicher Temperatur etwa 30 Minuten stehen, giesst es dann in Eiswasser, wobei sich ein schwach-gelber, krystallinischer Körper ausscheidet. Ausbeute 0.22 g., 88% der Theorie. Schmp. 70–78°. Umkrystallisiert aus Petroläther (40–60°). Schwach-gelbe, winzige Nadeln. Schmp. 77–79°. (Gef.: N, 12.61. Ber. für $\text{C}_4\text{H}_2\text{O}_4\text{N}_2\text{Se}$: N, 12.67%.)

Das 2,4-Dinitroselenophen ist ziemlich löslich in Alkohol und Methanol, leicht löslich

(6) V. Meyer, „Die Thiophengruppe“, S. 125, Braunschweig (1888).

in Benzol und schwer in Petroläther (unter 40°) sogar in der Wärme. Alkalien zersetzen dasselbe allmählich unter Kotfärbung. Löst man dasselbe in Methanol auf und fügt zu der Flüssigkeit ein Tröpfchen (nicht mehr!) Kalilösung, so erhält man eine schöne, rosarot gefärbte Lösung. Überschüsse von Alkali sowie Salzsäure heben die Färbung auf, welche indes bei vorsichtiger Neutralisation zurückkehrt. Wenn Spuren von Dinitroselenophen in die Nase gelangen, wie dies z.B. beim Ablösen vom Filter leicht vorkommt, so bewirken sie lebhaften Reiz zum Niesen. Am Lichte färbt sich das Dinitroselenophen nur sehr allmählich, aber es erweist sich weitaus beständiger als α -Nitroselenophen.

2-Brom-5-nitroselenophen (III). Man lässt eine Lösung von 0.5 c.c. rauchender Salpetersäure und 2 c.c. Essigsäureanhydrid zu einem Gemische von 0.5 c.c. 2-Bromselenophen und 2 c.c. Essigsäureanhydrid unter Umschütteln im Eiswasser allmählich zutropfen. Ist das ganze Nitriergemisch eingetragen, so lässt man es noch etwa 30 Minuten in Eiswasser stehen, giesst es dann in Eiswasser, und lässt es zur Lösung des Essigsäureanhydrids wieder einige Zeit stehen. Ausscheidung eines ölhaltigen, gelbfarbenen Körpers. Lässt man sich diesen in Petroläther (40–60°) auflösen, so wird ein harziger Teil unlöslich beseitigt. Nach Eindampfen des Lösungsmittels scheiden sich gelbe Nadelchen aus. Umkrystallisiert aus Ligroin. Schmp. 57–59°. (Gef.: N. 5.90. Ber. für $C_4H_2O_2NBrSe$: N, 5.49%.)

Das 2-Brom-5-nitroselenophen färbt sich allmählich im Lichte und zeigt keine Farbenreaktion mit Methanol und Alkali.

2-Brom-3,5-dinitroselenophen (IV). 5 c.c. rauchender Salpetersäure lässt man in 1 g. 2-Bromselenophen bei –15° unter Umschütteln langsam zutropfen. Dabei tritt eine heftige Reaktion ein. Das Reaktionsgemisch wird dann in Eiswasser gegossen, wobei, wie beim Nitrieren aromatischer Kohlenwasserstoffe, ein intensiver Bittermandelölgeruch auftritt und der Nitrokörper sofort zu braunen Klumpen erstarrt. Diese werden abfiltriert und ausgewaschen. Ausbeute 0.6 g. Umkrystallisiert aus Ligroin. Gelbe, federförmige Krystalle. Schmp. 126–128°. (Gef.: C, 16.63; H, 0.66; Br, 27.11; N, 9.56; Se, 26.22. Ber. für $C_4H_2O_2N_2BrSe$: C, 16.00; H, 0.34; Br, 26.67; N, 9.34; Se, 26.37%.)

Das Bromdinitroselenophen ist leicht löslich in Benzol, schwer in Petroläther (40–60°) und färbt sich allmählich beim Aufbewahren.

2-Chlor-3,5-dinitroselenophen (IV). 1 g. 2-Chlorselenophen wird mit rauchender Salpetersäure bei –15° nitriert und wie beim entsprechenden Bromderivat aufgearbeitet. Ausbeute 0.4 g. Schwach-gelbe, federförmige Krystalle. Schmp. 119°. (Gef.: Cl, 14.13. Ber. für $C_4H_2O_2N_2ClSe$: Cl, 13.90%.)

Dies ist leicht löslich in Benzol, ziemlich leicht in Äther und dem 2-Brom-3,5-dinitroselenophen in jeder Hinsicht sehr ähnlich.

2,5-Dibrom-3-nitroselenophen (V). 2 g. 2,5-Dibromselenophen werden in rauchender Salpetersäure unter Umschütteln nach und nach bei –17° aufgelöst und das Reaktionsgemisch sofort in Eiswasser gegossen, wobei das Produkt zu einem festen Krystallkuchen erstarrt. Er wird abgesaugt, mit Wasser gewaschen, und nach Trocknung aus Ligroin umkrystallisiert. Hell gelbe Nadelchen. Schmp. 83–85°. Ausbeute 0.7 g. (Gef.: N, 4.30. Ber. für $C_4H_2O_2NBr_2Se$: N, 4.19%.) Dies erweist sich als lichtbeständig und zeigt keine Farbenreaktion mit Methanol und Alkali.

II. Sulfonierung von Selenophen. *Bariumsalz der Selenophen-2-sulfonsäure* (VI). $C_4H_3SeSO_3Ba \cdot SO_3C_4H_3Se \cdot H_2O$. 1.3 c.c. konzentrierter Schwefelsäure (1.84) werden zu einer Lösung von 3 g. Selenophen und 8 c.c. Essigsäureanhydrid unter Umschütteln im

Eiswasser nach und nach versetzt. Das Reaktionsgemisch färbt sich allmählich braun. Man lässt dies bei gleicher Temperatur noch 1-2 Stunden stehen, giesst es dann in Eiswasser und lässt es wieder einige Zeit stehen. Zwecks Beseitigung der Essigsäure unterwirft man die wässrige Lösung der Wasserdampfdestillation. Die dabei erhaltene, rohe Selenophensulfonsäurelösung wird mit Bariumkarbonat gesättigt, von überschüssigem Bariumkarbonat abfiltriert und mit Tierkohle entfärbt. Zur farblosen Lösung wird dann eine kleine Menge Alkohol zugesetzt, indem das beigemengte disulfonsaure Barium, das in wässrigem Alkohol schwerlöslich ist, sich niederschlägt. Aus dem Filtrate kristallisiert sich im Vakuum das Salz über Schwefelsäure aus. Nachdem sich das Salz zum grössten Teile in Warzen ausgeschieden hatte, wurde es abgesaugt, über Chlorkalzium im Vakuum getrocknet und analysiert. Ausbeute 6.05 g., 95% der Theorie. (Gef.: H_2O , 3.17. Ber. für $(\text{C}_4\text{H}_3\text{SeSO}_3)_2\text{Ba} \cdot \text{H}_2\text{O}$: H_2O , 3.13%. Gef.: Ba. 24.79. Ber. für $\text{C}_8\text{H}_6\text{O}_6\text{S}_2\text{Se}_2\text{Ba}$: Ba, 24.64%.)

Kaliumsalz der Selenophen-2-sulfonsäure (VII). $\text{C}_4\text{H}_3\text{SeSO}_3\text{K} \cdot \frac{1}{4}\text{H}_2\text{O}$. Die wässrige Lösung des selenophen-2-sulfonsauren Bariums wird mit einer äquivalenten Menge Kaliumkarbonatlösung versetzt und vom Bariumkarbonat abfiltriert. Die Lösung des selenophen-2-sulfonsauren Kaliums lässt man sich im Vakuum über Schwefelsäure kristallisieren. Nachdem sich das Salz zum grössten Teile kristallin ausgeschieden hatte, wurde es abgesaugt, über Chlorkalzium im Vakuum getrocknet und analysiert. (Gef.: H_2O , 1.40; Ber. für $\text{C}_4\text{H}_3\text{SeSO}_3\text{K} \cdot \frac{1}{4}\text{H}_2\text{O}$: H_2O , 1.78%. Gef.: K, 15.83, 15.85. Ber. für $\text{C}_4\text{H}_3\text{O}_3\text{SSeK}$: K, 15.66%.)

Das monosulfonsaure Kalium ist ziemlich löslich im Alkohol und 100 Teile Alkohol lösen 2.33 g. Kaliumsalz, d.h. Löslichkeit = 2.33.

Selenophen-2-sulfochlorid (VIII). 4.6 g. gepulvertes und wohlgetrocknetes selenophensulfonsaures Kalium werden mit 5 g. Phosphorpentachlorid verrieben. Das Gemisch erwärmt sich, wird flüssig, und der Chlorwasserstoff entwickelt sich sehr heftig. Nachdem das meiste Phosphoroxychlorid verjagt ist, wird das Reaktionsgemisch in Eiswasser gebracht. Das Chlorid scheidet sich in halbfestem Zustande ab, äthert sich aus (Tierkohle) und wird über Glaubersalz getrocknet. Die ätherische Lösung wird freiwilligem Verdunsten überlassen. Ausbeute 3.7 g. Umkristallisiert aus Ligroin. Schmp. 31-32.5°. Das Sulfochlorid hat einen charakteristischen Geruch, ist löslich in gewöhnlichen, organischen Lösungsmitteln und zersetzt sich allmählich beim Aufbewahren.

Selenophen-2-sulfamid (IX). Zur Darstellung desselben werden 3 g. Selenophen-2-sulfochlorid mit 3 g. Ammoniumkarbonat unter zeitweiligem Erwärmen zerrieben, bis die Masse ganz fest geworden. Man wäscht dann mit kaltem Wasser aus, löst in heissem auf, kocht mit Tierkohle und filtriert heiss. Beim Erkalten entsteht ein Brei von feinen, weissen Kryställchen, aber beim Stehenlassen der heissen Lösung scheiden sich schöne, farblose, tafelförmige Kryställchen aus. Abgesaugt, nochmals umkristallisiert, getrocknet und analysiert. Ausbeute 1.5 g. Schmp. 157-159°. (Gef.: C, 22.93; H, 2.59; N, 6.59. Ber. für $\text{C}_4\text{H}_5\text{O}_2\text{NSSe}$: C, 22.88; H, 2.40; N, 6.66%.)

Selenophen-2-sulfamid ist schwer löslich in Äther; mit Isatin und konzentrierter Schwefelsäure erhitzt, ergibt es schön-violette Färbung.

Bariumsalz der Selenophen-2,4-disulfonsäure (X). $\text{C}_4\text{H}_2\text{Se}(\text{SO}_3)_2\text{Ba} \cdot \frac{2}{3}\text{H}_2\text{O}$. Zur Lösung von 3 g. Selenophen und 8 c.c. Essigsäureanhydrid werden 3 c.c. konzentrierter Schwefelsäure wie beim Darstellen der Monosulfonsäure versetzt. Man lässt das Reaktionsgemisch bei Zimmertemperatur noch 30 Minuten stehen und giesst es dann in Wasser

ein. Nach Lösen des Essigsäureanhydrids arbeitet man es wie bei der Monosulfonsäure auf. Die mit Tierkohle entfärbte Lösung des selenophendisulfonsauren Bariums versetzt man mit dem gleichen Volumen Alkohol und lässt es einige Zeit stehen. Das Salz kommt aus der Lösung in schönen, farblosen, winzigen Krystallen heraus. Man saugt sie ab, löst sie im Wasser auf und fällt das Salz mit Alkohol um. Abgesaugt, gewaschen mit Alkohol und getrocknet im Vakuum über Chlorkalzium. Ausbeute 8.1 g. (Gef.: H_2O , 9.19. Ber. für $\text{C}_4\text{H}_2(\text{SO}_3)_2\text{Ba} \cdot 2\frac{1}{2}\text{H}_2\text{O}$: H_2O , 9.56. Gef.: Ba, 33.02. Ber. für $\text{C}_4\text{H}_2\text{O}_6\text{S}_2\text{SeBa}$: Ba, 32.24%.)

Kaliumsalz der Selenophen-2,4-disulfonsäure (XI). $\text{C}_4\text{H}_2\text{Se}(\text{SO}_3\text{K})_2 \cdot \frac{1}{4}\text{H}_2\text{O}$. Man versetzt das selenophendisulfonsaure Barium mit der äquivalenten Menge Kaliumkarbonatlösung und filtriert es vom Bariumkarbonat ab. Wird dann die Lösung des selenophendisulfonsauren Kaliums mit etwa dem gleichen Volumen Alkohol versetzt, so scheiden sich farblose, winzige Krystalle aus, welche abgesaugt, mit Alkohol gewaschen, über Chlorkalzium im Vakuum getrocknet werden. (Gef.: H_2O , 1.24. Ber. für $\text{C}_4\text{H}_2\text{Se}(\text{SO}_3)_2\text{K}_2 \cdot \frac{1}{4}\text{H}_2\text{O}$: H_2O , 1.20%. Gef.: K, 21.04. Ber. für $\text{C}_4\text{H}_2\text{O}_6\text{S}_2\text{SeK}_2$: K, 21.31%.)

Das Kaliumsalz der Selenophendisulfonsäure ist schwerer löslich in Alkohol als das der Selenophenmonosulfonsäure und 100 Teile Alkohol lösen 0.17 g. Kaliumsalz, d.h. Löslichkeit = 0.17.

Selenophen-2,4-disulfochlorid (XII). 1 g. gepulvertes und wohlgetrocknetes Kaliumsalz wird mit 1.5 g. Phosphorpentachlorid in einer Porzellanschale unter mässigem Erwärmen zusammengerieben. Wird dabei entstandenes Phosphoroxychlorid durch gelindes, weiteres Erwärmen verjagt, so erstarrt die Masse beim Erkalten. Sie wird mit Äther ausgezogen, mit Tierkohle behandelt und getrocknet. Beim freiwilligen Verdunsten erhält man das Chlorid in schönen, weissen Tafelchen. Ausbeute 0.7 g. Umkrystallisiert dreimal aus Ligroin. Schmp. $70-72^\circ$. (Gef.: Cl, 21.20. Ber. für $\text{C}_4\text{H}_2\text{O}_4\text{Cl}_2\text{S}_2\text{Se}$: Cl, 21.62%.) Das Disulfochlorid ist leicht löslich in Benzol und zersetzt sich allmählich beim Aufbewahren.

Selenophen-2,4-disulfamid (XIII). 0.6 g. soeben beschriebenen Chlorids werden mit 0.5 g. Ammoniumkarbonat unter Erhitzen auf dem Wasserbade zerrieben, bis die Masse ganz fest geworden. Die Reaktionsmasse wird mit heissem Wasser aufgenommen, mit Tierkohle aufgeköcht; das Filtrat wird zur Krystallisation stehen gelassen. Schöne, weisse Nadelchen. Ausbeute 0.4 g. Umkrystallisiert nochmals aus Wasser. Schmp. $237-239^\circ$ unter Zersetzung. (Gef.: N, 9.61. Ber. für $\text{C}_4\text{H}_6\text{O}_4\text{N}_2\text{S}_2\text{Se}$: N, 9.69%.)

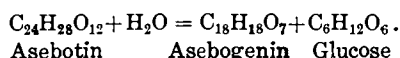
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STUDIES ON THE STRUCTURE OF ASEBOTIN, A COMPONENT OF ANDROMEDA JAPONICA THUMB.

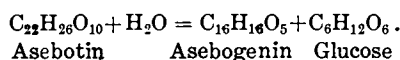
By Kunisaburo TAMURA.

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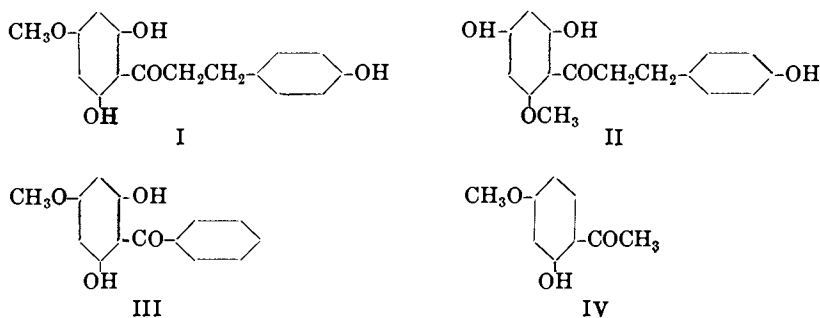
Asebotin is a component of *Andromeda japonica* Thumb, and has been investigated by several workers.⁽¹⁾ According to an investigation by Eykman it is a glucoside, which is decomposed by mineral acid in the following way :



The results obtained by the present author have altered the equation as follows :



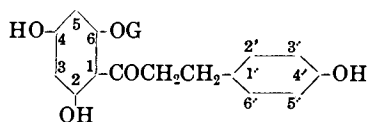
Asebotin (m. p. 147.5°) gave a reddish brown tinge with ferric chloride, but no colouration with metallic magnesium and hydrochloric acid. Asebogenin (m. p. 168°) has one methoxyl group and gave triacetylasebogenin (m. p. 66–67°) by acetylation. Triacetyl-asebogenin neither gave ferric chloride reaction nor decolourised potassium permanganate. Asebogenin gave phloroglucinol-monomethylether (b. p. 175–178°/7 m.m., m. p. 74–77°) as a phenolic substance as well as phloretic acid (m. p. 128°) as an acidic substance, when it was fused at 170–180° with potassium hydroxide in an atmosphere of hydrogen. Thus, it is possible to represent asebogenin by either of the two following formulas I and II :



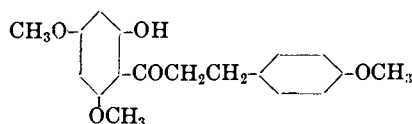
(1) Eykman, *Ber.* **16** (1883), 2769; E. Bourquelot and A. Fichtenholz, *Chem. Zentr.*, **83** (1912), I, 585, 733, 1224; Marc Bridel, *ibid.*, **102** (1931), I, 468; Marc Bridel and A. Kramer, *ibid.*, **103** (1932), I, 396; *ibid.*, **104**, (1933), II, 3289.

Generally speaking, hydroxyl groups occupy ortho-positions in relation to the carbonyl group in natural substances having both hydroxyl groups and methoxyl groups, as in cotoin (III)⁽²⁾, Päonol (IV)⁽³⁾, and flavones. Then it is possible to state that formula I represents the structure of asebogenin. This conclusion was confirmed by the following synthesis: iso-asebogenin (II) was synthesised by condensation of phloroglucinol-monomethyl-ether and phloretic nitrile in the presence of freshly fused zinc chloride (Hoesch's reaction)⁽⁴⁾, which melted at 201-202°.

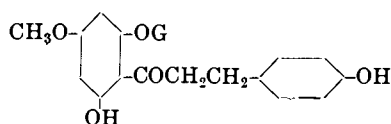
The position of glucose was confirmed by methylation of asebotin. When asebotin was methylated with methyl iodide and potassium carbonate in dry acetone, a colourless transparent syrup was obtained, which gave no ferric chloride reaction. On hydrolysis of this syrup with dilute sulphuric acid, colourless prismatic crystals (from alcohol) were obtained. These crystals melted at 109-110° alone and in admixture with 6-hydroxy-2, 4, 4'-trimethoxy-phenyl-propiophenone (VI) (m. p. 109-110°) which had been prepared by F. R. Johnson and A. Robertson⁽⁵⁾ to determine the position of glucose in phloridzin (V) in the same way. Therefore the position of glucose in asebotin proved to be "6" as in phloridzin.



V



VI



VII

G = Glucose

Thus, judging from the result obtained, asebotin can be regarded as phloridzin-monomethyl-ether (VII), as evidenced by the fact that asebotin gives the same reaction as phloridzin, turning yellow and precipitating an amorphous substance on treatment with boron acetic acid anhydride.⁽⁶⁾ However, the

(2) "Beilsteins Handbuch der Organischen Chemie", VIII, 419.

(3) *Ibid.*, VIII, 267.

(4) When a side chain is introduced in phloroglucinol-monomethyl-ether by Hoesch's reaction, it enters the ortho-position to methoxyl-groups completely or at least for the most part, *Ber.*, **58** (1925), 1691; **61** (1928), 2300; *Helv. Chim. Acta.*, **2** (1919), 486, 478.

(5) *J. Chem. Soc.*, **1930**, 21.

(6) *Ber.*, **54** (1921), 3020.

present author's view differs from that held by Marc Bridel and A. Kramer⁽¹⁾ who considered them to be identical, whereas, they differ, according to the present author's investigation, in that asebotin contains a methoxyl group in place of a hydroxyl group in phloridzin.

Experimental.

Isolation and Properties of Asebotin. Fresh leaves of *Andromeda japonica* Thumb. were extracted with warm water for 5 hours. The extraction was repeated again. When the resulting extract was concentrated on the water bath under reduced pressure and left to stand, asebotin separated out gradually in brown crystals. It was filtered, dried, and recrystallised from either water (50 c.c. per 1 g. asebotin) or a mixture of alcohol and water (charcoal). Asebotin was obtained in colourless long plates, m.p. 147.5°. The yield was 30 g. (pure asebotin) from 15 kg. of leaves. Asebotin is soluble in warm water, alcohol, and glacial acetic acid, but sparingly soluble in light petroleum, ether, benzene, and chloroform. It gave a reddish brown tinge with ferric chloride, and neither gave colouration with metallic magnesium and hydrochloric acid, nor reduced Fehling's solution. Yellowish colouration was given with the formation of an amorphous precipitate on treatment with boron acetic acid anhydride in acetic acid anhydride. $[\alpha]_D^{25} = -46.7^\circ$ (absolute alcohol, $c = 4.904$). Substance dried at the boiling point of toluene over phosphorous pentoxide was analysed (Found: C, 58.51, 58.26, 58.37; H, 6.15, 6.36, 6.42. Calc. for $C_{22}H_{26}O_{10}$: C, 58.63; H, 5.82%).

Hydrolysis of Asebotin. When asebotin (1 g.) was warmed on the water bath with 5% sulphuric acid (50 c.c.), at first it was dissolved to a great extent, then the solution became turbid with formation of asebogenin crystals. After two hours it was cooled and filtered. Yield of asebogenin was 0.63 g.

Qualitative Test of Glucose. Sulphuric acid was removed from the filtrate, from which asebogenin had been separated by filtration, with a solution of barium hydroxide. On drying the filtrate, it gave the sugar with yellowish resinous matter. When a part of the sugar was warmed on water bath with phenylhydrazine hydrochloride (2 parts) and sodium acetate (2 parts) in water (20 parts), yellowish glucosazone was formed, and it was filtered and washed with methyl alcohol and ether, melting point 209° alone and in admixture with the authentic specimen. The sugar gave neither Seliwanoff's reaction with resorcinol nor Ihl-Pechmann's diphenylamine reaction. On leaving the sugar with phenylhydrazine hydrochloride in water at room temperature, there was found no precipitate of phenylhydrazone.

Asebogenin. Asebogenin was crystallised from dilute alcohol (charcoal) in colourless long plates, m. p. 168°. It gave purple-reddish tinge with ferric chloride. It is soluble in acetic ester, acetone, methyl alcohol, ethyl alcohol, ether, and alkali, but sparingly soluble in chloroform, light petroleum, benzene, and toluene. On analysis, the result agreed with $C_{16}H_{16}O_5$, having one methoxyl group (Found: C, 66.19, 66.32; H, 5.55, 5.86; CH_3O , 10.6. Calc. for $C_{15}H_{13}O_4 \cdot OCH_3$: C, 66.64; H, 5.60; CH_3O , 10.76%).

Preparation and Properties of Acetylasebogenin. Acetic acid anhydride (3 c.c.) was added to a solution of asebogenin (0.5 g.) in pyridine (4 c.c.) and the solution was allowed

to stand overnight. When the reaction mixture was treated with water, a white crystalline mass separated. This was collected and dried. It was crystallised from alcohol in colourless prisms, melting at 76-77°. It did not give ferric chloride reaction and did not decolourise potassium permanganate in glacial acetic acid (Found: C, 63.39, 63.58; H, 5.63, 5.87. Calc. for $C_{22}H_{22}O_3$; C, 63.74; H, 5.35%).

Alkali Fusion of Asebogenin. Asebogenin (2 g.) was added gradually to fused potassium hydroxide which was prepared in a platinum crucible with potassium hydroxide (3 g.) and water (1.5 c.c.), and the mixture was held at 170-180° in an atmosphere of hydrogen. After 30 minutes, the fused mass was cooled. The yellowish product was dissolved in water, the solution was acidified with sulphuric acid, and sodium carbonate was added; the solution was extracted with ether, the ether was evaporated, and the residue was distilled under reduced pressure. A colourless oil distilled at 175-178°/7 mm. After some time it crystallised, m.p. 74-77°. The yield was 0.6 g. On analysis, it corresponded to $C_7H_8O_3$, having one methoxyl group. It is freely soluble in water, alcohol, and ether, and reduces Fehling's solution; it also gave purple-reddish tinge in pine shaving reaction. It tastes sweet. These data show that it is phloroglucinol-monomethyl-ether (Found: C, 59.75; H, 5.98; CH_3O , 21.31. Calc. for $C_6H_5O_2 \cdot OCH_3$: C, 59.97; H, 5.76; CH_3O , 22.15%).

Sodium carbonate solution, from which phloroglucinol-monomethyl-ether was extracted, was acidified with sulphuric acid, and extracted with ether; the ether was evaporated and the residue was crystallised from benzene in colourless crystals, m.p. 128°. The yield was 1.5 g. On analysis, it corresponded to $C_9H_{10}O_3$ and was found to be phloretic acid (Found: C, 64.46; H, 6.36. Calc. for $C_9H_{10}O_3$: C, 65.03; H, 6.07%).

This acid was methylated with dimethyl sulphate and sodium hydroxide to confirm the above view. The product was crystallised from alcohol in colourless needles, melting at 102-103° (Found: C, 66.53; H, 6.93; CH_3O , 17.10; molecular weight obtained by titration with N/10 NaOH, 178. Calc. for $C_9H_9O_2 \cdot OCH_3$: C, 66.63; H, 6.72; CH_3O , 17.21; mol. wt. 180).

Synthesis of Iso-asebogenin. To a solution of phloroglucinol-monomethyl-ether (1 g.) and phloretic acid nitrile (1 g.) in absolute ether (7 c.c.) a freshly fused anhydrous zinc chloride was added, and into this solution was passed a slow current of dry hydrogen chloride gas for 3 hours, while cooling with ice water. The mixture was allowed to stand overnight in a cool place. The reaction mixture separated in two layers, the lower layer consisting of yellowish semi-solid. After decantation of ether, the semi-solid mass was treated with water (12 c.c.). The oil, which separated on addition of water, crystallised gradually and completely. Colourless prisms thus obtained melted at 198-204° with decomposition. When the crystals were burned on a platinum spatula, it left white zinc oxide. Therefore, this substance is considered to be zinc chloride complex of ketimide chloride. When the zinc chloride complex was dissolved in water and the solution was warmed for one hour on the water bath, it became turbid, an oil separating finally. On cooling, this oil became crystalline and colourless needles crystallized out from the aqueous layer. The substance was recrystallised from methanol in colourless prisms, m.p. 201-202°. (7) It gave a purple-reddish tinge with ferric chloride (Found: CH_3O , 10.78. Calc. for $C_{15}H_{13}O_4 \cdot OCH_3$: CH_3O , 10.76%).

(7) The mother liquor was not investigated further.

The Position of Sugar. Methyl iodide (3 c.c.) was added to a solution of asebotin (3 g.) in dry acetone (20 c.c.) containing powdered potassium carbonate (6 g.) in suspension, and the mixture refluxed for 20 hours. After separation from potassium salts, the acetone and the excess of methyl iodide were removed by distillation. The colourless viscous residue, which could not be recrystallised, did not give a ferric chloride reaction. A solution of the product in a mixture of 50% methyl alcohol (25 c.c.) and 15% sulphuric acid (10 c.c.) was refluxed on the water bath for 30 minutes. On cooling, crystals separated, which crystallised from alcohol in colourless squat prisms, melting at 109–110° alone and in admixture with 6-hydroxy-2, 4, 4'-trimethoxy-phenyl-propiophenone,⁽⁵⁾ m. p. 109–110° (Found: C, 68.20; H, 6.42. Calc. for $C_{18}H_{20}O_5$: C, 68.32; H, 6.36%).

The author wishes to express his hearty thanks to Dr. T. Hoshino for his kind guidance during this investigation.

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THE THIRD ABSORPTION BANDS OF CO-ORDINATION
COMPOUNDS. I. $[\text{Co}(\text{NH}_3)_4\text{Cl NO}_2]\text{Cl}$ AND $[\text{Co}(\text{NO}_2)_6]\text{Na}_3$.

By Ryutaro TSUCHIDA and Shin KASHIMOTO.

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Most of the complex salts show in aqueous solutions two selective absorption bands⁽¹⁾ in the visible and the near-ultraviolet regions, but some of them give the third absorption bands. For instance, Y. Shibata⁽²⁾ has shown that nitro-ammine cobaltic compounds such as $[\text{Co}(\text{NH}_3)_4(\text{NO}_2)_2]^{(1)}\text{Cl}$, $[\text{Co}(\text{NH}_3)_3(\text{NO}_2)_3]$, and $[\text{Co}(\text{NH}_3)_2(\text{NO}_2)_4]\text{NH}_4$ have three absorption bands and thereby concluded that the third band is due to the pair of nitro-radicals co-ordinated in trans-positions to each other. Whereas the first and the second bands, especially the former, have frequently been investigated⁽³⁾, there have scarcely been any theoretical considerations as to the third band, except that of Y. Shibata⁽⁴⁾.

(1) Y. Shibata, *J. Chem. Soc. Japan*, **36** (1915), 118; etc.

(2) Y. Shibata, *J. Chem. Soc. Japan*, **36** (1915), 1246.

(3) Y. Shibata; *J. Faculty Sci., Imp. Univ. Tokyo*, (1915—); *J. Chem. Soc. Japan*, (1915—); J. P. Mathieu, *Bull. soc. chim.*, (5), **3** (1936), 463; A. Mead, *Trans. Faraday Soc.*, **30** (1934), 1052; J. Lifschitz, *Z. physik. Chem.*, **97** (1921), 1; etc.

(4) Y. Shibata, *J. Chem. Soc. Japan*, **36** (1915), 1243.

One of the authors⁽⁵⁾ has recently measured the absorption coefficients of trans-dichlorotetrammine cobaltic chloride $[\text{Co}(\text{NH}_3)_4\text{Cl}_2]^{(1)}\text{Cl}$ and showed that this salt has also the third absorption band. The author has thus been led to the conclusion that the theory of Shibata might possibly be extended to many other complex compounds besides the above mentioned nitro-ammines; in other words the theory might be applied not only to nitro-radicals but also to any other radicals which are co-ordinated by neutralizing the charge of the central metallic atom. The theory may, therefore, be extended to the effect that the third band is due to the pair of negative radicals co-ordinated in trans-positions to each other. The present investigation was undertaken to confirm the postulate. The extinction coefficients of $[\text{Co}(\text{NH}_3)_4(\text{NO}_2)_2]^{(1)}\text{Cl}$, $[\text{Co}(\text{NH}_3)_2(\text{NO}_2)_4]\text{NH}_4$, $[\text{Co}(\text{NO}_2)_6]\text{Na}_3$, and $[\text{Co}(\text{NH}_3)_4\text{Cl NO}_2]\text{Cl}$ were measured. The existence of the third bands is well established for the first two compounds, but not for $[\text{Co}(\text{NO}_2)_6]\text{Na}_3$. If the above mentioned postulate is right, the salt should have a third absorption band no matter what the configuration of NO_2 may be, and if Cl and NO_2 in $[\text{Co}(\text{NH}_3)_4\text{Cl NO}_2]\text{Cl}$ are co-ordinated in trans-positions to each other as is easily supposed from the process of its preparation, a third band should be expected also for this compound.

Experimental. (1) $[\text{Co}(\text{NH}_3)_4(\text{NO}_2)_2]^{(1)}\text{Cl}$ was prepared by the method of Jörgensen⁽⁶⁾. The extinction coefficients were measured for 0.001 mol/l. solution with varying thicknesses from 1 to 50 mm. The results are given in Fig. 1.

(2) $[\text{Co}(\text{NH}_3)_2(\text{NO}_2)_4]\text{NH}_4$ was prepared by the method of Jörgensen⁽⁷⁾ and the extinction coefficients were measured for 0.001 mol/l. solution with varying thicknesses from 1 to 50 mm. The absorption curve is shown in Fig. 2.

(3) $[\text{Co}(\text{NO}_2)_6]\text{Na}_3$ was prepared by the method of Büllmann⁽⁸⁾. The extinction coefficients were determined for concentrations between 0.0025 and 0.01 mol/l. and with varying thicknesses from 0.2 to 50 mm. The solutions were freshly prepared from time to time to avoid errors caused by considerably rapid decomposition of the salt. The results are shown in Fig. 2.

(4) $[\text{Co}(\text{NH}_3)_4\text{Cl NO}_2]\text{Cl}$ was obtained as an orange-red fibrous substance with silky lustre by the method of Jörgensen⁽⁹⁾. The measurements were done with concentrations between 0.0025 and 0.01 mol/l. and with varying thicknesses from 0.2 to 50 mm. The absorption curve is given in Fig. 1.

(5) R. Tsuchida, this bulletin, **11** (1936), 721.

(6) *Z. anorg. Chem.*, **17** (1898), 468.

(7) *Ibid.*, **17** (1898), 477.

(8) *Z. analyt. Chem.*, **39** (1900), 286.

(9) *Z. anorg. Chem.*, **5** (1894), 194; **7** (1894), 290; **17** (1898), 468.

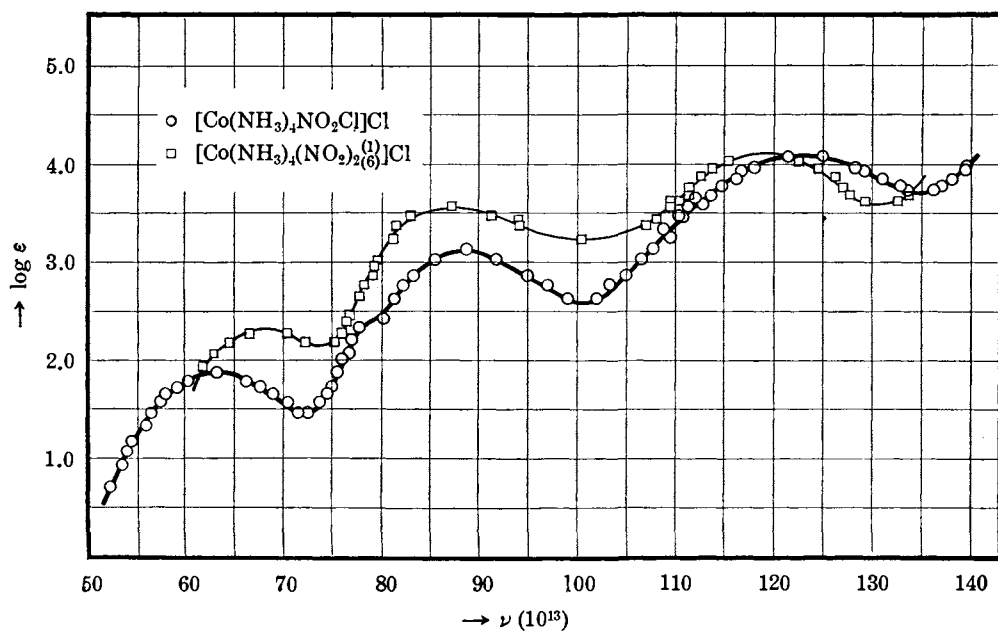


Fig. 1.

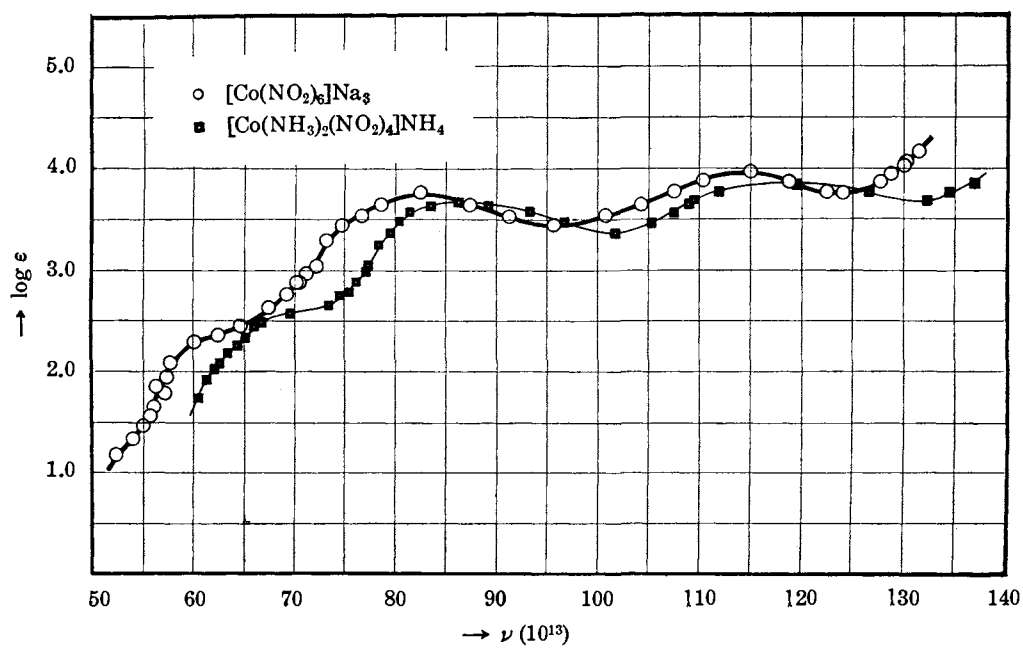


Fig. 2.

Results and Discussion. The frequencies for maximum absorption of these complex salts are summarized in Table 1 together with those of $[\text{Co}(\text{NH}_3)_4\text{Cl}_2]^{(10)}\text{Cl}$ and $[\text{Co}(\text{NH}_3)_3(\text{NO}_2)_3]^{(11)}$. The frequencies are shown as ν_1 , ν_2 , and ν_3 , the suffixes denoting the first, the second, and the third band respectively.

Table 1. Three Band Series.

	1st band		2nd band		3rd band		$\nu_2 - \nu_1$ (10^{13})	$\nu_3 - \nu_2$ (10^{13})	$\nu_3 - \nu_1$ (10^{13})
	ν_1 (10^{13})	$\log \epsilon$	ν_2 (10^{13})	$\log \epsilon$	ν_3 (10^{13})	$\log \epsilon$			
$[\text{Co}(\text{NH}_3)_4\text{Cl}_2]^{(10)}\text{Cl}$	45	1.2	63	1.37	96	3.16	18	33	51
$[\text{Co}(\text{NH}_3)_4\text{ClNO}_2]\text{Cl}$	63	1.87	89	3.13	123	4.10	26	34	60
$[\text{Co}(\text{NH}_3)_4(\text{NO}_2)_2]^{(10)}\text{Cl}$	68	2.32	87	3.54	120	4.11	19	33	52
$[\text{Co}(\text{NH}_3)_3(\text{NO}_2)_3]$	69	2.21	87	3.45	120	3.81	18	33	51
$[\text{Co}(\text{NH}_3)_2(\text{NO}_2)_4]\text{NH}_4$	68	2.56	86	3.67	119	3.85	18	33	51
$[\text{Co}(\text{NO}_2)_6]\text{Na}_3$	63	2.35	82	3.77	114	3.95	19	32	51

$[\text{Co}(\text{NH}_3)_4\text{ClNO}_2]\text{Cl}$ and $[\text{Co}(\text{NO}_2)_6]\text{Na}_3$ have thus been proved to have three bands each in the visible and the near-ultraviolet regions as had been expected. The third band of $[\text{Co}(\text{NO}_2)_6]\text{Na}_3$ may be explained as due to the pairs of either nitro-radicals or nitrito-radicals in trans-positions, but the colour of the salt favours the former view and accordingly the nitro-radicals are responsible for the third band as will be expected from the original theory of Shibata.

Whereas $[\text{Co}(\text{NH}_3)_4(\text{NO}_2)_2]^{(10)}\text{Cl}$ and $[\text{Co}(\text{NH}_3)_3(\text{NO}_2)_3]$ give their third bands at 120×10^{13} , nevertheless $[\text{Co}(\text{NH}_3)_2(\text{NO}_2)_4]\text{NH}_4$ shows its own at 119×10^{13} . The frequency 120×10^{13} may be assumed to be characteristic of the pair of nitro-radicals in trans-position to each other and the shift of the frequency towards longer wave-lengths may be explained as due to a disturbing effect on the pair of nitro-radicals by others which do not belong to the pair. In $[\text{Co}(\text{NH}_3)_3(\text{NO}_2)_3]$, however, the disturbing effect is small and the shift is almost imperceptible. As for $[\text{Co}(\text{NH}_3)_2(\text{NO}_2)_4]\text{NH}_4$, the shift is perceptible, indicating that the accumulation of negative charges in the complex radical gives rise to more or less instabilization. In $[\text{Co}(\text{NO}_2)_6]\text{Na}_3$, the disturbing effect is still greater than in $[\text{Co}(\text{NH}_3)_2(\text{NO}_2)_4]\text{NH}_4$, causing the shift

(10) *Loc. cit.*

(11) M. Kobayashi, unpublished.

to 114×10^{13} , and the higher instability may thereby be indicated. In $[\text{Co}(\text{NH}_3)_4\text{Cl}_2^{(1)}]\text{Cl}$ and $[\text{Co}(\text{NH}_3)_4\text{Cl NO}_2]\text{Cl}$, however, there will not exist such disturbing effect, and accordingly the frequencies 96×10^{13} and 123×10^{13} may be regarded as characteristic of the pair of two chlorine ions and that of a chlorine ion and a nitro-radical respectively.

Further we may point out some regularities among the frequencies for maximum absorption of those complex compounds in Table 1; viz., $\nu_3 - \nu_1$, $\nu_2 - \nu_1$, and $\nu_3 - \nu_2$ are 51×10^{13} , 18×10^{13} , and 33×10^{13} respectively, with the only exception of $[\text{Co}(\text{NH}_3)_4\text{Cl NO}_2]\text{Cl}$ for which $\nu_2 - \nu_1$ is 26×10^{13} .

Similar regularities may be found for other complex compounds. Absorption coefficients of a number of cobalt complex salts have recently⁽¹²⁾ been measured in this laboratory and among them some of pentammine and tetrammine series are exemplified in Table 2 and 3.

Table 2. Pentammine Cobaltic Series.

	1st band		2nd band		$\nu_2 - \nu_1 (10^{13})$
	$\nu_1 (10^{13})$	$\log \epsilon$	$\nu_2 (10^{13})$	$\log \epsilon$	
$[\text{Co}(\text{NH}_3)_5\text{NO}_3](\text{NO}_3)_2$	60	1.69	87	1.71	27
$[\text{Co}(\text{NH}_3)_5\text{NO}_2]\text{Cl}_2$	66	1.95	93	3.12	27
$[\text{Co}(\text{NH}_3)_5\text{ONO}]\text{Cl}_2$	64	1.74	91	2.79	27

Table 3. Tetrammine Cobaltic Series.

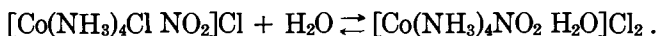
	1st band		2nd band		$\nu_2 - \nu_1 (10^{13})$
	$\nu_1 (10^{13})$	$\log \epsilon$	$\nu_2 (10^{13})$	$\log \epsilon$	
$[\text{Co}(\text{NH}_3)_4(\text{NO}_2)_2^{(1)}]\text{Cl}$	65	1.98	91	3.11	26
$[\text{Co}(\text{NH}_3)_4\text{CO}_3]\text{Br}$	57	2.03	83	2.01	26
$[\text{Co}(\text{NH}_3)_4\text{C}_2\text{O}_4]\text{Br}$	59	1.78	84	1.88	25
$[\text{Co}(\text{NH}_3)_4\text{Cl H}_2\text{O}_{(6)}^{(1)}]\text{Cl}_2$	50	1.30	75	1.76	25
$[\text{Co}(\text{NH}_3)_4\text{Cl H}_2\text{O}_{(2)}^{(1)}]\text{Cl}_2$	59	1.67	83	1.57	24
$[\text{Co}(\text{NH}_3)_4(\text{H}_2\text{O})_2^{(1)}]\text{Cl}_3$	60	1.40	84	1.48	24

For the pentammine series, $\nu_2 - \nu_1$ is 27×10^{13} and for the tetrammine series, $24 \sim 26 \times 10^{13}$. It is noteworthy that the monacido-pentammine and

(12) M. Kobayashi and others, unpublished.

the monacido-aquo-tetrammine salts form quite different series in regard to the value $\nu_2 - \nu_1$, while all the tetrammine salts belong to the same series in spite of their different charges of complex radicals. This fact is somewhat significant from the viewpoint of the stability of linkages between the central ion and the co-ordinated ions and molecules. It is still more remarkable that for the trans-diacido-tetrammine salts $\nu_2 - \nu_1$ is 18×10^{13} , whereas for the cis-diacido-tetrammine salts the value is 26×10^{13} .

Aqueous solutions of $[\text{Co}(\text{NH}_3)_4\text{Cl NO}_2]\text{Cl}$ behave as a compound of the tetrammine series so far as the first two bands are concerned. On the other hand the third band is observed for the same salt, as will be expected for a trans-diacido-tetrammine compound. This discrepancy may be explained as due to the following equilibrium⁽¹³⁾ which is set up immediately after dissolution in water.



The authors are preparing further investigation on this equilibrium.

Summary.

(1) In order to verify the postulate that the third band is due to a pair or pairs of negative radicals co-ordinated in trans-positions to each other, extinction coefficients of $[\text{Co}(\text{NO}_2)_6]\text{Na}_3$, $[\text{Co}(\text{NH}_3)_4\text{Cl NO}_2]\text{Cl}$, $[\text{Co}(\text{NH}_3)_4(\text{NO}_2)_2]^{(1)}\text{Cl}$, $[\text{Co}(\text{NH}_3)_2(\text{NO}_2)_4]\text{NH}_4$, etc. were measured.

(2) Aqueous solutions of $[\text{Co}(\text{NO}_2)_6]\text{Na}_3$ and $[\text{Co}(\text{NH}_3)_4\text{Cl NO}_2]\text{Cl}$ were proved to have the third bands as will be predicted from the postulate.

(3) Regularities among the frequencies of the first, the second, and the third band were pointed out, viz., for the cobalt complex salts, which show the third band, $\nu_3 - \nu_2$ and $\nu_2 - \nu_1$ are 33×10^{13} and 18×10^{13} , whereas for the pentammine and the tetrammine cobaltic salts, $\nu_2 - \nu_1$ is 27×10^{13} and $24 \sim 26 \times 10^{13}$ respectively.

The authors wish to express sincere thanks to Prof. Y. Shibata for his kind interest and also to Mr. M. Kobayashi for his assistance in the experimental work.

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(13) A. Werner, *Ber.*, **40** (1907), 4119; W. D. Harkins, R. E. Hall, and W. A. Roberts, *J. Am. Chem. Soc.*, **38** (1916), 2644.

STUDIES ON THE OILINESS OF LIQUIDS. II.

FRICTION COEFFICIENTS OF THE FILMS OF MONO- AND POLY-MOLECULAR LAYERS.

By Hideo AKAMATU and Jitsusaburo SAMESHIMA.

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It is well known that the friction between two solid surfaces greatly diminishes by the presence of a small amount of greasy matter at the sliding surfaces. Hardy found that the value of the coefficient of friction is practically independent of the quantity of the lubricating liquid, or the thickness of the film of liquid.⁽¹⁾ Langmuir devised a method of depositing monomolecular film of oleic acid on a glass plate.⁽²⁾ The friction coefficient of a glass reduces considerably by the presence of such a monomolecular film. Recently, this method has been improved by Blodgett and was made possible to deposit successive layers of fatty acid on a solid surface.⁽³⁾ The method is as follows. Let a small quantity of the fatty acid spreads on the surface of the water making monomolecular film. The area of the film is confined by using a boundary thread and a "piston oil" of oleic acid. Now a glass plate is dipped edgewise in such a water and withdrawn slowly, then a monomolecular film of fatty acid will be deposited on the glass plate. If this glass plate is dipped into the water again and withdrawn, then there deposit two more layers, the plate being covered with three molecular layers of fatty acid. If the process is repeated once more, then the number of layers becomes to five and so on.

By this method, we have made the films of known thickness on a glass plate, and have measured the coefficient of static friction of such a glass surface. The method of measuring of the static friction coefficient has already been described in the preceding report.⁽⁴⁾ The plate and the slider were cleaned by heating in chromic mixture for more than one hour, washing with soap solution, rinsing in running water and then drying in a current of the clean air. A microscope slide-glass was used as the sliding surface, and a watch glass as the slider. Blodgett's method has been conducted under the following conditions. The tap water was used for the underlying water of monomolecular floating film, the hydrogen concentration of which being

(1) Hardy and Doubleday, *Proc. Roy. Soc. (London)*, A, **100** (1922), 550.

(2) Langmuir, *Trans. Faraday Soc.*, **15** (1920), 68.

(3) Blodgett, *J. Am. Chem. Soc.*, **57** (1935), 1007.

(4) Sameshima, Kidokoro, and Akamatu, this Bulletin, **11** (1936), 659.

$pH = 7.8$ and containing some calcium ion. As the "piston oil" we used the oleic acid or the castor oil. The experiments were done at the room temperature.

The slide-glass was made clean by the above method, and one half of the surface was covered with the film of known thickness by Blodgett's method. The coefficients of friction were measured on the clean part and on the part covered with film. An actual example is shown in Table 1.

Table 1.

Surface of plate	Surface of slider	W (g.)	F (g.)	μ	Mean
Clean glass	Clean glass	20.6	25.52	1.24	1.04
		25.1	23.08	0.92	
		29.3	29.48	1.00	
		31.4	34.40	1.10	
Glass covered with the film of stearic acid of 1-molecular layer	Clean glass	25.1	3.15	0.13	0.11
		26.5	2.72	0.10	
		29.3	2.70	0.09	
		31.4	3.59	0.11	
The same of 3-molecular layer	Clean glass	20.6	2.41	0.12	

In this table are shown the conditions of surfaces of the plate and the slider, the weight of the slider, W , the tangential force acting to the slider, F , and the coefficient of friction, $F/W = \mu$.

The value of μ , thus, reduces to about one tenth by the existence of the monomolecular layer of stearic acid. This value, however, does not noticeably change by the increase of the thickness of film from 1-molecular to 3-molecular layer.

We have measured, in the next place, the coefficient of friction when the contact surface of the slider was covered with the monomolecular layer of stearic acid. The results are shown in Table 2.

From Table 1 and Table 2 we see that the value of μ is somewhat larger when the slider is covered with film and the plate is clean, than the case of the clean slider and covered plate. The slider surface is in contact with the

plate at a very small area if not at a point. So the monomolecular film of stearic acid on the slider is liable to be torn off at this contact point, and in consequence of this the friction becomes large. It is necessary, therefore, to deposit the film on the surface of plate in the study of the oiliness of films.

Table 2.

Surface of plate	Surface of slider	W (g.)	F (g.)	μ	μ Mean
Clean glass	Glass covered with the film of stearic acid of 1-molecular layer	26.2	8.53	0.33	0.34
		26.8	8.03	0.30	
		28.5	11.10	0.38	
Glass covered with the film of stearic acid of 1-molecular layer	Glass covered with the film of stearic acid of 1-molecular layer	25.7	2.42	0.09	0.11
		26.8	2.97	0.11	
		28.5	3.49	0.12	

The results of the measurements are summarized in Table 3. The data in this table have been obtained when the surface of plate is covered with the monomolecular film of the substances, the slider surface being clean. The "piston oil" used in the deposition of the film is also shown in the table.

From Table 3 we see that there are little differences of the coefficients of friction among these substances, provided that the thickness of film is 1-molecular. If the "piston oil" is changed from castor oil to oleic acid, there occurs, generally, a small change in the value of μ . Castor oil gives larger value of μ than oleic acid. This may be explained by the fact that oleic acid has greater surface pressure (about 30 dynes) than castor oil (about 17 dynes), so the former deposits the film in more compressed state than the latter.

Relatively large difference of μ is detected by the change of "piston oil" in the case of myristic acid. Myristic acid makes an expanded film and the compressibility of the film is larger than the other substances which make the condensed film.

The friction coefficients of the films thicker than 3-molecular layer are given in Table 4 and Table 5. The measurements have been done on palmitic acid and oleic acid. Oleic acid has been used for the "piston oil" in the deposition of films.

We see, from these tables, that there is almost no change in the value of μ , in spite of the change of thickness of the film. The presence of the film

Table 3.

Film substance	"Piston oil"	<i>W</i> (g.)	<i>F</i> (g.)	μ	μ Mean
Stearic acid	Castor oil	24.5	2.90	0.12	0.12
		25.1	3.15	0.13	
		31.4	3.59	0.11	
		32.8	3.68	0.11	
	Oleic acid	26.5	2.72	0.10	0.10
		29.3	2.70	0.09	
Palmitic acid	Castor oil	21.2	2.68	0.13	0.13
		26.7	3.15	0.12	
		30.9	3.53	0.11	
		31.0	4.31	0.14	
	Oleic acid	25.4	2.55	0.10	0.10
		29.0	2.75	0.09	
Myristic acid	Castor oil	22.6	4.71	0.21	0.20
		25.8	5.66	0.22	
		26.8	4.42	0.17	
	Oleic acid	21.9	2.65	0.12	0.11
		28.0	3.06	0.11	
		31.8	3.26	0.10	
Lauric acid	Castor oil	21.8	3.82	0.18	0.18
	Oleic acid	25.1	4.54	0.18	
		25.6	4.65	0.18	
Oleic acid	Castor oil	22.7	5.25	0.23	0.20
		26.6	4.78	0.18	
	Oleic acid	21.6	3.70	0.17	0.14
		21.6	2.39	0.11	
		24.3	4.28	0.18	
		24.3	2.15	0.09	
		32.1	4.27	0.13	
Ricinoleic acid	Castor oil	23.8	3.45	0.15	0.12
	Oleic acid	25.5	3.00	0.12	
		31.2	3.70	0.12	
Tripalmitine	Castor oil	20.9	3.12	0.15	0.14
		27.5	3.68	0.13	

Table 4.

Palmitic Acid Film.

Thickness of the film	W(g.)	F(g.)	μ	μ Mean
No film	(Table 1)			1.04
1-Molecular layer	(Table 3)			0.10
3-Molecular layer	25.4	2.66	0.11	0.09
	25.6	1.76	0.07	
	30.6	3.33	0.11	
	31.0	2.06	0.07	
5-Molecular layer	25.6	1.37	0.05	0.07
	27.5	2.10	0.08	
	29.0	2.26	0.08	
7-Molecular layer	23.3	1.30	0.06	0.06
	36.9	2.34	0.06	
9-Molecular layer	31.5	1.95	0.06	
11-Molecular layer	25.6	1.73	0.07	

Table 5.

Oleic Acid Film.

Thickness of the film	W(g.)	F(g.)	μ	μ Mean
No film	(Table 1)			1.04
1-Molecular layer	(Table 3)			0.14
3-Molecular layer	26.6	2.52	0.09	0.10
	26.6	2.43	0.09	
	29.1	3.70	0.13	
5-Molecular layer	25.3	3.54	0.14	0.16
	31.0	5.93	0.19	
7-Molecular layer	25.7	3.83	0.15	
9-Molecular layer	33.7	6.19	0.18	

of only 1-molecular layer reduces the friction coefficient to about one tenth of the clean glass surface, but no further reduction takes place by the increase of the thickness of film. This is a remarkable fact. In the film deposited by Blodgett's method, all of the oil molecules take the vertical position on the glass surface. The polar group of the oil molecule contacts with the surface of glass, and the nonpolar hydrocarbon group directs to the air. It is possible that such a regular arrangement of molecules favours the lubricating power more than the irregular arrangement. We can deposit the film on glass surface by means of the condensation of vapour or the evaporation of solvent from the solution. These methods, however, give less regular arrangement of molecules than Blodgett's method. On oleic acid the value of μ was measured to be about 0.3 in the case of the film deposited by the evaporation of the benzene solution. In the preceding paper, we reported that the value of μ of oleic acid is 0.29 when the glass surface is flooded with the liquid oil. Thus we see that the regular arrangement of oil molecules gives smaller friction coefficient than the irregular arrangement.

The present experiment has been done by the fund of Nippon Gakujutsu Shinkokwai (Foundation for the Promotion of Scientific and Industrial Research of Japan) for which the authors' thanks are due.

Summary.

(1) The static friction coefficients have been measured when the monomolecular films of some fatty acids, etc. are deposited on glass surface.

(2) The static friction coefficients have been measured on palmitic acid and oleic acid, when the film thickness increase from one to several molecular layers.

(3) The friction coefficient of the monomolecular film is about one tenth of that of the clean glass surface. The value shows no further reduction by the increase of the thickness of film.

(4) Regular arrangement of oil molecules in the film gives lower friction coefficient than the irregular one.

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ON THE STABILITY OF FOAM.

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It is a known fact that the foam of a liquid, for example the soap solution or beer, vanishes by adding a small quantity of an organic substance such as ethyl alcohol or ether. However there is no plausible explanation of this phenomena yet. So I started the following experiments.

When we shake the test tubes containing equal volumes of the liquids made from various proportions of butyl alcohol and water, and compare the heights of foam produced in them, the following is observed. The height of foam produced increases rapidly from zero by an addition of a minute quantity of butyl alcohol to water. On further addition of the alcohol, however, the height reaches a maximum and then falls again, finally tending to zero at the concentration at which the water is saturated with the alcohol. Further increase of the alcohol in water makes the system heterogeneous, from which, as well as from the homogeneous solution of water in butyl alcohol, no foam can be produced on shaking.

The same phenomenon is observed in some ternary systems. For example, when we shake a soap solution, a stable foam can be obtained. This foam vanishes instantaneously on adding a small quantity of butyl alcohol, but it can be reproduced when the solution is shaken again. If we continue to add butyl alcohol, a condition will be arrived at which the water is saturated with the alcohol and no foam can be produced on shaking.

It may be considered probable, from the above facts, that the homogeneity of a film plays an important rôle for the stability of the foam which it forms. That is to say, the foam of a homogeneous liquid mixture will be destroyed by adding one of the components, for the film of the foam becomes heterogeneous, being made of patches of the excessive component. In this case, the surface tension differs naturally in the different parts of a film. So the film, and accordingly the foam, will collapse. It can also be shown that a soap film made on a wire frame is torn off by touching with a drop of a liquid of low surface tension, alcohols for example. In general, such foam-depressant may be considered effective when it has a small solubility in water as well as a high surface activity.

A quantitative study is now being made on these phenomena.

The author is indebted to Prof. J. Sameshima for the inspection of the note.

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THE ADDITION OF HYDROGEN BROMIDE TO ALLYL BROMIDE IN THE PRESENCE OF VARIOUS SUBSTANCES.

III. A CONTRIBUTION TO THE ELUCIDATION OF THE SO-CALLED PEROXIDE EFFECT.

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The experiments described in this paper have been carried out with a view to elucidating the nature of the so-called peroxide effect in the addition of hydrogen bromide to allyl bromide. For the introduction to the present work the previous papers⁽¹⁾ may be consulted with.

The general procedure was as follows (compare the previous papers). Platinum black contained in the reaction tubes was heated at 250° in vacuum and then washed with hydrogen bromide gas. Allyl bromide (24 g. or 0.2 mol) was poured into the reaction tubes, which were filled beforehand with hydrogen bromide gas in experiments with platinum black. Then hydrogen bromide was introduced into the tubes cooled with solid carbon dioxide and chloroform, until the volume increase of the liquid reached 10 c.c. corresponding to 20 g. or 0.25 mol of hydrogen bromide. In exp. 1 allyl bromide and hydrogen bromide collected in the mixing tube were distilled in vacuum into the reaction tube as in the previous experiments.⁽²⁾ The mixtures were sealed in vacuum under cooling in liquid air. In exp. 1 air was allowed to enter the tube before sealing. The tubes were slipped into iron pipes and shaken at room temperature for three days. The contents were then treated as previous. Other particulars to individual cases will be given below. The results are shown in the accompanying table. The general decrease in the yields of the products compared with those obtained previously may be attributed to the fall of the room temperature.

The combined effects of platinum black and air were observed in exp. 1. The result, being very reasonable considering the results obtained with platinum black alone and with air alone (see the first paper), may be considered to represent simply the consequence of the competition of the two catalysts. Bromine was liberated, and its amount was roughly estimated to correspond to 45 c.c. of oxygen (2 Br : O) by the colorimetry of the wash

(1) This Bulletin, **11** (1936), 692, 754.

(2) As treated allyl bromide was used in all other experiments recorded in this paper, the distillation process was discarded.

No. of exp.	Treatment of allyl bromide and amount of Pt black, if added.	Products : dibromopropanes				Volume (c.c.) of O ₂ corresponding to liberated bromine
		Yield (%)	Boiling point (°C./mm.)	1, 3- (%)	1, 2- (%)	
1	Peroxide-free allyl bromide. Pt black 1.0 g. Air present.	30	38-49/16	39	61	45 (colorimetry)
2	Allyl bromide used immediately after passing O ₂ for six hours.	15	32-38/14	4	96	—
3	The same allyl bromide as 2. Pt black 0.5 g.	30	36-47.5/14	33	67	35 (colorim.)
4	Allyl bromide treated with O ₂ and placed in diffused light.	25	38-53.5/11	57	43	—
5	The same allyl bromide as 4. Pt black 0.5 g.	24	38-46/12	41	59	49 (iodometry) 48 (colorim.)
6	Allyl bromide treated with O ₂ and placed in diffused light.	41	40-55.5/12	70	30	—
7	The same allyl bromide as 6. Uncombined O ₂ removed. Pt black 0.5 g.	34	38-54.5/11	39	61	43 (iodom.) 36 (colorim.)

water of the reaction mixture against a standard bromine water. In experiments with peroxide-free allyl bromide, neither platinum black alone nor air alone has ever produced bromine from hydrogen bromide during the reaction.

A mixture of dibromopropanes (refractive index 1.5225, 1,3-compound 84%) (0.1 mol) was shaken with hydrogen bromide (0.1 mol), platinum black (0.5 g.), and dry air, by the same procedure as in the experiments of addition. The refractive index of the dibromopropane mixture was not changed by this treatment. The amount of bromine liberated corresponded to 14 c.c. of oxygen by colorimetry. This experiment shows that dibromopropanes are not isomerized by the action of any of platinum black, oxygen, and hydrogen bromide, and that bromine is produced from hydrogen bromide by the action of oxygen and platinum black even in the absence of the unsaturated compound, allyl bromide, the intermediate formation of a peroxide being unnecessary for the oxidation of hydrogen bromide.

The authors have made an interesting observation on the formation of a peroxide in allyl bromide. Even after oxygen was passed into allyl bromide

for six hours, the peroxide reaction with ammonium thiocyanate and ferrous ammonium sulphate was given only very slightly. When hydrogen bromide was added to allyl bromide treated with oxygen in this way, the result was quite normal (exp. 2),⁽³⁾ that is to say, the same as with untreated allyl bromide. Thus it was shown that oxygen was not combined with allyl bromide by mere passing of the former into the latter, and that, on introducing hydrogen bromide into allyl bromide at the temperature of solid carbon dioxide mixed with chloroform and then evacuating the mixture under cooling in liquid air, oxygen dissolved in allyl bromide was totally driven out. Nevertheless, when platinum black was put in the reaction tube beforehand and the addition was effected in the same way, a result similar to exp. 1 was obtained, bromine liberated corresponding to 35 c.c. of oxygen by colorimetry (exp. 3).⁽³⁾ The authors consider that the oxygen once dissolved in allyl bromide was retained by platinum black in some way or other at the low temperatures and given off again into the reaction mixture at room temperature. This assumption is supported by the fact that allyl bromide giving an intense colouration with ammonium thiocyanate and ferrous ammonium sulphate lost entirely the peroxide reaction on shaking with platinum black at room temperature for a few hours, showing that platinum black catalyzes the decomposition, rather than the formation, of the peroxide, and thus excluding the possibility of the fixation of oxygen by allyl bromide in the form of a peroxide with the aid of platinum black.

Now it has been found that light plays an important role in the formation of a peroxide in allyl bromide. Allyl bromide treated with oxygen in the dark for six hours did not give the peroxide reaction at all. When allyl bromide treated with oxygen was kept in diffused light for a few days, it gave an intense colouration with ammonium thiocyanate and ferrous ammonium sulphate, while a control substance (a portion of the allyl bromide treated with oxygen) placed in the dark during the same period gave no colouration and even after a month's standing in the dark at room temperature produced not the slightest peroxide reaction. The outdoor diffused light was naturally more effective for the peroxide formation than indoor light, but the direct sunlight caused the polymerization of allyl bromide. On adding hydrogen bromide to allyl bromide giving the peroxide reaction, uncombined oxygen being removed by evacuation under cooling in liquid air before (exp. 6)⁽³⁾ and after (exp. 4)⁽³⁾ the introduction of hydrogen bromide,⁽⁴⁾ the abnormal addition

(3) Exp. 2 and exp. 3 were carried out simultaneously with portions from the same specimen of treated allyl bromide; so were done exp. 4 and exp. 5; also exp. 6 and exp. 7. The difference in the yields between the last two groups of experiments may be, at least partly, due to the different temperatures of the room.

(4) In exp. 6 the tube was evacuated as usual also at sealing.

product (1,3-dibromopropane) undoubtedly predominated over the normal (1,2-dibromopropane). In exp. 5⁽³⁾ hydrogen bromide was added to allyl bromide containing the peroxide (and also uncombined oxygen) in the presence of platinum black, the mixture being evacuated only at sealing. In exp. 7,⁽³⁾ uncombined oxygen was removed from allyl bromide contained in a side tube provided especially for this purpose by evacuation under cooling in liquid air, and allyl bromide treated in this way was decanted in vacuum into the reaction tube containing platinum black. The results of exp. 5 and exp. 7 were similar to exp. 1, bromine being liberated in amounts shown in the table.

The results described above give an important suggestion. As mentioned above, a peroxide is formed from allyl bromide and oxygen only under the action of light, while the addition to peroxide-free allyl bromide in the presence of oxygen in the dark gives mainly 1,3-dibromopropane. Thus it is very probable that the effect may be attributed to the action of oxygen itself and not to any formed peroxide, because neither hydrogen bromide nor dibromopropanes can be considered to be capable of producing a peroxide from allyl bromide and oxygen. Moreover, platinum black possessing the power of decomposing peroxides and of accelerating the normal addition can not totally suppress the so-called peroxide effect by oxygen (exp. 1), allowing the formation of about 40% 1,3-compound. It may be rather suspected that peroxides are active because of the generation of oxygen by their decomposition, whether platinum black is present or not. In this connection it may be added that peroxide-containing allyl bromide had lost in fact the peroxide reaction after the action of hydrogen bromide, both in the presence and in the absence of platinum black. Experiments devised to furnish more definite indications on these points are now under way.

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THE PHOTOCHEMICAL DEHYDROGENATION OF
7-DEHYDRO-CHOLESTEROL.
(Preliminary Note.)

By Yoshiyuki URUSHIBARA and Toshio ANDO.

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7-Dehydro-cholesterol $C_{27}H_{44}O$ prepared by the method of A. Windaus, H. Lettré, and F. Schenck⁽¹⁾ was dehydrogenated photochemically in alcoholic solution in the presence of eosin according to the directions of H. H. Inhoffen⁽²⁾ for the preparation of ergopinacone from ergosterol. The flocculent needles which separated out in the course of a week's irradiation with the sunlight were collected, boiled with 95% alcohol, and washed with alcohol and then with ether. The substance obtained in this way melts and decomposes sharply at $182-183^{\circ}$ (corr.). For analysis the substance was dried in vacuum at 110° for 30 minutes (Found: C, 84.74; H, 11.14; molecular weight (Rast), 487. Calculated for $C_{54}H_{86}O_2$: C, 84.53; H, 11.31%; molecular weight, 767). If this substance is demonstrated to be the compound corresponding to ergopinacone, it may be called 7-dehydro-cholesteno-pinacone, and will be an important intermediate from cholesterol to its 10-desmethyl-derivatives analogous to those of ergosterol.

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(1) *Ann.*, **520** (1935), 98.

(2) *Ann.*, **497** (1932), 130.