THE SORPTION OF GAS BY CHARCOAL AS A DISSOLUTION PHENOMENON.

By **Jitsusaburo SAMESHIMA.**

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It is generally considered that the sorption of gas by charcoal is caused by the condensation of gas on the surface of the charcoal. Since Saussure's extensive research on this subject(1) nobody raise a doubt on the hypothesis of adsorption.(2) Recently, many suppositions have been proposed for the mechanism of sorption. Of them monomolecular film hypothesis of Langmuir(3) and polymolecular film hypothesis of Polanyi(4) are preeminent. None of them, however, do not sufficiently coinside with the results of experiments. McBain and others(5) have the opinion that one part of the gas absorbed is kept on the surface of the carbon and the other part diffuse into the mass of it.

I have studied the sorption of gas by charcoal for last several years(6) and recently was convinced that this phenomenon is caused by the dissolution of gas into the mass of charcoal. Of course the minimal quantity of gas may be adsorbed, positively or negatively, on the surface of the charcoal as is required by the Gibbs-Thomson's equation, but almost all quantity of gas absorbed is kept in the mass of charcoal as a solid solution. This has been proved by the facts described in this paper and by those which will be described in the later papers.

I have found no paper except Homfray's one(7) which deals the sorption of gas by charcoal as a dissolution phenomenon. There is no follower of Miss Homfray since the publication of her paper sixteen years ago, and only the adsorption hypothesis prevails throughout the scientific world.

Velocity of Sorption of Carbon Dioxide by Charcoal under Constant Pressure. The velocity of sorption of gas by charcoal was already

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(1) Saussure, *Gilb. Ann.*, 70 (1814), 113.

(2) The term "adsorption" was firstly used by Kayser, *Wied. Ann.*, 14 (1881), 450. For earlier literatures see, Mülfarth, *Ann. Physik,* [4], 3 (1900), 328.

(3) Langmuir, *J. Am. Chem. Soc.*, 40 (1918), 1361.

(4) Polanyi, *Ber. deut. physik. Ges.*, 16 (1914), 1012; *Z. Elektrochem.*, 18 (1916), 55 & 26 (1920), 370.

(5) McBain, *Phil. Mag.*, 18 (1909), 916; *Z. physik. Chem.*, 68 (1909), 471; *Nature,* 117 (1926), 550. Gouy, *J. d. Phys.,* [4], 9 (1910), 457. Firth, *Z. physik. Chem.*, 86 (1914), 294. Sheldon, *Phys. Rev.*, 19 (1922), 253.

(6) Sameshima and Hayashi, *Science Reports of the Tohoku Imperial University,* 12 (1924), 289.

(7) Homfray, *Z. physik. Chem.*, 74 (1910), 129. See Coolidge, *J. Am. Chem. Soc.*, 48 (1926), 1795.

measured by numerous authors,(1) but their experiments were not suited for the present purpose. I have measured the velocity of sorption of carbon dioxide by the cane sugar charcoal.

The charcoal was made by heating the pure saccharose from Merck in a porcellain crucible to red heat and then transfered into a quartz tube and again heated in vacuo to 1,000° for 30 minutes. The carbon dioxide was made by the action of the hydrochloric acid on the marble and passed through the sodium bicarbonate solution, concentrated sulphuric acid and phosphorus pentoxide successively. The gas was, then, frozen by liquid air, exhausted, and finally sublimed in vacuo.

The weight of charcoal was determined in the following manner. The sample is introduced into a small tube, which is then connected to an evacuating system. Heat to 300’ and evacuate to a pressure less than 0.001 mm., and then hermetically sealed and weighed. The tube is then cut open and the charcoal is transfered into the measuring apparatus (A in Fig. 1). The emptied glass tube and the pieses of glass are weighed and subtracted from the former value. Of course the correction for the bouyancy of the air must be applied.

The measuring apparatus is shown in Fig. 1. A is a vessel containing the known quantity of charcoal. This is heated to 300° by an electric furnace and evacuated by using a mercury diffusion pump for 30 minutes after the pressure diminishes less than 0.001 mm. The stopcock B and C are then closed, and the carbon dioxide gas is introduced through the cock D into the graduated burette E. The burette E consists of three parts, the upper part is made of a capillary tube of 2.3 mm. diameter, and the middle part an ordinary gas burette, and the lower part a ten c.c. burette of 7 mm. diameter.

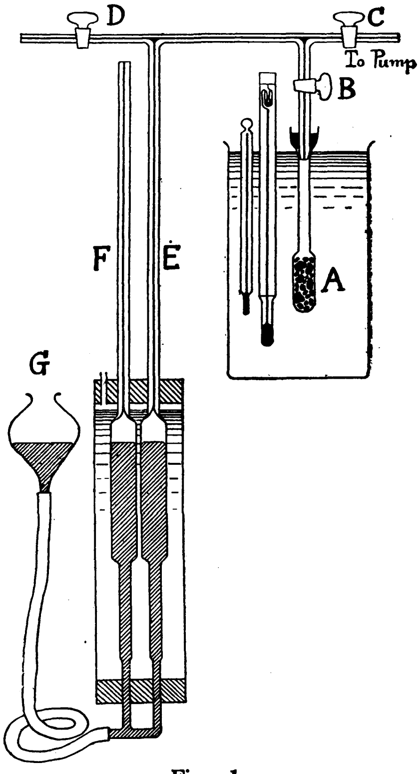

Fig. 1.

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(1) Giesen, *Ann. Physik*, 10 (1903), 833. Bergter, *Ann. Physik*, 37 (1912), 472. Harned, *J. Am. Chem. Soc.*, 42 (1920), 372. Driver and Firth, *J. Chem. Soc.*, 121 (1922), 2409. Gustaver, *Kolloidchem. Beihefte*, 15 (1922), 185. Iliin, *Z. physik. Chem.*, 107 (1923), 145. Rowe, *Phil. Mag.*, [7], 1 (1926), 659.

The latter two parts are kept in a water mantle as shown in the figure to prevent the change of temperature of the gas. A thermostat is brought to A by which it is kept to 25.00°, the constancy of temperature is indicated by a Beckmann thermometer. Now the cock B is opened and the carbon dioxide gas enters into the vessel A and is absorbed by the charcoal. The mercury reservoir G is raised to keep the gas pressure as constant as possible. The pressure of gas is read by the open manometer F and a barometer. The manometer F is made of three glass tubes of the same diameters to E as shown in the figure. The whole apparatus was calibrated with mercury before being assembled. This enabled the volume of gas in the different sections of the apparatus to be reduced separately to 0°C. from their observed temperatures.

The volume of the charcoal itself has been calculated assuming the density of charcoal to be 2.10(1). Some investigators(2) gave lower values for the density of charcoal, but the above given value is considered to be most reasonable from the fact that the charcoal has essentially identical nature to graphite.(3) The results are shown in Table 1. After the first series of observations had finished, the tube A was heated to 300° and evacuated for 30 minutes and then the second series of observations has been undertaken. Quite reproducible results were obtained as shown in the table.

TABLE 1.

Quantity of charcoal used in the experiments = 0.8604 gr.

	Time.		Volume of CO_2 absorbed by 1 gr. of charcoal at 25.00° (N.T.P.), in c.c.	Pressure of gas in mm. Hg.
	Min.	Sec.		
First series.		26	36.88	763.3
		59	43.48	763.3
	2	40	47.67	763.3
	3	10	48.11	763.3
	4	45	48.99	763.3
	95		52.58	762.3
	180		52.98	761.3
	1630		53.87	760.2
	3120		53.90	755.5

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(1) Howard and Hulett, *J. Phys. Chem.* **28** (1924), 1082.

(2) Cude and Hulett, *J. Am. Chem. Soc.*, **42** (1920), 391. Harkins and Ewing, *J. Am. Chem. Soc.*, **43** (1921), 1787.

(3) Debye and Scherrer, *Physik. Z.*, **18** (1917), 300. Asahara, *Japanese Journal of Chemistry*, **1** (1922), 35.

TABLE 1. (*Continued.*)

	Time.		Volume of CO_2 absorbed by 1 gr. of charcoal at 25.00° (N. T. P.), in c.c.	Pressure of gas in mm. Hg.
	Min.	Sec.		
Second series.		33	39.32	760.0
	2	50	47.86	760.0
	10	27	50.26	760.0
	12	25	50.44	760.0
	13	45	50.57	760.0
	15	20	50.75	760.0
	22	12	51.18	760.0
	25	55	51.36	760.0
	35	0	51.65	760.0
	40	30	51.77	760.0
	49	30	51.95	760.0
	65		52.24	760.0
	91		52.52	760.0
	146		52.85	760.0
	199		53.06	760.0
	220		53.11	760.0
	257		53.16	760.0
	281		53.22	760.0
	353		53.32	760.0
	387		53.37	760.0
Third series.		15	34.38	768.2
		25	37.91	768.2
		44	42.22	768.2
		61	44.37	768.2
	4	25	48.81	760.0
	26	10	51.25	757.7
	32	20	51.59	760.0
	35		51.71	760.0
	40		51.78	760.0
	42		51.89	760.0
	55		52.13	760.0
	79		52.42	760.0
	196		53.12	760.0
	294		53.23	760.0
	315		53.28	760.0
	365		53.33	760.0
	1470		53.95	761.4
	1610		53.95	760.0
	3090		54.04	760.0
	3205		54.03	760.0

After the sorption had been measured, the charcoal was powdered in an agate mortar as fine as possible. The powdered charcoal was put into a glass-tube and was connected to an evacuating system, heat to 300° and evacuated for 30 minutes, then hermetically sealed and weighed, in the same manner as in the case of granular charcoal. The powder was transfered into the vessel A in Fig. 1 and then measured the quantity of absorption of carbon dioxide gas. The results are shown in Table 2.

TABLE 2.

Quantity of powder charcoal used in the experiments = 0.8752 gr.

Time. Min.	Time. Sec.	Volume of CO_2 absorbed by 1 gr. of powder charcoal at 25.00° (N.T.P.) in c.c.	Pressure of gas in mm. Hg.
	22	44.54	760.0
	33	46.63	760.0
	43	47.68	760.0
	57	48.73	760.0
2	48	51.01	760.0
3	54	51.38	760.0
5	8	51.74	760.0
7	0	52.09	760.0
10	50	52.43	760.0
18	20	52.72	759.7
29	30	52.94	760.0
41		53.11	760.0
100		53.33	760.0
140		53.44	760.0
235		53.52	760.0
295		53.55	760.0
1440		53.85	760.0
1785		53.91	760.0
2880		54.01	760.0
2910		54.00	760.0
2975		53.97	760.0
3110		53.97	760.0

Graphically it becomes as Fig. 2. In this figure the logarithm of the time in seconds is taken in abscissa and the absorbed volume of carbon dioxide in ordinate.

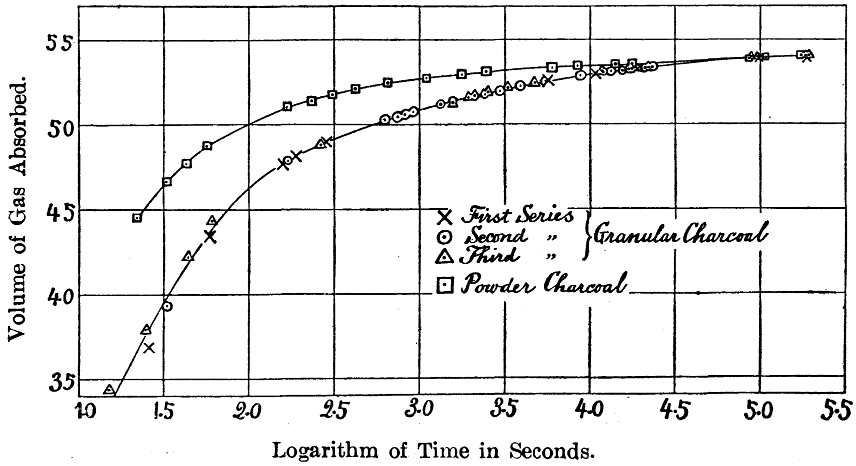

Fig. 2.

We see, from the above results, that the absorbed quantity of carbon dioxide by granular charcoal and by powder charcoal are quite the same. Moreover, the powder charcoal absorbs the gas more rapidly than the granular one. If we assume that the gas dissolves into the charcoal, then the above phenomena can be explained very smoothly. The dissolved quantity of gas depends only upon the amount of charcoal, and does not depend upon the surface area of it. So the same amount of charcoal absorbs the same quantity of gas, so long as the purity and the chemical nature of the carbon are the same, no matter what the surface area may be. By powdering the charcoal, the surface area must increases, so the velocity of dissolution must, of course, increases. From the adsorption hypothesis, the adsorbed quantity of gas must increases or decreases⁽¹⁾ by powdering the substance, but in my experiment it is not so. Quantitative discussions may appear in a later paper.

The Amounts of Carbon Dioxide Absorbed by Various Kinds of Charcoals.⁽²⁾ The absorptive capacities were measured of carbon dioxide by the various kinds of charcoals and the results are shown in Table 3. In each case the capacities were measured after the charcoals had been heated to 300° in vacuo.

TABLE 3.

Material from which the charcoal was obtained	Treatment.	Temp. °C.	Press. mm.	Volume of CO_2 absorbed by 1 gr. of charcoal (N.T.P.) c.c.	Ash content %
Bamboo wood.	The material was carbonized at 400°–500°, and then heated to 800° for 1 hour.	20.1	759	44.8	3.0
Cherry wood.	do.	22.0	758	43.0	1.5
Ebony wood.	do.	25.0	758	36.7	14.0
Cork.	do.	24.0	756	49.0	7.2
Cocoanut shell.	do.	23.2	754	46.3	2.8
Rice.	do.	25.0	755	46.0	1.7
Soy-bean.	do.	16.2	765	3.6	20.5
Kahlbaum's "Kohle activ".	—	23.3	758	44.2	6.1
Bamboo wood.	The charcoal was boiled with aqua regia, washed with water and heated to 300°	25.0	758	43.4	0.8

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(1) See Freundlich, "Kapillarchemie" 3rd. ed. (1923), p. 177.

(2) More detailed descriptions are found in the *Journal of the Chemical Society of Japan* (in Japanese), 47 (1926), 715.

TABLE 3. (*Continued.*)

Material from which the charcoal was obtained	Treatment	Temp. °C.	Press. mm.	Volume of CO_2 absorbed by 1 gr. of charcoal (N.T.P.) c.c.	Ash content. %
Cane sugar.	The sugar was carbonized in a crucible and then heated to 1,000° in vacuo for 30 minutes.	25.0	760	54.0	0
Carbon* monoxide soot.	CO was decomposed by hot iron. The charcoal was treated with HCl.	25.5	759	7.1	5.9 (Fe_2O_3)
Naphthalene** soot	———	25.0	762	38.0	—
Anthracite.	Anthracite was treated with HNO_3 and heated to 1,000°	20.2	765	45.6	8.1

* By the courtesy of Dr. Asahara in the Institute of Physical and Chemical Research.

** Made in the Laboratory of Prof. Michaelis in Aichi Medical University, Nagoya.

We see from Table 3 that the amount of absorbed carbon dioxide at ordinary temperatures (20–25°) by various kinds of charcoals are nearly equal in each other, viz. 35–50 c.c., notwithstanding the materials from which the charcoals have been made are so divergent. In the case of the soy-bean charcoal, the ash content is so high as 20% and such an impure charcoal cannot be compared with other purer charcoals. The bamboo charcoal was made by the carbonization of the hard fibrous stem of that tree, the sugar charcoal was made by the carbonization of the fused mass of sugar, while naphthalene soot by the imcomplete oxidation of the combustible vapour. It is not conceivable that so different materials give the charcoals of nearly same surface area. The surface area must, of course, be different in each charcoals, while they show nearly equal absorptive capacities. This fact can only be explained by the dissolution theory and not by the adsorption theory. The content of ash and other impurities will change the absorptive capacities of the charcoals, just as the dissolved salts or alcohol diminishes the solubility of hydrochloric acid gas in the water. The " activation " process is probably a process of removing the impurities and enlarging the surface area by etching which will enable the ability of rapid absorption of the gas.

One gram of the pure cane sugar charcoal absorbs 54.0 c.c. of carbon dioxide (N.T.P.) at 25.0° and under the gas pressure of 760 mm. We may take this quantity as the solubility of carbon dioxide in pure charcoal. For impure charcoal the solubility of gas will change according to the amounts, the chemical nature and the state of existence (i.e. physical mixture, solid solution or compound) of the impurities. The soy-bean charcoal and the carbon monoxide soot are the examples of the great effect of impurities. The carbon dioxide is an unsuitable gas to test the effect of impurities, because CaO, MgO etc. in the ash will chemically absorb this gas. The experiments for other gases will be undertaken later.

Absorptions of Carbon Dioxide by Charcoal at Various Temperatures and Pressures.(1) The determinations were made of the absorption amounts of carbon dioxide by another sample of bamboo charcoal at different temperatures and pressures and the results are summarized in Table 4.

Table 4.

Volumes of CO_2 absorbed by 1 gr. of bamboo charcoal (N.T.P.) in c.c.

Press. \ Temp.	0°	10°	20°	30°	40°
50 mm.	15.5	11.7	9.0	6.3	3.6
100 mm.	22.1	17.4	13.7	10.1	6.3
200 mm.	30.0	24.8	20.1	15.4	10.6
300 mm.	35.0	29.4	24.5	19.2	14.2
400 mm.	38.8	32.8	27.9	22.3	17.1
500 mm.	41.6	35.6	30.8	25.0	19.4
600 mm.	43.9	38.1	33.1	27.1	—

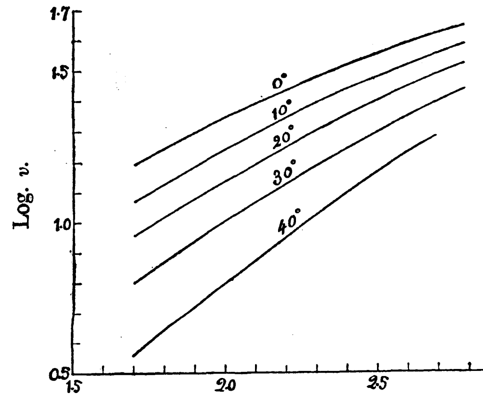

Fig. 3.

If we plot the logarithm of the volume against the logarithm of the pressure, Fig. 3 is obtained. Form Fig. 3 we see that the Freundlich's formula can hardly be applied in this case.

Numerous authors have tested whether the Henry's law can be applied for the absorption of gases by solids. In the case of hydrogen the law is applicable,(2) *but in other gases it is not* so. In Fig. 3 we see that the tangent of curves approach to unity at the high temperature and low pressure, for example at 40’ it becomes,

$$\frac{d(\log v)}{d(\log p)} = \frac{4}{5}, \qquad \text{or} \qquad v = kp^{0.8}$$

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(1) This experiment was done in 1922 in the Chemical Laboratory of the Tohoku Imperial University, Sendai.

(2) Titoff, *Z. physik Chem.*, 74 (1910), 641.

where v denotes the absorbed volume of gas, p the pressure and k a constant. The charcoal absorbs too much carbon dioxide to be applied the Henry's law, just as the cases of the dissolutions of ammonia or hydrochloric acid gas in the water. The amount of absorbed gas increases by lowering the temperature, which is quite similar to the dissolution of gas in water. There are parallelisms between the temperature effect on the absorption of gas by charcoal and by water.

Change of Absorption Amount by the Change of Modification. It is generally known that a substance in amorphous modification absorbs much gas than its crystalline modification.(1) It is doubtful that there is really amorphous substance in solid modification from the standpoint of the phase rule, X-ray analysis or colloid chemistry. Some of them may be the supercooled liquids and others may be the imperfect crystals of somewhat irregular atomic arrangements. But in any case, the so-called amorphous substance is the modification which will be situated between the perfect crystalline phase and the liquid phase. So it is expected that the solubility of gas by the amorphous modification is greater than that by the crystalline one, and probably less than that by the liquid if a comparison at the same temperature could be done. The absorptions of gases by silica gel, alumina or some of the fine powder of metals may ascribe to this cause.

The author wishes to express his thanks to Dr. G. Asahara and Dr. T. Totsuka for furnishing some of the charcoals. The author's thanks are also due to Mr. M. Kishino and Mr. T. Watanabe for their assistances in the experiments.

Summary.

1. The velocities of absorptions of carbon dioxide by the granular and the powder charcoals have been measured.
2. The velocity of absorption by the granular charcoal is smaller than that by the powder one.
3. It was confirmed that the absorption amounts by the granular and by the powder charcoal are the same.
4. The solubility of carbon dioxide in one gram of pure cane sugar charcoal at 25.0° and under 760 mm. has been determined to be 54.0 c.c. (N.T.P.).
5. The amounts of absorptions of carbon dioxide by various kinds of charcoals have been measured. Most of them absorb nearly equal amount of the gas, notwithstanding the divergence of the materials from which the charcoals were made.
6. The amounts of absorptions of carbon dioxide by bamboo charcoal at various temperatures and pressures have been measured.

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(1) See Freundlich "Kapillarchemie" 3rd. ed. (1923), p. 178.

7. The fact that the amorphous substance absorbs more gas than the crystalline one has been interpreted.

8. All of the facts mentioned above favoured the dissolution theory for the sorption of gas by charcoal.

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SPECTROCHEMICAL STUDIES OF HYDROXYAZO-COMPOUNDS. PART II.⁽¹⁾

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and Tamimatsu ENDO.

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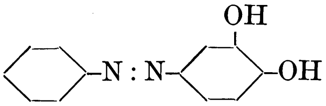
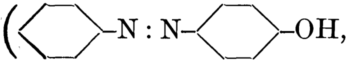
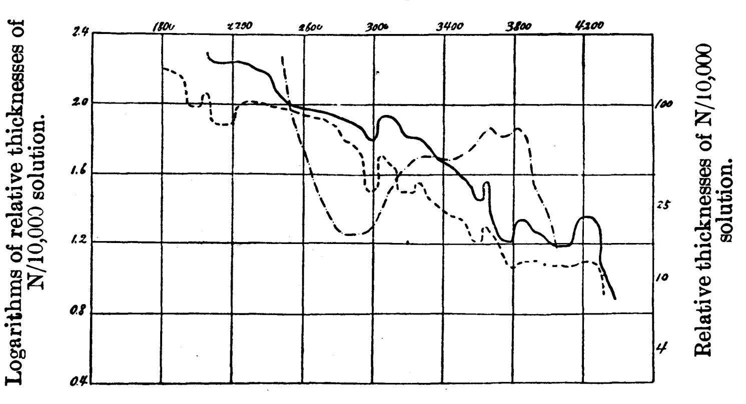
1. Benzeneazocatechol[2] (Benzeneazopyrocatechin),



Although the addition of KOH to this substance induces a change of colour in the solution from yellow to orange, only a slightly bathochromic influence can be observed from the absorption curve (Fig. 1). When we compare Fig. 1 with the absorption curve of No. 1 compound (, Fig. 1 in Part I of this paper), we can ascertain a considerable difference between them. We think this is due to the hydroxyl-group of the meta-position with respect to the azo-group. Then,



1. Benzeneazocatechol. { ——— Neutral solution.
{ - - - - - 0.05 N. alkaline solution.
1 (Part I). p-Hydroxyazobenzene. —·—·— Neutral solution.

Fig. 1.

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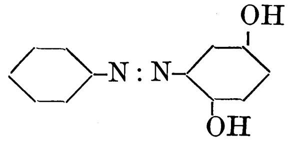
(1) Part I of this paper has been published in this journal 1 (1926), 260. N.B. In this paper, in the 12th line from the bottom on page 261, the phrase "the bathochromic and hyperchromic influences are easily observed" should be changed to "the bathochromic influence is easily observed".

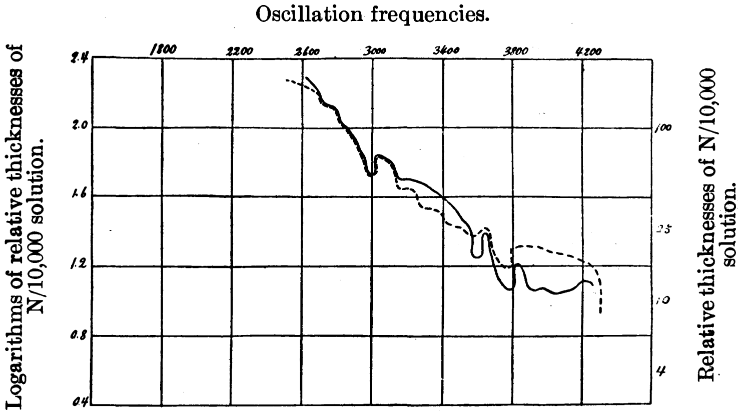
(2) Beilstein, "Handbuch der Organischen Chemie", IV (1899), 1440.

A-form is naturally assigned to the neutral solution, but the orange alkaline solution is perhaps the mixture of A-form and R-form.

2. Benzeneazoquinol⁽¹⁾
(Benzeneazohydroquinone),



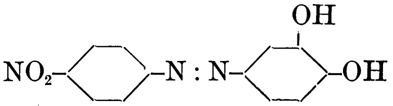
This substance is hardly affected in colour by the addition of KOH, and its absorption curves (Fig. 2) are also represented as can be expected. Only A-form exists in the solution of this compound.

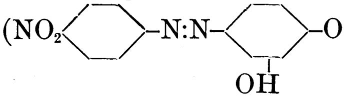


2. Benzeneazoquinol. { —— Neutral solution. ------ 0.05 N. alkaline solution.

Fig. 2.

3. p-Nitrobenzeneazocatechol⁽²⁾
(p-Nitrobenzeneazopyrocatechin),



Bathochromic and hyperchromic effects through alkali are observed in the solution of this compound. As the range of the red coloured solution is quite short, it changes into blue very quickly. N/1,000 alkaline solution is already blue, but this blue solution loses its shade, changes into reddish brown after standing one day, and can no more regain its former shade. We may give A-form to the neutral solution and B-form to the blue alkaline solution. According to the meta hydroxyl with respect to the azo-group, a great difference can be observed between the absorption curve of this compound (Fig. 3) and that of No. 5 compound (), in Part I of this paper.

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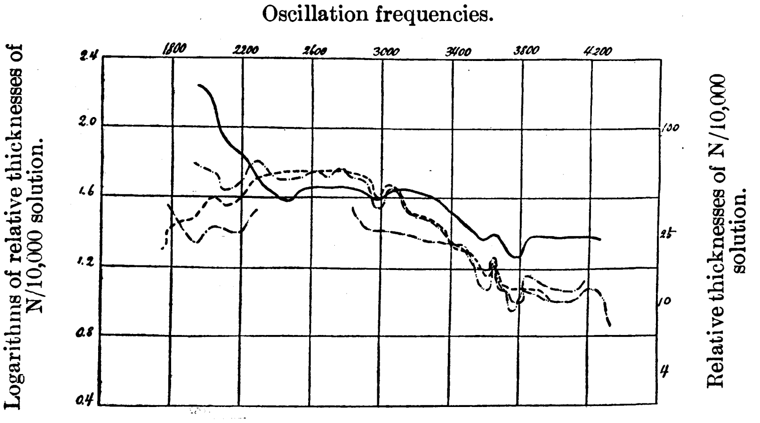
(1) Beilstein, " Handbuch der Crganischen Chemie ", IV (1899), 1447.

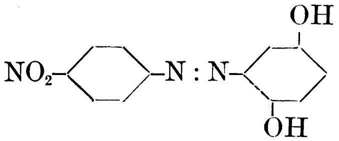
(2) Ibid., IV (1899), 1440.



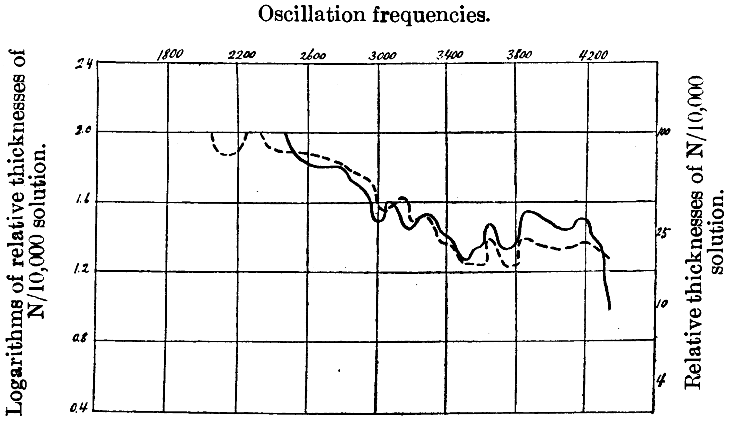
3. p-Nitrobenzeneazo-catechol.
—— Neutral solution.
- - - - - 0.048 N. alkaline solution.
—·—·— „ „ (after 3 days.)
—··—··— „ „ (after 4 days.)

Fig. 3.

4. p-Nitrobenzeneazoquinol(1) (p-Nitrobenzeneazohydroquinone),



We notice a slight change in colour through KOH, that is, by the addition of an alkali, a yellowish red neutral solution becomes orange, but this orange returns to yellow after one day and deos not take the former shade again. Then A-form can be assigned to the neutral solution, and probably R-form to the orange state (Fig. 4.).



4. p-Nitrobenzeneazoquinol.
—— Neutral solution.
- - - - - 0.05 N. alkaline solution.

Fig. 4.

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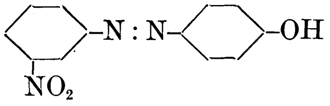
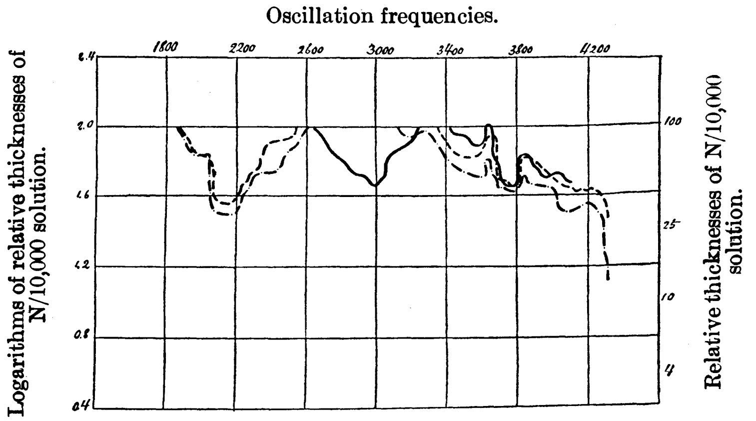
(1) Beilstein, "Handbuch der Organischen Chemie", IV (1899), 1447.

5. m-Nitrobenzeneazophenol,(1)



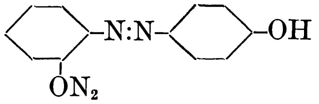
The yellow neutral solution changes into red when an alkaline solution is added. The bathochromic influence due to KOH can clearly be seen in the absorption curve (Fig. 5). We can certainly give A-form to the neutral solution and R-form to the alkaline solution which cannot have B-form owing to the meta nitro-radical with respect to the azo-group.



5. m-Nitrobenzeneazophenol. { ——— Neutral solution.
- - - - - 0.033 N. alkaline solution
— · — · — 0.166 N. alkaline solution

Fig. 5.

6. o-Nitrobenzeneazophenol(1)



The very same colour changes in No. 5 compound can be easily observed in this case, that is, we recognise bathochromic and hyperchromic effects when the solution is alkaline, but can never get the blue solution. Therefore, A- and R-forms only exist in o-Nitrobenzeneazophenol solution (Fig. 6).

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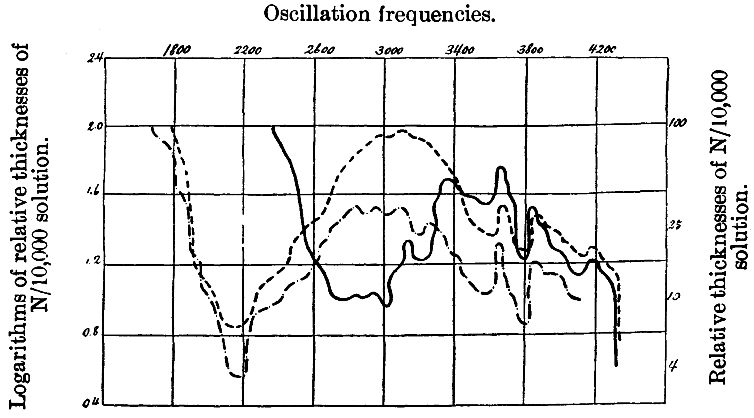
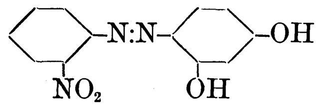
(1) Beilstein, "Handbuch der Organischen Chemie", IV (1899), 1410.



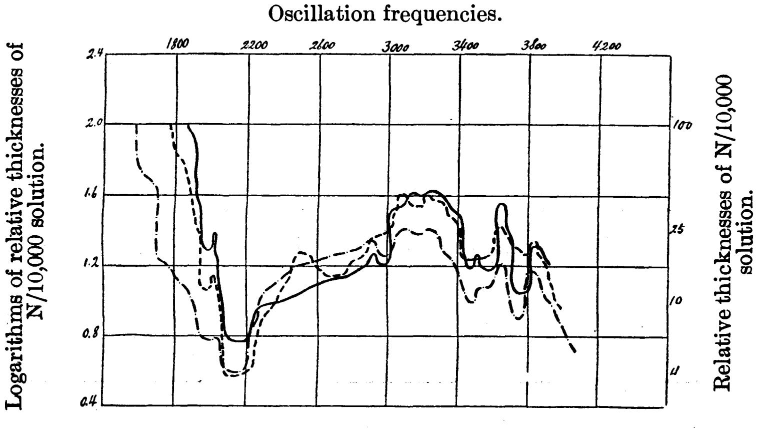
6. o-Nitrobenzeneazophenol. { ——— Neutral solution. - - - - - 0.05 N. alkaline solution. —·—·— 1.44 N. alkaline solution.

Fig. 6.

7. o-Nitrobenzeneazoresorcinol,(1)



Only the red alkaline solution of this compound can be easily obtained, and A- and R-forms can be respectively given to the neutral and alkaline solutions (Fig. 7). It is, therefore, proved that the nitro-radical which is in the ortho-position with respect to azo-group cannot take the isonitro-structure (See No. 6 compound).



7. o-Nitrobenzeneazoresorcinol. { ——— Neutral solution. - - - - - 0.0567 N. alkaline solution. —·—·— 1.12 N. alkaline solution.

Fig. 7.

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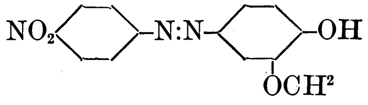
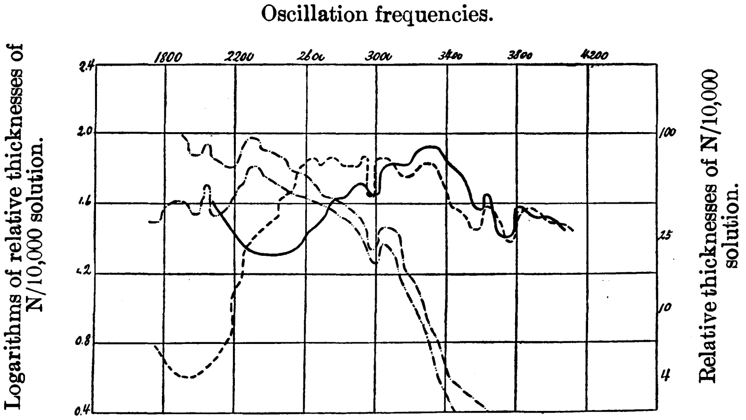
(1) Obtained from o-nitraniline and resorcinol.

8. p-Nitrobenzeneazoguaiacol,(1)



The yellow neutral solution changes into red by the addition of alkali like many other hydroxyazo-compounds. In this case, fairly remarkable bathochromic and hyperchromic influences through alkali can be found, and of course, A- and R-forms can be respectively assigned to the two different coloured solutions. (Fig. 8).

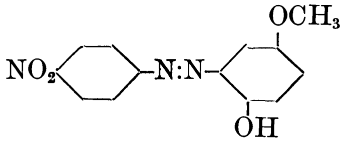


8. p-Nitrobenzeneazoguaiacol. { ——— Neutral solution.
{ - - - - - 0.8 N. alkaline solution.

9. p-Nitronenzeneazohydroquinone mono-methyl ether. { —·—·— Neutral solution.
{ —··—··— 0.045 N. alkaline solution.

Fig. 8.

9. p-Nitrobenzeneazohydroquinone mono-methyl ether,(2)



The yellowish red neutral solution changes first into purple by the addition of alkali, and then, after one hour turns brownish yellow. Slight bathochromic and hyperchromic effects due to alkali can be observed in that case (Fig. 8). From the absorption curve, we will give A-form to the neutral solution and R-form, not B-form, to the alkaline solution.

Dyeing Department, Tokyo Higher Technical School.

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(1) Obtained from p-nitraniline and guaiacol.

(2) Obtained from p-nitraniline and hydroquinone mono-methyl ether, which is synthetized with hydroquinone, sodium-methylalcoholate and methyliodide.

ACTION CATALYTIQUE DE LA TERRE ACIDE JAPONAISE SUR LE L-LINALOL.

(RECHERCHES SUR L'ESSENCE DE CAMPHRE VII)

Par **Kashichi ONO** et **Zensuke TAKEDA**.

Reçu le 8 décembre 1926. Publié le 28 janvier 1927.

L'un de nous a indiqué dans le précédent mémoire⁽¹⁾ que les alcools terpéniques cycliques se transforment en hydrocarbures correspondants par déshydratation catalytique de la terre acide Japonaise. On sait déjà que le linalol se transforme sous l'action du chlorure de zinc ou du bisulfate de potassium en dipentène et terpinène⁽²⁾ ou l'anhydrogéraniol.⁽³⁾ Le but de notre étude est de rechercher, si les reactions entre le linalol et la terre acide Japonaise se passent d'une manière analogue.

Partie expérimentale. Le prodiut employé est le " linalol pur extra " qui montre les constantes physiques suivantes,

$d_4^{15} = 0.8731$; $n_D^{19} = 1.4647$; $[\alpha]_D = -14.2'$

Soumis d'abord à la distillation fractionnée, nous avons pris pour nos essais exclusivement la fraction 197–199° pour laquelle nous avons trouvé les propriétés suivantes,

$d_4^{22.5} = 0.8604$; $n_D^{22.5} = 1.4610$; $[\alpha]_D = -15.26°$; R.M. $= 49.158$

500 gr. de l-linalol et 50 gr. de la terre acide Japonaise⁽⁴⁾ sont chauffés à 159° au bain d'huile en agitant vigoureusement comme il avait été décrit dans le précédent memoire. Après avoir chauffé pendant 85 minutes la réaction devint violente et un produit huileux commença à distiller. Le liquide distillé et le residue sont ensuite traités par la vapeur d'eau.

(I) 100 gr. ($d_4^{23} = 0.8602$; $n_D^{25} = 1.4694$) de produit ont été rectifiés sous 20–22 mm. qui donnent les fractions suivantes,

	Fraction.	Rendement.	n_D^{25}
(I)	30—70°	0.4 gr.	1.4711
(II)	70—80°	18.8	1.4715
(III)	80—8 °	15.8	1.4721
(IV)	85—90°	4.5	1.4720
(V)	90—95°	3.2	1.4691
(VI)	95—100°	8.6	1.4649

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(1) Ce journal, 1 (1926), 248.

(2) Bertram et Walbaum, *J. prakt. Chem.*, II, **45** (1892), 601.

(3) Semmler, *Ber.*, 24 (1891), 682.

(4) Pour nos essais la terre acide Japonaise a été desséchée à 100°.

(*suite*)

	Fraction.	Rendement.	n_D^{25}
(VII)	100—105°	21.2 gr.	1.4629
(VIII)	105—110°	7.1	1.4678
(IX)	110—115°	4.7	1.4741
(X)	115—120°	4.3	1.4781
(XI)	120—125°	2.2	1.4787
(XII)	125—130°	0.6	1.4788
(XIII)	au-dessus 130°	4.7	1.5011

Le mélange des fractions (I) à (IV) a été soumis cinq fois à la distillation fractionnée sous 21 mm. et nous pouvions en obtenir cinq fractions

A	60—65°	0.2 gr.
B	65—68°	5.4
C	68—70°	6.1
D	70—72°	6.0
E	72—74°	2.6

Après redistillation de la fraction (B), $d_4^{22.5} = 0.8175$; $n_D^{22.5} = 1.4670$; $[\alpha]_D = +3.83°$; R. M. = 46.201, en présence du sodium métallique, nous arrivions à séparer une fraction principale bouillante vers 67–68° sous 21 mm., pour laquelle nous avons trouvé les constantes physiques suivantes qui nous indiquent des données très voisines du myrcène. P. E. = 67–68° sous 21 mm. ou 169–171° sous 762 mm.; $d_4^{19} = 0.8097$; $n_D^{19} = 1.4674$; R. M. = 46.635; $[\alpha]_D = \pm 0$.

Analyse: 0.1165 gr. subst. donne 0.3743 gr. CO_2 et 0.1145 gr. H_2O. (Trouvé, C = 87.61; H = 10.99. Calculé pour $C_{10}H_{16}$, C = 88.15; H = 11.85 %).

La fraction (C) bouillante vers 68–70° sous 21 mm., $d_4^{20.5} = 0.8296$; $n_D^{22} = 1.4729$; R. M. = 46.024 est probablement un mélange d'hydrocarbures terpéniques cycliques et oléfiniques.

La fraction (D) bouillante vers 70–72° sous 21 mm., $d_4^{22} = 0.8408$ $n_D^{21} = 1.4771$; R. M. = 45.755; $[\alpha]_D = +5.92°$, est identique au limonène. A la rectification sous pression ordinaire sur du sodium métallique on obtient un d-limonène bouillant vers 175–176° sous 765 mm., $d_4^{21} = 0.8416$; $n_D^{21} = 1.4767$; R. M. = 45.646; $[\alpha]_D = +6.27°$.

Analyse: 0.2008 gr. subst. donne 0.6476 gr. CO_2 et 0.2156 gr. H_2O. (Trouvé, C = 87.94; H = 12.00. Calculé pour $C_{10}H_{16}$, C = 88.15; H = 11.85 %). Pour l'identification complète de notre limonène, nous l'avons transformé en tetrabromure fondant à 104–105°.

Nous avons constaté que la fraction (VII) contient encore une quantité notable de linalol bouillant vers 97–99 sous 21 mm., $d_4^{23} = 0.8617$; $n_D^{23} = 1.4650$; $[\alpha]_D = -10.50°$

Le mélange des fractions (IX) à (XIII) est chauffé pendant quatre heures au bainmarie à 80° avec l'anhydride phtalique en présence du benzène déshydré et on a laissé reposer une nuit. Après avoir separé l'excès d'anhydride phtalique par filtration, on a chassé le benzène dans le vide et on a extrait l'huile residuelle avec l'éther. La solution ethérée est traitée à plusieurs reprises par une solution de carbonate de soude pour éliminer l'éther phtalique acide du géraniol. On lave ensuite la solution éthérée avec de l'eau, et après l'avoir séchée sur du sulfate de sodium anhydre, on a chassé l'éther.

En distillant le residu sous 20 mm., on obtient les fractions suivantes :

		n_D^{18}
103—108°	0.1 gr.	1.4790
108—110°	2.9	1.4812
110—115°	0.9	1.4827
115—120°	1.1	1.4841
au-dessus 120°	6.4	——

La fraction bouillante vers 108–110° est identique au terpinéol $C_{10}H_{18}O$.

Analyse : 0.1302 gr. subst. donne 0.3694 gr. CO_2 et 0.1304 gr. H_2O. (Trouvé, $C = 77.36$; $H = 11.19$. Calculé pour $C_{10}H_{18}O$, $C = 77.92$; $H = 11.78$ %) $d_4^{18} = 0.9362$; $n_D^{18} = 1.4812$; R. M. = 46.873, calc. pour $C_{10}H_{18}O$. $F_1 = 47.238$; $[\alpha]_D^{18} = +14.03°$.

En traitant cette fraction par l'isocyanate de phényle, on obtient la phényluréthane de *α*-terpinéol, fondant à 112–113° trouvé identique au produit déjà obtenu par Wallach et Kerkhoff.(1)

La solution alcaline qui contient le géraniol, est acidulée par l'acide sulfurique dilué, et on l'extrait à l'éther. La solution éthérée est traitée par la soude et le liquide, qui contient maintenant le sel sodique est evaporé sous pression réduite. On obtient une masse cristalline brune claire qu'on saponifie par la potasse alcoolique à 10 pour 100. Après évaporation de l'alcool on y ajoute de l'eau et extrait la solution deux fois à l'éther. La solution éthérée est lavée à l'eau, séchée sur du sulfate de sodium anhydre. On chasse l'éther et le résidu huileux qui posséde l'odeur de géraniol, a donné, en distillant sous 20 mm., les fractions suivantes.

		n_D^{18}
à 122°	0.2 gr.	1.4773
122—125°	1.0	1.4776
125—128°	0.3	1.4778
au-dessus 128°	0.8	

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(1) *Liebig's Ann. Chem.*, 275 (1893), 104.

Nous avons constaté que la fraction bouillante vers 122–125° sous 20 mm. est identique au géraniol avec les propriétés suivantes, $d_4^{18} = 0.8822$; $n_D^{18} = 1.4776$; R.M. = 49.424, calc. pour $C_{10}H_{18}O\,F_2 = 48.971$; $[\alpha]_D = \pm 0$.

Analyse: 0.1419 gr. subst. donne 0.4062 gr. CO_2 et 0.1429 gr. H_2O. (Trouvé, C = 78.06; H = 11.25. Calculé pour $C_{10}H_{18}O$, C = 77.92; H = 11.78 %).

(II) 90 gr. du résidu jaunâtre visqueux de la distillation à la vapeur d'eau ($d_4^{22} = 0.9164$; $n_D^{22.5} = 1.5061$; l'indice l'acétyle = 72.35, c'est-à-dire 21.04 % de l'alcool $C_{15}H_{26}O$), sont distillés sous 18—20 mm. et ils ont donné les fractions suivantes,

105—115°	0.2 gr.	160—185°	0.6 gr.
115—125°	0.9	185—200°	20.7
125—140°	0.9	200—210°	13.2
140—160°	1.2		

Les deux fractions (185–200° et 200–210°) sont encore distillées sous 20 mm.

135—184°	0.7 gr.	193—196°	4.8 gr.
184—187°	3.3	196—200°	7.8
187—190°	6.0	200—204°	1.7
190—193°	3.4	204—207°	1.2

La fraction bouillante vers 187–190° sous 20 mm. est identique à l'alcool sesquiterpénique oléfinique $C_{15}H_{26}O$.

Analyse: 0.1329 gr. subst. donne 0.3929 gr. CO_2 et 0.1391 gr. H_2O. (Trouvé, C = 80.62; H = 11.70. Calculé pour $C_{15}H_{26}O$, C = 81.01; H = 11.78 %). $d_4^{21.5} = 0.90197$; $n_D^{22} = 1.4942$; R. M. = 71.743, calc. pour $C_{15}H_{26}O\,F_3 = 71.594$.

La fraction bouillante vers 196–200° sous 20 mm. semble identique à l'oxyde diterpénique déjà obtenu par Semmler et Jonas.(1)

Analyse: 0.1301 gr. subst. donne 0.3989 gr. CO_2 et 0.1387 gr. H_2O. (Trouvé, C = 83.61; H = 11.92. Calculé pour $C_{20}H_{34}O$, C = 82.63; H = 11.81 %). $d_4^{21.5} = 0.9186$; $n_D^{21} = 1.4946$; R. M. = 92.083, calc. pour $C_{20}H_{34}O\,F_2 = 90.851$; $[\alpha]_D = \pm 0$.

Il résulte de l'étude entreprise que l'action de la terre acide Japonaise sur l-linalol est demontrée par une réaction des déshydratations, par une transposition intramoléculaire, par la formation d'un noyau et par une polymérisation.

Laboratoires de Saiséi-shono Kwaisha à Kobe.

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(1) *Ber.*, 52 (1914), 2079.

THE APPLICATION OF THE PERKIN REACTION TO PHENOLIC ALDEHYDES.

By **Shintaro OGAWA.**

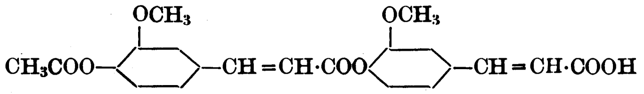
Received December 14, 1926. Published January 28, 1927.

It has been shown by Tiemann and his collaborators(1) that acetyl derivatives of hydroxycinnamic acids are formed when phenolic aldehydes, such as vanillin and p-hydroxybenzaldehyde, are heated with acetic anhydride and fused sodium acetate. However, the melting points of the acetyl derivatives obtained by this method were always not sharp. This fact was accounted for by Vorländer(2) as due to the characteristic nature of liquid crystals in the case of p-acetyloxycinnamic acid, and by Kobayashi in the case of acetylferulic acid(3), as a special peculiarity of the acid. According to my observation, I am inclined to the opinion that these substances are impure.

The author applied Perkin's reaction to vanillin and p-hydroxybenzaldehyde respectively, and subjected the products to fractional crystallisation. In the former case, the condensation product was separated into two substances and in the latter, into three.

The product obtained from vanillin consisted of a mixture of acetylferulic acid, $C_{12}H_{12}O_5$, m. p. 195–195. 5,° and substance (A) of unknown structure, $C_{22}H_{20}O_8$, m. p. 250° (decomp.), which are separated by fractional crystallisation from alcohol and glacial acetic acid, the latter being the less soluble.

The presence of one acetyl, one carboxyl and two methoxyl groups in the latter substance was proved and, on hydrolysis, it was converted into ferulic acid in an almost quantitative yield. From these facts and from its method of formation it seemed possible that the constitutional formula of this substance might be (I), although the number of double bonds was not determined.



(I)

Owing to the decomposition of this acid at the melting point, it seemed desirable to prepare at first its stable derivative for indentification. The methyl ester was first synthesised by the action of diazomethane on the acid and found to be suitable for this purpose, the melting point being 204–205.5°.

The methyl ester of the substance corresponding with formula (I) was synthesised by the condensation of acetylferuloyl chloride with ferulic acid

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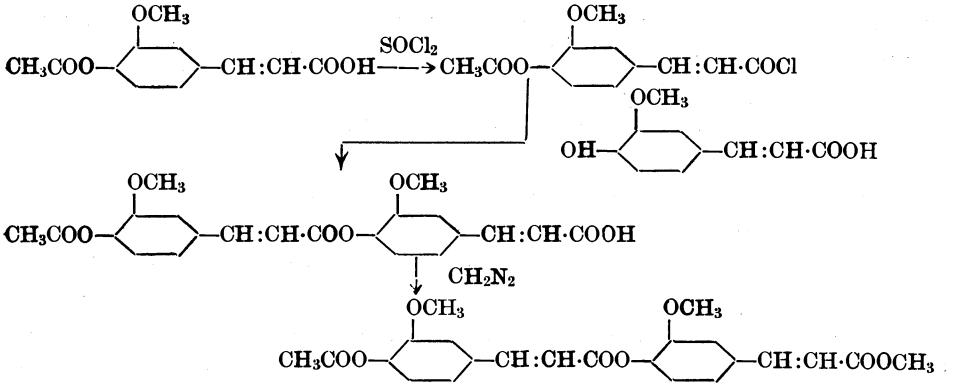
(1) *Ber.*, 10 (1877), 65; 11 (1878), 647.

(2) *Ber.*, 39 (1906), 808.

(3) *Bulletin of the Institute of Physical and Chemical Research* (in Japanese), 4 (1925), 575.

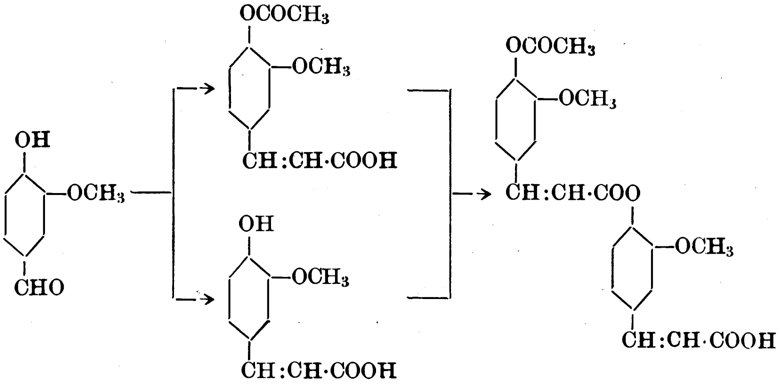
in the presence of pyridine and subsequent methylation with diazomethane, as shown in the following scheme :



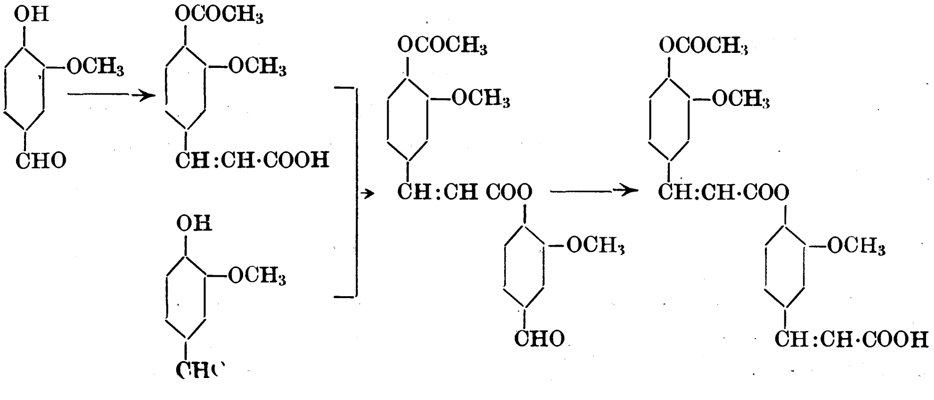
This synthetic methyl ester was identical in every respect with the methyl ester of substance (A).

The mechanism of the formation of substance (A) is accounted for by one of the following schemes, viz. (B) or (C) :

(B)



(C)



This view receives some support from the fact that the derivatives of cinnamic acid were the sole products of the action of acetic anhydride and fused sodium acetate on derivatives of vanillin which contain no phenolic hydroxyl, such as acetylvanillin and veratraldehyde.

In the case of p-hydroxybenzaldehyde, the condensation product was separated into three substance, (a) m.p. 205–205.5°; (b) m.p. 222–223° (decomp.); and (c) m.p. 231° (decomp.).

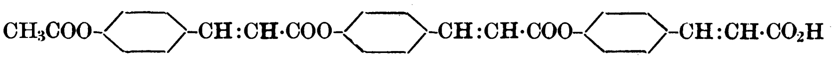
Substance (a) had the composition, $C_{11}H_{10}O_4$, and was identified as p-acetyloxycinnamic acid by analysis, molecular weight determination and by the fact that it was converted into p-hydroxycinnamic acid by hydrolysis in a good yield.

Substance (b), $C_{20}H_{16}O_6$, gave, on hydrolysis, p-hydroxycinnamic acid in an almost quantitative yield and was converted into its methyl ester, $C_{21}H_{18}O_6$, m.p. 166–167°. It is very probable judging by analogy with the case of vanillin that the constitutional formula of this substance would be 4-p-acetyloxycinnamoyl oxycinnamic acid (II),


(II)

The author synthesised the methyl ester corresponding with formula (II) in an exactly similar manner to the preparation of methyl acetylferuloylferulic acid. The synthetic methyl 4-p-acetyloxycinnamoyloxycinnamate was identical in all respects with the methyl ester of substance (b).

Substance (c) was insoluble in almost all organic solvents or camphor, and slightly soluble in hot nitrobenzene. As its molecular formula has not yet been determined, an empirical formula, $C_{29}H_{22}O_8$, only is at present assigned to it. It was converted into p-hydroxycinnamic acid by treatment with caustic soda and yielded a methyl ester having an empirical formula, $C_{30}H_{24}O_8$, when methylated with diazomethane. The author considers it to be best represented by formula (III).


(III)

The mechanism of the formation of substance (b) is explained as in the case of that of acetylferuloylferulic acid, and in the support of this view, the condensation product with anisaldehyde was only 4-methoxycinnamic acid.

The application of Perkin's reaction to the other phenolic aldehydes are now in progress.

Experimental Part.

The Application of the Perkin Reaction to Vanillin. *Isolation of Acetylferuloylferulic Acid,* $[(CH_3CO_2)(CH_3O)C_6H_3\,CH{:}CH{\cdot}CO_2](CH_3O)C_6H_3{\cdot}CH{:}CH{\cdot}CO_2H$. Vanillin (225 gr.) was heated with a mixture of acetic anhydride (675 gr.) and fused sodium acetate (225 gr.) in an oil-bath for 6 hours, when yellow crystals melting at 186–193°, were obtained, which on fractionally recrystallising from alcohol (95%) separated into three fractions: (a) m.p. 190–194°, 70 gr.; (b) m.p. 194–195.5°, 49 gr; and (c) m.p. 223–229°, 10 gr. The last fraction was further recystallised from alcohol and then from glacial acetic acid, from which it separated in faint, yellow crystals melting at 250° (decomp.). (Found: C=64.21; H=5.10. Mol. wt., by Rast's method(1), 413.6. $C_{22}H_{20}O_8$ requires C=64.07; H=4.86%; Mol. wt.=412.2),

Hydrolysis. The substance was hydrolysed by means of a 10% aqueous sodium hydroxide on a wire-gauze and on acidification with hydrochloric acid and recrystallisation of the product from dilute alcohol, faint, yellow crystals, m.p. 167.5–168°, were obtained and found to be identical with ferulic acid.

Determination of Groups. The acetyl group was determined by F. Kögl & P. P. Postowsky's method(2) and the methoxyl groups, by the micro-Zeisel method (Pregl, "Die Quantitative Organische Mikroanalyse". p. 178). (Found: CH_3CO = 10.52 ; 10.23 ; CH_3O = 14.97 ; 15.13. $C_{18}H_{11}O_6(OCH_3)_2(CH_3CO)$ requires CH_3CO=10.44 ; CH_3O=15.06%). The numbers of the carboxyl group were determined by conversion into its Ba-salt and subsequent analysis. (Found: CO_2H=10.98. $C_{21}H_{19}O_6(CO_2H)$ requires CO_2H=10.91%).

The Methyl Ester. The substance was esterified with diazomethane in ethereal suspension. After evaporating the ether and recrystallising the product from a mixture of ether and benzene, faint, yellow crystals, m.p. 204–205.5°, were obtained. No alternation of melting point was observed on mixing it with a specimen which was obtained synthetically by the method described on p. 21.

Synthesis of Methyl Acetylferuloylferulate. *Acetylferuloyl chloride,* $(CH_3CO_2)(CH_3O)C_6H_3CH:CH\,COCl$. Acetylferulic acid (2 gr.) was treated with thionyl chloride (6 gr.) in a water-bath. After evaporating the excess of thionyl chloride in a vacuum, the raw product was recrystallised from benzene, care being taken to avoid any access of moisture. Faint, brown crystals thus purified melted at 133°–134°:

5.568 mg. gave 3.035 mg. AgCl. (Found: Cl=13.49. $C_{12}H_{11}O_4Cl$ requires Cl=13.97%).

Methyl Acetylferuloylferulate, $[(CH_3CO_2)(CH_3O)C_6H_3\cdot CH:CH\cdot CO_2](CH_3O)C_6H_3CH:CH\,CO_2CH_3$. To a solution of 3 gr. of ferulic acid in 15 gr. of pyridine, kept at −15°, the acetylferuloyl chloride obtained from 5 gr. of acetylferulic acid was added and allowed to stand overnight. The product was acidified with dilute sulphuric acid and the precipitate was purified from acetone, glacial acetic acid and then from dilute alcohol. The product

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(1) *Ber.*, **55** (1922), 1051.

(2) *Ann.*, **440** (1924), 34.

thus purified was treated with an ethereal solution of diazomethane. After recrystallising from a mixture of ether and benzene, faint, yellow crystals, m.p. 204–205.5°, were obtained.

5,275 mg. gave 12.490 mg. CO_2 and 2.660 mg. H_2O. (Found : C=64.70 ; H=5.64. $C_{23}H_{22}O_8$ requires C=64.57 ; H=5.20%).

Application of the Perkin Reaction to the Derivatives of Vanillin not Containing the Free Phenolic Group. (*a*) *Application to Acetylvanillin.* After heating acetyl vanillin (2 gr.) with fused sodium acetate (1.56 gr.) and acetic anhydride (4.7 gr.) in an oil-bath and recrystallising the product from alcohol, faint, yellow crystals, m.p. 192–193.5°, (m.p. of acetylferulic acid is 195–195.5°), were obtained. However, no acetylferuloylferulic acid could be isolated.

(*b*) *Application to Veratraldehyde.* A mixture of veratraldehyde (10 gr.), fused sodium acetate (12 gr.) and acetic anhydride (27.6 gr.) was heated to boiling for 6 hours. After removing the excess of acetic anhydride, the reaction product was extracted with ether, washed well with water, dried and evaporated. On standing it in a vacuum desiccator, a small quantity of solid was separated from the residual oil and recrystallised from alcohol, from which it separated in colourless crystals, m.p. 181° (yield, 0.5 gr.). 3 : 4-Dimethoxycinnamic acid is stated by Milobedzka to melt at 180–181°.

Application of the Perkin Reaction to p-Hydroxybenzaldehyde. A mixture of p-hydroxybenzaldehyde (15 gr.), acetic anhydride (56 gr.) and fused sodium acetate (18.7 gr.) was heated at 195–200° for 6 hours. After removing the excess of acetic anhydride and boiling twice with water, the residue, m.p. 168–188°, (12 gr.) was separated at first into two parts by using boiling alcohol.

The Part Soluble in Boiling Alcohol. This part was again separated into two portions by using hot water, namely the fraction soluble and insoluble in hot water. On recrystallising each portion from alcohol, colourless crystals (a), m.p. 205.5–206°, were obtained from the former, and faint, yellow crystals (b), m.p. 222–223° (decomp.), from the latter :

4.029 mg. of subst. (a) gave 9.882 mg. CO_2 and 2.026 mg. H_2O ; 0.350 mg. in 3.945 mg. of camphor gave $\Delta t=15.6°$ (Found : C=64.02 ; H=5.38 ; Mol. wt.=227.5. $C_{11}H_{10}O_4$ requires C=64.07 ; H=4.86% ; Mol. wt.=206.8).

4.022 mg. of subst. (b) gave 10.085 mg. CO_2 and 1.805 mg. H_2O ; 0.105 mg. in 2.070 mg. of camphor gave $\Delta t=5.6°$ (Found: C=68.19; H=5.00 ; Mol. wt.=362.3. $C_{22}H_{16}O_6$ requires C=68.16 ; H=4.58% ; Mol. wt.=352.1).

The Part Insoluble in Boiling Alcohol. As this part was insoluble in water or in most organic solvents, it was first freed from impurities by boiling it successively with water, with alcohol and with glacial acetic acid,

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(1) *Ber.*, **43** (1910), 2166.

and then recrystallised six times from nitrobenzene, when it separated as a grey, amorphous substance (c), m.p. 231° (decomp.):

4.733 mg. gave 12.139 mg. CO_2 and 2.026 mg. H_2O. (Found : C=69.94; H=4.57. $C_{28}H_{22}O_8$ reguires C=69.89; H=4.45%).

Hydrolysis. Each of these three substances was hydrolysed with a 15% aqueous sodium hydroxide, when in all these cases only one colourless substance, m.p. 206–207°, was obtained in the almost theoretical yield. G. Eigel⁽¹⁾ gave 206° as the melting point of p-hydroxycinnamic acid.

The Methl Ester of (b). Substance (b) was treated with diazomethane in ethereal suspension and the product then purified as in the preparation of methyl acetylferuloylferulate, when faint, yellow crystals, m.p. 166–167°, were obtained and produced no depression of the melting point by admixture with methyl 4-p-acetyloxycinnamoyloxycinnamate which was synthetically obtained by the method described later.

The Methyl Ester of (c). The methyl ester, prepared similarly as described above, melted at ca. 200° on being rapidly heated:

4.620 mg. gave 11.860 mg. CO_2 and 2.094 mg. H_2O. (Found : C=70.01; H=5.07. $C_{30}H_{24}O_8$ requires C=70.28; H=4.73%).

Synthesis of Methyl 4-p-Acetyloxycinnamoyloxycinnamate, $[(CH_3CO_2)C_6H_4{\cdot}CH{:}CH{\cdot}CO_2]\,C_6H_4{\cdot}CH{=}CH{\cdot}CO_2CH_3$.

Acetyloxycinnamoyl Chloride, $(CH_3CO_2)\,C_6H_4{\cdot}CH{:}CH{\cdot}COCl$. 4-Acetoxycinnamic acid (0.5 gr.) was converted into its acid chloride, by treating with 2.5 gr. of thionyl chloride similarly as in the preparation of acetylferuloyl chloride, when it separated in colourless crystals, m.p. 118–119°:

7.153 mg. gave 4.446 mg. AgCl. (Found : Cl=15.37. $C_{11}H_9O_3Cl$ requires Cl=15.78%).

Methyl 4-p-Acetyloxycinnamoyloxycinnamate. p-Hydroxycinnamic acid (0.062 gr.) was dissolved in a mixture of 0.6 gr. of pyridine and 3 c.c. of absolute ether and kept at −15°. On acidifying with dilute sulphuric acid, faint, yellow precipitate separated, which was recrystallised once from alcohol, and was employed in the preparation of the methyl ester with diazomethane without further purification. The raw product was twice recrystallised from alcohol, when it melted at 166–167°.

4.865 mg. gave 12.273 mg. CO_2 and 2.389 mg. H_2O. (Found : C=68.79; H=5.49. $C_{21}H_{18}O_6$ requires C=68.82; H=4.95%).

The Application of the Perkin Reaction to 4-Methoxybenzaldehyde.

Synthesis of 4-Methoxycinnamic acid, $(CH_3O)C_6H_4\,CH{:}CH\,CO_2H$. A mixture of 9 gr. of anisaldehyde, 30 gr. of acetic anhydride and 10 gr. of fused sodium acetate was heated to boiling for six hours. The reaction product thus

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(2) *Ber.*, 20 (1887), 2529.

obtained was treated in a similar manner to the purification of veratraldehyde. After removing the excess of acetic anhydride and boiling it with water, 0.6 gr. of faint, yellow crystals, melting at 165° to a milky liquid and becoming clear at 185°, were isolated from the crude product.

In conclusion, the author desires to express his sincere thanks to Professor Hiroshi Nomura for his kind guidance and encouragement.

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ON THE SO-CALLED DIETHYL DICYANOGLUTACONATE AND SOME OF ITS DERIVATIVES.

By **Yoshiyuki URUSHIBARA.**

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The diethyl dicyanoglutaconate was first prepared by G. Errera$^{(1)}$ and by Ruhemann and Browning$^{(2)}$ independently, by the action of ethyl cyanoacetate, sodium ethylate, and chloroform, the sodium derivative being formed intermediately. The formula I was given to the ester and II to the sodium derivative.

$$C_2H_5OOC—C(CN)=CH—CH(CN)—COOC_2H_5 \qquad I.$$
$$C_2H_5OOC—C(CN)=CH—CNa(CN)—COOC_2H_5 \qquad II.$$

Errera's observations are as follows: The diethyl sodio-dicyanoglutaconate is light yellow, glittering needles, has two molecules of water of crystallisation, when it is crystallised from water, and melts at about 265°C. By acidifying a warm aqueous solution of this sodium compound a yellow substance is precipitated, which is recrystallised from benzene and found to be pure diethyl dicyanoglutaconate.

(Found: $C=55.52$; $H=5.59$; $H=11.59$. $C_{11}H_{12}O_4N_2$ requires $C=55.93$; $H=5.08$; $N=11.86\%$)

The diethyl dicyanoglutaconate melts at 178–179°, is difficultly soluble even in hot benzene, easily soluble in alcohol but *decomposed*. By boiling the spirit solution, the diethyl dicyanoglutaconate is changed into another substance of the formula $C_{11}H_{16}O_6N_2$.

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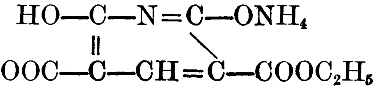
(1) *Ber.*, **31** (1898), 1241.

(2) *J. Chem. Soc.*, **73** (1898), 280.

He thought this substance was the diamide of the dicarboxyglutaconic ester but M. Guthzeit(1) showed that it was the ammonium salt of the diethyl dihydroxydinicotinate of the formula III.



III.

Ruhemann and Browning made similar observations and also obtained some pyridine derivatives. They state as follows:

"Ethylic dicyanoglutaconate dissolves readily in hot acetone, and crystallises from it in yellow, glittering plates which melt and decompose at 187–188°. It was found to contain a small quantity of another substance *which was not removed by repeated recrystallisation.* The following analytical results show that the percentage of carbon in different specimens of the product varies from the theoretical number by one to two percent."

(Found: C=54.07, 54.42, 55.22, 54.65; H=5.55, 5.38, 5.46, 5.42; N=11.50, 11.70 %).

By the action of ethyl cyanoacetate, sodium ethylate and carbon tetrachloride, Otto Dimroth(2) also obtained the same yellow sodium derivative, and from it the free ester melting at 181–183°. He observed that this substance showed a varying melting point according to the mode of heating. His analytical data is N=11.51 %.

G. Errera and F. Perciabosco(3) obtained the same yellow sodium compound by a long boiling of the triethyl sodio-dicyanoaconitate.

A Corrected Idea on the So-called Diethyl Dicyanoglutaconate. This compound was often prepared by the author according to the method of Errera for the purpose of obtaining any brominated derivatives by the action of bromine. The sodium derivative several times recrystallised from hot water was yellow needles, and its properties as well as those of the free ester agreed with the literatures.

After the obtainment of some new derivatives the starting substance, e.i. the diethyl dicyanoglutaconate seemed very doubtful in its chemical composition and constitution.

Preparation of Pure Substance. The diethyl dicyanoglutaconate precipitated from a hot aqueous solution of repeatedly recrystallised sodium derivative, washed with water, and dried, was dissolved in boiling absolute alcohol, filtered while hot and then cooled. The deposited crystals were collected, washed with ether, and dried.

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(1) *Ber.*, 32 (1899), 779.

(2) *Ber.*, 35 (1902), 2881.

(3) *Ber.*, 34 (1901), 3707.

0.2873 gr of subst. gave 29.2 c.c. of N_2 at 24° and 758 mm. (Found: N = 11.31. $C_{11}H_{12}O_4N_2$ requires N = 11.86 %.)

This was again recrystallised from pure acetone, and gave the following analytical result. 0.2616 gr. of subst. gave 26.5 c.c. of N_2 at 22° and 755 mm. (Found: N = 11.34 %.)

Once more recrystallised from acetone (that is once from alcohol and twice from acetone). 0.2014 gr. of subst. gave 20.0 c.c. of N_2 at 19.5° and 763 mm. (Found: N = 11.38 %).

Each time the taken substance was dried at 100° for half an hour in the stream of dry air, and weighed. After this treatment the yellow colour of the crystals became slightly deeper than before. Errera found in the substance crystallised from alcohol a carbon content too small by one to two percent, which he attributed to decomposition. Thus the determination of nitrogen seemed to lead to the same conclusion.

Another attempt of obtaining a pure substance was made by the replacement of chloroform with iodoform. The author found formerly that the tetraethyl sodio-dicarboxyglutaconate was obtainable in a purer state by using iodoform than by chloroform, and had lighter colour and somewhat higher melting point. In the case of the diethyl dicyanoglutaconate the same result was expected.

The sodium compound formed by using iodoform, after removing the usual red-coloured by-product by repeated recrystallisation from hot water, became nearly *colourless* crystals, melting at about 265°. On heating over 100° it turned yellow. With chloroform a *yellow* substance was always obtained, and thus it was ascertained that the colour was not essential, but caused by impurities. Between the melting point of the two kinds of preparations no remarkable difference was observed.

This colourless sodium compound was converted into the free ester by the ordinary procedure. The yellow crystals precipitated by hydrochloric acid were washed with water, dried, and recrystallised from pure acetone. This purified substance melted at 183° (corr.) and gave the following analytical result.

0.1495 gr. of substance dried at 100° gave 14.9 c.c. of N_2 at 20° and 766 mm. (Found: N = 11.43 %.)

This corresponds to the formula $C_{11}H_{12}O_4N_2 \cdot \frac{1}{2}H_2O$, which requires N = 11.43 %.

Composition of the So-called Diethyl Dicyanoglutaconate. The following facts suggest a great doubtfulness in the nature of this compound. (I) Its yellow colour, whilst the sodium derivative was ascertained to be colourless. cf. The tetraethyl dicarboxyglutaconate, which is colourless liquid and its sodium derivative is light yellow crystals. (2) Its high melting point, whilst the tetraethyl dicarboxyglutaconate and the triethyl α-cyano-γ-carboxyglutaconate are both liquid at the ordinary temperature. (3) When an aqueous solution of the sodium compound is acidified, the free ester separates out only after a while, not immediately. (4) Its small solubilities in various solvents. It is practically insoluble in benzene and ether, and only slightly soluble in cold alcohol and cold acetone. (5) The low value of nitrogen content. In both Errera's and Ruhemann's analytical data, the sodium derivative shows satisfactory numbers, while the free ester, obtainable by a simple treatment from the former, varies from the theoretical number by an impermissible amount.

The purest specimen obtained by using iodoform and recrystallised from acetone, contained 11.43 % of nitrogen as mentioned above, which corresponded to the formula $C_{11}H_{12}O_4N_2 \cdot \frac{1}{2}H_2O$. The contents of carbon and hydrogen were determined.

0.1959 gr. of substance dried at 100° gave 0.3868 gr. CO_2 and 0.0928 gr. H_2O. (Found: C=53.87; H=5.30. $C_{11}H_{12}O_4N_2 \cdot \frac{1}{2}H_2O$ requires C=53.88; H=5.31 %.)

There can be no hesitation in giving the formula $C_{11}H_{12}O_4N_2 \cdot \frac{1}{2}H_2O$ to the diethyl dicyanoglutaconate.

Errera and Ruhemann got probably only impure substances and calculated by an incorrect formula. One of Ruhemann's specimens, that showed the smallest contents of carbon (54.07 %) and nitrogen (11.50 %), although there is no knowing if the substances for both determinations belonged to the same specimen or not, may really be the purest, which he might considered as the least pure. Errera observed that the crystals from alcohol contained too small carbon, but did not noticed the presence of half a molecule of water. Ruhemann obtained an ammonia derivative of the formula $C_{11}H_{12}O_4N_2 \cdot NH_3 \cdot \frac{1}{2}H_2O$, but did not detect half a molecule of water contained in the original ester.

Constitution of the Diethyl Dicyanoglutaconate. The triethyl dicyanoaconitate [145–146°], $C_2H_5OOC{-}C(CN){=}C(COOC_2H_5){-}CH(CN){-}COOC_2H_5+\frac{1}{2}H_2O$(1), and the methenylbismalonitrile imidether [244°], $(CN)_2C{=}CH{-}CH(CN){-}C(NH){-}OC_2H_5+\frac{1}{2}H_2O$(2), obtained from the corresponding sodium derivatives by acidifying their aqueous solutions have also half a molecule of water. In both cases it was not determined whether the half molecule of water was the water of crystallisation or combined constitutionally. The present author made no close investigation of these two substances, but if such derivatives of the dinitrile of the glutaconic acid usually have half a

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(1) G. Errera und F. Perciabosco, *Ber.*, 34 (1901 , 3704.

(2) W. Zoernig, *J. prakt. Chem.*, 74 (1906), 435.

molecule of water when they are formed from the sodium derivatives by acidifying their aqueous solutions, it will not, probably, be a water of crystallisation.

Dehydration of the Ester. A substance dried in the desiccator at the ordinary temperature showed practically no decrease in weight on heating half an hour at 100° in the stream of dry air. 0.3114 gr. of the substance dried at 100° weighed 0.3108 gr. after one hour heating at about 130°, and 0.3104 gr. after more one hour heating at 150°, in the stream of dry air. The water in the diethyl dicyanoglutaconate was unremovable even by heating at 150°

Molecular Weight. Although the ester is not sufficiently soluble in boiling acetone, and the elevation of the boiling point is small, an ebullioscopic determination in this solvent was tried. The number 406 was obtained as the molecular weight, and it seemed that the diethyl dicyanoglutaconate had the molecular formula $(C_{11}H_{12}O_4N_2)_2H_2O$.

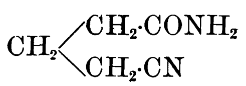
Chemical Properties. The sodium derivative of the diethyl dicyanoglutaconate does not evolve ammonia on heating with caustic alkali, but when the free ester is heated with caustic alkali, the ammoniacal odour is evidently perceived. Some of the nitrogen atoms in the free ester are more easily detached by alkali than those in the sodium compound. This indicates an undeniable difference in the constitution of these two compounds.

All these facts and the investigation of the bromine addition compound, which will be described later, show that the constitution of the diethyl dicyanoglutaconate will probably be represented by one of the following formulæ.

$$(C_{10}H_{12}O_4N)\text{—}C(NH)\text{—}O\text{—}C(NH)\text{—}(C_{10}H_{12}O_4N) \qquad \text{IV.}$$

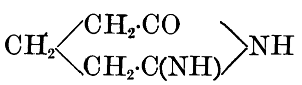
$$(C_{10}H_{12}O_4N)\text{—}CO\text{—}NH\text{—}C(NH)\text{—}(C_{10}H_{12}O_4N) \qquad \text{V.}$$

J. F. Thorpe(1) indicated that a nitrile of the formula VI would pass into an imino piperidine of the formula VII.



$$CH_2\left\langle\begin{array}{l}CH_2\cdot CONH_2\\ CH_2\cdot CN\end{array}\right.$$

VI.



$$CH_2\left\langle\begin{array}{l}CH_2\cdot CO\\ CH_2\cdot C(NH)\end{array}\right\rangle NH$$

VII.

In the present case the formula V is also more probable than IV, for it can be supposed that this compound would be formed by the condensation of a monoamide-mononitrile and a dinitrile.

This assumption is not contradictory to the fact that some pyridine derivatives were obtained from the ester, for a compound with such a constitution will easily be split into two similar molecules.

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(1) *J. Chem. Soc.*, **99** (1911), 422. Further cf. *J. Chem. Soc.*, **99** (1911), 1684; **115** (1919), 686; **117** (1920), 1465.

It is supposed that an analogous discussion may be made on the triethyl dicyanoaconitate and the methenylbismalonitrile imidether.

Action of Bromine on the Diethyl Dicyanoglutaconate. The diethyl dicyanoglutaconate was introduced in pure chloroform (about ten times in weight), and bromine (dehydrated by shaking with concentrated sulphuric acid) was added drop by drop. By the time when the quantity of bromine reached to four atoms to one molecule of the ester (refered to the formula $(C_{11}H_{12}O_4N_2)_2 H_2O$), the solid entered completely into solution, and during the addition of further four atoms of bromine, brick-red crystals were separating out. (In the dark the appearance of the crystals was somewhat delayed.) When the increase in amount of the crystals ceased, they were collected, washed with pure benzene (dehydrated on sodium) and dried in vacuum. When the brominated product was left in its mother liquor for a long time, it was accompanied by another substance, which also crystallised from the filtrate of the former and was considered to be the product of a secondary change.

This experiment was often repeated, and specimens of various purities were obtained. This substance melts at 146–149°, has a large proportion of free bromine, and is so unstable that it is decomposed in ether, alcohol, and water, but crystallises unchanged from a hot pure benzene solution on cooling. As shown in the following pages, this substance is transformed into the diamide hydrobromide, $C_{11}H_{16}O_6N_2 \cdot HBr$ and then into the picrate, $C_{11}H_{16}O_6N_2 \cdot C_6H_2(NO_2)_3OH$, which indicates that it is merely a molecular addition compound.

0.2247, 0.2028, 0.2960, 0.2750, 0.1199 gr. subst. (each belonging to a different specimen), gave 0.2809, 0.2483, 0.3730, 0.3457, 0.1520 gr. AgBr respectively. 0.1701, 0.6071, 0.4638 gr. subst. gave 19.8 (26.5°, 760 mm.), 29.4 (29°, 758 mm.), 24.4 c.c. (31°, 751 mm.) nitrogen respectively. (Found: Br=53.6, 52.10, 53.63, 53.50, 53.95; N=5.27, 5.24, 5.57 %).

Determination of Free Bromine. The iodometry was not successful in this case, for the liberation of iodine was incomplete. The method of analysis was as follows. The substance was weighed in a watch glass and placed in a beaker. A freshly prepared aqueous solution of sulphur dioxide, which should be free from sulphuric acid, was poured in the beaker and heated on the water bath. The crystals were dissolved to a colourless solution. Most of the excess of sulphur dioxide was then expelled by adding hydrochloric acid and heating. The formed sulphuric acid was determined as barium sulphate by the ordinary method. From the mother liquor of the barium sulphate a white substance crystallised out, which was identified with the diethyl dihydroxydinicotinate by its melting point (about 200°), and its reddish coloration on adding ferric chloride, the experimental fact described on p. 34 and 35 being taken into consideration. One molecule of barium sulphate corresponds to two atoms of bromine.

0.5004, 0.2887, 0.3617 gr. subst. gave 0.3287, 0.1910, 0.2397 gr. $BaSO_4$ respectively. (Found: Free Br=45.0, 45.3, 45.4. $(C_{11}H_{12}O_4N_2)_2H_2O.HBr.Br_6$ requires, total Br=53.3; free Br=45.7; N=5.33 %).

H. L. Wheeler and D. T. Walden⁽¹⁾ obtained many addition compounds of the general formula $(C_6H_5NHCOCH_3$ or derivative$)_2.HX.X_n$, where X represents Br or I, for instance, $(m\text{-}NO_2C_6H_4NHCOCH_3)_2HBr.Br_6$. At first they obtained some compounds of this series by the action of bromine on the meta-nitroacetanilide in chloroform. If the bromine was free from hydrogen bromide and the solvent was not attacked by bromine, no addition took place. Thus in carbon bisulphide they could not get the addition compounds. The present author also ascertained that the diethyl dicyanoglutaconate gave no addition compound in carbon bisulphide. But a long standing caused a substitution in a part of the substance and some brominated product separated out. The formula with two imino-groups given to the diethyl dicyanoglutaconate seems to be quite correct.

The Diamide Hydrobromide. When the bromine addition compound was introduced in commercial ether it changed into a white crystalline compound. This transformation was neither realised in absolute ether, nor in the presence of an excess of bromine, but promoted by light. Hence this reaction proceeded by liberating bromine and combining with water, and required more hydrogen bromide than the bromine addition compound originally contained. The ether in which the new substance was formed, was brown with bromine and left nearly no residue on evaporation. For the purpose of preparation it is better to use a sufficient amount of ether saturated with water. After the disappearance of the original brown crystals, the product is collected, washed with ether and dried. (The yield is theoretical, see under).

0.1369, 0.2952, 0.2206, 0.1460 gr. subst. gave 0.0733, 0.1587, 0.1173, 0.0785 gr. AgBr respectively. 0.1982, 0.2856 gr. subst. gave 14.3 (30°, 750 mm.), 20.7 c.c. (29°, 756 mm.) nitrogen respectively. (Found: Br=22.79, 22.88, 22.63, 22.88; N=7.73, 7.83. $C_{11}H_{12}O_4N_2.2H_2O.HBr$ requires Br=22.79; N=7.96 %).

This compound forms light, silky, white needles, does not show a sharp melting point, but decomposes to a dark red liquid when heated near 180°. It is soluble in water and alcohol, much more when heated, but insoluble in ether. The alcoholic solution is slightly fluorescent, and gives no coloration on adding ferric chloride. From a hot concentrated solution in water or

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(1) *Am. Chem. J.*, 18 (1896), 86.

alcohol the unchanged substance crystallises out on cooling. It dissolves also in hot concentrated hydrobromic acid (ca. 40 %) and crystallises from it unchanged. This substance does not liberate ammonia when boiled with caustic alkali, and only a long boiling with strong alkali decomposes it into ammonia and other substances. The aqueous solution is acidic and precipitates silver bromide on adding silver nitrate.

In every point it does not resemble⁽¹⁾ with the ammonium salt of the diethyl dihydroxydinicotinate, which was formed by adding two molecules of water to the diethyl dicyanoglutaconate in spirit solution but possesses a great likeliness for being a hydrobromide of an acid amide. Many acid amides give molecular compounds of the formula $2R.CONH_2.HX$ with hydrogen halide. Comparison of their properties with those of the present substance indicates that it belongs to the compound of this type, and it has two amide-groups in one molecule. The hydrohalides of amides are easily formed from nitriles in various reactions, where necessary water, or such substances as to give water by reaction, and hydrogen halide are present.⁽²⁾

The diethyl dicyanoglutaconate gave directly a slightly yellowish compound containing bromine and 7.86% of nitrogen, by the action of ether shaken with concentrated hydrobromic acid.

Moreover the hydrobromide gives the picrate of the formula $C_{11}H_{16}O_6N_2.C_6H_2(NO_2)_3OH$ which will be described in details in the following paragraphs.

Picrate of the Diamide. When the diamide hydrobromide was mixed with the picric acid both in alcoholic solutions, yellow, glittering needles separated out, which were collected, washed with alcohol several times and dried in the air-bath. This picrate melted at 196–197° (corr.) and contained no bromine, whilst the mother liquor showed the reaction of the bromine ions.

0.2214, 0.2189 gr. subst. gave 28.0 (26°, 754 mm.), 27.8 c.c. (25.5°, 755 mm.) nitrogen respectively. (Found: N=13.85, 13.97. $C_{11}H_{16}O_6N_2{\cdot}C_6H_2(NO_2)_3OH$ requires N=13.97%).

The value of carbon and hydrogen did not exactly agree with the formula, but was sufficient to exclude such a formula as $(C_{11}H_{12}O_4N_2)_2C_6H_2(NO_2)_3OH$, which requires N=14%.⁽³⁾

	Found	$C_{11}H_{16}O_6N_2{\cdot}C_6H_2(NO_2)_3OH$	$(C_{11}H_{12}O_4N_2)_2{\cdot}C_6H_2(NO_2)_3OH$
C	41.9%	40.7%	46.8%
H	3.5%	3.8%	3.9%

0.2146 gr. of the picrate weighed 0.2141 gr. after heating at 150° for half

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(1) See page 35.

(2) Colson, *Bull. soc. chim.*, [3] 17 (1897), 57. A. Pinner und Fr. Klein, *Ber.*, 10 (1877), 1896. F. Henle und G. Shupp, *Ber.*, 38 (1905), 1370.

(3) Nitro-compounds often give deviated results in analysis, unless a special care is taken.

an hour in the stream of dry air. Therefore the two molecules of water which came from the hydrobromide were not a water of crystallisation but combined constitutionally. The picrate agreed in appearance very closely with the picrates of the acetamide and formamide. The picric acid almost always gives the binary molecular compounds, when it enters into so-called picrates, whatever the constitution of the other substances may be. In this case the diamide also produced a binary compound, like the acetamide. The picrate is difficultly soluble in absolute alcohol, but easily soluble in hot spirit. It is not decomposed by, and when the two components are present also formed in, a moderately strong hydrobromic acid.

The same picrate was formed when the diethyl dicyanoglutaconate was mixed with the picric acid in alcohol containing some water. When the solutions of the diethyl dicyanoglutaconate and of the picric acid both in absolute alcohol were mixed, a brown clear solution resulted. On adding a few drops of water to this solution the picrate separated out in fine crystals immediately, whilst this picrate is more soluble in alcohol containing water than in absolute alcohol. Without the addition of water the picrate crystallised slowly taking water from surroundings.

0.1034 gr. of substance gave 13.0 c.c. of N_2 at 24.5° and 758 mm. (Found: $N=13.95\%$.) Melting point: 196.5°. The substance mixed with the picrate from the hydrobromide melted at 195.5°.

Finally the same picrate was formed when the bromine addition compound of the diethyl dicyanoglutaconate was mixed with the picric acid in alcoholic solution. Melting point: 195.5°. The substance mixed with the picrate from the hydrobromide melted at 196°.

The three compounds, diethyl dicyanoglutaconate, its bromine addition compound, and the diamide hydrobromide gave the same picrate.

Transformation of the Diamide Hydrobromide into the Diethyl Dihydroxydinicotinate. The diamide hydrobromide was boiled with dilute hydrobromic acid. It entered into solution at first, and in the course of a few minutes a solid separated, which rapidly increased in quantity. When cold this was collected. The mother liquor gave ammonia on heating with alkali. This substance was treated with cold concentrated hydrochloric acid. After adding water the solid was collected, washed and dried.

For comparison, the diethyl dihydroxydinicotinate was prepared by Ruhemann's method.(1) The substance obtained by the hydrolysis of the diethyl dicyanoglutaconate with dilute hydrobromic acid was not already the ammonium salt but the free diethyl dihydroxydinicotinate, for it gave no ammonia on heating with alkali, and the mother liquor gave it. But to

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(1) *J. Chem. Soc.*, 73 (1898), 284.

complete the reaction the solid was treated with cold concentrated hydrochloric acid, as described by Ruhemann. The substance obtained from the hydrobromide was compared with that from the diethyl dicyanoglutaconate, and found to be identical. The former, as well as the latter, was readily soluble in chloroform, gave the red coloration on adding ferric chloride, and melted at the same point (199° not corr.) The three compounds, the diethyl dicyanoglutaconate, its bromine addition compound, and the diamide hydrobromide, are all changeable into the diethyl dihydroxydinicotinate.

The ammonium salt of the diethyl dihydroxydinicotinate was prepared according to Errera's method(1) by the hydrolysis of the diethyl dicyanoglutaconate in spirit. On boiling, the solution of the diethyl dicyanoglutaconate in spirit became gradually colourless and a solid separated out, the mother liquor remaining colourless, whilst Errera observed that the mother liquor became intensively yellow, which was probably due to impurities.

This ammonium salt gave no product with picric acid in alcohol. By heating with caustic alkali it liberated ammnonia. By a dilute acid it was changed into the free ester, for by Ruhemann's method the ammonium salt was not obtained. On adding a ferric chloride solution to the substance suspended (not dissolved) in alcohol, at first no coloration, and then gradually reddish violet coloration occurred, which shows that the ammonium salt was transformed into the free ester by the ferric chloride solution.

The compound $C_{11}H_{16}O_6N_2$, which was obtained as its hydrobromide $C_{11}H_{16}O_6N_2 \cdot HBr$ and picrate $C_{11}H_{16}O_6N_2 \cdot C_6H_2(NO_2)_3OH$, differs from the ammonium salt of the diethyl dihydroxydinicotinate with the same composition and obtainable from the same mother substance, and is changeable into the diethyl dihydroxydinicotinate. Hence it can be no other compound than the diamide of the dicarboxyglutaconic ester, which corresponds to the formula $NH_2CO\text{–}C(COOC_2H_5)=CH\text{–}CH(COOC_2H_5)\text{–}CONH_2$ and should be called the "diethyl $\alpha\gamma$-dicarbamylglutaconate." No amide of this type has ever been obtained, and in cases where such amides should be formed, a ring formation or splitting into a propene chain took place.(2)

In those reactions producing the bromine addition compound of the diethyl dicyanoglutaconate, the diamide hydrobromide, and the picrate, no heat was applied. All the transformations proceeded at the ordinary temperature. Hence it is natural to suppose that there took place no extraor-

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(1) *Ber.*, 31 (1898), 1241.

(2) See page 27 and Errera, *Ber.*, 33 (1900), 2973; Ruhemann and Morrell, *J. Chem. Soc.*, 59 (1891), 743; ibid., 61 (1892), 791; ibid., 63 (1893), 874; Guthzeit und Laska, *J. prakt. Chem.*, 58 (1898), 419; Guthzeit und Haussmann, *Ann.*, 285 (1895), 61 u. 97. Further cf., J. F. Thorpe and his collaborators, *J. Chem. Soc.*, 85–117 (1904–1920), "The Formation and Reactions of Imino Compounds. Part I-Part XX".

dinary change as the ring formation. The free diamide has not yet been isolated.

The author expresses his hearty thanks to Prof. K. Matsubara, who gave kind suggestions and in whose laboratory these experiments were carried out.

Summary.

1. The so-called diethyl dicyanoglutaconate has the composition $(C_{11}H_{12}O_4N_2)_2H_2O$ and the constitution is considered to be represented by the formula $(C_{10}H_{12}O_4N)$–CO–NH–C(NH)–$(C_{10}H_{12}O_4N)$.

2. The diethyl sodiodicyanoglutaconate is colourless when pure.

3. By the action of bromine on the so-called diethyl dicyanoglutaconate an addition product is obtained, which has the composition $(C_{11}H_{12}O_4N_2)_2 \cdot H_2O \cdot HBr \cdot Br_6$. This is changed into the diamide hydrobromide, $C_{11}H_{16}O_6N_2 \cdot HBr$, in ether containing water.

4. The picrate of the diamide, $C_{11}H_{16}O_6N_2 \cdot C_6H_2(NO_2)_3OH$, is obtained from the diamide hydrobromide, from the bromine addition compound, and from the so-called diethyl dicyanoglutaconate. These three compounds are all changeable into the diethyl dihydroxydinicotinate.

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ON THE DENSITY OF THE WATER VAPOUR.(1)

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Received November 16, 1926. Published February 28, 1927.

Introduction. On the molecular state of the water vapour many discussions were published. But they cannot be said decisive. Some(2) of them claim the existence of polymerised molecules such as $(H_2O)_n$ besides single molecules H_2O in the water vapour, while others(3) refute them. Most of these discussions are based on the data calculated indirectly, for example the density of the water vapour under the orthobaric state calculated from the vapour pressure and the heat of vaporization. In fact the data(4) of the density of the water vapour directly measured are so scarce that they are not sufficient to be used in this discussion. The data of Kornatz,(5) however, are somewhat sufficient, which were used by Bose(6) to conclude the existence of twice polymerized molecules $(H_2O)_2$ in equilibrium with single molecules. According to his formula we can obtain so much $(H_2O)_2$ molecules as to 8.9% at 100° under one atmosphere. But presisely examining his formula, it is found that it does not reproduce the data of Kornatz correctly. Therefore we must make more careful measurement of the density of the water vapour, which I have undertaken.

Experimental. The apparatus is shown in Fig. 1, which has been designed after that of Prof. Sameshima(5) with some modifications. A is a glass vessel, whose volume above the mark *b* is accurately measured filling mercury at several temperatures. The stopper of the vessel carries two pieses of platinum wire sealed in, to which is hanged a small glass bulb containing an accurately weighed sample. The small glass bulb is wound round by fine platinum wire as shown in the separate figure. Through this wire electric current is passed to break the bulb in order to set free the water vapour into vessel A. The vessel A is immersed in a thermostat, the temperature of which is kept constant within one tenth degree $\left(\text{or } \pm\frac{1}{20}{}^{\circ}\right)$.

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(1) Translation of a paper published in the *Journal of the Chemical Society of Japan* (in Japanese), 44 (1923), 887.

(2) Winkelmann, *Wied. Ann.*, 9 (1880), 208; Oddo, *Gaz. chim. ital.*, 45 (1915), 319; Bose, *Z. Elektrochem.*, 14 (1908), 269; Weber, *Comm. Phys. Lab. Leiden*, No. 150.

(3) Kendall, *J. Am. Chem. Soc.*, 42 (1920), 2477; Menzies, *J. Am. Chem. Soc.*, 43 (1921), 851.

(4) Regnault, *J. de chim. et de phys.*, 15 (1845), 129; Horstmann, *Liebig's Ann. Chem., Sup. Bd.*, 6 (1868), 64; Kornatz, Inaug. Diss., Königsberg, 1908.

(5) Sameshima, *J. Am. Chem. Soc.*, 40 (1918), 1482.

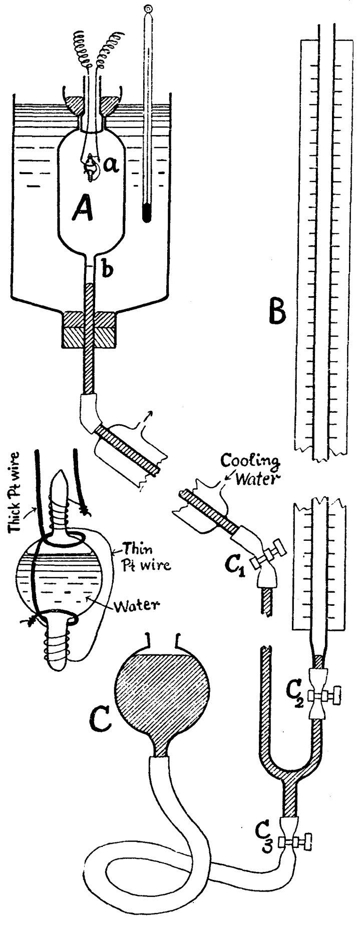

Fig. 1.

The liquid paraffine is used for the thermostat liquid, which is heated electrically. As the operating temperature lies so high as from 80° to 140°, the bath is carefully enveloped by thermal insulators, the electric current is continuously passed and only its small fraction is interrupted by means of a thermoregulator and a relay. The regulator is of ordinary type but the liquid filled is mercury only.

The measurement is carried out as follows. Raising the mercury reservoir C to fill the vessel A with mercury, we put the stopper fitted with the glass bulb already mentioned. Now lowering the reservoir, the vessel becomes to vacuum. This operation is repeated two or three times to get rid of any trace of gas occluded in the mercury or wall of the vessel. Adjusting the mercury level near the mark *b*, temperature of the thermostat is raised to the required temperature. Then adjusting the mercury level to the mark *b* accurately, the height of the mercury in the manometer B is noted. To make the change of the condition of the heated mercury column as small as possible, the connecting tube between A and B is covered with water jacket, and any moving of the heated part of mercury is avoided. For this purpose, in the case of breaking the glass bulb containing the sample, the connecting tube is shut at C_1 by means of a pinchcock. After the break, the counterbalancing mercury level in manometer B is aquired on several trials of slightly releasing the pinchcock at C_1.

The difference of the level in the manometer is reduced to the standard value with respect to temperature and gravity. This value (P) is the pressure exerted by the water vapour of w gr. The volume of the vapour V is that of the vessel subtracted by the net volume occupied by the glass of the sampling bulb, which always amounts to 0.03 c.c. And as the temperature of the bath (T) is known, we can calculate the apparent molecular weight (M) by the following equation

$$PV=\frac{w}{M}RT,$$

where $R=0.082068$ litre-atmosphere.

Following table contains the obtained value of M besides its percentage deviations from the ideal value 18.016. Here we find that no deviation exceeds one percent, and also in Fig. 2 it is shown that these deviations are of order comparable to that expected from the equation of state of water vapour. The lines in Fig. 2 represent the differences of the ideal density of water vapour and the densities calculated by means of van der Waals' equation

$$\left(P+\frac{a}{V^2}\right)(V-b)=rT,$$

where $a=0.01089$, $b=0.001362$⁽¹⁾, while the circlets represent the differences of the ideal density and the observed ones.

Temp. T-273.09	Volume of vapour (V) c.c.	Weight of water (w) gr.	Pressure (P) mm. Hg	Observed mol. wt. $M=\frac{wRT}{PV}$	Deviation from 18.016 (%)
80.03	312.28	0.04115	161.05	18.021	0.03
80.00	312.28	0.07188	280.3	18.085	0.38
100.03	306.07	0.03070	129.3	18.053	0.21
100.02	297.54	0.05170	226.4	18.060	0.24
99.99	306.07	0.08087	340.2	18.073	0.32
99.98	297.54	0.10050	435.2	18.060	0.24
100.00	311.68	0.12405	512.4	18.075	0.33
120.00	297.74	0.04959	226.4	18.037	0.12
120.03	297.74	0.10190	464.6	18.062	0.26
119.98	297.74	0.11160	508.7	18.064	0.27
119.99	297.74	0.11285	515.1	18.041	0.14
140.05	297.94	0.10730	513.2	18.083	0.37
140.00	297.94	0.11440	548.2	18.046	0.17
140.00	297.94	0.11623	556.8	18.052	0.20

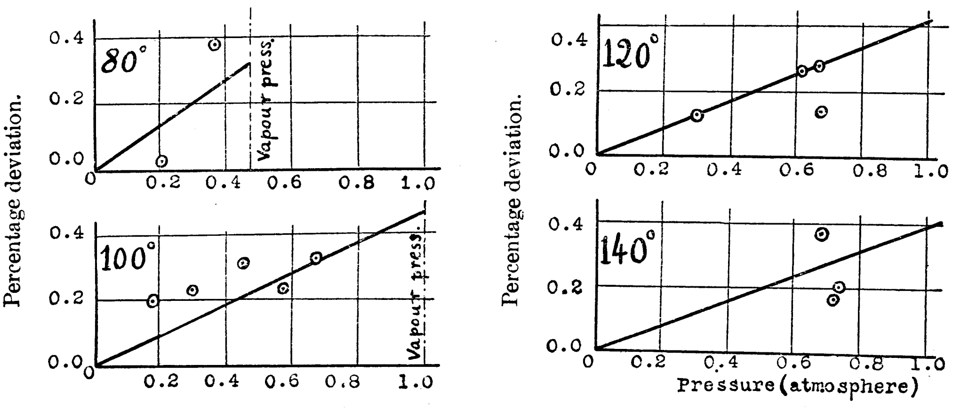

Fig. 2.

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(1) Landolt-Börstein, "Tabellen," 4th ed., p. 447.

Occationally, however, irregularly higher values of deviation were obtained. In these cases either the vassel A was not clear or the quantity of water was too much that the pressure exerted by it was very near or exceeded the saturated vapour pressure at the temperature. Moreover, on strongly illuminating the vessel we could detect film glittering on the wall of the vessel. Therefore the higher deviation must be caused by such adsorption of water vapour on the stained wall. Now as to the higher deviations found in Kornatz's data, I do not know how to explain it, as I am not available of his original paper.

We can conclude, therefore, from the above measurements that the water vapour consists of single molecules only.

In conclusion the author wishes to express his best thanks to Prof. J. Sameshima for his kind guidance during the investigation.

March 1923.

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THE EFFECT OF ALKALI ON THE OXIDATION OF FERROUS HYDROXIDE WITH AIR.

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Received December 24, 1926. Published February 28, 1927.

C. C. Palit and N. R. Dhar have found that some carbohydrates are oxydized by passing air through their solutions in the presence of ferrous hydroxide or sodium sulphite, and that the velocities of these induced oxidations increase with the increase of the concentration of caustic alkali almost in every case.(1) More or less similar results were obtained by Mittra and Dhar on the oxidation of nickelous hydroxide with air in the presence of ferrous hydroxide.(2) It may be supposed that the caustic alkali, which promotes the induced reaction is one of the substances which accelerate the primary reaction. In the case of ferrous hydroxide this expectation is more probable, for the reducing action of ferrous hydroxide increases as the concentration of alkali increases.(3) The present experiment has been

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(1) Palit and Dhar, *J. Phys. Chem.*, **29** (1925), 799; **30** (1926). 939.

(2) Mittra and Dhar, *Z. anorg Chem.*, **122** (1922), 146.

(3) Miyamoto, *Japanese Journal of Chemistry*, **1** (1922), 57; *Scientific Papers of the Institute of Physical and Chemical Research*, **1** (1922), 31.

undertaken to know the effect of alkali on the primary reaction, for the purpose of knowing its effect on the induced reaction above described. From the result of the experiment, it has been ascertained that the caustic alkali does not promote the oxidation, but on the contrary, it decreases the velocity of oxidation. This is one of the examples which show the possibility of the existence of substances which do not promote the primary reaction but accelerate the induced reaction, and the mechanism of this phenomenon may be explained by the theory of the transference of active states.(1)

Experimental. A certain amount of ferrous sulphate solution of known concentration is added to a known quantity of sodium hydroxide solution of known concentration, and air, purified by passing through an acidic solution of potassium bichromate and sodium hydroxide solution, is passed at constant velocity into the mixture. The total volume of the mixture was made to 40 c.c. in each case. The concentration of sodium hydroxide given in the following tables are those calculated after the addition of ferrous sulphate solution. After t minutes the air current is stopped and the contents of the vessel are dissolved by adding sulphuric acid, and the ferrous sulphate thus formed is titrated with potassium permanganate solution (0.1018 normal), the volume of which is given as v in the following tables. The values of k in the following tables were obtained graphically, and those of $v_{calc.}$ were calculated by the equation, $v_{calc.}=v_0-kt$, v_0 being the value of v at $t=o$.

TABLE 1.

Temp.$=20^\circ$C. Velocity of air$=7.78$ litres per hour. Concentration of alkali $(C_{NaOH})=2.240$ mol per litre. $k=0.140$ or $v_{calc.}=v_0-0.140\ t$.

t min.	v c.c.	$v_{calc.}$ c.c.	t min.	v c.c.	$v_{calc.}$ c.c.
0	9.11	—	0	12.60	—
6	8.10	8.27	6	11.50	11.76
8	8.00	7.99	8	11.32	11.48
10	7.74	7.71	10	11.18	11.20
12	7.54	7.43	12	10.97	10.92
15	7.05	7.01	15	10.66	10.50
0	10.83	—	0	18.20	—
6	9.90	9.99	6	17.11	17.36
8	9.65	9.71	8	16.99	17.08
10	9.30	9.43	10	16.69	16.80
12	9.20	9.15	12	16.51	16.52
15	8.79	8.73	15	16.12	16.10

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(4) Miyamoto, *Scientific Papers of the Institute of Physical and Chemical Research*, 4 (1926), 257.

From the above results we see that the velocity of oxidation of ferrous hydroxide with air is zero order with regard to the amount of ferrous hydroxide, or the amount of ferrous hydroxide oxidized is independent of the quantity of hydroxide present. This can be explained by considering that the oxidation takes place in the liquid phase and not on the surface of the solid phase, because in liquid phase the concentration of ferrous ion, although it is extremely small, will be constant during the process.

The Effect of Alkali. Table 2 shows the results of the measurements which were carried out in the sodium hydroxide solution of different concentrations. The values of k decrease with the increase of the concentration of the alkali.

TABLE 2.

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

C_{NaOH} mol/litre	t min.	v c.c.	$v_{calc.}$ c.c.		C_{NaOH} mol/litre	t min.	v c.c.	$v_{calc.}$ c.c.	
0.0048	0	9.11	—	$k=0.310$	0.870	0	9.06	—	$k=0.230$
	6	7.10	7.25			6	7.54	7.68	
	8	6.76	6.63			8	7.15	7.22	
	10	5.90	6.01			10	6.82	6.76	
	12	5.49	5.39			12	6.45	6.30	
	15	4.85	4.46			15	5.84	5.61	
0.0894	0	9.11	—	$k=0.300$	1.320	0	9.06	—	$k=0.203$
	6	7.15	7.31			6	7.66	7.84	
	8	6.60	6.71			8	7.28	7.44	
	10	5.96	6.11			10	7.10	7.03	
	12	5.61	5.51			12	6.69	6.62	
	15	4.85	4.61			15	6.20	6.01	
0.410	0	9.06	—	$k=0.278$	3.150	0	9.06	—	$k=0.110$
	6	7.20	7.39			6	8.25	8.40	
	8	6.65	6.84			8	8.07	8.18	
	10	6.41	6.28			10	7.97	7.96	
	12	5.65	5.72			12	7.76	7.74	
	15	5.06	4.89			15	7.58	7.41	

The Effect of Temperature. The results of the measurements at 30°C. and 40°C. are shown in Table 3. Thus the effect of temperature on the velocity of oxidation of ferrous hydroxide by the air is rather small.

TABLE 3.

Velocity of air = 7.78 litres per hour.

Temp. C°.	C_{NaOH} mol/litre	t min.	v c.c.	$v_{calc.}$ c.c.		Temp. C°.	C_{NaOH} mol/litre	t min.	v c.c.	$v_{calc.}$ c.c.	
30	2.240	0	9.05	—	$k=0.160$	40	2.240	0	9.02	—	$k=0.184$
		6	7.96	8.09				6	7.88	7.92	
		8	7.71	7.77				8	7.50	7.55	
		10	7.39	7.45				10	7.22	7.18	
		12	7.17	7.13				12	6.91	6.81	
		15	6.75	6.65				15	6.40	6.26	
30	0.870	0	9.05	—	$k=0.235$	40	0.870	0	9.02	—	$k=0.247$
		6	7.50	7.64				6	7.38	7.54	
		8	7.03	7.17				8	7.09	7.04	
		10	6.85	6.70				10	6.64	6.55	
		12	6.32	6.23				12	6.09	6.06	
		15	5.73	5.52				15	5.53	5.32	

$\frac{k_{30^\circ}}{k_{20^\circ}}=1.14$ and $\frac{k_{40^\circ}}{k_{30^\circ}}=1.15$ when $C_{NaOH}=2.240$ mol/litre.

$\frac{k_{30^\circ}}{k_{20^\circ}}=1.02$ and $\frac{k_{40^\circ}}{k_{30^\circ}}=1.05$ when $C_{NaOH}=0.870$ mol/litre.

The Effect of the Velocity of Air Current Passed. In the measurements above described, air was passed at the rate of 7.78 litres per hour. Table 4 shows the results obtained when the velocity of air current was changed. By comparing these values with those given in Table 1, it will be seen that the velocity of the oxidation increases slightly with the increase of the velocity of air current.

TABLE 4.

Temp. = 20°C. $C_{NaOH}=2.240$ mol per litre.

Velocity of air litre/hour	t min.	v c.c.	$v_{calc.}$ c.c.		Velocity of air litre/hour	t min.	v c.c.	$v_{calc.}$ c.c.	
6.67	0	8.95	—	$k=0.126$	10.00	0	8.90	—	$k=0.146$
	6	8.07	8.19			6	7.90	8.02	
	8	8.02	7.94			8	7.75	7.73	
	10	7.71	7.69			10	7.52	7.44	
	12	7.39	7.44			12	7.24	7.15	
	15	7.12	7.06			15	6.90	6.71	

Summary.

The velocity of the oxidation of ferrous hydroxide with air was found to be independent of the quantity of ferrous hydroxide in a definite volume.

The effect of temperature on the reaction was small.

Caustic alkali does not promote the oxidation, and on the contrary, it decreases the velocity of oxidation, notwithstanding the reducing power of ferrous hydroxide increases with the increase of the concentration of alkali. From this result, we may suppose that the increase of the velocity of oxidation of carbohydrates or nickelous hydroxide by the addition of caustic alkali is not due to the increase of the velocity of primary reaction.

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ÜBER DAS GLEICHGEWICHT DES SYSTEMS GLUKOSE-KOCHSALZ-WASSER.

Von **Shinnosuke MATSUURA.**

Eingegangen am 8 Januar 1927. Ausgegeben am 28 Februar 1927.

Man findet in der chemischen Literatur verschiedene Verbindungen zwischen Glukose und Natriumchlorid,⁽¹⁾ so z. B. $(C_6H_{12}O_6)_2\ NaCl{\cdot}H_2O$, $(C_6H_{12}O_6)_2\ 2NaCl{\cdot}H_2O$ und $(C_6H_{12}O_6){\cdot}2NaCl$, unter denen die erste, die von zwei Moleküle Glukose und einem Molekül Natriumchlorid gebildet ist, am sichersten bekannt ist, und schon im Jahre 1850 von Pasteur in diabetischem Harn aufgefunden wurde. Nach Städeler wird die zweite Verbindung, die durch die Vereinigung von je einem Molekül Glukose und Kochsalz gebildet ist, bei langsamem Verdunsten eines mit Natriumchlorid gesättigten, diabetischen Harns gewonnen. Was das Vorhandensein der dritten Verbindung anlangt, so ist es heute noch etwas zweifelhaft.

Die oben an erster Stelle genannte Verbindung $(C_6H_{12}O_6)_2\ NaCl{\cdot}H_2O$ soll auch bei der Darstellung der Glukose gebildet werden, indem man Stärke mittels Salzsäure spaltet und nachher die so erhaltene saure Lösung mit Soda neutralisiert. Da die phasengesetzliche Untersuchung über das System Glukose-Kochsalz-Wasser, vom technisch-chemischen Standpunkt betrachtet, wichtig und interessant zu sein scheint, so habe ich diese in der vorliegenden Arbeit unternommen.

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(1) Beilstein, " Handbuch der organischen Chemie," 3. Auflage (1893), I. S. 1046.

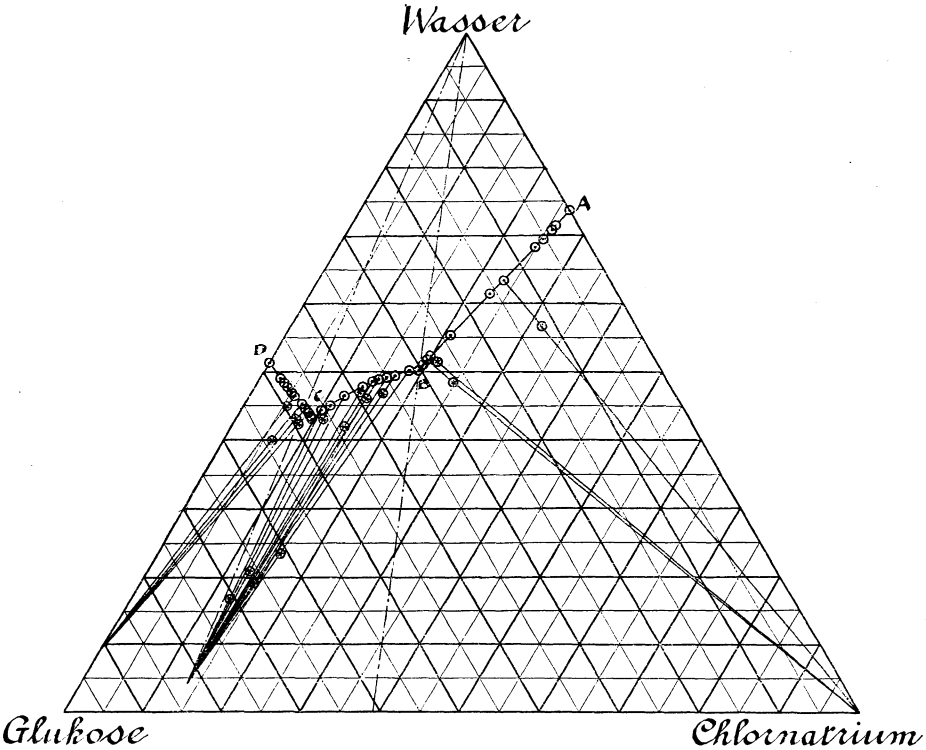
Beschreibung der Versuche. Die in dieser Untersuchung gebrauchte Glukose wurde von E. Merck und das Kochsalz von Kahlbaum bezogen. Die Glukose wurde vorher im Exsiccator auf Phosphorpentoxyd sorgfältig getrocknet.

Das Gemisch von Glukose-Kochsalz-Wasser wurde im Thermostat bei 24° etwa zwei Tage umgerührt und danach einige Stunden ruhig gelassen. Die klare Mutterlauge wurde alsdann herausgenommen und der Analyse unterworfen. Der Bodenkörper (mit etwas Lösung) wurde gleichfalls analysiert. Da ein an Glukose reicher Teill eicht die Erscheinung der Übersättigung zeigt, so musste man die Lösung mit einer Krystallsamen der Glukose impfen und einige Tage ruhig stehen lassen, bevor das Gleichgewicht zwischen fester und flüssiger Phasen vollständig hergestellt wurde.

Natriumchlorid wurde volumetrisch mit 1/10 N. Silbernitratlösung analysiert, indem man Kaliumchromatlösung als Indikator benutzte, und in dem Falle, wo eine grosse Menge der Glukose in der Lösung vorhanden war, noch einigen Tropfen der Salpetersäure dazu gefügt wurde. Die Glukose wurde folgedermassen bestimmt: Zur Glukose enthaltende Lösung wurde zuerst Schwefelsäure und dann Chromsäure zugefügt und dann erhitzt. Die dabei entweichenden Gase wurden zuerst durch ein mit Silbernitratlösung gefülltes Gefäss geleitet, um den beigemengte Chlorwasserstoff zu entfernen, und dann in eine 80 cm. lange, im vorderen Teil mit Kupferoxyd, und hinteren Teil mit einer Siberspirale versehene Verbrennungsrohr hineingeführt und verbrant. Nun wurde das Gas durch Trockenröhren mit konzentrierter Schwefelsäure und Calciumchlorid geleitet, schliesslich liess man das Kohlendioxyd, welches aus vollständiger Oxydation von Glukose resultierte, von der Kalilauge absorbieren. Die Glukosemenge wurde sodann aus dem Gewicht des Kohlendioxydes durch Rechnung festgestellt. Die Glukosemenge in die glukosereichen Teile wurden auch durch Polarimeter bestimmt. Die Kompositionsermitterung wurde anderseits dadurch bewerkstelligt, dass man Viskosität und spezifisches Gewicht der Lösung bestimmt, die durch Verdünnung der gesättigter Lösung oder durch Auflösung des Bodenkörpers (mit etwas Lösung) gewonnen werden, und die so erhaltenen Resultate in graphischer Darstellung bringt. In dieser Figur kann man die Komposition der gesättigten Lösung oder des Bodenkörpers (mit etwas Lösung) ablesen.

Die folgende Tabelle enthält die Komposition der gesättigten Lösung und des mit dieser im Gleichgewicht stehenden Bodenkörpers (mit etwas Lösung), welche in Gewichtprozent aufgestellt sind. Das graphische Dreieck wurde zeichnerisch nach Schreinemakers dargestellt.

Nummer	Lösung			Bodenkörper mit Lösung			Zusammensetzung der festen Phase aus Restanalysen ermittelt
	Glukose	Natriumchlorid	Wasser	Glukose	Natriumchlorid	Wasser	
1	0.00	26.48	73.52	—	—	—	
2	2.84	25.87	71.29	—	—	—	
3	3.58	25.58	70.84	—	—	—	
4	5.21	25.28	69.51	—	—	—	
5	6.82	24.85	68.33	—	—	—	
6	9.90	24.10	66.00	—	—	—	
7	13.09	23.38	63.53	11.70	31.52	56.78	NaCl
8	15.81	22.76	61.43	—	—	—	
9	19.77	21.90	58.33	—	—	—	
10	23.87	20.83	55.30	—	—	—	
11	27.81	19.87	52.32	27.39	21.06	51.55	„
12	28.35	19.85	51.80	26.57	24.86	48.57	„
13	29.47	19.50	51.03	—	—	—	NaCl + $[C_6H_{12}O_6]_2 \cdot NaCl \cdot H_2O$
14	31.70	18.10	50.20	60.74	15.71	23.55	$[C_6H_{12}O_6]_2NaClH_2O$
15	33.74	16.87	49.39	—	—	—	
16	33.76	16.84	49.40	36.59	16.59	46.82	„
17	34.92	15.98	49.10	66.35	14.45	19.20	„
18	35.98	15.12	48.90	38.00	15.00	47.00	„
19	36.90	14.50	48.60	43.69	14.39	41.92	„
20	38.67	13.61	47.72	39.61	13.40	46.99	„
21	41.62	11.92	46.46	66.28	12.70	21.02	„
22	44.05	10.95	45.00	46.02	11.00	42.98	„
23	45.60	10.24	44.16	70.79	12.31	16.90	„
24	47.35	9.57	43.08	—	—	—	$[C_6H_{12}O_6]_2NaCl \cdot H_2O$ + $C_6H_{12}O_6 \cdot H_2O$
25	47.38	9.22	43.40	—	—	—	
26	47.35	8.45	44.20	49.49	8.21	42.30	$C_6H_{12}O_6 \cdot H_2O$
27	47.23	8.28	44.49	49.34	7.67	42.99	„
28	47.73	7.65	44.62	—	—	—	
29	47.55	7.20	45.25	54.06	6.02	39.92	„
30	47.74	6.97	45.29	—	—	—	
31	48.08	5.60	46.32	49.74	5.30	44.96	„
32	48.17	5.01	46.82	—	—	—	
33	48.12	4.04	47.84	—	—	—	
34	48.13	3.27	48.60	—	—	—	
35	48.55	2.49	48.96	—	—	—	
36	48.68	0.00	51.32	—	—	—	



Die Punkten auf den Kurvenanteil AB in der Figur (1–11 in der Tabelle) wurden folgendermassen erhalten : man bereitet vorerst die Glukoselösung mit bekannter Konzentration und zufügt dieser verschiedene Mengen von Natriumchlorid, wobei die Glukose immer in der Lösung gelöst bleibt, und das Bodenkörper nur von Natriumchlorid besteht. Infolgedessen kann man die Menge der Glukose, die jedem Punkt auf den Kurvenanteil A B entspricht, durch Rechnung bekommen, wenn man nur die Natriumchloridmenge analytisch erkennt.

Die Glukosereichenteile in den Punkten auf den Kurvenanteil C D haben Neigung eine übersättigte Lösung zu ergeben, und die Löslichkeit von Glukose ist daher schwer zu bestimmen.

In dieser Weise, habe ich also als feste Phase nur eine Verbindung $(C_6H_{12}O_6)_2NaCl \cdot H_2O$ bei 24° gefunden, welche in Rhomboeder auskrystallisiert. Wie man aus der graphischen Darstellung ersieht, zerfällt es beim Auflösen in Wasser. Fügt man dagegen Natriumchlorid dazu, wird diese Verbindung wieder abgeschieden, da ihre Löslichkeit dabei stark vermindert wird. Die Verbindung $(C_6H_{12}O_6)_2 2NaCl \cdot H_2O$, die Städeler beschrieb, kann ich nicht bei 24° auffinden. Wahrscheinlich mag diese ein Gemenge von $(C_6H_{12}O_6)_2NaCl \cdot H_2O$

und NaCl sein. Die Verbindung $(C_6H_{12}O_6)2NaCl$ mag auch ein Gemenge sein, welches bei der Verdunstung der Lösung im Punkt B zuletzt entsteht.

Zusammenfassung.

1. Das heterogene Gleichgewicht des Systems Glukose-Kochsalz-Wasser wurde bei 24° untersucht.

2. Zwischen Glukose und Natriumchlorid ist nur eine Verbindung $(C_6H_{12}O_6)_2NaCl \cdot H_2O$ bei 24° existenzfähig.

3. Diese Verbindung zersetzt sich bei Auflösen in Wasser. Durch Zusatz von Kocksalz zu der Lösung wird jedoch dieselbe Verbindung wieder auskrystallisiert, weil ihre Löslichkeit dadurch stark vermindert wird.

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SPECTROCHEMICAL STUDIES OF HYDROXYAZO-COMPOUNDS. PART III.(1)

By **Taku UEMURA, Naomichi YOKOJIMA** and
Tamimatsu ENDO.

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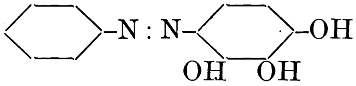
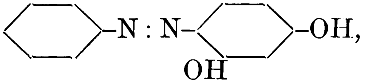
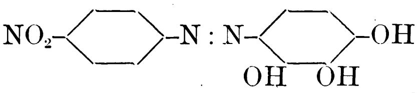
1. **Benzeneazopyrogallol,**(2) 

We can find very slight bathochromic and hyperchromic influences by the addition of alkali in the absorption curve (Fig. 1), and can hardly detect the change of colour in the solution. The marked difference from the absorption curves of No. 2 compound in Part I of this paper,  is probably due to the existence of the meta hydroxyl-group with respect to the azo-group in this compound. We can assign A-form to the neutral state, but the alkaline state is perhaps the mixture of A- and R-forms.

2. **p-Nitrobenzeneazopyrogallol,**(3) 

KOH changes the colour of the solution from yellowish red into brown

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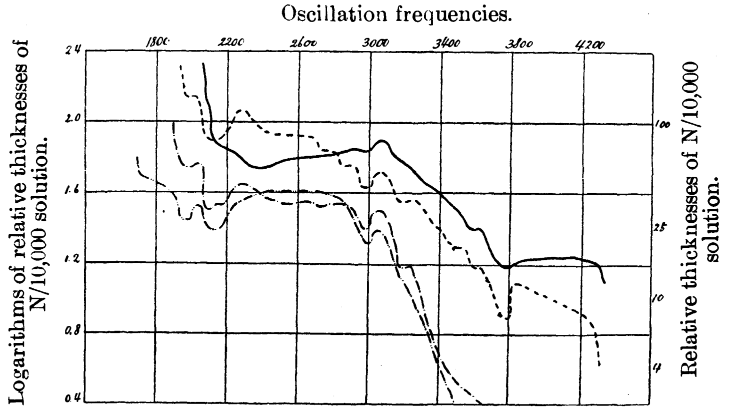
(1) Part I and Part II of this paper were published in this journal, 1 (1926), 260 and 2 (1927), 10 respectively.

(2) Beilstein "Handbuch der Organischen Chemie," IV (1899), 1450.

(3) Obtained from p-nitraniline and pyrogallol.

and soon into orange. A-form can be assigned to the neutral solution as usual, and R-form to the alkaline solution, but we think that on account of the meta hydroxyl with regard to the azo-group, B-form cannot be assigned in this case (Fig. 1).

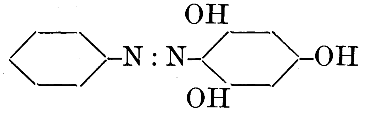


1. Benzeneazopyrogallol. { ——— Neutral solution. / - - - - 0.05 N. alkaline solution.

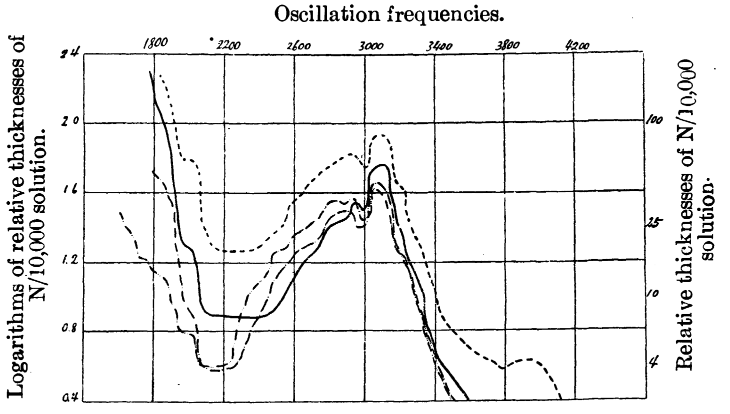
2. p-Nitrobenzeneazopyrogallol. { —·—·— Neutral solution. / —··—··— 0.0596 N. alkaline solution.

Fig. 1.

3. Benzeneazophloroglucinol,(1)



The yellow neutral solution does not change colour by the addition of potassium hydroxide solution. The hypochromic effect due to an alkali is rather exceptional (Fig. 2), but this is perhaps owing to a kind of destruction which has occurred in the molecule by the mutual hindrance of three movable hydrogen atoms in hydroxyl-groups.

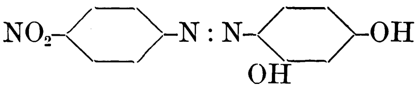


3. Benzeneazophloroglucinol. { ——— Neutral solution. / - - - - 0.05 N. alkaline solution.

4. p-Nitrobenzeneazo-phloroglucinol. { —·—·— Neutral solution. / —··—··— 0.05 N. alkaline solution.

Fig. 2.

4. p-Nitrobenzeneazophloroglucinol,(2)



By the addition of an alkali, only a slightly bathochromic effect can be

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(1) Obtained from aniline and phloroglucinol.

(2) Obtained from p-nitraniline and phloroglucinol.

seen in the absorption curve of this substance (Fig. 2), and this case, the yellowish red neutral solution changes into the orange red alkaline solution. Although we can give A- and R-forms to the two kinds of coloured solutions of this compound, it is almost safe to say that B-form is not represented owing to the mutual hindrance of labile hydrogen atoms.

All of the experimental results (Parts I, II, and III) may be summarized as follows:

No.		Compounds.	Colour of		Form to be assigned.
			Neutral solution.	Alkaline solution.	
Part I.	1	p-Hydroxyazobenzene.	y.	deep y.	A;R.
	2	Benzeneazoresorcinol.	y.	deep y.	A;R.
	3	Benzeneazo-p-cresol.	y.	r.	A;R.
	4	p-Nitrobenzeneazophenol.	y.r.	r.	A;R.
	5	p-Nitrobenzeneazoresorcinol.	r.y.	b.v.	A;R;B.
	6	m-Nitrobenzeneazoresorcinol.	y.	r.	A;R.
	7	p-Nitrobenzeneazo-p-cresol.	y.	v.	A;B.
Part II.	1	Benzeneazocatechol.	y.	o.	A;(A+R).
	2	Benzeneazoquinol.	light y.	nearly no change.	A.
	3	p-Nitrobenzeneazocatechol.	y.r.	b. (changeable).	A;B.
	4	p-Nitrobenzeneazoquinol.	y.r.	o. (changeable).	A;R.
	5	m-Nitrobenzeneazophenol.	y.	r.	A;R.
	6	o-Nitrobenzeneazophenol.	y.	r.	A;R.
	7	o-Nitrobenzeneazoresorcinol.	y.	r.	A;R.
	8	p-Nitrobenzeneazoguaiacol.	y.	r.	A;R.
	9	p-Nitrobenzeneazohydroquinone mono-methyl ether.	y.r.	p. (changeable).	A;R.
Part III.	1	Benzeneazopyrogallol.	y.	no change.	A;(A+R).
	2	p-Nitrobenzeneazopyrogallol.	y.r.	br. (changeable).	A;R.
	3	Benzeneazophloroglucinol.	y.	no change.	A.
	4	p-Nitrobenzeneazophloroglucinol.	y.r.	o.r.	A;R.

y. = yellow, r. = red, o. = orange, b. = blue, br. = brown, p. = purple, v. = violet.
y.r. = yellowish red, r.y. = reddish yellow, b.v. = bluish violet, o.r. = orange red.

Summary (Parts I, II, and III).

1. Tautomeric transpositions may take place in these hydroxyazo-compounds by the addition of a potassium hydroxide solution, with an accompanying change in colour.

2. We can respectively assign A(azo)-, R(red)-, and B(blue)-forms to these tautomers. (Sometimes we recognise more readily the mixture of these forms.)

3. Tautomerism is due to the labile hydrogen atoms in hydroxyl-groups which take the ortho- or para-position with respect to the azo-group.

4. The hydrogen atom which is in the meta hydroxyl-group with regard to the azo-group does not only move by itself, but moreover hinders the transposition of the other hydrogen atoms.

5. When there are many labile hydrogen atoms, mutual hindrance may occur.

6. B-form is sometimes produced only when there is a para nitroradical with regard to the azo-group.

7. Nitro-groups which take the ortho- or meta-position with respect to the azo-group do not change into the isonitro-structure.

8. The nitro-group has considerable bathochromic influence upon these hydroxyazo-compounds.

9. Generally only one absorption band exists in the solutions of these substances, but there are two bands when methyl-group is included.

The authors wish to express their hearty thanks to Prof. Yuji Shibata of the Tokyo Imperial University who offered them valuable advice in their researches.

The expenses of this study were defrayed partly through a grant from the Department of Education, and partly with the Research Fund of the School, for which we desire to tender our gratefulness.

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THE CONDENSATION OF PHENOLIC ALDEHYDES AND THEIR ETHERS WITH METHYL ETHYL KETONE.

By **Kenji IWAMOTO.**

Received December 29, 1926. Published February 28, 1927.

Harries and Müller(1) showed that, in the presence of an alkali, methyl ethyl ketone condenses with benzaldehyde to form the α-benzylidene derivative, $C_6H_5CH : CHCOC_2H_5$, and, in the presence of hydrochloric acid, to form the γ-benzylidene derivative, $C_6H_5CH : C(CH_3)COCH_3$. Ichikawa(2) reported that methyl ethyl ketone condenses with vanillin in the presence of an alkali, to yield 3-methoxy-4-hydroxystyryl ethyl ketone, $C_6H_3(OH)(OCH_3)CH : CHCOC_2H_5$, and, in the presence of hydrochloric acid, to give rise to the

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(1) *Ber.*, 35 (1902), 966.

(2) *Sci. Rep. Tohoku. Imp. Univ.*, 14 (1925), 127.

bimolecular compound, $C_6H_3(OH)(OCH_3)CH:CHCOC(CH_3):CHC_6H_3(OH)(OCH_3)$. Claisen and Claperède⁽¹⁾ found that, in the presence of hydrochloric acid, benzaldehyde condenses with acetone to form dibenzylidene acetone, $C_6H_5CH:CHCOCH:CHC_6H_5$, and Nomura and Hotta⁽²⁾ observed that divanillylidene acetone, $C_6H_3(OH)(OCH_3)CH:CHCOCH:CHC_6H_3(OH)(OCH_3)$, was formed by the condensation of vanillin with acetone in the presence of concentrated hydrochloric acid.

From these results, it appears that acetone condenses with benzaldehyde or with vanillin in the presence of hydrochloric acid, to form a bimolecular compound, arising from the condensation of two molecules of aldehyde and one of acetone, whilst, in the presence of hydrochloric acid, methyl ethyl ketone gives different condensation products, according as benzaldehyde or vanillin is condensed with it. Therefore, it seemed interesting to study the condensation of various phenolic aldehydes and their ethers with methyl ethyl ketone,—alkali, consentrated hydrochloric acid, or dry gaseous hydrogen chloride being used as the condensing agents.

The author condensed methyl ethyl ketone with protocatechualdehyde, veratraldehyde, piperonal, p-hydroxybenzaldehyde, anisaldehyde, m-hydroxybenzaldehyde, or with m-methoxybenzaldehyde under various conditions. The condensation may be represented by one of the following three cases :—

$$RCHO+CH_3COC_2H_5 \longrightarrow RCH:CHCOC_2H_5. \qquad (A.)$$

$$RCHO+CH_3COC_2H_5 \longrightarrow RCH:C(CH_3)COCH_3. \qquad (B.)$$

$$2RCHO+CH_3COC_2H_5 \longrightarrow RCH:CHCOC(CH_3):CHR. \qquad (C.)$$

The constitution of the products (A) and (B) was determined by analysis, and by the formation of oxime and dibromide, and they were differentiated from each other by using sodium hypochlorite, when substance (B) yielded chloroform and an acid with one fewer carbon atom than the original ketone, as shown in the following scheme :—

$$RCH:C(CH_3)COCH_3+3NaClO=RCH:C(CH_3)COONa+CHCl_3+2NaOH.$$

The compounds which were expected to be, on analysis, of the type (C) had no definite melting point and it was difficult to convert them into crystalline derivatives.

When protocatechualdehyde or veratraldehyde was condensed with methyl ethyl ketone in equi-molecular quantity in the presence of hydrochloric acid, a bimolecular compound of type (C) was obtained. In the case of p-hydroxybenzaldehyde or anisaldehyde, the condensation product, in the presence of hydrochloric acid, was a unimolecular compound when each molecule of aldehyde and ketone was used, and this was the case even when

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(1) *Ber.*, **14** (1881), 350.

(2) *Sci. Rep. Tohoku Imp. Univ.*, **14** (1925), 123.

half the quantity of the latter was used, i.e. a condition which is in favour of bimolecular formation of the compound. It thus follows that the formation of a bimolecular compound is not the effect of the hydroxyl or methoxyl group in para-position to the aldehyde group. On the contrary, it is the effect of the hydroxyl or methoxyl group in meta-position to the aldehyde group. In the support of this view, the substance of type (C) was the sole product of the condensation of methyl ethyl ketone with m-hydroxybenzaldehyde and its ether, in the presence of hydrochloric acid, even when each molecule of aldehyde and ketone, favourable to the formation of a unimolecular compound, was used.

In the presence of dilute alkali, the condensation products of methyl ethyl ketone with various aldehydes were found to be unimolecular compounds.

Experimental.

α-Methyl-3:4:3′:4′-tetramethoxydistyryl Ketone, $(CH_3O)_2C_6H_3CH:C(CH_3)COCH:CHC_6H_3(OCH_3)_2$. A mixture of veratraldehyde (3 gr.), methyl ethyl ketone (1.5 gr.) and concentrated hydrochloric acid (d=1.19; 6 c.c.) was allowed to stand for 6 days, and the black, violet product was ground in dilute alkali, collected, washed with water and dried. It was dissolved in benzene, boiled with the addition of animal charcoal, and after being filtered, precipitated with petroleum ether. On repeating this process, a dark, yellow, amorphous powder was obtained (Found: C=71.77; H=6.31. $C_{22}H_{24}O_5$ requires C=71.70; H=6.57%).

When half the above quantity of the ketone was used, the result was the same.

α-Methyl-3:4:3′:4′-tetrahydroxydistyryl Ketone, $(OH)_2C_6H_3CH:C(CH_3)CO CH:CHC_6H_3(OH)_2$. To an ice-cooled mixture of protocatechualdehyde (2 gr.; 1 mol.) and methyl ethyl ketone (1 gr.; 1 mol.), concentrated hydrochloric acid (d=1.19; 5 c.c.) was added. After standing for 6 days, the black mass was ground, collected and washed with water. It was dissolved in glacial acetic acid and precipitated with water. On repeating this operation, it separated as a black, violet powder, which, after being dried at 90–100° under reduced pressure, was analysed (Found: C=69.14; H=5.13. $C_{18}H_{16}O_5$ requires C=69.20; H=5.16%). On heating, this substance carbonises without melting.

The same result was obtained by using ½ mol. of the ketone and 1 mol. of the aldehyde.

The Methyl Ether, $(CH_3O)_2C_6H_3CH:C(CH_3)COCH:CHC_6H_3(OCH_3)_2$. α-Methyl-3:4:3′:4′-tetrahydroxydistyryl ketone was methylated with methyl sulphate and alkali. After being purified by dissolving it in benzene and precipitating it with petroleum ether, a brown, amorphous substance was obtained (Found : C=71.44 ; H=6.28. $C_{22}H_{24}O_5$ requires C=71.70 ; C=6.57%).

α-Methyl-p-methoxystyryl Methyl Ketone, $(CH_3O)\,C_6H_4CH:C(CH_3)\,COCH_3$. A mixture of anisaldehyde (27 gr.) and methyl ethyl ketone (15 gr.) was cooled in ice-water, saturated with dry hydrogen chloride, and allowed to stand overnight. The dark, green product was made alkaline and extracted with ether, washed with water and dried. After the removal of the ether, the residual oil was fractionated under a reduced pressure of 12 mm., when a faint, yellow oil (26 gr.) boiling at 278–281° passed over, which, on cooling, solidified to yellow crystals. These were recrystallised from a mixture of ether and petroleum ether with the addition of animal charcoal, when they separated in colourless crystals, m.p. 27.5–28° (Found : C=75.62 ; H=7.26. $C_{12}H_{14}O_2$ requires C=75.76 ; H=7.42%).

When concentrated hydrochloric acid was used instead of dry hydrogen chloride, the result was almost the same, but the yield was poor. When the quantity of the aldehyde was doubled in the above case, nothing definite could be isolated.

The Oxime, $(CH_3O)C_6H_4CH:C(CH_3)C(:NOH)CH_3$. A solution of the ketone (2 gr.), hydroxylamine hydrochloride (0.8 gr.) and sodium acetate (1.6 gr.) in dilute alcohol was boiled for 1½ hours under a reflux condenser. On recrystallising the crude product from alcohol, colourless needles, m.p. 126,5–128°, were obtained (Found : N=6.88. $C_{12}H_{15}O_2N$ requires N=6.83%).

The Dibromide, $(CH_3O)C_6H_4CHBrC(CH_3)BrCOCH_3$. To a chloroform solution of the ketone, a solution of bromine in the same solvent was added drop by drop, and allowed to stand for 10 minutes. The chloroform was removed under diminished pressure without the application of heat, and the residue was recrystallised from a mixture of ether and petroleum ether, when it separated in colourless crystals, m.p. 70.5–71°, which decomposed gradually (Found : Br=45.57. $C_{12}H_{14}O_2Br_2$ requires Br=45.67%).

Action of Sodium Hypochlorite. To a freshly prepared solution of sodium hypochlorite from bleaching powder and sodium carbonate, the ketone was added and warmed until the evolution of chloroform had ceased. The solution was acidified with dilute sulphuric acid and the precipitate was recrystallised from dilute alcohol, from which it separated in colourless crystals, m.p. 154.5–155° (Found : C=68.73 ; H=6.37. $C_{11}H_{12}O_3$ requires C=68.71 ; H=6.30%).

Perkin(1) gave 154° as its melting point.

p-Methoxystyryl Ethyl Ketone, $(CH_3O)C_6H_4CH:CHCOC_2H_5$. To a mixture of 50 c.c. of water and 20 gr. of a 10% solution of sodium hydroxide, 2

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(1) *J. Chem. Soc.*, 31 (1877), 411.

gr. of anisaldehyde and 1.1 gr. of methyl ethyl ketone were added. After shaking the whole for 2 days, the yellow crystals which separated were collected, washed with water and dried. Colourless scales, m.p. 58.5–59°, were obtained after recrystallisation from a mixture of ether and petroleum ether (Found: C=75.87; H=7.48. $C_{12}H_{14}O_2$ requires C=75.76; H=7.42%).

Ryan and Cahill⁽¹⁾ gave 53° as its melting point.

The Oxime, $(CH_3O)C_6H_4CH{:}CHC({:}NOH)C_2H_5$. This was prepared in the same way as α-methyl-p-methoxystyryl methyl ketoxime. It crystallised in colourless needles, m.p. 138–139°, from alcohol (Found: N=7.00. $C_{12}H_{15}O_2N$ requires N=6.83%).

The Dibromide, $(CH_3O)C_6H_4CHBrCHBrCOC_2H_5$. This compound was also synthesised in the same manner as its isomer. It is colourless crystals which decompose at 87.5° (Found: Br=45.58. $C_{12}H_{14}O_2Br_2$ requires Br=45.67%).

Ryan and Cahill described 85° as its melting point.

α-Methyl-p-hydroxystyryl Methyl Ketone, $(OH)C_6H_4CH{:}C(CH_3)COCH_3$. A well-cooled mixture of p-hydroxybenzaldehyde (5 gr.) and methyl ethyl ketone (3 gr.) was saturated with dry hydrogen chloride, when a green mass was obtained. After standing overnight, it was dissolved in dilute alkali solution, filtered, and acidified with dilute hydrochloric acid. The grey crystals which were deposited were collected and recrystallised from dilute alcohol with the addition of animal charcoal, when they separated in yellow crystals, m.p. 108.5–109.5° (Found: C=74.96; H=6.87. $C_{11}H_{12}O_2$ requires C=74.79; H=7.17%).

The condensation product was the same as that described above, when the condensation was effected with concentrated hydrochloric acid or when half the quantity of the ketone was used.

The Oxime, $(OH)C_6H_4CH{:}C(CH_3)C({:}NOH)CH_3$. This was prerared in the same manner as α-methyl-p-methoxystyryl methyl ketoxime. The oxime was colourless and melted at 147–148° (Found: N=7.39. $C_{11}H_{13}O_2N$ requires N=7.33%).

The Benzoyl Derivative, $(C_6H_6COO)C_6H_4CH{:}C(CH_3)COCH_3$. α-Methyl-p-hydroxystyryl methyl ketone was benzoylated by Schotten-Baumann's method and the raw product was recrystallised from dilute alcohol, from which it separated in colourless crystals, m.p. 124–125° (Found: C=77.26; H=6.02. $C_{18}H_{16}O_3$ requires C=77.11; H=5.76%).

The Methyl Ether, $(CH_3O)C_6H_4CH{:}C(CH_3)COCH_3$. α-Methyl-p-hydroxystyryl methyl ketone was methylated with methyl iodide and alcoholic potash and the crude product was recrystallised from a mixture of ether and

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(1) *J. Chem. Soc.*, 128 (1925), 1, 558.

petroleum ether, when it crystallised in colourless crystals, m.p. 27.5–28.5°. The melting point was not changed by admixture with α-methyl-p-methoxystyryl methyl ketone obtained by the condensation of anisaldehyde with methyl ethyl ketone.

α-Methyl-m : m′-dimethoxydistyryl Ketone, $(CH_3O)\,C_6H_4CH:C\,(CH_3)\,COCH:CHC_6H_4(OCH_3)$. An ice-cooled mixture of m-hydroxybenzaldehyde (1 gr.; 1 mol.) and methyl ethyl ketone (0.55 gr.; 1 mol.) was saturated with dry hydrogen chloride when a deep, scarlet, viscid oil was obtained. After being allowed to remain overnight, it was extracted with ether, washed with water and dried. The ether was removed and the residue was dissolved in benzene and precipitated with petroleum ether. On repeating this operation, a small quantity of yellow, amorphous substance was obtained, which, after being dried at 80–90° under reduced pressure, was analysed (Found: C = 77.78 ; H = 6.98. $C_{20}H_{20}O_3$ requires C = 77.88 ; H = 6.54%).

The same substance was obtained by condensing 1 mol. of the aldehyde with ½ mol. of the ketone.

α-Methyl-m : m′-dihydroxydistyryl Ketone, $(OH)C_6H_4CH:C(CH_3)COCH:CHC_6H_4(OH)$. To a mixture of m-hydroxybenzaldehyde (2 gr.) and methyl ethyl ketone (1.2 gr.), cooled in ice-water, 5 c.c. of concentrated hydrochloric acid (d = 1.19) was added and left for 6 days. The dark, brown mass thus obtained was treated similarly as in the case of the condensation product of protocatechualdehyde with methyl ethyl ketone, when a brick-red powder was obtained which was analysed after being dried at 80–90° for an hour under reduced pressure (Found: C = 77.25 ; H = 5.86. $C_{18}H_{16}O_3$ requires C = 77.11 ; H = 5.76%).

The product was the same on condensing half the quantity of the ketone with the aldehyde.

The Methyl Ether, $(CH_3O)C_6H_4CH:C(CH_3)COCH:CHC_6H_4(OCH_3)$. This substance was prepared by shaking the ketone with methyl sulphate and alkali, and purified by precipitating it from the benzene solution with petroleum ether as described in the case of α-methyl-3:4:3′:4′-tetramethoxydistyryl ketone, when it separated as a dark, yellow powder, which was analysed after being dried at 90–100° under reduced pressure (Found: C = 78.16 ; H = 6.25. $C_{20}H_{20}O_3$ requires C = 77.88 ; H = 6.54%).

3:4-Methylendioxystyryl Ethyl Ketone, $CH_2O_2C_6H_3CH:CHCOC_2H_5$. To a mixture of 100 c.c. of water and 20 c.c. of a 10% sodium hydroxide solution, 5 gr. of piperonal and 2.5 gr. of methyl ethyl ketone were added and allowed to stand for 2 days, when yellow crystals were separated. On recrystallising from dilute alcohol, they separated in yellow crystals, m.p. 101.5–102° (Found: C = 70.73 ; H = 5.99. $C_{12}H_{12}O_3$ requires C = 70.55 ; H = 5.93%).

Ryan and Cahill gave 101–102° as its melting point.

The Oxime, $CH_2O_2C_6H_3CH:CHC(:NOH)C_2H_5$. This was prepared by the same method as in the synthesis of p-methoxystyryl ethyl ketoxime. The crude product was recrystallised from alcohol in faint, yellow crystals, m.p. 173° (decomp.) (Found : N = 6.50 ; $C_{12}H_{13}O_3N$ requires N = 6.39%).

The Dibromide, $CH_2O_2C_6H_3CHBrCHBrCOC_2H_5$. This was synthesised by the same method as in the case of p-methoxystyryl ethyl ketone dibromide. It crystallised in colourless crystals, m.p. 93.5–94°, from a mixture of ether and petroleum ether (Found : Br = 43.94. $C_{12}H_{12}O_3Br_2$ requires Br = 43.92%).

In conclusion, the author wishes to express his hearty thanks to Professor Hiroshi Nomura under whose guidance this investigation was carried out.

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THE OCCURRENCE OF FREE PENTOSE IN BAMBOO SHOOTS. (STUDIES ON JAPANESE PLANTS. VIII.)(1)

By **Shigeru KOMATSU** and **Yasuo SASAOKA.**

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On the occurrence of free pentoses in plants, the evidence was offered by Davis and Sawyer,(2) as suggested by the work of de Chalmot,(3) from the Kröber-Tollens determination of pentoses in the extract of some vegetables, prepared with ammoniacal alcohol, and the contribution which supports this view was reported by A. G. Spoehr,(4) studying the carbohydrate economy of cacti. However, the treatment of the plant materials, employed by Davis and his co-workers, and Spoehr, as these were pointed out by D. T. Englis and C. Hale,(5) would then throw some doubt as to the conclusiveness of the evidence, owing to the fact that the desiccation of plant materials at high temperature,(6) and the use of ammonia and other weak alkalis for the extraction of sugars, could have given rise to a product which would lead to the

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(1) The articles I, II, III, IV, V, and VII have been published in *The Mem. Coll. Sci. Kyoto Imp. Univ.*, 6 (1923), 295; 7 (1923), 7; 9 (1925), 1; 8 (1925), 59; 223; 253.

(2) *J. Agr. Sci.*, 6 (1914), 406.

(3) *Am. Chem. J.*, 15 (1893), 21; 16 (1894), 16; *J. Am. Chem. Soc.*, 15 (1893), 618.

(4) "The Carbohydrate Economy of Cacti," (1919), p. 41.

(5) *J. Am. Chem. Soc.*, 47 (1925), 446.

(6) K. P. Link, ibid., 47 (1925), 470 and refer W. Stiles, "Photosynthesis," (1925), p. 145.

formation of furfural-like compounds by some intramolecular changes or some degradation of hexoses.

In view of these facts, it appears that the only reliable method for the evidence of the occurrence of free pentoses, must be based upon the isolation of these sugars of the expressed juice which was prepared on the spot where the plant materials were freshly gathered.

In the phytochemical study of bamboo shoots, one of the writers (S. K.) and Ch. Tanaka(1) have reported that the pentose-content, which was determined by Kröber-Tollens' method, was constant throughout the bamboo shoot life, and the conviction of the occurrence of pentose in the free state came to the writers from a consideration of the origin of the sugars in plant tissues, ascribing them to the metabolism of hexoses, but not to the photosynthesis of carbon dioxide. The endeavours by which free pentose was isolated, will open the way for some suggestion as to the provenance of pentoses in nature.

The material used in this experiment was the shoots of the Madake (*Phyllostachys quilioli, F. M.*), which were obtained from a bamboo grove in Yamanouchi, Kyoto, located two miles from the laboratory. The shoots were minced in a mincing machine within an hour of gathering, and the minced mass was pressed by means of a hydraulic press. The juice thus obtained was poured into absolute alcohol. The manipulation was carried out as rapidly as possible in order to avoid all danger from enzyme actions on the carbohydrates.

13 Kg. of shoots yielded 10 litres of the expressed-juice of a density of 1.02; and this juice contained 160 gr. of reducing sugar calculated to be d-glucose from its power of reducing Fehling's solution.

To the juice a sufficient quantity of alcohol (30 litres) was added, whereon a voluminous precipitate was formed, which was filtered, washed well with alcohol and the filtrate subjected to distillation under reduced pressure to distill off the alcohol, and then diluted with water. To get sugars only, a slight excess of basic lead acetate was added to precipitate glucuronic acid with some organic acids which occur in the juice and the precipitate was filtered off, the excess of lead was removed by hydrogen sulphide gas. The colourless solution was evaporated to syrup under reduced pressure and the reducing sugars were extracted with absolute alcohol, evaporated again to a thick syrup and treated with alcohol. The operation was repeated three times, and the final extract containing 111.68 gr. of d-glucose and 12.88 gr. of l-xylose calculated from the reducing power of Fehling's solution and from the quantity of furfural measured by Kröber-Tollens' method, was evaporated under reduced pressure to a thick syrup. After clarifying with basic lead

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(1) Loc. cit.

acetate, and an equal volume of glacial acetic acid was added to the syrup to crystallize the d-glucose, and actually 43 gr. of d-glucose. m.p. 145°, were isolated in a white crystalline state. The filtrate from the crystallized d-glucose, containing 49.5 gr. of reducing sugar, was diluted with water, and the acetic acid was expelled by distillation under reduced pressure, and the solution concentrated to 200 c.c.; it gave a polarization of $\alpha_D=26^\circ.9$ in a 1 dm. tube. Half of the sugar solution was diluted with water to make approximately a 10% aqueous solution, and about 5 gr. of top yeast were added, together with about 5 gr. of malt sprouts as a nitrogenous yeast food in order to ferment some hexoses remained in the solution with pentose. Fermentation proceeded at room temperature. After four days from the start, the fermentation had ceased and the solution was then cleared with a slight excess of basic lead acetate, the precipitate filtered, the excess of lead in the filtrate was precipitated by hydrogen sulphide gas, decolorized with active carbon and the solution again filtered. The solution freed from hydrogen sulphide, showed a polarization of $\alpha_D=19^\circ.2$ in a 1 dm. tube, contained 6.11 gr. and 6.13 gr. of l-xylose calculated from the reducing power of Fehling's solution, and the furfural-content by the Kröber-Tollens' method respectively. As concentrating the solution under reduced pressure, sugar was crystallized and the yield of the crude material was 5.4 gr. The sugar purified from its aqueous solution, melted at 145–150°, and showed a dextro-rotation in aqueous solution,

$$[\alpha]_D^{18}=\frac{0.39\times100}{2\times1.015}=+19.^\circ21$$

Analysis, ($C=39.95$; $H=6.65$), indicated that the sugar has the formula $C_5H_{10}O_5$ (it requires, $C=40.00$; $H=6.66\%$). For confirmation to be l-xylose, it was transformed into l-xylose osazone, m.p. 159°, and into xylonic acid by oxidation with bromine, and the latter was identified as the double salt of cadmium bromide with cadmium xylonate, following the method suggested by G. Bertrand.(1) It gave on analysis, $Br=20.78$; while theory requires $Br=21.32$ for $(C_5H_9O_6)_2Cd\cdot CdBr_2\cdot 2H_2O$.

The isolation of l-xylose in a crystalline state from the pressed juice of bamboo shoots was successful, and this is probably the first example that pentose has been obtained direct in crystalline form from vegetable tissues.

Moreover, it is noteworthy fact that glucuronic acid which was regarded as an intermediate product of glucose metabolism in nature, was isolated from the precipitate by basic lead acetate mentioned above. For the recognition of glucuronic acid,(2) the precipitate which formed by basic lead acetate, suspended in water was decomposed by means of hydrogen sulphide gas, and

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(1) *Bull. soc. chim.*, [3] 5 (1891), 556.

(2) Refer C. G. Schwalbe and G. A. Feldtmann, *Ber.*, 58 (1925), 1535.

the free acid in solution was isolated by converting it into barium salt of the phenylosazone⁽¹⁾ (m.p. 192°). The analytical results of the barium salt, $C_{36}H_{38}O_{10}N_8Ba$, are : $C=48.98$; $H=4.76$; $N=12.68\%$.

The discovery of these substances in such a vigorously growing part of the plant, should account for much of formation of pentoses by the metabolic changes of hexoses in plants.

In addition, pectinic substance was isolated in an impure state from the pressed juice of the shoots, which yields pentose by hydrolysis and mucic acid by oxidation.

In fact, pectines and mucilages,⁽²⁾ their basal molecule consists of xylose, glucose and glucuronic acid or arabinose, galactose and galacturonic acid, have been very generally occured in nature with the pentoses and hexoses. These facts strongly support the hypothesis of pentose formation above mentioned.

In conclusion, the writers desire to express their thanks to Mr. N. Iguchi for furnishing valuable materials used in this investigation.

October 1926.

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(1) Goldschmidt, *Monatsh.*, 31 (1910), 477.

(2) F. Ehrlich, *Chem. Ztg.*, 44 (1917), 197; T. von Fellenberg, *Biochem. Z.*, 85 (1918), 82; W. H. Dore, *J. Ind. & Eng. Chem.*, 16 (1924), 1042 ; S. Komatsu and H. Ueda, *The Mem. Coll. Sci. Kyoto Imp. Univ.*, A, 8 (1925), 51; D. R. Nanji, F. I. Paton and A. R. Ling *J. Soc. Chem. Ind.*, 44 (1925), 253; J. W. Mikinney, *J. Soc. Chem. Ind.*, 45 (1926), 301.

ELECTRICAL CONDUCTIVITIES OF THE SALT SOLUTIONS CONTAINING AGAR.

By **Eiichi IWASE.**

Received December 29, 1926. Published March 28, 1927.

The fact that the gelatine-sol containing salt does not change its electric conductivity on gelatinisation was already noticed by Arrhenius⁽¹⁾. Laing and McBain⁽²⁾ observed that there is no distinction in electric conductivity between soap sol and gel at the same concentration and temperature. Soap, however, is a so-called colloidal electrolyte and differs somewhat from a hydrophile colloid. Hatschek and Humphry⁽³⁾ have recently reported that the conductivity of agar, water and copper sulphate mixture exhibits on gelatinising a slight but measurable alteration. My experiments have been undertaken to test such a case, and are described in the following lines.

Powdered agar from Merck was dispersed in distilled water or in aqueous salt solution by heating in a vessel provided with a condenser on a water bath. Special precaution was taken to prevent the evaporation of the water during the dispersion and the measurement. The electrodes of the conductivity cell were made of moderately thick well platinized platinum plates and wires. The measurements were carried out in a thermostat of 50°±0.05°C. Being cooled by water from outside of the conductivity cell, sol was transformed into gel always in the same condition. Two percent $CuSO_4 \cdot 5H_2O$ solution prepared at 30° was diluted up to 1/32 percent. 25 c.c. of these aqueous salt solutions were taken, and 0.5 gr. agar was added to each of them and dispersed as above mentioned. The conductivities were measured of these aqueous solutions and agar solutions in sol and gel states. The results are shown in Table 1.

TABLE 1.

Grams of $CuSO_4 \cdot 5H_2O$ in 100 c.c. of water	Specific conductivity (mho × 10^5)			
	Aqueous solution	Agar solution		
		Sol	Gel	Difference
2	1011	1016	1020	4
1	598.8	606.9	609.7	2.8
1/2	353.4	388.1	390.6	2.5
1/4	209.1	252.9	255.4	2.5
1/8	122.9	170.6	171.8	1.2
1/16	70.71	122.7	123.6	0.9
1/32	40.70	100.1	101.3	1.2
Distilled water	3.039			

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(1) Arrhenius, *Oefvers Stockholm Akad.*, **6** (1887), 121.
(2) Laing and McBain, *J. Chem. Soc.*, **117** (1920), 1506.
(3) Hatschek and Humphry, *Trans. Faraday Soc.*, **20** (1924), 18.

The same experiments were undertaken for other salts than $CuSO_4$, viz. K_2SO_4, KCl, KI, NaCl and KCNS solutions and the results are shown in Tables 2, 3, 4, 5, and 6 respectively. The data given in Table 2 are depicted in Fig. 1.

TABLE 2.

Conc. of K_2SO_4 normal	Specific conductivity (mho × 10^5)		
	Aqueous solution	Agar solution	
		Sol	Gel
0.2	3014	—	—
0.175	2685	—	—
0.15	2353	2270	—
0.125	2011	—	—
0.1	1656	1596	—
0.075	1289	—	—
0.05	898.5	869.2	—
0.025	481.7	486.6	490.0

TABLE 3.

Conc. of KCl millimol/litre	Specific conductivity (mho × 10^5)			
	Aqueous solution	Agar solution		
		Sol	Gel	Difference
20.0	417.6	465.8	468.3	2.5
17.5	366.2	—	—	—
15.0	315.1	369.0	370.7	1.7
12.5	264.2	—	—	—
10.0	213.6	273.0	275.2	2.2
7.5	164.2	—	—	—
5.0	109.6	176.2	177.6	1.4
2.5	57.11	126.2	127.5	1.3
1.25	29.09	99.06	100.2	1.1
0.625	15.60	—	—	—

TABLE 4.

Conc. of KI millimol/litre	Specific conductivity (mho × 10^5)			
	Aqueous solution	Agar solution		
		Sol	Gel	Difference
20.0	418.3	463.9	465.9	2.0
17.5	269.2	415.4	417.4	2.0
15.0	317.7	367.7	370.0	2.3
12.5	266.6	—	—	—
10.0	216.2	272.6	274.3	1.7
7.5	162.6	—	—	—
5.0	110.4	175.9	176.7	0.8
2.5	56.20	126.6	127.4	0.8
1.25	31.35	101.7	102.5	0.8
0.625	15.50	—	—	—

TABLE 5.

Conc. of NaCl millimol/litre	Specific conductivity (mho × 10^5)			
	Aqueous solution	Agar solution		
		Sol	Gel	Difference
20.0	356.0	409.1	410.7	1.6
17.5	313.1	366.7	369.1	2.4
15.0	269.1	—	—	—
12.5	226.4	285.0	285.8	0.8
10.0	183.5	245.3	246.3	1.0
7.5	138.8	—	—	—
5.0	94.08	160.4	161.2	0.8
2.5	48.90	117.7	118.4	0.7
1.25	25.76	96.25	97.10	0.7
0.625	13.87	—	—	—

TABLE 6.

Conc. of KCNS millimol/litre	Specific conductivity (mho × 10^5)			
	Aqueous solution	Agar solution		
		Sol	Gel	Difference
20.14	393.4	440.5	442.8	2.3
17.6225	345.5	—	—	—
15.105	298.5	352.3	354.8	2.5
12.5875	250.2	—	—	—
10.07	201.2	259.4	261.0	1.6
7.5525	152.9	—	—	—
5.035	103.2	168.7	169.9	1.2
2.5175	52.92	—	—	—
1.2588	27.30	96.74	97.07	0.3
0.6294	15.70	—	—	—

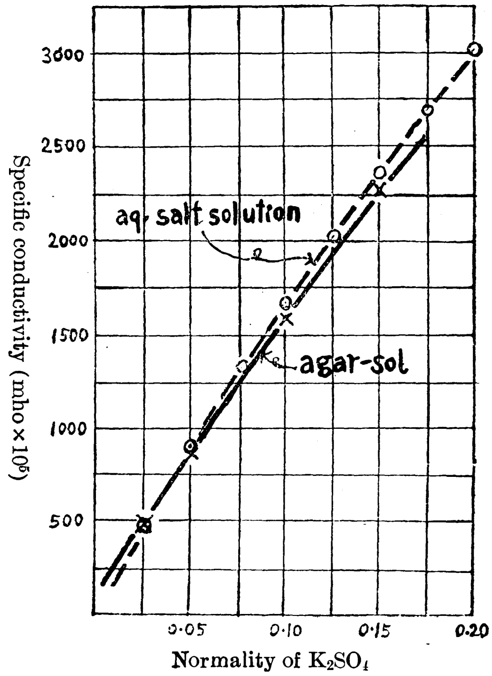

Fig. 1.

The conductivity of agar dispersed in distilled water has also been measured and the results are as follows. On ignition the agar has left ashes amounting from 3.5 to 4.0 percent.

TABLE 7.

Gram of agar in 25 c. c. of water	Specific conductivity (mho $\times 10^5$)		
	Sol	Gel	Difference
0.1	18.45	18.19	−0.26
0.2	33.34	33.09	−0.25
0.3	47.53	47.38	−0.15
0.4	61.14	61.29	+0.15
0.5	73.77	74.47	+0.70
0.7	95.94	97.36	+1.42
1.0	130.0	132.5	+2.5

All the measurements, in which 0.5 gr. agar were dispersed in 25 c.c. of salt solutions, have confirmed the results observed by Hatschek and Humphry with regard to conductivity alteration on sol-gel transformation, and at the same time support Prof. P.P. von Weimarn's opinion on this phenomena(1), which read " by the aggregation or growth of particles during gelation and the consequent reduction in surface, adsorbed electrolyte might be liberated, which would account for the higher conductivity of the gel." When we assume the agar sol and gel are heterogeneous system and the conductivity of agar-water-salt system is almost all ascribed to the dissolved salt, then we are capable of calculating the quantity of electrolyte adsorbed on the surface of agar particles. The value of conductivity of agar dispersed in pure water was subtracted from that of agar dispersed in salt solution, and the salt concentration corresponding to this conductivity value can be obtained from the curve of conductivity- salt concentration in pure aqueous solution which we can easily draw by the direct determination. The difference between the salt concentration thus obtained and that of the original may

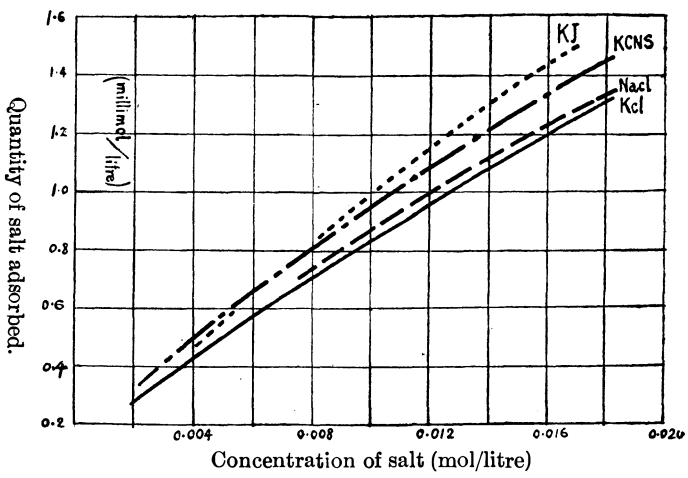

Fig. 2.

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(1) *Trans. Faraday Soc.* 20 (1924), 29.

be regarded as the adsorbed quantity of the salt on the agar particles. Fig. 2 shows the adsorption of salts due to two percent agar sols.

The author wishes to express his sincere thanks to Prof. J. Sameshima for his kind guidance throughout the present research. The author's thanks are also due to Prof. P. P. von Weimarn for his kind advices.

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THE PHOTOCHEMICAL REACTIONS OF COLOURING MATTERS.

I. THE REVERSIBLE PHOTOCHEMICAL REACTION OF MALACHITE GREEN.

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As is well known, colouring matters have played important rôles in the developement of photochemistry both from technical and scientific standpoints, for most of them are more or less sensitive to light and moreover their colour changes offer very convenient analytical methods in spite of complexity of the molecules. Indeed the bleaching effect of light on colouring matters has been very often investigated, and the results of these investigations accord at one point that most of these reactions are photocatalytic. While there are so many photocatalytic reactions in general, very few reversible photochemical reactions are known. Very simple photochemical reactions, such as those of tautomeric changes, will perhaps be favourable for the study of fundamental laws of photochemistry, provided that it is furnished with an easy and simple analytical method.

Berl,(1) Lassareff,(2) and Gebhard(3) formerly studied on the reversibility of methylene blue and Chevreul(4) on Prussian blue. Later J. Lifschitz and Joffé(5) described about photochemical molecular rearrangements in triphenylmethane series in the case of leucocyanides and carbinol bases of the dyes in the solutions of alcohols, ether, chloroform and aqueous mineral acids. A similar reaction was reported by Holmes(6) who used triphenylmethane sulphonic acid.

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(1) Berl, *Ber.*, 43 (1910), 164.
(2) Lassareff, *Z. physik. Chem.*, 78 (1912), 661.
(3) Gebhard, *Z. physik. Chem.*, 79 (1912), 639.
(4) Chevreul, *Fortschritte der Physik*, (1891), 206.
(5) Lifschitz and Joffé, *Ber.*, 52 (1919), 1919; *Z. physik. Chem.*, 97 (1921), 426.
(6) Holmes, *J. Am. Chem. Soc.*, 44 (1922), 1002.

For the purpose of looking for a reversible photochemical reaction I have tried to expose aqueous solutions of various colouring matters contained in a quartz glass tube to the light of a quartz mercury lamp, and carefully measured their colour changes, using Nutting's spectro-photometer. In the course of these experiments, I have found that the colour of malachite green solution, contrary to expectation, became more intense after the exposure to the light of the mercury lamp. Repeating the same experiment with the dye in presence of various chemicals, I found that the dye solution, which was beforehand decolourised by adding alkali, regained its green colour when exposed to the light of the lamp, and loses its colour again in the dark. This reversible colour change of malachite green solution may be suitably observed in a quartz glass vessel illuminated with the light of iron or carbon arc, but the reaction occurs neither with diffused daylight nor with the light of ordinary electric lamp. Intense direct sunlight is able to cause the reaction even in a glass vessel.

Although the similar phenomena were observed in other colouring matters of triphenylmethane group such as fuchsin, methylviolet etc, the present study is concerned only with the experiments which were carried out with malachite green.

Experimental.

In the first place, velocities of the colour changes of malachite green solutions were determined in the following three cases, in using Nutting's spectro-photometer: 1) Decolourisation in alkaline medium. (NaOH was added) 2) Regaining of the colour when exposed to the light of quartz-mercury-vapour-lamp. 3) Reversed decolourisation in the dark.

Experiment 1. 0.0218 gr. of malachite green (from Grueber in Germany) was dissolved in one litre of distilled water and diluted to the four times of its volume.(1) To each 50 c.c. of this solution was added respectively 5 c.c. of NaOH solution of the concentrations of 0.05, 0.03, 0.025, 0.02, 0.015, 0.010, 0.005 and 0.003 normal and the velocities of decolourisation of these solutions were observed.

The absorption tubes of the photometer were furnished with water jackets through which water of constant temperature was allowed to circulate from a thermostat in order to keep the system in a constant temperature. The light absorption was observed at the spectrum region of wave length 600 $\mu\mu$, where exists the absorption maximum of malachite green and, therefore, observations may be very conveniently carried out even in such a dilute solution as this.

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(1) If the solution be in larger concentration, white precipitates would be produced when alkali is added, therefore the experiment must be carried out within the limit of solubility of this difficultly soluble, colourless matter.

As the concentration of the colouring matter is very small in comparison with that of NaOH, we can practically take this reaction as that of first order, leaving, as the further question, the doubt about which of catalytic or of second order is the real nature of this reaction.

The concentration of the substance, the absorption of which is to be measured, can be expressed as follows,

$$C = \frac{-2 \log \cos \alpha}{Ed} \quad \cdots\cdots\cdots\cdots\cdots\cdots(1)$$

where α is the angle of the rotation of Nicol's prism, C the concentration of the colouring matter, E the extinction coefficient of the solution, d the thickness of the liquid layer.

Therefore, the velocity constant of the reaction, $K = \frac{1}{t} \log \frac{C_0}{C}$ can be expressed in terms of cos α as follows,

$$K = \frac{1}{t} \{\log(-\log \cos \alpha_0) - \log(-\log \cos \alpha)\} \cdots\cdots(2)$$

TABLE 1.

t	α	-log cos α	log (-log cos α)	$\log \frac{C_0}{C}$	$K = \frac{1}{t} \log \frac{C_0}{C}$
0	85.0	1.0597	0.025	—	—
3	79.0	0.7194	$\bar{1}.857$	0.168	.056
6	70.6	0.4787	$\bar{1}.680$	0.315	.058
10	61.5	0.3213	$\bar{1}.507$	0.518	.052
16	47.5	0.1703	$\bar{1}.230$	0.795	.050
28	22.0	0.0328	$\bar{2}.516$	0.509	.054

The control observation which was specially planned, showed that the extinction coefficient was constant throughout the concentration used, that is, the Beer's law holds.

The velocity increases with the concentration of NaOH linearly as may be seen in Table 2.

TABLE 2.

NaOH	0.03 N	0.025 N	0.02 N	0.015 N	0.01 N	0.005 N	0.003 N
$K \times 10^3$	86	74	54	43	30	16	9.2

Experiment 2. The solution of malachite green which was previously decolourised by adding NaOH, was exposed to the light of a quartz-mercury-vapour-lamp (from Heraeus of Hanau, Germany) at the distance of 15 cm.

and after various intervals of time, a definite quantity of the solution was taken out of the reaction vessel and light absorption of this solution was measured in the same manner as in Experiment 1.

The mercury lamp with its illuminating part of 1.65 cm. in length was lighted with 100 volts D. C., the current being 3 amps. throughout the experiment. In ten minutes after the lamp had been started, its light became constant in intensity. Both of the reaction vessel and light thermostat were made of cylindrical tubes of quartz glass, the former being inserted in the latter, through which water of constant temperature was circulated from a larger thermostat by means of a pump. The solution was agitated with a stirrer during the exposure.

I have prepared three kinds of malachite green solutions with different concentrations, one of these (solution A) is in about the same concentration as in the Exp. 1, while those of the other two (solution B and C) are respectively in the two thirds and one half of the first. To each 250 c.c. of the solution A, B and C, 5 c.c. of 0.01 N. NaOH was added. The solutions thus decolourized were exposed to the light of the lamp, the intensity of which, being found to be too strong was reduced to one fourth by inserting a rotating sector with two 45° apertures (800–1000 rotations per min.) between the light source and the reaction vessel and the change of colour was observed, keeping temperature constant at 25°.

In this case, the velocity constant of the light reaction was calculated in the following way: in the first place, it was considered that the amount of light sensitive substances which suffer changes by light is proportional to the light energy absorbed and consequently the reaction velocity can be put,(1)

$$\frac{dM}{dt}=KA=KS(I_0-I) \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots \quad (3)$$

and if Beer's law holds

$$\frac{dM}{dt}=KS(I_0-I_0e^{-idc}) \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots \quad (4)$$

where M is the amount of the substance, and A the quantity of absorbed light. This relation is satisfied only in such a case that the reacting system is contained in a rectangular vessel and exposed to parallel beams of light which are perpendicular to the wall of the vessel. In the present experi-

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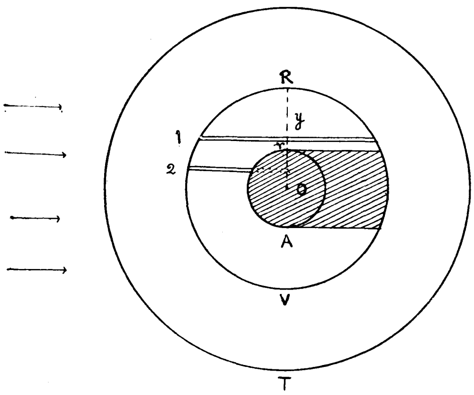
(1) Literatures on photochemical kinetics give us two different conceptions: 1. The equations of reaction velocity are same for photochemical and dark reaction. 2. The amount transformed is proportional to the absorbed light quantity. The light reaction of malachite green, however, being unimolecular, both of these conceptions lead us to the same conclusion.



Horizontal section of the apparatus.
T : Thermostat vessel.
V : Reaction vessel. (Radius R.)
A : Agitator. (Radius r.)

Fig. 1.

ment, however, the cylindrical vessel having been used, following considerations will be necessary for the calculation of the velocity constant.

Now if we take the elementary slices 1 and 2 in Fig. 1, their volumes are,

$$2\sqrt{R^2-y^2}\,h\,dy \quad \text{and} \quad \{\sqrt{R^2-y^2}-\sqrt{r^2-y^2}\}\,h\,dy \quad \ldots(5)$$

respectively, and the light absorbed by them are

$$I_0\left\{1-e^{-i\,2\sqrt{R^2-y^2}(b-x)}\right\}h.\,dy \quad \text{and} \quad I_0\left\{1-e^{-i\{\sqrt{R^2-y^2}-\sqrt{r^2-y^2}\}(b-x)}\right\}h.\,dy \quad \ldots\ldots(6)$$

Where b is the initial concentration of the substance, x the concentration of the substance formed, h the height of the part of the vessel exposed to the light, R and r the radii of the vessel and the agitator.

The equation (3) can be then, put as follows :

$$\frac{dM}{dt}=\frac{d\,V(b-x)}{dt}=K_0\Big[2\int_r^R I_0\left\{1-e^{-i\,2\sqrt{R^2-y^2}(b-x)}\right\}h.\,dy$$

$$+2\int_0^r I_0\left\{1-e^{-i\{\sqrt{R^2-y^2}-\sqrt{r^2-y^2}\}(b-x)}\right\}h.\,dy\Big] \ldots\ldots(7)$$

where $$e^{-i\,2\sqrt{R^2-y}(b-x)}=1-i\,2\sqrt{R^2-y^2}(b-x)+\frac{[i\,2\sqrt{R^2-y^2}(b-x)]^2}{1\cdot 2}- \quad \ldots(8)$$

$$e^{-i\{\sqrt{R^2-y^2}-\sqrt{r^2-y^2}\}(b-x)}=1-i\{\sqrt{R^2-y^2}-\sqrt{r^2-y^2}\}(b-x)$$

$$+\frac{[i\{\sqrt{R^2-y^2}-\sqrt{r^2-y^2}\}(b-x)]^2}{1\cdot 2}- \quad \ldots\ldots(9)$$

and if i or b is very small, we can neglect higher terms and consequently the equation (7) becomes

$$\frac{d(b-x)}{dt}=\frac{K_0}{V}\,2I_0h\Big[\int_r^R i\,2\sqrt{R^2-y^2}.dy+\int_0^r i\{\sqrt{R^2-y^2}-\sqrt{r^2-y^2}\}dy\Big](b-x)$$

$$=a\ \text{constant}\times(b-x)=K(b-x) \quad \ldots\ldots(10)$$

and finally the equation of the velocity constant can be put as

$$K=\frac{1}{t}\,[\log b-\log(b-x)] \quad \ldots\ldots(11)$$

where b and x can be expressed in terms of log cosα as in Experiment 1.

Although the extinction coefficient of the solution could not yet been determined, it is evident, however, that the concentration of the light sensitive substance is very small in this experiment and higher terms of the equations (8) and (9) may be neglected.

Velocity constants were thus calculated according to the equation (11) and pretty constant values were obtained as will be seen in Table 3, etc, giving rather smaller values at the beginning of the reaction.

It must be noted here that, the thermostat vessel used being cylindrical, the refraction of light beams at the wall of the vessel must be taken into consideration in the above calculations, but this was neglected for the sake of simplification, incident rays being assumed to be parallel.

TABLE 3.

Time (min)	2	4	6	8	10	12	14	16	18
K × 10³ (A)	35	44	51	53	51	51	50	—	—
K × 10³ (B)	35	43	43	51	51	53	59	—	53
K × 10³ (C)	39	41	45	52	58	61	59	54	—

In order to study the effect of the concentration of alkali, 5 c.c. of 0.03 and 0.02 N. NaOH were respectively added to each 250 c.c. of the solution A and the same experiment as mentioned above was done. It was, however found that in these cases there was good accordance of the observed values with those of Table 3, that is to say, the light reaction is independent of the concentrations of alkali present.

TABLE 4.

Time (min)	1	2	4	6	8	10	12	16
K × 10³ (0.02)	34	37	43	47	51	56	58	56
K × 10³ (0.03)	34	35	36	39	45	51	57	56

The temperature coefficient was then determined at 25° and 35° in using the solution A added with 0.01 N. NaOH and it was proved that the light reaction is practically not effected by the raise of temperature, at this interval, although more accurate experiment on this account will be necessary for its support.

TABLE 5.

Time (min)	2	4	6	8
K × 10³ (25°)	34	51	49	49
K × 10³ (35°)	32	42	49	49

Finally the effect of light intensity on the light reaction was also examined. The light of three different intensities of 1/2, 1/4 and 1/8 were applied to the solution C added with 0.01 N. NaOH, and it was found that the velocity of the light reaction is exactly proportional to the light intensity as will be expected.

Experiment 3. Five c.c. of 0.01 N. NaOH was added to each 50 c.c. of the solution A and C and these mixtures which show moderate reaction velocities were transferred into absorption tubes, after having exposed to the light of the mercury lamp until the green colour of these solutions took maximum intensity, and then the light absorption was measured in definite time interval in exactly the same manner as in Experiment 1. (Table 6)

TABLE 6.

Time (min.)	10	20	30	40	60	90	100	120	150	170	180
$K \times 10^3$ (sol. A)	76	62	—	58	56	—	57	—	56	—	55
$K \times 10^3$ (sol. C.)	53	58	59	55	59	59	—	55	52	52	—

The reaction velocity increases linearly with the concentrations of NaOH added as was proved in Experiment 1, only slightly differing in the angle of inclination. (Table 7)

TABLE 7.

$K \times 10^3$	76	65	40	30	19	7.8	5.6
Conc. of alkali	0.03	0.025	0.02	0.015	0.01	0.005	0.003

Discussion of Experimental Results. In Experiment 1, the decolourisation velocity of malachite green in presence of alkali was proved to be proportional to the concentration of sodium hydroxide added and the reaction may be taken as of first order, on the contrary to the results obtained by Mueller(1) and by Gerlinger,(2) who calculated the velocity constant by electrochemical method. But it must be taken in mind that my experiment has been carried out in excess of alkali in comparison with that of light sensitive substance. If this photochemical reversible reaction of malachite green, however, is considered to be a tautomeric change of colour-base as was indicated by Hantzsch and Osswald,(3) it seems more probable that the reaction is of first order, alkali acting itself catalyticaly.

Experiment 3 may be discussed exactly the same way as in Fxperiment

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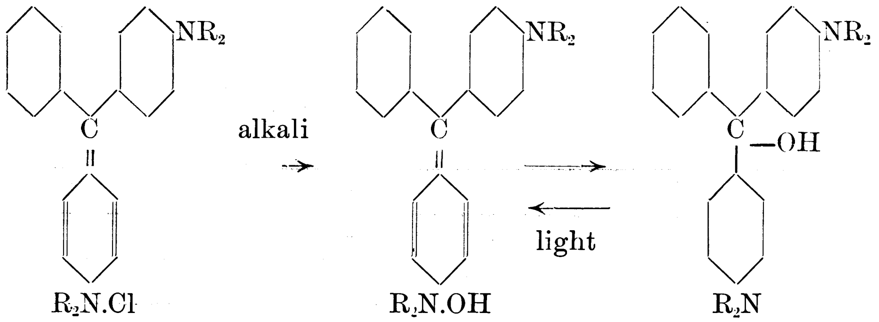
(1) W. J. Mueller, *Ber.*, 43 (1910), 2609.

(2) P. Gelinger, *Ber.*, 37 (1904), 3958.

(3) A. Hantzsch u. G. Osswald, *Ber.*, 33 (1900), 278.

1, if we consider that the coloured substance produced by light (Exp. 2) is a ammoniumbase, its decolourising velocity in the dark increasing linearly with the concentration of alkali added.

Hantzsch and Osswald have proved that in malachite green as well as in triphenylmethane dyes two kinds of modification are possible, one being in coloured and unstable ammonium-base and the other colourless and stable pseudo-ammonium-base type (carbinol type):



Salt of dye

Coloured ammonium base

Colourless pseudo ammonium base

If it is allowed to adopt these formulae, the coloured substance which is produced by the action of light can be considered to be this unstable coloured ammonium-base, and the other formed by the decolourisation in the dark will then be the stable colourless pseudo-ammonium-base.

In Experiment 2 it was observed that the linear relation holds between the intensity of the light and the reaction velocity. I have carried out the further experiments with the intention of finding out the limit at which the equation of zero order would be satisfied when factors such as thickness of liquid layer and the light intensity were changed. But sufficient data for this purpose have not yet been obtained.

The temperature coefficient of the velocity constant of the light reaction per ten degrees has been shown to be unity in the interval between 25° and 35°C, and this fact can be taken as a strong support that the reaction which we are now dealing with, is of pure photochemical one. The velocity of the dark reaction, which is quite insignificant as long as the concentration of alkali is small, increases rapidly in raising its concentration as well as temperature, while the light reaction is neither influenced by the temperature nor by the concentration of alkali.

So far as the visible part of the spectrum concerned, the absorptions are quite same in both cases of original colouring matter solution and the photo-product. Absorption spectrum of ultraviolet region was also studied in using the quartz spectrograph (Adam Hilger), and iron arc as the light source. But I failed to obtain a good photography of the absorption spectrum; the concentration of the substance having been very small, no distinct absorption band was to be detected on the plates.

As for the wave lengths of the most effective light, it will require further studies. Only it may be said that the optimum part lies in the ultraviolet region of spectrum, because the solution contained in an ordinary glass tube is not effected by illuminating with the light of iron arc, while it is easily coloured if a quartz glass vessel is used. Intense direct sunshine or the light from a mercury lamp of high intensity has shown, however, the colouring effect even in an ordinary glass vessel.

The author desires to express his best thanks to Dr. S. Iimori of the Institute, and to Dr. N. Yamaga of the Research Laboratory of the Hiratsuka Explosive Factory of the Imperial Japanese Navy for helps and facilities which they have given him in completing this research.

Summary.

1. The photochemical reversible reaction of the alkaline solution of malachite green was studied with the quartz-mercury-lamp, and its nature was discussed.

2. The reaction velocities were determined both in the light and the dark reaction, using Nutting's spectro-photometer. The former is proportional to the intensity of light and the latter to the concentration of the alkali added.

3. The temperature coefficient of the reaction velocity of the light reaction was found to be unity at the interval between 25° and 35° C.

4. Equation of the reaction of first order was derived with approximation for the light reaction.

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THE EFFECT OF ALKALI ON THE OXIDATION OF SODIUM SULPHITE WITH AIR.

By **Susumu MIYAMOTO.**

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It was described in the previous paper(1) that C. C. Palit and N. R. Dhar found(2) that some carbohydrates are oxidized with air in the presence of sodium sulphite and that the oxidation is accelerated on adding caustic alkali. They further measured the amount of sodium sulphite oxidized with air in the presence of carbohydrates and found that on adding caustic alkali the velocity of the oxidation of sodium sulphite decreases.(3) But it is not clear whether the retardation is the effect of the induced reaction or caustic alkali.

S. L. Bigelow(4) studied the catalytic action of many substances on the oxidation velocity of sodium sulphite with air, but the effect of alkali was not studied well. A. Titoff(5) studied the same phenomena also. In his experiment the oxidation was carried out in water which had been previously saturated with oxygen, that is, he studied the oxidation as a homogeneous reaction.

The purpose of this study is to know the effect of alkali more precisely by a modified method, and to discuss the promoting action of alkali on the induced oxidation, found by Dhar and Palit.

Experimental. The experimental procedure was quite the same with that described in the previous paper, only a large test-tube (diameter, 3 cm.) was used instead of an Erlenmeyer flask (100 c.c.), which was used in the previous experiment, for the vessel in which the oxidation takes place. Air, washed by acidified potassium dichromate solution and alkali, was passed at constant velocity into the solution of sodium sulphite of known concentration. The total volume of the solution was made to 40 c.c. in each case. After t minutes the air current was stopped and the total amount of the solution was poured into a known quantity of iodine solution, acidified with hydrochloric acid, and the excess of iodine was titrated back by means of sodium thiosulphate solution. In the following tables, v is the volume of sodium thiosulphate solution of 0.09962 normal which is equivalent to the

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(1) S. Miyamoto, This journal, 2 (1927), 40

(2) Palit and Dhar, *J. Phys. Chem.*, 29 (1925), 799; 30 (1926), 939.

(3) *J. Phys. Chem.*, 30 (1926), 948.

(4) Bigelow, *Z. physik. Chem.*, 26 (1898), 493.

(5) Titoff, *Z. physik. Chem.*, 45 (1903), 641.

amount of sodium sulphite; k is calculated by $k=\frac{1}{t}(v_0-v)$, v_0 being the value of v at $t=0$, and $v_{calc.}$ is obtained by $v_{calc.}=v_0-kt$, using the mean value of k.

TABLE 1.

Temp: 20°C. Air: 7.78 litres per hour. $C_{NaOH}=0$.

t min.	v c.c.	$v_{calc.}$ c.c.	k
0	16.71	—	—
10	13.42	13.41	0.329
15	11.87	11.76	0.322
20	10.03	10.11	0.334
30	7.40	6.81	0.310
0	29.16	—	—
8	26.48	26.52	0.335
10	25.75	25.86	0.341
12	25.12	25.20	0.337
15	24.05	24.21	0.341
24	21.49	21.24	0.320
0	38.64	—	—
9	35.73	35.67	0.323
12	34.54	34.68	0.342
22	31.56	31.38	0.322
		Mean:	0.330

Table 1 shows that the amount of sodium sulphite oxidized with air is independent of its concentration. This fact coincides with that obtained by Bigelow,(1) and can be explained by assuming that the velocity of the dissolution of oxygen into the solution is much slower than that of the oxidation of sodium sulphite.

The Effect of Alkali. The oxidation in sodium hydroxide solution of various concentrations was measured. The results are shown in Table 2.

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(1) Bigelow, *Z. physik. Chem.*, **26** (1898), 518.

TABLE 2.

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

C_{NaOH} normal	t min.	v c.c.	$v_{calc.}$ c.c.	k	C_{NaOH} normal	t min.	v c.c.	$v_{calc.}$ c.c.	k
	0	13.23	—	—		0	14.25	—	—
0.02888	9	10.52	10.55	0.301	0.7219	8	12.57	12.55	0.210
	15	8.87	8.76	0.297		12	11.68	11.69	0.214
	25	5.63	5.78	0.304		14	11.30	11.27	0.210
	30	4.23	4.29	0.300		16	10.66	10.84	0.224
	35	3.20	2.80	0.287		25	9.10	8.92	0.206
			Mean	0.298				Mean	0.213
	0	12.05	—	—		0	12.37	—	—
0.05173	9	9.41	9.57	0.293	1.1011	9	10.77	10.85	0.178
	12	8.71	8.74	0.278		12	10.26	10.34	0.176
	15	7.95	7.91	0.273		15	9.86	9.83	0.167
	20	6.60	6.53	0.273		20	9.12	8.99	0.163
	30	4.11	3.77	0.265		30	7.52	7.30	0.162
			Mean	0.276				Mean	0.169
	0	12.18	—	—		0	12.17	—	—
0.1810	9	9.70	9.79	0.276	1.810	9	11.26	11.28	0.1011
	12	8.90	9.00	0.273		12	11.01	11.00	0.0967
	15	8.35	8.20	0.255		15	10.59	10.69	0.1053
	20	6.88	6.88	0.265		20	10.24	10.19	0.0965
	30	4.50	4.23	0.256		30	9.32	9.20	0.0950
			Mean	0.265				Mean	0.0989
	0	13.98	—	—					
0.5173	10	11.66	11.67	0.232					
	12	11.10	11.21	0.240					
	15	10.42	10.51	0.237					
	20	9.56	9.36	0.221					
	30	7.29	7.05	0.223					
			Mean	0.231					

Thus the sodium hydroxide diminishes the oxidation velocity of sodium sulphite. This will be explained by assuming the caustic alkali diminishes the dissolution velocity of oxygen into the solution. This assumption will also explain why the oxidation velocity of ferrous hydroxide(1) with air decreases with the increase of the concentration of caustic alkali, although its reducing power increases. Anyhow the increase of the induced oxidation of carbohydrates in the presence of sodium sulphite on adding caustic alkali is not due to the increase of the velocity of the primary reaction. Sodium

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(1) S. Miyamoto, This journal, 2 (1927), 40.

hydroxide can be regarded as one of the substances which accelerate the induced reaction but not the primary reaction. The mechanism of this kind of promoters of induced reaction can be explained by the theory of the transference of active states.(1)

The Effect of Temperature. The results of the measurements at 30°C. and 40°C. are shown in Table 3. The effect of temperature was very small.

$$\frac{k_{30^\circ}}{k_{20^\circ}}=\frac{0.345}{0.330}=1.05,\quad \frac{k_{40^\circ}}{k_{39^\circ}}=\frac{0.382}{0.345}=1.11 \quad \text{when } C_{\mathrm{NaOH}}=0$$

$$\frac{k_{30^\circ}}{k_{20^\circ}}=\frac{0.265}{0.231}=1.15,\quad \frac{k_{40^\circ}}{k_{30^\circ}}=\frac{0.301}{0.265}=1.14 \quad \text{when } C_{\mathrm{NaOH}}=0.5173 \text{ Normal}$$

TABLE 3.

Air : 7.78 litres per hour.

Temp. C.	C_{NaOH} normal	t min.	v c.c.	$v_{calc.}$ c.c.	k
30°C	0	0	13.69	—	—
		9	10.52	10.58	0.352
		12	9.37	9.55	0.360
		15	8.50	8.51	0.346
		20	7.00	6.79	0.335
		30	3.78	3.11	0.330
					Mean 0.345
30°	0.5173	0	13.69	—	—
		9	11.18	11.30	0.279
		12	10.57	10.51	0.260
		15	9.73	9.71	0.264
		20	8.42	8.39	0.264
		30	6.01	5.74	0.256
					Mean 0.265
40°	0	0	11.84	—	—
		9	8.24	8.40	0.400
		12	7.35	7.26	0.374
		15	5.82	6.11	0.401
		20	4.52	4.20	0.366
		25	2.61	2.29	0.369
					Mean 0.382
40°	0.5173	0	11.41	—	—
		9	8.62	8.70	0.310
		12	7.64	7.80	0.314
		15	7.07	6.89	0.289
		20	5.07	5.39	0.311
		30	3.00	2.38	0.280
					Mean 0.301

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(1) S. Miyamoto, *Scientific Papers of the Institute of Physical and Chemical Research,* 4 (1926), 257.

The Effect of the Velocity of Air Passed. Table 4 is the results measured when air was passed at the rate of 6.67 and 10 litres per hour. By comparing this with Table 1, it will be seen that the oxidation velocity increases with the increase of the velocity of air current passed.

TABLE 4.

Temp: 20°C. $C_{NaOH}=0$.

Air litres per hour	t min.	v c.c.	$v_{calc.}$ c.c.	k
6.67	0	13.57	—	—
	9	10.87	10.87	0.300
	12	9.84	9.97	0.311
	15	9.20	9.07	0.291
	20	7.18	7.57	0.313
	30	5.00	4.57	0.286
				Mean 0.300
10.0	0	12.98	—	—
	9	9.68	9.79	0.367
	12	8.65	8.73	0.361
	15	7.70	7.67	0.352
	20	5.98	5.90	0.350
	30	2.75	2.36	0.341
				Mean 0.354

Summary.

1. The oxidation velocity of sodium sulphite with air was independent of its concentration.
2. Caustic alkali diminishes the velocity of the oxidation.
3. The effect of temperature was small.

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THE FORMATION OF OXY-DERIVATIVES OF DIPHENYLENE OXIDE FROM RESORCIN.

By Yojiro TSUZUKI.

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It was reported(1) that resorcin undergoes a certain reduction and condensation under the influence of blue oxide of tungsten between 500° and 550°, giving rise to the formation of a new compound which was supposed to be 2,6-dioxydiphenyl. With the view of ascertaining this constitution and whether there is any other product or not, and also of inquiring into the mechanism of this formation, this reaction was further examined by the suggestion of Professor B. Kubota.

The reaction was carried out exactly in the same manner as described in the previous paper. After the whole of the reaction products was subjected to steam distillation until no crystalline substance deposited in the condenser and the distillate showed no marked phenolic reaction, the remainder in the distilling flask was made strongly acidic with hydrochloric acid and the steam distillation was continued. By means of this steam distillatin it was found that there existed two products, one of which distils with steam though it goes on very slowly, and the other remains in the residual liquid. The former, melting at 138–138°.5, gave a monomethoxy-derivative $C_{12}H_7O(OCH_3)$ by being treated with sodium hydroxide and dimethylsulphate, whilst when heated with zinc dust diphenylene oxide was produced. The latter, melting at 241–242°, gave a dimethoxy-derivative $C_{12}H_6O(OCH_3)_2$ and diphenylene oxide by being treated in the same way. These facts lead us to suppose that the one compound melting at 138–138°.5 is evidently a monoxy-diphenylene oxide which contains two hydrogen atoms less than dioxy-diphenyl in the previous paper and the other melting at 241–242° a dioxy-diphenylene oxide.

Thus it seems to me that the production of benzene, phenol, diphenylene oxide, monoxy- and dioxy-diphenylene oxide may be regarded as the result of the normal action (dehydration) of the catalyst, accompanied by its secondary action (reduction), the processes of which being represented by the following schemes :

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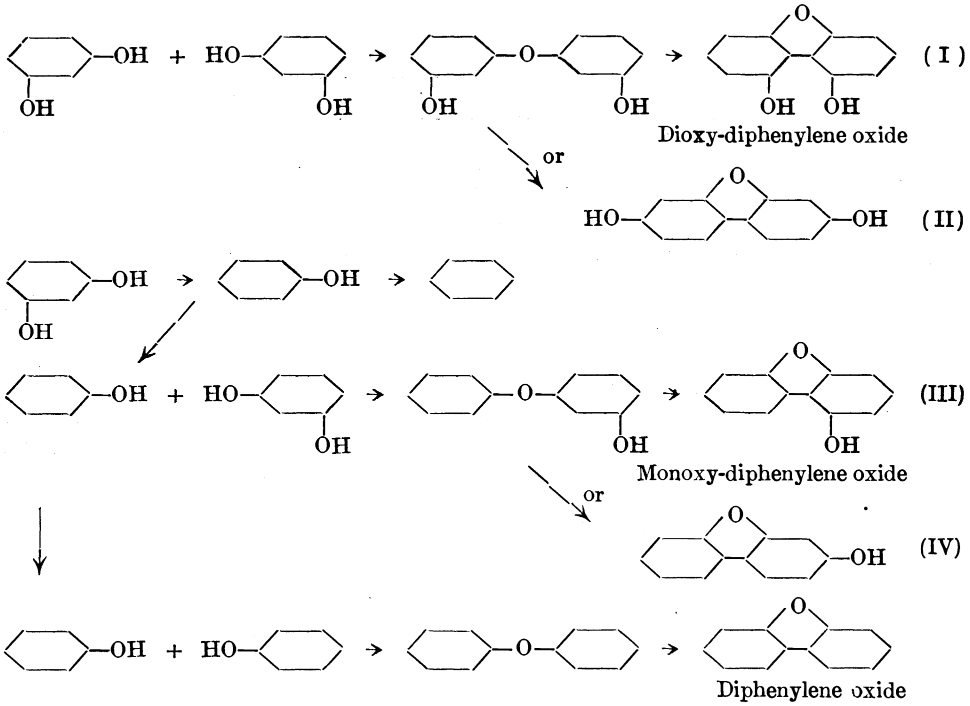
(1) Kubota, Fujimura and Akashi, *Scientific Papers of the Institute of Physical and Chemical Research*, 2 (1925), 185.



The well known formation of diphenylene oxide from phenol by means of lead oxide(1) or aluminium oxide(2) and also from diphenyl ether by means of heating(3) is suggestive of a remarkable tendency of the newly combining phenyl groups occupying ortho position with respect to the bridge oxygen atom. On the other hand, absorption curves show in their forms much resemblance to those of o-oxy-derivatives of diphenyl but not to those of p-oxy-derivatives(4), and those of acetyl derivatives are in good agreement with that of diphenylene oxide. Besides, it has been shown(4) that phenyl malonic acid was produced on oxidising the hexahydro-derivative of the compound melting at 138–138°.5. From this fact it is clear that the compound melting at 138–138°.5 is 2-oxydiphenylene oxide (formula III). From this point of view the formula I (2,2′-dioxydiphenylene oxide) becomes highly probable as that of the dioxy-diphenylene oxide) becomes highly probable as that of the dioxy-diphenylene oxide.

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(1) Graebe, *Ber.*, **7** (1874), 396.

(2) Sabatier and Maihe, *Compt. rend.*, **151** (1910), 429; *Bull. soc. Chim.*, **11** (1912), 843; *Compt. rend.*, **155** (1912), 260; **158** (1914), 608.

(3) Graebe u. Ullmann, *Ber.*, **29** (1896), 1876.

(4) Kubota, Fujimura and Akashi, loc. cit.

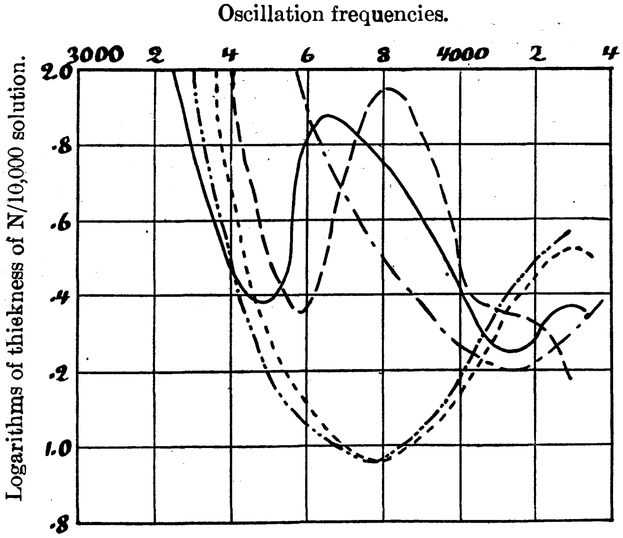
Experimental.

Monoxy-diphenylene Oxide. *The Methoxy-derivative.* Oxydiphenylene oxide (0.1 gr.) obtained by passing resorcin vapour over blue oxide of tungsten at 500–550° as descrived in the paper cited above, was dissolved in a sodium hydroxide solution and a drop of dimethyl sulphate was added. The solution was warmed, when some white crystals separated out. Being recrystallised from dilute alcohol, it separated out in small plates melting at 93–94.° Yield 0.08 gr. It is soluble in alcohol and ether, but insoluble in water. 2.503 mg. and 2.398 mg. substance gave 3.086 mg. and 2.862 mg. AgI. (Found: $-OCH_3=16.29$ and 15.77. $C_{12}H_7O(OCH_3)$ requires $-OCH_3 = 15.66\%$.)

From this result the formula $C_{12}H_7O(OH)$ becomes more probable as that of the compound melting at 138–138°.5 than $C_{12}H_8(OH)_2$ which was reported in the previous paper.

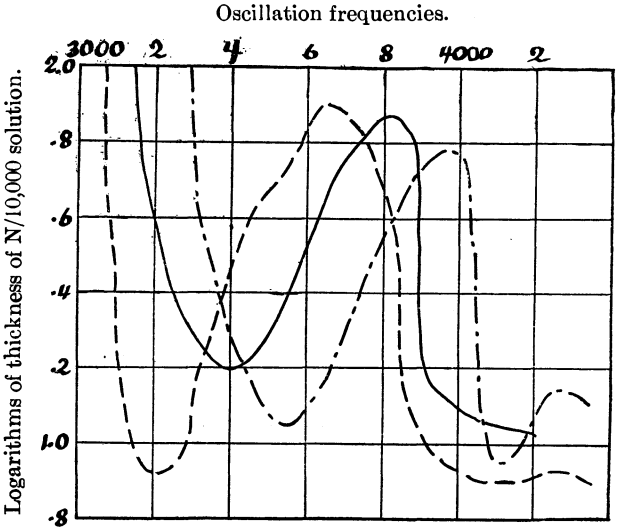
Nitro-derivative. Oxy-diphenylene oxide (16 mg.) was dissolved in glacial acetic acid and some drops of concentrated nitric acid were added. The solution on being warmed on the water bath yielded 10 mg. of fine yellow crystals. Upon recrystallisation from hot petroleum ether, it separated out in small prisms becoming dark brown at about 200° and melting with decomposition at 216–217°. 1.300 mg. gave 0.112 c.c. of N_2(20°, 754 mm.). (Found: $N=9.87$, $C_{12}H_6N_2O_6$ requires $N=10.22\%$). It is soluble in alcohol and in almost all other organic solvents, but insoluble in water. This substance appears to be 3,5-dinitro-oxydiphenylene oxide.

Dioxy-diphenylene Oxide. The reaction products which were obtained by passing resorcin vapour over the catalyst at 500–550° were subjected to steam distillation until no crystalline substance deposited in the condenser and the distillate showed no marked phenolic reaction. The remainder in the distilling flask was made strongly acidic with hydrochloric acid and the steam distillation was continued so long as oxy-diphenylene oxide came out. The residual liquid was filtered from a tarry matter while still hot and was allowed to stand a mean while, when some brown prisms separated out. These were dissolved in hot water, treated with animal charcoal and recrystallised, but the faint brown colour was not removed off. It is soluble in alcohol, ether and hot water, but scarcely soluble in cold water, thuogh it is more soluble than oxy-diphenylene oxide. With a ferric chloride solution it gives a green colour turning to a light brown on the addition of sodium carbonate solution. It becomes almost colourless at 100° and melts at 241–242°. On being dehydrated over P_2O_5 at 100° under a diminished pressure, 5.31 mg. of the substance lost 0.22 mg. of water. (Found: $H_2O=4.31$; $C_{12}H_8O_3 1/2 H_2O$ requires $H_2O=4.15\%$).



—·—·— = Diphenyl.
———— = o-Oxydiphenyl.
- - - - - = p-Oxydiphenyl.
— — — = 2,2′-Dioxydiphenyl.⁽¹⁾
——·—·— = 4,4′-Dioxydiphenyl.

Fig. 1.



—·—·— = Diphenylene oxide.
———— = Monoxydiphenylene oxide.
- - - - = Dioxydiphenylene oxide.

Fig. 2.

Molecular weight was determined by K. Rast's method. 0.14 mg. of substance in 1.94mg. of camphor gave $\Delta t = -13.°0$. (Found: M=210. $C_{12}H_8O_3$ requires M=200.)

The Dimethoxy-derivative. The dioxy-diphenylene oxide was treated with sodium hydroxide and dimethyl sulphate as described in the case of oxy-diphenylene oxide, when fine crystals were obtained. It was recrystallised from dilute alcohol, when it separated out in small plates melting at 150°. It is soluble in alcohol and ether, but insoluble in water. 2.123 mg. of substance gave 4.348 mg. AgI. (Found: $-OCH_3=27.06$. $C_{12}H_6O(OCH_3)_2$ requires $-OCH_3=27.20\%$).

The Acetyl-derivative. The dioxy-diphenylene oxide was warmed on the water bath with an excess of acetyl chloride, and that part of acetyl chloride, which was not used in the acetylation was for the most part driven off by diminishing pressure while still hot, when a residue consisting

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(1) In practice, its dimethoxy derivative was observed, for dioxydiphenyl was not easily obtained.

of fine crystals was obtained. It was recrystallised from dilute acetic acid, when it separated out in small plates melting at 138°. 0.190 mg. of substance in 2.682 mg. of camphor gave $\Delta t = -10°.0$. (Found: M=283. $C_{12}H_6O(OCOCH_3)_2$ requires M=284.)

The Zinc Dust Distillation. The dioxy-diphenylene oxide was intimately mixed with zinc dust and was gradually heated in a small test tube, when a colourless oil solidifying to a crystalline state in the upper part of the tube was found to distil off. This product was washed with sodium hydroxide solution and was recrystallised from dilute alcohol, when it separated out in scaly crystals melting at 80–81°. Its properties were found in good agreement with those of diphenylene oxide.

Absorption Curve. The results of a comparative study of the absorption curves of diphenylene oxide, oxy-diphenylene oxide, dioxy-diphenylene oxide and their acetyl derivatives are shown in the figures which, as already pointed out, give an indication of the fact that the compound meltings at 138–138°,5 and at 241–242° are both derivatives of diphenylene oxide whose hydroxyl groups are attached to the ortho position with respect to the other phenyl group. The curves of the two acetyl derivatives of oxy-diphenylene oxides are not especially drawn in the diagram as they are superposed on that of diphenylene oxide. All observations of absorption spectra were made in alcoholic solutions.

The author's best thanks are due to Professor B. Kubota under whose kind guidance the present investigations were carried out.

Summary.

The substance which was formerly supposed as 2,6-dioxydiphenyl was shown to be 2-oxydiphenylene oxide (III).

A new phenol was obtained, the formula of which was shown to be dioxydiphenylene oxide $C_{12}H_6O(OH)_2$. Two hydroxy groups seem to be in 2 and 2′ positions from the mechanism of its formation and its absorption spectrum.

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ÜBER DAMPFDRUCKMESSUNGEN WÄSSRIGER BLAUSÄURE BEI 18°C.

Von Manjiro SHIRADO.

Eingegangen am 15. Februar 1927. Ausgegeben am 28. April 1927.

Einleitung. Der Dampfdruck der reinen wasserfreien Blausäure wurde bereits von versiedenen Autoren bestimmt.(1) Die Dampfdrucke wässriger Blausäure haben Bussy und Buignet(2) bei 13.25°C. von 44.2% bis 75.0% bestimmt, sonst haben wir keine Literaturangaben über Dampfdrucke wässriger Blausäure gefunden, was uns veranlasste, Messungen des Dampfdruckes wässriger Blausäure bei 18.0°C. durchzuführen.

Darstellung der Blausäure. Zur Darstellung wässriger und wasserfreier Blausäure gibt es verschiedene Methoden.(3) Eine geeignete Apparatur hat bereits Gattermann(4) angegeben, an der wir einige zweckmässige Änderungen ausgeführt haben.

Die Methode der Darstellung wässriger und wasserfreier, reiner Blausäure aus möglichst reinen Stoffen haben wir untersucht. Anfangs haben wir nach Clark aus Cyankalium und Weinsäure die wässrige Blausäure dargestellt, aber die Reaktion war zu langsam, denn erst nach 5 stündigem Destillieren erhielten wir eine Ausbeute von 80% ; die Konzentration der Blausäure in den Destillaten betrug nur ungefähr 14%. Dann haben wir die Ferrocyankalium und Phosphorsäure-Methode versucht. Nach unserem Verfahren, das nur 2 Stunden in Anspruch nahm, ergab sich eine Ausbeute von ungefär 85%, die Blausäure-Konzentration war 55–60%. Zu 150–180 c.c. dieser wässrigen Blausäure wurde zur Conservierung ein Tropfen 83%iger Phosphorsäure zugefügt. Die Flasche wurde in Wasser gestellt und vor dem Tageslicht geschützt.

Zu den Dampfdruckmessungen der wässrigen Blausäure (bis zu 50%)

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(1) Bussy und Buignet, *Ann. chim.*, [4] 3 (1864), 245; Gautier, *Ann. chim.*, [4] 17 (1869), 103; Isambert, *Compt. rend.*, 94 (1882), 958; *Ann. chim. phys.*, [5] 28 (1883), 332; R. Hara und H. Sinozaki, *Journ. Ind. Chem. Japan*, 26 (1923), 884; Diese Zeitschrift, 1 (1926), 59; G. Bredig und L. Teichmann, *Z. Elektrochem.*, 31 (1925), 450; J. H. Perry und Frank Porter, *J. Amer. Chem. Soc.*, 48 (1926), 299.

(2) Bussy und Buignet, loc. cit.

(3) Gattermann, *Ann.*, 357 (1907), 318; Wade & Panting, *J. Chem. Soc.*, 73 (1898), 255; E. Schmidt, *Ber.*, 55 (1922), 97; R. Hara & Sinozaki, *Journ. Chem. Ind. Japan*, 26 (1923), 884 oder *The Technology Reports of the Tohoku Imperial University*, Vol. 4, No. 3 (1924), 38; G. Bredig und L. Teichmann, *Z. Elektrochem.*, 31 (1925), 449.

(4) Gattermann, loc. cit.

wurde die Vorratslösung entsprechend verdünnt. Für die Messungen der höherprozentigen Blausäure haben wir die wasserfreie Blausäure aus der 55%igen Blausäure durch Umdestillieren dargestellt. Zu dieser wasserfreien Blausäure wurde ein Tropfen 83%iger Phosphorsäure (1 Tropfen auf ca. 150–180 c.c.) hinzugefügt, und die Flasche wieder in Wasser aufbewahrt. Beim Gebrauch wurde diese Vorratslösung zweckmässig verdünnt.

Das Umdestillieren geschah folgendermassen: Aus einem 200 c.c. Destillationsrundkolben von Jenaer-Glas wurde destilliert, das Glas durch zwei Waschflaschen geleitet, deren erste mit feinkörnigem, reinem $CaCl_2$ und deren zweite mit feinkörnigem, reinem $CaCO_3$ gefüllt waren. Diese zwei Flaschen waren auf 40–45°C. in einem Wasserbad erwärmt; im ersten Gefäss sollte der Wasserdampf absorbiert, im zweiten die Spuren Salzsäure oder Phosphorsäurenebel niedergeschlagen werden. Das Gas wurde weiter durch einen Schlangenkühler geleitet, dabei verflüssigt und im Vorratsgefäss aufgefangen. Der Destillationskolben wurde in einem Wasserbad erwärmt; alle Gefässe wurden durch Glasschliffe miteinander verbunden.

Das spez. Gewicht der nach vorbeschriebener Methode dargestellten Blausäure fanden wir zu 0.6919 bei 18.0°C., die Analyse ergab 100.06% HCN.

Apparatur und Arbeitsweise. Sehr vorteilhaft ist es, den Dampfdruck, namentlich wenn er sehr klein ist, nicht direkt zu messen, sondern ihn zu berechnen aus dem Gewicht des Dampfes, der mit einer grossen, durch die Flüssigkeit geleiteten Menge eines indifferenten Gases von bekanntem Volumen mitgeführt wird. Es ist natürlich dafür zu sorgen, dass das durchgeleitete Gas auch wirklich mit dem Dampf gesättigt ist. Die Menge des Dampfes kann entweder direkt bestimmt werden aus der Gewichtszunahme des Absorptionsgefässes oder auf analytischem Wege durch quantitative Bestimmung in Form hierzu geeigneter (Titrimetrisch usw.) Reaktionen. Diese Methode, welche man das dynamische Verfahren nennt, hat verschiedene Vorteile. Nach diesem Prinzip haben wir die Dampfdruckmessungen wässriger Blausäure ausgeführt.

Die Lösung der wässrigen Blausäure von bekannter Konzentration wurde in Sättigungsgefässe, welche aus 2 Winkler-Spiralen einem Spiralabsorptionsrohr und zuletzt einer Sicherheitsflasche bestanden, gebracht. Ein Knallgasstrom passierte der Reihe noch drei Sättigungsgefässe und eine Sicherheitsflasche die mit der Lösung gefüllt waren. Der gelöste Stoff wird hauptsächlich den ersten Gefässen entnommen werden, und die Lösung in der Sicherheitsflasche wird ihre Konzentration bei richtigem Verhältnis nur unbedeutend ändern. Die Konzentration der Lösung in der Sicherheitsflasche wurde vor und nach dem Versuche bestimmt, und erwies sich fast stets unverändert.

Sättigungsgefässe und Sicherheitsflasche befanden sich in dem Wasserbade des Thermostaten. Die Versuchstemperatur betrug bei allen Messungen 18.0°C. Die Veränderung der Temperatur des Thermostaten während unserer Versuche war maximal ±0.05°C.

Das mit Wasserdampf und Blausäure gesättigte Knallgas passierte ein mit Kalilauge gefülltes Absorptionsgefäss und ein Chlorkalciumrohr. In diesen wurde die mitgeführte Blausäure und der Wasserdampf zurückgehalten. Zwischen Sicherheitsflasche und Absorptionsgefäss stand ein Wassermanometer, mit Hilfe dessen der Gasdruck genau gemessen wurde, gleichzeitig wurde der Atmosphärendruck abgelesen. Um den Verlust von Blausäure- und Wasserdampf zu vermeiden, wurde zwischen Manometer und Gasleitungsrohr ein Kapillarrohr ausgesetzt. Durch Wägung des Absorptionsgefässes und des CaCl$_2$-Rohrs vor und nach dem Versuche wurde die Gesamtmenge der Blausäure und des Wassers erhalten. Weiter wurde durch Titration der Lösung im Absorptionsgefäss die Blausäuremenge bestimmt. Die Differenz ergab die Wassermenge. Während unserer Versuche war die Zimmertemperatur immer 1–2° höher als die des Thermostaten, so wurde die Kondensation von Blausäure- und Wasserdampf vermieden. Für die Verbindung aller im Thermostaten befindlichen Gefässe und des Absorptionsgefässes verwendeten wir Glasschliffe; als Dichtungsmittel gebrauchten wir eine Mischung von Paraffin und Vaselin.

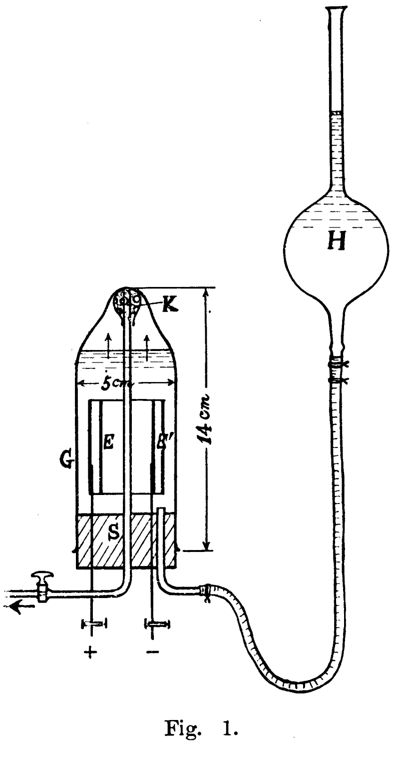

Fig. 1.

Dass die Blausäure mit Alkali sehr leicht polymerisiert, ist schon bekannt. Nach unseren Verfahren wurde der Blausäuredampf im Absorptionsgefäss mit der Kalilauge neutralisiert, deshalb mussten wir die Versuche rasch ausführen, besonders schnell mussten die Dampfdruckmessungen bei höheren HCN-Konzentrationen erfolgen. Aus diesem Grund nahmen wir möglichst verdünnte Kalilauge (siehe Tabelle 1).

Bei dynamischen Verfahren ist bekanntlich genaue Bestimmung eines Gasvolumens nötig. Nach einiger Erfahrung konstruierten wir einen Knallgasentwickler. In Fig. 1 ist G eine Glasglocke von 14 cm. Höhe und 5 cm. Durchmesser, verschlossen mit einem guten Gummistopfen S, durch den zwei konzentrisch ineinander gestellte Nickelelektroden E und E′ gehalten wurden, welche in verdünnte Kalilauge von 15% tauchten; durch den Stopfen wurden noch zwei Glasrohre durchgeführt, wovon das eine mit Hilfe von Gummischlauch mit einem mit Kalilauge gefüllten Druckheber H verbunden war, das andere bis in den engeren Raum der Glocke reichte (vgl. Fig. 1). An das Ende dieses Rohrs wurde eine Glaskugel K mit einigen Öffnungen aufgesetzt. Um den mit dem entwickelten Knallgas mitgeführten Wassernebel möglichst zurückzuhalten, wurde der Raum zwischen der Kugel und dem Glasrohr mit Glaswolle ausgefüllt. Durch dieses Rohr wurde das entwickelte Knallgas aus der Glocke nach dem Trockenrohr, welches mit wasserfreiem, feinem Chlorkalzium und Natronkalk gefüllt war, geleitet. In dieser Weise wurde das vollständig getrocknete Knallgas erst in die Sättigungsgefässe durch ein feines Kapillarrohr hindurchgeleitet. Die Sättigungsgefässe bestanden aus einer Winkler-Spirale von 35 c.c. Inhalt, einem 60 oder 90 c.c. fassenden Spiralabsorptionsrohr (das kleinere wurde jeweils für konzentriertere Lösungen, das grössere für verdünntere Lösungen benutzt) und schliesslich aus einer 20 c.c. Winkler-Spirale; als Sicherheitsflasche diente eine Waschflasche von 30 c.c. Inhalt. Um eine vollständige Sättigung des Gases mit HCN zu erreichen, war es nötig, dasselbe möglichst lange mit der Flüssigkeit in Berührung zu lassen. Fig. 2 zeigte das Spiralabsorptionsrohr. Mittels des Druckhebers H (Fig. 1) und mit Hilfe des Kapillarrohrs konnten wir das Knallgas gleichmässig und mit beliebiger Geschwindigkeit hindurchleiten.

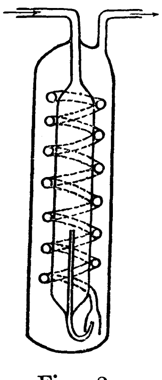

Fig. 2.

In den Stromkreis, der den Knallgasentwickler betätigte, waren ausserdem noch eingeschaltet ein Amperemeter, sowie ein Regulierwiderstand zur groben Einstellung, und zur genauen Messung des Stromes ein Kupfercoulometer. Die Füllung des letzteren hatte die Zusammensetzung, wie sie Öttel angiebt. Das Kupfercoulometer diente dazu, um aus der abgeschiedenen Kupfermenge nach Beendigung eines jeden Versuches die angewandte Knallgasmenge zu berechnen. In unseren Versuchen mit verdünnten Lösungen von Blausäure arbeiteten wir so, dass erst die Sättigungs-und Sicherheitsflasche einige Minuten in den Thermostaten getaucht wurden, dann wurde das Knallgas hindurchgeleitet; erst einige Minuten später schlossen wir des Absorptionsgefäss an. Dann wurde, sobald die erste Blase von Knallgas in dem Absorptionsgefäss erschien, gleichzeitig mit Hilfe eines Umschalters das Kupfercoulometer eingeschaltet⁽¹⁾; in konzentrierten Lösungen arbeiteten wir so, dass nach einigen Minuten langem hindurchleiten von Knallgas durch die Sättigungsgefässe der Glashahn zwischen Wassermanometer und Absorptionsgefäss geschlossen wurde dann, sobald das Wassermanometer den zum Durchperlen nötigen Gasdruck erreicht hatte (z. B. für 5% Kalilauge im Absorptionsgefäss war der Druck ca. 50 mm. H_2O, für 10% Kalilauge 53 mm. H_2O, für 20% 55 mm. H_2O), wurde das Absorptionsgefäss angesetzt und der Hahn geöffnet, wobei gleichzeitig das Kupfercoulometer eingeschaltet wurde.

Vorher mussten wir das Absorptionsgefäss und das $CaCl_2$ -Rohr genau abwiegen. Vor dem Versuch war das Absorptionsgefäss und das $CaCl_2$ -Rohr anfänglich mit Luft gefüllt, nach dem Versuch statt dessen mit Knallgas. Dieser Unterschied war ziemlich gross (etwa 23 mg.). Um diese Differenz zu vermeiden, gingen wir dazu über, in beiden Fällen das mit Luft gefülltem Gefäss zu wägen.

Die Berechnung der Partialdampfdrucke aus der Beobachtungsresultaten ergibt sich aus den Gasgesetzen folgendermassen: Waren a die Menge HCN und b die Menge H_2O in gr., welche vom Knallgasvolumen v c.c. (nach der Sättigung) bei normalen Bedingungen mitgeführt wurden, und p der Gasdruck in mm. Hg bei 0°C., so ist der Partialdruck der Blausäure:

$$p_{\mathrm{HCN}} = \frac{a}{27.02} \cdot \frac{p}{\left(\frac{a}{27.02} + \frac{b}{18.016} + \frac{v}{22412}\right)}$$

und derjenige des Wassers:

$$p_{\mathrm{H_2O}} = \frac{b}{18.016} \cdot \frac{p}{\left(\frac{a}{27.02} + \frac{b}{18.016} + \frac{v}{22412}\right)}$$

(p_{HCN} und $p_{\mathrm{H_2O}}$ jeweils in mm. Hg ausgedrückt), folglich der Gesamtdampfdruck:

$$P = p_{\mathrm{HCN}} + p_{\mathrm{H_2O}}.$$

Analysenmethode. Das Prinzip der Analyse der Blausäure besteht in der Absorption in Kalilauge, wobei sich eine Kaliumcyanid-Lösung bildet, welche mit einer eingestellten Lösung von Silbernitrat mit Hilfe von Kaliumjodid als Indikator bei Gegenwart von Ammoniak titriert wird (Methode nach Liebig⁽²⁾).

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(1) Das Kathodenblech wurde einige Minuten vor Beginn des Versuches in die Lösung getaucht. In unserem Falle betrug der Cu-Verlust 1.4 mg., wenn die Kathode sich 1 h. in der Lösung befand, während die abgeschiedene Kupfermenge mindestens 200 mg. betrug (s. Tab. 1), so dass der Unterschied vernachlässigt werden konnte.

(2) Liebig, *Ann. Chem. Pharm.*, 77 (1851), 102; Treadwell, "Lehrbuch der analytischen Chemie", II, S. 617 (1923).

Für die Urlösung zur Einstellung der $AgNO_3$-Lösung wurde chemisch reines NaCl von Merck genommen, einmal umkristallisiert, getrocknet und zerkleinert. Von diesem NaCl wurde eine n/50-Lösung hergestellt und gegen diese mit Hilfe von Fluorescein (Fluoresceinnatrium) als Indikator(1) n/50 $AgNO_3$-Lösung titriert. Diese $AgNO_3$-Lösung diente für die Titration der Blausäurelösung. Von dem zu unseren Versuchen dienenden HCN-Lösungen nahmen wir die Proben mittels einer 5 c.c.-Pipette, die zweimal sorgfältig geeicht war. Um die Ausflussgeschwindigkeit beliebig einstellen zu können, setzten wir auf das obere Ende mittels Druckschlauch eine Kapillare auf.

Mittels eines Schraubenquetschhahns konnten wir die Ausflussgeschwindigkeit beliebig regeln. Auf diese Weise war eine grosse Genauigkeit der Probenahme gewährleistet.

Zur Probenahme wurde ein Überschuss von etwa 20% der Kalilauge zur Neutralisation der Bläusaure in den Messkolben hineingegossen und zweckmässig verdünnt. Mit Hilfe der Pipette wurden von der Probelösung, die eine Temperatur von genau 18°C. hatte, 5 c.c. genau gemessen; dann wurde die noch übrige Lösung aus der Pipette völlig durch Ausfliessen lassen entfernt, und der HCN-Dampf in der Pipette mit Hilfe von destilliertem Wasser absorbiert und in den Kolben hineingespült; durch Schütteln wurde gut neutralisiert, auf bestimmtes Volumen verdünnt, wieder gut geschüttelt und dann analysiert. Die Lösung des Absorptionsgefäss, die gut neutralisiert worden war, wurde auf bestimmtes Volumen verdünnt und ebenfalls analysiert.

Die Messkolben und Büretten, die für die Analyse gebraucht wurden, wurden sorgfältig geeicht; auch wurde die Temperaturkorrektion der Lösungen ausgeführt. In allen Fällen waren mindestens 20 c.c. der verwendeten $AgNO_3$-Lösung zur Titration nötig. Der Endpunkt der Titration war deutlicher bei elektrischem Licht als bei Tageslicht zu erkennen.

Experimentelle Resultate der Dampfdruckmessungen. Die mit unserer Versuchsanordnung gewonnenen Resultate sind in Tabelle 1 und 2 zusammengefasst. In Tabelle 2 haben Spalte I gibt Konzentrationen der Blausäure in den Versuchslösungen. In Spalte II finden wir den Gesamtdampfdruck bei 18° in mm. Hg. Dieser berechnet sich aus den entsprechenden Partialdampfdruck bei 18°, die in Spalte IIIa bezw. IVa enthaltenen und nach den Formeln S.89 berechnet sind. IIIa gibt die beobachtenden Werte von p_{HCN} wieder, die sich aus Spalte IX der vorhergehenden Tabelle in der angebenen Weise nach den Formeln S.89 berechnet. IVa ist aus der Differenz der Werte aus Tabelle 1, Spalte VIII und IX berechnet. Spalte IIIb bezw. IVb enthalten die korrigierten Werte, welche aus Kurven

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(1) K. Fajans und O. Hassel, *Z. Elektrochem.*, 29 (1923), 495.

TABELLE 1.

I Konz. der Blausäure in Gew. %	II Arbeitszeit in Min.	III Stromstärke für Coulometer in Amp.	IV Gewichtszunahme der Kathode	V Knallgasmenge in norm. Beding. in c.c.	VI Gasdruck* in mm. Hg	VII Konz. der Kalilauge ins Abs. Gefäss in %	VIII Gew. Zunahme ins Abs. Gefäss (Wägung)	IX Blausäuremenge (Analyse)	X Wassermenge (Differenz)
4.996	300	0.20	1.3688 g	723.9	751.8	20	0.1748 g	0.1605 g	0.0143 g
9.703	180	0.20	0.8443	446.5	751.5	20	0.2299	0.2204	0.0095
14.488	180	0.13	0.5742	303.7	750.3	20	0.2416	0.2348	0.0068
19.675	180	0.13	0.5888	311.4	750.1	20	0.3278	0.3190	0.0088
20.054	180	0.20	0.8010	423.6	749.6	20	0.4573	0.4497	0.0076
26.90	180	0.10	0.3566	188.6	754.0	10	0.2415	0.2351	0.0064
33.01	180	0.08	0.2869	151.72	749.6	10	0.2203	0.2147	0.0056
47.64	180	0.08	0.2874	152.0	751.6	10	0.2472	0.2405	0.0067
47.93	180	0.08	0.2838	150.08	750.9	20	0.2461	0.2383	0.0078
49.20	150	0.09	0.3390	179.27	750.5	20	0.2918	0.2860	0.0058
60.23	60	0.21	0.2816	148.9	759.2	6	0.2529	0.2490	0.0039
60.76	60	0.20	0.2467	130.46	458.6	5	0.2233	0.2203	0.0030
69.67	60	0.20	0.2891	152.9	760.0	6	0.2700	0.2652	0.0048
70.93	60	0.20	0.2583	136.6	761.2	5	0.2468	0.2427	0.0041
79.54	60	0.20	0.2718	143.7	754.5	6	0.2943	0.2906	0.0037
80.18	60	0.20	0.2603	137.65	762.3	5	0.2777	0.2740	0.0037
88.55	60	0.20	0.2774	146.7	754.0	6	0.3576	0.3542	0.0034
89.64	60	0.20	0.2527	133.64	760.8	5	0.3240	0.3162	0.0078
100.00	105	0.10	0.2060	108.94	754.1	5	0.4057	(0.3822)	(0.0235)
100.00	120	0.20	0.5074	268.3	760.7	20	0.9412	—	—

* „Gasdruck" bezeichnet die Summe von Atmosphärendruck, abgelesen am Barometer, und dem in der Apparatur herrschenden Überdruck, abgelesen am Wassermanometer.

graphisch interpoliert sind, die mit den Werten der Spalten IIIa bezw. IVa gerechnet wurden. IIIc und IVc sind die Differenzen der Werte aus IIIa und IIIb bezw. IVa und IVb.

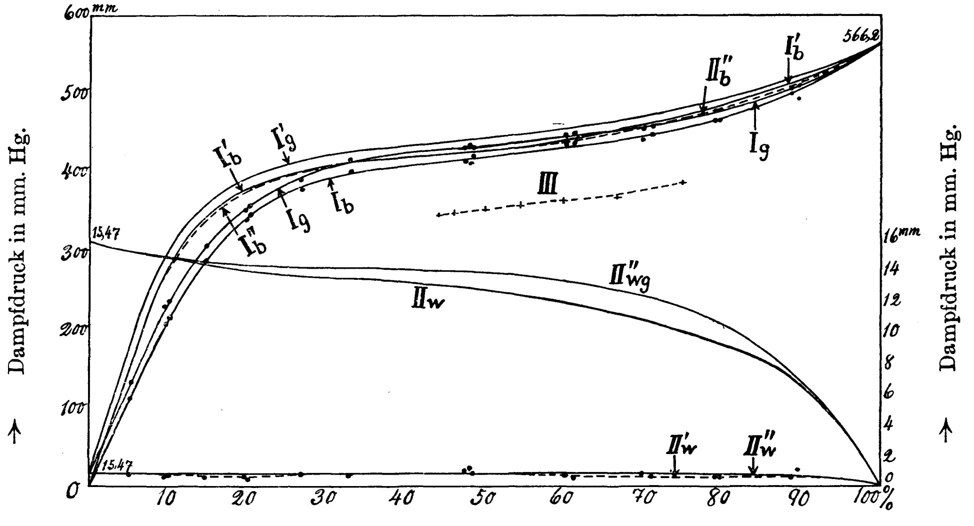
TABELLE 2.

I Konzentration des HCN in Gew. %	II Gesamtdampfdruck P (Wägung) in mm.	III Partialdruck p_{HCN}			IV Partialdruck p_{H_2O}		
		a. Gefund. Werte (Analyse) in mm.	b. Korr. Werte in mm.	c. Diff. in mm.	a. Gefund. Werte (Diff.) in mm.	b. Korr. Werte in mm.	c. Diff. in mm.
4.996	129.7	114.4	114.4	0	15.3	15.3	0
9.703	228.1	214.3	214.0	−0.3	13.8	14.5	+0.7
14.488	300.8	288.3	287.0	−1.3	12.5	14.3	+1.8
19.675	352.0	338.1	341.0	+2.9	13.9	12.5	−1.4
20.054	355.7	346.9	344.0	−2.9	8.8	11.5	+2.7
26.90	390.8	375.5	380.0	+4.5	15.3	13.0	−2.3
33.01	411.9	396.4	396.4	0	15.5	13.5	−2.0
47.64	434.1	416.7	419.0	+2.3	17.4	15.4	−2.0
47.93	435.6	415.2	419.3	+4.1	20.4	15.0	−5.4
49.20	433.0	420.2	419.4	−0.8	12.8	14.9	+2.1

TABELLE 2. *Fortsetzung.*

I Konzentration des HCN in Gew. %	II Gesamtdampfdruck P (Wägung) in mm.	III Partialdruck p_{HCN}			IV Partialdruck p_{H_2O}		
		a. Gefund. Werte (Analyse) n mm.	b. Korr. Werte in mm.	c. Diff. in mm.	a. Gefund. Werte (Diff.) in mm.	b. Korr. Werte in mm.	c. Diff. in mm.
60.23	445.4	435.2	430.0	−5.2	10.2	14.3	+4.1
60.76	446.3	437.4	430.5	−6.9	8.9	14.4	+5.5
69.67	453.3	441.3	443.7	+2.4	12.0	10.5	−1.5
70.93	458.0	446.7	446.2	−0.5	11.3	10.0	−1.3
79.54	476.0	467.1	466.0	−1.1	8.9	8.0	−0.9
80.18	478.4	468.9	468.9	0	9.5	8.0	−1.5
88.55	505.1	497.9	497.9	0	7.2	7.0	−0.2
89.64	510.2	(492.0)	502.5	(+10.5)	(18.2)	7.0	(−11.2)
100.00	569.7	(525.2)	566.2	(+41.0)	(44.5)	—	—
100.00	566.2	—	—	—	—	—	—

Der geringe conservierende Zusatz einer Spur wässriger Phosphorsäure kann nach unserer Schätzung den Dampfdruck der Blausäure nur um ungefähr 0.1 % vermindert haben und ihr Einfluss auf den Dampfdruck des Wassers dürfte auch, erst bei einem Wassergehalt der Blausäuremischung von weniger als 5 % Wasser merklich werden.



→ Gewicht- und Mol % der Blausäure.

Fig. 3.

Die erhaltenen Werte wurde noch auf Molenbrüche umgerechnet. Die so erhaltenen Resultate sind auch noch in Fig. 3 graphisch dargestellt. Die Abszisse gibt die Zusammensetzung der Lösungen in Gewicht- oder Molprozent HCN an, die Ordinate den Dampfdruck in mm. Hg. Von den ausgezogenen Kurven gibt Ig und I′g die Gesamtdrucke an, Ib und I′b die Partialdrucke des Cyanwasserstoffs. IIw und II′w sind noch die Partialdrucke des Wassers eingetragen worden.

Wegen Polymerisation der Blausäure in dem Kalilaugegefäss, waren die Partialdampfdruckmessungen des HCN und H_2O manchmal ungenau. In der Sättigungsgefässe und der Sicherheitsflasche selbst niemals Polymerisation beobachtet wurde, aber in dem Absorptionsgefäss mit 10 %-iger KOH ergab sich durch Polymerisation eine leicht goldgelbe Färbung, wenn wir lange arbeiteten. Stärkere Lauge von etwa 20 % vertiefte diese Nuance bis zu Braun. In diesem Falle lagen die gefundenen Werte für Blausäure tiefer als die mit verdünnter KOH erhaltenen.

Diskussion. Wie die Fig. 3 zeigt, sind die Partialdruckkurven des HCN und H_2O beide positiv, ebenso natürlich auch die Gesamtdruckkurve. Letztere zeigt in ihren Verlauf einen Wendepunkt. Nach Duhem(1) besteht zwischen den Partialdrucken und der molaren Zusammensetzung der Flüssigkeit die einfache Beziehung:

$$\frac{d \ln p_1}{d \ln x} = \frac{d \ln p_2}{d \ln (1-x)}$$

Diese totale Differentialgleichung ist rechnerisch nicht lösbar. Dagegen kann man nun, wie man an der leicht umgeformten Gleichung:

$$\frac{p_1}{p_2} = -\frac{x}{(1-x)} \cdot \frac{\frac{dp_1}{dx}}{\frac{dp_2}{dx}}$$

sieht, auf graphischen Weg zum Ziel gelangen (Näherungsmethode von Marshall(2) und Bose(3)). Wir erzielten nach 3 maliger Anwendung des Verfahrens folgende Werte:

TABELLE 3.

x Molbr. HCN in Flüssigkeit	$P_{ges.}$ in mm. beob.	Partialdrucke bei 18.0° C.					
		p_{HCN} in mm.			p_{H_2O} in mm.		
		ber.	beob. (aus der Kurve)	Diff.	ber.	beob. (aus der Kurve)	Diff.
0.00	—	0	0	0	15.48	—	—
0.05	182	167.0	167.0	0	15.0	15.1	+0.1
0.10	298	283.4	283.4	0	14.6	14.7	+0.1
0.15	362	347.7	349.5	+1.8	14.3	14.2	−0.1
0.20	393	378.9	381.0	+2.1	14.1	13.8	−0.3

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(1) Duhem, "Potential Thermodynamique," Paris, 1886.

(2) A. Marshall, *J. Chem. Soc.*, 89 (1906), 1350.

(3) Bose, *Physik. Z.*, 8 (1907), 350.

TABELLE 3. *Fortsetzung.*

x Molbr. HCN in Flüssigkeit	$P_{ges.}$ in mm. beob.	Partialdrucke bei 18.0° C.					
		p_{HCN} in mm.			p_{H_2O} in mm.		
		ber.	beob. (aus der Kurve)	Diff.	ber.	beob. (aus der Kurve)	Diff.
0.25	412	398.0	398.5	+0.5	14.0	13.5	−0.5
0.30	423	409.1	409.1	0	13.9	13.3	−0.6
0.35	431	417.2	417.2	0	13.8	13.2	−0.6
0.40	435	421.3	421.3	0	13.7	12.9	−0.8
0.45	439	425.4	425.4	0	13.6	12.7	−0.9
0.50	444	430.6	430.6	0	13.4	12.4	−1.0
0.55	448	434.8	434.8	0	13.2	12.0	−1.2
0.60	454	441.0	442.0	+1.0	13.0	11.6	−1.4
0.65	461	448.5	451.0	+2.5	12.5	11.1	−1.4
0.70	470	458.0	462.0	+4.0	12.0	10.4	−1.6
0.75	481	469.8	474.0	+4.2	11.2	9.8	−1.4
0.80	494	483.8	488.0	+4.2	10.2	9.0	−1.2
0.85	508	499.3	503.0	+3.7	8.7	7.9	−0.8
0.90	525	518.4	521.0	+2.6	6.6	6.4	−0.2
0.95	544	540.5	540.5	+0.5	4.0	4.0	0
1.00	566.2	566.2	566.2	0	0	0	0

Wie man sieht, sind Abweichungen merklich, was wohl auf die Assoziation sowohl des HCN wie auch des H_2O zurückzuführen ist.

Diese Resultate wurden wieder in Fig. 3 dargestellt. Die Kurve I″b bezw. II″w zeigen die berechneten Werte von p_{HCN} und p_{H_2O}, während in Kurve II″wg die Kurve II″w 20 mal vergrössert dargestellt wurde.

Bussy und Buignet⁽¹⁾ haben nach der statischen Methode die Dampfdrucke bei 13.25° C bestimmt. Ihre Resultate, umgerechnet auf Gewicht %, und diese Werte sind durch Kurve III dargestellt (vgl. Fig. 3).

Die Messungen erstrecken sich nur über ein kleines Gebiet, und erhalten keine Angabe über den Dampfgehalt, scheinen aber mit unseren Messungen durchaus verträglich.

Die mit der Mitführungsmethode (dynamisch) von uns erhaltenen Dampfdruck bei 18.0° für reine HCN (566.2 mm.) stimmen mit den von Bredig und Teichmann (567 mm.), sowie Hara und Sinozaki (565.5 mm.) nach der statischen Methode beobachteten Werten vorzüglich überein.

Zusammenfassung.

1) In vorliegender Arbeit ist der Dampfdruck und die Zusammensetzung des Dampfes über wässriger Blausäure bei 18.0° C. bestimmt worden.

2) Die beobachteten Partialdrucke weichen an den Enden der Kurve von den aus der gefundenen Gesamtdrucken nach der Marshall-Bose'schen Näherungsverfahren berechneten Partialdrucken merklich ab, während die Übereinstimmung in den mitteren Teilen vorzüglich ist.

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(1) Bussy und Buignet, loc. cit.

Diese Arbeit wurde im physikalische chemische Institut der Technischen Hochschule in Karlsruhe ausgeführt. Den Herren Prof. Dr. G. Bredig und Prof. Dr. E. Elöd sage ich meinen herzlichsten Dank für die Anregung und ihr Interesse an meiner Arbeit.

August 1926. Technische Hochschule, Karlsruhe i. B.,
Deutschland.

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

By Toshizo TITANI.

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Although numerous works on the viscosity of liquids have been published, very few of these researches are extended over a wide temperature range.(1) It was with the object of making up this deficiency that the writer undertook a series of determinations of viscosities of pure liquids above their boiling points. These experimental researches were followed by a study on the relation between viscosity of liquids and their volume and temperature.

Experimentals.

Preparation of Material. The materials used in this experiment are methyl-acetate, carbon-tetrachloride, fluorobenzene, chlorobenzene, and ethyl alcohol, of which the first four are usually regarded as normal liquids.

Methyl-acetate. A specimen from Merck was treated repeatedly with phosphorus pentoxide and finally fractionated. B.P. = 57.0°±0.01.

Carbon-tetrachloride. A pure specimen was obtained from Kahlbaum, which, being dehydrated over phosphorus pentoxide, boiled quite constantly. B.P. = 76.75°±0.00.

Fluorobenzene. This compound was prepared as described by Holleman and Beekman(2) by the action of concentrated hydrofluoric acid on benzenediazofluoride (C_6H_5.N.N.F.). Having been dried over calcium chloride, it was purified by fractional distillation. B.P. = 84°.8±0.05.

Chlorobenzene. A specimen from Kahlbaum was dehydrated over phosphorus pentoxide and purified by fractional distillation, until a product of quite constant boiling point was obtained. B.P. = 131°.74±0.01.

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(1) Stoel, Diss. Leiden, (1891); *Comm. Phys. Lab. Univ. Leiden*, **2** (1891); de Haas. ibid., **12** (1894); Warburg and v. Babo, *Wied. Ann.*, **17** (1882), 390; A. Heydweiller, *Wied. Ann.*, **55** (1895), 561; ibid., **59** (1896), 198; P. Phillips, *Proc. Roy. Soc. (London)*, (A) **87** (1912), 48

(2) Holleman and Beekman, *Rec. trav. chim.*, **23** (1905), 231; ibid., **24** (1905), 26.

Ethyl alcohol. Pure absolute alcohol from Merck was purified as described by Thorpe and Rodger⁽¹⁾ by distilling several times over freshly burnt quicklime. B.P. = 78°.27±0.02.

Description of Apparatus. At first several observations were made with methyl-acetate and fluorobenzene after the mercury-method described by A. Heydweiller.⁽²⁾ But as this method contains several difficulties and inaccuracy, a new apparatus was devised, by means of which the viscosities of the other three liquids were determined above their boiling points.

The appearance of the viscosimeter is shown in Fig. 1. Two parallel capillaries which have exactly equal inner diameter of 0.326 mm. and almost equal length (33 mm. and 32 mm.) are connected with each other by two U-tubes having uniform diameter of 4 mm. The total length of the upper U-part is 20 cm. and the lower 6 cm. The viscosimeter is cleaned by sucking successively hydrochloric acid, chromic acid, distilled water, alcohol and benzene and finally dry air through the annexed tube A or B (shown by dotted lines in the figure). Both limbs of the viscosimeter are so made as to exert equal resistance to the passing fluids.

It is then filled in the following manner: Having sealed the tube B, proper quantity of liquid is poured or distilled in through the other tube A. Both menisca of the liquid are gently heated with a little flame and brought to boiling, to expel all air in the tube, and, while still boiling, the neck of the tube A is sealed up.

To determine the viscosity of liquid thus filled, the viscosimeter is turned at an angle over 90 degrees, say, to the left side, so that most part of the liquid is collected in one of its limbs. Bringing it again in the vertical position, the left meniscus begins to descend, and the differences of the both menisca ($2H_1$ and $2H_2$) are determined at two different times (θ_1 and θ_2). Then the viscosity (η) of the liquid is calculated by the following formula:

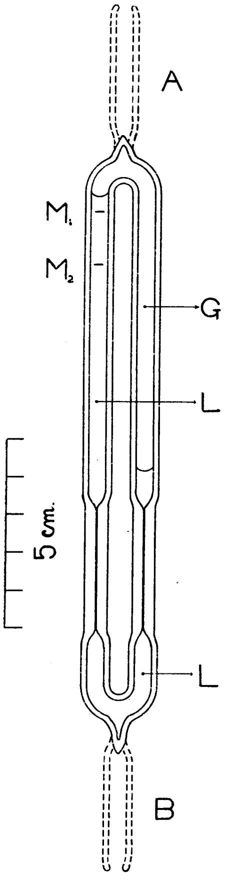

Fig. 1.

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(1) Thorpe and Rodger, *Phil. Trans.*, (A) 185 (1894), 532.

(2) loc. cit.

$$\eta = k.\ \frac{\theta_2 - \theta_1}{\log(H_1+\Delta_1)-\log(H_2+\Delta_2)}.\ (D_l - D_g)\ .\ (1+\alpha\, t)\times 10^{-5} \dots\dots\dots (1)$$

The deduction of this formula will be given later. The coefficient k is a viscosimeter-constant and independent of the temperature and the nature of the liquid employed. Δ_1 and Δ_2 are corrections due to kinetic energy, D_l and D_g are respectively the density of the liquid and vapour, α the linear expansion coefficient of glass and t the temperature of the liquid.

In order to use the same part of the viscosimeter tube in a series of observations, a pair of marks (M_1 and M_2) was etched on one of the limbs. The time of passage of the meniscus through these marks was recorded by means of a stop-watch and, at the same time, the hights of marks M_1 and M_2 and also that of the level of equilibrium were measured by a cathetometer. The values of H_1 and H_2 in the equation (1) are known from these readings.

As the apparatus is closed completely, the measurement can be done under moderately high pressure above the normal boiling point. The one and the same viscosimeter tube can repeatedly be used by opening the side tubes and filling with other substances.

With this viscosimeter several difficulties, which arise from the use of Heydweiller's, can be overcome. Above all, the viscosity of many substances such as acids and halogen or sulphur compounds, which attack mercury at all temperatures or when heated, can safely be determined by this method.

The viscosimeter was kept in a constant known temperature by heating it in a vapour-jacket, (Fig. 2). The lower end of the jacket tube G is bent and blown in a pear shaped bulb as is shown in the figure, while the upper end of which is closed by a stopper perforated with two holes. A metal rod R passes through one of the holes and is centered by two sets of small metallic pieces of the star shape. The viscosimeter V is fixed to the metal rod by a hook and a spring. Through the other hole in the stopper passes a small glass tubing T. This is connected to the pump and a big air reservoir for damping the fluctuation of pressure. Thus the liquid L in the bottom boils under reduced pressure at constant temperature. The uniformity of the temperature along the viscosimeter is secured by a wider cylindrical glass tube M placed outside the jacket tube. The temperatures are measured by a normal thermometer hanged just behind the viscosimeter.

The jacket tube is provided with a Liebig's condenser C and kept in a vertical position by the large stand P and clamps A_1 and A_2 as is shown in the figure. The stand is fixed to the table F by two steel hinges H, so that the whole apparatus may be turned about one of the edges of the stand-plate *S*. By this means the liquid in the viscosimeter can easily be collected in one (left one in the figure) of its limbs without allowing the liquid in the bulb to flow out nor stop boiling.

The Theory of Measurement.(1) If the difference of menisca at the time θ be $2H$ and the radius of the wider tube of the viscosimeter be R, the amount of decrease of the potential energy dE_p in the time $d\theta$ will be:

$$dE_p = -2\pi \,.\, R^2 \,.\, g \,.\, (D_l - D_g) \,.\, H \,.\, dH.$$

in which D_l and D_g are respectively the density of the liquid and vapour, g the acceleration of gravity.

The increase of kinetic energy dE_k of this system in the time $d\theta$ is mainly due to that of the liquid in both capillaries. Denoting their common radius by r, this will be:

$$dE_k = 2\pi \,.\, D_l \,.\, \frac{R^6}{r^4} \,.\, \left(\frac{dH}{d\theta}\right)^2 . \, dH.$$

The difference of the above two quantities will be the amount of energy dW which is converted into heat in the capillaries by internal friction. If the lengthes of the two capillaries are l_1 and l_2, this energy due to viscosity will amount to:

$$dW = -8\pi . (l_1 + l_2) \,.\, \eta \,.\, \frac{R^4}{r^4} \,.\, \frac{dH}{d\theta} \,.\, dH.$$

Since the algebraic sum of the above three quantities will be equal to zero, we obtain the following equation:

$$\frac{dH}{d\theta} = - \frac{g . (D_l - D_g)}{4 (l_1 + l_2) \,.\, \eta} \,.\, \frac{r^4}{R^2} \,.\, H \,.\, \times$$
$$\left\{1 - \frac{1}{g . H} \,.\, \frac{D_l}{D_l - D_g} \,.\, \frac{R^4}{r^4} \,.\, \left(\frac{dH}{d\theta}\right)^2\right\} \dots (2)$$

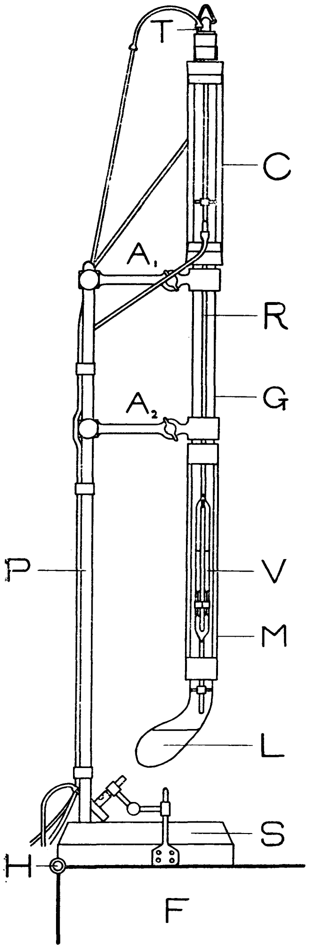

Fig. 2.

For the sake of simplicity, putting

$$A = \frac{4 (l_1 + l_2) \,.\, \eta}{g \,.\, (D_l - D_g)} \,.\, \frac{R^2}{r^4} \dots\dots\dots (3), \qquad B = \frac{1}{g} \,.\, \frac{D_l}{(D_l - D_g)} \,.\, \frac{R^4}{r^4} \dots\dots\dots (4)$$

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(1) The method of calculation used by Heydweiller was adopted. For details, see the original paper already cited.

the equation (2) becomes

$$\frac{dH}{d\theta} = -\frac{H}{A} + \frac{B}{A} \cdot \left(\frac{dH}{d\theta}\right)^2$$

As a solution of this differential equation, under suitable neglection we obtain :

$$\frac{\theta}{A} = -\ln H . \left(1 + \frac{B}{A^2} . H\right) + \text{Const.}$$

If H_1 and H_2 correspond respectively to θ_1 and θ_2, from the above we have :

$$A = \frac{\theta_2 - \theta_1}{\ln H_1' - \ln H_2'} \dots\dots\dots\dots\dots\dots\dots\dots\dots\dots (5)$$

In this relation

$$H' = H + \frac{B}{A^2} H^2 = H + \Delta,$$

the second term of which is evidently a correction due to the loss of the kinetic energy and can be computed by means of a successive approximation. (see equations (3) and (4)).

Let the quantities without index be refered to t° and those with index 0 to 0°, and the linear expansion coefficient of glass be α, from equations (3) and (5) we have :

$$\eta = k . \frac{\theta_2 - \theta_1}{\log H_1' - \log H_2'} . (D_l - D_g) . (1 + at) \times 10^{-5} \dots\dots\dots (1)$$

in which

$$k = 0.4343 . \frac{1}{A_0} . \frac{\eta_0}{D_{l0} - D_{g0}}$$

$$= 0.4343 . \frac{g}{4\,(l_{10} + l_{20})} . \frac{r_0^4}{R_0^2}.$$

This equation is identical with that which has already been given above.

Results. For the measurements of heights an accurate cathetometer made by Société Genevoise was used and times were recorded by a stop-watch provided with a stripping-index so as to eliminate errors due to inertia.

For example, the result obtained with carbon-tetrachloride will be cited below.

TABLE 1.

Carbon-tetrachloride.

t° C.	θ sec.	H_1 mm.	H_2 mm.	Δ_1 mm.	Δ_2 mm.	H_1' mm.	H_2' mm.	log η/k
20.00	52.0	36.7	22.7	0.4	0.1	37.1	22.8	$\bar{3}.5929$
30.00	46.7	36.1	22.1	0.5	0.2	36.6	22.3	$\bar{3}.5335$
30.00	47.1	36.0	22.0	0.5	0.2	36.5	22.2	$\bar{3}.5348$
40.00	42.9	35.3	21.3	0.6	0.2	35.9	21.5	$\bar{3}.4761$
40.00	43.2	35.2	21.2	0.6	0.2	35.8	21.4	$\bar{3}.4776$
50.00	40.0	34.3	20.3	0.7	0.2	35.0	20.5	$\bar{3}.4218$
50.00	40.0	34.3	20.3	0.7	0.2	35.0	20.5	$\bar{3}.4218$
60.00	37.4	33.5	19.5	0.8	0.3	34.3	19.8	$\bar{3}.3750$
60.00	37.6	33.4	19.4	0.8	0.3	34.2	19.7	$\bar{3}.3757$
70.00	35.6	32.6	18.6	0.9	0.3	33.5	18.9	$\bar{3}.3298$
76.75	34.2	32.0	18.0	1.0	0.3	33.0	18.3	$\bar{3}.2952$
80.00	33.5	31.6	17.6	1.0	0.3	32.6	17.9	$\bar{3}.2768$
90.00	32.5	30.7	16.7	1.1	0.3	31.8	17.0	$\bar{3}.2378$
100.00	31.5	29.6	15.6	1.3	0.3	30.9	15.9	$\bar{3}.1915$
110.0	30.9	28.6	14.6	1.3	0.3	29.9	14.9	$\bar{3}.1551$
120.0	30.5	27.5	13.5	1.4	0.3	28.9	13.8	$\bar{3}.1158$
130.0	30.6	26.35	12.35	1.45	0.35	27.8	12.7	$\bar{3}.0836$
140.0	31.0	25.2	11.2	1.5	0.3	26.7	11.5	$\bar{3}.0488$
150.0	31.8	23.9	9.9	1.5	0.3	25.4	10.2	$\bar{3}.0154$
160.0	33.1	22.5	8.5	1.5	0.2	24.0	8.7	$\bar{3}.9767$
170.0	35.6	21.1	7.1	1.5	0.2	22.6	7.3	$\bar{4}.9483$
180.0	39.0	19.5	5.5	1.4	0.1	20.9	5.6	$\bar{4}.9114$

The values of t and H are means of several observations. It will be seen that the time of flow decreases slowly up to 120° and then increases. Such were also seen in the other observations and will be ascribed to the combined effect of the diminution of viscosity and density of the liquid with temperature. Therefore the values of Δ_1 and Δ_2, the corrections due to the loss of kinetic energy, have maxima at high temperatures.

To calculate the absolute values of the viscosities by the equation (1), the value of the viscosimeter-constant k must be determined. For this purpose the results obtained below the boiling point (76.75°) were compared with those of Thorpe and Rodger :(1)

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(1) T.E. Thorpe and J.W. Rodger, *Phil. Trans.*, (A), **185**, (1894), 397; ibid., **189**, (1897), 71.

TABLE 2.

Temp. t°C.	log η (Thorpe and Rodger)	log η/k (Titani)	log k (Difference)
20	$\bar{3}.9863$	$\bar{3}.5929$	0.3934
30	$\bar{3}.9251$	$\bar{3}.5335$	0.3916
30	$\bar{3}.9251$	$\bar{3}.5348$	0.3903
40	$\bar{3}.8681$	$\bar{3}.4761$	0.3920
40	$\bar{3}.8681$	$\bar{3}.4776$	0.3905
50	$\bar{3}.8152$	$\bar{3}.4218$	0.3934
50	$\bar{3}.8152$	$\bar{3}.4218$	0.3934
60	$\bar{3}.7661$	$\bar{3}.3750$	0.3911
60	$\bar{3}.7661$	$\bar{3}.3757$	0.3904
70	$\bar{3}.7193$	$\bar{3}.3298$	0.3895
			Mean 0.3916

In the case of ethyl alcohol, a similar comparison with the same authors' values gave log $k = 0.3936$, the average of the two being log $k = 0.3926$, which value was used in the case of chlorobenzene, where no reliable standard data below the boiling point were found. The values of viscosity of the above three substances expressed in dyne per square centimeter are summarised below, together with those of methyl-acetate and fluorobenzene which were formerly determined by Heydweiller's method. The values of density necessary for the determination of viscosity were all obtained from the data of S. Young.(1) The viscosities in the second column are the values directly observed and those in the third (or fourth) are the values interpolated (or slightly extrapolated) from curves. In the fourth (or fifth) column are given the results obtained by other observers for the purpose of comparison.

TABLE 3.

Methyl-acetate. B.P. = 57°.0.

Temp. t°C.	η Observed value	Temp.	η From curves	η Thorpe and Rodger(2)
		0	—	0.00478
19.5	0.00386	10	—	0.00425
20.3	0.00382	20	0.00381	0.00381
34.5	0.00328	30	0.00344	0.00344
		40	0.00312	0.00312

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(1) S. Young, *Sci. Proc. Roy. Dublin Soc.*, [New Series] 12 (1909—1910), 374.

(2) loc. cit. These values were used to compute the viscosimeter-constant.

TABLE 3. *Continued.*

Methyl-acetate.

Temp. t°C.	η Observed value	Temp.	η From curves	η Thorpe and Rodger
46.1	0.00294			
		50	0.00284	0.00284
56.7	0.00267			
60.3	0.00258	60	0.00258	——
65.0	0.00249			
		70	0.00237	——
80.4	0.00217	80	0.00217	——
		90	0.00198	——
		100	0.00182	——
110.2	0.00167	110	0.00166	——
		120	0.00154	——
		130	0.00142	——
139.0	0.00132	140	0.00130	——

TABLE 4.

Carbon-tetrachloride. B.P. = 76°.75.

Temp. t° C.	η Observed value	η From curves	η Thorpe and Rodger
0.00	——	——	0.01347
10.00	——	——	0.01133
20.00	0.00965	0.00969	0.00969
30.00	0.00843	0.00843	0.008415
40.00	0.00739	0.00739	0.00738
50.00	0.00651	0.00651	0.006535
60.00	0.00585	0.00585	0.005835
70.00	0.00527	0.00524	0.00524
76.75	0.00486	0.00486	0.00488*
80.00	0.00466	0.00468	——
90.00	0.00426	0.00426	——
100.00	0.00383	0.00384	——
110.0	0.00352	0.00352	——
120.0	0.00322	0.00323	——
130.0	0.00299	0.00299	——
140.0	0.00276	0.00276	——
150.0	0.00255	0.00255	——
160.0	0.00234	0.00234	——
170.0	0.00219	0.00217	——
180.0	0.00201	0.00201	——

* Extrapolated value.

TABLE 5.

Fluorobenzene. B.P. = 84.°8.

Temp. t° C.	η Observed values	Temp. t° C.	η From curves	η Meyer and Mylius⁽¹⁾
		0	—	0.00755*
		10	—	0.00647
		20	0.00598	0.00584
25.7	0.00561			
		30	0.00532	0.00519
		40	0.00478	0.00471
46.8	0.00443			
		50	0.00428	0.00427
60.5	0.00388			
		60	0.00389	0.00388
64.7	0.00371			
		70	0.00357	0.00355
80.4	0.00330	80	0.00329	0.00327
		90	0.00300	—
100.2	0.00275	100	0.00275	—
110.0	0.00249	110	0.00250	—
		120	0.00231	—
130.8	0.00213	130	0.00214	—
136.1	0.00203			
136.3	0.00202	140	0.00198	—
		150	0.00182	—
155.2	0.00176			
		160	0.00168	—
		170	0.00156	—
182.0	0.00141	180	0.00144	—

* Recalculated from the values $1/\eta$ given by Meyer and Mylius.

TABLE 6.

Chlorobenzene. B.P. = 131.°74.

Temp. t° C.	η Observed values	η From curves	η Meyer and Mylius
10.0	—	0.00907	0.00912*
12.5	0.00876	—	—
20.0	0.00799	0.00799	0.00805
30.0	0.00715	0.00705	0.00710
40.0	0.00631	0.00631	0.00638
50.00	0.00571	0.00567	0.00580
60.00	0.00512	0.00515	0.00526
70.00	0.00472	0.00471	0.00481
80.00	0.00431	0.00431	0.00441
90.00	0.00397	0.00397	0.00405
100.00	0.00367	0.00367	0.00376
110.0	0.00339	0.00339	0.00351
120.0	0.00313	0.00313	0.00327
130.0	0.00292	0.00293	0.00306
131.7	0.00287	0.00288	—

* Interpolated from the curve drawn with the data given by Meyer and Mylius (loc. cit.).

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(1) J. Meyer and B. Mylius, *Z. physik. Chem.*, 95 (1920), 349. These values were used to compute the viscosimeter-constant.

TABLE 6. *Continued.*

Chlorobenzene. B.P. = 131°.74.

Temp. $t°$ C.	η Observed values	η From curves	η Meyer and Mylius
140.0	0.00273	0.00274	——
150.0	0.00257	0.00256	——
160.0	0.00239	0.00239	——
170.0	0.00222	0.00223	——
180.0	0.00209	0.00209	——
190.0	0.00196	0.00196	——
200.0	0.00186	0.00185	——
210.0	0.00173	0.00173	——
220.0	0.00162	0.00163	——
230.0	0.00155	0.00153	——
240.0	0.00144	0.00144	——

TABLE 7.

Ethyl alcohol. B.P. = 78°.27.

Temp. $t°$ C.	η Observed values	η From curves	η Thorpe and Rodger
0.00	——	——	0.01770
10.00	——	——	0.01449
20.00	——	——	0.01192
30.00	0.00991	0.00991	0.009895
40.00	0.00823	0.00825	0.008275
50.00	0.00701	0.00701	0.006975
60.00	0.00591	0.00591	0.005915
70.00	0.00503	0.00503	0.005045
78.27	0.00442	0.00446	0.00441*
80.00	0.00435	0.00435	——
90.00	0.00376	0.00376	——
100.00	0.00325	0.00325	——
110.0	0.00285	0.00283	——
120.0	0.00247	0.00248	——
130.0	0.00217	0.00217	——
140.0	0.00193	0.00191	——
150.0	0.00166	0.00166	——

* **Extrapolated value.**

Summary.

1. The viscosities of methyl-acetate and fluorobenzene were determined above their boiling points after the method described by A. Heydweiller.

2. To overcome several difficulties which arise from the use of his apparatus, a new viscosimeter was devised.

3. By means of this apparatus, the viscosities of carbon-tetrachloride, chlorobenzene and ethyl alcohol were determined above their boiling points.

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

The Institute of Physical and Chemical Research,
January, 1927. Hongo, Tokyo.

SOME NEW METALLO-ORGANIC OXONIUM SALTS.(1)

By **Taichi HARADA.**

Received June 24, 1926. Published April 28, 1927.

Introduction. Trimethyltin iodide, $(CH_3)_3SnI$, is a colorless liquid becoming brown under the action of sunlight. On withdrawing from the light the solution becomes colorless again. On renewed exposure the color again appears.

After some time small amounts of colorless crystals appear in the solution. This action was first noticed by Callis in 1922.(2)

He thought that the crystalline compound might be an iodonium salt, $((CH_3)_3Sn)_2I\text{-}I$, formed by molecular rearrangement under the action of sunlight. It was considered worth while to study the crystalline compound formed in this photo-chemical reaction. It was, therefore, decided that a more extensive investigation on this subject should be carried out.

When the compound was analysed for iodine, a value in the neighborhood of 19.5 % was obtained in place of 43.63 % as required for a compound of the iodonium type.

Analysis for tin indicated the presence of three atoms of tin per atom of iodine. It was concluded, therefore, that the formula is inapplicable.

The formula, $((CH_3)_3Sn)_2O.(CH_3)SnI, H_2O$, for the compound is proposed by the author from the following experimental facts.

Purified trimethyltin iodide did not give the appearance of any crystals. It was, therefore, thought that the crystalline compound must have been formed by the interaction of impurities which accompanied in its preparation.

An experiment, therefore, was made of a mixture of trimethyltin iodide and tetramethyltin and exposed to the sunlight and moist air. A considerable amount of crystals appeared from the solution whose properties and analysis of tin and iodine contents proved to be identical with those of

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(1) This paper incorporates partly a paper published by Kraus and Harada on the *Journal of the American Chemical Society*, 47 (1925), 2416 under the title of "Compounds formed between trimethyltin hydroxide and trimethyltin halides."

(2) Callis, Dissertation, Clark University, 1922.

the compound accidentally obtained from the impure solution by the action of sunlight.

Properties. The compound is readily soluble in water and alcohol and only slightly soluble in such organic solvents as benzene and ether.

Its aqueous solution is slightly acidic. It decomposes slowly at above 143° C. and melts at about 150° C., depending upon the rate of heating into trimethyltin iodide and trimethyltin hydroxide with a little trace of white substance.

When the aqueous solution of the compound was treated with silver hydroxide, silver iodide was precipitated. On evaporation of the clear filtrate on the water bath it did not leave any substance. However, a peculiar odour was noticed during the evaporation. The volatile substance, therefore, was collected by means of a condenser, in the form of colorless crystals.

The examination of the crystalline compound showed that it was trimethyltin hydroxide. With silver nitrate solution it readily precipitates silver iodide, but on standing or heating, the solution and the precipitate becomes dark brown. The quantitative analysis for iodine and tin conforms the following formula :(1)

$$((CH_3)_3Sn)_2O \cdot (CH_3)_3\,Sn\,I,\ H_2O. \qquad (I)$$

Sometimes lumpy crystals appeared from the solution which, perhaps, may be the same in an impure state. These were, therefore, dissolved in alcohol and heated, the solution then becoming brown and relatively strong acidic. From this solution, on cooling, colorless crystals were obtained as short needles. This compound is somewhat difficultly soluble in water and alcohol, insoluble in ether and benzene, melts and at the same time decomposes at 221° C. (incorrected). Its aqueous solutions show much stronger acidic properties than that of the first type of compound. When treated with silver nitrate, silver iodide is immediately precipitated. With silver hydroxide it precipitates silver iodide, and from the clear filtrate only trimethyltin hydroxide was again obtained in the pure state by distillation, as in the case of the first compound.

It was found that the contents of tin and iodine agrees to the following formula :(2)

$$((CH_3)_3Sn)_2O \cdot HI,\ H_2O \qquad (II)$$

If the proposed formula (I) is correct, it might be expected that the compound, $((CH_3)_3Sn)_3O$, or compounds, $((CH_3)_3Sn)_2O$ and $(CH_3)_3Sn$, in

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(1) Preparation and analytical results, see Kraus and Harada, *J. Am. Chem. Soc.*, 47 (1925), 2416.

(2) Kraus and Harada, ibid.

liquid ammonia would be obtained by treating with equivalent amount of sodium to the iodine.

Since the compound of type (I) is soluble in liquid ammonia, while the compound of type (II) such as, iodide and bromide are practically insoluble, an experiment was carried out with the iodide, $((CH_3)_3Sn)_2O-(CH_3)_3Sn\,I$, H_2O, as follows:

To one molecular proportion (4.03 gr.) of the compound in liquid ammonia solution one molecular proportion of metallic sodium (0.15 gr. by weight) was added little by little. A white precipitate was immediately formed. The solvent was evaporated at room temperature giving the reaction mixture which was washed with water, until it was free from sodium iodide and other dissolved impurities. Thus trimethyltin group, $(CH_3)_3\,Sn$, and its oxide, $((CH_3)_3\,Sn)_2\,O$, were obtained in the quantity expected. The following reaction probably has taken place:

$$[((CH_3)_3\,Sn)_3\,O]\,.\,I+Na \rightarrow [((CH_3)_3\,Sn)_3\,O] \rightarrow ((CH_3)_3\,Sn)_2\,O+(CH_3)_3\,Sn$$

Same substances were obtained from the action of the compound on trimethyltin sodium which was prepared according to Kraus and Sessions.⁽¹⁾ The reaction may have taken place as follows:

$$((CH_3)_3\,Sn)_3\,O\,.\,I+(CH_3)_3\,Sn\,Na \rightarrow ((CH_3)_3\,Sn)_2\,O+2\,(CH_3)_3\,Sn+Na\,I$$

Formations. $((CH_3)_3\,Sn)_2\,O\,.\,(CH_3)_3\,Sn\,X$, H_2O. It was found that when one molecular proportion of trimethyltin halide was treated with two molecular proportions of trimethyltin hydroxide in hot benzene solution, a crystalline compound was formed whose properties appeared to be identical with those of the compound previously obtained by the action of sunlight on impure trimethyltin halide, and on analysis gave similar results.

From trimethyltin free group: A quantity of trimethyltin group, $(CH_3)_3\,Sn$, which was obtained by either of the following reactions:

(I) $(CH_3)_3\,Sn\,OH+Na \rightarrow (CH_3)_3\,Sn+Na\,OH$

(II) $(CH_3)_3\,Sn\,X+Na \rightarrow (CH_3)_3\,Sn+Na\,X$

in liquid ammonia, was dissolved in moist benzene, along with trimethyltin halide, and this solution was subjected to oxidation in the dark. After some days crystals appeared. However, with dry benzene solution powder-like precipitate was formed, which when treated with alcoholic solution or water, became crystallized. These crystals were similar to those previously obtained.

$((CH_3)_3\,Sn)_2\,O\,.\,HX$, H_2O: When one molecular proportion of trimethyltin hydroxide or oxide was treated respectively with one molecular proportion of trimethyltin halide, under relatively hot alcoholic solution, or

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(1) *J. Am. Chem. Soc.*, 47 (1925), 2361.

of halogen acid, these compounds were formed in crystalline form. The chlorine compound such as $((CH_3)_3\,Sn)_2\,O\,.\,HCl\,,\,H_2O$ was prepared when one molecular proportion of trimethyltin hydroxide was treated with one molecular proportion of trimethyltin chloride in hot dry benzene. A heavy liquid, however, settled which readily absorbed water and immediately gave the crystalline compound. It shows, therefore, that water is necessary for the formation of all these crystalline compounds as their water of crystallization. The direct determination of the water of crystallization of these compounds was not carried out, since the compounds are slightly volatile and decomposible over dehydrating agents.

If the proposed formula (I) and (II) are correct, the compounds might be expected to dissociate according to the equations:

$$\begin{array}{llll} \text{I.} & ((CH_3)_3\,Sn)_3\,O\,.\,X & \rightleftarrows & ((CH_3)_3\,Sn)_2\,O + (CH_3)_3\,Sn\,X \\ & \text{or} & \rightleftarrows & ((CH_3)_3\,Sn)_3\,O + X \\ \text{II.} & ((CH_3)_3\,Sn)_2\,O\,.\,HX & \rightleftarrows & ((CH_3)_3\,Sn\,OH + (CH_3)_3\,Sn\,X \\ & \text{or} & \rightleftarrows & ((CH_3)_3\,Sn\,OH + (CH_3)_3\,Sn\,X \end{array}$$

Trimethyltin halides possess a high degree of hydrolysis in aqueous solutions, and trimethyltin oxide with water decomposes into the hydroxide which is a weak base.

The aqueous solution of the first type of halide is weakly acidic, because with silver hydroxide, as already described, on standing or heating becomes alkalline, owing to the formation of the base and which decomposes into trimethyltin hydroxide according to the following equation:

$$((CH_3)_3\,Sn)_2\,O\,.\,(CH_3)_3\,Sn\,I + Ag\,OH \rightarrow ((CH_3)_3\,Sn)_2\,O\,.\,(CH_3)_3\,Sn\,OH + H_2O \rightarrow 3\,(CH_3)_3\,Sn\,OH.$$

Concerning the second type of compound it may be regarded that the compound formed between one molecule of a weak base and one molecule of a strong acid is more stable than that of the first type of compound.

They conduct electric current in alcohol, water, acetone and liquid ammonia solutions while trimethyltin halide and hydroxide are poor conductors in the same solutions. Further discussion of this subject will be presented in a subsequent paper.

It, therefore, appears that the compounds in question are salts of an oxonium type.

Accordingly, the following conclusion is reached: That the formation of the compound between trimethyltin iodide and tetramethyltin taking place under sunlight may be represented by the following equation scheme:

1. $2\,(CH_3)_3\,Sn\,I \underset{\text{dark}}{\overset{\text{light}}{\rightleftarrows}} ((CH_3)_3\,Sn)_2 + I_2$
2. $((CH_3)_3\,Sn)_2 + I/2\ 0_2 \rightarrow ((CH_3)_3\,Sn)_2\,O$

On the other hand the free iodine reacts slowly with tetramethyltin as follows:

3. $I_2 + CH_3\,Sn\,(CH_3)_3 \rightarrow (CH_3)_3\,Sn\,I + CH_3\,I$

and $(CH_3)_3\,Sn\,I$ undoubtedly reacts with trimethyltin oxide to form the salt.

4. $((CH_3)_3\,Sn)_2\,O + (CH_3)_3\,Sn\,I \rightarrow ((CH_3)_3\,Sn)_2\,O\,.\,(CH_3)_3\,Sn\,I$

Summary

The formation of the compound, $((CH_3)_3\,Sn)_2\,O.\,(CH_3)_3\,Sn\,X,\,H_2O$, from trimethyltin halide by the action of sunlight in the presence of air have been studied and the mechanisms of the formation were interpreted. Identical products have been prepared by the following methods: (A) By oxidizing of trimethyltin group along with trimethyltin halide in benzene solution in the dark, and (B) by treating two molecular proportions of trimethyltin hydroxide with one molecular proportion of trimethyltin halide in hot benzene solution.

2. Compounds exhibit salt-like properties, being readily soluble in water, alcohol, acetone and liquid ammonia, and insoluble in benzene and ether. They conduct electric current appreciably in their solutions.

3. When the liquid ammonia solution is treated with an equivalent amount of metallic sodium in respect to the iodine trimethyltin oxide, $((CH_3)_3\,Sn)_2\,O$, and trimethyltin group, $(CH_3)_3\,Sn$, are produced.

4. Compounds of the type, $((CH_3)_3\,Sn)_2\,O\,.\,HX,\,H_2O$, have been prepared by treating of one molecular proportion of trimethyltin hydroxide with one molecular proportion trimethyltin halide or one molecular proportion of trimethyltin oxide with one molecular proportion of halogen acid under suitable conditions.

5. They are salt-like properties, being soluble in water and alcohol, and insoluble in nonionizing solvents such as benzene and ether.

6. Their melting points and stabilities are higher than those of the type, $((CH_3)_3\,Sn)_2\,O\,.\,(CH_3)_3\,Sn\,X,\,H_2O$.

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ETUDES DE DÉRIVÉS DU FURFURAL.

IV. DES DÉRIVÉS NITRÉS DE LA SÉRIE DU FURYLÉTHYLÈNE.

Par **Itizo KASIWAGI.**

Reçu le 8, mars 1927. Publié le 28, avril 1927.

Nous avons réussi à préparer des dérivés nitrés de la série du furyléthylène à partir du furfural d'une part et de l'autre de dérivés nitrés avec des atomes d'hydrogène rendus mobiles par l'introduction des groupes nitrés dans leurs molécules.

Les catalyseurs que l'on a employés pour cette nitration indirecte sont des bases de nature variable, agissant comme déshydratants. On peut exprimer les réactions par les formules suivantes :

$$\text{F–CHO} + \text{R}(\text{NO}_2)_n\cdot\text{CH}_3 = \text{H}_2\text{O} + \text{F–CH=CH–R}(\text{NO}_2)_n{}^{(1)}$$
$$\text{F–CHO} + \text{R–CH}_2\text{–NO}_2 = \text{H}_2\text{O} + \text{F–CH=C}(\text{R})\,\text{NO}_2$$

En résumant, on donnera ci-dessous les résultats expérimentaux avec les principaux catalyseurs :

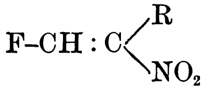
TABLE 1.

Substances soumises à la condensation avec le furfural	Catalyseurs	Dissolvant ou milieu où la réaction a eu lieu
Dinitro-2.4-toluène	Pipéridine	Sans dissolvant
Trinitro-2.4.6-toluène	Pipéridine	Sans dissolvant
Nitrométhane	Alcali caustique	Milieu aqueux
Nitrétane	Alcali caustique	Milieu aqueux
Phényl-nitrométhane	Méthylamine naissante	Sans dissolvant

Par conséquent on obtient les produits de condensation dans deux types : savoir des dérivés du furyl-polynitrophényl-ethylène

$$\text{F–CH}:\text{CH}\cdot\text{R}(\text{NO}_2)_n$$

et dérivés du furyl-nitréthylène



$$\text{F–CH}:\text{C}\begin{cases}\text{R}\\ \text{NO}_2\end{cases}$$

Ceux-ci possèdent une propriété singulière : leurs solutions alcooliques de couleur jaune assez intense, perdent leur couleur avec de l'alcali caustique, et elles la regagnent avec de l'acide minéral. Cette réaction est général pour le furylnitréthylène, le furylnitropropylène, le furyl-phényl-nitréthylène, etc.

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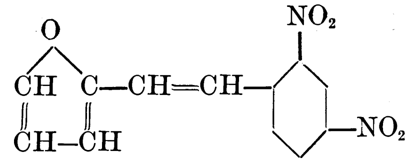
(1) F- indique le groupe furylique monovalent $\text{C}_4\text{H}_3\text{O}$-.

Partie Experimentale.

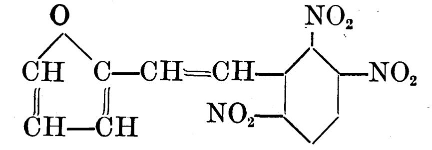


Furyl-1-dinitro-2'.4'-phényl-2-éthylène, Le dinitro-2.4-phényléthylène, dérivé phénylique correspondant, fut préparé la première fois par J. Thiele et R. Escales(1) à partir de la benzaldéhyde et le dinitrotoluène au moyen de la pipéridine, et ainsi ils montrèrent la mobilité des atomes d'hydrogène du groupe méthylé du toluène dinitré. D'après leur méthode le furfural est soumis à réagir sur le dinitro-2.4-toluène et sur le trinitro-2.4.6-toluène sous la catalyse de la pipéridine, en donnat le furyl-dinitrophényl-éthylène et le furyl-trinitrophényl-éthylène.

Voici le mode opératoire : on met dans un flacon le furfural et le toluène dinitré en proportion équimoléculaire, et on chauffe soigneusement jusqu'à 130°. Quand les deux corps fondent et se dissolvent l'un dans l'autre, on ajoute quelques gouttes de pipéridine. Après plusieurs heures de chauffage, on met de l'alcool pour dissoudre le produit de réaction. A froid une masse cristallisée se dépose, que l'on décolore avec du noir animal. (Commodément on peut abréger l'opération en ajoutant le noir animal et l'alcool à la fois).

Cette substance est cristallisée en aiguilles orangées, fondant à 135-135.5°, et soluble dans l'alcool chaud.

Analyse. Trouvé, $N=10.5, 11.1$. Calc. pour $C_{12}H_8O_6N_2$, $N=10.9\%$. Le rendement ateint à 67 pour 100.



Furyl-1-trinitro-2'.4'.6'-phényl-éthylène, A partir du furfural et du trinitro-2.4.6-toluène(2) on obtient ce corps par la même opération que le corps dinitré. Aiguilles rouges, fusible à 123-124°. Au cours de notre travail, M. Pastak a préparé ce corps, en condensant les deux substances dissoutes dans la pyridine avec de la pipéridine comme catalyseur.(3)

Il est à noter que je n'ai pas réussi à obtenir le furyl-dinitro-2-6-phényl-éthylène, en travaillant similairement, tandis que la benzaldéhyde donne le stilbène dinitré correspondant.(4)

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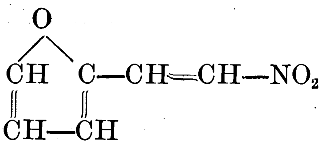
(1) Thiele et Escales, *Ber.*, 34 (1901), 2842.

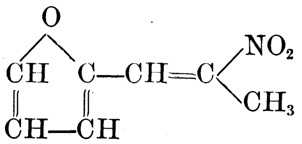
(2) C. Haussermann, *Z. angew. Chem.*, 4 (1891), 661.

(3) J. A. Pastak, *Bull. soc, chim*,, [4], 39 (1926), 75.

(4) P. Pfeiffer et J. Monath, *Ber.*, 39 (1906), 1305.



Furyl-1-nitro-2-éthylène, Ce corps a été bien étudié par de nombreux auteurs,(1) parmi lesquels Thiele et Landers nous ont donné une excellante méthode,(2) d'aprés laquelle nous avons préparé ce dérivé furyl éthylénique.

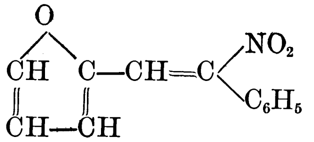


Furyl-1-nitro-2-propène-1, La méthode de Thiele et Landers(2) a été trouvée applicable avec avantage pour obtenir ce nouveau composé à partir du furfural et du nitréthane en milieu alcalin.

On dissout 2.0 gr. die nitréthane dans une solution aqueuse de potasse caustique. En ayant mis de la glace pilée, on ajoute 2.0 gr. de furfural fraîchement distillé, et on agite pendant plusieurs heures à la machine. En acidifiant avec de l'acide étendu, la solution se trouble fortement, et une substance jaune pâle cristallise rapidement. En recristallisant par l'essence de pétrole, on obtient des gros cristaux rhombiques qui fondent à 48–48.5°.

Analyse. Trouvé, N = 9.3. Calc. pour $C_7H_7O_3N$, N = 9.2%

Cette substance est très soluble dans l'alcool, l'essence de pétrole, l'acide acétique, etc. La solution dans l'acide acétique se teint en rouge brunâtre avec de l'aniline, mais la coloration est beaucoup moins intense que celle de la solution correspondante de furfural qui est formée avec de l'aniline en présence d'acide acétique.



Furyl-1-phényl-2-nitro-2-éthylène, Il semble que le meilleur catalyseur soit la méthylamine pour condenser le furfural et le phénylnitrométhane.

Nous avons préparé ce corps d'après Knoevenagel et Walter.(3) Le phénylnitrométhane (1.4 gr.), le furfural (1.0 gr.), le chlorure de méthylammonium (0.1 gr.) et un peu de carbonate de sodium sont introduits dans un petit flacon. Abandonnés à froid, on voit dans trois jours se former des cristaux jaunes et séparation d'eau. On met ce mélange dans une glacière.

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(1) Priebs, *Ber.*, 18 (1885) 1362; Bouveault et Wahl, *Compt. rend.*, 135 (1902), 41.

(2) Thiele et Landers, *Ann.*, 369 (1909), 303.

(3) Knoevenagel et Walter, *Ber.*, 37 (1904) 4502.

Au bout d'une semaine le mélange se cristallise prèsque totalement. Après une semaine encore on place les cristaux sur une plaque poreuse. Le poids obtenu est de 2 gr. et son point de fusion est 81.5–84°. Celui du corps cristallisé dans l'alcool est 87–87.5°. Lames minces jaunes.

Analyse. Trouvé, $N=6.9$. Calc. pour $C_{12}H_9O_3N$, $N=6.5\%$

Cette substance est soluble dans l'alcool chaud. Sa solution alcoolique a une propriété singulière, comme décrite haut. De jaune clair elle devient incolore avec de l'alcali caustique, et elle regagne sa couleur originale avec de l'acide. Cette réaction est génerale pour les dérivés nitrés de la chaine latérale.

Haute Ecole Polytéchnique de Yokohama.

A SIMPLE PROCEDURE OF SEMI-QUANTITATIVE SPECTRAL ANALYSIS OF CALCIUM, STRONTIUM, BARIUM AND LITHIUM.

By Kunizô HUKUDA.

Received December 25, 1926. Published May 28, 1927.

In the course of a research on the permeability of the frog-skin, it occurred to me to analyse very dilute solutions of alkali and alkali-earth metals. In this case, I applied the spectral analysis introducing some improvements in its practical procedure, which enabled me to perform the semi-quantitative analysis, and the results thus obtained were accurate enough for the purpose of biochemical studies. On account of the simplicity of the method, which may be carried out even in a laboratory not equipped with modern spectroscopical instruments, I believe, it is worth describing.

Apparatus Employed. An induction coil which can discharge through the maximum spark gap of 3.5 cm. is connected to a fulgurator, the positive pole of which comes from the bottom of the vessel containing the solution to be tested, and its point protrudes slightly above the liquid surface. The distance between the poles is adjusted to be 1–2 mm., whichever gives the best result. In the primary circuit of the induction coil stands a battery, as well as a reversing key (Fig. 1).

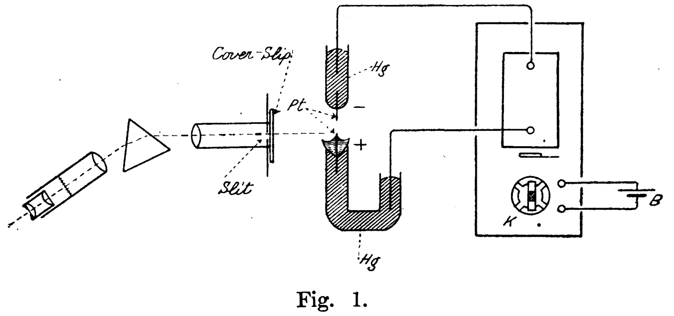

Fig. 1.

By this arrangement, in which the poles are reversed(1) to the usually adopted system, the spark is highly luminous at the anode and the spectral

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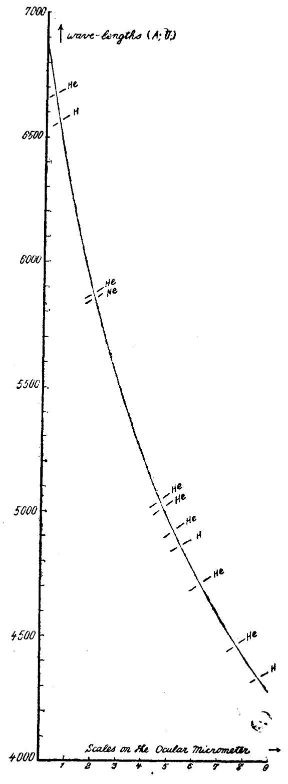
(1) This process differs from the well-known "procédé du spectre de renversement" after Lecoq de Boisbaudran in the respect, that in that classical method the solution itself serves as the anode, and it is the luminesced part of the solution that is observed spectroscopically.

lines thus observed, in directing carefully the collimator of the spectroscope towards the point of the anode, are quite specific to the metal in the solution, accompanied by a number of non-specific lines. The spectroscope employed was an ordinary prism spectroscope of low dispersion, D_1 and D_2 lines of sodium being just possibly resolved.



F ig. 2.

The Determination of the Wave-lengths. As the standards of the wave-lengths of spectral lines, some neon-, helium- and hydrogen- lines were used; these spectral lines of known wave-lengths[1] were observed through an eye-piece provided with an ocular micrometer on its focal plane, in adjusting the direction of the telescope such that the yellow line of neon (5852.4 Å) comes just upon the scale division 2.00 (Fig. 2), and a curve which represents the relation between the wave-lengths (ordinates) and the micrometer scales (abscissae) was drawn. By the aid of the ocular micrometer and this reference curve, the wave-length of any unknown line is easily determined approximately.

As we are dealing with the spark spectrum across air between the platinum electrodes, it is expected that the lines due to air and platinum present themselves constantly as non-specific lines. Care must be taken, therefore, not to confuse them with those to be identified in the practise of analysis. The most marked of them are,

Colour	λ observed.	λ identified.(2)	Probable source
Green	5685	5686, -80	N
Green	5008	5001, -05,-07,-11	N
Blue	4862	4854	Pt
Blue	4712	4705, -10	O(?)
Blue	4660	4662	O(?)
Blue	4650	{4642, -51 {4643, -55	O(?) N
Blue	4484	4478	N

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(1) Baly, "Spectroscopy." 3rd ed., Vol. I, p. 126 (1924).

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

Furthermore, in the fulgurator filled with a solution, there always appears a red line, $\lambda = 6563$ due to hydrogen, even when filled with distilled water; and it is also quite difficult to suppress the appearance of the D-doublet lines, because of their very high sensibility.

For the determination of wave-lengths of those spectral lines that are situated in the red to yellow region, another simple method is applicable. The fulgurator, namely, is put close in front of the slit of the collimator, which is protected by a micro cover-slip from being soiled; and a neon lamp ("Glimlamp") stands behind the fulgurator. By such an arrangement any metallic line in this region, which is to be identified, may be found between two neon lines with known wave-lengths. We estimate by interpolation how far the line in question is located from one of the neon lines, say that having a shorter wave-length, and we can thus easily calculate the approximate wave-length of the metallic line.

In relation to this it may be worth remarking here that the "Glimlamp" gives 21 neon lines to the left of the yellow line ($\lambda=5852.4$)(1) inclusive, two of which—the one $\lambda=5364.9$ and the other probably composed of $\lambda=5606.4$ and $\lambda=5602.4$, but fused together owing to the low resolving power of our apparatus—are not found listed in some current text-books, while the line $\lambda=7032.4$ was not visible to the author.

Identification of the Specific Lines. By either of the two methods above mentioned, the wave-lengths of spectral lines of several metals produced by our reversed pole procedure are determined and thus identified, taking the Kayser's table(2) or Eder and Valenta's atlas(3) as reference. The results are given below:

LiCl, 1/750 M. Two lines are to be observed: an orange line is found between two neon lines, $\lambda=6143$ and $\lambda=6096$, while a red line is situated just resolvably close to the neon line $\lambda=6717$. Thus the estimated and identified wave-lengths of these red and orange lines are as follows:

Colour	λ estim.	λ ident.
Red	6712	6708
Orange	6101	6104

LiCl, 0.11 M. In this case also two and no more lines came to sight. They are, as identified by the reference curve,

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(1) Baly, loc. cit., p. 37 (1924).

(2) Kayser, loc. cit.

(3) Eder u. Valenta, "Atlas typischer Spectren," (1911).

Colour	λ estim.	λ ident.
Red	6715	6708
Orange	6100	6104

KCl, 1/750 M. No lines characteristic to this metal were observed, although persisting lines are expected at $\lambda=4047$ and $\lambda=4044$.

RbCl, 1/750 M. and *CsCl,* 1/750 M. In both cases, no specific lines bright enough to be utilised for our purpose, were detected.

$MgCl_2$, 1/750 M. Three lines of greenish blue colour were observed. They are so highly characteristic in their arrangement that we can recognise them at the first glance. The determination of their wave-lengths gave the following results.

Colour	λ estim.	λ ident.
Greenish blue	5177	5184.
„	5170	5173
„	5166	5167

$BaCl_2$, 1/750 M. The following six lines were observed:

Colour and intensity	Position compared with Ne-lines
Red	Almost superposing on the line 6506.5
Bright orange	„ 6143.0
Pale yellow	„ 5852.4
Brilliant green	——
Brilliant blue	——
Brilliant indigo	——

Besides these lines, no bands were detected. The character of the barium spectrum obtained by this method shows thus more resemblance to its spark spectrum than to the flame spectrum.

$BaCl_2$, 0.09 M. In this concentration, barium chloride solution, if in a favourable condition, gives a number of distinct lines, the wave-lengths of which were determined as follows:

Colour	λ estim.	λ ident.
Red	6595	6595
»	6505	6499,-97
Orange	6137	6142
Striated in the orange region	6105	6111
	6060	6063
	6007	6019
	5993	5997
	5965	5972
Striated in the yellow region	5848	5854
	5828	5826
	5779	5778
Green	5537	5536
Blue	4935	4934
»	4920	4900,-03 (?)
Indigo	4556	4554

$SrCl_2$, 1/750 M. In this dilution, only few lines and bands were observed, namely two (sometimes more) weak green lines, two or more blue lines and one intense indigo line. Besides these lines, a striated red band and a distinct narrow orange band were visible.

$SrCl_2$, 0.1 M. The following numerous lines and bands were observed:

Colour and character	λ estim.	λ ident.
Red band	6880–6770	Band No. 1.
" "	6745–6640	" No. 2.
" "	6630–6555	" No. 3.
Red line	6460	6464,-66
Red band	6460–6420	Band No. 4.
Red line	6350	6346
Red band	6350–6310	Band No. 5.
Red line	6240	6229
Red band	6240–6207	Band No. 6.
" "	6105–6015	Band No. 7.
Orange-red line	6055	6059
Orange band	5975–5936	5970,-5940
Green line	5537	5543
" "	5518	5522
" "	5503	5504
" "	5476	5481
Blue line	5259	5259
" "	5237	5239
" "	5226	5230,-22
" "	4956	4962
" "	4871	4876,-72
" "	4831	4832
" "	4813	4812
" "	4793	4784
" "	4747	4742
" "	4723	4722
Indigo line	4612	4608
Violet line	—	4306
" "	—	4216

$CaCl_2$, 1/750 M. The following lines and bands were detectable:

Colour and character	Intensity
Orange-red line	Very weak, often invisible when the lamp is lighted.
Green line	
Red to orange band	Quite intense.
Narrow green band	

$CaCl_2$, 0.1 M. The wave-lengths of the following lines and bands were determined:

Colour and character	λ estim.	λ ident.
Red band	6525–6363	
Intense red band	6310–6157	
Lines in the intense red band	6250 6202 6180	6265 6202 6180
Orange line	5938	5933
Orange band	6155–5890	
Green band	5576–5493	
Lines in the green band	5559 5520	5543 5517

Accuracy and Limit of Application of this Method. In order that this spectroscopical method may be utilised for the semi-quantitative analysis of certain metals from salt solutions, its accuracy should be determined beforehand with solutions containing the salts in various known dilutions. And it is recommended to list the results in reference tables characterising the arrangement and apparatus made use of by each worker. In the author's own case, it proved as shown in the following tables, in which the degrees of brightness of the lines and bands are marked with – (invisible), ± (hardly visible), + (visible), + + (bright) and + + + (brilliant). The results obtained with lithium, barium, strontium and calcium were satisfactory:

Colour and wave-length	Relative concentration (1 = 1/750 M.)					
	0.025	0.05	0.1	0.25	0.5	1
Lithium chloride:						
Red, 6708	–	±	+	+	+ +	+ +
Orange, 6104	–	–	±	+	+	+ +
Barium chloride:						
Red, 6499–7	–	–	–	–	+	+
Orange, 6142	–	–	±	+	+	+ +
Yellow, 5854	–	–	–	–	–	+
Green, 5536	–	–	+	+	+ +	+ + +
Blue, 4934	–	–	+	+	+ +	+ + +
Violet, 4554	–	–	–	–	+	+ +
Strontium chloride:						
Red bands	–	–	±	+	+	+ +
Orange band	–	–	–	±	+	+ +
Green lines	–	–	–	–	±	±
Blue lines	–	–	–	–	±	±
Indigo, 4608	–	–	±	+	+ +	+ + +
Violet, 4306	–	–	–	+	+ +	+ + +
Violet, 4216	–	–	–	+	+ +	+ + +

Colour and wave-length	Relative concentration (1 = 1/750 M.)					
	0.025	0.05	0.1	0.25	0.5	1
Calcium chloride:						
Intense red band	−	−	−	+	+	++
Orange band	−	−	±	+	+	++
Green band	−	−	−	±	+	+

The probable limits of detection of Ca, Sr and Ba by this method, calculated in terms of mg. of the metals in 1 c.c. of solution and compared with those of Bunsen's classical method as well as of Riesenfeld and Pützer's process, are shown below:

	Bunsen's flame analysis.	Riesenfeld & Pützer.	Present author.
Ca	0.2 mg in 1 c.c.	0.002	0.013
Sr	0.6 "	0.03	0.029
Ba	14 "	0.006	0.018
Li	—		0.0009

According to the description of Riesenfeld and Pfützer,(1) their method, which is often quoted as a process representing the highest sensibility attainable by the spectral analysis, requires at least about 1 c.c. of the solution to be tested, while in the present procedure, only 0.1 c.c. or even a smaller quantity of solution is sufficient to carry out one test, owing to the small capacity of the fulgurator-vessel.

Summary.

1. A simple procedure of the semi-quantitative spectral analysis has been described.

2. This procedure consists in observing salt solutions fulgurated in a special fulgurator, with the electrodes reversed, i. e. the anode in the solution.

3. Accuracy and limit of application of this method were carefully studied and it was found that this is especially suited for the analysis of minute quantities of lithium, calcium, strontium and barium.

In carrying out this study, the author owes much to the suggestion and encouragement of Prof. Hashida and Prof. Nagai, as well as to the kind interest and care taken by Prof. Y. Shibata of the Faculty of Science of this University. Sincere thanks are also expressed here to the friendship of Dr. Shinki of the Military Institute for Scientific Research.

Physiological Institute, Faculty of Medicine,
Tokyo Imperial University.

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(1) Riesenfeld and Pfützer, *Ber.*, 46 (1913), 3140.

DAS SPEZIFISCHE GEWICHT WÄSSRIGER BLAUSÄURE.

Von **Manjiro SHIRADO.**

Eingegangen am 15. Februar 1927. Ausgegeben am 28. Mai 1927.

Das spezifische Gewicht wässriger Blausäure von 1 bis 16% HCN bei 15.56°C. hat bereits Ure⁽¹⁾ gemessen, kürzlich haben Walker und Marvin⁽²⁾ eine interessante und mühevolle Arbeit veröffentlicht, weiter haben Gay-Lussac⁽³⁾, Bleekrode⁽⁴⁾, Meyer-Hopf⁽⁵⁾ und Enklaar⁽⁶⁾ das spezifische Gewicht reiner Blausäure gemessen. Aber das spezifische Gewicht von 0 bis 100 % -ige Blausäure bei bestimmter Temperatur ist noch unbekannt. Wir mussten das spezifische Gewicht wässriger Blausäure messen.

Die wässriger und wasserfreier Blausäure aus chemische reines Ferrocyankalium und Phosphorsäure dargestellt (vgl. M. Shirado, diese Zeitschrift, 2 (1927), 85).

Das spezifische Gewicht wässriger Blausäure haben wir mit einem Kugelförmigen Pyknometer⁽⁷⁾ gemessen; sein Inhalt ist ca. 25 c.c. Die zu messende Lösung wurde ungefähr 10–15 Minuten in den Thermostaten von 18.0°C. gehängt, dann in das Pyknometer mittels Pipette möglichst schnell eingefüllt und der eingeschliffene Stopfen, der ein Thermometer trug, eingesteckt. Das Pyknometer stand dabei in einem Gefäss, das mit Wasser von 18.0°C. gefüllt war. In diesem Gefäss wurde das Pyknometer in das Wägezimmer getragen, gut getrocknet und schnell gewogen. Die Messung 100 % -iger Blausäure bei 18.0°C. war äusserst schwer; entweder kamen einigen Blasen in den Hals des Pyknometers oder einige Tropfen der Blausäure spritzten aus dem Kapillarrohr heraus, da ja der Siedepunkt reiner Blausäure bei 25.7°C. liegt. Aber nach einiger Erfahrung konnten diese Schwierigkeiten überwunden werden durch möglichst schnelles Füllen und schnelles Abwiegen.

Folgende Tabelle enthält die Ergebnisse der Messung. Fig. 1. zeigt die Abhängigkeit des spez. Gewichtes von der Konzentration.

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(1) „Chemiker Kalender," II, S. 275 (1926).
(2) M. Walker und C.J. Marvin, *Ind. Fng. Chem.*, 18 (1926), 139.
(3) Gay-Lussac, *Ann. chim.*, [1] 95 (1815), 145.
(4) Bleekrode, *Jahresbericht über die Fortschritte der Chemie,* 1884, S. 284.
(5) K.H. Meyer und H. Hopf, *Ber.*, 54 (1921), 1712.
(6) C.J. Enklaar, *Rec. trav. chim.*, 42 (1923), 1006.
(7) Vergl. Stähler, „Handbuch d. Arbeitsmethoden" III (1), S. 40, Fig. 6, Form 3.

Tabelle 1.

Spezifisches Gewicht wässriger Blausäure(1) bei 18.0°C.

Gewichtsprozent	Spez. Gewicht $\left(\frac{18^\circ}{18^\circ}\right)$	Spez. Gewicht $\left(\frac{18^\circ}{4^\circ}\right)$	
		In der Luft.	Reduzierte Werte auf den leeren Raum.
5.052 %	0.9927	0.9914	0.9914
9.770	0.9841	0.9827	0.9828
10.04	0.9838	0.9824	0.9825
14.58	0.9732	0.9718	0.9719
19.70	0.9593	0.9579	0.9580
20.29	0.9578	0.9565	0.9565
26.90	0.9376	0.9363	0.9364
33.01	0.9167	0.9154	0.9155
39.26	0.8987	0.8975	0.8976
46.01	0.8757	0.8745	0.8747
47.68	0.8658	0.8646	0.8648
52.00	0.8518	0.8506	0.8508
55.37	0.8428	0.8416	0.8418
60.23	0.8290	0.8279	0.8281
60.76	0.8270	0.8259	0.8261
69.50	0.7953	0.7942	0.7945
70.93	0.7925	0.7914	0.7917
79.54	0.7598	0.7587	0.7590
80.18	0.7582	0.7572	0.7574
88.55	0.7289	0.7279	0.7282
89.64	0.7265	0.7255	0.7258
100.00	0.6919	0.6909	0.6913

Zwischen 27 % und 100 % HCN-Gehalt ist die Abhängigkeit des spezifische Gewichts von der Konzentration annähernd linear; unterhalb 27 % biegt die Kurve merklich ab.

Die Punkte, die Walker und Marvin bei 18°C. gefunden haben, liegen alle genau auf der von uns gefundenen Kurve (siehe Fig. 1). Das spezifische Gewicht reiner Blausäure hat Gay-Lussac bei 18°C. zu 0.6969 gefunden, während wir bei 18.0°C. in der Luft $D^{18.0}_{18.0} = 0.6919$ und $D^{18.0}_{4} = 0.6909$ ge-

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(1) Die Blausäure enthielt zwecks Conservierung eine Spur Phosphorsäure. Eine Überschlagsrechnung ergab, dass die zugesetzte wässrige Phosphorsäure (spez. Gew., 1.7) bei 100 % Blausäure den 1/1220 Teil ihres Gewichtes ausmachte, was höchstens das spez. Gewicht der 100 % Blausäure schätzungsweise um 5 Einheiten der 4. Decimale und bei verdünnten Blausäure proportional um weniger vermehrt hat. Wir haben dafür keine Korrektion an die beobachteten Werte angebracht.

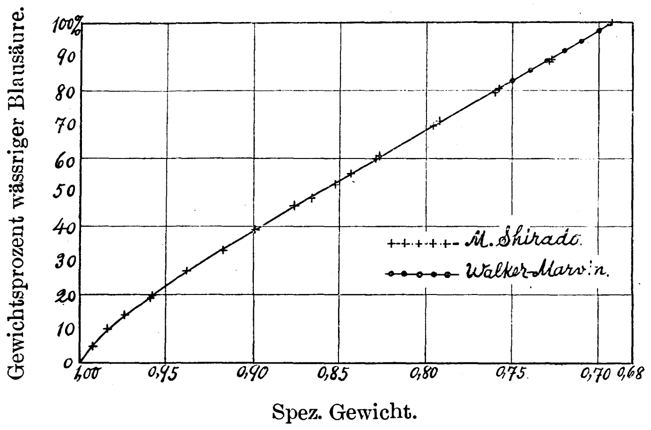

Fig. 1.

funden haben und die reduzierten Werte auf den leeren Raum $D_4^{18.0} = 0.6913$ berechnet haben. Es ist interessant zu erwähnen, dass Walker und Marvin bei 18°C. 0.693 für 99.8 % -ige Blausäure gefunden haben⁽¹⁾ und dass durch Extrapolieren ihrer Werte auf 100 % -ige Blausäure sich 0.692 ergibt. Dieses Resultat stimmt überein mit unseren Werten. Enklaar⁽²⁾ hat $D_4^{16.4} = 0.6936$ mit einem Temperaturkoeffizienten von 0.0013 gefunden. Aus diesem Werte wird $D_4^{18.0} = 0.6915$ erhalten, während wir aus $D_{18.0}^{18.0}$ den Wert $D_4^{18.0} = 0.6913$ berechnen. Dieses Resultat stimmt gut überein mit unseren Werten.

August 1926.

Physik. Chem. Institute der Technische Hochschule,
Karlsruhe i. B., Deutschland.

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(1) M. Walker und C.J. Marvin, loc. cit., 18 (1926), 140.

(2) C.J. Enklaar, loc. cit.

THE ACTIVITY OF PHENOL IN AQUEOUS SALT SOLUTIONS(3)

By Kwantaro ENDO.

Received March 2, 1927. Published May 28, 1927.

The fact, that the solubility of non-electrolytes is lowered by the presence of neutral salts, is well known(4) under the term "salt action" or "salting out." For the study of this problem, partition experiments are

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(3) Read before the Chemical Society of Japan, February, 1925.

(4) Rothmund, "Löslichkeit."

often made. In my previous work(1) the molecular states of phenol in benzene and in water were determined by the partition experiments. In the present paper the studies of salt action on phenol will be described.

Partition of Phenol between Benzene and Aqueous Solutions of Neutral Salts. The measurements were carried out at 25°C. in the same manner as described in the previous paper. All the salt used were purifed by recrystallisation. The results are shown in the following tables, where B and C represent the molar concentrations of phenol in the benzene and in the aqueous layer respectively, while S represents the moler concentration of the added salt.

TABLE 1.

Salt	Conc. of salt. mols (S)	Liquids. B=Benzene layer. C=Water layer.	Conc. of phenol. mols.				
NaCl	2.0	B	1.5142	0.7590	0.4383	0.2052	—
		C	0.1282	0.0912	0.0656	0.0379	—
	1.0	B	1.4573	0.7187	0.4126	0.1913	—
		C	0.1851	0.1316	0.0913	0.0518	—
	0.5	B	1.4180	0.6946	0.3948	0.1839	—
		C	0.2244	0.1557	0.1091	0.0593	—
NaBr	2.589	B	0.9316	0.6444	0.4186	—	—
		C	0.0883	0.0738	0.0562	—	—
	1.2945	B	0.8842	0.6077	0.3916	0.1937	—
		C	0.1357	0.1106	0.0832	0.0498	—
	0.6472	B	0.8513	0.5825	0.3734	—	—
		C	0.1686	0.1357	0.1014	—	—
$NaNO_3$	3.0	B	1.1931	0.9045	0.6256	0.2872	0.1399
		C	0.1159	0.1023	0.0827	0.0484	0.0280
	2.0	B	1.1583	0.8756	0.6029	0.2757	0.1334
		C	0.1507	0.1313	0.1050	0.0599	0.0344
	1.0	B	1.0911	0.8205	0.5757	0.2604	0.1257
		C	0.1902	0.1651	0.1326	0.0752	0.0421
	0.5	B	1.0697	0.8025	0.5614	0.2519	0.1225
		C	0.2117	0.1830	0.1469	0.0837	0.0453
	0.25	B	1.0559	0.7907	0.5535	0.2437	0.1198
		C	0.2251	0.1949	0.1547	0.0882	0.0481
Na_2SO_4	1.007	B	1.3138	0.8178	0.6493	0.3419	—
		C	0.1008	0.0820	0.0689	0.0458	—
	0.5166	B	1.1606	0.6111	0.3193	—	—
		C	0.1505	0.1071	0.0684	—	—
	0.2583	B	1.1210	0.5851	0.3812	0.1380	—
		C	0.1901	0.1331	0.1004	0.0451	—
	0.1292	B	1.0978	0.5698	0.3705	0.1342	—
		C	0.2133	0.1484	0.1112	0.0489	—

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(1) K. Endo, this journal, **1** (1926), 25.

Salt	Conc. of salt. mols.	Liquids. B=Benzene layer. C=Water layer.	Conc. of phenol. mols.				
KCl	2.0990	B	1.4956	0.7445	0.4302	0.2012	—
		C	0.1468	0.1058	0.0771	0.0419	—
	0.9917	B	1.4399	0.7083	0.4043	0.1887	—
		C	0.2025	0.1420	0.0996	0.0544	—
KBr	2.3533	B	0.8331	0.5215	0.2767	—	—
		C	0.1165	0.0885	0.0568	—	—
	1.1766	B	0.7978	0.4957	0.2597	—	—
		C	0.1518	0.1143	0.0738	—	—
	0.5883	B	0.8372	0.5726	0.3667	0.1804	—
		C	0.1827	0.1457	0.1081	0.0630	—
KNO_3	2.0007	B	1.4505	0.7159	0.4094	0.1910	—
		C	0.1919	0.1344	0.0945	0.0521	—
	0.9989	B	1.4127	0.6897	0.3927	0.1828	—
		C	0.2297	0.1606	0.1112	0.0603	—
K_2SO_4	0.50305	B	1.1489	0.6033	0.3951	0.1442	—
		C	0.1622	0.1149	0.0866	0.0389	—
	0.25136	B	1.2083	0.7396	0.3774	0.1369	—
		C	0.2063	0.1601	0.1043	0.0462	—

The data for NaCl in Table 1 are shown graphically in Fig. 1, which represents three B–C curves (namely $S=2$, $S=1$ and $S=0.5$), in comparison with the theoretical curve of $S=0$ drawn according to the equation(1)

$$B = 2.272C_0 + 37.71C_0^3$$

where C_0 denotes the molar concentration of phenol in the aqueous layer without any salt. As we see in the figure, all the B–C curves deviate leftward from the theoretical curve of $S=0$ and the deviation increases with the amount of the salt added. Obviously this shows the decrease of phenol concentration in the aqueous layer and the increase in the benzene layer by the addition of sodium chloride, that is, salting out. The degree of salting out increases with the increase of the salt concentration. The same can be stated as to other salts. Curves are here omitted.

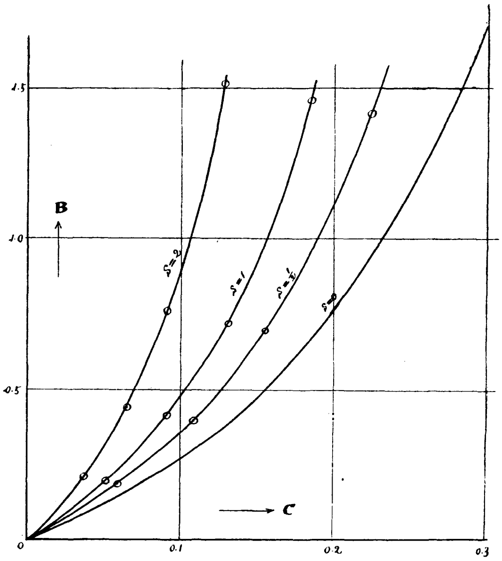

Fig. 1.

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(1) Endo, loc. cit.

Thorne⁽¹⁾, studying the solubility of ether in the aqueous solution of sodium chloride, confirmed that the oldest empirical law of Setschenow is valid in his case, namely,

$$\frac{1}{S}\log\frac{\eta_0}{\eta} = k \quad \text{or} \quad \eta = \eta_0 e^{-kS},$$

where η_0 and η denote the solubilities of non-electrolytes in pure water and in aqueous salt solutions respectively, while k is a constant.

Now in the present case, I have also found this logarithmic formula quite valid. For example the case of sodium chloride is shown in Table 2, where the calculations were made with regard to the three horizontal lines (namely $B=1.0$, $B=0.7$ and $B=0.4$) in Fig. 1.

TABLE 2.

S	C	$\log C$	$\log C_0 - \log C$	$\frac{1}{S}\log\frac{C_0}{C}=\beta$
$B=1.0$				
0	$0.2320=C_0$	$\bar{1}.3655$	—	—
0.5	0.1905	$\bar{1}.2799$	0.0856	0.1712
1.0	0.1570	$\bar{1}.1959$	0.1696	0.1696
2.0	0.1060	$\bar{1}.0253$	0.3402	0.1701
$B=0.7$				
0	$0.1913=C_0$	$\bar{1}.2817$	—	—
0.5	0.1560	$\bar{1}.1931$	0.0886	0.1772
1.0	0.1290	$\bar{1}.1106$	0.1711	0.1711
2.0	0.0870	$\bar{2}.9395$	0.3422	0.1711
$B=0.4$				
0	$0.1345=C_0$	$\bar{1}.1287$	—	—
0.5	0.1100	$\bar{1}.0414$	0.0873	0.1746
1.0	0.0895	$\bar{2}.9518$	0.1769	0.1769
2.0	0.0612	$\bar{2}.7867$	0.3420	0.1710
mean $\beta=0.172$				

Thus the constancy of β is satisfactory. Similarly the values of β for other salts are constant. They are shown in Table 3, where their differences are also indicated.

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(1) Thorne, *J. Chem. Soc.*, **119** (1921), 262.

TABLE 3.

The values of β and their differences.

Anions / Cations	Cl'	Cl'-NO_3'	NO_3'	Br'-NO_3'	Br'	$\frac{1}{2}SO_4''$-Br'	$\frac{1}{2}SO_4''$
$Na^{\cdot}$	0.172	0.059	0.113	0.042	0.155	0.055	0.210
$Na^{\cdot}$-$K^{\cdot}$	0.039	—	0.033	—	0.044	—	0.030
$K^{\cdot}$	0.133	0.053	0.080	0.031	0.111	0.069	0.180

We see in this table that β is an additive property.

Next we will consider the thermodynamical meanig of this law. Let X represent the chemical potential of phenol in the aqueous salt solution and Z be that quantity for unit concentration. Then

$$X = Z + RT \ln C$$

where T denotes the absolute temperature and R is the gas constant. If these corresponding quantities in the absence of salt are indicated by suffix 0, then

$$X_0 = Z_0 + RT \ln C_0.$$

Along a horizontal line in Fig. 1,

$$X = X_0 = \text{constant},$$

therefore

$$Z - Z_0 = RT(\ln C_0 - \ln C) = RT \ln \frac{C_0}{C}$$

From the above observation

$$\frac{1}{S} \log \frac{C_0}{C} = \beta \quad \text{or} \quad \frac{1}{S} \ln \frac{C_0}{C} = 2.303\, \beta.$$

Hence

$$\frac{Z - Z_0}{S} = a.$$

where $a = 2.303\, \beta RT$, which is constant for a constant temperature.

Thus the elevation of the chemical potential of phenol for unit concentration by the addition of a neutral salt is proportional to the salt concentration.

Now we can obtain the equation of B–C curves in Fig. 1. As indicated already,

$$B = 2.272\, C_0 + 37.71\, C_0^3,$$

while

$$\log \frac{C_0}{C} = \beta S \quad \text{or} \quad C_0 = 10^{\beta S} C.$$

Therefore

$$B = 2.272 \times 10^{\beta S} C + 37.71 \times 10^{3\beta S} C^3 \quad \cdots\cdots\cdots\cdots\cdots\cdots (1)$$

This equation (1) is found quite valid. For example, the case of $NaNO_3$ is shown in Fig. 2, where the curves have been drawn according to the equation (1) and the observed points are denoted by circlets.

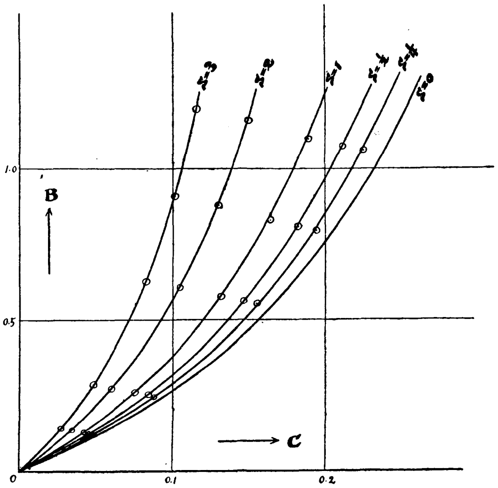

Fig. 2.

The Effect of Sodium Nitrate on the Depression of Freezing Point of Aqueous Phenol Solution. In the first place, the measurements on the depression of freezing point of the aqueous solution of sodium nitrate alone were made in the same manner as described in my previous paper, although on this same topic there are sevaral previous reports of experiments which are sometimes not accurate. The results are shown in Table 4, whereafter the molar concentrations are calculeted in mol per 1000 grams of water.

TABLE 4.

Depression of freezing point of the aqueous solution of $NaNO_3$.

Water gr.	$NaNO_3$ gr.	Molar concentrations of $NaNO_3$ S	Depressions of freez. pt. by $NaNO_3$ in degree. D_S.
499.4	2.3105	0.0542	0.189
499.4	4.6406	0.1093	0.373
499.4	8.5151	0.2006	0.670

In the next place, the cryoscopic measurements of the aqueous solution of both phenol and sodium nitrate were made, the result of which are shown in Table 5.

TABLE 5.

Depression of freezing point when both phenol and $NaNO_3$ are simultaneously dissolved in water.

Water gr.	Phenol gr.	Molar conc. of phenol (C)	$NaNO_3$ gr.	Molar conc. of $NaNO_3$ (S)	Depression of freez. pt. in degree. D_{P+S}
499.5	10.198	0.217	0.	0.	$0.388 = D_P$
499.5	10.198	0.217	3.7495	0.0883	0.695
499.5	10.198	0.217	6.9650	0.1640	0.952
499.5	10.198	0.217	9.9715	0.2348	1.185

Subtracting the depression of phenol alone (D_P), from that by the combination of the two solutes (D_{P+S}) in Table 5, the depression apparently due to sodium nitrate is obtained as shown in Table 6, provided that the depression is the additive property of solutes.

TABLE 6.

Portions of depression apparently due to $NaNO_3$ when $C=0.217$.

S	$D_{P+S}-D_P$
0	0
0.0883	0.307
0.1640	0.564
0.2348	0.794

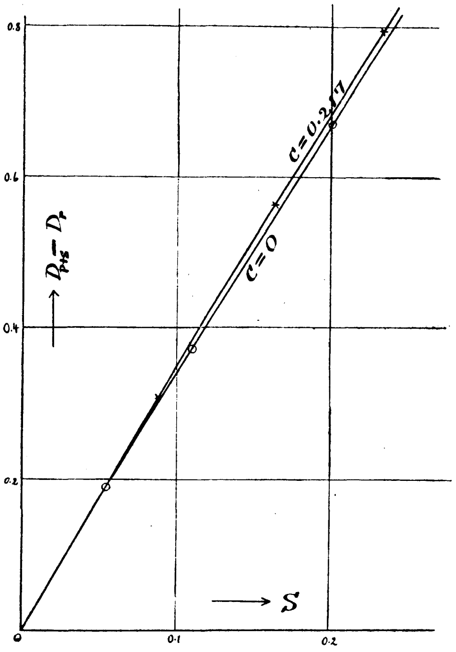

Fig. 3.

These depressions in Table 6 and those in Table 5, which are really due to sodium nitrate, are compared graphically in Fig. 3.

If the additivity holds in this case as assumed, the two curves must coincide, but we see a small discrepancy in the concentrated part. In the first section of this paper, I reached the conclusion that the chemical potential of phenol can be expressed in the following formula,

$$X = Z_0 + aS + RT\ln C$$

or

$$X = Z_0 + RT\ln\left(e^{\frac{a}{TR}S}C\right).$$

Now, as $e^{\frac{a}{RT}S}$ is so-called "activity coefficient," the activity of phenol and consequently, the depression of freezing point due to phenol must increase when a salt is added (that is, $S>0$). And so the above discrepancy of the curves should become perceptible when S is sufficiently great. Actually the curve $C=0.217$ deviates upwards from the curve $C=0$ and the deviation gradually increases with the concentration of sodium nitrate. Therefore, Fig. 3 offers a qualitative proof for the above equation obtained from the study of partition.

However, when the concentration of salt is small, owing to the small value of $\frac{a}{RT}$, the activity coefficient is nearly equal to unity and the effect of salt is negligible. That is why we cannot perceive the discrepancy at the dilute part in Fig. 3.

Summary.

1. From the measurements on the partition of phenol between benzene and the aqueous solutions of neutral salts, it has been found that the following logarithmic law practically holds,

$$\frac{1}{S} \log \frac{C_0}{C} = \beta$$

Applying this to the equation of the chemical potential of phenol it becomes

$$\frac{Z-Z_0}{S} = a.$$

We have also obtained an equation of phenol distribution between benzene and water in the presence of neutral salts at 25°C :

$$B = 2.272 \times 10^{\beta S}C + 37.71 \times 10^{3\beta S}C^3.$$

2. From the measurements of the freezing points of the aqueous phenol solutions in the presence of a neutral salt, it has qualitatively been proved that the chemical potential of phenol can be expressed in the following formula,

$$X = Z_0 + aS + RT \ln C$$

and the activity coefficient of phenol is, therefore, to be expressed as

$$e^{\frac{a}{RT}S}.$$

The author's thanks are due to Prof. K. Ikeda for his kind guidance in the present investigation.

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THE DENSITIES OF MAGNESIUM AT ITS MELTING POINT.

By Hikozô ENDO.

Received March 30, 1927. Published May 28, 1927.

Introduction. Most of the well-defined properties of elements change periodically when they are arranged in order of their atomic weight, for example, atomic volume, specific gravity, melting point, magnetic susceptibility, electric and thermal conductivities, compressibility, arc spectra etc.

When the numerical values are plotted against the atomic weights, the curve obtained is broken up into periods, the shape of period varying according to the property tabulated.

The present writer⁽¹⁾ also stated the periodicity of the change of volume of elements on melting to their atomic weights as illustrated in Fig. 1.

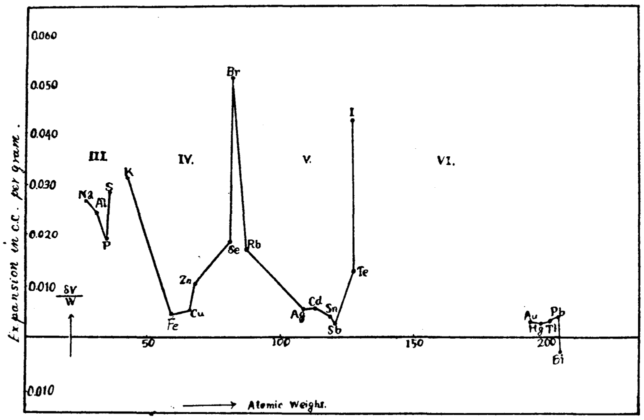

Fig. 1.

The first period in the curve corresponds to the third series of the Mendelejeff's periodic table. A complete short period contains eight elements and a complete long period, eighteen, which are made up of series connected by a transition groups of three elements. Within any one period, whether short or long, there is no sudden change in chemical and physical properties in general as we pass from one element to the next in order. But when we pass from one period to the next, there is a sudden change in the properties of consecutive elements. These sudden changes in the properties correspond in Fig. 1 to sudden change in the direction of the curves. In the Mendelejeff's table, the elements which are located near one another have general resemblance in their properties. From Fig. 1, therefore, it is highly probable that the amount of volume change on melting per unit mass of magnesium will intermediate between those of sodium and aluminium. The volume change on melting per one gram of sodium is 0.0243 c.c. and that of aluminium 0.0267 c.c., hence that of magnesium will be about 0.0255 c.c.

The value of volume change can be obtained if we were able to measure the densities of magnesium at its melting point both in the solid and the liquid states. But the density of magnesium at high temperature has not

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(1) H. Endo: *Sci. Rep. Tohoku Imp. Univ.*, **13** (1924), 193; The eighty-eighth report of the Research Institute for Iron, Steel and Other Metals.

yet been determined. So the author has calculated the densities of magnesium at its melting point under the assumption that the above value of the volume change is reasonable.

Experimental. The density of solid at its melting point might easily be calculated from the mean coefficient of cubical expansion of magnesium from room temperature to the vicinity of its melting point. The mean coefficient of linear expansion of the metal has been measured accurately with the dilatometer constantly used in our Institute.(1) The measurement was always made in a vacuum high enough to avoid the oxidation of the specimen. The rate of heating was slow, the whole time required for heating the specimen from room temperature to 600°C. extending over three hours. From the observed data, the elongation $\delta l/l$ of the specimen, whose length is l, was calculated. The mean coefficients of linear expansion of magnesium at various temperatures measured with the apparatus are illustrated in Fig. 2.

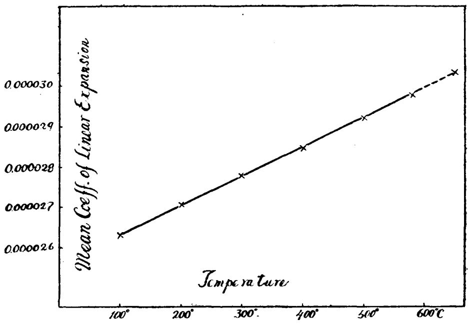

Fig. 2.

The melting point of the metal is 650°C. and, therefore, the mean coefficient of expansion between 20°C. and 650°C. can be deduced by extraporation, thus it has been known to be 0.00003025. Then the mean coefficient of cubical expansion will be calculated as follows:—

$$\beta = 3\alpha = 0.00003025 \times 3 = 0.00009075.$$

The specific volume of the solid state of magnesium at its melting point is 0.60724 c.c. that is:

$$V_s = V_{20}(1 + \beta t) = 0.5744(1 + 0.00009075 \times 630) = 0.60724$$

where V_{20} is the specific volume of the metal at 20°C. The density of the solid state at the melting point is reciprocal of the specific volume that is:—

$$\rho_s = \frac{1}{V_s} = \frac{1}{0.60724} = 1.6468$$

The Density of Magnesium in Liquid State at its Melting Point. The density of the liquid state of the metal at its melting point can easily be calculated from the density of solid state and the amount of the change of volume per unit mass on melting which described above. The writer published the results of measurements of the change of volume in several

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(1) *Sci. Rep. Tohoku Imp. Univ.*, 6 (1917), 203.

metals and alloys during solidification with a thermo-balance.(1) The result was that, with the exception of bismuth and antimony, all of the metals and alloys studied show the contraction during solidification. Therefore it may reasonably be assumed that the magnesium also expands during melting, and the amount of it is 0.0255 c.c. per gr. which was derived from the periodic curve described above.

Then the specific volume of the liquid state of magnesium at its melting point is,

$$V_l = 0.60724 + 0.0255 = 0.63274 \text{ c.c.}$$

And the density of the liquid magnesium at its melting point is,

$$\rho_l = \frac{1}{V_l} = \frac{1}{0.63274} = 1.5804.$$

The mean coefficients of linear expansions at several temperatures which have been obtained by measurements are tabulated in the following table.

Temp. C.	Mean linear exp. coeff.	Temp. C.	Mean linear exp. coeff.
20~100	0.0000263	20~500	0.0000292
20~200	0.0000271	20~580	0.0000299
20~300	0.0000278	20~650	0.0000303
20~400	0.0000284		

Density of solid magnesium at 20°C = 1.7410
Density of solid at melting point = 1.6468
Density of liquid at melting point = 1.5804.

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Tohoku Imperial University, Sendai.

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(1) K. Honda, *Sci. Rep. Tohoku Imp. Univ.*, 4 (1915), 97.

ON THE PRESERVATION OF THE STANDARD SOLUTION OF OXALIC ACID AND ON THE READING OF THE BURETTE.(2)

By **Saburo ISHIMARU.**

Received April 6, 1927. Published May 28, 1927.

As is generally known, the solution of oxalic acid is widely used as an important standard in volumetric analysis, though it is necessary to prepare it frequently anew on account of its tendency to decomposition, but

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(2) This paper was published in Japanese in the *Journal of the Chemical Society of Japan*, 43 (1922), 767.

very few books on analytical chemistry describe the method of preservation of this solution.

The addition of alcohol was formerly proposed by Hartly⁽¹⁾ and thymol by Gerland⁽²⁾ as preserving agents. Riegler⁽³⁾ on the other hand, described that a solution containing 50 c.c. of conc. sulphuric acid in 1 litre did not alter its titre after a year. Treadwell⁽⁴⁾ recommended the same precaution in his famous book of analytical chemistry, and advised not to use old solutions prepared in the usual manner without any preserving agent, on the basis of his observation that an oxalic acid solution prepared according to the method of Riegler lost, after eight months' standing, only 0.07% of its original strength, while one containing no sulphuric acid lost 0.57%.

Werner⁽⁵⁾ and Blass⁽⁶⁾ attributed the cause of the decomposition of oxalic acid to the action of a micro-organism, Bizio,⁽⁷⁾ Fleury⁽⁸⁾ and Gigli⁽⁹⁾ expressed the opinion that the concentrated solutions were not subject to the influence of the harmful micro-organism and Duclaux⁽¹⁰⁾ and Jorissen⁽¹¹⁾ described about the action of light upon it.

As the degree of the deterioration observed by Treadwell and Riegler in the oxalic acid solution containing sulphuric acid was too small to be in accordance with the author's experience, it was suspected that there might have been something wrong with their observations. The author also wondered why the two investigators had used so large a quantity of conc. sulphuric acid as 50 cc. for the purpose of preservation, though as a matter of course, a small quantity of it must have exerted a sufficiently disinfecting effect.

The experiments to be here described were carried out by the present author, in order to clear up the points in question, by a thoroughly systematical investigation, with the view that the most important of the influential factors as regards the preservation of the standard oxalic acid solution would probably be the action of light.

Two series of 0.1 N solutions of oxalic acid, with and without the addition of the various quantities of conc. sulphuric acid were prepared from

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(1) *Chem. News*, 37 (1878), 9.
(2) *J. Soc. Chem. Ind.*, 10 (1891), 25.
(3) *Z. analyt. Chem.*, 35 (1896), 522.
(4) „Lehrbuch der analytischen Chemie," 7th ed. II, p. 499.
(5) *Arch. Pharm.*, [3], 2 (1873), 522.
(6) Ibid., [3], 3 (1873), 310.
(7) *Z. analyt. Chem.*, 9 (1870), 392.
(8) *J. pharm. chim.*, [5], 7 (1883), 383; *Chem. Zentr.*, (1883), 547.
(9) *Apoth. Zt.*, 7 583; *Chem. Zentr.*, (1893), I, 11.
(10) *Comp. rend.*, 103 (1886), 1010.
(11) *Z. angew. Chem.*, (1899), 521.

Kahlbaum's purest oxalic acid ("Zur Analyse"): the one series was kept in ordinary colorless reagent bottles, while the other, in reagent bottles completely wrapped with black paper.

For the sake of studying the disparity, if any, between the degrees of the deterioration of the solutions differing in purity, the duplicates of the whole series were made from oxalic acid of the pure commercial grade.

All the bottles were kept in rows, on the laboratory shelves, which were beyond the reach of the *direct* sun light. From time to time, the rate of decomposition was measured, by titration with a standard solution of potassium permanganate, standardized against the pure oxalic acid solution, *freshly* prepared each time from Kahlbaum's preparation ("Zur Analyse").

In order not to exclude the chance of development of the microorganism, the investigation was begun in April and continued till September; the reagent bottles were simply closed with glass stoppers applying neither special sealing nor sterilization, so that the conditions would be kept the same, as far as possible, with those prevailing in the ordinary analytical practice.

TABLE 1.

(Oxalic acid: Kahlbaum, "Zur Analyse." Containers: ordinary colorless reagent bottles.)

No. of experiment.	Conc. H_2SO_4 in L. cc.	Normality.				
		1st day.	47th day.	90th day.	148th day.	Difference.
1	0	0.0991	0.0991	0.0991	0.0987	−0.0004
2	2	0.0992	0.0990	0.0986	0.0981	−0.0011
3	10	0.0990	0.0983	0.0980	0.0951	−0.0039
4	20	0.0992	0.0972	0.0941	0.0900	−0.0092
5	40	0.0992	0.0965	0.0929	0.0890	−0.0102
6	100	0.0992	0.0941	0.0887	0.0827	−0.0165

TABLE 2.

(Oxalic acid: commercial. Containers: ordinary colorless reagent bottles.)

No. of experiment.	Conc. H_2SO_4 in L. cc.	Normality.				
		1st day.	48th day.	91st day.	149th day.	Difference.
7	0	0.0993	0.0993	0.0986	0.0982	−0.0011
8	2	0.0993	0.0987	0.0980	0.0975	−0.0018
9	10	0.0993	0.0985	0.0970	0.0955	−0.0038
10	20	0.0993	0.0978	0.0960	0.0943	−0.0050
11	40	0.0990	0.0970	0.0938	0.0908	−0.0082
12	100	0.0991	0.0960	0.0927	0.0899	−0.0092

From the figures given in Tables 1 and 2, it is clearly shown that, contrary to the general belief now prevailing among chemists, the plain aqueous solutions are comparatively most stable (Nos. 1 and 7), and the solutions become more and more unstable as the quantities of sulphuric acid added are increased (No. 12 lost more than 9%, while No. 6 even 16% or so, of the original strength). Accordingly the method, recommended by Treadwell and Riegler, of adding sulphuric acid to the standard solution of oxalic acid and keeping it in the ordinary *colorless* bottle, is altogether of no practical value as a means of preservation.

It will also be seen that in the presence of fairly large quantities of sulphuric acid, the solutions of Kahlbaum's purest oxalic acid (Nos. 4–6) are less stable than those of the pure commercial sample (Nos. 10–12).

TABLE 3.

(Oxalic acid: Kahlbaum, "Zur Analyse." Containers: reagent bottles wrapped with black paper.)

No. of experiment.	Conc. H_2SO_4 in L. cc.	Normality.				
		1st day.	47th day.	90th day.	148th day.	Difference.
13	0	0.0992	0.0992	0.0992	0.0992	0.0000
14	2	0.0990	0.0992	0.0990	0.0992	+0.0002
15	10	0.0992	0.0992	0.0991	0.0995	+0.0003
16	20	0.0990	0.0992	0.0991	0.0995	+0.0005
17	40	0.0992	0.0992	0.0992	0.0995	+0.0003
18	100	0.0994	0.0992	0.0992	0.0993	−0.0001

TABLE 4.

(Oxalic acid: commercial. Containers: reagent bottles wrapped with black paper.)

No. of experiment.	Conc. H_2SO_4 in L. cc.	Normality.				
		1st day.	48th day.	91st day.	149th day.	Difference.
19	0	0.0993	0.0992	0.0992	0.0994	+0.0001
20	2	0.0991	0.0993	0.0992	0.0995	+0.0004
21	10	0.0991	0.0992	0.0992	0.0995	+0.0004
22	20	0.0993	0.0992	0.0992	0.0994	+0.0001
23	40	0.0991	0.0992	0.0991	0.0995	+0.0004
24	100	0.0993	0.0993	0.0991	0.0996	+0.0003

The results given in Tables 3 and 4 indicate, that the plain aqueous solutions of oxalic acid, kept in the bottles completely wrapped with black paper, without any precaution for excluding the influence of the micro-organism, are all strikingly stable, entirely regardless of the difference in the grades of purity of the materials (Nos. 13 and 19); even those containing large quantities of sulphuric acid are also stable when kept in the *black* bottles (Nos. 18 and 24).

The negligible increase, observed in the concentrations of these solutions, must naturally be explained to be due partly to the experimental error and partly to the slight evaporation during the extreme heat in the summer. Had the bottles, with specially well ground and perfectly fitted stoppers, instead of the *ordinary* reagent bottles, been used in the above experiment for keeping the solutions, the concentrations would doubtless have remained absolutely the same.

From the results stated thus far, it is clearly established, that the standard solution of oxalic acid should always be kept in a bottle carefully wrapped with black paper, and that the addition of sulphuric acid is entirely unnecessary.

What then was the reason which led Treadwell and Riegler to such an erroneous conclusion? It seems very plausible, in the light of the author's observation recorded above, that the two investigators accidentally kept their solutions for the experiments of preservation, in a more or less dark place—most probably inside the laboratory table.

On the Reading of the Burette.

For the purpose of making the reading of the burette easy and accurate, there have been many devices proposed, such as the use of a mirror, etc., but none of them satisfies the following five conditions at the same time, namely, (1) constancy of the background of the meniscus, (2) deep coloration of the meniscus, (3) facility of fixing the position of the experimenter's eye, (4) easy and comfortable reading of the graduations of the burette, none of them being covered from sight, and lastly (5) no necessity of holding it by hand.

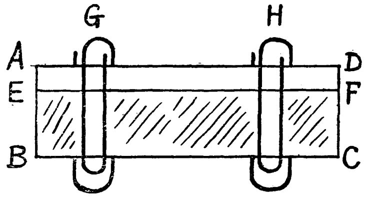

Fig. 1.

The device to be here described, is the one constantly used by numerous workers, in this laboratory of analytical chemistry for several years and found to answer all the requirements enumerated above.

A piece of paper ABCD, measuring 22 cm. x 8 cm., is cut from a name card, as shown in the accompanying figure, on which is pasted a strip of black glazed paper EBCF, measuring 1.5 cm. x 8 cm.: then a strip of transparent colorless celluloid plate, having exactly the same size as the glazed paper EBCF, is fastened by two paper clips, G and H, to the card, so that the edges of the glazed paper and celluloid perfectly coincide on the line EF, between which the burette is inserted. When it is moved until the meniscus seems to touch the line EF, the afore-mentioned conditions are satisfied simultaneously and the reading is made exceedingly easy and accurate.

Summary.

(1). The standard solution of oxalic acid should always be kept in a reagent bottle carefully *wrapped with black paper*. The solution thus preserved does not change its strength, irrespective of the presence or absence of sulphuric acid. Hence the old standard solution kept in a black bottle can as well used for titration.

(2). The method of preservation of the oxalic acid solution, described in Treadwell's "Analytical Chemistry" is not appropriate; the addition of sulphuric acid is not only unnecessary but *objectionable*, because the velocity of decomposition of the oxalic acid solution kept in a *colorless* bottle, becomes greater with the increase in the concentration of sulphuric acid added.

(3). A convenient device for the correct reading of the burette is described.

In conclusion, the author wishes to express his heartfelt thanks to Prof. M. Kobayashi for valuable suggestions during the work.

September, 1922.

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ÜBER DIE DICHTE VON SYSTEM DES NIKOTIN-WASSERS.

Von **Naoyasu SATA.**

Eingegangen am 10. April 1927. Ausgegeben am 28. Mai 1927.

Einleitung. Das abnorme Verhalten des Systems von Nikotin-Wassers nämlich betreffend ihre Lösungskurve wohl bekannt ist und besonders durch frühere Beobachtung von Hudson(1) und die spätere von Tsakalotos(2). Die beiden beobachtete in diesem Falle noch interessante Frscheinung, dass

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(1) *Z. physik. Chem.*, 47 (1904), 113.

(2) *Bull. soc. chim.*, 5 (1909), 397; Z. physik. Chem., 60 (1907), 567; *J. Chem. Soc.*, **115** (1919), 104; Bakhuis Roozeboom, „Heterogenen Gleichgewichte,“ 2 Heft, 2 Teil (Systeme mit zwei flüssigen Phasen, von E.H. Büchner), Braunschweig, 1918.

dieses über ca. 60°C. in zwei flüssigen phasen getrennte System bei ca. 90°C. der Platzwechsel der beiden Phasen geschiet während es über 210°C. sich wieder zu homogener System mischt. Wenn es tatsächlich der Fall ist, und anstatt der Lösungskurve mit der Dichte-Temperaturkurve gezeichnet wird, so sollte es zwischen 60°C. und 210°C. 8-artig werden und deren Kleuzpunkt soll mit dem Platzwechselpunkt übereinstimmen.

Um das genannte Verhalten betreffend die Dichtemessung bei der gleichmässig hohen Temperatur (näher und über den Siedepunkt der Flüssigkeit) durch eine experimentele Untersuchung graphisch darzustellen, nahm ich die vorliegend Arbeit vor.

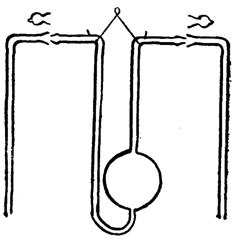

Fig. 1.

Versuchsmethoden. *Pyknometer:* Von 30°C. bis 95°C. gebraucht ich gewöhnlichen Pyknometer von Sprengelschem Rohr, mit geschliffenem Stöpsel und Einleitungsrohr (Fig. 1). Über 100°C., also das Wasser wird siedende Hitze, müssen wir Apparat mit eigentümlicher Einrichtung gebrauchen wie Fig. 2.

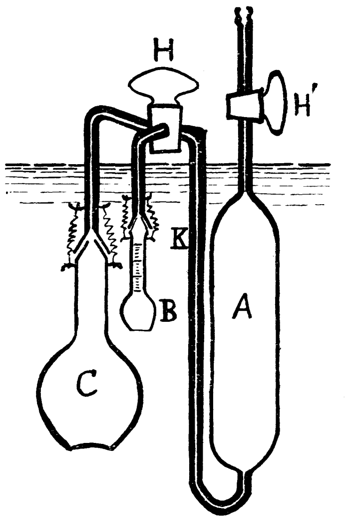

Fig. 2.

A : Gleichgewichtsgefäss.
B : Pyknometer.
C : Reservoir.
H : Dreiweghahn.
H': Hahn.

Anwendungsmessmethode, wie folgt: Erstens evakuiert man A, B und C durch H, H' mit dem Pumpen, hier schliesst man Dreiweghahn H, dann leitet Nikotin-Wasser Gemisch im Gleichgewichtsgefäss A ein, taucht man ganzen Apparat im Thermostat, wiederholt geschüttert bis das System das Gleichgewicht erreicht. (Es erkannt mit der klaren Aufscheidung der zwei flüssigen Phasen.)

Hier öffnet man Dreiweghahn H zum C, gibt die nichtgleichgewichte Teile in Kapillarrohr K in C auf, dann H zum B öffnet, füllt Pyknometer B ein, Skalen des Pykometerhalses lese und wäge.

Für Messungen oberer Phasen, gibt man ganze Unterphase in das Reservoir auf und säugt im Pyknometer obere Phase allein.

Thermostat: Unter 100°C., gewöhnlichem Wesserbade ist es gebräuchlich, nur aber ihre Oberfläche mit Paraffinöl bedeckt um Verdampfung des

Wassers zu verhindern. Über 100°C. benutzte ich Paraffinölbade mit elektrischer Heitzung und Temperaturregulierung, wie bei Dr. Shirai.(1)

Materien. *Nikotin:* Kahrbaum Präparate wird gebraucht. Durch Destillation unter vermindertem Druck in einem Wasserstoffstrome erhalten wir ganz farblose Flüssigkeit, aber es färbt sich bräunlich trotz der Aufbewahrung im Exikator im Dunkel. Deswegen am Anfang jeder Versuchen musste wieder destilliert werden.

Wasser: Man verwendet destilliertes Wasser mit genügendem Sieden, um gelöste Kohlensäure etc. zutreiben.

Versuchsresultaten. 1-*Versuchsreihe:* Dichte des Nikotin-Wasser Gemisches jedes Vol. % zwischen 30°C. und 60°C. gemessen.

Tabelle 1.

°C vol.% Nikotins	30	40	50	60
0	0.99567	0.99225	0.98807	0.98324*
10	1.00234	1.99856	0.99453	0.98968
20	1.00888	1.00410	0.99886	0.99353
30	1.01513	1.00953	1.00381	0.99755
40	1.02118	1.01449	1.00784	1.00065
50	1.02646	1.01903	1.01033	1.00299
60	1.03023	1.02156	1.01280	1.00407
70	1.03101	1.02228	1.01247	1.00406
80	1.02788	1.01830	1.00875	0.99979
90	1.01773	1.00979	1.00132	0.99280
100	1.00124	0.99383	0.98630	0.97890

* Landolt Tabellen.

Dieser wurde graphisch wie Fig. 3 dargestellt.

2-*Versuchsreihe:* Jeder Gemisch wird zwischen 60°C. und 65°C. in zwei flüssigen Phasen getrennt. Da über diese Temperatur die Gemische in zwei flüssigen Phasen im Gleichgewicht sich vorfindet, so ist eines mit Wasser gesättigte Nikotin Phase und anders mit Nikotin gesättigte Wasser Phase. Im folgendern sind die Dichte jeder Phasen bei jeder Temperaturen im Gleichgewicht dargestellt.

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(1) Diese Zeitschrift, **2** (1927), 38.

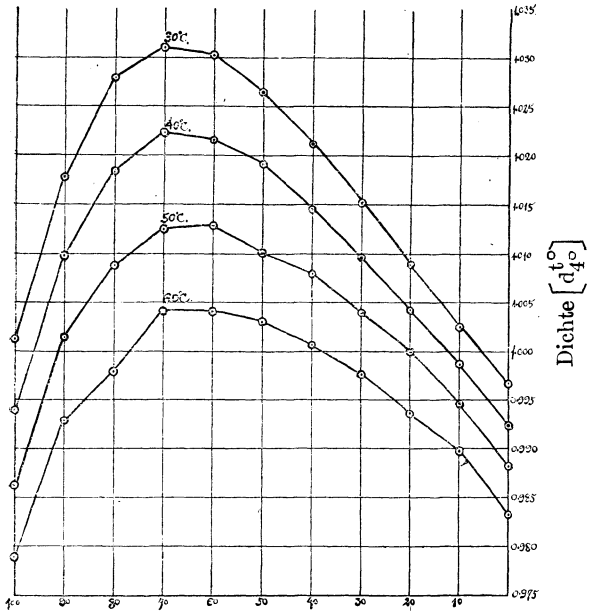

Fig. 3.

Tabelle 2.

°C.	Obere Phase. (mit Nikotin gesättigte Wasser-schicht.)	Untere Phase. (mit Wasser gesättigte Nikotin-schicht.)
65	0.98918	0.99907
70	0.98467	0.99491
75	0.98077	0.98904
80	0.97761	0.98438
85	0.97397	0.97832
90	0.97103	0.97368
95	0.96709	0.96744

3-*Versuchsreihe :* In dieser Reihe wurde genau ebenso wie in 2-Versuchsreihe die Dichte beiden Phasen von 100°C. bis 120°C. gemessen nur aber im Gebrauche von genanntem eigentümlichem Apparat, wegen des Über-Siedepunkt des Wassers.

Tabelle 3.

°C.	Untere Phase. (mit Nikotin gesättigte Wasser-schicht.)	Obere Phase. (mit Wasser gesättigte Nikotin-schicht.)
100	0.96420	0.9619
105	0.9607	0.9576
110	0.9571	0.9521
115	0.9534	0.9477
120	0.9497	0.9432

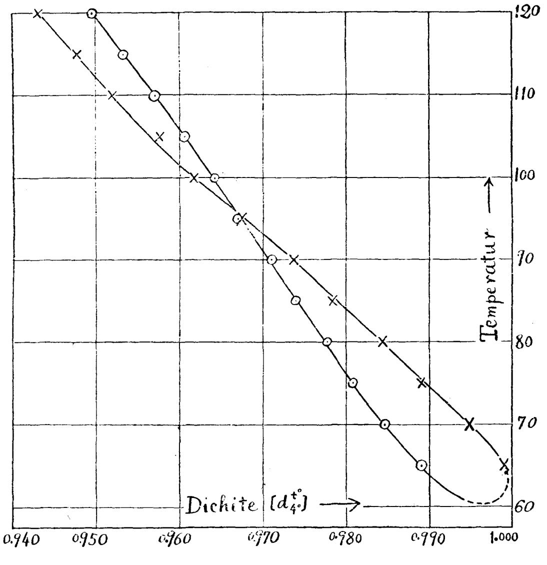

Fig. 4.

Tabelle 2 und 3 wird graphisch wie Fig. 4 dargestellt.

Zusammenfassung.

1. Die Dichte der Nikotin-Wasser Gemischen wurden in der Temperaturbereich von 30°C. bis 120°C. gemessen.

2. Vor Trennung in zwei Phasen, nämlich zwischen 30°C. und 60°C. (Fig. 3) Dichte-Vol. % Kurven haben ein Maximum, derer Krümmungen mit der Temperaturerhöhung grösser werden, und zeigen, dass nach der Trennung in zwei Phasen konstante Dichte haben, unabhängig von Verhältnisgehalt der Komponente.

3. Dichte-Temperatur Kurve nach der Trennung in zwei flüssigen Phasen wurde wie 8–artig übergezeugt. (Fig. 4)

4. Beim Kreuzpunkt der Kurve (Fig. 4) müssen die beiden Phasen ganz gleiche Dichte haben und muss der Platzwechsel beider Phasen, deswegen hier geschehen, deren Temperatur als 96°C. nach der Fig. 4 bestimmt wird.

Die vorliegende Arbeit wurde unter Leitung von meinem hochverehrten Lehrer Herrn Prof. J. Sameshima ausgeführt, welchem ich für seine froundliche Anregung und Unterstützung dabei zu herzlichem Dank verpflichtet bin.

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ON W. A. NOYES' METHOD OF PREPARING ETHYL CYANACETATE.

By Yoshiyuki URUSHIBARA.

Received April 4, 1927. Published May 28, 1927.

L. Vaninò describes in his "Präparative Chemie" W. A. Noyes' method for the preparation of ethyl cyanacetate.(1) But the condensation of the ester prepared by this method and triethyl ortho-formate by means of acetic anhydride(2) produced a substance which on analysis gave such numbers as if it were the *methyl* ethoxy-methylene-cyanacetate $CH_3OCO-C(=CHOC_2H_5)-CN$, the condensation product of methyl cyanacetate and triethyl ortho-formate.(3)

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(1) Original note: *J. Am. Chem. Soc.*, 26 (1904), 1545.

(2) In a manner similar to that described by E. Gregoire de Bellemont, *Bull. Soc. Chim.*, [3], 25 (1901), 18.

(3) *Bull. soc. chim.*, [3], 25 (1901), 21.

	C_2H_5OCO-C (=$CHOC_2H_5$)-CN	CH_3OCO-C (=$CHOC_2H_5$)-CN	Fonnd		
			I	II	III
C	56.77	54.19	54.72	55.21	—
H	6.56	5.81	5.93	6.04	—
N	8.28	9.03	—	—	9.22

Thus it is very probable that this cyanacetic ester contained methyl cyanacetate. This can be easily understood if we consider that the ester was prepared by boiling ethyl chloracetate and potassium cyanide in methyl alcohol. Some of the ethyl group of the ester was replaced by the methyl group of the methyl alcohol, which has been ascertained by the following analysis and measurement of density.

A precise determination of nitrogen content of the cyanacetic ester in question showed that this preparation contained about equal parts of ethyl and methyl esters.

	$CNCH_2CO_2CH_3$	$CNCH_2CO_2C_2H_5$	Found		
			I	II	III
N	14.14	12.39	13.32	13.26	13.28

Methyl cyanacetate was prepared from methyl chloracetate by using methyl alcohol as the solvent.⁽¹⁾

D_4^{17} of methyl cyanacetate = 1.133

D_4^{17} of the ester prepd. by Noyes' method = 1.114

The real ethyl cyanacetate was prepared from ethyl chloracetate by the action of potassium cyanide in absolute ethyl alcohol.⁽²⁾

Potassium cyanide is difficultly soluble in ethyl alcohol, while soluble in methyl alcohol, but the yield of cyanacetic ester is scarcely diminished by replacing methyl alcohol by ethyl alcohol.

D_4^{20} of the ester prepd. by Noyes' method = 1.110

D_4^{20} of ethyl cyanacetate = 1.063

The investigation on the diethyl dicyanoglutaconate, the details of which were given in the previous paper,⁽³⁾ always started from the cyanacetic ester prepared by Noyes' method. In all cases only the ethyl compound, e.i. diethyl sodio-dicyanoglutaconate, was obtained, the yield being sometimes over 60 % of the theoretical amount. Hence we must consider that the

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(1) and (2). These esters were fractionated two times under diminished pressure and sufficiently pure for synthetical purposes, but probably not for a precise determination of a physical constant.

(3) This Journal, 2 (1927), 26.

methyl ester contained in the ester mixture was again converted into ethyl ester, for the reaction giving diethyl sodio-dicyanoglutaconate was always carried out in ethyl alcohol. As long as the ester prepared by Noyes' method is used in ethyl alcohol, the absurdity of this method cannot be suspected. It can be foreseen that the ester mixture must give the *dimethyl* sodio-dicyanoglutaconate when it reacts with chloroform and sodium methylate in methyl alcohol. This compound, e.i. dimethyl sodio-dicyanoglutaconate had not been known, but was easily synthesised by using methyl cyanacetate in methyl alcohol.(1) The ester mixture prepared by Noyes' method also gave the same dimethyl sodio-dicyanoglutaconate when it was treated with chloroform and sodium methylate in methyl alcohol. J. C. Hessler and R. M. Lamb(2) observed that they obtained *methyl* esters of alkylcyanacetic acids by alkylation of ethyl cyanacetate in methyl alcoholic solution, but when one experiment was carried out on the alkylation of methyl cyanacetate in ethyl alcohol, the products remained methyl esters. But in the present case the replacement of the alcohol group of the cyanacetic ester seems to be reversible.

$$CNCH_2CO_2CH_3 + C_2H_5OH \rightleftarrows CNCH_2CO_2C_2H_5 + CH_3OH.$$

It is also not impossible that the replacement may occur in the reaction product rather than the cyanacetic ester, and a little amount of water or any other substance may act as a catalyser.

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Tokyo Imperial University.

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(1) The details will be given in another paper.

(2) *J. Am. Chem. Soc.* 43 (1921), 205.

THE FORMATION OF A COMPLEX ION IN THE AQUEOUS SOLUTION OF SILVER NITRATE AND PHENOL.

By Kwantaro ENDO.

Received March 2, 1927. Published June 28, 1927.

In the study⁽¹⁾ of the salting out effects of neutral salts on the aqueous phenol solution, the silver nitrate has been found to be an exception in that it showed the opposite effect. It is natural to think this "salting in" effect as due to some chemical combinations between phenol and silver nitrate in the aqueous solution. The following studies were made to solve this problem.

I. The Effect of Silver Nitrate on the Partition of Phenol between Benzene and Water. The experiments on the partition of phenol between benzene and the aqueous solution of silver nitrate were carried out at 25°C. in the same manner as described in the previous paper.⁽²⁾ The results are shown in Table 1, where *B* and *C* represent the molar concentrations of phenol in the benzene and in the aqueous layer respectively and *S* denotes that of silver nitrate.

TABLE 1.

Partition of phenol between benzene and water in the presence of $AgNO_3$.

Mol. conc. o $AgNO_3$ S	2.0		1.0		0.5		0.25	
	benzene layer	aqueous layer	benzene layer	aqueous layer	benzene layer	aqueous layer	benzene layer	aqueous layer
	B	*C*	*B*	*C*	*B*	*C*	*B*	*C*
Molar concentration of phenol in	0.8213	0.8517	1.1136	0.5966	0.9177	0.3637	0.9561	0.3092
	0.5688	0.6965	0.7675	0.5139	0.6716	0.3139	0.6429	0.2303
	0.[illegible]647	0.5049	0.5665	0.4190	0.3905	0.2181	0.4189	0.1866
	0.2836	0.4129	0.3862	0.3197	0.1982	0.1303	0.2111	0.1174
	0.1229	0.2056	0.1697	0.1588	0.0963	0.0680	0.1079	0.0564
	0.0615	0.0988	0.0813	0.0829				

Plotting *B-C* curves, we obtain Fig. 1, where the observed points are denoted by circlets. In Fig. 1, the most left-sided curve, which represents the case without silver nitrate, is taken from the previous paper.⁽²⁾ As we see in the figure, the curve moves to the right as the concentration of silver

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(1) K. Endo, *J. Chem. Soc. Japan*, **47** (1926), 374; This Journal, **2** (1927), 124.

(2) K. Endo, This Journal, **1** (1926), 25.

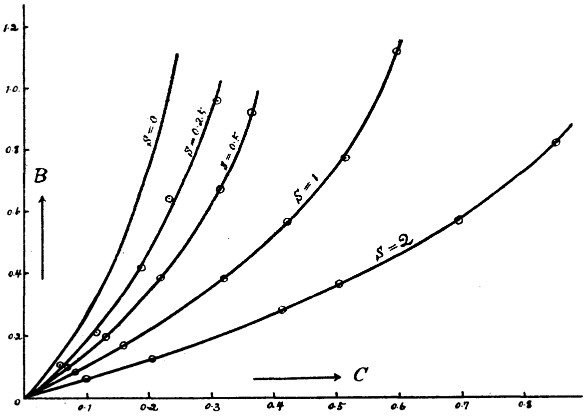

Fig. 1.

nitrate increases, that is, the solubility of phenol in the aqueous layer increases by the addition of silver nitrate. Obviously this effect is in the sense opposite to those of many other normal salts, namely, opposite to "salting out." The reason for this may be easily understood if we assume that some chemical combinations between phenol and silver nitrate (such as, the formation of a complex ion) occur in the aqueous layer. To solve this problem, I have studied, in the next place, the depression of freezing point of the aqueous solution of these substances.

II. The Effect of Silver Nitrate on the Depression of Freezing Point of the Aqueous Phenol Solution. The experiments were carried out in the similar manner as described in the previous paper. The results are shown in the following tables, where D_{P+A}, D_P and D_A represent the depressions of freezing point of the aqueous solutions of phenol in addition to silver nitrate, of phenol alone, and of silver nitrate alone, respectively.

TABLE 2.

Depression of freezing point of the aq. solution of $AgNO_3$.

Water gr.	$AgNO_3$ gr.	Molar conc. of $AgNO_3$ S	Depression (in degree) D_A
499.4	2.1370	0.0252	0.088
499.4	5.2475	0.0619	0.215
499.3	8.1625	0.0962	0.325
499.3	13.0165	0.1535	0.506
499.3	20.2700	0.2384	0.751

The data in Table 2 are also shown graphically by the curve $C=0$ in Fig. 2.

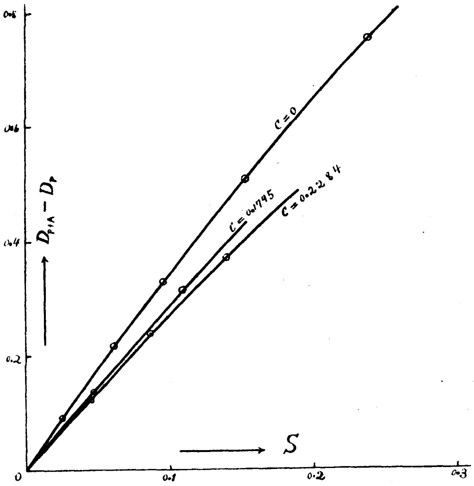

Fig. 2.

TABLE 3.

Depression of freezing point when both phenol and silver nitrate are dissolved simultaneously in water.

Water gr.	$AgNO_3$ gr.	Phenol gr.	D_{P+A} (in degree)
499.5	5.8815	2.4515	0.327
499.4	8.0345	5.7585	0.513
499.3	3.9570	8.4313	0.461
499.3	9.2870	8.4313	0.638
499.4	3.8176	10.7330	0.530
499.4	7.3333	10.7330	0.645
499.4	11.8433	10.7330	0.777

The data of Table 3 are compared in Table 4 with the summe of the individual depressions by phenol and by silver nitrate, which are obtained graphically, the former from Fig. 3 in the previous paper⁽¹⁾ and the latter from Fig. 2 in the present paper.

TABLE 4.

C	S	D_{P+A}	D_P	D_A	D_P+D_A
0.0522	0.0693	0.327	0.101	0.240	0.341
0.1226	0.0947	0.513	0.228	0.321	0.549
0.1795	0.0467	0.461	0.325	0.161	0.486
0.1795	0.1095	0.638	0.325	0.368	0.693
0.2284	0.0450	0.530	0.407	0.155	0.562
0.2284	0.0864	0.645	0.407	0.295	0.702
0.2284	0.1396	0.777	0.407	0.463	0.870

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(1) K. Endo. This Journal, **1** (1926), 28.

Here does not hold the additivity. This is shown more clearly in Fig. 2, where the ordinate denotes $D_{P+A}-D_P$ and the abscissa the molar concentration of silver nitrate. These deviations, as in the case of partition, are in the direction opposite to those of normal cases (e. g. sodium nitrate⁽¹⁾) and are moreover far greater than the latter. Such a decrease of depression must be considered as being due to the decrease of the number of dissolved particles by some chemical combinations, while all the ionised particles, on the other hand elevate⁽²⁾ the activity of phenol.

III. Determination of the Chemical Equation. The aqueous solution of silver nitrate and phenol is neutral and colourless, and as no compound between these substances can be separated out in any solid state, we can not determine its formula by chemical analysis. So we are obliged to rely upon the cryoscopic method for this purpose. The observations were made in the following two extreme cases.

a) *When the concentration of silver nitrate is very small compared with that of phenol:*—In this case we may assume that the whole of silver nitrate combines with phenol. As phenol associates in triple molecules⁽³⁾ in a small degree, there holds the following relation in the non-combined portion of phenol,

$$c_3 = Kc_1^3,$$

where c_1 and c_3 represent the molar concentrations of monomolecular and trimolecular phenol respectively and K the association constant. Although the initial concentration of phenol (C) is great compared to that of silver nitrate (x), its absolute value is not great. And moreover the value of K is small, so we can put

$$c_3 = KC^3$$

without introducing any serious error, because here we need only the approximate estimation and not the exact evaluation for our purpose. Thus the following depressions of freezing point are expected corresponding to the respective assumed equations.

(1) Let the aquation be

$$AgNO_3+C_6H_5OH=[Ag.C_6H_6O]^{\cdot}+NO_3',$$

then the depression of freezing point is to be expressed by

$$D_{P+A}/k = c_1+c_3+C_{[Ag.C_6H_6O]^{\cdot}}+C_{NO_3'},$$

where $C_{[Ag.C_6H_6O]^{\cdot}}$ and $C_{NO_3'}$ denote the ionic concentrations of $[Ag.C_6H_6O]^{\cdot\cdot}$

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(1) See the first foot-note of this paper.

(2) Ditto.

(3) K. Endo, This Journal, 1 (1926), 25.

and NO_3' respectively, and $k=1.86$. Here small correction terms due to the change of activities⁽¹⁾ by the presence of ions are also neglected.

Now $C = c_1+3c_3+C_{[\mathrm{Ag.C_6H_6O}]^{\cdot}}$, and $C_{[\mathrm{Ag.C_6H_6O}]^{\cdot}} = C_{\mathrm{NO_3}'} = x$.

So $D_{P+A}/k = C-2c_3+x = C(1-2KC^2)+x$.

Hence $\left(\dfrac{\partial D_{P+A}}{\partial x}\right)_{x=0} = k.$

Therefore, the $D_{P+A}-x$ curve must have a tangent k at $x=0$.

(2) $$\mathrm{AgNO_3+C_6H_5OH = C_6H_5OAg+H^{\cdot}+NO_3'},$$

then, by the treatment similar to (1), we obtain the following results,

$$D_{P+A}/k = C(1-2KC^2)+2x$$

and $$\left(\frac{\partial D_{P+A}}{\partial x}\right)_{x=0} = 2k.$$

If C_6H_5OAg dissociates further in two ions,

$$\left(\frac{\partial D_{P+A}}{\partial x}\right)_{x=0} = 3k.$$

(3) $$\mathrm{AgNO_3+2C_6H_5OH = [Ag.(C_6H_6O)_2]^{\cdot}+NO_3'},$$

then $D_{P+A}/k = C(1-2KC^2)$, and $\left(\dfrac{\partial D_{P+A}}{\partial x}\right)_{x=0} = 0.$

(4) $$\mathrm{AgNO_3+3C_6H_5OH = [Ag.(C_6H_6O)_3]^{\cdot}+NO_3'},$$

then $$\left(\frac{\partial D_{P+A}}{\partial x}\right)_{x=0} = -k.$$

And so forth.

Now these are tested by observations, the results of which are shown in Table 5.

TABLE 5.

Depression of freez. pt. when the conc. of $AgNO_3$ is very small compared with that of phenol.

Water gr.	Phenol gr.	$AgNO_3$ gr.	x Molar conc. of $AgNO_3$	$D_{P+A}-D_P$ in degree
455.3	27.29	0.679	0.0088	0.017
455.3	27.29	1.352	0.0175	0.033
455.3	27.29	2.172	0.0281	0.051

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(1) loc. cit.; Debye & Hückel, *Phys. Z.* **24** (1924), 185.

From Table 5 we obtain Fig. 3 by plotting $D_{P+A}-D_P$ against x, which becomes, as we see, a straight line represented by an equation

$$D_{P+A}-D_P = kx.$$

Its tangent is therefore

$$\left(\frac{\partial D_{P+A}}{\partial x}\right) = k.$$

which agrees whith the case of (1).

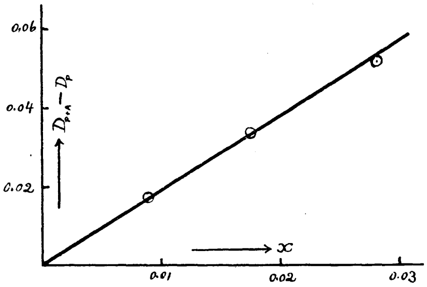

Fig. 3.

b) *When the concentration of phenol is very small compared with that of silver nitrate:*—The chemical equation,

$$\mathrm{AgNO_3+C_6H_5OH = [Ag.C_6H_6O]^{\cdot}+NO_3'}$$

which has been proved in the last case, is tested also in this case, where we can assume that the whole of phenol combines with silver nitrate.

According to the conductivity experiments of Werner,⁽¹⁾ the complex salts are to be considered strong electrolytes, while according to Debye and Hückel,⁽²⁾ all strong electrolytes make the perfect dissociation in the aqueous solution and the activity coefficient f_i (for the i-th ion) due to the electric field of ions is given by

$$f = e^{-Az^2\sqrt{\Sigma z_i^2 C_i}},$$

where z_i and C_i denote, respectively, the valency and the concentration of the i-th ion and A is a constant for a constant temperature. Thus,

$$D_{P+A} = k(f_1C_{\mathrm{Ag^{\cdot}}}+f_2C_{\mathrm{NO_3'}}+f_3C_{\mathrm{[Ag.C_6H_6O]^{\cdot}}}).$$

As to the valencies of these ions,

$$z_1 = z_2 = z_3 = 1$$

and moreover there is the relation with regard to the analytical concentration (S) of silver nitrate,

$$\Sigma C_i = C_{\mathrm{Ag^{\cdot}}}+C_{\mathrm{NO'_3}}+C_{\mathrm{[Ag.C_6H_6O]^{\cdot}}} = 2S.$$

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(1) Werner, „Neuere Anschauungen auf dem Gebiete der anorganischen Chemie.“

(2) loc. cit.

So, $$f_1 = f_2 = f_3 = e^{-A\sqrt{2S}} = f.$$

Hence, $$D_{P+A}/k = f(C_{\mathrm{Ag}^{\cdot}} + C_{\mathrm{NO}_3'} + C_{[\mathrm{Ag.C_5H_6O}]^{\cdot}}) = 2fS.$$

Consequently, $$\left(\frac{\partial D}{\partial x}\right)_{x=0} = 0$$

where x represents the molar concentration of the added phenol. The experimental results are shown in Table 6 and are depicted in Fig. 4, where a straight line, given by

$$D_{P+A} - D_A = kx,$$

is also drawn for the sake of comparison.

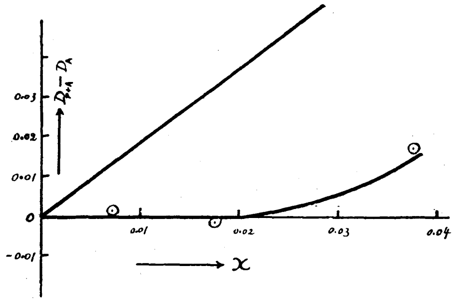

Fig. 4.

TABLE 6.

Depression of freez. pt. when the conc. of phenol is very small compared with that of silver nitrate.

AgNO gr.	Water gr.	Phenol gr.	x	$D_{P+A}-D_A$
5	35.602	0.0245	0.0073	0.001
5	35.602	0.0585	0.0175	0.002
5	35.602	0.1257	0.0375	0.017

In the vicinity of the origin, Fig. 5 shows actually a horizontal line in good agreement with our theory,

$$\left(\frac{\partial D_{P+A}}{\partial x}\right)_{x=0} = 0.$$

Thus the above chemical equation has been confirmed in the both extreme cases.

IV. Calculation of the Equilibrium Constant. As we have proved in the extreme cases that the chemical reaction,

$$\mathrm{AgNO_3 + C_6H_5OH = [Ag.C_6H_6O]^{\cdot} + NO_3'}$$

occurs in the aqueous solution, we shall next calculate the equilibrium constant in the intermediate cases (Table 3).

The association of phenol and the increase of activity of phenol due to the added salt are all negrected in the following calculations and the theory of strong electrolytes for dilute solutions by Debye and Hückel is applied, for here we treat dilute solutions in the cryoscopic measurements. For the calculation of the equilibrium constant, the following ionic equation has been used,

$$\mathrm{C_6H_5OH+Ag^{\cdot} = [Ag.C_6H_6O]^{\cdot}}.$$

As to the analytical concentrations of silver nitrate (S) and phenol (C), the following relations hold,

$$S = C_{\mathrm{NO_3'}} = C_{\mathrm{Ag^{\cdot}}} + C_{\mathrm{[Ag.C_6H_6O]^{\cdot}}},$$

$$C = C_P + C_{\mathrm{Ag.C_6H_6O]^{\cdot}}},$$

where C_P denotes the non-combined portion of phenol. For the depressions of freezing point by S moles of silver nitrate (D_A) and by C moles of phenol plus S moles of silver nitrate (D_{P+A}), respectively,

$$D_A = k(f_1C'_{\mathrm{A}\cdot} + f_2C_{\mathrm{NO_3'}}) = 2kfS,$$

$$D_{P+A} = k(f_1C_{\mathrm{A}\cdot} + f_2C_{\mathrm{NO_3'}} + f_3C_{\mathrm{[Ag.C_6H_6O]^{\cdot}}} + C_P) = 2kfS + kC_P.$$

Then $(D_{P+A}-D_A)/k = C_P$(1)

$$C - C_P = C_{\mathrm{[Ag.C_6H_6O]^{\cdot}}}$$

$$S - C_{\mathrm{[Ag.C_6H_6O]^{\cdot}}} = C_{\mathrm{Ag^{\cdot}}}.$$

By these three equations, we can obtain the equilibrium constant K_0 at 0°C as follows,

$$K_0 = \frac{C_P f C_{\mathrm{Ag^{\cdot}}}}{fC_{\mathrm{[Ag.C_6H_6O]^{\cdot}}}} = \frac{C_P C_{\mathrm{Ag^{\cdot}}}}{C_{\mathrm{[Ag.C_6H_6O]^{\cdot}}}}.$$

Table 7 has been calculated from the data given in Table 4.

TABLE 7.

Calculation of the equilibrium constant.

S	C	D_{P+A}	D_A	C_P	$C_{\mathrm{[Ag.C_6H_6O]^{\cdot}}}$	$C_{\mathrm{Ag^{\cdot}}}$	K_0
0.0693	0.0522	0.327	0.240	0.0445	0.0077	0.0616	0.36
0.0947	0.1226	0.513	0.321	0.1010	0.0216	0.0731	0.33
0.0467	0.1795	0.461	0.161	0.1646	0.0149	0.0318	0.35
0.1095	0.1795	0.638	0.368	0.1470	0.0325	0.0770	0.35
0.0450	0.2284	0.530	0.155	0.2095	0.0189	0.0261	0.29
0.0864	0.2284	0.645	0.295	0.1943	0.0341	0.0523	0.30
0.1396	0.2284	0.777	0.463	0.1730	0.0554	0.0342	0.26
						Mean K_0 = 0.32	

In spite of several neglections, the constancy of K_0 is satisfactory.

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(1) In the actual calculation C_P was determined graphically from the experimental D_P-C_P curve. (loc. cit.)

Summary.

1. From the measurement of partition of phenol between benzene and the aqueous solution of silver nitrate, it was found that the silver nitrate elevates considerably the solubility of phenol in the aqueous solution contrary to the salting out effects of other ordinary salts.

2. From the measurements of the depression of freezing point of the aqueous solutions of these substances, it has been proved that the "salting in" action of silver nitrate is due to the formation of a complex ion, $[Ag.C_6H_6O]^{\cdot}$, in the aqueous solution and the chemical equilibrium,

$$A\dot{g}+C_6H_5OH = [Ag.C_6H_6O]^{\cdot},$$

is established there.

The author's thanks are due to Prof. K. Ikeda for his kind guidance in the present investigation.

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THE EFFECT OF CAUSTIC ALKALI ON THE OXIDATION OF STANNOUS CHLORIDE WITH AIR.

By **Susumu MIYAMOTO.**

Received March 17, 1927. Published June 28, 1927.

S. W. Young(1) studied the effect of many substances on the oxidation of stannous chloride solution with free oxygen, but he did not studied the effect of alkali. The present research was carried out to know the effect of alkali by a modified method in connection with the former study on the effect of alkali on the oxidation of sodium sulphite with air.(2)

Experimental. The experimental procedure was quite the same with that described in the previous paper. Air was passed at constant velocity into the mixture of stannous chloride and sodium hydroxide solution. The total volume of the mixture was made to 40 c.c. in each case. A part o sodium hydroxide is used for the precipitation of stannous hydroxide, and the excess of alkali was given as C_{NaOH} in the following tables. After t-minutes the air current was stopped and the total amount of the mixture, acidified with hydrochloric acid, was poured into a known quantity of

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(1) *J. Am. Chem. Soc.*, **23** (1901), 119 and 450.

(2) Miyamoto, This Journal, **2** (1927), 74.

iodine solution and the excess of iodine was titrated back with sodium thiosulphate solution. In the following tables, v is the volume of sodium thiosulphate solution of 0.0996 normal, equivalent to the amount of stannous chloride; k was calculated by $k=\frac{1}{t}(v_0-v)$, v_0 being the value of v at $t=0$, and $v_{calc.}$ was obtained by $v_{calc.}=v_0-kt$, using the mean value of k.

Table 1 shows that the oxidation velocity is independent of the amount of stannous hydroxide. When the concentration of alkali is less than about 0.2 normal in the given condition, the mixture contains white precipitates of stannous hydroxide, and the phenomenon can be explained by considering that the oxidation takes place only in the liquid phase. But in more

TABLE 1.

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

C_{NaOH} Normal	t min.	v c.c.	$v_{calc.}$ c.c.	k
0.0217	0	12.08	—	—
	20	10.90	11.02	0.0590
	25	10.69	10.75	0.0556
	30	10.52	10.49	0.0520
	35	10.20	10.22	0.0537
	0	8.37	—	—
	20	7.37	7.31	0.0500
	30	6.85	6.78	0.0507
	0	5.61	—	—
	20	4.55	4.55	0.0530
	30	4.09	4.02	0.0507
			Mean:	0.0531
0.1081	0	11.94	—	—
	9	9.82	9.87	0.236
	12	9.19	9.18	0.229
	15	8.59	8.49	0.223
	20	7.40	7.34	0.227
	30	4.98	5.04	0.232
	0	6.23	—	—
	12	3.45	3.47	0.232
	17	2.33	2.33	0.229
			Mean:	0.230

C_{NaOH} Normal	min.	v c.c.	$v_{calc.}$ c.c.	k
0.5500	0	11.43	—	—
	10	9.13	9.28	0.230
	12	8.86	8.85	0.214
	15	8.29	8.20	0.209
	20	7.40	7.13	0.202
	30	4.61	4.98	0.227
	0	23.14	—	—
	20	18.42	18.84	0.236
	30	17.00	16.69	0.205
	0	7.57	—	—
	10	5.48	5.42	0.209
	15	4.46	4.34	0.207
			Mean:	0.215

concentrated alkaline solutions all the precipitates dissolve, forming stannites, and it should be explained as in the case of sodium sulphite.[1]

The Effect of Sodium Hydroxide. The measurements were carried out in alkaline solutions of various concentrations, and the results are given in Table 2 and Fig. 1. The oxidation velocity of stannous hydroxide with air

TABLE 2.

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

C_{NaOH} Normal	t min.	v c.c.	$v_{calc.}$ c.c.	k
0.00595	0	11.39	—	—
	40	10.47	10.49	0.0230
	50	10.26	10.27	0.0226
	60	10.06	10.05	0.0222
	70	9.87	9.82	0.0217
			Mean:	0.0224
0.0217	See Table 1.			0.0531
0.04057	0	12.22	—	—
	20	10.32	10.43	0.0950
	25	10.13	9.99	0.0836
	30	9.53	9.54	0.0897
	35	9.11	9.09	0.0889
			Mean:	0.0893
0.1081	See Table 1.			0.230
0.1706	0	11.95	—	—
	10	9.19	9.38	0.276
	15	8.17	8.09	0.252
	20	6.88	6.81	0.254
	25	5.50	5.52	0.258
	30	4.57	4.24	0.246
			Mean:	0.257
0.2204	0	12.32	—	—
	9	9.88	9.99	0.271
	12	9.20	9.21	0.260
	14	8.85	8.69	0.256
	20	7.24	7.14	0.254
	24	6.24	6.10	0.253
			Mean:	0.259
C_{NaOH} Norma	t min.	v c.c.	$v_{calc.}$ c.c.	k
0.3252	0	12.18	—	—
	9	9.80	9.97	0.264
	12	9.20	9.23	0.248
	15	8.54	8.49	0.243
	20	7.40	7.26	0.239
	25	6.33	6,03	0.234
			Mean:	0.246
0.5500	See Table 1.			0.215
1.130	0	12.65	—	—
	10	10.90	10.97	0.175
	12	10.68	10.63	0.164
	15	10.10	10.13	0.170
	20	9.29	9.29	0.168
	30	7.77	7.61	0.163
			Mean:	0.168
1.704	0	12.02	—	—
	20	9.32	9.50	0.135
	25	8.87	8.87	0.126
	30	8.36	8.24	0.122
	36	7.69	7.48	0.120
			Mean:	0.126
2.312	0	7.53	—	—
	10	6.49	6.53	0.104
	12	6.37	6.33	0.0967
	15	5.92	6.03	0.107
	20	5.63	5.53	0.0950
	27	4.93	4.84	0.0963
			Mean:	0.0998

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(1) Previous paper.

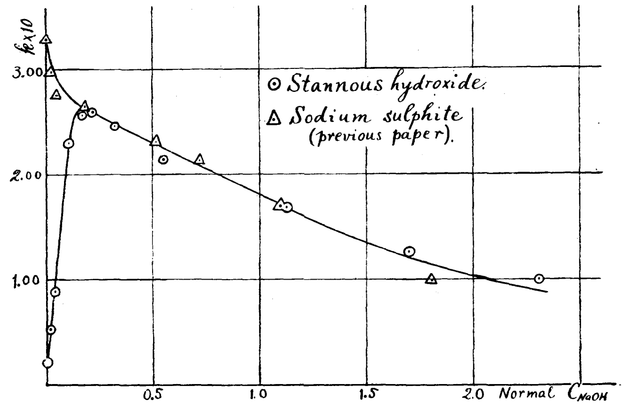

Fig. 1.

increases rapidly with the increase of the concentration of alkali until it attains a certain value and then decreases slowly. It was observed that the mixture contains white precipitates until the oxidation velocity attains almost its maximum value. In more concentrated alkaline solutions, all the stannous hydroxide dissolves forming stannites and the oxidation velocity was found to be the same as that of sodium sulphite. The results can be explained as follows.

The oxidation velocity increases until it attains the dissolution velocity of air with the increase of the concentration of alkali, which causes the formation of stannites. When the concentration of alkali increases still more, the dissolution velocity of air decreases, and consequently the oxidation velocity decreases. This assumption, which was also employed for the explanation of the oxidation velocity of sodium sulphite, was ascertained by the coincidence of their velocity constants as shown in Fig. 1. The values thus obtained can be regarded as the dissolution velocity of oxygen, when air was passed into 40 c.c. of solution in a test tube (diameter 3 cm.) through a glass tube (inside diameter=4 mm. outside diameter=6 mm.) at the rate of 7.78 litres per hour. From Fig. 1 we can calculate the approximate values of dissolution velocity of oxygen under the condition above described. Thus,

C_{NaOH} Normal	k	Dissolution velocity of oxygen
0.50	0.230	5.7×10^{-6} mols per minute.
1.00	0.180	4.5×10^{-6}
1.50	0.136	3.4×10^{-6}

The Effect of Temperature. The oxidation velocities at 30°C. and 40°C. are given in Table 3. The effect of temperature was small.

TABLE 3.

Velocity of air = 7.78 litres per hour.

Temp.	C_{NaOH} Normal	min.	v c.c.	$v_{calc.}$ c.c.	k
30°C.	0.0217	0	11.57	—	—
		30	8.99	9.16	0.0860
		35	8.76	8.76	0.0803
		40	8.56	8.36	0.0753
		50	7.61	7.56	0.0792
				Mean:	0.0802
30°C.	0.5500	0	11.14	—	—
		12	8.22	8.26	0.243
		15	7.44	7.54	0.247
		20	6.40	6.34	0.237
		25	5.32	5.14	0.233
				Mean:	0.240
40°	0.0217	0	10.35	—	—
		15	8.82	8.88	0.1020
		20	8.41	8.39	0.0970
		25	7.86	7.90	0.0996
		40	6.65	6.44	0.0925
				Mean:	0.0978
40°C.	0.5500	0	12.02	—	—
		10	9.17	9.22	0.285
		15	7.81	7.82	0.281
		20	6.50	6.42	0.276
		25	5.07	5.02	0.278
				Mean:	0.280

$$\frac{k_{30^\circ}}{k_{20^\circ}}=\frac{0.0802}{0.0531}=1.51 \quad \frac{k_{40^\circ}}{k_{30^\circ}}=\frac{0.0978}{0.0802}=1.22 \quad \text{When } C_{NaOH}=0.0217 \text{ normal}$$

$$\frac{k_{30^\circ}}{k_{20^\circ}}=\frac{0.240}{0.215}=1.12 \quad \frac{k_{40^\circ}}{k_{30^\circ}}=\frac{0.280}{0.240}=1.17 \quad \text{When } C_{NaOH}=0.5500 \text{ normal}$$

The Effect of the Velocity of Air Passed. It will be seen from Table 4 that a small change of the velocity of air current has not much influence on the oxidation velocity.

TABLE 4.

Temp. = 20°C. $C_{NaOH} = 0.5500$ Normal.

Velocity of air litres/hour	t min.	v c.c.	$v_{calc.}$ c.c.	k
6.67	0	11.31	—	—
	15	8.13	8.26	0.212
	20	7.11	7.25	0.210
	25	6.43	6.23	0.195
	30	5.35	5.22	0.199
			Mean:	0.203
10.00	0	11.81	—	—
	9	9.65	9.70	0.240
	15	8.35	8.30	0.231
	20	7.19	7.13	0.231
	25	5.96	5.96	0.234
			Mean:	0.234

Summary.

(1) The oxidation velocity of stannous chloride in alkaline solutions with air was studied. It was found to be the same as that of sodium sulphite when the concentration of alkali is greater than about 0.2 normal under the given condition.

(2) The effect of temperature was small.

(3) The dissolution velocity of oxygen in alkaline solutions was calculated indirectly.

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THE VISCOSITY OF LIQUIDS ABOVE THEIR BOILING POINTS. PART II.(1)

By Toshizo TITANI.

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Relation between Viscosity and Volume or Temperature.

1. Definition of Molecular and Specific Fluidity. The coefficient of viscosity η is defined by the formula:

$$R = \eta \cdot \frac{dv}{dz} \cdot A.$$

where R is tangential resistance, $\frac{dv}{dz}$ velocity gradient along the normal and A area. Therefore, it may also be defined as follows: we consider at first an unit cube (Fig. 1.) filled with a viscous substance. The viscosity of the substance is measured by the tangential resistance R on the upper plane of the cube, when it moves with unit velocity in respect to the lower.

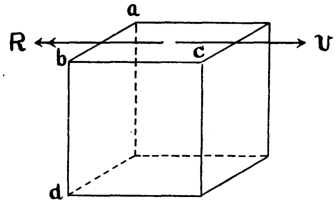

Fig. 1.

In order to express the viscosity in a molecular term, Thorpe and Rodger(2) proposed the molecular viscosity, which is defined by the product $\eta . V^{\frac{2}{3}}$, V being molecular volume, so that the molecular viscosity after Thorpe and Rodger is equal to the resistance when the sliding surface contains equal number of molecules, i.e. when in Fig. 1. $ab = bc = V^{\frac{1}{3}}$ while $bd=1$. The conception of this quantity seems not to be adequate, since, although equal number of molecules are arranged for different substances along ab and bc, it is not so in the direction bd. The expression $\eta . V^{\frac{2}{3}}$ may strictly be called molecular surface viscosity. The true molecular viscosity should be defined as follows: the molecular viscosity is measured by the resistance when the same number of molecules are arranged also in the direction of normal bd, i.e. when $ab=bc=bd = V^{\frac{1}{3}}$ in Fig. 1. Putting $ab=bc=bd = V_1^{\frac{1}{3}}$ where V_1 is specific volume, specific viscosity may similarly be defined.

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(1) Part I, This Journal, 2 (1927), 95.

(2) Thorpe and Rodger, *Phil. Trans.*, (A), 185 (1894), 397.

As the term of molecular viscosity are already conventionally understood in the sense of Thorpe and Rodger, the writer proposes to introduce the new proper definition for molecular and specific fluidity as the reciprocal of the above two quantities.

The coefficient of fluidity, denoted by ϕ, is the reciprocal of the coefficient of viscosity, so that it may be defined as the velocity v given to the upper plane referred to the lower (Fig. 1), by unit tangential force applied to the upper plane. Consequently, molecular fluidity Φ is measured by the sliding velocity given by unit tangential force applied to a plane containing the same number of molecules for different substances, the velocity being referred to another fixed plane, the distance between the two planes also having the same number of molecules. In Fig. 1., when $ab=bc=bd=V^{\frac{1}{3}}$, the velocity v measures molecular fluidity Φ. Specific fluidity Φ_1 is similarly defined as the velocity v in Fig. 1. when $ab=bc=bd=V_1^{\frac{1}{3}}$.

These two quantities can be calculated from the value of viscosity η or fluidity ϕ and molecular V or specific volume V_1 from the following relations:

$$\Phi=\frac{\phi}{V^{\frac{1}{3}}}=\frac{1}{\eta\,.\,V^{\frac{1}{3}}}\quad\cdots\cdots(1)$$

$$\Phi_1=\frac{\phi}{V_1^{\frac{1}{3}}}=\frac{1}{\eta\,.\,V_1^{\frac{1}{3}}}\quad\cdots\cdots(2)$$

2. Relation between Molecular Fluidity and Molecular Volume. As the relation between viscosity η and specific volume V_1, Batschinski(1) put forward the following experimental formula:

$$\eta=\frac{c}{(V_1-\omega)}\quad\cdots\cdots(3)$$

where c and ω are constants. This relation seems to have little theoretical lucidity, since viscosity in the left side is referred to unit cube, while specific volume in the right side being referred to one gram.

We will consider the molecular fluidity defined above as regards its relation to the molecular volume. Suppose the upper plane of the cube in Fig. 1 is displaced in reference to the lower by the amount du during the time $d\theta$ by unit tangential force applied to the upper plane. Then the displacement du measures the amount of shear of the vertical side. Therefore it seems plausible to assume this displacement to be proportional to the free space in the plane cbd, i.e. the area of the plane decreased by the amount proportional to the section of molecules:

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(1) Batschinski, *Z. physik. Chem.*, **84** (1913), 643.

$$du = K.(V^{\frac{2}{3}} - B^{\frac{2}{3}}).d\theta.$$

where K and B are constants. Dividing both sides with $d\theta$ and taking into consideration that $\frac{du}{d\theta}$ is equal to molecular fluidity Φ, the above relation becomes,

$$\Phi = K.(V^{\frac{2}{3}} - B^{\frac{2}{3}}) \dots\dots\dots\dots\dots\dots(4)$$

The constant B is the limiting value of the molecular volume of liquid as its molecular fluidity approaches zero, and it is therefore called effective molecular volume. Calling the difference $(V^{\frac{2}{3}} - B^{\frac{2}{3}})$ the molecular free area, the above relation may be expressed as follows: the molecular fluidity varies directly as the molecular free area.

Similarly, for the specific fluidity we obtain the following relation:

$$\Phi_1 = K_1.(V_1^{\frac{2}{3}} - B_1^{\frac{2}{3}}) \dots\dots\dots\dots\dots\dots(5)$$

were K_1 and B_1 are constants having similar meanings as K and B and being related with them by the equations:

$$K_1 = M.K, \quad \text{and} \quad B_1 = \frac{B}{M}.$$

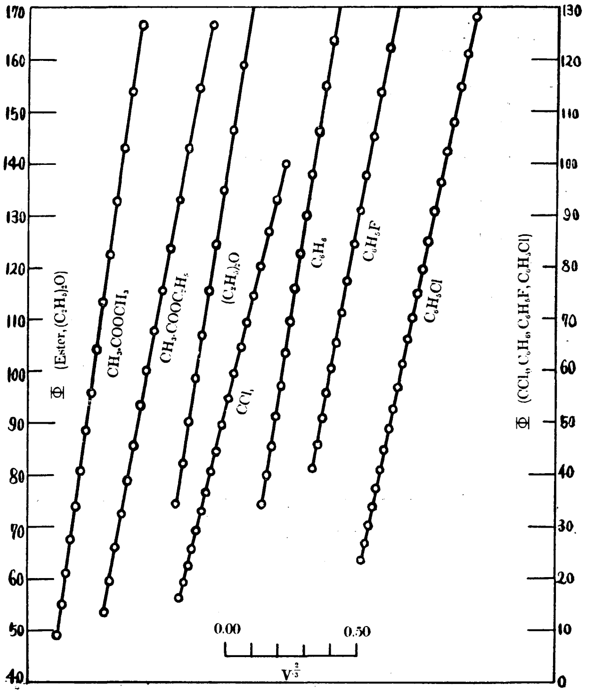

Fig. 2.—The volume relation for organic liquids extended over boiling points.

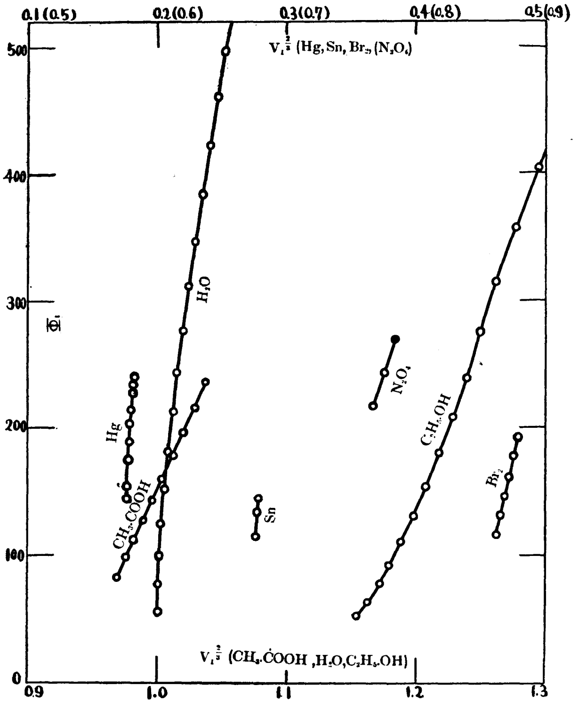

Fig. 3.—The volume relation for abnormal and inorganic liquids.

where *M* being the molecular weight. The above two relations (4) and (5) will be called the volume relation.(1) This is graphically summarised in Figs. 2. and 3., the details of numerical data are given in later tables. The volume relation is found to be satisfied by many substances. The calculated values of molenular or specific fluidity seldom deviate from the observed values by more than one per cent. Few substances for which the agreement is not good include alcohols, water and mercury, so long as being tested.

Multiplying both sides of the equation (5) with $V_1^{\frac{1}{3}}$ and inverting it, we have:

$$\eta = \frac{\frac{1}{K_1}}{(V_1 - B_1^{\frac{2}{3}}.V_1^{\frac{1}{3}})} \qquad \text{.....................(6)}$$

Comparing this expression with that of Batschinski (3), we see that a constant ω in the latter corresponds to a variable $B_1^{\frac{2}{3}}.V_1^{\frac{1}{3}}$ in the former (6).

---

(1) Although the definition of molecular or specific fluidity and their relation to volume need the data of density, this is not accompanied by introduction of a new unknown quantity, since the value of density is always necessary for the measurement of viscosity.

The effect due to this difference in formula may not be large until a comparison is done over a wide temperature range up to the critical point, but in this case a remarkable difference would appear between the values calculated by each equation.

3. Relation between Molecular Fluidity and Temperature. Viscosity or fluidity is one of the properties which change most remarkably with temperature, and as regards their variation with temperature, so many equations have been proposed that one can hardly decide which one is to be preferred.

If the volume relation obtained above be correct from the freezing point up to the critical, the molecular fluidity would approach zero at a certain low temperature, while near the critical it would increase very rapidly to a certain critical value. As one of the formula satisfying these conditions and containing constants as few as possible, the following relation is proposed:

$$\log(\Phi_K - \Phi) = \frac{1}{5}\log(T_K - T) + \text{Const.}$$

or

$$(\Phi_K - \Phi) = C.(T_K - T)^{\frac{1}{5}} \dots\dots\dots\dots (7)$$

where T_K is critical temperature, Φ_K the value of molecular fluidity at this point, C a constant. Similarly, for the specific fluidity:

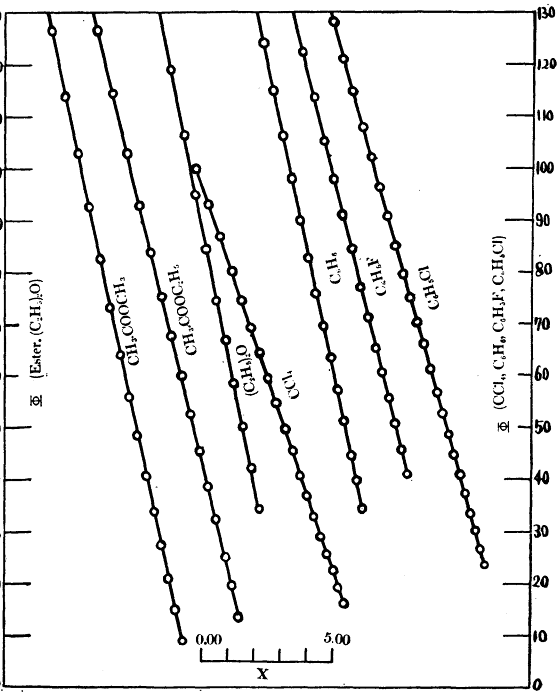

Fig. 4.—The temperature relation for organic liquids extended over boiling points.

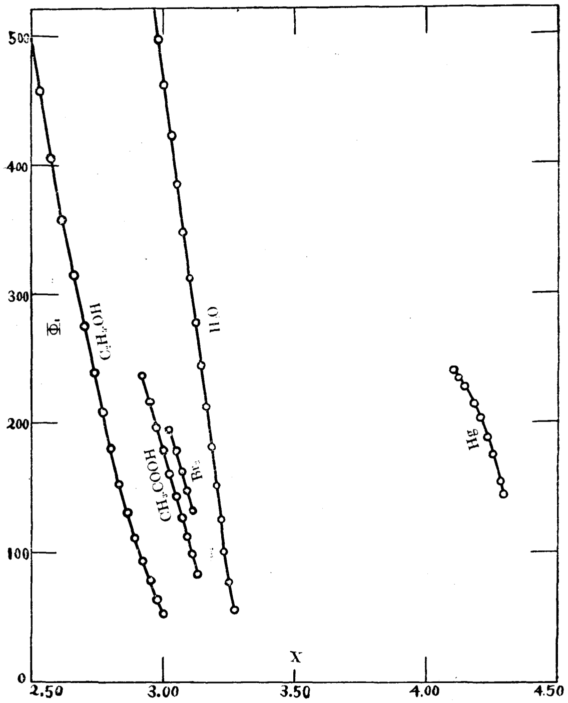

Fig. 5.—The temperature relation for abnormal and inorganic liquids.

$$(\Phi_{1K}-\Phi_1) = C_1.\,(T_K-T)^{\frac{1}{3}}\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots(8)$$

where respective quantities are each referred to one gram and—

$$C_1 = M^{\frac{1}{3}}.\,C. \qquad \Phi_{1K} = M^{\frac{1}{3}}.\,\Phi_K.$$

M being the molecular weight. These relations will be called temperature-relation. The temperature relation was found to be satisfied by many substances with a few exceptions (alcohols, water and mercury so long as being tested) as being shown graphically in Figs. 4. and 5. and numerically in later tables.

Notation:—t: Temperature in Celcius degree.

Φ: Molecular fluidity observed.

Φ_V: Molecular fluidity calculated from volume.

Φ_T: Molecular fluidity calculated from temperature.

Constants K, C etc. were determined graphically. Most of the necessary data were taken from the papers of S. Young,[1] Thorpe and Rodger,[2]

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[1] Density: S. Young, *Sci. Proc. Roy. Dublin Soc.*, **12** (1909–1910), 374.

[2] Viscosity: Thorpe & Rodger, *Phil. Trans.*, (A), **185** (1894), 397; ibid., **189** (1897), 71.

A. Heydweiller[(1)] and the writer's own.[(2)] A few others were from the Tables of Landolt-Börnstein-Roth, 5 edition.

Normal Pentane.

$$\Phi_V = 31.8\,(V^{\frac{2}{3}} - 95.50^{\frac{2}{3}}).$$

$$\Phi_T = 795.4 - 251\,(197{,}2 - t)^{\frac{1}{5}}.$$

t	Φ	Φ_V	Φ_T
0	73.36	73.5	73.5
10	80.87	80.7	80.7
20	88.59	88.7	88.5
30	96.47	96.4	96.7

Isopentane.

$$\Phi_V = 32.1\,(V^{\frac{2}{3}} - 96.10^{\frac{2}{3}}).$$

$$\Phi_T = 799.5 - 254\,(187.8 - t)^{\frac{1}{5}}.$$

t	Φ	Φ_V	Φ_T
0	75.82	75.8	75.9
10	83.71	83.7	83.7
20	91.85	91.7	91.9
30	99.86	100.3	99.7

Normal Hexane.

$$\Phi_V = 25.4\,(V^{\frac{2}{3}} - 112.6^{\frac{2}{3}}).$$

$$\Phi_T = 702.6 - 219\,(234{,}8 - t)^{\frac{1}{5}}.$$

t	Φ	Φ_V	Φ_T
0	50.16	50.3	50.2
10	55.77	55.9	55.7
20	61.60	61.6	61.7
30	67.63	67.7	67.7
40	73.98	73.8	74.1
50	80.63	80.5	80.7
60	87.46	87.7	87.5

Normal Heptane.

$$\Phi_V = 21.7\,(V^{\frac{2}{3}} - 129.9^{\frac{2}{3}}).$$

$$\Phi_T = 660.1 - 204\,(266.85 - t)^{\frac{1}{5}}.$$

t	Φ	Φ_V	Φ_T
0	36.84	36.8	36.5
10	41.40	41.4	41.4
20	46.20	45.9	46.2

Normal Heptane.
(continued)

30	51.21	51.5	51.3
40	56.32	56.5	56.4
50	61.81	62.2	61.9
60	67.54	67.4	67.4
70	73.37	73.3	73.3
80	79.62	79.5	79.5
90	85.90	85.3	86.3

Normal Octane.

$$\Phi_V = 18.6\,(V^{\frac{2}{3}} - 147.9^{\frac{2}{3}}).$$

$$\Phi_T = 612.9 - 188\,(296.2 - t)^{\frac{1}{5}}.$$

t	Φ	Φ_V	Φ_T
0	26.26	25.8	26.1
10	30.02	29.7	30.1
20	34.06	34.1	34.3
30	38.15	38.5	38.5
40	42.48	42.5	42.8
50	46.97	47.2	47.3
60	51.60	52.0	51.9
70	56.48	56.7	56.9
80	61.56	61.8	62.0
90	66.92	66.9	67.3
100	72.46	72.7	72.5
110	78.18	78.3	78.1
120	84.57	84.0	84.0

Methyl-formate.

$$\Phi_V = 43.8\,(V^{\frac{2}{3}} - 52.04^{\frac{2}{3}}).$$

$$\Phi_T = 729.5 - 229\,(214.0 - t)^{\frac{1}{5}}.$$

t	Φ	Φ_V	Φ_T
0	59.60	59.7	59.8
10	66.27	66.3	66.2
20	72.98	72.7	72.8
30	79.47	79.7	79.7

Ethyl-formate.

$$\Phi_V = 34.0\,(V^{\frac{2}{3}} - 69.60^{\frac{2}{3}}).$$

$$\Phi_T = 696.1 - 218\,(235.3 - t)^{\frac{1}{5}}.$$

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(1) Viscosity above boiling points: A. Heydweiller, *Wied. Ann.*, 55 (1895), 561; ibid., 59 (1896), 198.

(2) Viscosity above boiling points: the writer, this paper part I. (loc. cit.)

Ethyl-formate.
(continued)

t	Φ	Φ_V	Φ_T
0	46.32	46.2	46.3
10	51.96	52.2	51.8
20	57.66	57.7	57.7
30	63.72	63.9	63.7
40	70.00	69.8	70.0
50	76.28	76.3	76.6

Propyl-formate.

$$\Phi_V=27.5\ (V^{\frac{2}{3}}-86.82^{\frac{2}{3}}).$$

$$\Phi_T=649.3-202\ (264.85-t)^{\frac{1}{5}}.$$

t	Φ	Φ_V	Φ_T
0	32.83	32.9	32.7
10	37.40	37.3	37.4
20	42.17	42.3	42.4
30	47.19	47.2	47.4
40	52.47	52.5	52.5
50	57.85	57.9	58.0
60	63.50	63.5	63.6
70	69.37	69.3	69.4
80	75.54	75.5	75.5

Methyl-acetate.

$$\Phi_V=37.1\ (V^{\frac{2}{3}}-68.93^{\frac{2}{3}}).$$

$$\Phi_T=742.4-233\ (233.7-t)^{\frac{1}{5}}.$$

t	Φ	Φ_V	Φ_T
0	49.14	48.9	48.8
10	55.00	54.8	54.8
20	61.09	61.1	61.0
30	67.35	67.4	67.6
40	73.89	74.2	74.4
50	80.78	81,3	81.4
60	88.47	88.5	88.8
70	95.81	96.0	96.4
80	104.0	104.4	104.6
90	113.3	112.5	113.0
100	122.6	121.7	122.1
110	132.7	131.7	131.6
120	142.9	142.3	141.9
130	153.8	153.9	152.9
140	166.6	166.6	164.7

Ethyl-acetate.

$$\Phi_V=28.2\ (V^{\frac{2}{3}}-86.10^{\frac{2}{3}}).$$

$$\Phi_T=674.4-211\ (250.1-t)^{\frac{1}{5}}.$$

Ethyl-acetate.
(continued)

t	Φ	Φ_V	Φ_T
30	53.53	54.1	53.9
40	59.73	59.7	59.5
50	66.03	65.7	65.6
60	72.41	71.7	71.7
70	78.83	78.8	78.2
80	85.59	85.0	85.1
90	92.68	92.0	92.0
100	100.1	99.1	99.5
110	107.7	107.1	107.4
120	115.5	115.5	115.8
130	123.8	124.4	124.6
140	132.9	133.4	134.0
150	143.1	144.6	144.2
160	154.5	155.9	155.4
170	166.7	168.7	167.4
180	179.9	182.3	180.7

Propyl-acetate.

$$\Phi_V=23.8\ (V^{\frac{2}{3}}-104.2^{\frac{2}{3}}).$$

$$\Phi_T=630.0-196\ (276.2-t)^{\frac{1}{5}}.$$

t	Φ	Φ_V	Φ_T
0	26.93	26.7	26.7
10	31.04	31.0	31.2
20	35.40	35.4	35.7
30	40.09	40.2	40.4
40	44.83	45.0	45.2
50	49.77	50.1	50.3
60	55.00	55.4	55.5
70	60.36	60.8	60.8
80	66.00	66.4	66.7
90	72.19	72.6	72.4
100	79.30	78.6	78.6

Methyl-propionate.

$$\Phi_V=28.9\ (V^{\frac{2}{3}}-85.04^{\frac{2}{3}}).$$

$$\Phi_T=669.2-208\ (257.4-t)^{\frac{1}{5}}.$$

t	Φ	Φ_V	Φ_T
0	37.82	37.8	37.9
10	42.80	43.0	42.9
20	48.06	47.9	48.0
30	53.26	53.0	53.3
40	58.79	58.7	58.9
50	64.46	64.7	64.6
60	70.49	70.5	70.5
70	76.85	76.5	76.8

Ethyl-propionate.

$$\Phi_V=23.5\ (V^{\frac{2}{3}}-102.9^{\frac{2}{3}}).$$

$$\Phi_T=628.5-195\ (272.9-t)^{\frac{1}{5}}.$$

Ethyl-propionate.
(continued)

t	Φ	Φ_V	Φ_T
0	29.94	29.8	29.8
10	34.22	34.3	34.2
20	38.69	38.6	38.9
30	43.43	43.3	43.6
40	48.30	48.4	48.6
50	53.37	53.7	53.6
60	58.60	58.9	58.8
70	64.19	64.2	64.2
80	70.01	69.9	69.9
90	76.05	76.0	75.8

Methyl-butyrate.

$$\Phi_V=23.6\,(V^{\frac{2}{3}}-102.7^{\frac{2}{3}}).$$

$$\Phi_T=623.5-193\,(281.3-t)^{\frac{1}{5}}.$$

t	Φ	Φ_V	Φ_T
0	27.43	27.4	27.3
10	31.55	31.9	31.5
20	35.91	36.0	36.0
30	40.48	40.6	40.6
40	45.20	45.5	45.3
50	50.08	50.4	50.2
60	55.22	55.4	55.2
70	60.50	60.5	60.4
80	66.16	65.8	65.8
90	72.01	71.4	71.5
100	77.82	77.2	77.3

Methyl-isobutyrate.

$$\Phi_V=23.8\,(V^{\frac{2}{3}}-102.9^{\frac{2}{3}}).$$

$$\Phi_T=624.0-194\,(267.55-t)^{\frac{1}{5}}.$$

t	Φ	Φ_V	Φ_T
0	30.84	30.6	30.7
10	35.20	35.2	35.2
20	39.72	39.8	39.8
30	44.43	44.7	44.6
40	49.38	49.8	49.6
50	54.59	54.8	54.7
60	59.89	60.1	60.0
70	65.54	65.5	65.5
80	71.48	71.5	71.4
90	77.82	77.3	77.3

Ethyl-ether.

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

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

Ethyl-ether.
(continued)

t	Φ	Φ_V	Φ_T
0	74.40	74.3	74.2
10	82.24	82.4	81.8
20	90.16	89.9	89.7
30	98.42	98.3	97.9
40	106.8	107.3	106.6
50	115.4	116.0	115.9
60	124.6	125.1	125.4
70	135.0	135.3	135.8
80	146.6	145.9	146.9
90	159.1	158.8	158.5
100	172.6	171.8	171.2

Carbon-tetrachloride.

$$\Phi_V=20.4\,(V^{\frac{2}{3}}-88.88^{\frac{2}{3}}).$$

$$\Phi_T=470.7-147\,(283.15-t)^{\frac{1}{5}}.$$

	Φ	Φ_V	Φ_T
0	16.31	16.1	16.1
10	19.32	19.5	19.3
20	22.50	22.6	22.6
30	25.75	26.4	26.1
40	29.27	29.6	29.6
50	33.08	33.6	33.3
60	36.65	37.3	37.2
70	40.74	41.4	41.1
80	45.41	45.3	45.2
90	49.65	49.7	49.5
100	54.82	54.2	53.9
110	59.50	58.6	58.6
120	64.49	63.8	63.7
130	69.29	68.8	68.5
140	74.64	74.3	73.9
150	80.33	79.9	79.7
160	87.02	85.5	85.7
170	93.22	92.1	92.2
180	100.0	98.6	99.2

Benzene.

$$\Phi_V=34.4\,(V^{\frac{2}{3}}-82.21^{\frac{2}{3}}).$$

$$\Phi_T=756.6-236\,(288.5-t)^{\frac{1}{5}}.$$

t	Φ	Φ_V	Φ_T
20	34.62	34.3	34.3
30	39.92	39.7	39.8
40	45.47	45.8	45.4
50	51.18	51.6	51.3
60	57.18	57.7	57.3
70	63.37	63.3	63.5
80	69.58	69.9	70.0
90	75.95	75.3	75.6
100	82.75	83.3	83.6

Benzene.
(continued)

110	90.10	90.4	91.0
120	97.95	98.0	97.6
130	106.3	106.0	106.6
140	115.1	114.9	115.0
150	124.3	124.0	123.9
160	134.1	132.9	133.3
170	144.6	143.4	143.2
180	156.4	153.7	154.0

Fluorobenzene.

$$\Phi_V = 28.8\,(V^{\frac{2}{3}} - 85.51^{\frac{2}{3}}).$$

$$\Phi_T = 647.3 - 200\,(286.55 - t)^{\frac{1}{5}}.$$

t	Φ	Φ_V	Φ_T
30	41.19	40.9	40.9
40	45.66	45.6	45.6
50	50.81	50.3	50.5
60	55.71	55.5	55.6
70	60.38	60.8	61.1
80	65.25	65.9	66.5
90	71.22	72.1	72.3
100	77.32	78.2	78.1
110	84.45	84.4	84.5
120	91.11	91.2	91.0
130	97.81	98.4	97.8
140	105.2	105.7	105.0
150	113.7	113.4	112.6
160	122.4	122.8	120.7
170	131.0	130.4	129.2
180	141.0	139.6	138.4

Chlorobenzene.

$$\Phi_V = 24.5\,(V^{\frac{2}{3}} - 94.12^{\frac{2}{3}}).$$

$$\Phi_T = 601.1 - 179\,(359.2 - t)^{\frac{1}{5}}.$$

t	Φ	Φ_V	Φ_T
10	23.70	23.6	23.6
20	26.81	27.0	27.0
30	30.29	30.5	30.4
40	33.66	34.0	34.0
50	37.42	37.5	37.5
60	41.06	41.2	41.2
70	44.74	45.0	45.1
80	48.72	48.8	48.9
90	52.70	53.0	53.0
100	56.80	56.8	57.0
110	61.27	61.2	61.3
120	66.10	65.7	65.6
130	70.31	70.5	70.3
140	74.89	75.1	75.0
150	79.74	79.8	79.9
160	85.13	84.9	84.7
170	90.84	90.2	90.2
180	96.49	95.8	95.7
190	102.3	101.6	101.5
200	107.9	107.8	107.6
210	114.8	114.4	113.9
220	121.2	120.9	120.7
230	128.3	128.5	127.7
240	135.5	136.8	135.3

For the following substances quantities are all referred to one gram and this is meant by the index 1 under the symbol.

Acetic acid.

$$\Phi_{1V} = 2250\,(V_1^{\frac{2}{3}} - 0.8997^{\frac{2}{3}}).$$

$$\Phi_{1T} = 2291 - 705\,(321.6 - t)^{\frac{1}{5}}.$$

t	Φ_1	Φ_{1V}	Φ_{1T}
20	83.32	83	82
30	97.74	96	97
40	112.0	112	113
50	127.2	127	128
60	143.1	144	144
70	159.7	160	162
80	177.6	178	178
90	196.2	196	197
100	215.7	215	215
110	235.8	234	234

Bromine.

$$\Phi_{1V} = 4400\,(V_1^{\frac{2}{3}} - 0.2868^{\frac{2}{3}}).$$

$$\Phi_{1T} = 2273 - 688\,(302.2 - t)^{\frac{1}{5}}.$$

t	Φ_1	Φ_{1V}	Φ_{1T}
0	117.0	117	117
10	132.3	132	132
20	147.1	147	147
30	162.0	161	161
40	177.5	177	178
50	193.6	194	194

Nitrogen peroxide.

$\Phi_{1V}=3250\,(V_1^{\frac{2}{3}}-0.5855^{\frac{2}{3}})$.

t	Φ_1	Φ_{1V}
0	216.6	217
10	242.9	243
20	270.4	270

Molten Tin.

$\Phi_{1V}=16000\,(V_1^{\frac{2}{3}}-0.1247^{\frac{2}{3}})$.

t	Φ_1	Φ_{1V}
280	113.8 (110.4?)	111
296	114.7	115
357	134.0	134
389	145.1	144

?: Extrapolated from the other temperatures.

From above results, it may be concluded that equations (4), (7), etc. expressing the relations among molecular fluidity $({}^{1}/_{\eta}.\,V^{\frac{1}{3}})$, molecular volume and absolute temperature hold good for most substances except a few which include alcohols, water and mercury.

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

April, 1927.

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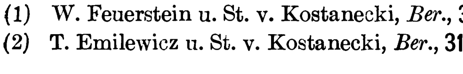
Hongo, Tokyo.

SYNTHESE VON 3',4'-METHYLENDIOXYFLAVON, 3',4'-METHYLENDIOXYFLAVONOL, 3',4'-DIMETHOXYFLAVON UND 3',4'-DIMETHOXYFLAVONOL.

Von Shizuo HATTORI.

Eingegangen am 11. April 1927. Ausgegeben am 28. Juni 1927.

Zum Zweck der Verwendung zu meiner spektrographischen Untersuchung habe ich die oben genannten Flavone und Flavonole neu synthetisiert. Die Synthese der ersten Verbindung hatten W. Feuerstein und St. v. Kostanecki⁽¹⁾ schon früher versucht, aber es resultierte aus dem 2-Acetoxy-3',4'-methylendioxychalkondibromid beim Behandeln mit Kalilauge kein entsprechendes Flavon, sondern das gelbe Piperonalcumaranon,  $C_6H_4\left<\begin{matrix}O\\CO\end{matrix}\right>C:CH\cdot C_6H_3\left<\begin{matrix}O\\O\end{matrix}\right>CH_2$. Diese Darstellungsweise⁽²⁾ eines

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(1) W. Feuerstein u. St. v. Kostanecki, *Ber.*, 32 (1899), 315.

(2) T. Emilewicz u. St. v. Kostanecki, *Ber.*, 31 (1898), 696.

Flavons aus o-Acetoxychalkondibromid geht sehr glatt bei 7-Oxyflavon⁽¹⁾ (aus 2-Acetoxy-4-äthoxychalkondibromid) und 7-Äthoxy-4-methoxyflavon⁽²⁾ u.s.w., dagegen schlägt die Methode fehl bei Flavon⁽³⁾ (aus 2-Acetoxychalkondibromid), 4′-Methoxyflavon⁽⁴⁾ (aus 4′-Methoxy-2-acetoxychalkondibromid) und bei 3′,4′-Methylendioxyflavon, wobei hauptsächlich Cumaranonderivate nebst einer gelingen Menge von Flavonen entstehen.

In vorliegenden synthetischen Versuchen habe ich eine schöne von A. Löwenbein⁽⁵⁾ aufgefundene Reaktion angewandt, welche in Dehydrierung eines Flavanons durch Einwirkung des Phosphorpentachlorids besteht. Diese Methode der Flavonsynthese ist als die beste zu empfehlen, wenn man das Flavanon schon in den Händen hat. Durch diese Methode konnte auch die Synthese des 3′,4′-Methylendioxyflavons leicht durchgeführt werden.

Die Flavonole sind auch nach der Methode von Kostanecki⁽⁶⁾ synthetisiert; nämlich eine Umwandlung von Flavanon über Isonitrosoflavanon in Flavonol, welche Reaktion auch glatt vor sich ging.

Versuche.

3′,4′-Methylendioxyflavanon. Eine heisse Lösung von 3′,4′-Methylendioxy-2-oxychalkon⁽⁷⁾ vom Schmp. 140° in Alkohol wird mit 10 proz. Schwefelsäure versetzt und auf dem lebhaft siedenden Wasserbade 24 Stunden lang erhitzt. Beim Erkalten scheiden sich weisse Nadeln vom Flavanon aus, die mit etwas unverändertem Chalkon beigemengt sind. Nach vollständigem Abscheiden filtriert man sie ab, spült mit Wasser zur Befreiung von Schwefelsäure aus und trocknet in einem Exsikkator. Dann wird die Krystallmasse beim gelinden Erwärmen in verhältnismässig viel Schwefelkohlenstoff gelöst und stehen gelassen, wobei das schwerer lösliche Flavanon in derben weissen Tafeln auskrystallisiert, dagegen das unveränderte Chalkon in Lösung bleibt. Dieses erstere wird aus 80 proz. Alkohol umkrystallisiert, woraus sie in glänzenden farblosen prismatischen Nadeln ausscheiden. Aus noch wasserärmerem Alkohol erhält man sie in hübschen, glitzernden, kurzen Prismen. Beide sind vom Schmp. 127–128°. ($C_{16}H_{12}O_4$. Ber.: C = 71.64, H = 4.46; Gef.: C = 71.73, H = 4.77%).

Mit conz. Schwefelsäure betupft, färben sich die Krystalle frisch ziegelrot.

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(1) T. Emilewicz u. St. v. Kostanecki, loc. cit., S. 698.
(2) St. v. Kostanecki u. F. Wosius, *Ber.*, 32 (1899), 321.
(3) T. Emilewicz u. St. v. Kostanecki, loc. cit., S. 696.
(4) F. Herstein u. St. v. Kostanecki, *Ber.*, 32 (1899), 318.
(5) A. Löwenbein, *Ber.*, 57 (1924), 1515.
(6) St. v. Kostanecki u. Szabrânski, *Ber.*, 37 (1904), 2819.
(7) W. Feuerstein u. St. v. Kostanecki (loc. cit.) gaben den Schmp. 137–138°.

3',4'-Methylendioxyflavon. 0.5 gr. des Flavanons wird in 5 c.c. reinem Benzol auf einem schwach siedenden Wasserbade gelöst, der Lösung 1.25 gr. Phosphorpentachlorid zugesetzt und weiter erhitzt. Bald färbt sich die Lösung rotbraun um, und es scheidet sich rotbraune Krystallmasse ab. Nach 10 Minuten werden sie scharf abgesaugt, mit wenig Benzol ausgewaschen und in 3 c.c. Alkohol eingetragen. Sie löst sich dabei mit gelinder Wärmeentwickelung. Diese alkoholische Lösung erstarrt nach einigen Sekunden zu einem gelben Krystallbrei. Dies wird sofort abfiltriert und mit wenig kaltem Alkohol gewaschen, wobei die rote schmierige Substanz in Lösung geht. Die hinterbleibende gelblich gefärbte Krystallmasse wird aus Alkohol umkrystallisiert, in welchem sie etwas schwer löslich ist. Man erhält sie ganz rein durch weitere Umkrystallisationen aus Ligroin. Sehr feine farblose Nadeln vom Schmp. 206°. ($C_{16}H_{10}O_4$. Ber.: $C=72.18$, $H=3.76$; Gef.: $C=72.05$, $H=4.10\%$).

Mit conz. Schwefelsäure betupft, lösen sich die Krystalle mit gelber Farbe darin auf. Mit Eisenchlorid zeigt die Substanz keine Färbung. In sehr verdünnter alkoholischer Lösung tritt eine ziemlich intensive blaue Fluorescenz auf.

3',4'-Methylendioxyflavonol. Auf einem kochenden Wasserbade werden einer Lösung von 3,'4'-Methylendioxyflavanon (2 gr.) in Alkohol (120 c.c.) abwechselnd conz. Salzsäure (20 gr.) und Amylnitrit (3 gr.) in kleinen Portionen zugesetzt. Beim Erkalten scheiden sich sofort gelbe Nadeln reichlich aus. Man filtriert sie ab, wäscht mit Wasser, trocknet und krystallisiert aus Alkohol um. Blassgelbe Nadeln vom Schmp. 214–215°.

Zuerst hielt ich diese Substanz für das 3',4'-Methylendioxy-3-isonitrosoflavanon als die natürliche Folge der Reaktion. Beim Ausführen der Mikro-Dumas-Bestimmung verriet sich, aber, die Abwesenheit von Stickstoff in ihrem Molekül. Auch die Elementaranalyse ($C_{16}H_{10}O_5$. Ber.: $C=68.08$, $H=3.54$; Gef.: $C=68.25$, $H=4.10\%$) und der höher liegende Schmelzpunkt weisen darauf hin, dass es hierbei das 3',4'-Methylendioxyflavonol vorliegt, welches bei diesem Vorgange direkt entstanden ist, ohne dass das Isonitrosoflavanon als Zwischenprodukt abgefangen werden konnte.

Mit conz. Schwefelsäure betupft, färbt sie sich rotbraun; die Lösung ist auch von gleicher Farbe. Mit Eisenchlorid erzeugt sie eine bräunlich violette Färbung, ähnlich wie alle andere Flavonole. Sehr verdünnte alkoholische Lösung liefert eine grünlich blaue Fluorescenz.

3',4'-Methylendioxyflavonolmethyläther. Das Flavonol wird in methylalkoholischer Lösung mit Diazomethan methyliert. Aus Alkohol umkrystallisiert, bildet der Methyläther weisse Prismen vom Schmp. 155°. ($C_{17}H_{12}O_5$. Ber.: 10.4%. OCH_3; Gef.: 10.5%. OCH_3).

Die Substanz zeigt keine Farbenreaktion mit Ferrichlorid: mit conz. Schwefelsäure betupft, färbt sich die Krystallmasse braunrot, wie es bei den vorigen Substanzen der Fall ist.

3',4'-Dimethoxy-2-oxychalkon. Eine Lösung von Veratrumaldehyd (12.5 gr.) und 2-Oxyacetophenon (10 gr.) in Alkohol wird mit 50 proz. wässriger Natronlauge (25 gr. Natriumhydroxyd) versetzt und auf einem Wasserbade unter Rückfluss drei Stunden lang erhitzt. Das erhaltene gelbe krystallinische Natiumsalz des Chalkons wird mit verdünnter Salzsäure zersetzt und das nun frei gewordene Chalkon aus absolutem Alkohol umkrystallisiert. Gelbrote, sechsseitige Plättchen vom Schmp. 117°. ($C_{17}H_{16}O_4$. Ber.: C=71.8, H=5.6; Gef.: C=71.71, H=5.96%).

In alkoholischer Lösung gibt es mit Eisenchlorid eine braune Färbung. Mit conz. Schwefelsäure betupft, färben sich die Krystalle rotbraun.

3',4'-Dimethoxy-2-acetoxychalkon. Das Chalkon wird mit siedendem Essigsäureanhydrid unter Zusatz von einigen Tropfen Pyridin leicht acetyliert. Das Produkt wird aus Alkohol mehrmals umkrystallisiert. Farblose, sechsseitige Plättchen vom Schmp. 90°. ($C_{19}H_{18}O_5$. Ber.: C=69.6, H=5.5; Gef.: C=69.3, H=5.6%).

3',4'-Dimethoxyflavanon. 3',4'-Dimethoxy-2-oxychalkon (3 gr.) wird auf einem siedenden Wasserbade in 150 c.c. Alkohol gelöst, der Lösung wird 10 proz. Schwefelsäure eingetropft, bis eine bleibende weisse Trübung entsteht. Dieselbe wird durch weitere Zugabe von einiger Menge Alkohol wieder in Lösung gebracht, und man fährt mit dem Erhitzen fort. Nach 20-stündigem Sieden wird die nun hellgelbe Lösung in eine offene Schale hineingegossen und stehen gelassen. Dabei scheiden sich blassgelbe glitzernde schuppenartige Krystalle aus, welche abgesaugt, mit Wasser gewaschen und in warmem Schwefelkohlenstoff gelöst werden. Nach kurzer Zeit beginnt die Ausscheidung von weissen Krystallen, welche aus Alkohol in farblosen monoklinen Tafeln auskrystallisierten. Schmp. 126°. ($C_{17}H_{16}O_4$. Ber.: C=71.8, H=5.6; Gef.: C=71.98, H=6.31%).

Die Substanz gibt keine Farbenreaktion mit Eisenchlorid; mit conz. Schwefelsäure betupft, färben sich die Krystalle rotbraun.

3',4'-Dimethoxyflavon. Das Flavanon wird wie bei dem 3',4'-Methylendioxyflavon in benzolischer Lösung mit Phosphorpentachlorid behandelt. Die Phosphorverbindung wird durch Eintragen in wenig kalten Alkohol zersetzt. Diese alkoholische Lösung wird in viel Wasser eingetragen, gelinde erwärmt und mit Glasstab an den Wandungen gerieben. Bald scheiden sich weisse feinwollige Nadeln aus, welche nach mehrmaligen Umkrystallisieren aus Alkohol weisse prismatische Nadeln vom Schmp. 156° geben. ($C_{17}H_{14}O_4$. Ber.: C=72.3, H=4.9; Gef.: C=72.02, H=5.11%).

Mit conz. Schwefelsäure wird die Verbindung mit rotgelber Farbe aufgenommen; mit Eisenchlorid entsteht keine Färbung in alkoholischer Lösung. Selbst eine sehr verdünnte alkoholische Lösung zeigt eine blaue Fluorescenz, wie es bei dem 3′,4′-Dimethoxyflavon der Fall ist.

3′,4′-Dimethoxy-3-isonitrosoflavanon. Eine siedende alkoholische Lösung von 3′,4′-Dimethoxyflavanon wird mit Amylnitrit und conz. Salzsäure sukzessiv in kleinen Portionen versetzt. Nach dem Erkalten wird die Reaktionsflüssigkeit in viel Wasser eingegossen. Die zuerst weiss trübende Flüssigkeit scheidet beim Stehen übernacht gelbe amorphe Masse ab, welche trotz wiederholten Versuchen nicht zur Krystallisation gebracht werden konnte und deshalb durch Fällen mit Essigsäure aus der Lösung in verdünnter wässriger Natronlauge gereinigt wurde. Sie schmilzt unscharf bei 125–127°. ($C_{17}H_{15}O_5N$. Ber.: N = 4.4; Gef.: N = 4.7%).

3′,4′-Dimethoxyflavonol. Das Isonitrosoflavanon wird wie bei dem 3′,4′-Methylendioxyflavonol behandelt. Aus Alkohol umkrystallisiert, stellt das Flavonol gelbe Nadeln vom Schmp. 202° dar. ($C_{17}H_{14}O_5$. Ber.: C = 68.45, H = 4.69; Gef.: C = 68.18, H = 6.64%).

Mit conz. Schwefelsäure werden die Krystalle auch rotbraun gefärbt; mit Eisenchlorid tritt eine braunviolette Färbung auf. In sehr verdünnter alkoholischer Lösung zeigt die Substanz eine schwach grünlichgelbe Fluorescenz.

3′,4′-Dimethoxyflavonolmethyläther. Das Flavonol wurde in einem Gemisch von Methylalkohol und Aceton gelöst und mit Diazomethan methyliert. Aus Alkohol umkrystallisiert, stellt der Methyläther gelblich gefärbte Warzen von feinen Nadeln dar. Schmp. 168–169°. ($C_{18}H_{16}O_6$. Ber.: 9.9%. OCH_3; Gef.: 9.7%. OCH_3).

Die Substanz zeigt keine Phenolreaktion mit Eisenchlorid.

Zum Schluss sei es mir gestattet, dem Herrn Prof. K. Shibata für seine gütige Leitung und Anregung meinen Dank auszusprechen.

März 1927.

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ON THE BASIC NITROGEN COMPOUNDS FROM FUSHUN SHALE TAR, I.(1)

By **Takashi EGUCHI.**

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The presence of nitrogen compounds in shale tar has long been recognized, but little is known of their chemical nature, owing to the fact that they may be present in tar in an amount rarely exceeding 1% and that the character of the bases would vary according to the conditions of the distillation of the shale, such as the type of retort used, the temperature and the time of heating.

Moreover, in the begining of the tar industry, the nitrogen constituents of shale or of coal were utilized by transforming them into ammonia, and the use of high temperature in distillation, tends to increase the yield of ammonia at the expense of the basic compounds normally found in the tars, which are for the most part relatively unstable toward heat.(2)

Since the Great War, the rapid increase in the consumption of gasoline, making heavy demands on pyridine bases as denaturants for the grain alcohol which is used as one of the constituents of some gasoline substitutes, opens the way for scientific researches into the nature of the nitrogenous substances in tars.(3)

Pyridine and its homologues have already been reported as present in Scottish and American Shale Oils; T. C. Garrett and J. A. Smythe(4) who worked on the basic constituents extracted from Scottish shale tar, have reported that pyridine, 2-methyl pyridine, 2:6-dimethyl pyridine, 2:4-dimethyl pyridine, 2:5-dimethyl pyridine, 2:3-dimethyl pyridine and 2:4:6-trimethyl pyridine were composed of the "green naphtha," with about a 0.3 per cent. yield by volume.

G. C. Robinson and his co-workers(5) have comfirmed that the bases of the isoquinoline series occurred in basic fractions boiling at 270° and 390°. The basic nitrogen compounds of American shale oil,(6) especially of the oil of the Colorado field, according to the investigations which are being carried

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(1) Contribution from the Scientific Research & Experimental Branch, Imperial Naval Fuel Depot, No. 1.

(2) P. E. Spielmann, "The Constituents of Coal Tar," (1924), 157; R. H. Mckee, "Shale Oil" (1925), 116.

(3) E. H. Leslie, "Motor Fuels," (1923), 13 & 482.

(4) *J. Chem. Soc.*, **81** (1902), 449; **83** (1903), 763.

(5) R. H. Mckee, "Shale Oil," (1925), 175.

(6) Ibid., p. 120.

out in the Chemical Engineering Laboratories of Columbia University, seem to be composed mostly of pyridine and its homologues, but not of the quinoline or the isoquinoline bases. It is remarkable, though the significance of the basic compounds in the natural product is not immediately apparent, that the majority of the nitrogen compounds in the shale oil are nitrogen-ring compounds, but not substitution products of the aromatic series as we noticed of the nitrogen bases occur in petroleum.(1)

The low temperature tar of Fushun coal, according to Y. Oshima and K. Ishibashi,(2) contains 0.67% of basic substances and among these substances 2-methyl pyridine, 3:4-dimethyl pyridine and 2:4:6-trimethyl pyridine were confirmed to occur, and the presence of aniline and its homologues were also confirmed. To our interest, the crude tar of Fushun shale has the highest nitrogen base content of any known, viz., 2–4%. It stands in nitrogen content near to Californian petroleum, which is 2.39%.(3)

The isolation in a pure state of the nitrogenous substances from the Fushun shale oil, and the study of the chemical and physical properties of the purified substances, aroused the writer's interest, in relation to some evidences for the significance of the presence of nitrogenous compounds in tar, which might give some suggestion for the consideration of the mechanism of the chemical processes in the distillation of the shale, and the present investigation was undertaken.

The crude tar used for the experiment was obtained by the distillation of Fushun shales of the composition (A & B) in the vertical retort, the Oakbank Retort, in Scotland, which shows the following properties:(4)

	A.	B.
Water	3.04%	2.67%
Volatile matter.	21.05%	15.89%
Fixed carbon.	4.47%	1.34%
Ash.	71.41%	80.10%

Tar. C=83.80; H=11.53; N=0.45; O=3.63; S=0.59; $d_4^{15}=0.864$.

	Fractions.	Yield (Vol.)
1.	— 200°	3%
2.	200° - 250°	25%
3.	250° - 300°	27%
4.	300° - 350°	23%
5.	above 350°	22%

600 litres of the crude tar were fractionated under atmospheric pressure

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(1) Engler-Höfer, "Das Erdöl," I. (1913), 479.

(2) *J. Soc. Chem. Ind. Japan,* 29 (1923), 445.

(3) C. F. Mabery & L. G. Wesson, *J. Am. Chem. Soc.,* 42 (1920), 1014.

(4) Refer: T. Kimura, *Reports of Invest. (Japanese) Central Lab., South Manchuria Railway Co. Ltd.,* 10 (1925), 507.

TABLE 1.

Fraction.	Distillate in gr.	$\frac{dw}{dT}$	d_4^{25}	n_D^{25}	Mol. wt.
128°–130°	32.5	16.3	0.9420	1.4970	95.4
130–132	8.8	4.4	0.9441	1.4970	
132–134	4.0	2.0	0.9476	1.4963	
134–136	1.5	0.8			
136–138	2.0	1.0	0.9376	1.4965	
138–140	2.0	1.0			
140–142	5.0	2.5	0.9328	1.4977	
142–143	17.7	17.7	0.9322	1.4979	
143–144	70.0	70.0	0.9320	1.4980	103.3
144–145	44.5	44.5	0.9330	1.4979	
145–146	15.0	15.0	0.9363	1.4973	
146–148	20.0	10.0	0.9312	1.4979	
148–150	11.5	5.8	0.9367	1.4958	
150–153	12.5	4.1	0.9312	1.4962	
153–156	15.3	5.1	0.9305	1.4964	
156–157	9.5	9.5	0.9265	1.4972	
157–158	39.3	39.3	0.9271	1.4969	
158–159	104.4	104.4	0.9260	1.4977	110.0
159–160	74.0	74.0	0.9265	1.4977	
160–161	14.	14	0.9312	1.4979	
161–163	26	13	0.9269	1.4979	
163–165	26	13	0.9272	1.4975	
165–167	18	9	0.9235	1.4975	
167–169	36	18	0.9214	1.4974	
169–170	29	29	0.9201	1.4973	
170–171	70	70	0.9180	1.4976	120.0
171–172	73	73	0.9185	1.4981	120.1
172–173	37	37	0.7202	1.4985	121.7
173–174	32	32	0.9213	1.4990	121.4
174–175	24	24	0.9240	1.4990	121.6
175–176	29	29	0.9242	1.4989	121.4
176–177	24	24	0.9271	1.4988	121.7
177–178	28	28	0.9268	1.4986	121.5
178–179	34	34	0.9241	1.4986	123.0
179–180	23	23	0.9237	1.4977	125.3
180–182	23	12	0.9186	1.4976	127.4
182–184	22	11	0.9194	1.4975	131.1
184–186	45	23	0.9145	1.4977	132.1
186–187	30	30	0.9133	1.4182	131.9
187–188	52	52	0.9173	1.4985	133.3
188–189	29	29	0.9178	1.4991	131.7
189–190	41	41	0.9191	1.4994	132.1
190–191	29	29	0.9188	1.4996	131.9
191–192	26	26	0.9212	1.5000	131.8
192–193	15	15	0.9249	1.5001	133.4
193–194	16	16	0.9258	1.5001	133.9
194–196	24	12	0.9251	1.5001	133.9
196–198	20	10	0.9285	1.5022	137.2
198–200	14	7	0.9313	1.5032	137.2
200–202	61	31	0.9261	1.5042	141.5
202–204	49	25	0.9268	1.5041	141.6
204–206	32	16	0.9257	1.5043	140.9
206–208	25	13		1.5050	142.1
208–210	16	8		1.5060	
210–214	24	6		1.5065	
214–218	29	7		1.5086	

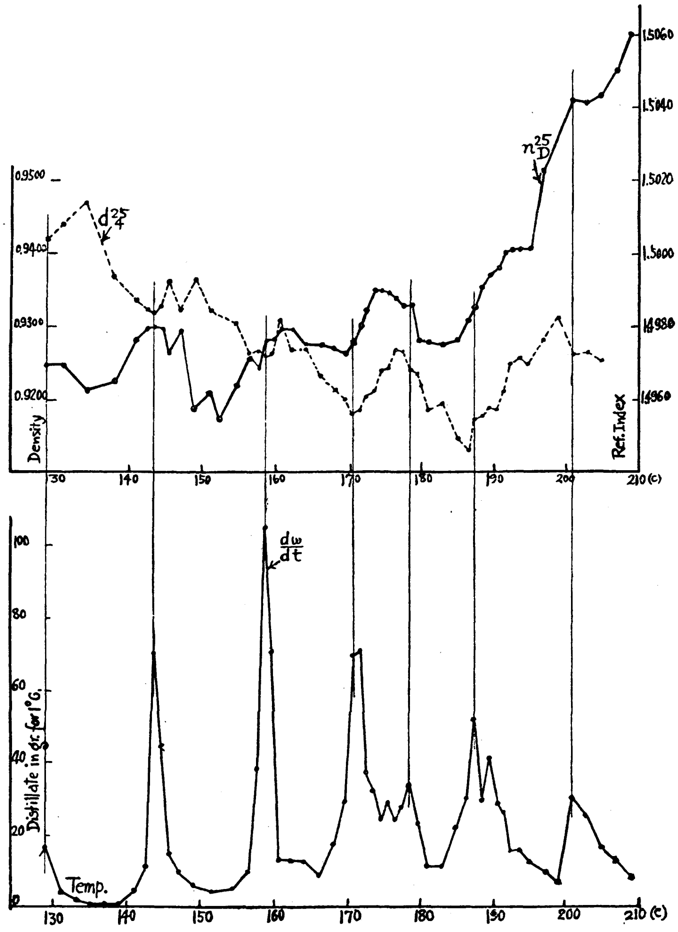

Fig. 1.

and thereby 106 litres of the fraction b. p. 220°–250° were obtained which were used in this experiment, and treated with 30% sulphuric acid to extract the basic substance; the crude base recovered amounted to 3550 c.c., (corresponding to about 0.6% by volume of the crude tar used), and they were distilled out between 100°–280°, and the specific gravity was about 0.979 at 15°. The nitrogen bases occurring in the fraction faintly show pyrrol reactions, but negatively the carbylamine reaction for primary amines and the Liebermann nitroso reaction for secondary amines. The presence of the tertiary bases of the pyridine series is shown in the behavior toward picric acid, ferrocyanic acid and mercuric chloride.

For the isolation of individual bases in an approximately pure state, 1965 gr. of the basic fraction boiling to 220°, was subjected to fractional distillation; it was fractionated carefully three times in a flask with a Norton & Otten's Six-column dephlegmator of 45 cm. length, and then seven successive fractional distillations through Hempel's glass dephlegmator of 120 cm. length, 2 cm. diameter, which contains 600 glass beads of 4 mm. diameter, the operation was continued at the rate of one or two drops of distillate every two seconds, and the results of the 10th distillation, the weight of each distillate, the ratio of weight and temperature range dw/dt, specific gravity, and index of refraction are shown in Table 1. The temperature-weight curve of the results shown in Fig. 1 shows the seven maxima which indicate the presence of some definite compounds in the regions.

1. **2-Methyl Pyridine.**⁽¹⁾ 2-Methyl pyridine which was assumed to be composed of the fraction, b. p. 128°–130°; $d_4^{25}=0,9420$; $n_D^{25}=1.4970$, 30 gr. of the fraction dissolved in dilute hydrochloric acid were added to 181 gr. of mercuric chloride dissolved in 2000 c.c. of water, and on standing the solution for a while at 20°C., 215 gr. of prismatic crystals of the double salt of mercury chloride were deposited. On purifying by recrystallisation twice from a dilute acidic solution, the pure double salt of melting-point 153°–154°, was isolated, the yield was 180 gr. On analysis, Hg was found to be 69.06%, while theory requires 69.67% for $C_6H_7N \cdot HCl \cdot 2HgCl_2$.

To liberate the free base, 60 gr. of sodium hydroxide were added to 180 gr. of the purified salt dissolved in 2000 c.c. of water, the free base extracted with benzene, distilled off the solvent, after fixed with hydrochloric acid, decomposed with caustic soda, dried with fused caustic potash and then distilled. It distilled completely at 129°.20–129°25 under 758.5 mm. and show the following physical constants:

d_4^{25}(in vacuo)$=0.9400$; $n_D^{25}=1.4983$; $n_C^{25}=1.4939$; $n_F^{25}=1:5097$; $n_{G'}^{25}=1.5197$.

0.1320 Gr. of the subst. gave 0.3745 gr. CO_2 and 0.0895 gr. H_2O. 0.2500 Gr. subst. gave 33.0 c.c. N_2 at 25° and 671 mm. (Found: C=77.42; H=7.59; N=15.15; Mol. wt., 93.8. C_6H_7N requires C=77.36; H=7.58; N=15.05%; Mol. wt., 93.1).

It was identified as 2-methyl pyridine by the oxidation of 3 gr. of the purified base with a 2% aqueous solution of 10.4 gr. potassium permanganate, the pyridine-2-carboxylic acid, thus obtained, was purified by converting it into the copper salt with a copper acetate solution. The copper salt, showing the characteristic appearance of the bluish-violet platy crystals of the salt of pyridine-2-carboxylic acid, was analysed for confirmation with the following results:

0.113 Gr. of the salt gave 0.0115 gr. loss on heating, 0.1694 gr. CO_2, 0.0252 gr. H_2O and 0.0258 gr. CuO. (Found: C=41.53; H=2.53; Cu=18.52;

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(1) P. E. Spielmann, "The Const. Coal Tar," (1924), 183.

$H_2O=10.33$. ($(C_5H_4N{\cdot}CO_2)_2Cu{\cdot}2H_2O$ requires $C=41.90$; $H=2.35$; $Cu=18.50$; $H_2O=10.48\%$).

The free acid isolated from the copper salt shows a reddish yellow colour reaction with ferrous sulphate.

2. **2:6-Dimethyl Pyridine.**(1) The fractions (1) b. p. 143°–144°; $d^{25}_4=0.9320$; $n^{25}_D=1.4980$; (2) b. p. 144°–145°; $d^{25}_4=0.9330$; $n^{25}_D=1.4979$ were regarded as a mixture of mono- and dimethyl pyridine from their physical constants and the molecular weight determination (mean Mol. wt. 103), and 40 gr. of the former fraction and 50 gr. of the latter were combined together, dissolved in a dilute hydrochloric acid solution, to which 250 gr. of mercuric chloride in total were added in several doses and 185 gr. of platy crystals of the double salt were obtained. Purifying twice from the dilute acidic solution, 171 gr. of pure salt of a melting point 191°–191°.5 were obtained, which on analysis, agrees in compostion with the formula $C_7H_9N{\cdot}HCl{\cdot}HgCl_2{\cdot}H_2O$. ($Hg=46.85$; $Cl=24.61\%$). 170 gr. of the pure salt were decomposed with a concentrated sodium hydroxide solution, and the free base was dried over fused caustic potash and distilled. 39.5 gr. of the pure base, thus obtained, were distilled out completely at 143°.85–143°.87 under 757.4 mm.

It was a non-disagreeable odours oil, completely miscible with water at 25°, and showed the following constants:

d^{25}_4 (in vacuo)$=0.9183$; $n^{25}_D=1.4953$; $n^{25}_C=1.4910$; $n^{25}_F=1.5065$; $n^{25}_{G'}=1.5164$.

0.0967 Gr. subst. gave 0.0738 gr. H_2O and 0.2780 gr. CO_2. 0.2951 Gr. subst. gave 38.8 c.c. N_2 at 29° and 759 mm. (Found: $C=78.41$; $H=8.54$; $N=13.32$; Mol. wt., 106.5. C_7H_9N requires $C=78.45$; $H=4.47$; $N=13.08\%$; Mol. wt., 107.1)

5 Gr. of the base were oxidized with 35 gr. of potassium permanganate in dilute solution, and dipicolinic acid formed by the oxidation, was obtained, and this was recrystallized from the aqueous solution. The yield was 5.3 gr. It melts at 238°.5, whereas Conrad & Epastein(2), and Collie(3) have recorded its melting point as 237° and 236°, respectively. The acid recrystallized from boiling alcohol, was found to melt at 226°.5–227°, as stated by A. Ladenburg & C. F. Roth(4) (226°) and also by C. Paal and C. Demeler(5), (226°–227°) for the melting point of the same acid.

On analysis of the acid with m. p. 226°, the results obtained were:

0.1008 Gr. subst. gave 0.1858 gr. CO_2 and 0.0278 gr. H_2O. (Found: $C=50.27$; $H=3.09$. $C_5H_3N(CO_2H)_2$ requires $C=50.28$; $H=3.02\%$)

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(1) P. E. Spielmann, loc. cit., P. 187.

(2) *Ber.*, 20 (1887), 162.

(3) *J. Chem. Soc.*, 59 (1891), 177.

(4) *Ber.* 18 (1885), 52.

(5) Ibid., 30 (1897), 1502.

3. **2:4-Dimethyl Pyridine.**(1) Both of the two fractions (1) b. p. 158°–159°; $d_4^{25}=0.9260$; $n_D^{25}=1.4977$, (2) b. p. 159°–160°, $d_4^{25}=0.9265$; $n_D^{25}=1.4977$, seem to be a mixture of lutidines and collidines as indicated by the mean molecular weight 110. To isolate the lutidine-2:4-dimethyl pyridine, in a pure state, the mixed oil derived from 55 gr. of the first fraction, and 55 gr. of the second, dissolved in a dilute hydrochloric acid solution, was added to the solution of 544 gr. of mercuric chloride dissolved in 8 litres of hot water. Long needle crystals (m. p. 124°) of glasswool-like lustre were deposited, recrystallized twice from hot water, and 240 gr. of the pure double salt of mercuric chloride with a melting-point of 131°–132° were obtained. It gave Hg=57.17, on analysis, which corresponds to Hg=56.94 for $C_7H_9N\cdot HCl\cdot 2HgCl_2\cdot H_2O$. 210 gr. of the salt were decomposed with 600 c.c. of a 10% caustic soda solution, and 30.5 gr. of a colourless base were separated, and this was dried with fused caustic potash and distilled.

It distilles completely at 157°.83–157°.85 under 758 mm., and dissolves in an equal quantity of water at 35° and shows these constants:

d_4^{25} (in vacuo)=0.9271; $n_D^{25}=1.4984$; $n_C^{25}=1.4942$; $n_F^{25}=1.5095$; $n_{G'}^{25}=1.5190$.

0.1184 Gr. subst. gave 0.3392 gr. CO_2 and 0.0915 gr. H_2O. 0.3319 Gr. subst. gave 40.2 c.c. N_2 at 33° and 760 mm. (Found: C=78.13; H=8.65; N=13.27; Mol. wt., 106.5. C_7H_9N requires C=78.45; H=8.47; N=13.08%; Mol. wt., 107.1)

The base was identified as 2:4-dimethyl pyridine by oxidation, 4 gr. of the base with an aqueous solution of 28 gr. potassium permanganate, and the dicarboxylic acid obtained by the oxidation was converted into the copper salt with copper acetate, which was separated into two crops by their solubility in water, the one being cobalt-coloured crystals which are insoluble in water, and the other bluish green crystals, more soluble in water than the former, and the yield is 2.3 gr. and 3.1 gr., respectively.

On analysis 0.1024 gr. of the former salt gave 0.1496 gr. CO_2, 0.0264 gr. H_2O and 0.0192 gr. CuO. (Found: C=39.84; H=2.89; Cu=15.21. $(C_5H_3N\cdot CO_2H\ CO_2)_2Cu.H_2O$ requires C=40.61; H=2.44; Cu=15.37%)

The free acid recovered from the copper salt by means of hydrogen sulphide gas, shows the melting point (244°) of 2:4 lutidinic acid.

The second copper salt also gave 2:4 lutidinic acid with a m. p. of 247° and the analytical results of the free acid and its copper salt, agree well with those of the acid mentioned in the literature.

0.1665 Gr. subst. gave 0.0131 gr. loss on heating at 96° for 4 hours, and 0.0533 gr. CuO. (Found: Cu=27.76. $C_5H_3N.(CO_2)_2.Cu.H_2O$ requires Cu=27.81 %).

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(1) P. E. Spielmann, loc. cit., p. 186.

0.1002 Gr. free acid gave 0.0103 gr. loss on heating at 110° for 3 hours. 0.0873 Gr. dried acid gave 0.1623 gr. CO_2 and 0.0250 gr. H_2O. (Found: C=50.70; H=3.28. $C_5H_3N.(CO_2H)_2.H_2O$ requires 10.28 % of the water of crystallization).

4. **2:6-Methyl Ethyl Pyridine.** The mother liquor separated from the crystals of the double salt of mercuric chloride of 2:4 dimethyl pyridine hydrochloride, remains on concentration a colourless oily salt which liberates a base of disagreeable odour, even when the salt is diluted with water. The free base which is composed mostly of methyl ethyl pyridine with some dimethyl pyridine, was treated in a benzene solution with picric acid to remove the latter base completely from the former by converting it into picrate which is slightly soluble in solvents and methyl ethyl pyridine was isolated in a free state from the amorphous picrate which remained in the mother liquor separated from dimethyl pyridine picrate in an benzene solution. The yield is 10 gr. and in consequence of the small quantity of the substance no accurate reading of the boiling point was possible; it distiles at 160°–161° und 760 mm., dissolves in 55 times of water at 30°, and shows the following constants: $d_4^{25}=0.9207$; $n_D^{25}=1.4950$; $n_C^{25}=1.4908$; $n_F^{5}=1.5057$; $n_{G'}^{25}=1.5151$.

0.1073 Gr. subst. gave 0.3114 gr. CO_2 and 0.0881 gr. H_2O. 0.3537 Gr. subst. gave 36.2 c.c. N_2 at 29° and 759 mm. (Found: C=78.93; H=9.19; N=11.56; Mol. wt., 118. $C_8H_{11}N$ requires C=79.27; H=9.16; N=11.57%; Mol. wt., 121.1)

The base was confirmed as 2:6-methyl ethyl pyridine, by oxidation of 2.5 gr. of the base with 27 gr. potassium permanganate, the free dicarboxylic acid purified from the copper salt isolated from the oxidation product was found to melt at 227°.

5. **2:4:6: Trimethyl Pyridine.** For isolation of this base in a pure state, two fractions, 50 gr. of one fraction with a b.p. of 170°–171°; $d_4^{25}=0.9180$; $n_D^{25}=1.4976$; Mol. wt. 120, and 50 gr. of the other with a b.p. of 171°–172°; $d_4^{25}=0.9185$; $n_D^{25}=1.4981$: Mol. wt. 120, combined together and treated with a mercuric chloride solution, and collected a crop of platy crystals with a m.p. of 156° deposited on each addition of the mercuric chloride. The yield was 240 gr. On purifying, 205 gr. of the crystals melting at 157°–157°.5 were obtained, and these gave Hg=56.71 ($C_8H_{11}N.HCl.2HgCl_2.1/2H_2O$ requires Hg=56.54 %).

The free base isolated in pure state from 200 gr. of the purified salt as usual amounted to 32.5 gr. It distils completely at 170.47°–170.51° under 762.3 mm. and has a nondisagreeable characteristic odour. It dissolves in 30 times of water at 20° and shows the following constants:

d_4^{25}(in vacuo) = 0.9101; n_D^{25} = 1.4959; n_C^{25} = 1.4919; n_F^{25} = 1.5069; $n_{G'}^{25}$ = 1.5164.

0.1055 Gr. subst. gave 0.3061 gr. CO_2 and 0.0862 gr. H_2O. 0.3150 Gr. subst. gave 32.0 c.c. N_2 at 25° and 767 mm. (Found: C = 79.13; H = 9.15; N = 11.75, Mol. wt., 121.8. $C_8H_{11}N$ requires C = 79.27; H = 9.16; N = 11.57%; Mol. wt., 121.1).

For identification of the base to be 2:4:6-trimethyl pyridine, 5 gr. of the purified base were oxidized with an aqueous solution of 53 gr. of potssium permanganate, and pyridine-2:4:6 tricarboxylic acid resulted by oxidation of the base purified from its silver salt, was found to melt at 227°.5. The yield was 5.3 gr.

0.1000 Gr. subst. gave 0.1441 gr. CO_2 and 0.0341 gr. H_2O. (Found: C = 39.30; H = 3.82. $C_5H_2N(CO_2H)_3.2H_2O$ requires C = 38.85; H = 3.61%).

The nitrogeous substances were isolated by extraction from the fraction b.p. 220°–250°, of Fushun shale oil by dilute sulphuric acid, liberation with alkali, drying and fractionation. Fach fraction is treated in its dilute hydrochloric acid solution with mercuric chloride, from which the bases were separated as a double salt of mercuric chloride, purified from the dilute acid solution, and finally they were again liberated in a free state by alkali, and distilled. 2-Methyl pyridine, 2:6-dimethyl pyridine, 2:4-dimethyl pyridine, 2:6-methyl ethyl pyridine and 2:4:6-trimethyl pyridine were proved to occur in the tar and identified by oxidation with a potassium permanganate solution, transforming them to the corresponding carboxylic acids.

The writer's samples which were isolated from the shale tar were in a highly purified state and no work of preparation of auch highly purified bases of the pyridine series has been described except that of J. G. Heap, W.I. Jones and J.B. Speakman.(1) They prepared the bases of the pyridine series from tar by fractionation and purification through the zinc chloride compounds.

In the following table, the physical constants of the writer's samples are shown with those of the bases of the pyridine series obtained by other chemists.(2)

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(1) *J. Am. Chem. Soc.*, 43 (1921), 1926.

(2) K. V. Auwers & R. Kraul, *Z. physik. Chem.*, 116 (1925), 448; Landolt-Börnstein-Roth, "Tabellen."; "International Critical Tables." I.; T. C. Garrett and J. A. Smythe Loc. cit.

TABLE 2.

	Pyridine	2-Methyl Pyridine	2-6-Dimethyl Pyridine	2-4-Dimethyl Pyridine	2-6-Methyl-ethyl Pyridine	2-4-6-Trimethyl Pyridine
b. p.	(1) 115°–6°	129°.5 (763 mm.)	142°.5	159°–.5°	—	170°.5 (763 mm.)
	(2) 115°.3 (760 mm.)	128°–9° (760 mm.)	137°.5 (about)	157°.1 (760 mm.)	—	—
	(3) 115°.3 (760 mm.)	129°.3 (759 mm.)	143°.9 (758 mm.)	157°.9 (758 mm.)	160°–1°	170°.5 (762 mm.)
d_4^{25}	(2) 0.9776	0.9404	0.9200	0.9273	—	—
	(3) —	0.9400	0.9183	0.9271	0.9207	0.9101
n_C^{25}	—	1.4939	1.4910	1.4942	1.4908	1.4919
n_D^{25}	—	1.4983	1.4953	1.4984	1.4950	1.4959
n_F^{25}	—	1.5097	1.5065	1.5095	1.5057	1.5069
$n_{G'}^{25}$	—	1.5197	1.5164	1.5190	1.5151	1.5164
$M\alpha$	23.89 (A)	28.82	33.77	33.64	38.08	38.60
MD	24.04	29.04	34.02	33.88	38.36	38.86
$M\beta$	24.55	29.60	34.67	34.52	39.06	39.59
$M\gamma$	24.96	30.09	35.24	35.06	39.67	40.22
$M\gamma$-$M\alpha$	1.07 (B)	1.27	1.47	1.42	1.59	1.62
$M\beta$-$M\alpha$	0.66	0.78	0.90	0.88	0.98	0.99
(C)	-1.44	-0.82	-0.51	-0.58	-0.42	-0.25
″	—	-0.90	-0.43	-0.56	-0.60	-0.18

(1) F. C. Garrett and J. A. Smythe, loc. cit.
(2) J. G. Heap, W. I. Jones and J. B. Spielman, loc. cit.
(3) Writer.
(A) & (B) Landolt, Börnstein-Roth: Tabellen.
(C) K. V. Auwers & R. Kraul; *Z. Physik. Chem.*, **116** (1925), 448.

As will be seen in the forgoing table, the molecular refractive power and the dispersive power of the bases for the α, β and γ hydrogen lines and also the sodium D line have been determined, since Brühl(1) has already shown that these physical constants offer and excellent means of determining the structure of organic compounds, especially as dispersive power is more readily influenced by constitution than refractivity.

The average value for the refractive effect of the hydrogen lines α, β, γ and the sodium D line of the CH_2 group which combined with the α or γ position of the pyridine nucleus, has been calculated,(2) and the increment for the α position compared with the γ position varies about 0.13 to 0.18.

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(1) *Z. physik. Chem.*, **7** (1891), 140; **16** (1895), 201; **79** (1912), 481.
(2) Refer: K. V. Auwers and R. Kraul, Ibid., **116** (1925), 448; *Ber.*, **57** (1924), 457.

There is no doubt that the effect of CH_2 depends to a certain extent on the position by which it combines with the carbonatom of the pyridine nucleus of the compounds, and it was able more exactly to elucidate the constitutive nature of the properties in the molecular dispersive power than in the molecular refractive power.

In conclusion, the writer wishes to express his gratitude to Vice-Admiral G. Yamashita, Director of the Imperial Naval Fuel Depot, Rear-Admiral T. Kishida, Chief of the Oil Department and Engineer Captain Viscount M. Kawase, Chief of the Scientific Research & Experimental Branch for their Kindness in enabling him to take part in this research, and also to Professor S. Komatsu of the Kyoto Imperial University, whose advice and encouragement have been invaluable.

The Scientific Research and Experimental Branch,
The Imperial Naval Fuel Depot, Tokuyama.

SYNTHESIS OF RED DISPERSOIDAL SOLUTIONS OF GOLD BY MEANS OF AQUEOUS EXTRACTS FROM FRESH LEAVES OF PLANTS.

By **Eiichi IWASE.**

(Under the direction of Prof. P.P. von Weimarn)

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1. Introduction. Aqueous extracts from shavings of wood(1) of twelve different kinds, as well as from Japanese tea,(2) have already been used with success by Prof. P.P. von Weimarn for producing red dispersoidal solutions of gold. Recently, A.M. Janek by applying aqueous extracts from tobacco obtained red dispersoidal gold solutions.(3)

Being convinced a priori that also *fresh* leaves would prove successful, Prof. P.P. von Weimarn suggested the author to test experimentally the synthesis of red dispersoidal gold solutions by means of aqueous extracts from fresh leaves of the following trees: cherry, pine, maple, bamboo, and camellia.

2. Method Employed. 10 Gr. freshly collected leaves, washed thoroughly, and cut to pieces, were immersed in 100 c.c. boiling distilled water, and were allowed to boil for 10 minutes. The extract was then filtered from leaves through filter No. 602 e.h. Shleicher and Schuell, and was used immediately after filtration.

The object of my investigation being the obtaining of red solutions with the highest degree of dispersity possible, I followed, in carrying out the experiments, the rules established by Prof. P.P. von Weimarn, and described in his papers, " Studien über dispersoide Synthese des Goldes."(4)

All my experiments, therefore, were carried out as follows: to 500 c.c. of vigorously boiling(5) common distilled water contained in a one-litre beaker of ordinary glass, were added, as rapidly as possible, (by dumping) successively: 10 c.c. 0.1 % gold-salt solution (1 gr. $AuCl_4H \cdot 4H_2O$ in 1 litre of common distilled water), and 10 c.c. aqueous extract from leaves of the selected plant. The mixture was allowed to continue boiling until, through

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(1) P.P. von Weimarn, *Reports of the Imperial Industrial Research Institute, Osaka,* **3**, No. 10 (January 1923), p. 45.

(2) P.P. von Weimarn, ' Kolloides und kristalloides Lösen und Niederschlagen," Kyoto, (1921), p. 409.

(3) A.M. Janek, *Kolloid Z.*, **41** (1927), 242.

(4) P.P. von Weimarn, *Kolloid Z.*, **33** (1923), 74 & 228; **36** (1925), 1; **39** (1926), 166 & 278.

(5) Under the conditions of my experiments, 10 minutes' time was required for attaining a vigorous boiling of 500 c.c. water.

evaporation, it became reduced to half of the original volume (i.e. approximately, to 260 c.c.). The results of the experiments are perfectly reproducible on condition that all the manipulations in experimenting are exactly the same. Time intervals necessary to produce the appearance of colour, or its change, coincide in the experiments repeated.

3. **Experiments with Aqueous Extracts from Leaves of a Cherry-tree.** The extraction was made from very young leaves of a Japanese cherry-tree; the extract obtained being yellow. The following table illustrates the course of changes in colour of the reacting mixture:

Time indications by the clock:	Colour of the reacting mixture:
10 hrs. 49 min. (The moment of pouring the gold-salt solution, and the extract, into the vigorously boiling water).	Almost colourless.
10 hrs. 49 min. 3 sec.	Pink.
10 hrs. 53 min.	Red (between 29 and 33, according to the standard given by Wilhelm Ostwald)(2)
11 hrs. 13 min. (The solution has evaporated to half of its former volume).	Red of stronger intensity, with a violet tinge (between 33 and 38).

The solution was kept in a hermetically stoppered vessel, and, after the lapse of two weeks, the red colour (between 33 and 38) of the solution had suffered no appreciable change; at the bottom of the vessel only traces of a precipitate were perceptible, under the form of several small flakes.

4. **Experiments with an Aqueous Extract from Pine-needles.** The extract was of a bluish colour, with a whitish opalescence (turbidity). The course of changes in colour of the reacting mixture is demonstrated in the following table:

Time indications by the clock:	Colour of the reacting mixture:
10 hrs. 21 min. (The moment of pouring the gold-salt solution, and the extract, into the vigorously boiling water).	Almost colourless.
10 hrs. 21 min. 3 sec.	Light-red.
10 hrs. 21 min. 30 sec.	Red (between 29 and 33).
10 hrs. 44 min. (The solution has evaporated to half of its original volume).	A more intense red. (33).

A gradual intensifying of the violet tinge with the increase in concentration of gold in the solution, takes place here also, though to a lesser

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(1) Wilhelm Ostwald "Die Farbenfibel", 10 Ed. (1924), p. 19.

degree than in the case of cherry-tree. The solution was kept in a hermetically stoppered vessel, and after the lapse of two weeks, the red colour (33) of the solution had suffered no appreciable change; no precipitate was observed.

5. Experiments with an Aqueous Extract from Leaves of a Maple. Very young leaves of a Japanese maple tree were taken for the preparation of an extract which possessed a red colouring (29 according to Wilhelm Ostwald's standards). The course of changes in colour of the reacting mixture may be observed in the following table:

Time indications by the clock:	Colour of the reacting mixture:
11 hrs. 10 min. (The moment of pouring the gold salt solution, and the extract, into the vigorously boiling water).	Almost colourless.
11 hrs. 10 min. 2 sec.	Pink.
11 hrs. 11 min.	Red (33)
11 hrs. 30 min.	Violet (between 38 and 42)
11 hrs. 32 min.	Violet (42)
11 hrs. 34 min. (The solution has evaporated to half of its original volume).	Violet (46)

The solution was kept in a hermetically stoppered vessel, and after the lapse of two weeks, the solution was of a blue colour (between 46 and 50); and a bluish-white precipitate had formed at the bottom.

6. Experiments with an Aqueous Extract from Bamboo Leaves. When observed in greater depth the extract from leaves of a bamboo was of a light-brown colour, while in a thin layer it appeared olive. The course of changes in colour of the reacting mixture is clearly seen in the following table:

Time indications by the clock:	Colour of the reacting mixture:
1 hr. 38 min. (The moment of pouring the gold-salt solution, and the extract, into the vigorously boiling water).	Almost colourless.
1 hr. 38 min. 5 sec.	Light-red with an orange tinge.
1 hr. 45 min.	Red (between 29 and 33).
1 hr. 57 min. (The solution has evaporated to half of its former volume).	A more intense red (between 29 and 33).

The solution was kept in a hermetically stoppered vessel, and after the lapse of two weeks, the red colour (between 29 and 33) had suffered no appreciable change; no precipitation was observed.

7. Experiments with an Aqueous Extract from Leaves of the Camellia. An aqueous extract from camellia leaves was of a greenish-yellow colour, and possessed a marked opalescence (turbidity.) The course of changes in colour of the reacting mixture may be understood from the following table :

Time indications by the clock:	Colour of the reacting mixture:
11 hrs. 16 min. (The moment of pouring the gold-salt solution, and the mixture, into the vigorously boilling water.)	Almost colourless.
11 hrs. 16 min. 2 sec.	Pink.
11 hrs. 16 min. 30 sec.	Ruby-red (between 25 and 29).
11 hrs. 45 min. (The solution has evaported to half of its original volume).	More intensely ruby-red (29).

Experiments with the extract from camellia leaves result in a dispersoidal gold solution of the purest and brightest red colour, as compared with the red colour of resulting solutions from other extracts experimented upon. The solution was kept in a hermetically stoppered vessel, and after the lapse of two weeks, the bright red colour of the solution (29) had suffered no appreciable change ; no precipitate was observed.

8. Conclusion. The results of the experiments mentioned above, permit one to draw the conclusion that aqueous extracts from *fresh* leaves of plants common to our gardens (e.g. cherry, pine, maple, bamboo, camellia) may serve as reagents for producing red dispersoidal solutions of gold. Though the red colouring of the solutions just described do not acquire in beauty, the brilliant red colour (between 25 and 21) of certain dispersoidal gold solutions prepared by the tartrates-method of Prof. P.P. von Weimarn,(1) the colour of the dispersoidal gold solution obtained by means of extract from camellia leaves represents nevertheless a sample of a pure ruby-red.

The investigation was carried out in the Dispersoidological Department of the Imperial Industrial Research Institute of Osaka. The author wishes to express his cordial thanks to the Head of this Dapartment, Prof. P.P.

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(1) P.P. von Weimarn "Kolloides und kristalloides Lösen und Niederschlagen", Kyoto, (1921), p.740; *Kolloid Z*, 36 (1925), 5. Tartaric acid (not the tartrates) had already been used (1857) for the preparation of solutions of colloidal gold by M. Faraday, though he failed to prepare either red, or any stable colloidal solutions. M. Faraday describes the results of his experiments in the following words: "Tartaric acid being added to a weak solution of gold gradually reduced it. The amethystine tint produced by diffused particles first appeared, and then a blue deposit of larger particles, whilst the side and bottom of the glass became covered by an adhering film of finer particles, presenting the perfect ruby tint of gold". Quoted in E. Hatschek's "The Foundations of Colloid Chemistry" London, (1925), p. 82.

von Weimarn, under whose kind guidance the present work was performed. The author's best thanks are due to the President of the Imperial Industrial Research Institute of Osaka, Dr. Eng. I. Shoji.

April, 1927.

Dispersoidological Department of the Imperial Industrial
Research Institute, Osaka.

ON THE OXIDATION OF THE MIXTURE OF STANNOUS CHLORIDE AND SODIUM SULPHITE IN ALKALINE SOLUTION WITH AIR.

By **Susumu MIYAMOTO.**

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Introduction. It was described in the previous papers that the oxidation velocity of sodium sulphite(1) or stannous chloride(2) in alkaline solution with air is independent of their concentrations, unless their concentrations are extremely small, and that their velocity constants decrease with the increase of the concentration of alkali and coincide with each other, when the concentration of sodium hydroxide is greater than about 0.2 normal under the condition of the previous study. To explain these results an assumption was proposed that the velocity of the dissolution of oxygen into the solution is smaller than that of the oxidation of these compounds.

If this assumption be correct, the oxidation velocity of the mixture of sodium sulphite and stannous chloride in alkaline solution with air can not be greater than that of each. The present research was undertaken to ascertain this assumption, but the results were not simple; the oxidation of the mixture seems to be a kind of induced reaction.

Method of Observation. Air, washed by an acidic solution of potassium dichromate and sodium hydroxide solution, was passed through a mixture of stannous chloride and sodium sulphite in sodium hydroxide solution of known concentration at the rate of 7.78 litres per hour.

The total volume was made to 40 c.c. in each case. After t minutes, air current was stopped and the total amount of the mixture was poured into a known quantity of iodine solution, acidified with hydrochloric acid, and the excess of iodine was titrated back with sodium thiosulphate solution. In

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(1) S. Miyamoto, this Journal, 2 (1927), 74.

(2) S. Miyamoto, this Journal, 2 (1927), 155.

the following tables, v is the volume of sodium thiosulphate solution of 0.0996 normal which is equivalent to the total amount of sodium sulphite and stannous chloride; k was calculated by $k = \frac{1}{t}(v_0 - v)$, v_0 being the value of v at $t = 0$, and $v_{\mathrm{calc.}}$ was obtained by $v_{\mathrm{calc.}} = v_0 - kt$, using the mean value of k. Initial amounts of sodium sulphite and stannous chloride are given by $v_{0\,(\mathrm{Na_2SO_3})}$ and $v_{0\,(\mathrm{SnCl_2})}$.

TABLE 1.

Temp. = 20° C. C_{NaOH} = 0.525 normal. Air = 7.78 litres per hour.

$v_0(\mathrm{SnCl_2})$ c.c.	$v_0(\mathrm{Na_2SO_3})$ c.c.	t min.	v c.c.	$v$calc. c.c.	k
—	0	From Fig. 1 in the previous paper,			0.220.
13.89	0.53	0	14.42	—	—
		10	12.50	12.49	0.192
		15	11.51	11.52	0.194
		20	10.52	10.56	0.195
		30	8.69	8.63	0.191
				mean:	0.193
10.89	0.74	0	11.63	—	—
		10	9.71	9.73	0.192
		20	7.87	7.83	0.188
		30	5.93	5.93	0.190
				mean:	0.190
10.89	2.76	0	13.65	—	—
		10	11.63	11.66	0.202
		20	9.67	9.67	0.199
		30	7.81	7.68	0.195
				mean:	0.199
11.61	4.76	0	16.37	—	—
		10	14.26	14.31	0.211
		20	12.13	12.25	0.212
		30	10.48	10.19	0.196
				mean:	0.206
9.13	5.40	0	14.53	—	—
		10	12.38	12.52	0.215
		25	9.61	9.50	0.197
		35	7.88	7.49	0.190
				mean:	0.201
7.24	5.84	0	13.08	—	—
		10	11.14	11.18	0.194
		20	9.34	9.28	0.187
		30	7.43	7.38	0.188
				mean:	0.190

TABLE 1. (*Continued.*)

Temp. = 20° C. $C_{NaOH} = 0.525$ normal. Air = 7.78 litres per hour.

$v_0(SnCl_2)$ c.c.	$v_0(Na_2SO_3)$ c.c.	t min.	v c.c.	$v_{calc.}$ c.c.	k
7.95	11.46	0	19.41	—	—
		10	17.28	17.38	0.213
		20	15.41	15.35	0.200
		30	13.55	13.32	0.195
				mean:	0.203
10.31	16.12	0	26.43	—	—
		10	24.32	24.38	0.211
		20	22.26	22.33	0.209
		30	20.58	20.28	0.195
				mean:	0.205
4.44	8.74	0	13.18	—	—
		10	11.30	11.41	0.188
		20	9.59	9.64	0.180
		30	8.27	7.87	0.164
				mean:	0.177
3.77	10.80	0	14.57	—	—
		10	12.82	12.87	0.175
		20	11.35	11.17	0.161
		40	7.63	7.77	0.174
				mean:	0.170
1.26	19.94	0	22.20	—	—
		10	20.96	—	0.124
		20	18.80	—	0.170
		30	16.63	—	0.186
1.23	13.64	0	14.87	—	—
		10	13.61	—	0.126
		20	11.52	—	0.168
		40	7.49	—	0.185
0.48	13.52	0	14.00	—	—
		10	12.42	—	0.158
		20	10.73	—	0.164
		40	6.75	—	0.181
0	—	From Fig. 1 in the previous paper,			0.220.

TABLE 2.

Temp. = 20°C. C_{NaOH} = 0.752 normal. Air = 7.78 litres per hour.

$v_0(SnCl_2)$ c.c.	$v_0(Na_2SO_3)$ c.c.	t min.	v c.c.	$v_{calc.}$ c.c.	k
—	0	From Fig. 1 in the previous paper,			0.199
11.72	0.39	0	12.11	—	—
		10	10.31	10.35	0.180
		15	9.50	9.47	0.174
		20	8.59	8.59	0.176
		30	6.91	6.83	0.173
				mean:	0.176
11.88	1.39	0	13.27	—	—
		10	11.45	11.52	0.182
		20	9.78	9.77	0.175
		30	8.20	8.02	0.169
				mean:	0.175
9.11	4.45	0	13.56	—	—
		10	11.72	11.82	0.184
		15	10.94	10.95	0.175
		20	10.00	10.08	0.175
		30	8.70	8.34	0.162
				mean:	0.174
1.27	11.99	0	13.26	—	—
		10	12.23	—	0.103
		20	10.30	—	0.148
		30	8.60	—	0.155
1.14	19.22	0	20.36	—	—
		10	19.35	—	0.101
		20	17.85	—	0.126
		30	15.54	—	0.161
0.50	14.47	0	14.97	—	—
		10	13.50	—	0.147
		20	11.59	—	0.169
		30	10.11	—	0.162
0	—	From Fig. 1 in the previous paper,			0.199.

TABLE 3.

Temp. = 20°C. C_{NaON} = 1.092 normal. Air = 7.78 litres per hour.

$v_0(SnCl_2)$ c.c.	$v_0(Na_2SO_3)$ c.c.	t min.	v c.c.	vcalc. c.c.	k
—	0	From Fig. 1 in the previous paper,			0.164
12.37	1.13	0	13.50	—	—
		10	12.10	12.08	0.140
		20	10.54	10.66	0.148
		30	9.24	9.24	0.142
		40	7.96	7.82	0.139
				mean:	0.142
8.34	4.46	0	12.80	—	—
		10	11.42	11.42	0.138
		20	9.93	10.02	0.144
		30	8.78	8.63	0.134
				mean:	0.139
3.48	8.04	0	11.52	—	—
		15	9.45	9.54	0.138
		25	8.27	8.32	0.130
		40	6.36	6.24	0.129
				mean:	0.132
1.46	13.33	0	14.79	—	—
		10	13.64	—	0.115
		20	12.15	—	0.132
		30	10.84	—	0.132
1.39	19.49	0	20.88	—	—
		10	19.68	—	0.120
		20	18.04	—	0.142
		30	16.75	—	0.138
1.09	12.93	0	14.02	—	—
		10	12.85	—	0.117
		20	11.52	—	0.125
		30	10.21	—	0.124
0	—	From Fig. 1 in the previous paper,			0.164

As is seen in tables 1, 2 and 3, the results are complex. When the initial concentration of stannous chloride is not small, the oxidation velocity of the mixture is independent of their concentrations, and is rather smaller than that of sodium sulphite or stannous chloride in alkaline solution. When the initial concentration of stannous chloride is small, the oxidation of the mixture takes place slowly first and increases with time.

The author has an opinion to explain these results by the transference of active states quite the same way as induced reaction,(1) but the theoretical discussion is left for the later study.

Summary.

1. The oxidation velocity of the mixture of sodium sulphite and stannous chloride in alkaline solution with air was studied.

2. When the initial concentration of stannous chloride is not small, the oxidation velocity is independent of their concentrations and is smaller than that of each.

3. When the initial concentration of stannous chloride is small, the oxidation of the mixture takes place at a slow rate first, and increases with time.

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(1) S. Miyamoto, *Scientific Papers of the Institute of Physical and Chemical Reserch*, 4 (1926), 257.

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

By Toshizo TITANI.

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1. **Specific Fluidity of Liquid Carbon dioxide.** P. Phillips(2) determined the viscosity of carbon dioxide at several temperatures under high pressures. Calculating the specific fluidity Φ_1 from his data and plotting it against the specific surface $V_1^{\frac{2}{3}}$, every point falls almost on a straight line as will be seen from Fig. 1. In the table below, the observed values of specific fluidity are compared with those calculated from the equation(3)

$$\Phi_1 = K_1 (V_1^{\frac{2}{3}} - B_1^{\frac{2}{3}}) \cdots\cdots\cdots\cdots (1).$$

where $K_1 = 3060, \quad B_1 = 0.669.$

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(2) P. Phillips, *Proc. Roy. Soc.*, (A), 87, (1912), 48.

(3) Cf. Part II of this paper, this journal, 2 (1927), 161.

TABLE 1.

Liquid Carbon dioxide.

20° C.

Pressure Atm.	$\Phi_1 \times 10^{-1}$	
	Observed	Calculated
83	114.4	111
72	121.0	118
59	131.4	131

30° C.

110.5	120.3	123
104	125.6	127
96	131.6	134
90	140.8	139
82	151.1	148
80	157.7	152
76	166.2	162
74	176.2	168
73	181.5	172
72	187.6	180

32° C.

Pressure Atm.	$\Phi_1 \times 10^{-1}$.	
	Observed.	Calculated.
120	117.3	124
112	124.1	128
104	131.3	133
93	143.5	144
87	151.5	154
84	157.2	161
80	164.4	172
76	196.3	197

35° C.

114.5	131.4	135
109	137.1	140
96	151.2	156
88	169.8	172
85	187.6	184

40° C.

112	155.3	155
108	163.0	161
100	178.0	180
94	201.7	205

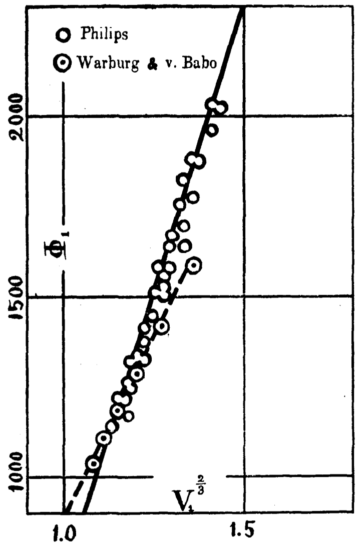

Fig. 1:—Volume Relation for Liquid Carbon dioxide.

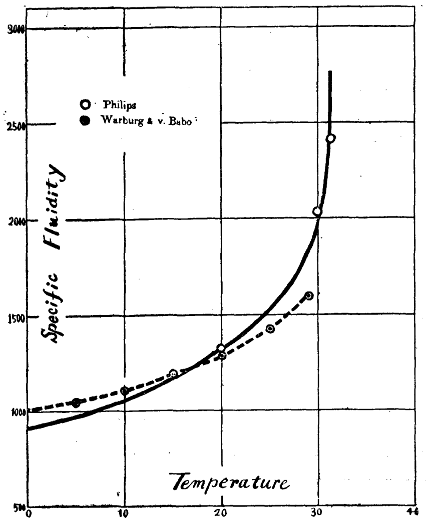

Fig. 2:—Orthobaric Specific. Fluidity of Liquid Carbon dioxide.

The specific fluidity for orthobaric volume(1) was found from equation (1) and, plotting it against the temperature, a full curve shown in Fig. 2 was obtained. The two observed (at 20° and 30°) and one estimated value (at critical point 31.°35) of P. Phillips, shown by circles, fall almost on the curve.

The viscosity of carbon dioxide under orthobaric state were early determined by Warburg and v. Babo.(2) Using their data, we have the dotted lines shown in Figs. 1 and 2. A remarkable discrepancy between the observed values of respective authors may probably be due to difference of specimen employed.

2. Comparison of Volume and Temperature Relations of Molecular Fluidity. In part II(3) of this paper we obtained as a relation between molecular volume V and molecular fluidity Φ:

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

where K and B are constants, and as its relation to temperature T:

$$\Phi = \Phi_k - C\,(T_k - T)^{\frac{1}{3}} \cdots\cdots\cdots\cdots\cdots\cdots (3).$$

were Φ_k and T_k are critical and C an arbitrary constant. The same form of relations hold also with specific fluidity.

(A). Putting $\Phi = 0$ in equation (3), we have the temperature t_s, where viscosity becomes infinity. This temperature t_s is found to be very near the freezing point t_F for many substances except a few. (see Table 2, column 2 and 3). Exact agreement between calculated and observed freezing point can not be expected, since t_s is to be a solidifying temperature of a substance, regarding it as quite isotropic.

(B). T_s is almost equal to $\frac{7}{20}$ of the critical temperature T_k, both being measured in absolute scale. (see Table 2, column 4).

(C). The term B in equation (2) represents the molecular volume when viscosity becomes infinity. Therefore, this should be the molecular volume V_s at the temperature t_s. In order to compute the density at the temperature t_s the rule of Cailletet and Mathias modified by S. Young(4) was used. The agreement between B and V_s is very satisfactory, the difference being all far less than 1%, as will be seen from the columns 5 and 6 in Table 2.

(D). The critical value of molecular fluidity Φ_{kT} in equation (3) is compared with Φ_{kv} found from equation (2) by putting critical volume in it. (see Table 2, columns 7 and 8). The agreement between two sorts of Φ_k is

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(1) Amagat, *Compt. rend.*, **114** (1892) 1093.

(2) Warburg & v. Babo, *Wied. Ann.*, **17** (1882), 390.

(3) loc. cit.

(4) S. Young, *Sci. Proc. Roy. Dublin Soc.*, **12** (1909—1910), 374.

satisfactory, if it be taken into account that the magnitude of these quantities is remarkably effected by a slight change in the values of other constants.

TABLE 2.

Substance.	t_F	t_s	$\frac{T_s}{T_k}$	B	V_s	Φ_{kv}	Φ_{kT}
Pentane.	−130.8°	−122.4°	0.321	95.5	95.0	796	795
Isopentane.	−158.05	−121.2	0.330	96.1	95.5	790	800
Hexane.	− 94.3	−105.2	0.331	112.6	111.6	710	703
Heptane.	− 90.0	− 89.6	0.340	129.9	129.1	674	660
Octane.	− 56.5	− 71.9	0.353	147.9	147.3	637	613
Methyl-formate.	− 99.75	−114.1	0.326	52.0	51.7	745	730
Ethyl-formate.	− 80.5	− 96.6	0.347	69.6	70.0	699	696
Propyl-formate.	. .	− 77.9	0.363	86.8	85.5	651	649
Methyl-acetate.	− 98.05	− 94.8	0.351	68.9	68.7	760	742
Ethyl-acetate.	− 83.4	− 83.7	0.362	86.1	86.0	675	674
Propyl-acetate.	. .	− 66.6	0.376	104.2	104.0	644	630
Methyl-propionate.	. .	− 88.5	0.348	85.0	84.5	684	669
Ethyl-propionate.	− 73.9	− 75.4	0.362	102.9	102.4	638	628
Methyl-butyrate.	. .	− 70.7	0.365	102.7	102.5	631	624
Methyl-isobutyrate.	. .	− 76.7	0.363	102.9	102.4	634	624
Ethyl-ether.	−116.2	−123.6	0.320	85.7	85.3	797	791
Carbon-tetrachloride.	− 22.95	− 53.3	0.395	88.9	88.6	459	471
Benzene.	5.484	− 50.0	0.397	82.2	81.9	737	757
Fluorobenzene.	− 41.2	− 68.6	0.335	85.5	85.0	648	647
Chlorobenzene.	− 45	− 67.9	0.325	94.1	93.7	611	601
Acetic acid.	+16.67	− 40.6	0.391	(0.900)	(0.898)	(2428)	(2291)
Bromine.	− 7.3	− 91.4	0.316	(0.287)	(0.289)	(2027)	(2273)

Note:—Numbers in brackets represent the quantities referred to one gram,

(E) The comparison of the two sorts of relations, (2) and (3), was done over a wide range of temperature. The result for ethyl ether is given in Fig. 3, as an example, where the following numerical equations[1] already obtained have been used.

$$\Phi_v = 33.8\,(V^{\frac{2}{3}} - 85.69^{\frac{2}{5}}) \cdots\cdots\cdots (4).$$

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

Equation (4) is given in full line and equation (5) in dotted. The agreement between the two is generally good, except near the critical tempereture. In this region errors of calculation becomes very large, since the term $(T_k - T)^{\frac{1}{5}}$ in equation (3) becomes very small and volume in equation (2) changes rapidly.

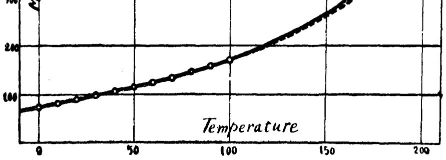

Fig. 3:—Comparison of Volume and Temperature Relations with Ethyl ether.

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(1) Part II. of this paper cited above.

3. Relation between Orthobaric Volume and Temperature. At low temperatures the orthonaric volume of liquid increases slowly with rise of temperature, but at higher temperatures the rate of increase becomes greater. For the purpose of calculation an algebraic expression is usually employed, the number of terms increasing with the range of temperature.

Eliminating the term of molecular fluidity Φ from the two equations (2) and (3) cited above, we have

$$V^{\frac{2}{3}} = V_k^{\frac{2}{3}} - A\,(T_k - T)^{\frac{1}{5}}. \quad \cdots\cdots(6).$$

where V is molecular volume and A a constant.(1)

Similarly, for specific volume V_1:

$$V_1^{\frac{2}{3}} = V_{1k}^{\frac{2}{3}} - A_1\,(T_k - T)^{\frac{1}{5}}. \cdots\cdots(7).$$

TABLE 3.

Chlorobenzene.

t° C	$V^{\frac{2}{3}}$		Δ	V		Δ
	Obs.	Calc.		Obs.	Calc.	
0	21.51	21.49	− 2	99.72	99.61	− 1
10	21.65	21.63	− 2	100.7	100.7	0
20	21.81	21.77	− 4	101.7	101.6	− 1
30	21.93	21.91	− 2	102.7	102.5	− 2
40	22.07	22.06	− 1	103.7	103.6	− 1
50	22.21	22.21	0	104.7	104.7	0
60	22.37	22.36	− 1	105.8	105.8	0
70	22.52	22.52	0	106.9	106.9	0
80	22.68	22.68	0	108.0	108.0	0
90	22.84	22.85	+ 1	109.1	109.2	+ 1
100	23.00	23.03	+ 3	110.4	110.5	+ 1
110	23.18	23.21	+ 3	111.6	111.9	+ 3
120	23.37	23.38	+ 1	112.9	113.2	+ 3
130	23.56	23.58	+ 2	114.4	114.5	+ 1
140	23.74	23.77	+ 3	115.7	115.9	+ 2
150	23.94	23.98	+ 4	117.1	117.4	+ 3
160	24.15	24.19	+ 4	118.7	119.0	+ 3
170	24.36	24.42	+ 6	120.2	120.7	+ 5
180	24.59	24.65	+ 6	122.0	122.4	+ 4
190	24.83	24.89	+ 6	123.7	124.3	+ 6
200	25.08	25.15	+ 7	125.6	126.2	+ 6
210	25.35	25.41	+ 6	127.7	128.0	+ 3
220	25.62	25.69	+ 7	129.7	130.2	+ 5
230	25.93	25.98	+ 5	132.1	132.4	+ 3
240	26.26	26.30	+ 4	134.7	134.9	+ 2
250	26.61	26.65	+ 4	137.3	137.6	+ 3
260	27.01	27.01	0	140.3	140.4	+ 1
270	27.42	27.40	− 2	143.5	143.4	− 1
329.2	31.29	31.01	−28	175.0	172.7	−23
348.8	34.57	33.84	−73	203.3	196.8	−65
358.8	40.29	39.58	−71	255.7	249.1	−66
359.2 (critical)	45.60	45.82	+22	307.9	310.2	+23

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(1) $A = \frac{C}{K}$ and $A_1 = \frac{C_1}{K_1}$.

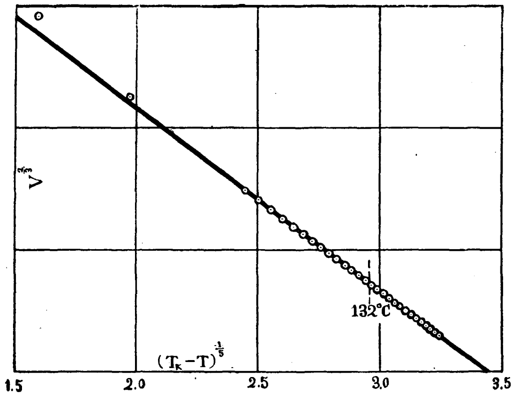


Fig. 4:—Rule (6) for Chlorobenzene.

These relations were found to hold with good accuracy over a wide range of temperature, except near the critical point. As an example, the result for chlorobenzene is given in Fig. 4 and Table 3. For calculation the following numerical equation was used.

$$V^{\frac{2}{3}}=310.2^{\frac{2}{3}}-7.50\ (359.2-t)^{\frac{1}{5}}.$$

It will be seen from the above table, that the agreement between observed and calculated values is very good up to near the critical temperature, where a deviation of about 1 to 3 % appears. If suitable correction terms be added, the relation would give a very satisfactory result. This relation suggests the means of calculating the density of liquid and vapour respectively, if it be employed together with the rule of Cailletet and Mathias expressing the sum of two density as a function of temperature.

Summary.

1. The volume relation of molecular or specific fluidity holds good even when the viscosity changes remarkably with pressure.
2. The volume and temperature relations give results which agree well with each other in all respects.
3. From the two sorts of relations concerning the viscosity, the following equation was obtained,

$$V_k^{\frac{2}{3}}-V^{\frac{2}{3}}=A\,(T_k-T)^{\frac{1}{5}}.$$

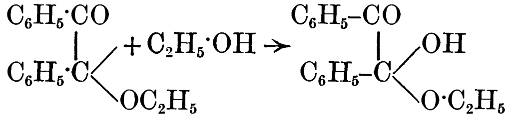
which was found to hold with good accuracy.

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

May, 1927.

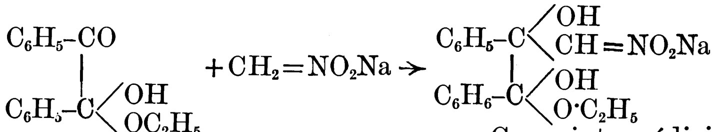
The Institute of Physical and Chemical Research,
Hongo, Tokyo.

Le nitrométhane sodé *à froid* et le nitréthane *à chaud* n'ont jamais donné la condensation analogue avec le benzile, et, au contraire, ils agissent suivant la formule II. La première phase de la réaction semble l'addition d'une molécule d'alcool sous l'action des corps nitrés sodés :



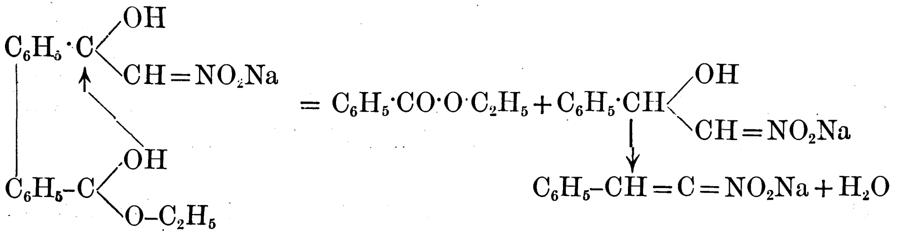
La deuxième paraît intéresser l'autre groupe carbonyle du benzile par addition d'une molécule des corps sodés, qui réagissent sur lui dépendamment de leur nature chimique.

Le nitrométhane semble posséder une affinité si grande pour le sodium, que la réaction marche comme ci-dessous:

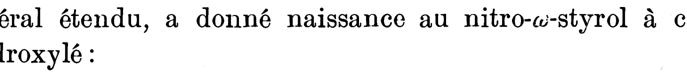


Corps intermédiaire

Bien que ce corps intermédiaire soit imaginaire, il subit aussitôt un dédoublement comme l'indique l'équation suivante par migration de l'atome d'hydrogène du groupe hydroxylé attaché au carbone auquel le groupe éthoxylé est lié :

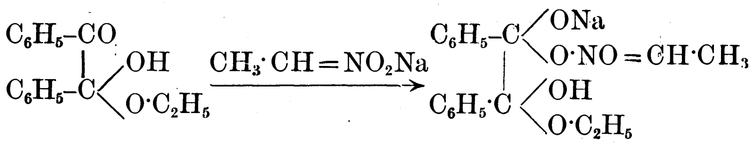


En vérité, nous avons obtenu comme produits finals de réaction d'un côté du benzoate d'éthyle en solution alcoolique, et de l'autre le dépôt d'une poudre contenant de l'azote et du sodium (les dosage de celui-ci ont donné toujours les valeurs entre $C_6H_5.CH(OH).CH=NO_2Na$ et $C_6H_5.CH=C=NO_2Na$). Cette poudre sodée, dissoute dans de l'eau, et décomposée par un acide minéral étendu, a donné naissance au nitro-ω-styrol à côté de son dérivé hydroxylé:



$$C_6H_5{\cdot}CH=C=NO_2Na \xrightarrow{H_2O} C_6H_5{\cdot}CH=CH{\cdot}NO_2$$

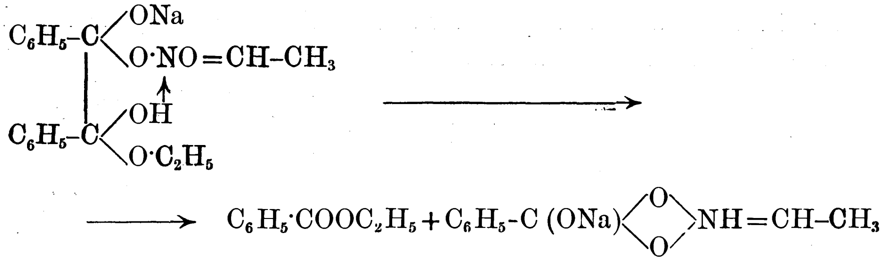
Quant au nitréthane, son affinité pour le sodium paraît être moins grande en sorte que son addition a lieu defféremment de son homologue inférieur. Par l'addition le nitréthane serait lié au benzile par l'un des atomes d'oxygène du groupe nitré :



$$\begin{array}{l} C_6H_5{-}CO \\ \quad | \\ C_6H_5{-}C{<}\begin{smallmatrix}OH\\O{\cdot}C_2H_5\end{smallmatrix} \end{array} \xrightarrow{CH_3{\cdot}CH=NO_2Na} \begin{array}{l} C_6H_5{-}C{<}\begin{smallmatrix}ONa\\O{\cdot}NO=CH{\cdot}CH_3\end{smallmatrix} \\ \quad | \\ C_6H_5{\cdot}C{<}\begin{smallmatrix}OH\\O{\cdot}C_2H_5\end{smallmatrix} \end{array}$$

Corps intermédiaire

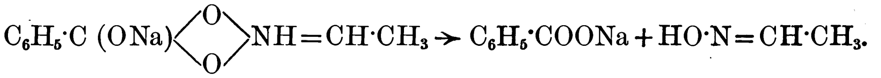
Similairement on trouve du benzoate d'éthyle dans la solution alcoolique, et, par conseque nt, la réaction a dû être complété jusqu'au point du dédoublement de ce produit intermédiaire en benzoate d'éthyle et un corps sodé :



$$\begin{array}{l} C_6H_5{-}C{<}\begin{smallmatrix}ONa\\O{\cdot}NO=CH{-}CH_3\end{smallmatrix} \\ \quad | \qquad \uparrow \\ C_6H_5{-}C{<}\begin{smallmatrix}OH\\O{\cdot}C_2H_5\end{smallmatrix} \end{array} \longrightarrow$$

$$\longrightarrow C_6H_5{\cdot}COOC_2H_5 + C_6H_5{-}C\,(ONa){<}\begin{smallmatrix}O\\O\end{smallmatrix}{>}NH=CH{-}CH_3$$

Le dernier corps sodé, intermédiaire, avait probablement la constitution cidessus, car il a donné avec un acide minéral de l'acide benzoique, et son eau-mère donnait une série de réactions : elle réduit le nitrate d'argent ammonical ; elle forme avec l'iode l'iodoforme *à froid,* dont l'odeur est remplacée *à chaud* par une odeur désagréable ; elle sent l'acétate d'éthyle quand on l'oxyde avec de l'eau oxygénée et qu'on chauffe avec de l'alcool, etc. Il semble qu'elle contienne de l'acétaldéhyde (ou bien de l'acéaldoxime),



$$C_6H_5{\cdot}C\,(ONa){<}\begin{smallmatrix}O\\O\end{smallmatrix}{>}NH=CH{\cdot}CH_3 \rightarrow C_6H_5{\cdot}COONa + HO{\cdot}N=CH{\cdot}CH_3.$$

Plus haut nous avons étudié les réactions du nitrométhane et du nitréthane sodés sur le benzile, et il est certainement remarquable que le dédoublement cité a lieu dans tous cas *par la migration d'atome d'hydrogène* (marqué par ↑ dans les formules ci-dessus).

De plus la même réaction n'a pas eu lieu au moyen de l'amidure de sodium dans un dissolvant inerte (comme dans le benzène) ni à froid ni à chaud, mais il se produit généralement la transformation benzilique. On peut maintenant tirer la conclusion que l'addition de l'alcool et la scission du benzile soient catalysées par le nitrométhane et le nitréthane sodés.

Partie expérimentale.

I. **Le nitrométhane sur le benzile.** Dans 50 c.c. d'alcool absolu on dissout 1.1 gr. de sodium métallique, et on ajoute à froid 3.1 gr. de nitrométhane (dissout dans de l'alcool), qui est sodé tout de suite, en déposant une masse blanche. Celle-ci est refroidie au moyen de l'eau glacée. Puis on met 10 gr. de benzile (dissout en 50 c.c. d'alcool à chaud), et l'on secoue vigoureusement. La réaction a lieu avec dégagement de chaleur, et les réactifs se dissolvent presque entièrement. Après quelques minutes la solution commence à se troubler, en déposant une poudre sodée blanche, que l'on laisse dans une glacière pendant la nuit. On filtre le produit de réaction rapidement à la trompe à eau. On a traité séparémment les deux portions ainsi obtenues :— le résldu et le filtrat.

Traitement du filtrat :—Du filtrat on chasse l'alcool autant que possible par la distillation, et on met de l'éther pour faire déposer le corps sodé qui a été dissout dans l'alcool et dans le produit liquide. On filtre de nouveau à la trompe à eau. Ce corps sodé est dissout dans de l'eau glacée et acidifié, en donnant une substance cristallisée, fusible à 110° environ. Elle fond aprés recristallisation dans l'eau chaude, à 119–120°, et se trouve être l'acide benzoique par le point de fusion de son mélange avec l'acide pur. La quantité de cette portion d'acide obtenu n'a été que 0.1–0.2 gr.

Après avoir chassé le dissolvant on distille le filtrat éthéré sous pression réduite, et l'on obtient une huile incolore bouillante à 100–103° sous 19 mm. Le rendement en huile est 5 gr. Cette huile a une odeur caractéristique et elle bout à 211° sous la pression ordinaire (corrigé), et elle ne contient pas d'azote.

Analyse. Trouvé :

$C=72.04$, $H=6.67$. Calc. pour $C_9H_{11}O_2$: $C=72.00$, $H=6.67\%$.

La valeur analytique et les propriétés de cette huile montrent que c'est du benzoate d'éthyle. De plus elle donne de l'acide benzoique quand elle soumise à l'hydrolyse par de la potasse alcoolique.

Traitement du corps sodé :—Le corps sodé que l'on obtient par filtration du produit de réaction est une poudre légèrement jaune brunâtre et à odeur piquante. Après avoir bouilli avec de l'éther, on filtre la poudre, lave avec de l'éther, et on la sèche sur une assiette poreuse *rapidement*, car elle s'altère assez vite par exposition à l'air humide. Cette poudre contient de l'azote et du sodium dont la teneur est trouvée *tout de suite après le lavage à l'éther* toujours très près de 12.9 pour 100, mais elle va jusqu'à 13.5 pour 100 au bout de 24 heures.

Cette poudre est dissoute dans de l'eau tout de suite après le lavage, et décomposée à froid par un acide minéral étendu, en donnant un corps cristallisé qui est fusible à 56–57° après la recristallisation dans l'alcool. De plus ce corps cristallisé a la propriété d'irriter l'épiderme et les muqueuses—surtout celles des yeux. Le rendement, 2 gr.

Analyse. Trouvé : $N=9.7$. Calc. pour $C_8H_7O_2N$: $N=9.4\%$.

Par les propriétés et l'analyse du corps obtenu on peut admettre du nitro-ω-styrol, et cela se trouve vérifier par le point de fusion du mélange de ce corps avec le nitrostyrol préparé d'après la méthode de Johan Thiele.(1).

Le rendement en était toujours pauvre comme on voit en haut. Du fait que l'eau-mère était fortement troublée, on a pensé à l'existence d'une certaine quantité d'un corps peut être le nitro-styrol.

Extrait à l'éther, on obtient une certaine quantité d'une huile jaune. De nouveau, au lieu de faire cristalliser le nitrostyrol du corps sodé, on décompose celui-ci sous une couche d'éther par un acide minéral étendu. De la solution éthérée on a, par distillation sous 4 mm., une huile jaune bouillante à 120–150° (5 gr.), de laquelle on obtient, en outre du nitrostyrol fusible à 56–57°, une huile bouillante à 140–150° sous 4 mm. Celle-ci semble l'alcool nitré correspondant, qui devient, par la deshydratation, le nitrostyrol, qui se produit en chauffant l'alcool dans un tube à éssai. On y observe de l'eau condensée au-dessus du tuyau, quand la température monte vers à 120°. On a chauffé encore quelque temps à 150°, et le corps devient peu à peu en substance fusible à 56–57°.

II. **Le nitréthane sur le benzile.** Le nitréthane n'a pas réagi sur le benzile *à froid*, mais *à chaud.* On a préparé le nitréthane sodé en dissolvant 0.6 gr de sodium métallique dans 20 cc. d'alcool absolu et y ajoutant 1.8 gr. de nitréthane. Sur le nitréthane sodé ainsi obtenu on verse la solution alcoolique de benzile chaude (5 gr.), et l'on chauffe pendant 2 jours sur B.M. à l'abri de l'aire humide. Au bout de ce temps on voit la solution se colorer en brun, et il se dépose une poudre fine au fond du flacon. On sépare la poudre de la portion alcoolique comme le nitrométhane sur cette dione.

Traitement du corps sodé :—La poudre déposée (dosage de sodium : 19.1–19.4 pour 100) n'est pas affectée à l'air humide autant que celle que l'on obtient avec le nitrométhane, et elle donne avec l'eau une solution trouble, de laquelle on obtient par l'action d'un acide minéral l'acide benzoique (fusible à 117–119°) qui fond, après avoir recristallisé dans l'eau chaude, à 119–120°, et étant mélangé avec un échantillon pur, à 119–120°. Le poids obtenu de ce corps est 2 gr. environ.

Avant la décomposition de la solution trouble citée plus haut elle devient claire par extraction à l'éther en donnant par l'action d'un acide minéral l'acide benzoique assez pur. (La solution éthérée a laissé, le dissolvant étant chassé, une trace d'huile qui sent le benzoate d'éthyle). Le filtrat de l'acide benzoique donne une série de réactions, comme décrites ci-dessus.

Traitement du filtrat :—En opérant similairement on obtient à coté d'une petite quantité de poudre sodée (qui donne aussi de l'acide benzoique par

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(1) J. Thiele, *Ber.*, 32 (1899), 1293.

décomposition) une huile à odeur spéciale (2–3 gr. de 5 gr. de benzile), qui bout à 109–110° sous 30 mm. Cette huile a été trouvée être le benzoate d'éthyle par l'hydrolyse en acide benzoique.

Résumé.

1. Le nitrométhane sodé réagit sur le benzile à la fois en le scindant et en condensant avec la benzaldéhyde ainsi engendrée, en donnant naissance au benzoate d'éthyle et au nitro-ω-styrol sodé.

2. Le nitréthane réagit sur le benzile à la fois le scindant et en oxydant la benzaldéhyde engendrée, en donnant naissance au benzoate d'éthyle et à l'acide benzoique (sous la forme de benzoate de sodium).

Haute Ecole Polytéchnique de Yokohama.

ON THE CATALYTIC ACTION OF JAPANESE ACID CLAY UPON CINEOL. (STUDIES ON CAMPHOR OILS, VIII.)

By **Kashichi ONO and Shuei MIYAZAKI.**

Received May 14, 1927. Published July 28, 1927.

In the previous investigation,(1) K. Ono supposed the formation of monoterpene such as dipentene as the intermediate product of the reaction of Japanese acid clay upon cineol, but he could not isolate it. Afterwards K. ONO(2) confirmed that the Japanese acid clay is a catalyst for dehydration of varionos terpene alcohols in the liquid system.

On the other hand, Wallach and Brass(3) have shown that cineol changes into dipentene in the presence of zinc chloride. These facts naturally lead us to suppose that the dehydration of cineol would take place in the presence of Japanese acid clay. This view was found to be correct from the following experiment.

500 Gr. of cineol ($d_4^{20}=0.9245$; $n_D^{20.5}=1.4590$; $[\alpha]_D=\pm 0$) were treated with 150 gr. of Japanese acid clay (dried at 100°) in a manner analogous to that described in the previous communication. After 2 hours (temperature of oil bath is 180°), the violent reaction took place and 102 gr. of oily product ($d_4^{22}=0.8670$; $n_D^{23}=1.4720$) and 5.24 gr. of water were obtained.

(I) After removing unchanged cineol with 50% solution of resorcine, the product was subjected to steam distillation. 60 Gr. of the oily distillate after having been dried with anhyd. sodium sulphate was distilled under 760 mm.

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(1) *The Memoirs Coll. Sci. Kyoto Imp. Univ.*, A, **7** (1924), 360.

(2) This Journal, **1** (1926), 248: **2** (1927), 16.

(3) *Ann.*, **225** (1888), 268.

Fraction.	Yield.	d.	n_D
173—175°	8.4 gr.	$0.8642\ (\frac{17.5}{4})$	1.4718
175—177°	31.4	$0.8488\ (\frac{20}{4})$	1.4720
177—180°	13.2	$0.8649\ (\frac{17.5}{4})$	1.4740
above 180°	5.7	———	———

The fraction boiling at 175–177' was analyzed with the following result. 0.1012 Gr. subst. gave 0.3263 gr. CO_2 and 0.1092 gr. H_2O. (Found, C=87.73, H=12.07. $C_{10}H_{16}$ requires C=88.15, H=11.85 %). Molecular refraction 44.91. $C_{10}H_{16}F_2$ requires 45.24.

The compound seems, so far as studied, to be identical with dipentene. For comfirmation, it was converted into tetrabromoderivative, it melted at 124.5–125° and was proved to be identical with dipentene-tetrabromide by a direct comparison with a pure specimen.

(II) The part remaining in the reaction flask was extracted with ether. On distilling off ether, the residue⁽¹⁾ was subjected to steam distillation. 70 Gr. of the oily distillate ($d_4^{21}=0.8415$; $n_D^{20}=1.4746$) were twice redistilled on metallic sodium under 767 mm.

Fraction.	Yield	$d\frac{18.5}{4}$	n_D^{18}
170—173°	3.3 gr.	0.8327	1.4700
173—175°	41.0	0.8376	1.4732
175—177°	11.3	0.8434	1.4780
above 177°	3.7	——	——

From its chemical behaviour the fraction boiling at 173–175° was found to consist of p-cymene. In order to remove some terpenic compounds, the p-cymene fraction was treated with a diluted permanganate solution in cold, and then transformed into barium salt of p-cymene-disulphonic acid following the direction given by M. Phillips.⁽²⁾

0.3163 Gr. subst. gave 0.1699 gr. $BaSO_4$. (Found, Ba=31.66. $C_{10}H_{12}(SO_3)_2Ba$ requires Ba=31.99 %).

The residue by the steam distillation was a yellow viscous oil with a fluorescence and confirmed to be composed mostly of dipinene⁽³⁾ by distilling it.

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(1) The residue did not contain any cineol.

(2) *J. Am. Chem. Soc.*, 46 (1924), 689.

(3) C.S. Venable, *J. Am. Chem. Soc.*, 45 (1923), 733.

From these experimental results it appears evident that the main portion of cineol changes into dipentene, p-cymene and dipinene by the action of Japanese acid clay. The formation of p-cymene may be assumed to be formed by the decomposition of dipinene.

$$(C_{10}H_{16})_2 \rightarrow C_{10}H_{16} + C_{10}H_{18}$$

dipinene p-cymene Δp-menthene (?)

Laboratory of Saisei-Shono Kwaisha, Kobe.

A METHOD OF DETERMINING OF MOLECULAR WEIGHT OF ORGANIC SUBSTANCES IN SMALL QUANTITIES BY MEANS OF FREEZING POINT DEPRESSION.

By **Bennosuke KUBOTA** and **Takeo YAMANE.**

Received May 30, 1927. Published July 28, 1927.

The molecular weight of minute quantities of valuable organic material can be determined by one of the two methods described recently by K. Rast(1) and F. Pregl.(2) The Pregl's method is an improved modification of the ordinary ebullioscopic method using a Beckmann's thermometer, and the Rast's is amazingly simple, using camphor as solvent and an ordinary apparatus for the determination of melting point as the means of measurement. Though both are quite excellent, the utility of the former is diminished by the difficulty in the performance of experiments and that of the latter is limited not only by the small choice of available solvents, but also often by the instability of the substance to be investigated at such a high temperature as the melting point of camphor.

It seemed to us that in spite of some investigators' examinations, the thermo-junction(3) and the Beckmann's thermometer(4) had no practical use for the micro-cryoscopic purpose, and that the electric resistance thermometer which was constructed with silver wire(5) by Mr. T. Ikebe in the Institute of Physical and Chemical Rasearch showed such an excellence in the determination of the temperature of small quantities of liquid that we were induced to attempt molecular weight determinations of organic substances in small quantities by the depression of freezing point.

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(1) *Ber.*, 55 (1922), 1051 and 3727.

(2) " Die Quantitative Org. Mikroanalyse," 1923.

(3) Y. Yamaguchi, *J. Tokyo Chem. Soc.*, 37 (1916), 727.

(4) Drucker, *Biol. Zentralblatt.*, 33 (1913), 99.

(5) Silver wire was prefered to platinum one because the latter is expensive.

By means of the apparatus, which is shown in the following figures, a molecular weight determination was carried out by introduction of 4 to 8 mg. of substance into about 1 c.c. of solvent. It gave quite satisfactory results without disadvantages already mentioned.

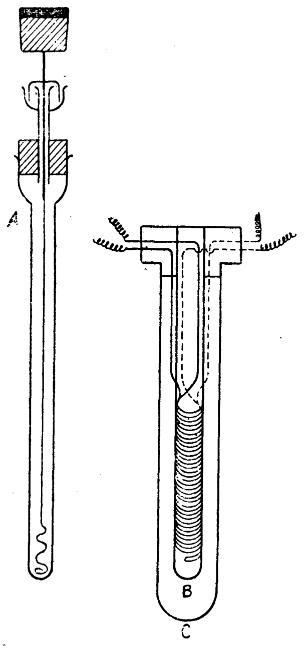

Fig. 1. (½ of actual size.)

It consists of an inner tube *A* which serves to freeze the solvent and is provided with a stirrer of platinum wire connected to a small glass rod. *A* is nicely fitted to the thin walled glass tube *B* which is coiled arround with silver wire of about 2 meters long and 0.11 m. in diameter, and is fixed in the air-jacketing tube *C* with a frame of ebonite. *C* is held in a Dewar's vessel containing the freezing mixture whose temperature depends upon the solvent.

For the measurement of resistance, the Müller type bridge of Leed and Northrup Co. was used, and as the resistance of the thermometer *B* changes with temperature practically in accordance with the formula $R_t = R_0(1+at)$, R_0 and R_t being resistances in ohms of the silver wire at 0° and $t°$ respectively, the change of its resistance per 1° was at first determined by two observations at 0°, the ice-water temperature, and at 8°.813, the room temperature, as follows:

$$R_0 = 1.2471, \qquad R_{8.813} = 1.2956$$

$$\frac{R_{8.813} - R_0}{8.813} = \frac{1.2956\text{–}1.2471}{8.813} = 0.0055$$

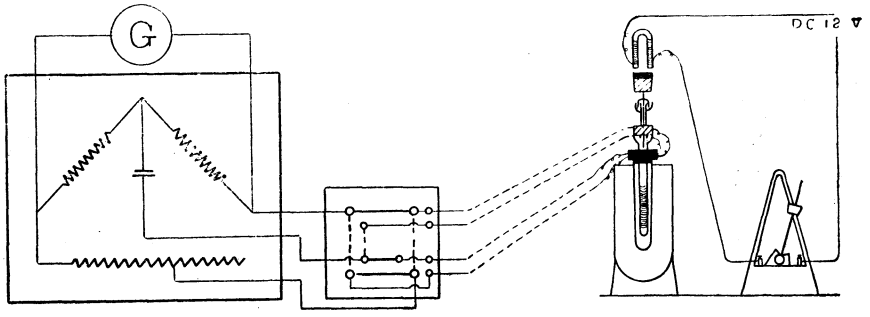

Fig. 2.

Now as much solvent was weighed in the tube *A* as its volume was enough to cover the whole length of the silver wire coil of the tube *B*. While agitating the solution with the stirrer of platinum wire which moves up and down by the action of a small electro-magnet and a iron piece, the resistance was observed.

The thermometer changed its resistance gradually and passed a maximum and a minimum point just like the reading in the Beckmann's thermometer. The maximum point was naturally taken as the resistance at the freezing point of the solvent.

A was then removed, the solvent was again melted and the solid substance previously weighed in a small glass tube (about 20 mm. long and 1.5 mm. in diameter) opened in both ends was introduced. When the dissolution was complete, the readings of the new value of the resistance were taken as before.

Thus the depression of freezing point $\varDelta t$ was easily calculated as follows:

$$\frac{R_t - R_n}{0.0055} = \varDelta t,$$

where R_t = resistance at the freezing point of the solvent, R_n = resistance at the freezing point of the solution, and the molecular weight of the substance was found from the usual formula. The results obtained with benzene, nitrobenzene and ethylene bromide as solvents are as follows.

(A). Benzene as solvent.

Molecular depression = 50.0 M = Molecular weight.

1. Acetanilide, 0.00404 gr. in 0.734 gr. of benzene.
   $R_t = 1.26961$. $R_n = 1.26848$. $\varDelta t = 0.^{\circ}206$
   Calc. $M = 135$. Found $M = 134$.
2. Naphthalene, 0.00705 gr. in 0.761 gr. of benzene.
   $R_t = 1.26937$. $R_n = 1.26742$. $\varDelta t = 0.^{\circ}360$.
   Calc. $M = 128$. Found $M = 127$;
3. Picric acid, 0.00820 gr. in 0.691 gr. of benzene.
   $R_t = 1.26892$. $R_n = 1.26747$. $\varDelta t = 0^{\circ}.264$
   Calc. $M = 229$. Found $M = 225$.
4. Phthalic anhydride, 0.00536 gr. in 0.666 gr. of benzene.
   $R_t = 1.26980$. $R_n = 1.26831$. $\varDelta t = 0^{\circ}.271$.
   Calc. $M = 148$. Found $M = 148$.

(B) Nitrobenzene as solvent.

Molecular depression = 70.0.

1. Acetanilide, 0.464 gr. in 0.884 gr. of nitrobenzene.
   $R_t = 1.27126$. $R_n = 1.126973$. $\varDelta t = 0^{\circ}.278$.
   Calc. $M = 135$. Found $M = 132$.
2. Naphthalene, 0.00720 gr. in 0.878 gr. of nitrobeneze.
   $R_t = 1.27140$. $R_n = 1.26890$. $\varDelta t = 0^{\circ}.454$.
   Calc. $M = 128$. Found $M = 126$.

(C). Ethylene bromide as solvent.

Molecular depression = 118.0.

As the second apparatus which was used was a little larger than the first one and, moreover, the specific gravity of ethylene bromide was comparatively large (2 18), a somewhat large quantities of the solvent had to be taken. The change of resistance per 1° of the thermometer was 0.01507.

1. Acetanilide, 0.00958 gr. in 2.972 gr. of solvent.
   $R_t = 4.03145$. $R_n = 4.02736$. $\Delta t = 0^\circ.272$
   Calc. $M = 135$. Found $M = 140$.
2. Naphthlene, 0.01795 gr. in 2.850 gr. of solvent.
   $R_t = 4.03159$. $R_n = 4.02273$. $\Delta t = 0^\circ.595$
   Calc. $M = 128$. Found $M = 126$.
3. Diphenyl, 0.01180 gr. in 3.031 gr. of solvent.
   $R_t = 4.03091$. $R_n = 4.02650$. $\Delta t = 0^\circ.293$
   Calc. $M = 154$. Found $M = 158$.

We wish to express our deepest obligation to Mr. T. Ikebe for his kindness in constructing the apparatus for us and also our best thanks to Dr. N. Watanabe and Mr. S. Sugimoto, in the Department of Commerce and Industry, for his kindness in placing the resistance bridge to our disposal.

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A RELATION BETWEEN ORTHOBARIC DENSITIES.

PART II.

By **Jurô HORIUCHI.**

Received July 11, 1927. Published August 28, 1927.

The writer has derived in his foregoing paper(1) the following relation between orthobaric densities,

$$\psi = RT \ln V_g/V_l = A(1/(V_l-E)-1/(V_g-E)) \cdots\cdots\cdots\cdots\cdots\cdots (1)$$

where ψ denotes the internal heat of vaporization of hypothetical infinitesimal molecules, while A and E denote characteristic constants for individual substance, and V_l and V_g the molecular volume of liquid and vapour respectively. There have been given 21 cases of actual calculations to prove validity of equation (1). In the present work 22 more substances have been taken. Some of them which are provided with full data of orthobaric densities have been treated just in the same manner as before. For the others, of which only vapour tension and liquid density are given, the vapour density was calculated from vapour tension applying gas law below boiling point, and for those substances whose vapour densities only are given in a certain range of temperature, liquid densities were estimated by Cailletet-Mathias' rule from the vapour densities and a few known data of liquid densities. The calculations have been done with following 22 substance; carbon dioxide,(2) nitrous oxide, ammonia, sulphur dioxide, phosgene, n-pentane, n-hexane, di-isopropyl, n-heptane, di-isobutyl, fluorobenzene, bromobenzene, iodobenzene, chloroform, carbon disulphide, methyl formate, methyl propionate, methyl isobutylate, ethyl acetate, ethyl propionate, propyl acetate, and acetone. In this paper, however, abridged data(3) are shown to save the space.

In the following tables Q_M, Q_z, D_l and D_g denote $RT \ln\frac{V_g}{V_l}$, $A\left(\frac{1}{V_l-E}-\frac{1}{V_g-E}\right)$, and densities of liquid and vapour respectively.

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(1) *J. Chem. Soc. Japan*, 47 (1926), 587; this journal, 1 (1926), 189.

(2) By Cailletet-Mathias' data, while in the previous paper by those of Amagat.

(3) Full data will be published in the *Journal of the Chemical Society of Japan* in Japanese.

TABLE 1. Carbon dioxide.

t°C	D_l	D_g	Q_M	Q_z
−23.0	0.998	(0.0475)	1514	1495
− 2.2	(0.898)	0.1040	1179	1179
15.9	0.796	(0.1726)	878	881
25.0	(0.685)	0.2543	587	585
28.9	(0.608)	0.3118	400	407

Critical temperature = 31.0°C,(1) $A=35270$, $E=21.1$.
(Cailletet and Mathias, *J. Phys.*, (2) 5 (1886), 549).
Parenthesis in the table show numbers computed by empirical equations given by the observers.

TABLE 2. Nitrous oxide.

t°C	D_l	D_g	Q_M	Q_z
−23.5	(1.017)	0.0413	1590	1597
−12.2	(0.964)	0.0566	1471	1470
− 1.5	(0.907)	0.0785	1321	1330
9.2	(0.838)	0.1066	1157	1159
19.8	0.758	(0.1476)	953	949
25.4	(0.690)	0.1782	803	795

Crit. temp. = 36.5°C,(2) $A=56770$, $E=8.89$.
(Cailletet and Mathias, ibid.)
Parenthesis in the table show numbers computed by empirical equations given by the observers.

TABLE 3. Ammonia.

t°C	D_l	D_g	Q_M	Q_z
−50	*1.4241	*2550	3322	3316
−20	*1.5033	* 612	3026	3026
+10	*1.6006	* 205.0	2731	2727
40	*1.7251	* 82.8	2409	2407
78.7	0.5120	0.0322	1935	1943
121.3	0.3831	0.1024	1035	1071

Crit. temp. = 132.9°C,(3) $A=47490$. $E=9.98$.
Numbers with asteriscs express the specific volume given by Osborne and Van Dusen(4); while the others are the densities obtained by Berthoud.(5)

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(1) Cardoso and Bell. *J. chim. phys.*, 10 (1912), 497; Landolt, "Tabellen," 5 ed., p. 258.
(2) Cardoso and Arni, *J. chim. phys.*, 10 (1912), 504; Landolt, "Tabellen," 5 ed., p. 262.
(3) Cardoso and Giltay, *J. chim. phys.*, 10 (1912), 514; Landolt, "Tabellen," 5 ed. p. 255.
(4) *Bur. Stannds Bull.*, 14 (1917), 414; "Tables Annuales," 5 (1925), 20.
(5) *J. chim. phys.*, 16 (1918), 429.

TABLE 4. Sulphur dioxide.

t°C	D_l	D_g	Q_M	Q_z
7.3	(1.4162)	0.00624	3024	3018
21.7	1.3757	(0.0105)	2857	2864
37.5	(1.3306)	0.0169	2696	2697
58.2	(1.2653)	0.0310	2443	2463
82.4	1.1845	(0.0525)	2202	2186
120.45	1.0166	(0.1268)	1628	1629
140.8	0.8690	(0.2250)	1131	1142
154.9	0.6483	0.4017	407	425

Crit. temp. = 157.15°C,⁽¹⁾ $A=77740$, $E=19.54$.
(Cailletet and Mathias, *Compt. rend.*, **102** (1887), 1563; Landolt, "Tabellen," 5 ed., p. 281.)
Parenthesis denote the numbers obtained by interpolation.

TABLE 5. Phosgene.

t°C	D_l	D_g	Q_M	Q_z
60.3	1.2780	0.0193	2779	2777
100.1	1.1655	0.0493	2347	2347
130.0	1.0637	0.0905	1975	1973
170.6	0.8219	0.2424	1077	1081
181.6	0.7089	0.3276	697	715

Crit. temp. = 187°C,⁽²⁾ $A=116200$, $E=28.09$.
(Patterno and Mazzuccuelli, *Gazz. Chim.*, **50** (1920), 38; "Tables Annuales," 5 (1925), 20.

TABLE 6. n-Pentane.

t°C	D_l	D_g	Q_M	Q_z
0	0.64539	(0.0007844)	3645	3642
40	0.6 62	0.003361	3234	3239
80	0.5624	0.01012	2821	2817
120	0.5107	0.0250	2358	2355
160	0.4394	0.0591	1727	1745
197.1	0.2560	0.2090	190	203

Crit. temp. = 197.2°C, $A=21690$, $E=53.62$.
(Young, *Sci. Proc. Roy. Dublin Soc.*, **12** (1910), 374).
Parenthesis denote the data calculated from vapour pressure.

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(1) Cardoso and Bell, loc. cit.; Landolt, "Tabellen," 5 ed., p. 261.

(2) Critical temperature mentioned here as well as those hereafter, if not otherwise described, are the data given by the observer of the densities.

TABLE 7. n-Hexane.

t°C	D_l	D_g	Q_M	Q_z
0	0.6769	(0.0002319)	4332	4324
30	0.6505	(0.0008523)	3999	3999
60	0.6221	0.002488	3656	3668
90	0.5918	0.00585	3325	3337
120	0.5588	0.01202	3000	2998
150	0.5207	0.02299	2627	2627
180	0.4751	0.04228	2179	2194
210	0.4124	0.07899	1584	1624

Crit. temp. = 234.8°C, $A = 276000$, $E = 64.48$.
(Young, ibid.)
Parenthesis denote the numbers calculated from vapour pressure.

TABLE 8. Di-isopropyl.

t°C	D_l	D_g	Q_M	Q_z
0	0.67948	(0.0003876)	4055	4040
30	0.6525	(0.001311)	3742	3741
60	0.6243	0.003479	3437	3439
90	0.5931	0.007782	3129	3125
120	0.5589	0.01555	2799	2798
150	0.5197	0.02825	2450	2439
180	0.4705	0.05216	1981	2000
226.5	0.2967	0.1848	470	499

Crit. temp. = 227.35°C, $A = 264400$, $E = 62.58$.
(Young, ibid.)
Parenthesis denote the numbers calculated from vapour pressure.

TABLE 9. n-Heptane.

t°C	D_l	D_g	Q_M	Q_z
30	0.6951	(0.0003115)	4628	4620
60	0.6491	(0.001015)	4279	4273
90	0.6218	0.002703	3926	3931
120	0.5926	0.006075	3580	3585
150	0.5598	0.01222	3217	3226
180	0.5232	0.02242	2838	2834
210	0.4793	0.04005	2384	2414
240	0.4177	0.07446	1759	1789

Crit. temp. = 266.85°C, $A = 340500$, $E = 75.90$.
(Young, ibid.)
Parenthesis denote the numbers calculated from vapour pressure.

TABLE 10. Di-isobutyl.

t°C	D_l	D_g	Q_M	Q_z
90	0.6328	0.002239	4074	4072
120	0.6046	0.005219	3714	3725
150	0.5732	0.01070	3348	3361
180	0.5383	0.01959	2984	2979
210	0.4970	0.03484	2552	2551
240	0.4434	0.06223	2003	2017
270	0.3482	0.1387	1047	1092

Crit. temp. = 276.8°C, $A = 381000$, $E = 86.98$.
(Young, ibid.)

TABLE 11. Fluorobenzene.

t°C	D_l	D_g	Q_M	Q_z
0	1.04653	(0.0001180)	4935	4935
30	1.0104	(0.0004908)	4598	4598
60	0.9744	(0.001503)	4288	4284
90	0.9366	0.003846	3967	3971
120	0.8955	0.008347	3654	3650
150	0.8519	0.01629	3329	3326
180	0.8037	0.02911	2989	2983
210	0.7480	0.04968	2605	2601
240	0.6789	0.08403	2131	2140
270	0.5739	0.1535	1424	1456

Crit. temp. = 286.55°C, $A = 221600$, $E = 46.87$.
(Young, ibid.)
Parenthesis denote the numbers calculated from vapour pressure.

TABLE 12. Bromobenzene.

t°C	D_l	D_g	Q_M	Q_z
50	1.4546	(0.0001321)	5979	5979
80	1.4142	(0.0004722)	5620	5643
110	1.3729	(0.001307)	5299	5320
140	1.3293	(0.003021)	4999	4999
170	1.2847	0.006562	4649	4681
200	1.2385	0.01209	4354	4371
230	1.1876	0.02079	4046	4040
260	1.1310	0.03427	3706	3687

Crit. temp. = 397°C, $A = 312100$. $E = 55.73$.
(Young ibid.)
Parenthesis denote the numbers calculated from vapour pressure.

TABLE 13. Iodobenzene.

t°C	D_l	D_g	Q_M	Q_z
80	1.7391	(0.0002018)	6357	6357
110	1.6932	(0.0006307)	6014	6024
140	1.6453	(0.001622)	5684	5697
170	1.5972	(0.003542)	5384	5384
200	1.5470	0.007278	5040	5063
230	1.4941	0.01295	4749	4745
260	1.4384	0.02200	4430	4423

Crit. temp. = 448°C, A = 367100, E = 5957.
(Young, ibid.)
Parenthesis denote the numbers calculated from vapour pressure.

TABLE 14. Chloroform.

t°C	D_l	D_g	Q_M	Q_z
−53.6	1.62580 (T)	0.00001340 (D)	5120	5115
−51.0	1.62075 (I)	0.00001639 (D)	5079	5079
−45.0	1.60988 (T)	0.00002593 (D)	5005	5002
−37.2	1.59511 (T)	0.00004563 (D)	4907	4903
−17.5	1.5559 (I)	0.0001667 (D)	4645	4645
− 6.2	1.53811 (T)	0.0003095 (D)	4517	4535
5.0	1.51700 (I)	0.0005281 (R)	4403	4406
12.87	1.50175 (Ty)	0.0007596 (R)	4315	4316
15.00	1.49739 (T.H.)	0.0008174 (R)	4290	4291

Crit. temp. = 260.0°C,(1) A = 167800, E = 40.60.

(D) : From vapour pressures given by Drucker and Kangro, *Z. physik. Chem.*, **90** (1915), 513.
(R) : From vapour pressures given by Rex, *Z. physik. Chem.*, **55** (1906), 358.
(T) : Timmermanns, *Sci. Proc. Roy. Dublin Soc.*, **13**, 326; "Tables Annuales," **3** (1914), 10.
(Ty): Tyrer, *J. Chem. Soc.*, **99** (1911), 871.
(H): Herz and Rathmann, *Chem. Zt.*, **146**, 1417; "Tables Annuales," **3** (1914), 10.
(T.H.): Mean of the densities given by (T) and (H).
(I): Interpolated from the data given in the above papers as well as the followings. Isnardi, *Z. Physik*, **9** (1922), 158; Faust, *Z. physik. Chem.*, **79** (1912), 97; Dolezalek and Schulze, *Z. physik. Chem.*, **83** (1913), 67; Flecker and Tyrer, *J. Chem. Soc.*, **103** (1913), 52; Tyrer, *J. Chem. Soc.*, **104** (1914), 2534.

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(1) Sajetschewsky, *Kiewer. Univers. Unters.*, 1878, No. 4 & No. 8; Landolt, "Tabellen" 5 ed., p. 257.

Table 15. Carbon disulphide.

t°C	D_l	D_g	Q_M	Q
−14.1	1.31324	0.00030170	4301	4306
− 3.06	1.29680	0.00051030	4209	4209
+ 8.26	1.28004	0.00079920	4121	4128
16.37	1.26807	0.0010964	4058	4059
22.44	1.25909	0.0013642	4011	4011
57.08	1.20484	0.0040642	3732	3736
78.82	1.17021	0.0072888	3558	3554
99.24	1.13583	0.011671	3389	3389
130.48	1.07964	0.021660	3117	3137

Crit. temp. = 273.05°C,⑴ $A = 149500$, $E = 23.22$

Densities of vapour were given by Battelli⑵ for the whole range of temperature. Densities of liquid have been estimated by Cailletet-Mathias' rule. Densities of liquid from 0° to 35° have been found from the following papers: Bugarsky, *Z. physik. Chem.*, **71** (1910), 705; Dawson, *J. Chem. Soc.*, **97** (1910), 1041; Tyrer, *J. Chem. Soc.*, **97** (1910), 2620; De Leeuw, Dissert. Amsterdam, **1910**, 22; "Tables Annuales," **1** (1912), 11.

Table 16. Methyl formate.

t°C	D_l	D_g	Q_M	Q_z
0	1.00319	(0.000687)	3956	3956
30	0.9598	0.002291	3638	3636
60	0.9133	0.006039	3324	3323
90	0.8634	0.01350	3002	3001
120	0.8070	0.02688	2659	2654
150	0.7403	0.05063	2256	2259
180	0.6521	0.09434	1762	1754
210	0.4857	0.2188	765	803

Crit. temp. = 214.0°C, $A = 125200$, $E = 28.21$.

(Young, ibid.)

Parenthesis denote the numbers calculated from vapour pressure.

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(1) Battelli, *Mem. Torino*, (2) **42** (1891), 1; ibid., **41** (1890), 1; Landolt, "Tabellen," 5 ed., p. 281.

(2) Ibid.

TABLE 17. Methyl propionate.

t°C	D_l	D_g	Q_M	Q_z
70	0.8537	0.002331	4026	4026
100	0.8137	0.005741	3678	3678
130	0.7705	0.01214	3326	3324
160	0.7221	0.02356	2936	2945
190	0.6657	0.04320	2518	2532
220	0.5938	0.07812	1988	2011
250	0.4655	0.1675	1063	1110

Crit. temp. = 257.4°C, $A=222400$, $E=47.99$.
(Young, ibid.)

TABLE 18. Methyl i-butylate.

t°C	D_l	D_g	Q_M	Q_z
90	0.8069	0.003361	3957	3957
120	0.7680	0.007628	3604	3606
150	0.7248	0.01533	3244	3237
180	0.6767	0.02869	2847	2847
210	0.6200	0.05141	2392	2403
250	0.5021	0.1218	1473	1519

Crit. temp. = 267.55°C, $A=270600$, $E=58.29$.
(Young, ibid.)

TABLE 19. Ethyl acetate.

t°C	D_l	D_M	Q_M	Q_z
10	0.9127	(0.000213)	4707	4700
40	0.8762	(0.000840)	4327	4328
70	0.8376	0.002561	3950	3964
100	0.7972	0.006158	3608	3609
130	0.7533	0.01314	3245	3246
160	0.7033	0.02577	2847	2853
190	0.6441	0.04751	2398	2415
210	0.5944	0.07128	2037	2029
249	0.3839	0.2288	537	570

Crit. temp. = 250.1°C, $A=221300$, $E=49.40$.
(Young, ibid.)
Parentesis denote the numbers calculated from vapour pressure.

TABLE 20. Ethyl propionate.

t°C	D_l	D_g	Q_M	Q_z
90	0.8077	0.002674	4122	4127
120	0.7692	0.00620	3767	3766
150	0.7267	0.01292	3390	3391
180	0.6795	0.02469	2986	2986
210	0.6243	0.04464	2534	2550
240	0.5501	0.08230	1938	1974
270	0.4018	0.1957	777	831

Crit. temp. = 272.9°C, $A = 281600$, $E = 58.29$.

TABLE 21. Propyl acetate.

t°C	D_l	D_g	Q_M	Q_z
90	0.8079	0.002457	4184	4184
120	0.7702	0.005760	3826	3824
150	0.7297	0.01195	3459	3460
180	0.6835	0.02268	3068	3065
210	0.6301	0.04115	2623	2628
240	0.5586	0.07576	2038	2067
270	0.4333	0.1661	1031	1093

Crit. temp. = 276.2°C, $A = 283700$, $E = 58.70$

TABLE 22. Acetone.

t°C	D_l	D_g	Q_M	Q_z
−83.4	0.90321 (T)	0.000000317	5605	5558
−78.0	0.900 (S)	0.000000608	5511	5511
−63.3	0.88150 (T)	0.00000287	5269	5254
−50.0	0.8670 (K)	0.00000967	5058	5058
−37.2	0.85337 (T)	0.00002490	4897	4894
−30.0	0.8463 (K)	0.00004056	4807	4799
−13.0	0.83105 (D)	0.0001185	4587	4620
− 6.2	0.81943 (T)	0.0001768	4479	4486
5	0.8081 (B)	0.0002985	4365	4365
10	0.8038 (B)	0.0003793	4310	4301

Crit. temp. = 234.4°C,(1) $A = 152700$, $E = 36.80$.

D_g was calculated from vapour tensions given by Drucker and Kangro, ibid.

(T): Timmermanns, ibid.
(K): Körber, *Ann. Phys.*, 37 (1912), 1014; "Tables Annuales," 3 (1914), 10.
(S): Stern, *Z. physik. Chem.*, 81 (1913), 441.
(D): Dutich, *Verh. K. Akad. Wet. Amsterdam*, 11, 44; "Tables Annuales" 3 (1914), 10.
(B): Bramley, *J. Chem. Soc.*, 109 (1916), 434.

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(1) Galizine, *Wied. Ann.*, 41 (1890), 620.

Table 1—22 show that the concordance of RT ln $\frac{V_g}{V_l}$ with A $\left(\frac{1}{V_l-E}-\frac{1}{V_g-E}\right)$ is excellent except at temperatures immediately near the critical temperature. Moreover, as vapour densities are calculated from vapour tensions at low temperatures, it is evident that following equation (2), which was derived from equation (1) as a vapour tension formula in the previous work, agrees with experimental data.

TABLE 23. Summary of constant E.

Substance	$E_{calc.}$	$E_{add.}$	$V_{P=\infty}$	V_K	E/V_K
Hydrogen	4.20	—		70.3	0.060
en	9.68	8.0		74.5	0.130
Ni	12.8	—		90.1	0.142
Argo	10.3	—		75.2	0.137
Carbon dioxide	21.1	21.6		94.8	0.223
Nitrous oxide	8.87	—		107	0.083
Ammonia	9.98	—		72.0	0.139
Sulphur dioxide	19.54	—		125.0	0.156
Phosgene	28.09	28.9		192.7	0.146
n-Pentane	53.62	54.0		310	0.173
i-Pentane	53.8	54.0		308	0.175
n-Hexane	64.48	65.0		367	0.176
Di-isopropyl	62.58	65.0		357	0.175
Heptane	75.90	76.0		427	0.178
n-Octane	87.0	86.9		491	0.177
Di-isobutyl	86.98	86.9		482	0.180
Benzene	41.51	41.5		256	0.162
Hexamethylene	52.6	52.3		308	0.171
Fluorobenzene	46.87	46.7		271	0.173
Chlorobenzene	50.15	51.0		308	0.163
Bromobenzene	55.73	55.4		323	0.172
Iodobenzene	59.57	59.7		351	0.170
Chloroform	40.60	37.7		—	—
Carbon tetrachloride	44.32	46.9		276	0.161
Carbon disulphide	23.22	—		202	0.115
Stannic chloride	58.43	—		351	0.166
Methyl formate	28.21	25.9		172	0.164
Methyl acetate	37.8	37.0		228	0.166
Methyl propionate	47.99	48.0		282	0.169
Methyl butylate	59.2	59.0		340	0.174
Methyl i-butylate	58.29	59.0		339	0.169
Ethyl formate	37.8	37.0		229	0.165
Ethyl acetate	49.40	48.0		286	0.173
Ethyl propionate	58.29	59.0		344	0.168
Propyl formate	46.5	48.0		285	0.163
Propyl acetate	58.7	59.0		346	0.170
Ethyl ether	50.0	47.0	49.9 (Tas.)	286	0.174
Acetone	36.80	34.0	35.6 (Tas.)	—	—
Methyl alcohol	24.40	26.7	23.1 (Tam.)	118	0.207
Ethyl alcohol	37.8	37.7	33.6 (Tam.)	167	0.226
Propyl alcohol	48.6	48.7		220	0.221
Acetic acid	30.0	—		171	0.175

Additive constants.

(H) = −0.54	(F) = 4.35	Double bond = − 4.6
(C) = 12.1	(Cl) = 2 × (F) = 8.70	Hydroxyl group = 16.2
(O) = 4.0	(Br) = 3 × (F) = 13.05	Ring formation = − 13.7
	(J) = 4 × (F) = 17. 4	

$$\ln P = \ln \frac{RT}{V_l} - \frac{1}{RT}\,\frac{A}{V_l - E} \tag{2}$$

Table 23 is the summary of the values of E hitherto obtained for 42 substances. In this work, besides that of carbon dioxdie shown in Table 1, the constants of carbon tetrachloride and benzene were recalculated by more careful computation, and are shown in the table.

E_{calc} in the second column is the values directly calculated. E_{add} in the third column which show pretty good agreement with E_{calc}, were calculated from additive constants shown at the bottom of the table. These constants consist of 6 fundamental numbers, and enable us to calculate constant E for 33 different substances. The values for C and H have been estimated from the data for normal hydrocarbons. The constant for a double bond was calculated assuming the benzene contains three of them. The group -CO-O- in esters was regarded to consist of two normal oxygen and a double bond. The constants for Cl are approximately the same for $COCl_2$, $CHCl_3$, CCl_4 etc.. It is interesting that the constants of halogenobenzenes are very accurately expressed by assuming to their constants 1, 2, 3, 4, times of that of fluorine respectively. $V_{p=\infty}$ in the fourth column denotes the volumes of liquids extrapolated to infinitely large pressure. The data adopted are of Tammann⁽¹⁾ and of Tashiro⁽²⁾, the latter being very close to E_{calc} in the case of ethyl ether and acetone. In the fifth, there are shown critical volumes calculated from data given in Landolt-Börnstein's table. Values of E/V_k in the last column are almost universally constant for normal liquids, the mean value of which being 0.170.

In the previous work, it was derived a reduced equation from equation (1), taking into account that the ratio $\frac{T_k}{\sqrt{AP_k}}$ are universally constant as well as $\frac{E}{V_k}$. The total summary of values for the constant A and $\frac{T_k}{\sqrt{AP_k}}$ are given in Table 24. This table shows that the constancy of the value $\frac{T_k}{\sqrt{AP_k}}$ for normal liquids is satisfactory, the following value having been obtained for their mean through the total data:

$$\frac{T_k}{\sqrt{AP_k}} = 0.1765.$$

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(1) *Ann. Phys.* **87** (1912), 975.

(2) *Bulletin of the Institute of Physical and Chemical Research* (in Japanese), **6** (1927), 105.

Teble 24. Summary of constant A.

Substance	A	$\frac{T_k}{\sqrt{AP_k}}$
Hydrogen	3958	0.148
Oxygen	18160	0.162
Nitrogen	17520	0.164
Argon	17440	0.165
Carbon dioxide	35270	0.189
Nitrous oxide	56770	0.154
Ammonia	47490	0.176
Sulphur dioxide	77740	0.175
Phosgene	116200	—
n-Pentane	216900	0.176
i-Pentane	204300	0.174
Hexane	276000	0.177
Di-isopropyl	264400	0.176
Heptane	340500	0.178
Octane	355900	0.180
Di-isobutyl	381000	0.180
Benzene	218200	0.174
Hexamethylene	249700	0.175
Fluorobenzene	221600	0.178
Chlorobenzene	292700	0.175
Bromobenzene	312100	0.179
Iodobenzene	367100	0.178
Chloroform	167800	0.176
Carbon tetrachloride	232500	0.172
Carbon disulphide	149500	0.166
Stannic chloride	307600	0.176
Methyl formate	125200	0.179
Methyl acetate	173700	0.178
Methyl propionate	222400	0.179
Methyl butylate	276700	0.179
Methyl i-butylate	270600	0.179
Ethyl formate	174000	0.178
Ethyl acetate	221300	0.180
Ethyl propionate	281600	0.179
Propyl formate	232700	0.173
Propyl acetate	283700	0.179
Ethyl ether	185600	0.181
Acetone	152700	0.169
Methyl alcohol	78950	0.205
Ethyl alcohol	105900	0.200
Propyl alcohol	143500	0.197
Acetic acid	151100	0.202

The writer wishes to express his sincere thanks to Prof. M. Katayama for his kind guidance throughout the present study.

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THE VISCOSITY OF LIQUIDS ABOVE THEIR BOILING POINTS. PART IV.⁽¹⁾

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In part II of this paper we have obtained the following equations expressing the relations between the molecular fluidity Φ defined as $\frac{1}{\eta . V^{\frac{1}{3}}}$ and molecular volume V or temperature T:

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

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

where K and C are arbitrary constants and Φ_K, T_K critical constants. As regards the specific fluidity Φ_1 referred to one gram, we have obtained exactly the same form of equations, which contain specific volume V_1 and constants K_1, C_1 and Φ_{1K} instead of K, C aud Φ_K. In the present paper some properties of the constants in the above equations will be considered.

First of all the constant B, an effective molecular volume, in equation (1) is of additive nature.⁽²⁾ In the following table the observed values of B are compared with those calculated by adding respective elementary parts :—

C=6.9, H=5.1, O=7.5, Cl=20.0, F=10.5, double linking=3.0, iso-grouping=0.

TABLE 1. Additivity of constant B.

Substance	Formula	$B_{\text{obs.}}$	$B_{\text{calc.}}$	Δ
Pentane	C_5H_{12}	95.5	95.7	+0.2%
Isopentane	C_5H_{12}	96.1	95.7	−0.4
Hexane	C_6H_{14}	112.6	112.8	+0.2
Heptane	C_7H_{16}	129.9	129.9	0
Octane	C_8H_{18}	147.9	147.0	−0.6
Methyl-formate	$C_2H_4O_2$	52.0	52.2	+0.4
Ethyl-formate	$C_3H_6O_2$	69.6	69.3	−0.4
Propyl-formate	$C_4H_8O_2$	86.8	86.4	−0.5
Methyl-acetate	$C_3H_6O_2$	68.9	69.3	+0.6
Ethyl-acetate	$C_4H_8O_2$	86.1	86.4	+0.3
Propyl-acetate	$C_5H_{10}O_2$	104.2	103.5	−0.7
Methyl-propionate	$C_4H_8 O_2$	85.0	86.4	+1.7
Ethyl-propionate	$C_5H_{10}O_2$	102.9	103.5	+0.6
Methyl-butyrate	$C_2H_{10}O_2$	102.7	103.5	+0.8
Methyl-isobutyrate	$C_5H_{10}O_2$	102.9	103.5	+0.6
Ethyl ether	$C_4H_{10}O$	85.7	86.1	+0.5
Carbon tetrachloride	CCl_4	88.9	86.9	−2.2
Benzene	C_6H_6	82.2	81.0	−1.3
Fluorobenzene	C_6H_5F	85.5	86.4	+1.0
Chlorobenzene	C_6H_5Cl	94.1	95.9	+1.9
Acetic acid	$C_2H_4O_2$	54.0	52.2	−3.3
Carbon dioxide	CO_2	29.5	27.9	−5·4

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

(2) It was shown by Batschinski that the constant ω in his formula is also of additive nature. *Z. physik. Chem.*, **84** (1913), 643.

The constants K, C, B and Φ_K in equations (1) and (2) have been reduced by using critical constants from the standpoint of corresponding states. The results are shown in Table 2 and 3.

1). The constant B has a dimension of volume, so that it can be reduced by dividing it with the critical molecular volume V_K :—

$$b_r = \frac{B}{V_K}.$$

2). From the form of equations (1) and (2) it will easilly be seen that the constants K and C can be reduced as follows:

$$k_r = \frac{K.V_K^{\frac{2}{3}}}{\Phi_K},$$

$$c_r = \frac{C.T_K^{\frac{1}{5}}}{\Phi_K},$$

where T_K represents the critical temperature and Φ_K the critical molecular fluidity.

3). The dimension of viscosity η is equal to that of momentum divided by area and from the kinetic theory of gases the velocity v in the momentum may be considered to be proportional to $\sqrt{\frac{T}{M}}$ where T is absolute temperature and M the molecular weight so that :(1)

$$[\eta] = \frac{[\text{Momentum}]}{[\text{Area}]} = \frac{[M][v]}{[V]^{\frac{2}{3}}} = \frac{[M]^{\frac{1}{2}}[T]^{\frac{1}{2}}[R]^{\frac{1}{2}}}{[V]^{\frac{2}{3}}} \quad \cdots\cdots\cdots\cdots\cdots(3),$$

where V represents volume and R the gas constant.

Using the above relation, the constants K and C may also be reduced as follows:

$$k_r' = K.M.^{\frac{1}{2}} T_K.^{\frac{1}{2}} V_K^{\frac{1}{3}},$$

$$c_r' = \frac{C M^{\frac{1}{2}} T_K^{\frac{7}{10}}}{V_K^{\frac{1}{3}}}.$$

4). From equations (2) and (3) we obtain the following reduced form of the constant Φ_K,

$$\varphi'_{Kr} = \frac{\Phi_K M^{\frac{1}{2}} T_K^{\frac{1}{2}}}{V_K^{\frac{1}{3}}}$$

The reduced constants obtained above have actually been calculated for various substances and tabulated below together with the actual constants.

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(1) This result has already been pointed out by K. Onnes, *Comm. Phys. Lab. Univ. Leiden*, 2 (1891).

As the values of Φ_K in k_r and c_r, those calculated from equations (1) and (2) have respectively been used.

TABLE 2. Actual constants.

Substance	K	B	C	Φ_K
Pentane	31.8	95.50	251	795.4
Isopentane	32.1	96.10	254	799.5
Hexane	25.4	112.6	219	702.6
Heptane	21.7	129.9	204	660.1
Octane	18.6	147.9	188	612.9
Methyl-formate	43.8	52.04	229	729.5
Ethyl-formate	34.0	69.60	218	696.1
Propyl-formate	27.5	86.82	202	649.3
Methyl-acetate	37.1	68.98	233	742.4
Ethyl-acetate	28.2	86.10	211	674.4
Propyl-acetate	23.8	104.2	196	630.0
Methyl-propionate	28.9	85.04	208	669.2
Ethyl-propionate	23.5	102.9	195	628.5
Methyl-butyrate	23.6	102.7	193	623.5
Methyl-isobutyrate	23.8	102.9	194	624.0
Ethyl ether	33.8	85.69	250	791.0
Carbon tetrachloride	20.4	88.88	147	470.7
Benzene	34.4	82.21	236	756.6
Fluorobenzene	28.8	85.51	200	647.3
Chlorobenzene	24.5	94.12	179	601.1
Acetic acid	(2250)	(0.8997)	(705)	(2291)
Bromine	(4400)	(0.2868)	(688)	(2273)
Carbon dioxide	(3060)	(0.669)	—	—

Note: Numbers in brackets represent quantities referred to one gram.

TABLE 3. Reduced constants.

Substance	k_r	$k'_r \times 10^{-4}$	b_r	c_r	$c'_r \times 10^{-4}$	$\varphi'_{Kr} \times 10^{-4}$
Pentane	1.84	3.98	0.308	1.08	2.34	2.16
Isopentane	1.85	3.95	0.312	1.08	2.34	2.16
Hexane	1.83	3.81	0.306	1.08	2.22	2.05
Heptane	1.83	3.80	0.304	1.09	2.22	2.04
Octane	1.82	3.74	0.302	1.09	2.32	2.12
Methyl-formate	1.82	4.17	0.302	1.08	2.43	2.24
Ethyl-formate	1.82	4.04	0.304	1.09	2.40	2.21
Propyl-formate	1.83	3.94	0.305	1.09	2.35	2.15
Methyl-acetate	1.82	4.39	0.303	1.09	2.57	2.35
Ethyl-acetate	1.82	3.99	0.301	1.09	2.40	2.20
Propyl-acetate	1.82	3.96	0.302	1.10	2.34	2.13
Methyl-propionate	1.82	4.10	0.302	1.09	2.41	2.21
Ethyl-propionate	1.81	3.89	0.299	1.09	2.32	2.12
Methyl-butyrate	1.82	3.92	0.302	1.10	2.33	2.13
Methyl-isobutyrate	1.83	3.90	0.304	1.09	2.30	2.10
Ethyl ether	1.83	4.12	0.304	1.08	2.42	2.24
Carbon tetrachloride	1.88	3.89	0.322	1.11	2.34	2.11
Benzene	1.86	4.58	0.321	1.11	2.76	2.28
Fluorobenzene	1.83	4.32	0.315	1.10	2.54	2.32
Chlorobenzene	1.83	4.41	0.306	1.08	2.57	2.38
Acetic acid	1.86	3.93	0.316	1.10	2.20	1.99
Bromine	1.95	4.29	0.339	1.08	2.67	2.47
Carbon dioxide	1.85	3.67	0.311	—	—	—
Mean	1.84	4.03	0.308	1.09	2.40	2.19

It will be seen from the above table that the respective constant becomes independent of the nature of the substance when it is expressed in reduced value.

Batschinski(1) also calculated the ratio $\frac{\omega}{V_{1K}}$ with various substances, where ω being the limiting volume in the rule proposed by him. This ratio should, according to him, as average be 0.307. Calculating the ratio with liquid carbon dioxide using the data actually measured by P. Phillips(2) near the critical point, it becomes 0.350. In the writer's case, using the same data, the ratio $\frac{B_1}{V_{1K}}$ is 0.311, which is only 1% greater than the average value 0.308.(3)

Reducing the respective quantities and constants in equations (1) and (2) by using the critical constants we have:

$$\frac{\Phi}{\Phi_K}=\frac{KV_K^{\frac{2}{3}}}{\Phi_K}\left\{\left(\frac{V}{V_K}\right)^{\frac{2}{3}}-\left(\frac{B}{V_K}\right)^{\frac{2}{3}}\right\},$$

$$1-\frac{\Phi}{\Phi_K}=\frac{CT_K^{\frac{1}{5}}}{\Phi_K}\left(1-\frac{T}{T_K}\right)^{\frac{1}{5}},$$

or for the sake of brevity,

$$\varphi_r=k_r(v_r^{\frac{2}{3}}-b_r^{\frac{2}{3}}) \cdots\cdots\cdots\cdots(4),$$

$$1-\varphi_r=c_r(1-t_r)^{\frac{1}{5}}\cdots\cdots\cdots\cdots(5),$$

where φ_r, t_r etc. represent reduced quantities or constants.

Using relation (3) stated above, equations (1) and (2) may also be reduced as follows:

$$\frac{\Phi.M.^{\frac{1}{2}}T_K^{\frac{1}{2}}}{V_K^{\frac{1}{3}}}=K.M.^{\frac{1}{2}}\,T_K.^{\frac{1}{2}}\,V_K^{\frac{1}{3}}\left\{\left(\frac{V}{V_K}\right)^{\frac{2}{3}}-\left(\frac{B}{V_K}\right)^{\frac{2}{3}}\right\},$$

$$\frac{\Phi_K M^{\frac{1}{2}}T_K^{\frac{1}{2}}}{V_K^{\frac{1}{3}}}-\frac{\Phi M^{\frac{1}{2}}T_K^{\frac{1}{2}}}{V_K^{\frac{1}{3}}}=\frac{CM^{\frac{1}{2}}T_K^{\frac{7}{10}}}{V_K^{\frac{1}{3}}}\left(1-\frac{T}{T_K}\right)^{\frac{1}{5}},$$

or

$$\varphi'_r=k'_r(v_r^{\frac{2}{3}}-b_r^{\frac{2}{3}})\cdots\cdots\cdots\cdots(6),$$

$$\varphi'_{Kr}-\varphi'_r=c'_r(1-t_r)^{\frac{1}{5}}\cdots\cdots\cdots\cdots(7),$$

where φ'_r, k'_r etc. represent reduced quantities or constants which are different from φ_r, k_r etc.

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(1) loc. cit.

(2) P. Phillips, *Proc. Roy. Soc.*, (A) 87 (1912), 48.

(3) Cf. paragraph 2 part II of this paper cited above.

It has already been shown that the constants k_r, k'_r, c_r, c'_r, and φ'_{Kr} have universal values independent of the nature of the substance, so that above equations (4), (5), (6) and (7) may be considered to express the theory of corresponding states for molecular or specific fluidity.

Summary.

1. The constant B, the effective molecular volume, is additive.
2. The respective constant in the volume and temperature relations becomes independent of the nature of the substance when it is expressed in reduced form.
3. From the volume and temperature relations of the molecular fluidity the reduced equations of the following form have been obtained.

$$\varphi_r=k_r(v_r^{\frac{2}{3}}-b_r^{\frac{2}{3}}).$$

$$1-\varphi_r=c_r(1-t_r)^{\frac{1}{5}}.$$

$$\varphi'_r=k'_r(v_r^{\frac{2}{3}}-b_r^{\frac{2}{3}}).$$

$$\varphi'_{Kr}-\varphi'_r=c'_r(1-t_r)^{\frac{1}{5}}.$$

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

July, 1927.
The Institute of Physical and Chemical Research,
Hongo, Tokyo.

SPECTROCHEMICAL STUDIES OF HYDROXYAZO-COMPOUNDS. PART IV.⁽¹⁾

By **Taku UEMURA** and **Shozo TABEI.**

Received June 11 1927. Published August 28, 1927.

One of the authors⁽²⁾ has already written on the tautomeric changes of some hydroxyazo-compounds and given them three different formulas according to their conditions.

We have now studied more in detail about the influences of methyl-group on these hydroxyazo-compounds, for as we have seen in a previous

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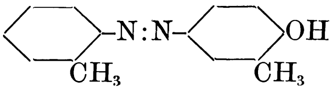
(1) Read before the Chemical Society of Japan, June 11, 1927.

(2) Uemura, Yokojima and Tan, This journal, **1** (1926), 260.
Uemura, Yokojima and Endo, ibid., **2** (1927), 10 & 48.

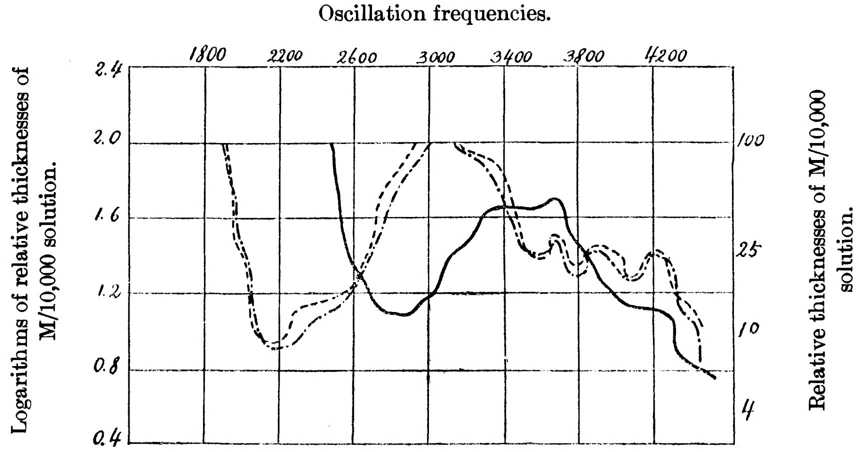
paper,(1) benzeneazo-p-cresol and p-nitrobenzeneazo-p-cresol have two absorption bands while the other compounds have but one. We have thought this was perhaps due to the methyl-group in the two above-mentioned hydroxy-azo-compounds. In the present paper, we shall describe tolueneazo-cresols.

Experimental.

1. o-Tolueneazo-o-cresol,(2)



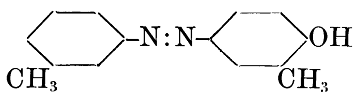
The neutral solution of this compound is light yellow and by adding KOH-solution it becomes yellowish orange even a concentrated (0.5 N.) alkaline solution. We may assign A(azo)-form(3) to the neutral solution and R(red)-form(3) to the alkaline.



1. o-Tolueneazo-o-cresol. { —— Neutral solution.
----- 0.02 N. alkaline solution.
—·— 0.1 N. alkaline solution.

Fig. 1.

2. m-Tolueneazo-o-cresol,(4)



The absorption curve of this compound (Fig. 2) is almost the same type as that of No. 1 compound. The colour change of this solution through alkali is also nearly the same as that of No. 1. When we compare the neutral solution curve of this compound with that of p-hydroxyazobenzene,(5)

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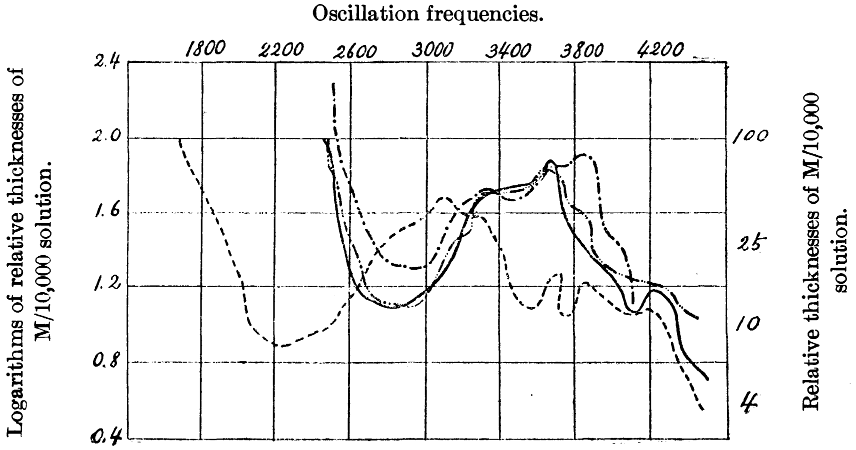
(1) This journal, 1 (1926), 262 & 265.
(2) Noelting and Werner, *Ber.*, 23 (1890), 3259.
(3) This journal, 1 (1926), 261.
(4) Jacobson, *Ann.*, 287 (1895), 185.
(5) This journal, 1 (1926), 262.

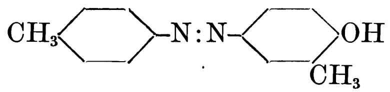
a considerably hyperchromic effect can be recognised, and the corresponding curve of benzeneazo-o-cresol(1) almost coincides with that of this compound. It seems to us that, although the methyl-group has a hyperchromic effect, yet it is still negligible against an already methylated compound.

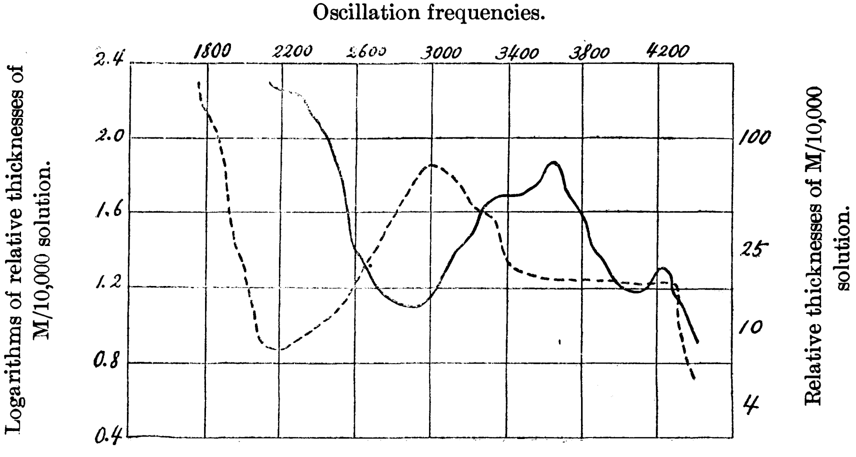


2. m-Tolueneazo-o-cresol. { ——— Neutral solution.
{ - - - - - 0.05 N. alkaline solution.
1 (Part I). p-Hydroxyazobenzene. —·—·— Neutral solution.
(Next report). Benzeneazo-o-cresol. —··—··— Neutral solution.

Fig. 2.

3. **p-Tolueneazo-o-cresol,**(2)





3. p-Tolueneazo-o-cresol. { ——— Neutral solution.
{ - - - - - 0.05 N. alkaline solution.

Fig. 3.

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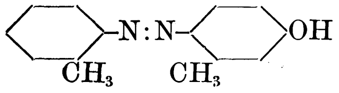
(1) Details about this compound will appear in the next report.

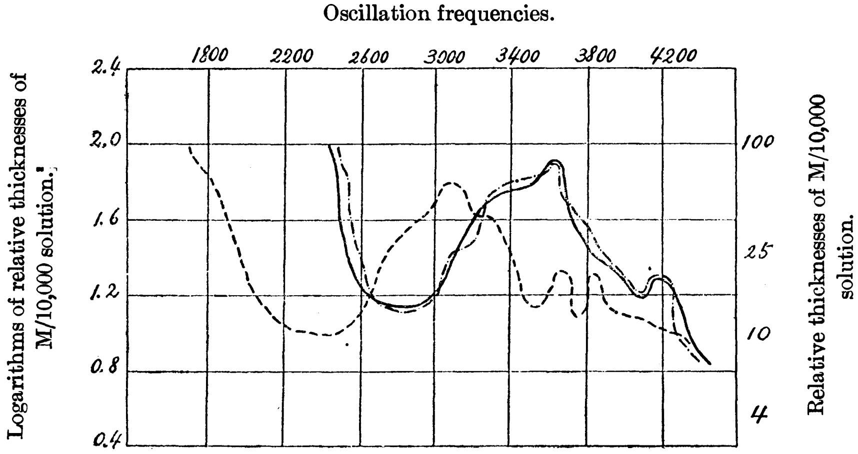
(2) Noelting and Werner, *Ber.*, **23** (1890), 3261.

When this compound is neutral in solution, it is slightly yellow, but becomes yellowish orange by odding KOH. We may clearly recognise the bathochromic and hyperchromic influences due to an alkali in the absorption curve (Fig. 3).

4. **o-Tolueneazo-m-cresol,**⑴



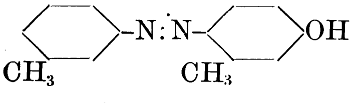
The yellow neutral solution of this compound changes into a deeper shade by the addition of alkali and this bathochromic effect can also be observed in its absorption curve. As Fig. 4 shows, we can likewise conclude that the influence of the methyl-group is similar to No. 2 oompound. We may also see the position effect of the methyl-group in the cresol ring is very slight.



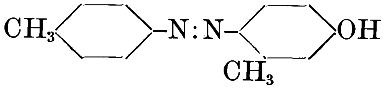
4. o-Tolueneazo-m-cresol. { ——— Neutral solution.
{ - - - - - 0.05 N. alkaline solution.
(Next report). Benzeneazo-m-cresol. —·—·— Neutral solution.

Fig. 4.

5. **m-Tolueneazo-m-cresol,**⑵



6. **p-Tolueneazo-m-cresol,**⑶



These two compounds have nearly the same type as No. 4 compound in their absorption curve (Fig. 5 and Fig. 6) of the neutral solution. We think

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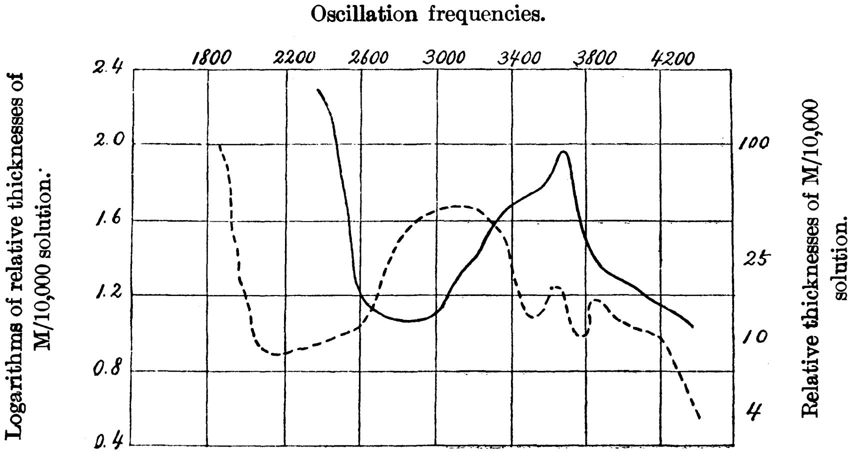
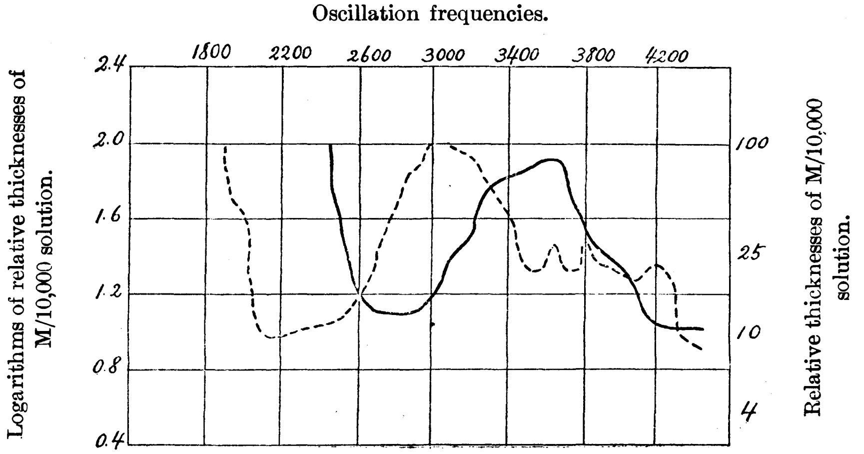
(1) Jacobson, *Ann.*, 287 (1895) 186.
(2) Jacobson, ibid., 287 (1895), 187.
(3) Jacobson, ibid., 287 (1895), 189.

this indicates the no position influence of the methyl-group in the toluene ring. As for the colour change, these compounds in solution are about the same as in No. 4 compound.



5. m-Tolueneazo-m-cresol. { ——— Neutral solution. / - - - - - 0.05 N. alkaline solution.

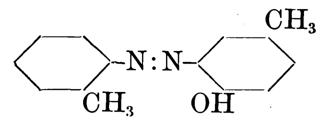
Fig. 5.



6. p-Tolueneazo-m-cresol. { ——— Neutral solution. / - - - - - 0.05 N. alkaline solution.

Fig. 6.

7. o-Tolueneazo-p-cresol,⑴



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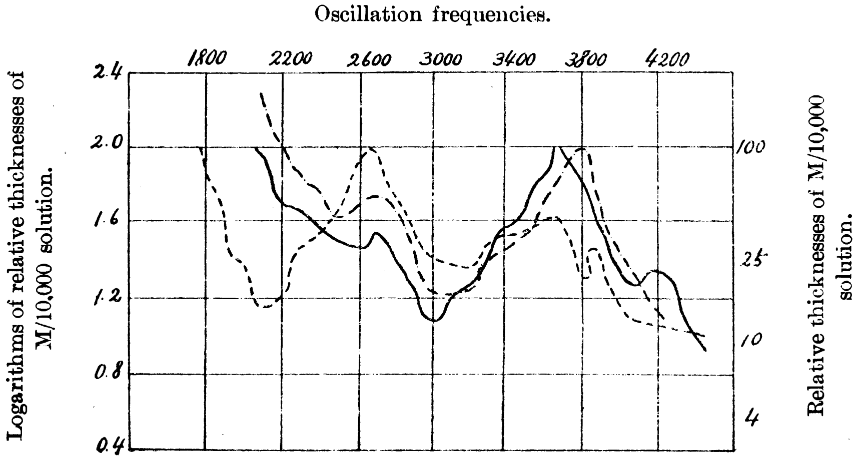
(1) Noelting and Werner, *Ber.*, 23 (1890), 3263.

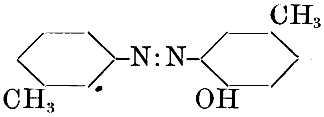
This compound has a hydroxyl-group in an ortho position with respect to the azo-group in cresol ring and has two absorption bands as is to be expected, and two bands more obvious can be also observed in the alkaline solution (Fig. 7). When we compare this absorption curve with that of benzeneazo-p-cresol,(1) the slight bathochromic and hyperchromic influences can be seen, and this is probably an effect of the methyl-group in the toluene ring. As the absorption curve of o-hydroxyazobenzene cannot yet been obtained, we are not here in a position perfectly to ascertain our point of issue like in the case of No. 2 compound.



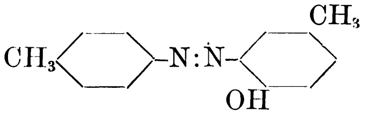
7. o-Tolueneazo-p-cresol. { ——— Neutral solution.
{ - - - - - 0.05 N. alkaline solution.
3 (Part 1). Benzeneazo-p-cresol. —·—·— Neutral solution.

Fig. 7.

8. m-Tolueneazo-p-cresol,(2)



9. p-Tolueneazo-p-cresol,(3)



In these cases, we discover nearly the same absorption curves as that of No. 7 compound, that is, these compounds have two absorption bands in their solution. The bathochromic effect by the addition of alkali is remarkably observed in their absorption curves (Fig. 8 and Fig. 9). The neutral

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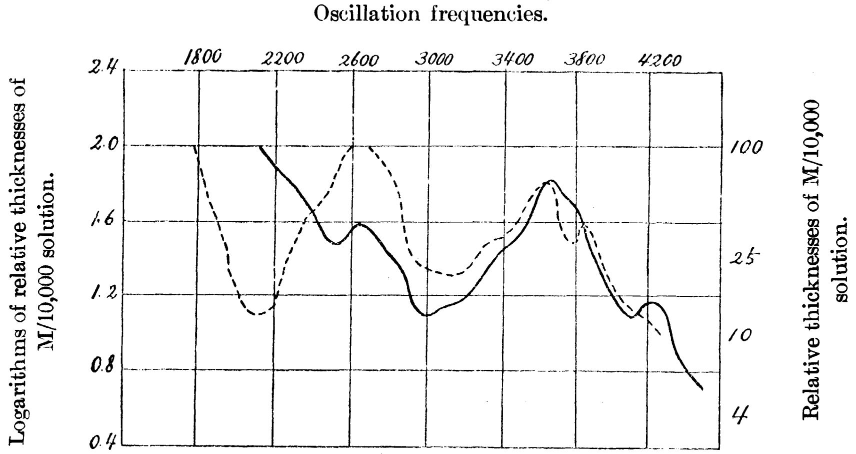
(1) This journal, 1 (1926), 263.

(2) Jacobson and Piepenbrink, *Ber.*, 27 (1894), 2703.

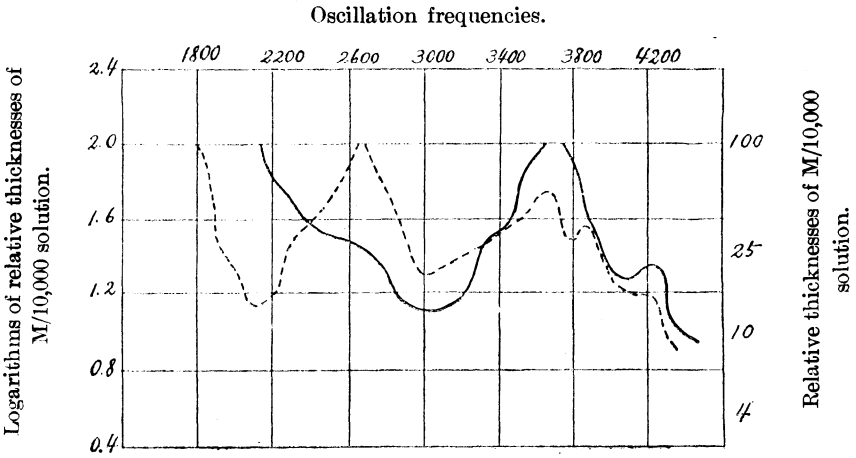
(3) Obtained from p-toluidine and p-cresol.

solutions of these two compounds are yellow like No. 7 compound and become orange when they are alkaline.



8. m-Tolueneazo-p-cresol. { —— Neutral solution. ----- 0.1 N. alkaline solution.

Fig. 8.



9. p-Tolueneazo-p-cresol. { —— Neutral solution. ----- 0.1 N. alkaline solution.

Fig. 9.

Summary.

(1) Tautomeric transformations may occur when the neutral solution of these tolueneazo-cresols change into the alkaline.

(2) The dilute neutral solution of these compounds is generally yellow and becomes deep yellow or orange when the solution is alkaline.

(3) We can respectively give A(azo)- and R(red)-forms⁽¹⁾ to these tautomers.

(4) There is one absorption band when hydroxyl-group in cresol ring takes para-position with regard to the azo-group, and two bands when ortho-position.

(5) The methyl-group has a hyperchromic influence, but when added to an already methylated compound, it ceases to be effective in the absorption curve.

(6) So far as the present studies are concerned, the methyl-group does not specially represent its influence with regard to the position.

We should like to express our hearty thanks to Prof. Yuji Shibata of the Tokyo Imperial University for the interest he has taken in the progress of these experiments. We are also indebted to the Department of Education and the School for a financial grant received in the pursuance of this research.

Dyeing Department, Tokyo Higher Technical School.

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(1) loc. cit.

ON THE SO-CALLED DIETHYL DICYANOGLUTACONATE AND SOME OF ITS DERIVATIVES. II.

By Yoshiyuki URUSHIBARA.

Received July 14, 1927. Published August 28, 1927.

In the previous paper(2) on the same subject the author pointed out the incorrectness of the view hitherto held on the composition and constitution of the so-called diethyl dicyanoglutaconate and described some of its derivatives. The results which were not referred to then, and those obtained further by the continued investigation will be noted in this paper.

The starting substance of the investigation on the diethyl dicyanoglutaconate, the cyanacetic ester, has been always prepared by Noyes' method.(3) That this method produces the mixture of methyl and ethyl esters, and that this fact has no direct effect upon the results, were explained in a separate paper.(4)

In order to distinguish the so-called diethyl dicyanoglutaconate from the real diethyl dicyanoglutaconate, which is not known in its free state, the former is followed by the word " semihydrate " according to the composition, but it must be remembered that the half molecule of water can not be removed.

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(2) This journal, 2 (1927), 26.
(3) *J. Am. Chem. Soc.*, 26 (1904), 1545.
(4) This journal, 2 (1927) 143.

The mechanism of the formation and the yield of the diethyl sodio-dicyanoglutaconate. In the condensation of ethyl cyanacetate, chloroform, and sodium ethylate, the reaction producing the diethyl sodio-dicyanoglutaconate, the mixture is brought to violent boiling when it is heated on the water bath, whereby apparently causing the escape of chloroform and diminishing the yield of the product. In fact, if the reaction is moderated by avoiding violent boiling, the yield of purified sodium compound is better (60% of the theoretical amount) than that attained by Errera (40%).(1) But the yield is not improved, even if the less volatile iodoform is used. Addition of chloroform in excess seems also to be of no use. The calculated amount of chloroform is sufficient to bring the mass nearly to neutral reaction, and the quantity of separated sodium chloride is not too small. Hence, it is probable that a side reaction occurs between chloroform and sodium ethylate, yielding the orthoformic ester, which the more prevails over the desired reaction, when the more rapidly heat is applied.

On the other hand, that the orthoformic ester is at first produced from chloroform and three-fourth of the sodium ethylate, and then it is condensed with cyanacetic ester by the action of remaining sodium ethylate, seems to be suggested by the following facts: Chloroform, carbon tetrachloride, and ethyl trichloracetate, give all the same compound, triethyl orthoformate, by the action of sodium ethylate, while all these three substances give the same diethyl sodio-dicyanoglutaconate by the action of ethyl cyanacetate and sodium ethylate.(2)

An experiment was carried out on the condensation of orthoformic ester and cyanacetic ester by means of sodium ethylate, but such did not take place. Hence, in the condensation of chloroform, sodium ethylate, and cyanacetic ester, the portion changed into orthoformic ester is lost, the corresponding amount of cyanacetic ester taking no part in the reaction. By the use of excess of chloroform and sodium ethylate, the amount of excess being in the proportion of one molecule to three, an increased yield of diethyl sodio-dicyanoglutaconate referred to the amount of the cyanacetic ester was obtained (70% of the theoretical amount.)

The formation of the diethyl sodio-dicyanoglutaconate by the condensation of ethyl cyanacetate and ethyl trichloracetate by means of sodium ethylate. The condensation of diethyl malonate and ethyl trichloracetate by means of sodium ethylate gives the tetraethyl sodio-dicarboxyglutaconate,(3) the same compound that is formed by using chloroform instead of ethyl trichloracetate. With a somewhat hopeless

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(1) *Ber.*, 31 (1898), 1241.

(2) *Ber.*, 35 (1902), 2881; and see under.

(1) Ruheman, *Ber.*, 29 (1896), 1017.

expectation of obtaining the triethyl dicyanoaconitate, the condensation of ethyl cyanacetate and trichloracetate was tried. But the experiment showed that the product was nothing but the diethyl sodio-dicyanoglutaconate. 0.4570 Gr. of the substance decreased in weight by 0.0557 gr. after dehydration at 120°. (Found: $H_2O=12.2$. $C_{11}H_{11}O_4N_2Na \cdot 2H_2O$ requires $H_2O=12.24\%$.) 0.2024 Gr. of the dehydrated substance gave 0.0528 gr. of Na_2SO_4. (Found: $Na=8.5$. The formula requires $Na=8.9\%$.)

The triethyl sodio-dicyanoaconitate has the formula $C_{14}H_{15}O_6N_2Na.\frac{1}{2}H_2O$, which requires $H_2O=2.65$; $Na=6.79\%$.)

Colour of the diethyl sodio-dicyanoglutaconate. In the previous paper it was shown that this substance was obtained in colourless state from iodoform. But sometimes the same reaction produced a dark reddish substance which was not easily freed from the colouring matter. The specimen prepared from ethyl trichloracetate was greenish yellow. At any rate this sodium compound accompanies some impurities in varying colours according to the condition of the reaction. And it is difficult to remove entirely these colouring matters by repeated recrystallisation. But when the sodium compound was recrystallised by using animal charcoal several times, it became nearly colourless.

Metallic derivatives of the diethyl dicyanoglutaconate. Various metallic derivatives are known, but as all of them were prepared from yellow sodium derivative, and the yellow colour is not characteristic of this compound, the colours of other metallic derivatives have been investigated.

Silver derivative. When a cold aqueous solution of silver nitrate is added to a cold aqueous solution of the sodium derivative, a gelatinous precipitate is formed, which on heating changes into have been powder.

Copper derivative. Freshly precipitated copper derivative is a pink-red voluminous substance, which soon changes into reddish brown powder. When ammonia is added to the well-washed reddish brown copper derivative, it changes into white precipitate, the supernatant liquid being slightly blueish.

Ammonium derivative. The double decomposition of the silver derivative of the diethyl dicyanoglutaconate and ammonium chloride gave an ammonium derivative with properties similar to those of the sodium derivative. This ammonium derivative precipitates the diethyl dicyanoglutaconate semihydrate on acidifying its aqueous solution. It possesses the formula $C_{11}H_{12}O_4N_2 \cdot NH_3 \cdot 2H_2O$, but loses one molecule of water on heating at 130°.

0.1388 Gr. of the substance dried in the desiccator gave 16.9 c.c. of N_2 at 9° and 756 mm. (Found: $N=14.50$. $C_{11}H_{12}O_4N_2 \cdot NH_3 \cdot 2H_2O$ requires $N=14.53\%$). 0.1452 Gr. of the substance dehydrated at 130° gave 19.2 c.c. of N_2

at 13° and 760 mm. (Found: N = 15.55. $C_{11}H_{12}O_4N_2 \cdot NH_3 \cdot H_2O$ requires N = 15.50%.) This substance decomposed when heated at a higher temperature.

Ruhemann[(1)] abtained an ammonium derivative by dissolving the diethyl dicyanoglutaconate semihydrate in aqueous ammonia. His compound has the composition $C_{11}H_{12}O_4N_2 \cdot NH_3 \cdot \frac{1}{2}H_2O$ and melts and decomposes at 162–163°. This is probably the ammonium derivative of the diethyl dicyanoglutaconate *semihydrate*, and the half molecule of water comes from the mother substance.

Incomplete hydrolysis of the diethyl dicyanoglutaconate semihydrate. Complete hydrolysis gives the diethyl dihydroxy-dinicotinate (diethyl 2.6-dioxypyridine-3.5-dicarboxylate).[(2)] The author obtained the hydrobromide and the picrate of diethyl dicarbamylglutaconate by the hydrolysis of the bromine addition compound of diethyl dicyanoglutaconate semihydrate, and transformed the hydrobromide into the diethyl dihydroxydinicotinate. The experiments show that this diamide is formed intermediately during the direct hydrolysis of diethyl dicyanoglutaconate semihydrate by dilute hydrochloric acid.

The semihydrate was hydrolysed by boiling in dilute hydrochloric acid and dissolved in it. Prolonged boiling produces the ultimate product, i.e., diethyl dihydroxydinicotinate, which separates out in white crystals from the boiling liquid. Before the appearance of this substance the boiling was stopped and the solution was cooled. A cryslalline substance was obtained and it gave a picrate identical in melting point with the picrate of diethyl dicarbamylglutaconate (197°).

Trial of synthesizing the real diethyl dicyanoglutaconate. According to L. Claisen[(3)] the diethyl diacetylglutaconate is formed in a moderate yield when orthoformic ester and acetic anhydride are heated with an excess of acetoacetic ester, and in a good yield when the ethoxymethylene-acetoacetic ester is introduced into the alcoholic solution of sodioacetoacetic ester. In the latter case the sodium derivative is formed, and from it the free ester is botained by treating with acid.

The diethyl sodio-dicyanoglutaconate does not give the corresponding free ester, but the semihydrate. The mixture of ethyl cyanacetate, triethyl orthoformate, and acetic anhydride, in the proportion of 2 mols : 1 mol : 3 mols, was boiled for two hours and distilled in vacuo (ca. 20 mm.) until the temperature reached 120°. By treating there sidue of the distillation with an alcoholic sodium ethylate solution, the diethyl sodio-dicyanoglutaconate was obtained, and on acidifying its aqueous solution the diethyl

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(1) *J. Chem. Soc.*, 73 (1898), 283.

(2) *J. Chem. Soc.*, 73 (1898), 284.

(3) *Ann.*, 297 (1897), 1.

dicyanoglutaconate semihydrate was precipitated. The formation of the diethyl sodio-dicyanoglutaconate probably owed to the presence of the real diethyl dicyanoglutaconate. But as it is possible that the ethoxymethylene-cyanacetic ester and cyanacetic ester were present in the residue and they produced the diethyl sodio-dicyanoglutaconate by the action of sodium ethylate, the formation of the real diethyl dicyanoglutaconate can not be insisted on.

The condensation of ethyl ethoxymethylene-cyanacetate and ethyl sodiocyanacetate. Another method for synthesizing such methenyl compounds consists in the condensation of ethoxymethylene compounds, and the corresponding sodio-compounds. This method was applied to the synthesis of the diethyl sodio-dicyanoglutaconate. Soon after the addition of ethyl ethoxymethylenecyanacetate to ethyl sodiocyanacetate in absolute alcohol, a crystalline substance separated out. On acidifying the aqueous solution of this substance the diethyl dicyanoglutaconate semihydrate was precipitated, which was quite identical with the specimen synthesized from chloroform.

The application of Claisen's condensation has enabled the author to synthesize all of the nitrile-esters of the dicarboxyglutaconic acid and the details will be given in another paper.

Dimethyl sodio-dicyanoglutaconate and its derivatives.(1) By the condensation of methyl cyanacetate and chloroform by means of sodium methylate in methyl alcohol the corresponding methyl compound was formed. Recrystallised from methyl alcohol, it was obtained as nearly colourless glittering crystals, which has the composition $C_9H_7O_4N_2Na{\cdot}2CH_3OH$, but easily loses a part of the alcohol of crystallisation. 0.5081 Gr. of the substance decreased by 0.1092 gr. on heating at 150–160°. (At a lower temperature the escape of the alcohol was incomplete.) (Found: $CH_3OH=21.52$. $C_9H_7O_4N_2Na\ 2CH_3OH$ requires $CH_3OH=21.77\%$.) 0.3819 Gr. of the substance freed from the alcohol of crystallisation gave 0.1159 gr. of Na_2SO_4. (Found: $Na=9.83$. $C_9H_7O_4N_2Na$ requires $Na=10.00\%$.) When this sodium compound is recrystallised from water and dried in the desiccator it contains about one molecule of water. 0.3821 Gr. of this substance decreased by 0.0265 gr. on heating at 150–160°. (Found: $H_2O=6.94$. $C_9H_7O_4N_2Na{\cdot}H_2O$ requires $H_2O=7.26\%$.)

By acidifying the hot aqueous solution of the dimethyl sodio-dicyanoglutaconate, yellow crystals of dimethyl dicyanoglutaconate semihydrate $C_9H_8O_4N_2\ \frac{1}{2}H_2O$ were precipitated.

0.2383 Gr. of the substance dried at 100–110° gave 26.3 c.c. of N_2 at 16.5°

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(1) Cf. this journal, 2 (1927), 145.

and 761 mm. (Found: N=12.85. $C_9H_8O_4N_2 \cdot \frac{1}{2}H_2O$ requires N=12.90%). This substance melts at 225° (corr.), is insoluble in absolute alcohol, methyl alcohol, benzene, and acetone even when boiled.

When bromine was added to the dimethyl dicyanoglutaconate semihydrate suspended in chloroform, the intermediate product was insoluble in this solvent and no distinct bromine addition compound was obtained. But the reaction proceeded in the same direction as in the case of the ethyl compound, which was ascertained as follows: After the addition of bromine the solid substance was collected and introduced into ether containing water. The white solid was dissolved in alcohol and the alcoholic solution of picric acid was added. At once a picrate precipitated, which proved to be the picrate of the dimethyl dicarbamylglutaconate.

0.1505 Gr. of substance gave 19.6 c.c. of N_2 at 15.5° and 751 mm. (Found: N=14.96. $C_9H_{12}O_6N_2 \, C_6H_2(OH)(NO_2)_3$ requires N=14.80%.)

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THE SURFACE AREA AND SORPTION.

By Michael TARLÉ.

Received July 22, 1927. Published September 28, 1927.

In the " Bulletin of the Chemical Society of Japan "(1) appeared an interesting report by Prof. Jitsusaburo Sameshima under the title : " The Sorption of Gas by Charcoal as a Dissolution Phenomenon." Prof. Sameshima made measurements of amounts of carbon dioxide absorbed by various kinds of charcoal (activated in the same way), and found, that the amounts absorbed are independent of the area of the surface of the charcoal ; therefore he considers the phenomenon of sorption not as a condensation of gas on the surface, but as a dissolution of the gas in the charcoal. In my opinion this deduction is based on misunderstanding : the interesting experiments of Prof. Sameshima do not prove the correctness of his point of view.

1. It is not quite clear in what way has been the amount of absorbed gas measured. The experimental part has been probably described in the former publications of Prof. Sameshima, which are inavailable for me at present. So far one can judge the volume absorbed has been measured indirectly and the measurements are partly based on the knowledge of the volume of the charcoal ; this volume is calculated under assumption that the density of the charcoal is 2.1. This assumption might be correct for highly active charcoals only ; in other words for charcoal, which has been heated for a rather long period of time (6 to 24 hours) at a temperature of 800–1000°C if, and as in experiments under discussion, has not been treated by chemical agents. Now, it is highly probable that being activated in this way, the raw charcoal changes its former structure and passes from the amorphous state to cristallinic (graphite). During this transition period —possibly under the influence of unsaturated atoms(2)—the charcoal has a high absorbing capacity. After the transition is finished and the whole of the charcoal is changed to graphite, the high active properties disappear. The process of transition can be followed by measurements of the true density of the charcoal, as has been shown by me in a paper submitted to the Anti-Gas Branch of the Chemical Warfare Department in London in 1918. I repeated now some of those measurements at the Research Laboratory of the Moukden Arsenal (in connection with an investigation of the velocity of sorption problem, soon to be

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(1) This journal 2 (1927), 1.

(2) O. Ruff, *Z. angew. Chem.*, 38 (1925), 1164.

published) and again found that the true density is a function of the duration and temperature of the activation process and is closely connected with the absorbing capacity. Different kinds of charcoal (of different origin and of different kind of activation) showed following results:

No.	Absorbing capacity for chlorine (%) A	True density(1) D	Volume of the pores per 1 gr. C	$\frac{A}{C}$
1	11.1	1.44	—	—
2	23.0	1.52	1.18	19.3
3	32.2	1.94	0.96	33.5
4	36.6	1.43	1.30	27.1
5	38.5	1.91	1.15	33.5
6	40.1	2.10	1.32	30.6
7	52.0	1.84	1.79	29.1

We see from this table that in only one case has been the density 2.1. As Prof. Sameshima activates his charcoal only *one* hour at 800°C. we may assume that its density has been lower than 2.1 (probably 1.7–1.9) and therefore the amounts of the absorbed gas (the absorbing capacities) are not represented quite correctly by the figures of Prof. Sameshima. The correction will vary with the kind of charcoal used and, although not a large one, may change the opinion "that the amounts of absorbed carbon dioxide... by various kinds of charcoals are nearly equal in each other." Furthermore we see from the above table that the rate "$A : C$" is nearly constant and from this we may assume, that —at least in some cases— the absorbing capacity is nearly proportional to the volume of the pores and therefore cannot be explained by the dissolution theory of Prof. Sameshima. His statement, that ".. It is not conceivable that different materials give the charcoals of nearly same surface area.." is also contradicted by facts. The activation process changes the original wood structure, the original difference of the structure with the progressing process disappears, the final density becomes about 2.1, the charcoal assumes the structure of the graphite. So the surface area (after activation) will depend not so much on the original structure, as on the method of activation. As the charcoals in the experiments of Prof. Sameshima has been activated in the same way the total absorbing capacity will not differ much from each other.

2. The second important point of the investigation of Prof. Sameshima is "that the absorbed amounts by the granular and by the powder charcoal are the same. ... The dissolved (absorbed ? M.T.) quantity of gas depends

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(1) These density figures are not absolutely correct, as we do not know the density of the liquid which filled the micropores and is compressed; but the volume of the micropores is evidently small comparing with the volume of the macropores. The mistake is also of a small order. See the investigation by Harkins and Ewing, *J. Am. Chem. Soc.*, **43** (1921), 1790.

only upon the amount of charcoal, and does not depend upon the surface area of it." This point is surely based on a misunderstood conception of the surface area of an absorber. The experimental method of Prof. Sameshima has been as follows. The amount of the gas absorbed by granulated charcoal has been measured, then the charcoal powdered (in a mortar, by hand), the charcoal heated, the gas removed, and the charcoal again brought in contact with gas. The first measurement of the absorbed amount gives practically the same result as the second one, and from this Prof. Sameshima concludes that the absorbing capacity is independent of the surface area, because the surface area of a powder is, in his opinion, much larger than that of the granules. This conclusion is incorrect, because for a very porous body both areas will be practically equal.(1) The surface area of a porous body consists of two areas: area of the external surface and that of the internal surface (interface), i.e. the surface of the macro- and micropores.(2) The second area is of another order of magnitude and incomparably larger than the first one; therefore the changing of the first area will have no practical influence upon the second one, which is not changed by grinding.

Let us make the following calculation. We take one piece of charcoal, a cube of 1 c.c., with an outside surface of 6 sq. cm. We do not know accurately the internal surface area; Lamb(3) assumes that it is equal to 100 sq. meters for 1 gr. of charcoal; Cude and Hulett(4) found it to be about 200 sq. meters; from the study of microphotograms taken at the Central Scientific Laboratory of the Russian War Office during the European war(5) I found the area of the macropores only to be about 10 sq. meters for 1 gr. of activated charcoal. If we take even this low figure as a base of our calculation and assuming that the apparent density is 0.5 we get for the total area—both external and internal—of our cube $6+50000=50006$ sq. cm. Now let us grind the charcoal. If we break it to 10000 small particles, each particle having a volume of 0.0001 c.c., the external surface of each particle will be $0.002116\times 6 =0.0127$ sq. cm. As we have 10000 such particles the external area will be equal to 127 sq. cm., and the total area will be $50000+127=50127$. So the change of the area produced by grinding equals to 0.2% of the area only. In other words the powdering produces a negligible effect upon the surface area and therefore the experiments of Prof. Sameshima do not prove the correctness of the dissolution theory.

Manchurian Arsenal, Moukden, China.

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(1) Cude and Hulett, *J. Am. Chem. Soc.*, 42 (1920), 398.

(2) Harkins and Ewing, *J. Am. Chem. Soc.*, 43 (1921), 1798.

(3) *J. Am. Chem. Soc.*, 42 (1920), 1146.

(4) Loc. cit.

(5) Prof. Chlopine, "The Foundations of the Anti-Gas Defence." Petrograd (Leningrad), 1926.

ON DR. TARLÉ'S PAPER ENTITLED "THE SURFACE AREA AND SORPTION."

By **Jitsusaburo SAMESHIMA.**

Received August 20, 1927. Published September 28, 1927.

I am glad to know that my paper under the title "The sorption of gas by charcoal as a dissolution phenomenon," which was published in the January number of this journal, has been read and criticised by Dr. Tarlé.(1) I can reply at once to the kind criticism of Dr. Tarlé.

1. In the first place, the method of measurement of the amount of absorbed gas was described in my paper (pages 2, 3 and Fig. 1). But I will explain it here again :—

Exactly weighed charcoal (evacuated, sealed in a tube and weighed) was put in the bulb A (cf. Fig. 1 in the paper cited above), and then evacuate the bulb A and the burette E. Close the cock B, introduce the carbon dioxide gas into the burette E and then close the cock D. Read the volume of the gas in the burette E after adjusting the pressure by the mercury reservoir G. Now open the cock B. Then the gas enters into the bulb A and is absorbed by the charcoal. The absorbed amount of gas can be traced time to time by reading the burette E. The final amount of absorption is known also by reading the burette E after sufficiently long time.

Now the absorbed amount of gas can be calculated as follows :—

$$V=v-v'-v'',$$

where V denotes the volume of gas absorbed by the charcoal taken,
v, the volume of gas introduced into the burette E,
v', the volume of gas remaining unabsorbed in the burette E,
v'', the volume of gas remaining unabsorbed in the bulb A.

The temperature and the pressure of the gas in various parts of the apparatus must, of course, be reduced to the same conditions, say 0°C. and 760 mm. The value of v'' can be obtained by the formula,

$$v''=(a-c)\frac{273.1P}{760T},$$

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(1) Former article in this journal.

where a denotes the capacity of the bulb A,
c, the volume of the charcoal,
P, the pressure of the gas,
T, the temperature of the gas in the bulb A.

Thus $(a-c)$ is the free space in the bulb A. A few of the actual data of observations are given in the following table (cf. Table 1 and Table 2 of the paper cited above).

	Time		v c.c.	v' c.c.	a c.c.	Wt. of charcoal gr.	c c.c.	v'' c.c.	V c.c.	Absorb. vol. for 1 gr. c.c.
	min.	sec.								
Granular charcoal. (third series)	—	15	53.200	19.071	6.046	0.8604	0.4097	5.220	28.909	34.382
	—	61	"	9.756	"	"	"	5.266	38.178	44.372
	4	25	"	6.041	"	"	"	5.165	41.994	48.808
	40	0	"	3.489	"	"	"	5.164	44.547	51.775
	79	0	"	2.930	"	"	"	5.164	45.106	52.424
	365	0	"	2.150	"	"	"	5.164	45.886	53.331
	3205	0	"	1.550	"	"	"	5.164	46.486	54.028
Powder charcoal.	—	22	53.837	9.697	6.046	0.8752	0.4168	5.158	38.982	44.540
	—	57	"	6.031	"	"	"	5.158	42.648	48.729
	5	8	"	3.398	"	"	"	5.158	45.281	51.738
	41	0	"	2.197	"	"	"	5.157	46.483	53.111
	100	0	"	2.006	"	"	"	5.158	46.673	53.329
	295	0	"	1.814	"	"	"	5.158	46.865	53.548
	3110	0	"	1.443	"	"	"	5.157	47.237	53.972

In this table the values of c (0.4097 and 0.4168) have been computed by the assumption that the density of charcoal is 2.10. Dr. Tarlé does not mention on the paper of Howard and Hulett.(1) It seems that their results are more trustworthy than any other density determinations ever published. They obtained the value 2.05—2.28 for the densities of various kinds of activated charcoals.

If we assume, however, the density to be 1.7 as Dr. Tarlé's opinion, then the values of c increase to 0.506 and 0.515 c.c. respectively. Accordingly V take lower values by 0.096 and 0.098 c.c. respectively than the values given in the table, which are 0.2% of the values of V. Then the absorbed volume of carbon dioxide by 1 gram of sugar charcoal at 25°C. and under 760 m.m. becomes 53.9 c.c. instead of 54.0 c.c. This is but small difference.

At any way, the question on the density of charcoal gives no serious effect on my result. My result are always referring to 1 gram of charcoal,

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(1) Howard and Hulett, *J. Phys. Chem.*, **28** (1924), 1088.

not 1 cubic centimeter of it. So the error which might come from the uncertainty of the density of charcoal is less than 0.2% in the final results. And in the comparison of the absorption velocities by granular and by powder charcoals, this uncertainty gives entirely no effect on the results, because the amounts of charcoals used are always nearly equal in granular and in powder ones.

The " activation," in my opinion, is nothing more than the purification process of the impure charcoal. This is analogous to the fact that the purified water dissolves much hydrochloric acid gas than the impure water. The ordinary charcoal contains much organic matters as well as inorganic " ash." These impurities can be removed by heating in the steam or in the air, or treating with chemicals etc. The amounts of impurities, however, can by no means be estimated by the elementary analysis. The surface area may somewhat increase by the partial oxidation of the charcoal, and this may result the increasing of the absorption velocity of gas in the " break point " experiment.(1)

Dr. Tarlé measured the volume of pores of charcoals. I do not know how these volumes were computed, but if he obtained these volumes from the differences of true densities and block densities (i.e. apparent densities), then it is almost meaningless to compare them with the absorption capacities. There is no relation between the surface area and the volume of pores which have been computed in such a manner. The surface area may depends upon the average volume of individual pore, but not the total volume of pores.

The charcoal probably changes its structure from amorphous to crystallinic by prolonged heating to the temperature higher than 1000°C., and this results the diminution of the absorption capacity of gas as was already described in the former paper (page 9).

2. It is true that the charcoal has a great numbers of small pores. But the surface area of it must, certainly, increase by grinding. In Dr. Tarlé's calculation, he considered that one cubic centimeter of charcoal produce 10000 particles by grinding. Then assuming the particles are cubic in form, the length of one side of these particles becomes, in average, 0.46 mm. This is evidently far from the truth. I have examined my powdered charcoal microscopically, and known that the particles range from 0.01 mm. down to those smaller than the lower limit of microscopical observation. Let us assume that the average length be 0.001 mm., then the number of particles derived from one cubic centimeter of charcoal is 10^{12}. Accordingly, the sum of the surface areas of these particles is, $6 \times 0.001^2 \times 10^{12} = 6 \times 10^6$ sq.

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(1) Chaney, Ray and John, *Ind. Eng. Chem.*, 15 (1923), 1244.

mm. = 6 sq. meter. If we assume that the total area of one gram of charcoal be 100 square meters,⁽¹⁾ and the block density of it be 0.5, then the increase of area by grinding amounts to 12% of the total area. The increase of area by grinding of the porous substance is less than that by grinding of the compact substance. So the above figure must be lowered to 6% or so. This is far above the experimental error of the determination of absorption capacity. In the present study, the experimental error is 0.2%. Even if the length of the particles be 0.01 mm. in average, the increase in area becomes to 0.6%, which still beyond the experimental error. Therefore the adsorption amount must increase by grinding if the adsorption theory be true.

The idea that the gas molecules condense on the surface of charcoal is merely a hypothesis. It is more natural, I think, to consider the absorption of gas by charcoal is caused by the dissolution than by the adsorption. There are numerous examples of absorption of gases by solid substances which can be explained by dissolution or compound forming theory, that is one phase theory, namely, the absorption of hydrogen by palladium, oxygen by silver, and hydrogen, carbon dioxide or water vapour by rubber etc.

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(1) Lamb and Coolidge, *J. Am. Chem. Soc.*, 42 (1920), 1168.
Garner, McKie and Knight, *J. Phys. Chem.*, 31 (1927), 641.

SPECTROCHEMICAL STUDIES OF HYDROXYAZO-COMPOUNDS, PART V.(2)

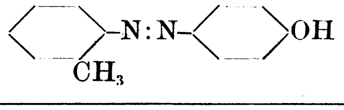
By **Taku UEMURA** and **Shozo TABEI.**

Received June 11, 1927. **Published September 28, 1927.**

Some influences with regard to the methyl-group in tolueneazo-cresols were mentioned in our previous paper,(3) and, in this paper, we shall continue the same subject.

Experimental.

1. **o-Tolueneazophenol,**(4)



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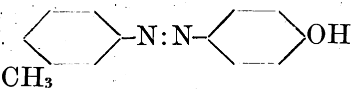
(2) Read before the Chemical Society of Japan, June 11, 1927.

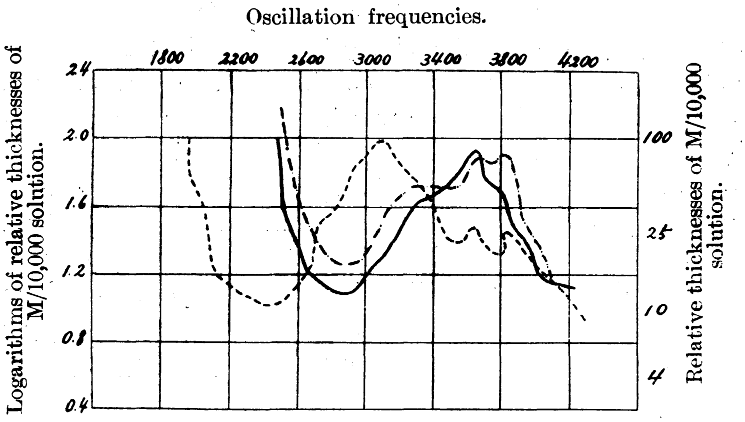
(3) Uemura and Tabei, This journal, **2** (1927), 229.

(4) Noelting and Werner, *Ber.*, **23** (1890), 3257; Paganini, Ibid. **24** (1891), 366.

2. m-Tolueneazophenol,(1)

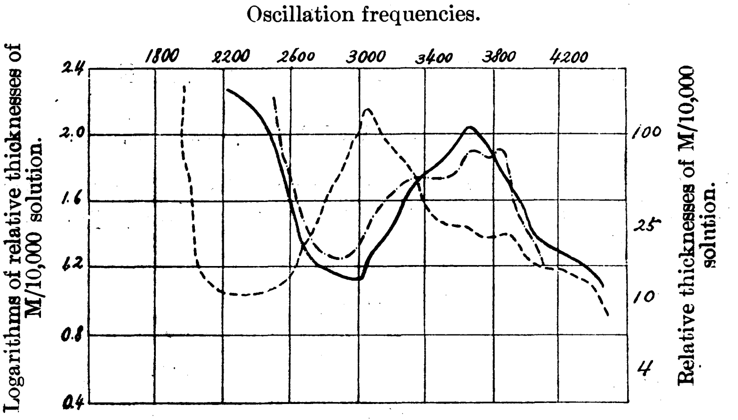


The neutral solutions of these two compounds are yellow and give a deeper shade by adding KOH. When we compare the neutral absorption curve of p-hydroxyazobenzene(2) with the absorption curves of these compounds, the hyperchromic influence due to the methyl-group can be distinctly observed (Fig. 1 and Fig. 2).



1. o-Tolueneazophenol. { ——— Neutral solution.
{ - - - - - 0.05 N. alkaline solution.
1(Part I).p-Hydroxyazobenzene. —·—·— Neutral solution.

Fig. 1.



2. m-Tolueneazophenol. { ——— Neutral solution.
{ - - - - - 0.05 N. alkaline solution.
1 (Part I). p-Hydroxyazobenzene. —·—·— Neutral solution.

Fig. 2.

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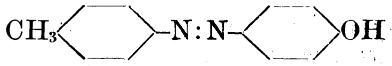
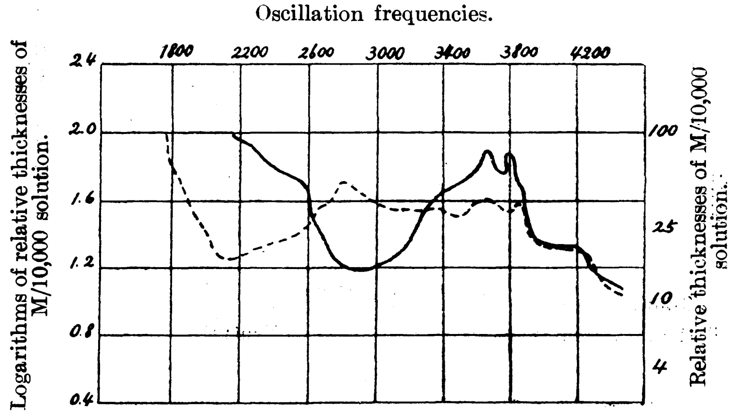
(1) Paganini, *Ber.*, 24 (1891), 368.
(2) This journal, 1 (1926), 262.

3. p-Tolueneazophenol,(1)



The absorption curves of this compound (Fig. 3) are slightly hypochromic than those of the previous two compounds. But, comparing the curve of p-hydroxyazobenzene(2) with these, we can observe an effect similar to the one we found in the cases of the two above-mentioned compounds.

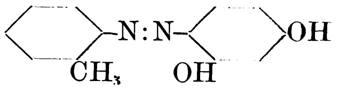
The colour of this alkaline solution is orange of a somewhat deeper shade than No. 1 and No. 2. By the addition of alkali, only a bathochromic effect can be shown in the absorption curves of these three tolueneazophenols.



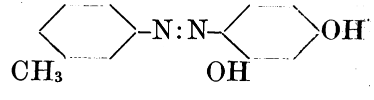
3. p-Tolueneazophenol. { —— Neutral solution
----- 0.05 N. alkaline solution.

Fig. 3.

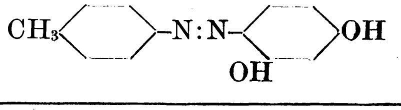
4. o-Tolueneazoresorcinol,(3)



5. m-Tolueneazoresorcinol,(4)



6. p-Tolueneazoresorcinol,(5)



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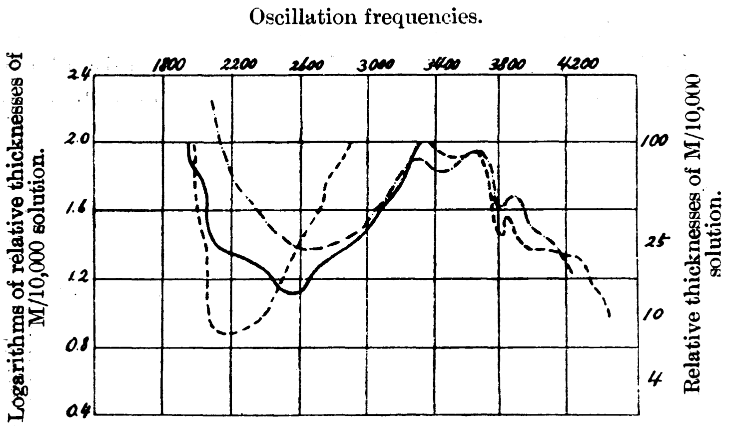
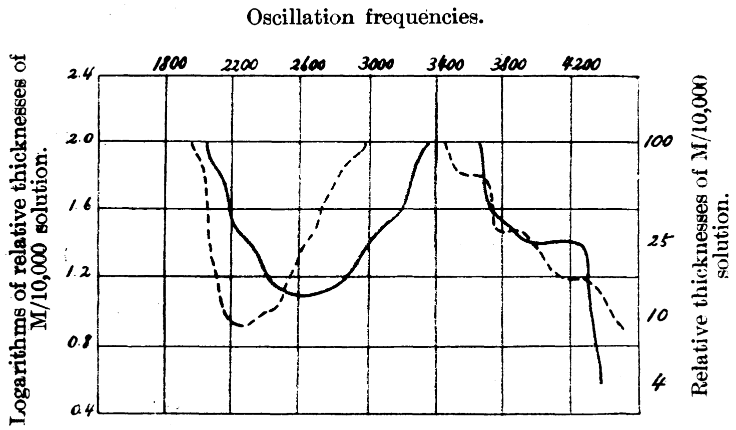
(1) Heumann and Oeconomides, *Ber.*, **20** (1887) 905; Kimich, Ibid., **8** (1875), 1030.
(2) Loc. cit.
(3) Wallach and Fischer, *Ber.* **15** (1882), 2825.
(4) Obtained from m-toluidine and resorcinol.
(5) Wallach, *Ber.*, **15** (1882), 2821.

These three compounds hardly produce any change in colour through alkali, and the hyperchromic influence can easily be recognised in their absorption curves (Fig. 4, Fig. 5 and Fig. 6). The hyperchromic effect due to the methyl-group may be detected in comparing it with benzeneazoresorcinol[1] (Fig. 4).



4. o-Tolueneazoresorcinol. { ——— Neutral solution.
----- 0.05 N. alkaline solution.
2 (Part I). Benzeneazoresorcinol. —·—·— Neutral solution.

Fig. 4.



5. m-Tolueneazoresorcinol. { ——— Neutral solution.
----- 0.05 N. alkaline solution.

Fig. 5.

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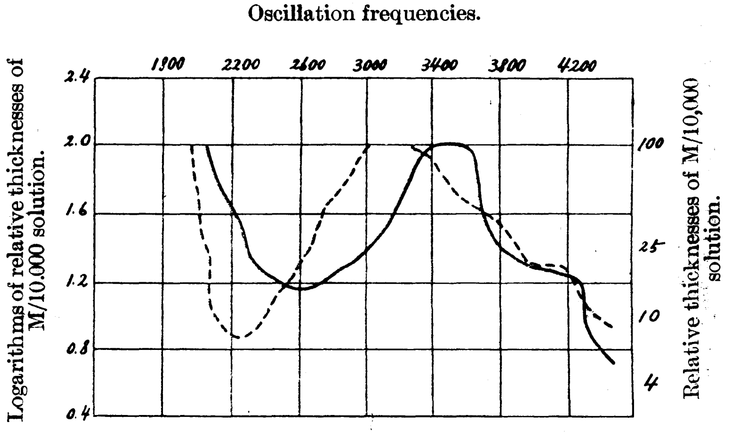
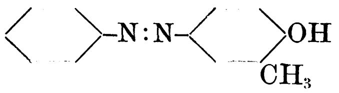
(1) This journal, 1 (1926), 262.



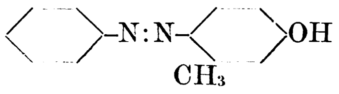
6. p-Tolueneazoresorcinol. { ——— Neutral solution. / - - - - - 0.05 N. alkaline solution.

Fig. 6.

7. **Benzeneazo-o-cresol,**(1)



8. **Benzeneazo-m-cresol,**(2)



These two compounds are light yellow in their neutral solution and change into a yellowish orange when KOH is added. Their absorption curves (Fig. 7 and Fig. 8) are quite different from benzeneazo-p-cresol,(3) and this must be owing to the position of the hydroxyl-group in the cresol ring. When it takes the para-position with respect to the azo-group (these two compounds), only one absorption band can be seen, while two bands are clearly represented in the case of the ortho-position (benzeneazo-p-cresol). Comparing these absorption curves with that of p-hydroxyazobenzene(4) (Fig. 7), we are able to find the hyperchromic influence which most likely comes from the methyl-group in the cresol ring.

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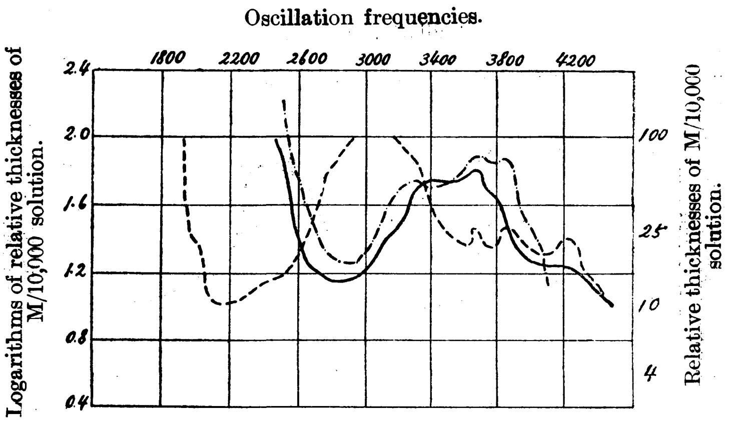
(1) Liebermann and Kostanecki, *Ber.*, **17** (1884), 131 & 879.
Noelting and Kohn, Ibid., **17** (1884), 363.

(2) Noelting and Kohn, Ibid., **17** (1884), 366.

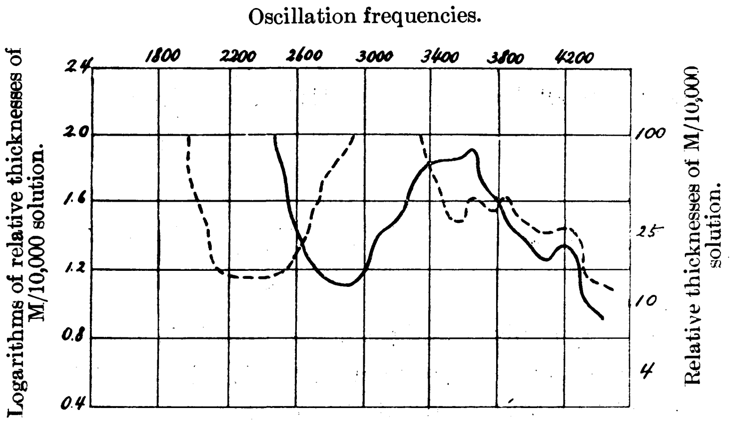
(3) This journal **1** (1926), 263.

(4) Loc. cit.



7. Benzeneazo-o-cresel. { ——— Neutral solution. ----- 0.05 N. alkaline solution.
1 (Part I). p-Hydroxyazobenzene. —·—·— Neutral solution.

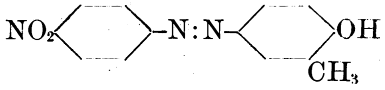
Fig. 7.



8. Benzeneazo-m-cresol. { ——— Neutral solution. ----- 0.05 N. alkaline solution.

Fig. 8.

9. p-Nitrobenzeneazo-o-cresol,⁽¹⁾



The yellow neutral solution changes into deep red when it is alkaline, but can not turn blue. When we compare the alkaline solution curve (0.002 N. KOH) of p-nitrobenzeneazophenol⁽²⁾ with the curve of this compound (Fig. 9), the hyperchromic effect due to the methyl-group can be recognised.

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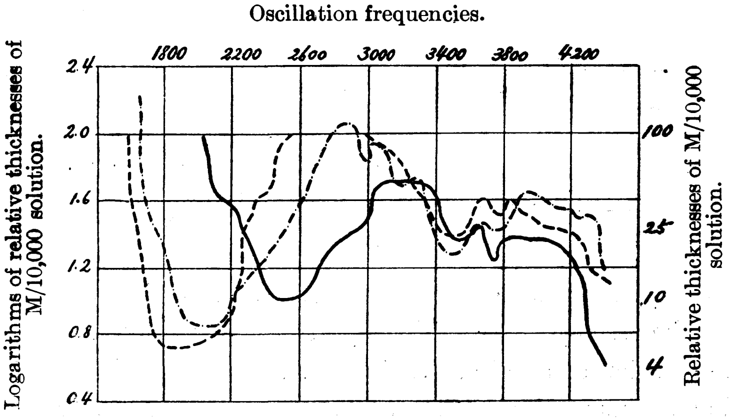
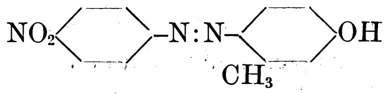
(1) Bamberger, *Ber.*, **28** (1895), 846.
(2) This journal, 1 (1926), 263.



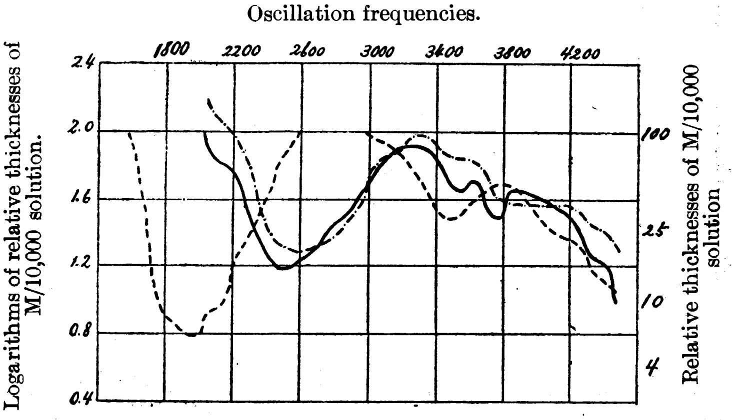
9. p-Nitrobenzeneazo-o-cresol. { ——— Neutral solution.
----- 0.002 N. alkaline solution.
4 (Part I). p-Nitrobenzeneazophenol. —·—·— 0.002 N. alkaline solution.

Fig. 9.

10. p-Nitrobenzeneazo-m-cresol,(1)



The colour change through alkali is just the same as No. 9 compound. This neutral curve (Fig. 10) is slightly more hyperchromic than that of p-nitrobenzeneazophenol.(2) As the nitro-radical is situated in the para-position with regard to the azo-group, hyperchromic and bathochromic influences somewhat greater than No. 7 and No. 8 compounds are observed in the absorption curves of No. 9 and No. 10 compounds.



10. p-Nitrobenzeneazo-m-cresol. { ——— Neutral solution.
----- 0.05 N. alkaline solution.
4 (Part I). p-Nitrobenzeneazophenol. —·—·— Neutral solution.

Fig. 10.

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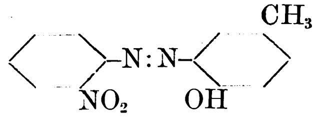
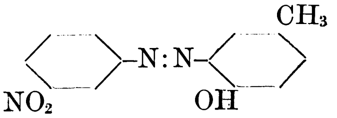
(1) Bamberger, *Ber.* 28 (1895), 847.
(2) Loc. cit.

11. o-Nitrobenzeneazo-p-cresol,(1)

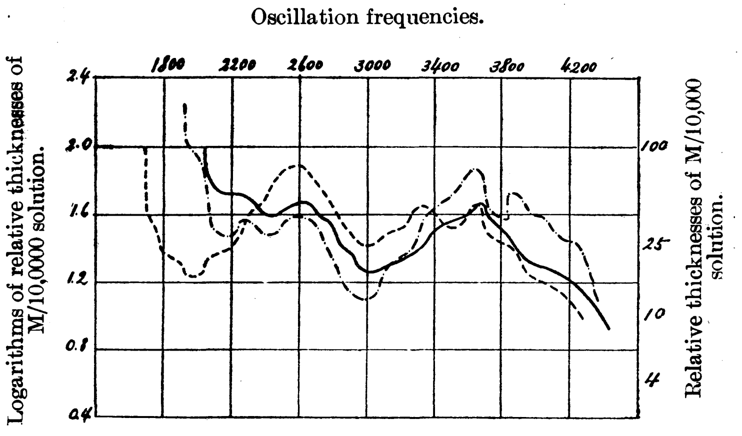


12. m-Nitrobenzeneazo-p-cresol,(2)



These compounds have two absorption bands owing to the hydroxyl which takes the ortho-position with respect to the azo-group.

By the addition of alkali to their neutral solution, the colour of these compounds changes yellow into red and only the bathochromic effect can be detected in their absorption curves, not the hyperchromic, like No. 9 and No. 10 compounds. This means probably that the hydroxyl situated in ortho-position with respect to the azo-group is less effective than the one in para-position, for the same relation is also preserved in the curve of p-nitrobenzeneazo-p-cresol.(3) And as for the nitro-radical, we may obtain a greater bathochromic curve when the para-position with regard to the azo-group is occupied by that group (Fig. 11 and Fig. 12).



11. o-Nitrobenzeneazo-p-cresol. { ——— Neutral solution.
{ - - - - - 0.05N. alkaline solution.
7 (Part I). p-Nitrobenzeneazo-p-cresol. —·—·— Neutral solution.

Fig. 11.

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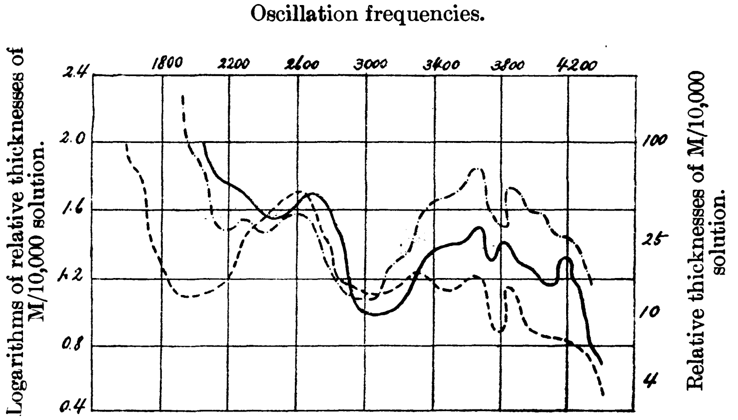
(1) Goldschmidt and Brubacher *Ber.* 24 (1891), 2308.

(2) Meldola and Hanes *J. Chem. Soc.*, 65 (1894), 838.

(3) This journal. 1 (1926), 265.



12. m-Nitrobenzeneazo-p-cresol. { ——— Neutral solution.
{ - - - - - 0.05 N. alkaline solution.
7 (Part I). p-Nitrobenzeneazo-p-cresol. —·—·— Neutral solution.

Fig. 12.

Summary.

(1) Tautomeric transformations may take place in these hydroxyazo-compounds.

(2) We may assign A (azo)-form⁽¹⁾ to the neutral solution and R (red)-form⁽¹⁾ to the alkaline.

(3) In general, one band can be shown in the absorption curves, except when the hydroxyl-group takes an ortho-position with regard to the azo-group.

(4) Hydroxyl- and nitro-radicals in para-position with respect to the azo-group are most effective in the absorption curve.

(5) The methyl-group has generally a hyperchromic influence upon the non-methylated compounds.

The writers gratefully acknowledge suggestions received from Prof. Yuji Shibata of the Tokyo Imperial University. The present investigations have been made possible through financial help from the Department of Education and from the School, for which we wish to express our sincere thanks.

Dyeing Department, Tokyo Higher Technical School.

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(1) This journal, 1 (1926), 261.

THE EFFECT OF HYDROCHLORIC ACID ON THE OXIDATION OF STANNOUS CHLORIDE WITH AIR.

By Susumu MIYAMOTO.

Received August 24, 1927. Published October 28, 1927.

The catalytic effects of many substances on the oxidation of stannous chloride in hydrochloric acid solution by means of free oxygen were studied by S. W. Young.(1) The present research was undertaken to know the effect of hydrochloric acid on the oxidation of stannous chloride with air more precisely by a new method in connection with the study on the effect of sodium hydroxide.(2) The experimental procedure is quite the same with that described in the previous paper.(3)

In the following tables, v is the volume of sodium thiosulphate solution of 0.0996 normal, which is equivalent to the quantity of stannous chloride; k_1 was calculated by $k_1=\frac{1}{t}(v_0-v)$, v_0 being the value of v at $t=o$; $\frac{k_2}{2.303}$ was calculated by $\frac{k_2}{2.303}=\frac{1}{t}\log\frac{v_0}{v}$ and $v_{calc.}$ was obtained by $v_{calc.}=v_0-k_1t$ or $v_{calc.}=v_0e^{-k_2t}$ using the mean value of k_1 or k_2.

TABLE 1.

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

C HCl normal	t min.	v c.c.	v calc. c.c.	k_1	$\frac{k_2}{2.303}$
0.00647	0	12.75	—	—	—
	60	11.68	11.74	—	0.000635
	120	10.71	10.81	—	0.000631
	150	10.32	10.37	—	0.000612
	0	13.59	—	—	—
	60	12.54	12.51	—	0.000582
	90	11.99	12.00	—	0.000604
	0	17.85	—	—	—
	60	16.40	16.43	—	0.000613
	90	15.82	15.77	—	0.000583
	150	14.86	14.41	—	0.000530
				—	mean: 0.000599

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(1) Young, *J. Am. Chem. Soc.*, **23** (1901), 119 & 450.

(2) S. Miyamoto, this journal, **2** (1927), 155.

(3) S. Miyamoto, ibid.

TABLE 1. (*Continued.*)

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

C HCl normal	t min.	v c.c.	v *calc.* c.c.	k_1	$\frac{k_2}{2.303}$
0.07117	0	12.17	—	—	—
	60	10.65	10.54	—	0.000963
	90	9.78	9.81	—	0.00106
	120	9.40	9.13	—	0.000935
	150	8.62	8.50	—	0.000999
	0	16.99	—	—	—
	60	14.68	14.72	—	0.00106
	90	13.49	13.70	—	0.00111
	150	11.55	11.86	—	0.00112
					mean: 0.00104
0.09672	0	11.56	—	—	—
	60	9.98	9.98	—	0.00106
	120	8.84	8.63	—	0.000971
	150	7.88	8.02	—	0.00111
	0	17.66	—	—	—
	60	15.50	15.25	—	0.000945
	100	13.69	13.84	—	0.00111
	160	11.61	11.95	—	0.00114
					mean: 0.00106
0.1359	0	12.01	—	—	—
	40	10.51	10.42	—	0.00145
	80	8.88	9.04	—	0.00164
	120	7.51	7.85	—	0.00170
	0	18.43	—	—	—
	60	15.19	14.90	—	0.00140
	80	13.96	13.88	—	0.00151
	120	12.10	12.04	—	0.00152
					mean: 0.00154
0.1682	0	7.52	—	—	—
	90	4.20	—	0.0369	0.00281
	0	12.73	—	—	—
	60	8.78	—	0.0658	0.00269
	120	6.01	—	0.0560	0.00272
	0	12.33	—	—	—
	70	7.73	—	0.0657	0.00290
	0	18.07	—	—	—
	30	15.83	—	0.0747	0.00192
	60	13.82	—	0.0708	0.00194
	90	11.14	—	0.0770	0.00233

TABLE 1. (*Continued.*)

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

C HCl normal	t min.	v c.c.	v calc. c.c.	k_1	$\frac{k_2}{2.303}$
0.3235	0	10.47	—	—	—
	20	8.39	8.35	0.104	—
	30	7.24	7.29	0.108	—
	50	5.04	5.17	0.109	—
	0	17.13	—	—	—
	40	12.65	12.89	0.112	—
	0	18.41	—	—	—
	15	16.87	16.82	0.103	—
	35	14.55	14.70	0.110	—
	50	13.66	13.11	0.0950	—
				mean: 0.106	
0.4587	0	11.13	—	—	—
	30	7.90	7.59	0.108	—
	40	6.74	6.41	0.110	—
	60	4.30	4.05	0.114	—
	0	17.21	—	—	—
	10	15.96	16.03	0.125	—
	20	14.85	14.85	0.118	—
	40	12.01	12.49	0.130	—
				mean: 0.118	
0.8151	0	11.84	—	—	—
	20	9.32	9.48	0.126	—
	30	8.10	8.30	0.125	—
	60	4.64	4.76	0.120	—
	0	18.02	—	—	—
	15	16.36	16.25	0.111	—
	25	15.14	15.07	0,115	—
	50	12.51	12.12	0.110	—
				mean: 0.118	

TABLE 1. (*Continued.*)

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

C HCl normal	t min.	v c.c.	v *calc.* c.c.	k_1	$\frac{k_2}{2.303}$
1.360	0	11.64	—	—	—
	15	9.88	9.91	0.117	—
	30	8.31	8.19	0.111	—
	45	6.96	6.46	0.104	—
	0	12.28	—	—	—
	15	10.53	10.55	0.117	—
	20	9.97	9.98	0.116	—
	45	7.38	7.10	0.109	—
	0	18.18	—	—	—
	40	13.23	13.58	0.124	—
	50	12.18	12.43	0.120	—
				mean: 0.115	
1.811	0	11.84	—	—	—
	20	9.12	9.20	0.136	—
	30	7.87	7.88	0.132	—
	40	6.60	6.56	0.131	—
	50	5.19	5.24	0.133	—
	0	18.18	—	—	—
	30	14.34	14.22	0.128	—
	50	11.68	11.58	0.130	—
				mean: 0.132	
2.262	0	12.66	—	—	—
	15	10.53	10.57	0.142	—
	30	8.58	8.49	0.136	—
	45	6.31	6.40	0.141	—
	50	5.70	5.71	0.139	—
	0	18.28	—	—	—
	30	14.08	14.11	0.140	—
	70	8.85	8.55	0.135	—
				mean: 0.139	

TABLE 2.

Temp. = 30°C. Air = 7.78 litres per hour.

C HCl normal	t min.	v c.c.	v calc. c.c.	k_1	$\frac{k_2}{2.303}$
0.00670	0	13.94	—	—	—
	60	12.37	—	0.0262	0.000865
	80	11.99	—	0.0244	0.000818
	150	10.60	—	0.0223	0.000793
	0	17.81	—	—	—
	50	16.43	—	0.0276	0.000700
	90	15.70	—	0.0234	0.000608
	140	14.68	—	0.0224	0.000600
0.1407	0	11.92	—	—	—
	26	9.80	—	0.0815	0.00327
	45	8.63	—	0.0731	0.00312
	80	7.05	—	0.0609	0.00285
	0	19.17	—	—	—
	20	17.20	—	0.0985	0.00235
	40	15.40	—	0.0943	0.00238
	70	14.28	—	0.0699	0.00183
0.2077	0	11.43	—	—	—
	20	9.30	—	0.107	0.00448
	40	7.48	—	0.0988	0.00460
	60	6.20	—	0.0872	0.00443
	0	18.26	—	—	—
	20	15.87	—	0.120	0.00305
	30	13.51	—	0.119	0.00327
	60	11.91	—	0.106	0.00309
0.2605	0	10.89	—	—	—
	15	8.91	8.97	0.132	—
	30	6.99	7.05	0.131	—
	45	5.45	5.13	0.121	—
	0	17.42	—	—	—
	15	15.60	15.50	0.121	—
	30	13.40	13.58	0.134	—
	45	11.50	11.66	0.131	—
				mean: 0.128	
0.3417	0	10.85	—	—	—
	15	9.00	9.03	0.123	—
	30	7.47	7.22	0.113	—
	45	5.92	5.40	0.110	—
	0	16.36	—	—	—
	15	14.32	14.54	0.136	—
	30	12.71	12.73	0.122	—
	45	11.00	10.91	0.119	—
				mean: 0.121	

TABLE 2. (*Continued.*)

Temp. = 30°C. Air = 7.78 litres per hour.

C HCl normal	t min.	v c.c.	v calc. c.c.	k_1	$\frac{k_2}{2.303}$
0.4297	0	12.34	—	—	—
	15	10.28	10.27	0.137	—
	30	8.32	8.20	0.134	—
	45	6.25	6.13	0.135	—
	0	18.78	—	—	—
	15	16.70	16.71	0.139	—
	30	14.45	14.64	0.144	—
	45	12.56	12.57	0.138	—
				mean: 0.138	
0.8527	0	12.47	—	—	—
	15	10.55	10.59	0.128	—
	20	10.03	9.97	0.122	—
	30	8.93	8.72	0.118	—
	45	6.62	6.84	0.130	—
				mean: 0.125	
1.276	0	11.89	—	—	—
	15	10.16	10.13	0.115	—
	20	9.49	9.55	0.120	—
	30	8.40	8.38	0.116	—
	45	6.73	6.62	0.115	—
				mean: 0.117	
1.699	0	12.47	—	—	—
	15	10.38	10.44	0.139	—
	20	9.77	9.77	0.135	—
	30	8.40	8.42	0.136	—
	45	6.64	6.39	0.130	—
				mean: 0.135	
2.122	0	12.19	—	—	—
	15	10.01	10.12	0.145	—
	20	9.45	9.43	0.137	—
	30	8.12	8.05	0.136	—
	45	6.16	5.99	0.134	—
				mean: 0.138	

TABLE 3.

Temp. = 40°C. Air = 7.78 litres per hour.

C HCl normal	t min.	c.c.	v *calc.* c.c.	k_1	$\frac{k_2}{2.303}$
0.00670	0	12.41	—	—	—
	40	11.37	—	0.0260	0.000950
	80	10.75	—	0.0208	0.000780
	120	9.86	—	0.0213	0.000832
	0	19.00	—	—	—
	40	17.62	—	0.0345	0.000819
	80	16.94	—	0.0258	0.000623
	120	15.99	—	0.0251	0.000624
0.04020	0	12.44	—	—	—
	40	10.87	—	0.0393	0.00146
	80	10.04	—	0.0300	0.00116
	120	9.37	—	0.0256	0.00103
	0	18.35	—	—	—
	50	16.37	—	0.0396	0.000992
	80	15.65	—	0.0338	0.000864
	130	14.90	—	0.0265	0.000696
0.0737	0	11.30	—	—	—
	40	9.56	—	0.0435	0.00182
	80	8.10	—	0.0400	0.00181
	120	7.57	—	0.0311	0.00145
	0	18.72	—	—	—
	40	16.43	—	0.0573	0.00142
	80	14.80	—	0.0490	0.00128
	120	13.74	—	0.0415	0.00112
0.0913	0	11.42	—	—	—
	40	9.44	—	0.0495	0.00207
	80	8.21	—	0.0401	0.00179
	120	7.41	—	0.0334	0.00157
	0	17.82	—	—	—
	40	15.28	—	0.0635	0.00167
	80	13.63	—	0.0524	0.00146
	120	12.63	—	0.0433	0.00125

TABLE 3. (*Continued.*)

Temp. = 40°C. Air = 7.78 litres per hour.

C HCl normal	t min.	v c.c.	v *calc.* c.c.	k_1	$\frac{k_2}{2.303}$
0.1407	0	12.54	—	—	—
	25	10.33	—	0.0884	0.00337
	50	8.92	—	0.0724	0.00296
	75	7.84	—	0.0627	0.00272
	0	18.14	—	—	—
	25	15.49	—	0.106	0.00274
	50	13.76	—	0.0876	0.00740
	75	12.50	—	0.0752	0.00216
0.2077	0	12.11	—	—	—
	20	9.63	—	0.124	0.00498
	40	7.79	—	0.108	0.00479
	60	6.35	—	0.0960	0.00467
	0	18.95	—	—	—
	20	16.22	—	0.137	0.00338
	40	13.96	—	0.125	0.00332
	60	12.04	—	0.115	0.00328
0.2605	0	12.39	—	—	—
	15	10.17	10.14	0.148	—
	30	8.00	7.89	0.146	—
	45	6.23	5.64	0.137	—
	0	18.52	—	—	—
	15	16.12	16.27	0.160	—
	30	13.84	14.02	0.156	—
	45	11.68	11.77	0.152	—
				mean: 0.150	
0.3417	0	11.62	—	—	—
	15	9.81	9.70	0.121	—
	30	7.88	7.78	0.125	—
	45	6.10	5.86	0.123	—
	0	18.89	—	—	—
	15	16.88	16.97	0.134	—
	30	15.01	15.05	0.129	—
	45	12.84	13.13	0.134	—
				mean: 0.128	

TABLE 3. (*Continued.*)

Temp. = 40°C. Air = 7.78 litres per hour.

C HCl norma	t min.	v c.c.	v. *calc.* c c.	k_1	$\frac{k_2}{2.303}$
0.4297	0	11.82	—	—	—
	15	9.64	9.66	0.145	—
	20	9.02	8.94	0.140	—
	30	7.33	7.50	0.150	—
	45	5.43	5.34	0.142	—
				mean: 0.144	
0.8527	0	12.07	—	—	—
	16	9.98	9.96	0.131	—
	20	9.41	9.43	0.133	—
	30	8.13	8.11	0.131	—
	46	6.01	6.00	0.132	—
				mean: 0.132	
1.276	0	11.63	—	—	—
	15	9.50	9.50	0.142	—
	20	8.79	8.79	0.142	—
	30	7.34	7.37	0.143	—
	45	5.33	5.24	0.140	—
				mean: 0.142	
1.699	0	11.97	—	—	—
	15	9.66	9.67	0.154	—
	20	8.97	8.91	0.150	—
	30	7.29	7.38	0.156	—
	45	5.13	5.08	0.152	—
				mean: 0.153	
2.122	0	11.94	—	—	—
	15	9.65	9.58	0.153	—
	20	8.90	8.80	0.152	—
	30	7.12	7.23	0.161	—
	45	4.68	4.87	0.161	—
				mean: 0.157	

As is seen in Table 1, 2 and 3, the oxidation velocity is independent of the concentration of stannous chloride when the concentration of hydrochloric acid is greater than about 0.25 normal under the condition of this experiment. This can be explained by the assumption that the oxidation velocity thus measured is no other than the dissolution velocity of oxygen into the solution.

When the concentration of hydrochloric acid is smaller than about 0.25 normal, the reaction seems to be between first and zero order. The concentration of hydrochloric acid, the initial values of which are given in the tables, can not be considered to be constant during the reaction; it decreases by the formation of stannic chloride. The decrease is not negligible when the concentration is smaller than about 0.25 normal, for in this region the oxidation velocity of stannous chloride increases rapidly with the increase of the concentration of hydrochloric acid. This will be one of the causes of the decrease of the values of k_1 or k_2 in Table 2 and 3 with time when the concentration of hydrochloric acid is small.

Anyhow from the above results it can be said that the oxidation velocity of stannous chloride increases rapidly with the increase of tho concentration of hydrochloric acid, until it reaches the dissolution velocity of oxygen into the solution, which is almost constant when the concentration of hydrochloric acid is greater than about 0.25 normal under the condition of this experiment.

By comparing Table 1, 2 and 3, it can be said that the effect of temperature on the reaction is small.

The Dissolution Velocity of Oxygen into Hydrochloric Acid Solution. The approximate values of the dissolution velocity of oxygen into hydrochloric acid of various concentrations, when air was passed into 40 cc. of the solution in a test tube (diameter = 3 cm.) through a glass tube (inside diameter = 4 mm., outside diameter = 6 mm.) at the rate of 7.78 litres per hour, were calculated from the above results.

The dissolution velocity, given in Table 4, when the concentration of hybrochloric acid is zero, was calculated from the oxidation velocity of sodium sulphite with air.(1) As is seen in Table 4 the dissolution velocity of oxygen into water decreases rapidly by adding hydrochloric acid until the concentration of hydrochloric acid reaches about 0.25 normal, and further addition of hydrochloric acid has almost no effect on the dissolution velocity, which is smaller than that into sodium hydroxide solution, calculated quite the same way in the previous paper.(2)

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(1) S. Miyamoto, this journal, 2 (1927), 74.

(2) S. Miyamoto, ibid., 2 (1927), 158.

TABLE 4.

Temp.	C HCl normal	k_1	Dissolution velocity of oxygen × 10^6 mols per minute
20°C.	0	0.330	8.2
	0.3235	0.106	2.6
	0.4587	0.118	2.9
	0.8151	0.118	2.9
	1.360	0.115	2.9
	1.811	0.132	2.3
	2.262	0.139	3.5
30°C.	0	0.345	8.6
	0.2605	0.128	3.2
	0.3417	0.121	3.0
	0.4297	0.138	3.4
	0.8527	0.125	3.1
	1.276	0.117	2.9
	1.699	0.135	3.4
	2.122	0.138	3.4
40°C.	0	0.382	9.6
	0.2605	0.150	3.7
	0.3417	0.128	3.2
	0.4297	0.144	3.6
	0.8527	0.132	3.3
	1.276	0.142	3.5
	1.699	0.153	3.8
	2.122	0.157	3.9

Summary.

1. The oxidation velocity of stannous chloride in hydrochloric acid with air was studied. When the concentration of hydrochloric acid is smaller than about 0.25 normal, the reaction seems to be between first and zero order. When the concentration of hydrochloric acid is greater than about 0.25 normal, the velocity is independent of the concentration of stannous chloride.
2. The effect of temperature is small.
3. The dissolution velocity of oxygen into hydrochloric acid of various concentrations was obtained indirectly.

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FORMATION OF THE RADIOACTIVE MANGANIFEROUS DEPOSITS FROM TANOKAMI, AND THE SOURCE OF MANGANESE IN THE DEEP-SEE MANGANESE NODULES.(1)

By **Satoyasu IIMORI.**

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In the previous paper(2) it has been shown that the feebly radioactive manganiferous deposit from the Tanokami district, Oomi Province, occurs in two modes, one in irregular masses charging narrow cracks of the hill-side rock, and the other in small nodular forms as one of the pebbly constituents of the gravel-beds of a stream. Both of them leave, on treatment with hydrochloric acid, a considerable residue of quartz grains with a large amount of faint yellowish green clayey matter. It so happens on close examination that this residue is practically identical with the fragments of rock body on the hill side, through which the deposit is disseminated. The rock, with which this manganiferous deposit is so intimately associated, seems to be consisted essentially of a kind of altered granitic rock, a marked feature being the presence of the above stated greenish clayey matter.

Similar manganese nodules, hitherto reported, have chiefly been found on the bottom of the deep sea and sometimes of particular creeks or rivers. The following will probably be the conspicuous cases so far as known, namely, those from the beds of Pacific Ocean(3) and of Loch Fyne in Scotland(4), from Onybygambach, New South Wales(5), and those found in Mesozoic deep-sea deposit from Borneo, Timor and Rotti(6), and on the bed of the River Vistula(7). All of these nodules are in accord with one another in respect of being largely composed of insoluble siliceous gangue and constantly containing a tolerable amount of iron besides manganese in the black portion soluble in hydrochloric acid. The proportion of the gangue varies of course considerably, but the composition of the soluble part is

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(1) Read before the Annual Meeting of the Chemical Society of Japan, April 5, 1927.

(2) This journal, **1** (1926), 43.

(3) J. Gibson, "Challenger Rept. Deep-Sea Deposits," (1891), 417-423; F. W. Clarke, "The Data of Geochemistry," (1924), 135. (Challenger Collection).
A. Agassiz, *Am. J. Sci.*, [4] **9** (1900), 33. (Albatross Collection).

(4) J. Y. Buchanan, *Chem. News*, **44** (1881), 253; *Proc. Roy. Soc. Edinburgh*, **18** (1890), 19.

(5) W. M. Doherty, *Australassian Assoc. Adv. Sci.*, **6** (1898), 339; *Am. J. Sci.*, [4], **9** (1900), 72.

(6) G. A. F. Molengreaff, *Proc. Roy. Acad. Amsterdam*, **18** (1915), 415; cf. "Neues Jahrb. Min. Geol"., (1916), II 233.

(7) E. Dittler, Tsch. Min. Mitt., **36** (1924), 164: cf. *J. Chem. Soc.*, **128** (1925), Abs. (ii), 322.

generally in close analogy in different sorts. The radium content of the nodules, however, has not been determined by the former investigators, except the ones from the bed of Pacific Ocean.(1) For the comparison of the chemical constituents, therefore, the original analyses by J. Gibson(2) and by J. Joly(3) made on the oceanic nodules from the Pacific Ocean, as well as that of the Tanokami nodules previously made by the author(4) are reproduced in the following tables.

Analyses of the soluble portion of the nodules.

Constituents Nodules from	MnO_2 & MnO	Fe_2O_3	Al_2O_3	PbO	CuO	ZnO NiO CoO	CaO	MgO	H_2O	Tl_2O	Acidic oxides	Total
The Tanokami Hill, Japan. (4)	59.8	14.6	9.9	4.8	(small)	3.7	—	—	7.2	—	—	(100)
The Pacific Ocean. (2)	52.4	27.0	6.3	0.1	0.7	2.7	4.0	4.6	—	0.06	2.0*	99.0

* MoO_3, V_2O_5, P_2O_5, SO_3, CO_2.

Amount of radium in the nodules

Manganese nodules from	Variety.	Amount of the insol. gangue. %	Radium content	
			Ra per gr. of the material. gr.	Ra per gr. of the soluble portion. gr.
Tanokami(4)	The hill-side deposit.	89.7	131×10^{-12}	1640×10^{-12}
	The river nodule.	68.9	115	388
Pacific Ocean(3)	Nodule, collected at a depth of 2750 fathoms.	16.0	24	29
	" " " " " 2370 fathoms. (off W. Coast of S. America.)	17.9	21	26

Although the two differ in certain particulars, as in lime, magnesia, thallia and acidic oxides, yet the general correspondence is remarkably close, and the presence of minor constituents, such as lead, copper, zinc, nickel, cobalt and radium, is strikingly harmonious. As regards the

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(1) J. Joly, *Phil. Mag.*, **16** (1908), 190.

(2) Loc. cit.

(3) Loc. cit.

(4) Iimori, loc. cit.

content of radium in the Tanokami nodules, attention has already been directed to the fact that the irregular masses of the manganiferous deposit occurring on the hill-side carry more radium than that in the nodules existing on the river bed, viz. the amount of radium in the former being about four times as much as that in the latter. This fact is possibly to be ascribed to the leaching action of stream water. The far less content of radium in the oceanic nodules will, therefore, be so explained that they have lost the greater part of the radium or uranium while lying on the bottom of the deep sea through a long period of geological time, and yet, as will be seen in the above figures, the richness in radium of the oceanic manganese nodules is obviously greater than that which we are aware of the rocks on the land, the average values being 1.7×10^{-12} and 1.1×10^{-12} grams radium per gram for igneous and sedimentary rocks respectively.(1)

Regarding the source of manganese which constitutes the deep sea nodules, no opinion seems yet to be substantially decisive. G. W. Gümbel supposes that the manganese is derived from submarine springs.(2) J. Murray attributes it to the product of the subaqueous decomposition of volcanic dêbris.(3) J. Y. Buchanan(4) and others(5) solely regard as due to the manganese dissolved in the sea water. Being formed, however, of the manganese universally dissolved, usually contained but in trace, in the sea water, the nodules would be found in everywhere of the bottom of the sea. But, in fact, such a mode of distribution has never been observed, and its sporadic occurrence in the bottom of the deep sea or special creeks shows, I suppose, that the manganese may probably be derived from certain manganese minerals, possibly peculiar ferromanganese minerals containing uranium, locally cropped out on the ocean floor.

Hence it will be so explicable that the manganese deposits from the Tanokami district should be formed by the same process as the cases of the sea nodules. While the region of the Tanokami hill and the neighbourhood had, once in early ages, been lying beneath the water, the veins and dykes of granitic pegmatite including the original manganese and iron bearing radioactive minerals, for instance, such as wolframite which is now sometimes found in this district in small quantity, were subjected to the aqueous alteration. Some of the constituents such as manganese, iron etc.

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(1) A. Z. Eve and D. Mc Intosh, *Phil. Mag.*, [6], **14** (1907), 231.

(2) *Jahr. Min.*, (1876), 869; cf. *J. Chem. Soc.*, **38** (1880), Abs., 16.

(3) *Proc. Roy. Soc. Edinburgh*, **9** (1876), 255; cf. *Bull. U. S. Geol. Survey*, **770** (1924), 135.

(4) *Proc. Roy. Soc. Edinburgh*, **18** (1890), 17; cf. *J. Chem. Soc.*, **60** (1891), Abs., 994.

(5) J. B. Boussingault, *Ann. Chim. Phys.*, (5) **27** (1882), 289; L. Dieulafait, *Compt. rend.*, **96** (1883), 718; R. Irvine and J. Gibson, *Proc. Roy. Soc. Edinburgh*, **18** (1890), 54; cf. *J. Chem. Soc.*, **60** (1891), Abs., 995; E. Dittler, loc. cit.

of the minerals imbedded in the rock went into solution and was precipitated with radium or uranium near its points of derivation between the cracks of the rock or around any nuclei which happened to be at hand, accordingly around the fragments of the altered rock yielding the radioactive manganiferous nodules. It will therefore be thought that the formation of the Tanokami nodules would never take place unter the stream water, seen at the present time, but in the quiet depths of the sea or lake throughout the geological ages. It would be expected, accordingly, that the rock body on the hill side of the Tanokami district have come up from the deep water, and the black impregnation on the rock blocks lying on the river bed, now frequently seen, will be due to the manganese and iron derived as the result of recent weathering and erosion from the above mentioned manganiferous deposits and nodules.

Finally, one thing which is much suggestive in this connection, is the origin of the radium contained in the oceanic water and the deep-sea deposits. It has been so considered by J. Joly(1) that the oceanic radium has entirely been supplied by the rocks and minerals on the land, having been leached by the rain water and poured by rivers into the sea. It may, however, be concluded from the foregoing considerations that some parts of the oceanic radium come from certain radioactive minerals cropped out sporadically on the bottom of the sea. In this way it will also easily be accounted for the less content of radium in the river water than that in the sea water. The critical revision of radium content in all the manganese nodules known is highly desirable.

The author's thanks are due to Prof S. Tsuboi of the Geological Laboratory, Tokyo Imperial University for his kind advices given on the examination of rocks.

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(1) J. Joly, "Radioactivity and Geology," (1909), p. 54.

THE GREEN KAOLIN FROM TANOKAMI. IDENTITY OF THE UNIVERSAL MINOR CONSTITUENTS OF THE IGNEOUS ROCK WITH THE CHROMOSPHERIC ELEMENTS OF THE SUN.⁽¹⁾

By Satoyasu IIMORI.

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The Composition of the Green Kaolin. The faint yellowish green clayey matter, which occurs almost constantly associated with the radioactive manganiferous nodules and deposits from Tanokami, Oomi Province and usually forms a part of the insoluble portion of the latter,⁽²⁾ has fully been analysed. The material used for the analysis was a comparatively large lump found on the hill side, where the radioactive manganiferous deposits are disseminated. It was of an amorphous character and not perfectly homogeneous. The specific gravity was determined as 2.71 with a hardness of about 2.5~3.5, and the streak was white. It gave the result of the second column in the following table, the third to the sixth showing the compositions of the various species of kaolin for the purpose of comparison.

Constituents	Analysis of the material. (%)	Kaolinite (monocl.)	Rectonite (amorph.)	Catlinite (amorph.)	Pyrophyllite (monocl.)
Loss on ignition <130°	0·23	$Al_2O_3 \cdot 2SiO_2$ $2H_2O$	$Al_2O_3 \cdot 2SiO_2$ H_2O	$Al_2O_3 \cdot 3SiO_2$ H_2O	$Al_2O_3 \cdot 4SiO_2$ H_2O
Loss on ignition >130°	3·56				
SiO_2	58·01	46·5	50·0	60·0	67·0.
Al_2O_3	35·79	39·5	42·5	34·0	28·0
Fe_2O_3	1·32		including Halloysite, Newtonite, $Al_2O_3 \cdot 2SiO_2$ xH_2O.		including Montmorillonite, $Al_2O_3 \cdot 4SiO_2$ xH_2O.
FeO	1·10				
Mn_3O_4	0·083				
Rare earths	0·040				
MgO	0·014				
(Total)	100·15	$\left(\frac{SiO_2}{Al_2O_3}=2\right)$	(„ =2)	(„ =3)	(„ =4)

The analysis clearly shows, setting aside the iron and other minor constituents, the character of this material as a kind of kaolin which has,

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(1) Read before the Annual Meeting of the Chemical Society of Japan, April 5, 1927.

(2) This journal, **1** (1926), 43.

however, neither composition of a kaolinite nor of a pyrophyllite but of the so-called catlinite. According to the descriptions cited in Dana's Mineralogy,(1) the latter is said to be no definite mineral species and pink in colour. The material analyzed is of a greenish colour, but its composition is in quite accord with that of the catlinite, the analysis nearly satisfying the formula $Al_2O_3 \cdot 3SiO_2 \cdot H_2O$.

The noteworthy feature of this kaolin is its containing a small quantity of rare earths which chiefly consist of the yttrium group. Examining spectrographically it shows that the rare earths separated contain a small amount of the terbium group and almost no member of the cerium group. The following indicate the partial analyses of rare earths.

The material taken. (gr.)	Rare earths found		Scandia separated from the rare earths obtained	
	(mg.)	(%)	(mg.)	(%)
28.60	13.2	0.046	0.096 (a)	0.00034
27.77	8.1	0.034	(<0.19) (b)	(<0.00080)

For the determination of the terbium earths, 0.0189 gr. of oxides of the rare earths freed from scandia was used. It gave 0.00146 gr. of oxides of the terbium group with a trace of the cerium group, both having been separated as the insoluble double potassium sulphates. The results is therefore represented as follows: 0.037% yttrium earths, 0.003% terbium earths, corresponding to 7.73% of the total rare earths, and less than 0.000x% scandia.

As to the carring out of the separation of the rare earths from the material, the following procedure was mainly employed as prescribed by W. F. Hillebrand.(2) The sample was first fused with fusing mixture. Eliminating silica and then heavy metals of the hydrogen sulphide group which were contained in small amounts, the rare earths with iron were precipitated by caustic potash. The precipitates thus obtained were treated with hydrofluoric acid so as to keep the iron, manganese, titanium, etc. in solution. The insoluble residue, mainly consisting of the fluorides of the whole rare earths, was decomposed with sulphuric acid in excess. The rare earths were then repeatedly precipitated by means of oxalic acid, after the sulphates have been dissolved in dilute hydrochloric acid. The oxalates were ignited for the oxides and weighed.

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(1) E. S. Dana, "System of Mineralogy," IV Edition, p. 696.

(1) *Bull. U. S. Geolog. Survey,* 700 (1919), 176.

To separate the scandium, the oxides of rare earths obtained were dissolved in hydrochloric acid. The excess of acid was removed by evaporation, and the scandium was precipitated as basic thiosulphate by the addition of 30 per cent sodium thiosulphate solution. The figure indicated with the mark (a) in the foregoing table was obtained according to P. and G. Urbain's process,⁽¹⁾ the scandium finally having been precipitated as phosphate by ammonium phosphate after the basic thiosulphate has been dissolved in hydrochloric acid and evaporated up to dryness. Another figure marked with (b) was tentatively obtained, roughly weighing the ignition product of the basic thiosulphate as crude oxide, as the precipitate yielded on the addition of sodium thiosulphate was too small.

The fractions obtained in the course of a duplicate analysis were examined spectroscopically using a large quartz spectrograph on Littrow mounting. The rare earth fraction showed the bulk of lines, including the whole principal lines given by Exner and Haschek, of scandium, yttrium, ytterbium, dysprosium, and also abundant lines of erbium, thullium, lutecium, terbium and gadolinium. The scandium fraction separated gave rather faintly a few of its lines, but none of other elements. The sulphide fraction of heavy metals, previously precipitated by hydrogen sulphide in acidic solution, gave the lines of copper and tin. In the precipitate obtained by ammonia from the main solution, after removal of the iron and aluminium by the succinate method, besides the lines of the above mentioned rare earths, those of nickel, cobalt, zink, titanium, zirconium, niobium, chromium, molybdenum, tungsten and ruthenium were detected, and a few lines of vanadium and lithium were also observed. Roughly having been determined, these minor constituents except the rare earths, computing as oxides, hardly amounted to 0.1~0.15 per cent of the material, hence they were omitted in the foregoing table of analysis for the convenience of manifestation.

Comparison of the Minor Constituents of the Igneous Rock with the Elements in the Solar Chromosphere. One of the well known elements existing in the highly ionized state in the high level region of the solar chromosphere is the scandium which is, as stated above, distinctly detected in the rare earth fraction of the green kaolin occurring associated with the radioactive manganiferous nodules from Tanokami. The whole chromospheric elements given by F. W. Dyson⁽²⁾ and S. A. Mitchell⁽³⁾ are conveniently tabulated as below, together with four other elements shown enclosed with the double lines.

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(1) *Compt. rend.*, **174** (1922), 1310.

(2) *Phil. Trans. Roy. Soc.*, A, **206** (1906), 403.

(3) *Astroph. Jour.*, **38** (1913), 407.

1 H	2 He		6 C			9 F					
11 Na	12 Mg	13 Al	14 Si	15 P	16 S	17 Cl					
	20 Ca	21 Sc	22 Ti	23 V	24 Cr	25 Mn	26 Fe	27 Ni	28 Co	29 Cu	30 Zn
	38 Sr	39 Y	40 Zr								
	56 Ba	57 ~ 71 Rare Es.									

The elements inside the single line enclosure in the above table are those which give most abundant or distinct lines in the spectrum of the chromosphere, and those inside the dotted line enclosure representing the elements which are mentioned to be observed rather faintly or in deficient numbers in the spectral lines of the chromosphere.

As a matter of fact, the elements detected in small amounts in the green kaolin and the manganiferous nodules previously descrived nearly coincide with the principal members of the chromospheric elements excepting carbon and helium, and on the other hand, with what are called the universal minor constituents of the igneous rock shown by H. S. Washington,(1) W. F. Hillebrand,(2) etc. which are nothing but those elements indicated in the above table including four more elements, phosphorus, sulphur, fluorine and chlorine. Judging from the numerous results of rock analyses, hitherto put forward by several investigators, the constant minor constituents of the majority of igneous rocks are quite particular and surely to be recognized, but why they are so universally distributed among the igneous rocks is now in dispute. As will be pointed out, however, it may be seen that the universal minor constituents of the igneous rock are in close agreement with the elements constituting the solar chromosphere, and the spectroscopical lacking in some elements such as phosphorus, sulphur, fluorine and chlorine in the chromosphere will not be serious, as they give very insignificant lines, or at times no line in their spectra.

Advocating the nebular hypothesis, when the earth was formed by cooling from a gaseous mass through the same state as the sun seen at the present time, the primeval atmosphere must have been quite unlike our present envelope, and we may suppose that it was probably the same as the present chromosphere of the sun. When the liquefaction commenced over the whole surface of the our globe in the earliest state under such an atmosphere as above, no doubt there must have been contained in the liquid crust the same elements as those in the primitive atmosphere, a hetero-

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(1) H. S. Washington, " Manual of the Chemical Analysis of Rocks," (1919), p. 17.

(2) W. F. Hillebrand, " The Analysis of Silicate and Carbonate Rocks," (1919), p. 25.

geneous equilibrium between both phases having been established. As the temperature of the earth has decreased and the liquefaction proceeded, the composition of the gas phase would then gradually have changed, according as the atmospheric elements have passed into the liquid phase. Hence all the rocks afterwards solidified out from the original surface magma must have more or less been contaminated with all of these primeval atmospheric elements.

According to the view set out above, though we have no clear evidence for it yet, it should possibly be considered that the presence of helium in certain non-radioactive minerals such as beryl, fluorite, sphene, etc. and in some natural gases may be ascribed to this notable one of the constituents of the primeval atmosphere supposed. The present is not the place for any extended discussion, but the close analogy between the universal minor constituents of the igneous rock and the chromospheric elements, if it might be apparent, will not be denial.

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ON THE NITRILE-ESTERS OF THE DICARBOXY-GLUTACONIC ACID.

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In the previous paper(1) dealing with the so-called diethyl dicyanoglutaconate the author showed that this substance has the composition $C_{11}H_{12}O_4N_2\cdot\frac{1}{2}H_2O$ instead of $C_{11}H_{12}O_4N_2$, and its constitution is represented by the formula $(C_{10}H_{12}O_4N)-C(=NH)-NH-CO-(C_{10}H_{12}O_4N)$. The triethyl dicyanoaconitate $C_2H_5OOC(CN)C=C(COOC_2H_5)-CH(CN)COOC_2H_5+\frac{1}{2}H_2O$(2), and the methenylbismalonitrile-imidether $(CN)_2C=CH-CH(CN)C(NH)-OC_2H_5+\frac{1}{2}H_2O$(3), are also combined with half a molecule of water. In order to examine the presence of such a tendency as of combining with water, and at the same time expecting some interesting results which would arise from their being the derivatives of glutaconic acid, the author synthesized and investigated the following nitrile-esters of the dicarboxyglutaconic acid.

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(1) This journal 2 (1927), 26.

(2) G. Errera und F. Perciabosco, *Ber.*, 34 (1901), 3704.

(3) W. Zoernig, *J. prakt. Chem.* 74 (1906), 435.

By the condensation of one of diethyl ethoxymethylene-malonate $(C_2H_5OOC)_2C=CHOC_2H_5$, ethyl ethoxymethylene-cyanoacetate $C_2H_5OOC(CN)C=CHOC_2H_5$, and ethoxymethylene-malonitrile $(CN)_2C=CHOC_2H_5$, with one of diethyl sodio-malonate $CHNa(COOC_2H_5)_2$, ethyl sodio-cyanoacetate $CHNa(CN)COOC_2H_5$, and sodio-malonitrile $CHNa(CN)_2$, nine methenyl compounds are to be formed, which are the nitrile-esters of the dicarboxyglutaconic acid. They are:

(I) Tetraethyl propylene-α, α, γ, γ-tetracarboxylate (or tetraethyl dicarboxyglutaconte), $(C_2H_5OOC)_2C=CH-CH(COOC_2H_5)_2$;

(II) Triethyl α-cyanopropylene-α, γ, γ-tricarboxylate (or triethyl α-cyano-γ-carboxyglutaconate), $(C_2H_5OOC)_2C=CH-CH(CN)COOC_2H_5$;

(III) Triethyl γ-cyanopropylene-α, α, γ-tricarboxylate, $C_2H_5OOC(CN)C=CH-CH(COOC_2H_5)_2$;

(IV) Diethyl α, α-dicyanopropylene-γ, γ-dicarboxyate, $(C_2H_5OOC)_2C=CH-CH(CN)_2$;

(V) Diethyl γ, γ-dicyanopropylene-α, α-dicarboxylate, $(CN)_2C=CH-CH(COOC_2H_5)_2$;

(VI) Diethyl α, γ-dicyanopropylene-α, γ-dicarboxylate (or diethyl dicyanoglutaconate), $C_2H_5OOC(CN)C=CH-CH(CN)COOC_2H_5$;

(VII) Ethyl α, α, γ-tricyanopropylene-γ-carboxylate, $C_2H_5OOC(CN)C=CH-CH(CN)_2$;

(VIII) Ethyl α, γ, γ-tricyanopropylene-α-carboxylate, $(CN)_2C=CH-CH(CN)COOC_2H_5$;

(IX) α, α, γ, γ-Tetracyanopropylene, $(CN)_2C=CH-CH(CN)_2$.

Of course the above condensations will give first the α-sodio-derivatives of these compounds. All of them, except (I) which is well known as the tetraethyl dicarboxyglutaconate, have never been closely investigated, and most of them have never been synthesized. Errera(1) carried out the condensation of diethyl ethoxymethylene-malonate with ethyl sodio-cyanoacetate, and the oily substance obtained by him was probably the nitrile-ester (II), but with no analytical determination of its composition, he transformed it into the diethyl dihydroxydinicotinate. The compound which had been considered to be the diethyl α, γ-dicyanopropylene-α, γ-dicarboxylate (VI), the so-called diethyl dicyanoglutaconate, was clearly explored by the author as stated above. The compound obtained by Zoernig(2) in the condensation of malonitrile, chloroform, and sodium ethylate was not the tetranitrile (IX), but its imidether semihydrate.

The first two compounds (I) and (II) are not described in this paper, because the tetraethyl dicarboxyglutaconate had no important relation to the

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(1) *Ber.*, **31** (1898), 1243.

(2) Loc. cit.

present investigation, and the triethyl α-cyanopropylene-α, γ, γ.tricarboxylate had been synthesized by Errera if not in a satisfying manner. The present author has synthesized the other seven compounds, or, strictly speaking, performed the seven condensations which would give the seven compounds.

The general procedure of the condensations of the ethoxymethylene compounds with sodium compounds was very simple.(1) These reactions proceeded smoothly at the ordinary temperature in the absolute alcoholic solutions. The resulting solutions of the sodium derivatives of the methenyl compounds were coloured more or less deep red, but, besides the inevitable formation of the colouring by-product which might be very small in quantity, no side reactions seemed to occur. On evaporating the alcohol in vacuo over sulphuric acid (heating was avoided in fear of any secondary reaction) the solutions left the crystalline mass of the sodium compounds. As these sodium compounds are generally easily soluble in water, a considerable loss could not be avoided in the recrystallisation from water.

Some of the sodium compounds were obtained in coloured appearance, and others in colourless state. From the analogy of the constitution all of them should be colourless and the colours of some of them must be due to impurities which can be difficultly removed.

(III) **Triethyl γ-cyanopropylene-α, α, γ-tricarboxylate.** Sodium was dissolved in absolute alcohol, and diethyl malonate was added. Ethyl ethoxymethylene-cyanoacetate in powder was added to this solution under cooling in ice water. The solution became red, and on evaporating the alcohol in vacuo over sulphuric acid, a coloured crystalline mass was obtained. After washing with ether the crystals were again dried over sulphuric acid. This crystalline sodium compound, triethyl α-sodio-γ-cyanopropylene-α, α, γ-tricarboxylate, is hygroscopic, and absorbs heat when dissolved in water. It gave an oily substance when its aqueous solution was acidified with dilute hydrochloric acid, which was extracted with ether. This ethereal solution was shaken with the aqueous solution of sodium carbonate and the aqueous layer was again acidified and extracted with fresh ether. This second ethereal solution was washed with water, dried with calcium chloride, and evaporated in vacuo. In this way an oily substance was obtained, which gradually crystallised on keeping it in the desiccator. After dried to a constant weight in vacuo in the desiccator it was analysed. 0.2378 Gr. of the substance gave 10.5 c.c. of nitrogen at 24.0° and 758 mm. (Found : $N=4.91$. $C_{13}H_{17}O_6N$ requires $N=4.94\%$.) According to the mode of formation and the expected result in analysis, this substance is the triethyl γ-cyanopropylene-α, α, γ-tricarboxylate, $C_2H_5OOC(CN)C=CH-CH(COOC_2H_5)_2$.

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(1) Cf L. Claisen, *Ann.*, **297** (1897), 1.

This substance has an acid character and dissolves in the aqueous solution of sodium carbonate, evolving carbon dioxide.

It can be induced from the studies on the following cases that the condensation of diethyl ethoxymethylene-malonate with ethyl sodio-cyanoacetate will give the same product as that described above, and there is no difference between triethyl α-cyanopropylene-α, γ, γ-tricarboxylate and triethyl γ-cyanopropylene- α, α, γ-tricarboxylate,

(IV) **Diethyl α, α-dicyanopropylene-γ, γ-dicarboxylate.** When diethyl ethoxymethylene-malonate was added to the alcoholic solution of sodio-malonitrile a reddish solution was obtained. The solution was filtered from a little amount of solid. The viscous mass which remained after the evaporation of the alcohol was dissolved in water and the solution was shaken with ether to remove substances soluble in ether. On adding dilute hydrochloric acid to the aqueous solution a brown oil separated, which was extracted with ether, but soon from both the aqueous and ethereal solutions colourless crystals separated out. As the colouring impurities were taken into ether, the crystals from aqueous solution were quite colourless, which were collected, washed with cold water and ether, and dried in vacuo over sulphuric acid. 0.1552 Gr. of the substance gave 14.2 c.c. of nitrogen at 23.5° and 760 mm.; 0.2359 gr. of the substance gave 0.4199 gr. of CO_2 and 0.1253 gr. of H_2O. (Found: N=10.23; C=48.56; H=5.94. $C_{11}H_{12}O_4N_2 \cdot 2H_2O$ requires N=10.29: C=48.51; H=5.93%.) This crystalline compound was not the diethyl α, α-dicyanopropylene-γ, γ-dicarboxylate $C_{11}H_{12}O_4N_2$, but the diethyl α, α-dicarbamyl-propylene-γ, γ-dicarboxylate, $(C_2H_5OOC)_2C=CH-CH(CONH_2)_2$. The oily substance which existed for a short time was probably the dinitrile.

When the viscous mass obtained by evaporation of alcohol from the condensation mixture was left in the desiccator for a few days, it took gradually crystalline form. This crystalline substance was twice recrystallised from a small amount of water. 0.3504 Gr. of the substance dried in vacuo over sulphuric acid decreased by 0.0116 gr. on dehydrating at 140–150°. (Found: $H_2O=3.31$. $C_{11}H_{11}O_4N_2Na \cdot \frac{1}{2}H_2O$ requires $H_2O=3.37\%$.) 0.3388 Gr. of the dehydrated substance gave 34.0 c.c. of nitrogen at 26° and 756 mm. (Fonnd: N=11.02. $C_{11}H_{11}O_4N_2Na$ requires N=10.9%.) According to the mode of formation this is diethyl α-sodio-α, α-dicyanopropylene-γ, γ-dicarboxylate.

(V) **Diethyl γ, γ-dicyanopropylene-α, α-dicarboxylate.** In the case of the condensation of ethoxymethylene-malonitrile with diethyl sodio-malonate, the resulting solution was not so intensely coloured as in the case of (IV) and the formed sodium compound crystallised easily on evaporating the solvent.

The sodium compound was dissolved in water and dilute hydrochloric acid was added. A brown oily substance deposited at once, but, on stirring, dissolved again in the mother liquor and soon colourless crystalline substance separated out, which was collected, washed with a small amount of water several times and dried in vacuo over sulphuric acid. 0.2596 Gr. of the substance gave 24.5 c.c. of nitrogen at 27.5° and 758.4 mm. (Found: $N=10.31$, $C_{11}H_{12}O_4N_2 \cdot 2H_2O$ requires $N=10.29\%$.)

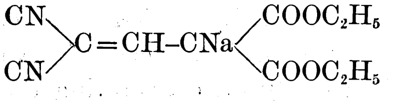
The compound obtained in this case was also a diamide. The constitution should be $(H_2NCO)_2C=CH-CH(COOC_2H_5)_2$, the isomer of $(C_2H_5OOC)_2C=CH-CH(CONH_2)_2$ described in (IV).

Recrystallised from alcohol, the sodium compound became nearly colourless crystals. 0.5245 Gr. of the substance dried at 150° gave 0.1413 gr. of Na_2SO_4. 0.3220 Gr. of the substance dried at 150° gave 32.5 cc. of nitrogen at 27° and 757 mm. (Found: $Na=8.72$; $N=11.03$. $C_{11}H_{11}O_4N_2Na$ requires $Na=8.92$; $N=10.9\%$.) The sodium compound crystallised from water contains half a molecule of water. 0.3440 Gr. of the substance decreased by 0.0113 gr. on dehydrating at 140–150°. (Found: $H_2O=3.29$. $C_{11}H_{11}O_4N_2Na \cdot \frac{1}{2}H_2O$ requires $H_2O=3.37\%$.) According to the mode of formation this is diethyl α-sodio-γ, γ-dicyanopropylene-α, α-dicarboxylate.

Considered from the mode of formation the two kinds of diamides described in (IV) and (V) may differ in the position of the double union only. But as it is expectable from the fact that the α- and γ-positions in glutaconic acid are the same,⁽¹⁾ these two diamides have been found identical. The one, the other, and their mixture melted at the same point 139-140°, solidified then and gradually decomposed when heating was continued.

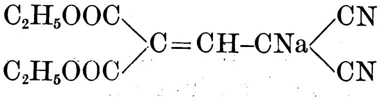
The coincidence in composition (water of crystallisation) of the sodium derivatives of diethyl α, α-dicyanopropylene-γ, γ-dicarboxylate and of diethyl γ, γ-dicyanopropylene-α, α-dicarboxylate suggested the identity of these two sodium compounds. Really they have been found identical. These two specimens of sodium compounds and their mixture melted at the same point 238–239° (not corr.). It is no wonder that the specimens of the identical sodium compounds gave the identical diamides.

For the identity of the α- and γ-positions in glutaconic acid $HOOCCH=CH-CH_2COOH$, it is necessary that at least one of the methylene hydrogen atoms remains unsubstituted. There exists, however, no mobile hydrogen atom in the sodium compounds as shown by the formulæ,



$$(CN)_2C=CH-CNa(COOC_2H_5)_2$$

(A)



$$(C_2H_5OOC)_2C=CH-CNa(CN)_2$$

(B)

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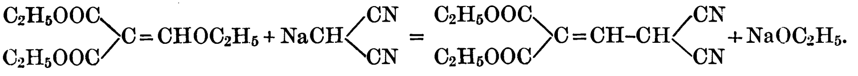
(1) J. F. Thorpe, *J. Chem. Soc.* 87 (1905), 1669.

The compound represented by (A) can not be identical with the compound represented by (B). Therefore the constitution of the sodium compounds formed through two ways of condensation must be limited to either of them. Whichever formula it may possess, how two ways of condensation led to the same product can be explained on the assumption that the condensation of an ethoxymethylene compound with a sodium compound proceeds in two stages. In the first stage sodium ethylate is split off from the ethoxymethylene compound and the sodium compound, for instance,

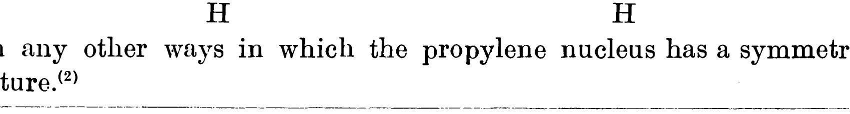


$$\begin{matrix}C_2H_5OOC\\C_2H_5OOC\end{matrix}\!\!>C=CHOC_2H_5+NaCH<\!\!\begin{matrix}CN\\CN\end{matrix} = \begin{matrix}C_2H_5OOC\\C_2H_5OOC\end{matrix}\!\!>C=CH-CH<\!\!\begin{matrix}CN\\CN\end{matrix}+NaOC_2H_5.$$

And then the sodium ethylate reacts with the methenyl compound, yielding the sodium derivative of the methenyl compound and alcohol. Now, the methenyl compound formed intermediately has the mobile hydrogen atom, and there is no difference between α- and γ-positions. Thus the condensation of diethyl ethoxymethylene-malonate with sodio-malonitrile and the condensation of ethoxymethylene-malonitrile with diethyl sodio-malonate will give the same intermediate compound, and the second stage of the condensation, where the mobile hydrogen atom is replaced by sodium, will be the same.

The identity of the diamides may not be directly due to their glutaconic structure, but to the identity of the sodium derivatives ; and the fundamental cause of the identity of the sodium compounds lies in their glutaconic structure. Although it is not yet decided whether the constitution of the sodium compound is (A) or (B) it can be safely said that the diamide $C_{11}H_{16}O_6N_2$ is the diethyl α, α (= γ, γ)-dicarbamylpropylene-γ, γ (= α, α)-dicarboxylate.

(VI) **Diethyl α, γ-dicyanopropylene-α, γ-dicarboxylate.** That the condensation of ethyl ethoxymethylene-cyanoacetate with ethyl sodio-cyanoacetate gave the same substance as that synthesized from ethyl cyanoacetate, chloroform, and sodium ethylate, was explained in the previous paper.(1) The constitutional formula previously given to the diethyl dicyanoglutaconate semihydrate can now be written in a more expanded form, for it has become known that the double bond of the propylene nucleus is not fixed. Thus in the following way :



$$\begin{matrix}CN\\C_2H_5OOC\end{matrix}\!\!>\underbrace{C-CH-C}_{H}<\!\!\begin{matrix}C(=NH)-NH-CO\\CO_2C_2H_5\quad C_2H_5O_2C\end{matrix}\!\!>\underbrace{C-CH-C}_{H}<\!\!\begin{matrix}CN\\COOC_2H_5\end{matrix}$$

or in any other ways in which the propylene nucleus has a symmetrical structure.(2)

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(1) This journal 2 (1927), 240.

(2) Cf. J. F. Thorpe, *J. Chem. Soc.*, 87 (1905) 1669.

(VII) **Ethyl α, α, γ-tricyanopropylene-γ-carboxylate.** The sodium derivative of this compound was obtained in coloured crystalline mass by the evaporation of alcohol from the red solution which resulted on adding ethyl ethoxymethylene-cyanoacetate to the alcoholic sodio-malonitrile. As this sodium compound was very easily soluble in water, alcohol, acetone, ethyl acetate, and pyridine, it was not recrystallised in fear of the loss of the substance. The crystalline mass was washed with ether, dried, and dissolved in cold water. On adding hydrochloric acid to the aqueous solution and rubbing the wall of the vessel with a glass rod, a crystalline precipitate in yellowish brown colour separated out, which was collected, washed with water, and dried in the desiccator. 0.1892 Gr. of the substance dried at 100° gave 36.1 c.c. of nitrogen at 22.5° and 751 mm. 0.2953 Gr. of the substance gave 0.5874 gr. of CO_2 and 0.1071 gr. of H_2O. (Found: N=21.20; C=54.27; H=4.06. $C_9H_7O_2N_3 \cdot \frac{1}{2}H_2O$ requires N=21.21; C=54.54; H=4.04%.) The obtained substance corresponded in composition to ethyl α, α, γ-tricyanopropylene-γ-carboxylate *semihydrate*. This specimen was yellowish brown and melted at about 190°.

In order to investigate whether this substance is identical with that obtained in the case of (VIII), the sodium compound prepared by another experiment was recrystallised three times from water, when it was obtained as greyish violet crystals. 0.5428 Gr. of the substance decreased by 0.0433 gr. on dehydrating at 130–140°% (Found: H_2O=7.98. $C_9H_6O_2N_3Na \cdot H_2O$ requires H_2O=7.86%.) The aqueous solution of this coloured sodium compound gave light green crystals of the semihydrate of the free nitrile-ester on acidifying.

When the sodium compound was dissolved by heating in a saturated aqueous solution of sodium chloride, the solution separated into two layers. The crystals which separated on cooling the solution in two layers were twice recrystallised from hot water. In this way nearly colourless crystals were obtained, which gave the light yellow semihydrate. This yellew specimen was probably the purest, but the colouring impurities in the brown or green specimen had nearly no perceptible effect on the melting point and the analytical results.

(VIII) **Ethyl α, γ, γ-tricyanopropylene-α-carboxylate.** By an analogous procedure the sodium derivative was obtained. This substance was easily soluble in water, acetone, ethyl acetate, and pyridine. On acidifying the aqueous solution of the sodium compound yellow crystalline substance precipitated, which was collected, washed with water, and dried in the desiccator. 0.1490 Gr. of the substance (no decrease in weight when dried at 120–130°) gave 27.7 c.c. of nitrogen at 22.5° and 755 mm. 0.1842 Gr. of the substance gave 34.6 c.c. of nitrogen at 23.5° and 754 mm. 0.2370 Gr. of the substance gave 0.4710 gr. of CO_2 and 0.0868 gr. of H_2O. 0.3022 Gr. of the substance gave 0.5991 gr. of CO_2 and 0.1100 gr. of H_2O. (Found : N=20.77, 20.83 ; C=54.22, 54.08 ; H=4.10, 4.07. $C_9H_7O_2N_3 \cdot \frac{1}{2}H_2O$ requires N=21.21; C=54.54 ; H=4.04%.) Decided from the analytical results this specimen was not pure and melted gradually by the time when the temperature reached 185°.

To obtain a pure specimen the preparation was repeated, when the sodium compound became quite colourless on recrystallising it twice from hot water. 0.3111 Gr. of the substance decreased by 0.0250 gr. on dehydrating at 130–140°. (Found: H_2O=8.04: $C_9H_6O_2N_3Na \cdot H_2O$ requires H_2O= 7.86%.) 0.2861 Gr. of the dehydrated substance gave 52.8 c.c. of nitrogen at 28.5° and 752.3 mm. (Found: N=19.88. $C_9H_6O_2N_3Na$ requires N=19.91%.) This purified sodium compound was transformed into the semihydrate of the free nitrile-ester. 0.1423 Gr. of the substance dried at 120° gave 27.4 c.c. of nitrogen at 27.5° and 759 mm. (Found: N=21.44. $C_9H_7O_2N_3 \cdot \frac{1}{2}H_2O$ requires N=21.21%.)

The semihydrate in (VII) stands in the same relation to the semihydrate in (VIII) as the diamide in (IV) to the diamide in (V). The yellow purest specimen of the semihydrate described in (VII), the yellow semihydrate from the purified sodium compound described in (VIII), and their mixture melted exactly at the same point 190° (corr.). The sodium derivatives obtained through two ways of condensation also coincided in water of crystallisation, and proved to be identical. These two specimens and their mixture melted at the same point 241–242° (not corr.). An analogous discussion may be made on these compounds, and it may be said that the compound obtained from the sodium derivative is the semihydrate of ethyl α, α, γ (= α, γ, γ)-tricyanopropylene-γ (= α)-carboxylate, and its constitution is represented by the formula $(C_8H_7O_2N_2)$–CO–NH–C(=NH)–$(C_8H_7O_2N_2)$.

(IX) α, α, γ, γ-Tetracyanopropylene. Soon after the addition of ethoxymethylene-malonitrile to the alcoholic solution of sodio-malonitrile, fine crystals separated out until the solution was filled with them, which were collected and recrystallised from hot water. In this way colourless fine needles of the sodium derivative of α, α, γ, γ-tetracyanopropylene were obtained, which had one molecule of water of crystallisation. 0.6551 Gr. of the substance decreased by 0.0648 gr. on heating at 135–140°. (Found: H_2O=9.89. $C_7HN_4Na \cdot H_2O$ requires H_2O=9.89%.) 0.1327 Gr. of the dehydrated substance gave 40.5 c.c. of nitrogen at 22.5° and 756 mm. (Found : N= 34.14. C_7HN_4Na requires N=34.15%.)

The alcoholic mother liquor of the crystallised condensation product gave a crystalline mass on evaporating it to dryness. The solid which remained undissolved when this crystalline mass was treated with hot water, was recrystallised from alcohol. 0.1581 Gr. of the substance gave 43.2 c.c. of nitrogen at 23.5° and 752 mm. 0.1138 Gr. of the substance gave 30.3 c.c. of nitrogen at 23° and 752.5 mm. (Found : $N=30.21, 29.55\%$.) This substance did not contain sodium, was not changed by treating with dilute hydrochloric acid, and melted at 211–212° without decomposition. 0.1133 Gr. of the substance treated with hydrochloric acid gave 30.5 c.c. of nitrogen at 26° and 757 mm. 0.2292 Gr. of the substance gave 0.4836 gr. of CO_2 and 0.0893 gr. of H_2O. 0.2194 Gr. of the substance gave 0.4617 gr. of CO_2 and 0.0860 gr. of H_2O. (Found: $N=29.60$; $C=57.56, 57.41$; $H=4.36, 4.39$. $C_7H_2N_4 \cdot C_2H_5OH$ requires $N=29.78$; $C=57.43$; $H=4.29\%$.) No investigation was made on the constitution and the mechanism of formation of this compound.

The sodio-tetracyanopropylene seemed to behave in a different manner towards hydrochloric acid. It deposited neither solid nor liquid, when acidified with the acid. The warm aqueous solution of the sodium compound, acidified with hydrochloric acid, gave the crystals of the original sodium compound on cooling. The acidified solution of this compound, after standing for three weeks, also gave the original substance on evaporating to dryness in the desiccator, the desiccator being filled with the fume of hydrochloric acid. But when the acidified solution of the sodium compound was extracted with ether several times and the aqueous layer was evaporated on the water bath, the residue consisted of sodium chloride alone. The ethereal solution was dehydrated with calcium chloride and evaporated in vacuo over sulphuric acid, when colourless crystals remained, which soon decomposed into a brown amorphous substance. Further the following experiment clearly shows the behaviour of the compound in question.

3.640 Gr. ($\frac{1}{50}$ mol.) of sodio-tetracyanopropylene $C_7HN_4Na \cdot H_2O$ were dissolved in water, acidified with hydrochloric acid, and shaken with ether five times. The aqueous layer was separated quantitatively and evaporated on the water bath, when 1.177 gr. of sodium chloride was obtained. The ethereal extracts were evaporated on the aqueous solution of 1.169 gr. ($\frac{1}{50}$ mol) of sodium chloride, so that the solute in the ethereal solution could enter into the aqueous layer as the ether was evaporated. After the disappearance of the ethereal layer, the aqueous solution was evaporated in vacuo in the desiccator in which concentrated sulphuric acid and soda-lime were placed. This solution, on evaporating to dryness, gave 3.643 gr. of sodio-tetracyanopropylene $C_7HN_4Na \cdot H_2O$. This experiment indicates the perfect reversibility of the reaction $C_7HN_4Na + HCl \rightleftarrows C_7H_2N_4 + NaCl$, and the distinct existence of the compound $C_7H_2N_4$ which matches hydrochloric acid in strength.

The equilibrium state in the aqueous solution containing C_7HN_4Na, HCl, $C_7H_2N_4$, and NaCl, probably owes its existence to the fact that the compound $C_7H_2N_4$ is soluble in water and has no tendency of combining with water and forming an insoluble substance as in the cases of other nitrile-esters of the dicarboxyglutaconic acid.

Triethyl cyanocarboxyglutaconate is so strong in acidity that it decomposes carbonates, forming its own salt, and tetracyanopropylene matches hydrochloric acid. The continued investigation on the acid character of the latter will bring some interesting results.

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

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THE CATALYSIS OF NICKEL ON THE THERMAL DECOMPOSITION OF METHANE.

By **Bunnosuke YAMAGUTI.**

Received October 1, 1927. Published November 28, 1927.

The catalytic decomposition of methane has been studied by Kunsetzow(1), Sabatier and Sendrens(2), Slater(3) and recently by Cantelo(4). Nickel is generally known as the most excellent catalyst for hydrogenation and dehydrogenation in organic chemistry. It is, however, to be remarked that the efficiency of the catalyst depends greatly upon the conditions of preparing and reducing of it.

As seen from Cantelo's experiment(4), nickel is the most efficient catalyst also for the thermal decomposition of methane. But it is doubtful whether the conditions to prepare an efficient catalyst may be identical both for methane decomposition and for hydrogenation or not, i.e. whether an catalyst suitable for hydrogenation may be equally efficient for methane decomposition or not. The author has made some investigations on this point.

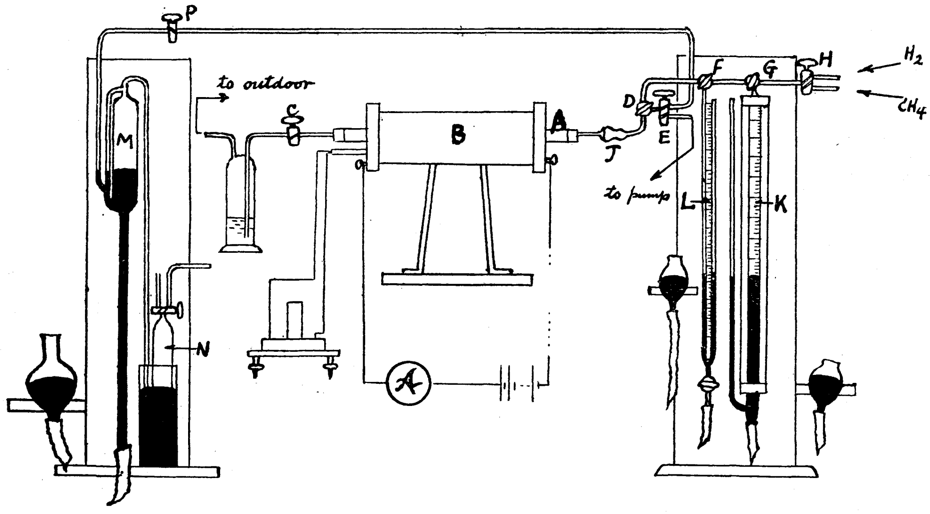

Fig. 1.

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(1) *Ber.*, **40** (1907), 2871.

(2) *Ann. chim. phys.*, **4** (1905), 435.

(3) *J. Chem. Soc.*, **109** (1916), 106.

(4) *J. Phys. Chem.*, **28** (1924), 1036.

Experimental Part.

In experiments the author has employed an apparatus shown in Fig. 1 which is practically identical with Slater's apparatus except some modifications.

The boats, filled with definite amounts of powdered catalyst are carefully pushed into the silica tube A (length 400 mm. and internal bore 15 mm.) through the joint J. Hydrogen is then passed through the cocks H, G, F and D for a definite time in order to reduce the catalyst, the silica tube being heated to a desired temperature by means of the electric furnace B. When the reduction finishes, stop-cocks C and F are closed and E opend, the whole is exhausted to a vacuum by an oil pump and further by the Töpler's pump M.

Methane is introduced into the burette K through the cock H. The mercury in the manometer must have been previously raised to the stop-cock F.

In the next place the electric furnace is adjusted by the help of a variable resistance to a desired temperature and then methane is introduced into the tube A through the cocks G and F until the manometer L shows the atmospheric pressure. Immediately, the methane in the tube is decomposed and the manometer L shows a gradual increase of the internal pressure. The reaction is allowed to proceed for the required time (10 minutes), and at the end of it, F is closed and E opened, thus allowing most of the gas to be drawn over into the vacuous portion of the Töpler's pump M.

Lastly, a sample of the gas is pumped out into the burette N and analysed for the determination of hydrogen content in it. The rate and degree of the decomposition of methane on each catalyst can be also examined, although in a rough manner, by observing the manometer L.

As it has been found very convenient for the experimental work to be possible to reproduce catalysts of consistent activity, the author has used the following method to prepare a catalyst according to E.F. Armstrong and T. P. Hilditch.(1) A boiling aqueous sodium carbonate is added in slight exess to a boiling solution of nickel sulphate. The precipitated hydroxide and basic carbonate are collected on a filter and throughly washed, until the filtrate shows no reaction for sulphate or carbonate, and then dried at 100°C.

Before proceeding to the study of the activity of the catalyst, the catalytic effect of the walls of the silica tube and porcelain boats employed has been examined in the absence of catalyst in various temperatures. The results are shown in Table 1.

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(1) *Proc. Roy. Soc.* (London), A. 103 (1923), 586.

TABLE. 1.

Reaction temperature	Hydrogen produced	Reaction temperature	Hydrogen produced
600°C	0.2%	850°C	3.4%
650	0.6	900	14.7
700	0.9	950	22.1
750	1.6	1000	37.5
800	2.1		

The amount of hydrogen produced in consequence of the decomposition of methane by the mere catalysis of the walls is thus found to be not more than 15% even at 900°C. and only 3.4% at 850°C.

For reducing the catalyst hydrogen is, in all the experiments, streamed through the tube at the rate of 1 litre per hour, as it has been ascertained by a preliminary experiment that this rate is nearly enough (see Table 2). In this case reducing is conducted at 600°C., streaming hydrogen over one gram of the catalyst for one hour.

TABLE. 2.

Velocity of H_2-stream	Hydrogen produced	Velocity of H_2-stream	Hydrogen produced
$1\frac{\text{litre}}{\text{hour}}$	15.60%	$4\frac{\text{litre}}{\text{hour}}$	16.01%
2	16.26	5	16.20
3	16.18		

The Effect of Reduction Temperature. The boats, each filled with 1.5 gr. of the catalyst is pushed into the reaction tube, and the catalyst is reduced by passing hydrogen through the tube at various temperature with the velocity of 1 litre per hour.

When the reduction finishes, the temperature of the furnace is raised to 850°C. and the activity of the catalyst is examined, introducing methane in the tube and allowing the reaction to proceed for 10 minutes.

Table 3 and Fig. 2 show the effect of reduction temperature of the catalyst on the yield of hydrogen.

TABLE 3.

Reduction temperature	Hydrogen produced	Reduction temperature	Hydrogen produced
300°C	22.10%	600°C	51.13%
400	32.54	700	48.50
500	41.75	800	46.51

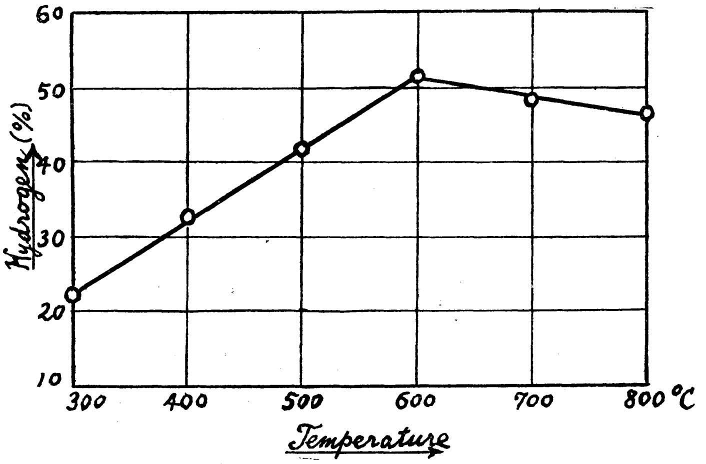

Fig. 2.

The catalyst becomes more active in a notable extent with the increase of reduction temperature until it reaches 600°C., while above this temperature its increase causes, on the contrary, a gradual decrease of activity. In order to give the highest activity to the catalyst, therefore, reduction must be conducted at 600°C. This conclusion is very interesting in contrast with the results obtained by many authors in the studies of hydrogenation where the optimal temperature of reduction has been determined to be about 400°C. and a catalyst reduced at above 500°C. has been generally known to be poor in activity.

The Effect of Reducing Duration. In order to know the effect of reducing duration, each catalyst reduced for different duration is tested on its activity in the same way as above. The result is shown in Table 4. and Fig. 3.

TABLE 4.

Reduction temperature: 600°C.
Reaction temperature: 850°C.
Reaction time: 10 minutes.

Reducing duration	Hydrogen produced	Manometer reading	Reducing duration	Hydrogen produced	Manometer reading
8 hour	45.99%	20 cm.	19 hour	53.55%	24 cm.
10	48.23	23	20	31.00	15
12	51.13	25	22	30.10	14
14	53.09	29	24	30.14	14
16	57.20	32	26	30.08	14
18	63.50	28.5 34.	30	30.20	14

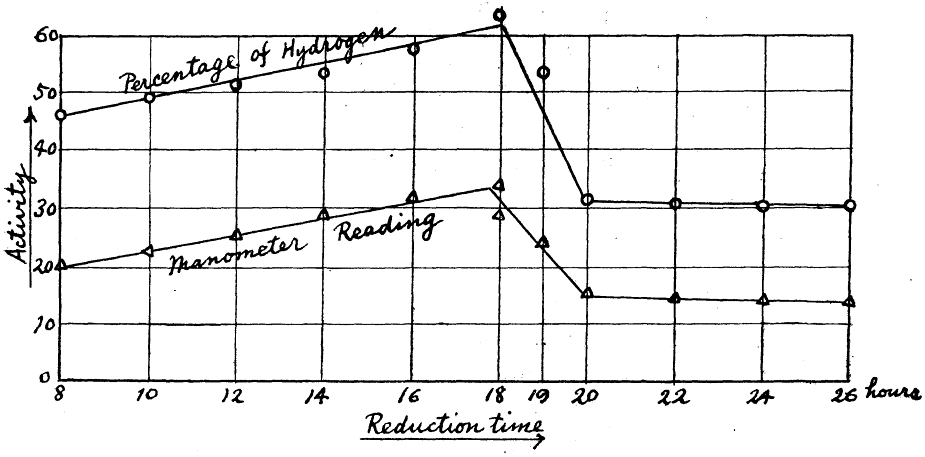

Fig. 3.

It is seen that the activity of the catalyst increases in proportion with duration of the reduction until it reaches to 18 hours, while a little longer reduction than that time causes, on the contrary, a sudden decrease of activity. The highest activity is thus obtained by reducing the catalyst for 18 hours. In order to determine the extent to which the reduction has taken place in the case of the maximum activity, the catalyst is analysed by the ferric chloride method for the determination of nickel in the presence of its oxide(1) and found to contain 79.5 per cent of the total nickel as reduced metallic one.

This result leads to the conclusion that also for the decomposition of methane, a partially reduced nickel catalyst (Ni-NiO) is better than a completely reduced one, what has been already ascertained in the case of hydrogenation by Boswell and other investigators.

The poor activity attained after 20 hours reduction is no more altered by reducing the catalyst further, and this seem to show that at least the surface of it has been completely reduced and accordingly has become very poor in activity.

The lower curve in Fig. 3 indicates the readings of the manometer in the experiments, of course giving a parallel result to that of the analysis.

The Durability of Activity. To study the durability of catalystic activity in an exact manner it is necessary to construct a more suitable apparatus than that described above. However, the author has tried to examine how the activity of the catalyst has been affected by the carbon deposited on its surface in consequence of the decomposition of methane, simply using the same apparatus as in the above cases.

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(1) Treadwell-Hall, " Analytical Chemistry," 1919, Vol. 2, p. 612.

Methane is introduced in the tube, as above described, which contains a boat filled with 1 gram of catalyst reduced at 600°C. for 9 hours, and the reaction is allowed to proceed at 850°C. After ten minutes the gas produced by the decomposition of methane is pumped out in the burette by the Töpler's pump and determined the hydrogen contained in it. Methane is again introduced in the same tube and after ten minutes the produced gas is similarly pumped out and analysed. In this manner the process has been repeated 30 times.

In the first time the manometer reading reaches 30 cm. corresponding to 57.5% yield of hydrogen and in the second time it decreases to 29 cm. corresponding to 56.8% hydrogen.

But in all the cases from the third to the thirtieth time, the manometer shows invariably the same reading with the second time, meaning no more decrease of the activity of the catalyst.

As the total quantity of methane used in the repeated reactions amounts to 3.6 litres of which about 40 per cent may be regarded to be decomposed into hydrogen and carbon, the amount of carbon deposited on one gram of the catalyst can be calculated approximately to be 0.6 gram. From this it is perceived that such a quantity of carbon deposit seems to have almost no effect on the activity of the catalyst.

In conclusion the author wishes to express his cordial thanks to Prof. M. Katayama for his valuable advices during the work and also to Mr. Z. Simizu for his earnest assistance.

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ON THE FICTITIOUS HEAT OF SOLUTION OF THALLOUS SULPHATE.

By **Fusao ISHIKAWA.**

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If we construct the following two reversible cells and apply the Gibbs-Helmholtz equation to them, we obtain the following relations (1) and (2).

Thallium amalgam saturated 50%	|	saturated solution with solid thallous sulphate	Hg_2SO_4	|	Hg	Cell A.
Thallium amalgam saturated 50%	|	solution of thallous sulphate of any desired concentration	Hg_2SO_4	|	Hg	Cell B.

for cell A $$Q_A = nF\left\{E_A - T\left(\frac{dE}{dT}\right)_A\right\} \quad \cdots\cdots\cdots\cdots\cdots\cdots\cdots(1)$$

for cell B $$Q_B = nF\left\{E_B - T\left(\frac{dE}{dT}\right)_B\right\} \quad \cdots\cdots\cdots\cdots\cdots\cdots\cdots(2)$$

in which Q_A or Q_B represents the quantity of heat corresponding to the chemical reaction in cell A or in cell B when nF of electricity be allowed to pass reversibly through each cell. Now if nF of electricity be taken out of call A and be passed through cell B in the opposite direction, both being carried out in a reversible manner, the chemical change which takes place in the whole system is the dissolution of n equivalents of thallous sulphate in the unlimited quantity of the solution in cell B. The heat corresponding to this change is nothing but the so-called differential heat of solution $(Q)_T$ and is given by the difference of equations (2) and (1).

$$(Q)_T = Q_B - Q_A = nF\left[(E_B - E_A) - T\left\{\left(\frac{dE}{dT}\right)_B - \left(\frac{dE}{dT}\right)_A\right\}\right] \quad \cdots(3)$$

If the saturated solution without the solid salt be used in cell B then $(Q)_T$ must be equal to the fictitious heat of solution $(F)_T$ and equation (3) will be transformed into the following form as in this case $E_A = E_B$,

$$(F)_T = nFT\left\{\left(\frac{dE}{dT}\right)_A - \left(\frac{dE}{dT}\right)_B\right\} \quad \cdots\cdots\cdots\cdots\cdots\cdots\cdots(4)$$

Besides, the fictitious heat of solution is also derived from the following relation

$$\left(\frac{dE}{dT}\right)_A = \left(\frac{dE}{dT}\right)_B + \left(\frac{dE}{dC}\right)_T \frac{dC}{dT}$$

combining this with equation (4), we obtain

$$(F)_T = nFT\left(\frac{dE}{dC}\right)_T \frac{dC}{dT} \quad \cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots(5)$$

The author had previously determined the fictitious heat of solution of thallous sulphate at 30°C. on the basis of relations (4) and (5) and the following values had been obtained.(1)

-14.73 cal./gr.	(from equation (4))
-14.74 cal./gr.	(from equation (5))

With the aid of equation (3) we can determine the differential heat of solution of an anhydrous salt at any desired concentration by measuring the

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(1) *Z. physik. Chem.*, **105** (1923), 155. The figures reported previously are corrected as given above owing to the alteration of the atomic weight of thallium.

electromotive forces and their temperature coefficients of cells *A* and *B*, but it is found to my reglet that equation (3) has a very limited scope of application, for the metal of the salt to be considered must show a well defined potential as the electrode, otherwise a large error can not be avoided in the result because equation (3) gives the differential heat of solution as a difference of two figures which are not far apart from each other. In the case of thallous sulphate, though thallium amalgam can show the very good constancy of potential, we can not determine the differential heat of solution in the wide range of concentration owing to its slight solubility, however, we can determine the differential heats of solution at several concentrations quite near to the saturation and then by the slight extrapolation the fictitious heat of solution may be evaluated and it might be without interest to compare the result with the previous one obtained by making use of equations (4) and (5).

Experimental.

The experimental methods had been described in the previous paper and will not be repeated here, only the results obtained being given in the following tables.

Cell *A*. (with the solid salt).

The figures shown in Table 1 were taken from the previous report.

TABLE 1.

Saturated solution, 5.826 gr. of Tl_2SO_4 in 100 gr. of solution at 30°C.

Temperature	Electromotive force (mean)	Calculated	Calc.—Obs.
27.5	1.05823	1.05811	− 0.00012
30.0	1.05889	1.05891	+ 0.00002
32.5	1.05972	1.05971	− 0.00001
35.0	1.06049	1.06051	+ 0.00002
37.5	1.06131	1.06131	0.0
40.0	1.06208	1.06211	+ 0.00003

The figures given in the third column were calculated by the following equation

$$E_A = 1.05891 + 0.000320\,(t-30).$$

Hence the temperature coefficient at 30°C. will be—

$$\left(\frac{dE}{dT}\right)_{A,\,30°} = 0.00032\frac{\text{volt}}{\text{degree}}$$

Cell *B*.

(with unsaturated solution of thallous sulphate).

In the following tables C denotes the concentration of the solution expressed in number of grams of solute in 100 gr. of solution.

TABLE 2.

$C=2.283$

Temperature	Cell 1.	Cell 2.	Mean	Calculated	Calc.—Obs.
25.0	1.07777	1.07774	1.07775	1.07775	0.0
27.5	1.08007	1.08004	1.08005	1.08005	0.0
30.0	1.08236	1.08234	1.08235	1.08235	0.0
32.5	1.08469	1.08468	1.08468	1.08465	− 0.00003
35.0	1.08695	1.08693	1.08694	1.08695	+ 0.00001

The relation between the electromotive force and the temperature can be represented as follows:

$$E=1.08235+0.00092\ (t-30).$$

Hence

$$\left(\frac{dE}{dT}\right)_{2.823}=0.00092\frac{\text{volt}}{\text{degree}}$$

TABLE 3.

$C=3.059$

Temperature	Cell 1.	Cell 2.	Mean	Calculated	Calc.—Obs.
25.0	1.07028	1.07037	1.07033	1.07033	0.0
27.5	1.07251	1.07261	1.07256	1.07256	0.0
30.0	1.07475	1.07484	1.07479	1.07479	0.0
32.5	1.07697	1.07707	1.07702	1.07702	0.0
35.0	1.07918	1.07925	1.07922	1.07925	+ 0.00003

The following equation may be derived from the observed electromotive forces.

$$E=1.07479+0.000892\ (t-30)$$

which gives

$$\left(\frac{dE}{dT}\right)_{3.059}=0.000892\frac{\text{volt}}{\text{degree}}$$

TABLE 4.

$C=5.110$

Temperature	Cell 1.	Cell 2.	Mean	Calculated	Calc.—Obs.
25.0	1.05751	1.05750	1.05750	1.05749	− 0.00001
27.5	1.05966	1.05963	1.05964	1.05964	0.0
30.0	1.06181	1.06177	1.06179	1.06179	0.0
32.5	1.06396	1.06393	1.06394	1.06394	0.0
35.0	1.06610	1.06606	1.06608	1.06609	+ 0.00001

The following equation describes the above data.

$$E=1.06179+0.00086\ (t-30)$$

Therefore

$$\left(\frac{dE}{dT}\right)_{5.110}=0.00086\frac{\text{volt}}{\text{degree}}$$

From the foregoing results we can compute the differential heat of solution of thallous sulphate at each concentration by substituting the numerical values for E_A, E_B, $\left(\frac{dE}{dT}\right)_A$ and $\left(\frac{dE}{dT}\right)_B$ in equation (3). The second column of the following table shows the differential heats of solution thus calculated ($nF=2\times 96494\times 0.2389$) except the last two which are the fictitious heats of solution obtained in the previous investigation.

TABLE 5.

Differential heat of solution per 1 gr. of thallous sulphate.

Temperature 30°C.

Concentration of solution (gr./100 gr. solution)	Differential heat of solution (cal.)	Calculated
2.283	− 14.47	− 14.41
3.059	− 14.38	− 14.48
5.110	− 14.68	− 14.66
5.826	− 14.73 − 14.74 (fictitious heat of solution)	− 14.72 (extrapolated)

In such a narrow range of concentration the differential heat of solution may be considered to be a linear function of the concentration and the following equation was obtained by applying the method of least squares to the observed values.

$$(Q)_{30^\circ}=-14.21-0.088\ C$$

The calculated values based on this equation are expressed in the third column of the table. Now by extrapolating the concentration to the saturation ($C=5.826$), the fictitious heat of solution may be obtained which is given in the last line of the same column and is found to be in good agreement with the previous result.

The experiments described in this article were carried out in the Van't Hoff Laboratorium, Utrecht and the author wishes his best thanks to Prof. Ernst Cohen and also to Dr. A. L. Th. Moesveld.

September 1927. The Institute of Physical and Chemical Research,
Hongo, Tokyo.

BEMERKUNGEN UEBER DIE ZUSTANDSGLEICHUNGEN DER ADSORBIERTEN PHASE.⁽¹⁾

Von **Bun-ichi TAMAMUSHI.**

Eingegangen am 6. Oktober 1927. Ausgegeben am 28. November 1927.

I.

Die Gibbsche Gleichung

$$u = -\frac{C}{RT}\frac{d\gamma}{dC} \cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots (1)$$

kann, wenn die Lösung so weit verdünnt ist, dass wir hier $C=dC$ bzw. $-d\gamma=\gamma_0-\gamma$ setzen können, wobei γ_0 die Grenzflächenspannung des reinen Lösungsmittels und γ die der Lösung bedeutet, in der folgenden Form:

$$(\gamma_0-\gamma)\frac{1}{u} = RT \cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots (2)$$

gefasst werden. Ferner ist $\gamma_0-\gamma$ gleich dem sogenannten „Gasdruck“ P_s, der parallel zur adsorbierenden Fläche auf 1 cm. wirkt, und $\frac{1}{u}$ ist gleich der molaren Oberfläche des Adsorbens A, d.h. diejenige Fläche, an der 1 Mol des gelösten Stoffes adsorbiert wurde. Somit haben wir:

$$P_sA=RT \cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots (3)$$

Traube⁽²⁾ hat auf Grund der Analogie zwischen dieser Formel und der

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(1) Die Gleichung, die in meiner früheren Arbeiten (diese Zeitschrift, 1 (1926), 185, u. 257) aufgestellt wurde, soll in dieser Mitteilungen noch näher diskutiert werden. Die Bezeichnungen sind dieselben, wie in den vorhergehenden Mitteilungen, wenn das Gegenteil nicht ausdrücklich ausgesprochen wird.

(2) *Lieb. Ann.*, **256** (1891), 27.

Gleichung des idealen Gases, $Pv=RT$ erklärt, dass die Erniedrigung der Grenzflächenspannung des Adsorbens auf der themischen Bewegung der gelösten Molekeln beruhe. Diese Formel ist jedoch, wie Traube bemerkt hat, nur für sehr kleine Werte von P_s gültig, und selbst wenn man für den Gibbschen Film die kinetische Theorie anwenden könnte, lässt sich doch nicht allgemein denken, dass sich die adsorbierten Moleküle im Film vollständig ebenso verhalten wie ein ideale Gas. Die Tatsache in der Traubeschen Versuchen, dass man P_sA/RT für mässig grösse Werte von P_s nicht gleich 1 setzen kann, ist derjenigen ganz ähnlich dass Pv/RT für reale Gase nie gleich 1 ist.

Volmer⁽¹⁾ hat dabei den Flächenbedarfseinfluss der gelösten Moleküle berücksichtigt und die folgende Gleichung thermodynamisch aufgestellt:

$$P_s(A-\beta)=RT \quad \cdots\cdots\cdots\cdots\cdots(4)$$

worin β die von 1 Mol des adsorbierten Stoffes bedeckten Fläche bedeutet. Diese Gleichung ist von Volmer für die Versuche von Traube⁽²⁾ und Szyszkowski⁽³⁾ angewandt und es ist gefunden worden, dass die Gleichung für nicht zu hohe Dichten in Übereinstimmung mit der Erfahrung steht.

Aber, wie Langmuir früher bemerkt hat, liegt der Grund dafür, dass ein unlöslicher Film nicht vollständig den Gasdruck aufweist, darin, dass zwischen den Hydrocarbonketten, die in der adsorbierten Phase angeordnet sind, eine Anziehungskraft zur Wirkung kommt. Die Existenz dieser intermolekülaren Kraft……entweder anziehende oder abstossende……kann man allgemein annehmen, wenn die Lösung nicht mehr sehr verdünnt ist. Wenn noch ein Dipolgas z.B. CO_2 an der Oberfläche der Kohle adsorbiert ist, wirkt deutlich eine elektrostatische Abstossungskraft zwischen den Molekülen, über diese Erscheinung wird später noch einmal bemerkt.

Jedenfalls muss man in der Aufstellung der Zustandsgleichung der adsorbierten Phase, ausser der thermischen Energie der gelösten Moleküle noch eine potentiale Energie in der Phase berücksichtigen, und diese Bahauptung stimmt mit der jetzt allgemein vertretenen Ansicht überein, dass die adsorbierten Moleküle in der Grenzfläche in einer bestimmten Orienteirung gelagert sind.

V. Cofman⁽⁴⁾ hat aus diesem Gesichtspunkte bemerkt, dass die Variabeln, die den Zustand des adsorbierten Films bestimmen sollen, P_s, A und E sein könnten, die eben P, v und T in der Zustandsgleichung der Gase entsprechen, und somit dass statt der Gleichung (3) die folgende Gleichung gegeben werden könne:

$$P_sA=aE\,(\text{oder } aE^2) \quad \cdots\cdots\cdots\cdots\cdots(5)$$

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(1) *Z. physik. Chem.*, **115** (1925), 253.
(2) Loc. cit.
(3) *Z. physik. Chem.*, **64** (1908), 385.
(4) *Nature*, **117** (1926), 755.

worin a eine Konstante und E eine neue Variable sei, deren reale Natur, als elektrochemische vermutet, aber noch nicht ganz erklärt geblieben ist.

Hierbei hat Cofman die Variable T ausgeschlossen. Ich möchte lieber annehmen, dass in der Zustandsgleichung der adsorbierten Phase zwei Glieder addiert gedacht werden können, von denen die eine die thermische Bewegung der Moleküle, die andere die potentiale Energie elektrostatischer Natur darstellt. Dann haben wir nun:

$$P_s A = RT + \psi(e) \cdots\cdots\cdots\cdots (6)$$

worin $\psi(e)$ eine Funktion bedeutet, deren analytische Darstellung nicht ganz einfach ist. Aber nach der Theorie des Dipols können wir den Wert dieser Funktion angeben nämlich:(1)

$$\varphi_d = -\frac{\mu^2}{h^3}(1+\cos^2\theta) \qquad \text{(ohne Polarisation)}$$

oder

$$\varphi_d = -\frac{\mu^2}{h^2}\left[\frac{2}{1-2\text{ɜ}}\cos^2\theta + \frac{1}{1-\varepsilon}\sin^2\theta\right] \qquad \begin{array}{l}\text{(mit Berücksichtigung}\\ \text{der Polarisation)}\end{array}$$

wobei μ das Moment des Dipols, h der Abstand zwischen beiden Dipolzentren, θ der Winkel, unter welchem die beiden Dipolachsen zur Geraden h geneigt sind, und ε eine Konstante ist, welche die Polarisation des Moleküls vertritt. Cos θ ist gleich null für die adsorbierten Moleküle, und φ_d kann gleich $k\theta_d$ gesetzt werden. Hier ist k die Boltzmannsche Konstante und θ_d ist eine für das Molekül charakteristische Konstante, die eine Dimension der Temperatur hat. Führen wir diesen Ausdruck in die obige Gleichung ein, so haben wir:

$$P_s A = RT + q\theta_d,$$

oder

$$P_s A = \left(1 + \frac{q\theta_d}{RT}\right)RT \cdots\cdots\cdots\cdots (7)$$

worin q einen anderen Koeffizient bedeutet. Ersetzen wir hierbei $1 + q\theta_d/RT$ durch i, so erhalten wir:

$$P_s A = iRT \cdots\cdots\cdots\cdots (8)$$

Wir ziehen noch gleichzeitig die Volmersche Korrektur in Betracht, und erweitern die Gleichung(2) zu:

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(1) E. Jacket, *Fortschr. d. Physik u. phys. Chem.* Bd. **18** (1925).

(2) Für den Fall der Adsorption von Kohlensäure an der Kohle, hat Magnus nach der Dipoltheorie die folgende Zustandsgleichung entwickelt:

$$\left(P_s - \frac{\alpha}{A^2}\right)(A-\beta) = RT$$

wobei $\alpha/A = \varphi_d$ ist, wenn φ_d die gesamte potentiale Energie der wechselseitigen Kraftwirkungen bedeutet. Es ist bemerkenswert, dass in dieser Gleichung die Korrektur für den Druck (wie in der van der Waalschen Gleichung) als eine Funktion der Fläche eingeführt ist. Aber wie man sofort erkennen kann, stimmt die Gleichung, wenn man β gegen A^2 vernachlässigt, mit der Gleichung (9) überein, da i gleich $1+\frac{q\Theta_d}{RT}$ bzw. $1+\frac{\varphi_d}{RT}$ ist. Vergl. A. Magnus, *Z. anorg. allgem. Chem.*, **158** (1926), 76.

$$P_s\,(A-\beta)=iRT \;\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots (9)$$

Diese Gleichung ist die, die ich in meiner früheren Arbeiten angenommen habe.

II.

Die Gleichung (9) können wir auch in folgender Form fassen:

$$\frac{P_sA}{RT}=\frac{P_s\beta}{RT}+i \;\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots (10)$$

die, wie man gleich sehen wird, der Amagatschen Gleichung für reale Gase entspricht, und neulich von Rideal⑴ für die adsorbierte Phase angewandt wurde. Die folgende Tabelle zeigt die Werte von β und i, die über die Versuche von Traube, Szyszkowski und anderen von den neben bezeichneten Verfasseren gerechnet wurden.

TABELLE.

Stoff	Grenzphase	$\beta \cdot 10^{+16}$ Fläche pro Molekül	i	Beobachtet von	Berechnet von
Essigsäure	Wasser-Luft	24.3	.97	Traube	Tamamushi
Propionsäure	„	24.3	.85	„	„
n-Buttersäure	„	24.3	.73	Szyszkowski	Rideal
n-Valeriansäure	„	24.3	.63	„	„
n-Kapronsäure	„	24.3	.43	„	„
Iso-Buttersäure	„	25.1	.78	„	„
Iso-Valeriansäure	„	25.1	.68	„	„
Iso-Kapronsäure	„	25.1	.48	„	„
Iso-Amylalkohol	„	—	.59	„	„
n-Buttersäure	Wasser-Benzol	24—25	1—.95	Harkins u. King	„
tertiär. Butylalkohol	Wasser-Quecksilver	24.0	.52	Gouy	„
tertiär. Amylalkohol	„	28.0	.46	„	„
Rohr Zucker	„	72.7	1.0	„	„
Pyridin	„	26.0	1.0	„	„
Dimethylanilin	Wasser-Benzol	75	.84	Mathews u. Stamm	Ch. Sen⑵
Dimethylanilin	Wasser-Heptan	51	.75	„	„
Essigsaüre	Wasser-Kohle	84	1.73	Schmidt	Tamamushi⑶

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(1) Rideal, " An Introduction to Surface Chemistry," Cambridge. (1926), p. 58.
(2) *Phil. Mag.*, [7], 17 (1927), 925.
(3) Loc. cit. Berechnet von der Gleichung (11).

Hierbei die letzte Reihe ist ausgenommen sind die Werte von i nicht grösser als 1. Diese Ergebnisse stimmen mit der Langmuirschen Meinung darin überein, dass zwischen den Ketten der adsorbierten Moleküle eine Anziehungskraft besteht. Und die Tatsache, dass sich der Wert von i mit dem Molekulargewicht der Fettsäuren regelmässig vermindert, deutet darauf hin, dass die wechselseitige Kraftwirkung als ein Mass für die Kapillaraktivität benutzt werden kann.

In der vorhergehenden Arbeit, habe ich von der Gleichung (9) und der Gibbschen Gleichung eine Adsorptionsisotherme, nämlich:

$$\frac{u}{1-u\beta}=KC^{\frac{1}{i}} \quad\cdots\cdots\cdots\cdots\cdots\cdots(11)$$

abgeleitet und gleicherweise von anderen Gleichungspaaren die Freundlichsche Formel, $u=aC^{\frac{1}{i}}$ gefunden. Wenn i in diesen Isothermen noch einen gleichen physikalischen Sinn, wie oben erläutert wurde, haben kann, so können wir aus den Werten von i, die jetzt immer grösser als 1 sind, behaupten, dass an der Adsorptionsphase z.B. Kohle-Essigsäure, eine abstossende Kraft zwischen den adsorbierten Molekülen zur Wirkung kommen muss. Also, wir sollen dabei eine andere Orientierung der Moleküle annehmen als die, die wir an der Grenzphase Wasser—Gas annehmen konnten. An der Oberfläche der Kohle, verhalten sich die Fettsäuren vielleicht ebenso wie Kohlensäure, die, wie oben gezitiert wurde, von Magnus ausführlich theoretisch behandelt ist. Also auf Grund der dipoltheoretischen Erklärung des Koeffizienten i, kann man die Zustandsgleichung (9) nicht nur für die Grenzphase Flüssig-gasförmig und Flüssig-flüssig sondern auch für die Grenzphase Fest-gasförmig oder -flüssig als allgemein gültig denken. Aber bei Adsorption spielt noch die Natur des Adsorbens eine wichtige Rolle, die im Falle der festen Körper wie Kohle besonders schwer zu definieren ist. Dann ist die ganze Erscheinung nicht so einfach. Die elektrostatische Natur der Adsorptionskraft scheint mir aber noch im allgemeinen nicht zweifelhaft, darüber sollen noch weitere Untersuchungen berichtet werden.

Herrn Prof. M. Katayama bin ich für seine freundlichste Unterstützung zu wärmesten Dank verpflichtet.

September, 1927. Berlin, Deutschland.

A NOTE ON SORPTION.

By Michael TARLÉ.

Received October 21, 1927. Published November 28, 1927.

In spite of the kind reply of Prof. Sâmeshima(1) I am still maintaining my opinion, that his experiments do not prove the correctness of the dissolution theory of sorption. The fact that the ratio—absorbing capacity : volume of the pores—for various kinds of charcoal is nearly constant, can not be explained by the theory, which considers the process of activation solely as a purification of the charcoal, without paying attention to the change of its structure.

Also one can not agree with the opinion that the grinding increases the surface area. The increase—if any—is extremely small, even if we assume with Prof. Sameshima that the number of particles derived from one cubic centimeter of charcoal is 10^{12}. The magnitude of the total area is not known and might be larger than 100 sq. meter. Lamb, Wilson and Chaney assume that it is equal to 1000 sq. meter for 1 c.c. of active charcoal(2). If we agree with this figure, the increase of area by grinding, as computed by Prof. Sameshima(3) will amount to 0.03% of the area. But it is useless to make such computations, as we do not know even the order of magnitude of the area. Freundlich says(4) : "…Deshalb ist es auch nicht gesagt, dass ein Zerpulvern des Adsorbens die adsorbierte Fläche vergrössert.…Wenn nur schon vorhandene innere wirksame Oberfläche zu äusserer Oberfläche wird, so macht dies für die Adsorptions-oberfläche nichts aus." What I tried to do in my precedent paper(5) was to show that in any case the grinding has a minimal effect upon the surface. We may assume that the dissolution of a gas plays in some cases a part in the phenomenon of sorption, but it is surely unsuitable to interpret it as a pure dissolution process, independent of the surface of the adsorbens.

Manchurian Arsenal, Moukden, China.

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(1) This journal 2 (1927), 246.

(2) *J. Ind. Eng. Chem.*, 11 (1919), 427.

(3) Loc. cit.

(4) " Kapillarchemie ", 3 ed. (1923), p. 177.

(5) This journal, 2 (1927), 243.

CONDENSATION OF ETHYL ACETOACETATE WITH SODIO-MALONITRILE. A VIEW ON THE EXPLANATION OF SIMILAR REACTIONS.

By **Yoshiyuki URUSHIBARA.**

Received September 22, 1927. Published November 28, 1927.

H. Rogerson and J. F. Thorpe⁽¹⁾ showed that ethyl sodio-cyanoacetate condenses with ethyl acetoacetate giving the sodium derivative of diethyl α-cyano-β-methylglutaconate $C_2H_5OOC(CN)CH{\cdot}C(CH_3){=}CHCOOC_2H_5$, but diethyl sodio-malonate does not react with ethyl acetoacetate. They explained the reactive nature of the sodium derivative of ethyl cyanoacetate on the assumption that this sodium compound reacts in the enolic form, whereas the corresponding sodium derivative of diethyl malonate is in the ketonic form. Further they indicated that so long as one of the methylene hydrogen atoms in ethyl acetoacetate remains unsubstituted, that is, so long as it is capable of reacting in an enolic form, it possesses the power of combining with ethyl sodio-cyanoacetate.

According to this indication ethyl sodio-cyanoacetate should give diethyl α,γ-dicyano-β-methylglutaconate $C_2H_5OOC(CN)C{=}C(CH_3){-}CH(CN)COOC_2H_5$, condensing with ethyl cyanoacetoacetate $CH_3CO{\cdot}CH(CN)COOC_2H_5$; and triethyl α-cyano-γ-carboxy-β-methylglutaconate $(C_2H_5OOC)_2C = C(CH_3) - CH(CN)COOC_2H_5$, condensing with diethyl acetylmalonate $CH_3CO{-}CH(COOC_2H_5)_2$. In this way some of the nitrile-esters of the β-methyldicarboxyglutaconic acid might be obtained, which the author intended to synthesize for the studies associated with the investigations on the nitrile-esters of the dicarboxyglutaconic acid.⁽²⁾

But from the reaction mixture of ethyl sodiocyanoacetate with ethyl cyanoacetoacetate in absolute alcohol or in benzene the free ethyl cyanoacetate and the sodium derivative of ethyl cyanoacetoacetate were obtained, and no condensation product. The migration of the sodium atom from ethyl cyanoacetate to ethyl cyanoacetoacetate can be explained on the consideration of the relative acidity⁽³⁾ of these two compounds, the former being less strong than the latter. Hence, though it may be a necessary condition, it is not sufficient for the condensation with ethyl sodio-cyanoacetate that ethyl acetoacetate or its substituted derivatives can react in an enolic form. It

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(1) *J. Chem. Soc.*, 87 (1905), 1685. Further cf. *Proc. Chem. Soc.*, 28 (1912), 51 and *J. Chem. Soc.*, 121 (1922), 2216.

(2) This journal, 2 (1927), 278.

(3) " Acidity " means the power of combining with sodium.

must be weaker in acid character than ethyl cyanoacetate. For this reason the condensation which can proceed between ethyl sodio-cyanoacetate and ethyl methyl- or ethyl-acetoacetate(1) did not occur between ethyl sodio-cyanoacetate and ethyl cyanoacetoacetate. The realisation of the condensation seems to depend not so much on the fact that the ethyl cyanoacetate exists in its sodium derivative at the first moment of the reaction, as on the fulfilment of the above condition. Thus Rogerson and Thorpe obtained the same condensation product by the reaction of ethyl cyanoacetate and ethyl sodio-acetoacetate, although in a small yield, as that from ethyl sodio-cyanoacetate and ethyl acetoacetate.

In the previous paper(2) the author showed that the sodium derivative of diethyl $\alpha,\alpha(=\gamma,\gamma)$-dicyanopropylene-$\gamma,\gamma(=\alpha,\alpha)$-dicarboxylate gives an oily substance on acidifying its aqueous solution, but soon the oil dissolves in the mother liquor and colourless crystalline compound is precipitated which is the diethyl $\alpha, \alpha(=\gamma, \gamma)$-dicarbamylpropylene-$\gamma, \gamma(=\alpha, \alpha)$-dicarboxylate, $(H_2NCO)_2$-CH–CH=C$(COOC_2H_5)_5$. In order to investigate whether the combination with water will occur in a compound constituted similarly, it was necessary to synthesize a suitable compound. If ethyl cyanoacetate in Rogerson and Thorpe's condensation can be replaced by malonitrile without causing the hindrance of the reaction, ethyl α, α-dicyano-β-methylpropylene-γ-carboxylate $(CN)_2CH{-}C(CH_3){=}CHCOOC_2H_5$ is to be formed, which will resemble in constitution with the above-mentioned compound. Really the condensation of ethyl acetoacetate with sodio-malonitrile gave a sodium compound, which, on treating with acid in an aqueous solution, was transformed into a free nitrile-ester. The latter is an oily substance and has the composition $C_9H_{10}O_2N_2$ as expected from the above constitutional formula. It possesses no tendency of combining with water to form a diamide.

The sodio-malonitrile can not react in the enolic form, but is capable of condensing with ethyl acetoacetate. Therefore, Regerson and Thorpe's explanation of the reactive nature of the sodium derivative of ethyl cyanoacetate does not seem to be appropriate. The sodium derivative of diethyl malonate did not condense with ethyl acetoacetate probably because diethyl malonate is weaker in acid character than ethyl cyanoacetate and was deprived of sodium atom by the latter.

Experimental Part. *Synthesis of Ethyl α,α-dicyano-β-methylpropylene-γ-carboxylate.*

Sodium (2.0 gr.) was dissolved in a small quantity of absolute alcohol and malonitrile (5.6 gr.) was introduced, when a part of the formed sodio-malonitrile crystallised out. On adding ethyl acetoacetate (11.0 gr.) to the

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(1) Rogerson and Thorpe, loc. cit

(2) This journal, 2 (1927), 278.

sodio-malonitrile, a clear solution resulted and a large quantity of heat was evolved. The solution was boiled for half an hour on the water bath and evaporated to dryness. A crystalline mass was obtained, which was recrystallised twice from a small amount of water. The aqueous solution of this sodium compound reacts alkaline. The purified sodium compound was dissolved in water and the solution was covered with ether and acidified with dilute hydrochloric acid. The ethereal extract was washed with water and dehydrated with calcium chloride. On evaporating the ether in vacuo, a brown coloured oily substance was obtained, which was well dried in vacuo. 0.3258 Gr. of the substance gave 46.5 c.c. of nitrogen at 26° and 758 mm. 0.2325 Gr. of the substance gave 0.5138 gr. of CO_2 and 0.1169 gr. of H_2O. (Found: $N=15.71$; $C=60.29$; $H=5.63$. $C_9H_{10}O_2N_2$ requires $N=15.73$; $C=60.65$; $H=5.66\%$.)

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

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ON CARBOLTHIONIC ACIDS AND THEIR ESTERS. PART IV. A NEW METHOD OF FORMATION FOR THIAMIDES AND THIOHYDRAZIDES.

By Yoshihito SAKURADA.

Received September 29, 1927. Published November 28, 1927.

Thiamides have hitherto been prepared either by the interaction between amides and phosphorus pentasulphide or by the addition-reaction of nitriles toward hydrogen sulphide. But both methods are not widely applicable, and as the consequence thiamides hitherto known have been very limitted in number.

Now the reactions(1) between carbolthionic esters (thiocarboxylic o-esters) and ammonia or amines, which take place in the ethereal solution so as to yield thiamides, were experimentally confirmed to afford a very widely applicable new method for formation of various thiamides.

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(1) *Mem. Coll. Sci. Eng., Kyoto*, 3 (1912), 248.

Phenylhydrazine also reacts upon carbolthionic esters in the ethereal solution just analogously and yields various thiohydrazides many of which are quite new substances hitherto unknown.

Those thiamides and thiohydrazides prepared according to this method are described below.

I. Thiamides.

1. *Thioacetoethylamide,* $CH_3CSNHC_2H_5$. When an ethereal solution of methylcarbolthionic propylester (thioacetic o-propylester) added with some ethylamine was left to stand for a few days it gradually lost its characteristic odour and colour, and a thick yellow oil having a peculiar odour separated out on the bottom of the flask. The oil was purified by washing it repeatedly with ether, and analysed.

0.1324 Gr. the substance gave 0.3136 gr. Ag_2S; S=30.64% (Calc. 31.08).

Thioacetoethylamide is a yellow viscous liquid with a characteristic odour, soluble in alcohol and nearly insoluble in water and ether. When warmed with alkali it decomposes evolving ethylamine.

2. *Thiopropioethylamide,* $C_2H_5CSNHC_2H_5$. This was obtained from ethylcarbolthionic propylester and ethylamine as a yellow viscous liquid resembling the corresponding thioacetamide in every respect.

0.0996 Gr. the substance gave 0.2131 gr. Ag_2S; S=27.68% (Calc. 27.36).

3. *Thiobenzo-ethylamide,* $C_6H_5CSNHC_2H_5$. This was prepared from phenylcarbolthionic butylester and ethylamine. It is also a yellow viscous liquid.

4. *Thiophenylaceto-ethylamide,* $C_6H_5CH_2CSNHC_2H_5$. This thiamide was also obtained as a yellow viscous liquid by the action of ethylamine upon benzylcarbolthionic isoamylester.

0.2184 Gr. the substance gave 0.2948 gr. Ag_2S; S=17.46% (Calc. 17.89).

5. *Thioparatolu-ethylamide,* $C_7H_7CSNHC_2H_5$. Paratolylcarbolthionic propylester and ethylamine were used for the preparation of the thiamide which was also found to be a yellow thick oil.

0.0159 Gr. the substance gave 0.0212 gr. Ag_2S; S=17.25% (Calc. 17.89).

6. *Thioaceto-isobutylamide,* $CH_3CSNHC_4H_9$. When prepared from methylcarbolthionic isoamylester and isobutylamine it was obtained as a yellow coloured oily substance.

0.1235 Gr. the substance gave 0.2293 gr. Ag_2S; S=24.02% (Calc. 24.44).

7. *Thiopropio-isobutylamide,* $C_2H_5CSNHC_4H_9$. For the preparation ethylcarbolthionic butylester and isobutylamine were used, and it was obtained as a yellow thick oil.

0.1048 Gr. the substance gave 0.1796 gr. Ag_2S ; $S=22.17\%$ (Calc. 22.08).

8. *Thiobenzo-isobutylamide,* $C_6H_5CSNHC_4H_9$. This was obtained as a yellow crystalline substance when phenylcarbolthionic methylester was treated with isobutylamine. It was purified by recrystallizing from a mixture of alcohol and ether, in the former of which it is very soluble while in the latter hardly soluble.

0.1417 Gr. the crystal gave 0.1783 gr. Ag_2S ; $S=16.28\%$ (Calc. 16.60).

9. *Thiophenylaceto-isobutylamide,* $C_6H_5CH_2CSNHC_4H_9$. This was prepared from benzylcarbolthionic isobutylester and isobutylamine. A very viscous yellow liquid.

0.1702 Gr. the substance gave 0.2041 gr. Ag_2S; $S=15.51\%$ (Calc. 15.47).

10. *Thioparatolu-isobutylamide,* $C_7H_7CSNHC_4H_9$. Paratolylcarbolthionic butylester and isobutylamine were used for the preparation. Yellow crystals with a peculiar odour.

0.0434 Gr. the crystal gave 0.0512 gr. Ag_2S ; $S=15.26\%$ (Calc. 15.47).

11. *Thioaceto-isoamylamide,* $CH_3CSNHC_5H_{11}$. This was prepared from methylcarbolthionic isobutylester and isoamylamine. A yellow thick liquid having a peculiar smell.

0.0702 Gr. the substance gave 0.1193 gr. Ag_2S ; $S=21.99\%$ (Calc. 22.08).

12. *Thiopropio-isoamylamide,* $C_2H_5CSNHC_5H_{11}$. Ethylcarbolthionic isoamylester and isoamylamine were used for this preparation and the amide was obtained as a yellow liquid.

0.0847 Gr. the substance gave 0.1306 gr. Ag_2S ; $S=19.95\%$ (Calc. 20.14).

13. *Thiobenzo-isoamylamide,* $C_6H_5CSNHC_5H_{11}$. For the preparation phenylcarbolthionic isoamylester and isoamylamine were used. It is a yellow crystalline substance.

0.1037 Gr. the crystal gave 0.1252 gr. Ag_2S ; $S=15.62\%$ (Calc. 15.47).

14. *Thiophenylaceto-isoamylamide,* $C_6H_5CH_2CSNHC_5H_{11}$. This was obtained from benzylcarbolthionic ethylester and isoamylamine as a yellow viscous liquid.

0.1894 Gr. the substance gave 0.2144 gr. Ag_2S ; $S=14.64\%$ (Calc. 14.49).

15. *Thioparatolu-isoamylamide,* $C_7H_7CSNHC_5H_{11}$. The thiamide was produced as a yellow crystalline substance when paratolylcarbolthionic methylester was treated with isoamylamine in an ethereal solution.

0.1042 Gr. the crystal gave 0.1143 gr. Ag_2S ; $S=14.19\%$ (Calc. 14.49).

II. Thiohydrazides.

Many thiohydrazides described below were prepared from carbolthionic esters by treating the latter with phenylhydrazine. They are all crystalline solids of light yellow colour easily decomposed by alkali and acid.

1. *Thioacetophenylhydrazide*, $CH_3CSNHNHC_6H_5$.
   0.0538 Gr. the substance gave 0.0801 gr. Ag_2S ; S=19.26% (Calc. 19.29).
2. *Thiopropiophenylhydrazide*, $C_2H_5CSNHNHC_6H_5$.
   0.1323 Gr. the substance gave 0.1837 gr. Ag_2S ; S=17.96% (Calc. 17.79).
3. *Thiobenzophenylhydrazide*, $C_6H_5CSNHNHC_6H_5$.
   0.0148 Gr. the substance gave 0.0159 gr. Ag_2S ; S=13.90% (Calc. 14.05).
4. *Thiophenylacetophenylhydrazide*, $C_6H_5CH_2CSNHNHC_6H_5$.
   Not analysed.
5. *Thioparatoluphenylhydrazide*, $C_7H_7CSNHNHC_6H_5$.
   0.0242 Gr. the substance gave 0.0249 gr. Ag_2S ; S=13.31% (Calc. 13.23).

The writer takes this opportunity of warmly thanking Professor M. Matsui for his kind assistance and encouragement throughout the work.

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ÉTUDES DE DÉRIVÉS DU FURFURAL.
V. ACTION DES COMPOSÉS ORGANOMAGNÉSIENS SUR LES CÉTONES FURYLIQUES ET CONSTITUTION DE LA FURYLIDÈNE-MÉTHYLÉTHYLCÉTONE.

Par **Itizo KASIWAGI.**

Reçu le 10 octobre 1927. Publié le 28 novembre 1927.

Le but de ce travail est (i) d'étudier l'influence du noyau furanique sur l'activité chimique du groupement carbonyle de quelques cétones furyliques saturées,(1) quand elles sont soumises à l'action des composés organomagnésiens, et (ii) d'appliquer le resultat ainsi obtenu pour constater la constitution de la furylidène-méthyléthylcétone.

Quant à l'action des composés organomagnésiens sur les dérivés furaniques, Douris a fait réagir l'halogénure d'éthylmagnésium sur le furfural,(2) et il a obtenu le furyl-éthyl-carbinol. Asahina et ses élèves ont préparé des cétones furyliques correspondant à la formule

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(1) Sur la terminologee voir ce journal, 1 (1926), 147.

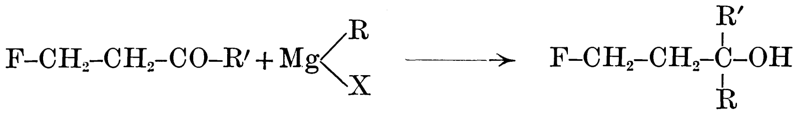
(2) *Compt. rend.*, 157 (1913), 722.

$F\text{-}CO\text{-}R$(1)

à partir de la pyromuconitrile et des composés organomagnésiens.(2) Plus tard R. Adams en collaboration avec J. S. Pierce a obtenu le furyl-éthyl-carbinol et le furyl-n-butyl-carbinol par l'action des composés alcoylmagnésiens sur le furfural.(3)

D'après ces études, il semble que les composés organomagnésiens réagissent normalement sur les dérivés furaniques, comme le furfural et la pyromuconitrile - c'est à dire que le noyau a peu d'influence sur le groupement carbonyle, et que celui-ci retient sa fonction vis-à-vis des composés organomagnésiens.

De notre expérience nous avons pu tirer la même conclusion : les furyl-éthyl-alcoyl-cétones et ses dérivés donnent avec les composés organomagnésiens les alcools tertiaires

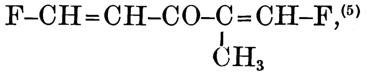


$$F\text{-}CH_2\text{-}CH_2\text{-}CO\text{-}R' + Mg\begin{matrix}R\\X\end{matrix} \longrightarrow F\text{-}CH_2\text{-}CH_2\text{-}\overset{R'}{\underset{R}{C}}\text{-}OH$$

Le rendement a été toujours satisfaisant. Dans ce mémoire les cétones non-saturées du type $F\text{-}CH{=}CH\text{-}CO\text{-}R$ sont exclues, car le groupement carbonyle voisin d'une double liaison réagit différemment que celui des cétones saturées, et nous reviendrons ailleurs sur ce sujet.

La tendance à se deshydrater des alcools ainsi obtenus croit avec les poids moléculaires, et elle est considérable chez les alcools ayant une chaine ramifiée en position α du groups hydroxylé. Nous y reviendrons plus loin.

En ce qui concerne la constitution de la furylidène-méthyléthylcétone que nous avons obtenue en condensant le furfural avec la méthyléthylcétone sous l'action de l'alcali caustique(4) à coté du dérivé bifurylique



$$F\text{-}CH{=}CH\text{-}CO\text{-}\underset{CH_3}{C}{=}CH\text{-}F,$$(5)

nous avons adopté *provisoirement* la constitution suivante :

$$F\text{-}CH{=}CH\text{-}CO\text{-}CH_2\text{-}CH_3$$

simplement à cause de son analogie avec la benzaldéhyde, qui, d'après Harries et Müller,(6) donne avec la méthyléthylcétone en *présence de l'alcali caustique* la phényl-1-pentène-1-one-3 :

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(1) Ce journal, 2 (1927), 110.

(2) *Arch. Pharm.*, 252 (1914), 341.—*Jour. Pharm. Soc. Japan*, 447 (1919). 357.

(3) *J. Am. Chem. Soc.*, 47 (1925), 1100 et 1102.

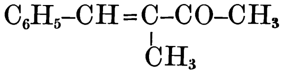
(4) Ce journal 1 (1926), 92.

(5) Recemment nous avons réussi á faire cristalliser ce corps. Ce fait indique que les atomes d'hydrogène des deux cotés du carbouyle de la cétone condensante sont remplaçables.

(6) *Ber.*, 35 (1902), 967.

$$C_6H_5\text{-}CH{=}CH\text{-}CO\text{-}CH_2\text{-}CH_3,$$

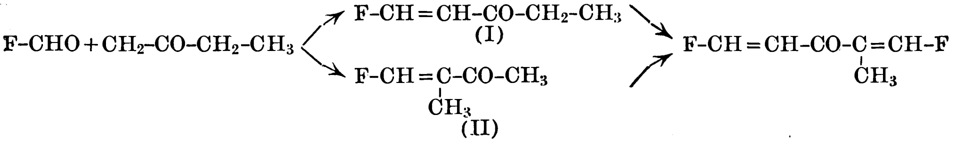
tandis qu'elle forme, au contraire, *avec le chlorure d'hydrogène* comme catalyseur la phényl-4-méthyl-3-butène-3-one-2 :



$$C_6H_5\text{-}CH{=}\underset{\displaystyle CH_3}{C}\text{-}CO\text{-}CH_3$$

isomère de la première.

Quant au furfural, nous avons préféré l'alcali caustique comme agent de condensation au chlorure d'hydrogène, car celui-ci ouvrirait le noyau furanique.(1) L'aldéhyde réagira sur la méthyléthylcétone de duex façons possibles:

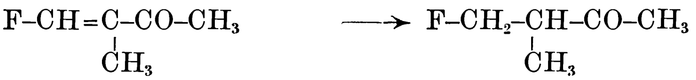


$$F\text{-}CHO + CH_2\text{-}CO\text{-}CH_2\text{-}CH_3 \begin{cases} \nearrow F\text{-}CH{=}CH\text{-}CO\text{-}CH_2\text{-}CH_3 \ \text{(I)} \\ \searrow F\text{-}CH{=}\underset{\displaystyle CH_3}{C}\text{-}CO\text{-}CH_3 \ \text{(II)} \end{cases} \longrightarrow F\text{-}CH{=}CH\text{-}CO\text{-}\underset{\displaystyle CH_3}{C}{=}CH\text{-}F$$

A quelle formule des deux (I) ou (II) correspond la furylidène-méthyléthylcétone que nous avons préparée ? Pour y répondre, voici l'explication de la réaction précédente : étant hydrogénée par l'amalgame de mercure, la furylidène-méthyléthylcétone donne la dihydrofurylidène-méthyléthylcétone, réaction représentée par une des formules suivante :

$$F\text{-}CH{=}CH\text{-}CO\text{-}CH_2\text{-}CH_3 \longrightarrow F\text{-}CH_2\text{-}CH_2\text{-}CO\text{-}CH_2\text{-}CH_3 \qquad \text{(III)}$$

ou

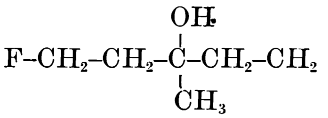


$$F\text{-}CH{=}\underset{\displaystyle CH_3}{C}\text{-}CO\text{-}CH_3 \longrightarrow F\text{-}CH_2\text{-}\underset{\displaystyle CH_3}{CH}\text{-}CO\text{-}CH_3$$

(IV)

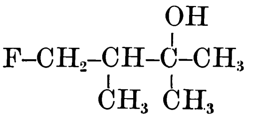
Le dihydrure ainsi obtenu(2) doit être l'un ou l'autre (III) ou (IV).

Comme nous l'avons écrit plus haut, ce dihydrure réagit normalement avec les composés organomagnésiens : l'iodure de méthyle donne le dihydrofurylidène-*diméthyl*-éthylcarbinol, tandis que le bromure d'éthyle le transforme en dihydrofurylidène-méthyl-*diéthyl*-carbinol. Le premier alcool a une constitution répondant à l'une des deux formules ci-desous :



$$F\text{-}CH_2\text{-}CH_2\text{-}\overset{\displaystyle OH}{\underset{\displaystyle CH_3}{C}}\text{-}CH_2\text{-}CH_2$$

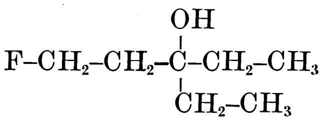
(V) ou



$$F\text{-}CH_2\text{-}\underset{\displaystyle CH_3}{CH}\text{-}\overset{\displaystyle OH}{\underset{\displaystyle CH_3}{C}}\text{-}CH_3$$

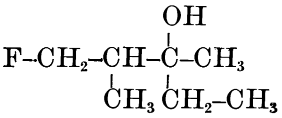
(VI)

et le second à (VII) ou (VIII) :



$$F\text{-}CH_2\text{-}CH_2\text{-}\overset{\displaystyle OH}{\underset{\displaystyle CH_2\text{-}CH_3}{C}}\text{-}CH_2\text{-}CH_3$$

(VII) ou



$$F\text{-}CH_2\text{-}\underset{\displaystyle CH_3}{CH}\text{-}\overset{\displaystyle OH}{\underset{\displaystyle CH_2\text{-}CH_3}{C}}\text{-}CH_3$$

(VIII)

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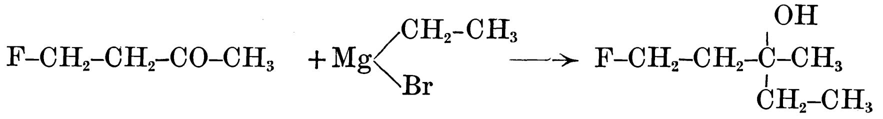
(1) W. Marckwald, *Ber.*, **20** (1887), 2813; E. A. Kehrer et E. Hofacker, *Ann.*, **294** (1897), 163; E. A. Kehrer et P. Igler. *Ber.*, **32** (1899), 1176; Thiele et Landers, *Ann.*, **369** (1909) 300.

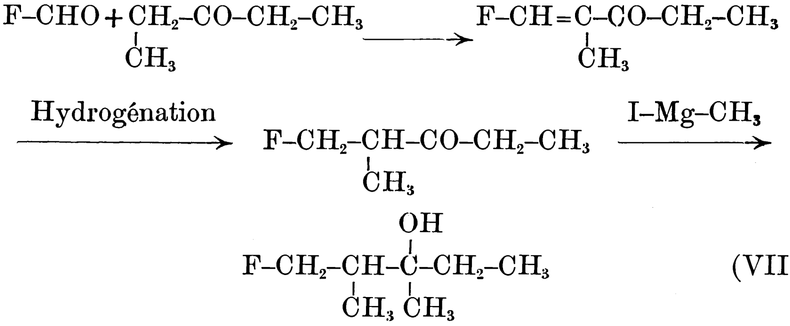
(2) Ce journal, **1** (1927), 93.

Cependant on peut préparer l'alcool exactement de la formule (V) à partir de la furylbutanone et du bromure d'éthyle :



$$F\text{-}CH_2\text{-}CH_2\text{-}CO\text{-}CH_3 + Mg\begin{cases}CH_2\text{-}CH_3\\ Br\end{cases} \longrightarrow F\text{-}CH_2\text{-}CH_2\text{-}\underset{\underset{CH_2\text{-}CH_3}{|}}{\overset{\overset{OH}{|}}{C}}\text{-}CH_3 \qquad (V')$$

De plus on peut obtenir facilement aussi le composé (VIII) similairement que (V'), à partir de la furyl-1-méthyl-2-penténone-3, qui est formée par condensation du furfural avec la diéthylcétone⁽¹⁾ :



$$F\text{-}CHO + \underset{\underset{CH_3}{|}}{CH_2}\text{-}CO\text{-}CH_2\text{-}CH_3 \longrightarrow F\text{-}CH{=}\underset{\underset{CH_3}{|}}{C}\text{-}CO\text{-}CH_2\text{-}CH_3$$

$$\xrightarrow{\text{Hydrogénation}} F\text{-}CH_2\text{-}\underset{\underset{CH_3}{|}}{CH}\text{-}CO\text{-}CH_2\text{-}CH_3 \xrightarrow{I\text{-}Mg\text{-}CH_3}$$

$$F\text{-}CH_2\text{-}\underset{\underset{CH_3}{|}}{CH}\text{-}\underset{\underset{CH_3}{|}}{\overset{\overset{OH}{|}}{C}}\text{-}CH_2\text{-}CH_3 \qquad (VIII')$$

Pour comparer les composés donnés plus haut, voici le résultat expérimental:

TABLE 1.

Substance	Points d'ébullition	d_4^{25}	n_D^{26}	Réfraction moléculaire	
				calc.	trouv.
(V) ou (VI)	82.5° sous 3.5 mm.	0.9923	1.4779	48.42	47.92
(VII) ou (VIII)	90-91.5° sous 3 mm.	0.9892	1.4800	53.03	42.26
(V')	83.5-84.5° sous 2 mm.	0.9926	1.4780	48.42	47.91
(VIII')	93° sous 3.5 mm.	0.9895	1.4800	53.03	52.25
Tous les composés sont incolores et possèdent une odeur camphrée très agréables, qai ne permet pas de les distinguer.					

La phényluréthane formée avec l'isocyanate de phényle sur (V) ou (VI) fond à 91–91.5°, et celle de (V') à 84–84,5°, tandis que le mélange des deux fond déjà vers 70°. Cependant les uréthanes de (VII) ou (VIII) et de (VIII') ne se forment pas avec la même facilité que celles de (V) ou (VI) et de (V'), mais les alcools perdent une molécule d'eau, qui donne, avec l'isocyanate de phényle, la diphénylurée symétrique.

Ainsi on établit que l'alcool obtenu de la dihydrofurylidène-méthyléthylcétone avec le bromure d'éthylmagnésium soit le composé (VIII), et non le

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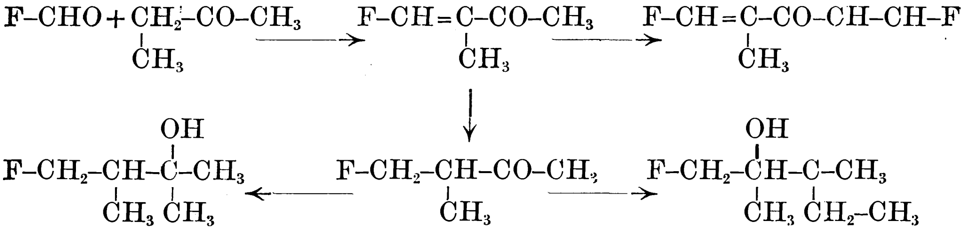
(1) Loc. cit.

composé (VII). Par consequent, la furylidène-méthyléthylcétone est la méthyl-2-furyl-1-butène-1-one-3 répondant à la formule (II). On peut donner ci-dessous comme résumé le cours des réactions que la furylidène-méthyléthylcétone subit :



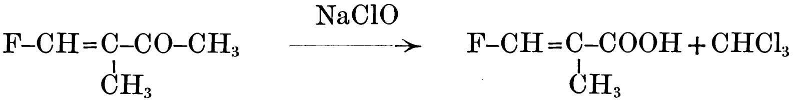
$$\begin{tikzcd}
F\text{-}CHO + \underset{CH_3}{CH_2}\text{-}CO\text{-}CH_3 \arrow[r] & F\text{-}CH{=}\underset{CH_3}{C}\text{-}CO\text{-}CH_3 \arrow[r] \arrow[d] & F\text{-}CH{=}\underset{CH_3}{C}\text{-}CO\text{-}CH\text{-}CH\text{-}F \\
F\text{-}CH_2\text{-}\underset{CH_3}{CH}\text{-}\overset{OH}{\underset{CH_3}{C}}\text{-}CH_3 & F\text{-}CH_2\text{-}\underset{CH_3}{CH}\text{-}CO\text{-}CH_3 \arrow[l] \arrow[r] & F\text{-}CH_2\text{-}\underset{CH_3}{CH}\text{-}\overset{OH}{\underset{CH_2\text{-}CH_3}{C}}\text{-}CH_3
\end{tikzcd}$$

différent que (V′) identique à (VIII′)

De plus on arriva aux même conclusions, quand on oxyde la furylidène-méthyléthylcétone par l'hypochlorite. C'est la méthode d'après laquelle Ludwig Diehl et Alfred Einhorn préparèrent en 1885 l'acide cinnamylidène-acétique et ses dérivés à partir de la cinnamylidène-acétone et de ses dérivés.(1) J'ai trouvé la méthode applicable également à la série furanique, p. e. la furylidène-acétone s'oxyde en furylacrylique et chloroforme :

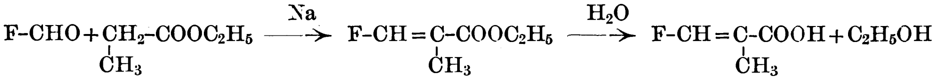
$$F\text{-}CH{=}CH\text{-}CO\text{-}CH_3 \xrightarrow{NaClO} F\text{-}CH{=}CH\text{-}COOH + CHCl_3$$

Les composés aromatiques contenant CH_3 lié au carbon voisin du groupement acétyle se comportent d'une façon analogue, en donnant les acides α-méthyles.(2) La furylidène-méthyléthylcétone, identique à la furyl-méthylbuténone, donnerait naissance à l'acide méthyl-α-acrylique :



$$F\text{-}CH{=}\underset{CH_3}{C}\text{-}CO\text{-}CH_3 \xrightarrow{NaClO} F\text{-}CH{=}\underset{CH_3}{C}\text{-}COOH + CHCl_3$$

En vérité la réaction semble avoir eu lieu suivant la formule, mais la cétone s'est décomposée plus profondément, et, par conséquent, le rendement en était pauvre. Pour l'identification, nous avons préparé ce même acide en condensant le furfural avec le propionate d'éthyle sous l'action de sodium métallique suivant la méthode donnée par Claisen qui prépara le furylacrylate d'éthyle à partir du furfural et de l'acétate d'éthyle(3):



$$F\text{-}CHO + \underset{CH_3}{CH_2}\text{-}COOC_2H_5 \xrightarrow{Na} F\text{-}CH{=}\underset{CH_3}{C}\text{-}COOC_2H_5 \xrightarrow{H_2O} F\text{-}CH{=}\underset{CH_3}{C}\text{-}COOH + C_2H_5OH$$

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(1) *Ber.*, 18 (1885), 2325.

(2) R. Stoermer et R. Wehln, *Ber.*, 35 (1902), 3551; K. Iwamoto, ce journal, 2 (1927), 54.

(3) Claisen, *Ber.*, 24 (1891), 143.

Le mélange des deux acides ainsi obtenus fond à la même température que les deux, mais le mélange du premier acid et de l'acide furylacrylique fond beaucoup plus bas.

En résumé, il est remarquable que le furfural se comporte différemment que la benzaldéhyde pour la condensation avec la butanone, et ceci est attribuable aux propiétés différentes des noyaux furanique et benzénique.

Partie experimentale.

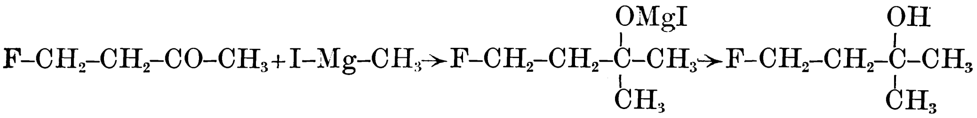
Action de l'iodure de méthylmagnésium sur la furylbutanene.—Dans un ballon muni d'un réfrigérant reversible, on introduit 1,5 gr. de magnésium et de l'éther, puis on fait tomber goutte à goutte l'iodure de méthyle. Quand le métal a entirèrement disparu, on ajoute peu à peu 6 gr, de furylbutanone dissoute dans de l'éther. On chauffe ensuite à l'ébullition pendant quelques heures, et, après avoir refroidi, on décompose le produit de réaction, en le versant sur une solution glacée de chlorure d'ammoniaque. On lave la solution éthérée avec de l'eau et on la sèche sur du sulfate de sodium anhydre. En fractionnant sous pression de 12 mm., on a obtenu 5 gr. d'huile incolore, bouillant à 99–102° qui est douée d'une odeur camphrée très agréable. Cette huile bout à 93.5–94° sous 8 mm.

Analyse. Trouvé : $C=69.71$ $H=9.09\%$ Calc. pour $C_9H_{14}O_2$:
$C=70.12$ $H=9.11\%$

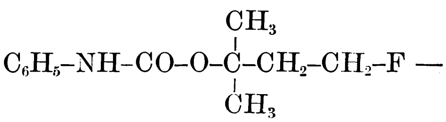
Réfraction moléculaire. $d_4^{25}=0.9972$, $n_D^{25}=1.4745$ (Abbe).

R. M. : trouvée, 43.44. Calc. pour $C_9H_{14}O^{<}O'F_2$, 43.80. Dépression, 0.36.

La réaction a donc marché normalement :

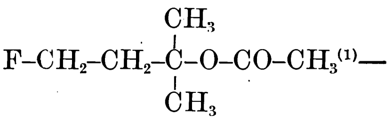


$$F\text{-}CH_2\text{-}CH_2\text{-}CO\text{-}CH_3 + I\text{-}Mg\text{-}CH_3 \rightarrow F\text{-}CH_2\text{-}CH_2\text{-}\overset{OMgI}{\underset{CH_3}{C}}\text{-}CH_3 \rightarrow F\text{-}CH_2\text{-}CH_2\text{-}\overset{OH}{\underset{CH_3}{C}}\text{-}CH_3$$



Phénluréthane de cet alcool, $C_6H_5\text{-}NH\text{-}CO\text{-}O\text{-}\overset{CH_3}{\underset{CH_3}{C}}\text{-}CH_2\text{-}CH_2\text{-}F$ — Elle s' obtient en chauffant le melange équimoléculaire de cet alcool et d'isocyanate de phényle pendant quelques heures. Recristallisée dans de l'alcool, on a plaques tétragonales, incolores, fondant à 126.5–127°.

Analyse. Trouvé : $N=4.9\%$ Calc. pour $C_{16}H_{19}O_3N$: $N=5.1\%$



Acétate, $F\text{-}CH_2\text{-}CH_2\text{-}\overset{CH_3}{\underset{CH_3}{C}}\text{-}O\text{-}CO\text{-}CH_3$(1)—Une huile d'odeur rance, bouillant à

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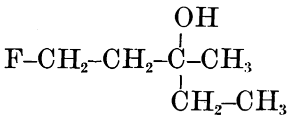
(1) D'après le méthode de J. Houben (*Ber.*, 39 (1906), 1736).

83–85 sous 3 mm. Rendement pauvre. $d_4^{25}=1{,}0188$ $n_D^{25}=1{,}4583$.

Action du bromure d'éthylmagnésium sur la furylbutanone.—La furylbutanone est traitée similairement par le bromure d'éthylmagnésium, et on en a obtenu une huile incolore bouillant à 83.5–84.5° sous 2 mm. Cette huile possède une odeur agréable cemme la précédente.

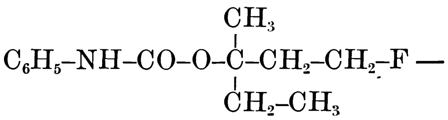
Analyse. Trouvé: C=71.15, H=9.71%. Calc. pour $C_{10}H_{16}O_2$:
C=71.43, H=9.42%

Réfraction moléculaire. $d_4^{25}=0.9926$, $n_D^{25}=1.4780$,
R. M.: trouvée, 47.91. Calc. pour $C_{10}H_{16}O'O'\,\digamma_2$, 48.42. Dépression 0.51.
Cett substance est donc le furyl-1-méthyl-3-pentanol-3,



$$\text{F--CH}_2\text{--CH}_2\text{--}\overset{\text{OH}}{\underset{\text{CH}_2\text{--CH}_3}{\text{C}}}\text{--CH}_3$$

que nous avons numéroté (V′).

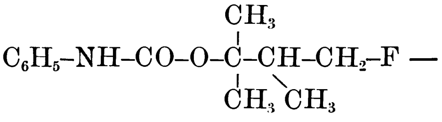
Phénooluréthane,  $C_6H_5\text{--NH--CO--O--}\overset{\text{CH}_3}{\underset{\text{CH}_2\text{--CH}_3}{\text{C}}}\text{--CH}_2\text{--CH}_2\text{--F}$ — Aiguilles fines blanches, fusible à 84.5–85°, et cristallisable dans l'alcool.

Action de l'iodure de methylmagnésium sur la dihydrofurylidène-méthyléthylcétone.—Dans un mémoire précédent, j'ai montré la méthode d'obtenir la furylidène-méthyléthylcétone ainsi que son dihydrure.(1) A partir de celui-ci nous avons obtenu au moyen de l'iodure de méthyimagnésium un alcool, dihydrafurylidène-*diméthyl*-éthyl-carbinol, que nous avons numéroté (V) ou (VI). On a 7 gr. de cet alcool de 9 gr. de la cétone.

Analyse. Trouvé: C=71.27, H=9.29%. Calc. pour $C_{10}H_{16}O_2$:
C=71.43, H=9.52%.

Réfraction moléculaire. $d_4^{25}=0.9923$, $n_D^{25}=1.4779$.
R. M.: trouvée, 47.92. Calc. pour $C_{10}H_{16}O\,O'\,\digamma_2$, 48.42. Dépression, 0.50.

Cet alcool est une huile incolore douée d'une odeur camphrée agréable. Le point d'ébullition est 82.5° sous 3.5 mm.

Phényluréthane,  $C_6H_5\text{--NH--CO--O--}\overset{\text{CH}_3}{\underset{\text{CH}_3}{\text{C}}}\text{--}\underset{\diagdown\,\text{CH}_3}{\text{CH}}\text{--CH}_2\text{--F}$ — Poudre blanche, fusible à 91–91.5°. Cristallisable dans l'alcool.

Action du bromure d'éthylmagnésium sur la dihydrofurylidène-méthyléthylcétone.—Ayant traité similairement le dihydrure avec le bromure d'éthylmagnésium, nous avons obtenu un alcool, dihydrofurylidène-méthyl-*diéthyl*-carbinol, qui a été numéroté (VII) ou (VIII). Cet alcool est

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(1) Loc. cit.

une huile sans couleur, bouillant à 90–91.5° sour 3 mm. et douée d'une odeur semblable aux précédentes.

Analyse. Trouvé: $C = 72.47$, $H = 9.83\%$. Calc. pour $C_{11}H_{18}O_2$:
$C = 72.53$, $H = 9.89\%$.

Réfraction moléculaire. $d_4^{25} = 0.9892$, $n_D^{25} = 1.4800$.

R. M.: trouvée, 52.26. Calc. pour $C_{11}H_{18}O{}^{\backprime}O' \ulcorner_2$, 53.03. Dépression, 0.77.

Action de l'isocyanate de phényle sur cet alcool,—Cet alcool ne forme pas l'uréthane avec l'isocyanate de phényle comme ses homologues inférieurs, mais il perd une molécule d'eau, qui forme avec l'isoeyanate de phényle la diphénylurée symétrique. Nous n'avons pas encore réussi à obtenir la phényluréthane, même quand nous avons fait réagir les deux réactifs dans la solution d'éther de pétrole de laquelle s'est déposé la diphénylurée.

Action de l'iodure de methylmagnésium sur la furyl-méthyl-pentanone.—La furyl-1-méthyl-2-pentanone-3 donne avec l'iodure de méthylmâgnésium un alcool, furyl-1-diméthyl-2.3-pentanol-3, désigné par (VIII′). Il est une huile d'odeur très agréable, bouillant à 93° sous pression de 3.5 mm. peu près constamment.

Analyse. Trouvé: $C = 62.67$, $H = 10.40\%$. Calc. pour $C_{11}H_{18}O_2$:
$C = 72.53$, $H = 9.89\%$.

Réfraction moléculaire. $d_4^{25} = 0.9895$, $n_D^{25} = 1.4800$.

R. M.: trouvée, 52.25. Calc. pour $C_{11}H_{19}O{}^{\backprime}O' \ulcorner_2$, 53.03. Dépression, 0.78.

Action de l'isocyanate de phényle sur cet alcool,—Il ne forme pas l'uréthane avec l'alcool ainsi obtenu ni directement ni en milieu d' éther de pétrole, mais il deshydrate l'alcool, en donnant la diphénylurée symétrique.

Oxydation de la furyl-buténone par l'hypochlorite de sodium. On chauffe un mélange de furyl-buténone et d'une solution aqueuse d' hypochlorite de sodium formé par le chlorure de chaux et le carbonate de sodium jusqu'au moment où le chloroforme finit de se dégager. La buténone se dissout dans la solution comme l'oxydation se poursuit. Le chauffage dure presque une heure. Ayant été refroidie et filtrée, la solution est acidulée par le gas SO_2, en déposant une masse blanche qui fond à 139.5–140°, après avoir été recristallisée dans de l'eau chaude. On a 60 pour 100 du rendement théorique.

Analyse. Trouvé: $C = 60.87$, $H = 4.28\%$. Calc. pour $C_7H_6O_3$:
$C = 60.87$, $H = 4.35\%$.

Cette substance est donc l'acide furyl-acrylique, $F{-}CH{=}CH{-}COOH$.

Oxydation de la furylidène-méthyléthylcétone par l'hypochlorite de sodium.—Nous avons montré que la furylbuténone s'oxyde facilement en acide furyt-acrylique par l'hypochlorite de sodium. La furylidène-méthyléthylcétone, son homologue, est donc soumise à l'oxydation à la même façon.

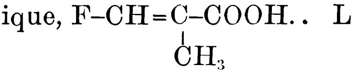
On la chauffe avec une solution d'hypochlorite pendant deux heures, et on a une masse grise, fondant à 86° environ. Fn décolorant avec du noir animal et en recrystallisant dans de l'eau chaude, on a une masse cristalline sans couleur, fusible à 110.5–111°. Rendement très pauvre.

Pour établir la constitution de cette substance, nous avons mesuré les points de fusion pe ses mélanffes avec les échantillons de constitutions connues.

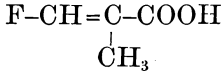
1° Un mélange avec de l'acide furylacrylique s'est ramoli déjà vers 90° et a fondu complètement à 130°.

2° Un autre avec de l'acide furyl-méthyl-α-acrylique fond à 114–115°.

Ainsi nous avons pu constater que ce produit d'oxydation est identique à l'acide furyl-méthyl-α-acrylique, $F{-}CH{=}\underset{\substack{|\\ CH_3}}{C}{-}COOH$.. L'acide furyl-méthyl-$\alpha$-acrylique que nous sommes servi pour constater de la constitution est obtenu à la façon suivante.

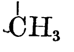


Acide furyl-méthyl-α-arylique, $F{-}CH{=}\underset{\substack{|\\ CH_3}}{C}{-}COOH$ D'après la méthode de Claisen,[1] pour préparer l'éther-sel d'acide furyl-acrylique par la condensation du furfural avec l'acétate d'éthyle, on met un atome de sodium métallique dans cinq molécules d'éther-sel propionique refroidis dans de l'eau glacée, et on fait tomber goutte à goutte une molécule de furfural. Ayant abondonné pendant la nuit, on décompose le produit de réaction, en ajoutant une molécule d'anhydride acétique. On le lave avec du carbonate de sodium, et avec de l'eau, et on le sèche avec du sulfate de sodium. Par réctification on a une huile bouillant à 103–104° sous 4.5 mm.



Analyse. Trouvé : $C=66.75$, $H=6.97\%$. Calc. pour $C_{10}H_{12}O_3$: $C=66.67$, $H=5.67\%$.

Cette substance est donc le furyl-méthyl-α-acrylate d'éthyle, $F{-}CH{=}\underset{\substack{|\\ CH_3}}{C}{-}COOC_2H_5$ et possède la propriété optique suivante :



Réfraction moléculaire. $d_4^{25}=1.0800$, $n_D^{25}=1.5418$.

R. M. : trouvée, 52.44. Calc. pour $C_{10}H_{12}O''O^{<}_{2}\ulcorner_3$, 48.08. Exaltation, 4.36.

L'exaltation considérable est bien concordante avec la constitution de l'éther-sel.

Par saponification avec de la potasse alcoolique, on a l'acide libre, aiguilles blanches fines, et fusibte à 115–115.5°. Par recristallisation dans de l'eau chaude, il fond à 116°.

Analyse. Trouvé : $C=63.63$, $H=5.84\%$. Calc. pour $C_8H_8O_3$: $C=63.16$, $H=5.26\%$.

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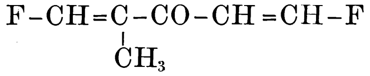
(1) Loc. cit.

On s'est servi de cet acide pour l'identificotion pour l'acide, produit d'oxydation de la furylidène-méthyléthylcétone.

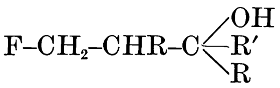
Difuryl-1·5-méthyl-2-pentadièn-1·4-one-3, 
$F-CH=\underset{\displaystyle CH_3}{\underset{|}{C}}-CO-CH=CH-F$

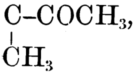
En enlevant la furylidène-méthyléthylcétone(1) par distillation, on a un résidu visqueux. Jusqu'à ce moment nous n'avons pas pu le cristalliser. Mais par distillation soignée, on sépare complètement si possible la cètone monofurylée que le résidu, en évitant même le signe de décomposition par surchauffage. Le résidu, étant abondonné dans une glacière, va cristalliser, et ensuite on met la masse cristallisée sur une plaque poreuse. On a des prismes jaunes, fusibles à 61°.

Analyse. Trouvé : $C=73.14$, $H=5.31\%$. Calc. pour $C_{14}H_{12}O_3$:
$C=73.68$, $H=5.26\%$.

Cette substance est recristallisable dans l'alcool éthylique, et se brunit à la longue.

Résumé.

1. Les composés du type $F–CH_2–CHR–CO–R'$ se comportent normalement, quand ils sont soumis à l'action des composés organomagnésiens, en donnant les alcools tertiaires du type 
$F–CH_2–CHR–C\begin{smallmatrix}\diagup OH\\ \leftarrow R'\\ \diagdown R\end{smallmatrix}$

2. La furylidène-méthylcétone, produit de condensation du furfural avec la méthyléthylcétone, est trouvée répondre à la formule F–CH= 
$F–CH=\underset{\displaystyle CH_3}{\underset{|}{C}}–COCH_3$, et non pas à $F–CH=CH–CO–CH_2–CH_3$.

3. Les cétones furyliques non saturées, $F–CH=CR–CO–CH_3$ sent oxydable par l'acide hypochloreux en milieu alcalin en acides furyl-acryliques, $F–CH=CR–COOH$.

4. Le furfural condense avec le propionate d'éthyle en présence de sodium métallique en acide furyl-méthyl-α-acrylique.

5. La difuryl-méthyl-penta-diénone a été isolée du résidu que l'on obtient du produit de condensation du furfural avec la méthyléthylcétone duquel on a enlève la furylidène-méthyléthylcétone.

Haute ecole polytechnique de Yokohama.

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(1) Loc. cit.

THE ESTIMATION OF GOLD AND SILVER IN SEA WATER.

By **Mataichi YASUDA.**

Received October 27, 1927. Published December 28, 1927.

In regard to the estimations of gold and silver in sea water, the method of Sonstadt(1) was published at the early time and at present this method is still used frequently. In recent time H. Koch(2) and F. Haber(3) have published new methods. Of course, it seems to be very excellent. But, I thought, some skillness is necessary to carry out their methods and to obtain some reliable results.

I tried to estimate the gold and the silver by an old method of Scheibler(4) by notice of Dr. S. Iimori, and modified it by adding mercuric chloride solution and reduced them with metallic magnesium and concentrated hydrochloric acid. By this treatment the mercury deposits in fine metallic particles which catch all the gold and the silver as amalgams. It seems to be very excellent in the point that the metals obtained as heavy black precipitates.

Prof. Dr. P. P. Weimarn suggested that the gold in the sea water should be exist in the following states: (1) from colloidal to suspensoid, (2) metallic state in quartz and other earths, (3) gold in the organic colloids, (4) dissolved ionic states of trivalent as $Au^{\cdot\cdot\cdot}$, (5) the same of monovalent as $Au^{\cdot}$. H. Koch thought, also, that the gold in sea water exists as ionic states, though it once changes to submicron particles by some organic reducing agents, it should be, again, convert into ionic state by oxidation. It is supposed that the cupric and the ferric ions exist in the sea water serves as the oxidising agent. My analytical method, however, can estimate all of the gold except that in the organic colloids. The detail of the method is given in the followings.

Two litres of sea water to be examined is taken into a separating funnel of 2.5 litres capacity, and add 4–5 grams of powdered or shaved metallic magnesium. The magnesium must, previously, be freed from any oily contaminations, by washing with ether two or three times, because the commercial magnesium is usually contaminated with machine oils etc. Then add 20 c.c. of 0.05 mol per litre solution of mercuric chloride, and 40 or 50

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(1) Sonstadt, *Chem. News*, 74 (1896), 316.

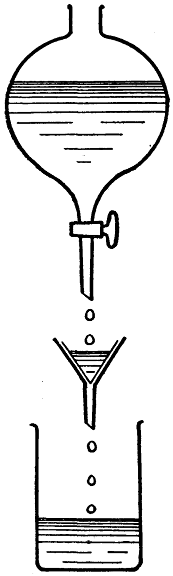
(2) H. Koch, *Kolloid Z.*, 22 (1918), 1.

(3) F. Haber, *Z. angew. Chem.*, 40 (1927), 303.

(4) Scheibler, *Ber.*, 2 (1869), 2. Villiers and Borg, *Compt. rend.*, 116 (1893), 1524.

c.c. of strong hydrochloric acid (38% HCl). Now strong effervescence takes place with the evolution of the hydrogen gas, and deposits the white mercurous chloride at once. The deposition, however, gradually change to grey colour by the formation of the metallic mercury. The fine particles of the mercury settle down catching all of the gold and silver as amalgams.

After the reactions has finished, the heavy black precipitate is filtered. The filtration is performed in the manner shown in the accompanied figure. When emptied, the separating funnel is washed once more with water and alcohol to remove all of the black matter.



The filter paper obtained by this way contains all of the amalgam of the precious metals, it dried and burnt, and enclosed the obtained ashes with pure lead sheet and put in a small crucible. Next heat the crucible with gas flame adding two grams of gold and silver free lead oxide to oxidize the remaining carbon, and to absorb the precious metals into the lead button. The button obtained by this way is cupelled on the bone ash in the muffle, and a small bead is obtained. The bead is weighed with a balance of 0.001 mg. sensibility, and then is taken into a small glass dish of 15 mm. diameter.

If the colour of the bead is white it is dissolved directly in a drop of nitric acid (specific gravity, 1.26). If the colour of the bead is yellow or yellowish green, it is dissolved in a drop of mercury (free from gold and silver, of course), and then is dissolved in a drop of nitric acid. The gold remains in a form of black powder by such treatment. Next dip the small dish into a large white porcelain dish filled with distilled water, and moved it by means of a small pincette coated with celluloid, to dissolve out the silver and the mercury nitrate, to and fro, up and down, in the water until the black residue of gold is purified sufficiently. It happens frequently, during this treatment, that the black residue floats out from the small dish. In such a case the black residue is collected with a small dust-pan with long handle made of white celluloid and a small feather under the observation by a lens, and then transfered into the small dish.

By this way all of the gold can be collected in the small dish, which is then evaporated to dryness, and heated to 250°C. After cooled in a desiccator, it is weighed. The heating should begin slowly, for otherwise the gold residue sometimes spring out and lost.

The blank tests of the method have been carried out on three percent solution of sodium chloride, in which the known quantities of gold chloride had been added. The results are shown in the following table.

TABLE 1.

Gold added in 3% NaCl solution (gr.)	Gold obtained (gr.)		Content of gold in the solution (mg. per cubic meter)
	I	II	
0.0000140	0.0000157	0.0000139	4.6
0.0000320	0.0000316	0.0000300	10.6
0.0000512	0.0000507	0.0000522	17.0

By this method I have estimated the gold and the silver in Japanese sea waters, and obtained the following results.

TABLE 2.

Place where the water was taken	One cubic meter of sea water contains	
	gold	silver
Kominato Bay	10. mg.	70. mg.
Kagoshima Bay	20. mg.	20. mg.
Sagami-Nada	3. mg.	—

Kominato Bay, a small sea port of Pacific coast south eastern way from Tokyo, 74 km. apart.

Kagoshima Bay, a gulf of south part of Kyûshû and there are city of Kagoshima and the volcano of Sakurajima.

Sagami-Nada, entrance sea of Tokyo Bay.

I am now endeavouring to estimate the precious metals in sea waters of the vicinity of Japan by the present method.

October 1927.

361 Ikejiri, Setagaya-machi,
near Tokyo.

SPECTROSCOPICAL STUDY OF AMINO-ACID ANHYDRIDES. II. LIGHT ABSORPTIONS OF SOME AMINO-ACIDS, THEIR ESTERS, PEPTIDES AND ANHYDRIDES.(1)

By **Yuji SHIBATA** and **Tei-ichi ASAHINA.**

Received November 24 1927. Published December 28, 1927.

In the preceding paper(2) we have described the results of spectrochemical studies on the constitution of some diketopiperazines, which are regarded, from the experimental and theoretical points of view of the recent protein chemistry, as the important fundamental molecules of protein substances. The conclusion, at which we have experimentally arrived, was that glycine anhydride, alanine anhydride and sarcosine anhydride are in the keto-form only, although they are often considered to take possibly the enolic form. Quite recently, however, E. Abderhalden and E. Schwab(3) have synthesised these compounds which have surely the enolic form, in using the other mode of preparation than those generally known.(4) This latter fact, that is to say, the new samples of diketopiperazines obtained by Abderhalden are not identical in their constitution with those hitherto known, seems to us to be in good accordance with our conclusion just mentioned.

In the present work, we have further carried out spectrochemical studies on various amino-acids, their esters, dipeptides and anhydrides. Among these compounds, tyrosine and phenylalanine containing chromophore groups in their molecules absorb selectively in ultraviolet: the absorption maximum of tyrosine exists at 3580 of frequency (Fig. 3), while those of phenylalanine are observed at 3780 and 3900 of frequencies (Fig. 1). These absorptions remain unchanged even when substitutions occur in the molecules of those amino-acids, so far as the substituents themselves contain no chromophores. Only phenylalanine anhydride shows an exceptional results : it has an end absorption only(5) and the characteristic absorption bands of phenylalanine are thus vanished on anhydride formation (Fig. 1).

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(1) Read before the annual meeting of the Chemical Society of Japan, April 5, 1927.

(2) This journal, **1** (1926), 71.

(3) *Z. physiol. Chem.*, **149** (1925), 100 & 298 ; **152** (1926) 80. Abderhalden, u. Gebelein, ibid., **152** (1926), 125.

(4) Compare E. Fischer, "Untersuchungen über Aminosäuren, Polypeptide und Proteine." Maillard, *Comp. rend.*, **153** (1911), 1078. Balbiano, *Ber.* **33** (1910), 2323; **34** (1911), 1501. K. Shibata, *Acta Phytochim.*, **2** (1925), 39.

(5) It is well known that diphenyl and triphenyl carbinol give no selective absorptions, although they contain two or more benzene nuclei in their molecules [Baly and Tuck, *J. Chem. Soc.*, **93** (1908), 1913. Baker, ibid., **91** (1907), 1495].

As for the absorption of tyrosine, we may expect that it will show an analogy with that of phenol, for the former contains phenol nucleus in its molecule. In fact, it was proved to be the case by Ward⁽¹⁾ and Blyth⁽²⁾ and further it was observed by Stenström and Reinhard⁽³⁾ that, when tyrosine and phenol were respectively dissolved in media with varying H-ion concentrations, the both substances display analogous changes in their extinction coefficients. Our present spectrochemical investigation confirmed too the results obtained by these authors.

Except tyrosine and phenylalanine, we have found that so far as our study concerns, there are neither amino-acids nor their derivatives which absorb selectively in any region of spectrum.

Experimentals.

Amino-acids.—*Glycocoll.* After careful recrystallisation from water, was studied in 1 mol solution in using the Adam-Hilger's quarz spectrograph; its spectrogram showed no selective absorption.

Alanine. Kahlbaum's synthetical pure material was recrystallised from water; its 0.1 mol solution gave no selective absorption.

Leucine. Crude *l*-leucine obtained by hydrolysis of gluten was recrystallised several times from water and dilute alcohol; 0.01 mol solution of this substance gave no selective absorption.

Phenylalanine. *l*-Phenylalanine obtained also by hydrolysis of gluten was purified as in the previous case; so purified sample showed the rotatory power $[\alpha]_D = -34°$, and absorption maxima at 3780 and 3900 of frequencies in 0.01 mol solution (Fig. 1). Synthetical racemic phenylalanine gave the identical absorption with the active body.⁽⁴⁾ The analogous phenomenon has previously been observed by one of the present authors (Y. Shibata) in the spectrochemical investigation of metallic complex salts; i.e., he found that the optically active cobalt-ammines absorb identically with their racemic modifications.

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(1) *Biochem. J.*, 17 (1923), 891.

(2) *J. Chem. Soc.*, 75 (1899), 1162.

(3) *J. Phys. Chem.*, 29 (1915), 1477.

(4) Racemic phenylalanine procured from Kahlbaum, when it was examined without any purification, gave thoroughly different absorption from the active substance (Fig. 2). On exhaustive extraction with ether we have obtained from this Kahlbaum's sample certain quantities of white non-nitrogenous substance with the melting point 132–133°. On removing this impurity, the racemic body showed quite the same absorption with the active compound (Fig. 6).

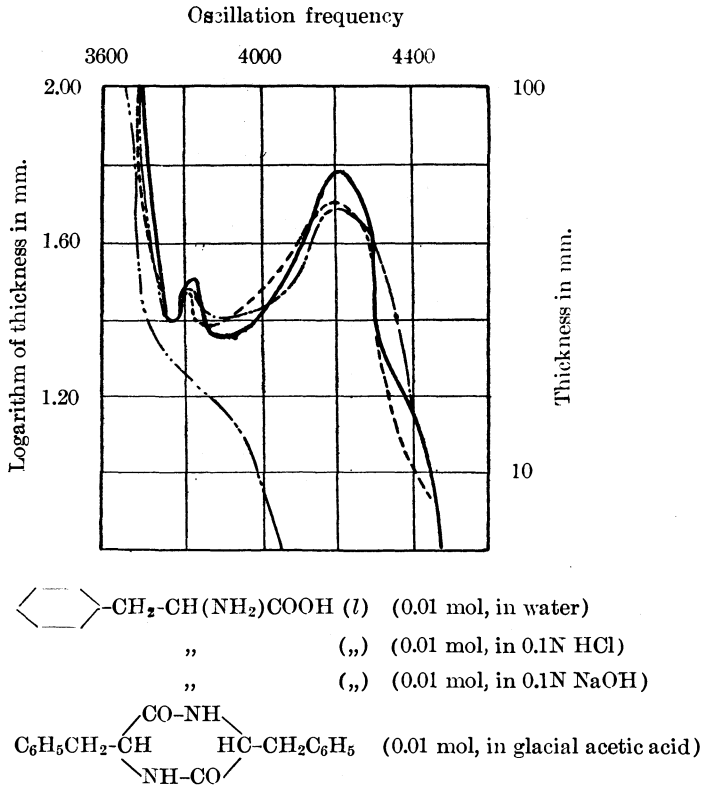

Fig. 1.

Tyrosine. *l*-Tyrosine was repeatedly recrystallised from water and examined; its absorption is mentioned in Fig. 3. It is known that, tyrosine shows, like phenol, different absorptions according to the varying P_H-value of the medium, especially in the alkaline side.⁽¹⁾ We have carried out, therefore, comparative studies between these two substances, both in 0.001 mol solution in 0.1 N sodium hydroxide and pure water. On changing the proportion between alkaline solution and water, i.e. on varying the P_H-value of the medium, shifts of absorption bands, quite parallel in both substances, were observed (Fig. 3, 4 and 5). It is obvious, therefore, that, the absorption of tyrosine is certainly due to the phenol nucleus in its molecule.

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(1) Stenström and Reinhard, loc. cit.

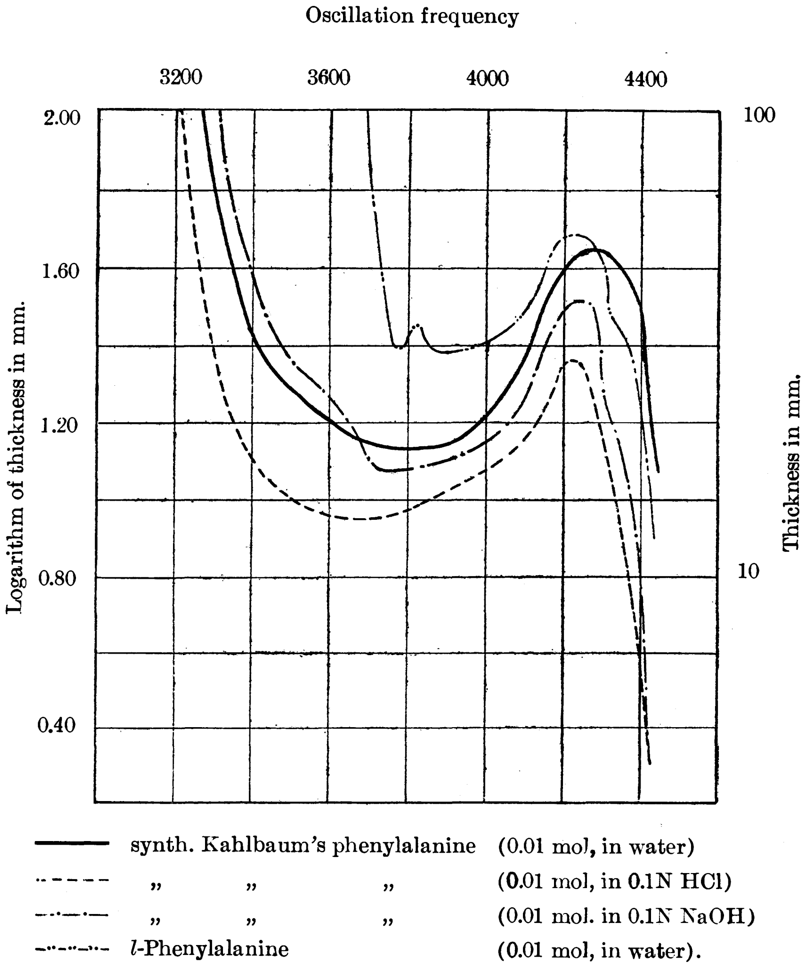
Oscillation frequency
3200
3600
4000
4400
2.00
1.60
1.20
0.80
0.40
Logarithm of thickness in mm.
100
10
Thickness in mm.
synth. Kahlbaum's phenylalanine (0.01 mol, in water)
" " " (0.01 mol, in 0.1N HCl)
" " " (0.01 mol. in 0.1N NaOH)
l-Phenylalanine (0.01 mol, in water).

Fig. 2

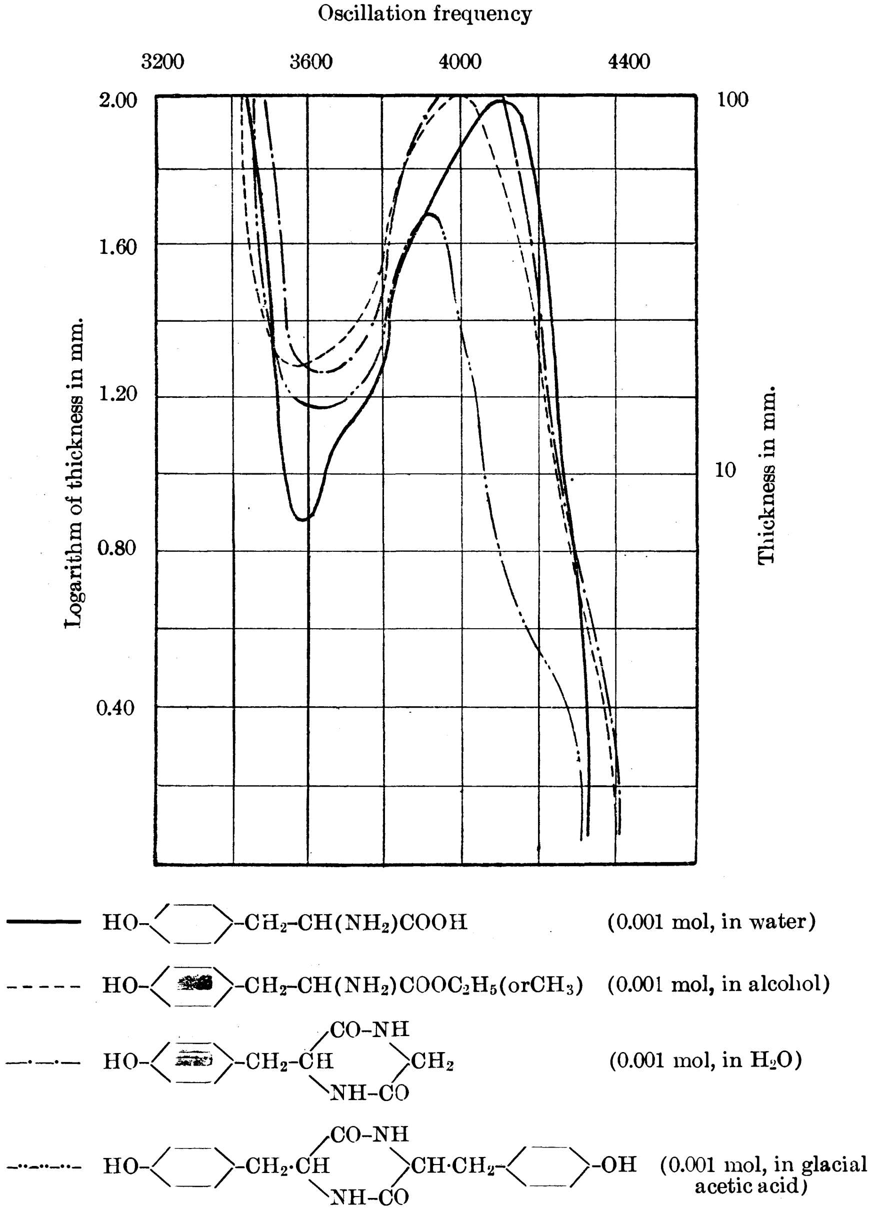
Oscillation frequency
3200
3600
4000
4400
2.00
1.60
1.20
0.80
0.40
Logarithm of thickness in mm.
100
10
Thickness in mm.
HO-C6H4-CH2-CH(NH2)COOH (0.001 mol, in water)
HO-C6H4-CH2-CH(NH2)COOC2H5(orCH3) (0.001 mol, in alcohol)
HO-C6H4-CH2-CH(CO-NH)(NH-CO)CH2 (0.001 mol, in H2O)
HO-C6H4-CH2·CH(CO-NH)(NH-CO)CH·CH2-C6H4-OH (0.001 mol, in glacial acetic acid)

Fig. 3.

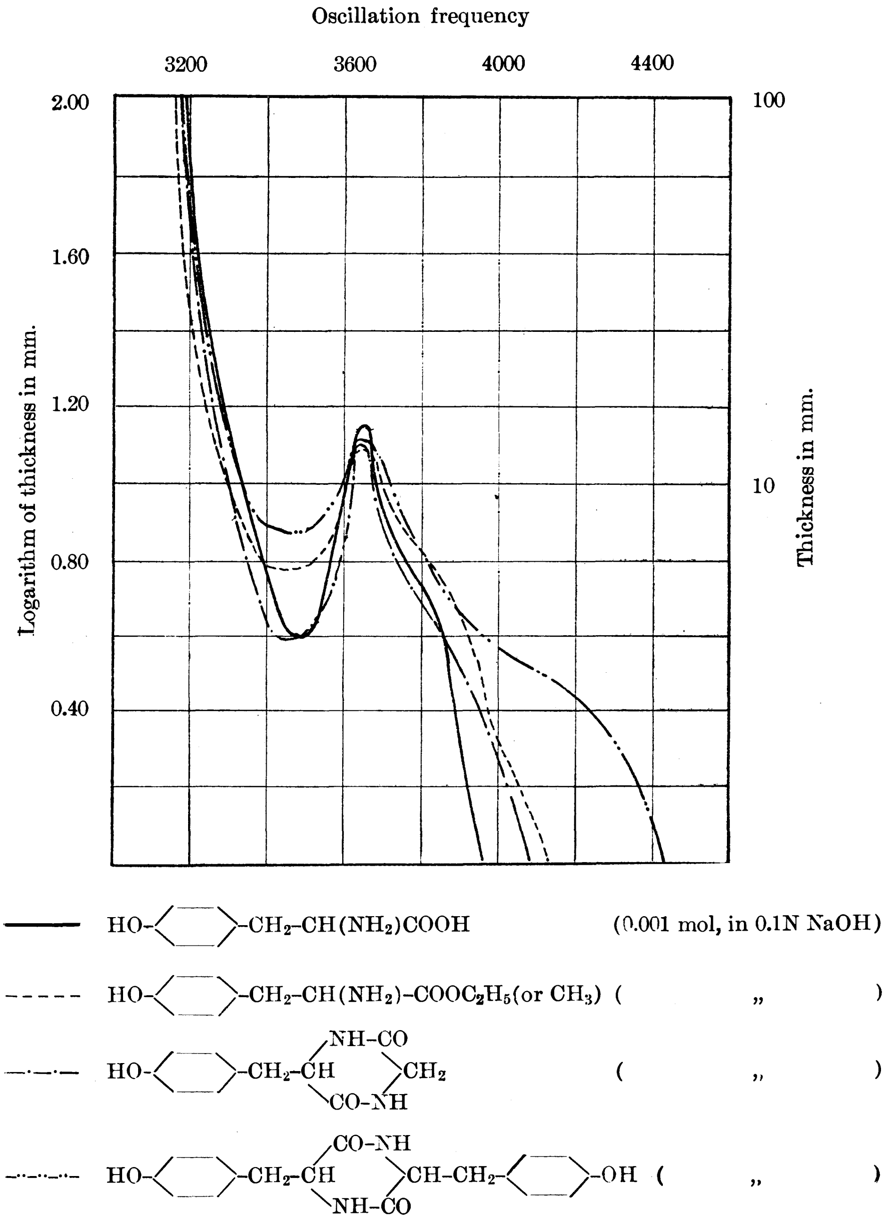
Oscillation frequency
3200
3600
4000
4400
2.00
1.60
1.20
0.80
0.40
Logarithm of thickness in mm.
100
10
Thickness in mm.
HO- -CH$_2$-CH(NH$_2$)COOH (0.001 mol, in 0.1N NaOH)
HO- -CH$_2$-CH(NH$_2$)-COOC$_2$H$_5$(or CH$_3$) („)
HO- -CH$_2$-CH NH-CO CH$_2$ CO-NH („)
HO- -CH$_2$-CH CO-NH CH-CH$_2$- -OH NH-CO („)

Fig. 4.

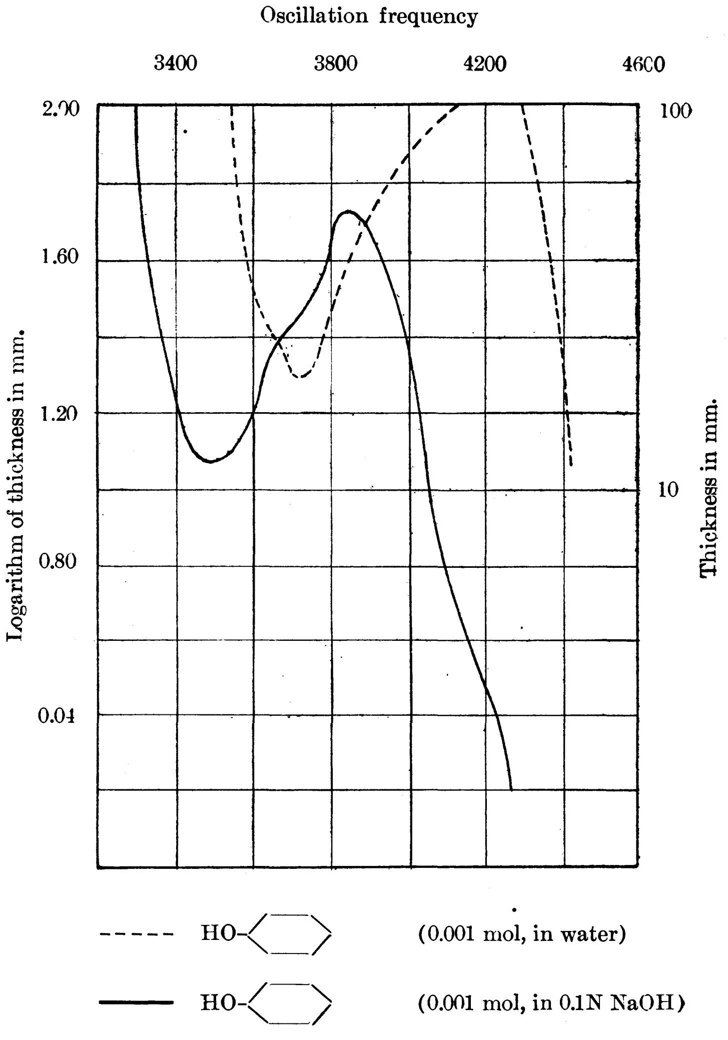
Oscillation frequency
3400
3800
4200
4600
2.00
1.60
1.20
0.80
0.04
Logarithm of thickness in mm.
100
10
Thickness in mm.
HO-
(0.001 mol, in water)
HO-
(0.001 mol, in 0.1N NaOH)

Fig. 5.

Esters of Amino-acids.—*Glycocoll ester.* Its hydrochloride was first prepared according to the method described by V. Auger(1) and it was then transformed into ester.(2) The solution of ester in alcohol which had been freshly redistilled over sodium gave no selective absorption.

Tyrosine esters, Ethyl and methyl esters of tyrosine were prepared according to mainly the methods given by E. Fischer(3) and his collaborators, only slight modifications being applied to it.

Ethyl-ester (m.p. 108°) and methyl-ester(4) (m.p. 133.5–134.5°) thus prepared and carefully purified, were dissolved in ethyl alcohol, both in 0.001 mol solution. Their absorption spectrograms coincide with each other (Fig. 3 and 4) and the shifts of these bands in alkaline solutions with the same P_H-value are also the same in both cases.

Dipeptides.—*Glycylleucine.* This substance was prepared according to the method given by E. Fischer(5); the crude sample thus obtained was once dissolved in a small bulk of water and rendered to crystallise out again by adding some quantities of 90% ethyl alcohol to the solution. 0.01 Mol aqueous solution of glycyl-*l*-leucine so purified gave no selective absorption.

Glycyl-l-phenylalanine. This substance was also prepared after Fischer's method(6) and purified by repeating the alternative dissolution in water and precipitation by adding alcohol. 0.01 Mol solution of this peptide gave the absorption identical with that of *l*-phenylalanine (Fig. 6).

Glycyl-d,l-phenylalanine. This peptide was prepared in the same manner as the case of active body, in using Kahlbaum's racemic phenylalanine as one component. The spectrogram of the solution of this substance was also identical with both the active compound and phenylalanine itself (Fig. 6).

Anhydrides.—*Glycyl-l-tyrosine anhydride.* This substance was prepared according to the method described by Fischer and Schrauth,(7) and spectroscopically studied in neutral and alkaline solutions; the former solution being made by dissolving 0.0110 gr. of the anhydride in 50 c.c. of pure water, while in the latter the same quantity of the substance being contained in 50 c.c. of 0.1 N sodium hydroxide solution. The absorptions of these two solutions were found to be identical respectively with the corresponding solutions of tyrosine itself (Fig. 3 and 4).

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(1) *Bull. soc. chim.*, [3], **21** (1899), 5.

(2) E. Fischer, *Ber.*, **34** (1901), 436.

(3) *Ber.*, **34** (1901), 433.

(4) E. Fischer u. Schrauth, *Ann.*, **354** (1907) 21.

(5) E. Fischer u. J. Steingroever, *Ann.*, **340** (1905) 157.

(6) Fischer u. Schoeller, *Ann.*, **357** (1907), 1.

(7) Fischer u. Schrauth, *Ann.*, **354** (1907), 21.

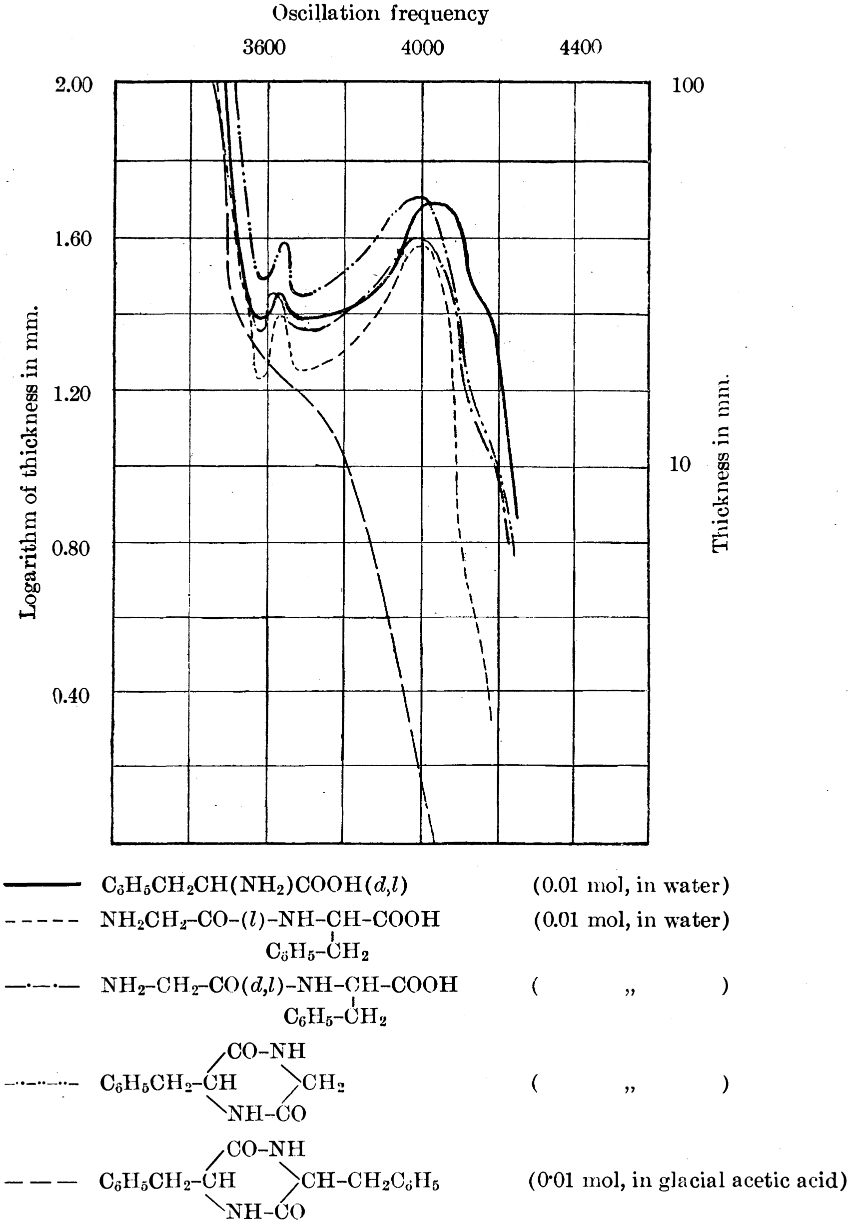

Fig. 6.

Tyrosine anhydride. This anhydride was prepared in two ways: we have namely followed faithfully the preparatory method given by Fischer and Schrauth,⁽¹⁾ and, on the other hand, tyrosine was heated in 8 times of

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(1) Fischer u. Schrauth, *Ann.*, **354** (1907), 21.

its weight of glycerol at 170°–180° for 25 hours. The glycerol solution so treated was added with alcohol in order to let separate out the desired anhydride, which was washed with hydrochloric acid to remove unchanged tyrosine and then was recrystallised from 25% ammonia solution.

These two samples,(1) however, gave the same spectrogram and further the shifts of their absorption bands in alkaline media were identical between them (Fig. 3 and 4), all these absorptions not differing from those of tyrosine itself and its derivatives.

Glycyl-l-leucine anhydride. 1 Gr. of glycyl-*l*-leucine was heated in 8 gr. glycerol at 170°–180° for 9 hours(2); crude anhydride thus obtained was carefully recrystallised from water (found, N=16.8, calc., 16.5%) and examined in 0.01 mol aqueous solution. This solution gave no selective absorption.

Leucine anhydride. 9 Gr. leucine was well shaken with 20 Gr. glycerol and the mixture was heated for 20 hours at 160°–170°. After cooling, a little water was added to the liquid and yellowish crystals were drained, and well washed with hot water in order to remove the adhering amino-acid (the yield of the substance was 6.6 gr., i.e., 85% of theory). In starting from racemic leucine and in following the same mode of preparation just described, leucine anhydride was prepared. (Found, N=12.5, calc., 12.4%) 0.005 Mol alcoholic solutions of both samples gave the same spectrogram without any selective absorption.

Glycyl-l-phenylalanine anhydride. This substance was prepared according to the method described by Fischer and Schoeller.(3) 0.01 Mol aqueous solution of this anhydride gave the identical absorption either with phenylalanine or with glycylphnylanine.

Phenylalanine anhydride. 3 Gr. *l*-phenylalanine suspended in 10 gr. glycerol was heated in an oil bath at 180°–200° for 3 hours, until the suspended matters were entirely disappeared and a clear solution with slightly yellowish colour was made. From this solution, after about half an hour, anhydride began to separate out as yellowish crystalline masses, which were drained, well washed with hot water and recrystallised from boiling alcohol in addition of animal charcoal. So purified colourless crystals of phenylalanine anhydride (found, N=9.58, calc., 9.53%) were dissolved in glacial acetic acid (0.01 mol). The spectrogram of this solution, as was remarked in the introductory part, gave no selective absorption. Only a few substances are known, which show no selective absorption, in spite of that they contain more than one benzene nucleus in their molecules. This anomality in light absorption of the substances of this category, such as diphenyl

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(1) Glacial acetic acid was used as solvent.

(2) Compare Abderhalden und Schwab, *Z. physiol. Chem.*, 148 (1925), 254.

(3) Fischer und Schoeller, loc. cit.

and some of triphenyl compounds probably is due to the relative position of phenyl groups in molecule.

Summary.

(1) Glycocoll, alanine, leucine, phenylalanine, tyrosine, glycocoll ester, tyrosine esters, glycylleucine, glycyl-*l*-phenylalanine, glycyl-*d,l*-phenyl alanine, glycyl-*l*-tyrosine anhydride, tyrosine anhydride, glycyl-*l*-leucine anhydride, leucine anhydride, glycyl-*l*-phenylalanine anhydride and phenylalanine anhydride were spectrochemically studied in aqueous, alcoholic or glacial acetic acid solutions.

(2) Among these compounds only those which contain phenyl and oxy-phenyl groups in their molecules show selective light absorptions; i.e., tyrosine, phenylalanine and their derivatives, except phenylalanine, anhydride absorb selectively.

(3) Although two phenyl groups exist in its molecule, phenylalanine anhydrid show only end absorption, perhaps due to the mutual effect of these two chromophores symmetrically situated to each other.

(4) Derivatives of either tyrosine or phenylalanine absorb identically with their mother substances.

(5) Other amino-acids, their esters, pepetides and anhydrides show no selective absorptions, as in the cases of glycocoll anhydride, alanine anhydride and sarcosine anhydride which were described in our previous paper.

(6) As for the constitution of amino-acid anhydrides, the same conclusion as was previously mentioned, may be applied again to the substances now studied, that is to say, all these anhydrides are in keto-form.

The experiments are going on with other amino-acid compounds and anhydrides. The authors' best thanks are due to Prof. Keita Shibata who was not unwilling to make valuable remarks and also to Dr. Yoshitaro Takayama who kindly supplied them with amino-acids. The cost of the present investigation was defrayed from the grant of the Imperial Academy of Science, for which they wish to record their gratefulness.

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