3,5-DIKETOPYRAZOLIDINE DERIVATIVES. I.

By Tokuichi TSUMAKI.

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When we try to obtain the acyl-derivatives of hydrazobenzene by substituting the hydrogen atoms attaching to the imino-groups in hydrazobenzene by acyl-groups, we sometimes obtain, as the results of the reaction, the derivatives of benzidine instead of those of hydrazobenzene. The difficulty to obtain the acyl-derivatives of the latter compound lies in the fact that the hydrazobenzene frequently undergoes benzidine transformation by various reagents.

D. Stern[1] carried out the reaction between hydrazobenzene and benzoyl chloride, and obtained contrary to his expectation dibenzoylbenzidine as a reaction product. In the case of the reaction between formic acid and hydrazobenzene, the analogous result was brought about, producing diformylbenzidine.

But several acyl-derivatives of hydrazobenzene are also obtained under suitable condition. For example, D. Stern obtained monoacetyl-hydrazobenzene under the action of acetic anhydride on hydrazobenzene, and also diacetyl-hydrazobenzene by heating the above two substances for a long time. C. A. Bischoff[2] obtained various bromoacyl-compounds from α-bromofatty acids and hydrazobenzene. J. Biehringer and A. Busch[3] produced monobenzoylhydrazobenzene by the action of benzoyl chloride on hydrazobenzene in alcohol in presence of slaked lime. H. P. Kaufmann[4] prepared acylated hydrazobenzenes by the action of succinyl chloride and o-phthalyl chloride respectively on hydrazobenzene in dimethylaniline.

The author carried out the reaction between malonyl chloride and hydrazobenzene in the ether solution under cooling, and was able to isolate the colourless crystals, melt at 178°, by extracting the white precipitate, instantly produced in the ether solution, with petroleum ether.

On close inspection, this substance was proved to be a heterocyclic compound, namely, 1,2-diphenyl-3,5-diketopyrazolidine produced by substituting the hydrogen atoms of imino-groups in hydrazobenzene according to the following equation. Benzidine hydrochloride was simultaneously formed.

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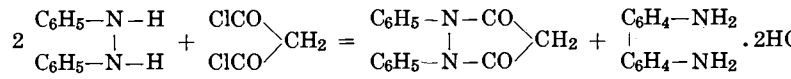
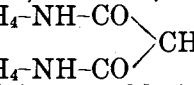
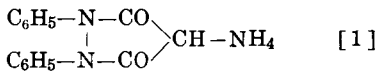
(1) Stern, *Ber.*, **17** (1884), 379.
(2) Bischoff, *Ber.*, **31** (1898), 3241.
(3) Biehringer and Busch, *Ber.*, **36** (1903), 137.
(4) Kaufmann, *Z. angew. Chem.*, **40** (1927), 69.



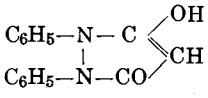
This compound forms colourless crystals and is soluble in alcohol, ether, acetone, chloroform and hot ligroin, while malonylbenzidine,  , prepared by Remfry[1] in 1911 has bluish gray colour, and is insoluble in almost all the ordinary organic solvents. The former bears some resemblance in its chemical properties to the derivatives of pyrazolone and pyrazolidone, especially to 1-phenyl-3,5-diketopyrazolidine described by Michaelis.[2]

It is insoluble in water, but soluble in alkali solution forming its salt. For example, the ammonium salt [1] is easily obtained as the colourless crystals, when the strong ammoniacal solution of diphenyl-diketopyrazolidine is evaporated up to dryness. M.p.: 138°–139°.

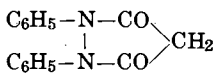


[1]

The constitution of diphenyl-diketopyrazolidine may be expressed as the enolic form [2], or the ketonic form [3], and the formation of salts may approve of the former formula.



[2]



[3]

But, the easiness with which diphenyl-diketopyrazolidine condenses with aldehydes, ketones and nitrous acid, as stated in the following, shows us the existence of a methylene group in this compound, the author, therefore, prefers the formula [3], and has expressed its ammonium salt as diketo-compound as above.

Diphenyl-diketopyrazolidine is fairly stable, and is not decomposed by dilute acid nor by alkali. From its alkali solution, it is reprecipitated as white crystals unaltered, after neutralizing the solution with acid. It seems to be decomposed by heating with conc. alcoholic potash solution, but neither hydrazobenzene nor benzidine can be detected in the decomposition product, which shows that the compound is not simply hydrolysed into its components.

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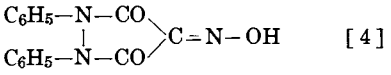
(1) Remfry, *J. Chem. Soc.*, **99** (1911), 621.

(2) Michaelis and Bermeister, *Ber.*, **25** (1892), 1502.

By the action of nascent nitrous acid, diphenyl-diketopyrazolidine forms isonitroso-compound; namely, 1,2-diphenyl-4-isonitroso-3,5-diketopyrazolidine [4].

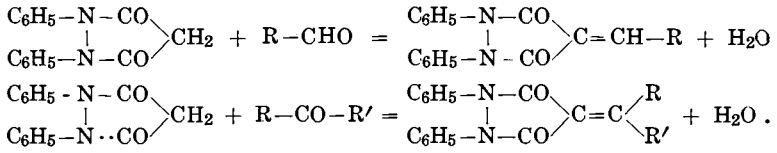


[4]

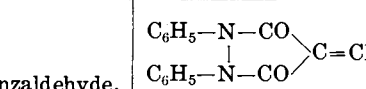
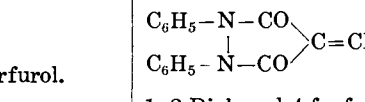
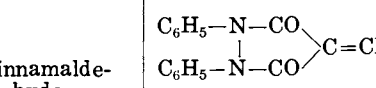
This compound contains two molecules of water of crystallization, and crystallizes in orange-red needles, while the anhydride forms dark red crystals and melts at 163°–164°.

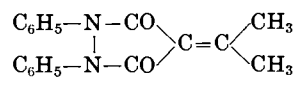
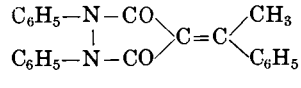
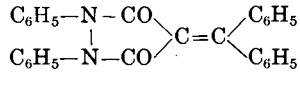
Diphenyl-diketopyrazolidine condenses with aldehydes and ketones forming various coloured substances. Its condensation with aldehydes is accomplished especially smoothly, and the products are obtained with good yields, only by heating the two components together on the water-bath for a short time; while its condensation with ketones requires more time and higher temperature.

At any late, the reactions with aldehydes and ketones are expressed by the following general formulae:—



The condensation products synthesised by the author are as follows.

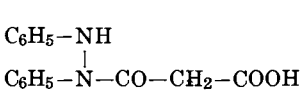
Aldehyde or ketone.	Condensation product.	M.p., °C.	Colour.
Benzaldehyde.	 [5] 1, 2-Diphenyl-4-benzylidene-3, 5-diketopyrazolidine.	164–165	Orange red.
Furfurol.	 [6] 1, 2-Diphenyl-4-furfurylidene-3, 5-diketopyrazolidine.	157–158	Dark red.
Cinnamaldehyde.	 [7] 1, 2-Diphenyl-4-cinnamylidene-3, 5-diketopyrazolidine.	190–192	Violet-tinged red.

Aldehyde or ketone.	Condensation product.	M.p., °C.	Colour.
Acetone.	 [8] 1, 2-Diphenyl-4-isopropylidene-3, 5-diketopyrazolidine.	113	Canary yellow.
Acetophenone.	 [9] 1, 2-Diphenyl-4-[α-phenylethylidene]-3, 5-diketopyrazolidine.	148–149	Yellow.
Benzophenone.	 [10] 1, 2-Diphenyl-4-[diphenylmethylene]-3, 5-diketopyrazolidine.	269	Reddish yellow.

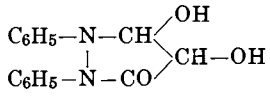
These products are easily decomposed by hot alkali solution, reproducing aldehydes or ketones.

In addition to diphenyl-diketopyrazolidine, another substance of colourless needles was obtained from the ethereal part of the product of the above-mentioned reaction between malonyl chloride and hydrazobenzene. It dissolves in caustic soda solution, and is reprecipitated by the addition of acid. It is soluble in ordinary organic solvents, but insoluble in ligroin, and its constituent corresponds to the formula $C_{15}H_{14}O_3N_2$. M.p.: 160°–162°.

From its mode of formation, the constitution of this compound may be conjectured to be [11] or [12].



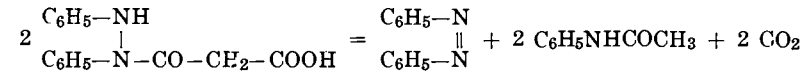
[11]



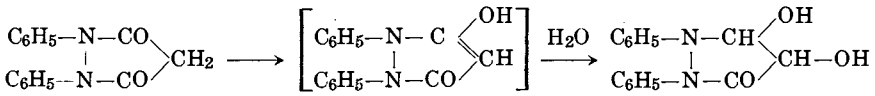
[12]

And if the former is true, it is expected that the compound will undergo the following decomposition on heating, forming azobenzene, acetanilide and carbon dioxide, in the same manner observed by Melms and others[1] on hydrazobenzene, or by Stern[2] on monoacetyl-hydrazobenzene.

(1) Melms, *Ber.*, **3** (1870), 554; Lermontow, *Ber.*, **5** (1872), 235.
(2) Stern, *Ber.*, **17** (1884), 379.



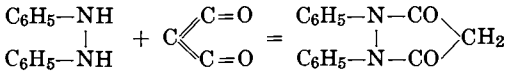
But in reality, nothing of these decomposition products could be detected. It is, therefore, presumed that the compound is [12], namely, the derivative of pyrazolidone, which undergoes complex decomposition under the influence of heat. Moreover, the same compound was produced when diphenyl-diketopyrazolidine, dissolved in the mixed solution of chloroform and alcohol, was allowed to stand for a few days after adding a few drops of dilute hydrochloric acid. In this case, diphenyl-diketopyrazolidine must be hydrated by the catalytic action of acid as in the following,



[3] [12]

On the other hand, the formation of [11] from diphenyl-diketopyrazolidine by hydrolysis with dilute hydrochloric acid is thought to be unprobable, as it is not hydrolysed into hydrazobenzene, as mentioned above, even with concentrated acid. In view of these facts, the compound in question is considered as [12], namely, 1, 2-diphenyl-3, 4-dihydroxy-5-pyrazolidone. It does not form isonitroso-compound with nitrous acid, as it has no methylene group in the molecule.

Parallel to the reaction between malonyl chloride and hydrazobenzene, the author carried out the reaction between carbon suboxide and hydrazobenzene, expecting that the reaction must be a suitable method for the preparation of diphenyl-diketopyrazolidine, as there is in this case no fear of benzidine transformation.



[3]

In fact, the same substances as were obtained by the action of malonyl chloride on hydrazobenzene, were also obtained in this case. But, the yields of them were very poor owing to the polymerization of the greater part of carbon suboxide into brownish black substance during the reaction.

Experimental Part.

A. The Reaction between Malonyl Chloride and Hydrazobenzene. *1,2-Diphenyl-3, 5-diketopyrazolidine*, [3]. Malonyl chloride, used as a

material for the reaction, was prepared principally according to the method described by Staudinger and Bereza.[1]

Fifty grams of powdered malonic acid and 160 gr. of thionyl chloride were heated in a flask under a reflux condenser for 60 hours at 40°, and then for 8 hours at 50°. The crystals of malonic acid went into solution forming the brownish liquid. It was then distilled under diminished pressure, and the fraction which boiled at 60° under 30 mm. pressure was collected as malonyl chloride.

A solution of 18.5 gr. of hydrazobenzene in 300 c.c. of ether was dropped from the tap-funnel into 200 c.c. of ether containing 10 gr. of malonyl chloride, and the white precipitate instantly produced in the flask was quickly filtered and well washed with ether, without exposing to moist air, as otherwise, the precipitate would change into a non-filterable viscous matter of brownish black colour. Diphenyl-diketopyrazolidine was obtained by extracting this precipitate with petroleum ether, and was recrystallized from ethyl alcohol. The yield was 6 gr. It crystallizes in colourless plates melting at 178°. It is insoluble in water and cold petroleum ether, but prettily soluble in alcohol and ether, and very soluble in acetone and chloroform. It dissolves in ammonia or in alkali solution, forming its salt.

Anal. Subst.=0.1095; CO_2=0.2862; H_2O=0.0490 gr. Found: C=71.28; H=5.01%. Calc. for $C_{15}H_{12}N_2O_2$: C=71.41; H=4.80%.

Subst.=0.1850 gr.; N_2=17.8 c.c. (12°, 763 mm.) Found: N=11.50%. Calc. for $C_{15}H_{12}N_2O_2$: N=11.11%.

1, 2-Diphenyl-3, 4-dihydroxy-5-pyrazolidone, [12]. The ethereal filtrate, obtained by filtering the above-mentioned precipitate by the reaction between malonyl chloride and hydrazobenzene, was washed with water to decompose the excess of malonyl chloride remained in the solution. It was then shaken with an one percent solution of sodium carbonate. The soda solution gave a light yellow precipitate when acidified with hydrochloric acid. The precipitate was dissolved in the least quantity of chloroform, and alcohol was added to it, and the solution was allowed to stand for one day. From this solution, 1,2-diphenyl-3,4-dihydroxy-5-pyrazolidone crystallized in colourless needles. It melts at 160°–162°. Before melting it seems to be somewhat decomposed. It is soluble in ether and chloroform, sparingly soluble in alcohol, ligroin and water.

Anal. Subst.=0.1204; CO_2=0.2956; H_2O=0.0550 gr. Found: C=66.94; H=5.08% Calc. for $C_{15}H_{14}O_3N_2$: C=66.67; H=5.18%.

Subst.=0.1454 gr.; N_2=12.8 c.c. (13°, 761 mm.) Found: N=10.45%. Calc. for $C_{15}H_{14}O_3N_2$: N=10.37%.

(1) Staudinger and St. Bereza, *Ber.*, **41** (1908), 4463.

The same compound was obtained from 1, 2-diphenyl-3, 5-diketopyrazolidine by dissolving the latter in the mixed solution of chloroform and alcohol, and allowing it to stand for a few days after the addition of a small quantity of dilute hydrochloric acid.

B. The Reaction between Carbon Suboxide and Hydrazobenzene. According to the method of Staudinger and Bereza,[1] dibromomalonic acid was treated with phosphorus pentachloride in ether, and the liquid which boiled at 74°–75° under 17 mm. pressure was collected as dibromomalonyl chloride; and was used as a material for the preparation of carbon suboxide.

To the flask containing 30 gr. of zinc granules, 450 c.c. of ether solution containing 45 gr. of dibromomalonyl chloride was added from the tap-funnel, and the evolved carbon suboxide gas and the vapour of ether were introduced to a condenser which was connected to another flask containing the ethereal solution of 20 gr. of hydrazobenzene and cooled with freezing mixture. A small amount of white precipitate was produced in the ethereal solution. 1,2-Diphenyl-3,5-diketopyrazolidine was obtained from this precipitate when recrystallized from petroleum ether. Hydrogen chloride gas was then passed through the ethereal solution in order to precipitate the excess of hydrazobenzene as benzidine hydrochloride. The ethereal solution was washed with water, and evaporated up to dryness, and the reddish brown residue was washed with petroleum ether to remove azobenzene included in it. A small amount of colourless needles was obtained from this brownish residue when recrystallized from alcohol, and this compound was proved to be identical with diphenyl-dihydroxypyrazolidone obtained from malonyl chloride and hydrazobenzene.

C. The Derivatives of 1,2-Diphenyl-3,5-diketopyrazolidine. *Ammonium salt of 1, 2-diphenyl-3, 5-diketopyrazolidine*, [1]. When the ammonical solution of diphenyl-diketopyrazolidine was allowed to stand in a vacuum desiccator furnished with soda lime till the solution was evaporated to dryness, the ammonium salt was remained as the colourless crystals. M.p.: 138°–139°.

Anal. Subst.=0.1262 gr.; N_2=17.1 c.c. (18.5°, 762 mm.) Found: N=15.70%. Calc. for $C_{15}H_{15}O_2N_3$: N=15.61%.

1,2-Diphenyl-4-isonitroso-3,5-diketopyrazolidine, [4]. To the caustic potash solution of 2 gr. of diphenyl-diketopyrazolidine, 0.6 gr. of sodium nitrite was added, and the excess of dilute hydrochloric acid was dropped

(1) Staudinger and St. Bereza, *Ber.*, **41** (1908), 4461.

to this solution under cooling. Isonitroso-compound was deposited out at once as a yellow precipitate, which gave the long needle crystals of orange colour on recrystallization from hot water. The yield was 0.5 gr. It contains two molecules of water of crystallization, and the anhydrous compound has dark red colour and melts at 163°–164°. It is soluble in alcohol, benzene, ether and hot water, but insoluble in ligroin.

Anal. Subst.=0.0253; lost at 100°=0.0029 gr. Found: H_2O=11.5%. Calc. for $C_{15}H_{11}O_3N_3 \cdot 2H_2O$: H_2O=11.4%.

Subst.=0.1424 gr.; N_2=16.7 c.c. (20.5°, 763 mm.) Found: N=13.47%. Calc. for $C_{15}H_{11}O_3N_3 \cdot 2H_2O$: N=13.25%.

1,2-Diphenyl-4-benzylidene-3,5-diketopyrazolidine, [5]. When 2.5 gr. of diphenyl-diketopyrazolidine and 2 gr. of benzaldehyde were heated on the water-bath, the former dissolved into the latter forming a dark red solution, which solidified on cooling to a dark red mass. It was pressed on a porous plate, and washed with alcohol until it smelt no longer of benzaldehyde. The yield was 2.8 gr. The compound has orange red colour, and melts at 164°-165°. It is very soluble in chloroform, moderately soluble in alcohol and ether, but insoluble in ligroin. By the action of hot caustic alkali, it is decolourized and decomposed into its components.

Anal. Subst.=0.1581 gr.; N_2=12.0 c.c. (26°, 764 mm.) Found: N=8.57%. Calc. for $C_{22}H_{16}O_2N_2$: N=8.24%.

1,2-Diphenyl-4-furfurylidene-3,5-diketopyrazolidine, [6]. When 2 gr. of diphenyl-diketopyrazolidine was heated with 1.6 gr. of furfurol on the water-bath for a while, a reddish brown mass was obtained. It was pressed on a porous plate, and washed quickly with alcohol to remove furfurol still adhering to it. The condensation product was left in an almost pure state. The yield was 2 gr. It was once more purified by dissolving it in alcohol and allowing it to stand after the addition of petroleum ether. The compound crystallized out as dark red prisms. It melts at 157°–158°; and is soluble in acetone, benzene and ether. but insoluble in water.

Anal. Subst.=0.1513 gr.; N_2=11.6 c.c. (26°, 763 mm.) Found: N=8.65%. Calc. for $C_{20}H_{14}O_3N_2$: N=8.48%.

1,2-Diphenyl-4-cinnamylidene-3,5-diketopyrazolidine, [7]. 2.5 gr. of diphenyl-diketopyrazolidine and 2.5 gr. of cinnamaldehyde were mixed and heated on a water bath for one hour. The mixture solidified to a dark red mass, which was purified by washing with petroleum ether and alcohol, and dried on a porous plate. The yield was 3 gr. It has a violet-tinged red colour, and is soluble in alcohol, ether and chloroform, sparingly soluble in

ligroin, but insoluble in water. M.p. : 190°–192°. Before melting it seems somewhat to decompose.

Anal. Subst.=0.1490 gr.; N_2=10.2 c.c. (26°, 763 mm.) Found : N=7.72%. Calc. for $C_{24}H_{18}O_2N_2$: N=7.65%.

1,2-Diphenyl-4-[α-phenylethylidene]-3,5-diketopyrazolidine, [9]. Two grams of diphenyl-diketopyrazolidine and 2 gr. of acetophenone were heated for one hour at 130°–180°. On cooling, the product solidified to a reddish brown viscous matter contaminating the yellow needle crystals. It was washed with ligroin, and on recrystallization from alcohol, it gave yellow needles, which melts at 148°–149°. The yield was 0.8 gr. It is soluble in ether and hot alcohol, but insoluble in water.

Anal. Subst.=0.0070 gr.; N_2=0.451 c.c. (23°, 764 mm.) (Pregl's method). Found : N=7.38%. Calc. for $C_{23}H_{18}O_2N_2$: N=7.91%.

1,2-Diphenyl-4-[diphenylmethylene]-3,5-diketopyrazolidine, [10]. Two grams of diphenyl-diketopyrazolidine and 2.8 gr. of benzophenone were fused together on the water-bath for one hour and a half and on a wire gauze, above 100°, for 1/2 hour. The product was extracted with alcohol, and this solution gave reddish yellow needle crystals when allowed to stand for one day. They were recrystallized once from alcohol. M.p. : 265°. The yield was 0.8 gr.

Anal. Subst.=0.0112 gr.; N_2=0.666 c.c. (23°, 758 mm.) (Pregl's method). Found : N=6.75%. Calc. for $C_{28}H_{20}O_2N_2$: N=6.73%.

In conclusion the author wishes to acknowledge his indebtedness to the Department of Education for a grant which has defrayed a part of the expense of this investigation.

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ON THE DISSOLUTION VELOCITY OF OXYGEN INTO WATER. PART IV.

By Susumu MIYAMOTO and Akira NAKATA.

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Introduction. The oxidation velocity of sodium sulphite, when the mixture of oxygen and air is passed into the solution through a narrow glass-tube under various conditions, and the dissolution velocity of oxygen

into water calculated from the observed value of the oxidation velocity, were reported in the previous papers.[1] In these measurements, the gas bubbles, which ascend in the solution, agitate the solution so violently that in the boundary surface layer a sufficient quantity of sodium sulphite is always present to react with the oxygen molecules which enter into the liquid phase, and the observed oxidation velocity of sodium sulphite gives the dissolution velocity of oxygen into water, when the concentration of sodium sulphite is not below a certain value.

It will be expected that the reaction velocity of the oxidation of sodium sulphite which takes place on the free surface layer of the solution in the atmosphere of oxygen will be independent of the contentration of sodium sulphite and give the dissolution velocity of oxygen into water, when the condition is satisfied under which a sufficient quantity of sodium sulphite is always present in the boundary surface layer.

As will be seen in the subsequent discussion, the dissolution velocity of oxygen, here described, is the value when the concentration of oxygen in the surface layer is maintained at zero.

It is intended in the present paper to report the observed oxidation velocity of sodium sulphite in the atmosphere of oxygen, studied under the following conditions and to give a theoretical consideration on the result.

The direct measurements of the rates of solution of oxygen into water were carried out by several writers.

Adeney and Becker[2] measured the dissolution velocity of oxygen into water from bubbles of known magnitudes. Davis and Crandall[3] carried out the direct measurement of the rates of solution of oxygen into water from the water surface of known area, the main body of water being agitated with a stirrer of special construction.

The initial rate of solution of oxygen into water, observed by these writers, should be equal to the dissolution velocity, calculated from the oxidation velocity of sodium sulphite, if the interpretation above described be acceptable. In Table 4 the values are compared.

Davis and Crandall explained the process of the dissolution velocity of a gas into a liquid by the two film theory,[4] and they assumed the surface of the liquid film is instantaneously saturated with the gas.

The existence of a thin film at the boundary surface may generally be accepted, but it will be difficult to explain the result of the present research

(1) Miyamoto and Kaya, this Bulletin, **5** (1930), 123; Miyamoto, Kaya and Nakata, ibid., **5** (1930), 229; Miyamoto and Kaya, ibid., **5** (1930), 321.

(2) *Phil. Mag.*, **38** (1919), 317; **39** (920), 385; **42** (1921), 87.

(3) *J. Am. Chem. Soc.*, **52** (193), 3757, 3769.

(4) Lewis and Whitman, *Ind. Eng. Chem.*, **16** (1924), 1215.

by the assumption that the surface of the liquid film is instantaneously saturated with the gas, for the oxidation velocity of sodium sulphite is independent of its concentrations. One of the present writers (Miyamoto) has a different opinion on the mechanism of the rate of solution of a gas into a liquid, a part of which is described in the later. The precise discussion on the dissolution theory of a gas will be given in another occasion.

The direct measurement of the rate of solution of oxygen into water was also carried out by Morgan and Pyne,[1] but in their paper the numerical value of the boundary surface area is not given.

Experimental. The apparatus graphically shown in Fig. 1, was employed for the reacting vessel. Oxygen gas, washed by acidified potassium bichromate and sodium hydroxide solutions, is passed at a high velocity through A into the apparatus, which contains 30–50 c.c. of water, for about 30 minutes. When the air in the apparatus has been completely replaced by oxygen, the stirrer S is put in motion at the rate of about 400 revolutions per minute, and a definite quantity of sodium sulphite solution is added in the water from B. The stop-watch is started when about the half volume of the sodium sulphite solution has been poured in the vessel. Oxygen gas is passed at the rate of about 10 liters per hour. The quantity of sodium sulphite added is separately determined by the usual method of iodmetry. The stirrer is made of glass and it is so situated that its wing is vertical to the boundary surface to avoid the disturbance of the surface area.

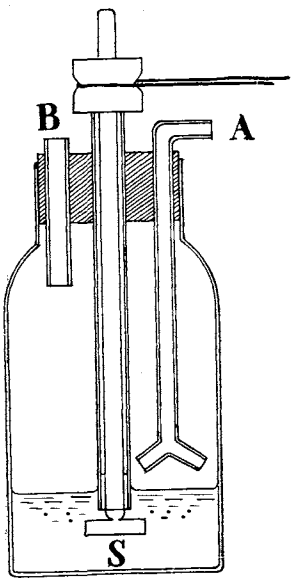

Fig. 1

After the elapse of t minutes, the oxygen current is stopped and nitrogen gas is passed from B at a high velocity to replace the oxygen in the apparatus quickly. The total quantity of the solution is poured into a known quantity of iodine solution, acidified with hydrochloric acid, and the excess of iodine is titrated back by means of sodium thiosulphate solution.

In Table 1, v is the volume of sodium thiosulphate solution of 0.1000 normal, equivalent to the amount of sodium sulphite remained in the vessel. The velocity constant k is calculated by

$$k=\frac{v_0-v}{t},$$

where v_0 is the value of v at $t=0$.

(1) *J. Phys. Chem.*, **34** (1930), 1818.

Table 1.

Temp.	p_{O_2} atm.	S cm.^{2}	t min.	v c.c.	$v_{calc.}$ c c.	k
15°C.	0.954	17.11	0	148.01	—	—
			50	137.17	137.11	0.217
			0	174.07	—	—
			50	163.05	163.17	0.220
			0	203.71	—	—
			50	193.10	192.81	0.212
			0	230.51	—	—
			50	219.58	219.61	0.219
			0	263.34	—	—
			50	252.30	252.44	0.221
					Mean	0.218
		26.31	0	145.26	—	—
			30	134.54	134.34	0.357
			0	145.41	—	—
			30	134.40	134.49	0.367
			0	179.96	—	—
			30	169.15	169.04	0.360
			0	227.06	—	—
			30	216.13	216.14	0.364
			0	263.06	—	—
			30	251.94	252.14	0.371
					Mean	0.364

Table 1.—(*Continued*)

Temp.	p_{O_2} atm.	S cm.^{2}	t min.	v c.c.	$v_{calc.}$ c.c.	k
25°C.	0.941	9.22	0	75.24	—	—
			90	54.06	54.45	0.235
			0	93·58	—	—
			90	75.58	72.79	0.225
			0	99.18	—	—
			90	78.58	78.39	0.229
			0	198.11	—	—
			90	177.49	177.32	0.229
			0	220.93	—	—
			96	198.00	198.75	0.239
					Mean	0.231
		17.11	0	134.65	—	—
			50	113.03	112.60	0.432
			0	139.29	—	—
			50	116.00	117.24	0.466
			0	159.77	—	—
			50	137.94	137.72	0.437
			0	185.22	—	—
			50	163.64	163.17	0.432
			0	189.57	—	—
			50	167.76	167.52	0.436
			0	240.14	—	—
			50	218.02	218.09	0.442
					Mean	0.441

Table 1.—(*Continued*)

Temp.	p_{O_2} atm.	S cm.^{2}	t min.	v c.c.	$v_{calc.}$ c.c.	k
25°C.	0.941	26.31	0	119.67	—·	——
			30	98.86	99.21	0.694
			0	121.87	——	——
			30	101.64	101.41	0.674
			0	133.33	——	——
			31	112.05	112.19	0.686
			0	134.67	——	——
			30	114.68	114.21	0.666
			0	140.08	——	——
			30	120.14	119.62	0.665
			0	164.57	——	——
			30	143.88	144.11	0.690
			0	189.52	——	——
			30	168.59	169.06	0.698
			0	209.11	——	——
			30	188.64	188.65	0.682
						Mean 0.682
		42.75	0	122.37	——	——
			20.33	99.83	100.01	1.109
			0	136.47	——	——
			20	113.96	114.47	1.126
			0	163.30	——	——
			50	108.83	108.30	1.089
			0	187.65	——	——
			51.5	130.92	131.00	1.102
			0	209.68	——	——
			50	154.97	154.68	1.094
			0	234.63	——	——
			50	179.86	179.03	1.083
						Mean 1.101

Table 1.—(*Concluded*)

Temp.	p_{O_2} atm.	S cm.^{2}	t min.	v c.c.	$v_{calc.}$ c.c.	k
35°C.	0.916	17.11	0	146.99	—	—
			50	114.88	113.69	0.642
			0	178.43	—	—
			50	146.22	145.13	0.644
			0	205.95	—	—
			50.33	171.15	172.43	0.691
			0	231.99	—	—
			50	198.62	198.69	0.667
			0	261.14	—	—
			50	226.82	227.84	0.686
					Mean	0.666
		26.31	0	147.92	—	—
			30	118.63	117.08	0.976
			0	204.35	—	—
			30.25	173.06	173.25	1.034
			0	235.54	—	—
			30	203.27	204.70	1.076
			0	262.06	—	—
			30	231.50	1.22	1.019
			0	288.99	—	—
			30	257.93	258.15	1.035
					Mean	1.028

The values of $v_{calc.}$ given in the Table, are obtained by

$$v_{calc.}=v_0-kt\ ,$$

using the mean value of k.

Under the present conditions, the oxidation velocity is independent of the concentration of sodium sulphite and is proportional to the boundary surface area, as will be seen in Table 1.

The result is easily interpreted by the assumption that the oxidation velocity of sodium sulphite, when it is independent of its concentrations, is not the real reaction velocity but the dissolution velocity of oxygen into water. Then the relation between the observed velocity constant and the dissolution velocity of oxygen is given by

$$D_0=\frac{1}{4}k\times 10^{-4}\text{ moles per minute, } \ldots\ldots\ldots\ldots (1)$$

where D_0 means the dissolution velocity of oxygen into water when its concetration in the surface layer is kept at zero.

The values of $k_{obs.}$ and the dissolution velocity D_0, calculated by the equation (1), are given in the 4th and the 6th column of Table 2.

In the 5th and the 7th column, the values of $k_{calc.}$ and $D_{calc.}$, calculated by the following linear equations with respect to the surface area S, are given.

$$k_{calc.}=0.0133\,S, \quad \ldots\ldots\ldots\ldots\ldots\ldots (2)$$

$$D_{0calc.}=0.332\times 10^{-6}\,S, \quad \ldots\ldots\ldots\ldots\ldots (3)$$

at 15°C.,

$$k_{calc.}=0.0258\,S, \quad \ldots\ldots\ldots\ldots\ldots\ldots (2')$$

$$D_{0calc.}=0.645\times 10^{-6}\,S, \quad \ldots\ldots\ldots\ldots\ldots (3')$$

at 25°C. and

$$k_{calc.}=0.0390\,S, \quad \ldots\ldots\ldots\ldots\ldots\ldots (2'')$$

$$D_{0calc.}=0.975\times 10^{-6}\,S, \quad \ldots\ldots\ldots\ldots\ldots (3'')$$

at 35°C. .

The surface area S is obtained by the measurement of the rise of the level for the addition of a definite volume of water into the vessel.

The partial pressure of oxygen, given in the 2nd column of Table 1 or 2, were calculated from the composition of the gas passed and for the vapour pressure of the solution the vapour pressure of pure water was employed as a first approximation.

Table 2.

Temp.	p_{O_2} atm.	S cm.^{2}	$k_{obs.}$	$k_{calc.}$	$D_{0\,obs.}$ moles/min.	$D_{0\,calc.}$ moles/min.
15°C.	0.954	17.11	0.218	0.228	5.45×10^{-6}	5.70×10^{-6}
		26.31	0.364	0.350	9.10 ,,	8.75 ,,
25°C.	0.941	9.22	0.231	0.233	5.78×10^{-6}	5.95×10^{-6}
		17.11	0.441	0.441	11.03 ,,	11.03 ,,
		26.31	0.682	0.679	17.05 ,,	16.98 ,,
		42.75	1.101	1.103	27.53 ,,	27.58 ,,
35°C.	0.916	17.11	0.666	0.667	16.65×10^{-6}	16.68×10^{-6}
		26.31	1.028	1.026	25.70 ,,	25.65 ,,

The observed result is graphically shown in Fig. 2 and Fig. 3.

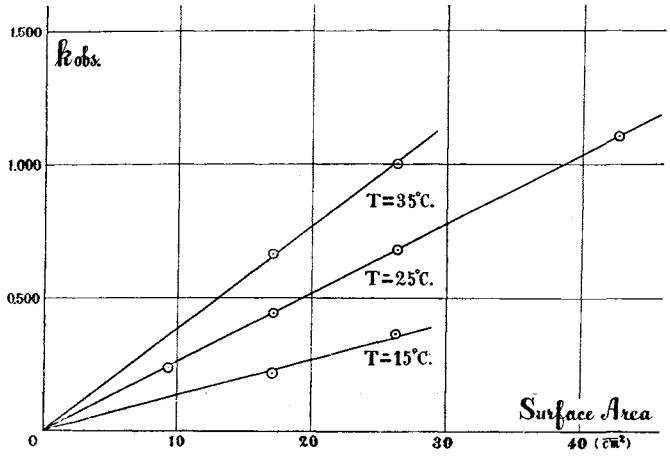

Fig. 2.

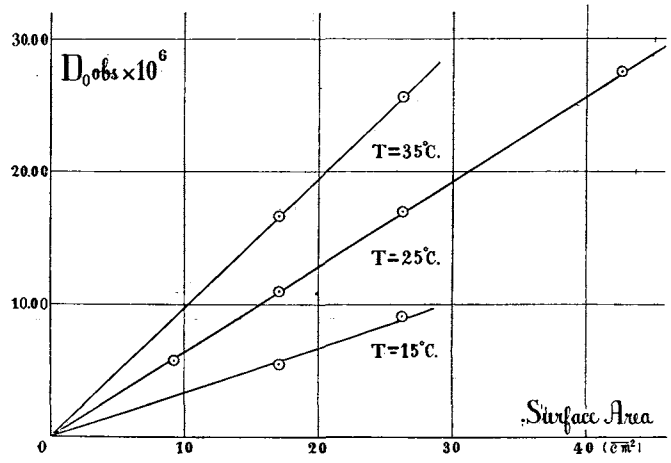

Fig. 3.

Theoretical. The dissolution velocity of a gas into a liquid can generally be given by

$$D=N''S-f(c)S, \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots \quad (4)$$

where N''=the number of the molecules which enter into the liquid phase through the unit boundary surface area per unit of time,

$f(c)$=the number of the molecules which leave the liquid phase through the unit boundary surface area per unit of time, and this value can be considered to be a function of the concentration of the gas in the surface layer,

S=the area of the boundary surface.

When the concentration of the gas in the surface layer is kept at zero, the dissolution velocity is represented by

$$D_0=N''S. \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots \quad (5)$$

This state is maintained so long as the sufficient quantity of a substance which reacts readily with the gas, be always present in the surface layer as in the case of the present experiment.

$$N''=\beta N', \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots \quad (6)$$

where N'=the number of the molecules which collide with the unit area of the boundary surface per unit of time,

β=the ratio of the number of the molecules which penetrate into the liquid phase and the number of the molecules which collide with the liquid surface.

By Maxwell's distribution law of velocities,

$$dN=\frac{N}{\sqrt{\pi}\,\alpha}e^{-\frac{u^2}{\alpha^2}}du\,, \quad \cdots\cdots (7)$$

where dN=the number of the molecules whose component of velocity parallel to one axis lies between u and $u+du$ among N molecules.

$$\alpha^2=\frac{2RT}{M}\,, \quad \cdots\cdots (8)$$

where R=the gas constant,
M=the molecular weight of the gas.

Then,

$$N'=\int_0^\infty \frac{N}{V\sqrt{\pi}\,\alpha}u\,e^{-\frac{u^2}{\alpha^2}}du=\frac{N\alpha}{2V\sqrt{\pi}}\,, \quad \cdots\cdots (9)$$

where N=Avogadro's constant,
V=the molar volume.

From (8) and (9),

$$N'=\frac{Np}{\sqrt{2\pi MRT}}\,. \quad \cdots\cdots (10)$$

Now the following assumption, which has great probability, is adopted. Among the molecules, which collide with the liquid surface, only those molecules, whose components of velocity vertical to the surface are greater than a threshold value u_0, are able to enter into the liquid phase. Then,

$$N''=\int_{u_0}^\infty \frac{N}{V\sqrt{\pi}\,\alpha}u\,e^{-\frac{u^2}{\alpha^2}}du=\frac{N\alpha}{2V\sqrt{\pi}}e^{-\frac{u_0^2}{\alpha^2}}\,, \quad \cdots\cdots (11)$$

or,

$$N''=\frac{Np}{\sqrt{2\pi MRT}}e^{-\frac{Mu_0^2}{2RT}}\,. \quad \cdots\cdots (12)$$

From (6), (10) and (12) we have,

$$\beta=e^{-\frac{Mu_0^2}{2RT}}\,. \quad \cdots\cdots (13)$$

From (5) and (12),

$$D_0=\frac{Np}{\sqrt{2\pi MRT}}e^{-\frac{Mu_0^2}{2RT}}S \text{ molecules / sec.}$$

$$=\frac{60p}{\sqrt{2\pi MRT}}e^{-\frac{Mu_0^2}{2RT}}S \text{ moles / min.} \quad \cdots\cdots\cdots (14)$$

From (1) and (14),

$$k=\frac{24p\times 10^{-5}}{\sqrt{2\pi MRT}}e^{-\frac{Mu_0^2}{2RT}}S. \quad \cdots\cdots\cdots (15)$$

When all the values except the surface area are kept at constant,

$$D_0=AS, \quad \cdots\cdots\cdots (16)$$

$$k=BS, \quad \cdots\cdots\cdots (17)$$

where A and B are constants.

Thus the experimental equations, above obtained, are theoretically endorsed.

The calculation of the threshold value u_0. From the equations (13) and (15),

$$\beta=\frac{\sqrt{2\pi MRT}}{24p_{o_2}\times 10^5}\frac{k}{S}, \quad \cdots\cdots\cdots (18)$$

$$u_0=\sqrt{\frac{-2RT\ln\beta}{M}}. \quad \cdots\cdots\cdots (19)$$

The value of β, which stands for the ratio of the number of the molecules of oxygen which enter into water and the number of the molecules of oxygen which collide with the liquid surface, can be calculated by the equation (18), using the experimentally obtained values of $\frac{k}{S}$, given in the equations (2), (2′) and (2″).

Then the threshold value u_0 can be calculated by the equation (19).

The values of β and u_0, thus obtained, are given in the 4th and the 5th column of Table 3.

The present calculation is based upon the assumption, that among the molecules of oxygen which collide with the water surface, only the molecule, whose component of velocity is greater than the threshold value u_0, can enter into the liquid phase.

Table 3.

Temp.	p_{O_2} atm.	$\frac{k}{S}$	β	u_0 cm./sec.	$\sqrt{\overline{c^2}}$ cm./sec.
15°C.	0.954	0.0133	1.258×10^{-8}	1.650×10^{5}	4.74×10^{4}
25°C.	0.941	0.0258	2.517×10^{-8}	1.646×10^{5}	4.82×10^{4}
35°C.	0.916	0.0390	3.974×10^{-8}	1.651×10^{5}	4.90×10^{4}

It was first expected that the value u_0 would depend upon the temperature, but the calculated values of u_0 at 15°C., 25°C. and 35°C. are almost identical. It was thus confirmed that the value u_0 is independent of the temperature within the observed region.

The root-mean-square velocity of oxygen molecules, calculated by

$$\sqrt{\overline{c^2}}=\sqrt{\frac{3RT}{M}},$$

is given in the last column of Table 3.

It follows from the present research that only the molecule of oxygen, whose vertical component of velocity is greater than approximately 3.4 times the root-mean-square velocity, can enter into water.

The initial rates of solution of oxygen into water. The initial rates of solution of oxygen into water should be equal to the value D_0, calculated from the maximum oxidation velocity of sodium sulphite, when the water employed is perfectly free from oxygen.

From the equations (3), (3′) and (3″), the dissolution velocity of oxygen from unit surface area per second can be calculated.

Becker[1] measured the absorption velocity of oxygen from air into alkaline water containing suspensions of ferrous hydroxide. It was confirmed that the absorption rate tend to a maximum, independent of further increases in the stirring speed, but the effect of the amount of ferrous hydroxide was not studied. The maximum value should be equal to the initial rates of solution into the alkaline solution. The dissolution velocity of oxygen into alkaline solution is not the same as that into water.[2]

In Table 4 the initial rates of solution of oxygen into water, directly observed, are given in comparison with the values, chemically obtained.

Adeney and Becker observed the initial rates of solution is independent of temperature, while the value, calculated from the oxidation velocity of sodium sulphite by the present writer, depends upon temperature.

(1) *Phil. Mag.*, **45** (1923), 581.
(2) Miyamoto, this Bulletin, **2** (1927), 74; **3** (1928), 98.

Table 4.

Observer	Method	Temp.	Initial rates of solution moles per cm.^{2} per sec.
Davis and Crandall	directly	25°C.	4.5×10^{-9}
,,	,,	25°C.	2.6×10^{-9}
Adeney and Becker	,,	35.1°C.	10.6×10^{-9}
,,	,,	25.2°C.	11×10^{-9}
,,	,,	15.5°C.	11×10^{-9}
,,	,,	2.5°C.	11.3×10^{-9}
Conant and Scherp	,,	25°C.	28×10^{-9}
,,	,,	25°C.	24×10^{-9}
Davis and Crandall	100 c.c. 1N-K_2SO_4 + $Fe(OH)_2$	25°C.	1.0×10^{-9}
Becker	100 c.c. water containing $Fe(OH)_2$ + KOH		5.2×10^{-9}
Miyamoto and Nakata	40 c.c. water containing	15°C.	5.53×10^{-9}
,,	Na_2SO_3 of various	25°C.	11.75×10^{-9}
,,	concentrations	35°C.	16.25×10^{-9}

Summary.

(1) The oxidation velocity of sodium sulphite was studied, when the condition is satisfied, under which the concentration of oxygen in the boundary surface layer is always zero. The oxidation velocity is independent of the concentration of sodium sulphite and is proportional to the boundary surface area.

(2) The theoretical considerations on the observed oxidation velocity was given.

(3) The assumption that only the molecule of oxygen, whose component of velocity vertical to the boundary surface is greater than a threshold value u_0 is able to enter into the liquid phase, was given, and the values of u_0 were calculated at 15°C., 25°C. and 35°C. from the experimentally obtained result.

The calculated value of u_0 is 1.65×10^5 cm. per sec. and is independent of the temperature within the observed region.

The authors wish to express their appreciation of a grant from the Department of Education for the expenses of this research.

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DISPERSOIDAL INVESTIGATIONS ON SELENIUM. I.

By Kiyoshi JUNA.

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Concerning the Influence of the Oxygen and the Carbon Dioxide Present in Air on the Formation of the Dispersed Phase of Selenium when Selenium Solution in Hydrazine Hydrate are poured into Water, Alcohol and Glycerine. Many researches have already been made on the formation of colloidal selenium solutions by pouring into water the selenium solutions in hydrazine hydrate. J. Meyer[1] explained the reaction of the formation of colloidal selenium as follows: ". . . . . Ganz analog wie das Selen verhält sich auch der Schwefel gegen Hydrazine·hydrate,

$$3NH_2NH_3OH + 3S = 2H_2NNH_3SH + H_2NNH_3SO_3H$$
$$6NH_2NH_3OH + 3S = 2(H_2NNH_3)_2S + (H_2NNH_3)_2SO_3 + 3H_2O.$$

. . . . . Beim starken Verdünnen dieser Lösungen erhält man nun kolloide Schwefel· und Selen·Lösung. Die Abscheidung der beiden Elemente ist darauf zurückzuführen, dass die oben gegebenen Reaktionsgleichungen nun von rechts nach links verlaufen . . . . ." A. Gutbier[2] and his collaborator studied also the method of the synthesis of colloidal selenium in aqueous and in alcoholic media.

Experimental. In the following table (this covers only one part of my experiments) are briefly described several experiments showing that the formation of colloidal selenium solutions is dependent principally on the influences of the oxygen and the carbon dioxide present in air.

Conclusion. In an atmosphere of nitrogen any formation of colloidal selenium solution is not to be observed on pouring selenium solutions in hydrazine hydrate into either water, alcohol or glycerine.

I wish to express here to Prof. P. P. von Weimarn my sincere gratitude for providing me with the theme for these investigations.

November 1930. Dispersoidological Department of the Imperial Industrial Research Institute of Osaka.

(1) Meyer, *Ber.*, **46** (1913), 3.
(2) Gutbier, *Ber.*, **47** (1914), 466; *Koll.-Zeitsch.*, **30** (1922), 103.

Table

Medium	In the absence of air; in an atmosphere of nitrogen	Influences of other gases than nitrogen		
		Air	Oxygen	Carbon dioxide
Water	0.2 c.c. $Se^{2\%}_{H.H.}$ ← 40 c.c. H_2O In an atmosphere of nitrogen, no colloidal selenium solutions are formed; but a clear brown solution is obtained.	0.05 c.c. $Se^{2\%}_{H.H.}$ ← 20 c.c. H_2O (In an atmosphere of nitrogen). When air is passed through the clear brown solution obtained, a brick-red colloidal selenium solution is formed.	0.2 c.c. $Se^{2\%}_{H.H.}$ ← 40 c.c. H_2O (In an atmosphere of nitrogen). When oxygen is passed through the clear brown solution, a brick-red colloidal solution of selenium is produced.	0.2 c.c. $Se^{2\%}_{H.H.}$ ← 40 c.c. H_2O (In an atmosphere of nitrogen). When carbon dioxide is passed through the clear brown solution, a brick-red colloidal selenium solution is formed.
Alcohol	0.2 c.c. $Se^{2\%}_{H.H.}$ ← 40 c.c. C_2H_5OH In an atmosphere of nitrogen, certain selenium compounds do not dissolve readily in alcohol and there results a dark-brown turbid suspension.*	0.3 c.c. $Se^{2\%}_{H.H.}$ ← 20 c.c. C_2H_5OH (In an atmosphere of nitrogen). When air is passed through the above dark-brown turbid suspension, it is transformed into a brick-red colloidal selenium solution, which appears blue in transmitted light.	0.2 c.c. $Se^{2\%}_{H.H.}$ ← 40 c.c. C_2H_5OH (In an atmosphere of nitrogen). When oxygen is passed through the above turbid suspension, a brick-red colloidal selenium solution is formed.	0.2 c.c. $Se^{2\%}_{H.H.}$ ← 40 c.c. C_2H_5OH (In an atmosphere of nitrogen). When carbon dioxide is passed through the above turbid suspension, a dark-red colloidal selenium solution is obtained, which appears blue in transmitted light.
Glycerine	0.2 c.c. $Se^{2\%}_{H.H.}$ ← 40 c.c. $C_3H_5(OH)_3$ In an atmosphere of nitrogen no colloidal selenium solution is formed; but there results a clear brown solution.	0.3 c.c. $Se^{2\%}_{H.H.}$ ← 20 c.c. $C_3H_5(OH)_3$ (In an atmosphere of nitrogen). When air is passed through the clear brown solution obtained, there is formed a brick-red colloidal solution of selenium.	0.2 c.c. $Se^{2\%}_{H.H.}$ ← 40 c.c. $C_3H_5(OH)_3$ (In an atmosphere of nitrogen). When oxygen is passed through the clear brown solution obtained, a brick-red colloidal selenium solution results.	0.2 c.c. $Se^{2\%}_{H.H.}$ ← 40 c.c. $C_3H_5(OH)_3$ (In an atmosphere of nitrogen). When carbon dioxide is passed through the clear brown solution, there is slowly formed a brick-red colloidal selenium solution.

In this table under $Se^{2\%}_{H.H.}$ is designated a 2% selenium solution in hydrazine hydrate.

* By the experiment is shown that the precipitate in the above suspension is decomposed by water containing CO_2 and O_2 from the air. The decomposition is accompanied by the formation of a colloidal selenium solution. After the dissolution of selenium in hydrazine hydrate, the solution was evaporated to dryness under reduced pressure in an atmosphere of nitrogen. To the dry residue obtained, absolute alcohol was added always in the nitrogen atmosphere. After the lapse of a day, the alcohol was filtered off and the residue on a filter paper was washed three times with alcohol, and water, containing CO_2 and O_2 from the air, was added. As a result of the addition of water, the residue suffered decomposition; the dispersed particles of selenium passed through the filter and there was obtained a beautiful, stable colloidal selenium solution of a brick-red colour.

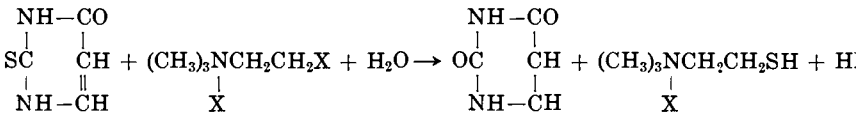
CHEMISTRY OF THIO-CHOLINE HALIDE (TRIMETHYL THIO-ETHYL AMMONIUM HALIDE). II.

NEW THIO-CHOLINE CHLORIDE AND ITS DERIVATIVES.

By Taichi HARADA.

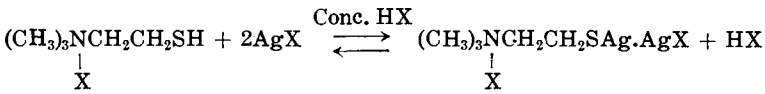
Received December 13, 1930. Published January 28, 1931.

In a previous paper[1] in this Bulletin the author described the preparation of thio-choline bromide and its silver derivatives. The present paper is the continuation of the research on thio-choline compounds. According to the author's previous paper the reaction between 2-thio-uracil and halogeno-choline chloride is represented by the following reaction equation:



The yield was rather small in the pure state owing to side reactions.

Thio-choline chloride forms colorless, transparent monoclinic plates. Above 200°C. thio-choline chloride decomposes slowly. It is interesting to note that the substance forms an addition compound with silver halides giving a complex salt and releasing hydrochloric acid; the reaction becomes decidedly acid. The change may be represented by the following equation:



The new complex compound is a lustrous asbestos-like crystalline salt. The reaction proceeds to the right when the solution is neutral at the start. The compound decomposes slowly into the original constituents under the action of a strong acid or with temperatures above 70°C. It ionizes in aqueous solution probably to form $((CH_3)_3NCH_2CH_2SAg.AgX)^+ + X^-$ ions.

Shortly after the author's first publication, Vickery and Leavenworth[2] reported that cysteine combines with silver sulphate to form a silver compound, $(C_3H_5O_2NS\ Ag)_2Ag_2SO_4$, similar to that of the choline.

Thio-choline halides are very soluble substances both in water and in ethyl alcohol while the silver derivatives are not. The solubility of the

(1) This Bulletin, **4** (1929), 171.

(2) *J. Biol. Chem.*, **83** (1929), 523; **86** (1930), 129.

chlorine compound of the silver derivative, however, is slightly greater in water than that of the corresponding bromide. As a material for the preparation of thio-choline chloride, chloro-choline chloride was prepared by condensation of trimethylamine with ethylene chloride according to the author's previous method for the bromide.[1]

The reaction equation may be represented as follows:

$$(CH_3)_3N + ClCH_2CH_2Cl \longrightarrow (CH_3)_3\underset{\displaystyle Cl}{\overset{|}{N}}CH_2CH_2Cl$$

Chloro-choline chloride decomposes slowly above 163°C. and at 242°C. melts and boils, the color becoming reddish brown. None of these compounds have definite decomposition or melting points.

Experimental Part.

Chloro-Choline Chloride. Forty grams of ethylene chloride were condensed with trimethylamine which was generated from a saturated aqueous solution containing thirty grams of trimethylamine hydrogen chloride in a well-stoppered pressure bottle with a rubber stopper which was framed with an iron cage. It was slowly heated in a water bath, then maintained for several hours at the boiling point of water. With such treatment chloro-choline chloride condensed in the form of a white snow-like salt. The substance obtained was washed with ether and dried over calcium chloride in a desiccator. The yield was forty grams. It can be recrystallized from 95 % ethyl alcohol in a large colorless monoclinic form. It decomposed above 163°C. (approximately), assuming a yellowish tint. At 242°C. (not sharp) it melts and boils changing its color into a reddish brown.

Anal. Subst.=0.2368, 0.1834; AgCl=0.4297, 0.3332 gr. (Carius' method). Found: Cl=44.85, 44.94%. Calc. for $C_5H_{13}NCl_2$: Cl=44.87%.

Thio-Choline Chloride. One molecular proportion (6 gr.) of Chloro-choline chloride was heated with one molecular proportion (5 gr.) of 2-thio uracil together with 25 c.c. of water in a sealed bomb tube at about 150°C. for one to three hours depending upon the size of the tube. After cooling, the sealed tube was opened and transferred to a beaker for the separation of the insoluble uracil formed. The solution was pale yellowish in color. The filtrate was neutralized with a solution of ammonia. The volume of the solution was reduced to a suitable amount on a steam bath. Cooling

(1) This Bulletin, **4** (1929), 171.

permitted further separation of the uracil. The total uracil obtained was 3.91 gr. in the impure state.

Fractional crystallization was then carried out as in the case of thio-choline bromide[1] on the filtrate from the impure uracil. This solution contains ammonium chloride, chloro-choline chloride, and thio-choline chloride. It was treated with butyl alcohol with or without ethyl alcohol and cooled with a mixture of salt and ice. By this repetition a small amount of the transparent colorless monoclinic crystalline form of the substance sought was obtained. The yield in the pure state was about 0.5 gr. It was noticed that some amount of the salt remained in the mother solution.

The compound is a very soluble substance both in water and in ethyl alcohol. Its isoelectric point was found to be at P_H 7.0. Above 200° C. (approximately), it decomposes slowly darkening in color and at 238°C. (not sharp) it melts and boils with a deep brown discoloration.

Anal. Subst.=0.2992; AgCl=0.2744 gr. Found: Cl=22.62%. Calc. for $C_5H_{14}NSCl$: Cl=22.78; S=20.59%.

Subst.=0.2020; AgCl=0.1862; $BaSO_4$=0.3040 gr. (Carius' method). Found: Cl=22.80; S=20.67%.

Silver Derivative of Thio-Choline Chloride. It was found that thio-choline chloride dissolves freshly prepared silver chloride in a slightly acidic or neutral solution giving a pale yellowish solution without any evolution of hydrogen, but with the formation of hydrochloric acid. An excess of freshly prepared silver chloride was dissolved in a solution of thio-choline chloride by constant stirring; the solution becomes a transparent pale yellow. The excess of silver chloride was separated simply by filtration. The filtrate was diluted with 95% alcohol, filtered again, then allowed to stand over-night. From this solution a white lustrous asbestos-like compound was crystallized out. It was separated by filtration, washed with water, alcohol, and ether. Finally it was dried over calcium chloride in a desiccator in the dark,

Second and third crops from the mother solution could be obtained. This was continued until no further separation was evident. The yield is approximately quantitative. It slowly decomposes above 70°C. (approximately); the color changes to gray and then to deep brown; it melts and boils turning dark brown above 228°C. (not sharp). In all probability, this is due mainly to its thermal decomposition products, thio-choline chloride and silver chloride. It ionizes in an aqueous solution, the chlorine-ion precipitating silver chloride from a solution of silver nitrate. The solubility

(1) Ibid, **4** (1929), 174.

of the compound in 100 c.c. of water at 37°C. was found to be 0.1215 gr. while the bromide compound appears to be almost insoluble, that is, 0.0326 gr. under the same conditions.

Hydrogen-ion concentration of the saturated solution of the compound at 37°C. gives P_H 6.9. The structural formula for the compound is still under investigation.

Anal. Subst.=0.1986; AgCl=0.1406 gr. Found: AgCl=70.79%. Calc. for $C_5H_{13}NSAg_2Cl_2$: AgCl=70.63; S=7.90%.

Subst.=0.2400; AgCl=0.1681; $BaSO_4$=0.1398 gr. (Carius' method). Found: AgCl=70.42; S=8.00%.

In concluding, the author withes to express his thanks to Prof. Kraus of Brown University, Prof. Stieglitz of Chicago University, and Dean Whitmore, School of Chemistry and Physics, Pennsylvania State College for valuable private advices regarding the constitution of the silver compound.

Summary.

1. Chloro-choline chloride was obtained by the condensation of trimethylamine with ethylene chloride. It decomposes slowly above 163°C. melting and boiling at 242°C. with a reddish brown discoloration.

2. Thio-choline chloride was prepared from chloro-choline chloride by the action of 2-thio uracil at 150°C. Its isoelectric point was found to be at P_H 7.0. It decomposes slowly above 200°C. (approximately), melting and boiling at 238°C.

3. Thio-choline chloride reacts with silver chloride to form $(CH_3)_3NCH_2CH_2SAg.AgCl$ (with Cl) whose solubility in water at 37° was found to be 0.1215 gr. It decomposes slowly above 70°C. (approximately), melting and boiling around 228°C.

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SOME CONDENSATIONS GIVING DIETHYL DICYANOGLUTACONATE.

By **Yoshiyuki URUSHIBARA.**

Received December 17, 1930. Published January 28, 1931.

The compound which had been called by the name of diethyl dicyanoglutaconate and to which formula $C_2H_5OCO(CN)C=CH-CH(CN)COOC_2H_5$ or $C_{11}H_{12}O_4N_2$ had been given, was found by the author to be a more complex compound with formula $(C_{11}H_{12}O_4N_2)_2\cdot H_2O$. The author calls it diethyl dicyanoglutaconate semihydrate, because in this compound half a molecule of water is combined with $C_{11}H_{12}O_4N_2$.[1] Many reactions are known, in which diethyl sodio-dicyanoglutaconate $C_{11}H_{11}O_4N_2Na$ is formed; but treated with a dilute acid, it is transformed, not to the corresponding free cyano-ester $C_{11}H_{12}O_4N_2$, but to the semihydrate $(C_{11}H_{12}O_4N_2)_2\cdot H_2O$. Hence, the compound with formula $C_{11}H_{12}O_4N_2$, to which the name diethyl dicyanoglutaconate should be given correctly, can not be obtained unless the synthesis is realized without the intermediate formation of the sodium compound. The following condensations were tried, and, in the first two, the formation of diethyl dicyanoglutaconate was ascertained. This compound was not isolated in a pure state, but its presence was proved by the precipitation of diethyl dicyanoglutaconate semihydrate on acidifying the alkali extract of the condensation products, for diethyl dicyanoglutaconate, if present, would dissolve in alkali carbonate forming its own alkali derivative, and the latter, treated with a dilute acid, would give the semihydrate according to the already known process.

(1) *Condensation of ethyl oxymethylene-cyanoacetate* $[HOCH=C(CN)COOC_2H_5]$ *with ethyl cyanoacetate* $[CNCH_2COOC_2H_5]$ *by the action of acetic anhydride.* The reaction was expected to proceed as follows:

$$C_2H_5OCO(CN)C=CHOH + CH_2(CN)COOC_2H_5 = H_2O + C_2H_5OCO(CN)C=CH-CH(CN)COOC_2H_5.$$

A mixture of ethyl oxymethylene-cyanoacetate, ethyl cyanoacetate, and acetic anhydride in molecular proportions was heated for one hour. Then the whole mass was shaken with an aqueous solution of sodium carbonate and ether. On acidifying the aqueous solution, a crystalline substance separated. This was found to be identical with diethyl dicyano-

(1) This Bulletin, **2** (1927), 26.

glutaconate semihydrate, for it melted at 182° and could be transformed into the characteristic picrate melting at 197°.[1]

(2) *Condensation of ethyl chloromethylene-cyanoacetate* [$ClCH=C(CN)COOC_2H_5$] *with ethyl chloro-cyanoacetate* [$ClCH(CN)COOC_2H_5$] *by the action of metallic copper.* Ethyl chloromethylene-cyanoacetate had not been known, but was easily obtained by the action of phosphorus pentachloride on ethyl oxymethylene-cyanoacetate. The mixture of ethyl oxymethylene-cyanoacetate and phosphorus pentachloride in molecular proportions was heated on the water bath. From the reaction product hydrogen chloride and phosphorus oxychloride were removed by heating it on the water-bath and sucking with a water jet pump, and the residue was distilled under diminished pressure. The most part distilled at 106–107° under 16 mm. pressure, and by redistillation the pure substance distilling at 105° under 12 mm. pressure was obtained.

Anal. Found: Cl=22.05, 21.97%. Calc. for $C_6H_6O_2NCl$: Cl=22.23%.

The condensation of ethyl chloromethylene-cyanoacetate and ethyl chlorocyanoacetate was tried at first with so-called molecular silver, but without success. Then metallic copper, which was prepared in fine powder by adding zinc dust to an aqueous solution of copper sulphate, was used. The reaction was too violent, and the whole mass frothed up owing to evolution of an enormous quantity of heat. So in another experiment caution was taken to avoid an excessive rise of temperature. The reaction mass was extracted with ether, and on evaporating the ethereal solution an oily substance was obtained. To examine the presence of diethyl dicyano-glutaconate in this oily substance, it was dissolved in ether, and the ethereal solution was shaken with an aqueous solution of potassium carbonate. A crystalline substance separated from the aqueous solution and proved to be the potassium derivative of diethyl dicyanoglutaconate, for, when its aqueous solution was acidifyed, the yellow crystals of diethyl dicyano-glutaconate semihydrate melting at 182° were obtained, and these gave the characteristic picrate melting at 197°.

The reaction can be represented by the following equation:

$$C_2H_5OCO(CN)C=CHCl + ClCH(CN)COOC_2H_5 + 2Cu \longrightarrow C_2H_5OCO(CN)C=CH-CH(CN)COOC_2H_5 + Cu_2Cl_2$$

(3) *Condensation of ethyl chloromethylene-cyanoacetate* [$ClCH=C(CN)COOC_2H_5$] *with ethyl cyanoacetate* [$CNCH_2COOC_2H_5$] *by the*

(1) This Bulletin, **5** (1930), 7.

action of pyridine. Because of the strong acid nature of ethyl oxymethylene-cyanoacetate it was expected that ethyl chloromethylene-cyanoacetate would act like an acid chloride, and would condense with ethyl cyanoacetate by the action of pyridine, just as acetyl chloride; that is, there must be an analogy between the following reactions:

$$CH_3COCl + CNCH_2COOC_2H_5 + C_5H_5N = C_5H_5NHCl + CH_3CO-CH(CN)COOC_2H_5,$$
$$C_2H_5OCO(CN)C=CHCl + CNCH_2COOC_2H_5 + C_5H_5N = C_5H_5N\cdot HCl + C_2H_5OCO(CN)C=CH-CH(CN)COOC_2H_5.$$

To a mixture of ethyl chloromethylene-cyanoacetate and ethyl cyanoacetate, pyridine was added gradually under cooling. The mixture became a dark red pasty mass. Water and ether were added to the mass, and the two liquids were separated. On acidifying the aqueous solution with dilute sulphuric acid a yellow solid was obtained; but this was found not to be diethyl dicyanoglutaconate semihydrate, but its alcoholic solution gave with picric acid the picrate $C_{11}H_{16}O_6N_2\cdot C_6H_2(NO_2)_3OH$ which is characteristic to diethyl dicyanoglutaconate semihydrate $(C_{11}H_{12}O_4N_2)_2\cdot H_2O$ and to diethyl dicarbamyl-glutaconate $C_{11}H_{16}O_6N_2$. Hence, although the obtained substance were neither of these compounds, it was probably a compound, or a mixture of compounds, which situate between these two in the degree of hydration, and can give the same picrate.

(4) *Condensation of ethyl ethoxymethylene-cyanoacetate* [$C_2H_5OCH=C(CN)COOC_2H_5$] *with ethyl cyanoacetate* [$CNCH_2COOC_2H_5$] *by the action of acetic anhydride and zinc chloride.* A mixture of ethyl ethoxymethylene-cyanoacetate, ethyl cyanoacetate, and acetic anhydride in molecular proportions was heated. No change was observed. Zinc chloride was added to the mixture, and boiling was continued for two hours. The mixture became very dark in colour, but no trace of diethyl dicyanoglutaconate was found in the reaction mass.

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

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(1) Cf. this Bulletin, **2** (1927), 239.

SINOMENIN UND DISINOMENIN. XXIII.[1] UEBER DIE IDENTITAET VON β-TETRAHYDRODESOXY-CODEIN UND DIHYDRO-THEBAKODIN.

Von Kakuji GOTO und Shingo MITSUI.

Eingegangen am 9. Januar 1931. Ausgegeben am 28. Februar 1931.

Kondo und Ochiai[2] haben zuerst das Sinomenin (I) der Clemmensenschen Reducierung unterworfen und berichtet dass dabei Desoxy-tetrahydrosinomenin (III), die *d*-Form von Dihydro-thebakodin, entstanden war. Als Beweise dafür dass die Phenolgruppe in 4 fortreduciert war, führten sie die Tatsachen an, dass die neue Base alkaliunlöslich war und keine Eisenchloridreaktion mehr zeigte. Als Beweis des Vorhandenseins einer sekundären Alkoholgruppe, ersetzten sie die letztere durch Chlor, obgleich das Chlorgehalt dieses Chlorids viel niedriger als das berechnete war.

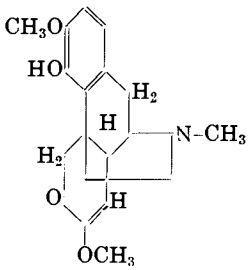
Diese Angabe war etwas erstaunlich, weil nach Ihnen das Sinomenin durch Zn-Amalgam schon seinen Phenolhydroxyl einbüsste, während seine Ketongruppe nur zum Alkohol reduciert wurde. Dieses Verhältnis veranlasste den Einen der Autoren[3] diese Reduktion zu wiederholen und er hat gefunden dass dabei nicht *d*-Dihydrothebakodin, sondern Desoxodemethoxy-dihydro-sinomenin (II), d.h. die *d*-Form von β-Tetrahydrodesoxycodein gebildet wurde. Das Vorhandensein des Phenolhydroxyls in dieser Desoxo-demethoxybase wird durch die unveränderte Diazoreaktion verratet. Die Tatsache, dass in dieser Verbindung die Ketongruppe zum Methylen reduciert wurde, geht aber auch aus ihrer anderen Darstellungsweise aus Demethoxydihydrosinomenin durch Phosphorpentachlorid und nachfolgende Reduktion hervor (siehe Versuchsteil).

Dann wendeten Kondo und Ochiai[4] einer neuen Auffassung zu, d.h. Dihydrothebakodin und β-Tetrahydrodesoxycodein eine und dieselbe Substanz sein müssen. Die Ähnlichkeit dieser zwei Substanzen ist sehr auffallend und man kann bloss aus den äusseren Eigenshaften, wie Krystallform, Schmelzpunkt, Drehungsvermögen u. s. w. nichts Sicheres beschliessen. Doch jederman, der die Originale[5] von Speyer und Siebert liest, kann nicht die Selbständigkeit von Dihydrothebakodin bezweifeln. Der Ersatz

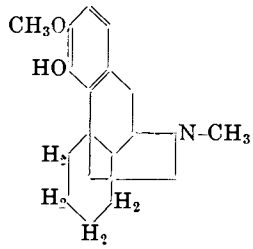
(1) Kitazato u. Goto, Die Sulfonierung der Alkaloide ist als XXII Mitteilung zu betrachten.
(2) *Ann.*, **470** (1929), 227; *Ber.*, **63** (1930), 646.
(3) Dieses Bulletin, **4** (1929), 244.
(4) *Ber.*, **63** (1930), 646.
(5) *Ber.*, **54** (1921), 1526.

von dem Hydroxyl mit Chlor mittelst Phosphorpentachlorids könnte nicht so leicht ausgeführt werden, wenn er einen Phenolhydroxyl darstellte. Der Schluss, zu dem Kondo und Ochiai gelangt haben, verlangt natürlich einen weiteren Stütz.

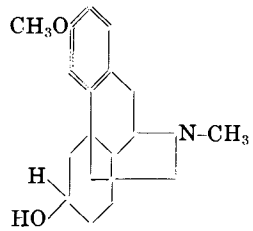
Wir versuchten das Problem aus einer anderen Seite auzugreifen. Glücklicherweise haben wir Demethoxy·dihydrosinomenin (V) und Desoxo·demethoxy·dihydrosinomenin (II) in einer genügenden Menge in Hand gehabt. Wenn wir diese zwei Substanzen der Tafelschen Elektro·reduktion unterwerfen, um zu sehen, ob dadurch der Phenolhydroxyl fortreduciert wird, so können wir darüber einen sicheren Schluss ziehen.



I.



II.



III.

IV.[1] Dihydrosinomenin $-CH_2\cdot CO\cdot C(OCH_3)H\cdot CH_2-$

V.[2] Desmethoxy·dihydro·sinomenin (*d*·Dihydrothebainon) $-CH_2\cdot CO\cdot CH_2\cdot CH_2-$

VI.[3] Demethoxy·dihydro·sinomeninol $-CH_2\text{-}CHOH\cdot CH_2\cdot CH_2-$

VII.[4] Sinomeninol $-CH_2\cdot C(OH)H\cdot C(OCH_3)=CH-$

VIII.[4] Dihydrosinomeninol $-CH_2\cdot C(OH)H\cdot C(OCH_3)H\cdot CH_2-$

IX.[5] Sinomeninhydrat $-CH_2\cdot CO\cdot C(OCH_3)(OH)\cdot CH_2-$

X.[5] α·und β·Demethoxy·sinomeninhydrat $-CH_2\cdot CO\cdot CH(OH)\cdot CH_2-$

Die Resultate dieser Reduktion werden in der folgenden Tabelle 1 zusammengefasst.

(1) Dieses Bulletin, **5** (1930), 282.
(2) Dieses Bulletin, **4** (1929), 244.
(3) Dieses Bulletin, **5** (1930), 282.
(4) Ibid.
(5) Dieses Bulletin, **4** (1929), 271.

Tabelle 1.

Substanz	Angewandte Menge (gr.)	Katholyt (25% H_2SO_4)	Zeitdauer (Stunden)	Stromkonz. per 100 c.c. (Amp.)	Ausbeute
[V]+[VI]*	8	160	3	9~9.5	[II] 1.2 gr. [VI] 2.7 gr.
[II]	6.8	140	3.5	10	[II] 60%
[VIII]	7.3	160	5	9.2	[VIII] 70%
[VII]	4.0	80	5	9~12	[VII] 75%
[IV]	10	150	4.5	10	[IV] 90% [VIII] sehr wenig
[I]	10	150	4	10.7	[IV] 3.4 gr.

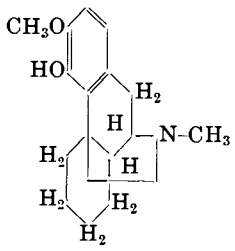
* Dass dieses Gemisch aus fast gleicher Menge von Demethoxy-dihydro-sinomenin und Demethoxy-dihydro-sinomeninol bestand, wurde durch Isolierung von Jodmethylat und Semicarbazon von dem ersteren quantitativ nachgewiesen [Dieses Bulletin, 5 (1930), 288]. Es ist klar, daher, dass 2.7 gr. von [VI] nicht durch die Reduktion von [V] gebildet wurden, sondern die unverändert zurückgewonnenen Substanz darstellten.

Die Ausbeuten, die in Prozentgehalt ausgedrückt wurden, bezeichnen die Mengen der unverändert zurückgewonnenen Substanzen.

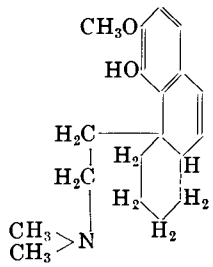
In diesen acht Versuchen, haben wir in keinem Fall die Alkoholbase isoliert, welche dem Dihydrothebakodin von Speyer und Siebert entspricht. Diazo-reaktion wurde sogar am jeden einzelnen krystallisierten Anteil geprüft, aber wir beobachteten keine Verminderung. Wir sind daher auch geneigt zu denken, dass Dihydro-thebakodin eine und dieselbe Substanz mit β-Tetrahydrodesoxykodein darstelle.

Natürlich ist die Reduktionsfähigkeit in der elektrolytischen Methode stark von der Natur von den Elektroden, vom elektrischen Strom, Temperatur u.s.w. abhängig und wir dürfen nicht einen voreiligen Schluss ziehen. Die Möglichkeit dass in Speyer und Siebertschem Fall, der Phenol-hydroxyl tatsächlich fortreduciert worden war, ist nicht ausgeschlossen. Doch wird unserer Schluss auch dadurch unterstützt dass die des-N-Methyl-base von Desoxo-demethoxy-dihydro-sinomenin schmilzt bei demselben Grad wie die des-N-Methyl-base von Dihydrothebakodin und dass der stickstofffreie Körper von dem ersteren fast denselben Schmelzpunkt wie der des lezteren besitzt. Diese frappante Übereinstimmung von Schmelzpunkt finden wir auch bei den des-N-Methyl-basen von Demethoxy-dihydrosinomenin und von Dihydrothebainon, welche beide ein optisches Paar[1] zueinander sind.

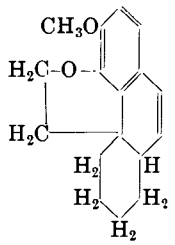
(1) Dieses Bulletin, **4** (1929), 271.



XI.



XII.



XIII.

Die Schwerreducierbarkeit von dem sekundären Alkohol auf dem elektrolytischen Weg führte uns zu prüfen, ob dasselbe Verhältnis in der Clemmensenschen Reduktion besteht. Schon lange hat Clemmensen[1] gezeigt dass der Hydroxyl nur dann fortreduciert wird, wenn er vicinal zu einem Keton steht und dass der Hydroxyl, der etwas entfernt davon liegt, wie bei ω-Aceto-propylalkohol, unberührt bleibt. Die Resultate unserer Versuche sind mit den obigen gut vereinbar und in der Tabelle 2 zusammengefasst.

Tabelle 2.

Substanz	Ausbeute	Unveränderte Subst. zuruckgewonnen.
1. Sinomenin.	25%	—
2. Dihydro-sinomenin.	30%	—
3. Demethoxy-dihydro-sinomenin.	30%	—
4. Sinomenin-hydrat	30%	—
5. α-Demethoxy-sinomenin-hydrat	50%	—
6. β-Demethoxy-sinomenin-hydrat	30% (Schmp. 141°)	—
7. Sinomeninol	—	60%
8. Dihydrosinomeninol	—	60%

Die Tatsache, dass α-Demethoxysinomeninhydrat auch zu Desoxo-demethoxy-dihydrosinomenin reduciert wurde, zeigt dass in dieser Substanze die Hydroxylgruppe mit dem Keton benachbart sein muss. Folglich wurde dadurch die Auffassung seiner Muttersubstanz, Sinomeninhydrats, als ein Semiacetal wieder auch einigermassen bestätigt.

(1) *Ber.*, **52** (1914), 681.

In ihren Abhandlung, haben Kondo und Ochiai die Bezeichung Dihydro·thebainan[1] für die β·Tetrahydrodesoxycodein und Dihydrothebakodin vor·geschlagen. Doch denken wir dass der Name etwas ungepasst sei. Der Name Thebainon ist schon lange in der Literature eingebürgert, und man versteht jetzt allgemein dass in Thebainon die Methyl·amino·äthyl·seiten·kette in einem anderen Ort als beim Dihydrothebainon angehängt ist, wie es C. Schöff sehr wahrscheinlich gemacht hat. Wir mögen hier den Name Dihydro·eu·thebainan vorschlagen, weil die Tatsache dass die genannte Seitenkette in Thebain und Dihydrothebainon in demselben Punkt C(13) verknüpft ist jetzt allgemain anerkannt.

Beschreibung der Versuche.

I. Tafelsche Reduktion von Sinomenin und Seiner Derivaten. Die Resultate sind in der Tabelle 1 zusammengefaszt. Als Beispiele, sei die Reducierung von Demethoxy·dihydrosinomenin (V) hier angeführt werden. Wegen der Erspärnis des Materials, wurde das Gemisch[2] von der Ketonbase (V) und der Alkoholbase (VI) ohne Trennung angewendet. Die Bleikathode wurde nach Tafel[2] sorgfältig präpariert. 8 gr. des Basen·gemisches, gelöst in 160 c.c. 25% Schwefelsäure, erfüllte das Kathoden·raum, und die Anodenflüssigkeit bestand aus 900 c.c. 10% H_2SO_4. Stroms·konzentration 9–9.5 amp. / 100 c.c. Dauer 3 Stunden.

Die Kathodenflüssigkeit wurde dann mit 160 c.c. 20% NaOH alkalisiert. Der Niederschlag wurde in wenig Salzsäure gelöst und wieder mit Natron·lauge gefällt. Die Fällung wurde mit viel Wasser gewaschen und dann aus Aceton unkrystallisiert. Ausbeute 1.2 gr. Schmp. 149° (Keine Erniederung in der Mischprobe mit der Substanz, gewonnen in II). Diazoreaktion noch erkennbar in 1 : 2,000,000 Verdünnung.

Das Jodmethylat schmolz bei 267° (aus Wasser), ebenso die Mischprobe mit demjenigen, gewonnen durch Clemmensenschen Methode.

Aus dem alkalilöslichen Teil, wurden 2.2 gr. reiner Demethoxydihydro·sinomeninol (VI) zurückgewonnen, nebst 0.5 gr. Kristalle von dem Gemisch von den beiden Basen. Gesamte Ausbeute 3.9 gr. d.h. etwa 50%.

Da die Alkoholbase, wie man aus der Tabelle 1 ersehen kann, sehr schwer nach Tafel reducierbar ist, muss zweifellos die gesammte Ausbeute an Desoxo·demethoxy·dihydrosinomenin aus der Ketonbase entstanden haben.

(1) *Ber.*, **63** (1930). 646.
(2) Siehe die Bemerkung zu Tabelle 1.
(3) *Ber.*, **33** (1900), 2226.

Bei der Prüfung der Diazoreaktion an einzelnen Krystallisationen ergab sich dass es nie eine Fraktion gab, in der die Reaktion abgeschwächt ist.

II. Ueberführung von Demethoxy-dihydrosinomenin (V; d-Dihydrothebainon) ins Desoxo-demethoxy-dihydro-sinomenin (II; d-β-Tetra-hydrodesoxycodein). Diese Umwandlung geschah ganz in derselben Weise wie M. Freund[1] in der Bereitung von β-Tetrahydro-desoxy-codein aus Codein angegeben haben. 10 gr. wohl getrockneter Demethoxy-dihydro-sinomenin wurden portionsweise in das eisgekühlte Gemisch von 11 gr. Phosphorpentachlorid und 60 c.c. Chloroform eingetragen. Nach dem Stehenlassen übernachts, wurde das Hydrochlorid der Base mit viel Aether als öliger Niederschlag gefällt. Der letztere wurde mit viel (150 c.c.) gesättigter Sodalösung auf dem Wasserbad digeriert. Das Dichlorid wurde dabei krystallinisch, aber nie rein genug zur Analyse.

Das Dichlorid wurde, daher, ohne weitere Reinigung, der katalytischen Reduktion mit kolloidalem Palladium (aus 0.5 gr. $PdCl_2$+ wenig Gummi arabicum) in essigsauer Lösung unterworfen. Die Aufnahme von Wasserstoff betrug auf etwa 1,000 c.c. in anderthalb Stunden. Die in der üblichen Weise daraus isolierte Base bildete vier=oder sechs=eckige Tafeln, schmolz bei 147–148° und zeigte alle dieselben Eigenschaften mit der, die durch Clemmensensche Reduktion gewonnen worden war. Ausbeute etwa 25%.

Anal. Subst.=7.092; CO_2=19.544; H_2O=5.551 mg. Subst.=7.437 mg.; N_2=0.319 c.c. (15°, 760 mm.) Gef.: C=75.16; H=8.63; N=4.91%. Ber. für $C_{18}H_{25}NO_2$ (287): C=75.26; H=8.71; N=4.88%.

Das Jodmethylat schmolz scharf bei 267–268° (aus Methanol).

III. Des-N-Methyl-desoxo-demethoxy-dihydro-sinomenin. Fünf gramm des Jodmethylates der Base (II) (Schmp. 267° aus Wasser) wurden in 20 c.c. Wasser heiss gelöst und unter Zusatz von 20 c.c. 50% KOH eine halbe Stunde im Glycerin-bad gekocht. Beim Sättigen der abgekühlten und mit Wasser verdünnten Lösung mit Kohlensäure, schied sich ein flockiger Präcipitat, welcher in Alkohol aufgenommen und dann in viel Aether eingegossen wurde. Beim Abdampfen des Aethers blieb ein Syrup, der sich durch Rühren mit Aether krystallisieren liess. Aus Methanol umkrystallisiert, bildete es lange Prismen die beim 147–148° scharf schmolzten. Ausbeute 0.4 gr. d.h. etwa 15% der Theorie. (Formel XII).

Anal. Subst.=4.52: CO_2=12.587; H_2O=3.742 mg. Subst.=5.286 mg.; N_2=0.218 c.c. (15°, 760 mm.) Gef.: C=75.95; H=9.19; N=4.72%. Ber. für $C_{17}H_{27}O_2N$ (301): C=75.75; H=8.97; N=4.65%.

(1) *J. prakt. Chem.*, **101** (1921), 21.

Der stickstofffreie Körper. Da das Jodmethylat der des-Base keine Neigung zur Krystallisation zeigte, wurde es sofort mit Kalilauge abgebaut. Das Jodmethylat, bereitet aus 0.9 gr. der des-Base und 0.8 gr. Jodmethyl, wurde mit 10 c.c. 25% Kalilauge 20 Minuten gelinde gekocht. Das beim Abkühlen erstarrende Öl wurde mit Wasser gewaschen und in Aether aufgenommen. Der gewaschene und getrocknete Aether liess eine krystallinische Masse hinter, die sich aus Methanol in langen, schönen Prismen krystallisieren lassen hat. Schmp. 107 ~ 108° (vorheriges Sintern bei 97~98°). Ausbeute mehr als 50% der Theorie. (Formel XIII).

Anal. Subst.=5.444; CO_2=15.945; H_2O=3.797 mg. Gef.: C=79.88; H=7.75%. Ber. für $C_{17}H_{20}O_2$ (256): C=79.69; H=7.81%. 0.0191 gr. Subst. in 0.1848 gr. Campher. Erniederung 16.4°. Mol. Gew. Gef. 252.

IV. Clemmensensche Reduktion von Sinomenin und seinen Derivaten. Zinc-amalgam wurde nach Clemmensen bereitet. Je 1 gr. der Substanz wurde mit Ueberschuss von diesem Amalgam und 10 c.c. Salzsäure (1:1) ein oder zwei Stunden auf dem Wasserbad erhizt. Nach dem Ende der Reduktion, wurde die salzsaure Lösung von dem Amalgam abgegossen und mit Wasser sorgfältig verdünnt, dabei fällt das $ZnCl_2$-Doppelsalz (?) der reducierten Base in syrupöser Form.

Das lelztere wurde in wenig Aceton gelöst und in viel Chloroform eingegossen. Wenn dabei zu viel ungelöste Substanz bleibt, wird die Operation einigermals wiederholt. Die Aceton-Chloroformlösung wurde dann mit verdünntem Ammoniak gründlich geschüttelt und mit Wasser gewaschen. Beim Abdampfen der getrockneten Chloroformlösung bleibt ein Syrup züruck, welcher sich aus Aceton in vier- oder sechseckigen Tafeln krystallisieren läszt. Schmp. 148°. Ausbeute gewöhnlich etwas 30% der Theorie.

Aus der salzsaure Lösung gewinnt man natürlich etwas mehr von dieser Substanz, aber durch die obige Arbeitsweise bekommt man schnell das reinste Examplar.

Die Resultate dieser Reduktion mit verschiedenen Derivaten des Sinomenins sind in der Tabelle 2 zusammengefasst.

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STUDIES ON THE CONSTITUENTS OF THE VOLATILE OIL FROM THE LEAF OF CHAMAECYPARIS OBTUSA, SIEB. ET ZUCC., F. FORMOSANA, HAYATA, OR ARISAN-HINOKI. I.

By Kinzo KAFUKU, Tetsuo NOZOE and Chuta HATA.

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It was S. Uchida[1] who first studied the oil of *Chamaecyparis obtusa*, Sieb. et Zucc. f. *formosana*, Hayata, or Arisan-Hinoki. His oil, however, consisted of the product of dry distillation of the wood, and he reported to have found *d*-α-pinene and *l*-cadinene in the oil. Nextly, R. Tsuchihashi and S. Tasaki[2] studied the oil obtained by steam distillation of old root-stumps of the same plant, and proved the presence of *d*-α-pinene, *d*-α-terpineol, isoborneol, *d*-cadinene, a dicyclic sesquiterpene alcohol, an acid of the formula $C_9H_{16}O_2$ or $C_9H_{14}O_2$, and a phenolic substance of the formula $C_{10}H_{12}O_2$. Later, N. Hirao[3] examined a similar oil and found camphene, borneol, camphor, and an acid of the formula $C_{10}H_{16}O_2$ aside from those previously mentioned. To this acid Hirao gave the name "chamaenic acid," he also suggested that terpinolene and β-terpineol might probably be present. In all of these cases, the main component of the oil were *d*-α-pinene, *d*-α-terpineol, and cadinene. More recently, S. Uchida[4] published the result of his studies of the oil from the leaves of Japanese Hinoki (*Chamaecyparis obtusa*, Sieb. et Zucc.) and the following constituents are stated to have been found: — *d*-α-pinene; *d*-limonene; borneol, bornyl acetate; bornyl nonylate; a tricyclic sesquiterpene with a little cadinene; a dicyclic sesquiterpene alcohol; a tetracyclic diterpene; a new acid $C_{16}H_{24}O_2$. The last substance was named "hinokic acid" by the author. In quantity, *d*-α-pinene, *l*-limonene, and bornyl acetate predominated.

So far as the present authors are aware, however, there has been no report concerning the constituents of Formosa Hinoki leaf oil, and the authors took to the study of this oil which turned out to be quite different in composition from those cited above.

The main constituents of the acidic part was an unsaturated fatty acid possessing the physical properties resembling those of the acid described by Tsuchihashi and Tasaki (loc. cit.), but the results of analyses, molecular

(1) *J. Soc. Chem. Ind. Japan*, **19** (1916), 611.
(2) *Report of Gov. Research Inst. Formosa*, **1** (1920).
(3) *J. Chem. Soc. Japan*, **47** (1926), 666, 743.
(4) *J. Soc. Chem. Ind. Japan*, **31** (1928), 650.

weight determinations, and the molecular refraction corresponded to $C_{10}H_{16}O_2$ instead of $C_9H_{16}O_2$ or $C_9H_{14}O_2$. Chamaenic acid described by Hirao (loc. cit.) could not be found in our oil. The following table shows the data as regards these acids.

Table 1.

	Tsuchihashi-Tasaki	Hirao	Kafuku-Nozoe-Hata
Origin	wood	wood	leaf
B. p.	134°–140°/5mm.	130°–134°/6mm.	133°–135°/6mm.
Density	0.9507 (24/4)	1.0092 (20/4)	0.9544 (20/4)
n_D	1.4784 (24)	1.5271 (20)	1.4732 (20)
Formula	$C_9H_{16}O_2$	$C_{10}H_{16}O_2$	$C_{10}H_{16}O_2$
Mol. refr.	—	51.10	49.40
Br-absorption	—	2 Br.	2 Br.
Coloration with $FeCl_3$	—	deep red	deep red

Our acid, which perhaps is an aliphatic acid of the terpene series, gave a deep red coloration with a drop of dilute alcoholic solution of ferric chloride, precisely as is stated by Hirao in case of chamaenic acid (loc. cit.)—and moreover, it deposited a minute quantity of dark red crystals; but, as regards the exact nature of this acid, we must leave it for the future study.

On fractionation of the acid-free oil, the fraction boiling between 165° and 175° showed a density too low for an ordinary terpene and moreover it was very unstable and liable to oxidize on exposure to the air and ready to undergo polymerization. With a view that it might contain some new terpenes possessing definite properties, we carefully fractionated it repeatedly over metallic sodium under partial vacua and obtained at last a hydrocarbon of a characteristic odor with following constants: Boiling point=86°—88° under 50 mm.; $d_4^{25}=0.8228$; $n_D^{25}=1.4686$; rotatory power$_D^{25}$ =about+35°.

From considerations of its molecular refraction, its bromine number, and its non-reducibility by sodium and alcohol, it becomes evident that the hydrocarbon is neither a menthene nor a mixture of cyclic and chain terpenes, but a hitherto unknown new terpene of monocyclic nature. The authors wish to propose the name "*chamene*" to this new terpene, which, so far as the authors are aware, has the lowest density among all naturally occurring monocyclic terpenes, as shown in Table 2.

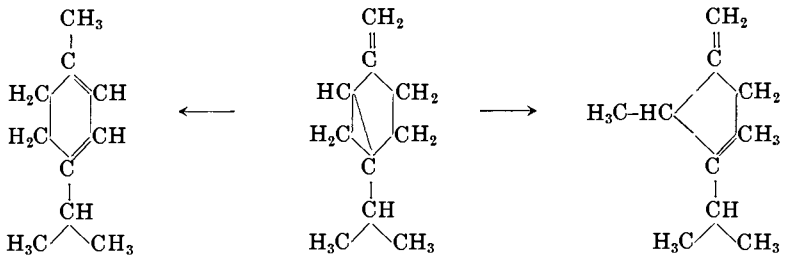
Table 2.

	B. p.	d_{20}	n_D^{20}	M.R.	M.R. as $C_{10}H_{16}$
Limonene	175°-176°	0.845	1.4746	45.24	45.24
Terpinolene	184°-188°	0.857	—	—	—
Terpinene	179°-181°	0.846	1.480	45.65	—
Phellandrene	170°-176°	0.845	1.4788	45.63	—
Sylvestrene	175°-176°	0.848	1.4753	45.23	—
Chamene	168°-170°	0.827	1.472	46.0	—

Chamene is easily oxidized on being kept in the air, thereby changing into a viscous oxygenous compound of higher density, and if shaken with an amount of dilute sulphuric acid it loses its optical activity and changes into another new terpene, to which we propose the name "*isochamene.*" Isochamene is fairly more stable than chamene but the physical properties remain almost unchanged, and it is not yet fully explained whether this change is due to isomerization or racemization. If alcoholic potash is used instead of dilute sulphuric acid, then an inactive diterpene "diisochamene" results.

Semmler,[1] on treating sabinene with concentrated formic acid at -20°C., obtained besides α-terpinene and formic ester of origanol (terpinenol-4), a hydrocarbon $C_{10}H_{16}$ with the following properties: Boiling point=50°-54° under 10mm., 169°-173° under 760mm.; d^{20}=0.829-0.831; n_D^{20}=1.470; α_D=+13°-+24°.

From the fact that this hydrocarbon showed a very low density and that its optical activity did not enfeeble even when it was boiled with an acid, and from the supposition that a semicyclic double linking is less influenced by acids than the cyclopropane ring, he assumed this hydrocarbon to be a derivative of cyclopentadiene of the formula (3) given below, but as to its chemical behaviors nothing is described in his paper:



(II) α-Terpinene ← (I) Sabinene → (III)

(1) *Ber.*, **39** (1906) 4414.

It is not difficult to consider that this hydrocarbon and chamene or isochamene to be in close connection,—although may or may not be the same substance,—as Semmler's formula is in accordance with such properties of chamene as the tendency to polymerize, isomerize or oxidize by itself. But it is absolutely necessary to determine at first whether this hydrocarbon does actually possess a pentamethylene ring, or not; and experiments are being carried out in this direction.

Fractions distilling below 158° had a fairly low specific gravity and were still unstable even though sabinene and chamene had been removed by repeated fractionations, which fact led us to test for the presence of, α-thujene and α-pinene. For this purpose we oxidized this fraction with dilute potassium permanganate and ketonic acids formed thereby were isolated as their semicarbazones. After repeated fractional crystallizations from dilute alcohol we succeeded in separating them into two parts, the one of which represented the semicarbazone of pinonic acid melting at 206°—207° while the other that of thujaketonic acid,[1] melting with decomposition at 180.5°—181.5°. Thus, it is most probable that α-thujene is contained in the oil, although any further identification could not be made.

An intermediate portion distilling between the terpene and terpene alcohol fractions possessed a characteristic pleasant odour reminding esters, so that it was saponified and a free alcohol of the formula $C_8H_{16}O$ was obtained. This alcohol represented an octenol, secondary in nature, but quite different from ordinary methyl heptenol. It had a peculiar musty odour and on oxidation with Beckmann's mixtures, it gave a product other than the ordinary methyl heptenone. The exact nature of this alcohol, however, could not be determined because of the small quantity available.

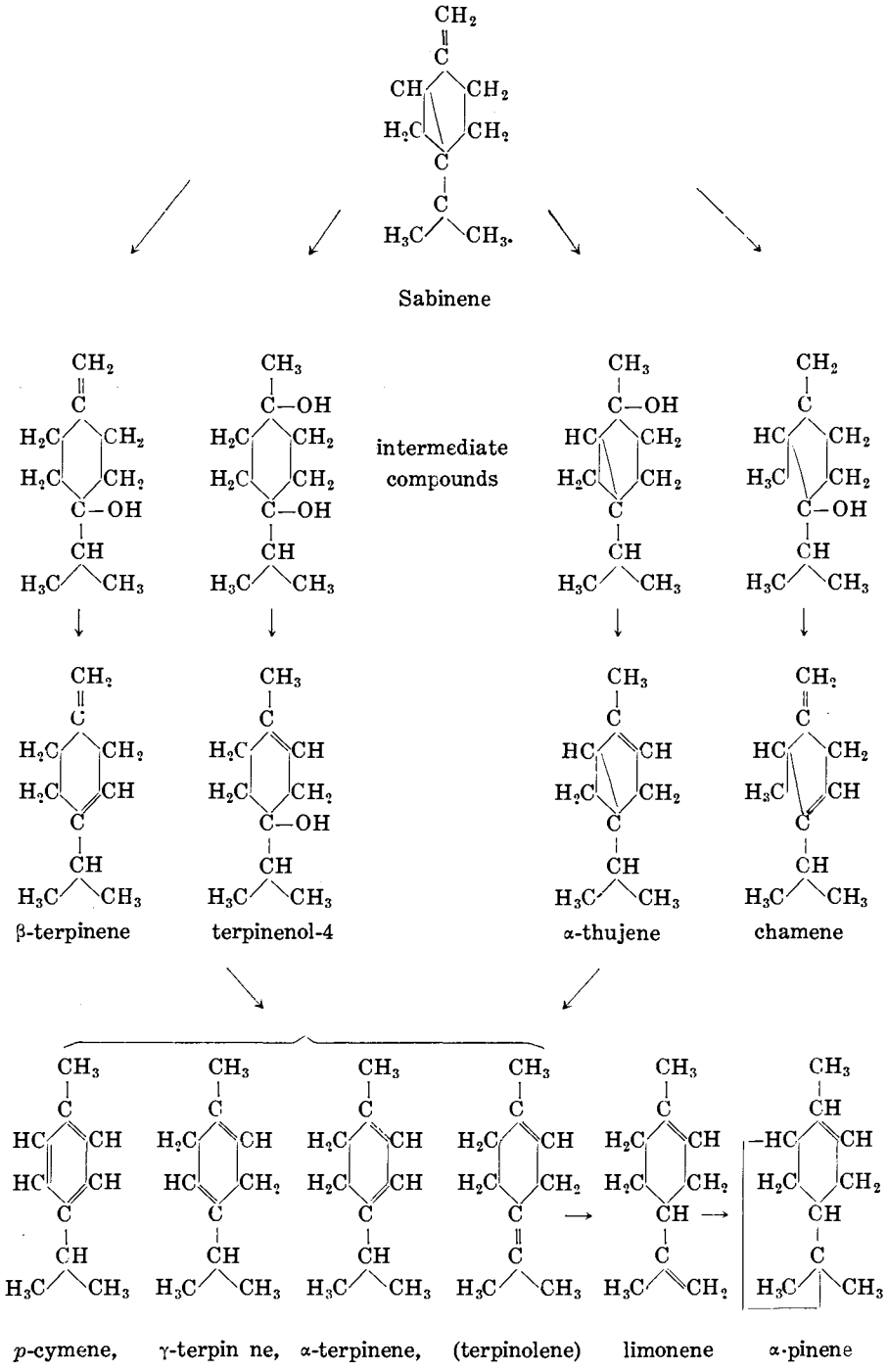
To summarize our results briefly:

1. The acidic portion which amounted to about 0.85% of the whole oil, consisted mainly of an unsaturated fatty acid of the formula $C_{10}H_{16}O_2$, and hinokic acid, $C_{16}H_{24}O_2$, melting at 165°—166°, together with a small quantity of an acid, probably caproic acid, and a trace of phenolic substances.

2. The terpene part occupied about 34% of the oil, of which about 50% consisted of d-sabinene, and 20—30% of a new terpene "*chamene*," the remainder represented d-α-pinene, p-cymene, α-terpinene, γ-terpinene, α-thujene, and a trace of dipentene.

3. The constitutional formula for chamene was partly deduced, but not yet fully established.

(1) Wallach (*Ber.*, **30**, 426), Thuja-ketonic Acid m.p.=182°-183°.
Semmler (*Ber.*, **35**, 552), Thuja-ketonic Acid m.p.=198.5°.


Sabinene
intermediate compounds
β-terpinene
terpinenol-4
α-thujene
chamene
p-cymene,
γ-terpin ne,
α-terpinene,
(terpinolene)
limonene
α-pinene

4. The terpene alcohol fraction occupied about 11.6% of the original oil, which consisted mainly of *d*-terpinenol—4. Besides, there were found a small amount of a laevo-rotatory alcohol of the formula $C_8H_{16}O$ and *l*-linalool, both for the most part in form of esters, and in addition to these a trace of borneol was found to present.

N. B. It is of interest that the chief constituents of the leaf oil, *d*-sabinene, *d*-chamene, and *d*-terpinenol-4, have never been found in the oils from root or wood, while *d*-α-pinene, dipentene, and α-terpineol which form the main part of the latter oils are to be found in the former oil either in very small quantities or not at all. Moreover, it seems peculiar, that almost all the constituents found in this oil are to some extent related to sabinene as may be seen from the scheme in the foregoing page.

Experimental.

The oil used for these experiments was obtained at Arisan (Mt. Ari) by steam distillation of the fresh leaves of "benihi" cypress or *Chamaecyparis Obtusa*, Sieb. et Zucc. f. *formosana*, Hay.; the yield amounting to 0.3% of the weight of live leaves. The oil had a characteristic pleasant odour and was of slightly yellow colour which gradually changed into deep red on standing. The properties of the oil were as follows: $d^{25}=0.8988$; $n_D^{25}=1.4878$; $\alpha_D^{25}=-5.83°$; Acid value=0.96; Ester value=12.63; Do. after acetylation=54.81.

The Acidic Part. The acid part was extracted from the oil by shaking with 5% caustic potash, and it was then regenerated from the aqueous solution in the usual way by means of carbon dioxide and dilute sulphuric acid. From 5 kg. of oil 12 gr. of the acidic part and 1.5 gr. of phenolic part were obtained.

This acidic mixture was fractionally distilled in vacuo three times successively, and from the fractions we could identify the following constituents:

i) *An Unsaturated Fatty Acid*, $C_{10}H_{16}O_2$. This formed the main fraction which had the following constants: B.p.=133°—135°; $d_4^{20}=0.9544$; $n_D^{20}=1.4732$; $\alpha_D=0°$; M.R.=49.40 as $C_{10}H_{16}O_2$, calculated value 48.99.

Anal. Subst.=0.1365; $CO_2=0.3558$; $H_2O=0.1233$ gr. Found: C=71.08; H=10.03%. Calc. for $C_{10}H_{16}O_2$: C=70.58; H=10.58%. Calc. for $C_{10}H_{18}O_2$: C=71.42; H=9.50%.

0.0999 gr. substance in carbon tetrachloride at 0°C. absorbed 0.0948 gr. bromine. Calculated for $C_{10}H_{16}O_2Br_2$: Br=0.0950 gr.

Molecular weight. 0.2067 gr. acid required 12.65 c.c. of normal caustic soda (N=0.969) for neutralization, corresponding to a molecular w ight of 168.6. $C_{10}H_{16}O_2=168.2$. 2.80 mg. of the silver salt gave 1.07 mg. silver, corresponding to a molecular weight of 168.4.

Neither an acid amide nor an anilide could be obtained in the crystalline form.

The solution of this acid gave an intense red coloration on shaking with a few drops of ferric chloride solution and deposited a small amount of dark red crystalline precipitate on standing, but the nature of this precipitate, however, has not been studied further.

ii) *Hinokic Acid.* The fraction boiling above 150° under 2 mm. pressure, solidified on standing and after recrystallization from dilute alcohol melted at 165°—166°. This acid is in all probability identical with Uchida's hinokic acid.

iii) Besides, there was a trace of lower fatty acid, which judging from the results of analyses of its silver salt, seemed likely to be caproic acid.

iv) Phenols, with lower boiling point, gave reddish violet coloration to alcoholic ferric chloride, while the higher ones, a deep bluish green on the same treatment, but on account of the small quantity we could not identify any of the individual phenols.

The Neutral Part. A preliminary examination has shown that the oil did not contain any noticeable quantity of aldehydes or ketones (shaking with concentrated sodium bisulphite solution), and moreover, that it was rather unstable to the action of the acid, so we fractionated the oil directly without any treatment beforehand.

2500 c.c. of the oil was fractionated carefully under reduced pressures, and after four consecutive fractionations the whole was divided into the following six sections:

Table 3.

(A)	40°— 80°/50 mm.	1362 gr.	34.1% (Terpenes)
(B)	80°—120°/50 mm.	456 gr.	11.4% (Terpene alcohols)
(C)	120°—140°/50 mm.	1607 gr.	40.2% (Sesquiterpenes)
(D)	140° –160°/50 mm.	394 gr.	9.6% (Sesquiterpene alcohols)
(E)	160°—180°/50 mm.	52 gr.	1.8% (Diterpenes)
(F)	The residue	16 gr.	0.4%

In all of the fractional distillations the authors used Widmer's fractionating column.

The Terpenes. The fraction (A) in the foregoing table was further fractionated over metallic sodium under 50 mm. pressure and separated into the following eleven fractions as shown below:

Table 4.

No.	B.p./50 mm.	Yield	d_4^{22}	n_D^{22}	α_D^{22}
1	76°— 78°	53 gr.	0.842	1.4651	+30.4°
2	78°— 80°	131	0.839	1.4662	+40.9°
3	80°— 82°	171	0·835	1.4673	+48.3°
4	82°— 84°	128	0.830	1.4685	+48.7°
5	84°— 86°	76	0.830	1.4698	+42.3°
6	86°— 88°	44	0.829	1.4705	+35.2°
7	88°— 90°	12	0.831	1.4712	+27.5°.
8	90°— 92°	40	0.833	1.4726	+20.4°
9	92°— 94°	50	0.837	1.4746	+13.1°
10	94°— 98°	67	0.847	1.4773	+ 5.5°
11	98°—106°	5	0.870	1.4740	+ 3.0°

The New Terpene "Chamene." As the fractions (3) to (7) had a very low specific gravity, and were liable to deposit a viscous liquid (not water) on exposure to the air, we studied these fractions first of all. These were once again repeatedly and systematically fractionated over metallic sodium and at last we could obtain a rather pure sample with the following constants: B.p. = 86°—88° under 50 mm., 168°—170° under 760 mm.; $d_4^{25} = 0.8228$; $n_D^{25} = 1.4686$; $\alpha_D = +35.0°$; M. R. = 46.00, calculated as $C_{10}H_{16}|_2^{=} = 45.2$.

As chamene was ready to oxidize in the air, the authors experienced difficulty in getting good results in analyses.

0.2745 gr. substance absorbed 0.7033 gr. bromine, the amount calculated for $C_{10}H_{16}Br_2$ being 0.6443 gr.

The hydrochloride was obtained by saturating the ethereal solution of the hydrocarbon with dry hydrogen chloride for two days in the cold. The product was a liquid which boiled at 80°—90° under 11 mm. pressure with a density 1.0196 at 25°C., and a refractive index 1.4783 at the same temperature. The molecular refraction found was 58.09 as $C_{10}H_{18}Cl_2$ or 50.58 as $C_{10}H_{17}Cl$, while those calculated were 55.91 as $C_{10}H_{18}Cl_2$ ($|^{=} = 0$) and 50.58 as $C_{10}H_{17}Cl$ ($|^{=} = 1$).

Attempts to reduce the hydrocarbon itself or this hydrochloride with sodium and alcohol were not effective; also all efforts to get characteristic crystalline substance proved unsuccessful.

Chamene, especially in the pure state, was very unstable and liable to change into a viscous liquid insoluble in the original terpene which seemed

likely to be a peroxide. As for the exact nature of the products of oxidation it should remain to be reported until the next opportunity.

Isomerisation of chamene was carried out by shaking 20 gr. of chamene with 20 c.c. of dilute sulphuric acid (1 :3) for two hours at room temperatures, when its optical activity all but disappeared and a new isomeric terpene was obtained, which was thoroughly washed with water, dried over anhydrous sodium sulphate, and then rectified in vacuo. This terpene, to which we suggest the name "*isochamene*," was found to possess the following constants: B.p.=88°–90° under 50 mm.; $d_4^{25}=0.8222$; $n_D^{25}=1.4726$; $\alpha_D^{25}=-0.27°$; M.R.=46.42, calculated as $C_{10}H_{16}\overline{|}_2=45.2$.

Anal. Subst.=0.1088; $CO_2=0.3475$; $H_2O=0.1123$ gr. Found: C=87.11; H=11.46%. Calc. for $C_{10}H_{16}$: C=88.23; H=11.77%.

Contrary to chamene, isochamene was found to be fairly more stable than chamene against the action of the air.

Polymerization of isochamene to its dimeride ensued when alcoholic sulphuric acid (1 : 1) was used instead of the aqueous in the experiment described above; the rotatory power being destroyed almost to nothing in half an hour with appreciable evolution of heat. The product represented a mixture of a diterpene with a little isochamene, which was rectified in the usual manner and the diterpene with the following properties was obtained: B.p. = 155°–156° under 4 mm.; $d_4^{20}=0.9150$; $n_D^{20}=1.5134$; $\alpha_D^{20}=-0.7°$; M.R.=89.40, calculated as $C_{20}H_{32}\overline{|}_3=88.76$.

The name "*diisochamene*" is given by the authors to this new diterpene as it was obtained by the condensation of two molecules of isochamene.

To a well-cooled mixture of a benzol solution of isochamene and a calculated amount of sodium nitrite solution under stirring, glacial acetic acid was added drop by drop, when the solution assumed a blue colour at first which gradually turned into yellow. No crystal formation set in before the solution was warmed once again to about 50° when it suddenly deposited a quantity of colourless needles which after recrystallization from dilute alcohol, melted at 154°–155°. Strangely enough, this crystal was proved to be identical with α-terpinene nitrosite by observing the mixed melting point with an authentic specimen of the same. Whether this nitrosite resulted from by-mixed terpinene really existent in the isochamene fraction or from an intramolecular rearrangement of isochamene nitrosite, is not clear, but from consideration of the feature and quantity of crystal formation, the latter course seems the more probable.

Chamene dissolved in acetic anhydride, if treated with a drop of concentrated sulphuric acid, a deep red coloration is produced.

The total amount of chamene in the oil perhaps amounted to 20—30% although the final product in the pure condition was rather small in quantity.

The Terpenes boiling lower than Chamene. The fractions of lower boiling terpenes—No. 1 to No. 6 were further fractionated under ordinary pressures over metallic sodium and they were divided into the following eleven fractions taking into consideration their optical activities:—

Table 5.

No.	α_D^{18}	B.p./760 mm.	n_D^{18}	d_4^{19}	Yield	M.R.
1	− 4°—+0°	153.0°—155.0°	1.4628	0.8463	14 gr.	44.6
2	+ 0°—+5°	155.0°—155.5°	1.4642	0.8475	20	44.3
3	+ 5°—+10°	155.5°—156.0°	1.4647	0.8477	13	44.3
4	+10°—+15°	156.0°—156.5°	1.4651	0.8477	21	44.4
5	+15°—+20°	156.5°—157·0°	1.4655	0.8474	29	44.4
6	+20°—+32°	157.0°—157.5°	1.4661	0.8469	24	44.5
7	+32°—+40°	157.5°—158.0°	1.4665	0.8462	18	44.6
8	+40°—+50°	158.0°—159.0°	1.4669	0.8453	35	44.6
9	+50°—+60°	159.0°—160.0°	1.4677	0.8435	30	44.8
10	+60°—+62°	160.0°—161.0°	1.4680	0.8425	15	44.9
11	+62°—+66°	161.0°—162.0°	1.4690	0·8420	150	45.0

From these fractions we could identify α-pinene, α-thujene, and *d*-sabinene.

α-Pinene. The presence of α-pinene was proved by preparing nitroso-chloride, nitrolbenzylamine, nitrolpiperidine, and pinonic acid melting at 106°—107°, 121°—122.5°, 118°—119°, and 206.5°—207 respectively.

d-Sabinene. Fraction (11) represented nearly pure sabinene, whose presence being confirmed by preparing the sparingly soluble sodium salt of sabinic acid, and the free acid melting at 58°—58.5° from the products of oxidation of the fraction with alkaline permanganate. Besides, we obtained sabina ketone and its semicarbazone (m.p. 141°—142°). It should be mentioned that our sabinene was found to possess the highest optical activity. The hitherto observed highest data being + 68.54°[1] while the authors' sabinene after careful rectifications showed the following constants: B.p.=161°—163°; $d_4^{17.5}$=0.8442; $n_D^{17.5}$=1.4695; $\alpha_D^{17.5}$=+72.94°; $[\alpha]_D^{17.5}$=+86.4°; M.R.=44.90, calc. as $C_{10}H_{16}$ $\overline{\overline{=}}$ 43.51.

(1) Ber. von Schimmel & Co. — Gildemeister u. Hoffmann, "Die Ätherischen Öle," Vol. 1, p. 356.

α-Thujene. A well-cooled mixture of the fractions No. 3 to No. 6 (45 gr.) was oxidized by means of alkaline permanganate solution, and the resulting oxidized products were treated in the usual manner and obtained 30 gr. of acid. This was extracted with ether and the extract was neutralized with sodium hydroxide. On evaporation 3.5 gr. of sodium sabinate separated out as crystals while from the filtrate 22 gr. of other acids were recovered. These gave on treatment with semicarbazide hydrochloride, about 12 gr. of a crystalline body melting at 190°—198°, seemingly a mixture of more than two semicarbazones. Thus, it was fractionally recrystallized from dilute alcohol and at last we obtained two different products, the one melting at 201°—203° and the other at 184°—186°. These were further fractionated in the same medium eight consecutive times and were differentiated into (a) the more difficultly soluble prismatic crystals—pinonic acid semicarbazone m.p. 206°—207°, and (b) the more easily soluble thin needle crystals melting with decomposition at 181°—181.5°. This latter melting point coincides with that of α-tanaceto-keto-carboxylic acid semicarbazone,[1] but whether it be such or not is not clear.

Anal. Subst. = 3.61 mg.; N_2 = 0.579 c.c. (30°, 759 mm.) Found: N = 16.95%. Calc. for $C_{11}H_{19}O_3N_3$: N = 17.4%.

The Higher Boiling Terpenes. The fractions (8), (9), (10), and (11), were further fractionated over metallic sodium into the following five fractions:

Table 6.

	B.p./760 mm.	Yield	n_D^{22}	d_4^{22}	α_D^{22}
1)	168°—172°	84 gr.	1.4710	0.8300	+30.0°
2)	172°—175°	16	1.4735	0.8354	+16.6°
3)	175°—178°	44	1.4759	0.8418	+ 8.5°
4)	178°—181°	45	1.4782	0.8471	+ 3.5°
5)	181°—	8	1.4832	0.8545	+ 1.1°

In the above, 1) consisted mainly of chamene, while 3) and 4) contained *p*-cymene, α-terpinene, γ-terpinene and dipentene. The first of these, *p*-cymene, was isolated after repeated treatments with dilute permanganate solution as a mobile, highly refracting liquid of the characteristic smell, from which on oxidation with a more concentrated solution of potassium

(1) Wallach, *Ber.*, **30**, 426.

permanganate, crystals of *p*-oxy-isopropyl-benzoic acid[1] (m.p. 115°—Misch-proben) was obtained. The presence of α-, and γ-terpinenes was proved by preparing $\alpha\alpha'$-dioxy-α-methyl-α'-isopropyl adipic acid[2] (m.p. 188°—189°—Mischproben) and γ-terpinene erythrite (m.p. 236°—238°—Mischproben) respectively. Dipentene was found in small quantity in 4) from which the tetrabromide could be prepared in the ordinary way.

The presence of Δ_3-, and Δ_4-carenes, α-, and β-phellandrenes was suspected and tests in these directions were made but without success.

The Terpene Alcohols. The fraction (B), which consisted mainly of terpene alcohols, was submitted to a careful and systematic fractionation under reduced pressures (at first under 12 mm., and finally under 50 mm. pressure), and ultimately it was divided into the following twelve fractions:

Table 7.

	B.p./50 mm.	Yield	d_4^{20}	n_D^{20}	α_D^{20}	Ester value
(1)	up to 105°	11 gr.	0.853	1.476	+ 2.5°	—
(2)	105°—112°	3	—	1.465	+ 3.8°	—
(3)	112°—115°	2	0.884	1.458	+ 4.9°	78.5
(4)	115°—118°	7	0.899	1.464	+ 9.5°	44.2
(5)	118°—121°	17	0.907	1.468	+13.5°	—
(6)	121°—124°	78	0.931	1.475	+20.1°	29.1
(7)	124°—127°	22	0.930	1.472	+19.2°	51.8
(8)	127°—130°	12	0.928	1.468	+14.5°	—
(9)	130°—133°	13	0.926	1.466	+ 4.3°	157.2°
(10)	133°—136°	5	—	1.467	+ 0.5°	157.8
(11)	136°—140°	6	0.932	1.477	- 12.5°	109.0
(12)	140°—145°	7	0.934	1.481	−25.6°	80.5

With these fractions the following identifications were made:

i) *An Octenol $C_8H_{16}O$ and its Ester.* The fractions (2) and (3) had a characteristic pleasant odour reminding the presence of an ester, therefore we mixed the fractions (1) to (4) and saponified the mixture by heating with alcoholic potash for two hours. The free alcohol thus obtained was purified by distillation in vacuo, the constants of which are: $d_4^{30}=0.8454$; $n_D^{30}=1.4441$; $\alpha_D^{30}=-10.62$.

Anal. Subst.=0.1189; CO_2=0.3290; H_2O=0.1298 gr. Found: C=75. 8; H=12.12%. Calc. for $C_8H_{16}O$: C=75.00; H=12.50%.

(1) Wallach, *Ann.*, **264** (1891), 10.
(2) Wallach, *Ann.*, **362** (1908), 297.

The purified alcohol had a peculiar not-unpleasant odour but reminding of mouldy cellar, did react with phthalic anhydride not at 100°C., but at 130° with formation of an ester-acid. The physical constants of this alcohol almost coincided with those of methyl heptenol, but these two differed distinctly in their odour as well as their behaviour towards Beckmann's chromic acid mixture,—the former in not giving the ordinary methyl heptenone while the latter did. The attempt to prepare crystalline derivatives from the alcohol were altogether futile.

ii) *d-Δ_1-Terpinenol-4.* The fractions (5) to (7) represented a free terpene alcohol with a little ester, so they were saponified to get rid of the latter, and then distilled, when, it was found that the main fraction boiled very constantly at 122°—123° under 50 mm. pressure. The properties of the main distillate are as follows: $d_4^{14}=0.9410$; $n_D^{14}=1.4806$; $\alpha_D^{14}=+23.58°$; M.R.=45.9°, calc. as $C_{10}H_{15}OH\,\overline{\overline{\Delta_1}}$ =45.04.

These constants agree fairly well with those of *d-Δ_1*-terpinenol-4 so the following derivatives were prepared for the identification. *Nitroso-chloride.* The nitrosochloride was prepared just in the same way as in the case of pinene, and was found to melt at 109°—110°. The nitrolpiperidin derived from this melted after purifications at 178°—179°, and showed no depression of the melting point on admixture with pure *β*-nitrolpiperidin of *i-Δ_1*-terpinenol-4 (m.p. 181°). *1, 2, 4-Trioxyterpane.* The alcohol, on treatment with an ice-cold, dilute, alkaline permanganate solution, gave 1, 2, 4-trioxyterpane[1] which melted after recrystallization from water at 115°—116° (with a molecule of water of crystallization) and after being dried at 80° in vacuo at 124°—125°.

iii) *Borneol.* In course of the above described experiment, during the steam distillation of the oxidized products, a small quantity of needle-like crystal was observed to separate out in the colder part of the receiver which on examination was found to possess an unmistakable odour of borneol.

iv) *l-Linalool and its Ester.* The fractions (9) and (10) consisted of esters of very pleasant smell which after saponification and subsequent extraction and distillation gave an alcohol having the characteristic odour of linalool with the following constants: B.p.=116°—118° under 50 mm.; $d_4^{20}=0.8695$; $n_D^{20}=1.4648$; $\alpha_D=-14.28°$.

The alcohol was identified as linalool by obtaining the phenyl urethane melting at 60°—63° whose melting point did not lower on admixture with a known sample of linalool phenyl urethane from 'Ho'-oil. Besides, it gave

(1) Wallach, *Ann.*, **356** (1907), 215; also K. Nagai, Investigation of Shogyu- and Yuju-oils (Monopoly Bureau, Government of Formosa, 1914).

rise to an unmistakable odour of citral on treatment with Beckmann's chromic mixture.

From the caustic residue of the saponification, the acidic constituents were recovered in the usual manner. The recovered acid possessed a smell more like caproic acid, but the analysis of the silver salt, however, showed that the greater part was acetic acid, viz. :—

4.82 mg. substance gave 3.04 mg. silver. Found: Ag=63.1%. Calc. for CH_3CO_2Ag: Ag=64.7%.

It follows that linalool existed in the oil chiefly as acetate and a fraction as an ester of higher fatty acid.

Attempts to prove the presence of α-terpineol as its phenyl urethane or its nitrosochloride did not succeed.

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DISPERSOIDOLOGICAL STUDY OF SILVER SALTS IN AQUEOUS ETHYL ALCOHOL, ACETONE AND PROPIONE SOLUTIONS. I.

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On the Complex[1] Solubility and on the Dispergation of an AgI-Precipitate in Aqueous Ethyl Alcohol and Acetone Solutions of KI.

Historical Introduction and Subject of Investigations. The colloidal synthesis of silver salts which are practically insoluble in an aqueous dispersion medium, was the subject of the classical investigations of

(1) By "complex solubility" P.P. von Weimarn designates the solubility of substance AB in solutions of substance AX or BY, with which AB forms complex molecules; the complex molecules become decomposed on the dilution of the solutions by the dispersion medium. In these cases of dissolution, crystals of substance AB are the solid phase (saturating substance).

A. Lottermoser[1]; who also established that e.g. for the cases of dispergation of an AgI-precipitate in *aqueous* KI solutions of progressively increasing concentrations,[2] the dispergation curves have a maximum point (see Curve A, Fig. 2).

The stability of colloidal solutions of silver salts is explained by Lottermoser (l.c.) by the adsorption of ions; owing to this adsorption the disperse particles acquire electrical charges which hinder coagulation.

P.P. von Weimarn[3] ascribes the causes of stability of these colloidal solutions to kinetic processes taking place on the surfaces of the disperse particles and in the dispersion medium; these processes are closely connected with the formation of complex molecules (e.g. AgI, KI).

On the ground of his investigations embracing the colloidal synthesis in mixtures of alcohols and water, of various salts (amongst them of AgI, AgBr, AgCl, silver-citrate and silver-tartrate) P.P. von Weimarn[4] had arrived at a series of conclusions, of these the two following are of special importance for the present investigations.

(1) Ability for complex-formation increases with decrease in the dielectric constant of the dispersion medium. For instance, in the aqueous ethyl alcohol solutions, the dielectric constant decreases with increase of the concentration of alcohol; therefore, with a certain[5] *constant* concentration of substance AX (or BY) in the solution, owing to increase in the complex-formation, the complex solubility of substance AB increases simultaneously with increase of the concentration of alcohol (e.g. $BaSO_4$ in an alcoholic-aqueous BaI_2 solution; AgI in an alcoholic-aqueous KI solution, etc.). These correlations are represented schematically in Fig. 1.

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(1) Lottermoser, *J. prakt. Chem.*, **72-73** (1905), 39 and 374; *Koll.-Zeitschr.*, **1** (1906), 11; *Z. physik. Chem.*, **60** (1907), 451; *Koll.-Zeitschr.*, **2** (1907), Suppl. I, IV; *Z. physik. Chem.*, **62** (1908), 359; *Koll.-Zeitschr.*, **3** (1908), 31; *Z. physik. Chem.*, **70** (1910), 239; *Koll.-Zeitschr.*, **5** (1909), 78; *Koll.-Zeitschr.*, **36** Erg. (1925), 230; *Collegium* (1925), 573; *Z. angew. Chem.*, **39** (1926), 347.

(2) Lottermoser, *Z. physik. Chem.*, **62** (1908), 376.

(3) P.P. von Weimarn, *J. Russ. Chem. Soc.*, **40** (1908), 1785; *Koll.-Zeitschr.*, **4** (1909), 123; "Kolloides und kristalloides Lösen und Niederschlagen," **2** (1921), Kyoto.

(4) P.P. von Weimarn, *News of the Ural Mining Institute*, **1** (1918-1919), Part III, 38; *Koll.-Zeitschr.*, **28** (1921), 99; **32** (1923), 147. For more details see P.P. von Weimarn's paper referred to in Footnote (1) in the next page.

(5) With weaker concentrations of substance AX or BY, the solubility of substance AB decreases according to the Nernst-Noyes' law. For more details, see P.P. von Weimarn's paper referred to in Footnote (1) in the next page.

(2) Increase in complex-formation and complex solubility of substance AB, when the concentration of alcohol in the alcoholic-aqueous solutions of substance AX (or BY) is increased, has an influence on the stability of colloidal solutions, in narrowing the region of concentrations of substance AX (or BY) within the limits of which the existence of a colloidal solution of substance AB is possible.

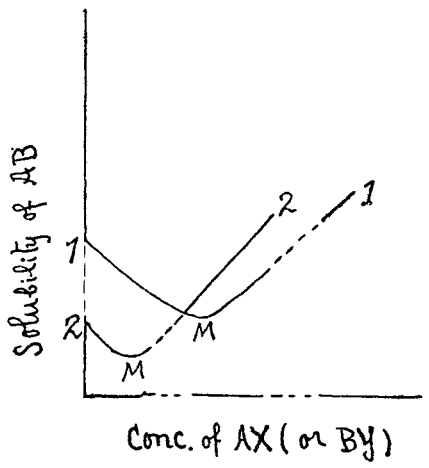
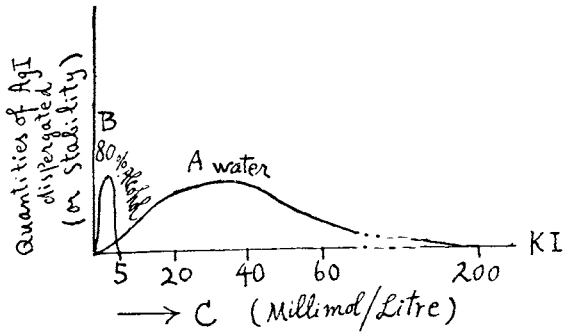


Fig. 1.

(After P.P. von Weimarn. Curve 1 M 1-dispersion medium, water; curve 2 M 2-dipersion medium, e.g. 80% alcohol).

These correlations in the case of AgI and KI are shown schematically in Fig. 2.

For a clear understanding of the stability of colloidal solutions in presence of complex-formation, P.P. von Weimarn in his recent paper[1] has especially stressed the great importance of quantitative investigations of complex solubility, of adsorption and of other variables. Prof. P.P. von Weimarn was kind enough to suggest to me a quantitative study of the following:



(Curve A, after A. Lottermoser; Curve B, after P.P. von Weimarn.)

Fig. 2.

(1) P.P. von Weimarn, "The influence of solubility, adsorption, complex-formation and solvation, upon the stability of the colloidal state." This paper will appear in the course of this year, in *Kolloidchemische Beihefte*.

1. The dispergation of *precipitates*[1] of different dispersities of AgI, AgBr, AgCl etc. in KI, KBr, KCl etc. ethyl alcoholic aqueous solutions with a progressively increasing concentration of alcohol.

2. The complex solubilities of the same substances.

3. The adsorption of the above-named dispergators.

4. The dispersoidal synthesis of practically insoluble silver salts, in aqueous acetone and propione (diethyl ketone) solutions.

The dielectric constants of acetone and propione are smaller than that of ethyl alcohol (ethyl alcohol, 26.5; acetone, 20.7 and propione, 17.0). Moreover, no investigations have been carried out up to the present upon the colloidal synthesis of practically insoluble silver salts in aqueous acetone and propione solutions.

Up to the present the author has completed the determination of the complex solubility of AgI[2] in aqueous ethyl alcohol and acetone solutions of KI,[3] as well as determining the AgI dispergation curves for these solutions.

Experimental Part.

§ 1. Complex Solubility, and the Dispergation Curve of AgI in Aqueous Ethyl Alcohol Solution of KI. An extremely pure AgI-precipitate was prepared for the experiments. It did not show traces of any admixtures ($AgNO_3$ or KI) even when tested by the most sensitive qualitative reactions. In order to reach such a high state of purity the AgI precipitate was washed during ten days with large amounts of water. Further the precipitate was thoroughly washed with ethyl alcohol and dried at 130°C. Micro-and ultramicroscopical investigations of this precipitate showed its polydispersity. A part of the crystals composing the precipitate were of colloidal dimensions, but the degree of their dispersity was not high. The size of other crystals of this AgI-precipitate was above the colloidal; nevertheless they were so small that only seldom could the regularity of their shape be established by microscopic examination under maximum magnification.

(1) Colloidal synthesis of practically insoluble silver salts in statu nascendi (by the double decomposition reaction) was the subject of P.P. von Weimarn's investigations (l.c.). P.P. von Weimarn will continue these researches, especially with aqueous solutions of propyl and butyl alcohols.

(2) On the complex solubility of $BaSO_4$ in alcoholic-aqueous solutions of BaI_2, $BaBr_2$ and $BaCl_2$, see the paper of P.P. von Weimarn and S. Ishii, which will appear in the course of this year, in *Kolloidchemische Beihefte*.

(3) I have also studied crystals of various complex compounds of AgI and KI; certain of these crystals proved to be sensitive to light. The results of this investigation will appear in my paper in the *Reports of the Imperial Industrial Research Institute of Osaka* (1931).

The experiments for the determination of AgI complex solubility in aqueous ethyl alcohol KI solutions were carried out as follows. About 3 gr. of AgI-precipitate and 100 c.c. KI-solution of a definite concentration were placed into a cylindrical glass vessel which after being carefully stoppered, was shaken for half an hour in a shaking machine. After shaking, the vessel containing the disperse system formed, was kept in a thermostat (20°C.) up to the time when complete precipitation of AgI disperse particles took place. The precipitation was regarded as completed when the supernatant solution no longer produced the Tyndall cone (in a dark room, under arc-lamp illumination). This solution, perfectly "optically void," was filtered and about 80 c.c. were taken for the determination of AgI and KI concentrations. After heating the solution in order to eliminate the alcohol, 300 c.c. water were added. The quantity of AgI (precipitated on the addition of water) was determined by gravimetric analysis; and that of KI in the filtrate by volumetric analysis according to Volhard. Complex solubilities, weaker than 1.10^{-4} mol per litre, were determined by tyndallimetry.

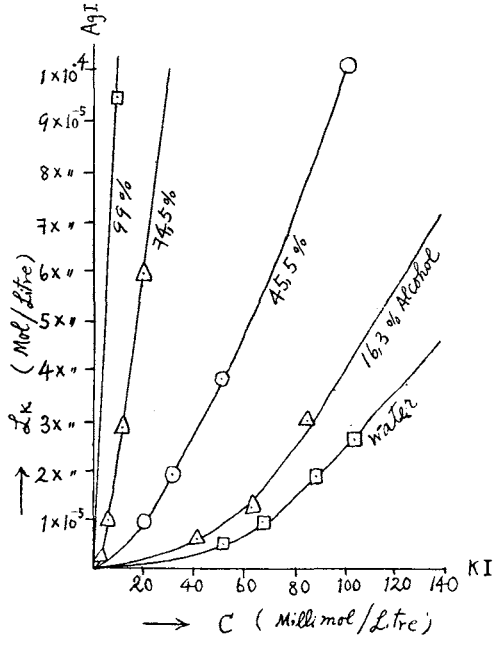


Fig. 3*a*.

In Figs. 3*a* and 3*b* are shown graphically the results obtained by the author (the coordinates for the curves in Fig. 3*a* are L_k, complex solubility in mol-liter, and C, concentration in millimol-liter of KI in the solution; for

the curves in Fig. 3*b* they are $\mathrm{Log}L_k$ and $\sqrt{C}$; the concentration of alcohol is expressed by weight percentage).

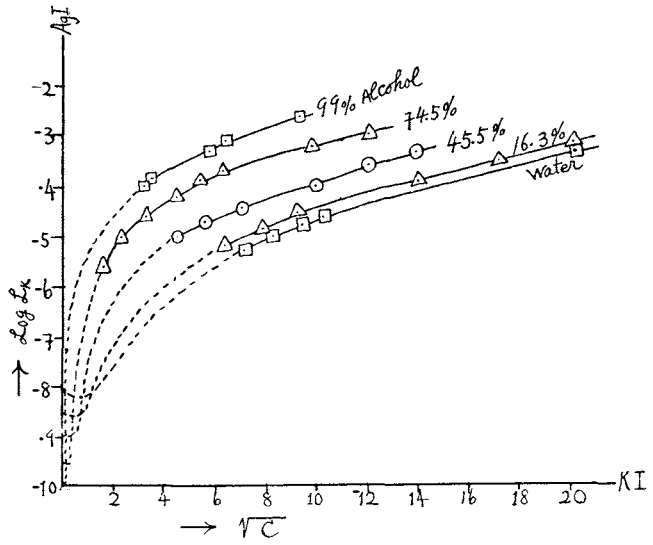


Fig. 3*b*.

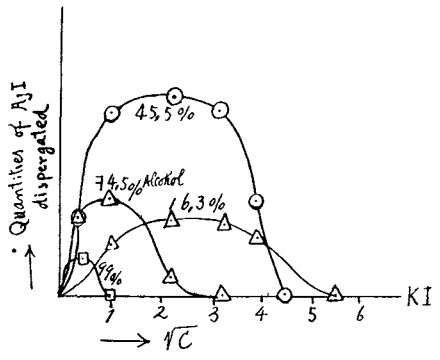


Fig. 4. (After one month)

The experiments on the dispergation of the AgI-precipitate in KI solutions were carried out as follows. A cylindrical glass vessel containing 1 gr. of AgI (powdered in an agate mortar) and 25 c.c. KI solution of a definite concentration was carefully stoppered and placed in a shaking machine for 20 minutes. The disperse system, obtained after shaking, was kept in a dark room. In Fig. 4 are represented graphically some of the results obtained by the author (the coordinates for the curves are $\sqrt{C}$ and quantities of AgI dispergated).

2. Complex Solubilities and the Dispergation Curves of AgI in Aqueous Acetone Solutions of KI. The same methods of investigation as those described in paragraph 1 have been employed. The results obtained are graphically represented in Figs. 5*a*, 5*b* and 6.

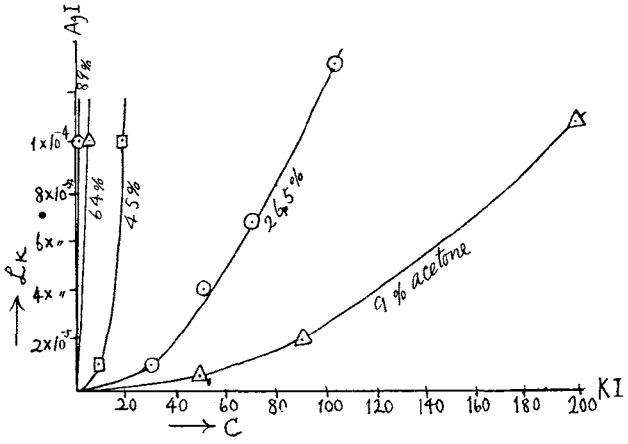


Fig. 5*a*.

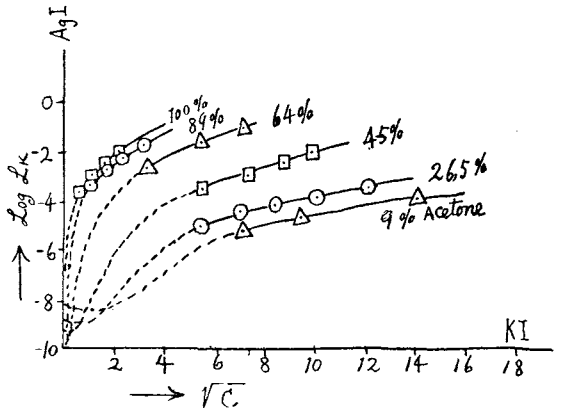


Fig. 5*b*.

When acetone is diluted with water, the strong fall in the complex solubility must correspond (see P. P. von Weimarn, Preface) to a strong increase of the dielectric constant in the acetone · aqueous mixtures, when the concentration of acetone is lowered. As is clear from the following Table such increase of the dielectric constant actually takes place.

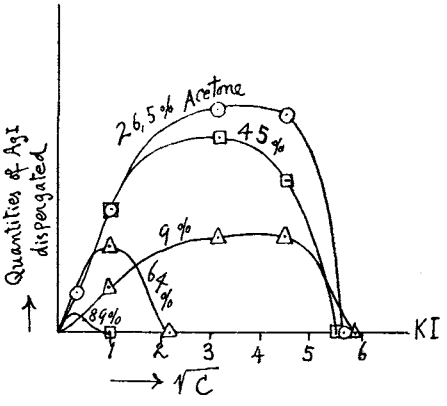


Fig. 6. (After one month)

Table 1.

Wt. % acetone	Dielect. const (19°C.)	Wt. % ethyl alcohol	Dielect. const. (20°C.)
0.	81.8	0.	81.9
25.0	67.7	—	—
50.0	51.2	50.0	49.4
80.0	32.2	80.0	34.1
100.0	20.7	100.0	26.5

Summary.

In this paper is given a graphical representation of quantitative data pertaining to:

1. The complex solubility of the AgI-precipitate in aqueous ethyl alcohol solutions of KI.
2. The dispergation process in the same solutions.
3. The complex solubility of the AgI-precipitate in aqueous acetone solutions of KI.
4. The dispergation process in the same solutions.

I wish to express here to Professor P.P. von Weimarn my sincere gratitude for suggesting the theme for these investigations.

January 1931. Dispersoidological Department of the Imperial Industrial Research Institute of Osaka.

ON THE COMPOSITION OF THE CYANIDE COMPLEX RADICAL OF METALS. PART II. CADMIUM CYANIDE COMPLEX RADICAL.

By Kosaku MASAKI.

Received January 26, 1931. Published February 28, 1931.

P. Walden[1] and V. Tafeln[2] stated that when a cadmium cyanide is dissolved in a solution of potassium cyanide, the molal ratio of combined cyanide to cadmium is four to one, corresponding to the formula $Cd(CN)_4^{--}$.

(1) *Z. anorg. Chem.*, **23** (1900), 375.
(2) *Ber.*, **35** (1902), 2668.

It may be due to the fact that the simplest of the double salts of potassium cyanide and cadmium cyanide is $2KCN \cdot Cd(CN)_2$.

Books of analytical chemistry[1] describe the following facts. By adding potassium cyanide to a solution of a cadmium salt, it produces white precipitate of amorphous cadmium cyanide and this cyanide is soluble in excess of the reagent.

$$Cd^{++} + 2CN^- \rightarrow Cd(CN)_2$$
$$Cd(CN)_2 + 2CN^- \rightarrow Cd(CN)_4^{--}$$

V. Tafeln[2] also stated that when a cadmium sulfocyanide is dissolved in a solution of potassium sulfocyanide, it produces potassium cadmium sulfocyanide, the formula of which is $Cd(CNS)_2 \cdot 2KCNS \cdot 2H_2O$, and moreover showed that there are the following complex compounds of cadmium.

(1) $Cd(CNS)_3M$ (2) $Cd(CNS)_4M_2$ (3) $Cd(CNS)_6M_4$

Composition of the Cadmium Cyanide Ion. In the present investigation, a simple titration method was used for the determination of the ratio of combined cyanide to cadmium in the complex ion. The method has already been described in the case of silver cyanide.[3] The results are shown in the following tables.

Table 1.

Sodium Cyanide and Cadmium Cyanide.

Cadmium mol per litre	Free cyanide mol per litre	Combined cyanide mol per litre		Ratio combined cyanide to cadmium
		Apparent	Actual*	
—	2.51344	—	—	—
0.16181	2.20600	0.30744	0.46925	2.90
0.15809	2.20516	0.30828	0.46637	2.95
0.13924	2.23496	0.27848	0.41772	3.00
0.08626	2.34437	0.16907	0.25533	2.96
0.03679	2.43986	0.07358	0.11037	3.00
0.02231	2.46772	0.04572	0.06803	3.05
0.01565	2.48057	0.03287	0.04852	3.10
—	1.48376	—	—	—
0.17050	1.16264	0.32112	0.49162	2.88
0.12759	1.21801	0.26575	0.39334	3.08
0.08714	1.29552	0.18824	0.27538	3.16
0.05070	1.37303	0.11073	0.16143	3.07

* The actual concentration of combined cyanide is equal to the apparent concentration plus the concentration of cadmium.

(1) For example, Treadwell, "Lehrbuch der analytischen Chemie," Vol. 1.
(2) *Z. anorg. Chem.*, **37** (1903), 447.
(3) This Bulletin, **4** (1929), 190.

The cadmium cyanide, $Cd(CN)_2$, has been prepared by decomposing barium cyanide with cadmium sulphate. It crystallizes in small colourless rhombic prisms. The barium cyanide, $Ba(CN)_2 \cdot 2H_2O$, has been obtained by passing hydrocyanic acid into a solution of barium hydroxide, the hydrocyanic acid being obtained by boiling the mixture of potassium ferrocyanide solution and sulphuric acid with the addition of cuprous chloride to decompose completely, thus:

$$K_4Fe(CN)_6 + 3H_2SO_4 = 6HCN + FeSO_4 + 2K_2SO_4$$

Table 2.

Sodium Cyanide and Cadmium Sulphate.

Cadmium mol per litre	Free cyanide mol per litre	Combined cyanide mol per litre	Ratio
—	1.82148	—	—
0.17895	1.30431	0.51717	2.89
0.12013	1.46710	0.35438	2.95
0.08544	1.56089	0.26059	3.05
0.05608	1.64268	0.17880	3.01
—	0.50935	—	—
0.08455	0.26021	0.24914	2.94
0.07383	0.29343	0.21593	2.92
0.06254	0.32111	0.18824	3.00
0.05154	0.35433	0.15502	3.00

Table 3.

Sodium Cyanide and Cadmium Chloride.

Cadmium mol per litre	Free cyanide mol per litre	Combined cyanide mol per litre	Ratio
—	1.82148	—	—
0.45695	0.53745	1.28403	2.81
0.27383	1.01368	0.80780	2.95
0.10658	1.49854	0.32294	3.03
—	1.48376	—	—
0.23133	0.80831	0.67545	2.91
0.15305	0.98548	0.49828	3.25
0.09789	1.17736	0.30640	3.13
0.05095	1.32989	0.15387	3.02

The cadmium sulphate and cadmium chloride which had been purified by recrystallization were used in these cases.

In all the above solutions the molal ratio of the combined cyanide to cadmium is three to one, indicating the formula to be $Cd(CN)_3^-$.

Stability of the Cadmium Cyanide Ion. There is, in the literature, no available information on the concentration of cadmium ion in cadmium cyanide solutions.

The author determined the potential differences between a cadmium electrode and various solutions of cadmium cyanide in sodium cyanide. The solutions used in these measurements were made by dissolving the appropriate amounts of pure cadmium cyanide in 50 c.c. of 0.77762 mol sodium cyanide solution. The electromotive force measurements were made at 25°C. by connecting a normal calomel electrode, through a saturated potassium chloride salt bridge, with an electrode of pure cadmium wire immersed directly in the solution, which being constantly stirred. The measured potentials remained constant over one hour. The data are summarized in Table 4.

Table 4.

$Cd(CN)_3^-$	CN^-	E	E_w	Cd^{++}	K
0.08920	0.22327	1.1567	0.8745	1.47×10^{-17}	5.45×10^{17}
0.07348	0.23097	1.1799	0.8977	1.12×10^{-17}	5.32×10^{17}
0.05502	0.24124	1.1851	0.9029	7.45×10^{-18}	5.26×10^{17}
0.02712	0.25661	1.1971	0.9149	2.90×10^{-18}	5.53×10^{17}

In Table 4, E is the measured electromotive force, and E_w is the potential of the cadmium electrode referred to the normal hydrogen electrode, taking the value for the single potential of the normal calomel electrode as -0.2822 volt.(1) The cadmium ion concentration, c, was found by the next equation

$$E_w = E_0 - 0.0295 \log c,$$

where E_0 is the standard electrode potential of the cadmium ion—cadmium electrode and is given by Lewis and associates as 0.3976 volt.(2) From the calculated value of (Cd^{++}), K can be determined from the expression:

(1) *J. Am. Chem. Soc.*, **42** (1920), 1128.

(2) Lewis and Randall, "Thermodynamics" (1923), p. 433.

$$K=\frac{Cd(CN)_3^-}{(Cd^{++})(CN^-)^3}$$

The fact that K remaines constant is an added evidence for the formula $Cd(CN)_3^-$.

Conclusion. The composition of the cadmium cyanide complex ion is probably $Cd(CN)_3^-$ at all concentrations.

The author wishes to express his appreciation to Prof. W.D. Bonner of the University of Utah, U.S.A., who suggested this research, and his best thanks to Prof. J. Sameshima and also to Prof. M. Yokoyama for the kind advice.

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ON THE ESSENTIAL OIL OF TAIWANIA CEDAR.

By Kinzo KAFUKU and Ryo KATO.

Received January 9, 1931. Published March 28, 1931.

The Taiwania cedar is one of the five big conifers indigenous to Formosa and is found along the central mountain range at an altitude of 6,000 to 7,000 ft. above sea level. It closely resembles Japanese Cryptomeria cedar (*Cryptomeria japonica*, D. Don.) in appearance, hence its Latin name,—*Taiwania Cryptomerioides*, Hayata. Its essential oil has hitherto never been studied but as it has a peculiar pleasant smell of its own, the authors undertook to investigate the nature of its volatile constituents, if any.

The material for examination forwarded by the Government Forestry Department at Taiheizan (Mt. Taihei) represented several root-stumps of a big, freshly hewn tree, of about 100 years of age, and they were chopped into small pieces of $1 \times 3 \times 8$ cm. in size, and put into a still. On prolonged steam distillation the authors obtained a very viscous oil of faintly yellow tinge with characteristic pleasant aroma, the yield amounting to 0.23% by weight of the material used. The oil, though very viscid, showed no tendency to deposit solid crystalline substance even on cooling with freezing mixtures. On fractional distillation it gave no terpene or terpene alcohol fractions, but seemed to consist practically of sesquiterpenes and sesquiterpene alcohols,—viz. about 34% cadinene, 2–3% humulene and caryophyllene, and 46% sesquiterpene alcohol. This last mentioned sesquiterpene alcohol closely resembled that isolated by L. Ruzicka[1] from West Indian sandalwood oil, in such respects as, the boiling point, the formation of hydrochloride, unaction towards phthallic anhydride, etc. etc. Thus, it is of interest whether this oil can be used or not as a substitute for the aforesaid oil for therapeutic purposes as a drug.

Experimental.

The oil directly after steam distillation, on being dried over anhydrous sodium sulphate, showed the following constants:—

d_4^{15}	0.9593
n_D^{15}	1.5104
α_D^{15}	-2.00°

(1) *Rec. trav. chim. Pay-Bas*, **47** (1928), 370, 381.

Acid value	0.38
Ester value	10.52
Do. after acetylation	83.00
Specific viscosity	137.1
Turbidity number (alcohol)	7.5(1)

On shaking the oil with 40% sodium bisulphite solution, no formation of crystalline precipitate was observed, from this it follows likely that the oil contained neither aldehyde nor ketone. The result of five consecutive fractional distillations with Widmer's dephlegmator, is shown below. (Diagrammatically in Fig. 1.)

Fraction	Boiling point	Pressure	Distillate %
(1)	113°—115°	10 mm.	0.28
(2)	115°—120°	do.	0.16
(3)	120°—125°	do.	1.13
(4)	125°—130°	do.	2.06
(5)	130°—133°	do.	21.00
(6)	133°—135°	do.	13.70
(7)	135°—140°	do.	0.49
(8)	140°—145°	do.	1.23
(9)	145°—150°	6 mm.	46.20

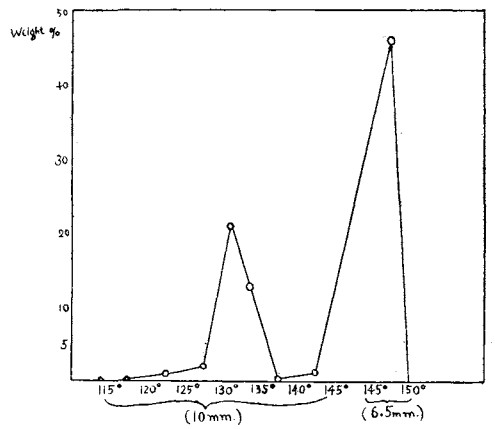


Fig. 1.

(1) Number of c.c. of water required to produce a permanent turbidity to 10 c.c. of an absolute alcohol solution of the oil in question (2 c.c. in 10 c.c. of alcohol).

The properties of these fractions are as follows:—

Fraction	d_4^{15}	n_D^{15}	α_D^{15}	M. R.
(1)	0.9104	1.4913	− 5.40°	—
(2)	0.9097	1.4979	− 1.40°	—
(3)	0.9089	1.5002	+ 1.08°	66.04 as $C_{15}H_{24}$
(4)	0.9134	1.5050	+ 7.20°	66.24
(5)	0.9189	1.5090	+35.20°	66.30
(6)	0.9215	1.5110	+54.60°	66.36
(7)	0.9641	1.5110	−17.40°	—
(8)	0.9715	1.5104	−33.40°	—
(9)	0.9742	1.5093	−40.46°	68.01 as $C_{15}H_{26}O$

It is noteworthy that in the foregoing table, the first two fractions and the last three are laevo-rotatory, while the rest are all dextro-rotatory, and that the fraction (5) which forms the greater part of the sesquiterpene fraction still contains oxygen to an extent of 2.6%, while the next (6) is practically pure hydrocarbon. From these, it follows that there may be a certain oxygenous compound of laevo-rotatory nature in the lower boiling portions. Whether this oxygenous compound be of terpenic alcoholic nature or not, we leave it for the future to decide.

The Sesquiterpenes. From considerations on the boiling behaviour and other physical constants, it seemed most probable that the fractions (3), (4), (5), and (6) consisted for the most part of dicyclic sesquiterpenes, so that the authors tested for the presence of caryophyllene and humulene with the fractions (3) and (4), and of cadinene with (5) and (6).

Thus, 0.5 gr. each of (3) and (4), was dissolved in an equal volume of absolute ether, and a dry current of nitrosyl chloride was passed in the cold as suggested by Ehestädt, and stood overnight in the ice chamber, then ether expelled and treated with methyl alcohol, when, an amount of crystalline substance separated out. Then it was fractionally recrystallized from methyl alcoholic solution and the resulting nitrosochloride tested for the melting point.

It was found that the nitrosochloride from (3) melted at 165°–166°, while that from (4) at 105°–106°. That the former was identical with humulene nitrosochloride, could be proved by the unlowering of its melting point on admixture with humulene nitrosochloride from oil of *chamaecyparis Obtusa*, Sieb. et Zucc., but the latter, on examination, seemed likely to be a mixture of cadinene nitrosochloride with some other higher-melting nitrosochloride.

Thus, they were once more fractionated under 10 mm. pressure, and it was possible to separate them into a lower boiling inactive, and a higher boiling active fractions. These afforded on treatment with nitrosyl chloride following Ehestädt's method,[1] two nitrosochlorides, the one melting at 165°–166°, and the other at 175°. The former was of course identical with humulene nitrosochloride, and the latter proved to be that of caryophyllene, which identity was affirmed by observing the mixed melting point with a known sample of caryophyllene nitrosochloride from Chamaecyparis oil. This latter nitrosochloride with m.p. 175°, showed an optical activity of +3.82° (0.423 gr. in 10 c.c. of chloroform).

Nextly an attempt was made to prepare nitrosites but it was altogether fruitless, and no crystalline substance could be obtained. But the action of cold glacial acetic acid solution of nitric acid on a mixture of 2 c.c. each of the sesquiterpene, isoamyl nitrite, and glacial acetic acid, afforded crystalline nitrosates from both, which after recrystallization from methyl alcohol, melted both at 162° and was proved to be humulene nitrosate (mischproben).

The fraction (5) was boiled over metallic sodium for six hours to get rid of oxygenous substances, and then rectified in vacuo, and in this way, a rather pure product with the following constants was obtained.

B.p.	130°—131.5° / 10 mm.
d_4^{20}	0.9183
n_D^{20}	1.5093
α_D^{20}	+34.62°
M.R.	66.36; 66.15 calc. as $C_{15}H_{24}$ $\equiv_2$.

On Liebermann's colour test, the hydrocarbon produced indigo blue colour which gradually turned into blue and then pink. If dissolved in chloroform and a drop of concentrated sulphuric acid added, it imparted to the solution a deep red coloration. This agrees with the behaviours of cadinene, so that tests in this direction were carried out. One gram of the sample was dissolved in an equal amount of absolute ether, and a current of dry hydrogen chloride gas was passed into the ice-cold solution, after twenty minutes an amount of crystals separated out which was kept overnight, then ether and hydrogen chloride driven off in vacuo, and the resulting semisolid mass was thoroughly washed with cold glacial acetic acid and then recrystallized from acetic ether. The white needle crystal thus obtained showed a melting point 117°—118°, whose identity with cadinene dihydrochloride could be proved by "mischproben" method.

(1) *Schimmels Report*, April **1910**, 164.

The nitrosate and the hydrobromide were prepared in the usual manner and after due purifications it was observed to melt at 110°—111° and 124°—125° respectively, which is in accordance with the data about the corresponding derivatives of cadinene. The fraction (6) had practically the same constants as this rectified product from (5) and on repeating the experiments as above, it gave precisely the same results. Only, it is worth mentioning, that in the second experiment, the hydrochloride (m. p. 117°—118°) offered an optical activity of −39.64° (in chloroform solution), and that the cadinene regenerated from this hydrochloride rotated a laevorotation of −47.42°, whereas the original sesquiterpene gave a rotatory power +56.60°. This is in accordance with the description by Semmler[1] that the hydrochloride obtained either from *d*- or *l*-cadinene, as well as the revived cadinene from the hydrochloride are all laevo-rotatory.

The oxidation of cadinene has been studied by L. Ruzicka and M. Stoll,[2] and by D. T. Gibson, J. M. Robertson, and J. Sword,[3] but no crystalline compound other than cadinene glycol has been obtained. The authors oxidized cadinene with acetone permanganate and obtained a substance melting at 142°—143° with a composition corresponding to the formula $C_{12}H_{22}O_2$. It was carried out in the following manner. To a mixture of 20 gr. of the rectified hydrocarbon from (6), 150 gr. of acetone, and 40 gr. of water under stirring, 20 gr. of finely powdered potassium permanganate was added in small portions and the temperature maintained at 30°—40° during the reaction. After the reaction was over, the mass was subjected to steam distillation to drive off acetone and unacted hydrocarbon, then the residue was extracted with ether. The ether extract was evaporated and distilled in vacuo, when, 12 gr. of unacted cadinene came over, and then about 4 gr. of higher-boiling oxidation product distilled at about 140° under 4 mm. pressure. This product was treated with petroleum ether when a crystalline substance deposited which melted at 142°—143° after purification. The substance, on analysis, showed the composition $C_{12}H_{22}O_2$.

Anal. Subst.=0.1088, 0.1103; CO_2=0.2895, 0.2930; H_2O=0.1070, 0.1100 gr. Found: C=72.56, 72.44; H=10.87, 11.08%. Calc. for $C_{12}H_{22}O_2$: C=72.70; H=11.10%.

As for the exact character of this substance the authors wish to communicate on the next available occasion, and retain it for the present.

The Sesquiterpene Alcohol. The fraction (9) practically consisted of sesquiterpene alcohol, as its physical properties as well as the analytical data show :—

(1) "Die ätherischen Oele," Bd. 2, S. 553.
(2) *Helv. Chim. Act.*, **7** (1924), 84.
(3) *J. Chem. Soc.*, **1926**, 164.

B.p.	145°—150°/6.5 mm.
d_4^{15}	0.9742
n_D^{15}	1.5093
α_D^{15}	−40.46°
M.R.	68.01; calculated as $C_{15}H_{26}O$ $\overline{\overline{\text{I}}}$ =68.12.

Anal. Subst.=0.1267; CO_2=0.3882; H_2O=0.1293 gr. Found: C=81.42; H=11.34%. Calc. for $C_{15}H_{26}O$: C=81.11; H=11.74%.

This fraction, on Liebermann's test, gave indigo blue colour at first which faded into pink, while the chloroformic solution, on addition of a few drops of concentrated sulphuric acid, turned into dark blue and changed into red in course of time.

Fifty grams of the fraction was boiled over a calculated amount of metallic sodium for 15 hours, the unacted oil was driven off in vacuo, the residual viscous mass of the alcoholate was decomposed by alcoholic sulphuric acid, then an excess of water was added and it was extracted with ether. The ethereal solution was washed out with water, dried, evaporated, and then distilled under a pressure of 6 mm. mercury. The distillate showed the following constants:—

B.p.	141°—143°/6 mm.
d_4^{30}	0.9692
n_D^{30}	1.5045
α_D^{30}	−42.56°
M.R.	67.88; calculated as $C_{15}H_{26}O$ $\overline{\overline{\text{I}}}$ =68.01.

Anal. Subst.=0.1355; CO_2=0.4032; H_2O=0.1439 gr. Found: C=81.15; H=11.79% Calc.: C=81.11; H=11.70%.

Three grams of this substance, dissolved in dry ether was treated with a current of dry hydrogen chloride, when, a quantity of crystalline compound precipitated. Ether and excess of hydrogen chloride was then driven off at room temperatures, and the crystalline substance remaining behind was well washed with cold glacial acetic acid, drained until dry on the porous porcelain plate and then recrystallized from acetic ether. The pure hydrochloride showed a melting point 117°—118°, and proved to be identical with cadinene dihydrochloride as no lowering of melting point occurred on mixing it with cadinene dihydrochloride from other sources. Exactly the same thing had been experienced by Semmler and Jonas[1] in handling the sesquiterpene alcohol from galbanum oil, and they had given the name "cadinol" to it. They had stated that it represented a tertiary sesqui-

(1) *Ber.*, **47** (1914), 2068.

terpene alcohol, and that it was liable to break into cadinene and water, but failed to prepare any definite crystalline derivatives therefrom. For the sake of comparison, their data as regards this sesquiterpene alcohol, and the authors' data are given below:—

	Semmler and Jonas	Kafuku and Kato
B.p.	155°—165°/15 mm.	141°—143°/6 mm.
d^{20}	0.9720	0.9692 ($_{30}$°)
n_D^{20}	1.50702	1.5045 ($_{30}$°)
α_D^{20}	+22°	−42.56° ($_{30}$°)
M.R.	67.97	67.88

With a view to obtain a crystalline phenyl urethane, the purified alcohol was let react with phenyl isocyanate. For this purpose, 2.2 gr. of the freshly distilled substance and 1.2 gr. of phenyl isocyanate was mixed in the warm and kept for 20 days in a desiccator, when the mixture congealed into a crystalline mass. Then, it was treated with petroleum ether and got rid of diphenyl urea in the usual manner, and at last, a crude phenyl urethane m.p.=128°–130° was obtained, which after recrystallizations from alcohol showed a melting point 134°–135°.

The attempt to prepare the benzoate, the acid phthalate, the paranitrobenzoate, the bromide, or the xanthogenate, turned out altogether to be futile, and no crystalline compound was obtained. Only, it is worthy of note that the petroleum ether solution of the sesquiterpene alcohol, on treatment with an aqueous chromic acid solution assumed a characteristic red colouration, which according to Wienhaus[1] showed the formation of chromic acid ester. Even though it was impossible to get any crystalline chromic ester, this colouration and its poor affinity towards phthalic anhydride suggests that the authors' sesquiterpene alcohol also to be of a tertiary nature.

Ten grams of the rectified product from (9) was oxidized in aqueous acetone solution with 25 gr. of potassium permanganate at 50°–60°, the resulting mass was steam distilled to expel the unoxidized oil, and then, the aqueous residue, as well as the manganic mud, were separately extracted with ether, the ethereal solutions united and evaporated, when a small quantity of a yellowish oil together with a little crystalline residue remained behind. On standing for a length of time, the whole coalesced into a gruel-like mass, which was dried on the clay plate and the crystalline body recrystallized from benzol. The resulting crystal melted at 170°, but, on account of the small quantity available, nothing has been done to determine the nature of the substance.

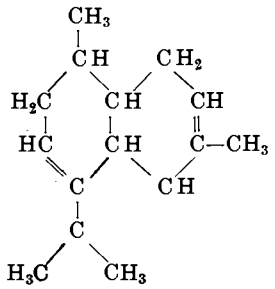
(1) *Ber.*, **47** (1914), 329.

Thirty grams of the substance was dissolved in an equal amount of pure formic acid, and warmed on the water bath for fifteen minutes, then the acid was neutralized with caustic soda, the hydrocarbon thus formed was extracted with ether, ether evaporated off, and the hydrocarbon boiled over metallic sodium at 165°–180° for 4 hours, and then rectified in vacuo. The distillate had the following properties:—

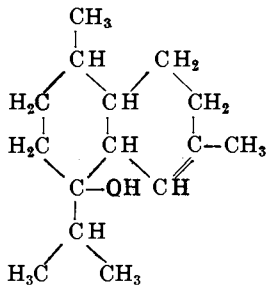
B.p.	134°—135°/10 mm.
d_4^{20}	0.9209
n_D^{20}	1.5100
α_D^{20}	−51.08°
M.R.	66.25 as $C_{15}H_{24}\overline{\overline{=}}$ =66.15

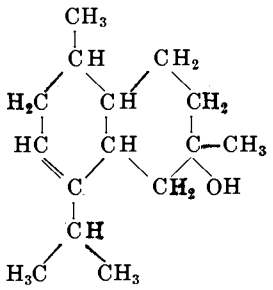
This hydrocarbon gave a dihydrochloride m.p. 117°–118°, and a dihydrobromide m.p. 124°–125°, which turned out to be identical with those of cadinene, (mischproben). Also a nitrosate melting at 110°–111° was obtained in the usual manner. From these it is obvious that the product of dehydration is cadinene.

From the foregoing experiments it seems possible that the authors' sesquiterpene alcohol might be identical with Semmler's cadinol, but considering the assumed constitutional formula for cadinene, there still remains much to be determined before the identity is claimed. Supposing the constitutional formula for cadinene to be

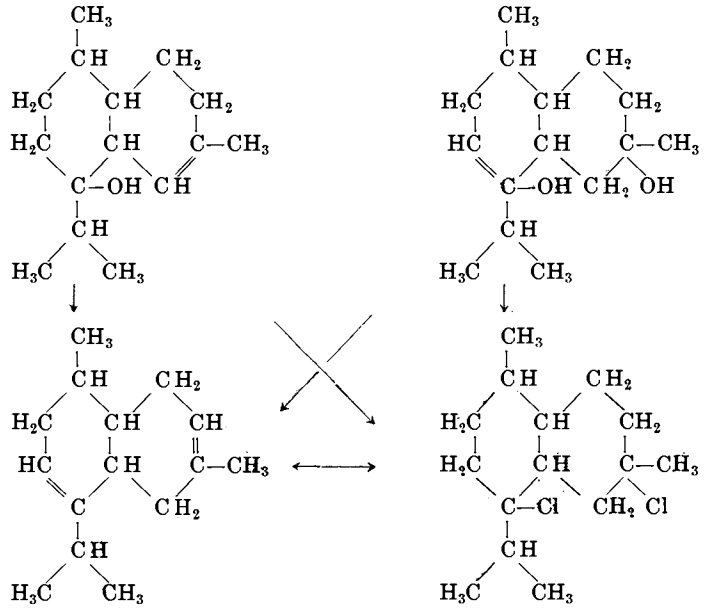


the following two sesquiterpene alcohols of the formulae





may both be responsible for the formation of cadinene dihydrochloride by the action of hydrogen chloride, and at the same time the dehydration to cadinene by formic acid, thus:—



It therefore remains for the authors to determine which of these two formulae should more reasonably be adopted for the sesquiterpene alcohol in question. The authors hope to discuss the subject by studying the oxidative disintegration of the alcohol on the next available opportunity. For the present, the authors wish to name their sesquiterpene alcohol as "taiwanol," as it originates from *Taiwania Cryptomerioides*, Hayata.

Summary.

1. The wooden chips of *Taiwania Cryptomerioides*, Hayata, gives on steam distillation 0.23% of an oil, consisting chiefly of sesquiterpene and sesquiterpene alcohol.

2. The sesquiterpenes in the oil are chiefly cadinene, with a little humulene and caryophyllene.

3. From the cadinene, a new oxidation product $C_{12}H_{22}O_2$ (m.p.=142°–143°) was obtained.

4. The sesquiterpene alcohol in the oil, to which the authors suggest the name "taiwanol," closely resembles cadinol of Semmler and Jonas. From cadinol no crystalline phenyl urethane could be obtained, but in case

of taiwanol, it affords a crystalline pheyl urethane melting at 134°–135°, and furthermore, it gives a neutral oxidation product (m.p. 170°) if oxidized with permanganate in acetone solution.

Department of Industry,
Government Research Institute of Formosa,
Taihoku, Formosa.

UEBER DIE ADSORPTION BISUBSTITIERTEN BENZOLEN.

Von Bun-ichi TAMAMUSHI.

Eingegangen am 7. Februar 1931. Ausgegeben am 28. März 1931.

In folgenden Untersuchungen wurde zuerst die Adsorption einiger bisubstitierten Benzolen: *o*-, *m*-, *p*-Nitrophenol, *o*-, *m*-, *p*-Nitranilin, *o*-, *m*-, *p*-Dinitrobenzol, durch Kohle in benzoligen Lösungen gemessen, und dazu wird eine theoretische Bemerkung gemacht.

I. Man schüttelte die 100 c.c. Lösung mit 10 gr. Tierkohle (von Merck) zusammen und bestimmte deren Solutgehalt gravimetrisch vor und nach der Adsorption, indem man das Lösungsmittel in einem Platintiegel bei niedriger Temperatur sorgfältig verdampfen liess.

Die folgenden Tabellen 1–3 zeigen die Ergebnisse, wobei c die Konzentration in Millimol in Litre and a die adsorbierte Menge in Millimol je Gramm Kohle bedeuten. Die Versuchstemperatur ist dabei auch angezeigt.

Tabelle 1.

$t = 25°C$.

Substanz	c	a
o-Nitrophenol	130.660	0.345
	58.993	0.180
	43.876	0.151
m-Nitrophenol	90.653	0.323
	20.144	0.144
p-Nitrophenol	68.344	0.374
	35.970	0.251
	20.144	0.173

Tabelle 2.

$t = 25°C.$

Substanz	c	a
o-Nitranilin	52.894	0.065
	34.059	0.043
	6.909	0.011
m-Nitranilin	52.885	0.094
	18.840	0.058
p-Nitranilin	23.188	0.102
	18.840	0.087

Tabelle 3.

t=18-20°C.

Substanz	c	a
o-Dinitrobenzol	58.929	0.048
	25.000	0.030
	8.344	0.015
m-Dinitrobenzol	54.762	0.018
	36.309	0.014
	11.902	0.009
p-Dinitrobenzol	55.953	0.030
	23.512	0.018
	11.309	0.012

Weiter, wie Fig. 1-3 zeigen, gilt durchaus die Freundlichsche Adsorptionsisotherm

$$a = k C^{\frac{1}{n}},$$

worin $\frac{1}{n}$ gleich 0.53 fuer Nitrophenol, 0.57—0.93 fuer Nitranilin und 0.36—0.57 fuer Dinitrobenzol.

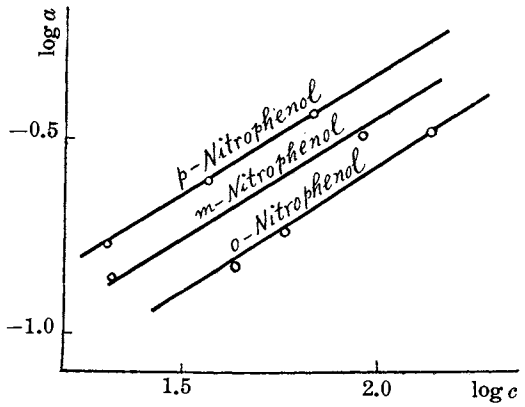

log a
−0.5
−1.0
p-Nitrophenol
m-Nitrophenol
o-Nitrophenol
1.5
2.0
log c

Fig. 1.

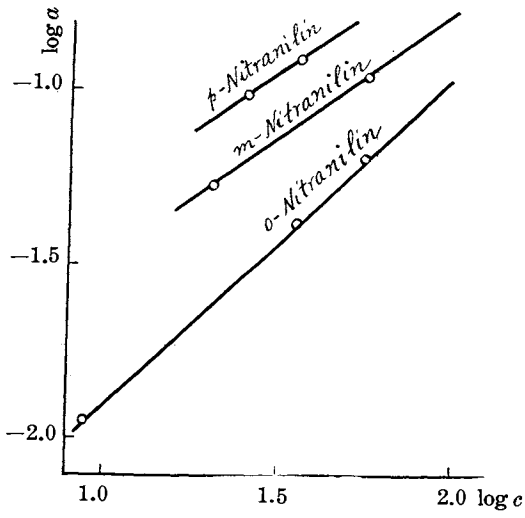

log a
−1.0
−1.5
−2.0
p-Nitranilin
m-Nitranilin
o-Nitranilin
1.0
1.5
2.0 log c

Fig. 2.

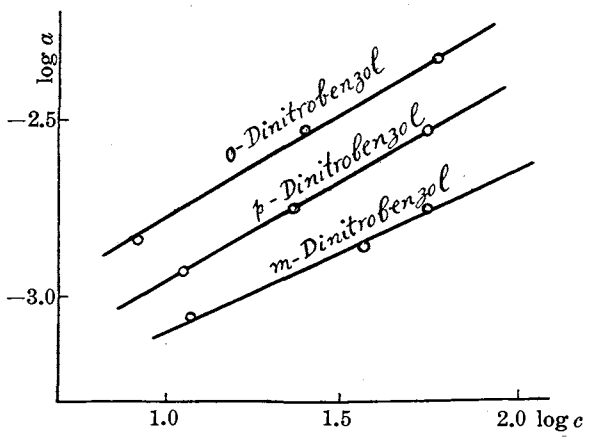


Fig. 3.

Die Adsorption vermindert sich in der Reihe $p > m > o$ bei Nitrophenol sowie bei Nitranilin, aber bei Dinitrobenzol in der Reihe $o > p > m$.

II. In Bezug auf diese experimentellen Ergebnisse, sei folgende Ueberlegung gestattet. Zunächst hat die Adsorption in Lösungen einen bekannten Zusammenhang mit der Löslichkeit, und es steht zu erwarten, dass die Substanz, welche schwerer löslich ist, stärker adsorbiert wird. Fuer den Fall von Nitrophenol sowie von Nitanilin gilt diese Regel qualitativ, da sich die Löslichkeit dieser Verbindungen in Benzol vergrössert in der Reihe $p < m < o$, während sich die Adsorption in dieser Reihe vermindert. Auch bei Dinitrobenzol, wurde *m*-Dinitrobenzol, das leichst löslich ist, am schwersten adsorbiert.

Unerwarteterweise wurde aber *o*-Dinitrobenzol, das beträchtlich leichter löslich ist als *p*-Dinitrobenzol, etwas stärker adsorbiert als *p*-Dinitrobenzol.

Diese letzte Regelwidrigkeit möchte ich provisorisch Dipoleffekt nennen, womit ich darauf hindeuten möchte, dass die Adsorptionskraft auch in Lösungen teilweise als elektrostatisch aufgefasst werden könnte, soweit wir die polaren Molekeln im Betracht nehmen.[1] Vermutlich werden also die Molekeln, die ein grosses Dipolmoment besitzen, durch Adsorbens stark angezogen, etwa aus dem analogen Grunde, weswegen bei solchen polaren Molekeln eine Molekülarassoziation erfolgt.

(1) Elektrostatische Theorien der Adsorptionskraft sind besonders bei Gas-fest Grenzfläche mit Erfolg aufgestellt worden. Verg. E. Hückel, "Adsorption u. Kapillarkondensation." (1928).

In den meisten Fällen, besonders wenn wir die Adsorption in wässerigen Lösungen studieren, wobei das Wasser selbst stark polar ist, würden die ganzen Verhältnisse kompliziert sein und kein Dipoleffekt wäre eindeutig bekannt. Doch dürfte dieser Effekt sich bemerkbar machen, wenn wir die Adsorption der polaren Molekeln in dipollosen benzoligen Lösungen untersuchen. Das natürliche Dipolmoment der Molekeln ist eigentlich auch in benzoligen Lösungen vielfach bestimmt worden.

Eine eingehende Diskussion ueber diese Frage soll hierbei nicht vorgenommen werden, da das experimentelle Material noch nicht genügt. In folgender Tabelle sind Schmelzpunkt, Löslichkeit (in Benzol), Molekularassoziation und Adsorption der bisubstitierten Benzolen zusammengestellt, damit wir einen charakteristischen Zusammenhang dieser Eigenschaften wahrnehmen können.

Der Pheil zeigt eine vergrössernde Reihe. Eindeutig ist der Zusammenhang fuer den Fall von Nitrophenol und Nitranilin. Wie es schon bekannt ist, sind Schmelzpunkt und Löslichkeit einander antiparallel,

Tabelle 4.

Substanz	S. P.[1]	D. M.[2] (10^{18})	M. A.[3]	L.[5] (gr.i. 100 c.c.)	A.[5]
o-Nitrophenol	45	3.10	1.02	70 ↑	
m-Nitrophenol	96	3.90	1.05	2.48	
p-Nitrophenol	113 ↓	5.05 ↓	1.09 ↓	1.33	↓
o-Nitranilin	72	4.45	1.04	14.23 ↑	
m-Nitranilin	112	4.72	1.08	2.15	
p-Nitranilin	118 ↓	7.1 ↓	1.25 ↓	0.53	↓
o-Dinitrobenzol	117 ↑	6.00 ↑	1.16 ↑	4.96	
m-Dinitrobenzol	91	3.7	1.04	34.37 ↑↓	↑↑
p-Dinitrobenzol	172 ↓	0.8	1.01	2.26 ↑	↓

(1) Schmelzpunkt. "Chemiker Kalender," 1931.

(2) Dipolmoment. Nitrophenol: J. W. Williams, *Fortschr. d. Chemie, Physik u. phys. Chemie*, Bd. 20, Ht. 5, 1930. Nitranilin und Dinitrobenzol: K. Höjendahl, *Phys. Z.*, **30** (1929), 391.

(3) Molekülarassoziation. Nitrophenol und Nitranilin, in etwa 50 Millimol benzoligen Lösungen: H. Shiba, Unveröffentlichte Arbeiten. Herr Shiba hat neulich die Molekülarassoziation zahlreicher polaren organischen Verbindungen ebullioskopisch untersucht. Dinitrobenzol: Nach meinen kryoskopischen Versuche in derselben Konzentration.

(4) Löslichkeit. Nitrophenol und Nitranilin: Nach meinen Versuche. Versuchstemperatur =25°. Dinitrobenzol: de Bryn, *Rec. Trav. Chim.*, **13** (1894), 116. Versuchstemperatur=18°.

(5) Adsorption. Verg. Tabelle 1-3.

während Dipolmoment bez. Molekülarassoziation mit dem Schmelzpunkt parallel stehen. Die Adsorption ist antiparallel mit Löslichkeit, somit parallel mit Dipolmoment.

Auch bei Dinitrobenzol sind Löslichkeit und Schmelzpunkt antiparallel einander, und zwar hat *m*-Verbindung ein Schmelzpunktsminimum bez. Löslichkeitsmaximum. Dipolmoment und Molekülarassoziation sind auch in diesem Falle einander parallel und vergrössern sich nach der Reihe $p < m < o$. Adsorption hat sein Minimum bei *m*-Verbindung, die am leichsten löslich ist, während fuer *o*- und *p*-Verbindung der Löslichkeits-einfluss von dem Dipoleffekt uebertroffen zu sein scheint.

Es sei an dieser Stelle Herrn Dr. H. Shiba mein Dank fuer seine freundliche Mitteilug ueber Molekülarassoziation ausgesprochen. Herrn Prof. M. Katayama bin ich fuer seine wertvollen Ratschläge zum wärmsten Dank verbunden.

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SINOMENINE AND DISINOMENINE. XXV. ON THREE DIFFERENT SINOMENINE-METHINES.

By Kakuji GOTO and Hideo SHISHIDO.

Received February 25, 1931. Published March 28, 1931.

In the previous note, published in 1926,[1] one of the authors (K.G.) reported preliminarily on the three different products of sinomenine [I], produced by the Hofmann decomposition. Now that the constitution of sinomenine is fairly well established,[2] we undertook the investigation again and could trace the relation of these three methines, the results of which will be published here with some necessary supplements and corrections to the former note.

When sinomenine iodomethylate was boiled with 2% NaOH (2 mol) for one minute, there is formed an iodine free substance, $C_{20}H_{25}NO_4$, of m.p. 179°. To this substance, formerly the name N-methyl-anhydro-sinomeninium-base and the constitution [II] had been given chiefly from the following three reasons.

(1) *Proc. Imp. Acad.*, **2** (1926), 167.
(2) In the XXIV report of this study, (*Ann.*, **485** (1931), 247), the results are partly summarized.

1. The extreme easy formation of this substance, compared with the other two methines.

2. The characteristic unstableness of this substance, which does not allow the recrystallization even from alcohol. This might indicate the splitting off of the double linking between $C_{(9)}$ and N.

3. Very weak halochromy with conc. H_2SO_4. All the methines of morphine and codeine are known to give strong colouration with this reagent.

Yet, the fact that the hydroiodide of this substance is totally different from the starting material was very singular, although this fact was not mentioned in that short note.

Now, we prepared the hydroiodide and iodomethylate of this substance carefully and found that these two salts give the same weak halochromy with conc. H_2SO_4. In addition to this, the fact that the iodomethylate of this substance is transformed into the iodomethylate of the secoud methine by cold 10% NaOH, which give an intense blue halochromy with H_2SO_4, reminded us of the transformation of α-methyl-morphi-methine into β-methyl-morphi-methine by alcoholic alkali. We are, therefore, inclined now to give this substance the methine constitution [III] and call it sinomenine-achro-methine.

As its iodomethylate, the sinomenine-achro-methine itself can be transformed into the methine, which gives an intense blue colour with conc. H_2SO_4. This methine was called α-sinomenine-methine in the previous note, but we wish to call it now sinomenine-violeo-methine, in order to avoid confusion with the prefixes of the six methyl-morphi-methines, since the relation of each sinomenine methine to the corresponding methyl-morphi-methine is not exactly determined. We believe, however, that the sinomenine-violeo-methine corresponds to the β-methyl-morphi-methine from the reasons, which will be given later.

From sinomenine iodomethylate, another methine, which gives a strong red halochromy against conc. H_2SO_4, is obtainable. At first, this methine was obtained by boiling sinomenine iodomethylate with 5% NaOH (5 mol) for a short time. In this treatment this methine is produced side by side with the violeo-methine, the yield of the both methines being extremely small (5—7%). Now, it was found that the crude sinomenine-achro-methine, recrystallized from alcohol and kept for years, transforms itself partly into this methine. That in this transformation, the sodium bicarbonate, which might be attached to the crude methine, may be the cause, was proved by the experiment that the iodomethylate of the achro-methine could be turned into that of this methine by boiling in methyl-

alcohol, added with a bit of sodium bicarbonate. This third methine was called β-sinomenine-methine in the previous note, but we propose now the new name sinomenine-roseo-methine for it. The iodomethylate of this roseo-methine was transformed, then, into that of violeo-methine by cold 10% NaOH.

The relation of these three sinomenine-methines is given in the Table 1 and their properties are summarized in the Table 2.

Table 1.

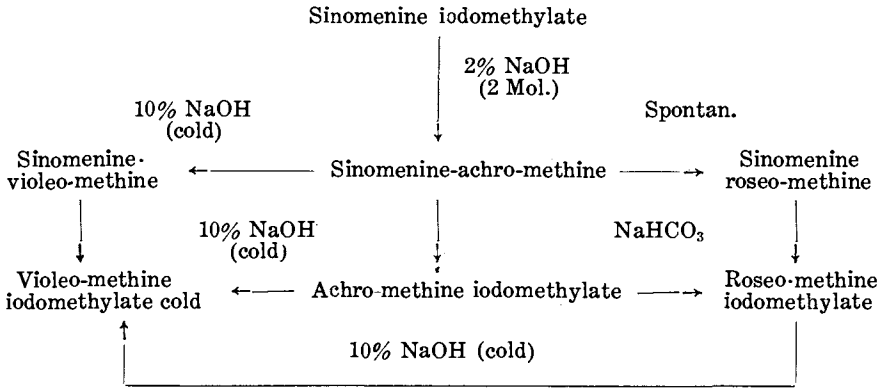


Table 2.

Substance Former names*	Sinomenine-achro-methine N-methyl-anhydro-sinomeniniumbase	Sinomenine-roseo-methine β-Sinomenine methine	Sinomenine-violeo-methine α-Sinomenine methine
M. p.	179°	163°**	172°—173°
Sol. in ether	easier soluble	difficultly sol.	almost not
$[\alpha]_D$	+72.58°	+135.70	+434.78°
Diazo-reaction	2,000,000th	100,000th	2,000,000th
Conc. H_2SO_4	faintly yellow	carmin red	deep blue
Fuming HCl	lyra	yellowish red	deep blue
M.p. of iodomethylate	212° (fr. water)	277° (fr. methanol)	209° (from water)
$[\alpha]_D$	−33.00°	−48.26°	+373.36°
The above three reactions are same with their corresponding free bases.			

* *Proc. Imp. Acad.*, **2** (1926), 167.

** M.p. 263° in the above note is clearly a misprint.

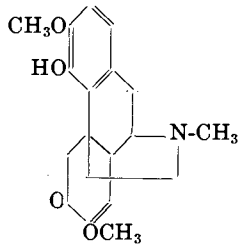
As regards the constitution of these three methines, we will now provisionally give the following explanation. In these three methines, no dislocation of the attaching groups and the linking point of dimethyl-aminoethyl group seems to have occurred. For, the achro-methine and the violeo-methine (iodomethylate) could be very easily decomposed into sinomenol by the same methods as with the sinomenine itself. Though the roseo-methine has not been decomposed, the same argument could be applied to it, since its iodomethylate could be transformed into that of the violeo-methine. The cause of the difference in these three methines then may be due to the displacement of the double linkings, as Knorr and Robinson suspected to be the case in methyl-morphi-methines.

Now, we feel it is almost doubtless that the sinomenine-violeo-methine corresponds to the β-methyl-morphi-methine from the following considerations.

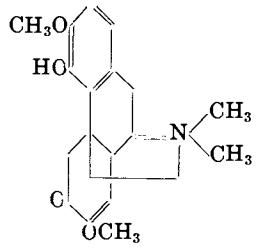
1) Its mode of formation (cold 10% NaOH).
2) Its high specific rotatory power.
3) Its intense blue halochromy with conc. H_2SO_4 and with fuming HCl.

R. Robinson,[1] based on the study of neopine, gave to the β-methyl-morphi-methine the constitution [VI]. This constitution seems to explain partly its high specific rotatory power as well as its intense halochromy. If this conception is not errornous, the sinomenine-violeo-methine may possess the constitution [V]. [2]

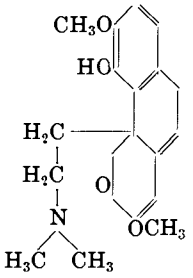
The question, which of the remaining two sinomenine-methines corresponds to the α-methyl-morphi-methine is difficult to say. But, from (1) its



I.



II.*

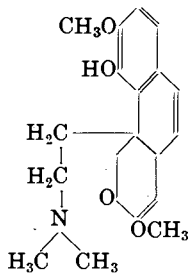


III.

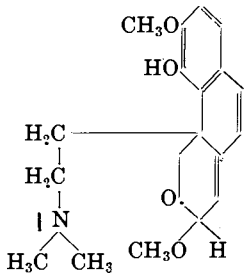
* Partly modified, with necessary corrections.

(1) R. Robinson, J. C. Smith, *J. Chem. Soc.*, **1926**, 903; compare also E. Speyer, Koulen, *Liebig's Annalen*, **438** (1924), 34, and R. S. Cahn, *J. Chem. Soc.*, **1926**, 2562.

(2) An objection to this explanation may be the transposition of the double linking from α, β- to β, γ-position relating to the ketone group. But, after the text-book of Meyer-Jacobson (2. Edition, I, 1, p. 947), such a transposition is not without examples in unsaturated acids.



IV.



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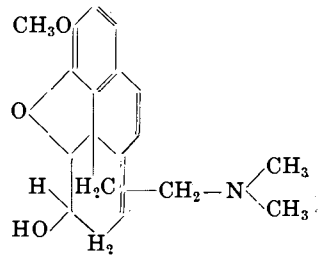

VI.

very easy formation and (2) its very weak halochromy aganinst conc. H_2SO_4, we wish to give the constitution [III] to the sinomenine-achro-methine, taking the new double linking between C (9) and C (14). It is remarkable that all the derivatives of sinomenine, which have not the double linking in C (7) and C (8), stand stronger against the Hofmann decomposition. The iodomethylates of dihydro-sinomenine, of its demethoxy- and demethoxy-desoxo-derivatives are opend successfully in their C (9) and N-linking by boiling with 16.6% KOH over thirty minutes. This shows that the double linking in C (7) and C (8) makes easy the opening of the ring. If so, why should not the new double linking conjugate to the old one and enter between C (9) and C (14)? If we assume the double linking in C (9) and C (10) in the habitual way, the easy formation of the achro-methine could not be explained.

The position C (9) and C (14) is also convenient to explain the extremely weak halochromy of the substance. All the other methines of sinomenine series, which are produced by boiling 16.6% KOH or 25% NaOH over thirty minutes, give strong yellowish red or red halochromy against conc. H_2SO_4. This property is partaken by other hydrated phenanthrenes, which have a double linking in α, β-position to the not hydrated benzene nucleus, say, meta-thebainone[1] and benzylidene-*d*-thebenone.[2]

It may not be unreasonable to seek, therefore, the cause of the very weak halochromy of the achro-methine in the different position of the double linking from that of all the other methines.

As to the roseo-methine, we wish to give the constitution [IV] to it. The rearrangement of a β, γ-double linking to the benzene nucleus into the α, β-position by the action of alkali is well known in eugenol and allyl-benzene. Whether this arrangement could be effected by a so mild reagent as $NaHCO_3$ is a question. Yet, seeing that the yield in this rearrangement

(1) C. Schöpf, H. Perrey, *Liebig's Annalen*. **483** (1930), 170.
(2) H. Wieland, M. Kotake, *Liebig's Annalen*, **444** (1925), 90.

is far less than the quantitative and that the roseo-methine gives an intense red halochromy as almost all the other methines, we propose this explanation for the present.

It seems to us that there must be some means, by which the above hypothesis can be verified or not. For example, the reductive method, which was so useful in determining the C (7)—C (8) position of the double linking in sinomenine, may be applied to the above three methines. Yet, all the preliminary experiments, carried out for the purpose, gave very unpromissing results, and we are forced to be satisfied with the above hypothetical explanations for the present. But the question whether the stage of sinomenine-achro-methine is passed or to be isolated in future in the methines, derived from morphine or condeine remains to be an interesting problem.

Experimental.

1. Sinomenin-achro-methine, [III]. Sinomenine iodomethylate (2 gr.) is boiled with 2% NaOH (20 c.c.; 2 mol) for one minute. The brownish coloured liquid is quickly cooled with water and saturated with CO_2 gas.

The reddish brown precipitate is then washed with hot water and dried on a porous plate. It is already crystalline. The raw yield amounts to 80% of the theoretical.

The purification is best effected through its sodium salt. When the crude product was poured on with ice-cold 10% NaOH, there is formed almost colourless phenolate of the substance. The latter is quickly collected on a glass-filter, washed with alkali and then redissolved in water. When the aqueous solution is again saturated with CO_2 gas, the achro-methine crystallises out in faintly brownish[1] flat prisms. One more recrystallization from much ether turns the substance into long prisms. They are still faintly coloured. This seems to be due to some impurity, which is quickly formed by the decomposition of the achro-methine itself. M.p. 179° (sintering at 173°). Its halochromy in conc. H_2SO_4 is very faintly yellow (almost colourless), so it is named sinomenine-achro-methine.

The properties of this methine is given in the first column of the Table 1.

Anal. Found: C=69.80, 70.10; H=7.05, 7.32; N=4.18; Methoxyl=18.15%.
$C_{20}H_{25}NO_4$=343 requires: C=69.97; H=7.28; N=4.08; Methoxyl=18.07%.
Sp. rotatory power, in chloroform: $[\alpha]_D^{16} = +(0.43 \div 0.1481) \times (25 \div 1) = +72.58°$.

(1) This brownish red substance seems to be produced by a partial decomposition of the achro-methine and gives a deep green halochromy with conc. H_2SO_4. The achro-methine seems to be turned into this substance at its melting point, but the substance itself could not be yet obtained in a crystalline form.

Hydro·iodide: long prisms, m.p. is very unsharp, but lies at 115~118° (sintering at 80°). Halochromy in conc. H_2SO_4 or in fuming HCl is the same with the free methine. (Found: I=27.18. $C_{20}H_{25}NO_4 \cdot HI$ requires I=26.96%) Hydro·chloride and hydrobromide is too hygroscopic for the analysis.

Iodomethylate: is prepared in methyl·alcohol without heating. It melts at 212° with decomposition. Halochromy is same as above.

Anal. Found: C=51.93, 51.98; H=5.76, 5.98; N=2.99; Methoxyl=12.48; I=26.09%. $C_{21}H_{28}NO_4I$=484.9 requires: C=51.96; H=5.77; N=2.89; Methoxyl=12.78; I=26.17%.

Sp. rotatory power, measured in water: $[\alpha]_D^{17}=(-0.11\div0.3333)\times(50\div0.5)=-33.00°$

Oxime: prepared in the ordinary way at room temperature. Recrystallisable from methylalcohol and ether into prisms collected in rosettes. Decomposes at 204~205° (losing water at 120°). (Found: N=7.79%. Calc. for the monoxime: N=7.82%).

Decomposition of the achro·methine with 66% KOH resp. with benzoyl·anhydride gave the same sinomenol resp. dibenzoyl·sinomenol as with sinomenine itself, the yield also being almost equal with the latter. The amine, evolved in the potash fusion, was also dimethyl·ethyl·amine. (The auri·chloride decomposed at 220° and the platini·chloride decomposed at 239°).

2. **Sinomenine-roseo-methine.** [IV]. The free base of this substance is formed, when the sinomenine iodo·methylate is decomposed with 5% NaOH (5 mol). But from the crude achro·methine, recrystallized from alcohol and kept for years, it was accidentally isolated in ca. 10% yield. The change might have been effected through the sodium bicarbonate, attached to the crystalls. This point was made clear with their iodomethylates. (See later on).

It is yellowish, melts at 163° and gives an intense red (carmin) halochromy in conc. H_2SO_4 and an yellowish red in fuming HCl. It is, therefore, called sinomenine·roseo·methine.

For the properties, see the second column of the Table 1.

Anal. Found: C=69.78; H=7.16; N=4.10; CH_3O-=18.24%. $C_{20}H_{25}NO_4$=343 requires: C=69.97; H=7.28; N=4.08; CH_3O-=18.07%.

Sp. rotatory power, measured in chloroform:

$$[\alpha]_D^{16}=(+1.03\div0.0759)\times(10\div1)=+135.70°$$

Iodomethylate. It was first noticed that the iodomethylate of the crude achro·methine, when prepared by boiling in methyl·alcohol, contains sometimes the iodomethylate of the roseo·methine. Therefore, in order to

transform the iodomethylate of the achro-methine into that of the roseo-methine, the former was boiled in ten times its weight of methyl alcohol with a bit of sodium bicarbonate for one hour and was set aside, after being filtered from the bicarbonate. On the next day, the crystalls deposited on the bottom was collected and recrystallized from methyl alcohol. It forms yellow long prisms, which melt and decompose at 276°. Admixture with the iodomethylate obtained in 1926, did not lower the melting point. Halochromy is the same with the free roseo-methine.

Anal. Found: C=52.05; H=5.88; N=2.84; CH_3O=12.42; I=26.05%.
$C_{21}H_{28}NO_4I$=484.9 requires: C=51.96; H=5.77; N=2.89; CH_3O=12.78; I=26.17%

Sp. rotatory power, measured in water: $[\alpha]_D^{17}=(-0.25\div0.1295)\times(25\div1)=-48.26°$

To prove the point, that the sodium bicarbonate effect this change, the pure achro-methine iodo-methylate was boiled in methyl alcohol without the addition of $HNaCO_3$. It was found that the iodomethylate, chrystallized out from the solution gave only the faintly yellow halochromy and melted also at 212°.

The yield of the roseo-methine was not good and the decomposition trial was not carried out with it. But the fact that it stands between the achro- and violeo-methines was proved by turning its iodomethylates into that of the violeo-methine by the action of cold 10% NaOH.

The only anormality of this methine is in the very diminished diazo-reaction, compared with the other sinomenine derivatives with the free C(1). We hope to clear away this question by a further study in a near future.

3. Sinomenine-violeo-methine. [V]. It was noticed, at the beginning of the study of sinomenine, that the action of boiling caustic alkali turns sinomenine into the substance which gives an intense bluish halochromy with conc. H_2SO_4. The substance, which is the cause of this colour, as well as its iodomethylate were isolated six years ago. This time, it was obtained from the achromethine and the relation was clearly settled.

When the achro-methine (1 gr.) is kept overnight in 10% NaOH (8 c.c.) and methyl-alcohol (4 c.c.) and then saturated with CO_2 gas, a precipitate is formed in the ice-cooled solution. This is collected and crystallized from chloroform by the addition of much ether. Yield about 20%, but, as will be described later, the change is almost the theoretical with the iodo-methylate. It forms flat prisms and melts at 172~173°. It gives an intense blue halochromy with conc. H_2SO_4 as well as with fuming HCl. Hence the name sinomenine-violeo-methine is given.

The properties of this substance is given in the third column of the Table 1.

Anal. Found: C=70.03, 69.32; H=7.25, 7.20; N=4.23; CH_3O—=18.19%.
$C_{20}H_{25}NO_4$=343 requires C=69.97; H=7.28; N=4.08; CH_3O—=18.07%
Sp. rotatory power, measured in chloroform:

$$[\alpha]_D^{17}=(+0.19\div 0.2185)\times(250\div 0.5)=+434.78^\circ$$

The iodomethylate is formed from that of the achro-methine in an almost theoretical yield by the action of the cold 10% NaOH (5 times). The change seems to be complete in a few hours, judged from the halochromy, but the mixture is better to be left stand overnight for the precaution. It is well cooled with ice and saturated with CO_2 gas. As this substance is most difficultly soluble in water of the three, it crystallises out almost completely. It is colourless prisms collected in a form of a fun. M.p. 209° (dec., from water). Halochromy is the same as the free methine.

Anal. Found: C=51.84, 51.85, 51.60; H=6.01, 6.11, 6.20; N=2.99; CH_3O=12.64; I=26.29%. $C_{21}H_{28}NO_4I$=484.9 requires: C=51.96; H=5.77; N=2.89; CH_3O=12.78; I=26.17%.

Sp. rotatory power, measured in water: $[\alpha]_D^{17}=(+0.30\div 0.1607)\times(100\div 0.5)=+373.36^\circ$

The violeo-methine iodomethylate is already decomposed into sinomenol by boiling 3.3% NaOH for an hour (m.p. 172°). The use of 20% NaOH in this decomposition turns the greater part of sinomenol into disinomenol. This easy splitting off of the side chain is undoubtedly due to the strong tendency to aromatize of the nuclei II and III of the hydrated phenanthrene, since it contains a ketone group, which can enolize in presence of alkali. This is the reason why we must effect the transformation of the achro-methine into the violeo-methine in the cold.

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ON THE COMPOSITION OF THE CYANIDE COMPLEX RADICAL OF METALS. PART III. ZINC CYANIDE COMPLEX RADICAL.

By Kosaku MASAKI.

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F. Kunschert[1] stated that when a zinc salt is dissolved in a solution of potassium cyanide, the molal ratio of combined to uncombined zinc is usually four to one, though sometimes three to one, and he showed that the salt $K_2Zn(CN)_4$ will be separated to about 16% in KCN and $KZn(CN)_3$, and moreover, in concentrated solutions there exist such ion or salt as $Zn(CN)_4^{--}$, $K_2Zn(CN)_4$ or $BaZn(CN)_4$.

Book of analytical chemistry[2] describes as the followings: It produces white precipitate of zinc cyanide by adding potassium cyanide to a solution of a zinc salt. In this case, the reaction take places are:

$$Zn^{++}+2CN^- \rightleftarrows Zn(CN)_2$$
$$Zn(CN)_2+2CN^- \rightleftarrows Zn(CN)_4^{--}$$

Composition of Zinc Cyanide Ion. A simple titration method has been employed to determine the ratio of combined cyanide to zinc in the complex ion. The method has already been described in the cases of silver cyanide[3] and cadmium cyanide.[4] Zinc cyanide has been prepared from the dilute solution of zinc sulphate and sodium cyanide solution. It is white amorphous precipitate. The results are summarized in the following tables.

Table 1.

Sodium Cyanide and Zinc Cyanide.

Zinc mol per litre	Free cyanide mol per litre	Combined cyanide mol per litre		Ratio combined cyanide to zinc
		Apparent	Actual*	
0.2850	1.1288	0.5978	0.8828	3.09
0.2377	1.2322	0.4944	0.7321	3.08
0.1779	1.3637	0.3629	0.5408	3.04

* This Bulletin, **6** (1931), 61.

(1) *Z. anorg. Chem.*, **41** (1904), 351.
(2) For example, Treadwell, "Lehrbuch der analytischen Chemie," Vol. 1.
(3) This Bulletin, **4** (1929), 190.
(4) This Bulletin, **6** (1931), 60.

Table 1.—(*Concluded*)

Zinc mol per litre	Free cyanide mol per litre	Combined cyanide mol per litre		Ratio combined cyanide to zinc
		Apparent	Actual	
0.1199	1.4809	0.2457	0.3656	3.05
0.0770	1.5742	0.1524	0.2294	2.98
0.2469	0.5614	0.5030	0.7499	3.00
0.2005	0.6614	0.4030	0.6035	3.01
0.1853	0.6955	0.3689	0.5543	2.99
0.1767	0.7146	0.3498	0.5265	2.98
0.1524	0.7627	0.3017	0.4541	2.98
0.2003	0.2386	0.4418	0.6421	3.27
0.1735	0.3178	0.3626	0.5361	3.09
0.1482	0.3766	0.3038	0.4520	3.05
0.1110	0.4562	0.2242	0.3552	3.02
0.0937	0.4996	0.1808	0.2745	2.95

Table 2.

Sodium Cyanide and Zinc Sulphate.

Zinc mol per litre	Free cyanide mol per litre	Combined cyanide mol per litre	Ratio
0.2436	0.0754	0.9890	4.05
0.2159	0.1869	0.8765	4.06
0.1835	0.3231	0.7413	4.04
0.1721	0.3726	0.6918	4.02
0.1366	0.5167	0.5477	4.01
0.0942	0.6872	0.3772	4.00
0.0635	0.8088	0.2556	4.02
0.1415	0.2726	0.5906	4.17
0.1077	0.3938	0.4694	4.34
0.0793	0.5364	0.3268	4.12
0.0894	0.0503	0.3688	4.11
0.0807	0.0963	0.3228	4.00
0.0570	0.1927	0.2264	3.97
0.0466	0.2389	0.1802	3.86

Table 3.

Sodium Cyanide and Zinc Acetate.

Zinc mol per litre	Free cyanide mol per litre	Combined cyanide mol per litre	Ratio
0.0907	0.4944	0.3688	4.06
0.0692	0.5950	0.2682	3.87
0.0351	0.7458	0.1404	4.00
0.0258	0.7710	0.0922	3.58

In the above experiments, the molal ratio of combined cyanide to zinc is three to one in the case of zinc cyanide and sodium cyanide, and four to one is other cases, corresponding to the formulas $Zn(CN)_3^-$ and $Zn(CN)_4^{--}$ respectively.

Stability of the Zinc Cyanide Ion. There is available in the literature very little information on the concentration of zinc ion in zinc cyanide solution. Kunschert[1] stated that the zinc ion concentration is 3×10^{-19} in a molal solution of cyanide ion and 0.1 molal solution of complex ion, which he regards as $Zn(CN)_3^-$. He gives as the stability constant 3.3×10^{17}.

The author have consequently made a series of determinations of the potential differences between a zinc electrode and various zinc salts in sodium cyanide solution. The solutions used in these measurements were made by dissolving the appropriate amounts of pure $Zn(CN)_2$ and $ZnSO_4$ in 100 c.c. portions of 0.5177 molal sodium cyanide solution. The electromotive force measurements were made at 18°C by connecting a normal calomel electrode, through a normal potassium chloride salt bridge, with an electrode of pure zinc rod immersed directly in the solution, which being constantly stirred. The data are summarized in Tables 4 and 5.

Table 4.

$Zn(CN)_3^-$	CN^-	E	E_w	Zn^{++}	K
0.03916	0.15687	1.5471	1.2649	2.717×10^{-18}	3.73×10^{18}
0.02385	0.16079	1.5522	1.2700	1.799×10^{-18}	3.18×10^{18}
0.02000	0.16472	1.5556	1.2734	1.371×10^{-18}	3.27×10^{18}

(1) *Z. anorg. Chem.*, **41** (1904), 351.

Table 5.

$Zn(CN)_4^{--}$	CN^-	E	E_w	Zn^{++}	K
0.03460	0.10442	1.5532	1.2710	1.668×10^{-18}	1.77×10^{20}
0.02428	0.10589	1.5588	1.2766	1.068×10^{-18}	1.81×10^{20}

In Tables 4 and 5, E are the measured electromotive forces and E_w are the potentials of the zinc electrode referred to normal hydrogen electrode, taking the value for the single potential of the normal calomel electrode as 0.2822 volt.(1) The zinc ion concentration, C, was found by the next equation.

$$E_w = E_0 - 0.02885 \log c$$

where E_0 is the standard electrode potential of the zinc ion-zinc electrode which is given as 0.7581 volt.(2) From the calculated value of (Zn^{++}), K can be determined from the expression:

$$K=\frac{Zn(CN)_3^-}{(Zn^{++})\ (CN^-)^3} \text{ and } K=\frac{Zn(CN)_4^{--}}{(Zn^{++})\ (CN^-)^4}$$

Table 6.

$Zn(CN)_3^-$	CN^-	E	E_h	E_{Zn}	H^+	Zn^{++}	K
0.03916	0.15687	1.5471	−0.3157	1.2324	1.14×10^{-11}	4.94×10^{-17}	2.05×10^{17}
0.02385	0.16079	1.5528	−0.3158	1.2364	1.13×10^{-11}	2.64×10^{-17}	2.14×10^{17}
0.02000	0.16472	1.5556	−0.3159	1.2397	1.12×10^{-11}	2.02×10^{-17}	2.20×10^{17}

Table 7.

$Zn(CN)_4^{--}$	CN^-	E	E_h	E_{Zn}	H^+	Zn^{++}	K
0.03460	0.10442	1.5532	−0.3130	1.2402	1.41×10^{-11}	1.95×10^{-17}	1.47×10^{19}
0.02428	0.10589	1.5588	−0.3132	1.2456	1.39×10^{-11}	1.27×10^{-17}	1.51×10^{19}

(1) Lewis and Randall, "Thermodynamics" (1923), p. 407.
(2) Ibid., p. 420.

In Tables 6 and 7, E is the measured electromotive force; E_h the correction required to give the potential (E_{Zn}) referred to the normal hydrogen electrode, and K the stability constant. The hydrogen ion concentrations in these solutions were calculated from the ionization constant of HCN[1] as 2.06×10^{-9} and that for water[2] as 1.005×10^{-14}.

From the law of mass action we have obtained for the dissociation of hydrocyanic acid:

$$\frac{(CN^-)\,(H^+)}{(HCN)}=K \quad \cdots\cdots\cdots\cdots\cdots\cdots\cdots \quad (1)$$

and, since $$(H^+)\,(OH^-)=K_w \quad \cdots\cdots\cdots\cdots\cdots\cdots\cdots \quad (2)$$

we have $$\frac{(CN^-)}{(HCN)}=\frac{K}{K_w}(OH^-) \quad \cdots\cdots\cdots\cdots\cdots\cdots \quad (3)$$

The concentration of the undissociated sodium cyanide may be neglected, since the salt may be regarded as completely dissociated. The hydrolysis of sodium cyanide takes place according to the equation.

$$NaCN+H_2O=HCN+NaOH$$

and the sodium hydroxide may, also be regarded as completely dissociated. Therefore, the concentration of the OH ion produced by the hydrolysis is equal to the concentration of the undissociated HCN produced at the same time according to the equation.

$$CN^-+H_2O=OH^-+HCN \quad \cdots\cdots\cdots\cdots\cdots\cdots \quad (4)$$

Now, from (3) we have

$$(HCN)=(OH^-)=\frac{(CN^-)}{(OH^-)}\times\frac{K_w}{K}$$

so $$(CN^-)=\frac{K(OH^-)^2}{K_w} \text{ or } (OH^-)^2=\frac{(CN^-)\,K_w}{K} \quad \cdots\cdots \quad (6)$$

Therefore, the concentration of the hydrogen ion was calculated from the equations (6) and (2) and the value of E_h was calculated by the next equation.

$$E_h=0.02885\log(H^+)$$

To determine the zinc ion concentration we may write,

$$E_{Zn}=E_o-0.02885\log c$$

(1) Lewis and Randall, "Thermodynamics" (1923), p. 589.
(2) Ibid., p. 486.

where E_0, the standard electrode potential of Zn^{++}, is taken as 0.7581 volt. From the calculated value of Zn^{++}, K can be determined from the above expression.

The fact that K remaines constant are an added evidence for the formulas $Zn(CN)_3^-$ and $Zn(CN)_4^{--}$.

Conclusion. The composition of the zinc cyanide complex ion are probably $Zn(CN)_3^-$ and $Zn(CN)_4^{--}$ at all concentrations.

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STUDIES ON THE VOLATILE CONSTITUENTS OF THE LEAF OF *CHAMAECYPARIS FORMOSENSIS*, MATSUM.

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Chamaecyparis formosensis, Matsum. or "benihi" is a conifer indigenous to Formosa and one of the most important timber trees of the island. Its older growths are found along the central mountain range at an altitude of 7000 to 8500 ft. above sea level. Most of these trees are gigantic in size, the biggest tree on Mt. Ari is said to be more than two thousand years old and measures indeed 160 ft. in height and 25 ft. in diameter. The leaf of this conifer has a peculiarly pleasant odour of its own, but as to the nature of its volatile constituents, nothing has yet been reported. The authors, with a view to study such, distilled the live leaves of freshly felled trees on Mt. Ari with steam then and there, and could obtain a quantity of a reliable material for examination, in form of a faintly reddish coloured mobile oil with the characteristic odour, the yield of the oil amounting to 0.16% as referred to the whole weight of the leaf. This oil, on being stood in the air, was liable to oxidize and thicken into a viscid dark reddish-brown mass, however, without any appreciable change in odour. The properties of the oil, a week after its preparation, were as follows :

d_4^{24}	n_D^{24}	α_D^{24}	Acid value	Ester value	Do. after acetylation
0.8645	1.4724	-24.67°	1.06	5.78	26.35

This oil consisted for the most part of terpenes, with smaller quantities of terpene alcohols, sesquiterpenes, and sesquiterpene alcohols. In addition

to these, the authors could detect the presence of minute quantities of a crystalline ketone, a liquid acid and a solid phenol. The ketone had a melting point 139°–140° and boiled between 157° and 161°. The authors propose to name this ketone "benihione." The liquid acid and the solid phenol showed a remarkable resemblance to citronellic acid and homopyrocatechin respectively but on account of the small quantity of the substance available, it was impossible to carry out any positive means of identification. Among the terpenes, there predominated a highly active *l*-α-pinene in quantity, while *l*-camphene, dipentene, α- and γ-terpinene were also present with a little cineol. The terpene alcohol fraction represented chiefly borneol and its esters, while in the sesquiterpene fraction the authors detected cadinene and humulene. The highest boiling fraction as a whole seemed to consist of a dicyclic sesquiterpene alcohol of a tertiary nature perhaps identical with "cadinol" of Semmler and Jonas.[1]

Experimental.

Acids and Phenols. 2800 gr. of the crude oil was shaken on the machine with a quantity of 3% caustic alkali solution and acids and phenols were regenerated from this aqueous layer in the usual manner. After due purifications 2.14 gr. of acidic and 1.2 gr. of phenolic portions were obtained. Both of these were reddish black in colour but smelled differently,—the former was of a strong fatty odour while the latter reminded of pyrocatechin and cresol at the same time.

The Acid. The acidic portion on fractionation in a small distilling apparatus came over chiefly between 135° and 136° under 6 mm. pressure, and the distillate was found to possess the following characteristics:—

d_4^{24}	n_D^{24}	Acid value	Bromine value	Ag % of Ag-salt
0.9507	1.4800	330.2	935	38.9

The molecular weight calculated as a monobasic acid from the above data is 169.6 corresponding to a formula $C_{10}H_{18}O_2$(M.W.=170); the calculated value of Ag (%) from $C_{10}H_{17}O_2Ag$ is 38.96% agreeing well with the experimental result. The bromine value points to the presence of one ethylene linkage, as such requires 940.2 for $C_{10}H_{18}O_2\overline{|}\overline{=}$. The odour of this acidic fraction reminded of citronellic acid, but attempts to prepare its acid amide and other derivatives turned out to be futile.

(1) *Ber.*, **47** (1914), 2063.

The Phenol. The phenolic portion showed a marked tendency to get darker in colour and to resinify on exposure to the air. On fractional distillation under 8 mm. pressure it furnished the following fractions :—

	B. p./8 mm.	d_4^{24}	n_D^{27}	Colour Reactions		
				aqueous $FeCl_3$	alcoholic $FeCl_3$	vanillin+HCl
(1)	123°—130°	0.974	1.5000	red	green	blue
(2)	130°—135°	0.973	1.4959	,,	,,	purple
(3)	135°—150°	0.976	1.5010	,,	,,	,,
(4)	150°—156°	0.978	1.5013	,,	,,	,,

(3) and (4), on cooling to—5°C., deposited a quantity of scaly crystals which, after purifications showed a melting point 57°-62°, and seemed likely to be homopyrocatechin (m.p.=63°), but owing to the lack of material no further means of identification were possible.

The Neutral Part. The lye-washed neutral oil was almost devoid of the reddish tinge as seen in the crude state, and represented a golden yellow transparent oil of the following properties :—

d_4^{24}	n_D^{24}	α_D^{21}	η_{24}	Ester value	Do. after acetylation
0.8654	1.4717	−28°	1.00	5.75	26.44

This oil was four times fractionated under 3 mm. pressure using Wiedmer's fractionating column, when the fractions with the following characteristics came over :—

	B. p./3 mm.	n_D^{28}	d_4^{29}	α_D^{29}	Yield %
(1)	31°— 40°	1.4640	0.8505	−39.40°	83.70
(2)	40°— 50°	1.4725	0.8584	— 2.86°	0.57
(3)	50°— 55°	1.4788	0.8621	— 1.23°	0.42
(4)	55°— 60°	1.4839	0.8771	— 1.03°	0.25
(5)	60°— 65°	1.4902	1.0049	+ 0.85°	0.11
(6)	65°— 70°	1.4870	1.0114	+ 0.30°	0.07
(7)	70°— 80°	1.4683	0.9263	+ 7.20°	0.14
(8)	80°— 85°	1.4706	0.9322	— 0.30°	0.88
(9)	85°— 90°	1.4715	0.9319	— 0.45°	0.67
(10)	90°— 95°	1.4740	0.9299	−12.44°	0.28

	B. p. / 3 mm.	n_D^{28}	d_4^{29}	α_D^{29}	Yield %
(11)	95°—100°	1.4782	0.9281	−17.68°	0.11
(12)	100°—105°	1.4892	0.9152	−27.00°	0.78
(13)	105°—110°	1.4989	0.9053	−30.25°	2.87
(14)	110°—115°	1.5030	0.9054	−13.43°	3.97
(15)	115°—120°	1.5050	0.9141	+18.82°	2.51
(16)	120°—125°	1.5048	0.9331	+27.08°	0.32
(17)	125°—130°	1.5040	0.9478	+13.60°	0.32
(18)	130°—135°	1.5033	0.9583	− 7.00°	0.99
(19)	135°—140°	1.5052	0.9680	−19.59°	1.03

In the above, we notice that maxima of the amount of distillate per degree occur at (1), (8), (14), and (19), while maxima and minima of refractive indices and densities are observable at (1), (5), (7), (15), (19), and (1), (6), (13), (19) respectively. It is also of interest that while most of the fractions are laevo-rotatory, strongly dexro-rotatory fractions are met with at (7) and (16). These features are graphically shown in Fig. 1.

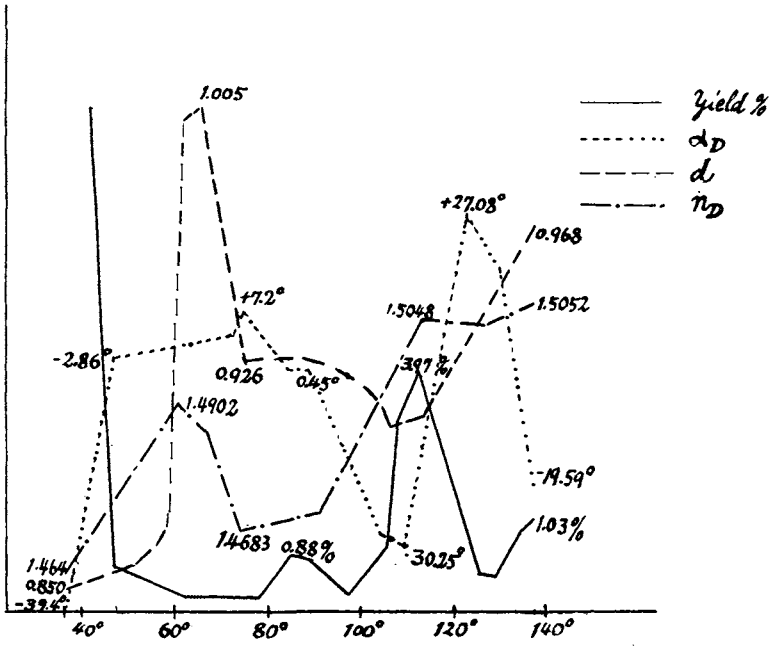

Fig. 1.

The Terpenes. Fractions (1) and (2), which represented the greater part of the terpenic constituents, were boiled over metallic sodium for 6 hours under 70 mm. pressure, and then fractionally distilled under the atmospheric pressure using Wiedmer's column for dephlegmation. After seven successive fractionations the greater part accumulated at the 156°–157° fraction and showed the following properties :—

d_4^{31}	n_D^{31}	α_D^{31}	$[\alpha]_D$	M.R.	M.R. calc.
0.8483	1.4608	−40.78°	−48.07°	43.98	43.54 as $C_{10}H_{16}$

That this fraction represented *l*·*α*·pinene is almost self·evident, but in order to prove its identity more rigorously, the following derivatives were prepared from it :

(*a*) *Pinene Hydrochloride.* On passing dry hydrogen chloride gas through well-cooled hydrocarbon, a quantity of the crystalline hydrochloride was obtained, which after recrystallizations from alcohol, melted at 128°C., and showed no depression of the melting temperature on admixture with a known sample of pinene hydrochloride. Its specific rotation in alcoholic solution amounted to−31.25°. (0.817 gr. of the crystal in 8.02 c.c. of alcohol.)

(*b*) *Pinonic Acid.* By oxidizing 25 gr. of the hydrocarbon with 83 gr. of potassium permanganate in 500 c.c. of water at 5°–10°C., and treating the product of oxidation in the usual manner, a syrupy acidic substance was obtained, which on rectification under 4 mm. pressure, distilled chiefly at 194°–199°. This distillate, on being kept for three weeks in an ice·cold chamber, deposited a mass of crystals with m.p. 67°–69°. The residual fluid part showed a specific rotation−25.0° and afforded a semicarbazone (m.p.=203.5°) and an oxime (m.p.=189°–190°). The oxime was insoluble in glacial acetic acid and its specific rotation amounted to +38.40° in alcoholic solution. All these data agree with the previous data about pinonic acid.

(*c*) *Pinene Nitrosochloride.* By passing a current of dry nitrosyl chloride into a well·cooled ethereal solution of the terpene (1 : 1), and subsequently adding an equal volume of cold absolute alcohol. The needle crystals thus precipitated were filtered, washed, redissolved in chloroform, and reprecipitated by methyl alcohol. The purified product showed a melting point 89°–90°, which even after several successive purifications remained unaltered. This is in accordance with the results of Tsuchihashi·

Tasaki[1] and of Lynn[2] who worked with highly active pinenes from Chamaecyparis obtusa, Sieb. et Zucc., and from *Chamaecyparis Lawsoniana*, (Murr.) Parl. respectively. It is worthy of note that in the present case up to 38% by weight of the nitrosochloride was obtainable, whereas it is generally stated that the preparation of nitrosochloride from highly active pinenes are accompanied by difficulties. Our nitrosochloride showed a specific rotation −292°. (2.00 gr. in 15.03 c.c. of chloroform.)

(*d*) *Nitrosopinene.* Two grams of the nitrosochloride was heated for five hours on the water bath with 2 gr. of metallic sodium and 5 c.c. of 85% alcohol, the whole mass was then thrown into 25 c.c. of water and kept for six days in the ice chamber, when a quantity of crystals separated out. These crystals after recrystallizations from acetic ester showed a melting point 129°–131°.

(*e*) *Pinene Nitrolbenzylamine.* On treating 1 gr. the nitrosochloride with 1 gr. of benzylamine and 5 c.c. of alcohol in the warm, crystals of the benzylamine were obtained, which after recrystallizations melted at 143°–145°. This melting point is somewhat too high for the ordinary pinene nitrolbenzylamine—122°–123°, but coincides with the data of Lynn who prepared it from pinene of Chamaecyparis Lawsoniana.

The next fraction b.p. 157°–161° seemed to consist of mixtures of pinene and camphene, and by carrying out the hydratation according to Bertram and Walbaum, isoborneol was duely identified, (phenylurethane m.p. 136°–137°), while by oxidizing it with concentrated aqueous permanganate pinonic acid could be obtained. Attempts to prove nopinene or sabinene proved to be fruitless.

The portion boiling between 173° and 175° gave dipentene tetrabromide (m.p. 124°) on treatment with bromine. The odour of this fraction reminded the presence of cineol in it, and analyses also revealed the presence of some oxygenated substances, thus:—

Sample	CO_2	H_2O	C %	H %	O %
0.2021	0.6241	0.2037	84.21	11.19	4.60
0.1673	0.5169	0.1689	84.26	11.21	4.53

So, the fraction was shaken with 50% resorcinol solution when a small quantity of cineol-like substance could be regenerated from this resorcinol

(1) *Report of Dep't of Industry, Gov. Research Inst. of Formosa* No. 1, p. 119.
(2) *Ber. Schmmel & Co.*, **1919** S. 132.

solution. In order to identify cineol, it was treated with iodol and a iodol compound was obtained which melted at 107°–110°. On account of the small quantity no further purifications were possible, but it is most likely that this was cineol-iodol. (m.p.=112°).

The next two fractions b.p. 175°–180° and 180°–187° were twice rectified and a main fraction with the following properties was obtained :

B. p. / 757 mm.	d_4^{23}	n_D^{13}	α_D^{23}
179°—182°	0.8503	1.4766	—3.65°

This gave two crystalline products on oxidation with dilute permanganate solution, the one melting at 235°–236° and the other at 186°–188°. The first of these corresponded to terpinene erythritol while the latter to α-α'-dihydroxy-α-methyl-α'-isopropyl-adipic acid. These results show that the fraction consisted of α- and γ-terpinenes.

Benihione. The fractions (2)–(5) contained a crystalline ketonic compound soluble in dilute $NaHSO_3$-solution, and on being regenerated from such solution a crystalline substance was obtained, which after recrystallization from 70% ethyl alcohol melted at 139°–140°C. This substance does not reduce Tollen's solution, but an attempt to prepare its semicarbazone resulted in a failure.

The Terpene Alcohols and Esters. The fractions (8), (9), and (10) represented terpene alcohols and esters as their saponification values before and after acetylation clearly showed :—

	Sap, V.	Sap. V. a. acet'n
(8)	88	132.4
(9)	99	129.8
(10)	86	146.3

These were separately fractionated under 15 mm. pressure, and rectified three times in the same manner, when the laevorotatory part accumulated at higher boiling fraction, thus,—

	B. p. / 15 mm.	Distillate gr.	d_4^2	n_D^{28}	α_D^{28}
(a)	97°— 99°	16	0.9324	1.4705	+ 7.64°
(b)	101°—102.5°	17	0.9354	1.4695	+ 3.16°
(c)	106°—107°	9	0.9297	1.4712	—11.40°

All of these fractions did not congeal even when they were cooled to −20°. On treatment with phenyl isocyanate each gave the same phenyl urethane melting at 137°C, showing the presence of borneol or isoborneol in every one of them. Nextly, they are benzoylated after Schotten-Baumann, and after standing over night, the products were subjected to steam distillation. Then the residues from steam distillation were separately saponified with excess of alcoholic potash and steam distilled for the second time. The distillates were then ethered out, the ethereal solutions evaporated, when, from each of them crystals of borneol separated out. It was identified as such by testing the melting point and preparing the phenyl urethane. By directly saponifying the fractions and testing for the acids contained therein, the authors could detect formic and acetic acids. (Reducing action towards $HgCl_2$; behaviour of the silver salt analyses of silver salts);

The Sesquiterpenes. The fractions (12), (13), and (14) consisted chiefly of sesquiterpenes but contained small quantities of alcoholic and ester constituents, so they were boiled for 6 hours under reduced pressures over metallic sodium at 80°-90° and then carefully fractionated seven times under reduced and atmospheric pressures. The resulting distillates showed the following properties :—

	B. p.	gr.	d_4^{24}	n_D^{27}	α_D^{26}	M. R.
(i)	Up to 257°	3.5	—	—	—	—
(ii)	257° - 259°	4.8	0.9016	1.4970	−24.36°	66.20
(iii)	259°—260°	1.0	—	—	—	—
(iv)	260°—263°	29.0	0.9046	1.5004	−19.30°	66.38
(v)	263°—264°	3.0	—	—	—	—
(vi)	264°—267°	71.0	0.9065	1.5030	+ 4.99°	66.52
(vii)	267°—268°	8.0	—	—	—	—
(viii)	268°—273°	10.0	0.9096	1.5050	+21.04°	66.53

Fractions (ii) and (iv) gave liquid hydrochloride while (vi) and (viii) deposited cadinene dihydrochloride on treatment with dry hydrogen chloride. The cadinene dihydrochloride showed a specific rotation $[\alpha]_D = -31,49°$ (0,1023 gr. in 7.00 c.c. chloroform) and a melting point 117°C.

Fractions (ii) and (iv) gave a nitrosochloride which dissolved with difficulty in ether or alcohol but easily in chloroform, and melting at 173°-175°. It was optically inactive. Action of hydrogen chloride on these fractions produced no dihydrochloride. Also no isocaryophyllene alcohol could be obtained by applying Aschan's hydratation method.

The nitrosite was obtained by adding 5 c.c. of glacial acetic acid into a well-cooled mixture of 3 c.c. of the substance in 3 c.c. of petroleum ether (b.p. 60°–70°) with some saturated solution of sodium nitrite in water, and stood over night at 5°C. A blue crystalline substance separated out, which was filtered, washed, and dried. It melted at 116°–118°C. When this was recrystallized from absolute alcohol, two kinds of crystals were obtained; viz.: a faintly blue-coloured crystal melting at 164°–166°, and a colourless needle crystal melting at 140°–141C°. These results agree with the description by A. Chapman[1] about the recrystallization of humulene nitrosite from ethyl alcohol.

Nextly, the nitrosate was prepared by the action of a mixture of nitric and acetic acids (1:1) on a solution of the hydrocarbon in amyl nitrite and glacial acetic acid (5:5:8). The white crystalline substance obtained, melted at 163°C. The nitrosate and the nitrosite were optically inactive.

The Sesquiterpene Alcohol. The fractions (18) and (19) were rectified twice under 12 mm. pressure and a main fraction with the following characteristics was obtained:

B. p./12 mm.	d_4^{23}	n_D^{23}	α_D^{23}	M. R.	M. R. calc.
154°—156°	0.9695	1.5059	−14.00°	68.05	68.12 as $C_{15}H_{26}O$ $\left\vert\overline{\overline{1}}\right.$

These data show that the fraction consists of a sesquiterpene alcohol of the bicyclic nature. On Liebermann's test it exhibited a beautiful green colour at first, which gradually changed into blue and then greyish violet. It did not react with phthallic anhydride neither in benzol solution nor without the solvent by heating to 130°, from which it seems probable that this alcohol represented a tertiary alcohol.

By the action of dry hydrochloric acid gas on this fraction an almost quantitative yield of cadinene dihydrochloride (m.p. 118°) resulted, while by dehydratation with sulphur it afforded cadaline, its identity proved as its picrate. From these behaviours it is most probable that this alcohol is identical with cadinol of Semmler and Jonas.[2]

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1) *J. Chem. Soc.*, **67**, 60; Ibid., **1928**, 133;
(2) Loc. cit.

ON THE FORMATION OF BENZENE-(PENTANONE-3-YLENE)$_{1,2}$

By Bennosuke KUBOTA and Toshizo ISEMURA.

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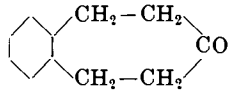
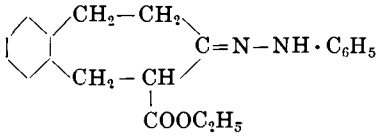
With the view of inquiring into the conditions of the formation of rings which can be attached to the ortho-positions of benzene nucleus, and the effects of benzene nucleus on the odour of alicyclic poly-membered rings, the synthesis of benzene-(alcanone-x-ylene)$_{1,2}$ was attempted. In the present communication a result of the formation of benzene-(pentanone-3-ylene)$_{1,2}$



is briefly descrived.

As to the seven-membered ring compounds of the type above mentioned, A. F. Titley[1] had previously showed, in the course of his investigations of conditions of formation of rings attached to the *o*-, *m*-, and *p*-positions of the benzene nucleus, the synthesis of phenylhydrazone of ethyl 3-ketophen-heptamethylene-2-caboxylate



by the application of the Dieckmann reaction (the action of sodium on *o*-phenylenedipropionic ester in toluene at 100°), though the pure ketone-carboxylate had not been isolated. Thus the formation of benzene-(pentanone-3-ylene)$_{1,2}$ was examined by means of dry distillation of thorium salt of *o*-phenylenedipropionic acid. The *o*-phenylenedipropionic acid was prepared by Perkin's method[2], but as it was found after a few experiments that the large excess of concentrated alkali solution did not act to give a good yield of the acid, the method was slightly modified as descrived in the experimental part. The action of alkali on ethyl *o*-xylenedimalonate was precisely investigated by Mr. H. T. Lo who previously reported the results in this Bulletin.[3] Being carefully saponified with a dilute potassium hyd-

(1) Titley, *J. Chem. Soc.*, **1928**, 2571.
(2) Perkin, *J. Chem, Soc.*, **53** (1888), 18; Titley, *J. Chem. Soc.*, **1928**, 2578.
(3) This Bulletin, **5** (1930), 326.

roxide solution, acidified with a dilute sulphuric acid, and then extracted with either, *o*-xylenedimalonate gives really *o*-xylenedimalonic acid which crystallises from the mixture of chloroform and benzene in colourless microscopic crystals melting at 156° with decomposition. When the therium *o*-phenylenedipropionate, which was prepared by neutrallising the acid with a caustic soda solution and then adding a thorium chloride solution, was subjected to the dry distillation in diminished pressure, it begins to decompose at 200° in the temperature of the oil bath and a yellowish oil which distils between 155 and 175° are collected. The product is soluble in almost all common organic solvents and recrystallised with much difficulty from petroleum ether. It crystallises in large plates melting at 41–42°. On elemental analysis of itself and its phenylhydrazone, and the determination of the molecular weight, it proved to be nothing but benzene·(pentanone·x·3·ylene)$_{1\cdot2}$. As Ruzicka[1] showed in his excellent researches on higher carbonatom rings that alicyclic ketones which have carbon atoms from C_5 to C_{12} have the odour of bitter almond and peppermint. It may be seen somewhat interesting to indicate that the ketone obtained also has the striking smell of them, though we must naturally have many further investigations in order to know what influences are exerted upon the odour of alicyclic rings by an aromatic one consolidated into them.

Experimental.

Ethyl *o*-xylenedimalonate. The preparation of this ester was carried out exactly as described by Perkin,[2]

$$C_6H_4(CH_2Br)_2 + 2\,NaCCl(COOC_2H_5)_2 \longrightarrow C_6H_4[CH_2-CCl(COOC_2H_5)_2]_2$$

$$C_6H_4[CH_2-CCl(COOC_2H_5)_2]_2 \xrightarrow{Zn+CH_3COOH} C_6H_4[CH_2\cdot CH(COOC_2H_5)_2]_2,$$

but as it was found difficult to isolate *o*-phenylenedipropionic acid from ethyl *o*-xylenedimalonate in the quantity showed by the author and also found that the cause was to use concentrated alcoholic potash, the investigation of which was previously reported by Mr. H. T. Lo in this bulletin,[3] the method of its preparation was modified as described below.

***o*-Phenylenedipropionic acid.** In a flask provided with a reflux condenser. ethyl *o*-xylenedimalonate was boiled with a little excess of dilute

(1) Ruzicka, *Bull. Soc. Chim.*, **43** (1928), 1145.
(2) Loc. cit.
(3) Loc. cit.

alcoholic potash (about 2%) calculated from the following formula for some hours on a water bath and the hydrolysis was completed.

$$C_6H_4[CH_2\cdot CH(COOC_2H_5)_2]_2 + 4KOH = C_6H_4[CH_2CH(COOK)_2]_2 + 4C_2H_5OH$$

Being added some water, the reaction mixture was carefully evaporated on a water bath until the solution gained the former volume and was acidified with dilute sulphuric acid. *o*-Xylenedimalonic acid thus produced in the solution was extracted three or four times with ether. The etherial solution was washed with water and the ether was then distilled off, when a slightly yellowish crystalline mass remained, consisting of mainly *o*-xylenediomalonic acid accompanied by a small quantity of *o*-phenylenedipropionic acid and a tarry matter. In preparing *o*-phenylenedipropionic acid, it is enough to heat the product in an oil bath at the temperature between 120° and 165° when a considerable evolution of carbon dioxide take place and nearly pure *o*-phenylenedipropionic acid is formed, which crystallises from water in small colourless needles melting at 160–162°. Neverthless when the product consisting of mainly *o*-phenylenedimalonic acid is recrystallised from the mixture of chloroform and benzene, pure *o*-xylenedimalonic acid, $C_6H_4[CH_2\cdot CH(COOH)_2]_2$, is obtained. It crystallises in colourless microscopic crystals which melts at 156° with the evolution of carbon dioxide and transforming to *o*-phenylenedipropionic acid.

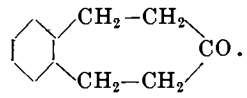
Seven membered ring. *o*-Phenylenedipropionic acid is carefully neutrallised with a dilute caustic soda solution and a solution of thorium chloride is added, whereby thorium *o*-phenylenedipropionate is precipitated in a voluminous white crystalline mass. It is collected, washed with water, and dried in an air bath at 100°. On dry distillation under diminished pressure (about 0.1 mm.), the salt begun to decompose when the temperature of the oil bath was raised to about 200°, and the following fractions were collected,

(1) 155—175° (2) 174—190°.

The first fraction (1) was a yellowish liquid which crystallised in colourless plates when it was left to cool. The second fraction (2) was a brown liquid which did not crystallise, even if it was left to cool. But when it was fractionated again under the same pressure (0.1 mm.), a yellowish liquid boiling at 155–175° which was quite identical to the first fraction (1) was obtained as the main product.

The product dissolves easily in almost all common organic solvents, though it can be recrystallised with much difficulty from hot petroleum ether, when it forms colourless plates melting at 41–42°. The crystals have

a strong smell of bitter almond and peppermint and on analysis proved to be those of benzene·(pentanone·3·ylene)$_{1.2}$



Anal. Subst. = 2.466; CO_2=7.474; H_2O=1.775 mg. Found: C=82.64; H=7.98%. Calc. for $C_{11}H_{12}O$: C=82.50; H=7.50%.

Molecular weight was determined by K. Rast's method, using camphor as solvent, 0.264 mg. in 3.099 mg. of solvent gave $\Delta t = 21.1°$. Molecular weight found 166 4· $C_{11}H_{12}O$ requires 160.

An alcoholic solution of the product produced a white turbidity on the addition of a dilute alcoholic solution of phenylhydrazine hydrochloride and sodium acetate, which being allowed to stand for a few hours, collected into a precipitate. This was filtered and recrystallised from alcohol, when it formed colourless crystals melting at 85° and on analysis it proved to be nothing but phenylhydrazone of benzene·(pentanone·3·ylene)$_{1.2}$.

Anal. Subst.=2.25 mg.; N_2=0.228 c.c. (19°, 749.2 mm.) Found: N_2=11.4%. Calc. for $C_{17}H_{18}N$: N=11.2%.

Authors wish to acknowledge their obligations to Mr. R. Yokowo for his kind assistance in this research.

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OXIDATION OF METHANE TO CARBON MONOXIDE AND HYDROGEN.

By Kiyoshi YOSHIKAWA.

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Attention has recently been called to the methane-oxygen reaction as a source of hydrogen-carbon monoxide mixtures. Patart[1] obtained a suitable mixture for the catalytic synthesis of methanol by incomplete combustion of methane. The methane, mixed with half its volume of oxygen was injected into coke maintained at 1000°. Brownlee and Uhlinger[2] employed a method of obtaining carbon monoxide, hydrogen and nitrogen from the products of combustion of internal combustion engines. This method of incomplete combustion of methane was proposed in many patents,

often combined with the process using the reaction between methane and steam, but few information has been made on the scientific works with regard to the oxidation of methane to carbon monoxide and hydrogen.

The present work was undertaken to investigate the reaction at atmospheric pressure with the view of obtaining the efficient catalysts to accelerate the reaction or to cause it to take place at lower temperatures. The experiments were carried out by a flow method at 800—1000°, with and without catalysts, using methaner-air and methane-oxygen mixtures. It was found that nickel and cobalt were efficient catalysts and their activity was promoted by the addition of various oxides. The most efficient catalysts of those studied were nickel-thoria and nickel-silica. In the presence of those catalysts, the reaction proceeds at 850—900° almost quantitatively as shown in the following equation

$$2\,CH_4 + O_2 = 2\,CO + 4\,H_2$$

Without a catalyst, the analysis of the effluent gas reveals that the greater part of methane was unchanged at 1000°.

Experimental.

Methane was obtained from a cylinder of natural gas from the Kashiwazaki Province and gas mixtures containing 2 volumes of methane and 5 volumes of air, and 2 volumes of methane and 1 volume of oxygen, were used. The oxygen was obtained from cylinder of that gas. The gases were allowed to pass at the rate of 15 *l.* per hour over a catalyst which was placed centrally in the porcelain reaction tube in the gas furnace. The temperature was measured by means of a platinum and platinum-rhodium thermo-couple. The off gas was collected and analyzed. Analysis was carried out with an usual method, and hydrogen and methane were determined by oxidation with copper oxide at 300° and 550° respectively. Confining fluid was water.

In the experiments 3—5 gr. of oxides were carried on 5 gr. of small grains of pumice which gave a layer of a catalyst of 14 cm., when packed into a reaction tube. The temperature was raised to 800—1000° and gases were allowed to pass over the catalyst. During the reaction, easily reducible oxides in catalysts were reduced and converted to metals. In the case of nickel catalyst, experiments were carried on also with the catalyst which

(1) Brit. Pat., 247,176.
(2) U. S. Pat., 1,107,581.

was reduced at 400° with hydrogen before the commencement of the reaction. The catalyste were prepared by the following methods:—

Nickel oxide—Ignition of nickel nitrate.
Cobalt oxide—Ignition of cobalt nitrate.
Iron oxide—Ignition of iron oxalate.

The mixed catalysts were prepared by the ignition of nickel or cobalt nitrate with nitrates of other metals. (in the case of mangan and magnesium the formates were used.) Nickel-silica and cobalt-silica catalysts were prepared by the ignition of the nitrates with anhydrous silicic acid.

The results obtained are given in Tables 1, 2 and 3. As may be seen from Table 1, when the mixture of methane and air is used, without a catalyst, hydrogen appears at 800° only in 4% in effluent gas and at 1000° in 12%. The use of nickel and cobalt catalysts greatly accelerates the reaction and lowers the reaction temperatures. Iron catalyst is not suitable because it favours the production of carbon dioxide. It is clear from the

Table 1.

Methane-air mixture, rate of flow 15 *l.* per hr. with catalysts, 30 *l.* per hr. without a catalyst.

Catalysts	Original gas / Temp.	CO_2	Heavy hydrocarbons	O_2	CO	H_2	CH_4	N_2
		0	0	14.3	0	0	28.6	57.1
Without catalysts	800°	1.1	1.1	1.4	9.1	4.2	19.0	64.2
	900°	.7	.9	0	10.7	8.1	16.2	63.2
	1000°	.9	1.1	0	10.8	12.4	14.2	60.6
Ni (reduced at 400°)	900°	4.1	0	.3	10.5	20.7	13.6	50.8
	1000°	2.4	0	0	14.4	30.7	8.	44.4
Ni	900°	2.4	0	.3	14.3	33.1	6.9	43.0
	1000°	.9	0	.8	18.7	38.9	2.4	38.3
Co	900°	3.0	0	.1	16.8	36.2	4.9	39.0
	1000°	.5	0		18.5	38.4	3.1	39.5
Fe	900°	8.1	.3	.5	2.2	2.2	23.3	63.4
	1000°	6.6	.1	.5	5.0	11.0	18.4	58.4

Table 2.

Methane-air mixture, rate of flow 15 *l.* per hr.

Catalysts	Original gas / Temp.	CO_2	Heavy hydrocarbons	O_2	CO	H_2	CH_4	N_2
		0	0	14.3	0	0	28.6	57.1
Ni—ZnO 0.1*	900°	1.9	0	0	17.3	39.2	2.3	39.3
	1000°	2.6	0	0	15.6	38.2	3.9	39.7
Ni—BeO 0.1	900°	2.6	0	0	15.9	35.6	3.2	42.7
	1000°	1.1	0	0	18.2	40.9	2.0	37.8
Ni—MnO 0.1	900°	1.7	0	0	17.9	38.1	2.4	39.9
	1000°	1.0	0	0	17.9	38.5	2.9	39.7
Ni—Cr_2O_3 0.05	900°	0.8	0	0	19.3	37.9	1.5	40.5
	1000°	0.4	0	0	19.5	39.6	1.3	39.2
Ni—Al_2O_3 0.2	900°	1.3	0	0.1	18.6	38.0	1.3	40.7
	000°	0.3	0	0	19.2	40.4	1.8	38.3
Ni—MgO 0.1	900°	2.4	0	0	18.2	37.4	1.2	40.8
	1000°	0.5	0	0	19.3	41.0	1.4	37.7
Ni—CeO_2 0.1	900°	1.0	0	0.2	18.8	38.3	1.4	40.3
	1000°	0.9	0	0.1	18.8	41.3	1.2	37.7
Ni—ThO_2 0.1	900°	0.2	0	0.2	19.1	38.1	2.1	40.3
	1000°	0	0	0.2	19.4	40.5	1.6	38.3
Ni—ThO_2 0.1	850°	0.3	0	0	19.1	39.0	1.4	39.2
	900°	0	0	0.1	19.5	39.9	1.3	39.2
Ni—SiO_2 0.01	850°	2 2	0	0.4	16.6	36.0	1.6	43.1
	900°	0.4	0	0	19.0	39.5	1.4	39.7
Ni—SiO_2 0.05	850°	0.5	0	0.1	19.1	38.8	1.3	40.2
	900°	0.1	0	0.2	19.3	39.4	1.4	39.6
Ni—SiO_2 0.1	850°	0.6	0	0	19.1	38.9	2.3	39.4
	900°	0.3	0	0.5	19.6	39.3	2.1	39.2
Ni—SiO_2 0.2	850°	1.3	0	0	18.8	39.0	1.8	38.1
	900°	0.4	0	0.2	19.2	40.2	1.7	38.3
Ni—SiO_2 1.0	850°	1.1	0	0	18.4	40 4	1.3	38.9
	900°	0.2	0	0.3	19.1	40.3	1.4	38.7
Co—ThO_2 0.1	850°	2.4	0	0.1	17.4	40.1	1.2	38.8
	900°	3.0	0	0	16.6	42.6	1.5	36.3
Co—SiO_2 0.1	850°	1.1	0	0	17.9	38.0	2.5	40.5
	900°	0.8	0	0.5	19.1	38.1	1.6	39.9

* The figure indicates gram molecule of the oxide added to 1 gram atom of Ni or Co.

Table 2.—(*Concluded*)

Catalysts	Original gas / Temp.	CO_2	Heavy hydrocarbons	O_2	CO	H_2	CH_4	N_2
		0	0	14.3	0	0	28.6	57.1
$Ni-ThO_2-CeO_2$ 0.1 0.1	900°	0.9	0	0	19.2	40.0	1.0	38.9
	1000°	0.5	0	0	19.5	41.8	1.0	37.2
$Ni-ThO_2-CeO_2$ 0.1 0.01	900°	0.6	0	0.1	19.5	39.1	1.3	39.4
	1000°	0.2	0	0.2	19.8	40.2	1.2	38.4
$Ni-ThO_2-Al_2O_3$ 0.1 0.1	900°	1.8	0	0	17.9	38.9	1.2	40.2
	1000°	0.7	0	0	19.3	40.2	1.0	38.8
$Ni-SiO_2-ThO_2$ 0.1 0.02	850°	0.2	0	0.2	18.3	38.9	2.7	39.7
	900°	0.2	0	0.1	19.6	40.2	0.9	39.0
$Ni-SiO_2-MgO$ 0.1 0.02	850°	0.3	0	1.1	19.5	36.5	2.8	39.8
	900°	0	0	0.2	19.5	38.3	1.4	40.6

Table 3.

Methane-oxygen mixture, rate of flow 15 *l.* per hr.

Catalysts	Original gas / Temp.	CO_2	Heavy hydrocarbons	O_2	CO	H_2	CH_4	N_2
		0	0.4	30.8	0	0	61.6	7.2
$Ni-ThO_2$ 0.1	850°	0.3	0	0.1	29.2	62.7	2.8	4.9
	900°	0	0	0.4	29.0	64.0	2.3	4.3
	Original gas / Temp.	0	0.4	32.5	0	0	61.2	6.9
	850°	0.7	0	0.1	30.8	59.3	3.5	5.1
	900°	0.4	0	0	30.6	61.4	3.1	4.5

results in Table 2 the addition of other oxides increases the catalytic activity of nickel and cobalt. The most efficient catalysts are nickel-thoria and nickel-silica. As shown in Table 3, when the mixture of methane and oxygen is used, the similar results are obtained with nickel-thoria catayst.

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STUDIES ON THE CONSTITUENTS OF THE VOLATILE OIL FROM THE LEAF OF CHAMAECYPARIS OBTUSA, SIEB. ET ZUCC., F. FORMOSANA, HAYATA, OR ARISAN-HINOKI. PART II.

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In the previous paper, the authors and C. Hata have reported on the terpenic as well as the terpenic alcoholic constituents of the essential oil from the leaf of "arisan-hinoki" or *chamaecyparis obtusa*, Sieb. et Zucc. f. *formosana*, Hayata.[1] The present paper is its sequel and deals with the higher boiling ingredients of the same. As regards the high-boiling constituents of similar essential oils, R. Tsuchihashi and S. Tasaki[2] have reported that cadinene and a dicyclic sesquiterpene alcohol-chamaecypariol were present in the wood oil from the same plant as the authors', while S. Uchida,[3] who examined the leaf oil of "hinoki" or Japanese *chamaecyparis*, has proved, besides cadinene, a tricyclic sesquiterpene, a dicyclic sesquiterpene alcohol, and an inactive tetracyclic diterpene in it. The present authors' oil, however, showed a marked difference from the foregoing in various respects, a brief account of which will be described first.

The authors' sesquiterpene fraction, which occupied about 38% by weight of the whole oil, consisted for the most part of three sesquiterpenes, among which the most predominating was a new tricyclic sesquiterpene, the rest represent *d*-cadinene and another tricyclic sesquiterpene. The name "sesquichamene" is suggested by the authors to this predominant tricyclic sesquiterpene. From point of view of physical constants, sesquichamene is almost identical with many of the hitherto known sesquiterpenes of the tricyclic class, such as cedrene,[4] tricyclogurjunene,[5] or longifolene,[6] but it differs decidedly from the others in many chemical behaviours. The most characteristic of all is that it gives a crystalline nitrosochloride which melts with decomposition at 78°-79°C. It is rather unstable and cannot be kept for more than a few hours even in the purest state, but, unstable as it is, it should be remarked, that this is the only crystalline nitrosochloride ever prepared out of tricyclic sesquiterpenses. The nitrolbenzylamine can also be prepared from this nitrosochloride. It

(1) This Bulletin, **6** (1931), 40.
(2) *Report of Govern. Research Inst. Formosa* (1920).
(3) *J. Soc. Chem. Ind. Japan*, **19** (1916), 611.
(4) Semmler, *Ber.*, **40** (1907), 3521; **45** (1912), 355.
5) Semmler, *Ber.*, **47** (1914), 1029, 1141.
6) Simonsen, *J. Chem. Soc*, **117** (1920), 570; **123** (1923), 2642.

melts at 158°-159°C. The nitrosochloride dissolves readily in chloroform and acetone forming blue solutions, from which the original nitrosochloride can be reprecipitated by the addition of ethyl or methyl alcohol, and thus it can be purified by repeating this treatment. It should be remembered, however, that the nitrosochloride is also very unstable in the dissolved state, and the blue colour of the solutions rapidly fades away into yellow minute by minute, and once it becomes yellow, then the reprecipitation impossible.

Sesquichamene slowly oxidizes in the air, and the yield of the characteristic nitrosochloride is maximal only directly after its distillation but declines steadily and ultimately into nil on standing. By oxidizing sesquichamene with potassium permanganate in acetone solution, a glycol melting at 89°-91°. a diketone whose disemicarbazone melting with decomposition at 233°, and a crystalline substance of an undefined nature, have been obtained. By the action of alcoholic sulphuric acid, sesquichamene undergoes isomerization and gives rise to an isomer which should be named "isosesquichamene." Isosesquichamene has a far lower rotatory power and a greater stability than the original sesquichamene. It should be noted that in our sesquiterpene fraction, a small quantity of isosesquichamene was found to be present. Whether this sesquiterpene had been present in the original oil, or had it arisen from sesquichamene during the processes of fractional distillations, remains to be discussed later. Uchida's tricyclic sesquiterpene also seems possibly to be the same, but in his case, it is to be anticipated that it resulted from sesquichamene by the action of heat, as his fractionations were carried out under the atmospheric pressure. Table 1 shows the physical constants and the melting points of characteristic derivatives of hitherto known tricyclic sesquiterpenes and those of sesquichamene and isosesquichamene:

Table 1.

	Cedrene	Tricyclogurjunene	Longifolene
	(Semmler)[4]	(Semmler)[5]	(Simonsen)[6]
B. p.	121°—124°/12	120°—123°/13	150°—151°/35
d	0.9354/15	0.9348/15	0.9284/30
n_D	1.5030	1.5028	1.495/30
α_D	−56° (86°)	+74.5°	+42.7°
Hydrochloride	liq.	liq.	59°—60°
Ketone $C_{15}H_{24}O$	43°	43°	....
Semicarbazone	242°—243°	237°	....
Diketone	....	....	94°—95°
Disemicarbazone	234°	....	....
Glycol	168° (172°)	....	....
Nitrosochloride	....	....	....
Nitrolbenzylamine	....	....	....

Table 1.—(*Concluded*)

	Sesquichamene (Authors')	Isosesquichamene (Authors')	Isosesquichamene[3] (Uchida)
B. p.	$122°-123°/_{12}$	$129°-131°/_{12}$	$265°-268°/_{760}$
d	$0.9277/_{28}$	$0.9320/_{20}$	$0.9367/_{20}$
n_D	$.1.5012/_{28}$	$1.5109/_{21}$	$1.5009/_{20}$
α_D	$-89.4°/_{28}$	$-8.5°/_{21}$	$-15.7°$ (alcohol)
Hydrochloride	liq.	liq.	liq.
Ketone $C_{15}H_{24}O$	....	....	....
Semicarbazone	....	....	....
Diketone	....	....	....
Disemicarbazone	233° (dec.)	....	....
Glycol	89°—91° (dec.)	....	....
Nitrosochloride	78°—79° (dec.)	....	....
Nitrolbenzylamine	165°—166° (dec.)	....	....

The sesquiterpene alcohol fraction amounted to about 8% of the whole oil and contained a dextro-rotatory dicyclic sesquiterpene alcohol and cadinol. Besides, it contained also a very small quantity of tricyclic sesquiterpene alcohol which was not cedrol. The dicyclic sesquiterpene alcohol present was probably identical with that which had been found by Uchida in Japanese chamaecyparis oil. The only definitely identified compound among these was cadinol.

The diterpene fraction was very poor, amounting to only 1% of the original oil. Its physical properties showed that it consisted mainly of a laevo-rotatory tetracyclic diterpene. Its rotatory power, however, on treatment with acids, or by the action of heat, went diminutive and gave rise to an inactive diterpene which was most probably identical with Uchida's inactive diterpene in the above-mentioned oil. We wish to propose the name "chamaecyparene" to this active diterpene, and also the name "isochamaecyparene" to the racemized or isomerized inactive diterpene. The following table shows the physical properties of the dicyclic sesquiterpene alcohol and the diterpene obtained by Uchida and by us:

Table 2.

	Sesquiterpene Alcohol		Diterpene	
	(Uchida)	(Authors')	(Uchida)	(Authors')
B. p.	$290°-295°/_{760}$	$146°-148°/_{12}$	$340°-343°/_{760}$	$185°-186°/_{12}$
d	$0.9599/_{4}$	$0.9492/_{25}$	$0.9624/_{15}$	$0.9648/_{25}$
n_D	$1.5020/_{20}$	$1.4995/_{25}$	$1.5190/_{20}$	$1.5158/_{25}$
α_D	$+18°$ (alcoh.)	$+4.0°$	$\pm 0°$	$-25.1°$

Experimental.

The Sesquiterpene Fraction. After eight consecutive systematic fractional distillations under 12 mm. pressure (the last three times over metallic sodium) the following eleven fractions were obtained:—

	B. p./$_{12}$ mm.	Distillate	n_D^{25}	d_4^{25}	α_D^{25}	M. R.
(1)	115°–120°	10	1.4940	0.9240	−37.0°	64.27
(2)	120°–122°	34	1.4990	0.9272	−51.8°	64.60
(3)	122°–124°	467	1.5031	0.9297	−85.8°	64.87
(4)	124°–126°	57	1.5035	0.9283	−70.6°	65.01
(5)	126°–128°	14	1.5048	0.9274	−52.8°	65.22
(6)	128°–130°	8	1.5049	0.9261	−31.5°	65.32
(7)	130°–132°	31	1.5062	0.9244	−13.7°	65.59
(8)	132°–134°	24	1.5075	0.9232	+18.0°	65.59
(9)	134°–136°	68	1.5073	0.9226	+43.1°	65.84
(10)	136°–140°	23	1.5056	0.9238	+44.2°	65.56
(11)	140°–142°	18	1.5024	....	+14.0°	....

A glance at these constants enables us to notice that the main constituent is represented by the fraction (3) where a preponderating maximum of the quantity of distillate as well as maxima of density and laevo-rotation are to be observed. From considerations of the molecular refraction it is evident that the predominant sesquiterpene belongs to the tricyclic class. The fraction (9) is also peculiar, corresponding to a small maximum of the quantity of distillate, a minimum of density, and a maximum of the dextro-rotation. This fraction should represent a dicyclic sesquiterpene as its molecular refraction is much greater than that of the fraction (3).

Sesquichamene. On rectification of the fraction (3), its physical constants exhibited the following values:

B. p. 122.5°–123.5°/$_{12\,mm.}$; n_D^{28} 1.5021; d_4^{28} 0.9277; α_D^{28} −89.85°;

M. R. found 64.81, calculated as $C_{15}H_{24}\left|\overline{=}_1\right.$ 64.45;

Anal. Subst. = 0.1627; CO_2 = 0.5254; H_2O = 0.1687 gr. Found: C = 88.01; H = 11.52%. Calc. for $C_{15}H_{24}$: C = 88.16; H = 11.84%.

Sesquichamene Nitrosochloride. A pure, freshly distilled sesquichamene was dissolved in twice its volume of absolute ether, and a current of

dry nitrosyl chloride gas was passed through the cold solution contained in a vessel surrounded by freezing mixtures. After a while, the vessel became filled with crystals. The vessel was left in the cold for half an hour more, and then the crystals were filtered, washed with cold ether and alcohol, and dried in vacuo. The yield of this crystalline substance amounted to about 75-80%. It was then purified by reprecipitating its chloroformic solution with methyl alcohol, and was obtained as colourless needles melting with methyl alcohol, and was obtained as colourless needles melting with decomposition at 77.5°-78.5°. A very pure sample obtained by repeating this process several times, could be kept for three to five hours without any appreciable decomposition. It is very soluble in chloroform and benzol, pretty soluble in petroleum ether, ethyl acetate, aceton, and ether, but very slightly so in methyl alcohol, ethyl alcohol, and water.

Sesquichamene Nitrolbenzylamine. A weighed quantity of the nitroso-chloride was suspended in a small volume of alcohol to which a slight excess of an alcoholic solution of benzylamine was slowly added in the cold. The crystals of the nitrosochloride was seen to disappear gradually as the temperature of the solution reached the room temperature, and then the product of reaction was precipitated by adding water thereto, filtered, washed with ether, and recrystallized from dilute alcohol. Sesquichamene nitrolbenzylamine thus prepared melted with decomposition at 165°-166°.

By the action of sodium nitrite and glacial acetic acid on sesquichamene, a semicrystalline deposit of sesquichamene nitrosite was obtained, but no further means of purification was possible as the crude nitrosite, on dissolving it in any of the ordinary solvents, was liable to pass into the oily state never to crystallize again. The preparation of the nitrosate was also tried but with negative results.

Oxidation of Sesquichamene. A mixture of 40 gr. of sesquichamene, 250 gr. acetone, and 80 c.c. of water was put into a vessel and kept agitated. To this mixture 80 gr. of finely powdered potassium permanganate was added in small portions, the temperature being kept under 40° the while. In half an hour the reaction was over, so the solution was filtered, the precipitate of manganese dioxide thoroughly extracted with hot acetone, the acetone solutions combined, evaporated, and then the whole mass was subjected to steam distillation. Nextly the products of reaction were divided into an acidic and a neutral portions in the usual manner.

The neutral products were collected and they were fractionated by three successive fractional distillations, when the fractions with following properties came over :—

	B. p.	Pressure	gr.	n_D^{28}	α_D^{28}
(1)	up to 140°	12 mm.	5	1.5140	- 80.0°
(2)	140°—155°	,,	2	1.5067	....
(3)	155°—160°	,,	7	1.5028	−89.3°
(4)	160°—165°	,,	11	1.5040	−79.3°
(5)	165°—170°	,,	1	1.5044	....
(6)	170°—175°	,,	2	1.5059	....
(7)	175°—180°	,,	1	1.5068	....
(8)	161°—163°	4 mm.	26	1.5090	−21.3°

The residue from these distillations represented a solid mass, which when extracted with acetone while hot, left a white powder. This powder was soluble in chloroform and benzol, but insoluble in alcohol, acetone, or ethyl acetate. The chloroformic solution, on addition of methyl alcohol, deposited an oil which solidified in course of time but looked possibly amorphous. It sintered at 220° and melted with decomposition at 240°-245°.

The fraction (8) on standing gave a little crystalline deposit which could not be separated from its mother liquor by ordinary filtration on account of its excessive viscidness. Therefore, it was dissolved in 3-5 volumes of petroleum ether and kept still for a length of time in the ice box, until at last an aggregation of fine needle crystals separated out. It was filtered and washed with ice-cold petroleum ether, and then recrystallized from hot petroleum benzine. It melted at 89°-91°.

Anal. Subst. = 3.333 mg.; CO_2 = 9.20 mg.; H_2O = 3.311 mg. Found: C = 75.35; H = 11.12%. Calc. for $C_{15}H_{26}O_2$: C = 75.6; H = 10.9%.

The fractions (3) to (8) were treated with solutions of sodium acetate and semicarbazide hydrochloride and the crystalline deposit formed thereby filtered, washed with alcohol and ether, and dried. From each of the fractions the same semicarbazone resulted which melted with decomposition at 233°. It differed from hydrazodicarbonamide (m.p. 257°) in being insoluble in all ordinary organic solvents and also in its crystalline form and solubility in hot water. The result of analysis is as follows :—

1.89 mg. substance gave 0.414 c.c. nitrogen (23.5°C; 765.4 mm.).

	Found	$C_{17}H_{30}O_2N_6$	$C_{17}H_{28}O_2N_6$	$C_{16}H_{28}O_2N_6$	$C_{16}H_{26}O_2N_6$
N%:	24.9	24.0	24.1	25.0	25.2

It follows that the substance in question was either a semicarbazide-semicarbazone of an unsaturated monoketone $C_{14}H_{20}O$ or a disemicarbazone of a diketone $C_{14}H_{20}O_2$. But since this substance was not soluble in mineral acids, it is to be expected that this substance represents a disemicarbazone of a diketone or a keto-aldehyde.

Isosesquichamene. Shaking with aqueous sulphuric acid brought no action on sesquichamene, but when alcoholic sulphuric acid was used, its optical activity gradually demolished. Thus, 25 gr. sesquichamene was treated with 10 gr. of alcoholic sulphuric acid (1:1) at 40°-50°, when in course of 1.5 hours its activity depressed to the value -9.5°. It was then twice rectified over metallic sodium and a main fraction with the following properties was obtained :—

B. p. 129°—131°/12 mm.; $n_D^{21.5}$ 1.5109; $d_4^{21.5}$ 0.9320; $\alpha_D^{21.5}$ −8.52°;
M. R. Found : 65.60. Calc. : 64.79 as $C_{15}H_{24}\overline{|}_1$; 65.60 as $C_{15}H_{24}\overline{|}_2$.

This sesquiterpene showed a fairly more stable quality against the action of the air but afforded no crystalline hydrochloride by treatment with hydrogen chloride gas.

d-*Cadinene.* The fractions (9) and (10) when dissolved in twice the volume of absolute ether, treated with a current of dry hydrogen chloride gas, and kept in cold for two days, deposited a quantity of needle crystals on evaporating off ether. After recrystallization from alcohol these crystals melted at 118°-119°, and were proved to be identical with cadinene dihydrochloride, as they showed no depression of the melting point on admixture with pure cadinene dihydrochloride from known source. From these fractions no nitrosite, nitrosate or nitrosochloride could be obtained in the crystalline state.

The fraction (7) gave neither hydrochloride nor nitrosochloride on usual treatment. Judging from its physical constants it seems most probable that it contained isosesquichamene.

The Sesquiterpene Alcohol and Diterpene Fractions. The portion containing sesquiterpene alcohols and diterpenes was fractionated six times under 12 mm. pressure and separated into the following eleven fractions, the physical constants of which are tabulated below :—

	B. p./12 mm.	Distillate	n_D^{25}	d_4^{25}	α_D^{25}
(1)	136°—140°	17 gr.	1.5018	0.9388	+14.8°
(2)	140°—145°	23	1.5006	....	+ 8.3°
(3)	145°—149°	55	1.5001	0.9482	+ 3.5°
(4)	149°—151°	15	1.5021	....	+ 5.6°
(5)	151°—154°	35	1.5033	0.9680	+ 7.8°
(6)	154°—157°	39	1.5062	0.9773	+ 8.8°
(7)	157°—159°	11	1.5113	0.9824	− 5.3°
(8)	159°—163°	23	1.5130	0.9860	−10.4°
(9)	163°—170°	5	1.5170	....	−20.0°
(10)	170°—180°	11	1.5184	....	−23.6°
(11)	180°—186°	22	1.5185	0.9650	−22.8°

d-Cadinol. On rectification the fractions (5) and (6) gave a main part having the following characteristics:

B.p. 146°—148°/12 mm.; $n_D^{22.5}$ 1.5043; $d_4^{22.5}$ 0.9706; α_D^{22} +7.76°;
M.R. Found: 67.91. Calc. as $C_{15}H_{26}O$ 68.12.

By the action of hydrogen chloride, cadinene dihydrochloride melting at 118°-119° resulted, which showed no depression of melting point on mixing it with a pure specimen obtained from known sources. This fraction gave no other characteristic derivatives.

From considerations of physical properties, the fraction (3) and (8) seemed likely to consist of sesquiterpene alcohols of dicyclic and tricyclic structure respectively, but all attempts to get definite proofs failed.

The fraction (11) was further rectified in vacuo and a main fraction consisting chiefly of diterpenes was obtained. It showed the following constants:—

B.p. 185°—186°/12 mm.; n_D^{25} 1.5185; d_4^{25} 0.9648; α_D^{25} −25.1°;
M.R. Found: 85.56. Calc. as $C_{20}H_{32}\equiv_1$ 85.21.

On treatment with alcoholic sulphuric acid (1:1), the optical activity of the diterpene enfeebled pretty rapidly. Also on heating it to 350° for several hours inactiviation ensued.

Thanks are due to Mr. Chuta Hata who assisted the authors' experiments most assiduously.

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DENSITIES OF ISOPROPYL AND n-BUTYL ALCOHOLS AT LOW TEMPERATURES.

By Tokuzô TONOMURA and Kôe UEHARA.

Received April 4th, 1931. Published May 28th, 1931.

Densities of isopropyl- and n-butyl alcohols were determined with the pycnometers made of pyrex glass as shown in Fig. 1. The pycnometer has a bulb of about 3.5 c.c. capacity which is connected to a capillary tube, whose inner diameter is 0.2 cm. and whose length 20 cm. Two marks (a and b) were etched on the capillary tube.

Fig. 1.

The volumes of the pycnometers are calibrated with mercury according to the method proposed by K. Issac and I. Masson.[1] The schematic diagram of the calibration apparatus is shown in Fig. 2. The pycnometer, mounted vertically in a water jacket kept at constant temperature, is connected to a two way capillary stopcock (A), one way of which is connected through a trap (B) to a mercury diffusion pump, by which the pycnometer can be evacuated. When the pycnometer has been completely exhausted, the stopcock (A) is turned 180° and the mercury in the cup (D) is allowed to enter in it by the other way of the stopcock. The cup (D), which is to be taken out and weighed, is placed in a bottle with a rubber stopper (E), so that the cup can be kept free from all dirty substances that may prevent accurate weighing. By means of the glass tube (C) with two stopcocks, one being connected to a pump and the other to atmosphere, the pressure of the bottle is regulated in order that the mercury in the pycnometer is allowed down to an appropriate position, say a. The volume of the bulb is thus determined by the difference of the weight of mercury in D before and after emptying the pycnometer with mercury. The total volume and the volume of the every cm. of the capillary tube between the marks a and b are similarly determined. In all cases the height of the meniscus of mercury and the mark a or b are read by a cathetometer. With the data thus obtained the correction for the capillary at the position l cm. from the mark a is calculated and plotted against l.

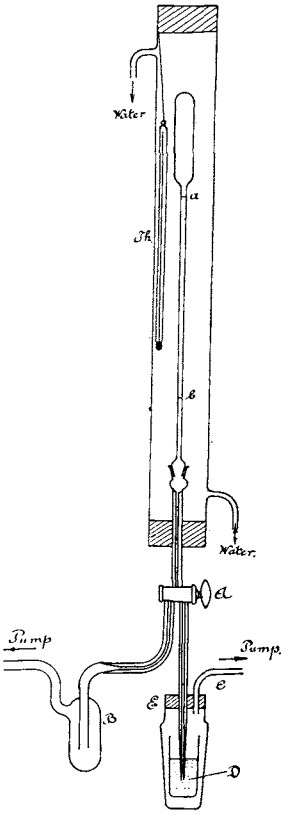

Fig. 2.

After the pycnometer has been allowed to cool several times to the temperature of liquid air, its volume is again determined. It is thus ascertained that the hysteresis of volume change of pycnometer is negligibly small. (The difference of volume before and after is 1 parts in 15000.)

(1) *J. Phys. Chem.*, **28** (1924), 166.

The volume of the sample filled in the pycnometer at the temperature t is calculated as follows.

$$V=V_0(1-3\alpha t)+vl(1-2\alpha t)+\Delta v_I+\Delta v_{II} \quad \ldots\ldots \quad (1)$$

where V_0 is the volume of bulb at 0°, v, the mean volume of the capillary tube per cm., l, the distance between a and the meniscus of the liquid filled in the pycnometer, Δv_I, the above mentioned correction of volume of the capillary tube at the position l, Δv_{II}, the correction of volume of the meniscus given in the Int. Nat. Crit. Table, Vol. 1, p. 73., α, the expansion coefficient of the glass.

The expansion coefficient α of the glass is determined, by using ethyl ether as a standard. Ether is filled in the pycnometer as described below and with the aid of formula (1), neglecting the expansion coefficient of the glass, the apparent volumes at several temperatures of ether are calculated. The true volumes of ether at corresponding temperatures are calculated from the data given by Keyes and Felsing.[1] From the differences between the true and apparent volumes of ether, the contraction of the pycnometer is calculated, assuming the contraction to be linear to temperature. The linear expansion coefficient of the glass thus found is 5.1×10^{-7}.

All the materials used for the present experiments are Kahlbaum extra pure chemicals. After dehydrating by anhydrous calcium oxide, they have the following boiling point: isopropyl alcohol, 81.9°–82.4°/768.6 mm., corr. and red. b.p.=81.9°C; n-butyl alcohol, 116.7°–117.0°/757.0 mm., corr. and red. b.p.=117.0.

The loading apparatus of the sample is shown in Fig. 3. It is made of ordinary glass except the portion below D, which is made of pyrex glass and they are sealed together at D with pyrex-ordinary glass graded sealing. The sample loads first in A, removes any gases dissolved by evacuation, distills twice at ordinary temperature under vaccum using liquid air as cooling reagent for condenser. Each time first and last one fourth of distillate are rejected. When the proper quantities of the sample have condensed in the pycnometers, they are sealed off at a. The pycnometers with sample are then immersed vertically in the cryostat.

The cryostat is constructed according to R. Hara and H. Shinozaki[2] and its temperature is kept constant within 0.05°. Its temperature is determined by a platinum-resistance thermometer from Leeds and Northrup Co., which has been calibrated at the normal boiling point of oxygen (-182.97°), the normal sublimation point of carbon dioxide (-78.5), the ice point and

(1) *J. Am. Chem. Soc.*, **41** (1919), 589.
(2) *J. Soc. Chem. Ind. of Japan*, **29** (1926), 269.

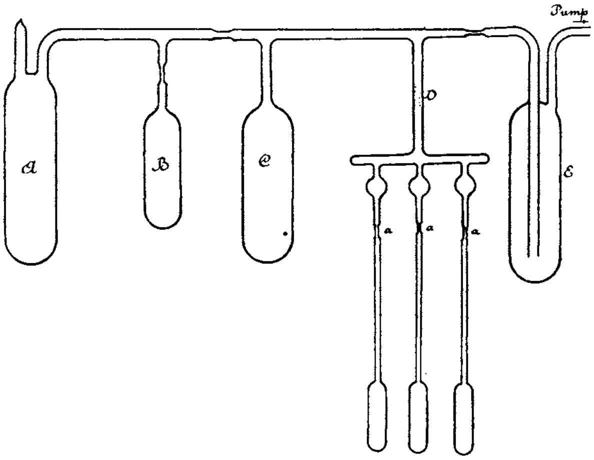

Fig. 3.

boiling point of water. It has the resistance of 2.5089 (r_0) at 0° and the resistance (r) at any temperature t is calculated by the following formula.

$$r/r_0=1+3.97186\cdot10^{-3}t+6.148\cdot10^{-7}t^2+5.08\cdot10^{-12}t^4 \quad . \ . \ . \quad (2)$$

Cylindrical Dewar vessel of the cryostat is silvered except the spaces of about 1 cm. wide along the mother line of the vessel, through which the meniscus of the pycnometer is observed from outside by a cathetometer, so as to calculate the volume of the sample in the pycnometer by the formula (1).

The densities at each temperature can be expressed by

$$D=w/V. \quad . \quad (3)$$

where w is the weight of the sample in the pycnometer which is determined by emptying the pycnometer after the observations. The results given in the following tables and in Fig. 4 are the mean values of several independent results with different pycnometers.

D (calc.) in the third columns of Tables 1 and 2 are calculated by the following formulae, which have been obtained from the observed data with the aid of the method of least square.

For isopropyl-alcohol,

$$D=0.80430-0.0008201\,t-0.000001405\,t^2$$

Table 1. Densities of Isopropyl-alcohol.

Temp.	Density (obs.)	D (calc.)	Pycnometer
— 0.00	0.80430		5, 6 and 8
— 7.02	0.81083	0.81005	6
— 10.02	0.81234	0.81243	6
— 10.26	0.81293	0.81256	1
— 10.57	0.81376	0.81295	6
— 17.17	0.81884	0.81834	1 and 6
— 20.77	0.82167	0.82127	6
— 28.09	0.82742	0.82723	2 and 5
— 41.85	0.83855	0.83840	6
— 43.75	0.83938	0.83991	2 and 5
— 44.25	0.84037	0.84031	1 and 6
— 54.17	0.84810	0.84831	2 and 5
— 54.95	0.84869	0.84894	1 and 6
— 65.80	0.85723	0.85762	5
— 76.80	0.86603	0.86645	5
— 90.82	0.87725	0.87762	1 and 6
—106.03	0.89030	0.89967	6

Table 2. Densities of n-Butyl-alcohol.

Temp.	Density	D (calc.)	Pycnometer
0.00	0.82380		2, 2, 5 and 8
—11.28	0.83264	0.83259	2, 5 and 6
—18.14	0.83852	0.83831	5 and 6
—23.30	0.84197	0.84193	2 and 6
—32.87	0.84936	0.84934	2 and 6
—37.70	0.85305	0.85307	2 and 6
—38.36	0.85349	0.85358	2 and 6
—39.45	0.85448	0.85442	2 and 6
—45.70	0.85932	0.85923	2 and 6
—55.33	0.86654	0.86662	2 and 6
—55.44	0.86676	0.86671	2 and 6
—69.06	0.87729	0.87701	2 and 6
—75.58	0.88241	0.88211	2 and 6
—80.80	0.88607	0.88607	2 and 6

and for n·butyl·alcohol,

$$D=0.82380-0.0007819\,t-0.000000129\,t^2$$

Table 3 contains the calculated densities from the above formulae at temperature of round numbers.

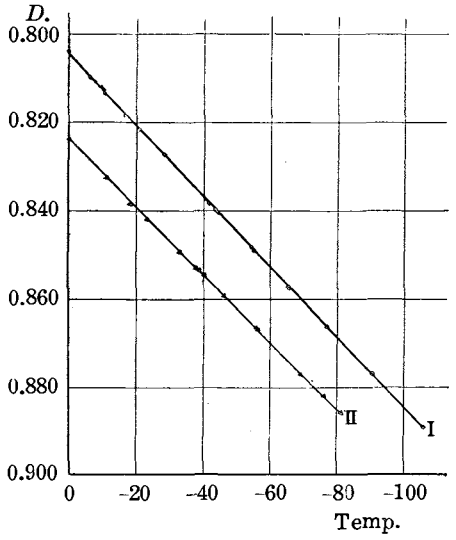

Fig. 4.

Table 3. Densities of Isopropyl·and n·Butyl·alcohol.

Temp.	Isopropyl-alcohol	n-Butyl-alcohol	Temp.	Isopropyl-alcohol	n-Butyl-alcohol
0.00	0.80430	0.82380	— 50.00	0.84179	0.86258
— 5.00	0.80836	0.82771	— 55.00	0.84516	0.86642
— 10.00	0.81236	0.83161	— 60.00	0.84845	0.87025
— 15.00	0.81628	0.83550	— 65.00	0.85167	0.87407
— 20.00	0.82014	0.83939	— 70.00	0.85482	0.87790
— 25.00	0.82392	0.84327	— 75.00	0.85790	0.88171
— 30.00	0.82764	0.84714	— 80.00	0.86091	0.88552
— 35.00	0.83128	0.85101	— 85.00	0.86389	
— 40.00	0.83486	0.85487	— 90.00	0.86672	
— 45.00	0.83837	0.85873	— 95.00	0.86953	
			—100.00	0.87226	
			—105.00	0.87401	

In conclusion, the present authors acknowledge the helpful guidance of Prof. S. Mitsukuri, who also kindly paid a part of the expenses of the experiments from the research fund granted to him from the Imperial Academy and from the Saito Gratitude Foundation.

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VISCOSITIES OF ISOPROPYL AND n-BUTYL ALCOHOLS AT LOW TEMPERATURES.

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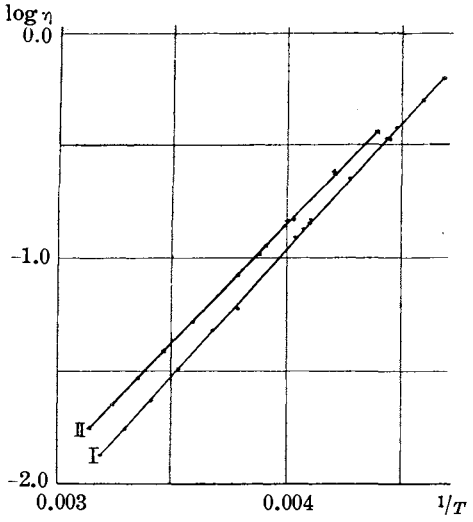
The viscosities of isopropyl- and n-butyl alcohols at low temperatures were determined by the present author with the modified Ostwald's viscosimeters that were reported in the previous papers.[1], [2] The results were summarized in Tables 1 and 2, and shown in the accompanying figure. The



I Isopropyl-Alcohol.
II n-Butyl-Alcohol.

(1) S. Mitsukuri and T. Tonomura, *J. Chem. Soc. of Japan*, **48** (1927), 335.
(2) S. Mitsukuri and T. Tonomura, Ibid., **50** (1929), 120.

densities of the alcohols were taken from the data given by T. Tonomura and K. Uehara.[1] The constants of the viscosimeters were given in Table 4 of the previous paper.

Table 1.

The Viscosities of Isopropyl-alcohol.

Temp. °C	Density	Time of fall sec.	Viscosity C.G.S.	Viscosimeter
0.00	0.8043	118.10	0.04510	3
− 0.20	0.8045	123.20	0.04706	3
− 6.77	0.8099	155.75	0.05989	3
− 9.38	0.8120	172.30	0.06643	3
−16.32	0.8177	224.58	0.08719	3
−19.15	0.8200	248.40	0.09676	3
−20.40	0.8211	262.83	0.10247	3
−24.07	0.8240	304.47	0.11870	3
−27.48	0.8267	117.74	0.13331	4
−29.29	0.8282	128.57	0.14205	4
−29.50	0.8284	376.29	0.14300	3
−39.14	0.8362	194.47	0.22273	4
−43.80	0.8400	241.17	0.27385	4
−47.36	0.8428	290.35	0.3351	4
−49.83	0.8448	322.43	0.3731	4
−55.33	0.8492	427.77	0.4976	4
−59.83	0.8529	544.30	0.6358	4

Table 2.

The Viscosities of n-Butyl-alcohol.

Temp. °C	Density	Time of fall sec.	Viscosity C.G.S.	Viscosimeter
0.00	0.8238		0.05186	(Thorpe and Rodger)
−14.12	0.8348	211.40	0.08379	3
−20.72	0.8399	90.32	0.10391	4
−22.31	0.8412	281.41	0.11240	3
−22.38	0.8412	95.50	0.11004	4
−29.65	0.8469	124.48	0.14440	4
−30.12	0.8472	126.40	0.14668	4
−40.74	0.8553	199.01	0.23314	4
−40.89	0.8556	197.39	0.23133	4
−50.92	0.8633	305.27	0.36100	4

(1) T. Tonomura and K. Uehara, this Bulletin, **6** (1931), 118.

The relations between the viscosities and the temperatures were expressed by the following formula, where A, B and C were the constants.

$$\log \eta = -A + B/(T-C)$$

The values of the constants were given in the Table 3.

Table 3.

Alcohol	A	B	C
Isopropyl	5.4727	1127.09	0
n-Butyl	5.0562	1051.65	5.2

The author here expresses his gratitude to Prof. S. Mitsukuri, under whose helpful guidance the present experiments were carried out.

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SINOMENINE AND DISINOMENINE. PART XXVI. ON THE DECOMPOSITION OF SINOMENINE WITH DIMETHYL-SULPHATE.

By Kakuji GOTO and Kenjiro TAKUBO.

Received April 8th, 1931. Published May 28th, 1931.

In the XXV report of this study,[1] the Hofmann decomposition of sinomenine with the use of methyliodide and alkali was reported. In this communication, the same reactions were repeated with dimethylsulphate and alkali, and the results obtained partly ascertained those of the last report, but in regard to the nitrogen free substance, a new diphenanthryl derivative, different from the disinomenol, was obtained. These results are, for brevity's sake, summarized in the following way.

1. Sinomenine metho-sulphate [I] is best obtained by adding dimethyl-sulphate to the aqueous suspension of sinomenine and by precipitating the metho-sulphate by sodium carbonate solution. In this way, the yield is almost quantitative. The metho-sulphate shows the diazo-, $FeCl_3$, and

(1) This Bulletin, **6** (1931), 79.

$FeK_3(CN)_6 + CO_3Na_2$ reactions just as sinomenine hydrochloride itself and behaves against hot, dilute alkali in the same way as the iodomethylate does.

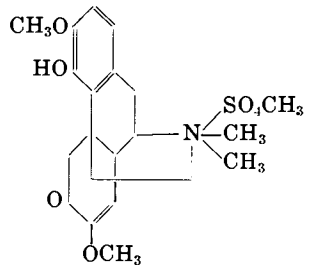
2. When sinomenine is methylated by dimethyl sulphate and caustic alkali at low temperature (cooling with ice-water), methyl-sinomenine metho-sulphate [II] is produced. The success of the reaction depends largely on the condition of the experiment, and the yield is very poor (15%). The trial to prepare this metho-sulphate from methyl-sinomenine in the way given [I] was unsuccessful.

3. The difficulty of the above reaction [2] lies chiefly in the easy opening of C_9–N linking of the metho-sulphate by the caustic alkali at the room temperature. In the latter condition, two kinds of methyl-sinomenine methine metho-sulphates, namely, the methyl-sinomenine-roseomethine-methosulphate and the methyl-sinomenine-violeo-methine-metho-sulphate [III] were isolated. Of these two, the former was more difficulty obtainable and in numerous experiments, it was obtained only twice (yield about 5%). The metho-sulphate of the methyl-sinomenine-violeomethine is, however, obtainable from sinomenine-achro-methine by dimethyl-sulphate and caustic soda at 0°C in a yield 60%.

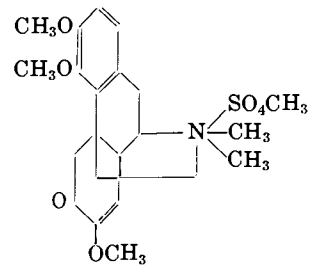
4. When the methyl-sinomenine-violeo-methine metho-sulphate is decomposed by boiling caustic soda (2–25%), a nitrogen-free substance ($C_{24}H_{30}O_8$; m.p. 310°) is produced. From the elemental analysis, the methoxyl content and the molecular weight determination, it must be a double molecular monomethyl-sinomenol. The linking point is supposed to be C_5, adjuscent to the free phenol group, which is newly formed from the original ketone group. The substance is named, therefore, 4,4′-dimethyl-bis-(5,5′)-sinomenol. This point was supported by the fact that the 4,4′, 6,6′-tetramethyl-bis-(5,5′)-sinomenol is quite different from the tetra-methyl-disinomenol, obtained from sinomenine or disinomenine by the boiling 66% KOH and the followed methylation.

5. The above tetramethyl-bis-(5,5′)-sinomenol can be obtained directly from sinomenine by dimethyl-sulphate and alkali at the room temperature, if the reaction mixture is kept for a long time. This shows that the methyl-amino-ethyl-side chain of sinomenine is in a condition, which can be easily splitted off in the course of the aromatisation.

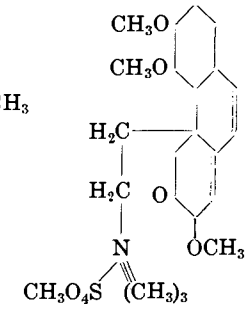
6. When the reaction mixture of sinomenine, dimethyl sulphate and caustic alkali is boiled, then the mixture of dimethyl-sinomenol and tetra-methyl-bis-(5′5′)–sinomenol is obtained. This fact shows that there must be produced also the monomolecular 4-methyl-sinomenol, which perhaps on account of its low melting point could not be isolated in crystalline condition up to present.



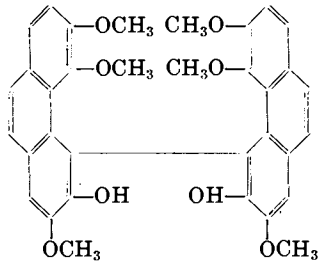
[I]



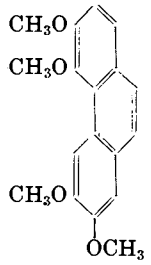
[II]



[III]



[IV]



[V]

7. By the present study, the following change in the nomenclature applied in the preliminary report appeared in *Proc. Imp. Acad.*, 2 (1926), 167 were necessitated.

The new nomenclature	To be abolished
1) Methyl-sinomenine-violeo-methine-metho-sulphate	1) α-Methyl-sinomenine-methine-methyl-sulphate
2) Methyl-sinomenine-roseo-methine-metho-sulphate	2) β-Methyl-sinomenine-methine-methyl-sulphate
3) 4, 4′-Dimethyl-bis-(5, 5′)-sinomenol	3) Trimethoxy-keto-vinyl-phenanthrene-tetrahydride
4) Tetramethyl-bis-(5, 5′)-sinomenol	4) α-Tetramethoxy-vinyl-phenanthrene-dihydride
5) Dimethyl-sinomenol	5) β-Tetramethoxy-vinyl-phenanthrene-dihydride m.p. 122°

Experimental.

1. **Sinomenine-methyl-methosulphate** [I]. Sinomenine hydrochloride (13.3 gr.) in an aqueous solution (80 c.c.) was added with anhydrous sodium carbonate (2 gr), and to this suspension of the free base, dimethyl sulphate

(9 c.c.) was added and well stirred. To the clear solution, which is produced in half an hour, a saturated sodium carbonate solution (40 c.c.) is added. After several hours, the precipitate is collected and recrystallized from ten parts of water. M.p. 265°C (decomposes). Yield quantitative. It gives no halochromy with conc. H_2SO_4 and HCl.

Anal. Found: C = 55.50; H = 6.23; N = 3.05; S = 7.06; CH_3O- = 20.53%.
$C_{21}H_{27}O_8NS$ requires C = 55.48; H = 6.58; N = 3.07; S = 7.03; CH_3O- = 20.39%.

2. Methyl-sinomenine-methyl-metho-sulphate. Sinomenine hydrochloride (10 gr) in an aqueous solution (70 c.c.) was added with anhydrous Na_2CO_3(1.5 gr in 20 c.c. water). This fine suspension of sinomenine was methylated with dimethyl sulphate (30 c.c.) and 33% NaOH (26 c.c.), given alterately in small portions, until the diazo-reaction disappeared. The reaction mixture was then extracted with chloroform sixteen times. By evaporating the dried chloroform, 1.5 gr. of the methyl-sinomenine methosulphate was obtained. It is hygroscopic, but recrystallisable from methanol into colourless prisms, melting at 245°. It gives no reaction for phenol group.

Anal. Found: CH_3O- = 25.89%. 4 CH_3O- in $C_{22}H_{29}O_8NS$ requires CH_3O- = 26.38%.

3. Methyl-sinomenine-violeo-methine-methyl-metho-sulphate [III].

(A) From sinomenine hydrochloride. The condition of the methylation is almost the same as (2), only the reagents being used in a somewhat larger quantity and the reaction mixture was warmed at 45° for some time. After six hours, the mixture was saturated with CO_2, added with Na_2CO_3 (saturated; 20 c.c.) and extracted with chloroform. The methosulphate is then precipitated from the chloroform solution (1 part) by ether (4 parts). Recrystallized from alcohol, it forms beautiful long prisms, which melts and decomposes at 204° sharply.

The substance is, however, better to be prepared from the sinomenine-achro-methine, as follows.

(B) Crude sinomenine-achro-methine (4.5 gr) is dissolved in 10% NaOH (15 c.c.) and set aside for 1.5 hours. (This treatment changes the achromethine into the violeo-methine). Then, the solution is methylated with dimethyl sulphate (15 c.c.) and 30% NaOH (15 c.c.) under ice-cooling. The reaction is completed by letting the mixture stand at the room temperature for three hours.

The yield is 2.5 gr, namely 60% of the theoretical.

The metho-sulphate dissolves deep blue in conc. H_2SO_4 and fuming HCl respectively.

Anal. Found: C = 57.28; H = 6.87; N = 3.02; S = 6.69; CH_3O- = 25.15 %. $C_{23}H_{33}O_8SN$ = 483 requires C = 57.14; H = 6.83; N = 3.02; S = 6.63; $CH_3O-(4)$ = 25.67 %.

Sp. rotatory power, measured in water,

$$[\alpha]_D^{13} = +(7.14 \div 0.1492) \times (10 \div 1) = +478°$$

Sp. rotatory power, measured in chloroform,

$$[\alpha]_D^{20} = +(5.70 \div 0.245) \times (25 \div 1) = +581.6°$$

4. Methyl-sinomenine-roseo-methine-methyl-methosulphate. Sinomenine (10 gr) was methylated with dimethyl-sulphate (50 c.c.) and 30% NaOH (68 c.c.) in an aqueous suspension (120 c.c.) The solution was nearly neutralized, added with saturated Na_2CO_3 solution (30 c.c.) and boiled for two hours. By extracting the cooled solution with chloroform, a reddish syrup (3.5 gr) was obtained from which on standing long separated first the crystals of methyl-sinomenine-violeo-methine-methyl-metho-sulphate. The alcoholic filtrate therefrom deposited, also on long standing, rhombic plates of the methyl-metho-sulphate of methyl sinomenine-roseo-methine. M.p. 178°. The substance dissolves deep red in conc. H_2SO_4 and in fuming HCl.

Anal. Found: N = 2.99; CH_3O- = 24.38 %. Calculated: N = 2.99; $CH_3O-(4)$ = 25.67 %.

5. 4,4'-Dimethyl-bis-(5.5')-sinomenol [IV]. Methyl-sinomenine-violeo-methine-methyl-metho-sulphate was boiled with ten times its weight of 2% NaOH for 20 minutes. The amine evolved was absorbed in dilute HCl. The aqueous part was extracted with chloroform, and the residue of the evaporation of the chloroform was recrystallised from glacial acetic acid or chloroform. It forms long colourless prisms, which melt at 310°. Yield ca. 20%. It dissolves in conc. H_2SO_4 brownish, and gives a green precipitate on diluting with water, but it does not show the sinomenol-reaction.

Anal. Found: C = 71.96; H = 5.27; CH_3O- = 32.86 %. $C_{34}H_{30}O_8$ = 566
Requires: C = 72.05; H = 5.30; $CH_3O-(6)$ = 32.68 %.

Mol. Weight after Rast's,

$$M = (0.263 \div 2.478) \times 100 \times (400 \div 6.3) = 674.$$

The amine evolved was identified as trimethyl amine from the m.p. of its auri-chloride (m.p. 251°) and platini-chloride (m.p. 245°). It is clear that the trimethyl-amine is produced from the $CH_3 \cdot CH_2 \cdot N(CH_3)_3OH$ secondarily.

6. 4,4′-Dimethyl-6,6′-diacetyl-bis-(5,5′)-sinomenol. 4,4′-Dimethyl-bis-(5,5′)-sinomenol [IV] gives this diacetylated substance, when boiled with acetic anhydride, added with Na-acetate for one hour. It is recrystallised from methanol in long prisms, m.p. 230°.

Anal. Found: C = 69.72, 69.85; H = 5.48, 5.52; CH_3O- = 28.63 %. $C_{38}H_{34}O_{10}$ requires: C = 70.15; H = 5.23; $CH_3O-(6)$ = 28.61 %.

7. Tetramethoxy-bis-(5,5′)-sinomenol. (A). Sinomenine HCl (20 gr) was methylated in an aqueous solution (100 c.c.) with dimethyl sulphate (53 c.c.) and 33% NaOH (79 c.c.) On standing this mixture for three weeks, a yellow crystalline substance was deposited on the bottom. The latter was dissolved in chloroform and precipitated with ethyl alcohol into long colourless prisms. M.p. 280°, but the substance recrystallised from acetone (1500 parts) melted at 283°C. Yield ca 2.2 gr. i.e. 13% of the theoretical.

(B). As the above preparation requires much time, it is better to boil the filtrate of the preparation, described in [3, B] with 33% NaOH (7 c.c.). As this filtrate contains some methyl-sinomenine-metho-sulphate and Na-CH_3-sulphate, so it gives tetramethyl-bis-(5,5′)-sinomenol in a tolerably good yield.

The substance is easily soluble in chloroform but very difficulty in alcohol, acetone (1:1 500) and ether. It dissolves in conc. H_2SO_4 brown and gives a green precipitate on diluting with water. Very resistent against $KMnO_4$. It has no rotatory power, showing that the sidechain must have been splitt off completely.

Anal. Found: C = 72.55, 72.34; H = 5.81, 6.18; CH_3O- = 41.64 %. $C_{36}H_{34}O_8$ = 594 requires: C = 72.46; H = 5.79; $CH_3O-(8)$ = 41.75 %.

Mol. Weight after Rast's,

$$M = (0.227 \div 2.142) \times 100 \times (400 \div 6.1) = 695.$$

Sp. rotatory power, measured in chloroform,

$$[\alpha]_D^{18} = (0 \div 0.1057) \times (10 \div 1) = 0.$$

8. In the preparation of 7, (A), we obtain a mixture of dimethyl-sinomenol and tetramethyl-bis-(5,5′)-sinomenol in different proportions,

when we boil the methylating mixture, using the dimethyl·sulphate and cautic alkali in different proportions. This shows that there must be the formation of the monomolecular 4·methyl·sinomenol in the above treatment, but the latter is not obtained in crystalline form yet. The substance, given in Proc. Imp. Acad. 2, (1926) 169, as β·tetramethoxy·vinyl·phenanthrene·dihydride (m.p. 122°), turned out to be nothing but dimethyl·sinomenol itself. The analysis made clear this point.

Anal. Found: C=72.38, 72.34; H=6.38, 6.18%. Calc. for $C_{18}H_{18}O_4$: C=72.45; H = 6.08%.

9. Dimethyl-sinomenol chinone. The alkaline filtrate from the preparation 7, (A), was diluted and oxidised with a dilute $KMnO_4$ solution, so long as the latter is still decolourised. Ether extracts therefrom a deep red substance (prisms) in a minute quantity. It melts at 266°C and forms a phenazine, which melts at 184°C. The mixed m.p. showed the substance is dimethyl·sinomenol·chinone, reported already in this Bulletin 4 (1929), 169.

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ON THE DISSOLUTION VELOCITY OF OXYGEN INTO WATER. PART V. THE OXIDATION VELOCITY OF SODIUM SULPHITE SOLUTION BY OXYGEN IN THE PRESENCE OF THE MOLECULAR FILM OF FATTY ACID.

By Susumu MIYAMOTO, Tetsuo KAYA and Akira NAKATA.

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Introduction.

H. Davis and R. Schuler[1] carried out a research on the rate of absorption of the gaseous olefins into sulphuric acid solution and found that the specific absorption coefficient (volume of gas absorbed per second per square centimeter of surface) was not appreciably affected by the agitation of the main body of the liquid. Ethylene was absorbed by concentrated sulphuric acid as rapidly when the acid was quiescent as when it was stirred (without breaking the surface or changing its area) at 400 revolution per minute.

H. Davis and G. Crandall[2] studied the rate of the solution gaseous olefines into sulphuric acid solution with an apparatus newly devised, and obtained exactly the same result as that of the above mentioned experiment.

According to Nernst,[3] an unstirred stationary liquid layer exists at the upper surface of liquid which is in contact with gas.

Whitman and Keats[4] extended the theory of Nernst, and proposed an assumption that whenever a liquid and a gas come into contact there exists on the gas side of the interface a layer of gas in which motion by convection is slight compared with that in the main body of the gas, and similarly on the liquid side of the interface there is a surface layer of the liquid which is practically free from mixing by convection.

The theoretical interpretations of the rate of absorption of gaseous olefins by sulphuric acid solution and of the rate of absorption of carbon dioxide by sodium hydroxide solution, given by Davis and Crandall,[5] are based on the theory of whitman and Keats, the two-film theory.

Davis and Crandall[5] have made two suppositions; firstly that the reactions take place instantaneously in the liquid film, and secondly that the

(1) *J. Am. Chem. Soc.*, **52** (1930), 721.
(2) Ibid., **52** (1930), 3757.
(3) *Z. physik. Chem.*, **47** (1904), 52.
(4) *J. Ind. Eng. Chem.*, **14** (1922), 185.
(5) Loc. cit.

upper surface of the liquid film, which is not disturbed by the agitation of the main body of the liquid, is kept at the saturated state with the gas. From these assumptions it is quite easy to see that the velocity of the absorption depends only upon the velocity of diffusion of the gas molecules and that of the molecules of the reacting substances through the stationary liquid film. Davis and Crandall[1] proposed the following equation for the initial rate of absorption of gas into a well-stirred liquid when any irreversible chemical reactions taking place are instantaneous, compared with the rate of solution of the gas.

$$\frac{1}{S}\left(\frac{dn}{dt}\right)_{Initial} = k(c_\infty + c_m) ,$$

where $\frac{1}{S}\left(\frac{dn}{dt}\right)_{Initial}$ is the initial rate of absorption of the gas per unit area of the surface, S the area of the boundary surface, k a constant, c_∞ the saturation concentration of the dissolved gas and c_m the concentration of the reacting solute.

The oxidation of sodium sulphite solution[2] by means of oxygen is quite an analogous phenomenon. But from the results of the experiments of the present writers[2] it was found that the velocity of the oxidation of sodium sulphite solution does not increase above a certain maximum value, however much the concentration of sodium sulphite be increased.

The above mentioned equation, proposed by Davis and Crandall, will be unsuitable for the interpretation of this phenomenon, and it might be immediately supposed that it would be necessary to make suppositions different from those proposed by Davis and Crandall in order to interprete the velocity of oxidation of sodium sulphite solution.

The following facts were already ascertained by one of the present writers (Miyamoto) experimentally.

(1) The maximum velocities of the oxidation of sodium sulphite, stannous hydroxide and ferrous hydroxide in sodium hydroxide solutions are identical under the comparable conditions.[3]

(2) The velocities of oxidation of these oxidizable substances do not increase above this maximum value with the increase of the concentration of these substances, as was above mentioned.

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(1) Loc. cit.

(2) S, L. Bigelow, *Z. physik. Chem.*, **26** (1898), 493; S. Miyamoto, this Bulletin, **2** (1927), 74; S. Miyamoto and T. Kaya, ibid., **5** (1930), 123; S. Miyamoto, T. Kaya and A. Nakata, ibid., **5** (1930), 229; S. Miyamoto and T. Kaya, ibid., **5** (1930), 321; S. Miyamoto and A. Nakata, ibid., **6** (1931), 9.

(3) S. Miyamoto, this Bulletin, **2** (1927), 74; ibid., **2** (1927), 155; ibid., **3** (1928), 98; ibid., **3** (1928), 137.

(3) The total oxidized quantity of these substances during a definite time interval does not increase by mixing them.[1]

(4) The maximum oxidation velocity of sodium sulphite solution is proportional to the area of the interface of oxygen and the solution.[2]

From these facts one of the present writers (Miyamoto) made the assumption that the maximum velocity of oxidation of sodium sulphite solution will be equivalent to the initial rate of solution of oxygen into water, in the surface of which no free oxygen is present.

This supposition was endorsed by the comparison[2] of the initial rate of solution of oxygen into water obtained from the result of the direct measurement by several writers[3] with that calculated from the velocity of oxidation of sodium sulphite solution.

For the theory of the rate of solution of gases into liquids, proposed by one of the present writers[4] (Miyamoto), a part of which was stated in the previous paper, it is a matter of indifference whether the thin liquid film (the diffusion layer), at the upper surface of the liquid phase, is agitated by the stirring of the main body of the liquid or not. Only the second supposition, proposed by Davis and Crandall, that the upper surface of the liquid film is instantaneously saturated with the gas, seems to be unprobable for the interpretation of the velocity of oxidation of sodium sulphite solution.

If the thin stationary liquid film be really not disturbed by the agitation of the main body of the liquid, as was supposed by several writers, the occurrence of the following phenomenon will be expected.

When the molecules of fatty acid were placed at the upper surface of sodium sulphite solution by a proper method, they occupy a certain area of the surface, undisturbed by the agitation of the main body of the solution, and the velocity of oxidation of sodium sulphite solution, which is equivalent to the initial rate of solution of oxygen under certain conditions, will change as a result of the alteration of the area of the free boundary surface between gas and liquid. Then it will be possible to calculate the effective area of a molecule of fatty acid from the measurement of the velocity of oxidation of sodium sulphite solution in the presence of a measured quantity of fatty acid, as the maximum velocity of the oxidation of sodium sulphite solution was confirmed to be proportional to the area of the boundary surface.

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(1) S. Miyamoto, this Bulletin, **2** (1927), 191; ibid., **4** (1929), 132.

(2) S. Miyamoto and A. Nakata, ibid., **6** (1931) 9.

(3) Adeney and Becker, *Phil. Mag.*, **38** (1919), 317; **39** (1920), 385; **42** (1921), 87; Davis and Crandall, *J. Am. Chem. Soc.*, **52** (1930), 3757, 3769.

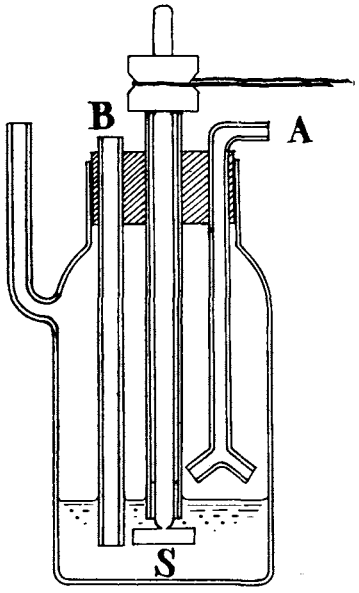
(4) Loc. cit.,

The cross-sections and the length of many organic compounds were obtained from the result of excellent physical experiments by Langmuir[1] and by Adam.[2]

The present research was carried out with the expectation that the relation between the effective cross-section of the molecule of fatty acid, which will be calculated from the measurement of the velocity of the oxidation of sodium sulphite solution in the presence of the molecules of fatty acid, and the real cross-section obtained from the result of physical experiment will be obtained.

Experimental.

The apparatus, graphically shown in the accompanying figure, was employed as the reacting vessel. The apparatus has nearly the same construction as that employed in the previous research.[3] The important difference, which will be seen by the comparison of the present apparatus with that stated in the previous paper, is that the lower end of the tube B is dipped in the solution in the present case.



The experimental method is as follows.

A definite quantity of fatty acid was dissolved in a definite volume of purified, newly distilled benzene, and by means of a calibrated pipette a few drops of the bezene solution of fatty acid was added on the measured quantity of water contained in the vessel, which was placed in a water thermostat. Air, washed by acidified potassium bichromate and sodium hydroxide solutions, was passed at a high velocity through A for about an hour to remove benzene completely from the apparatus. After the benzene has been perfectly evaporated off, oxygen, washed by the above mentioned reagents, was passed into the apparatus at a high velocity through A for about thirty minutes. When the air in the apparatus has been entirely replaced by oxygen, the

(1) *J. Am. Chem. Soc.*, **39** (1917), 1848.
(2) *Proc. Roy. Soc.*, **99** A (1921), 336; **101** A (1922), 452, 516; **103** A (1923), 676, 687.
(3) S. Miyamoto and A. Nakata, This Bulletin, **6** (1931), 11.

stirrer is put in motion at the rate of about 400 revolutions per minute and the rate of the passage of oxygen was regulated at about 15 liters per hour.

The stop-watch was started when about half the volume of sodium sulphite solution had been added in the vessel through B, the total volume of the solution being made up to 40 c.c. . The quantity of sodium sulphite solution added was determined separately by the usual method of iodometry.

When t-minutes have elapsed, the revolution of the stirrer and the current of oxygen were stopped and nitrogen gas was passed from A in the apparatus at a high velocity to drive the oxygen out as quickly as possible.

The vessel was then taken out and the total quantity of the solution was poured into a known quantity of iodine solution, acidified with hydrochloric acid. After the reacting vessel had been repeatedly washed with distilled water, the excess of iodine was titrated back by means of sodium thiosulphate solution of 0.1000 normal.

Representative results of the experiments are given in Tables 1 and 2.

In the tables, v is the volume of sodium thiosulphate solution of 0.1000 normal, equivalent to the quantity of sodium sulphite remained in

Table 1. (Temp. = 25°C)

No.	Conc. of stearic acid solution moles / liter	Stearic acid solution taken c.c.	S_{acid} cm.^{2}	S_0 cm.^{2}	t min.	v c.c.	k	$\frac{k}{S_0}$
1	0	0	0	26.31	—	—	0.682	0.0259
2	0.879×10^{-4}	0.050	5.60	25.60	0 30	207.69 188.80	0.630	0.0246
3	,,	0.050	5.60	,,	0 30	211.29 190.51	0.693	0.0271
4	,,	0.100	11.20	,,	0 30	203.64 184.01	0.654	0.0255
5	,,	0.200	22.30	,,	0 30	205.25 184.37	0.696	0.0272
6	8.06×10^{-4}	0.050	51.30	,,	0 30	231.18 211.80	0.646	0.0252
7	,,	0.200	205.10	,,	0 30	207.68 188.01	0.656	0.0256
8	43.72×10^{-4}	0.034	189.10	,,	0 30	227.48 208.02	0.649	0.0254
9	,,	0.200	1113.00	,,	0 30	206.50 187.00	0.650	0.0254

Table 2. (Temp. = 25°C)

No.	Conc. of palmitic acid solution moles / liter	Palmitic acid solution taken c.c.	S_{acid} cm.^{2}	S_0 cm.^{2}	t min.	v c.c.	k	$\frac{k}{S}$
1	0	0	0	26.31	—	—	0.682	0.0259
2	1.125×10^{-4}	0.033	4.72	25.5	0 30	232.47 212.22	0.675	0.0265
3	3.707×10^{-4}	,,	15.57	,,	0 30	237.25 217.54	0.657	0.0258
4	8.125×10^{-4}	,,	34.12	,,	0 30	236.28 217.05	0.641	0.0251
5	18.37×10^{-4}	,,	77.14	,,	0 30	236.58 217.51	0.636	0.249
6	41.60×10^{-4}	,,	174.70	,,	0 30	232.09 213.77	0.611	0.0240

the solution, when t-minutes has passed from the moment at which the oxidation had taken place.

The values k, given in the third column of the tables, were calculated according to the equation.

$$k = \frac{v_0 - v}{t},$$

where v_0 is the value of v at $t = 0$.

The values of S_{acid}, given in the 4th column of the tables, stand for the area, which would be occupied by the molecules of fatty acid added, if they formed a monomolecular film, and the values were calculated in the following manner.

According to the investigations of Langmuir[1] and Adam,[2] when a few drops of benzene solution of fatty acid was placed on the surface of water, the molecules of fatty acid are arranged not indiscriminately but perpendicular to the surface and parallel to each other after the benzene has been evaporated off.

If the thin stationary layer at the surface of the solution be not disturbed by the agitation of the main body of the solution with a stirrer, the orientation of the molecules of fatty acid will take place during the present observation in exactly the same way as in the case of quiescent water. From

(1) Loc. cit.
(2) Loc. cit.

this assumption the values S_{acid} were calculated from the quantity of fatty acid solution taken and the area of the cross-section of each molecule, for which 21×10^{-16} cm^2., obtained by Adam,[1] was adopted for stearic acid and palmitic acid.

The area of the boundary surface between liquid and gas in the absence of the molecules of fatty acid was calculated by exactly the same process, as that stated in the previous paper,[2] and the value is given as S in the 5th column of the tables.

The value of k in the absence of the molecules of fatty acid, given in the tables, is the value already obtained in the previous experiment.[3]

As will be seen in the tables, the difference between the value of k observed in the absence of fatty acid and that observed in the presence of fatty acid lies in the range of experimental error, and it may be described that the presence of the molecules of fatty acid has virtually no effect on the oxidation velocity of sodium sulphite solution, which will be equivalent to the rate of solution of oxygen into water, which is free from oxygen, under the condition of the present experiments.

Discussion.

The molecules of these fatty acids employed will form a monomolecular or multimolecular film on the upper surface of the liquid after the complete evaporation of benzene. In the case of the experiments Nos. 2–5 in Table 1 and Nos. 2–3 in Table 2, a part of the boundary surface is covered with the monomolecular film, and in the case of the experiments Nos. 6–9 in Table 1 and Nos. 4–6 in Table 2, the total area of the boundary surface is occupied by the multimolecular film of the fatty acid.

According to the experiments of Adam,[4] the molecules of these fatty acids have the following magnitude.

	Cross section.		Length.
	Head. cm^2.	Chain. cm^2.	cm.
Palmitic acid.	25.1×10^{-16}	21.0×10^{-16}	23.7×10^{-8}
Stearic acid.	25.1×10^{-16}	21.0×10^{-16}	26.2×10^{-8}

(1) Loc. cit.
(2) Loc. cit.
(3) Loc. cit.
(4) Loc. cit.

The calculation of the thickness of the assumed stationary liquid film[1] was carried out by Brunner[2] and by Davis and Crandall,[3] and was based upon the assumption that the rate of solution of gases into liquids is no other than the velocity of diffusion of the gas molecules through the stationary liquid film at the interface. According to these writers, the thickness of the stationary liquid film is about $2\times10^{-3}-2\times10^{-2}$ cm., which naturally depends upon the rate of revolution of the stirrer in the main body of the liquid.

If the assumption, that a stationary film exists at the interface, be acceptable, the multimolecular film of fatty acid, whose thickness is a minute portion of that of the stationary film, will occupy the area of the upper surface of the interface during the measurements of the present experiments, undisturbed by the agitation of the main body of the liquid. From this consideration it will quite be probable to expect that the presence of the multimolecular film of fatty acids at the upper surface will have some effect on the rates of solution of gases into liquids.

The result of the present experiments was contrary to this expectation, and it will be difficult to interprete the present result by the ordinary theory, which is based upon the supposition of the presence of a stationary liquid film.

One of the present writers (Miyamoto) has an opinion that it will be very probable to interprete the process of solution of gases into liquids by the assumption that among the molecules which collide with the liquid surface only those molecules, whose components of velocity at right angles to the boundary surface are greater than a threshold value u_0, are able to enter into the the liquid phase. According to this supposition, the rate of solution will be expressed by

$$D_0 = N''S - N'''S,$$

where N'' is the number of the molecules which enter into the liquid phase through the unit area of the boundary surface per unit of time, N''' the number of the molecules which leave the liquid phase through the unit area of the boundary surface per unit of time and S the area of the boundary surface.

So long as the concentration of the gas in the liquid phase is maintained at zero, the rate of solution is given by

$$D_0 = N''S,$$

(1) Nernst, *Z. physik. Chem.*, **47** (1904), 52; Whitman and Keats, *J. Ind. Eng. Chem.*, **14** (1922), 185.
(2) *Z. physik. Chem.*, **47** (1904), 99.
(3) *J. Am. Chem. Soc.*, **52** (1930), 3760.

N''' being zero under this condition.

As was stated in the previous paper,[1] the oxidation velocity of sodium sulphite solution of proper concentration is equivalent to the value D_0, when the main body of the liquid is well agitated with a stirrer.

According to this theory of the rate of solution of gas into liquid, it is quite enough for the interpretation of the result of the present experiments if only one of the following assumptions be satisfied.

(1) The value u_0 does not differ whether the molecules of fatty acids are present or not.

(2) The liquid film at the interface is not stationary and the molecules of fatty acids are covered with the solution when the main body of the solution is agitated.

The present writers consider that the first assumption will be inadequate to be adopted.

If the second supposition be satisfied, the total area of the boundary surface is not altered by the addition of fatty acids, and the concentration of oxygen at the upper surface will be kept at zero by the presence of the sufficient quantity of sodium sulphite to react with all of the molecules of oxygen which enter into the liquid phase, so long as the main body of the liquid is well agitated with a stirrer.

It is then quite clear that the presence of the molecules of fatty acids will have no effect on the velocity of the oxidation of sodium sulphite solution, which is equivalent to the initial rate of solution of oxygen into water, D_0, under the present conditions.

For this interpretation it is of no use to investigate whether the molecules of fatty acids, covered with the solution, remain in the upper layer of the liquid or go down into the main body of the liquid during the experiments.

From the discussion, above stated, it seems that the supposition of the existence of the stationary liquid film of proper thickness, proposed by several writers, the diffusion theory, will be unfavourable to the interpretation of the result of the present experiments.

As the conclusion of the present research it will be possible only to describe that the thickness of the stationary liquid film, if it exist, should be smaller than the length of the molecule of palmitic acid, 23.7×10^{-8} cm., when the main body of the liquid is well agitated with a stirrer.

Although the present research failed to produce the expected result, the phenomenon observed will be one of the important experimental facts,

(1) Loc. cit.

which will be employed for the discussion of the process of solution of gasses into liquids.

As a result of the present research, it can be said that, under the conditions of the study on the rate of oxidation of sodium sulphite solution, carried out by Miyamoto and his collaborators, stationary liquid film does not exist at the boundary surface, and therefore the results of the experiments can not be interpreted by the classical theory, based upon the assumption that the phenomenon is the rate of diffusion through a stationary film at the interface.

Summary.

(1) The monomolecular or multimolecular films of stearic acid or of palmitic acid were formed at the upper surface of sodium sulphite solution, and the velocity of the oxidation of sodium sulphite solution was studied, the main body of the solution being well agitated with a stirrer of special construction. It was confirmed that the velocity of the oxidation of sodium sulphite solution by oxygen, observed in the presence of the molecules of these fatty acids, and that observed in the absence of the molecules of the fatty acids, are almost identical under the conditions above described.

(2) A short discussion on the result of the present experiments was made.

The assumption, that a stationary liquid layer is present at the interface between gas and liquid, seems to be unfavourable to the interpretation of the phenomenon observed by the present writers. It was stated that the assumption, that the molecules of fatty acid at the upper surface of the liquid will also be agitated by the stirring of the main body of the liquid and covered with the solution, has great probability for the interpretation of the result of the present experiments.

(3) The mechanism of solution of gas into liquid was shortly discussed.

A part of the opinion of one of the present writers (Miyomoto) on the rate of solution of gases into liquids was described.

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SOLUBILITIES OF METALLIC CYANIDES.

By Kosaku MASAKI.

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In the author's previous paper[1] the solubilities of cyanide and thiocyanate of silver in water were published. Sherrill[2] determined the solubility of mercuric cyanide in water. But we have no information on the solubilities of cyanides of other metals. Author measured, hence, the solubilities of cyanides of cadmium, zinc, nickel, and cobalt.

In order to determine these solubilities the following cells are used.

Cd (amalgam), Cd^{++} (a_1) || Ca^{++} (a_2), Cd (amalgam)
Zn (amalgam), Zn^{++} (a_1) || Zn^{++} (a_2), Zn (amalgam)
Ni (amalgam), Ni^{++} (a_1) || Ni^{++} (a_2), Ni (amalgam)
Co (amalgam), Co^{++} (a_1) || Co^{++} (a_2), Co (amalgam)

The following two equations have been used to determine the electromotive force.

$$E_c = \frac{RT}{2F} \ln \frac{a_2}{a_1} \quad \cdots\cdots (1)$$

$$E_l{}^{(3)} = \frac{\frac{\Lambda_C}{V_C} - \frac{\Lambda_A}{V_A}}{\Lambda_C + \Lambda_A} \frac{RT}{F} \ln \frac{a_2}{a_1} \quad \cdots\cdots (2)$$

where E_c represents the electromotive force of electrodes, E_l, the liquid potential at the contact of two solutions, a_1 and a , the activities of cadmium-, zinc-, nickel-, and cobalt-salts, and also Λ_C and Λ_A are the ionic conductances of the cation and of the anion, and V_C and V_A are the valences of the cation and of the anion respectively, the term Λ_A was replaced by the mean value of the two anion conductances.

Experimental.

Cyanides of cadmium, zinc, nickel and cobalt were prepared from the dilute solutions of corresponding potassium salt by precipitating with purified sulphates of these metals respectively. Potassium salts used were

(1) This Bulletin, **5** (1930), 345.
(2) *Z. physik. Chem.*, **43** (1903), 735.
(3) Noyes and Sherrill: Chemical Principles, p. 263 (1922).

of Kahlbaum and purified by recrystallization. The precipitated salts were further purified by washing with conductivity water.

Cadmium chloride, zinc chloride, nickel nitrate, and cobalt nitrate were purified by washing five times with conductivity water. Conductivity water used in the experiments had a specific conductance of 1.5×10^{-6}.

The amalgams were made by electrolysing a 10% solutions of pure cadmium sulphate, zinc sulphate, nickel nitrate, and cobalt nitrate with mercury as a cathode, and the amalgams contained about 2.5% of metals. The cells used were of ordinary form. The electromotive force of the cells were measured after being kept in a thrmostat at $18°\pm0.1$ for about one hour. Constants necessary to carry out the calculation are given in the Tables 1 and 2.

Table 1.

Salt	Moles per litre of water	Activity coeff.	Activity
$CdCl_2$	0.01	0.532(1)	5.32×10^{-3}
$ZnCl_2$	0.0033	0.799(2)	2.63×10^{-3}
$Ni(NO_3)_2$	0.005	0.776(3)	3.88×10^{-3}
$Co(NO_3)_2$	0.01	0.380(4)	3.80×10^{-3}

Table 2.

Ion	Ionic Conductance at 18°C.	Ion	Ionic Conductance at 18°C.
Cd^{++}	46.4	Cl^-	65.5
Zn^{++}	47.0	CN^-	58.6
Ni^{++}	44.0	NO_3^-	61.8
Co^{++}	43.0		

The values in Table 2 were taken from the data of Noyes and Falk(5), except that for the cyanide ion which was determined by the following method.

(1) *J. Am. Chem. Soc.*, **41** (1919), 1787.
(2) Lewis and Randall "Thermodynamics" p. 420 (1923).
(3) and (4) The values were calculated from the data of "Thermodynamics" p. 382 (1923).
(5) *J. Am. Chem., Soc.*, **34** (1912), 459.

The conductivity was measured by the ordinary bridge method, using the cell of uniform diameter. The assembly for the measurements consisted of measuring bridge with a thin wire platinum-iridium, resistance wire, oscillater, and a tunable telephone. The slide wire and the resistance box were calibrated before the conductivity work was begun. The cell constants of the conductivity cell were determined with 1/50 normal solution of potassium chloride. The specific conductance of the sodium cyanide solutions were measured at $18° \pm 0.1°$ C. after being kept in the thermostat for one hour. The results are summarized in the Table 3.

Table 3.

Concentration of NaCN	Cell Constant	Specific Conductance		Equivalent Conductance
		appearent	corrected	
1 Mol	0.228	73188×10^{-6}	73186×10^{-6}	73.186
0.1	0.228	7843×10^{-6}	7841×0^{-6}	78.41
0.01	0.228	829.9×10^{-6}	828.4×10^{-6}	82.84
0.001	0.228	95.76×10^{-6}	94.26×10^{-6}	94.26

We obtained 102 as the value of Λ_∞ at the infinite dilution of sodium cyanide by extrapolation from the data in Table 3, and subsequently 58.6 as the value of ionic conductance of CN^-.

Calculation.

The measured electromotive forces are as follows:

	Cell	E at 18°C.
(1)	Cd (amalgam), Cd $(CN)_2$ (sat) ‖ Cd Cl_2 (0.01 M), Cd (amalgam)	0.02700
(2)	Zn (amalgam), Zn $(CN)_2$ (sat) ‖ Zn Cl_2 (0.0033 M), Zn (amalgam)	0.08705
(3)	Ni (amalgam), Ni $(CN)_2$ (sat) ‖ Ni $(NO_3)_2$ (0.005 M), Ni (amalgam)	0.04300
(4)	Co (amalgam), Co $(CN)_2$ (sat) ‖ Co $(NO_3)_2$ (0.01 M), Co (amalgam)	0.05050

We have the equation (3) by adding the equations (1) and (2).

$$E = E_c - E_l = \left[\frac{1}{2} - \frac{\frac{\Lambda_C}{V_C} - \frac{\Lambda_A}{V_A}}{\Lambda_C + \Lambda_A} \right] \frac{RT}{F} \ln \frac{a_2}{a_1} \quad \cdots\cdots\cdots (3)$$

(1) For the 0.01 molal solution of cadmium chloride, the value of activity a_2 is 5.32×10^{-3} and the values of Λ_C and Λ_A at 18°C. are 46.4 and 62.05, respectively and

$$0.02700=\left[\frac{1}{2}-\frac{\frac{46.4}{2}-62.05}{46.4+62.05}\right]0.0577\ \log\frac{5.32\times10^{-3}}{a_1}$$

then, we obtain

$$a_1=1.51\times10^{-3}$$

(2) For the 0.0033 molal solution of zinc chloride, the value of activity is 2.63×10^{-3} and the value of Λ_C and Λ_A at 18°C. are 47 and 62.05. Therefore,

$$0.08705=\left[\frac{1}{2}-\frac{\frac{47}{2}-62.05}{47+62.05}\right]0.0577\ \log\frac{2.63\times10^{-3}}{a_1}$$

then

$$a_1=4.49\times10^{-5}$$

(3) For the 0.005 molal solution of nickel nitrate, the value of activity is 3.88×10^{-3} and the values of Λ_C and Λ_A at 18°C. are 44 and 60.2. Then,

$$0.0430=\left[\frac{1}{2}-\frac{\frac{44}{2}-60.2}{44+6.02}\right]0.0577\ \log\frac{3.88\times10^{-3}}{a_1}$$

and

$$a_1=5.35\times10^{-4}$$

(4) For the 0.01 molal solution of cobalt nitrate, the value of activity is 3.80×10^{-3} and the values of Λ_C and Λ_A at 18°C. are 43 and 60.2, therefore,

$$0.0505=\left[\frac{1}{2}-\frac{\frac{43}{2}-60.2}{43+60.2}\right]0.0577\ \log\frac{3.80\times10^{-3}}{a_1}$$

and

$$a_1=3.77\times10^{-4}$$

Summary

(1) Ionic conductance of CN^- was determined.

(2) The activities, i.e. solubilities of cyanides of cadmium, zinc, nickel, and cobalt were calculated.

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

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OBSERVATIONS ON THE ABSORPTION SPECTRA OF THE RARE EARTHS. I.

By Yasumitsu UZUMASA and Hisateru OKUNO.

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It has been confirmed by several investigators that the absorption bands of neodymium shift toward the longer wave-lengths by increasing the concentration and Beer's law holds only from a definite concentration down. Selwood[1] recently observed that for neodymia and other rare earths investigated increasing concentration is accompanied by a change of molecular volume and molecular refraction and a slight shift of absorption bands. He explained the phenomenon on the basis of the theory of the deformation of the electron shells. It is also well known that the bands of neodymium salts are shifted toward the red on the addition of a common ion. As Quill and Selwood with Hopkins[2] have concluded there may be more than one influence to deal with the phenomenon but the changes of the bands produced here may be possibly attributed to the deformation of the electron shells again since the shifts become more apparent with increasing amount of a common ion added. Changes somewhat similar to those produced on the addition of a common ion are expected to appear if the oppositely charged ions, i.e., Nd^{+++} and NO_3^- for example, are brought close enough to one another to cause distortion of the electron arrangement by any other means than changing concentration or adding a common ion and this will be performed by using a solvent having a smaller dielectric constant than water. Jones[3] studied the absorption spectra of the solu-

(1) *J. Am. Chem. Soc.*, **52** (1930), 3112, 4308.
(2) Ibid., **50** (1928), 2929.
(3) Carnegie Institution of Washington Publication, No. 130, No. 160.

tions of the rare earths and some other comparatively rarer elements and suggested the formation of solvates. No observations were made, however, as to the existence of any general relation between the changes of the bands and the nature of the solvents used. H. Schaeffer[1] states that the absorption spectra of the rare earths are influenced by solvents, both organic and inorganic, and the displacements of the bands caused by the solvents with the lowest refractive indices are in general the greatest. Schaeffer's experiments were carried out with neodymium and didymium. Didymium is as well known a mixture of impure neodymium and praseodymium while neodymium used in his investigation is not believed to be absolutely free from other earths. It was therefore desired in the present investigation to examine conclusively if the changes of the bands are connected with any properties of the solvent used when the observations are made with pure neodymium.

Experimental.

The spectra were photographed by a Hilger spectrograph of constant deviation type and also by a Zeiss hand spectroscope combined with a camera, using a tungsten incandescent lamp as the source of illumination. A Baly absorption tube with quartz end plates was used throughout. The neodymium and praseodymium were purchased from Adam Hilger Ltd. They are the oxides prepared by Luigi R lla and believed by him to have not more than 0.01% total impurities.

Neodymium- and praseodymium nitrates in various organic solvents.

Nitric acid was added to 0.15 gr. pure neodymium oxide until the latter completely dissolved. After the excess of the acid was removed by evaporation the salt was dissolved in water and diluted to 50 c.c. The same amount of the oxide was converted into nitrate in the similar way and the salt dissolved in 50 c.c. pure acetone, thus the concentration of the two solutions being exactly the same, i.e., 0.019 mol. When these two solutions were compared with the spectrograph, there were observed in the acetone solution unmistakable broadenings and shifts of the bands toward the red. As will be seen in Fig. 1, the band at 5800 Å region becomes so markedly intensified in the acetone solution that one may take it more concentrated with respect to neodymium than the water solution. Again a series of nitrate solutions was prepared, using glycerol, methyl alcohol, ethyl alcohol and acetone as

(1) *Physik. Z.*, **7** (1906), 822.

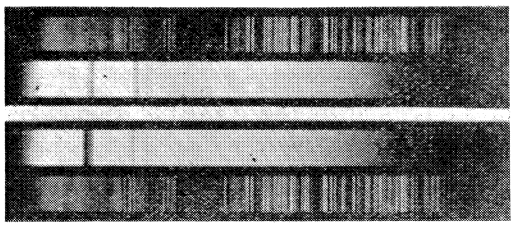

Fig. 1. Absorption bands of neodymium nitrate.

solvent respectively and their spectra were examined. Since each of them contains 0.15 gr. of neodymium as oxide, their concentrations should be the same while their bands are as shown in Fig. 2 more or less shifted and diffused toward the red. All these photographs were taken through 25 mm. of the solutions.

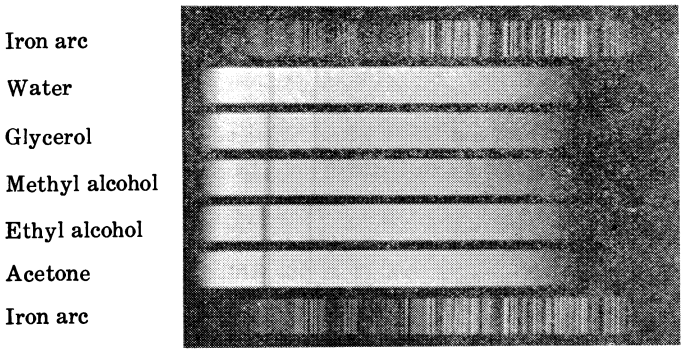

Fig. 2. Absorption bands of neodymium nitrate dissolved in various solvents.

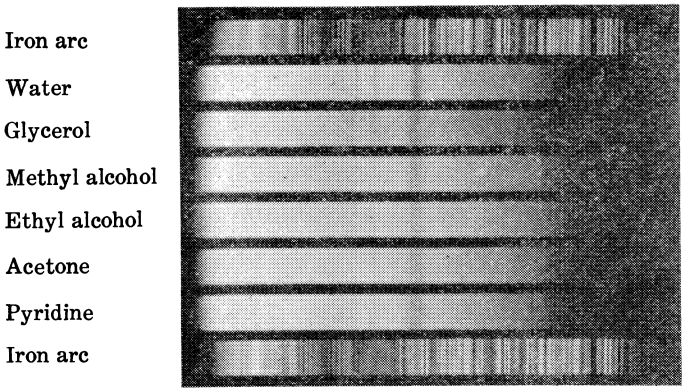

Fig. 3. Absorption bands of praseodymium nitrate dissolved in various solvents.

The similar effect was observed with praseodymium. Fig. 3 shows the absorption bands of praseodymium nitrate in water, glycerol, methyl alcohol, ethyl alcohol, acetone and pyridine respectively. Each solution contains 0.15 gr. of praseodymium as oxide and the spectrograms were taken through 30 mm. of the solution. The displacements are not so distinct as with neodymium but all the bands are more or less broadened and diffused, the effect being most pronounced in the acetone and pyridine solutions. The shift of the narrow band at 4819 Å can be most easily observed.

Influence of common ion in acetone solution.

It was next desired with interest to examine the influence of magnesium nitrate on the bands of neodymium nitrate in the acetone solution. As reported in the paper of Quill and others[1] magnesium nitrate as well as nitric acid produces a marked effect of displacing the bands of neodymium nitrate toward the red. Fig. 4 shows the shifts produced by magnesium nitrate in the water solution, the concentration of which is 0.012 mol. with

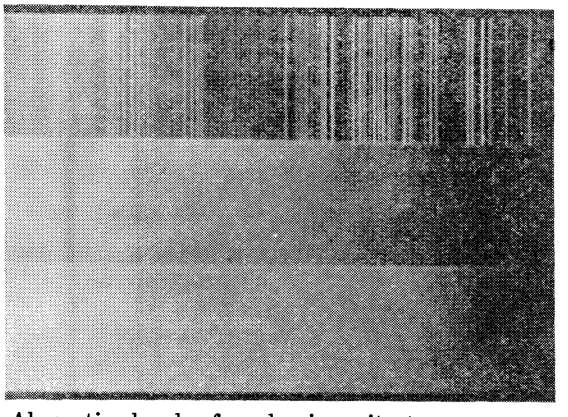

Fig. 4. Absorption bands of neodymium nitrate dissolved in water.

respect to neodymium and 0.496 mol. with respect to magnesium. The photographs were taken through a depth of 70 mm. When acetone is used as solvent, the broadenings take place in the presence of magnesium nitrate in a slightly different manner. The solution contains the same amount of neodymium and magnesium and was photographed through the same depth as before, i.e., 70 mm., while all the bands are more or less broadened and above all the band at 5750 Å region is unmistakably spread out on both sides.

(1) loc. cit.

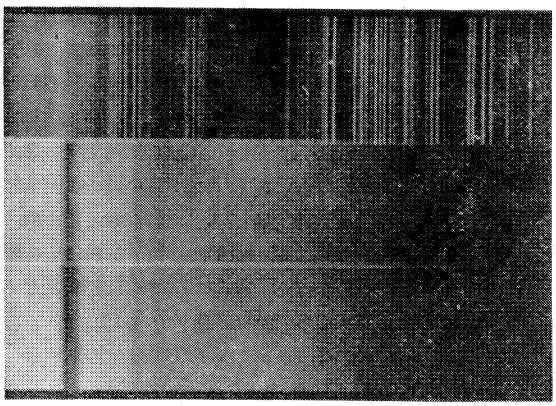

Fig. 5. Absorption bands of neodymium nitrate dissolved in acetone.

Discussion.

It was found in the present investigation that the displacements of neodymium bands are most pronounced when acetone or ethyl alcohol is used while the shifts produced by methyl alcohol or glycerol are less marked, the effect of the latter being the smallest. In the accompanying table are shown the displacement of the bands at 5800 Å in various solvents and the refractive indices of these solvents. No regularity can be observed between these two quantities, however.

Table

Solvent	Shift of the band at 5800 Å region (1)	Refractive index (20°C) (2)	Dielectric constant (20°C) (3)
Water	0	1.333	80.0
Glycerol	17 Å	1.4729	43.0
Methyl alcohol	26 Å	1.329	33.7
Ethyl alcohol	43 Å	1.361	25.7
Acetone	43 Å	1.3591	21.4
Pyridine	—	1.509	12.5

The oppositely charged ions may approach to one another with decreasing dielectric constant of the solvents in which they dissolve. If the defor-

(1) The measurements are approximate as the edges are diffused.
(2) International Critical Tables, Vol. I.
(3) ibid., Vol. VI.

mation of the electron shells should cause the changes of the absorption bands, these changes might be the greatest when the solvent with the largest dielectric constant is used. The present investigation shows that this is exactly the case. As shown in the third column of the table, the dielectric constants decrease as the shifts increase. No photometric examinations were made with the spectrograms taken and it seems rather hasty to postulate any quantitative relation between these two quantities. In view of what has been observed, however, it is suggested that the displacement produced is possibly connected with the dielectric constant of the solvent.

Addition of magnesium nitrate to the acetone solution of neodymium nitrate produces a considerable change, not similar but slightly different from that produced in the water solution. Dissociation of neodymium nitrate as well as magnesium nitrate is supposed to be very small in the acetone solution and the effect of magnesium nitrate thus added may greatly differ from that of the so-called "common ion" added to the dilute water solution. It is still probable that the salt added may affect the electron arrangement of neodymium somehow so that it produces a change in the absorption spectra. It is known that for a given normality the changes produced by magnesium nitrate are slightly more pronounced than those produced by nitric acid. This fact suggests that a metal ion, dissociated or undissociated, might play a part. The further investigation is under way with the intension of finding the influence of foreign substances on the bands of neodymium.

The writer wishes to express his appreciation to Professor G. Nakamura for the use of the spectrograph.

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THE REACTION BETWEEN BENZYL CHLORIDE AND WATER.

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The heterogeneous reaction which takes place at a liquid·liquid interface has been studied by several workers. In the majority of these cases, however, at least one of the reactants is solute molecules or ions dissolved in two immiscible solvents.

The object of the following experiments is to investigate the case where the immiscible liquids themselves react with each other at there interface. The reaction chosen as one of such cases was the hydrolysis of benzyl chloride by water according to the equation:

$$C_6H_5\cdot CH_2Cl + H_2O \rightarrow C_6H_5\cdot CH_2OH + HCl.$$

This reaction has been already studied by G. Harker,[1] who observed rather remarkable facts that benzyl chloride is not acted on by steam but decomposed by water with constant velocity. The present authors were interested to investigate the course of the reaction with water phase as well as vapour phase, of which only the former reaction is here published as they are obliged to interrupt the experiment. Since benzyl chloride is known to be practically insoluble in water, it will be sufficient to take only the surface reaction in consideration. In the present experiment a known volume of distilled water has been placed on the top of benzyl chloride, the former being stirred with constant rate, and the concentration of hydrochloric acid in it has been determined frequently at different intervals by measuring its electrical conductivity.

Measurements.

A hard glass powder bottle of half liter capacity whose cross-sectional area is 40.0 sq. cm. was used as a reacton vessel. The vessel was closed with a cork stopper holding a thermometer (T), a platinum electrode (E), a small glass stirrer (S) and a fine glass tube (I), as is shown in Fig. 1, b. The two blades of the stirrer stand vertical so as not to disturb the interface of the two liquids.

A weighed quantity of 250 c.c. of distilled water is placed in the reaction vessel which is immersed right up to the neck in a water thermostat. On the other hand a pear shaped vessel (B) with a glass stopper, in which 50 c.c. of benzyl chloride (Schering-Kahlbaum's purest for scientific purposes) is placed, is also immersed in the thermostat. To the bottom opening of the above vessel (B) is connected a rubber tubing (R) with a rubber clip (P) and a glass tube (I), the latter being placed in the reaction vessel through the cork stopper. When the temperature becomes constant the pear shaped vessel (B) is somewhat lifted up and by opening the rubber clip (P) benzyl chloride is allowed to flow into the bottom of the reaction vessel. The tube (I) is then lifted slightly above the interface in order not to disturb it. The stirrer (S) is then started.

(1) *J. Chem. Soc.*, **125** (1924) 500.

The upper end of the stirrer rod is connected through a short rubber tubing (C) co-axial with a pivot of a wooden pulley, which is coupled with another wooden pulley fixed to the axis of a large stirrer of the thermostat. Since the thermostat-stirrer is driven by a small electric motor and regulated so as to rotate with constant rate (100 turns per min.), the rate of rotation of the glass stirrer in the reaction vessel can be controlled at will by choosing a pair of wooden pulleys having a suitable ratio of diameters.

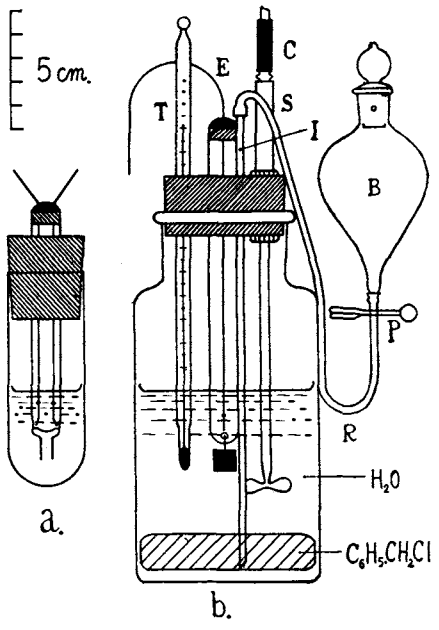

Fig. 1.

The electrical conductivity of the aqueous layer was successively measured by means of a well calibrated Wheatstone's bridge with simultaneous record of time. The concentration of hydrochloric acid was calculated in mol/liter from the observed specific conductance by dividing it with the corresponding molecular conductance and multiplying with 1000. The viscosity of the reacted solutions was found to be identical with the hydrochloric acid solution of the same concentration and distilled water in the limits of the experimental errors.

The necessary data of molecular conductance were determined by the writers at 30° and 50°C. The reaction vessel itself was used as a conductivity cell at 30°C., but as it required a considerable amount of solutions, a

30.0° C.

m	0.000168	0.0002958	0.0005915	0.001183	0.005915	0.001183	0.05915
Λ	450	449	447	450	448	441	423

50.0° C.

m	0.000333	0.000998	0.00333	0.00998	0.0333	0.0998
Λ	570	570	570	560	540	506

small cell with the same electrode (shown in Fig. 1, a) was specially made for this purpose at 50°C. The values obtained are given in the following table, where m expresses the concentration of hydrochloric acid in mol/liter and Λ stands for the molecular conductance.

The conductivity measurement was started when the concentration of hydrochloric acid reached the lower limit of concentration in the control measurement of molecular conductance given above, namely $m = 0.000168$ at 30.0°C. and $m = 0.000333$ at 50.0°C. At first an experiment was done at 18°C. by using the molecular conductance data of Goodwin and Haskell,[1] but the rate of reaction at this temperature was so small that it required whole day to reach the limit just mentioned. All the other experiments, therefore, were carried out at 30° and 50°C., where this period varied from two hours to half an hour according to the temperature and the speed of stirring. Some of the results of the experiments are shown, as examples, by the curves in Figs. 2 and 3, where the figure on each curve indicates the number of revolution of the stirrer per minute. Full data will be given in later tables.

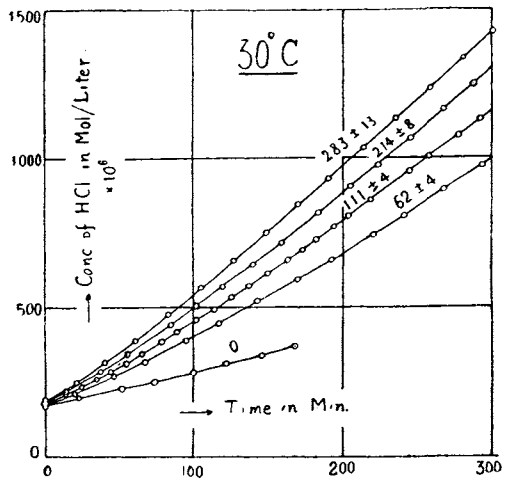

Fig. 2.

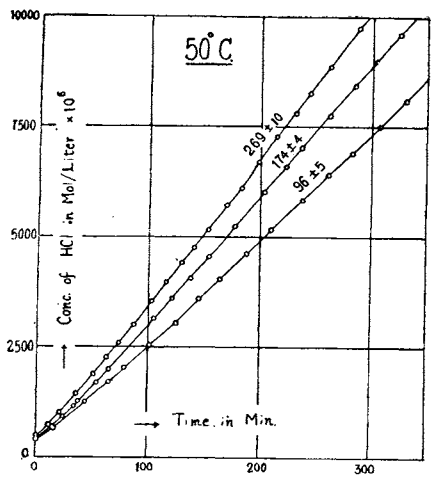

Fig. 3.

It will be seen from these curves that the rate of increase of hydrochloric acid is largely affected by the speed of stirring and, moreover, it increases with time, tending to become constant gradually.

(1) *Phys. Rev.*, **19** (1904), 369.

Results and Discussion.

The experimental results may be accounted for by assuming an adsorption film (A.F.) and a diffusion film (D.F.) in the aqueous part along the interface with benzyl chloride, as is shown in Fig. 4. These films may be movable as a whole but any configurations in the interior of them are supposed to be just like as on solid adsorbents.

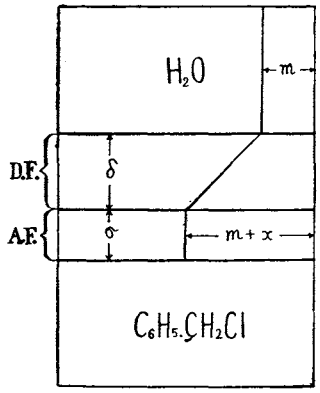

Fig. 4.

Since the reaction is a surface one and adsorbed molecules at the interface are supposed to hinder the progress of hydrolysis, its rate may be expressed by $H-kx$, where x denotes the concentration of adsorbed molecules of hydrochloric acid, H and k being constants at a given temperature. Let m express the concentration of hydrochloric acid in the bulk of aqueous layer whose volume is V, then the rate of increase of the total amount of hydrochloric acid in it is equal to $V\frac{dm}{dt}$, where t denotes the time. The difference of the above two quantities may be equal to the rate of increase of hydrochloric acid in the adsorption film (A.F.), whose thickness is put as σ:

$$S\sigma\frac{d(m+x)}{dt} = H-kx-V\frac{dm}{dt}, \quad \cdots\cdots\cdots\cdots\cdots (1)$$

where S denotes the area of the interface, $(m+x)$ being the actual concentration of hydrochloric acid in the adsorption film.

On the other hand, the rate of increase of hydrochloric acid in the bulk of the aqueous layer is equal to the amount which passes upwards in unit time through the diffusion film (D.F.). This amount is, however, proportional to the area of the interface S, the diffusion coefficient of hydrochloric acid D in water and the concentration gradient in the diffusion film whose thickness is δ:

$$V\frac{dm}{dt} = \frac{D\cdot S}{\delta}\cdot\left\{(m+x)-m\right\} = \frac{D\cdot S}{\delta}x. \quad \cdots\cdots\cdots\cdots (2)$$

Solving this equation for x and putting the result in equation (1) we have

$$S\sigma\frac{dx}{dt} = H-V\left(1+\frac{k\delta}{D\cdot S}+\frac{S\sigma}{V}\right)\frac{dm}{dt}. \quad \cdots\cdots\cdots\cdots (3)$$

Differentiating equation (2) with regards to t and substituting equation (3) in it we have

$$\frac{d^2m}{dt^2}+\frac{D}{\delta\sigma}\left(1+\frac{k\delta}{DS}+\frac{S\sigma}{V}\right)\frac{dm}{dt}=\frac{D}{\delta\sigma V}H. \quad \cdots\cdots\cdots (4)$$

As the solution of this differential equation we obtain

$$\frac{dm}{dt}=A-Ce^{-Bt}, \quad \cdots\cdots\cdots\cdots\cdots\cdots\cdots (5)$$

where C is an integration constant and

$$A=\frac{H}{V\left(1+\frac{k\delta}{DS}+\frac{S\sigma}{V}\right)}, \qquad B=\frac{D}{\delta\sigma}\left(1+\frac{k\delta}{DS}+\frac{S\sigma}{V}\right). \quad \cdots (6)$$

But, since $\frac{S\sigma}{V}$ is very small compared with unity, equations (6) may be written in the form:

$$A=\frac{H}{V\left(1+\frac{k\delta}{DS}\right)}, \qquad B=\frac{D}{\delta\sigma}\left(1+\frac{k\delta}{DS}\right). \quad \cdots\cdots\cdots (7)$$

The relation between m and t is obtained by integrating equation (5)

$$m=At+\frac{B}{C}e^{-Bt}+K, \quad \cdots\cdots\cdots\cdots\cdots\cdots\cdots (8)$$

where K is an integration constant.

Equation (8) was tested by comparing the calculated values of m with those observed. The results are very satisfactory as is shown in the following tables, in which N denotes the number of revolution of the stirrer per minute. The constants in equation (8) were computed in the following manner: The value of A which is equal to the reaction rate after sufficiently long time (cf. eq. (5)), can be directly known from the slope of the straight portion of the $t-m$ curve shown for example in Figs. 2 and 3. Then by plotting the value of log $(A-dm/dt)$ against the time t we obtain a straight line (cf. eq. (5)), whose slope gives the value of B, C being known from the point of the line on the abscissa.

18.0°C. $N = 109 \pm 2$*

$A = 1.00 \times 10^{-6}$
$K = 978 \times 10^{-6}$

t min.	$m \times 0^6$ (obs.)	$m \times 10^6$ (calc.)	Δ
0	980.8	978	−3
32	1014	1010	−4
72	1047	1050	+3
98	1071	1076	+5
128	1109	1106	−3
163	1144	1141	−3
203	1179	1181	+2
248	1225	1226	+1

* Continued from the last day.

30.0°C. $N = 0$.

$A = 1.69 \times 10^{-6}$, $B = 0.00352$,
$C = 0.689 \times 10^{-6}$, $K = -22 \times 10^{-6}$.

t min.	$m \times 10^6$ (obs.)	$m \times 10^6$ (calc.)	Δ
0	170.7	173	+2
23	199.3	197	−2
52	230.2	229	−1
74	251.3	254	+3
100	285.4	284	−1
122	313.1	311	−2
146	340.3	342	+2
168	370.2	370	0

30.0°C. $N = 62 \pm 2$.

$A = 3.90 \times 10^{-6}$, $B = 0.00440$,
$C = 1.897 \times 10^{-6}$, $K = -260 \times 10^{-6}$,

t min.	$m \times 10^6$ (obs.)	$m \times 10^6$ (calc.)	Δ
0	173.4	172	−1
13	199.3	198	−1
22	218.3	218	0
33	242.4	242	0
45	270.6	270	−1
55	293.0	294	+1
66	319.4	320	+1
77	346.7	348	+1
92	385.8	387	+1
110	434.8	435	0
125	476.4	477	+1
143	526.9	528	+1
163	586.0	587	+1
179	633.4	634	+1
194	680.6	681	0
208	723.8	725	+1
227	787.2	785	−2
246	846.3	846	0
267	914.7	914	−1
280	957.9	958	0

30.0°C. $N = 62 \pm 1$.

$A = 3.82 \times 10^{-6}$, $B = 0.00440$,
$C = 1.910 \times 10^{-6}$, $K = -260 \times 10^{-6}$.

t min.	$m \times 10^6$ (obs.)	$m \times 10^6$ (calc.)	Δ
0	175.3	175	0
20	213.2	214	+1
47	270.6	273	+2
68	318.6	322	+3
95	391.4	389	−2
117	447.3	447	0
143	521.8	518	−4
170	595.5	596	0
192	661.8	661	−1
220	743.4	745	+2
241	805.7	811	+5
268	893.7	898	+4
294	975.0	982	+7

30.0°C. $N = 60 \pm 2$.*

$A = 3.77 \times 10^{-6}$, $K = 4219 \times 10^{-6}$.

t min.	$m \times 10^6$ (obs.)	$m \times 10^6$ (calc.)	Δ
0	4215	4219	+ 4
18	4281	4287	+ 6
42	4383	4377	− 6
66	4473	4468	− 5
85	4528	4539	+11
104	4624	4611	−13
121	4663	4675	+12
140	4764	4747	−17
163	4848	4834	−14
193	4936	4947	+11
215	5050	5029	−21
253	5145	5173	+28
273	5243	5248	+ 5
295	5335	5331	− 4
319	5425	5422	− 3
346	5518	5523	+ 5

* Continued from (62±1) over a night.

30.0°C. $N = 101 \pm 5$.

$A = 4.01 \times 10^{-6}$, $B = 0.00449$, $C = 1.845 \times 10^{-6}$, $K = -224 \times 10^{-6}$.

t min.	$m \times 10^6$ (obs.)	$m \times 10^6$ (calc.)	Δ
0	186.4	187	+1
17	224.5	225	0
36	269.2	270	+1
55	314.9	318	+3
73	361.7	366	+4
92	421.5	417	−5
111	476.4	471	−5
137	553.5	548	−6
154	598.8	600	+1
171	656.1	653	−3
188	706.0	707	+1
206	765.2	765	0
224	823.9	824	0
241	876.6	881	+4
262	946.2	953	+7
281	1015	1018	+3
304	1096	1100	+4

30.0°C. $N = 111 \pm 4$.

$A = 4.03 \times 10^{-6}$, $B = 0.00640$, $C = 1.688 \times 10^{-6}$, $K = -89 \times 10^{-6}$.

t min.	$m \times 10^6$ (obs.)	$m \times 10^6$ (calc.)	Δ
0	176.7	175	−2
14	210.7	209	−2
25	236.2	237	+1
35	260.9	263	+2
45	288.3	290	+2
55	313.1	317	+4
66	347.5	350	+2
79	387.2	388	+1
89	416.7	419	+2
102	457.6	459	+1
114	493.6	497	+3
126	534.6	537	+2
137	573.1	573	0
150	617.0	616	−1
163	660.1	661	+1
173	693.6	695	+1
182	728.6	726	−3
194	770.5	769	−2
204	805.7	805	−1
219	860.2	859	−1
245	956.1	953	−3
258	1002	1002	0
278	1074	1076	+2
292	1130	1129	−1

30.0°C. $N = 161 \pm 5$.

$A = 4.15 \times 10^{-6}$, $B = 0.00972$, $C = 1.852 \times 10^{-6}$, $K = -26 \times 10^{-6}$.

t min.	$m \times 10^6$ (obs.)	$m \times 10^6$ (calc.)	Δ
0	165.0	165	0
20	212.8	211	−2
43	277.4	278	+1
64	340.3	342	+2
83	401.4	403	+2
107	485.7	485	−1
142	608.8	611	+2
163	685.8	689	+3
181	757.9	758	0
202	840.4	839	−1
225	928.5	929	0
247	1015	1016	+1
267	1094	1096	+2
288	1173	1171	−2
310	1274	1269	−5
333	1366	1364	−2

30.0°C. $N = 209 \pm 3$.

$A = 4.36 \times 10^{-6}$, $B = 0.00979$,
$C = 1.709 \times 10^{-6}$, $K = -10 \times 10^{-6}$.

t min.	$m \times 10^6$ (obs.)	$m \times 10^6$ (calc.)	Δ
0	166.5	166	−1
11	195.7	196	0
22	228.3	228	0
31	254.9	255	0
45	297.8	299	+1
56	332.0	336	+4
71	388.6	388	−1
84	434.8	434	−1
99	489.2	489	0
110	532.0	530	−2
123	579.2	579	0
134	620.4	622	+2
146	667.4	670	+3
169	764.2	765	+1
180	806.9	806	−1
192	858.8	855	−4
206	913.1	912	−1
220	969.8	970	0
231	1015	1016	+1
246	1081	1080	−1
261	1144	1143	−1

30.0°C. $N = 214 \pm 8$.

$A = 4.31 \times 10^{-6}$, $B = 0.00921$,
$C = 1.796 \times 10^{-6}$, $K = -11 \times 10^{-6}$.

t min.	$m \times 10^6$ (obs.)	$m \times 10^6$ (calc.)	Δ
0	184.5	184	−1
14	220.5	220	−1
38	288.3	290	+2
56	346.7	346	−1
85	441.9	442	0
102	505.0	505	0
120	569.0	571	+2
140	644.6	646	+1
159	718.1	719	+1
184	817.7	818	0
205	904.1	903	−1
224	978.4	979	+1
246	1068	1069	+1
268	1163	1161	−2
288	1245	1244	−1
305	1317	1316	−1
325	1405	1400	−5

30.0°C. $N = 283 \pm 13$.

$A = 4.55 \times 10^{-6}$, $B = 0.01117$,
$C = 1.514 \times 10^{-6}$, $K = 48 \times 10^{-6}$.

t min.	$m \times 10^6$ (obs.)	$m \times 10^6$ (calc.)	Δ
0	187.3	190	+3
21	250.2	249	−1
41	316.7	313	−4
61	391.4	387	−4
83	476.4	472	−4
105	567.8	568	0
127	660.1	657	−3
149	750.6	750	−1
170	842.9	845	+2
190	930.3	931	+1
214	1034	1034	0
236	1134	1141	+7
259	1231	1228	−3
281	1336	1340	+4
301	1423	1423	0
325	1530	1529	−1

30.0°C. $N = 283 \pm 3$.

$A = 4.50 \times 10^{-6}$, $B = 0.01117$,
$C = 2.084 \times 10^{-6}$, $K = -20 \times 10^{-6}$.

t min.	$m \times 10^6$ (obs.)	$m \times 10^6$ (calc.)	Δ
0	166.0	167	+1
11	194.8	195	0
23	230.7	228	−3
35	264.1	264	0
48	304.4	304	0
60	346.7	346	−1
72	391.4	388	−3
84	433.1	431	−2
96	476.4	476	0
108	521.8	522	0
121	573.7	573	−1
135	628.3	628	0
151	690.9	695	+4
166	756.8	756	−1
182	822.6	824	+1
198	890.8	892	+1
213	956.1	956	0
235	1049	1052	+3
253	1131	1129	−2

50.0°C. $N = 96 \pm 5$.

$A = 24.31 \times 10^{-6}$, $B = 0.0237$,
$C = 8.792 \times 10^{-6}$, $K = 52 \times 10^{-6}$.

t min.	$m \times 10^6$ (obs.)	$m \times 10^6$ (calc.)	Δ
0	425.1	423	− 2
15	674.2	677	+ 3
44	1251	1253	+ 2
65	1706	1712	+ 6
79	2036	2029	− 7
101	2539	2534	− 5
125	3127	3110	−17
145	3596	3589	− 7
164	4040	4047	+ 7
188	4632	4627	− 5
210	5164	5160	− 4
238	5826	5839	+13
261	6403	6397	− 6
283	6923	6933	+10
307	7508	7515	+ 7
331	8091	8098	+ 7
358	8754	8756	+ 2

50.0°C. $N = 174 \pm 4$.

$A = 29.53 \times 10^{-6}$, $B = 0.0283$,
$C = 11.00 \times 10^{-6}$, $K = 13 \times 10^{-6}$.

t min.	$m \times 10^6$ (obs.)	$m \times 10^6$ (calc.)	Δ
0	401.4	401	0
14	688.2	687	− 1
24	918.1	919	+ 1
38	1269	1267	− 2
54	1692	1692	0
65	1998	1995	− 3
105	3127	3134	+ 7
121	3596	3600	+ 4
138	4060	4059	− 1
154	4559	4566	+ 7
177	5226	5234	+ 8
203	6012	6009	− 3
223	6587	6600	+13
237	7023	7012	−11
262	7746	7750	+ 4
285	8433	8429	− 4
304	8989	8991	+ 2
325	9614	9611	− 3
348	10310	10293	−17
370	11000	10943	−57

50.0°C. $N = 269 \pm 10$.

$A = 33.64 \times 10^{-6}$, $B = 0.0279$,
$C = 12.42 \times 10^{-6}$, $K = 50 \times 10^{-6}$.

t min.	$m \times 10^6$ (obs.)	$m \times 10^6$ (calc.)	Δ
0	493.2	496	+ 3
11	744.0	748	+ 4
21	1015	1005	−10
36	1438	1424	−14
51	1893	1874	−19
63	2271	2246	−25
74	2569	2596	+27
87	2998	3016	+18
103	3523	3540	+17
116	3966	3971	+ 5
130	4420	4435	+15
141	4760	4803	+43
153	5164	5204	+40

50.0°C. $N = 269 \pm 10$.

(Continued)

t min.	$m \times 10^6$ (obs.)	$m \times 10^6$ (calc.)	Δ
170	5719	5773	+54
183	6220	6210	−10
198	6699	6714	+15
214	7268	7250	−18
231	7788	7822	+34
244	8258	8260	+ 2
262	8880	8865	−15
288	9743	9739	− 4
316	10730	10680	−50
337	11450	11390	−60
359	12100	12130	+30
383	13010	12940	−70

Table of Constants.

Temp.	N	$A\times10^6$	B	$C\times10^6$	$K\times10^6$
18.0°C.	109± 2*	100	—	—	978
30.0°C.	0	1.69	0.00352	0.689	− 22
	62± 2	3.90	0.00440	1.897	−260
	62± 1	3.82	0.00440	1.910	−260
	60± 2*	3.77	—	—	4219
	101± 5	4.01	0.00449	1.845	−224
	111± 4	4.03	0.00640	1.688	− 89
	161± 5	4.15	0.00972	1.852	− 26
	209± 3	4.36	0.00979	1.709	− 10
	214± 8	4.31	0.00921	1.796	− 11
	283±13	4.55	0.01117	1.514	48
	283± 3	4.50	0.01117	2.084	− 20
50.0°C.	96± 5	24.31	0.0237	8.792	52
	174± 4	29.53	0.0283	11.00	13
	269±10	33.64	0.0279	12.24	50

* After sufficiently long time.

It will be seen from the above tables that the values of A and B increase not only with rise of temperature but also with the speed of stirring. And, moreover, the effect of stirring on A is more prominent at higher temperatures. On the contrary the same effect on B decreases with rise of temperatures, showing a tendency that B becomes independent of the speed of stirring at sufficiently high temperatures. These facts may be accounted for by equation (7) at least qualitatively, taking into considerations the fact that the const nts H and k have a property of reaction coefficient and δ, the thickness of the diffusion film, becomes smaller when the speed of stirring increases.

It is clear from the above data that the reaction is not of zero order as was mentioned by Harker. The reaction can be supposed quite naturally to be of constant velocity if we neglect the adsorption and assume the reaction to be completely irreversible. Nevertheless the result of experiments makes it necessary to assume the presence of an adsorption layer and the hindrance of reaction by adsorbed molecules.

The writers desire to express their thanks to Professor M. Katayama for the interest he showed in the work.

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THE SOLUBILITIES OF THIOCYANATE OF METALS.

By Kosaku MASAKI.

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The author published on the solubilities of cyanide of metals in the previous paper[1]. Böttger[2] determined the solubility of lead thiocyanate in water by the method of using dissociation constant. But on the solubilities of thiocyanate of other metals, we have no information.

In this investigation, the solubilities of lead thiocyanate and cadmium thiocyanate were determined by the same method in the previous paper, and also the solubilities of zinc thiocyanate and cobalt thiocyanate were measured by means of the determination of specific conductances.

(1) Lead thiocyanate and Cadmium thiocyanate.

Lead chloride and lead thiocyanate were prepared from the dilute solutions of potassium salts by precipitating with purified lead acetate, and then precipitated lead salts were further purified with conductance water. Cadmium thiocyanate was prepared from the barium thiocyanate solution by precipitating with purified cadmium sulphate, and cadmium chloride was purified by washing with conductance water.

The amalgam employed are contained 2.5% of lead and cadmium, and also the cells used were of ordinary form.

The following cells are used to determine the solubilities of lead thiocyanate and cadmium thiocyanate.

(1) Pb (amalgam), Pb $(SCN)_2$ (sat.) || $PbCl_2$ (sat.), Pb (amalgam)

(2) Cd (amalgam), Cd $(SCN)_2$ (sat.) || $CdCl_2$ (0.01 M), Cd (amalgam)

The measured electromotive forces of the cells are 0.001917 and 0.1136 volt at $18° \pm 0.1°C$. respectively and constants necessary to carry out the calculation are given in Tables 1 and 2.

Table 1.

Salt	Moles per litre of water	Activity coeff.	Activity
$PbCl_2$	0.039	0.39[3]	$1.521 \cdot 10^{-2}$
$CdCl_2$	0.01	0.532[4]	$5.32 \cdot 10^{-3}$

(1) This Bulletin, **6** (1931), 143.
(2) *Z. physik. Chem.*, **46** (1903), 603.
(3) *Z. physik. Chem.*, **56** (1906), 645.
(4) *J. Am. Chem. Soc.*, **41** (1919), 1787.

Table 2.[1]

Ion	Ionic conductance at 18°C.	Ion	Ionic conductance at 18°C.
Pb^{++}	60.2	Cl^-	65.5
Cd^{++}	46.4	SCN^-	56.7

In the previous paper, we obtained the following equation.

$$E = E_c - E_l = \left[\frac{1}{2} - \frac{\frac{\Lambda_C}{V_C} - \frac{\Lambda_A}{V_A}}{\Lambda_C + \Lambda_A}\right]\frac{RT}{F}\ln\frac{a_2}{a_1}$$

(1) Solubility of lead thiocyanate

$$0.001917 = \left[\frac{1}{2} - \frac{\frac{60.2}{2} - 61.1}{121.3}\right]0.0577\log\frac{1.521\times10^{-2}}{a_1}$$

$$a_1 = 1.37\times10^{-2}$$

(2) Solubility of cadmium thiocyanate

$$0.11360 = \left[\frac{1}{2} - \frac{\frac{46.4}{2} - 61.1}{107.5}\right]0.0577\log\frac{5.32\times10^{-3}}{a_1}$$

$$a_1 = 2.51\times10^{-5}$$

The calculated value of the solubility of lead thiocyanate is in good agreement with the value of Böttger (1.35×10^{-2}).

(2) Zinc thiocyanate and Cobalt thiocyanate.

Zinc thiocyanate and cobalt thiocyanate were prepared from the barium thiocyanate solution by precipitating with purified zinc sulphate and cobalt sulphate.

The conductivities of zinc thiocyanate and cobalt thiocyanate were measured at 18°±0.1°C. by the same method in the previous paper. The

(1) *J. Am. Chem. Soc.*, **34** (1912), 459.

specific conductances of zinc thiocyanate and cobalt thiocyanate were 6.55×10^{-2} and 1.496×10^{-1} respectively, and also the cell constant was 0.228. The conductivity water which used in this investigation had a specific conductance of 1.5×10^{-6}.

The solubilities of zinc thiocyanate and cobalt thiocyanate were calculated by the equation, $n = \frac{1000k}{\Lambda_\infty}$, and the values of Λ_∞ obtained by the addition of the ionic conductances are 103.7 for zinc thiocyanate and 99.7 for cobalt thiocyanate.

(1) Solubility of zinc thiocyanate

$$n = \frac{1000 \times 6.55 \times 10^{-2} \times 0.228}{103.7} = 1.44 \times 10^{-1}$$

(2) Solubility of cobalt thiocyanate

$$n = \frac{1000 \times 1.496 \times 10^{-1} \times 0.228}{99.7} = 3.41 \times 10^{-1}$$

Summary.

(1) The solubilities of lead thiocyanate and cadmium thiocyanate were determined by the potentiometric method.

(2) The solubilities of zinc thiocyanate and cobalt thiocyanate were determined by the measurements of the specific conductances.

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SORPTION OF GAS BY MINERAL. III. SILICIC ACID MINERALS.

By Jitsusaburo SAMESHIMA.

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In the first report of this series the results of experiments were described on heulandite and chabazite,[1] and in the second report on laumontite.[2] The present paper deals with the experiments on some silicic acid minerals.

(1) Sameshima, this Bulletin, **4** (1929), 96
(2) Sameshima, this Bulletin, **5** (1930), 303.

The minerals tested are two kinds of chalcedonies, common opal, diatomaceous earth, natural silica gels and siliceous sinter. The gas used is ammonia, which has been prepared from ammonium chloride and lime, and dehydrated by potassium hydroxide, frozen and fractionated twice with liquid air.

The apparatus and the method of measurements are quite the same with those which were described already.[1] The experiments have been done at 25°C. and under about one atmospheric pressure of gas.

Chalcedony A. The mineral from Morofuno, Ibaraki Prefecture has been used. It is a translucent hard matter. The mineral lost 0.26% by weight on evacuating and heating to 300°C. The loss probably due to the evaporation of water which is contained in the mineral. The mineral which was dehydrated at 300°C. has been tested for the sorption of ammonia. The results are shown in Table 1.

Table 1. Chalcedony A.

Time in min. (t)	Pressure of gas in mm.	Volume of NH_3 (N.T.P.) sorbed at 25°C. by 1 gr. of chalcedony, in c.c. (x)	
		Observed	Calculated
0.5	763.3	0.19	—
3.	763.3	0.28	0.21
10.	763.3	0.42	0.43
60	762.9	0.70	0.76
155	762.4	0.93	0.94
1335	759.3	1.39	1.34
4285	758.5	1.56	1.56
$x = 0.43 \log t.$			

In this table, the first column shows the time in minutes after the contact of mineral to ammonia, the second column the pressure of ammonia gas, the third column the volume of ammonia sorbed at 25°C. by the dehydrated material which has been obtained by treating one gram of air-dry mineral at 300°C. and evacuating, the figures being the volumes in c.c. reduced at normal temperature and pressure, and the fourth column the values calculated by the equation given at the bottom of the table, x being the volume of ammonia sorbed and t the time.

(1) Sameshima, this Bulletin, **2** (1927), 2; **4** (1929), 97.

Chalcedony B. Another sample of calcedony was tested, the locality of which being Akadani, Niigata Prefecture. The mineral is found as gravel of spherical shape the diameter of which being about 2-4 cm. and is called "sorobandama-ishi." It is a hard, translucent matter. The loss of weight by heating to 300°C. and evacuation amounts to 0.65%. The volumes of ammonia sorbed by one gram of air-dry mineral after dehydrating at 300°C. are given in Table 2.

Table 2. Chalcedony B.

Time in min. (t)	Pressure of gas in mm.	Volume of NH_3 (N.T P.) sorbed at 25°C. by 1 gr. of chalcedony, in c.c. (x)	
		Observed	Calculated
0.67	758.3	0.44	—
3	758.3	0.71	0.70
6.5	758.3	0.89	0.89
14	758.2	1.08	1.08
23	758.2	1.19	1.20
29	758.1	1.26	1.26
55	757.9	1.44	1.42
90	757.9	1.56	1.54
313	757.8	1.83	1.85
$x = 0.57 \log t + 0.43$			

Thus chalcedony B absorbs more ammonia than chalcedony A, being parallel to the water contents of them.

Opal. The mineral from Hoosaka, Fukushima Prefecture has been used. It has a milky colour and a glassy lustre, and is like the boiled white-of-egg in appearance. The mineral contains much water than chalcedony. By heating to 300°C. and subjecting to evacuation its weight decreased to the amount of 5.01%. The substance thus dehydrated has been used for the experiment. It is, therefore, expected that more ammonia will be sorbed by this mineral than chalcedonies. The results are shown in Table 3.

The values in Tables 1 to 3 have been depicted in Fig. 1, taking the logarithm of time against the volume of ammonia sorbed. The straight lines are drown by the equations given under each table. The observed values are, quite satisfactorily, on the straight lines, excepting first one or two values in each series.

Table 3. Opal.

Time in min. (t)	Pressure of gas in mm.	Volume of NH_3 (N.T.P.) sorbed at 25°C. by 1 gr. of opal, in c.c. (x)	
		Observed	Calculated
0.5	745.9	2.52	—
2	745.9	3.07	2.93
10	745.8	3.71	3.68
30	745.6	4.20	4.20
60	745.2	4.52	4.52
120	744.6	4.84	4.84
240	743.9	5.17	5.17
1460	755.6	5.99	6.02
4320	764.9	6.55	6.52
$x = 1.08 \log t + 2.60$.			

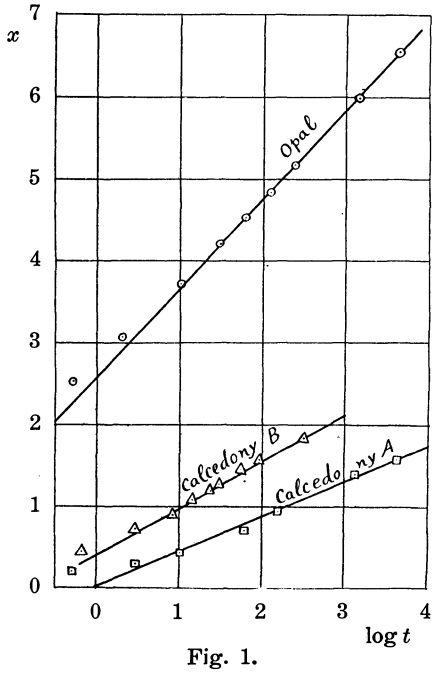

Fig. 1.

Diatomaceous Earth. The diatomaceous earth from Saigo, Oki Islands has been used. The mineral was dehydrated by heating to 300°C. and subjecting to evacuation, the decrease in weight being 10.12%. Thus a con-

siderable amount of water is contained in this mineral. Accordingly, as seen from Table 4, the amount of ammonia sorbed is also relatively high. The values are shown in Table 4 and Fig. 2.

Table 4. Diatomaceous Earth.

Time in min. (t)	Pressure of gas in mm.	Volume of NH_3 (N.T.P.) sorbed at 25°C. by 1 gr. of air-dry earth after being dehydrated, in c.c. (x)	
		Observed	Calculated
0.5	752.4	11.69	—
2	752.4	14.20	14.87
5	752.3	15.46	15.43
10	752.2	15.92	15.86
30	751.8	16.61	16.54
60	751.2	16.97	16.97
120	750.9	17.33	17.39
240	749.4	17.67	17.82
1560	753.6	18.86	18.97
4330	763.5	19.57	19.60
7370	769.1	19.93	19.93
11635	766.3	20.21	20.21
18850	747.3	20.47	20.51
$x = 1.42 \log t + 14.44$			

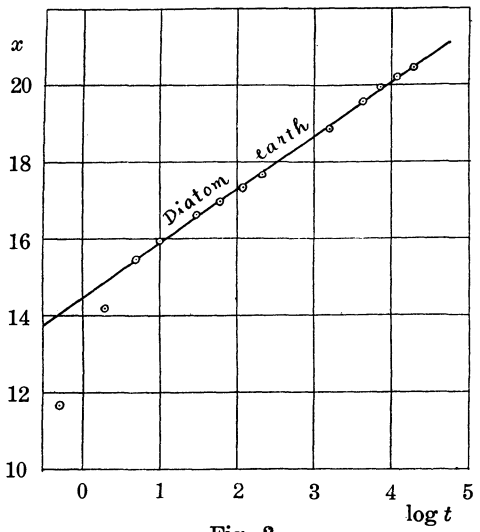

Fig. 2.

Siliceous Sinter and Natural Silica Gels. The three minerals which are described in the following lines were obtained from Nakabusa Hot Spring, Nagano Prefecture, The spring from which these minerals have been deposited, is erupting in boiling state, the temperature of which being 95°C. The altitude is about 1500 metres from sea level. Total solid matter in 100,000 parts of spring is 68 in which 24 parts are SiO_2. The value of P_H of the spring is 8.9.

In the course of flowing down the mountain side the temperature of spring descends and the deposition of silica takes place. The silica deposits in gel form of soft, gelatinous appearance of various colours. It is not a pure silica gel, but contains a considerable amount of organic matters like fungi, which may accelerate the deposition of silica from spring. The gel was dried in open air and the air-dry substance was analysed giving the following results.

Weight loss by heating at 150°C. and subjecting to evacuation :	5.03%
Ignition loss (mainly organic matter) :	12.50%
SiO_2 :	77.35%
Al_2O_3 and Fe_2O_3 :	2.66%
CaO :	0.54%
Total	97.98%

The remainder (about 2%) is probably NaCl etc.

The silica which is found underneath of the layer of gelatinous deposit is like a soft cheese in appearance. It is probable that this cheese-like silica was produced as the result of the loss of elasticity by the death of fungi in the gelatinous silica. At the bottom of the spring flow or the dry places near the spring there is much quantity of siliceous sinter which is generally a hard white, bone-like matter.

Measurements were done on these three kinds of silicas. They were dehydrated by heating at 150°C. and evacuating and then measured the sorption of ammonia. The loss of weight by dehydration for gelatinous gel, cheese-like gel and hard sinter amount to 5.03, 4.01 and 3.44% respectively. The results of measurements are shown in Tables 5, 6, 7 and Fig. 3.

Theoretical. The mechanism of sorption of gas by porous matter has already been discussed.[1] The following equation for the velocity of sorption has been proposed in case of the sorption of ammonia by charcoal.[2]

$$x = K \log t + k,$$

(1) Sameshima, this Bulletin, **4** (1929), 125; *Chem. News*, **139** (1929), 61.
(2) Sameshima, this Bulletin, **5** (1930), 173.

Table 5. Gelatinous Silica Gel.

Time in min. (t)	Pressure of gas in mm.	Volume of NH_3 (N.T.P.) sorbed at 25°C. by 1 gr. of air-dry gel after being dehydrated, in c.c. (x)	
		Observed	Calculated
1	757.6	18.95	—
5	757.6	23.73	—
10	757.6	25.66	—
25	757.5	28.14	28.69
71	757.9	31.01	31.14
200	759.0	33.68	33.58
1470	762.0	38.31	38.27
2850	769.7	39.76	39.84
4520	770.0	41.08	40.92
5790	761.2	41.59	41.50
8840	766.2	42.39	42.50
10130	759.1	42.66	42.82
$x = 5.42 \log t + 21.11$			

Table 6. Cheese-like Silica Gel.

Time in min. (t)	Pressure of gas in mm.	Volume of NH_3 (N.T.P.) sorbed at 25°C. by 1 gr. of air-dry gel after being dehydrated, in c.c. (x)	
		Observed	Calculated
1	761.8	23.96	—
5	761.8	27.73	—
10	761.8	29.02	—
30	761.7	30.91	30.57
62	761.8	32.38	32.33
120	762.1	33.85	33.94
210	762.1	35.20	35.30
1370	762.5	39.55	39.87
2810	754.8	41.48	41.61
5700	761.4	43.44	43.33
12930	759.0	45.36	45.33
17200	761.4	46.04	46.02
22930	765.7	46.70	46.72
41680	759.6	48.00	48.17
$x = 5.60 \log t + 22.30$			

Table 7. Hard Siliceous Sinter.

Time in mm. (t)	Pressure of gas in mm.	Volume of NH_3 (N.T.P.) sorbed at 25°C. by 1 gr. of air-dry mineral after being dehydrated, in c.c. (x)	
		Observed	Calculated
1	759.9	6.53	—
5	759.9	8.22	—
15	759.8	9.49	—
70	759.3	11.85	—
220	759.7	14.20	—
1665	760.1	19.05	19.14
2990	752.9	20.97	21.18
4555	754.5	22.44	22.63
8895	764.3	25.07	24.96
12900	771.3	26.40	26.26
15790	759.2	27.06	26.95
20275	763.1	27.91	27.83
29130	758.4	29.12	29.08
36210	752.4	29.80	29.84

$x = 8.00 \log t - 6.63$

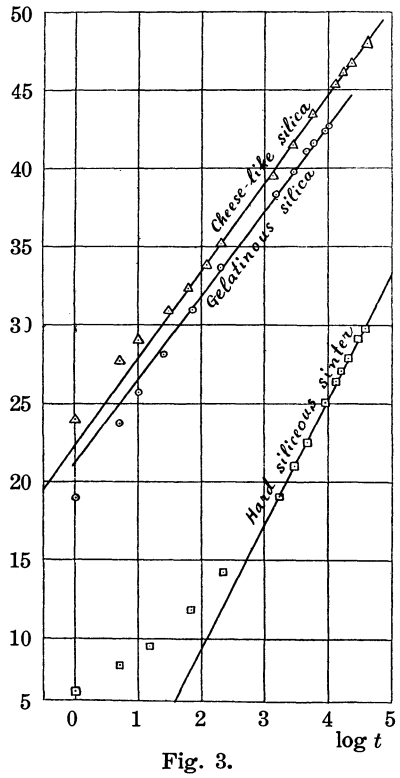

Fig. 3.

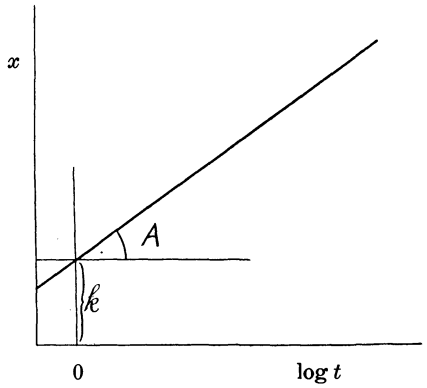

Fig. 4.

where x is the quantity of gas sorbed at time t, and K and k are the constants. This equation shows a straight line on a diagram drawn x against $\log t$ (Fig. 4). The trigonometrical tangent of the angle A between the straight line and the $\log t$ axis gives the value of K. The value of x cutting by the straight line at $\log t=0$ gives the value of k. As shown in Figs. 1, 2 and 3, this equation can be applied in the present experiments. And by the above manner we can easily evaluate the values of K and k from the observed line. The equations thus obtained were given under each table of observed data.

At the initial stage of sorption the velocity is not expressed by the equation as seen from the figures. In the case of sorption of ammonia by sugar charcoal such a non-linear part lasted about one hour.[1] In the present cases, it lasts shorter period, excepting siliceous sinter, thus 2-3 minutes for chalcedonies, 5 minutes for opal, 2 minutes for diatomaceous earth, and 10 minutes for silica gel, while 200 minutes for siliceous sinter.

The entering of gas molecules into relatively large openings among solid molecules are accomplished in relatively short time. This part of sorption cannot be expressed by the present equation and deviate from the straight line relation. But the latter part of sorption can thus well be expressed by our derived equation.

Summary.

1. Sorption of ammonia by dehydrated materials of chalcedonies, opal, diatomaceous earth, natural silica gels and siliceous sinter have been measured.

2. All these substances sorb considerable amounts of ammonia at ordinary temperature.

3. The sorption velocity can be expressed by the equation

$$x=K \log t+k,$$

where x is the sorption amount at time t, and K and k are the constants.

Chemical Institute, Faculty of Science,
Tokyo Imperial University.

(1) Sameshima, this Bulletin, **5** (1930), 179.

ON THE THERMAL DECOMPOSITION OF AROMATIC ETHERS UNDER HIGH HYDROGEN PRESSURE.

By Toru OGAWA.

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It is a well known fact that diethyl ether on being heated to 550°–770° C., decomposes into ethane and acetaldehyde[1]; anisol[2] yields phenol and ethylene at 380–460°, and cyclohexyl phenyl ether decomposes at high temperatures into phenol and cyclohexene.[3]

Aromatic ethers such as diphenyl ether, as noticed by Graebe, on pyrolysis, yields diphenyleneoxide and other polymers with a small quantity of phenol and benzene.[4] This result seems to differ from that obtained with the aliphatic ethers or aliphatic and aromatic ethers mentioned above, and polymerization of diphenyl ether in the pyrolysis may be attributed to the weakness of the combining affinity of the hydrogen atom in the para or ortho position for the carbon atom, effected by the disruption of the linking between the carbon and the oxygen atom in the molecule.

The thermal decomposition of ethers should be promoted in the presence of catalysts and in fact, aliphatic ethers in the presence of Japanese acid clay are decomposed into alcohols and olefines at 200°[6]; phenyl methyl ether by potash fusion at 180° produces phenol and anisol; and diphenyl ether by contact with metallic sodium heated to 180°–200°, is decomposed into phenol and benzene.[7] The decomposition of diphenyl ether into phenol and benzene is promoted in the presence of reduced nickel and hydrogen, as observed by S. Komatsu and M. Masumoto[8], this decomposition being evidently accompanied by hydrogenation of the benzene nucleus:

$$C_6H_5\,O\,C_6H_5 \longrightarrow C_6H_{11}OH + C_6H_{12}$$

It is, therefore, very interesting to study the pyrolysis of aromatic ethers in the presence of hydrogen under pressure, and in the present re-

(1) *Ann.*, **14** (1835), 134; U. Nef. Ibid., **318** (1901), 198; E. Peytral, *Bull. Soc. Chim.*, **4** (1924), 35.
(2) Meyer u. Hofmann, *Monatsh.*, **38** (1917), 343.
(3) Skraup u. Beifuss, *Ber.*, **60** (1927), 1070.
(4) *Ber.*, **29** (1896), 1877.
(5) R. Nakai, This Bulletin, **5** (1930), 136.
(6) K. Kashima, Ibid., **5** (1930), 25.
(7) P. Shöringen, *Ber.*, **56** (1923), 176; K. Ziegler u. F. Thielmann, Ibid., **56** (1923), 1740.
(8) This Bulletin, **5** (1930), 241.

search, diphenyl ether, diphenylene oxide, α- and β-dinaphthylene oxides are used as the experimental material.

When diphenyl ether was heated in an autoclave at 500° for 1 hour with hydrogen under 100 atmospheric pressures at 0°, 90% of the ether was transformed into benzene and phenol, although W. Ipatiew[1] has reported that no appreciable reaction took place under such conditions.

The fact that the mol ratio of benzene, phenol and water in the reaction product is 1 : 0.4 : 0.3 indicates that in the pyrolysis the following reaction (1)

$$C_6H_5\,O\,C_6H_5 + H_2 = C_6H_5OH + C_6H_6 \quad \ldots\ldots\ldots\ldots \quad (1)$$

will be accompanied by either reaction (2) or (3) :—

$$C_6H_5\,O\,C_6H_5 + H_2 = 2C_6H_6 + H_2O \quad \ldots\ldots\ldots\ldots \quad (2)$$

$$C_6H_5OH + H_2 = C_6H_6 + H_2O \quad \ldots\ldots\ldots\ldots \quad (3)$$

K. Kashima[2] and R. Nakai[3] have already claimed in the report on their experiments on aliphatic and aromatic ethers, that reaction (2) will take place mostly at higher temperatures, and reaction (3), in spite of the fact that it was not observed as expected in an experiment made by A. Kling and D. Florentin[4], was actually noticed by the writer and Takahashi[5] on heating phenol with hydrogen at 460°—490° for $2\,^1/_2$ hours under 100 atmospheric pressures at 0°, the result being a fruitful yield of benzene and water.

Thus, the pyrolysis of diphenyl ether in the presence of hydrogen may be assumed to proceed mostly by reactions (1) and (2) and partly by reaction (3).

Decomposition of diphenylether at 250°, however, in the presence of reduced nickel and hydrogen under 100 atmospheric pressures at 0° is observed to produce cyclohexane and cyclohexanol in equimolecular quantities (0.65 mol), which result is on the whole very similar to that obtained by S. Komatsu[6] and W. Ipatiew[7], in which hydrogenation in the benzene nucleus happens first and is followed by the disruption of the linking between the oxygen and carbon atoms, thus :

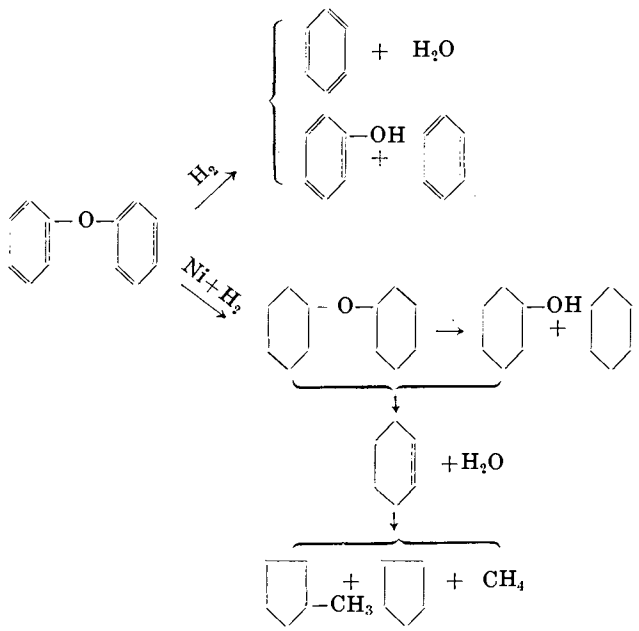
$$C_6H_5{\cdot}O{\cdot}C_6H_5 + H_2 \rightarrow C_6H_{11}{\cdot}O{\cdot}C_6H_{11} \rightarrow C_6H_{11}OH + C_6H_{12}$$

(1) *Ber.*, **60** (1927), 1963.
(2) Loc. cit.
(3) „ „
(4) *Internat. Conf. Bit. Coal.*, **11** (1928), 523.
(5) Unpublished.
(6) Loc. cit.
(7) *Ber.*, **41** (1908), 1001.

When the reaction was conducted at 500° C, methane, cyclopentane, methyl-cyclopentane and water were observed to occur in the reaction product with the yield in mol ratio, 2 : 0.2 : 0.4 : 1 respectively.

The formation of methyl-cyclopentane and cyclopentane is explained by assuming that cyclohexene which is formed as an intermediate product by dehydration from cyclohexanol or dicyclohexyl ether is in turn decomposed into cyclopentane and its derivative, as reported by S. Inoue[1] and by the writer and T. Yokota[2] in connection with their catalytic reaction of benzene and phenol under high temperature and high pressure in the presence of reduced nickel and hydrogen.

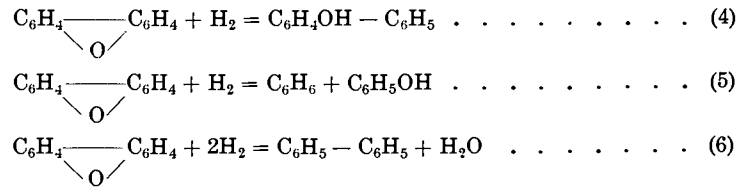
The chemical changes of diphenyl ether under high temperature and high hydrogen pressure with or without reduced nickel may be summarized as in the following scheme :—



When diphenylene oxide is treated with hydrogen at 500°C for 5 hours under 100 atmospheric pressures at 0°, benzene (0.14 mol), phenol (0.13 mol), *o*-hydroxydiphenyl (0.2 mol) and a small quantity of diphenyl are obtained with 30% of unchanged oxide in the reaction product.

(1) This Bulletin, **1** (1926), 157.
(2) Ibid., **5** (1930), 266.

The main reaction in this case is represented analogously with the case of diphenyl ether, by the following scheme:



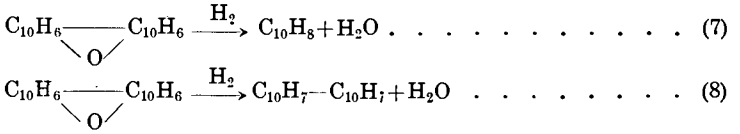
$$C_6H_4\!<\!\!\begin{matrix}\text{——}C_6H_4\\ O\end{matrix}\!\!> + H_2 = C_6H_4OH - C_6H_5 \quad \ldots\ldots\ldots\ldots (4)$$

$$C_6H_4\!<\!\!\begin{matrix}\text{——}C_6H_4\\ O\end{matrix}\!\!> + H_2 = C_6H_6 + C_6H_5OH \quad \ldots\ldots\ldots\ldots (5)$$

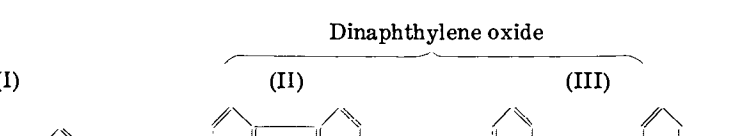
$$C_6H_4\!<\!\!\begin{matrix}\text{——}C_6H_4\\ O\end{matrix}\!\!> + 2H_2 = C_6H_5 - C_6H_5 + H_2O \quad \ldots\ldots\ldots\ldots (6)$$

In other words, the disruption of the linking between the carbon and oxygen atoms proceeds first under the experimental conditions mentioned above; the effect of this is to weaken the linking connecting the two benzene nuclei, with the result that reaction (5) takes place properly, and the reactions (4) and (6) are compatible with reactions (1) and (2) in the case of diphenyl oxide.

When 20 gr. of α- or β-dinaphthylene oxide were treated under conditions similar to those employed in the case of diphenylene oxide, the α-compound was decomposed completely into methane (3.8 gr.), benzene homologue (3.4 gr.), naphthalene (5.4 gr.) and a small amount of β-β'-dinaphthyl, and the β-isomer was converted into methane (4.8 gr.), benzene homologue (3.5 gr.), naphthalene (4.8 gr.), α-α'-dinaphthyl (2.5 gr.) and perylene (1.5 gr.), but no trace of naphthol was formed in either case. These results indicate that the behaviour of these two naphthylene oxides is not entirely the same as that of diphenylene oxide though they present by the anologous chemical constitutions (I), (II) and (III).



$$C_{10}H_6\!<\!\!\begin{matrix}\text{——}C_{10}H_6\\ O\end{matrix}\!\!> \xrightarrow{H_2} C_{10}H_8 + H_2O \quad \ldots\ldots\ldots\ldots (7)$$



$$C_{10}H_6\!<\!\!\begin{matrix}\text{——}C_{10}H_6\\ O\end{matrix}\!\!> \xrightarrow{H_2} C_{10}H_7\text{—}C_{10}H_7 + H_2O \quad \ldots\ldots\ldots\ldots (8)$$

Diphenylene oxide α β

A free naphthylene radical (4) which is formed by disruption of the linking between the carbon and oxygen atoms and that between the carbon and carbon atoms connecting the two naphthalene nuclei, will decompose more

easily than the phenylene radical (5) into methane and benzene homologue, and such a tendency of the free radical to decompose may be anticipated from the thermal reaction of naphthalene and benzene.

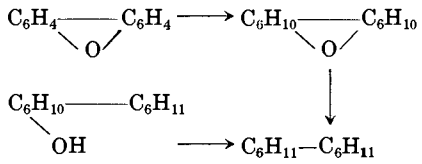
(V) (IV)

In the presence of nickel and hydrogen, diphenylene oxide was converted at 200°C and 280°C into *o*-hydroxydicyclohexyl and dicyclohexyl. The reaction products differ in quantity according to the reaction temperature, as may be seen in the Table 1 and the experimental results

Table 1.

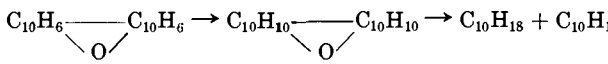
	$C_6H_4\!\!<\!\!\begin{matrix}\\O\end{matrix}\!\!>\!\!C_6H_4+H_2$	$\longrightarrow C_6H_{10}(OH)-C_6H_{11}$	+	$C_6H_{11}-C_6H_{11}+H_2O$	
200°	1 mol.	8.4 mol.	0.47 mol.	0.33 mol.	0.15 mol.
280°	1 mol.	9.3 mol.	0.25 mol.	0.54 mol.	0.69 mol.

indicate that the conversion of the ethylene oxide into dicyclohexyl is favorable at higher temperatures, due to dehydration of either *o*-hydroxydicyclohexyl or dicyclohexylene oxide, which are evidently formed by the catalytic hydrogenation of the oxide:



Such an interpretation of the chemical changes occurring during the catalytic hydrogenation of the ethylene oxide may be applied to the catalytic reaction of α- and β-dinaphthylene oxides in the presence of reduced nickel. As a matter of fact, α-dinaphthylene oxide does not present any change in the presence of reduced nickel at 225°, while the β-isomer is transformed first into octa-hydrodinaphthylene oxide at 200°. At 500°, formation of methane, cyclohexane homologue, decalin and tetralin was noticed, and the reaction is explained by assuming that hydronaphthylene, formed as an intermediate reaction product by dehydration of hydronaphthalene oxide, was converted into tetralin and decalin by catalytic reduction on the one

hand, and on the other decomposed into methane and cyclohexane homologue; this assumption is based on the fact that naphthalene is converted by catalytic hydrogenation under high pressure and temperature into methane and cyclohexane homologue.

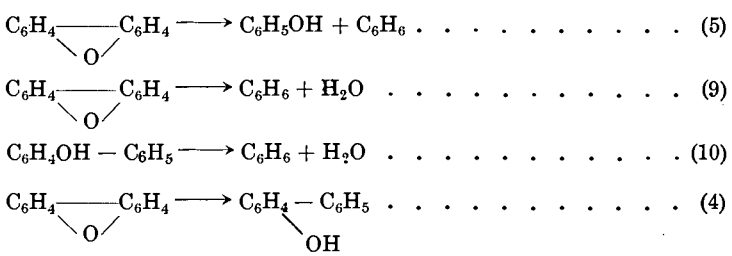


In order to investigate the catalytic effects of reduced copper, ferric oxide and Japanese acid clay on the thermal decomposition of diphenylene oxide, it was treated in the presence of each of these catalysts and of hydrogen at 500° under 100 atmospheric pressures at 0°. The reaction product was observed to consist, in each case, of benzene, phenol, diphenyl and *o*-hydroxydiphenyl, and the amount of water and of benzene produced by the reaction was greatest with Japanese acid clay, ferric oxide and copper following in that order, as will be seen from the following Table 2.

Table 2.

Catalyst	Water produced %	mol ratio of benzene and phenol
—	0.7	1.2 : 1
Cu	3.4	2.1 : 1
Fe_2O_3	5.4	2.7 : 1
Japanese acid clay	6.0	4.1 : 1

From these experimental results, the writer is inclined to believe that the chemical reaction of diphenylene oxide in the presence of a catalyst and hydrogen under high temperature and pressure, proceeds by the processes represented as follows:



The reactions (9) and (10) which are not occur at 280° and 100 atmospheric pressures at 0° with or without reduced nickel, are promoted in the presence neither copper oxide, ferric oxide nor Japanese acid clay heated at 500°C.

Experimental.

The apparatus employed in the experiments consisted of a cylindrical autoclave of about 2.5 litres capacity, which was heated externally by electric resistance, and mounted horizontally so to rotate, as may be seen in the Fig. 1.

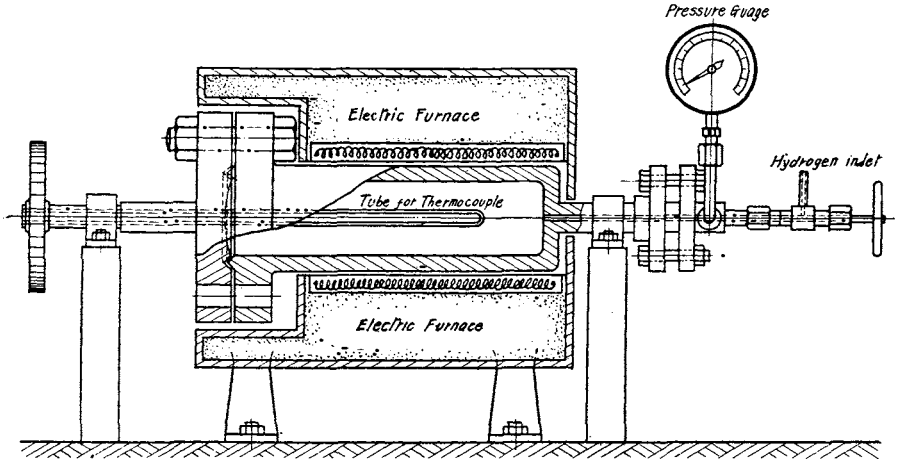


Fig. 1.

In each experiment, the sample, with or without a catalyst (10%) was put into the autoclave, hydrogen was introduced from a cylinder to produce 100 atmospheric pressures at 0°C, and this was heated to the required temperature. The changes in the pressure during the reaction were observed at intervals of 5 minutes. When the reaction was finished, the volume and the density of the gas in the apparatus were measured, and the chemical composition of the gas and liquid or solid reaction products was examined carefully by chemical and physical methods.

1. Diphenyl Ether. (A) Diphenyl ether (50 gr.) prepared[1] from monochlorobenzene and phenol by the catalytic action of copper, showing m. p. 28.0°; b. p. 247°–249 (760 mm.), $d_4^{30} = 1.0711$; $n_D^{30} = 1.5773$, was heated with hydrogen at 490° for 1 hour under a pressure of 100 atmos-

(1) F. Ullmann and P. Sponagel, *Ber.*, **38** (1905), 2211.

pheres at 0°. A fall of 6 atmospheric pressures was observed, which corresponds to 1.2 gr. or 2 mol hydrogen, and the gas in the autoclave was determined to be composed of 99.4% hydrogen and 0.3% saturated hydrocarbon, probably methane.

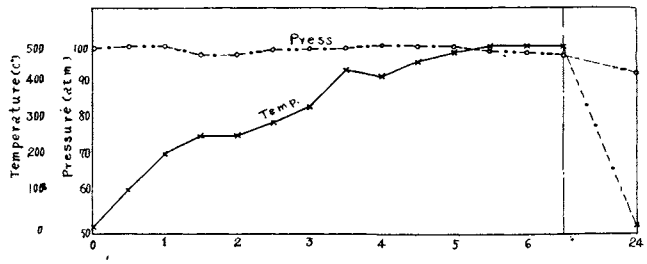


Fig. 2.

The liquid substance (45 gr.) produced by the reaction with water (1.5 gr.), was divided by fractional distillation into the following 3 fractions.

Fraction	B. p.	Yield (gr.)	d_4^{25}	n_D^{25}	Remarks
1	75°—85°	22	0.8724	1.4970	Benzene
2	180°—190°	11	—	1.5411	Phenol
3	250°—260°	6.5	1.0724	1.5779	Diphenyl-ether

Fractions (1) and (2), as indicated by their physical constants, are assumed to be composed of benzene and phenol respectively, and this was confirmed in the case of the former substance by changing it into nitrobenzene, and of the second by the reaction with ferric chloride and caustic soda.

The third fraction agrees in its constants with diphenyl ether.

(B) *In the presence of reduced nickel.* (1) When 50 gr. of the sample were heated at 250° for 2 hours with hydrogen under 100 atmospheric pressures at 0°, in the presence of reduced nickel (5 gr.) which had been previously prepared from nickel oxide by reduction with hydrogen at 280°, a fall of 22 atmospheric pressures was noticed.

The amount of hydrogen absorbed and that of the gases produced during the reaction were found by calculation to be 4.8 gr. (8.0 mol.) and

2.9 gr. respectively (Fig. 3) from the analytical results of the gas in the autoclave:

$$CO=0.1\,;\quad H_2=98.4\,;\quad C_nH_{2n+2}=1.5:$$

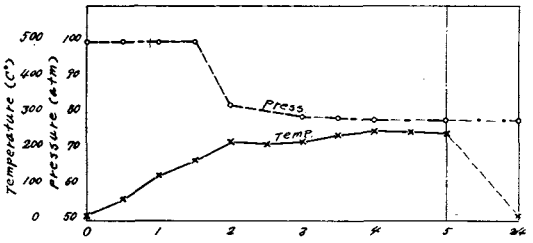


Fig. 3.

The liquid reaction product (47.5 gr.) separated from water (0.2 gr.) and the catalyst, was fractionated into 3 parts:

	B.p.	Yield
1	70°—175°	40 gr.
2	175°—250°	2.5 ,,
3	above 250°	1.0 ,,

After repeated fractionation, the physical constants of each fraction were studied:

Fraction	B. p.	Yield (gr.)	d_4^{25}	n_D^{25}	Remarks
1	79°—85°	14.5	0.7769	1.4241	Cyclohexane
2	158°—165°	20.0	0.9464	1.4610	Cyclohexanol
3	238°—242°	1.5	0.989	1.470	Dicyclohexyl-ether

Fraction 1 was confirmed to be composed of cyclohexane from its behaviour towards bromine or a mixture of nitric and sulphuric acids, and also from its physical constants. The phys cal properties of the 2nd fraction agree with those of pure cyclohexanol ($d_4^{25}=0.9469$; $n_D^{25}=1.4635$).

The third fraction was assumed from the physical constants to be composed of dicyclohexyl ether, which has been prepared by S. Komatsu and M. Masumoto[1] from diphenyl ether by catalytic reduction.

(1) S. Komatsu and M. Masumoto, loc. cit.

(2) Diphenyl ether (50 gr.) was heated at 500° for 2 hours with reduced nickel (5 gr.) and hydrogen under a pressure of 100 atmospheres, the fall in the pressure was 28.5 atm. at 0°, (Fig. 4) and 7 gr. of hydrogen (12 mol) were used in the reduction, and the gaseous product was composed of hydrogen and methane in the proportion H : CH_4 = 92.7 : 7.3.

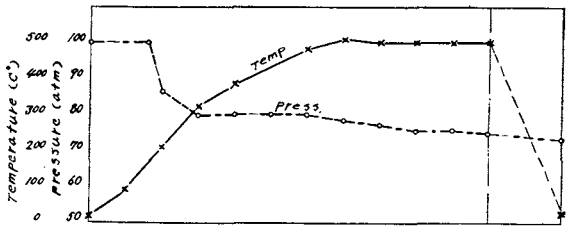


Fig. 4.

5.4 Gr. of water and 13.6 gr. of liquid substance were obtained from the autoclave, with 22.0 gr. of liquid substance of low boiling point, which escaped with the gaseous products from the autoclave when it was opened, and were absorbed with active carbon. The liquid reaction product found in the autoclave was all distilled at below 120°, and was fractionated carefully, and the physical constants of each fraction studied :

Fraction	B. p.	Yield (gr.)	d_4^{15}	n_D^{15}	Remarks
1	55°—65°	5.0	0.7556	1.4160	Cyclopentane
2	65°—75°	3.0	0.7633	1.4214	Methyl-cyclopentane
3	75°—78°	0.5	0.7769	1.4242	Cyclohexane

Fractions 1, 2 and 3 were identified by their physical constants and chemical properties with cyclopentane, methyl cyclopentane and cyclohexane respectively.

The liquid reaction substance found in the gaseous products, was also examined and found to be composed of cyclopentane and methyl cyclopentane by the usual treatment, as will be seen in the following table :—

Fraction	B.p.	Yield (gr.)	d_4^{15}	n_D^{15}	Remarks
1	55°—65°	2.0	0.7545	1.4142	Cyclopentane
2	65°—75°	1.2	0.7635	1.4218	Methyl cyclopentane

2. Diphenylene Oxide. Diphenylene oxide prepared from phenol by destructive distillation with lead oxide, and purified by fractional distillation and recrystallization from alcohol solution, shows b.p. 284° (760 mm); m.p. 83°; m.p. of picrate 99°.

When 50 gr. of the sample was heated with hydrogen at 500° for 2 hours under a pressure of 100 atmospheres at 0°, no appreciable change in the pressure was noticed, and therefore, it was heated again with a new supply of hydrogen, at 500°C for 2 hours (Fig. 5), and 1.5 gr. (2.5 mols.) of hydrogen were utilized in the reaction.

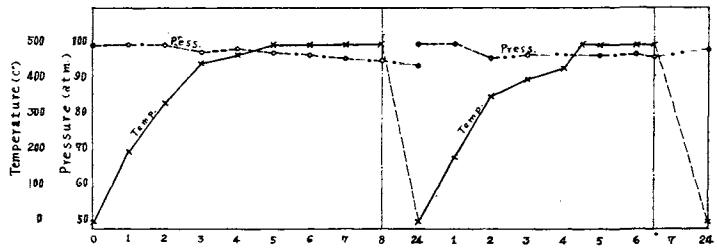


Fig. 5.

The gas in the autoclave consisted only of hydrogen.

An oily reaction product (43 gr.) separated from water (0.4 gr.) was fractionated into 4 fractions with the follwing physical constants:

Fraction	B.p.	Yield (gr.)	d_4^{25}	n_D^{25}	Remarks
1	75°—90°	3.3	0.7819	1.4919	Benzene
2	170°—190°	3.5	1.0356	1.5358	Phenol
3	260°—280°	10	—	—	—
4	280°—290°	13.7	—	—	—

Fractions 1 and 2 were confirmed to be composed of benzene and phenol respectively.

Fraction 3 melting at 70°—80°, was treated with a dilute caustic alkali solution, and the amorphous substance separated on acidifying the solution with acid, was recrystalized from petroleum ether in colorless needle crystals which melted at 58° and boiled at 283°, 760 mm. These physical properties of the writer's sample being different from those of *o*-hydroxy-

diphenyl mentioned by Hönigschmidt[1] (b.p. 275°, m.p. 56°) and Hirsh[2] (m.p. 67°), it was analysed with the following results :

Subst. = 0.1045 ; CO_2 = 0.3240 ; H_2O = 0.0570 gr. Found : C = 84.55 ; H = 6.06.
Calc. for $C_{12}H_{10}O$: C = 84.70 ; H = 5.88.

Fraction (4) consists of a substance which shows m.p. 83°, after being purified from an alcohol solution, it was identified with diphenylene oxide.

(B) *In the presence of reduced nickel.* (1) 100 Gr. of diphenylene oxide were heated at 200° for 3 hours with hydrogen and reduced nickel under 100 atmospheric pressures at 0°. The fall in the pressure was 45.3 atmospheres which correspond to 10 gr. or 8.5 mol of hydrogen (Fig. 6).

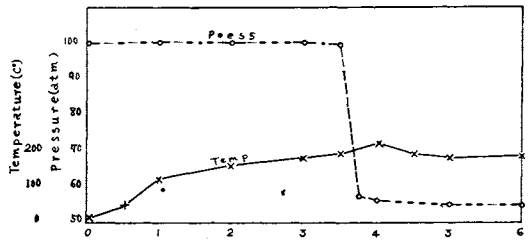


Fig. 6.

The gas in the autoclave was composed of hydrogen.

The liquid reaction product (107.0 gr.) separated from water (2.7 gr.) was fractionated carefully and the physical constants of the main fraction studied :

Fraction	B.p.	Yield (gr.)	d_4^{25}	n_D^{25}
1	Below 255°	7.3	—	—
2	255°—265°	32.5	0.9391	1.4898
3	265°—275°	51.1	0.9791	1.4962
4	Over 275°	2.0	—	—

The third fraction was a colorless liquid with a characteristic odour, showing no coloration with ferric chloride and no reaction with hydroxylamine ; the analytical results are as follows :

(1) Hönigschmidt, *Monatsh.*, **22** (1901), 568.
(2) Hirsh, *Ber.*, **23** (1890), 3710.

Subst. = 0.1056; CO_2 = 0.3028; H_2O = 0.1141 gr. Found: C = 78.2; H = 12.1
Calc. for $C_{12}H_{22}O$: C = 79.12; H = 12.09.

These results agree fairly well with those of *o*-hydroxydicyclohexyl mentioned by Wallach.[1]

The second fraction was assumed to be a mixture of *o*-hydroxydicyclohexyl ($C_{12}H_{22}O$, C = 79.1; H = 12.1) and dicyclohexyl ($C_{12}H_{22}$, C = 86.7; H = 13.3) from its physical constants and the analytical results:

Subst. = 0.1423; CO_2 = 0.4197; H_2O = 0.1692 gr. Found: C = 80.4: H = 13.3.

(2) When 100 gr. of diphenylene oxide were heated at 280° for 2 hours with hydrogen and reduced nickel under a pressure of 100 atmospheres at 0°, there was a fall of 50 atmospheric pressures, which indicated that 10.7 gr. (9 mol.) of hydrogen were absorbed.

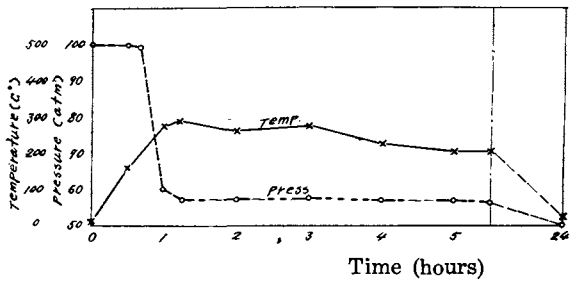


Fig. 7.

104.0 Gr. of liquid reaction product was obtained, with 7.3 gr. of water, and the former was fractionated carefully and the physical constants of each fraction studied:

Fraction	B. p.	Yield (gr.)	d_4^{25}	n_D^{25}
1	Below 237°	1.2	—	—
2	237°—240°	53.8	0.8958	1.4794
3	240°—245°	19.8	0.9049	1.4811
4	245°—250°	6.6	0.9253	1.4842
5	Over 250°	5.0	0.9485	1.4881

(1) O. Wallach, *Ber.*, **40** (1907), 70.

The 2nd fraction, which showed no reaction with a mixture of nitric and sulphuric acids, gave the following analytical results:

Subst. = 0.1378; CO_2 = 0.4342; H_2O = 0.1617 gr. Found: C = 85.9; H = 13.1.
Calc. for $C_{12}H_{22}$: C = 86.74; H = 13.26.

These experiments indicate that the fraction consisted of dicyclohexyl.

The 3rd fraction was assumed to be a mixture of dicyclohexyl and hydroxydicyclohexyl from its physical constants.

(3) When 50 gr. of diphenylene oxide were heated with hydrogen and nickel at 500° for one hour under pressure, the fall in pressure was observed to be 28.5 atmospheres. (Fig. 8).

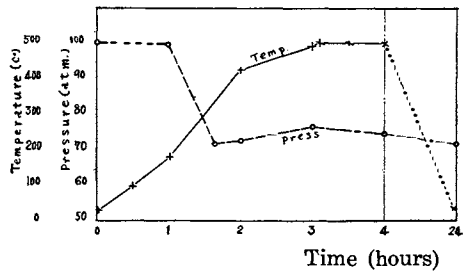


Fig. 8.

From the composition of the gas in the autoclave shown in the table, the amount of hydrogen absorbed by the reaction was calculated and found to be 7.8 gr. (13 mol.)

H_2	C_nH_{2n}	C_nH_{2n+2}	n
87.7	—	12.3	1.4

Liquid product (22.0 gr.) and water (4.8 gr.) were obtained by the reaction and the former was fractionated repeatedly and the physical constants of each fraction were studied:

Fraction	B. p.	Yield (gr.)	d_4^{15}	n_D^{15}	Remarks
1	68°—75°	8.7	0.7662	1.4226	Methyl-cyclopentane
2	78°—82°	2.5	0.7844	1.4279	Cyclohexane

Fractions 1 and 2, as their physical constants indicate, are composed of methylcyclopentane and cyclohexane respectively. Moreover, 7.4 gr. of

methyl-cyclopentane (b.p. 50—75°, $d_4^{15} = 0.7635$; $n_D^{15} = 1.4218$) were isolated from 19.6 gr. of the liquid reaction product which escaped with hydrogen gas from the autoclave when it was opened, and absorbed by active carbon.

(C) *In the presence of ferric oxide.* Diphenylene oxide (50 gr.) was heated at 500° for 5 hours with hydrogen and ferric hydroxide ignited at 350°, under pressure, and no appreciable change in the pressure was noticed, as is indicated in Fig. 9. The gas in the autoclave was composed of,

CO_2	CO	H_2	C_nH_{2n}	C_nH_{2n+2}	n
—	0.2	97.5	—	2.3	1.5

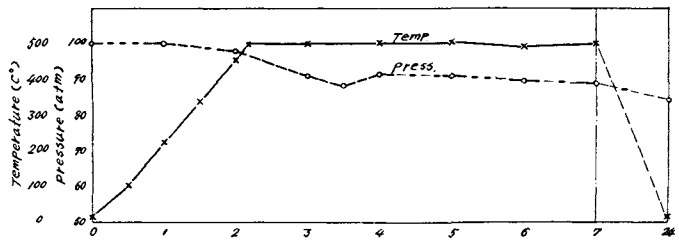


Fig. 9.

An oily reaction product (37.2 gr.) separated from water (2.7 gr.) was fractionated and the physical constants of each fraction studied:

Fraction	B.p.	Yield (gr.)	d_4^{25}	n_D^{25}	Remarks
1	75°—85°	6.5	0.8580	1.4820	Benzene
2	175°—200°	3.0	1.0335	1.5369	Phenol
3	200°—260°	3.5	—	—	—
4	260°—280°	11.0	—		Mixture of *o*-hydroxydiphenyl and diphenyl
5	280°—290°	2.0	(83°)		Diphenylene oxide

Fractions 1 and 2, as indicated by their physical constants are composed of benzene and phenol respectively, and this was confirmed by chemical methods. The 4th fraction was treated with dilute caustic alkali solution, to separate *o*-hydroxydiphenyl from diphenyl, and the former showed b.p.

283°, (760 mm), m.p. 58° after purification and a part insoluble in alkali, which melted at 70° after being purified by distillation and crystallization, was confirmed to be diphenyl.

Fraction 5 was assumed to be composed mostly of diphenylene oxide from its melting point, which showed no depression on mixing with pure diphenylene oxide.

(D) *In the presence of reduced copper.* Diphenylene oxide (50 gr.) was heated at 500° for 3 hours with hydrogen under 100 atmospheric pressures at 0°, in the presence of reduced copper (5 gr.) which had been previously prepared from copper oxide by reduction with hydrogen at 200°.

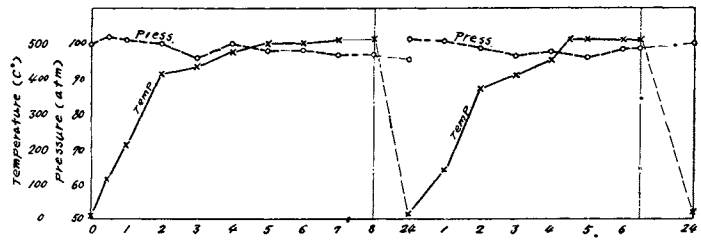


Fig. 10.

The gas in the autoclave was composed of hydrogen and saturated hydrocarbon, and the hydrogen absorbed by the reaction was calculated as 5 mols.

H	C_nH_{2n+2}	n
97.4	2.6	1.1

40 Gr. of the oily reaction product with 1.7 gr. of water were obtained, and were fractionated:

Fractions 1 and 2 were assumed by their physical constants to be composed mainly of benzene and phenol respectively.

Fraction	B.p.	Yield (gr.)	d_4^{25}	n_D^{25}	Remarks
1	75°—82°	6.8	0.8659	1.4904	Benzene phenol
2	170°—190°	3.8	1.0414	1.5428	*O*-hydroxy diphenyl
3	220°—280°	18	—	—	Diphenyl
4	Above 280°	2	—	—	Diphenylene oxide

O-hydroxydiphenyl and a small quantity of diphenyl were isolated from fraction (3).

(E) *In the presence of Japanese acid clay.* (3) Diphenylene oxide (50 gr.) was heated at 500° for 10 hours with hydrogen under pressure in the presence of Japanese acid clay (5 gr.). (Fig. 11).

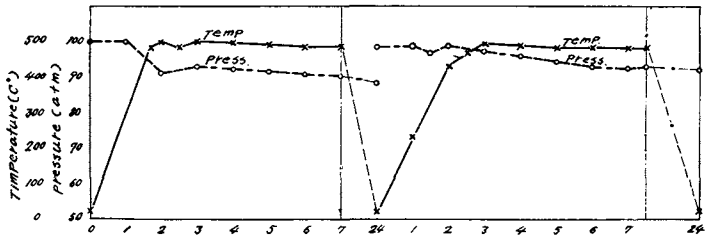


Fig. 11.

From the composition of the gases in the autoclave we learned that the loss of hydrogen was 11 mol but 6.9 gr. of saturated hydrocarbon were generated by the reaction.

	H_2	C_nH_{2n+2}	n
I	97.4	2.6	1.1
II	98.3	1.7	—

27 Gr. of an oily substance with 3.0 gr. of water were obtained by the reaction, and the former was fractionated carefully and the physical constants of each fraction studied:

Fraction	B.p.	Yield (gr.)	d_4^{25}	n_D^{25}	Remarks
1	79°—85°	7.5	0.8683	1.4925	Benzene
2	175°—185°	2.3	1.0227	1.5310	Phenol
3	260°—300°	15.0	(60°—70°)		Mixture of *o*-hydroxydiphenyl and diphenyl
4	280°—300°	2.3	(82°—83°)		Diphenylene oxide

Fractions 1 and 2, as their physical constants indicate, are composed of benzene and phenol respectively. From the 3rd fraction, *o*-hydroxydiphenyl and diphenyl were isolated, and the 4th fraction was assumed to be composed mainly of diphenylene oxide.

3. **Dinaphthylene Oxide.** α- and β-Dinaphthylene oxides were prepared[1] from the corresponding naphthol (α or β) by distillation with lead oxide, and purified by treating with alkali solution and recrystallization from hot benzene solution.

	α-Dinaphthylene oxide	β-Dinaphthylene oxide
B. p.	255°–260° (5 mm)	250°–260°–(5 mm)
M. p.	181°	155°
M.p. of picrate	173°	158.5°

(A) *α-Dinaphthylene Oxide.* (1) α-Dinaphtylene oxide (20 gr.) was heated at 500° for 3 hours with hydrogen under 100 atm. pressures at 0° and the fall in the pressure was 14 atmospheres. (Fig. 12).

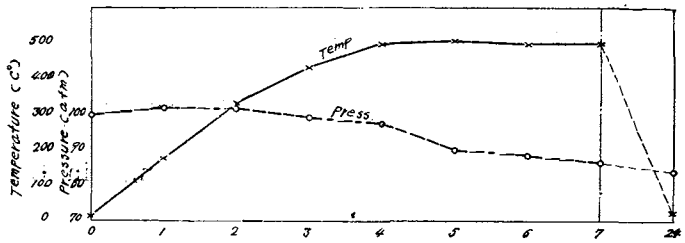


Fig. 12.

The gas in the autoclave was composed of hydrogen (89.7%) and saturated hydrocarbons (10.3% ; n=1) and the latter amounted to 3.8 gr.

Liquid product, (16.8 gr. $d_4^{25}=0.9801$; $n_D^{25}=1.5840$), was fractionated :

Fraction	B.p.	Yield (gr.)	d_4^{25}	n_D^{25}
1	80°—125°	2.7	0.8802	1.4956
2	125°—140°	0.7	0.8894	1.5080
3	180°—200°	1.0		
4	200°—250°	5.4		
5	250°—280°	0.6		
6	residue	2.8		

Fractions 1 and 2 were assumed to be composed of benzene and its homologue by their physical constants and also by the formation of nitro-compounds with a mixture of sulphuric and nitric acids, and of benzoic and phthalic acids on oxidation by potassium permanganate solution.

(1) W. Knecht u. J. Unzeitig, *Ber.* **13**, 1724; C. Graebe, Ann., **209** (1881). 132; O. Hönigschmidt, *Monatsh.*, **22** (1901), 561; O. Eckstein, *Ber.*, **38** (1905), 3661.

Fraction 3 which showed no reaction with ferric chloride solution or alkali solutions, yielded a small amount of naphthalene on distillation.

Fraction 4, on recrystallization from hot alcohol yielded white crystals melting at 80°, and was confirmed to be hydro-naphthalene by conversion into picrate melted at 149°. From the higher fraction, 0.5 gr. of white tabular crystals with a pale blue fluorescence was isolated which melted at 184° after being recrystallized from hot alcohol solution and gave an organe yellow picrate melting at 184°. It was assumed to be β·β′-dinaphthyl, and to confirm this assumption, it was analysed:

Subst. = 0.0142; CO_2 = 0.0290; H_2O = 0.0076 gr.

Found: C = 94.1; H = 5.9; Calc. for $C_{20}H_{14}$; C = 94.48; H = 5.52.

(2) *In the presence of nickel.* α-Dinaphthylene oxide (20 gr.) was heated with hydrogen at 225° for 2 hours in the presence of reduced nickel under 100 atm. pressures at 0°, no appreciable change in the substance being noticed.

(B) *β-Dinaphthylene Oxide.* (1) β-Dinaphthylene oxide (20 gr.) was heated at 500° for 3 hours under the same conditions as above, and the fall in the pressure was 18 atm. at 0° (Fig. 13).

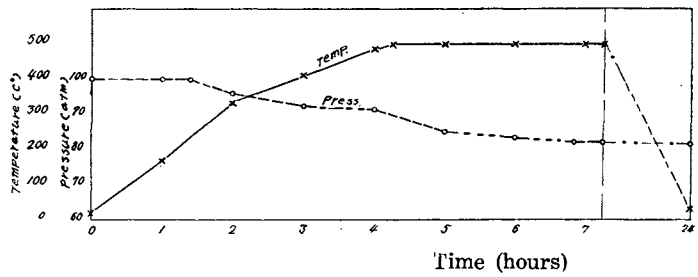


Fig. 13.

From the composition of the gases in the autoclave [hydrogen (86.3 %) and methane (13.7 %)], the amount of hydrogen absorbed and of methane produced were calculated and found to 1.6 gr. (11.5 mol.) and 4.8 gr. (4.3 mol.) respectively.

The oily reaction product (14.7 gr.) was fractionated with the following result:

Fraction	B.p.	Yield (gr.)	d_4^{25}	n_D^{25}
1	100°–150°	2.5	0.8719	1.4963
2	150°–180°	1.0	0.8894	1.5058
3	180°–200°	1.3		
4	200°–250°	4.8		
5	250°–280°	0.7		
6	120°–250° (4 mm)	2.5		
7	250°–320° (4 mm)	1.5		

The first fraction was confirmed to be composed of benzene homologues by chemical methods as in the case of the α-compound.

The amount of fractions 3 and 5 was very small, and no alkali-soluble matter was observed to occur.

Fraction 4 was confirmed to be composed of naphthalene. From fraction 6, white tabular crystals melting at 156°, identical in their properties with α-α'-dinaphthyl, were obtained and analysed:

Subst. = 0.1215; CO_2 = 0.4215; H_2O = 0.0561 gr. Found: C = 94.6; H = 5.2.
Calc. for $C_{20}H_{14}$; C = 94.48; H = 5.52.

Fraction 7, a reddish viscous liquid, yielded yellowish tabular crystals on being treated with benzene solution and then acetic acid; they melted at 247° and formed a deep brown picrate melting 250°. These facts and the colour reaction to conc. sulphuric acid indicate that the compound is identical with perylene.

(2) β-Dinaphthylene oxide (20 gr.) was heated with hydrogen in the presence of reduced nickel at 200° for 2 hours, the fall in the pressure being 11 atmospheres. (Fig. 14).

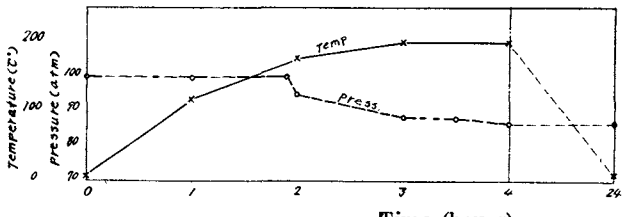


Fig. 14.

A colourless jelly-like matter which distilled out at 225°–280° (6 mm), was obtained as a reaction product. The yield was 17 gr. On analysis it gave the following results:

Subst. = 0.1106; CO_2 = 0.3509; H_2O = 0.0729 gr. Found: C = 86.52; H = 7.37.

On treating the product with hot alcohol, 5 gr. of white needle crystal melting at 140° were isolated.

Subst. = 0.1069; CO_2 = 0.3396; H_2O = 0.0708 gr. Found: C = 86.6; H = 7.4.
Calc. for $C_{20}H_{20}O$: C = 86.95; H = 7.24.

It yielded an orange yellow picrate which melted at 145.5°–146.5° (not sharp). From these results the needle crystals were assumed to be octahydrodinaphthylene oxide.

(3) When 20 gr. of β-dinaphthylene oxide were heated at 500° for one hour in the presence of reduced nickel under high pressure, the hydrogen lost and the methane generated were found, by calculation, to be 2.5 gr. (16.5 mol.) and 5.5 gr. respectively (Fig. 15), since the gaseous reaction product was composed of 87 % hydrogen and 12.3 % methane.

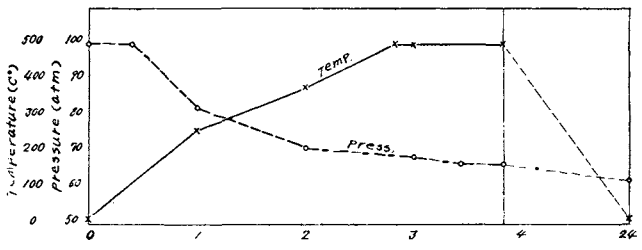


Fig. 15.

A pale yellow liquid product (13.9 gr.) was fractionated as usual, and the physical constants of each fraction studied:

Fraction	B.p.	Yield (gr.)	d_4^{25}	n_D^{25}
1	67°—90°	1.2	0.7623	1.4204
2	90°—160°	2.6	0.8246	1.4615
3	160°—190°	2.3	0.8584	1.4831
4	190°—197°	0.7	0.9074	1.5010

Fractions 1 and 2 were assumed by their physical constants to be composed of cyclohexane and its homologue, and this was confirmed by transforming them into benzene $n_D^{25}=1.4995$ and toluene $n_D^{25}=1.4955$ respectively by dehydrogenation with reduced nickel heated at 350°.

Fractions 3 and 4 were assumed to be composed of decalin and tetralin by the study of their physical constants, and also of their catalytic oxidation into naphthalene by contact with reduced nickel at 350°.

In conclusion, the writer wishes to express his gratitude to Vice-Admiral S. Kishimoto, Director of the Imperial Naval Fuel Depot, who gave him permission to publish this paper; to Engineer-Captain Viscount M. Kawase, Chief of the Scientific Research and Experimental Branch, for their kindness in enabling him to take part in this work; and also to Professor S. Komatsu of the Kyoto Imperial University, whose advice and encouragement have been invaluable.

March 1931. Naval Fuel Depot, Imperial Japanese Navy,
Tokuyama.

UNTERSUCHUNGEN ÜBER SINOMENIN.
(XXVII. MITTEILUNG.)

Ueber den Hofmannschen Abbau des Sinomenin-hydrat-dioxims.

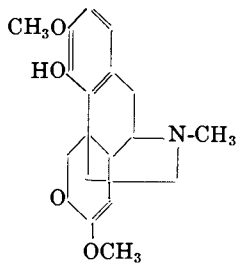
[Aus d. Chem. Laborat. d. Kitasato-Institutes].

Von **Kakuji GOTO** und **Shingo MITSUI.**

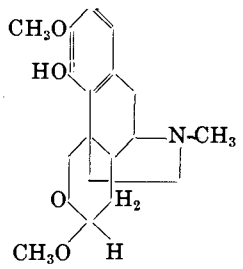
Eingegangen am 18 Mai. 1931. Ausgegeben am 28 August, 1931.

1. *Der Hofmannsche Abbau von Sinomenin-hydrat-dioxim.*

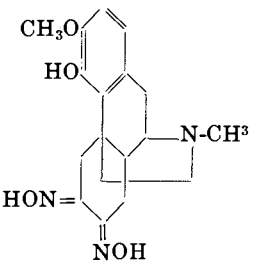
In der XII. Mitteilung[1] dieser Untersuchung hat Einer der Autoren (K. Goto) auf folgende Umwandlungen berichtet.



[I]



[II]



[III]

Kocht man nun Sinomenin-hyrat-dioxim [III] mit 16.5 Proc. Kalilauge 1 Stunde lang, so erhält man in guter Ausbeute viel sandige Krystallen, denen nach wiederholter Verreinigung und Analyse $C_{18}H_{21}O_3N_3$, eine um H_2O geringere Formel als das Dioxim zukommt. Die Erklärung ist mit grosser Wahrscheinlichkeit darin zu finden, dass dabei ein Furazankern durch Abspaltung von 1 Mol H_2O aus den beiden ortho-ständigen Isonitrosogruppen (6, 7) entsteht.

Die vorliegende Substanz sollte streng genommen Sinomenin-hydrat-dioxim-anhydrid genannt werden ; hier wollen wir aber sie der Bequemlichkeit halber einfach als Sinomeninon-furazan bezeichnen, und ihr die Formel [IV] zuschreiben.

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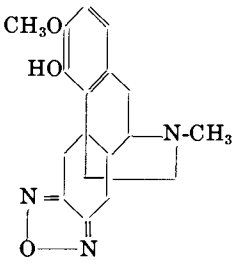
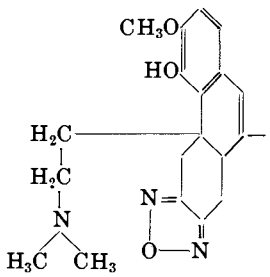
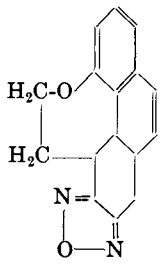
(1) K. Goto u. H. Suzuki: Dies Bull. **50** (1929), 487.



[IV]



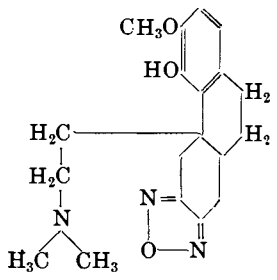
[V]



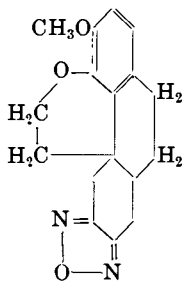
[VI]

Zum Hofmannschen Abbau von Sinomeninon-furazan zersetzt man besser das Jodmethylat von Sinomenin·hydrat·dioxim [III] direkt mit 16.5 Proc. Kalilauge. Dabei bildete sich der Furazankern unter gleichzeitiger Absprengung der C (9)–N Bindung, was sich durch elementare Analyse und Halochromieeintritt erkennen liess. Wir wollen dieses Methin als Sinomeninon·furazan·methin [od. des-N·methyl·sinomeninon·furazan] bezeichnen [V]. Sodann wurde die Substanz [V] in das Jodmethylat umgewandelt, und wieder mit 16.5 Proc. Kalilauge gekocht. Dabei entsteht Dehydro-*l*·thebenon·keton·(7)·dioxim·anhydrid, kurz Dehydro-*l*·thebenon·keton·(7)·furazan [VI] genannt, unter Abspaltung von Trimethylamin.

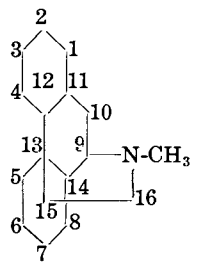
Da die Substanz [VI] in kalten Lösungsmitteln sehr schwer löslich und nicht zur katalytischen Hydrierung, geeignet war, wurde Sinomeninonfurazan [III] zunächst zu Dihydro·Sinomenion·furazan·methin [VII] reduziert, und das Jodmethylat des letzteren wurde durch Kalilauge abgebaut. Das Jodmethylat wurde dabei in *l*-Thebenon·keton·(7)·furazan [VIII] und Trimethylamin abgespalten.



[VII]



[VIII]

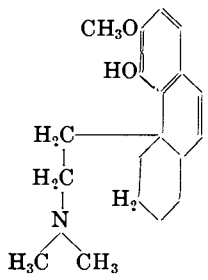


Im allgemeinen, zeigt der Furazankern gegen mehrere chemische Reagenzen eine ausserordentliche Resistenz, und es fehlt uns zurzeit ein positiver Beweiss, dass wir hier wirklich mit dem Dioxim·anhydrid tun.

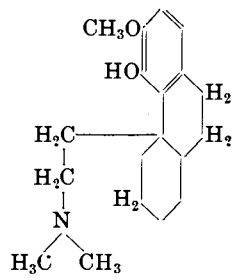
Aber die Tatsache dass das einzelne Glied dieser Furazan-reihe die vom entsprechenden Dioxim um 1 Mol H_2O geringere Formel besitzt, beweist vielleicht die Zutrefflichkeit von unserer Annahme. Was den Ätherringschluss zwischen der Seitenkette und dem Phenolhydroxyl angeht so ist er dadurch unterstützt einerseits, dass der betreffende stickstofffreie Körper keine Diazoreaktion mehr zeigt, anderseits dass in ganz analoger Weise *l*-Thebenon bzw. Dehydro-*l*-thebenon aus Demethoxy-dihydro-sinomenin ableiten liessen.

2. Thebenan

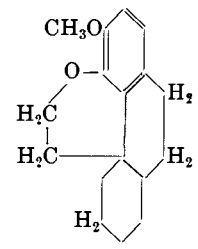
Über den Hofmannschen Abbau des Desoxo-demethoxy-dihydro-sinomenins haben wir bereits in der XXIII. Mitteilung[1] kurz berichtet. Im vorliegenden Versuche haben wir die Abbau-methode einigermassen verbessert (s. Versuchsteil), und ausserdem durch katalytische Hydrierung das Desoxo-methoxy-dihydro-sinomenin-methinin die entsprechende Dihydro-des-N-Base [X] übergeführt, deren Jodmethylat durch kochen mit Alkali in *l*-Thebenan [XI] überging.



[IX]



[X]



[XI]

3. Über die schrittweise optische Umkehrung der l-Thebenon-keton-(7)-furazan bzw. Thebenanreihe und den Drehungssinn der asymmetrischen C-Atomen im Sinomenin.

Wir haben bereits in der XXIV. Mitteilung folgende zwei Tatsachen bemerkt.

(1) Bei den Umwandlungen, Sinomenin (−) zu *l*-Thebenon (−), findet in einzelner Stufe eine regelmässige Umkehrung des Drehungssinns statt.

(1) K. Goto u. S. Mitsui: Dies Bull., **53** (1931), 106.

(2) Dagegen ist bei der Umwandlung, Demethoxy-dihydro-sinomenin-methin (−) zu Dehydro-*l*-thebenon (−), nur die Zunahme der Drehungsgrösse zu beobachten.

Dieser Umstand lässt sich leicht erklären, wenn man annimmt, dass einerseits die Doppelbindung auf das benachbarte asymmetrische C-atom exaltierend einwirkt oder dessen Drehungssinn umkehrt, und dass anderseits die asymmetrischen C-Atomen C_{13} u. C_{14} im Sinomenin in der Drehungsrichtung sich entgegengesetzt orientiert sein müssen.

Die spez. Drehungen der in (1) und (2) angeführten Verbindungen werden in folgender Tabelle zusammengefasst.

Subst.	Spez. Drehuug	Halochromie mit konz. H_2SO_4
[III]	+127.8°	Fade gelb
[IV]	+136.2°	–
[V]	+ 49.9°	Rot
[VI]	−485.2°	Gelbrot
[VII]	+ 21.9°	–
[VIII]	−120.4°	–
Demethoxy-desoxo-dihydro-sinomenin	+ 43.2°	–
[IX]	− 65.2°	–
Dehydro-thebenan	−175.7°	Fuchsin rot
[X]	− 77.9°	–
[XI]	− 3.14°	–

Wie man aus der obigen Tabelle ersieht, zeigen auch die Thebenan- bzw. Furazanreihe, mit einziger Ausnahme des Sinomeninon-furazan-methins [V], eine auffallende Analogie mit der Thebenonreihe. Nun lässt sich diese Umkehrung im Lichte der folgenden Annahmen mit Hilfe der Exaltationshypothese der Doppelbindung allein wahrscheinlichst erklären.

Annahme 1. Im Sinomenin dreht C_{13} nach rechts, während C_{14} nach links.

Annahme 2. Die Entstehung des Ätherringschlüsses drückt das Drehungsvermögen des betreffenden asymmetrischen C-atoms (C_{13}) herab, oder umkehrt, oder exaltiert das Drehungsvermögen des benachbarten C-atoms (C_{14}).

Zunächst wird die Linksdrehung des Sinomenins [I] (−73.9°) durch die exaltierende Wirkung der Doppelbindung in C_7–C_8 auf die Linksdrehung von C_{14} erklärt, weil alle Derivate des Sinomenins, in denen diese Doppelbindung aufgelöst ist, ausnahmslos nach rechts dreht.

Im Sinomenin mag also mit grosser Wahrscheinlichkeit angenommen werden,

$$C_9(+) + C_{13}(+) < C_{14}(-) + \Delta^{6,7}$$

$$C_9(+) + C_{13}(+) > C_{14}(-)$$

Zweitens muss die Linksdrehung der des-N-Base der Dihydro-sinomeninreihe einerseits durch das Verschwinden des Asymmetricität des $C_9(+)$ und anderseits durch den exaltierenden Einfluss der neu eingetretenen Doppelbindung in C_9—C_{10} auf $C_{14}(-)$ verursacht werden.

Deshalb folgt,

$$C_{13}(+) < C_{14}(-) + \Delta^{9,10}$$

Übrigens entsteht bei der katalytischen Hydrierung dieser des-N-Base, immer eine rechts-drehende Dihydro-des-N-Base.

Also $$C_{13}(+) > C_{14}(-)$$

Inzwischen drehen *l*-Thebenon bzw. *l*-The benan nach links. Dazu mag wenigstens eine oder mehrere Momente, auseinandergesetzt in der Annahme 2 in Betracht kommen, d.h. der Ätherringschluss deppressiert die Drehungskraft von $C_{13}(+)$, od. umkehrt, od. exaltiert diejenige von $C_{14}(-)$.

Die obige Betrachtung lässt sich natürlich nur in dem einfachsten Fall der Morphinalkaloide anwenden, z.B. in der Umwandlung von Sinomenin zu *l*-Thebenon u. s. w. In dem verwickelteren Fall, z.B. in Drehungssinn des einzelnen Methylmorphinmethins, scheint der optische Antagonismus selbst zwischen Morphinalkaloiden und Sinomenin teilweise verschwindet oder am wenigstens verdeckt zu sein. Unter den drei Sinomeninmethinen, scheint das Violeomethin aus seiner Darstellungsmethode, am nächsten dem β- oder δ-Methyl-morphimethin zu stehen, doch dreht das erstere stark nach rechts ebenso wie die letzteren. Der wirkliche Drehungssinn der Kohlenstoffatome C_{13} und C_{14} wird nur dann endgültig bestimmt, wenn man die zweite und dritte Kerne des Phenanthrens glücklich öffnen lässt. Bis dahin, müssen wir mit der Annahme gegnügt sein dass in Sinomenin vielleicht C_{13} nach rechts und C_{14} nach links drehen und daher in Morphinalkaloide diese zwei C-Atome im entgegengesetzten Sinne drehen müssen.

4. Einige Derivate von l-Thebenon.

Wir haben, nach der Vorschrift von Wieland und Kotake,[1] aus *l*-Thebenon die folgende vier Derivate dargestellt: *l*-Thebenon-keton,

(1) *Liebig's Ann.* **444** (1925), 91.

dessen Dioxim, Isonitroso-*l*-thebenon, und dessen Oxim. Diese vier Substanzen stimmten in ihrer Schmelzpunkten und Analysen mit den entsprechenden Derivaten von *d*-Thebenon, welche die genannten Autoren aus Thebain dargestellt haben, vollkommen überein. Also bleibt nun kein Zweifel übrig, dass das *l*-Thebenon aus Sinomenin nichts anders als der optische Antipod des *d*-Thebenons aus Thebain ist.

Beschreibung der Versuche

1. **Sinomeninon-furazan** [IV]. Das Sinomeninon-hydrat-dioxim wird mit der 10 fachen Menge 16.5 Proc. Kalilauge gekocht. Dabei scheidet sich das Furazan schon nach einer Viertelstunde sandig aus. (Diese sandigen Krystallen stellen schon das Furazan selbst, und nicht dessen Phenolate dar.) Nach 1 stündigem Kochen werden die Krystallen abgesaugt, mit Wasser gut nachgewaschen. Zur Vollständigen, Entfernung der Lauge werden sie in wenig Wasser suspensiert, und mit Kohlensäure gesättigt. Man krystallisiert sie aus wenig Methylalkohol um. Prachtvolle Prismen vom Schmelzp. 223°~5°. (Zers. 240°). Ausbeute etwa 65 Proc.

6.979 mg. Subst.: 16.949 mg. CO_2, 4.081 mg. H_2O. — 2.823 mg. Subst.: 0.302 ccm N_2 (11°, 762.7 mm.) $C_{18}H_{21}O_3N_3$ (327) Ber. C 66.06 H 6.42 N 12.84 Gef. C 66.23 H 6.49 N 12.74. Spez, Drehung. 0.6044 g Subst., 10 cm Chloroform, 1 dm-Rohr. Abgelesener Winkel +8.23°. $[\alpha]_D^{19} = +136.2°$.

2. **Sinomeninon-furazan-methin** [V]. Dies lässt sich leichter durch Abbau des Sinomenin-hydrat-dioxim-jodmethylats darstellen. Das Dioxim wird mit gleicher Menge Methyljodids in Methylalkohol 1 Stundelang gekocht. Nach dem Verdampfen des Methylalkohols krystallisiert das Jodmethylat in farblosen Prismen aus. Schmelzp. 218°~220° (Zers.)

0.0668 g Subst.: 0.0321 g. AgJ.
$C_{19}H_{26}O_4N_3J$ (487) Ber. 26.08 Gef. 25.97

Das Jodmethylat wird in derselben Weise wie 1 abgebaut. Das abgeschiedene Produkt wird aus Methylalkohol umkrystallisiert. Schöne Prismen vom Schmelzp. 226°~227°, (Zers). die mit konz. H_2SO_4 und rauch. HCl tiefrote Halochromie zeigen. Ausbeute etwa 60 Proc.

7.813 mg. Subst.: 19.187 mg. CO_2, 4.575 mg. H_2O — 5.572 mg. Subst.: 0.585 ccm N_2 (14.2°, 764 mm.)
$C_{19}H_{23}O_3N_3$ (341) Ber. C 66.80 H 6.74 N 12.32
Gef. „ 66.98 „ 6.51 „ 12.34
Spez. Drehung. 0.3318 g Subst. 25 ccm Chloroform, 1 dm-Rohr. Abgelesener Winkel +0.66°. $[\alpha]_D^{19} = +49.9°$.

3. **Dehydro-*l*-thebenon-keton-(7)furazan** [VI]. Da das Jodmethylat von Sinomeninon-furazan-methin schwer zur Krystalisation zu bringen ist, wird der vom Methyljodid völlig abgetrennte Rückstand in ganz analoger Weise wie 1 bzw. 2 abgebaut.

Während des Kochens erstarrt das zunächst abgeschiedene Öl schon zur krystallinischen Masse. Nach 20 Minuten wird die Flüssigkeit mit Kohlensäure gesättigt und abgesaugt.

Die Substanz lässt sich aus Methylalkohol in flachen Prismen umkrystallisieren, und schmilzt bei 200°. (sintern ab 197°. Das aus Eisessig umkrystallisierte Präparat zeigt auch denselben Schmelzpunkt). Ausbeute 1.2 g aus 2.5 g des-N-Base, d.h. etwa 60 Proc.

Schwer löslich in kaltem Methylalkohol und Eisessig. Löst sich in konz. H_2SO_4 und rauch. HCl mit einer schönen gelb-roten Färbung.

Beim 2 Stündigem Kochen mit 5 Proc. H_2SO_4 erhält man die unveränderte Substanz quantitativ zurück.

9.622 mg. Subst.; 24.392 mg. CO_2, 4.852 mg, H_2O. — 3.200 mg. Subst.: 0.25 ccm. N_2 (5°, 760 mm).

$C_{17}H_{16}O_3N_2$ (296) Ber. C 68.92 H 5.41 N 9.46
Gef. „ 69.14 „ 5.60 „ 9.51

Spez. Drehung. 0.3969 g. Subst., 10 ccm. Chloroform, 1 dm-Rohr. Abgelesener Winkel −19.26°. $[\alpha]_D^{19} = -485.2°$.

Der basische Antheil, der beim obigen Abbau überdestilliert worden ist, wird in verdünnter Salzsäure aufgenommen und in Goldsalz übergeführt. Aus dem Schmelzpunkt (242°~3° zers.) und dem Goldgehalt wird es als Trimethylamin erkannt.

11.760 mg. Subst.: 5.825 mg. Au.
$C_3H_9N.\ AuCl_4H$ Ber. Au. 49.42 Gef. Au 49.53.

4. **Dihydro-sinomeninon-furazan-methin** [VII]. Es ist nicht uns gelungen, Dehydro-*l*-thebenon-keton-(7)-furazan auf katalytischen Wege in *l*-Thebenon-keton-(7)-furazan überzuführen, weil das erstere weder in Alkohol noch in Eisessig lösen wollte. Deshalb hat man zunächst Sinomenion-furazan-methin zur Reduktion unterworfen und das dabei entstehende Dihydromethin abgebaut. 1.8 g. Sinomenion-furazan-methin werden in 100 ccm. 1 Proc. Essigsäure unter Zusatz von 0.05 g. $PdCl_2$ und 0.5 g. Kohle (Merck) unter Wasserstoff geschüttelt, wobei in $^1/_2$ Stunde 140 ccm. Wasserstoff (etwa die berechnete Menge) aufgenommen werden.

Die vom Palladium-Kohle abfiltrierte Lösung wird mit Soda ausgefällt. Die Fällung wird zuerst mit Äther, dann mit Chloroform extrahiert. Gesammte Ausbeute 1.4 g., d.h. über 80 Proc. Die Krystallen werden in

Methylalkohol heiss gelöst, woraus sie in farblosen Prismen auskrystallisiert. Sie färbt sich merklich braun gegen 203° und schmilzt bei 205°~207°. Löst in konz. H_2SO_4 schwach rot. (Es ist wohl zur etwa beigemengten Verunreinigung von der nicht hydrierten Base zurückzuführen).

8.488 mg. Subst.: 20.705 mg. CO_2, 5.569 mg. H_2O — 5.420 mg. Subst.: 0.552 ccm. N_2 (9.5°, 767.5 mm.)
$C_{19}H_{25}O_3N_3$ (343) Ber. C 66.47 H 7.29 N 12.24
Gef. „ 66.53 „ 7.29 „ 12.28

Spez. Drehung. 0.1050 g. Subst., 10 ccm Chloroform, 1 dm-Rohr. Abgelesener Winkel +0.23°. $[\alpha]_D^{19} = +21.9°$.

5. *l*-Thebenon-keton-(7)-furazan [VIII]. 1 g. Dihydro-sinomeninon-furazan-methin wird in 10 ccm. Methylalkohol mit 1 g. Methyljodid unter Rückfluss gekocht. Das Jodmethylat wurde sofort mit 16.5 Proc. Kalilauge gekocht. Zunächst sammelt sich ein Öl auf der Oberfläche, welches schon nach 5 Minuten in Krystallen übergeht. Man saugt die Krystallen ab, und wäscht mit viel Wasser wiederholt nach.

Zum Umkrystallisieren werden sie in 3 ccm. Eisessig gelöst, dann mit 1 ccm. Wasser ausgefällt.

Besser werden sie noch einmal durch wenig Methylalkohol gereinigt. Schmelzp. 148°. (Sintern ab 140°.) Ausbeute 0.6 g., d.h. etwa 65 Proc.

8.363 mg. Subst.: 20.935 mg. CC_2, 4.434 mg. H_2O.—3.776 mg. Subst.: 0.289 ccm. N_2 (6°, 759 mm).
$C_{17}H_{18}O_3N_2$ (298) Ber. C 68.46 H 6.04 N 9.39
Gef. „ 68.27 „ 5.89 „ 9.27

Spez. Drehung. 0.2650 g. Subst., 10 ccm Chloroform, 1 dm-Rohr. Abgelesener Winkel—3.19°. $[\alpha]_D^{19} = -120.4°$.

6. Desoxo-demothoxy-dihydro-sinomenin-methin [IX]. Über die Darstellung haben wir bereits in dies Bul. **52**, 106, (1931) mitgeteilt. Inzwischen verfährt man besser, wenn man das Jodmethylat mit 16.5 Proc. Kalilauge $1^1/_2$ Stundenlang kocht. Dabei tritt die Ausscheidung der des-N-Base schon nach 20 Minuten ein.

Ausbeute über 60 Proc. Die elementare Analyse ist in der oben genannten Berichte angegeben.

Spez. Drehung. 0.3710 g. Subst., 10 ccm Methylalkohol, 1 dm-Rohr. Abgelesener Winkel -2.42°. $[\alpha]_D^{19} = -65.2°$.

7. Dehydro-thebenan [IX]. Wir wollen den stickstofffreien Körper der in 6 geschilderten des-Base (dies Bul. **52**, 107, 1931) als Dehydro-thebenan bezeichnen.

Spez. Drehung. 0.0962 g. Subst.; 10 ccm. Methylalkohol, 1 dm-Rohr. Abgelesener Winkel -1.69°. $[\alpha]_D^{19} = -175.7°$.

Der basische Anteil wird in Goldsalz umgewandelt. Sowohl aus dem Schmelzpunkt (242°~243° zers.) als auch aus dem Au Gehalt liegt hier einwandfrei Trimethylamin vor.

3.616 mg. Subst.: 1.784 mg. Au. C_3H_9N. $AuCl_4H$ Ber. 49.41 Gef. 49.06.

8. **Demethoxy-desoxo-dihydro-sinomenin-dihydro-methin** [X]. 4 g. Desoxo-demethoxy-dihydro-sinomenin-methin werden in etwa 150 ccm. verdünter Salzsäure mit 0.1 g. $PdCl_2$ und 1 g. Kohle unter Wasserstoff geschüttelt, wobei die Aufnahme von Wasserstoff 275 ccm. (etwa die berechnete Menge) beträgt. Im Laufe der Reduktion scheidet sich schon das Chlorhydrat der hydrierten Base aus. Man isoliert in gewöhnlicher Weise das Reaktionsprodukt. Aus Äther umkrystallisiert, stellt sie wohl ausgebildete Prismen vom Schmelzp. 161° dar. Zeigt keine Halochromie mit konz. H_2SO_4 und rauch. HCl. Ausbeute ziemlich gut.

5.814 mg. Subst.: 16.025 mg. CO_2, 4,862 mg. H_2O. — 4.671 mg. Subst.: 0.177 ccm. N_2 (6°, 759 mm.)

$C_{19}H_{29}O_2N$ (303) Ber. C 75.25 H 9.57 N 4.61
Gef. „ 75.17 „ 9.29 „ 4.59

Spez. Drehung. 0.2280 g. Subst., 25 cm. Chloroform-Methylalkohol gemisch, 1 dm-Rohr. Abgelesener Winkel +0.71°. $[\alpha]_D^{19} = +77.9°$.

9. **Thebenan** [XI]. Man bereitet auf [X] auf gewöhnlichem Wege dessen Jodmethylat, und setzt das letztere zum Abbau aus.

Das dabei entwickelte Amin wird in verdünnter Salzsäure aufgenommen. Der stickstoffefreie Körper wird mit Äther extrahiert und mit verdünnter Salzsäure nachgewaschen. Nach dem Abdampfen des Äthers und längerem Stehen im Vakuum-Exikator in der Kälte erhält man grosse, lange, farblose Prismen, welche keine Halochromie mit konz. H_2SO_4 mehr zeigen. Die Substanz schmilzt schon bei Herausnahme aus dem Exikator nieder, und die Analyse wurde mit der bei 70° getrockneten Substanz ausgeführt.

6.328 mg. Subst.: 17.730 mg. CO_2, 4.863 mg. H_2O.

$C_{17}H_{22}O_2.\frac{1}{2}H_2O$ (267) Ber. C 76.41 H 8.61
Gef. „ 76.41 „ 8.54

Spez. Drehung. 0.5103 g. Subst., 10 ccm. Methylalkohol, 1 dm-Rohr. Abgelesener Winkel -0.16°. $[\alpha]_D^{17} = -3.14°$.

Die salzsaure Lösung des abgespaltenen Amins wird zum Trocknen verdampt. Das hinterbleibende Amin-chlorhydrat wird einmal durch Methyl-alkohol gereinigt und in Goldsalz übergeführt, welches sowie aus dem Schmelzpunkt (243°) als aus Analyse als Trimethylamin erkannt.

6.438 mg. Subst.: 3.179 mg. Au.
$C_3H_9N.AuCl_4H$ Ber. 49.42 Gef. 49.38

10. ***l*-Thebenon-keton.** Man bereitet diese Substanz nach der Vorschrift von Wieland und Kotake durch Chromsäureoxydation in Eisessig. Dabei verdampft man besser den Eisessig nicht, sondern man extrahiert sofort mit Essigäther aus und wäscht mit viel verdünnter Natronlauge nach. Die beim Abdunsten des Äthers schon auskrystallisierende Masse wird aus Methylalkohol umkrystallisiert. Prismen vom Schmelzp. 187°. Ausbeute beträgt etwa 50 Proc.

7.742 mg. Subst.: 20.155 mg. CO_2, 4.370 mg. H_2O
$C_{17}H_{18}O_4$ (286) Ber. C 71.33 6.29
Gef. „ 71.00 6.27

Dioxim. Das Oxim wird auch nach der Angabe der genannten Autoren dargestellt.

Beim Abdestillieren des Methylalkohols tritt das Oxim in Krystallen auf. Das aus Methylalkohol unkrystallisierte Präparat besitzt denselben Schmelzpunkt wie das von Wieland und Kotake. Erweicherung gegen 160° und Zersetzung auf 255°~260°.

2.862 mg. Subst.: 0.206 ccm. N_2 (12.5°, 750 mm.).
$C_{17}H_{20}O_4N_2$ Ber. N 8.86 Gef. N 8.38.

11. **Isonitroso-*l*-thebenon.** Wird auch nach der Vorschrift der beiden Autoren durch Einwirkung von metallischem Na und Amylnitrit in Äther bereitet. Die Ausbeute beträgt etwa 10 Proc. im besten Falle. Gelbliche Prismen vom Z.p. 165°.

4.399 mg. Subst.: 0.171 ccm. N_2 (11.5°, 769 mm.)
5.402 mg. Subst.: 0.211 ccm. N_2 (10°, 770 mm.)
$C_{17}H_{19}O_4N$ (301) Ber. N 4.65. Gef. N 4.65, N 4.71.

Dioxim. Ebenso nach Wieland und Kotake hergestellt. Aus der Methylalkoholischen Lösung krystallisiert, beim Zusatz von überschüssigen Äther, das Dioxim in Rosetten vom Z.p. 241°~242° aus.

3.002 mg. Subst.: 0.232 ccm. N_2 (19°, 758.6 mm.)
$C_{17}H_{20}O_4N_2$ (316) Ber. N 8.86 Gef. N 8.83.

DIPOLE MOMENT AND MOLECULAR ORIENTATION AT LIQUID-GAS INTERFACE.[1]

By Bun-ichi TAMAMUSHI.

Received June 2nd, 1931. Published August 28th, 1931.

This paper contains a short discussion on questions of molecular orientation at the surface of some polar liquids, treated in connection with the theory of liquid crystals.

According to the determination of total surface energies of homologous fatty acids by Hunten and Maas,[2] it is evident that the molecules of these substances are orientated parallel to each other at their surfaces, though in statistical sense, and this anisotropic structure seems to have some analogies with that of liquid crystals. The same will hold also in the case of homologous alcohols or esters.

Now, applying the theory of Langevin and Born[3] to the surface of fatty acids, alcohols and esters, the dipole moment of their molecule has been calculated by the following relation:

$$\mu^2 = \frac{9\,kMT^*}{4\pi N\rho},$$

where k means Boltzmann's constant, N Avogadro's number, M the molecular weight, ρ the density, and T^* the temperature at which the anisotropic molecular orientation would spontaneously disappear.

T^* is not known experimentally and for the present purpose, it was assumed that it can be substituted by the critical temperature of the substance. And consequently, the density was extrapolated from the measured ones to the critical point. In the following table, the calculated dipole moments are shown in comparison with those which have been determined experimentally by several authors.

The theory and the experiment are consistent in approximation, but the calculated dipole moments are found always smaller than the experimental. This reveals that the theory which takes merely the electric moment of single molecule into consideration is a rough approximation, and that to attain a better theory, we had to consider still other factors which might affect the mutual orientation of molecules. Of these factors

(1) This paper is a preliminary one. Further studies will be done.

(2) K. W. Hunten and O. Mass, *J. Amer. Chem. Soc.*, **51** (1929), 153.

(3) M. Born, *Ann. d. Phys.*, **55** (1918), 222.

Substance.	$\mu \cdot 10^{18}$ theor.	$\mu \cdot 10^{18}$ exp.
Methyl Alcohol	2.1	1.64 Debye 1.15 Ebert·Hartel 1.73 Höjendahl
Ethyl Alcohol	2.5	1.64 Debye 1.35 Ebert·Hartel 1.72 Höjendahl
Propyl Alcohol	3.0	1.66 Debye „ Höjendahl 1.48 Ebert·Hartel
Buthyl Alcohol	—	1.61 Ebert·Hartel
Acetic Acid	2.9	1.17 Ebert·Hartel 0.74 Wolf(1)
Propionic Acid	2.4	1.54 Smyth 0.63 Wolf(2)
Butylic Acid	2.7	0.68 Wolf(3)
Formic Acid Methylester	2.4	1.21 Ebert-Hartel 1.37 Smyth
Acetic Acid Ethylester	3.3	1.34 Ebert·Hartel 1.74 Williams 1.83 Wolf-Briegelb
Formic Acid Amylester	4.4	1.66 Ebert-Hartel

(1) (2) (3) These are the dipole moment of a single molecule. In benzene solution of fatty acids we measure in fact, however, the moment of a double associated molecule, which must be somewhat greater than the former one.

the following may be mentioned: (a) Geometrical form of a molecule, (b) Location of natural electric moment in a molecule, (c) Dielectric polarisation due to inner and outer molecular fields, (d) Existence of associated or polymerized molecules. Further the thermal agitation, which balances with the attractive cohesion must of course be taken in account.

Ebert and v. Hartel,(1) who have discussed the theory of Born in the very case of liquid crystals, like also to consider the problem of molecular anisotropy not so simple as it was treated by Born. Jung(2) has developed a dipole theory of fine structure of liquid surface, but his theory remains too as a first approximation by the same reason that I have mentioned above.

Thus the general theory of molecular orientation is far from completion; we can get in some cases, however, a schematic idea of definite mutual orientation of polar molecules at liquid·gas interface.

(1) L. Ebert and v. Hartel, *Physik. Z.*, **28** (1927), 786.
(2) G. Jung, *Z. physik. Chem.*, **123** (1926), 281.

Higher fatty acids or alcohols, whose molecules have their polar group at the chain end, will orientate themselves parallel to each other and will form the first bimolecular layer at the surface as schematically shown in Fig. 1. In the figure the arrow denotes the location and the direction of natural electric moment in a molecule.

In the case of any esters of symmetric form like cetylpalmitate $CH_3(CH_2)_{14}CO_2(CH_2)_{15}CH_3$ for example, the molecules will orientate themselves according to the following scheme (Fig. 2), forming the first monomolecular layer at the surface.

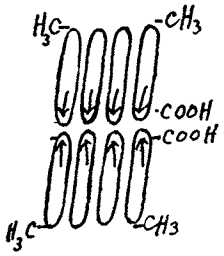


Fig. 1.

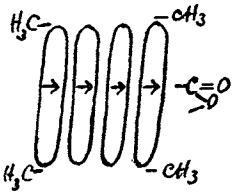


Fig. 2.

It is to be remarked that these schematic ideas are comparable with the results of röntgenographical investigations of fatty acids and esters in thin films.(1)

Lastly, with regard to the Langmuir-Adam's monomolecular layer at the adsorption surface, the theoretical treatment would be more difficult as the matter is complicated by the existence of interaction between molecules of different kinds.

June 1st.

The Musashi Higher School,
Tokyo-Nakaarai.

(1) J. J. Trillart, Activation et structure des molécules, 439, Paris 1928.

STUDIES ON THE ASYMMETRIC OXIDATION. PART II.

By Yuji SHIBATA, Yasuo TANAKA and Shiro GODA.

Received June 3rd, 1931. Published August 28th, 1931.

In the preceding preliminary note, one of the present authors (Yuji Shibata), together with Ryutaro Tsuchida, described of the experiments on the asymmetric oxidation,[1] which was accomplished by oxidising synthetic racemic 3,4-dioxy-phenylalanine with optically active *l*-diethylenediamine-monoammonio-monochloro-cobaltic bromide, [Co $\underline{en}_2 \cdot NH_3 \cdot Cl$] Br_2. In observing, time after time, the rotation changes of the solution containing the substances just mentioned, they came to the conclusion that *l*-dioxy-phenylalanine was oxidised more rapidly than its *d*-form by *l*-cobaltic complex salt.

Now we carried out an analoguous study in using *d*-catechin and *d*-and *l*-form of the same cobaltic complex salt that was employed as oxidiser in the former investigation, for the purpose of determining, if possible, the velocity constants of the oxidising reaction in two systems of (*d*-catechin + *d*-complex salt) and (*d*-catechin+*l*-complex salt). For the reason of complexity of the reaction, in which the oxidation product of catechin suffers very probably further changes such as decomposition or polymerisation, etc., we failed to calculate velocity constants desired. But, in comparing the curves obtained by tracing the successive changes of rotation angles, we could distinctly recognise that *d*-catechin is oxidised with different velocities by *d*- and *l*-complex cobaltic salts, *d*-complex showing to behave more actively than *l*-complex towards *d*-catechin.

Then we tried to carry out an experiment of the same reaction between *d*-catechin and the racemic compound of the same cobaltic complex salt, and thus we could find a very interesting fact: namely, in this case, the oxidation reaction took a course closely resembling to that of the system of (*d*-catechin + *l*-complex), as if there is none of *d*-complex salt in the solution. This somewhat curious result, however, may easily be understood, if we take into consideration the recent work of Willstätter and his collaborators on the asymmetric hydrolysis of mandelic ester by an esterase extracted from liver[2]. They found, namely, that if racemic mandelic ester is subjected to the action of the esterase, *d*-ester will be hydrolysed more

(1) This Bulletin, **4** (1929), 142; compare Y. and K. Shibata: Untersuchungen über die oxydasenartigen Wirkungen gewisser Metallkomplexsalze, *Acta Phytochimica*, **4** (1929) No. 3.

(2) *Ber.* **61** (1928), 886.

quickly than *l*-ester, but the relation is quite reversed, when the isolated *d*- and *l*-ester are separately put under the action of the hydrolytic enzyme: in this latter case, *l*-ester is hydrolysed more rapidly than *d*-ester.

These authors explained this quite unexpected result in considering as follows: the apparent velocity of an enzyme action should involve two factors, that are (1) affinity relation, which take its appearence between enzyme and substrate at first and (2) the reaction velocity proper to that system. In considering, therefore, that the affinity between *d*-ester and esterase is larger than that between *l*-ester and esterase, while the velocity of hydrolysis of *l*-ester by the same esterase surpasses that of *d*-ester, the experimental results obtained by them will readily be explained.

In adopting this theory, our experimental results on asymmetric oxidation may equally be interpreted, because if we consider that the affinity between *d*-catechin and *l*-complex salt is superior to that between *d*-catechin and *d*-complex salt, it should be expected that the oxidising effect of *l*-complex salt on *d*-catechin molecules must prevail over that of *d*-salt, when the solution contains the racemic compound.

Now then, for velocity determination of the oxidation reaction, we took the other method than rotation measurements: we observed namely the quantities of oxygen absorbed in the course of the oxidation reaction, in making use of Warburg's apparatus, which was slightly modified in its shape and dipped entirely, even its capillary manometer, in a thermonstat of 20°. In this way, we were able again to find a distinct difference in oxidation velocities of *d*-catechin respectively by *d*- and *l*-cobaltic complex salts, the results showing a good accordance with the former investigation of the measurement of rotation changes. In this case, too, we could not calculate the velocity constants for the same reason that was above described; anyhow we could here add one more example of asymmetric oxidation and establish the further analogies between the actions of natural enzymes and those of some metallic complex salts.

Experimental.

(1) Measurements of rotation changes of solutions containing *d*-catechin and respectively *d*-, *l*- and *r*-diethylene-diamine-monoammonio-monochloro-cobaltic bromide.

As was shown in our preceding investigations[1], the oxidation performed by some metallic complex salts is strongly influenced by the PH-

(1) loc. cit.

value of solutions: it will namely be accelerated by OH-ions and retarded by H-ions. In order to find, therefore, the optimum value of PH in carrying out the experiments of this sort, we have preliminarily made a series of measurements, in which the PH-value of solutions were rendered respectively 7, 7.5 and 6 by adding varying quantities of the buffer solution of $NaH_2PO_4 + NaOH$.

Table 1.

Rotation changes of the solutions containg *d*-catechin (0.6%), *d*-[Co en$_2$NH$_3$Cl] Br$_2$ (0.3%) and phosphate buffer (0.05 Mol).

PH = 6		PH = 7		PH = 7.5	
Time (hour)	Angle	Time (hour)	Angle	Time (hour)	Angle
0.0	+0.26	0.0	+0.27	0.0	+0.28
5.0	.19	0.5	.26	0.5	.25
9.0	.20	1.0	.19	1.0	.20
12.0	.20	1.5	.13	1.5	.06
22.0	.12	2.0	.08	2.0	−0.05
24.0	.09	2.5	.06	2.5	.13
26.0	.06	3.0	.05	3.0	.17
29.0	.04	4.5	−0.02	4.0	.25
34.0	.00	5.0	.02	4.5	.24
49.0	−0.01	6.0	.02	5.0	.22
54.0	+0.01	7.0	.04	5.5	.22
		8.0	.06	6.0	.20
		10.0	.08	7.0	.16
		12.0	.10	8.0	.16
		25.0	.08	10.0	.17
		30.0	.08	11.0	.14
		53.0	.02	12.0	.14
				13.0	.12
				25.0	.04
				27.0	.04
				30.0	.01
				51.0	.00

From the courses of the reactions shown by the rotation-time curves I and II, it will easily be seen that *d*-catechin in neutral or slightly alkaline solution produces at first a certain substance with laevo-rotatory power in undergoing oxidation by the cobalt complex salt and this latter product loses slowly its optical activity, while, in slightly acidic solution, it appears that the oxidation of *d*-catechin by the cobalt salt does not practically proceed, although the curve III shows that there is observed a slight decrease of dextro-rotation in the solution mixture. The following studies were, therefore, carried out always with the solutions of PH = 7.5.

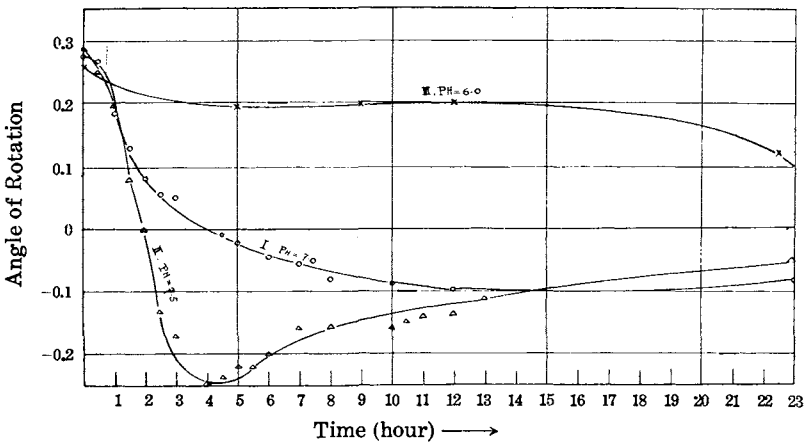


Fig. 1.

Table 2.

Rotation changes of the solutions containing *d*-catechin (0.4%) and respectively *d*-, *l*- and r- [Co $\underline{en}_2NH_3Cl]Br_2$ (0.25%) and phosphate buffer (PH = 7.5).

Time (hour)	Angles of rotation		
	d-complex	*l*-complex	*r*-complex
0.0	+0.19	−0.09	+0.04
0.5	.19	—	—
1.0	.16	.13	−0.01
1.5	.09	.19	—
2.0	.03	.25	.13
2.5	−0.03	.29	—
3.0	.06	.32	.20
3.5	.11	.34	.21
4.0	.16	.37	.23
4.5	.16	—	.24
5.0	.17	.35	.23
5.5	.18	—	—
6.0	—	.32	.21
6.5	.17	—	—
7.0	—	.29	.20
7.5	.15	—	—
8.0	—	.28	—
9.0	—	—	.18
10.0	.12	.25	.17
11.0	—	.23	.16

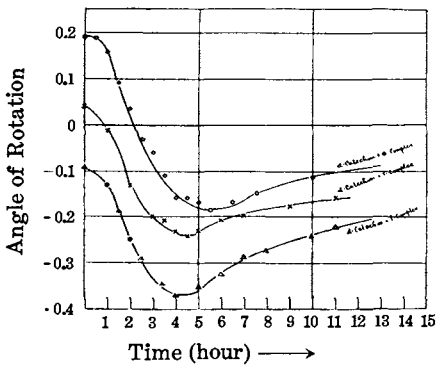


Fig. 2.

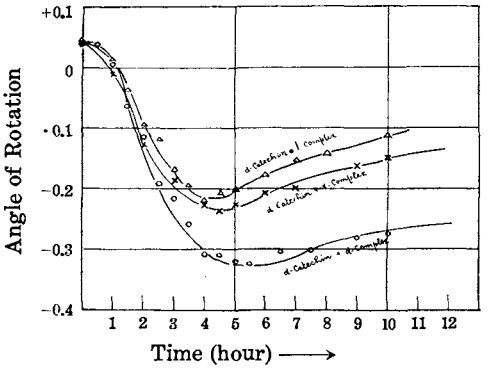


Fig. 3.

The curves shown in Fig. 2 are nothing but the graphical representation of numerical data in Table 2. In order that the amounts of the oxidation product of catechin in these three cases may be compared with readiness, we have reproduced these curves in bringing them at the same origin (Fig. 3). It must only be taken in mind that, if optical activities of *d*- and *l*-complex salts remain constant throughout the reaction, the curves in Fig. 3 may be taken for comparison just as it is; but, in fact, the complex salts used as oxidiser somewhat decompose in the course of reaction, instead of behaving normally as catalyser. Therefore, when it concerns to the true amounts of rotation of the oxidation products, the curves for *d*- and *l*- complex salts should be a little drawn near to each other. At any rate, it will be clear enough to be noticed that the oxidation of *d*-catechin by *d*- and *l*-cobalt complex salts takes place asymmetrically. Further it will readily be recognised that the course of the oxidation of *d*- catechin by *r*-complex salt remarkably accesses to that of the system of (*d*- catechin + *l*-complex), instead of taking its way at the middle position of the other two. With regard to this latter fact, we have already discussed in the introductory part.

(2) Measurement of the oxygen quantities absorbed by the solutions containing *d*-catechin+*d*- [Co $\underline{en}_2NH_3Cl]Br_2$ and *d*-catechin+*l*- [Co $\underline{en}_2NH_3Cl]Br_2$.

In the measurements of the pressure depression in the Warburg's apparatus, that indicates the quantities of oxygen absorbed in the course of an oxidation reaction, if its capillary manometer will be put outside the

thermostat, the pressure-time curve, which represents the reaction course, takes a zigzag shaped path. If the whole apparatus, however, is dipped in the thermostat, as is the case in our actual experiment, the results become well concordant and reproduceable, giving always smooth curves.

We have carried out the measurements with three apparatus of different capacities, catechin solution being put in a main bulb, complex salt solution in a side bulb and alkali liquor* in a small cylinder which is fused at the middle position of the bottom of the main bulb. Their volumes were as follows :

No. 1, solution= 5.0 c.c.; air=ca. 43 c.c.; alkali liquor=2 c.c.

No. 2, solution= 5.0 c.c.; air=ca. 38 c.c.; alkali liquor=2 c.c.

No. 3, solution=10.0 c.c.; air=ca. 97 c.c.; alkali liquor=1 c.c.

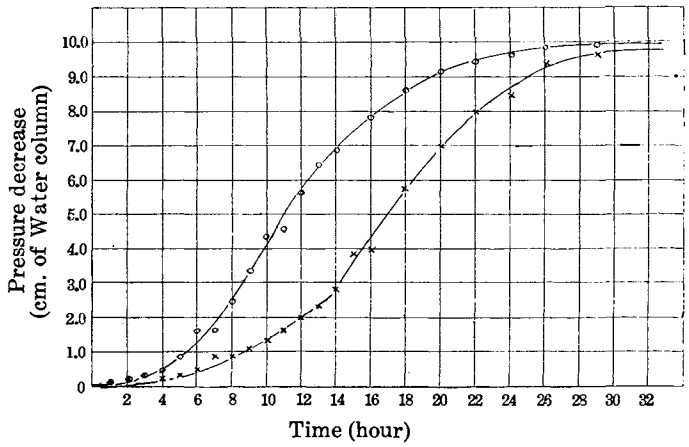
In Table 3 and Fig. 4, we mentioned only the result of determination executed with the apparatus No. 2, because the other results were so similar with this that they are not here worth noting.

Table 3.

(Temp. = 20°C)

Time (hour)	Press. depression (cm. of water column)		Time (hour)	Press. depression (cm. of water column)	
	d-complex	*l*-complex		*d*-complex	*l*-complex
0	0.00	0.00	11	4.60	1.72
1	0.08	0.06	12	5.66	2.01
2	0.10	0.06	13	6.50	2.32
3	0.27	0.28	14	6.99	2.75
4	0.41	0.33	16	7.93	3.95
5	0.90	0.31	18	8.60	5.91
6	1.57	0.42	20	9.20	7.00
7	1.60	0.90	22	9.39	8.01
8	2.51	0.91	24	9.60	8.40
9	3.42	1.22	26	9.81	9.58
10	4.41	1.35	29	9.92	9.60

* This concentrated alkali solution is provided for the purpose of absorption of CO_2 produced in the course of oxidation of catechin.



○ *d*-catechin+*d*-complex salt.
× *d*-catechin+*l*-complex salt.

Fig. 4.

Two curves in the above Figure indicate distinctly again that the velocity with which *d*-catechin is oxidised by *d*-cobaltic complex salt is larger than that by *l*-complex salt.

Summary.

The catalytic oxidation of *d*-catechin by *d*- and *l*- [Co en$_2$NH$_3$Cl] Br$_2$ was studied. The course of these oxidation reactions were observed in two different ways: one of the methods was the measurements of rotation changes of solutions containing *d*-catechin and *d*- or *l*-cobaltic complex salt, and the other was the determinations of oxygen quantities absorbed by those solutions during the oxidation reactions. In both cases we could confirm that the oxidation takes place always asymmetrically, *d*-complex salt oxidising *d*-catechin more rapidly than *l*-complex salt.

Further we studied the oxidation of *d*-catechin by racemic [Co en$_2$NH$_3$Cl] Br$_2$ and could confirm that the oxidation in this case goes on very similarly with the system of (*d*-catechin+*l*-complex salt), instead of taking an average course of those shown respectively by *d*- and *l*-complex salts. Concerning to the cause of this result, it was discussed from the point of view of natural enzyme actions.

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THE ACTION OF LIGHT ON CATALYTIC OXIDATION BY SOME METALLIC COMPLEX SALTS.

(Preliminary Note)

By Yuji SHIBATA and Shiro GODA.

Received June 3rd, 1931. Published August 28th, 1931.

Since some ten years, Yuji Shibata, Keita Shibata and their collaborators have published a series of papers on the investigations of an enzyme-like oxidising action shown by some metallic complex salts.[1] In studying this interesting reaction from various sides, especially from the investigations of its chemical kinetics, they came to a conclusion that the oxidation just mentioned must be produced by activated water-molecules and the role of complex salt added appears to be of rendering water-molecules catalytically active.

The present experiment has been carried out to study the influence of light energies on this catalytic oxidation, for the purpose of ascertaining what region of light spectrum will be effective to promote this reaction, that is to say, is it either the light which is absorbed by the complex salt used as oxidiser, or the light of longer wave-lengths which is absorbed by water-molecules? In this preliminary work, we used, as colour filters, plates of ordinary window glass (opaque for the ultra-violet light of wave-lengths shorter than $\lambda = 3300$ Å), ruby glass (transparent for light of wave lengths longer than $\lambda = 5900$ Å), green glass (transparent between $\lambda = 5860$ Å $-$ 3250 Å), and finally 20% copper sulphate solution of 12 m.m. layer.

The reaction bulb of Warburg's apparatus which was used in our recent investigation of asymmetric oxidation[2] was illuminated by a Mazda-lamp of 100 W., in putting the colour filter between the light source and the reaction bulb. In this way, *d*-catechin was oxidised by racemic [Co $en_2NH_3Cl]Br_2$ and the pressure-depression (namely oxygen obsorption) in the apparatus was recorded time after time; the curves thus obtained are given in Fig. 2. As will easily be seen in these curves, the reaction velocity under green light is distinctly inferiour to those under red and white lights.

(1) Y. Shibata und K. Shibata: Untersuchungen über die oxydasenartigen Wirkungen gewisser Metallkomplexsalze; *Acta Phytochimica*, **4** (1929), 363. Compare also Y. Shibata and R. Tsuchida; Studies on Asymmetric Oxidation; This Bulletin, **4** (1929), 142 and **6** (1931), 210. The references of papers on this subject which have been published in the Japanese language on the Journal of the Chemical Society of the Japan since 1920 are fully given in the papers just mentioned.

(2) Y. Shibata and S. Goda: Studies on asymmetric Oxidation. Part II., loc. cit.

On the other hand, we have observed the absorption spectrum of the solution of diethylenediamine·monoammonio·monochloro·cobaltic bromide and confirmed that the solution shows two absorption bands at $\lambda = 5000$ Å and $\lambda = 3640$ Å[1], both of which are just contained in the spectrum region transmitted by the green filter, while the red filter entirely absorbs that part of spectrum, where stand these two bands. From these results it may surely be insisted that excited molecules of water (under red and white lights) are more effective than equally excited molecules of the complex salt (under green light) for promotion of oxidation of *d*·catechin*. Then we carried out another experiment in making use of 20% $CuSO_4$·solution (liquid layer =12 m.m.) as the filter, because it is well known that this solution absorbs almost completely the infra·red and red part of spectrum, transmitting all other rays of shorter wave·lengths than yellow.

The pressure·time curve obtained under the $CuSO_4$·filter coincides very well with that under the green filter, or, in the other words, the light which lacks the infra·red and red parts in its spectrum is always less effective for promotion of this reaction than the light containing the infra·red and red rays.** Thus we are now convinced that our earlier explanation on this oxidation reaction was quite correct: namely it deals with the action of activated water·molecules and the reaction may perhaps be represented by the following scheme:

$$R + 2\,H\cdot OH + \frac{1}{2}O_2 = R(OH)_2 + H_2O$$

or further

$$R(OH)_2 = RO + H_2O$$

The ordinary associated molecules of water will be activated (very probably dissociated into monomolecular state) in coming to contact with some metallic complex salts which are endowed with this nature. Only the mechanism of this latter action is not yet quite clear.

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(1) Compare Y. Shibata: Recherches sur les spectres d'absorption des ammine-complexes metalliqes, I, *Jonrn. Coll. Scien. Imp. Univ., Tokio,* **37** (1915), Art. 2.

* The absorption spectrum of catechin has been studied by T. Tasaki *Acta Phytochimica,* **3** (1927), and it was found that the dilute solution of this substance shows an absorption band at $\lambda = 278$ Å. Therefore, in the present case, where an ordinary electric lamp is applied as the light source, the excitation of catecin-molecules is out of question.

** Transparency of ordinary glass for infra·red rays of comparatively short wavelengths was proved by W. Coblentz: Investigation of Infra·red spectra, Part III, p. 65.

Experimental.

(1) Absorption spectrum of Diethylenediamine - monoammonio - monochloro-cobaltic bromide. 1/100 Mol. aqueous solution of the cobaltic complex salt was prepared and its absorption spectrum was photographed in using a quartz spectrograph of Adam-Hilger; the absorption curve was then made according to the Hartley-Baly system. As was mentioned in Fig. 1, it contains two wide bands at $\lambda = 5000$ Å and $\lambda = 3640$ Å, both of which lie in the spectrum region transmitted by the green filter.

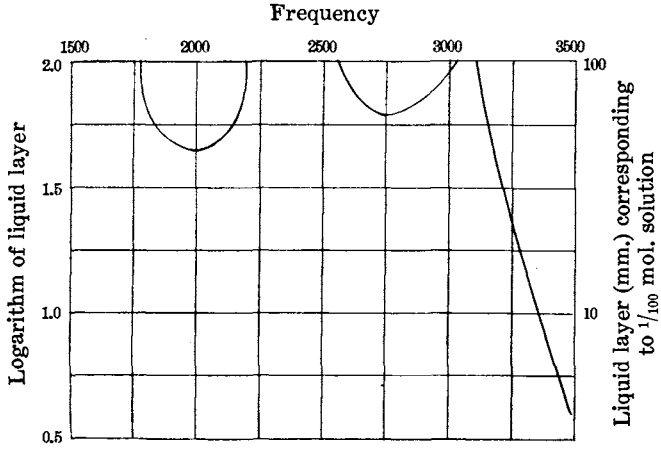

Fig. 1. Absorption curve of [Co en$_2$ NH$_3$Cl] Br$_2$

(2) Oxidation of catechin by [Co en$_2$ NH$_3$Cl] Br$_2$ under various colour filters. The procedure of this experiment and the apparatus used were quite the same as in the case of our recent investigation on asymmetric oxidation[1]: catechin (1/250 mol solution) was mixed with the complex salt (1/500 mol solution) in the presence of the phosphate buffer (PH = 7.5) in the reaction bulb of Warburg's apparatus. The pressure depressions in the course of each reaction were given in Table 1.

Table 1.

Time (hour)	Colourless filter	Ruby glass	Green glass	$CuSO_4$-Sol.
0	0.00	0.00	0.00	0.00
1	0.10	0.08	0.81	0.49
2	0.20	0.09	−0.61	−0.30
3	0.65	0.31	−0.31	−0.35
4	0.98	0.87	+0.09	+0.13

(1) Loc. cit.

Table 1.—(*Concluded*)

Time (hour)	Colourless filter	Ruby glass	Green glass	$CuSO_4$-Sol.
5	1.59	1.68	0.39	0.50
6	2.06	2.21	0.93	1.22
7	2.82	3.10	1.13	1.78
8	3.70	3.91	1.88	2.50
9	4.94	4.89	2.63	3.01
10	5.43	5.56	2.97	3.81
11	6.30	—	4.06	—
12	6.84	6.57	4.64	—
13	6.87	6.90	5.62	5.21
14	7.94	7.34	6.16	5.89
17	8.39	8.21	7.39	6.89
19	8.55	8.70	7.84	7.35
20	8.78	9.04	7.89	7.75
21	9.03	9.04	8.25	7.93
22	9.36	9.27	8.51	8.21
23	9.44	9.51	8.73	—
25	9.36	9.70	8.90	—

△ Colourless glass plate
○ Ruby glass plate
□ $CuSO_4$ solution (20%, 12 mm.)
× Green glass plate

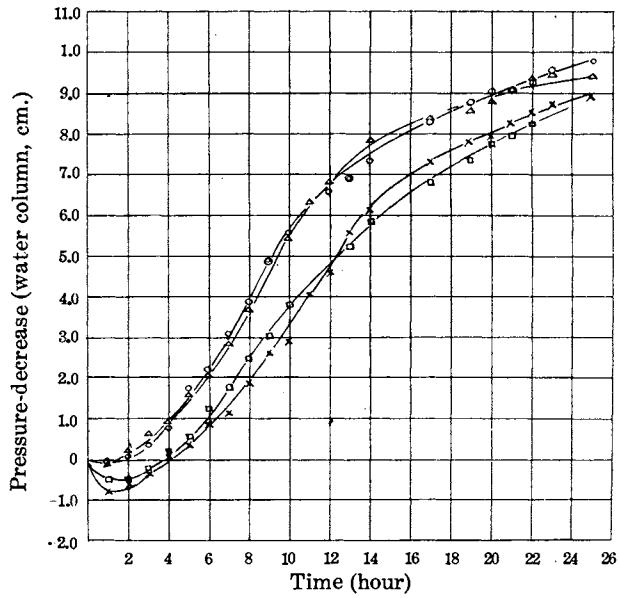

Fig. 2.

In the experiments above described, we observed, at the earlier stages of the oxidation reaction, slight increases of pressure in the apparatus; this inexplicable phenomanon has never been observed in our recent studies on asymmetric oxidation and will be left to later investigation.

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ÜBER DIE CAROTINOIDE VON CUCURBITA.

I. DIE PIGMENTE DER FRUCHT VON *CUCURBITA MAXIMA*, DUCH.

Von **Harusada SUGINOME** und **Kiyoshi UENO.**

Eingegangen am 11 Juni, 1931. Ausgegeben am 28 August, 1931.

Im Jahr 1885 hat Arnaud[1] einen kristallisierten Chlorophyllbegleiter untersucht und gefunden, dass dieser wahrscheinlich mit dem Farbstoff der Möhre (*Daucus carota*) und *Cucurbita pepo*, dem Carotin, identisch ist. Darüber gibt es aber keine ausführliche Beschreibung. Bisher untersuchten weder Chemiker noch Botaniker das Pigment im Fleisch von *Cucurbita*, als erster hat Ansai[2] Carotinosis, eine gelbe* Färbung der Haut, die durch das Essen von *Cucurbita* verursacht wird, darauf zurückgeführt, dass der gelbe Farbstoff durch die Schweiss-drüse ausgeschieden wird. Als Ausgangsmaterial hatte Genannter einen Extrakt benutzt, der durch Behandlung der Frucht von *Cucurbita maxima* mit Petroläther erhalten wurde. Die Isolierung der Farbstoffe im kristallisierten Zustande gelang bisher noch nicht.

Im folgenden sei über die Isolierung und über die Eigenschaften der Pigmente berichtet:

Die zerhackte Frucht wurde mit Aceton extrahiert und der mit diesem Extrakte ausgeführte Entmischungs-Versuch nach Sorby-Kraus-Willstätter ergab, dass die Frucht von *Cucurbita maxima* wenigstens ein sauerstoffreies und daneben ein sauerstoffhaltiges Pigment enthält. Da sie mit keinem der bekannten, wohldefinierten Carotinoiden des Pflanzenreichs übereinstimmen, geben wir ihnen die Namen Cucurbiten und Cucurbitaxanthin.

Neuerdings haben Kuhn, Winterstein und Kaufmann,[3] Zechmeister und Cholnoky,[4] zu gleicher Zeit und unabhängig, ein verestertes Carotinoid, Physalien, aus der Judenkirsche und der Bocksdornbeere gefunden.

Aus *Cucurbita maxima* wurde noch kein verestertes Carotinoid isoliert aber durch Behandlung der Mutterlauge des Cucurbitens mit methylalkoholischem Kali Palmitinsäure gewonnen. Es ist allerdings fraglich, ob die Palmitinsäure aus einem Farbstoff oder aus einem Begleitstoff der Carotinoide, wie Phytosterin, kommt.

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(1) *Compt. rend.*, **100** (1885), 751.

(2) *Japanese Journal of Medical Sciences.* V. Pathology, **1** (1928), 175.

* In Hokkaido sieht man oft Carotinosis der Bauern, welche dort in Herbst *Cucurbita maxima* zu essen pflegen.

(3) *Ber.*, **63** (1930), 1489.

(4) *Ann.*, **481** (1930), 42.

Cucurbiten kristallisiert aus Petroläther in dunkelbraun gefärbten rhombischen glänzenden Täfelchen mit starkem Pleochroismus. In der Durchsicht sind die Kristalle dunkelrot. Der Schmelzpunkt liegt bei 179–180° (unkorr.). 10 Kg. frische Frucht lieferten 0.18 g. reines Cucurbiten. Die Ausbeute an dem Farbstoff ist abhängig von der Reife der Frucht. Die Elementaranalyse ergibt als Bruttoformel des Cucurbitens $C_{40}H_{56}$. In Benzin ist es löslich, in Alkohol aber sehr wenig. In konzentrierte Schwefelsäure löst sich das Cucurbiten wie Carotin mit tiefindigoblauer Farbe. Auch die anderen Farbenreaktionen, mit Ausnahme jener mit Ameisensäure, erinnern an Carotin. Für den direkten Vergleich diente Carotin, welches aus *Daucus carota* gewonnen worden war.

Herr Prof. G. Nakamura hatte die Güte, die Absorptionskurven des von uns erhaltenen Cucurbitens und Carotins zu vergleichen im Versuchsteil sind diese wiedergegeben. Beide Absorptionskurven stehen zwar sehr nahe, aber jene des Carotins ist etwas nach rot verschoben.

Neuestens haben Karrer[1] und seine Mitarbeiter die Einheitlichkeit des Carotins bezweifelt, nachdem es ihnen gelungen ist, den Schmelzpunkt durch häufiges Umkristallisieren aus Petroläther auf 181–182° zu steigern. Die genannten Verfasser nahmen an, dass Carotin nach Willstätter und seinen Mitarbeitern[2] ein Gemisch aus α- und β-Carotin ist. Nach ihrer Beschreibung scheint β-Carotin noch nicht ganz rein dargestellt worden zu sein und sie vermuteten, dass β-Carotin in reinem Zustand optisch inaktiv sei. Doch steht Cucurbiten, so weit es den Schmelzpunkt betrifft, sehr nahe dem β-Carotin.

Der zweite Nebenfarbstoff in der Frucht von *Cucurbita maxima*, für den wir den Nahmen Cucurbitaxanthin vorschlagen, wurde mit einem Mengenverhältnis 1.6 : 1.0 (zugunsten des Cucurbitens) isoliert. Dieser Farbstoff ist unlöslich in Petroläther, wohl aber löslich in Methyl- und Aethylalkohol, Schwefelkohlenstoff und Chloroform. Aus Methanol kristallisiert es in ziegelroten körnigen Kristallen mit Metallglanz. Die Kristalle sind in der Durchsicht dunkelgelb. Der Schmelzpunkt liegt bei 180° (unkorr.) Cucurbitaxanthin besitzt die Zusammensetzung $C_{40}H_{56}O_2$ und gehört somit in die Gruppe der Xanthophylle. Es ist optisch aktiv, und zwar rechtsdrehend: $[\alpha]_C^{20°} = +105°$ (in Chloroform).

Bezüglich der Konstitution des Cucurbitens und Cucurbitaxanthins sind Untersuchungen im Gange.

(1) P. Karrer, *Z. angew. Chem.*, **42** (1929), 923: H. v. Euler, P. Karrer und M. Rydbom, Ber., **62** (1929), 2447; P. Karrer, A. Helfenstein, H. Wehrli, Ber., Pieper und R. Marf, *Helv.*, **14** (1931), 614.

(2) R. Willstätter und W. Mieg, *Ann.*, **335** (1907), 1; H. H. Escher, Dissertation Zurich. Polytechnikum (1909); R. Willstätter und H. H. Escher, *Z. Physiol. Chem.*, **64** (1910), 47.

Experimenteller Teil.

Isolierung der Farbstoffe. Als Ausgangsmaterial standen 130 Früchte von *Cucurbita maxima* zur Verfügung, die im letzten Herbst in der hiesigen Universitätsfarm gesammelt worden waren. Den Herrn G. Misonoo und K. Shirahama sind wir für ihre freundlichen Bemühungen zu grossem Dank verpflichtet.

12.5 Kg. Fruchtfleisch, frei von Chlorophyll, wurden durch die Hackmaschine getrieben und 24 Stunden lang unter 10 l. Aceton stehen gelassen, und dann abgesaugt. Die Extraktion wurde noch viermal wiederholt. Das Lösungsmittel wurde unter Stickstoff bei vermindertem Druck und bei 30–40° derart abdestilliert, dass von ihm nur sehr wenig zurückblieb, um so die nächste Operation zu erleichtern. Der etwas acetonhaltige rotbraune Rückstand wurde in Petroläther (Sdp. bis 60°) aufgenommen. Nach dem Trocken über Natriumsulfat wurde unter Stickstoff bei vermindertem Druck der Petroläther abdestilliert. Der rotbraune zähe Rückstand wog 21.5 g. Dieser Rückstand wurde wieder mit 800 ccm. Petroläther behandelt, wodurch unlösliche rotbraune körnige Kristalle von Cucurbitaxanthin abgetrennt wurden. Die Ausbeute an diesem betrug 0.14 g. Die tief gefärbte Petrolätherlösung wurde mit 80% igem Methanol entmischt, dann über Natriumsulfat getrocknet. Durch Abdestillation unter Stickstoff im Vakuum gewinnt man einen rotbraunen Kristallbrei, der 20.0 g. wog. Bei der Aufbewahrung in der Kälte (–15°) vermehrten sich die metallglänzenden Kristalle, welche mit Hilfe von wenig Petroläther rasch abgesaugt wurden. Um den farblosen Begleiter zu lösen, wurde mit kaltem Lösungsmittel gewaschen. Die Ausbeute betrug 0.23 g. Dieses rohe Cucurbiten wurde mit Petroläther umgelöst. Schmp. 178.5–179.5°. Nach noch zweimaliger Umkristallisation zeigte die Substanz einen konstanten Schmelzpunkt: 179–180°. Da der Schmelzpunkt etwas abhängig von der Art des Erhitzens ist, führten wir das Schmelzpunktröhrchen in das bis 165° vorerwärmte Bad ein.

Cucurbiten, in solcher Weise gewonnen, ist löslich in Petroläther, Aceton, Chloroform und Schwefelkohlenstoff, schwer löslich in Alkohol. Die petrolätherische Lösung ist weinrot, wenn sie konzentriert ist, aber in der Verdünnung orangegelb.

Anal: Subst. = 4,154, 4,200, 4,342; CO_2 = 13.615, 13,772, 14,199; H_2O = 3,954, 4,045, 4,138 mg. Gef.: C = 89.39, 89.43, 89.19; H = 10.65, 10.78, 10.66%. Ber. für $C_{40}H_{56}$: C = 89.48; H = 10.52%.

Die Analyse wurde von Herrn K. Saito ausgeführt, wofür wir ihm auch an dieser Stelle unseren besten Dank aussprechen.

Darstellung des Carotins. Nach Kohl[1] und Euler und Nordensen[2] wurden 50 kg. Möhren in dünnen Scheiben zerschnitten und drei Stunden lang in Wasser gekocht und gut abgepresst; der Presskuchen wurde mit Sand verrieben und in dünner Schicht auf Blechen bei 50° getrocknet. Das trockene Material wurde mit Petroläther (Sdp. bis 50°) perkoliert und eingedampft. Es blieb ein rotbrauner Kristallbrei zurück. Nach der Aufbewahrung in der Kälte wurde dieser abgesaugt. Zur Reinigung wurden die Kristalle in Petroläther unter Rückflusskühlung gelöst, hierbei blieben wenige schwerlösliche rotbraune Kristalle, die bei ca. 178-180° schmolzen. Beim Erkalten der Lösung scheidet sich wohl Carotin als auch ein farbloser Begleiter aus.

Um den Begleiter zu trennen, saugt man nur die rotbraunen leichten Täfelchen, die in der Lösung suspendiert sind, ab, während, farblose rhombische dipyramidale schwere Kristalle am Boden bleiben, welche bei 117–118° schmelzen. Carotin in solcher Weise dargestellt, zeigt einen Schmp. 167–168° (unkorr.), bei 165° tritt aber leichte Sinterung ein. Ausbeute 0.9 g.

Nach noch dreimaligem Umkristallisieren aus demselben Lösungsmittel schmiltzt das Carotin bei 170–171° (unkorr.). Bestimmt man mit einem abgekürzten Normalthermometer in einem bis 165° vorerwärmten Bad, so liegt der Schmelzpunkt bei 173–174° wie schon Escher[3] feststellte. Zur Sicherheit kristallisierten wir das oben erwähnte Präparat nochmals aus Schwefelkohlenstoff-Alkohol um, das Carotin zeigte aber denselben Schmelzpunkt.

Die Analyse (K. Saito) des Farbstoffes ergab:

Subst.=4.247, 4.409, 4,370; CO_2=13.904, 14.496, 14.308; H_2O=4,144, 4,246, 4,236 mg. Gef.: C=89,48, 89,67, 89.30; H=10.92, 10.77, 10.85%. Ber. für $C_{40}H_{56}$: C=89.48; H=10 52%.

Aus dem Filtrat wurde ein farbloser Begleiter, in Nadeln kristallisiert, isoliert, dessen Schmelzpunkt bei 118-119° liegt.

Vergleich des Cucurbitens mit Carotin. Cucurbiten kristallisiert in rhombischen Täfelchen, während Carotin unter denselben Bedingungen in Rhomboedern kristallisiert. In der Durchsicht ist Cucurbiten dunkelrot, Carotin orangerot. Der Schmelzpunkt des Cucurbitens ist um ca. 10° höher als derselbe des Carotins. Die Analysenresultate der beiden Farbstoffe liegen innerhalb der Fehlergrenze. Gegen Luftsauerstoff ist Cucurbiten viel beständier als Carotin.

(1) Untersuchungen über das Carotin und seine physiologische Bedeutung in den Pflanzen.
(2) *Z. Physiol. Chem.*, **56** (1908), 223.
(3) *Z. Physiol. Chem.*, **83**, (1913) 206.

Farben-Reaktionen.[1] Alle Versuche mit Cucurbiten und Carotin sind unter genau denselben Bedingungen ausgeführt worden.

Eisenchlorid in Palmöl[2] (je 1 mg. Substanz in 1 g. Palmöl mit einigen Körnchen Eisenchlorid).

Cucurbiten: bläulichgrün.
Carotin: bläulichgrün (etwas rascher).

Konz. Schwefelsäure (je 1 mg. Substanz in 2 ccm).

Cucurbiten: blau, nach 24 Stdn., braunschwarz.
Carotin: blau, nach 24 Stdn., braunschwarz.

Ameisensäure (je 1 mg. Substanz mit 2 ccm. Kahlbaumscher Ameisensäure).

Cucurbiten: In der Kälte keine Reaktion, nach ca. 5 Minuten langem Kochen und kurzem Stehen: grüne Lösung → dunkelblau. (sehr beständig).
Carotin: In der Kälte keine Reaktion, nach ca. 5 Minuten langem und kurzem Stehen: rotbraune Lösung.

Dichloressigsäure (je 1 mg. Substanz in 0.5 ccm. Säure).

Cucurbiten: dunkelblau → blauschwarz.
Carotin: braun → braunschwarz → blauschwarz (rascher).

Konz. Schwefelsäure + Chloroform (je 0.5 ccm. gesättigte Chloroformlösung + 0.3 ccm. konz. Schwefelsäure).

Cucurbiten: Schwefelsäure indigoblau, Chloroform dunkelbraun.
Carotin: Schwefelsäure indigoblau, Chloroform braunschwarz.

Essigsäureanhydrid (je 0.5 ccm. gesättigte Chloroformlösung + 2 Tropfen Essigsäureanhydrid + 5 Tropfen konz. Schwefelsäure).

Cucurbiten: Schwefelsäure kobaltblau → blau → fast farblos.
Chloroform → grünblau.
Carotin: Schwefelsäure blauschwarz → indigoblau.

Rauchende Salpetersäure + Chloroform (je 1 ccm. gesättigte Chloroformlösung + 1 Tropfen Salpetersäure $d = 1.52$).

Cucurbiten: blau → blaugrün → gelblichbraun.
Carotin: blau → blaugrün → gelblichbraun.

Trichloressigsäure + Chloroform (je 1 mg. Substanz + 0.3 g. Säure + 0.5 ccm. Chloroform).

Cucurbiten: blau → braunschwarz → blauschwarz.
Carotin: blau → braunschwarz → blauschwarz.

Absorptionskurve I: Carotin in Alkohol (1:20000)
Absorptionskurve II: Cucurbiten in Alkohol (1:20000)

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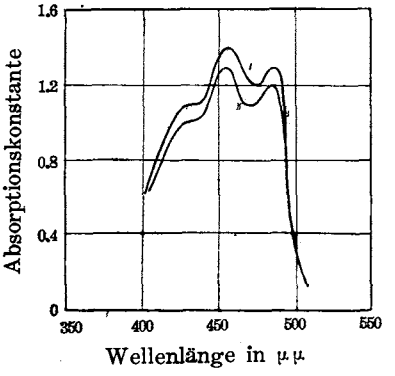
(1) Vgl.: R. Kuhn, A. Winterstein und W. Wiegand, *Helv.*, **11** (1928), 723.
(2) L. S. Palmer and W. E. Thrun: *J. Ind. Eng. Chem.*, **8** (1916), 614.



Optische Schwerpunkte des Cucurbitens:

$$487\mu\mu,\ 452\mu\mu,\ \text{und}\ 428\mu\mu.$$

Im Absorptionsspektrum der Alkohollösung finden wir Cucurbiten und Carotin sehr nahestehend. Für die Untersuchung wurden Hilgersche Sektor-Photometer und Spektrograph mit 90° Ablenkung benutzt. Als Lichtquelle hat uns die Nitralampe gedient.

Herrn Prof. Nakamura möchten wir für sein freundliches Entgegenkommen auch an dieser Stelle herzlich danken.

Cucurbitaxanthin. Das aus dem Extrakt durch Petroläther getrennte Pigment (0.14 g.), Cucurbitaxanthin, wurde mit 80% igem Methanol entmischt und aus Methanol umkristallisiert. Diese Cucurbitaxanthin kristallisiert in körnigen ziegelroten Kristallen mit Metallglanz. In der Durchsicht sind sie braungelb. Der Schmelzpunkt liegt bei 180°. Das Pigment ist löslich in Chloroform, Schwefelkohlenstoff, Methyl- und Aethylalkohol aber fast unlöslich in Petroläther; optisch ist es aktiv:

$$[\alpha]_c^{20^\circ} = \frac{+0.32^\circ \times 100}{0.602 \times 0.5} = +105.1^\circ$$

Nach der Umkristallisation aus Chloroform-Petroläther wurde es analysiert. (K. Saito).

Subst.=3.859; CO_2=11.926; H_2O=3.473 mg. Gef.: C=84.29; H=10.07%. Ber. für $C_{40}H_{56}O_2$: C=84.44; H=9.93%.

Cucurbitaxathin färbt sich mit Ameisensäure sofort grün. Beim Versetzen der Chloroformlösung mit einigen Tropfen konzentrierter Schwefelsäure zeigt es eine blaue, dann blauschwarze Färbung.

In der folgenden Tabelle werden Cucurbitaxanthin mit dem rechtsdrehenden Xanthophyll, Lutein[1] verglichen.

Name	Formel	Schmelzpunkt (korr.)	Drehungsvermögen in Chloroform	Kristallform aus Methanol
Cucurbitaxanthin	$C_{40}H_{56}O_2$	183°	+105° (C)	Körnig
Lutein	$C_{40}H_{56}O_2$	193°	+160° (Cd.)	Prismen

Behandlung der Mutterlauge des Cucurbitens mit methylalkoholischem Kali. Da aus der Mutterlauge des Cucurbitens kein Farbstoff in kristallisiertem Zustand isoliert worden war, wurde Hydrolyse ausgeführt.

Nach Zechmeister und Cholenoky[2] wurde die tiefe orangerot gefärbte Mutterlauge mit Petroläther auf 300 ccm. verdünnt und mit 100 ccm. 30% igem methylalkoholischem Kali unterschichtet und bei 25° stehen gelassen. Nach einigen Stunden ging der grösste Teil des Farbstoffes in die untere Schicht über und gleichzeitig erschien eine weisse wachsartige Substanz an den Glaswandungen und an der Berührungsfläche der beiden Schichten. Nach 24 Stunden wurde die wachsartige Substanz filtiert, mit Petroläther gewaschen und dann in Wasser gelöst. Nun wurde mit Salzsäure angesäuert, mit Aether (Tierkohle) extrahiert und der mit Natriumsulfat getrocknete Extrakt eingedampft. Es hinterblieben ca. 2 g. braune Kristalle, Schmp. 58–61°. Nach dreimaligem Umkristallisieren aus 70% igem Alkohol, unter vermindertem Druck abdestilliert und dann noch einmal aus demselben Lösungsmittel umkristallisiert, erhielten wir schneeweisse glänzende Kristalle, die bei 62–63° schmolzen. Mit gereinigter Kahlbaumscher Palmitinsäure entstand keine Depression.

Subst.=4.007; CO_2=11.003; H_2O=4.599 mg. Gef.: C=75.10; H=12.84%. Ber. für $C_{16}H_{32}O_2$: C=74.93; H=12.59%. (K. Saito).

Die alkalische methylalkoholische Lösung wurde mit Aether überschichtet. Mit Schwefelsäure angesäuert, scheidet sich Natriumsulfat aus und der Farbstoff geht in die obere Schicht über. Die Aetherauszüge wurden gewaschen, getrocknet und eingeengt. Bei der Aufbewahrung in der Kälte kristallisierte kein Farbstoff, sondern eine farblose Substanz aus. Diese wurde mit Methylalkohol abgesaugt. Durch Umkristallisation aus Aceton wurden farblose Kristalle, die bei 152° unscharf schmolzen, gewonnen. Diese Kristalle zeigten sich unter dem Mikroskop als ein Gemisch aus Täfelchen und Nadeln.

(1) R. Kuhn, A. Winterstein und E. Lederer, *Z. Physiol. Chem.*, **197** (1931), 141.
(2) *Ann.*, **481** (1930), 53.

Die petrolätherische Lösung wurde mit 80% igem Methanol entmischt, gewaschen, getrocknet und eingedampft. Es wurden aber keine Kristalle von Cucurbitaxanthin gewonnen.

Nach erfolgter Hydrolyse wurde alle gefärbte Substanz in Aether aufgenommen und mit 20% igem methylalkoholischem Kali noch einmal, wie oben erwähnt, behandelt. Durch diese Behandlung wurde etwas mehr Palmitinsäure und farblose Substanz gewonnen, aber kein kristallisierter Farbstoff.

Der grösste Teil der Kosten dieser Untersuchungen wurde durch Gelder aus der Kaiserlichen Akademie gedeckt. Für diese Beihilfe möchten wir auch an dieser Stelle unseren ergebensten Dank aussprechen.

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SINOMENINE AND DISINOMENINE. PART XXVIII. ON HOFMANN DECOMPOSITION OF DIHYDROSINOMENINE.

By Kakuji GOTO and Hideo SHISHIDO.

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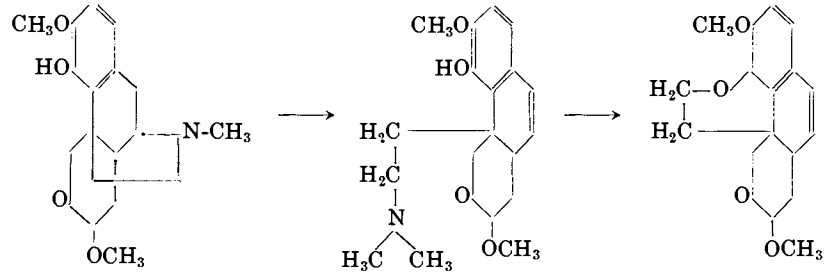
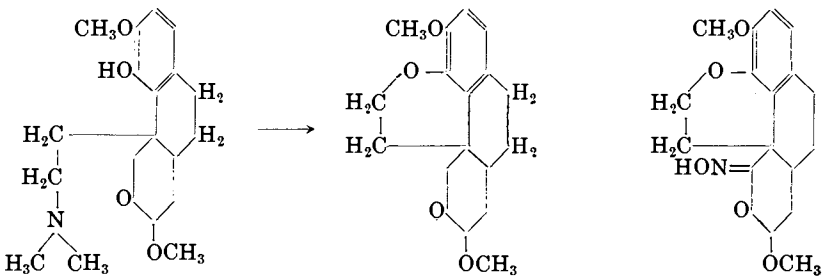
On Hofmann decomposition of sinomenine and its derivates, several communications have been published by us. In the present communication, dihydrosinomenine [I] was decomposed into the 7-methoxy-dehydro-*l*-thebenone [III] and into the 7-methoxy-*l*-thebenone [V] by the following process.



I. II. III.



IV. V. VI.

One remarkable feature in the above decomposition is that the sense of the optical rotation is inverted step by step from sinomenine to 7-methoxy-*l*-thebenone. The same phenomenon was observed in the *l*-thebenone and the *l*-thebenane series. As we have shown already, this inversion could be explained by the exalting action of the double bond only if we assume that

1. in sinomenine, $C_{(13)}$ is + and $C_{(14)}$ is −
2. the formation of an ether ring between OH in (4) and the side chain diminishes or inverts the rotatory power of $C_{(13)}$ or exalts that of $C_{(14)}$.

This hypothesis, which assumes $C_{(13)}$ to be + and $C_{(14)}$ to be − in sinomenine (hence $C_{(13)}$ to be − and $C_{(14)}$ to be + in morphine series) can be, however, applied only to the simplest cases such as the thebenone and thebenane series. In the three sinomenine methines, reported in the XXVth communication, this hypothesis is already faced with a grave difficulty. Of these three methines, sinomenine·violeo-methine seems to be most akin to the β- or δ·methylmorphi·methines, from the mode of its preparation and from its properties. But here it seems that the optical antagonisms between morphine and sinomenine series disappears or at least strongly diminishes. For, sinomenine·violeo·methine as well as its methyl-ether·methosulphate are strongly dextrorotatory (>300°) just like β- or δ·methyl·morphi·methines. This may be due partly to the fact that in morphine series there are two more asymmetric carbon atoms [$C_{(5)}$ and $C_{(6)}$] than in sinomenine. Yet, the ultimate reaction, we presume, must be sought in

(1) the influence of phenyl nucleus,
(2) the influence of the ring formation, viz. the nitrogenous ring, the ether ring and the hydrated third ring of the phenanthrene and
(3) the double linking,

as we have already mentioned.

The 7·methoxy·*l*·thebenone forms an isonitroso derivative by the action of amylnitrite and Na in ether. Although this isonitroso·derivative can not be obtained in a crystallised state, yet from the determination of N and methoxyl, it is clear that the isonitroso group must have been introduced in $C_{(5)}$. Then our assumption that the side·chain in sinomenine must be attached to $C_{(13)}$, made principally from its very easy splitting off, even by boiling 2% caustic soda in case of the sinomenine·violeo-methine, seems justly to have been added with a new proof.

Experimental

1. **Dihydrosinomenine-methine [II].** Dihydrosinomenine iodomethylate (5 gr.) is boiled with 16.5% KOH (30 c.c.) for 70 minutes. The liquid is then diluted with water (30 c.c.), well cooled and saturated with CO_2, by

which the suspended oil drops crystallise out. The crystals are collected, washed with water and dried on a porous plate. Yield almost quantitative. Recrystallised from ether, it forms colourless long prisms. M.p. 173°C. (sintering at 160°C.).

Anal.: Subst. = 3.986; CO_2 = 10.140; H_2O = 2.806 mg. Subst. = 6.424 mg.; N_2=0.218 c.c. (12°C., 762 mm.). Found: C=69.38; H=7.82; N=4.02%. Calc. for $C_{20}H_{27}NO_4$ (345): C=69.56; H=7.82; N=4.06%.

Spec. Rotation. (0.2111 gr. Subst. in 10 c.c. chloroform, 1-dm. tube.)
$\alpha = -1.78°$ $[\alpha]_D^{18} = -84.32°$

2. 7-Methoxy-dehydro-*l*-thebenone [III]. Dihydro-sinomenine methine (6 gr.) was first turned into its iodomethylate by methyl iodide (6 gr.) in boiling methanol (30 c.c.). After the methyl iodide is perfectly evaporated off, the residue was decomposed by boiling 16.5% aqueous KOH (63 c.c.) for 35 minutes. The amine was caught in dilute HCl in this operation. The nitrogen free substance was then extracted with ether, after the free KOH was fixed with CO_2. It forms colourless prisms from ether. Yield 3.4 gr. M.p. 118°C. (Sinters at 113°C).

Anal.: Subst. = 5.989; CO_2 = 15.773; H_2O = 3.642 mg. Found: C = 71.83; H = 6.76%. Calc. for $C_{18}H_{20}O_4$ (300): C = 72.00; H = 6.67%.

Spec. Rotation. (0.2986 gr. Subst. in 10 c.c. chloroform, 1-dm. tube.)
$\alpha = -8.54$ $[\alpha]_D^{18} = -286.00°$

Oxime. 0.2 Gr. subst. was boiled in alcoholic solution (10 c.c.) with $NH_2OH \cdot HCl$ (0.4 gr.) and Na-acetate (0.4 gr.) for 2 hours. The crystals, deposited on evaporation of the alcohol, was well washed and recrystallised from alcohol. Prisms, which melt and decompose at 180°C.

Anal.: Subst. = 5.841 mg.; N = 0.213 c.c. (8°C., 760.4 mm.). Found: N = 4.38%. Calc. for $C_{18}H_{21}NO_4$ (315): N = 4.44%.

Nitrogenous substance. On evaporating the above hydrochloric acid, long needles of the hydrochloride of an amine was obtained, which was purified through absolute methanol. The chloro-aurate and the chloro-platinate melted at 246°C. and 249°C. respectively,

0.0907 Gr. chloro-aurate gave 0.0449 gr. Au. 0.0751 Gr. chloro-platinate gave 0.0278 gr. Pt. Found: Au=49.50; Pt=37.01%.

$[(CH_3)_3N \cdot HCl]\,AuCl_3$ and $[(CH_3)_3N \cdot HCl]_2\,Pt\,Cl_4$ require 49.37% Au and 36.97% Pt respectively.

3. **Dihydrosinomenine-dihydro-methine** [IV]. Dihydrosinomenine methine (2 gr.), dissolved in dilute HCl, was shaken in hydrogen atomosphere with $PdCl_2$ (0.1 gr.) and charcoal (1 gr.). The calculated quantity of hydrogen was absorbed in 5 minutes. The reduced methine was set free with Na_2CO_3 and extracted with ether, from which it separated out in prisms. M.p. 133°C. (sintering at 123°C.). Yield almost quantitative.

Anal.: Subst. = 3.586, 6.247; CO_2 = 9.08, 15.911; H_2O = 2.735, 4.633 mg. Subst. = 12.849 mg.; N_2 = 0.432 c.c. (12.1°C., 762 mm.). Found: C = 69.12, 69.46; H = 8.46, 8.24; N = 3.98%. Calc. for $C_{20}H_{29}NO_4$ (347): C = 69.16; H = 8.35; N = 4.03%.

Spec. Rotation: (0.4291 gr. Subst. in 10 c.c. chloroform, 1-dm. tube.)
$\alpha = +0.09$ $[\alpha]_D^{18} = +2.09°$

4. **7-Methoxy-*l*-thebenone** [V]. (*A*) *From the dihydromethine* [*IV*]. Dihydrosinomenine dihydromethine (1 gr.) was turned first into its iodomethylate in the same way as described in (2). The iodomethylate, which was not crystalline, was decomposed by boiling with 16.5% aqueous KOH in the same manner as described in (2). The 7-methoxy-*l*-thebenone crystallised out from ether in glistening, colourless, long prisms. Yield 0.37 gr. (ca. 50%). M.p. 128°C. (sintering at 122°C.).

The nitrogenous substance showed the same properties as that obtained in the reaction (2) and was purified in the same way.

0.0430 Gr. the chloroaurate gave 0.0212 gr. Au. 0.0585 Gr. the chloroplatinate gave 0.0216 gr. Pt. Found: Au = 49.30; Pt. = 36.92%. Calc.: Au = 49.37; Pt. = 36.97%.

(*B*) *From 7-methoxy-dehydro-l-thebenone.* 7-Methoxy-dehydro-*l*-thebenone (2 gr.) was reduced catalytically in the same way as described in (3). The calculated quantity of hydrogen was absorbed in 30 minutes. The reduced substance crystallised out from ether in glistening prisms. M.p. 128°C. (sintering at 123°C.). Yield almost quantitative.

The mixed m.p. of the substances from (A) and (B) was unaltered. Anal.: Subst. = 4.780; CO_2 = 12.526; H_2O = 3.115 mg. Found: C = 71.46; H = 7.24%. Calc. for $C_{18}H_{22}O_4$ (302): C = 71.52; H = 7.28%.

Spec. Rotation. (0.2885 gr. Subst. in 10 c.c. chloroform, 1-dm. tube.)
$\alpha = -4.26$ $[\alpha]_D^{18} = -147.66°$

Oxime. Prepared quite in the same way as described in (2). Recrystallised from ethylacetate, it forms thick tetragonal plates. M.p. 168°C. (sinters at 145°C.)

Anal: Subst. = 8.739 mg.; N = 0.317 c.c. (11.2 °C, 761 mm.). Found: N = 4.31%: Calc. for $C_{18}H_{23}NO_4$(317): N = 4.41%.

5. **Isonitroso-7-methoxy-*l*-thebenone** [VI]. 7-Methoxy-*l*-thebenone (1 gr.) was dissolved in ether (50 c.c.) and ca. 1 gr. of natrium-wire was driven into it. To the ice-cooled solution, amyl nitrite (1.5 gr.) was added little by little. After standing overnight, the yellow precipitate at the bottom was collected on a glass filter and disolved in ice-water. By passing CO_2 in this solution, a resinous precipitate was formed, which was collected and dried in a vacuum-desiccator. The dried substance dissolved almost completely in ether, but showed no tendency to crystallise from it, or from ethyl alcohol. The analysis was carried out with the well dried substance.

Anal.: Subst. = 5.506 mg.; N = 0.199 cc. (18.5 °C., 758 mm.). Subst. = 9.197; AgI = 12.882 mg. Found: N = 4.13; CH_3O—(2) = 18.51%. Calc. for $C_{18}H_{21}NO_5$(331): N = 4.22; CH_3O—(2) = 18.73

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ON THE COMPOSITION OF THE CYANIDE COMPLEX RADICAL OF METALS. PART IV.

NICKEL CYANIDE COMPLEX RADICAL.

By Kosaku MASAKI.

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H. E. Williams[1] showed that nickel cyanide dissolved very readily in a solution of an alkaline cyanide, forming an orange-red solution of a double nickel cyanide of type, $M_2Ni(CN)_4$.

The following description is found in the book of analytical chemistry.[2] It produces an apple-green gelatinous precipitate by adding potassium cya-

(1) Cyanogen Compounds p. 66 (1915).
(2) Treadwell, Lehrbuch der analytishen Chemie, Vol. 1.

nide to a solution of a nickel salt, and this cyanide is soluble in excess of the reagent.

$$Ni^{++} + 2CN^{-} \rightarrow Ni(CN)_2$$

$$Ni(CN)_2 + 2CN^{-} \rightarrow Ni(CN)_4^{--}$$

Composition of Nickel Cyanide Ion. Nickel cyanide has been prepared by adding a solution of an alkaline cyanide to an excess of a nickel sulphate solution. In this case, author had an apple-green gelatinous precipitate of nickel cyanide, The precipitated nickel cyanide was purified by washing with conductivity water. Also nickel sulphate and nickel nitrate were purified by recrystallization. Then the ratio of combined cyanide to nickel in the complex ion was determined by a simple titration method.[1]

The results are summarized in the following tables.

Table 1.

Sodium Cyanide and Nickel Cyanide.

Nickel mol per litre	Free cyanide mol per litre	Combined cyanide mol per litre	Ratio of combined cyanide to nickel
0.1535	1.3308	0.6293	4.09
0.1456	1.3517	0.5926	4.07
0.1298	1.3922	0.5205	4.01
0.1195	1.4156	0.4765	3.98
0.1665	1.0109	0.6693	4.02
0.1372	1.0728	0.5488	4.00
0.1038	1.1344	0.4204	4.05
0.0988	1.1476	0.3972	4.03
0.0581	0.6363	0.2330	4.01
0.0390	0.6754	0.1556	3.99
0.0237	0.7064	0.0941	3.97
0.0165	0.7225	0.0635	3.85

Author obtained red colour solutions by adding pure nickel cyanide to 1.6531 and 1.3472 molal solutions of sodium cyanide, and also an orange colour solution by using 0.7530 molal solution of sodium cyanide.

(1) This Bulletin, **4** (1929), 190; ibid., **6** (1931), 60; ibid., **6** (1931), 89.

Table 2.

Sodium Cyanide and Nickel Sulphate.

Nickel mol per litre	Free cyanide mol per litre	Combined cyanide mol per litre	Ratio
0.0804	1.3295	0.3236	4.02
0.0662	1.3767	0.2764	4.17
0.0638	1.4001	0.2530	3.96
0.0578	1.4354	0.2177	3.78
0.0556	0.8000	0.2236	4.02
0.0519	0.8059	0.2177	4.19
0.0472	0.8295	0.1941	4.11
0.0444	0.8353	0.1883	4.24
0.0389	0.4471	0.1529	3.93
0.0352	0.4589	0.1411	4.00
0.0317	0.4706	0.1294	4.08
0.0289	0.4824	0.1176	4.06

Table 3.

Sodium Cyanide and Nickel Nitrate.

Nickel mol per litre	Free cyanide mol per litre	Combined cyanide mol per litre	Ratio
0.0891	0.7269	0.3555	3.99
0.0731	0.7915	0.2909	3.98
0.0586	0.8488	0.2336	4.00
0.0549	0.8612	0.2212	4.03
0.0418	0.4544	0.1672	4.00
0.0379	0.4712	0.1524	4.02
0.0277	0.5124	0.1111	4.01
0.0212	0.5377	0.0859	4.05

In these cases of the Tables 2 and 3, author obtained red colour solutions by adding nickel sulphate or nitrate solution to the 1.0653 and 1.0824 molal sodium cyanide, and also orange colour solutions by adding nickel salts solutions to the 0.8000, 0.6000, and 0.6236 molal sodium cyanide solutions.

In all these experiments, the molal ratio of combined cyanide to nickel is four to one for all nickel salts, corresponding to the formula $Ni(CN)_4^{--}$. Hence it may be probably that the composition of the cyanide complex radical of nickel is $Ni(CN)_4^{--}$.

Stability of the Nickel Cyanide Ion. There is no available information on the concentration of nickel ion in nickel cyanide solution.

The potential differences between a nickel electrode and various solutions of nickel cyanide in sodium cyanide has been determined. The solutions used in these measurements were made by dissolving the appropriate amounts of pure nickel cyanide in 100 c.c. of 0.7852 mol NaCN solution. The electromotive force measurements were carried out at 25° C. by connecting a normal calomel electrode, through a normal KCl salt bridge, with an electrode of pure nickel wire immersed directly in the solution being constantly stirred. The obtained data are summarized in Table 4.

Table 4.

$Ni(CN)_4^{--}$	CN^-	E	E_w	Ni^{++}	K
0.06995	0.12511	0.7767	0.4946	4.92×10^{-10}	5.8×10^{13}
0.05316	0.14243	0.7863	0.5041	2.34×10^{-10}	5.6×10^{13}
0.02278	0.15591	0.7976	0.5154	7.33×10^{-11}	5.4×10^{13}

In Table 4, E is the measured electromotive force and E_w is the potential of the nickel electrode referred to the normal hydrogen electrode, taking the value of the single potential of the normal calomel electrode as -0.2822.[1] The nickel ion concentration was found by the equation.

$$E_w = E_o - 0.0295 \log c$$

where E_o is the standard electrode potential of nickel ion- nickel electrode and its value is 0.22 volt.[2] From the calculated value of (Ni^{++}), stability constant can be determined as follows:

$$K = \frac{Ni(CN)_4^{--}}{(Ni^{++})(CN^-)^4}$$

It will be noticed that K remains nearly constant in the Table 4. Therefore, we may conclude that in this case the complex ion is also $Ni(CN_4^{--})$.

Conclusion. The composition of the nickel cyanide complex ion is probably $Ni(CN)_4^{--}$ through all concentrations.

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(1) Lewis and Randall, Thermodynamics (1923), p. 407.
(2) Noyes and Sherrill, Chemical Principle (1920), p. 260.

ON THE OCCURRENCE OF A HYDROCARBON IN ISHINAGI LIVER OIL.

By Mitsumaru TSUJIMOTO.

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Of hydrocarbons occurring in the liver oils of animals, the most remarkable one is the highly unsaturated hydrocarbon, squalene, $C_{30}H_{50}$, which is contained in a fairly large number of shark liver oils, and although small in proportion, the saturated hydrocarbon, pristane, $C_{18}H_{38}$, usually accompanies squalene. In recent years, H. J. Channon and G. F. Marrian[1] found a hydrocarbon probably of the formula $C_{32}H_{54}$, $C_{33}H_{55}$ or $C_{34}H_{58}$, in the livers of man, sheep, horse, and pig; the present author in conjunction with K. Kimura[2] isolated a hydrocarbon, possibly corresponding to the formula $C_{35}H_{60}$, from the liver fat of sperm whale. However, so far as fish livers are concerned, no hydrocarbon has hitherto been discovered in them besides the above two hydrocarbons in shark liver oils. Recently I found a hydrocarbon in the liver oil of ishinagi, *Stereolepis ischinagi* (Hilgendorf). This oil, first investigated by me, is distinguished by the remarkable content of a vitamin A-like substance (liver resin), which sometimes amounts up to nearly 50% of the oil.[3] The amount of the hydrocarbon in the oil was small; it was highly unsaturated. Owing to the want of material, no definite formula has yet been assigned to it, but it appeared to be of a high molecular weight. The present paper is a preliminary report on this hydrocarbon.

Experimental Part.

The ishinagi liver oil used for the present investigation was a mixture of four samples of the oil prepared in the laboratory. It was a brownish red-yellow, viscous liquid, which appeared almost black in thick layer, and deposited an appreciable amount of solid fat in winter. An intense blue colouration was observed in the antimony trichloride test. The oil showed the following numbers:

d_4^{15}	0.9358	Saponif. value	146.2
n_D^{20}	1.5070	Iodine value (Hanus)	155·5
Acid value	11.8	Unsaponif. matter	22.36%

(1) *Biochem. J.*, **20** (1926), I, 409.

(2) *Chem. Umschau.*, **35** (1928), 317.

(3) Tsujimoto, *Chem. Umschau.*, **29** (1922), 385; S. Ueno, M. Yamashita and Y. Ôta, *J. Soc. Chem. Ind. Japan*, **31** (1928), 1193.

The fatty acids contained 68.5% of liquid acids, and consisted mainly of palmitic and oleic acids, together with stearic and clupanodonic acids. Hexadecenic acid and a small proportion of saturated acids higher than stearic were probably present.[1]

The unsaponifiable matter formed a reddish-orange, very viscous liquid. In order to separate the hydrocarbon, it was treated with methanol. 35 Gr. of the substance were heated with 350 c.c. of methanol, thereby complete solution occurred, but on cooling the solution became turbid, and an oily precipitate was gradually deposited. On standing over night, the supernatant liquid was decanted off; the precipitate was repeatedly washed with a small amount of methanol. In this way about 1 gr. of a yellow-orange, viscous liquid was obtained. It had an orange-yellow colour even after treatment with a pretty large amount of animal charcoal in ethereal solution. As the liquid was difficultly soluble in methanol, ethyl alcohol, and acetic anhydride, there was little doubt that it consisted mainly of hydrocarbon, but judging from its colour and colour reaction (Liebermann's), it appeared to be still impure. Owing to the difficulty of purification of such small material, it was analysed without further treatments as follows:

d_4^{17} 0.942 Iodine value (Hanus) 290.8

n_D^{17} ca. 1.54 ,, ,, (Rosenmund and Kuhnehenn) 310.0

Solidif. pt. Not solidified at 0°

Molecular weight. (1) 0.0114 gr. subst., 0.1307 gr. camphor (m.p. 177.7°), m.p. of the mixture 172°, depression 5.7°, mol. wt. 612. (2) 0.1442 gr. subst., 10.85 gr. benzol, depression 0.103°, mol. wt. 644.

Elementary analysis: Subst. = 0.1127; CO_2 = 0.3493; H_2O = 0.1187 gr. Found: C = 84.53; H = 11.79%.

Thus the substance had high specific gravity and refractive index, and as indicated by its iodine value, it was highly unsaturated. As the percentage of carbon and hydrogen amounted only to 96.32%, it was still impure to be taken as a hydrocarbon as had been anticipated.

Bromine addition compound. 0.1152 Gr. of the substance was dissolved in 10 c.c. of ether, and on cooling the flask with ice, a little excess of bromine was added. On standing for about one hour, the precipitate was collected on a filter and washed with ether; yield 0.1950 gr. or 169.3%. A white powder; on heating it became somewhat brown at 130°C., brown at 150°C., and turned black with sintering at 170°C. The bromine content was determined to be 67.07% (Carius).

(1) Tsujimoto, *Report of the Tokyo Imperial Industrial Laboratory*, Vol. **24** (1929), No. 4, p. 1.

Hydrogen chloride addition compound. 0.3 Gr. of the substance (not treated with animal charcoal) was dissolved in 10 c.c. of ether, and on well cooling, dry hydrogen chloride gas was passed into it to saturation. The solution showed various change of colour, and finally turned blackish violet. On standing for two hours, the precipitate was collected and washed with ether; yield 0.15 gr. On recrystallising it from acetone, a nearly white powdery substance was obtained. This sintered at above 120° C., and melted at 128–129°C. with bubbling (decomposition). The chlorine content was 30.85%.

Discussion.

The results of the above experiments were yet insufficient to determine the composition of the hydrocarbon. It was even questionable whether the substance consisted of a single compound. But assuming it to be so, the following two suggestions are possible, the decision of which I should postpone to further investigation:

(1) By assuming the high values of specific gravity, refractive index, and molecular weight to be due to some admixed impurities, and taking the halogen contents and the melting point of the comparatively pure bromine and hydrogen chloride addition compounds into consideration, it appears that the hydrocarbon closely resembles to that of the liver fat of sperm whale (loc. cit.), viz. Br content of $C_{35}H_{60}Br_{12}$=66.62%: Cl content of $C_{35}H_{60}6HCl$=30.42%.

(2) If we take the values of specific gravity, refractive index, and molecular weight to be nearly correct, then the substance is a compound higher than C_{40} atoms, and the number of double bonds must be more than six. The compounds nearly corresponding to these data are $C_{45}H_{76}$ (mol. wt. 616.6, iodine value 329.4 as eight double bonds) and $C_{46}H_{78}$ (mol. wt. 630.6, iodine value 322.1). The calculated halogen contents of the addition compounds are as follows:

	Br (%)		Cl (%)
$C_{45}H_{76}Br_{16}$	67.47	$C_{45}H_{76}8HCl$	31.23
$C_{46}H_{78}Br_{16}$	66.97	$C_{46}H_{78}8HCl$	30.75

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REACTION BETWEEN TRIMETHYLTIN HYDROXIDE AND METHYLIODIDE.

By Taichi HARADA.

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Some years ago[1] the author noticed that a beautiful crystalline compound forms when trimethyltin hydroxide and methyliodide are put together in an ethereal solution. Recently this subject was undertaken by Kraus and Bullard[2] by measuring the conductivity of the mixture of trimethyltin hydroxide and methyliodide in acetone solution. They assumed the increase of conductivity of the mixtures due to the formation of a salt having the formula, $((CH_3)_3SnOH)_2CH_3I$. This has lead my attention to further investigation of this reaction. The experimental results show that the crystalline compound is identical with the compound which was obtained by the reaction between trimethyltin hydroxide and trimethyltin iodide[3]. Therefore, the reaction may be formulated as follows:

$$(CH_3)_3SnOH + CH_3X \rightarrow (CH_3)_3SnX + CH_3OH$$
$$2(CH_3)_3SnOH + (CH_3)_3SnX \rightarrow ((CH_3)_3Sn)_3O \cdot X \cdot H_2O$$

Experimental.

Two molecular proportion of trimethyltin hydroxide and one molecular proportion of methyliodide in a large amount of ethyl ether were introduced into a round bottom flask and connected with reflux condenser and heated on a water bath for about three hours. The solution of the mixture was filtered through filter paper while it was hot. The clear solution was kept over night in open air. From this solution a beautiful prismatic compound crystallized out.

On analysis it appeared to be identical to the compound formed between trimethyltin hydroxide and trimethyltin iodide in benzene solution.

Anal: Subs. = 0.2144, 0.1998; AgI = 0.0771, 0.0718 gr. Found: I = 19.44, 19.43%. Calcd. for $C_9H_{29}O_2Sn_3I$: I = 19.46%.

Subs. = 0.3511; SnO_2 = 0.2442 gr. Found (Carius): Sn = 54.77%. Calcd. for $C_9H_{29}O_2Sn_3I$: Sn = 54.59%.

(1) T. Harada, Thesis, Clark University, Worcester, Mass., 1923.
(2) Kraus and Bullard, *J. Am. Chem. Soc.*, **52** (1930), 4057.
(3) Kraus and Harada, ibid., **47** (1925), 2416; Harada, this Bulletin, **2** (1927), 105.

The Conductance of the Compound: No special precautions were taken, since the purpose of measuring the conductance of the compound was to get a general idea of the composition of the compound. The specific conductances of 0.1 N and 0.0166 N solutions of the compound in water were found to be 7.43×10^{-4} and 1.51×10^{-4} respectively and 1.41×10^{-4} and 0.35×10^{-4} in ethyl alcohol respectively expressed as reciprocal ohms at 23°C.

The magnitude of the specific conductance in water is about five times larger than that in alcohol. In other words, the extension of the dissociation of the compound in alcohol is about one fifth lower than it is in water. The equivalent conductances of the compound in alcohol at the concentrations, therefore, are 14.1 and 21.0 respectively. The specific conductance decreases as dilution increases. However, the equivalent conductance increases with increasing dilution. Therefore, the compound appears to be a salt.

Summary.

The reaction between trimethyltin hydroxide and methyliodide was studied. The compound formed from the mixture was identical to the compound formed from trimethyltin hydroxide and trimethyltin iodide having the formula $((CH_3)_3Sn)_3OX$, H_2O.

The conductance of the compound was studied. The results indicate that the compound appears to be a salt.

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THE CATALYTIC HYDROGENATION OF AROMATIC HYDROCARBONS UNDER HIGH PRESSURE AND HIGH TEMPERATURE.

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Introduction

In connection with the hydrogenation of aromatic hydrocarbons, numerous methods have been suggested by Sabatier,[1] Ipatiew[2] and Schroeter,[3]

(1) Sabatier and Sendrens, *Compt. rend.*, **132** (1901), 1257.
(2) Ipatiew, *Ber.*, **40** (1907), 1281.
(3) Schroeter, *Ann.*, **426** (1922), 1

and their experimental studies indicate that the velocity of reduction is affected not only by the kind of catalyst employed and the pressure, but also by the chemical structure of the hydrocarbons. Very few investigators, however, have made a systematic survey of the relation between the catalytic reduction of aromatic hydrocarbons and their chemical constitution, and the present paper deals with this interesting problem.

Experimental.

The aromatic hydrocarbons which were used in the studies, were benzene, diphenyl, naphthalene, acenaphthene, anthracene, phenanthrene and pyrene, and they were all proved to be chemically pure except the phenanthrene, which contained a trace of a sulphur compound; their physical constants are shown in the table.

The reduced nickel used as a catalyst was made by heating nickel nitrate at about 300°C., and reducing it in a stream of hydrogen at 300°–320°C.; its activity was tested by its behaviour towards naphthalene.

Table 1.

Name	Appearance	d_4^{25}	n_D^{25}	B.P.	M.P.	Picrate	
						Appearance	M.P.
Benzene	Colourless liquid	0.8740	1.4972	—	—	—	—
Diphenyl	White thin plates	—	—	248–249 (756.5 mm.)	68.5–69.5	—	—
Naphthalene	White granular	—	—	212.5–213.5 (·58.2 mm.)	80–81	Pale yellow needles	150–150.5
Acenaphthene	White needles	—	—	266.5–267.5 (760.2 mm.)	93–94	Orange-red needles	160.8–161.8
Anthracene	White thin plates	—	—	—	212.5-213.5	Red needles	139–140
Phenanthrene	White powder	—	—	—	98–100	Orange yellow thin plates	141–142
Pyrene	Yellow tetrahedral crystals	—	—	about 280° (757.5 mm.)	148–149	Red needles	222-223

In the experiments, a weighed sample was placed in an autoclave with freshly reduced nickel in the proportion of 8% of the weight of the sample, and after the air in the autoclave had been replaced by hydrogen, the gas was subjected to the required pressure, and heated externally by electric resistance to a definite temperature. During the reaction, the apparatus was shaken by a machine to bring the substance in contact with the hydro-

gen, and the change of temperature and pressure in the reaction chamber was recorded every 15 minutes. When the pressure became constant, the autoclave was cooled and the reaction products separated and fractionated by distillation, and purified by distillation or recrystallization. Their physical and chemical properties were then studied.

In the hydrogenation of benzene with 76 hydrogen atmospheric pressures at 0°C., the reaction started at 40°C and the reaction velocity at 200° C. to form hexahydrobenzene was found by calculation to be $\frac{96 \text{ gr.}}{315 \text{ minutes}}=0.3$ (Fig. 1).

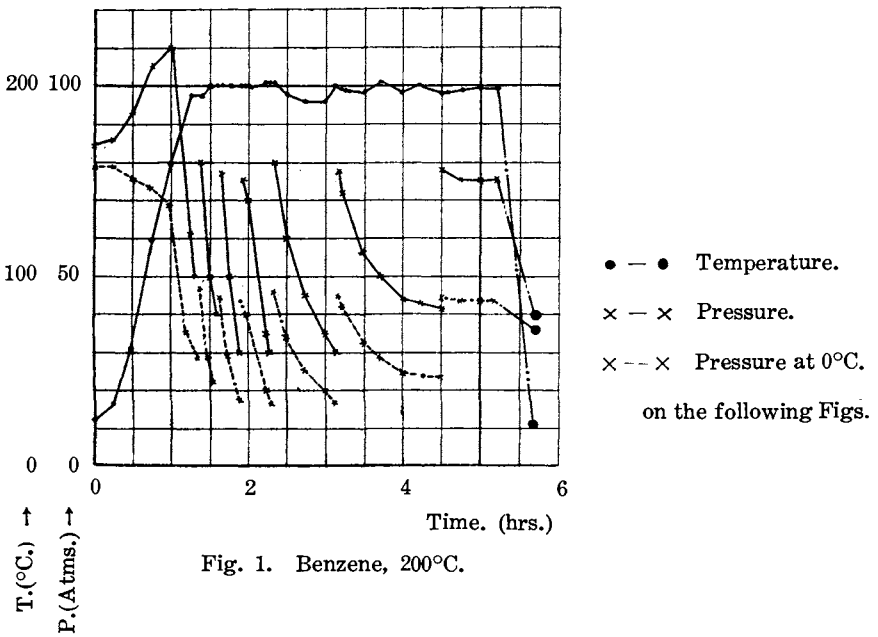


Fig. 1. Benzene, 200°C.

When diphenyl was hydrogenated catalytically with 95 hydrogen atmospheric pressures at 0°C., the initial temperature at which the reaction began was about 80°C., and dicyclohexyl was formed quantitatively at 200°C., the reaction velocity being $\frac{61}{225}=0.27$ (Fig. 2). Hydrogenation at 250°C. and under 95 hydrogen atmospheric pressures at 0°C., however, resulted in the formation of phenyl cyclohexane, owing to the partial oxidation of dicyclohexyl formed directly from diphenyl (Fig. 3). Naphthalene on reduction at 200°C. and under 91 hydrogen atmospheric pressures at 0°C., yields tetrahydronaphthalene which is converted into a

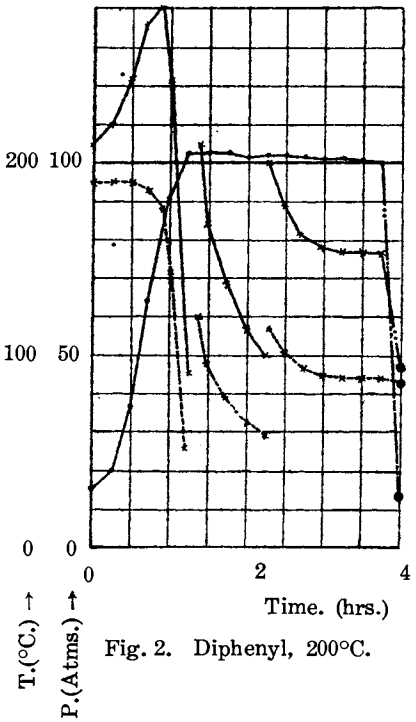


Fig. 2. Diphenyl, 200°C.

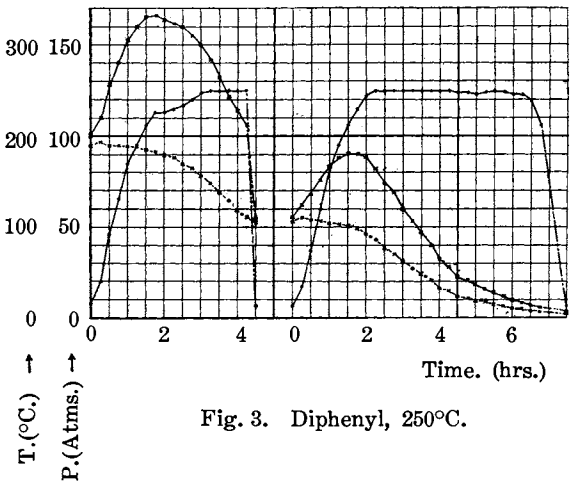


Fig. 3. Diphenyl, 250°C.

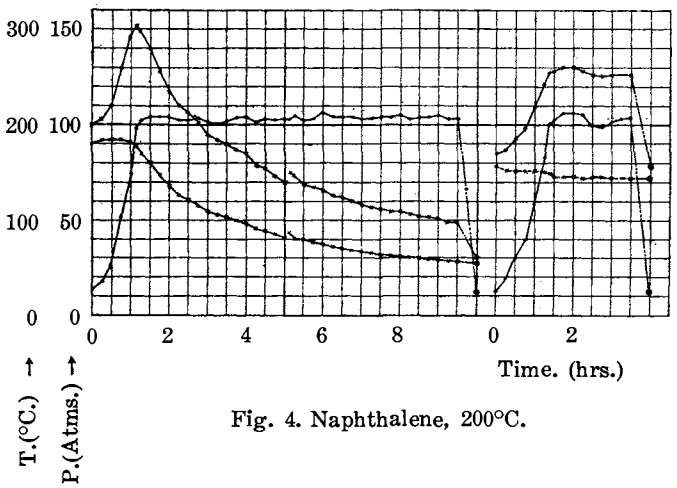


Fig. 4. Naphthalene, 200°C.

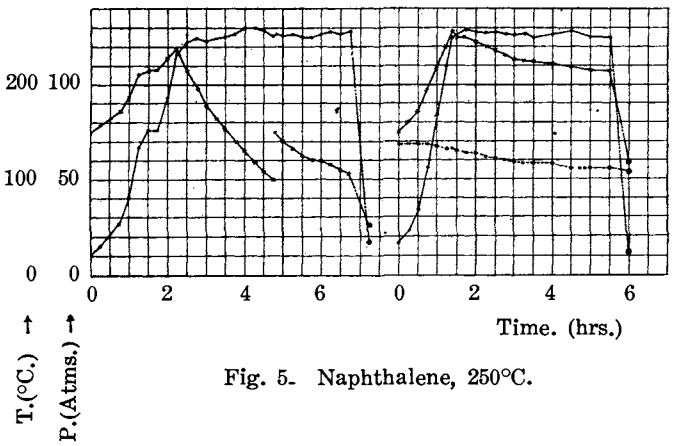


Fig. 5. Naphthalene, 250°C.

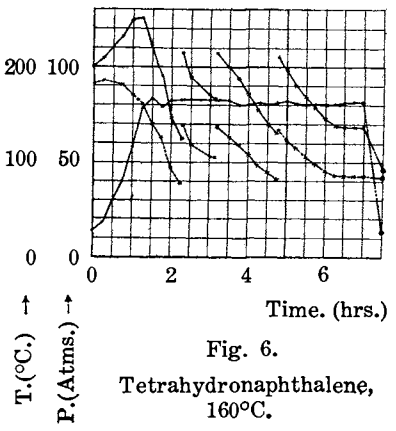


Fig. 6.
Tetrahydronaphthalene, 160°C.

decahydro-compound at 160°C. and under 91 atmospheric pressures. The hydrogenation of naphthalene seems to differ from that of tetrahydronaphtalene, the reaction in the former case having been observed to start with slow reaction velocity at about 140°C. under the conditions mentioned above, while that of tetrahydronaphthalene takes place at lower temperatures such as 80°C. (Figs. 4, 5, 6).

According to the principles of stereochemistry, there are two isomers in decahydronaphthalene, the cis- and trans-isomers, which have been studied by Mohr[1], Hückel[2], Willstätter[3], Eisenrohr[4], and Zelinsky[5]. The proportion of the cis- to the trans-isomer in the writer's sample was found to be 90 : 10, the calculation being made by the aid of the index of refraction and the specific gravity of the two isomers as observed by Willstätter and Hückel (See Table 2). The catalytic reduction of naphthalene at high pressure and high temperature seems to be similar, so far as the reaction product is concerned, to the case of the reaction of naphthalene with platinum and hydrogen at ordinary temperatures, but not the same as in Sabatier's method, in which the trans-isomer predominates in the reaction product.

Table 2.

	Decahydronaphthalene	
	Cis-form %	Trans-form %
Calc. from Willstätter's data		
of index of refraction	81	19
of specific gravity	97	3
Calc. from Hückel's data		
of index of refraction	62	38
of specific gravity	73	27

Acenaphthene on the other hand behaves quite differently from naphthalene in the catalytic reduction, though they show similar chemical structure; the absorption of hydrogen begins at about 80°C. under 94 atmospheric pressures at 0°C, and decahydroacenaphthene is produced at 200°C, the

(1) Mohr: *Ber.*, **55** (1922), 230.
(2) Hückel: *Ber.*, **58** (1925), 1449.
(3) Willstätter: *Ber.*, **56** (1923), 1388; **57** (1924), 683.
(4) Eisenrohr: *Ber.*, **57** (1924), 1639.
(5) Zelinsky: *Ber.*, **57** (1924), 2062.

reaction velocity being $\frac{103}{540} = 0.2$. The hydrogenation at higher temperatures (270°C.), however, produces tetrahydroacenaphthene due to the reverse reaction which occurs in the decahydro compound and which is favoured by higher temperatures (Fig. 7, 8).

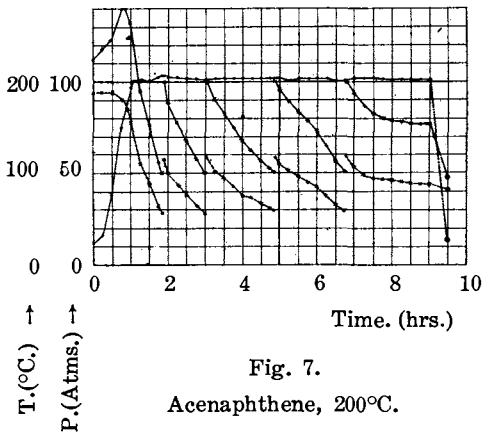


Fig. 7.
Acenaphthene, 200°C.

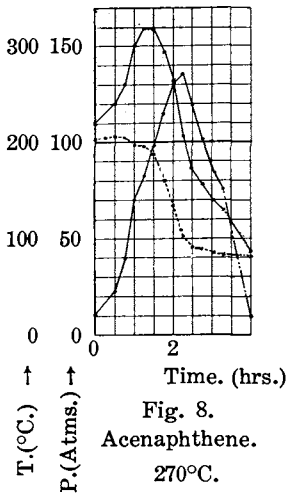


Fig. 8.
Acenaphthene.
270°C.

The reduction of anthracene is noteworthy in that the absorption of hydrogen begins at about 100°C. and the reaction by which the substance is converted into its octahydro-compound proceeds very quickly at 200°C., as was indicated by a fall of 30 atmospheric pressures in the pressure of the autoclave. Also, further reduction of the compound into perhydroanthracene will takes considerably longer time, as may be seen from Fig. 9.

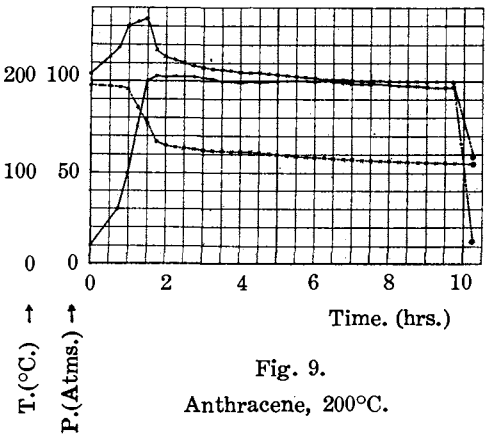
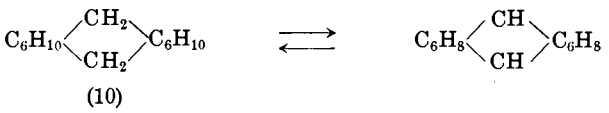


Fig. 9.
Anthracene, 200°C.

The reaction product consisted of three substances; the first was in the form of colourless crystals melting at 72°C., (Found: C=90.5; H=10.5) identified with the octahydroanthracene obtained by Godchot[1] and Schroeter[2]; the second, colourless crystals melting at 61°C., was proved to be perhydroanthracene by elementary analysis (Found: C=87.7; H=12.3); and the third, a liquid substance, was found by elementary analysis (Found: C=87.1; H=12.3) and by reference to its physical constants to be an isomeric substance with the perhydro-compound. The proportion of these substances in the reaction product was 1 : 3 : 2.

The fact that octahydroanthracene occurs with perhydro-compounds in the reaction product, indicates that two hydrogen atoms combined with carbon atoms, (9) and (10), in perhydroanthracene were removed on heating, as we experienced in the case of dihydroanthracene, resulting in octahydroanthracene as a reaction product.

(9)



(10)

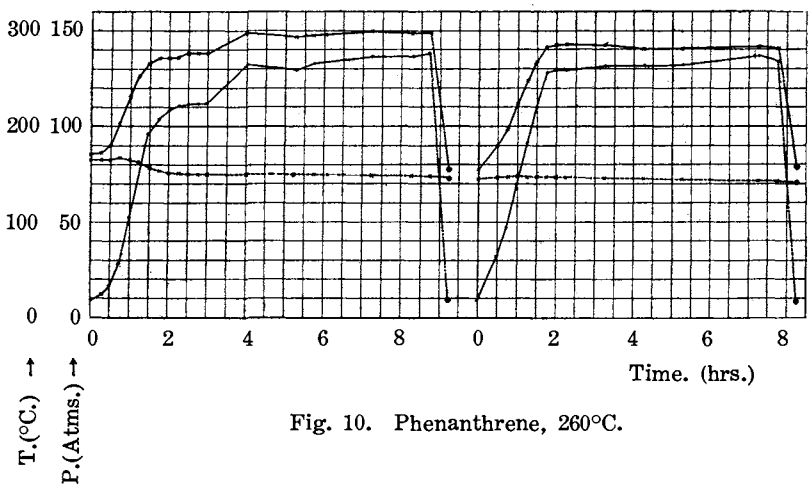


Fig. 10. Phenanthrene, 260°C.

(1) Godchot: *Ann. Chim.*, (8) **12** (1907), 1168.
(2) Schroeter: *Ber.*, **57** (1924), 2003.

In the reduction of phenanthrene, the reaction proceeded very slowly at 260°C. partly owing to the presence of some poisonous sulphur compound in it, and the product contained only 6% of tetrahydrophenanthrene (Fig. 10), which was separated from phenanthrene unchanged. The reduction was repeated with a new supply of hydrogen and reduced nickel, and octahydrophenanthrene was formed by heating at 175°C. for about 30 hours, which was identified from the physical properties. (Fig. 11).

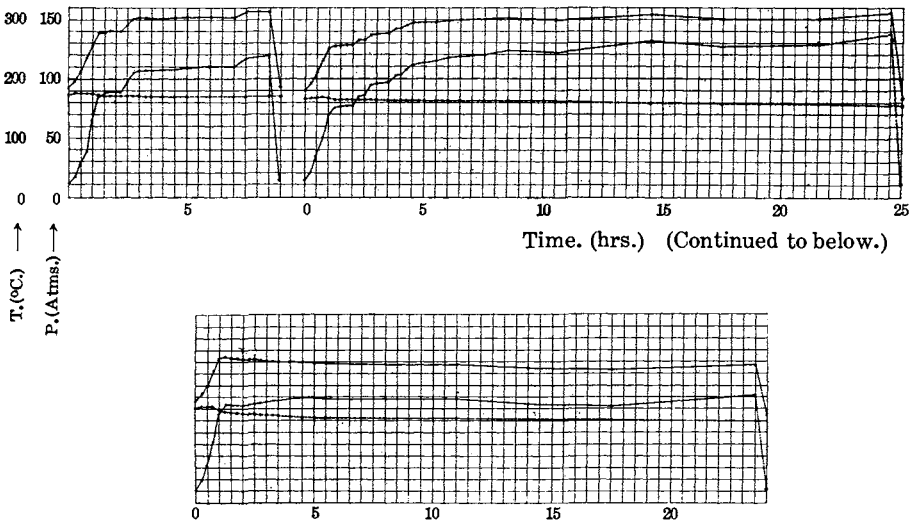


Fig. 11. Tetrahydrophenanthrene, 175°C.

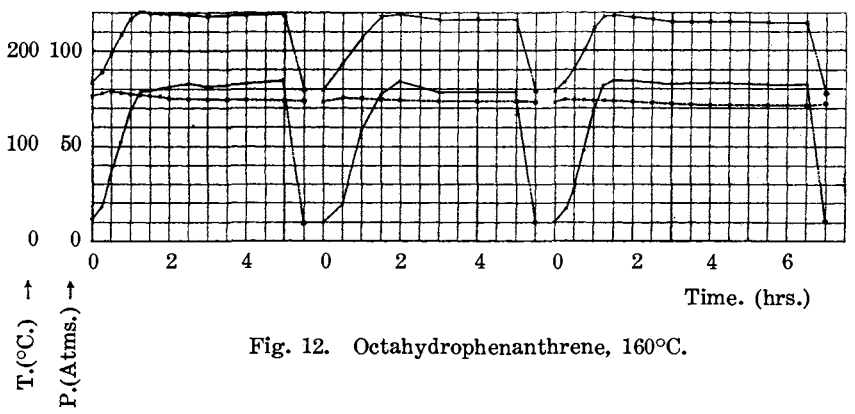
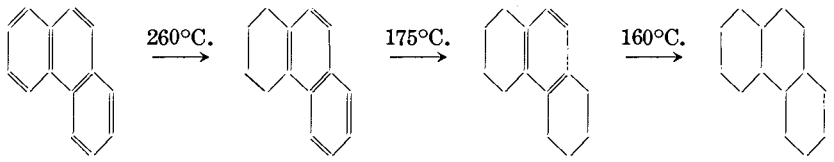


Fig. 12. Octahydrophenanthrene, 160°C.

To convert the octahydro-compound into perhydrophenanthrene, it was heated with hydrogen at about 160°C. for 5 hours under 77 atmospheric pressures at 0°C., and the yield of the pure compound was only 13% (Fig. 12). The catalytic reduction of phenanthrene may be represented by the following scheme:



Thus, the behaviour of phenanthrene towards reduced nickel and hydrogen at high temperature and high pressure, is, on the whole, similar to that of its isomeric anthracene, both being viewed as diphenylene compounds; the group CH=CH in the phenanthrene molecule, by which two benzene rings are joined, is very difficult to keep in a reduced state at higher temperatures since these two carbon atoms, as we noticed in the oxidation of phenanthrene, are situated in a more reactive state than the other carbon atoms due to lack of uniformity in distribution of energy in the molecule.

The hydrogenation of pyrene was more difficult than that of the other hydrocarbons. The hexahydro-compound was formed with theoretical

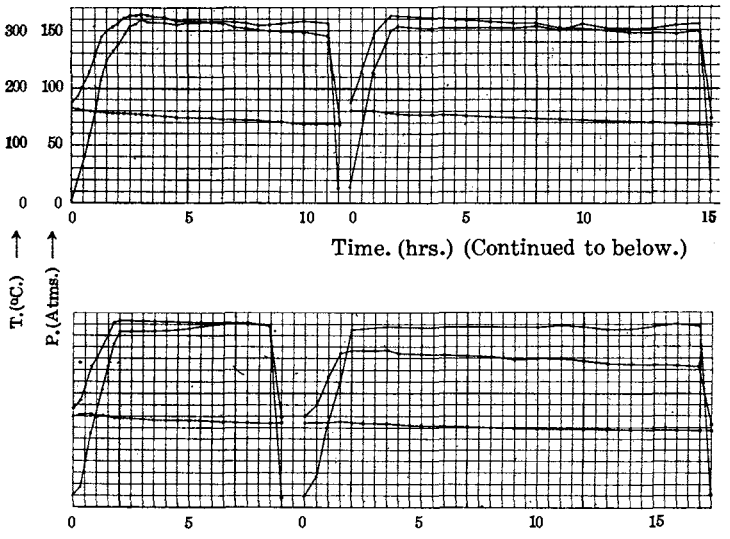


Fig. 13. Pyrene, 300°C.

yield when pyrene was heated with hydrogen at 300°C. for 52 hours under about 80 atmospheric pressures at 0°C. (Fig. 13); its physical properties, the results of elementary analysis (Found: C=92.2; H=7.7) and m.p. of picrate (118–119°C.) were identical with those of di-peri-di-trimethylene naphthalene obtained by Goldschmidt.[1]

Hexahydropyrene was regarded from the point of view of structure chemistry as a derivative of naphthalene or acenaphthene, and the catalytic reduction with reduced nickel and hydrogen at high temperature and pressure leads to a similar conclusion. When heated with hydrogen at 210°C. for 20 hours under 92 atmospheric pressures at 0°C., it yielded a substantial amount of decahydropyrene (Fig. 14), which was by further catalytic re-

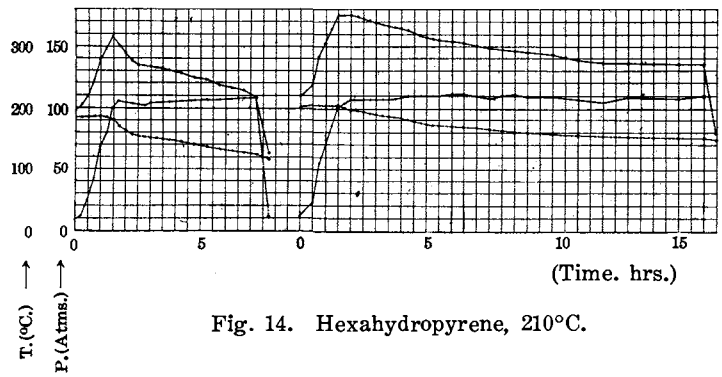


Fig. 14. Hexahydropyrene, 210°C.

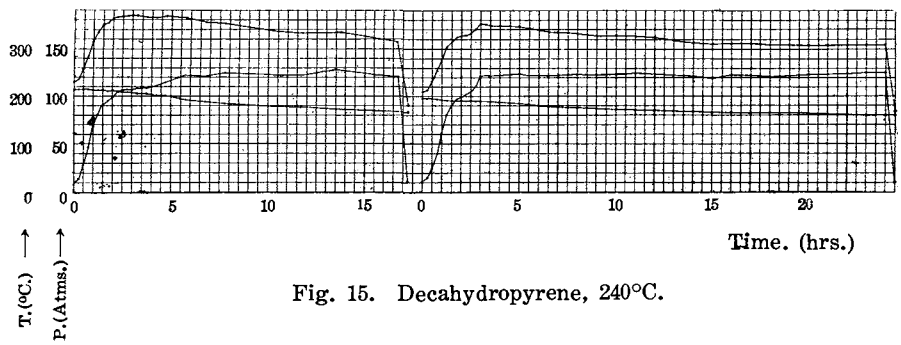


Fig. 15. Decahydropyrene, 240°C.

duction at 240°C. for 40 hours under 107 atmospheric pressures at 0°C., converted into perhydropyrene (Fig. 15). There are two isomeric forms of the perhydro-compound, the one consisting of colourless needles, m.p. 87–88°C., and the other being a liquid, b.p.=162–166°C. at 9.5 mm.; they were

(1) Goldschmidt: *Ann.*, **351** (1907), 218.

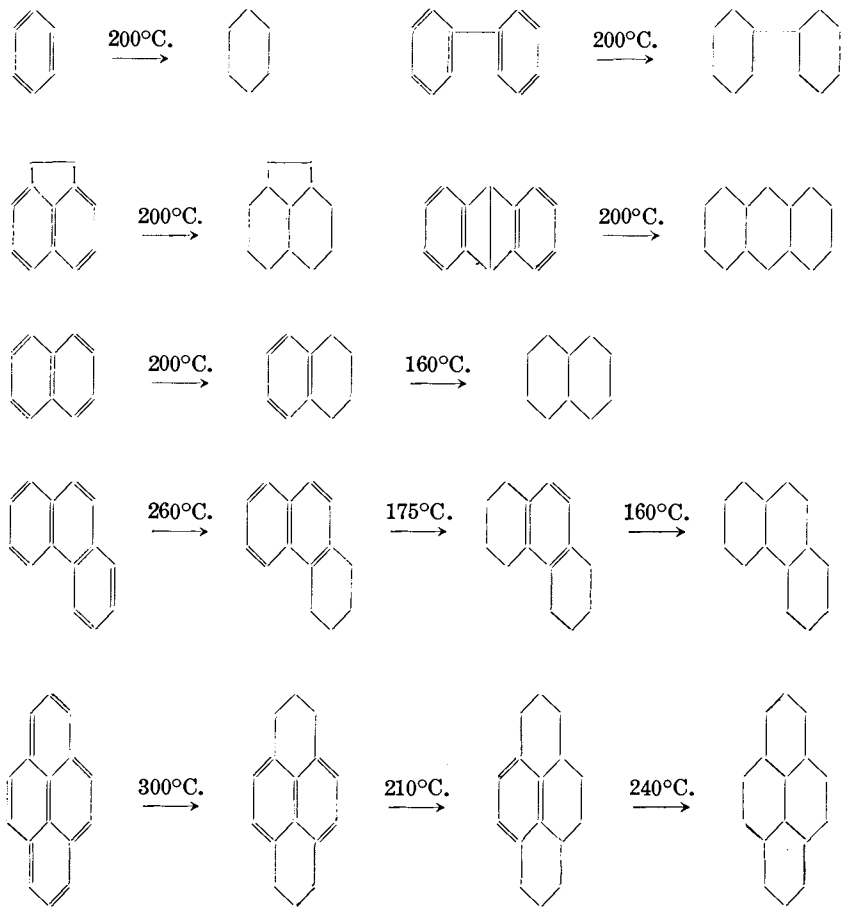
Table 3. The conditions and results of hydrogenation.

Number of experiment	Aromatic compound	Wt. (gr.)	Reaction temperature (°C)	Initial pressure at 0°C.	Hydrogen absorbed. atms. (obs.)	Hydrogen absorbed. atms. (calc.)	Time (hr.-min.)	Reaction product. Hydroaromatic compound	Yield (gr.)	d_4^{25}	n_D^{25}	M.R. obs.	M.R. calc.	B. P. (°C.)	M.P. (°C.)
7	Benzene	100	200	76	182	168	5–15	Hexahydrobenzene	96	0.7741	1,4235	27.69	27.70	80–80.5 (759.5 mm.)	
21	Diphenyl	65	„	95	115	98	3-45	Dicyclohexyl	61	0.8833	1.4772	53.20	53.22	231-233	
67	„	40	250	95	91	92	11–0	Phenylcyclohexane	37	0.9431	1.5313	52.56	51.82	234-236	
8	Naphthalene	100	200	91	71	67	13-0	Tetrahydronaphthalene	91	0.9675	1.5392	42.79	42.58	201.5–203.5	
9	„	„	250	69	74	67	12-15	Tetrahydronaphthalene	92	0.9678	1.5396	42.80	42.58	201.5–203.5	
18	Terahydro-naphthalene	„	160	91	119	97	7–0	Decahydronaphthalene	97	0.8881	1.4753	43.82	43.87	189-191	
22	Acenaphthene	„	200	94	168	142	9–0	Decahydroacenaphthene	103	0.9488	1.4996	51.24	51.06	235–237	
66	„	„	270	102	62	57	3–20	Tetrahydroacenaphthene	96	1.0065	1.5550	50.42	49.62	245–248	
31	Anthracene	28	200	97	42	41	9–45	Octahydroanthracene	7					160–163 (13 mm.)	72–73
								Perhydroanthracene	14					150–155 (13 mm.)	60.5-61
								Perhydroanthracene	4.5	0.9747	1.5275	60.67	60.25	150–155 (13 mm.)	
33	Phenanthrene	100	260	83	13	42	16-30	Tetrahydrophenanthrene	7.2	1.0777	1.6322	58.96	57.92	170–180 (18 mm.)	
43	Tetrahydro-phenanthrene	53	175	87	19	23	56–30	Perhydrophenanthrene	0.7	0.9630	1.5323	61.87	60.25	150-160 (18 mm.)	
								Octahydrophenanthrene	40	1.0232	1.5726	59.91	58.85	160–170 (18 mm.)	
44	Octahydro-phenanthrene	15	160	77	3	9	16–30	Perhydrophenanthrene	2.0	0.9609	1.5261	61.41	60.25	155–165 (25 mm.)	
39	Pyrene	65	300	82	39	39	51-30	Hexahydropyrene	65						131-132
40	Hexahydropyrene	93	210	92	60	38	23–15	Decahydropyrene	89	1.0522	1.5713	66.28	65.89	196.5–201.5 (18 mm.)	
41	Decahydropyrene	70	240	107	40	40	40–45	Perhydropyrene	50						86.8–87.8
								Perhydropyrene	14	0.9828	1.5228	67.84	67.29	162-166 (9.5 mm.)	

proved to isomers so by elementary analysis (Found: C=87.9; H=12.1 for solid isomer and C=87.8; H=12.1 for the liquid) and also by their physical properties.

The method described above for the hydrogenation of aromatic hydrocarbons in the presence of reduced nickel under high pressure and at high temperature, has many advantages when applied to the synthesis of hydroaromatic compounds compared with the method of Sabatier or those proposed by Ipatiew and others, but in order to get the required hydrogenated compounds the reduction procedure shown in the table should be adhered to.

Table 4.



As will be seen in the above tables, aromatic hydrocarbons made up of two or more benzene rings, may be divided into two groups from the point of view of catalytic hydrogenation; the one can be hydrogenated completely by one experimental condition as we noticed in the case of benzene, but in the case of the other group to which naphthalene and phenanthrene belong, complete hydrogenation can be achieved only through two or more steps of reaction, with changes in the experimental conditions, especially in the reaction temperature.

In conclusion, the writer wishes to express his gratitude to Vice-Admiral G. Yamashita and Vice-Admiral S. Kishimoto, the former and the present Director respectively of the Imperial Naval Fuel Depot, and to Engineer Captain Viscount M. Kawase, Chief of the Scientific Research and 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.

DENSITIES OF ALLYL ALCOHOL, METHYL-ETHYL KETONE AND TOLUENE AT LOW TEMPERATURES.

By Tokuzô TONOMURA and Kôe UEHARA.

Received July 27th, 1931. Published October 28th, 1931.

The densities of allyl alcohol, methyl-ethyl ketone, and toluene at low temperatures were determined by the sealed pycnometer method which was reported by the same authors in this Bulletin.[1] All the materials used in this experiment were Kahlbaum pure chemicals purified according to the usual methods.

The boiling points of the samples were as follows.

Allyl alcohol	Methyl-ethyl ketone	Toluene
96.5°–96.6° C / 755.0 mm.	79.4° C / 751 mm.	110.2° C / 753.1 mm.

The experimental results are shown in Tables 1, 2, and 3 and accompanying figure. Table 4 contains the densities at temperatures of round

Table 1. Densities of Allyl Alcohol.

Temp. (°C)	Density (obs.)	Density (calc.)	Pycnometer
0.00	0.87042		2 and 6
−10.43	0.87980	0.87959	6
−19.03	0.88739	0.88720	2
−21.40	0.88966	0.88930	6
−26.87	0.89457	0.89417	2
−40.13	0.90607	0.90606	2
−43.96	0.90974	0.90951	6
−48.54	0.91377	0.91365	2
−52.75	0.91746	0.91746	6
−59.12	0.92362	0.92327	2 and 6
−59.50	0.92402	0.92362	6
−65.78	0.92943	0.92936	2 and 6
−66.33	0.93020	0.92986	6
−68.60	0.93230	0.93194	6
−80.08	0.94260	0.94250	6

$$D = 0.870\,42 - 0.000\,875\,6\,t + 0.000\,000\,309\,t^2$$

(1) This Bulletin, **6** (1931), 118.

Table 2. Densities of Methyl-ethyl Ketone

Temp. (°C)	Density (obs.)	Density (calc.)	Pycnometer
0.00	0.82591		6 and 8
−14.41	0.83996	0.84007	8
−19.91	0.84503	0.84544	5
−25.50	0.85064	0.85089	5
−29.36	0.85454	0.85464	2 and 6
−30.70	0.85623	0.85594	5
−35.29	0.86070	0.86039	2 and 8
−37.58	0.86277	0.86259	5
−37.73	0.86288	0.86274	2 and 8
−37.95	0.86317	0.86296	2, 6 and 8
−45.37	0.87056	0.87011	5
−50.36	0.87521	0.87490	6 and 8
−55.35	0.88011	0.87968	5
−60.24	0.88481	0.88435	5
−62.03	0.88605	0.88606	6 and 8
−65.03	0.88924	0.88891	5
−77.83	0.90063	0.90103	5

$$D = 0.825\,91 - 0.000\,986\,6\,t - 0.000\,000\,274\,t^2$$

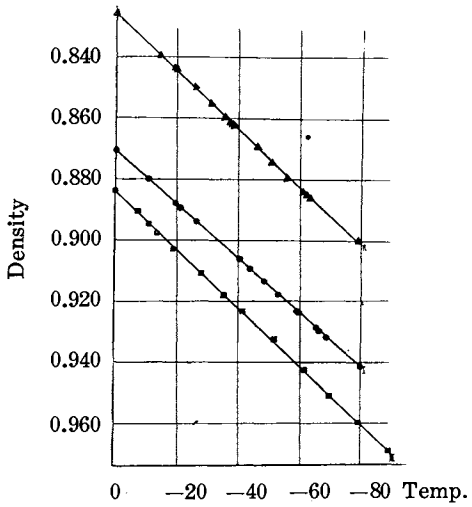
Table 3. Densities of Toluene.

Temp. (°C)	Density (obs.)	Density (calc.)	Pycnometer
0.00	0.88418		2, 6 and 8
−11.70	0.89618	0.89670	2, 6 and 8
−13.86	0.89830	0.89782	2, 6 and 8
−19.60	0.90368	0.90341	2, 6 and 8
−28.25	0.91170	0.91178	2, 6 and 8
−35.17	0.91825	0.91842	2, 6 and 8
−42.49	0.92491	0.92539	2, 6 and 8
−52.50	0.93423	0.93479	2, 6 and 8
−62.73	0.94393	0.94439	2, 6 and 8
−70.38	0.95132	0.95142	2 and 8
−79.41	0.95986	0.95978	2, 6 and 8
−89.27	0.96928	0.96874	8

$$D = 0.884\,18 - 0.000\,990\,6\,t - 0.000\,000\,487\,t^2$$

Table 4. Densities.

Temp. (°C)	Allyl alcohol	Methyl-ethyl ketone	Toluene
0.00	0.87042	0.82591	0.88418
−5.00	0.87481	0.83083	0.88912
−10.00	0.87921	0.83574	0.89404
−15.00	0.88362	0.84065	0.89893
−20.00	0.88805	0.84553	0.90380
−25.00	0.89250	0.85040	0.90864
−30.00	0.89697	0.85526	0.91346
−35.00	0.90145	0.86010	0.91825
−40.00	0.90594	0.86493	0.92303
−45.00	0.91045	0.86975	0.92777
−50.00	0.91497	0.87455	0.93249
−55.00	0.91951	0.87936	0.93719
−60.00	0.92407	0.88411	0.94186
−65.00	0.92864	0.88888	0.94651
−70.00	0.93323	0.89362	0.95114
−75.00	0.93783	0.89836	0.95574
−80.00	0.94245	0.90307	0.96031
−85.00	—	—	0.96486
−90.00	—	—	0.96939



I Allyl alcohol
II Methyl-ethyl Ketone
III Toluene

Fig. 1.

numbers, calculated by the empirical equations obtained by the least square method with the observed values.

The present authors express their gratitude to Prof. S. Mitsukuri's suggestions during the experiments.

July, 1931. The Laboratory of Theoretical Chemistry,
Faculty of Science, Tohoku Imp. Univ., Sendai.

AN ENZYME WHICH HXDROLYSES GLUCOSE-MONO-SULPHATE[1] : GLUCO-SULFATASE.

(Preliminary Communication).

By Tokuro SODA and Chikahiro HATTORI.

Received September 5th, 1931. Published October 28th, 1931.

Many studies on the enzymic hydrolysis of sulphuric acid esters were carried out especially by Neuberg and his co-workers. They have already discovered pheno-sulfatase[2] and recently chondro-sulfatase.[3] Another sulfatase is in myrosin. It splits sulphuric acid esters of the glucosides contained in mustard, but it is different from above sulfatases according to Neuberg and is called by him Senfölglukosido-sulfatase.

Glucose-mono-sulphate, synthetically prepared, was not fermented by yeast[4] and also Takadiastase which contains pheno-sulfatase has no power of hydrolysing it.

Yamazaki, in our laboratory, has examined the action of myrosin from mustard upon this compound, but unmistakable result was not obtained though after several weeks very faint hydrolysis was observed (unpublished). It was also noticed that when the solution of the barium salt of this ester was stored long while, some bacteria grew in it and at the same time the deposition of the barium sulphate was remarkable, but we could

(1) Neuberg and Liebermann: *Biochem. Z.*, **121** (1921), 326; Ohle: ibid., **131** (1922), 601, **136** (1923), 428; Soda: ibid., **135** (1923), 621.

(2) Neuberg and Kurono: *Biochem. Z.*, **140** (1923), 295; Neuberg and Linhardt: ibid., **142** (1923), 191; Noguchi: ibid., **143** (1924), 186, **144** (1924), 138; Neuberg and Simon: ibid., **156** (1925), 365; Rosenfeld: ibid., **157** (1925), 434; Neuberg and Wagner: ibid., **161** (1926), 492, **174** (1926), 457; Weinmann: ibid., **205** (1929), 214; Fromgageot: ibid., **208** (1929), 482; Nakamura: ibid., **175** (1926), 226.

(3) Neuberg and Hofmann: *Biochem. Z.*, **234** (1931), 345; Naturw., Heft 23/25 (1931), 484.

(4) Soda: *Biochem. Z.*, **135** (1923), 623.

not decide whether this was due to the bacterial action or merely natural decomposition.

Hirudo medicinalis when fed on the dilute solution of sodium salt of this ester, some increase of the sulphate ion was observed in a few days, yet we have not succeeded to prepare the enzyme solution from it.

At last we have experienced very strong hydrolysing power of snails. Those we collected were of Eulota spp.: *Eulota luhuana*, *Eulota quaesita* and *Eulota pelionphala*. They are commonly found in Tokyo districts, especially in rainy season. From these the enzyme solution was prepared by such a procedure as described in the experimental part. The enzyme solution was brought together with the substrate solution in a stoppered bottle and put aside at room temperature (22°—28°). Every day a portion of this mixture was drawn out and the sulphate ion was estimated after Dennis's nephelometric method of blood sulphate estimation.(1) To compare the turbidity we used a control instead of the standard sulphate solution which is used in the usual procedure. The control was made from a solution of the same composition as the reaction mixture, freshly prepared just before every estimation, applying the same technique as for the reaction mixture. In this way the effect of a trace of sulphate ion which could not be removed from the original solutions was cancelled, and thus the difference of the nephelometric readings corresponds the degree of the enzymic hydrolysis.

The series of data thus obtained are somewhat irregular but on the whole we can clearly recognize the progress of the hydrolysis. In good conditions about 10% of the applied glucose-mono-sulphate was found to be hydrolysed in the course of a week (for these estimations Fiske's benzidine titration method(2) was used).

The action of our enzyme upon the potassium salt of following esters was also examined in order to know its specificity: Ethyl-sulphate, phenol-sulphate, galactose-tetra-sulphate(3) and sucrose-sulphate.(4)

Ethyl-sulphate was not attacked throughout all the experiments, while it gave always positive results with glucose-mono-sulphate. Results with galactose-sulphate and sucrose-sulphate were sometimes negative and sometimes positive, but not very marked.

While phenol-sulphate was very strongly hydrolysed by Enzyme-B, it was only slightly decomposed by Enzyme-A and -D which were found to be very active toward glucose-mono-sulphate. For the preparation of Enzyme-A and -D we applied about the same procedure, but Enzyme-B was

(1) Dennis: *J. Biol. Chem.*, **49** (1921), 311.
(2) Fiske: ibid., **47** (1921), 26.
(3) Akamatsu: *Biochem. Z.*, **142** (1923), 181.
(4) Soda: ibid., **135** (1923), 621.

prepared by somewhat different way as is shown in experimental part. Thus it seems possible to differentiate the glucose-sulphate hydrolysing action of our enzyme from that of pheno-sulfatase; therefore it has, so far as we examined, specific action of hydrolysing glucose-mono-sulphate, and we wish to suggest for this new sulfatase a provisional name "Gluco-sulfatase." Its optimum pH seems to be about 7. We do not know yet whether this enzyme, as Neuberg's chondro-sulfatase, has the faculty of hydrolysing chondroitin-sulphuric acid. An experiment to decide this question is now going on.* Moreover it should also be investigated whether both the pheno-sulfatase action and gluco-sulfatase action of our enzyme due to the one and same enzyme or there exist two different and separable enzymes.

The authors wish to acknowledge their thanks to the Ministry of Education for a grant which partially covered the expenses of these experiments.

Experimental Part.

Preparation of enzyme solution. Snails were collected in Tokyo or its suburb. The first collection in which *Eulota pelionphala* predominated was treated as following: Snails were hungered for about a week in a cage, then their shells were removed (50 gr.) and crushed by freezing them in liquid air. Now 100 c.c. of water together with some coarse silica sand, kieselguhr and barium carbonate were added and ground in a mortar throughly by adding chloroform. After four days' autolysis, the enzyme solution was separated by means of the centrifugal machine. We labelled this preparation Enzyme-A.

Enzyme-B was prepared from the second collection, The most part of this collection were *Eulota luhuana*, and weighed 80 gr. when their shells removed. They were treated almost in the same manner as above described, by adding 160 c.c. of water, 15 gr. of kieselguhr and some silica sand, but in this case the addition of barium carbonate was omitted and toluene was used instead of chloroform.

The third collection (the most part *Eulota quaesita*): Snails were hungered for about two weeks, and they have lost much of their activity. They weighed 180 gr. in naked state and were ground in a mortar immediately, without freezing, to puree with some coarse silica sand and chloroform. This puree was kept at room temperature for about a week in a stoppered bottle.

* While this paper was under press, we have ascertained that the gluco-sulfatase did not hydrolyse chondroitin-sulphuric acid which was prepared from tracheal cartilage.

Enzyme-C was prepared from 60 gr. of this puree merely extracting with 120 c.c. of water. After some ten days, to another 60 gr. of the puree 10 gr. of kieselguhr, 10 gr. of barium carbonate and some water were added, ground in a mortar and subsequently by means of centrifugal machine the solution of Enzyme-D was separated.

Manipulations for the estimation of the increase of sulphate ion. For this estimation Dennis's method[1] was applied in the following manner: 2 c.c. of the reaction mixture (composition of which are given at each protocol) were drawn out every day. To this 5 c.c. of $HgCl_2$-HCl mixture were added and filtered through after half an hour with a small amount of animal charcoal (free from sulphate). Of this clear protein free solution 5 c.c. was taken out and then by adding 2.5 c.c. of ammonium nitrate solution and 2.5 c.c. of barium chloride solution the suspension of barium sulphate was formed. Turbidity thus produced was compared with that of the control by means of nephelometer. The control was made, by applying the same manipulation as above stated, from a solution of the same composition as the reaction mixture. This solution was made every time just before use by mixing the substrate solution and the enzyme solution which were kept at the same temperature as the reaction mixture.

I. Experiments with Enzyme-A.

Protocol No. 1. (June 25th, 23°C). The composition of the reaction mixture:

Enzyme solution	Water	Substrate solution
5 c.c.	5 c.c.	10 cc.

The approximate concentration of each substrate solution:

(1)	Sodium glucose-mono-sulphate	(Gl.)	2 %
(2)	Potassium phenol-sulphate	(Phen.)	5 %
(3)	Potassium galactose-tetra-sulphate	(Gal.)	5 %
(4)	Potassium sucrose-sulphate	(Suc.)	5 %
(5)	Potassium ethyl-sulphate	(Ethyl.)	7 %

Days	Gl.	Phen.	Gal.	Suc.	Ethyl.
1	9.2	7.8	10.0	6.1	9.7
2	8.9	8.9	6.7	9.8	10.4
4	4.5*	7.9	8.3	8.1	11.9
5	5.1*	7.3	7.8	8.9	11.9

(1) loc. cit.

* For these figures the control was set at 20.0 mm., as the turbidity was too high.

These figures are nephelometric readings in mm., those of controls being always set at 10.0 mm. This is understood in the following protocols too.

At the sixth day the decomposed amount of sulphate of glucose-mono-sulphate was estimated: 5 c.c. of the reaction mixture was treated with 2 c.c. of trichloroacetic acid (20%) and subsequently filtered through with animal charcoal (free from sulphate). With 5 c.c. of this protein-free filtrate the amount of sulphate was determined by Fiske's benzidine titration method.[1] 1.26 c.c. of NaOH solution (1 c.c. corresponds 0.311 mg. of sulphur) were used. From this value the amounts of sulphate hydrolysed in 1 c.c. of the original reaction mixture is calculated as follows:

$$0.311 \times 1.26 \times 7/5 \times 1/5 = 0.11 \text{ mg. as sulphur.}$$

After the acid hydrolysis of the protein-free filtrate the amount of sulphur was again determined in the same way. 1.14 Mg. of sulphur was found in 1 c.c. of the original reaction mixture. Therefore 0.11/1.14=9.7% of glucose-mono-sulphate ought to be hydrolysed by the enzyme. The influence of sulphate in the control was here neglected because of its small amount.

Protocol No. 2. (July 1st, 25°C.) The composition of the reaction mixture:

Enzyme solution	Buffer solution	Glucose-mono-sulphate (2%)
5 c.c.	5 c.c.	10 c.c

The buffer solution: 1/20 Mol. sodium acetate-acetic acid mixture, except for pH = 8 which was composed of 1/10 mol. ammonium chloride-ammonia.

	pH				
Days	4	5	6	7	8
1	10.6	8.8	8.2	7.6	7.2
2	11.4	10.6	9.4	7.3	8.1
3	9.5	8.9	7.4	6.4	8.4
5	7.4	7.5	6.8	5.0	6.5
6	8.3	7.6	6.7	5.5	7.4

At the seventh day the hydrolysed amount of sulphate was estimated, as in protocol No. 1, with the solution of pH=7. It was found that 12.5% of the total sulphur was titratable as free sulphate ion.

(1) loc. cit.

Protocol No. 3. (July 24th, 24°C.) The composition of the reaction mixture:

	Enzyme solution 10 c.c.	Substrate solution 10 c.c.	
Days	Gl. (6 %)	Phen.	Gal.
1	9.3	10.9	11.5
3	8.0	9.0	10.0
4	6.4	8.7	9.2
5	6.8	8.7	8.6
7	5.1	8.8	8.8

II. Experiments with Enzyme-B.

Protocol No. 4. (July 14th). This experiment was carried out in the thermostat at 35°C., the composition of the reaction mixture being the same as in protocol No. 2. Its pH was kept at 7.0.

Days	1	2	3	4	5
	6.8	3.3	4.5	7.4	6.6

As was expected the enzymic hydrolysis went on very rapidly for the first few days, but later on the nephelometric readings gradually increased as is seen in above data. This singularity is probably due to the natural decomposition of solutions from which the control was prepared owing to the high temperature. Because, both the turbidities increased steadily if we compared each of them separately with that of 1/2000 mol. potassium sulphate.

Protocol No. 5. (July 17th, 26°C.) The composition of the reaction mixtures was the same as that of Protocol No. 1.

Days	Gl. (6 %)	Phen.	Gal.	Suc.	Ethyl.
1	9.8	7.9	10.7	12.3	11.1
3	6.6	6.2	12.5	7.5	13.7

Protocol No. 6. (July 28th, 26°C.) The composition of the reaction mixtures was the same as that of Protocol No. 3.

Days	Gl. (3.8 %)	Phen.
1	8.9	10.3
3	8.7	10.2
4	7.7	4.7
6	7.2	4.5

III. Experiments with Enzyme-C and -D.

Protocol No. 7. (August 4th, 28°C.) The composition of the reaction mixtures was the same as that of Protocol No. 3.

	Enzyme-C		Enzyme-D	
Days	Gl.	Phen.	Gl.	Phen.
1	6.9	10.3	6.4	9.5
2	7.0	9.7	6.6	6.4
4	7.3	10.1	3.8	8.5

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ON THE RATE OF SOLUTION OF OXYGEN INTO WATER. PART VI. THE RATE OF ABSORPTION OF OXYGEN BY SODIUM SULPHITE SOLUTION.

By Susumu MIYAMOTO and Tetsuo KAYA.

Received July 30th, 1931. Published October 28th, 1931.

Introduction.

It was confirmed in the previous research[1] that the velocity of oxidation of sodium sulphite solution by oxygen, when the main body of the solution is well agitated with a stirrer of special construction, increases with the increase of the concentration of sodium sulphite as far as it attains a certain maximum value, which remains constant with the further increase of the concentration of sodium sulphite and that this maximum value is proportional to the area of the boundary surface.

The fact that the maximum rate of oxidation of sodium sulphite solution is proportional to the partial pressure of oxygen was also confirmed[2]. The interpretation on these experimental facts, given by the present writers, is based upon the assumption that the maximum rate of oxidation of sodium sulphite solution is equivalent to the rate of solution of oxygen into water, in the surface of which no free oxygen is present.

(1) S. Miyamoto and A. Nakata, this Bulletin, **6** (1931), 9.
(2) S. Miyamoto, T. Kaya and A. Nakata, ibid., **5** (1930), 229.

The comparison[1] of the rate of solution of oxygen, calculated from the maximum rate of oxidation of sodium sulphite solution, with the initial rate of solution of oxygen into pure water, obtained directly by several writers[2], confirmed that this assumption has great probability.

It is intended in the present paper to describe the results of the measurements of the rate of absorption of oxygen by sodium sulphite solution by the observation of the rate of the decrease of the volume of oxygen at constant temperature and pressure, which is in contact with sodium sulphite solution, the main body of which being well agitated with a stirrer of special constructions as in the previous research, and to discuss the phenomenon more precisely.

Experimental.

The apparatus employed is graphically shown in Fig. 1.

D is a gas burette (25 c.c.), E a glass tube of about the same magnitude as that of D, A and B stop-cocks, S a stirrer, whose wing is made to be at right angles to the boundary surface. The lower end of the outer tube of the stirrer is dipped in the solution to avoid the disturbance of the surface area, when it is put in motion, and the upper end of the tube is so constructed that the gas present in the vessel is separated with mercury from air, as will be seen in the figure.

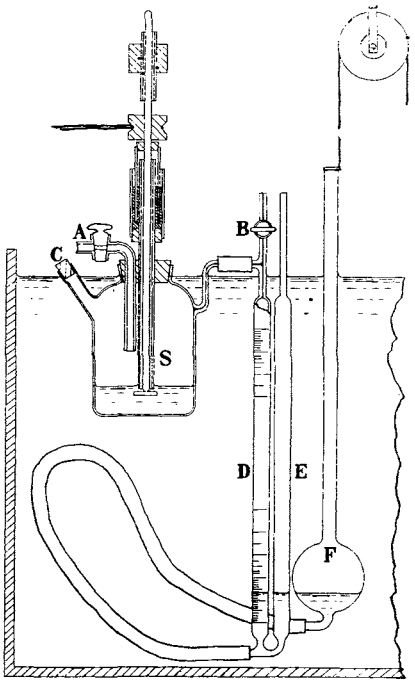

Fig. 1.

The measurements were carried out in the following manner.

All parts of the apparatus were placed in a water thermostat regulated at a constant temperature. The tubes D and E were filled with water saturated with oxygen by the elevation of the tube F, the stop-cock B being opened. A definite quantity of newly distilled water was poured into

(1) loc. cit.

(2) Adeney and Becker, *Phil. Mag.*, **38** (1919), 317; **39** (1920), 385; **42** (1921), 87, Davis and Crandall, *J. Am. Chem. Soc.*, **52** (1930), 3757, 3769.

the vessel through D, and oxygen gas, washed with acidified potassium bichromate solution and alkali, was passed through A into the vessel at a high velocity for about 30 minutes.

Oxygen gas employed is that manufactured from liquid air and its oxygen content was determined by analysis to be 97 per cent by volume. When the air in the vessel has been completely replaced with oxygen, the tube D was also filled with oxygen by lowering the tube F, and a definite quantity of sodium sulphite solution of known concentration was added into the vessel through C, the total volume of the solution being made up to 40 c.c.

The stop-cocks A and B were closed, the stirrer S was put in motion at about 400 revolutions per minute, and when the levels of water in D and E have been made to be at equal heights, the stop-watch was started. The levels of water in D and E were regulated to be always at equal heights by the elevation of the tube F and the height of water in the tube D was recorded from time to time. The rate of the decrease of the volume of oxygen at constant temperature and pressure was observed in this way.

Representative results are given in Table 1. The area of the interface is 27.75 cm^2. in each case.

Table 1.

Temp.	C_0 Na_2SO_3 normal	t min.	Δv cor. c.c.	$\Delta n \times 10^5$ moles	$\frac{\Delta n}{\Delta t} \times 10^5$ moles/min.
15°C.	0.3714	0	—	—	—
		20	4.17	18.59	0.929
		30	6.47	28.86	0.962
		40	8.70	38.81	0.970
		50	10.91	48.67	0.973
		60	13.13	58.61	0.976
					Mean 0.962
	0.5811	0	—	—	—
		30	6.21	27.71	0.924
		40	8.31	37.07	0.927
		50	10.45	46.65	0.933
					Mean 0.928
	0.6299	0	—	—	—
		10	2.05	9.13	0.913
		30	6.16	27.47	0.916
		40	8.26	36.84	0.921
		50	10.52	46.94	0.939
					Mean 0.922
					Mean Value = 0.937

Table 1—(*Continued*).

Temp.	C_0 Na_2SO_3 normal	t min.	Δv cor. c.c.	$\Delta n \times 10^5$ moles	$\frac{\Delta n}{\Delta t} \times 10^5$ moles/min.
20°C.	0.4356	0	—	—	—
		15	4.22	18.85	1.26
		25	7.24	32.28	1.29
		30	8.88	39.62	1.32
					Mean 1.290
	0.5050	0	—	—	—
		20	5.70	25.44	1.27
		40	11.75	52.44	1.31
		50	15.32	68.38	1.37
					Mean 1.317
	0.5800	0	—	—	—
		30	8.78	39.19	1.31
		40	11.89	53.07	1.32
					Mean 1.315
	0.7440	0	—	—	—
		10	3.02	13.48	1.35
		20	6.09	27.16	1.35
		30	9.34	41.66	1.39
					Mean 1.363
					Mean Value = 1.321
25°C.	0.4202	0	—	—	—
		20	7.95	35.47	1.77
		30	12.39	55.29	1.84
		40	16.89	75.38	1.88
					Mean 1.830
	0.4805	0	—	—	—
		10	4.06	18.12	1.81
		20	8.05	35.91	1.80
		30	12.39	55.31	1.84
					Mean 1.817
	0.4964	0	—	—	—
		10	3.82	17.05	1.70
		20	7.77	34.69	1.73
		30	12.21	54.48	1.82
		40	17.01	75.90	1.90
					Mean 1.788
	0.573	0	—	—	—
		10	4.27	19.05	1.91
		20	8.58	38.30	1.92
		30	13.02	58.11	1.94
					Mean 1.923

Table 1—(*Concluded*).

Temp.	C_0 Na_2SO_3 normal	t min.	Δv cor. c.c.	$\Delta n \times 10^5$ moles	$\frac{\Delta n}{\Delta t} \times 10^5$ moles/min.
25°C.	0.6110	0	—	—	—
		20	8.18	36.51	1.83
		30	12.30	54.91	1.83
		40	16.34	72.90	1.82
					Mean 1.827
	0.6281	0	—	—	—
		10	3.98	17.78	1.78
		20	8.10	36.16	1.81
		30	12.54	55.96	1.86
					Mean 1.817
	0.702	0	—	—	—
		10	4.43	19.76	1.98
		20	8.88	39.64	1.98
		30	13.44	59.96	2.00
					Mean 1.987
					Mean Value = 1.856
35°C.	0.499	0	—	—	—
		10	6.04	26.94	2.69
		15	9.21	41.11	2.74
		20	12.64	56.41	2.82
		25	16.15	72.08	2.88
					Mean 2.78
	0.633	0	—	—	—
		10	6.19	27.61	2.76
		15	9.37	41.80	2.79
		20	12.58	56.15	2.81
		25	15.86	70.76	2.83
					Mean 2.80
	0.715	0	—	—	—
		5	3.12	13.92	2.78
		10	6.30	28.11	2.81
		15	9.41	41.99	2.80
		20	12.65	56.44	2.82
		25	15.94	71.12	2.84
					Mean 2.81
					Mean Value = 2.797

Initial concentrations of sodium sulphite solutions employed are given in the second column of the table. The values Δv_{cor}, given in the fourth column of the table, are the quantity of oxygen absorbed during t- minutes

expressed by the volume of oxygen at 0°C. and 1 atmosphere, the vapour pressure of the solution and the barometric height being taken into calculation. The absorbed quantities of oxygen expressed in the unit of gram molecules are given in the fifth column of the table, the rate of absorption being given in the last column.

As was expected, the rate of absorption of oxygen by the solution is independent of the concentration of sodium sulphite. The rate of absorption does not increase with the increase of the concentration of sodium sulphite in the range of its concentrations, given in the table.

It was reported by Milbauer and Pazourek[1] that the rate of oxidation of sodium sulphite solution of high concentration is smaller than that of lower concentration. As was above described, the rate of absorption of

Table 2.

Temp.	C_0 Na_2SO_3 normal	t min.	Δv cor. c.c.	$\Delta n \times 10^5$ moles	$\frac{\Delta n}{\Delta t} \times 10^5$ moles/min.
15°C.	1.421	0	—	—	—
		10	1.19	5.29	0.529
		30	3.54	15.79	0.526
		40	4.65	20.74	0.519
		60	6.93	30.91	0.515
					Mean 0.522
	2.138	0	—	—	—
		10	0.46	2.06	0.206
		20	0.94	4.20	0.210
		30	1.42	6.34	0.211
		40	1.84	8.23	0.206
		50	2.29	10.20	0.204
		60	2.72	12.14	0.202
					Mean 0.2065
25°C.	1.425	0	—	—	—
		10	2.44	10.89	1.09
		20	4.87	21.75	1.09
		40	9.83	43.86	1.10
		60	14.67	65.45	1.09
					Mean 1.093
	2.140	0	—	—	—
		10	0.75	3.37	0.337
		20	1.46	6.51	0.326
		40	2.82	12.58	0.315
		60	4.32	19.30	0.322
					Mean 0.3250

(1) *Bull. Soc. Chim.*, **31** (1922), 676.

oxygen by sodium sulphite solution is independent of its concentration, when the concentration lies in the range of about 0.35—0.75 normal. The measurements were carried out when the concentration of sodium sulphite is comparatively high, and the representative results are given in Table 2. The phenomenon observed by Milbauer and Pazourek was confirmed. The rate of absorption of oxygen by sodium sulphite solution of high concentration decreases with the increase of the concentration of sodium sulphite.

It was ascertained by the preliminary experiments, that when the concentration of sodium sulphite solution is lower than about 0.35 normal, the rate of oxidation of sodium sulphite solution increases with the increase of the concentration of sodium sulphite as far as it attains the maximum value, given in Table 1.

Discussion.

From the results of the experiments above described, it will easily be seen that there are three different stages when the effect of the increase of the concentration of sodium sulphite solution on the rate of oxidation of sodium sulphite solution is observed. The behaviour is graphically shown in Fig. 2.

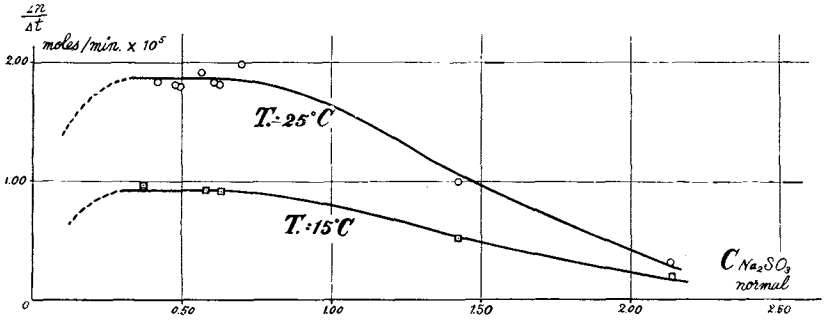

Fig. 2.

At low concentrations of sodium sulphite solutions, the rate of oxidation of sodium sulphite solution increases with the increase of the concentration of sodium sulphite as far as it attains a certain maximum value.

At middle concentrations of sodium sulphite solutions, the rate of oxidation of sodium sulphite solution is maximum and independent of the concentration of sodium sulphite.

At high concentrations of sodium sulphite solution the rate of absorption decreases with the increase of the concentration of sodium sulphite.

Under the conditions of the present experiments it was confirmed[1] that there exists no stationary liquid film at the interface, and according to the theory of one of the present writers (Miyamoto) the phenomenon can be interpreted in the following manner.

At low concentrations of sodium sulphite solution the number of the molecules of sodium sulphite at the upper surface layer is not sufficient to react with all of the molecules of oxygen, which enter into the liquid phase per unit time. Then in this case a part of the molecules of oxygen, which could not react with sodium sulphite, will go back into the gas phase, and a part of them diffuses into the main body of the solution. Under special condition, the upper surface of the liquid will be saturated with the molecules of oxygen in a short time, and a part of the molecules which diffuse towards the deeper layer of the liquid, will react with the molecules of sodium sulphite, which diffuse towards the reacting zone from the main body of the solution. Under this condition, the rate of solution may be expressed by the following equation, proposed by Davis and Crandall.[2]

$$\frac{1}{S}\left(\frac{dn}{dt}\right) = k\,(C_m + C_\infty),$$

where C_m is the concentration of sodium sulphite solution, C_∞ the saturation concentration of oxygen in water, S the area of the boundary surface, k a constant, n the number of moles of oxygen in the liquid phase.

When the quantity C_∞ is negligible compared with C_m, the equation becomes

$$\frac{1}{S}\left(\frac{dn}{dt}\right) = k\,C_m.$$

In the second stage, the number of molecules of sodium sulphite at the boundary surface is quite sufficient to react with all the molecules of oxygen, which enter into the liquid phase per unit of time, and therefore the concentration of oxygen at the interface is always kept at zero. Under these conditions, it will easily be accepted that the rate of oxidation of sodium sulphite solution, which is, in this case, equal to the rate of solution of oxygen into the solution, is equivalent to the rate of solution of oxygen into water, in the surface of which no free oxygen exists, and that the rate of absorption of oxygen by the solution is maximum, which is independent of the concentration of sodium sulphite.

(1) S. Miyamoto, T. Kaya and A. Nakata, this Bulletin, **6** (1931), 133.
(2) *J. Am. Chem. Soc.*, **52** (1930), 3769.

As was discussed in the previous paper,[1] the behaviour in this stage will be difficult to be interpreted by the ordinary diffusion layer theories, which are based on the assumption that the boundary surface is instantaneously saturated with gas.

The following equation[2] was proposed for the rate of solution of gas into liquid by one of the present writers (Miyamoto).

$$\frac{\Delta n}{\Delta t} = N'' - N''' \text{ moles/sec.}, \quad \cdots\cdots\cdots\cdots\cdots\cdots \quad (1)$$

where N'' is the number of moles of the gas which enters into the liquid phase per second, N''' the number of moles of the gas which leaves the liquid phase per second, and n the number of moles of the gas in the liquid phase.

When the concentration of the gas in the liquid phase is kept at zero, the equation (1) becomes

$$\left(\frac{\Delta n}{\Delta t}\right)_0 = N'' \text{ moles sec.}, \quad \cdots\cdots\cdots\cdots\cdots\cdots \quad (2)$$

According to the theory of one of the present writers,[3]

$$\left(\frac{\Delta n}{\Delta t}\right)_0 = N'' = \frac{60 p_{O_2}}{\sqrt{2\pi MRT}} e^{-\frac{Mu_0^2}{2RT}} S \text{ moles/min.}, \quad \cdots\cdots \quad (3)$$

where p_{O_2} is the partial pressure of the gas, M the molecular weight of the gas, R the gas constant, S the area of the boundary surface, and u_0 a constant.

The derivation of this equation is based upon the assumption that among the molecules, which collide with the liquid surface, only those, whose components of velocity at right angles to the surface are greater than a threshold value u_0, are able to enter into the liquid phase.

When the concentration of the gas in the liquid phase is not kept at zero, the rate of the escape of molecules of the gas from the liquid phase should naturally be taken into consideration as was described in the previous paper.[4]

At high concentrations of sodium sulphite solution, the concentration of oxygen at the liquid surface will also be kept at zero by the presence of

(1) S. Miyamoto, T. Kaya and A. Nakata, this Bulletin, **6** (1931), 133.
(2) S. Miyamoto and A. Nakata, ibid., **6** (1931), 18.
(3) S. Miyamoto and A. Nakata, this Bulletin, **6** (1931), 20.
(4) Ibid.

the sufficient quantity of sodium sulphite reacting with all the molecules of oxygen, which enter into the liquid phase per unit of time, so long as the main body of the liquid is well agitated with a stirrer, and the oxidation velocity of sodium sulphite solution will be equal to the rate of absorption of oxygen by the solution, which will be expressed by the above mentioned equation (3).

As the threshold value u_0 should be considered to depend upon the properties of the boundary surface, it may be expected with a high degree of probability that the value u_0 of pure water and that of the solution will have different values. From the equation (3), it is quite clear that the rate of solution of gases will depend upon the threshold value u_0. When the concentration of sodium sulphite is not very high, the minute difference of the nature of the boundary surface will have no appreciable effect on the value u_0, but at high concentration the threshold value u_0 will be influenced by the change of the nature of the interface. Therefore the present results of experiments may be explained by the assumption that the threshold value u_0 increases with the increase of the concentration of sodium sulphite. At high concentration of sodium sulphite the rate of solution of oxygen decreases in consequence of the increase of the value u_0.

In Tables 3 and 4, the results of the present experiments are given in comparison with the results of the experiments, reported in the previous paper.[1] The agreement will be satisfactory.

In the fifth column of Table 4, the threshold value u_0 at several temperatures, calculated by the equation (3), using the observed values of the rate of solution of oxygen into sodium sulphite solution, are given. The value u_0 was found to be independent of temperature within the region of the present experiments.

The value β given in the fourth column of the table, stands for the ratio of the number of molecules of oxygen which enter into water and the number of molecules of oxygen which collide with the liquid surface per unit of time, and was calculated by

$$\beta = e^{\frac{Mu_0^2}{2RT}} = \frac{1}{60}\,\frac{1}{S}\left(\frac{\Delta n}{\Delta t}\right)_0 \frac{\sqrt{2\pi MRT}}{p_{O_2}}\,.$$

In the last column of the table, the root-mean-square-velocity of oxygen at several temperatures, calculated by

$$\sqrt{\overline{C^2}} = \sqrt{\frac{3RT}{M}}$$

(1) Loc. cit.

Table 3.

Temp.	Method	S cm².	$\frac{\Delta n}{\Delta t}$ moles per min.	$\frac{1}{60}\frac{1}{S}\frac{\Delta n}{\Delta t}$ moles per sec. per cm².
15°C.	Volume decrease	27.75	0.937×10^{-5}	5.63×10^{-9}
	Iodometry	—	—	5.53×10^{-9}
20°C.	Volume decrease	27.75	1.321×10^{-5}	7.93×10^{-9}
25°C.	Volume decrease	27.75	1.856×10^{-5}	11.14×10^{-9}
	Iodometry	—	—	10.75×10^{-9}
35°C.	Volume decrease	27.75	2.797×10^{-5}	16.81×10^{-9}
	Iodometry	—	—	16.25×10^{-9}

Table 4.

Temp.	p_{O_2} atms.	Method	$\frac{1}{60}\frac{1}{S}\left(\frac{\Delta n}{\Delta t}\right)$ moles per sec. per cm².	β	u_0 cm. per sec.	$\sqrt{\overline{C^2}}$ cm. per sec.
15°C.	0.954	Volume decrease	5.63×10^{-9}	1.278×10^{-8}	1.649×10^{5}	4.737×10^{4}
		Iodometry	5.53×10^{-9}	1.258×10^{-8}	1.650×10^{5}	
20°C.	0.948	Volume decrease	7.93×10^{-9}	1.828×10^{-8}	1.647×10^{5}	4.778×10^{4}
25°C.	0.941	Volume decrease	11.14×10^{-9}	2.773×10^{-8}	1.641×10^{5}	4.818×10^{4}
		Iodometry	10.75×10^{-9}	2.517×10^{-8}	1.646×10^{5}	
35°C.	0.916	Volume decrease	16.81×10^{-9}	4.111×10^{-8}	1.650×10^{5}	4.898×10^{4}
		Iodometry	16.25×10^{-9}	3.974×10^{-8}	1.651×10^{5}	

are given. It follows from the present research that only the molecules of oxygen, whose components of velocity at right angles to the boundary surface are greater than approximately 3.4 times the root-mean-square-velocity, are able to enter into the liquid phase.

Summary.

(1) The rate of solution of oxygen into sodium sulphite solution of various concentrations was observed by the measurements of the decrease of the volume of gas phase at constant temperature and pressure.

(2) At low concentrations of sodium sulphite solution, the rate of solution of oxygen increases as the concentration of sodium sulphite increases. At middle concentrations, the rate of solution is maximum and independent of the concentration of sodium sulphite.

At high concentrations the rate of solution decreases with the increase of the concentration of sodium sulphite.

(3) A theoretical interpretation on the results of the present experiments was given.

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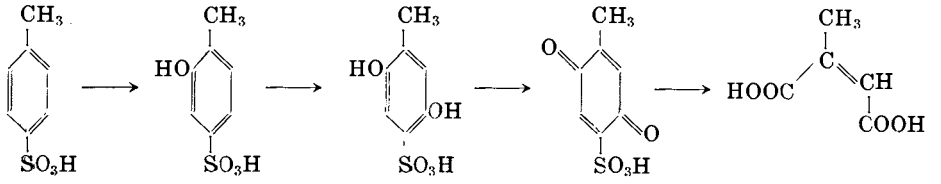
DIE ELEKTROCHEMISCHE OXYDATION DES TOLU-*p*-CHINONS.

Von Moriaki YOKOYAMA und Wataru ISHIKAWA.

Eingegangen am 31 August, 1931. Ausgegeben am 28 Oktober, 1931.

Wie einer der Autoren vor einiger Zeit an anderer Stelle[1] mitgeteilt hat, kann man durch elektrochemische Oxydation von 1-Methyl-benzol-sulfonsäure-(4) die Mesaconsäure erhalten. Die Entstehung wurde dabei nach folgendem Schema erklärt :

(1) M. Yokoyama, *Helv. chim. Acta.*, XIII (1930), 1257.



Es ist darnach anzunehmen, dass *o*-Kresolsulfonsäure[1] und Toluchinon bei elektrochemischer Oxydation auch Mesaconsäure ergaben. Daher haben wir vorliegende Untersuchung unternommen, um die Annahme über den Verlauf von *p*-Toluol-sulfonsäure zu stützen, und das bis jetzt wenig studierte Verhalten der Chinone[2] bei Einwirkung von anodischen Sauerstoff zu erkennen.

I. Elektrochemische Oxydation von Toluchinon.

Der elektrolytische Trog, der in einem grösseren Kühlgefäss stand, bestand aus einem cylindrischen etwa 200 cm^3 fassenden Glasgefäss, welches durch einen mehrfach durchbohrten Kautschukstopfen verschlossen wurde.

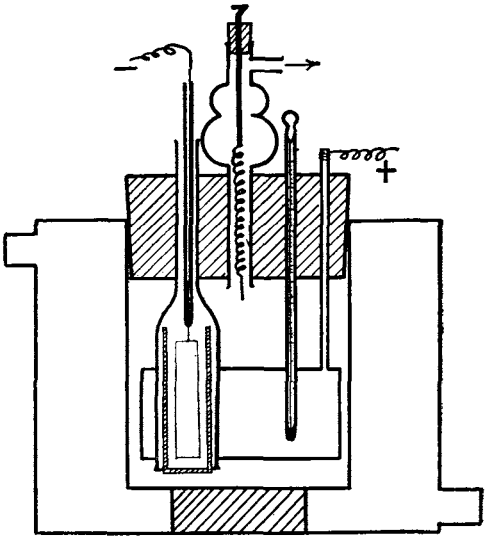


Fig. 1.

(1) Aus der *o*-Kresolsulfonsäure wurde die Mesaconsäure durch elektrochemische Oxydation erhalten. (ibid.).

(2) Ueber *o*-Xylochinon; M. Yokoyama, *Helv. Chem. Acta*, XII (1929), 771; Ueber Benzochinon; R. Kempf, *J. prakt. Chem.*, [2], **83** (1911).

Der Anolyt enthielt je 2.5 gm. Toluchinon[1] in 100 ccm 10 % iger Schwefelsäure, das Chinon war teilweise gelöst und teilweise suspendirt.

Wie Fig. 1 zeigt, befand sich die cylindrische Platinblechkathode in einem ebenfalls zylindrischen Tondiaphragma, welches mit einem Glasrohr bedeckt wurde um Gasdiffusion in den Anodenraum zu verhindern.

Der Katolyt war 10 % iger Schwefelsäure. Es wurde an einer cylindrischen Bleidioxydanode bei der anodischen Stromdichte von 0.05[1] Amp/cm^2. oxydiert. Der Elektrotyt wurde durch Eiswasserkühlung auf 10–12°C. gehalten.

Zur Erzielung einer ständigen Bewegung und einer dadurch feineren Suspension des Reaktionsgemisches wurden die Apparate auf der Platte einer kleinen Schüttelmaschine aufgestellte. Der gelb gefärbte Elektrolyt verblasste im Verlauf der Elektrolyse allmählich, bei längerer Elektrolyse verschwand die Suspension und schliesslich wurde die Flüssigkeit klar und farblos.

A. **Die gas-förmigen Reaktionspropukte:** Während der Elektrolyse wurde das Kathodengas ins Freie geleitet, das Anodengas aber durch den den Anodenraum verschliessenden Gummistoffen geführt war, in die auffangbürette von 1 L. Inhalt (A in Fig. 2).

Die kleine Gasauffangbürette (B) war notwendig, um das Anodengas dann aufzunehmen wenn ein Teil des Gases aus (A) zum Zweck der Analyse in das Azotometer (C) übergeführt wurde. Als Sperrflüssigkeit dieser Auffang- und Messapparatur diente gesättigte, Kohlendioxyd praktisch nicht absorbierende Natriumchloridlsg.[3] der einige Tropfen konz. Schwefelsäure und Phenolphthaleinlsg.[4] zugesetzt waren.

---

(1) Das nötige Toluchinon stellten wir anfangs aus *o*-Toluidin (Kahlbaum) nach Angaben von K. Schnitter dar (*Ber.*, **20** (1887), 2283), erzielten aber ein unbefriedigendes Resultat. Indessen lässt sich durch eine leichte Modification des Schnitterschen Verfahrens das Chinon aus dem Reaktionsgemisch leicht abtrennen. Diese kleine Abänderung bestand im Wesentlichen darin, dass bei der Isolierung des entstandenen Chinons die mühsame Aetherextraktion durch Vakuum Destillation ersetzt wurde. Dadurch erhielten wir so reine gelbe Krystalle von Toluchinon mit der Ausbeute von 70% , dass für gewöhnlichen Zweck die Reinigung nicht nötig war. Smp. 68°C .

(2) Bei den meisten Versuchen haben wir mit Stromdichten von 0.05=Amp/cm^2 gearbeitet um die Versuchszeit abzukürzen, obwohl die Stromausbeute mit $D_A = 0.0125$ Amp/cm^2 besser als die mit $D_A = 0.05$ Amp/cm^2 war., Wenn die Versuch bei $D_A = 0.0125$ Amp/cm$_2$ durchgeführt wurden, wird bei den gasanalytischen Resultaten speziell daraufhingewiesen.

(3) G. Hoffmann, *Z. angew. Chem.*, **39** (1926), 401.

(4) H. Tropisch, *Z. angew. Chem.*, **39** (1926), 23.

Ein aliquoter Teil des in der Literbürette (A) aufgesammelten Gases wurde, nach dem Lesen des genauen Volum durch Azotometer (C), in die mit 35 % iger Kalilauge gefüllte Bürette (D) mit Hilfe des Dreiweghahns übergeführt, um den Gehalt des Gases an Kohlendioxyd zu ermitteln. Der Gehalt des Anodengases an Sauerstoff wurde bestimmt in einer Hempelschen Gasabsorptionspipette, die nach Franzen[1] mit alkalischer Natriumhydrosulfitlsg. gefüllt war, und der Gehalt an Kohlenoxyd in einer gleichen Pipette, deren Füllung aus ammoniakalischer Kupferchlorürlsg. und Kupferdrahtnetzröllchen[2] bestand.

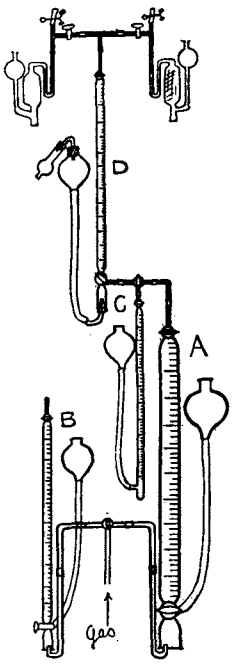


Fig. 2.

Einige Analysenresultät aus der grossen Reihe der durchgeführten Versuche wurden in der folgenden Tabelle zusammengestellt. Die Gasvolumina wurden darin auf 0° C und 760 mm Druck reduziert.

Wie aus der Tabelle (1) und (2), und Kurven (Fig. 3 und 4) ersichtlich, ist das Verhalten der Anodengase nicht so unverschiedlich, doch ist die Stromausbeute bei niedriger Stromdichte besser als die bei höherer. Die Menge des Kohlenoxyds ist fast konstant. Der Sauerstoff nimmt zunächst ab

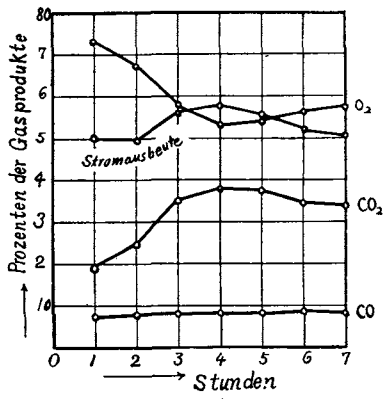


Fig. 3.

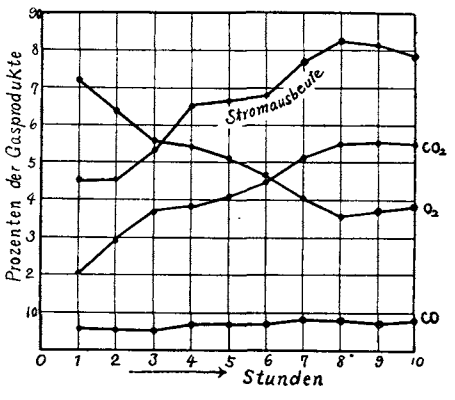


Fig. 4.

(1) Treadwell: Lehrbuch der Analyt. Chem. Bd II (11 Aufl.) 667.
(2) Ebenda 669.

Tabelle 1.

Stromstärke: 2.5 Amp. Stromdichte: 0.05 Amp. / cm.^{2}

Stunden	Gesamt Anodengas ccm.	Prozenten der aufgefangenen Gas- produkte			Verbrauchte O_2 in Zelle (ccm)(1)	Strom- ausbeute(2)
		CO_2	CO	O_2		
1	355.2	19.2	7.1	73.2	261.0	50.0
2	387.5	24.3	8.2	67.5	260.3	49.9
3	399.8	35.1	7.9	57.0	294.5	56.4
4	407.4	38.2	8.1	53.7	303.0	57.7
5	423.0	37.4	8.3	54.3	291.0	55.7
6	439.5	34.9	8.8	56.3	274.2	52.6
7	445.9	33.9	8.4	57.7	264.8	50.7

Tabelle 2.

Stromstärke: 0.625 Amp. Stromdichte: 0.0125 Amp. / cm^2.

Stunden	Gesamt Anodengas ccm.	Prozenten der aufgefangenen Gas- produkte			Verbrauchte O_2 in Zelle (ccm)(3)	Strom- ausbeute
		CO_2	CO	O_2		
1	98.8	20.4	7.4	72.4	58.8	45.2
2	106.1	29.4	6.8	63.8	62.5	45.8
3	106.1	36.1	6.4	57.6	69.0	53.0
4	82.5	38.2	7.6	54.2	85.6	65.7
5	84.8	41.2	7.5	51.3	86.8	66.6
6	88.9	45.2	7.0	47.8	87.8	67.5
7	73.5	51.1	8.4	40.5	100.5	76.5
8	80.9	55.3	8.0	36.7	106.5	82.0
9	60.5	55.3	7.6	37.1	100.6	81.5
10	75.5	54.0	8.0	38.0	101.6	78.2

(1) Die Werte wurden erhalten durch Subtraktion der aufgefangenen Sauerstoffvolumina von 522.6 ccm. (2.5 Amp. entwickeln pro Stunde nach dem Faraday'schen Gesetz 0.7462 gm. $O_2 = 522.6$ cm^3.)

(2) Der in der Zelle verbrauchte O_2 in Prozenten des elektrolytisch entwickelten Sauerstoffs.

(3) 0.625 Amp. entwickeln pro Stunde 0.1865 gm. O_2 entsprechend 130.6 ccm. und die Werte wurde berechnet wie Tabelle 1.

mit steigender Strommenge und erreicht einen Minimum Punkt, dagegen sind die Verhältnisse des Kohlendioxyds umgekehrt.

Aus diesen analytischen Daten, kann man vielleicht so folgen, dass aus Chinon zuerst Substanzen entstehen, die leichter als dieses Ausgangsmatial zu Kohlenoxyd und Kohlendioxyd abgebraut werden. In dem Masse, wie sich diese leichter oxydierbaren Körper (z.B. Ameinsensäure, Maleinsäure u.s.w.) in Anolyt anreichern, wird der elektrolytisch entwickelte Sauerstoff stärker verbraucht.

B. Die in Aether leicht löslichen Produkte. Nach beendeter Elektrolyse (Strommenge 30 F/Mol) wurde der Anolyt unmittelbar durch Ausschütteln mit Benzol vom unveränderten Chinon befreit. Der vom Chinon befreite Anolyt wurde von fünf einzelnen Versuchen gesammelt und mit Aether mehrmals ausgeschüttelt. Die Aetherlsg. hinterliess nach Entfernung des Aethers eine nach Ameisensäure riehende, braun gefärbte Flüssigkeit.

Um die Ameisensäure zu entfernen, wurde der Destillationsrückstand einige Mal mit frischem Aether geschüttelt und überdestilliert. Durch intensive Mischung der überdestillierten Aetherlsg. mit einem wässrigen Bariumcarbonatbrei, Trennen und Filtrieren der wässrigen Schicht und Verdampfen des Filtrats erhielten wir Bariumformiat. Nach der Entfernug der Ameisensäure erstarrte der Aetherrückstand zu einer krystallinischen Masse, die mit Wasser in einen schwer (a) und leicht löslichen Teil (b) zerlegt werden konnte. Der erstere betrug etwa 0.13 gm. und der zweite 1.9 gm.

(*a*) *Die in Wasser schwer lösliche Substanz:* Aus der schwer löslichen Substanz wurde wiederholtes Umkrystallisieren aus heissem Wasser und Vakuumsublimieren (13 mm.; 150°C.) ein weisses Krystallpulver erhalten, das Lackmuspapier rötete und zwischen 200° und 202°C. schmolz. Es war Mesaconsäure. In dieser Fraktion gab es noch eine fast schwarze krystallinische Masse, die unlöslich in heissem Wasser, löslich in Alkohol, nicht sauer gegen Lackmus war und bis 290 C°. nicht schmolz. Nach diesen Beobachtungen ist diese Substanz vermutlich ein Polymerisationsprodukte[1] von Toluchinon, entstanden infolge des Gegenwart von Schwefelsäure.

(*b*) *Die in Wasser leicht löslichen Produkte:* Diese Substanz wurde in wenig Wasser gelöst und mit Tierkohle unter Zusatz von etwa Schwefelsäure gereinigt. Aus der gereinigten Lsg. wurde durch mehrmalige Ausäthern eine weisse Substanz erhalten, die im Wesentlichen aus Maleinsäure bestand. Daraus stellten wir mit Hilfe von Bariumcarbonat das schön krystallisierende Bariumsalz der Säure her. Durch Lösen in verd. Essig-

(1) Spica, *Gazzetta Chimica Italiana*, **12**, 225. (Beilstein, 4 Aufl., VII, 646).

säure (50 %) wurde das Bariumsalz vom anderen in 50% Essigsäure schwer löslichen und als Reaktionsprodukte möglichen dicarbonsauren Salzen getrennt. Nach dem Eindampfen des Filtrats blieb ein weisser krystallinischer Rückstand, der mit wenig Wasser aufgenommen und mit Schwefelsäure vorsichtig vom Barium freigemacht wurde. Aus der so erhaltenen Lsg. erhielten wir weisse schönen Krystalle, die nach nochmaligem Umkrystallisieren aus Aether bei 130°C. schmolzen.

Die in verdünnter Essigsäure schwer löslichen Bariumsalze konnten wir einstweilen wegen Substanzmangels nicht weiter identifizieren.

C. **Die mit Aether nicht extrahierbaren Produkte:** Eine Probe des nach der Extraktion mit Aether zurückgebliebene Teils des Anolyten wurde eingedampft und geglüht; sie schwärzte sich beim Glühen stark unter Verkohlungserscheinungen. Der Anolyt enthielt also noch organisches Material.

Der Anolyt wurde deshalb zunächst mit der berechneten Menge von Bariumcarbonat von der Hauptmenge Schwefelsäure befreit und das Filtrat vom Bariumsulfat mit Tierkohle gereinigt. Dann wurde die Flüssigkeit mit Bleiacetatlsg. behandelt, um eventuell vorhandene Traubensäure über ihr Bleisalz zu isolieren. Das abfiltrierte und gut ausgewaschene Bleisalz wurde mit Schwefelwasserstoff in heisser wässriger Suspension zerlegt, das Sulfid filtriert und die Flüssigkeit im Vakuum eingedampft. Der Rückstand wurde in einer kleinen Menge Wasser gelöst und im Vakuum-Exssikator eingedunstet. Hier schieden sich aus der braunen Flüssigkeit fast weisse Krystalle von Traubensäure aus, die auf Ton abgepresst und aus Wasser unter Anwendung von Tierkohle umkrystalliert wurden. Die Krystalle schmolzen bei 197°–200°C. unter Schäumen.

Identifizierung der Oxydationsprodukte.[1]

(*a*) *Ameisensäure.* Das Bariumsalz wurde nach zweimaligem Umkrystallisieren aus Wasser im Vakuum über Schwefelsäure bis zur Gewichtskonstantz getrocknet; die Analyse ergab folgende Werte:

0.1739 gm. gaben durch Abrauchen mit Schwefelsäure 0.1777 gm. $BaSO_4$. Gef.: Ba = 60.13% . Ber. für $(CHO_2)_2Ba$: Ba = 60.42% .

Die Säure schied aus Mercurichloridlsg. Mercurochlorid ab und reduzierte Silbernitratlsg.

(*b*) *Mesaconsäure.* Sie wurde durch Sublimation im Vakuum (13 mm.; Badtemp. 140°-150°C.) gereinigt. Smp. 201°C. (er sollte bei 204.5°C.[2] liegen); der Mischschmelzpunkt ergab mit einen käuflichen Präparat (von Kahlbaum) 202°C.

(1) Die zur Identifizierung gebrauchte Oxydationsprodukte wurden durch mehrmaligen Versuchen erhalten.

(2) H. Mottern u. G. Keeman, *J. Am. Chem. Soc.*, **53** (1931), 2347.

Anal: Subst. = 0.1165, 0.0991; CO_2 = 0.1968, 0.1671; H_2O = 0.0457, 0.0422 gr.

0.1378 gm Subst. verbrauchten 41.6 ccm 0.05-N Natronlauge.

Gef.: C = 46.07, 45.99; H = 4.39, 4.76%; Aeq-Gew. = 66.25. Ber. für $C_5H_6O_4$: C = 46.14; H = 4.65%; Aeq-Gew. = 65.02.

(*c*) *Maleinsäure.* Bei Vakuumsublimation mit Phosphorpentoxyd (13 mm. Druck und 80°-110°C.), lieferte sie ein Sublimat von Maleinsäureanhydrid[1] in schönen Krystallen. Das bei 51°C. schmolz. Das Bariumsalz wurde nach dem Trocknen[2] bei 100°C. der Analyse unterworfen.

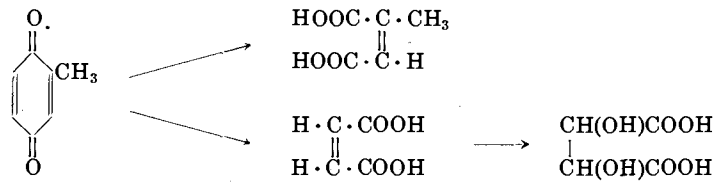
Subst. = 0.2106; CO_2 = 0.1343; H_2O = 0.0303 gm. Subst. = 0.1914; $BaSO_4$ = 0.1641 gm. Gef.: C = 17.39; H = 1.61; Ba = 50.45%. Ber. fur $C_4H_2O_4Ba+H_2O$: C = 17.82; H = 1.50; Ba = 50.98%.

(*d*) *Traubensäure.* Diese wurde durch den Schmelzpunkt (gegen 201°C.), durch die Art des Schmelzens (unter charakteristischem Gasblasen) und durch die Reaktion ihrer wässrigen Lsg. mit Gypswasser (Fällung feiner nadelformiger Krystalle) charakterisiert. Das mit Bariumacetat erhaltene Bariumsalz[3] wurde nach dem Trocknen über Schwefelsäure der Analyse unterworfen.

Subst. = 0.1901; CO_2 = 0.0974; H_2O = 0.0520 gm. Subst. = 0.1211; $BaSO_4$ = 0.0828 gm. Gef.: C = 13.98; H = 3.06; Ba = 40.23. Ber. fur $C_4H_4O_6Ba+3H_2O$: C = 14.14; H = 2.97; Ba = 40.47%.

Die elektrochemische Oxydation von Tolu-*p*-Chinon der Oxydation nicht stand hält, sondern weiterm Abbau unter Bildung von Maleinsäure, Ameisensäure neben Mesaconsäure, Kohléndi- und Kohlenmonoxyd unterworfen ist. Die Maleinsäure gibt durch weitere Oxydation Traubensäure, Ameisensäure, u.s.w.

Unter Zusammenfassung aller bischerigen Beobachtungen lässt sich einstweilen folgendes Schema über den Oxydationsverlauf, (wobei die letzten Stufen Ameisensäure, Kohlenoxyd und Kohlendioxyd noch nicht berücksichtigt sind), aufstellten:



(1) R. Kempf, *J. prakt. Chem.* (2), **78** (1908), 239; *Ber.*, **39** (1906), 3722.

(2) D. Vorländer, *Ann.*, **280** (1894), 192. vgl. auch Kekulé u. Strecker; *Ann.*, **223** (1884), 185.

(3) Lossen u. Riebensahm, *Ann.*, **292** (1896), 313.

II. Elektrochemische Oxydation der Maleinsäure.

Da nach obigen Versuchen anzunehmen ist, dass die Traubensäure durch weitere Oxydation der Maleinsaure entstanden ist, so wurde auch diese Säure elektrolytich oxydirt.

Die Apparatur und die Elektrolysebedingungen waren dem vorigen Analog.

2 gm. Maleinsäure (Kahlbaum) wurden in 100 ccm 10% iger Schwefelsäure gelöst und bei 10°–13°C. (unter Eiswasserkühlung) an einer Bleidioxydanode mit der anodischen Stromdichte 0.05 Amp/cm² oxydirt; die Kathode war ein Platinblech, der Katholyt 10% iger Schwefelsäure.

A. Die gasförmigen Reaktionsprodukte: Kohlenmonoxyd und Kohlendioxyd erhielten wir auch bei diesen Versuchen. Die gasanalytischen Resultate sind in der folgenden Tabelle zusammengestellt.

Tabelle 3.

Stromstärke: 2.5 Amp. Stromdichte: 0.05 Amp./cm.²

Stunden	Gesamt Anodengas ccm	Prozenten der aufgefangenen Gas- produkte			Verbrauchte O_2 in Zelle (ccm)(1)	Strom- ausbeute(1)
		CO_2	CO	O_2		
1	398.3	34.9	6.6	58.5	283.5	55.3
2	428.0	31.5	7.6	60.9	260.5	50.0
3	450.0	29.1	8.0	62.9	238.5	46.6
4	484.9	25.9	5.3	63.3	214.3	41.2
5	485.0	22.9	4.9	67.2	195.5	37.5
6	422.0	14.9	2.0	85.1	162,8	31.2

In Vergleich mit früheren Anodengasanalyse ist die Gasabscheidung im Verlauf dieser Elektrolyse analog.

B. Die in Aether löslichen Produkte: Die zugeführte Strommenge 14 F/Mol. Die aus dem Anolyten durch mehrmalige Extraktion mit Aether erhaltene Mischung von Stoffen erwies sich nach Entfernung des Aethers als eine stechend nach Ameisensäure riechende Flüssigkeit. Daraus erhielten wir auch Bariumformiat (etwa 1 gm für 5 einzelne Versuche) nach gleicher Behandlung wie der Oxydation von Toluchinon. Nach der Ab-

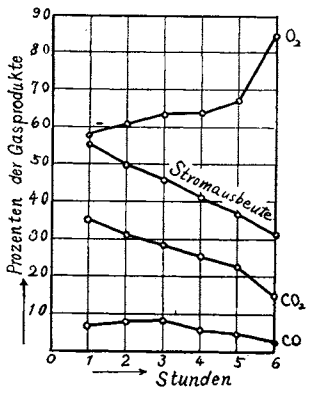


Fig. 5.

(1) Die Werte wurden berechnet wie Tabelle 1.

scheidung der Ameisensäure erstarrte die Flüssigkeit zu schönen Krystallnadeln (etwa 3.2 gm für 5 einzelne Versuche), deren Smp. zwischen 125° und 142°C war (keine einheitlichen Subst.).

Zwecks Isolierung der Maleinsäure (Ausgangsmaterial) von anderen Reaktionsprodukten stellten wir Bariumsalz dieser Substanz dar. Aus diesem Salze erhielten wir nach der bei der Oxydation von Tolu·*p*·chinon bereits erwähnten Behandlung etwa 2.6 gm unveränderte Maleinsäure. Nach diesen Beobachtungen müssen noch andere Produkte existieren, deren Natur wir einstweilen noch nicht ermitteln können.

C. **Die durch Aether nicht extrahierbaren Produkte:** Aus der nach der Extraktion mit Aether zurückgebliebenen Anodenflüssigkeit erhielten wir nach der im Abschnitte I (C) geschilderten Methode auch traubensaures Blei (1.9 gm für 5 einzelne Versuche). Nach Abscheidung des Blei durch Schwefelwasserstoff stellten wir weisse Krystalle der freien Traubensäure her, die nach Umkrystallisieren aus heissem Wasser bei 202° C. unter Schäumen schmolzen. Die Säure[1] wurde nach den Trocknen über Schwefelsäure analysiert.

Subst. = 0.1791; CO_2 = 0.2075; H_2O = 0.0663 gm. Gef.: C = 31.42; H = 4.18%.
Ber. für $C_4H_6O_6$: C = 31.98; H = 4.04%.

Wie die näheren Verhältnisse bei der Oxydation der Maleinsäure zur Traubensäure sind, ob die weitere Produkte liefert und wie das Verhalten der freien Mesaconsäure bei Einwirkung von anodischem Sauerstoff ist, sollen die bereits im Gang befindlichen Versuch klären.

Zusammenfassung.

(1) Bei der elektrochemischen Oxydation von Tolu·*p*·chinon an der Bleidioxydanode in verdünnter Schwefelsäure wurden die folgenden Oxydationsprodukte erhalten: Ameisensäure, Mesaconsäure, Traubensäure, Maleinsäure, Kohlendioxyd und Kohlenoxyd.

(2) Maleinsäure wurde bei den gleichen Bedingung wie bei der Oxydation des Toluchinons elektrochemisch oxydiert, und ergab auch Ameisensäure, Traubensäure, CO_2 und CO. Dadurch wurde Beziehungen zwischen Toluchinon und seinen elektrochemischen Oxydationsprodukten aufgeklärt.

(3) Der kinetische Verlauf der Gasabscheidung an der Anode während der Elektrolyse wurde analytisch verfolgt.

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(1) Die Säure wurde durch vielmalige Elektrolyse aufgesammelt.

STUDIES ON THE FUSED PRODUCTS OF Cr_2O_3-SiO_2 SYSTEM.

By Yohei YAMAGUCHI and Haruo NAKAZAWA.

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Glasses coloured by various metal oxides were known from ancient time, but there are, however, only few studies on the colouring of fused silica glass. Copper and cobalt oxides give red and blue silica glass respectively. Chromic oxide has a special property of producing many kinds of colours on silica glass. Experimental conditions affect on the colours of silica glass containing chromic oxide, since black, green and other colours are obtained by the different treatments. The following studies were carried out to make clear the special and complex properties of the obscure Cr_2O_3-SiO_2 system.

Experimental.

The materials used are an ordinary chromic oxide for chemical use and natural quartz sands which were purified by hydrochloric acid. The mixture of a definite proportion of these materials was fused by an electric furnace of high voltage. The experimental results are as follows.

When the temperature of the mixture is nearly to the melting point of silica (1700°C.) or a little higher, there is no chemical reaction between two oxides. And it is observed that the chromic oxide powder, owing to its high melting point (ca. 2000°C.), was heterogeneously distributed in the fused silica. Subsequently a homogeneous fused product should be obtained by raising temperature far above 1700°C. The product thus obtained was striped on the whole by the consequence of high viscosity of fused silica and inhomogeneity of the temperature raised, and the initial granular form of the chromic oxide was not found in it as in the first case.

The colour of the fused product depends upon the concentration of chromic oxide, the temperature of the fusion and the cooling velocity of the heated mass. At a very high temperature and with a low concentration of chromic oxide (about 0.5%) it gives a transparent and homogeneous mass of blue, violet or reddish brown colour. High concentrations of the oxide (few percent) give non-transparent products, and their colours are too many to point out strictly. But it may be said that by the rapid cooling the product is black and glassy, and by the slow cooling dark blue, reddish brown or dark green and brittle. The relation between the experimental conditions and the colours of the fused product may be summarized as follows.

(A). Low concn. of Cr_2O_3	Transparent, glassy and homogeneous mass with a colour of blue, violet or reddish brown.
(B). High concn. of Cr_2O_3 and rapid cooling	Glassy and apparently black mass, its thin plate is, however, transparent and reddish brown.
(C). High concn. of Cr_2O_3 and slow cooling	Non-transparent and not glassy mass of dark green, dark blue, reddish brown etc.

A beautiful green glass can not be obtained by one heating operation, but it is occasionally obtained only by the second heating. This second heating operation upon the fused product will be mentioned by the term of "reheating" in this paper. No characteristic changes were observed on the reheated products of (A) and (B) to 1700°C., but a remarkable change was found on (C). By the reheating of (C) somewhat below the melting point of silica it becomes a very brittle and pure green mass. When the temperature of the reheating was elevated to 1700°C., it, however, becomes a very beautiful green and glassy fused mass which may be useful to ornaments.

Microscopic Studies of the Fused Products. A petrographic microscope was used to examine the products. (A) is completely transparent under the microscope. And considering that there is no compound between two oxides and are many varieties of the colour, it is perhaps the colloidal solution of chromic oxide in fused silica. (B) is also glassy and its thin plate is homogeneous and reddish brown, but it contains very little particles of chromic oxide which is a small fraction of its initial quantity.

The studies by the petrographic microscope were almost limited to (C), since the very beautiful green and glassy fused mass was obtained by its reheating. Fig. 1, 2, 3 and 4 are the examples of (C). Figs. 2 and 4 are those of under the crossed Nicols. In the figures only needle-like crystals are found, but the crystals are not really needle and are very thin plate of which section appears needle-like. The form of the crystal is shown by the following diagram. This crystal is a very thin tridymite. The main part of the chromic oxide mixed are distributed in the tridymite as little green crystals which can be observed by the microscope. The other small part of it exists homogeneously in the same tridymite with the different colours like (A) and (B). The occurrence of chromic oxide in two different kinds in the fused product as above may be the reason why so many varieties of (C) are obtained. By the ratio of the both kinds of the oxide and by the size of the particle, it can be conceived to be obtained so

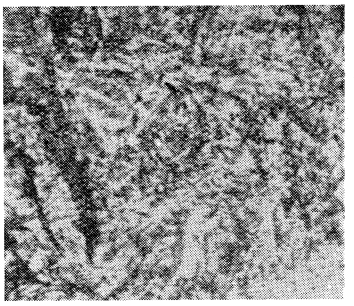


Fig. 1. (×1000)

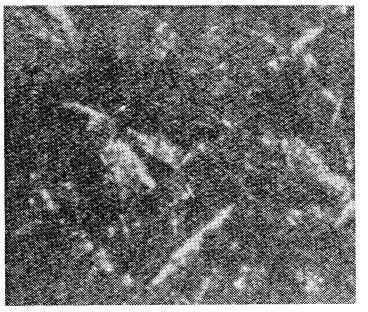


Fig. 2. (×1000).

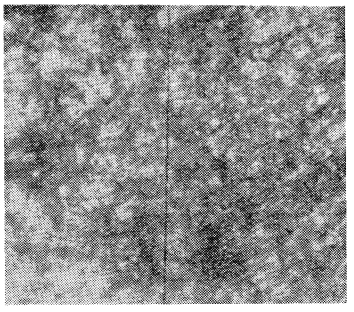


Fig. 3. (×1000)

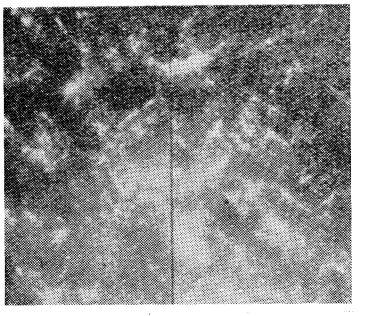
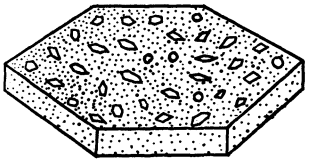


Fig. 4. (×1000)



Diagram

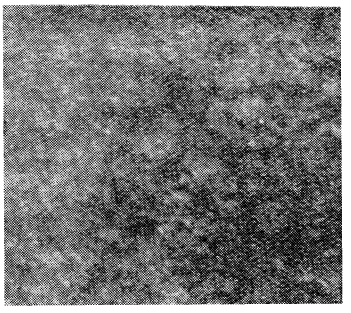


Fig. 5. (×1000)

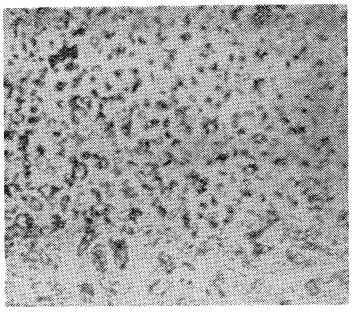


Fig. 6. (×1000)

many colours of the fused products as they can not be expressed by proper words.

The mechanism of the second reheating operation on the product is explained by the results of the microscopical studies. Fig. 5 shows a product of which the colour changed from reddish brown to green and the crystal of chromic oxide did not disappear. In this case it was known that the transformation of tridymite to cristobalite occurred and the main part of the chromic oxide which existed as green crystals remained in the cristobalite as before, and the other small part of the oxide disappeared which gave the different coloured products. Thus the change of colours of (C) to pure green by reheating can be well explained. When the temperature is raised over the melting point of cristobalite but not far over, the cristobalite becomes silica glass and the above pure green crystals of chromic oxide distribute in it, and the beautiful green and glassy fused product will be obtained by rapid cooling. Fig. 6 shows the portion of the reheated mass which contains the specially big, hexagonal, tabular and green crystals of chromic oxide.

Discussion.

Considering that the crystal of chromic oxide is different from its initial form by the cooling velocity, it may be seen that at high temperature chromic oxide dissolves in silica of fused state and recrystallizes as the temperature falls. The nature of the particles produced by the recrystallization of chromic oxide depends upon the concentration of the oxide and especially upon the cooling velocity by the consequence of very high viscosity of fused silica. The formations of (A), (B) and (C) may be explained by this view.

Efforts to obtain cristobalite by the cooling of the fused Cr_2O_3-SiO_2 system was in vain, because it always accompanys the formation of silica glass or tridymite (by the proper cooling velocity crypto-crystalline tridymite) contrary to the Ostwald's principle. The colour change by the reheating process is an interesting phenomenon. It is perhaps related to the fact that the recrystallization of chromic oxide in tridymite is not fully developed but completely in cristobalite by the natures of its crystal structure.

The experiments on obtaining the fused products were carried out in the laboratory of the Institute of Physical and Chemical Research at Hongo, Tokyo, since it was very convenient to use a special apparatus to get easily the products of high melting point.

Summary

(1) The mixtures of chromic oxide and silica were electrically fused and by the experimental conditions the products of different colours were obtained.

(2) The beautiful green and glassy fused product was obtained only by the second reheating process.

(3) The products of different colours were examined by the petrographic microscope.

(4) The experimental conditions to obtain the each product of different colours were discussed.

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ON THE UNSAPONIFIABLE MATTER OF CALAMARY OIL.

By Mitsumaru TSUJIMOTO.

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The general properties of calamary oil obtained chiefly from the liver of *Ommastrephes sloani pacificus* (Steentrup) have already been reported in a previous paper.[1] The oil contained more than 4% of unsaponifiable matter. As no investigation on the unsaponifiable matter of the oils of Cephalopoda has yet been found, the present experiment was made in order to compare its composition to those of the liver oils of Elasmobranch fishes and Crustacea ("taraba-kani"), which contain the alcohols of the selachyl alcohol group (monoglyceryl ethers) as invariable constituents.[2]

Experimental Part.

1. Material. The calamary oil used for this experiment was prepared at Hokkaidô, and had the following properties:

d_4^{15}	0.9298	Saponification value	175.8
n_D^{20}	1.4828	Iodine value	184.1
Acid value	20.5	Unsaponif. matter	4.50%

(1) Tsujimoto and K. Kimura, *J. Soc. Chem. Ind. Japan*, **30** (1927), 865.
(2) Tsujimoto, ibid., **31** (1928), 1191; **32** (1929), 1139.

The unsaponifiable matter was separated by saponifying the oil with alcoholic potash, and extracting the soap solution with ether. The total amount of ether used was 3200-3400 c.c. per 100 gr. of the oil. By this operation 68 gr. (3.4%) of the unsaponifiable matter were obtained from 2000 gr. of the oil.

2. Examination of the Composition of the Unsaponifiable Matter. The unsaponifiable matter was warmed with methanol. On cooling the deposited crystals were separated, and the mother liquor concentrated; by repeating this treatment several times the final solution was cooled with ice to separate solid constituents as completely as possible. Thus the following three parts were obtained: (1) Solid part A, 35 gr., (2) Solid part B, 8 gr., (3) Liquid part, 20 gr.

(*1*) *Solid Parts.* The solid part A was that part which deposited firstly from the methanol solution, and amounted more than the half of the unsaponifiable matter. It formed white crystals of m.p. above 100°C. After recrystallisation it melted at 148.5°C., and by mixed test it was confirmed to be cholesterol. The amount of cholesterol determined by digitonin method was 48.0% of the unsaponifiable matter.

The solid part B was obtained by concentrating the mother liquor from cholesterol. The crude product formed fine orange-yellow crystals and melted below 100°C. By recrystallising it from methanol, 5.5 gr. of fine white crystals were obtained. This was acetylated by heating it with five times by weight of acetic anhydride, and 6.3 gr. of the acetyl product were fractionated under 4 mm. pressure as follows (the temperature soon rose up to above 200°C.):

	Yield (gr.)	Appearance	M. p.	Saponif. value
(1) Until 230°	1.9	White solid	30°	272
(2) 230-238°	2.1	,,	30°	270
(3) Residue	2.1	Dirty orange-yellow solid	—	—

From the above result, it appears that the fractions consist mainly of the acetyl derivatives of chimyl and batyl alcohols, as may be seen from the following numbers:

		M.p.	Saponif. value
Chimyl acetate,	$C_{19}H_{38}O(OCOCH_3)_2$	ca. 22-22.5°	280.3
Batyl acetate,	$C_{21}H_{42}O(OCOCH_3)_2$	33.9-34.4°	262.0

The boiling point of these compounds is 235–249°C./5mm.

As the fractions had nearly identical properties, they were mixed for further examination. When calculated from saponification value, the substance contained nearly equivalent parts of chimyl and batyl alcohols.

The free alcohols obtained by saponification were fractionally crystallised from 95% alcohol, and separated into the following three parts: (1) First crop, 1.8 gr., white, lustrous crystals, m.p. 64–65°C., (2) Second crop, 0.7 gr., similar crystals, m.p. 61°C., (3) Third crop, m.p. 59.5–60°C.

By recrystallisation the first crop yielded 1.1 gr. of crystals of m.p. 65°C.; so no elevation of m.p. was observed. This substance contained no cholesterol, and the mixed test (equal parts) with batyl alcohol (m.p. 70–70.5°C.) was 63.5°C., showing a little depression.

Anal. Subst. = 0.1092; CO_2 = 0.2870; H_2O = 0.1268 gr.

Found: C = 71.68; H = 12.99%. Calc. for $C_{21}H_{44}O_3$: C = 73.18; H = 12.88%.

Thus the substance mainly consisted of batyl alcohol, but it probably contained some impurity of smaller number of carbon atoms.

The second and third crops probably consisted of chimyl and batyl alcohols; the mixed test of the latter with chimyl alcohol (m.p. 60–60.5°C.) was 58°C. Although not isolated, the presence of chimyl alcohol is highly probable from the high saponification value of the acetyl compound.

(2) *Liquid Part.* Although this was mentioned as "liquid" part, it really still contained solid constituents, and formed an orange yellow semi-solid at the ordinary temperature. It had iodine value 73.0, and acid value 4.3. It was acetylated, and 22.4 gr. of the acetyl compound were firstly distilled under 4.5 mm. pressure until the boiling point rose to 250°C. (bath temperature 290°C.), the orange-yellow coloured distillate amounting to 18 gr. (80.4%). The residue (4 gr.) formed a dark brown crystalline semi-solid; this contained vitamin substance (liver resin). The distillate was then fractionated under ca. 4 mm. pressure as the following table.

The high saponification values of the higher fractions pointed the presence of the compounds of dihydric alcohols, and the comparatively low iodine values indicated the admixture of the compounds of saturated alcohols. The each fraction contained also small amount of free acids.

Fractions (2) and (3). These were mixed and saponified. On extracting the alkaline soap solution with ether, the free alcohol was obtained; yield, 1.8 gr., an orange-yellow crystalline mass. This was dissolved in 90% acetone, and cooling with ice, the deposited crystals were separated. The liquid part obtained from the filtrate was dissolved in 80% acetone, and

cooling with ice and salt, further amount of solid part was separated. So finally 0.5 gr. of liquid part was obtained.

	Yield (gr.)	Appearance	Acid value	Saponif. value	Iodine value	n_D^{20}
(1) Until 180°	2.0	Orange-yellow liquid	5.2	164	45	1.4528
(2) 180–190°	1.3	,,	6.3	188	33	1.4504
(3) 190–200°	1.1	,,	6.8	199	37	1.4510
(4) 200–210°	1.3	,,	10.2	218	41	1.4520
(5) 210–220°	1.2	,,	7.9	224	45	1.4540
(6) 220–230°	2.8	,,	7.0	246	48	1.4550
(7) 230–245°	5.3	,,	5.5	248	53	1.4571
(8) Residue	3.0	Dirty brownish yellow semi-solid	—	—	—	—

The solid part thus separated, on recrystallisation from 90% acetone, melted at 49.5–50°C., and showed no depression of m.p. on the mixed test with cetyl alcohol.

Anal. Subst. = 0.1432; CO_2 = 0.4131; H_2O = 0.1823 gr.

Found: C = 78.68; H = 14.25%. Calc. for $C_{16}H_{34}O$: C = 79.25; H = 14.14%.

The substance was therefore confirmed to be cetyl alcohol.

The liquid part was of an orange-yellow colour, and had iodine value 76.4 and n_D^{20} 1.4696. On brominating it in petroleum ether solution, a somewhat appreciable amount of precipitate was formed. On hydrogenation the yield of solid product was small, so that the exact determination of m.p. was not possible. It appears, however, very probable that the liquid part contained oleyl alcohol.

Fractions (6) and (7). These were mixed and refractionated under 5 mm. pressure. The second fraction (ca. 3 gr.) boiling at 230–245°C. was an orange-yellow liquid of saponif. value 240.2, iodine value 53.9, and n_D^{20} 1.4572. The free alcohol (semi-solid) obtained by saponification was dissolved in 90% acetone, and by cooling with ice the deposited solid (probably batyl alcohol) was separated. The liquid part obtained from the filtrate amounted to 1.3 gr. It was an orange-yellow liquid of iodine value 73.0 and n_D^{20} 1.4725. A little precipitate was formed by brominating it in petroleum ether solution.

Anal. Subst. = 0.1240; CO_2 = 0.3326; H_2O = 0.1362 gr.

Found: C = 73.15; H = 12.29%. Calc. for $C_{21}H_{42}O_3$: C = 73.61; H = 12.36%.

This substance was hydrogenated with platinum black as catalyser; the hydrogenated product on recrystallisation from alcohol melted at 64°C. and showed no depression on the mixed test with batyl alcohol. So the original substance was confirmed to be selachyl alcohol.

The first fraction (until 230°C./5mm.) of the refractionation had saponif. value 239.4, iodine value 45.8, and n_D^{20} 1.4550. The chief constituent of this fraction would also be selachyl alcohol.

The fractions (4) and (5) were not examined, but judging from their properties they consisted probably of mixtures of the acetyl compounds of cetyl, batyl and selachyl alcohols, and possibly also of oleyl and chimyl alcohols.

The compounds of alcohols of higher unsaturation were also present. The low saponification value of the fraction (1) appeared somewhat abnormal. Probably it contained not acetylated alcohols, or hydrocarbons, but the want of material prevented further examination.

Summary.

(1) The unsaponifiable matter of calamary oil contained 48% of cholesterol.

(2) Besides cholesterol, the presence of cetyl, batyl and selachyl alcohols has been confirmed. Oleyl and chimyl alcohols were probably present. A small amount of the alcohols of higher unsaturation appeared also to be present.

(3) The occurrence of the alcohols of the selachyl alcohol group (monoglyceryl ethers) in calamary oil indicates the wide distribution and vital importance of these compounds as constituents of liver oils of various marine animals.

The author desires to express his hearty thanks to Prof. Kôkichi Ôshima for the kind supply of the sample of calamary oil used for this investigation.

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STUDIES ON THE REACTIONS BETWEEN GAS AND SOLID. PART I. VELOCITY OF ABSORPTION OF MOISTURE BY QUICKLIME.

By Takeo AONO.

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1. Velocity of Absorption of Moisture at Constant Vapour Pressure.

Method of the Experiment. Fine CaO powder of 100 gr. contained in a 500 c.c. beaker (sectional area = 79.4 cm^2.) was placed in a glass vessel with some water in the bottom. The change of weight was measured occasionally. This experiment was set about on Dec. 11th, 1929, and by dint of the warming equipment of the chamber, the temperature did not deviate much from the mean temperature of 14°C. during the whole course of time.

Result of the Experiment. The relations between the weight increase and time are shown in Table 1.

Table 1.

Time in days (t)	5	10	20	30	40	50	60	74
Weight increase (W_t) (obs.)	8.2	16.6	23.7	28.9	32.3	34.0	35.1	36.3
Weight increase calc. by eqn. (1).	8.4	14.8	23.7	29.0	32.2	34.1	35.2	36.2
Difference	+0.2	− 1.8	0.0	+ 0.1	− 0.1	+ 0.1	+ 0.1	− 0.1

From this result the following experimental formula was obtained:

$$W_t = 37.0\,(1-e^{-0.0510t}) \quad \ldots\ldots\ldots\ldots\ldots\ldots \quad (1)$$

The calculated value by this equation shows a coincidence with the observed one. (See Table 1 and Curve A of Fig. 1).

Consideration of the Results. If the temperature, humidity, surface nature and other conditions are kept constant, the velocity of absorption of moisture by CaO may be considered to follow the equation:

$$\frac{dW_t}{dt} = k_1(W_\infty - W_t) \quad \ldots\ldots\ldots\ldots\ldots\ldots \quad (2)$$

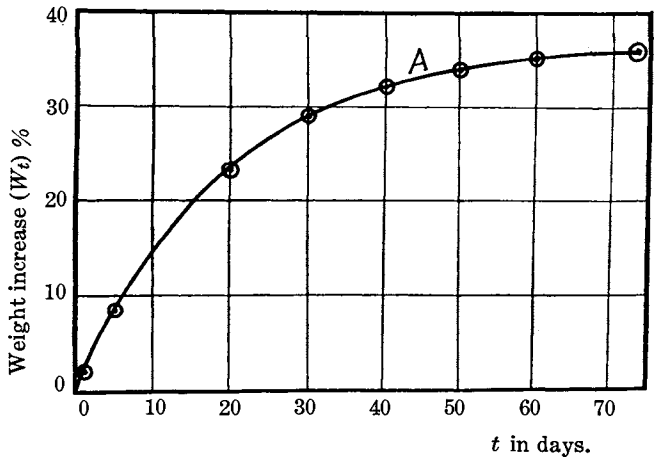

Fig. 1. Absorption of moisture by CaO at constant humidity.

where W_t: weight of moisture absorbed by 100 gr. of CaO during the t (days); W_∞: means $(\lim_{t\to\infty} W_t)$; $(W_\infty - W_t)$: absorbing capacity of the CaO in future; k_1: a constant, indicating the rate of absorption.

From the equation (2) we have

$$W_t = W_\infty(1-e^{-k_1 t}) \quad \cdots\cdots\cdots\cdots\cdots\cdots \quad (3)$$

and

$$k_1 = \frac{1}{0.4343t}\log_{10}\left(\frac{W_\infty}{W_\infty - W_t}\right) \quad \cdots\cdots\cdots\cdots \quad (4)$$

Equation (3) quite agrees with equation (1) in the form, and we have $k_1 = 0.0510$ and $W_\infty = 37.0$.

W_∞ cannot be calculated by the equation

$$CaO + H_2O = Ca(OH)_2 \quad \cdots\cdots\cdots\cdots\cdots\cdots \quad (5)$$

to be equal to 32.14, because there may be some parts of moisture, which are merely adsorbed on the surface, and which make W_∞ greater than 32.14. The value: $37.0-32.14 = 4.86$, can therefore be regarded as the part due to adsorption.

2. Relations between the Velocity of Absorption of Moisture and Temperature and Humidity.

Method of the Experiment. Each 10 gr. of CaO powder, contained in a weighing tube of 4.9 cm^2 wide, was placed in a vessel each containing sul-

phuric acid or some salt solution of a known concentration, and the increase of weight was measured occasionally, at 10, 20, 30 and 40°C. respectively. Special care was taken to equalize the fineness and compactness of the powder.

Results of the Experiment. The results are shown in Tables 2 to 5.

Table 2. Temp. = 9.9 ± 0.9°C. (corresponding to Fig. 2)

Solution		Water	Sulphuric acid	
concentration %		100	43.75	66.0
vapour tension (mm. Hg)		9.1	4.4	1.1
humidity %		100	48 3	12.1
	time hrs.			
weight increase (gr.)	19.75	0.0756	0.0319	0.0095?
	25.25	0.1021	0.0425	0.0087
	43.25	0.1919	0·0752	0.0137

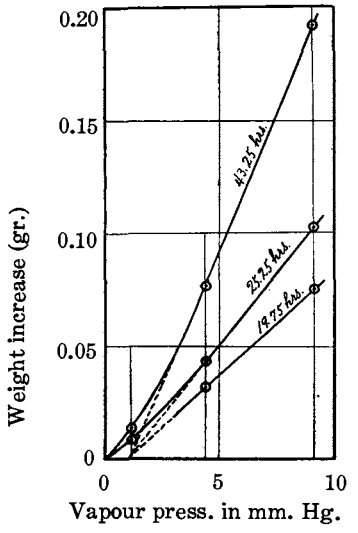

Fig. 2. Relation btw. absorption of moisture and humidity. Temp. = 9.9 ± 0.9°C.

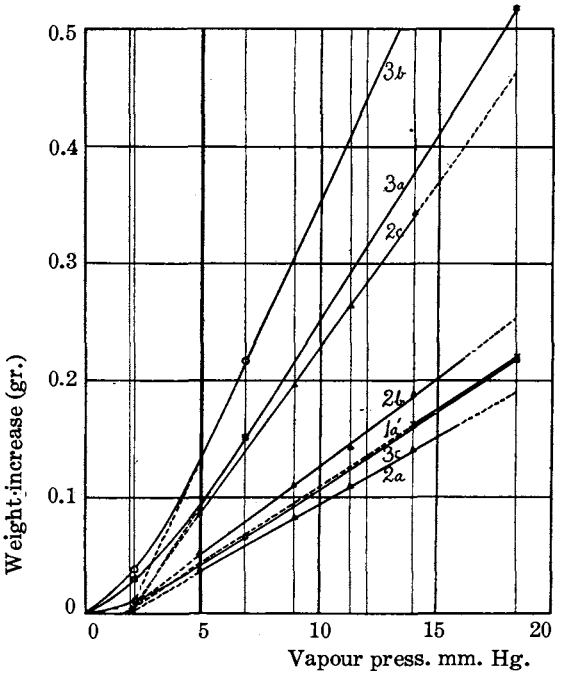

Fig. 3. Relation btw. absorption of moisture and humidity. Temp. = 20.8 ± 0.3°C.

Table 3. Temp. = 20.8±0.3°C. (Fig. 3)

Solution			H_2O	NaCl	NH_4NO_3	H_2SO_4				
concentration %			100	Sat.	Sat.	37.69	43.75	50.00	55.00	65.20
vapour press. mm. Hg			18.4	14.0	12.0	11.3	8.86	6.8	4.9	2.1
humidity %			100	74·6	65.2	61.4	48.2	37.0	26.6	10.3
weight increase (gr.)	No.	time (hrs.)								
	1_a	22.5		0.1615						
	2_a	17.9		0.1399		0.1075	0.0823		0.0356	
	2_b	23.66		0.1877		0.1419	0.1085		0.0509	
	2_c	40.5		0.3414		0.2625	0.1953		0.0853	
	3_a	43.8	0.5017					0.1496		0.0291
	3_b	60.9	0.7207					0.2151		0.0412
	3_c	17.0	0.2171		0.1311			0.0641		0.0107

1_a: very compactly charged,

3_c: very coarsely charged.

Table 4. Temp. = 30.3±0.5°C. (Fig. 4)

Solution			H_2O	NH_4NO_3	H_2SO_4	
concentration. %			100	Sat.	50	66
vapour pressure mm. Hg.			32.4	19.3	12.1	3.5
humidity %			100	59.5	37.3	10.8
weight increase (gr.)	No.	time (hrs.)				
	1_a	17.25	0.3967	0.2188	0.1188	0.0215
	1_b	22.92	0.5436	0.2969	0.1646	0.0289
	1_c	40.17	0.9280	0.5480	0.3012	0.0522
	1_d	45.50	1.1163			
	1_e	28.83	1.7112			
	1_f	89.83	2.1658			

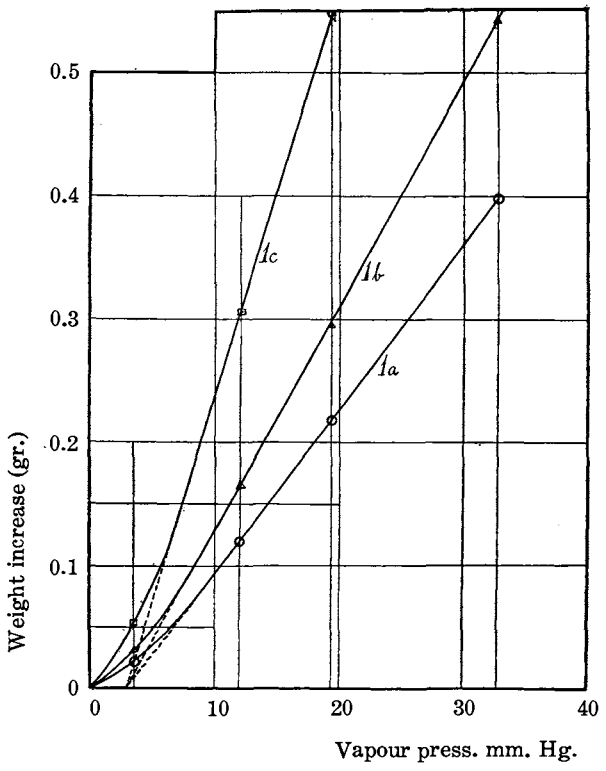

Fig. 4. Relation btw. absorption of moisture and humidity.
Temp. = 30.3 ± 0.5° C.

Table 5. Temp. = 39.9±0.1°C.

Solution		H_2O	NaCl	H_2SO_4	
concentration %		100	Sat.	50.0	66.0
vapour pressure mm.Hg		55.0	41.2	21.3	5.4
humidity %		100	74.9	38.6	9.8
weight increase (gr.)	time hrs.				
	18.08	0.8417	0.5760	0.2464	0.0481

Theoretical Part

The increase of weight (W_t) of quicklime due to moisture must be the sum of water adsorbed by CaO, water chemically combined to form $Ca(OH)_2$ (W_t') and hygroscopic water on the $Ca(OH)_2$ (w_t). It may be assumed that the water adsorbed by CaO is relatively small because it soon combines with CaO to form $Ca(OH)_2$, and $Ca(OH)_2$ formed absorbs rapidly the hygroscopic water, the quantity of which must be considerable. Then we have

$$W_t = W_t' + w_t \quad \cdots\cdots (6)$$

This w_t may be regarded to consist mainly of the water adsorbed on the surface of $Ca(OH)_2$, and as $Ca(OH)_2$ produced from the CaO forms very fine powders, the area of the surface may be regarded to be proportional to the mass. Then from Langmuir's equation of the adsorption isotherm we have

$$w_t = \lambda W_t' \quad \cdots\cdots (7)$$

$$w_t = \left(\frac{\lambda' h}{1+ah}\right) W_t' \quad \cdots\cdots (8)$$

where a and λ' are constants and h is the vapour pressure. From equations (6) and (8) we have

$$W_t = W_t'(1+\lambda) = W_t'\left(1+\frac{\lambda' h}{1+ah}\right) \quad \cdots\cdots (9)$$

and combining this equation to equation (2), we have

$$\frac{dW_t'}{dt} = k_1(W_\infty' - W_t') \quad \cdots\cdots (10)$$

where $W_\infty' = \dfrac{W_\infty}{1+\lambda} = 32.14\%$ of initial weight of pure CaO.... (11)

Assuming that the velocity of formation of $Ca(OH)_2$ is proportional to the vapour pressure h, namely

$$k_1 = \alpha_1 h \quad \cdots\cdots (12)$$

At the earlier stage of slaking, where W_t' is negligibly small compared with W_∞', we have

$$\frac{dW_t'}{dt} = \alpha_1 h W_\infty' \quad \cdots\cdots (13)$$

or

$$W_t' = \alpha_1 h W_\infty' t \quad \cdots\cdots (14)$$

and from (9) and (14),

$$W_t = \alpha_1 W'_\infty ht\left(1+\frac{\lambda' h}{1+ah}\right) \quad \text{..... (15)}$$

or

$$\omega \equiv \frac{W_t}{h} = \alpha_1 W'_\infty t\left(1+\frac{\lambda' h}{1+ah}\right) \quad \text{..... (16)}$$

Taking a certain value of ω' corresponding to h', we have, for every common time t,

$$\frac{h-h'}{\omega-\omega'} = \left(\frac{1+ah'}{\alpha_1 W'_\infty \lambda' t}\right)(1+ah) \quad \text{..... (17)}$$

Therefore, if the equation (15) truely holds, $\frac{h-h'}{\omega-\omega'}$ must be in linear relation with h.

Now, discussing this relation from the observed values:

From	Table 3 No. 3c (20°C.)				Table 4 No. 1a (30°C.)				Table 5 (40°C.)			
h_{mm}.	2.1	6.8	12.0	18.4	3.5	12.1	19.3	32.4	5.4	21.3	41.2	55.0
$\frac{h-h'}{\omega-\omega'}\times 10^{-3}$	—	1.09	1.69	2.43	—	2.34	3.05	4.72	—	5.95	7.03	7.77

we see that $\frac{h-h'}{\omega-\omega'}$ stands in linear relation with h (Fig. 5) and therefore that the equation (15) holds, and consequently the above assumptions are quite plausible.

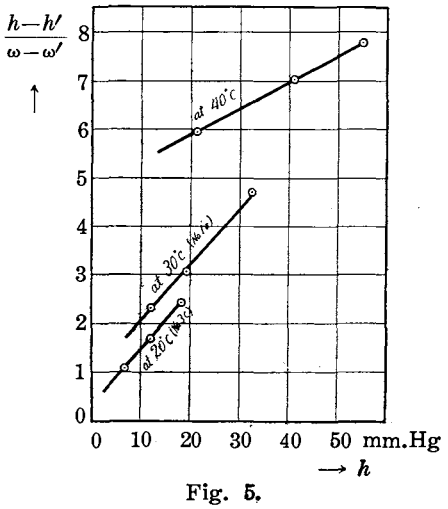

Fig. 5.

For the equation of absorption of moisture by quicklime at constant temperature we have the following general equations

$$\frac{dW_t}{dt} = \alpha_1 h\left\{(1+\lambda)W'_\infty - W_t\right\} \quad \cdots\cdots\cdots\cdots\cdots\cdots \quad (18)$$

and

$$W_t = (1+\lambda)W'_\infty\left\{1-e^{-\alpha_1 ht}\right\} \quad \cdots\cdots\cdots\cdots\cdots\cdots \quad (19)$$

where

$$\lambda = \frac{\lambda' h}{1+ah}.$$

Summary

(1) From the experimental study, it has been found that the mechanism of absorption of moisture by quicklime can be explained as follows: free CaO absorbs moisture to form $Ca(OH)_2$, the velocity of which being proportional to the humidity, and the $Ca(OH)_2$ formed, getting off from the mother CaO in fine powders, and swelling in its volume, quickly adsorbs moisture, the amount of which being proportional to the amount of $Ca(OH)_2$ formed.

(2) The general equation of the velocity of the increase of weight at constant temperature has been given as

$$\frac{dW_t}{dt} = \alpha_1 h\left\{(1+\lambda)W'_\infty - W_t\right\}$$

and

$$W_t = (1+\lambda)\,W'_\infty\left\{1-e^{-\alpha_1 ht}\right\},$$

where

$$\lambda = \frac{\lambda' h}{1+ah},$$

(3) The effect of temperature elevation has also been studied.

Grateful acknowledgment is made to Dr. M. Katayama, Prof. of the Tokyo Imperial University, for giving valuable suggestions, and to Mr. K. Hibi, Director of the Denki-Kagaku-Kogyo Co., Tokyo, who gave the author the opportunity of the accomplishment of this work and allowed him to publish this report.

VAPOUR PRESSURE, SURFACE TENSION AND DENSITY OF OSMIUM TETROXIDE.

By Eijiro OGAWA.

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Introduction.

There are two different theories on the constitution of osmium tetroxide. Sugden says that it must be a semi-polar compound while Sidgick asserts that it must be a covalent compound. Sidgick states, according to his valency theory, as follows. As the elements of first subgroup of 8th group, iron, ruthenium and osmium, have eight electrons more than an innert gas, they might be expected to show the valency of eight, especially in 8-covalent compounds which could be formed directly without coordination. But by the covalency rule it appeares that the maximum covalency of an atom is 2 for hydrogen, 4 for the elements from lithium to fluorine, 6 for the elements from potassium to bromine, and 8 for the elements from rubidium to uranium. So the elements which can form 8-covalent compounds directly without coordination are ruthenium and osmium only. We find that osmium formes an octafluoride OsF_8 which is very stable and volatile compound, having the vapour pressure 552.5 mm. at 38.0°C.

It is at least probable that we should assign a similar 8-covalent structure to osmium in the tetroxide OsO_4, and write it $\begin{matrix} O & & O \\ \diagdown & & \diagup \\ & Os & \\ \diagup & & \diagdown \\ O & & O \end{matrix}$ and not $\begin{matrix} O & & O \\ \diagup & & \diagdown \\ & Os & \\ \diagdown & & \diagup \\ O & & O \end{matrix}$. This is supported by the fact that ruthenium, which also can be 8-covalent, likewise forms a volatile tetroxide, while iron, which is limited to a covalency of six, does not.

But the result of the measurement of parachor by Sugden and the isolation of the compounds by Krauss which indicate that osmium tetroxide must be unsaturated coordination compound are strong objections to the covalency theory. Sugden got 154.0 as the parachor of osmium tetroxide using the data measured by Wartenberg. If we assume that the osmium has an octet, there must be four semi-polar links (or coordinate links according to Sidgick) in the molecule. And the value for osmium will be:

$$Os = 154.0 - 4 \times 20.0 + 4 \times 1.6 = 80.4 .$$

On the other hand, if the molecule is analogous to OsF_8, and has four true double links, we should have, according to Sugden's values:

$$Os = 154.0 - 80.0 - 4 \times 23.2 = -18.8.$$

Sugden said that there is no other evidence of the value of parachor of osmium, but from rough data for the neighbouring elements it should be between 60 and 100. Hence he concluded that the formula $\begin{matrix} O \\ O \end{matrix}\!\!>\!Os\!<\!\!\begin{matrix} O \\ O \end{matrix}$ is correct. According to Sidgick, Sugden's argument seems at first sight conclusive, but on close examination it will be noted that there is some difficulty. In the first place, the close agreement between theory and observation which he obtained with the other substances cannot be adduced here, for lack of other data as to the parachor of osmium. Secondly, in all the substances for which the agreement was found to be close, there is the evidence of the presence (in every atom except hydrogen) of an octet.

Hence Sidgick said that there is no proof that his values hold good when the valency group exceeds eight, it should be expected that this would affect the molecular volume, and that in addition to the constitutive factors of the parachor already mentioned, another would be needed to allow for the change in size of the valency group. This would presumably be negative: the high stability and screening effect of the octet as compared with any other arrangement of the outer electrons suggest that when there is a larger valency group the external field is stronger, and the attached atoms are more closely held; just as it is found that in zinc, where the group next to the valency electrons is eighteen, the volume is much smaller than in calcium, where it is eight. In osmium tetroxide, if the metal is really eight covalent, there is an extreme case of this effect, since the valency group has expanded from eight to sixteen, and it may be concluded that if this occurred, it would considerably reduce the parachor, so that the fact that such a formula would give a negative value for the parachor of osmium if no allowance is made for the change in the valency group, is not conclusive evidence that the formula is wrong.

As the second evidence that supports Sugden's theory F. Kräuss and D. Wilken[1] reported the isolation of following compounds which indicate that osmium tetroxide is unsaturated co-ordination compound, namely:

$K_2[OsO_4(OH)_2]$, $Cs_2[OsO_4(OH)_2]$, $(NH_4)_2[OsO_4(OH)_2]$,

$Ba[OsO_4(OH)_2]$, $Cs_2[OsO_4, F_2]$, $Rb_2[OsO_4, F_2]$,

(1) *Z. anorg. allgem. Chem.*, **145** (1925), 151.

This fact is a strong objection to Sidgick's theory. In short, this question is not yet solved. It is very desirable to measure the parachor of osmium octafluoride. But the measurements of surface tensions and densities are very difficult according to its nature. But if we assume that osmium octafluoride has the same surface tension and density as osmium tetroxide, so we shall find as its parachor 212. Hence the parachor of osmium is

$$212.0-25.7\times 8 = 6.4\,.$$

The author wanted to carry out more accurate measurements on parachor and measured surface tensions and densities of osmium tetroxide between its melting point and boiling point. Krauss also reported the enantiotropic isomerism of ruthenium tetroxide and osmium tetroxide. The author wanted to investigate this point thoroughly and measured vapour pressure of osmium tetroxide by the statical method using a spring manometer.

Existence of Enantiotropic Isomers of Osmium Tetroxide. The chief points by which Krauss asserts the existence of enantiotropic isomers of osmium tetroxide are as follows.

(I) Existence of white and yellow isomers. The melting point of the white one is 39.5°C. and the yellow is 41.0°C.

(II) Different vapour pressure of them.

(III) Formation of both compounds by raising or lowering the temperature.

But the present author could not recognize isomers by his experiments which will be described in details in the following lines.

(I) By Krauss osmium tetroxide obtained by heating the metal in oxygen stream is crystals of white needles and melts at 39.5°C. It solidifies in light yellow mass on cooling. When heated again, the solidified yellow mass does not melt at 39.5°C., but melts at 41.0°C.

According to the author's results, osmium tetroxide obtained by sublimation is white needles, and by heating it melts to a yellow transparent liquid. It solidifies in transparent light yellow mass or white opaque mass, according to its quantity and its cooling velocity. The melting point was observed under a microscope which is kept in a thermostat providing a thermometer standardized at P. T. R. The sublimated white needles did not melt at 39.5°C., but melted at 40.6—40.7°C. The solidified light yellow mass gave the same melting point.

(II) Krauss measured vapour pressures up to its melting point by Hüttig's[1] method and indicated that the white compound has higher vapour pressure than yellow as follows.

White osmium tetroxide.

I		II		III	
0°	2.0 mm.	0°	2.0 mm.	0°	2.0 mm.
10°	3.5	13°	4.0	8°	3.0
18°	5.0	31°	7.5	18°	5.0
29°	7.0	34°	8.5	24°	6.0
36°	9.0			32°	8.0

Yellow osmium tetroxide.

I		II		III	
0°	0.5 mm.	0°	0.5 mm.	0°	0.5 mm.
12°	2.0	8°	1.5	18°	2.5
18°	3.0	16°	2.5	23°	4.0
28°	5.0	31°	6.0	26°	4.5
35°	7.5			36°	8.5

His result of each experiment shows good coincidence and both vapour pressure curves coincide at 41.0°C. But it will be seen later that there are wide differences between these and the author's results, which have been obtained by statical measurements. So the author considers that the above result may not represent the saturated vapour pressures.

(III) Further by Krauss the yellow osmium tetroxide changes into the white form in liquid air and becomes very breakable with a glass rod. This white form also melted at 39.5°C. According to the author's result, however, the yellow form did not change its colour by leaving in liquid air for twenty hours and melted at 40.6°C.

Therefore, the enantiotropic isomerism of osmium tetroxide will be denied by the present author.

Experimental.

Measurement of Vapour Pressure of Osmium Tetroxide. Vapour pressures were measured by Ruff and Tschirch[2], and Wartenberg.[3] The values

(1) *Z. anorg. allgem. Chem.*, **114** (1920).
(2) *Ber.*, **46** (1913), 929.
(3) *Ann.*, **440** (1924), 97.

measured by Ruff using the dynamical method of A. Smith and A. Merzies[1] are as follows.

Temperature °C.	95°	115°	125°	135°
Pressure mm.	275	482*	640.4	779

The values measured by Wartenberg extend over a wide range above and below the melting point. He measured vapour pressures of solid osmium tetroxide by dynamical method passing the stream of ozone at the temperatures 0°, −19.6° and −38.0°C.

Temperature °C.	0°	−19.6°	−38.0°
Pressure mm.	0.775	0.115	0.0137

The empirical formula is

$$\log P_{atm} = -13500/4.57\,T + 7.83\,.$$

Therefore the mean heat of sublimation is 13500 cal.

The values of vapour pressures of liquid osmium tetroxide were obtained by the dynamical method of A. Smith.

Temperature C°.	40.2	51.0	51.6	62.0	62.2	67.8	91.0	96.2	96.8	132.0	136.4
Pressure mm.	11.0	32.0	33.0	59.5	61.0	79.0	205.4	250.4	258.4	714.6	757.4

The August's empirical formula is

$$\log P_{atm} = -10100/4.57\,T + 5.49\,.$$

He gave 40.1°C. as the melting point and 129.0°C.** as the boiling point from the above values.

The author carried out the following experiment in order to obtain the more accurate values, as there are marked differences between the values of Ruff and Wartenberg.

Preparation of Osmium Tetroxide. It was prepared by heating the metal in oxygen stream. The sublimated tetroxide condenses at the cold part. It is necessary to shut off the moistures, as the tetroxide decomposes by small quantity of water giving the violet substance. (It may be osmium dioxide).

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(1) *J. Am. Chem. Soc.*, **32** (1920), 907.

* We find in the original paper the value 182 instead of 482.

** The melting point should be above 136.4 according to vapour pressures.

Method of Measurement. As the tetroxide has a strong oxidizing power and attacks mercury violently staining its surface, so it is impossible to measure pressures directly with mercury. Therefore the author used a glass spring manometer. On its preparation and employment he owes much Mr. K. Arii,[1] Assistant Professor of Tohoku Imperial University, and wishes to express his sincere thanks.

At first the whole apparatus is evacuated to a high vacuum such as 0.0005 mm. Hg. Then *B*, containing the tetroxide, is connected and by warming *B* the tetroxide is distilled into *A*, which is cooled with freezing mixtures of sodium chloride and ice, and the whole apparatus evacuated again (Fig. 1). Then sealed at *a*. After keeping the vacuum of 0.0005 mm. for 30 minutes the apparatus is sealed at *b* and *c*. The position of the needle *d*, that indicates the zero-point, is determined accurately by means of a fixed telescope, before introducing the tetroxide. The sensibility of a spring manometer used is 0.01 mm. Hg. The thermometer used was compared with a P.T.R. thermometer. The temperature of the thermostat is carefully regulated. For example, at 130°C. it is regulated within ±0.02°C. The internal diameter of the mercury manometer is 15 mm. A cathetometer was used for the reading of pressure.

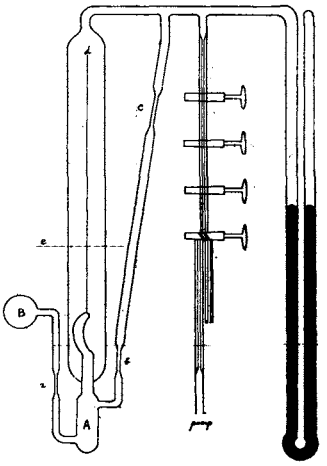

Fig. 1.

Results. There was no difference between the value after 2 hours and after 24 hours even at the lowest temperature 15.89°C. This proves that the time necessary to reach the equilibrium is very short. The values observed at each temperature are mean values of several observations for one day and night. Though osmium tetroxide is very stable compound, for precaution's sake, for example, from 70.15°C. the temperature was turned back to the previous temperature 60.10°C. and the value was compared with the former value in order to examine whether or not the dissociation takes place. Results are all negative. The pressures given in Table 1 were added necessary corrections. The relation between $\frac{1}{T}$ and $\log P$ is given in Fig. 2.

(1) *Bull. of the Institute of Phys. and Chem. Research,* Vol. 8, No. 7.

Table 1.

Temperature °C.	T	$\frac{1}{T}$	$P_{mm.}$	$\log P$
15.89	288.99	0.0034603	5.37	0.72997
21.92	295.02	33896	7.95	0.90037
26.95	300.05	33328	11.03	1.04258
31.97	305.07	32778	15.08	1.17840
36.99	310.09	32249	21.05	1.32325
40.01	313.11	31938	25.09	1.39950
43.02	316.12	31634	28.84	1.46000
47.04	320.14	31236	35.64	1.55194
53.07	326.17	30659	47.12	1.67321
60.10	333.20	30012	64.44	1.80916
70.15	343.25	29133	100.18	2.00078
85.22	358.32	27908	181.04	2.257776
100.29	373.39	26782	300.46	2.477784
115.00	388.10	25767	483.89	2.684751
130.00	403.10	24808	746.18	2.872848

Melting Point. The melting point determined by the relation between $\frac{1}{T}$ and $\log P$ is 40.7°C., and that from a microscopic observation is 40.6° or 40.7°C.

Wartenberg determined it as 40.1°C. from the vapour pressure curve, but this value is not correct, because his vapour pressure curve is somewhat different from author's result. The author can not agree with Krauss' values 39.5° and 41.0°C. owing to above reason.

Boiling Point. The value obtained by the graph is 131.2°C. Krauss' value is 134°C.

Empirical Formula below Melting Point. The August's formula has been obtained by an assumption that the heat of sublimation is constant in the range of temperature measured. The calculated values well coincide with the observed ones.

$$\log P = -\frac{2542.01}{T} + 9.51791 .$$

Table 2.

Temp.	15.89	21.92	26.95	31.97	36.99	40.01
$P_{obs.}$	5.37	7.95	11.02	15.08	21.05	25.09
$P_{calc.}$	5.27	7.97	11.11	15.33	20.90	25.07

Therefore the mean heat of sublimation is 11640 cal.

Empirical Formula above Melting Point. The relation between log P and $\frac{1}{T}$ was indicated in Fig. 2. It is composed of two straight lines in-

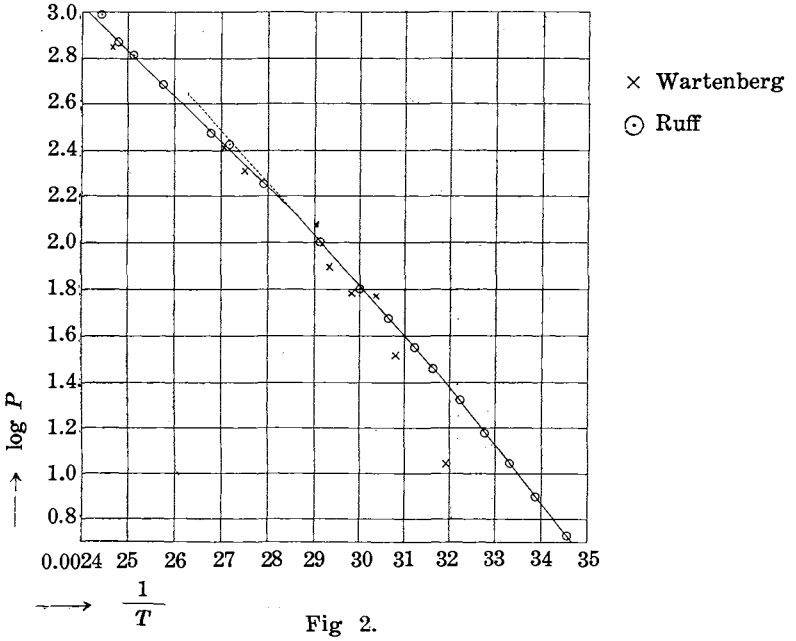

Fig 2.

tersecting at about 72°C. It cannot be decided with this result only, whether any change takes place in a liquid at 72°C. or the actual relation is not a straight line, but is a curve owing to gradual decrease of the heat of vaporization. If we assume a transition point at about 72°C. and apply August's formula, we obtain the following two relations.

$$\log P = -2167.22/T + 8.31658 \text{ (below 72°C)} \quad \ldots\ldots\ldots \text{ I}$$

$$\log P = -1977.39/T + 7.77704 \text{ (above 72°C)} \quad \ldots\ldots\ldots \text{ II}$$

The mean heat of vaporization will be obtained by these equations

$$\Delta H = 9923 \text{ cal.} \quad \text{(from I)}$$

$$\Delta H = 9054 \text{ cal.} \quad \text{(from II)}$$

The difference between them indicates the heat of transformation.

If the relation between $\log P$ and $\frac{1}{T}$ is not a straight line, the following Nernst's formula will be obtained.

$$\log P = -2592.66/T + 1.75 \log T - 0.0062662\,T + 7.26716 .$$

Table 3 shows the comparisons between observed and calculated values.

Table 3.

C°	$P_{obs.}$	$P_{calc.}$ by I or II	$P_{calc.}$ by Nernst's formula
43.02	28.84	28.89	28.53
47.04	35.64	35.24	35.24
53.07	47.12	47.00	47.10
60·10	64.44	64.91	65.00
70.15	100.18	100.65	100.10
85.22	181.04	181.36	180.40
100.29	300·46	302.83	305.52
115.00	483.89	480.73	484.61
130.00	746.18	743.93	739.37

Further, the heat of vaporization in a narrow range of temperature is given by the following relation

$$\Delta H = 4.5787 \frac{T_1 T_2}{T_2 - T_1} \log \frac{p_2}{p_1} .$$

As the range is narrow, ΔH may be assumed as a heat of vaporization at a mean temperature instead of a mean heat of vaporization within this range of temperature.

The heat of vaporization at the melting point found from the above data by extrapolation is 10100 cal. The difference (1540 cal.) between the heat of sublimation (11640 cal.) and the heat of vaporization (10100 cal.)

shows the heat of fusion of osmium tetroxide. If we put the heat of vaporization at boiling point equals to that at 122.5°C., we get as Trouton's constant,

$$\frac{\Delta H}{T} = \frac{8982}{404.3} = 22.2 .$$

The heat of vaporization obtained by extrapolation, from Table 4 is $\Delta H = 8700$ cal. and Trouton's constant becomes

$$\frac{\Delta H}{T} = \frac{8700}{404.3} = 21.5 .$$

Table 4.

Temperature range	Mean temperature	ΔH
43.02— 60.10	51.56	9859 cal
60.10— 85.22	72.66	9763
85.22—115.00	100.11	9129
115.00—130.00	122.50	8982

Thus we know that osmium tetroxide is a normal liquid at its boiling point.

By Wartenberg's measurement the heat of vaporization is 10100 cal. and the heat of sublimation is 13500 cal., so the heat of fusion is 3400 cal. This value coincides well with his value $3410 \pm 2\%$ cal. obtained by a calorimetric observation.

The author cannot agree with 10100 cal. for the heat of vaporization at the melting point, because the heat of vaporization decreases as the temperature rises. The mean heat of vaporization between 51.0° and 62.0°C. using Wartenberg's value becomes 12170 cal. The difference between 13500 cal. and 12170 cal. is 1330 cal. So we know that the heat of fusion measured by Wartenberg is incorrect.

The vapour pressure at 25°C. obtained by interpolation is 9.91 mm. So

$$OsO_4(s) = OsO_4(g) , \qquad \Delta F_{298.1} = 2572 .$$

Further, the vapour pressure at 25°C. of the super-cooled liquid obtained also by extrapolation is 11.02 mm.

$$OsO_4(1) = OsO_4(g) , \qquad \Delta F = 2509 .$$

Thus the free energy change between solid and liquid tetroxide at 25°C. is

$$OsO_4(s) = OsO_4(l), \qquad \Delta F_{298.1} = 63.$$

The specific heats of liquid and solid osmium tetroxide are unknown. If we assume that there are no differences between them.

$$\Delta H_0 = 1540 \text{ cal.}, \qquad \Delta F = 1540 + IT.$$

And $\Delta F = 0$ at 40.7°C., then $I = -4.91$.

Therefore $OsO_4(s) = OsO_4(l), \qquad \Delta F_{298.1} = 77.$

The results obtained from both calculations are concordant.

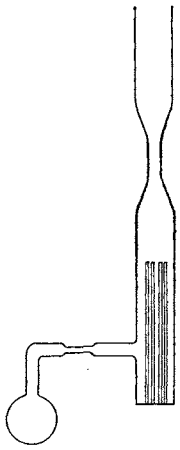

Fig. 3.

Measurement of Surface Tension. It was found by the above experiment that the decrease of the heat of vaporization of osmium tetroxide is remarkable with the rise of temperature. To ascertain this point on the one hand and to make sure Wartenberg's value on the other hand, its surface tensions and densities were measured. The measurements were carried out by the method of a capillary rise in a sealed tube. The glass capillary used has the same radius at its both ends. The radius of the wider tube was calibrated by measuring the weight and length of the mercury thread put into it. A good concordant value, 0.611 mm., was obtained.

The radius of the narrow one was calculated from the surface tension of benzene. Benzene used was "Kahlbaum zur Analyse" and dehydrated by sodium. The difference in height was 8.52 mm. at 25°C.

$$a^2 = \frac{H}{\frac{1}{b_1} - \frac{1}{b_2}} \qquad \cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots \quad (1)$$

where a^2 is the specific cohesion; H is the difference in height between the lowest points on the menisci; and b_1, b_2 are the radii of curvature at these points respectively. On the other hand

$$a^2 = \frac{2\gamma}{g(D-d)}.$$

where γ is the surface tension and D and d are the densities of liquid and vapour respectively. The surface tension of benzene is 28.23 at 25.00°C. The densities of liquid and vapour are 0.87345 and 0.00044 respectively. Hence

$$a^2 = 0.06592 .$$

If we put $\frac{1}{b_2} \fallingdotseq \frac{1}{r_2}$ in the equation (1), we obtain as $\frac{1}{b_1}$ 2.898. Hence b_1 is 0.345 mm. If we put $b_1 \fallingdotseq r_1$ and approximately calculate twice from Bashforth and Adam's table, we obtain $r_1 = 0.343$ mm. as a mean value. From these values of r_1 and r_2, we obtained the value of the surface tension of water as 70.93 at 34.32° while Richards' value by the method of the capillary rise is 70.72.

Osmium tetroxide was distilled into the tube which has two capillary tubes in it, Fig. 3, and the apparatus was sealed at a and kept in vacuum of 0.0005 mm. for 30 minutes and sealed at b. Thus we measured the capillary rise under its own vapour pressure. The apparatus was kept in a thermostat at a constant temperature and after 15 minutes several observations were carried out. The results obtained are shown in Table 5.

Table 5.

t° C.	$H_{mm.}$	$a^2_{mm.^2}$	γ dyne/cm.	$\gamma^{5/6}$
43.00	3.05	0.02323	49.24	25.72
50.00	3.00	0.02284	48.10	25.23
58.00	2.97	0.02261	47.25	24.85
67.00	2.91	0.02214	45.87	24.24
75.00	2.88	0.02191	45.03	23.87
85.00	2.79	0.02120	43.15	23.04
95.00	2.72	0.02066	41.62	22.36
105.00	2.65	0.02021	40.13	21.69
115.00	2.58	0.01956	38.59	20.99
130.00	2.44	0.01845	35.79	19.71
150.00	2.33	0.01760	33.32	18.57

The surface tensions at 50.0° and 100.0°C obtained by Wartenberg are 49.8 and 42.2 respectively.

Generally there are a following relation in a normal liquid.

$$\gamma = \gamma_o(1-T_r)^{\frac{6}{5}}$$

where γ_0 is the surface tension at absolute zero and T_r is reduced critical temperature. On osmium tetroxide the relations between $\gamma^{\frac{5}{6}}$ and t show two straight lines of different inclinations intersecting at about 75°C. The discussion on the liquid state will be described later.

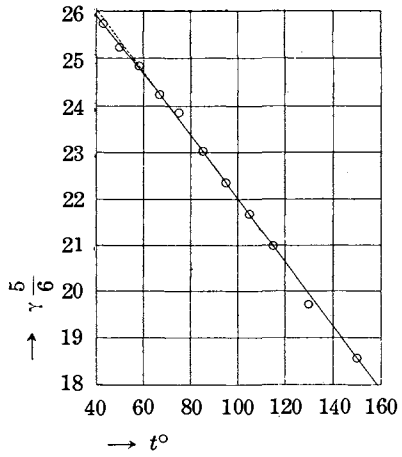

Fig. 4.

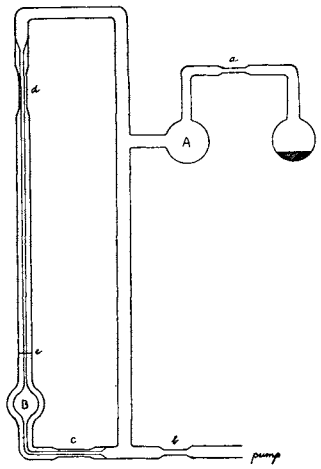

Fig. 5.

Measurement of Densities. The experiment was carried out only on liquid osmium tetroxide. After the sample was distilled into A, it was sealed at a and evacuated to vacuum of 0.0005 mm., and it was cooled with a freezing mixture of NaCl and ice and then sealed at b. By warming A the melt was transfered into B up to slightly above the mark e and was sealed at c and d. (Fig. 5). The capillary rise was read by a cathetometer with an accuracy of 0.01 mm. The apparatus was immersed in a thermostat. The capillary used has a length of about 7 cm. and its mean radius is 0.695 mm. by several observations with mercury. After the measurement ended, it was cut at a little above e and its capacity up to e is measured with water several times (V mm^3.). The coefficient of expansion of glass was taken as 2.5×10^{-5}.

The density of vapour is calculated by the following formula

$$d_b = 0.0122 \frac{M}{T_b}$$

$$\log_{10} \frac{d}{d_b} = 5\left(\frac{T}{T_b} - 1\right).$$

where d_b is the vapour density at the boiling point, M the molecular weight and T_b the boiling point.

The results are shown in Table 6. At the last column values of parachor are given, $p = \frac{M\gamma^{\frac{1}{4}}}{D-d}$. Its mean value was obtained only from the values above 75°C.

Table 6.

t °C	$V_{mm.^3}$	D	d	$D-d$	$(D-d)^{\frac{10}{3}}$	P
43.00	646.95	4.3224	0.0006	4.3218	131.46	156.2
50.00	651.14	4.2946	0.0008	4.2938	128.66	156.3
58.00	656.12	4.2620	0.0010	4.2610	125.42	156.8
67.00	661.75	4.2257	0.0012	4.2245	121.86	157.0
75.00	667.02	4.1923	0.0015	4.1908	118.67	157.5
85.00	673.49	4.1521	0.0021	4.1500	114.86	157.2
95.00	680.25	4.1108	0.0027	4.1081	111.04	157.6
105.00	687.04	4.0702	0.0036	4.0666	107.34	157.7
115.00	694.38	4.0271	0.0048	4.0223	103.49	157.9
130.00	705.81	3.9619	0.0074	3.9545	97.79	157.6
150.00	721.96	3.8733	0.0131	3.8602	90.23	158.4
						157.7

The value of parachor calculated by Sugden from Watenberg's data is 154.0 and the densities obtained by Wartenberg at 42° and 100° are 4.44 and 4.19 respectively.

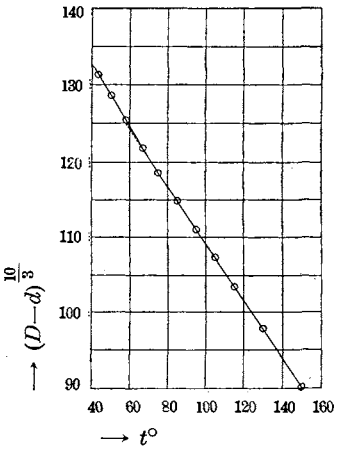

Fig. 6.

For a normal liquid, generally, there is a relation,[1]

$$D-d = D_o(1-T_r)^{\frac{3}{10}}$$

where D_0 is the density at absolute zero, and T_r the reduced critical temperature. That is to say, there is a linear relation between $(D-d)^{\frac{10}{3}}$ and temperature. For osmium tetroxide this relation holds good at above 75°C. but the line bends below 75°C. This fact is also in parallel to the results on vapour pressure and surface tension measurements.

Liquid State of Osmium Tetroxide. It has been known by the measurement of the

(1) Sugden, *J. Chem. Soc.*, **1927**, 1780.

vapour pressure that the relation between $\log p$ and $\frac{1}{T}$ can be expressed by two straight lines intersecting at about 70°C. The Trouton's constant is 21~2. The tetroxide, therefore, is a normal liquid at its boiling point.

In the measurement of the surface tension the relation $\gamma=\gamma_o(1-T_r)^{\frac{6}{5}}$ holds at above 75°C. and at below 70°C. separately, showing two straight lines. The same fact is observed in the measurement of densities. The relation $D-d = D_o(1-T_r)^{\frac{3}{10}}$ holds good at above 75°C.

According to Walden[1] there is a following relation at its boiling point for a normal liquid.

$$\frac{Ma^2}{T} = K = 1.162 .$$

where a^2 is the specific cohesion at its boiling point. For osmium tetroxide

$$a^2 = 1.867 , \qquad K = 1.177 .$$

Therefore this relation also indicates that the substance is a normal liquid at its boiling point. Putting these facts together, osmium tetroxide must be a normal liquid at above 75°C. In the following Katayama's equation which indicates the relation between a molecular surface energy and temperature, the constant K' is 2.12 for a normal liquid in most cases.

$$\gamma\left(\frac{M}{D-d}\right)^{\frac{2}{3}} = k'(T_c-T)$$

where T_c is the critical temperature. If the liquid associates, the degree of association is given by $x=\left(\frac{2.12}{k}\right)^{\frac{3}{2}}$, where k is the value found by experiment. In the following table k and x for osmium tetroxide are given.

t °C.	43.00	67.00	95.00	115.00	150.00
k	1.68	1.91	1.95	1.97	
x	1.42	1.17	1.13	1.11	

As the value of 2.12 varies somewhat according to a kind of a molecule, so it may be said that the tetroxide is a normal liquid at a high temperature. It will be concluded that the abnormalities observed in the measurements of the vapour pressure, the surface tension and the density are due to an association. This indicates that this compound has somewhat a polar character.

(1) *Z. physik. Chem.*, **65** (1908), 129, 257.

Critical Temperature. Wartenberg measured the critical temperature and found to be of 405°C. The author extrapolated the value by the relations $\gamma = \gamma_0(1-T_r)^{\frac{6}{5}}$ and $D-d = D_0(1-T_r)^{\frac{3}{10}}$ and found the values 422°C. and 388°C. respectively. There is a great difference between them, but this is inevitable because the temperature range of measurements is narrow. The mean value of them is 405°C. We adopt this value, though it is not so accurate.

Summary.

(I) The structure of osmium tetroxide was discussed.

(II) It was made clear that the phenomenon of an enantiotropy of osmium tetroxide set forth by Krauss did not exist.

(III) The vapour pressure of osmium tetroxide was measured between 15° and 130°C. Melting point, boiling point, heat of sublimation, heat of vaporization, heat of fusion, and free energy change among solid, liquid and vapour were determined.

(IV) Surface tensions and densities from melting point up to 150°C. were determined.

(V) Osmium tetroxide in liquid state somewhat associates below 70°C., though it is a normal liquid above 75°C.

(VI) The critical temperature was determined as 405°C.

July 1931.

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STUDIES ON THE REACTIONS BETWEEN GAS AND SOLID. PART II. ABSORPTION OF CO_2 BY CaO AND $Ca(OH)_2$.

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1. Absorption of CO_2 by CaO. Fine powders of lime (100 gr.) were placed in dry CO_2 and the change of weight was measured at 14°C. The results are given in Table 1.

Table 1.

Time in days	1	3	5	9	17	30	50	96	150	222	302
Increase in weight (%)	0.305	1.115	1.457	2.048	2.272	2.332	2.378	2.470	2.694	3.130	3.618

From the results it is clear, as it is ever said, that dry CO_2 does not react with dry CaO, or the velocity is very small at common temperature. The initial change of weight might be caused by a lack of care in the experiment, namely the CaO might have absorbed some moisture during its weighing, or the CO_2 gas might have contained a trace of water vapour, though it had been dried with sulphuric acid.

The rapid decrease of the carbonation velocity will be due to the facts, that the carbonation takes place only on the surface of CaO, and its rate of proceeding inwards is very slow. Hence, if the surface is covered with $CaCO_3$, the carbonation will practically cease.

This will also be true in the case of carbonation of CaO at high temperatures. To confirm this the following experiment was carried out. 7.0473 Gr. of CaO was heated in a stream of dry CO_2 for 2.5 hours, the temperature being kept at 600°C., and 0.5302 gr. of CO_2 was combined. The product was placed with untreated lime side by side, in an atmosphere which was saturated with water vapour at 50°C., and the rate of absorption of moisture was measured. At first the rate of absorption by the carbonated lime was exceedingly small. For example, the increase of weight of the carbonated lime was only 0.5% after 17 hours, while the untreated one increased 10.5%. But afterwards the rate increased more and more approaching to that of the untreated one. This fact shows that the carbonated lime has a coating of $CaCO_3$ on its surface, and is protected from water vapour. But after a certain time the water adsorbed on the surface will reach the fresh part of lime by diffusion through the coating of $CaCO_3$.

Quick lime with water changes to slaked lime with an increase of volume. Thus the crust of $CaCO_3$ is cracked off from the surface of lime and the slaking of quicklime proceeds more and more rapidly.

2. Absorption of Moist CO_2 by $Ca(OH)_2$ and its Velocity. Each 10 gr. of $Ca(OH)_2$, which had been kept in a saturated water vapour for 7 days to absorb moisture, were placed in an atmosphere of a constant composition of air and CO_2 which was saturated with water vapour (the total pressure was equal to 1 atm.) at 14°C. and their increase of weight was measured after 2 hours.

The results are shown in Table 2.

Table 2.

Absorption of moist CO_2 by 10 gr. of moist $Ca(OH)_2$ in 2 hours.
Relation between increase of weight and concn. of CO_2.

Concentration. C. (vol. % of CO_2)	1.33	3.87	6.44	13.0	32.0	64.7	78.5	100
Increase of weight % (W_t) obs.	1.21	2.88	5.47	9.40	16.84	24.63	26.26	—
Increase of weight calc. from eq. (1)	1.08	3.00	4.80	8.88	17.37	24.78	26.35	27.99
Difference	+0.13	−0.12	+0.67	+0.52	−0.53	−0.15	−0.09	—

In this table the volume concentration, C %, of CO_2 was calculated from the partial pressure of CO_2 saturated with water vapour by the following equation:

$$C = \frac{p_{CO_2}}{P} \times 100 = \frac{p(P-p_{H_2O})}{P^2} \times 100,$$

where P is the total pressure; p the partial pressure of moist CO_2; and p_{CO_2} and p_{H_2O} the partial pressure of CO_2 and H_2O respectively.

In the previous paper[1] on the absorption of moisture by CaO the author has obtained the following equation:

$$W_t = W_{h,\infty}(1-e^{-\alpha_1 ht}) \quad \cdots\cdots\cdots\cdots\cdots\cdots \quad (1)$$

(1) This Bulletin, **6** (1931), 294.

where W_t is the increase of weight in per cent in the time t, $W_{h,\infty}$ is $\lim_{t\to\infty} W_t$, α is the velocity constant of absorption of moisture, and h is vapour pressure.

From the analogy of the character of reaction, a similar relation has been assumed for the absorption of CO_2

$$W_t = W_\infty(1-e^{-\beta_1 Ct}) \quad \cdots\cdots\cdots\cdots\cdots\cdots \quad (2)$$

where C denotes the concentration of CO_2 in the moist air. The value of W_∞ cannot be calculated directly from the chemical equation: $Ca(OH)_2+CO_2=CaCO_3+H_2O$, because water is adsorbed and expelled during the experiment. As the materials were always saturated with moisture, the value of W_t, however, may be regarded as a measure of CO_2 absorbed, since the water will evaporate by local heating, and the product will be $CaCO_3$ keeping a quantity of H_2O and CO_2 corresponding to the adsorption equilibrium, the total increase of weight being thus proportional to the CO_2 combined. Putting $W_\infty=30.0$ by inspection, we have from the experimental data the following equation:

$$W_t = 30.0(1-e^{-0.0135Ct}) \quad \cdots\cdots\cdots\cdots\cdots\cdots \quad (3)$$

The value of W_t calculated from this equation, shown in Table 2 and Fig. 1, agrees fairly well with that of observed. Hence the following differential form will also be true:

$$\frac{dW_t}{dt} = \beta_1 C(W_\infty - W_t) \quad \cdots\cdots\cdots\cdots\cdots\cdots \quad (4)$$

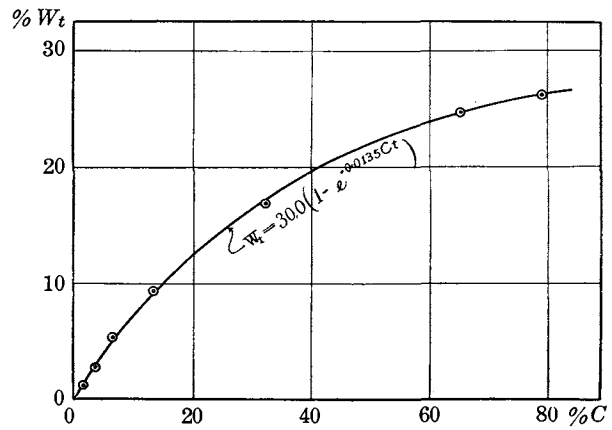

Fig. 1.

Relation btw. concn. of CO_2 and absorption of CO_2 in 2 hrs.

3. **Absorption of Dry CO_2 by $Ca(OH)_2$ and its Velocity.** 132.14 Gr. of $Ca(OH)_2$, prepared from 100 gr. of CaO and equivalent water, were placed in a desiccator with $CaCl_2$. It was evacuated and CO_2 (dried by conc. H_2SO_4) was introduced into it. The increase of weight was measured from time to time. The results are given in Table 3 and Fig. 2.

Table 3.

Days	1	2	4	6	8	11	16	26	39	60	124	221	301
Increase of weight %.	31.80	35.82	42.18	40.38	38.81	37.16	36.16	35.96	35.82	35.64	35.63	35.49	35.39

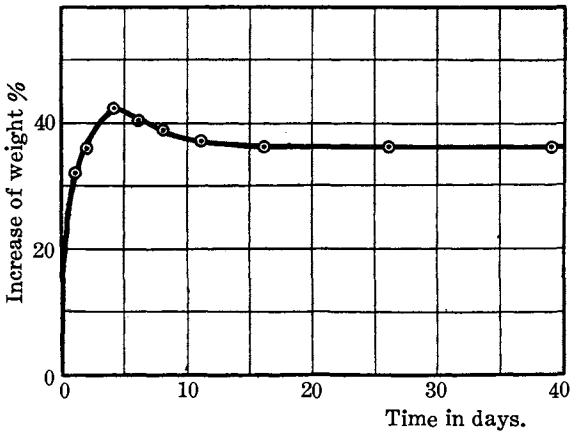

Fig. 2.

Absorption of CO_2 by dry $Ca(OH)_2$.

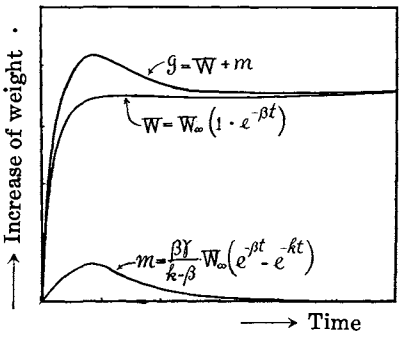

Fig. 3.

When dry $Ca(OH)_2$ reacts with CO_2 to form $CaCO_3$, setting equivalent molecules of water free, the water will be kept by the surrounding lime for a time and then given off. The curve of indicating the change of weight with time will therefore have a point of maximum and inflexion. Its character will be shown in Fig. 3, curve g. This curve is obtained as the sum of two curves W and m, where W shows the weight of CO_2 absorbed and m that of water remaining.

The velocity of absorption of CO_2 by $Ca(OH)_2$ is, from the former experiment, given by the equation

$$\frac{dW_t}{dt} = \beta(W_\infty - W_t) \quad \cdots\cdots (4)$$

or

$$W_t = W_\infty(1-e^{-\beta t}) \quad \cdots\cdots (5)$$

where W_∞ is, from the equation $Ca(OH)_2+CO_2=CaCO_3+H_2O$, equal to 35.1%. The velocity of liberation of water is theoretically

$$\frac{dw_t}{dt} = \gamma\left(\frac{dW_t}{dt}\right) = \beta\gamma W_\infty e^{-\beta t} \quad \cdots\cdots (6)$$

where $\gamma=18.02/25.98$ and therefore $\gamma W_\infty=24.3\%$. The velocity of evaporation of water will be given by the equation

$$-\frac{dm_t}{dt} = km_t - \gamma\frac{dW_t}{dt'} = km_t - \beta\gamma W_\infty e^{-\beta t} \quad \cdots\cdots (7)$$

where m_t is the amount of water held by the material at time t. By integrating the equation (7) m_t may be calculated.

$$m_t = e^{-\int k dt}\left[\int e^{\int k dt}(\beta\gamma W_\infty e^{-\beta t})\,dt + \text{const.}\right]$$

$$= m_o e^{-kt} + \frac{\beta\gamma}{k-\beta}W_\infty\left[e^{-\beta t} - e^{-kt}\right] \quad \cdots\cdots (8)$$

where m_o means m_t at $t=0$. The total increase of weight after the time t is therefore

$$g_t = W_t + m_t$$

$$= W_\infty + \left(\gamma W_\infty\frac{\beta}{k-\beta} - W_\infty\right)e^{-\beta t} - \left(\gamma W_\infty\frac{\beta}{k-\beta} - m_o\right)e^{-kt} \quad \cdots (9)$$

$$= 35.1 + \left(24.3\frac{\beta}{k-\beta} - 35.1\right)e^{-\beta t} - \left(24.3\frac{\beta}{k-\beta} - m_o\right)e^{-kt} \quad \cdots (9')$$

If $m_o = 0$, then $g_t = g_t'$

$$g_t' = 35.1 + \left(24.3\frac{\beta}{k-\beta} - 35.1\right)e^{-\beta t} - 24.3\frac{\beta}{k-\beta}e^{-kt} \quad \cdots\cdots (9'')$$

The character of the curve for equation (9) agrees with that of experimentally obtained. The equation (9) may be applied to any reactions of this sort.

These experiments were carried out in the research laboratory of the Electrochemical Manufacturing Co. Ltd., Tokyo, before April 6th, 1930 and reported to the board of directors of the Co. on that day. Grateful acknowledgment is made to Dr. M. Katayama, Prof. of the Tokyo Imperial University, for giving valuable suggestions, and to Mr. K. Hibi, Director of the Co., who gave the author the opportunity of the accomplishment of this work and allowed him to publish this report. Mr. I. Kobayashi assisted the author in this experiments.

Summary.

(1) It was determened experimentally that the velocity of absorption of CO_2 by $Ca(OH)_2$ is proportional to the concentration of CO_2 (or partial pressure of CO_2) in the air, and to the absorbing capacity of the substance:

$$\frac{dW_t}{dt} = \beta C(W_\infty - W_t)$$

(2) For the change of weight due to the absorption of dry CO_2 by dry $Ca(OH)_2$ the following equation was proposed

$$g_t = W_\infty + \left(\frac{\beta}{k-\beta}\gamma W_\infty - W_\infty\right)e^{-\beta t} - \left(\frac{\beta}{k-\beta}\gamma W_\infty - m_o\right)e^{-kt}.$$

and was also experimentally discussed.

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ON THE DIBASIC ACIDS IN JAPAN WAX.

By Mitsumaru TSUJIMOTO.

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Japan wax is obtained in Japan exclusively from the berries (mesocarps) of "Hazé-noki," *Rhus succedanea L.* (Anacardiaceae). The statement often mentioned in foreign books that the wax is prepared from many species of the genus Rhus is erroneous. *Rhus succedanea* grows chiefly in the south-western parts of the country, and so the wax industry is conducted in Kiushiu and Shikoku. Formerly in more northern parts of the country, "Urushi" wax was prepared from the berries of *Rhus vernicifera L.*, but this industry has now nearly ceased to exist. The production of Japan wax has appreciably diminished than in former times; nevertheless it is one of the most important fats produced in Japan.

It is strange to note that the chemical examination of Japan wax has but rarely been undertaken by native chemists; in 1911 the author[1] reported experiments on the general properties and chemical composition of the wax, and recently I. Sakuma[2] made an extensive investigation on the colouring matter and the bleaching of the wax.

The discovery of a dibasic acid in Japan wax is due to L. E. Eberhardt,[3] who observed the occurrence of an acid (m.p. 117.5°C.) belonging to the oxalic acid series and assigned to it the chemical formula $C_{18}H_{36}(CO_2H)_2$. In 1900 A. C. Geitel and G. van der Want[4] made a closer study on the chemical composition of Japan wax. On dissolving the insoluble fatty acids in alcohol, and fractionally precipitating the acids with magnesium acetate in hot solution, they obtained an acid of m.p. 117°C., palmitic acid, and impure oleic acid. They named the high melting acid "japanic acid" ("Japan-säure"), and by the determination of neutralisation value, etc., confirmed its formula to be $C_{20}H_{40}(CO_2H)_2$. Further they described the separation of the acid as potassium salt, the formation of a ketone $C_{20}H_{40}CO$ (m.p. 82–83°C.) from it on strong heating, and also the probable occurrence of the acid as a mixed glyceride with palmitic acid in the wax. R. Schaal[5] fractionated the Japan wax fatty acids under diminished pressure and obtained

(1) *J. Soc. Chem. Ind. Japan*, **14** (1911), 321.
(2) Scientific Report of Kiriu Higher Technical School, No. 3 (1929).
(3) Diss. Strasburg, 1888.
(4) *Z. prakt. Chem.*, **61** (1900), 151.
(5) *Ber.*, **40** (1907), 4784.

homologues of higher dibasic acids. The chief acid was $C_{19}H_{38}(CO_2H)_2$ (m.p. 117–117.5°C.), but $C_{18}H_{36}(CO_2H)_2$ and $C_{17}H_{34}(CO_2H)_2$ were also present. E. Tassily[1] also fractionated the methyl esters of Japan wax fatty acids and identified japanic acid, $C_{21}H_{40}O_4$, and two lower homologues.

The present author[2] isolated high melting acids (m.p. 119–121°C.), which he considered to consist mainly of japanic acid, and calculated its amount in the wax as ca. 2%. It should be noted that the melting points of these acids were far higher than those mentioned in the literature, but at that time no further experiment was performed as to their chemical composition. At present even in the standard works on fats and oils, the formula for so-called japanic acid is somewhat indefinite, either $C_{21}H_{40}O_4$ or $C_{22}H_{42}O_4$ being adopted.

The experiments described in this paper are the continuation of the investigation made some twenty years ago. The result shows that the main constituent of the dibasic acids in Japan wax is heneicosane dicarboxylic acid. $C_{23}H_{44}O_4$, accompanied probably by eicosane dicarboxylic acid, $C_{22}H_{42}O_4$.[3] Further a peculiar property of Japan wax dibasic acids is mentioned.

Experimental Part.

(I) Matetial. The samples of Japan wax were procured from Higo Seirô Kaisha (Higo Wax Manufacturing Company) of Kumamoto, Kiushiu. Nine samples of raw or fresh wax (Ki-rô)[4] and one sample of bleached wax (Sarashi-rô) were used. Among others the following three samples were chiefly used.

(1) No. 1. New berry wax; pale brownish yellow colour.

(2) No. 2. Old berry wax; colour nearly the same as No. 1.

(3) No. 3. New berry wax; brownish yellow colour.

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(1) *Bull. Soc. Chim.*, Bd. **9–10** (1911), 608.

(2) Loc. cit.

(3) After the present paper (in Japanese) had been published in the Report of Tokyo Imperial Industrial Laboratory, Vol. 25, No. 4 (1930), I have noticed the investigation of B. Flaschenträger and F. Hall (*Chem. Zentr.*, 1930, Bd. II, 2761). The result obtained by them agrees in many respects with that of my experiments.

(4) "Ki-rô" is the name given to an unbleached, raw or fresh Japan wax. When the berries of *Rhus succedanea* are stored, the colouring matter in them become gradually insoluble in the wax in the preparation. The wax obtained from new or fresh berries has usually a dark brown colour, and is called "Shinmi-rô" (new berry wax). The wax from the berries stored beyond the next rainy season in this country (June to July) is called "Komi-rô" (old berry wax), and has a far lighter colour. Notwithstanding many disadvantages, it is customary for the wax manufacturers to keep the berries until they become "Komi" (old berry). Sometimes they are stored for several years. Then they are called "Ô-komi" (literally "great" old berry, "Ô" is used here in the sense of "very"); the wax from them, "Ô-komi-rô", has the lightest brownish or greenish yellow colour.

Characteristics, etc. of the Waxes.

	No. 1.	No. 2.	No. 3.
d_4^{100}	0.8626	0.8627	0.8620
M.p.	52–52.5°	49.5–50°	50–50.5°
Acid value	4.5	7.8	3.1
Saponif. value	205.7	207.5	206.7
Iodine value (Wijs)	18.8	17.5	20.2
Hehner value	94.56	94.64	95.14
Unsaponif. matter	0.60%	0.60%	0.51%

The fatty acids[1] gave the following numbers:

	No. 1.	No. 2.	No. 3.
M.p.	59–59.5°	60.5–61.5°	60–61°
Neutralisation value	213.2	212.3	210.5
Iodine value (Wijs)	19.5	17.8	19.9

The comparatively high iodine values are due to the admixture of the kernel oil of the berry. The iodine values of many samples of the wax formerly determined by me ranged 10.3–13.8. The characteristics of Japan wax cited in foreign books are usually those which were determined on the bleached wax. As by bleaching process (insolation), fairly profound changes of the composition occur, the numbers are quite different from that of the genuine wax.

(II) Approximate Quantitative Determination of the Dibasic Acids. As japanic acid appears not the only dibasic acid in Japan wax, this name is reserved for a while, and "Japan wax dibasic acids" or simply "dibasic acids" are used in the following description. To investigate the dibasic acids, it is firstly most important to know at least their rough amount in the wax. By utilizing their difficult solubility in petroleum ether, the author has devised the following procedure as the approximate determination of these acids.

About 1 gr. of the Japan wax fatty acids is accurately weighed in a small flask, and 50 c.c. of petroleum ether (b.p. until 80°C.) are added. The flask is repeatedly immersed in a water bath at 40–50°C., and shaken to dissolve the acids.[2] It is necessary to cork the flask to prevent the evaporation of petroleum ether, but the cork is often removed to diminish the internal pressure caused by the expansion of the solvent. The main part of the dibasic acids remains as a fine precipitate. The flask is next cooled in ice-water for 30 minutes, thereby the dibasic acids are completely

(1) In this report, the "fatty acids" mean the insoluble acids plus unsaponifiable matter.

(2) This warming is necessary in order to disintegrate the mass of the acids. By direct treatment of the acids with petroleum ether at 25°C, there is some possibility that a part of palmitic acid remains enveloped in the dibasic acids.

precipitated together with palmitic acid. Then the flask is put in water at 25°C. for one hour with frequent shaking. By this treatment the precipitated palmitic acid is again dissolved in petroleum ether leaving the dibasic acids. The solution is filtered through a tared Gooch crucible[1] kept at about 25°C. by suitable arrangement. As the dibasic acids are deposited as a colloid-like state, the filtration presents some difficulty. The liquid is finally sucked with a pump, and the precipitate washed three times with each 5 c.c. of petroleum ether. The crucible with the precipitate is dried at 90°C. to a constant weight. As it is difficult to transfer all the precipitate to the crucible, a portion of the dibasic acids adhering to the flask is weighed separately, and its weight is added to that of the main part.

The dibasic acids are slightly soluble in petroleum ether; for example, 100 c.c. of the latter (b.p. until 80°C., d_4^{25} 0.6493) dissolve 0.0045 gr. of the acids (refined specimen) at 25°C. As the above method has been proposed only as a rough determination, no correction is made for the loss caused by this solubility. Moreover, oxidised acids, colouring matter, and other impurities are also precipitated, and these would make the apparent weight of the dibasic acids rather higher.

By the above mentioned concentration, palmitic acid does not deposit even when the solution is cooled to 20°C., so that more or less lowering of temperature on filtering is of no consequence. Also sterol in the unsaponifiable matter does not precipitate by this treatment.

In a test made with a sample of a known composition (palmitic acid 80%, oleic acid 15%, dibasic acids 5%), it was found that the dibasic acids can be determined with an error of about within 0.5%. So the method is sufficient satisfactory for the approximate determination of these acids. The results obtained on a number of commercial unbleached Japan wax are given in the following table:

Waxes	Data	Percentage of the dibasic acids in the fatty acids
No. 1	Samples mentioned above	5.6
,, 2		5.9
,, 3		5.2
,, 4	Kumamoto; old berry	6.0
,, 5	Saga; new berry	6.1
,, 6	Nagasaki; new berry	6.7
,, 7	Kagoshima; "Ô-komi"	5.9
,, 8	,, ; new berry	5.3

N. B. No. 7 is free from the kernel oil; it had the iodine value 12.5.

(1) As filtering materials, a filter paper (its circumferential part pasted to the bottom of the crucible) and asbestos fibres are used.

Besides the above samples, a wax from the Prefecture of Kumamoto was found to contain 7.2% of the dibasic acids. This rather abnormally high content is probably due to the difference of the variety of "Haze" tree. To determine the acid content in genuine wax prepared in the laboratory, a sample of the wax was extracted from the mesocarps of new berries from a district of Kiushu, and it was treated with animal charcoal. The fatty acids from this wax contained 5.2% of the dibasic acids. The latter melted at 107–108°C and had the neutralisation value 288. So they consisted of nearly pure compounds.

By calculating from the Hehner value (mean 94.7), the contents of the dibasic acids in the Japan waxes mentioned in the above table amount to 4.9–5.8%. It will be seen from the above that the amount of the dibasic acids in Japan wax is far greater than hitherto considered.

In the case of bleached wax, the method could not be recommended, since oxidised acids produced by insolation are difficultly soluble in petroleum ether. An experiment gave the number 6.5%, which appeared to be somewhat high.

(III) Preparative Separation of the Dibasic Acids. Geitel and van der Want separated so-called japanic acid by utilizing the difficult solubility of its potassium salt in alcohol.[1] The mixed fatty acids are dissolved in 95% alcohol so as to form 10% solution, and the solution is neutralised with alcoholic potash. The potassium salt of the dibasic acid separates as a precipitate. The solution is then filtered in a hot funnel at 50–62°C., thereby the salt remains on the filter. This is finally decomposed with hydrochloric acid. The drawbacks of this method are the necessity of neutralising the total acids, the difficulty of filtration owing to colloidal nature of the precipitate, and bad yield.

It is clear that the dibasic acids may be prepared in some quantity by applying the procedure of the above mentioned determination on a large scale, but obviously a very large amount of the solvent is required. However, on extracting the mixed fatty acids in a Soxhlet apparatus, about 2% of the crude dibasic acids may be obtained as an insoluble residue. After several trials, the author recommends the following methods as preparative separation in laboratory.

(1) Separation by means of Lead Salt. The dibasic acids are fractionally precipitated with a calculated quantity of lead acetate in alcoholic solution.

(1) The salt is readily soluble in dilute alcohol.

10 Gr. of Japan wax fatty acids are dissolved in 100 c.c. of 95% alcohol. To this solution is added a solution of 0.6 gr. of lead acetate (which corresponds to about 7% of the dibasic acids) in 10 c.c. of the alcohol. The mixed solution is warmed on a water bath to above 70°C., and then rapidly filtered on a hot funnel kept a little above 70°C. The precipitate on the filter is returned to the flask, and treated with 20 c.c. of the alcohol and filtered as before. The precipitate is then decomposed with hydrochloric acid.

The lead salt of palmitic acid is soluble in 95% alcohol at 70°C. The repetition of the treatment is to remove palmitic acid as completely as possible from the precipitate. By this method, about 5.6% of the crude dibasic acids were obtained from the fatty acids of the wax No. 3.

Instead of lead, the salts of alkaline earths, magnesium, or zinc may probably be used. Indeed, Geitel and van der Want used magnesium acetate for such purpose. Sodium salt was found to be unsuitable.

(2) *Separation by means of the Distillation of Esters.* This is of course not novel, since it was already applied by Tassily, but the method is most convenient for preparative purpose. The following is an example.

1000 Gr. of Japan wax are heated with 1000 gr. of methanol containing 2.5% of HCl on a water bath for 12 hours to ensure methanolysis. The methyl esters are liquid in summer season. They are distilled under 5–5.5 mm. pressure until the temperature rises to 185°C. (bath temperature 230°C.) thereby more than 80% of the esters distil over. The residue which contains the dibasic acids is saponified, and the free acids are extracted in a Soxhlet apparatus with petroleum ether to dissolve admixed palmitic and oleic acids. An experiment by this method gave 50 gr. or 5% of the crude dibasic acids.

The reason why the distillation is interrupted at 185°C., is to avoid the decomposition of the acids by overheating. But in the experiments made recently, the distillation was carried out up to 205°C/3 mm. without apparent defect, so that more than 90% of the distillate were obtained. It seems also that the distillation may even be continued up to higher temperatures, until the esters of the dibasic acids themselves distil over. In this case, however, there is much fear for decomposition, especially if the esterification is not complete, and the quantity is large.

Technically it will be most simple to distil the free fatty acids, but particular care should be necessary, since if we accept the statement of Geitel and van der Want, japanic acid forms a ketone at high temperature.

(IV) **On the Chemical Composition of the Dibasic Acids.** It has been described in the introductory remark that the chemical formula of japanic

acid is somewhat indefinite, either C_{21} or C_{22} formula being adopted. It is rather doubtful too whether there occur in reality the homologues of japanic acid in Japan wax. It should also be noted that the samples of the foreign investigators appear to have been bleached waxes, which certainly must have contained many impurities formed by bleaching process. In view to obtain the dibasic acids more easily free from such impurities, the author made experiments on raw or fresh, unbleached waxes.

(*1*) *Experiment 1.* Firstly the dibasic acids were separated according to the classic method of Geitel and van dar Want. The temperature of filtration was kept at 55-60°C. It has been observed that the potassium salt remains dissolved at above 70°C., but the solution becomes turbid at 65°C., and an appreciable precipitate is formed already at 62°C.

About 3 gr. of the salt were obtained from 100 gr. of the fatty acids of the wax No. 1. After thrice recrystallisation, the free acids melted at 119–120°C., and had the neutralisation value 294.4[1]

Anal. Subst. = 0.1082; CO_2 = 0.2854; H_2O = 0.1126 gr. Found: C = 71.94; H = 11.65%.

The substance corresponded, therefore, mainly to $C_{23}H_{44}O_4$. The m.p. was higher than those recorded in the literature.

The calculated numbers for the high members of the dibasic acids are as follows:

	Mol. wt.	Neutr. value	C (%)	H (%)
$C_{21}H_{40}O_4$	356.3	315.0	70.72	11.31
$C_{22}H_{42}O_4$	370.3	303.0	71.29	11.43
$C_{23}H_{44}O_4$	384.3	292.0	71.81	11.54

(*2*) *Experiment 2.* 50 Gr. of the fatty acids of the wax No. 3 were treated by the lead salt separation method, and the crude dibasic acids were decolourised with animal charcoal; yield, 2.8 gr. After thrice recrystallisation from alcohol, the purified acids (0.8 gr.) formed white crystals of m.p. 119–120°C. and the neutralisation value 288.9.

Anal. Subst. = 0.1287; CO_2 = 0.3385; H_2O = 0.1350 gr. Found: C = 71.73; H = 11.74%.

The mother liquor gave on concentration 0.9 gr. of white crystals; on washing with petroleum ether, they melted at 111–112°C., and had the neutralisation value 287.3.

(1) In alcoholic solution, the potassium salt separates out as a precipitate. In order to observe the accurate end of titration, the addition of a little water to dissolve it is necessary.

So the result of the analysis and the neutralisation values of these substances corresponded to those of $C_{23}H_{44}O_4$.

(3) *Experiment 3.* By the procedure mentioned in the ester distillation method (until 185°C./5 mm.), 48.5 gr. of the crude product were obtained from 1000 gr. of the methyl esters of the wax No. 2. This was dissolved in 95% alcohol, treated with animal charcoal, and then recrystallised from about 10 times of its quantity of the alcohol. The crystals were separated into two parts : first crop (A), 20 gr., m.p. 114–115°C., and second crop (B), 19 gr., m.p. 112–113°C. The crystals were very fine, and presented difficulty on filtration.

(a) Purification by Recrystallisation. The crude acids were purified by repeated recrystallisation from 95% alcohol.

(1) Purification of the Part A. At the beginning, 5 gr. of it were crystallised from 100 c.c. of the alcohol. The recrystallisation was repeated six times, using about 20 times of alcohol for each crop of crystals.

	M.p.	Neutr. value[1]
1st recrystallisation	115°	—
2nd ,,	116–120°	285
3rd ,,	117–120°	286
4th ,,	121–122°	290
5th ,,	122–123°	288
6th ,,	122–123.5°	289

After 3rd recrystallisation, the m.p. became almost constant. The neutralisation values corresponded nearly to that (292.0) of $C_{23}H_{44}O_4$.

Two analyses of the last (6th) substance were as follows :

Subst. = 0.1190 and 0.1282; CO_2 = 0.3107 and 0.3343; H_2O = 0.1226 and 0.1353 gr.
Found : C = 71.21 and 71.12; H = 11.53 and 11.81%.

The results corresponded to $C_{22}H_{42}O_4$ rather than $C_{23}H_{44}O_4$. But judging from the neutralisation value, the substance has been considered to consist mainly of $C_{23}H_{44}O_4$.

(2) Purification of the Part B. 5 Gr. of the substance were recrystallised.

	M.p.	Neutr. value
2nd recrystallisation	109–109.5°	288
3rd ,,	112–113.5°	290

(1) The saponification values of these compounds were usually a little higher, but as errors may more likely be involved in the determination, they were omitted in this paper.

Although the m.p. was low, the neutralisation value corresponded to $C_{23}H_{44}O_4$.

(b) Purification by the Fractional Distillation of the Esters. As by the purification by crystallisation, there may be some doubt as to the individuality of the compound obtained, the substance was esterified and fractionally distilled under diminished pressure. The methyl ester was prepared by heating the substance with an excess of methanol (containing HCl) for 3 hours on a water bath.

(1) Distillation of the Ester of the Part A. 14.8 Gr. were distilled under 5 mm. pressure. The distillation began at the temperature 270°C. (last temp. 280°C.). The distillates formed white crystalline solids.

	Dist. temp.	Yield (gr.)	M.p.	Solidif. p.	Saponif. value
(1)	Until 240°	2.9	54.5°	—	269
(2)	240-250°	7.7	56.3°	ca. 55°	274
(3)	250-252°	2.1	57.8°	ca. 56.5°	275
(4)	Residue	1.7	—	—	—

The following are the calculated numbers for the methyl esters of C_{21} to C_{23} dibasic acids :

	Mol. wt.	Saponif. value
$C_{21}H_{38}O_4(CH_3)_2$	384.3	292.0
$C_{22}H_{40}O_4(CH_3)_2$	398.4	281.7
$C_{23}H_{42}O_4(CH_3)_2$	412.4	272.1

The saponification values of the above distillates nearly corresponded to that of the C_{23} formula.

The free acids obtained by saponification from the distillates had the following properties :

	M.p.	Solidif. p.	Neutr. value
Acid from fraction (1) (Once recrystallisation from alcohol)	113-114°	—	293
Acid from fraction (2) (Twice recrystallisations from alcohol)	Mainly liquid at 118°; became clear at 121°	Became turbid at 111°; solidified at 109°	292
Acid from fraction (3) (Twice recrystallisations from alcohol)	Liquid at 122; clear at 123.5°	Deposited crystals at 116°; solidified at 114°	293

Anal. of the acid from (3). Subst. = 0.1348; CO_2 = 0.3516; H_2O = 0.1390 gr.
Found : C = 71.14; H = 11.54%.

All the neutralisation values corresponded to that of $C_{23}H_{44}O_4$, but the result of the analysis approached rather to the C_{22} formula.

The free acid from the distillation residue melted after purification at 117°C., and showed the neutralisation value 265. This value nearly corresponded to that (263.2) of $C_{26}H_{50}O_4$. The actual occurrence of such an acid in the wax is, however, very doubtful.

(2) Distillation of the Ester of the Part B. 14.5 Gr. were used. The distillation (5mm.) began at the bath temperature 258°C. (last temp. 280°C). The distillates were white crystals.

	Dist. temp.	Yield (gr.)	M.p.	Solidif. p.	Saponif. value
(1)	Until 240°	5.8	50.8°	—	260
(2)	240-251°	7.1	56°	ca. 54°	275
(3)	Residue	1.0	—	—	—

The fraction (1) seemed fairly impure. The saponification value of (2) nearly corresponded to that of the C_{23} formula.

The properties of the free acids obtained from the distillates were examined:

	M.p.	Solidif. p.	Neutr. value
Acid from fraction (1) (Once recrystallisation)	115-116°	—	286
Acid from fraction (2) (Once recrystallisation)	113-113.5°	—	299
Acid from fraction (2) (Twice recrystallisations)	114°	ca. 104°	303

The acid from the fraction (1) had unexpectedly higher m.p. than that from (2). In spite of the fact that the saponification value of the latter fraction nearly corresponded to that of the C_{23} formula, the neutralisation value of its free acid coincided to that (303.0) of $C_{22}H_{42}O_4$.

From the results of the distillation, it appeared that the acids in the part A mainly consisted of $C_{23}H_{44}O_4$, while those of the part B contained an appreciable amount of $C_{22}H_{42}O_4$.

Summarising the results of the experiments made on the composition of the dibasic acids, it has been concluded that the main constituent of the acids is $C_{23}H_{44}O_4$, but probably the acid $C_{22}H_{42}O_4$ also occurs in a fair proportion. It seems rather doubtful that the acids of consecutive even and odd numbers occur in one and same wax, but actually no proof has been obtained to negate it, inasmuch as there is no sufficient ground to consider $C_{22}H_{42}O_4$ to be a mixture of $C_{21}H_{40}O_4$ and $C_{23}H_{44}O_4$, and still less to presume $C_{23}H_{44}O_4$ as a mixture of $C_{22}H_{42}O_4$ and $C_{24}H_{46}O_4$.[1]

(1) The dibasic acids in Urushi wax appears to consist chiefly of $C_{22}H_{42}O_4$.

(V) On a Peculiar Property of the Dibasic Acids. In the experiments on the dibasic acids, the author has observed the following interesting facts:

1. The structure of the solidified Japan wax fatty acids is very fine, and in spite of its brittleness, it has still a peculiar coherency and tenacity.

2. When freed from the dibasic acids, the crystals of the fatty acids became large and coarse, and nearly lose the coherency and tenacity.

As a matter of fact, by adding the dibasic acids, the fatty acids regained their original properties. To observe more closely the effect of the addition on various fatty and waxy substances, the following experiments were performed. The dibasic acids used in these experiments melted at 118–119°C., and had the neutralisation value 294; the structure was observed after well cooling of the melted mass.

(1) Japan wax fatty acids freed from the dibasic acids. M.p. 56.5°C.; markedly crystalline with various speckled structure. To them were added:

(a) Dibasic acids 1%. Crystals became finer, but still pretty crystalline.

(b) Dibasic acids 2%. Very fine crystals; became totally homogeneous mass; whiteness (opacity) increased. M.p. 60°C.(1)

(2) Palmitic acid. Coarse, needle-shaped crystalline mass (markedly on the surface).

(a) 2% Addition. Crystals became fairly fine, and the surface smoother.

(b) 5% Addition. Became fine, white crystalline mass with a waxy smooth surface.

(3) Stearic acid. The effect was greater than in the case of palmitic acid.

(4) Hardened herring oil. M.p. 54°C.; this had originally a fine crystalline structure, but the 2% addition made its appearance more waxy.

(5) Fatty acids from the hardened herring oil. M.p. 53.-54°C.; also a fine crystalline structure; the 2% addition had a pretty effect, but not so marked.

(6) Hardened sperm oil. M.p. 54°C.; coarse, beautiful crystalline structure.

(a) 1% Addition. Crystals became finer, and opacity increased.

(b) 2 %Addition. A marked effect; became a very fine crystalline, homogeneous structure.

(7) Paraffin. M.p. 52°C.; had a marked transparency.

(a) 2% Addition. Crystals became finer, and opacity (whiteness) increased.

(b) 4% Addition. Became a markedly white, homogeneous structure.

Thus it may be observed that the dibasic acids have a peculiar property to make the crystalline structure of fatty and waxy substances finer and more opaque; they also give to the substances a certain coherency and tenacity. Nor do the added acids separate out from the mass on long keeping.

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(1) The addition did not materially raised the m.p.; so in the following the description of the m.p. of the mixtures is omitted.

In the literature on fats, we find as the "hardening agent" ("Härtungsmittel") for candle materials, such substances as sebacic acid and stearic anilide. According to the author's experiments, they are, however, far less effective than the Japan wax dibasic acids. The same is true for dihydroxystearic acid.

A characteristic property of Japan wax that it may be kneaded between fingers to a "mochi" (rice-cake)-like mass without adhering, is due to the presence of the dibasic acids as glycerides. Many other solid fats, for instance, hardened fish oils, are usually brittle, and at the same time become very sticky and unpleasantly adhere to the fingers.

The fact that the glycerides of the dibasic acids are really responsible for this property, has been experimentally proved by the author by synthesizing two fats from the following fatty acid compositions by heating them with the equivalent parts of glycerol in sealed tubes to 200–205°C. :

(a) Palmitic acid 80; oleic acid 15 parts.

(b) ,, ,, ,, ; ,, ,, ,, ; dibasic acids 5 parts.

Whereas the fat from (a) was brittle and sticky, that from (b) exhibited nearly the same property as Japan wax.(1)

This peculiar property could not be considered to be specific to the dibasic acids of Japan wax, but probably it will be common to the higher members of the dibasic acids. Possibly this property of the dibasic acids may find applications in industry.

Summary.

(1) As "japanic acid" of Geitel and van der Want appears not the only dibasic acid in Japan wax, this name has been reserved for a while, and the expression of the "Japan wax dibasic acids" or more simply the "dibasic acids" is used in this paper.

(2) Basing on the difficult solubility of the dibasic acids in petroleum ether, a method for their approximate determination has been proposed. The results obtained by this method show that the content of the dibasic acids in the mixed fatty acids of Japan wax amounts to 5–6%, which are far greater than hitherto considered.

(3) For the preparative separation of the dibasic acids, the lead salt precipitation method and the ester distillation method have been found to be most convenient.

(1) The synthesized fats appeared to consist chiefly of diglycerides, but the effect of the dibasic acids as glycerides may be recognized as proved.

(4) As the results of the chemical examination of the dibasic acids, it has been concluded that the main constituent of the acids is heneicosane dicarboxylic acid, $C_{23}H_{44}O_4$, but probably eicosane dicarboxylic acid, $C_{22}H_{42}O_4$, also occurs in a fair proportion.

(5) As a peculiar property of the dibasic acids, it has been found that the comparatively small addition of them to fatty and waxy substances makes the crystalline structure of these substances finer and more opaque, and at the same time gives certain coherency and tenacity.

(6) The characteristic property of Japan wax that it may be kneaded to a "mochi"-like mass without adhering to the fingers is due to the presence of the glycerides of the dibasic acids.

In conclusion the author desires to thank Mr. Takenori Honda, Director of the Higo Wax Manufacturing Company, who kindly supplied him the samples of Japan wax used in the present investigation.

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ON THE DIBASIC ACIDS IN A FEW SUMACH BERRY WAXES.

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In the preceding paper the author has reported the investigation made on the dibasic acids in Japan wax ("hazé" wax), which is obtained in this country exclusively from the berries of "hazé" tree, *Rhus succedanea L.* It will be then natural to consider that whether such acids also occur in the waxes from other species of sumach trees. This is important and interesting from genetic relation of the trees, when we recollect that same or similar substances are often produced in plants of closely allied species. To contribute to this question, the author has tried experiments on the waxes (correctly, fats) from the berries of the following four species of Japanese sumach trees :[1]

(1) Besides the waxes from these four species, the fat from the berries of "nurudé", *Rhus semialata Murr., var. Osbeckii DC.* was also examined. The fat formed a brownish green-yellow semi-solid of the saponification value 199.2 and the iodine value 83.3. The petroleum ether insoluble substance in the fatty acids from this fat amounted only to 0.77%, and the dibasic acids appeared not to be present.

1. "Urushi-noki," *Rhus vernicifera DC.* This tree gives the well-known Japanese lacquer ("urushi") as the excretion of the stem. It chiefly grows in the northern part of Japan, and reaches to a height of 20–30 feet.

2. "Yama-hazé," *Rhus sylvestris S. et Z.* This is widely distributed in the country, and reaches to a height of more than 20 feet. Its berries resemble those of hazé, but are smaller.

3. "Yama-urushi," *Rhus trichocarpa Miq.* Chiefly grows in mountainous districts, and reaches to about 10 feet. The berries are far smaller than hazé berries.

4. "Tsuta-urushi," *Rhus toxicodendron L., var. vulgaris Pursh., f. radicans Engl.* This is a viny shrub growing in mountainous districts. The size of the berries resembles to that of yama-urushi.

Excepting yama-urushi wax, the occurrence of the dibasic acids has been confirmed in the other three waxes.

Experimental Part.

(I) **The Sumach Berries.** The berries of urushi and yama-urushi were procured from Fukushima Prefecture, while those of yama-hazé and tsuta-urushi were purchased from Kiso district of Nagano Prefecture. Although different in sizes, the berries somewhat resembled each other and also to hazé berries, and formed fairly flat, irregular ellipsoidal shapes with more or less pointed ends. The sizes, weights and analyses, etc., of the berries are given in the following table:

		Urushi	Yama-hazé	Yama-urushi	Tsuta-uruchi
Size (mm.)	Length	7–9	7–8	3–5	3.5–4
	Width	6–9	7–8	4–6	4–5
	Thickness	ca. 4	3–3.5	ca. 3	2.5–3
Weight of 100 berries (gr.)		7.76	7.34	2.17	2.61
Ratio of shell(1) to kernel		46.2 : 53.8	27.6 : 72.5	20.5 : 79.5	39.5 : 60.5
Analysis of shell					
Moisture (%)		5.22	4.06	5.52	3.18
Crude wax (%)		41.23	47.61	51.54	67.81

(1) Shell means exocarp and mesocarp. But in the cases of the berries of yama-hazé, yama-urushi and tsuta-urushi, the exocarps were for the most part lost during transportation.

(II) Properties of the Sumach Berry Waxes. The waxes were obtained by extracting the shells (chiefly mesocarps) of the berries with ether.

Properties of the Waxes.

	Urushi	Yama-hazé	Yama-urushi	Tsuta-urushi
Colour	Brownish yellow	Brownish black	Dark brown	Brownish black
d_4^{100}	0.8653	0.8679	0.8639	0.8895
M.p.	52.5–53°	51–52°	49–50°	38–39°
Acid value	3.1	6.2	14.1	—
Saponif. value	209.5	202.9	205.2	208 (?)
Iodine value (Wijs)	12.9	24.9	16.8	82 (?)
Unsaponif. matter (%)	0.62	—	0.78	—

Properties of the Fatty Acids.[1]

	Urushi	Yama-hazé	Yama-urushi	Tsuta-urushi
M.p.	62°	56–57°	54–55°	ca. 51–52°
Neutralisation value	212.9	214.1	212.6	212 (?)
Iodine value (Wijs)	12.8	14.6	17.1	26
Petroleum ether insoluble substance (crude dibasic acids) (%)	6.3	1.6	1.9	6.3

The crude tsuta-urushi wax contained the Japanese lacquer in appreciable proportion, so that only ambiguous results were obtained in the determination of the characteristics.

(III) Examination of the Occurrence of the Dibasic Acids.

(*1*) *Urushi wax.* By the lead salt precipitation method, 3.17 gr. of the crude dibasic acids (animal charcoal treated) were obtained from 50 gr. of the fatty acids. After fourth recrystallisation from 95% alcohol, the substance (0.8 gr.) melted at 117–118°C., and had the neutralisation value 301.3.

Anal. Subst. = 0.1148; CO_2 = 0.2980; H_2O = 0.1175 gr. Found: C = 70.96; H = 11.45%. Calc. for $C_{22}H_{42}O_4$: C = 71.29; H = 11.43%.

The further recrystallisations gave the following results:

	M.p.	Neutr. value
5th recrystallisation	119–120°	300.4
6th ,,	120-121°	299.1

So the substance appeared to consist chiefly of $C_{22}H_{42}O_4$.

(1) The fatty acids of yama-hazé and tsuta-urushi waxes were treated with animal charcoal before determination.

The mother liquors up to 4th recrystallisation were united, which on concentration gave 0.83 gr. of crystals of m.p. 116–117°C. and the neutralisation value 301.8. This neutralisation value also corresponded to that of the C_{22} formula.

(2) *Yama-hazé wax.* 50 Gr. of the methyl esters of the fatty acids were distilled under 6 mm. pressure until the temperature rose to 190°C. (bath temperature 225°C.), thereby 82.6% of the esters distilled over. The residue (6.4 gr.) was saponified, and the free acids (4.8 gr.) were dissolved in 250 c.c. of petroleum ether. After standing over-night the insoluble part (1.8 gr.) was dissolved in alcohol, treated with animal charcoal, and crystallised from alcohol. The refined substance (0.37 gr.) formed a grayish white powder of m.p. ca. 111°C. and the neutralisation value 280.6. After further decolourisation and recrystallisation, the substance (0.26 gr.) showed the m.p. 111–112°C. and the neutralisation value 290.1. The mixed test with the Japan wax dibasic acids (m.p. 123.5°C.) was 114–115°C.

From the above results, it appears that the chief constituent of the dibasic acids in yama-hazé wax is $C_{23}H_{44}O_4$.

(3) *Yama-urushi wax.* 10 Gr. of the fatty acids were treated with petroleum ether, and 0.2344 gr. of the insoluble substance was obtained. After decolourisation and recrystallisation it melted at 102°C., and had the neutralisation value 223.4. Although the want of the material prevented further investigation, the occurrence of a substance, which was difficultly soluble in petroleum ether and had the m.p. above 100°C., has been confirmed. Whether this consisted of dibasic acids or not, was, however, undecided.

(4) *Tsuta-urushi wax.* 100 Gr. of the methyl esters of the fatty acids[1] were distilled under 5 mm. pressure in the like manner as in the case of yama-hazé wax until the temperature rose to 180°C. (bath temp. 225°C.). By this operation 62% of the esters distilled over, and the residue (37 gr.) formed a brownish black, viscous liquid. The free acids obtained by saponification from the residue were dissolved in 500 c.c. of petroleum ether, and standing overnight, the insoluble substance (7 gr.) was separated from almost black mother liquor. By crystallising this substance from 100 c.c. of 95% alcohol, about 1.6 gr. of blackish brown crystals was obtained. These were treated with animal charcoal, and twice recrystallised from alcohol. The final refined product (0.7 gr.) melted at 117–118°C., and had the neutralisation value 286.7; the mixed test with the dibasic acids of Japan wax was 121–121.5°C. So the substance was confirmed to be $C_{23}H_{44}O_4$.

(1) The distillate consisted chiefly of the methyl ester of myristic acid.

Summary.

(1) The crude dibasic acids in urushi wax amounted to about 6.3% of the fatty acids. Their chief constituent appeared to be eicosane dicarboxylic acid, $C_{22}H_{42}O_4$.

(2) Yama-hazé and tsuta-urushi waxes also contained the dibasic acids, which amounted respectively to about 1.6 and 6.3% of the fatty acids. They consisted mainly of heneicosane dicarboxylic acid, $C_{23}H_{44}O_4$.

(3) The fatty acids of yama-urushi wax gave a small amount of a substance of m.p. 102°C. Whether this consisted of the dibasic acids or not, was, however, undecided.

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