

BULLETIN OF THE CHEMICAL SOCIETY OF JAPAN

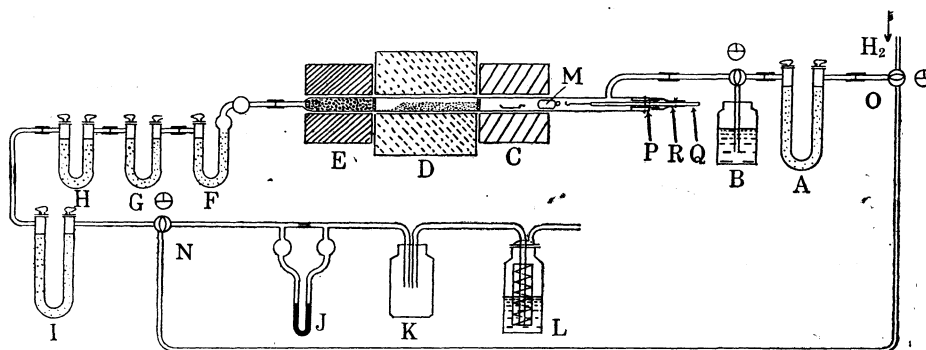
Direct Determination of Oxygen in the Organic Compounds by the Hydrogenation. I. Search of the Optimum Analytical Conditions.

By Kiyoshi MORIKAWA, Toraki KIMOTO and Ryonosuke ABE.

(Received November 21, 1940.)

The direct determination of oxygen in the organic compounds by the hydrogenation method according to Meulen⁽¹⁾ was examined in details. Inaba and Abe⁽²⁾ succeeded in the analysis of saccharose which was considered to be a difficult one. W. R. Kirner,⁽³⁾ however, could not obtain good results with saccharose and he discussed the problem of application of corrections obtained in the blank experiments. We, therefore, hoped to reexamine and clear up these points by experiments and also by theoretical consideration of this hydrogenation method.

Experimental Details. (1) *The apparatus used is shown in Fig. 1. It is essentially the same as Russel and Fullton's⁽⁴⁾ apparatus.*



A: CaCl_2 or NaOH granules	F, G, H: CaCl_2 or NaOH granules	M: Quartz plug
B: Conc. H_2SO_4	I: CaCl_2 tube	N: Three way cock
C: Sample heating furnace	J: Flowmeter	O: Three way cock
D: Cracking furnace	K: Empty bottle	P: Rubber stopper
E: Reduction furnace	L: Conc. H_2SO_4	Q: Glass tube
		R: Rubber tube

Fig. 1. Apparatus.

(1) H. Meulen: *Rec. trav. chim.*, **53** (1934), 118; *Bull. Soc. Chim.*, [5] **2** (1935), 1692.

(2) T. Inaba and R. Abe: *J. Soc. Chem. Ind., Japan*, **39**, 91 B (1936).

(3) W. R. Kirner: *Ind. Eng. Chem., Anal. Ed.*, **9** (1937), 535-539.

(4) W. W. Russel, J. W. Fullton: *Ind. Eng. Chem., Anal. Ed.*, **5** (1933), 384.

(2) *The catalyst*: The cracking (Pt-silica gel) and reducing (Ni-thoria) catalysts were prepared according to Russel's procedure⁽⁴⁾. The latter was reduced with hydrogen at 350°C. for 3 hours and then at 500°C. for 12~15 hours, thereby the water formed by reduction of catalyst would be less than one mg. per hour. After 7-10 analyses the Pt-silica gel catalyst was covered with free carbon deposit and lost its activity and, therefore, it was required to revive it by burning the carbon deposit with streaming air.

(3) *The analytical procedure* was essentially the same as Inaba and Abe's.⁽²⁾

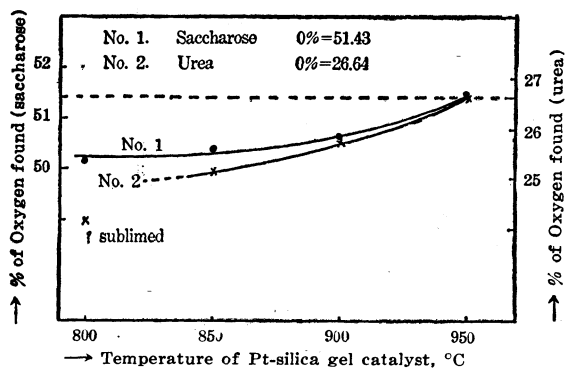
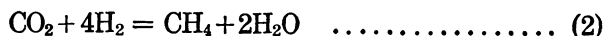
(4) *The absorbent*: Calcium chloride was used for typical substances which contained only carbon, hydrogen and oxygen, and caustic soda or soda lime, for nitrogen containing samples, the latter was preliminarily treated with dried ammonia gas.

(5) *The samples* were all Merck's preparations and were dried on phosphorus pentoxide in the Abderhalden vacuum drying apparatus.

Experimental Results. The optimum analytical conditions were searched with saccharose and the results obtained were given in Fig. 2-5.

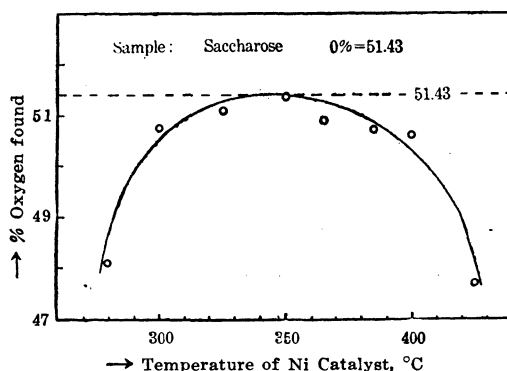
(1) *Cracking temperature*: Under 950°C. the analyses gave lower results, indicating the incomplete cracking of organic vapours (Fig. 2).

(2) *Reducing temperature*: The temperature around 350°C. was found to be satisfactory (Fig. 3). Under 300°C. the reducing velocity on Ni-catalyst was too slow and above 400°C. the equilibrium conditions of the following reactions became unsatisfactory for complete conversion of carbon oxides.



Analytical conditions: Temp. of Ni catalyst 350 C; hydrogen streaming velocity 5 l/hr; analytical time, saccharose 60 min., urea 80 min.

Fig. 2. Influence of Temperature of Pt-silica Gel Catalyst.



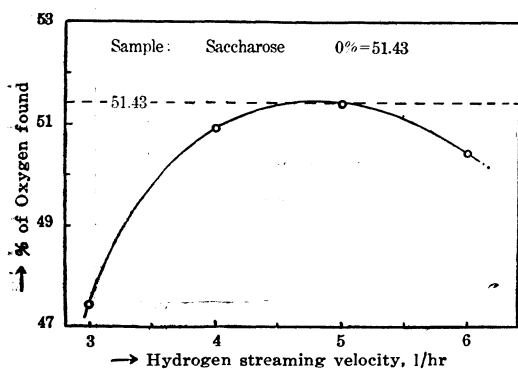
Analytical conditions: Temp. of Pt-silica gel catalyst 950 C; hydrogen streaming velocity 5 l/hr; analytical time 60 min.

Fig. 3. Relation between Reduction Temperatures and % of Oxygen found.

(3) *Streaming velocity of hydrogen*: Around 5 l./hr. was found to be best suited (Fig. 4). When the hydrogen streamed too slowly the

vapour pressure of carbon oxides became too high and, therefore, equilibrium conditions of reaction (1) and (2) became unfavourable for the analytical purpose.

(4) *Amount of sample taken*: The optimum amount of sample to be taken were investigated, and the product of the weight (in gram) and the oxygen content (in percentage) of the sample taken was expressed as K . Only when K was below 12, saccharose and urea gave good results as shown in Fig. 5.



Analytical conditions: Temp. of Pt-silica gel catalyst 950°C; temp. of Ni catalyst 350°C; analytical time 60 min.

Fig. 4. Influence of Hydrogen Streaming Velocity.

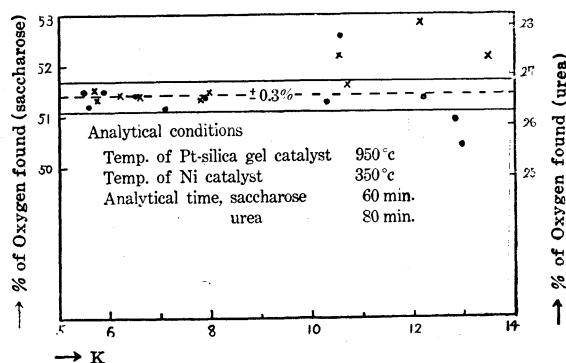


Fig. 5. Influence of weight of sample.

(5) Typical results with several compounds containing only carbon, hydrogen, and oxygen are shown in Table 1.

(6) Typical results with several compounds containing only carbon, hydrogen, oxygen, and nitrogen are indicated in Table 2.

Table 1. Analyses of CHO compounds.

Analytical conditions: Pt-silica gel temp. 950°C., Ni-catalyst temp. 350°C., hydrogen streaming velocity 5 l./hr., time required for these runs 60 min.

Expt. No.	Sample		Water obtained g.	Blank value mg.	Oxygen found %	Error %
	Kinds	Wt. g.				
58	Saccharose (0% = 51.43)	0.1070	0.0642	2.2	51.50	+0.07
57		0.1121	0.0670	2.2	51.34	-0.09
25		0.1152	0.0688	2.0	51.50	+0.07
56		0.1282	0.0772	3.0	51.40	-0.03
24		0.1537	0.0912	2.2	51.42	-0.01
				mean	51.43	+0
78	Benzoic Acid (0% = 26.22)	0.0869	0.0265	0.8	26.26	+0.04
94		0.1000	0.0315	1.7	26.46	+0.24
76		0.1144	0.0346	0.8	26.32	+0.10
92		0.1153	0.0354	1.7	25.96	-0.26
				mean	26.25	+0.03

Table 1.—(Concluded)

Expt. No.	Sample		Water obtained g.	Blank value mg.	Oxygen found %	Error %
	Kinds	Wt. g.				
67	α -Naphthalic Acid (0% = 18.60)	0.1002	0.0237	3.5	18.52	−0.08
97	β -Naphthalic Acid (0% = 18.60)	0.0752	0.0174	1.7	18.54	−0.06
105		0.1027	0.0237	2.2	18.59	−0.01
104		0.1113	0.0259	2.5	18.67	+0.07
106		0.1148	0.0262	2.2	18.56	−0.04
				mean	18.58	−0.02
63	Anthraquinone (0% = 15.38)	0.0642	0.0129	1.8	15.36	+0.02
64		0.0799	0.0163	2.2	15.56	+0.18
65		0.0993	0.0196	2.2	15.56	+0.18
62		0.1163	0.0222	2.0	15.43	+0.05
				mean	15.48	+0.10
C-9	Cellulose (indirect method) (0% = 50.17)	0.1932	0.1069	3.1	49.88	−0.29
C-10		0.2441	0.1403	2.1	50.23	+0.11
				mean	50.08	−0.09

Table 2. Analyses of CHON compounds.

Analytical condition: Pt-silica gel temp. 950°C., Ni-catalyst temp. 350°C., hydrogen streaming velocity 5 l./hr., time required for these runs 80~90 min.

Expt. No.	Sample		Water obtained g.	Blank value mg.	Oxygen found %	Error %	Absorbent
	Kinds	Wt. g.					
116	Urea (0% = 26.64)	0.1147	0.0355	2.0	26.71	+0.07	Granules of caustic soda
119		0.1325	0.0416	2.0	26.54	−0.10	„
118		0.1329	0.0422	2.0	26.84	+0.22	„
117		0.1478	0.0434	2.0	26.68	+0.04	„
135		0.2252	0.0688	1.3	26.62	−0.02	Soda lime
136		0.2446	0.0750	1.3	26.79	+0.15	„
				mean	26.70	+0.06	
121	Dimethyl-glyoxime (0% = 27.57)	0.0809	0.0258	2.0	27.77	+0.20	Granules of caustic soda
140		0.1170	0.0383	2.0	27.88	+0.31	Soda lime
139		0.1198	0.0396	2.0	27.55	−0.02	„
				mean	27.73	+0.16	
L-3	Beech-Lignin (indirect method) (0% = 30.66)	0.1234	0.0423	0.1	30.47	−0.19	Granules of caustic soda
L-6		0.1432	0.0500	0.9	30.51	−0.15	„
				mean	30.49	−0.17	

Discussion of Results. (1) *Analysis of saccharose*: W. R. Kirner⁽³⁾ was inclined to believe that saccharose left much carbon residues which retained some oxygen very tenaciously and thus gave lower values than the calculated ones. Russel, Fullton⁽⁴⁾ and Inaba, Abe⁽²⁾ and the authors all employed Pt-silica gel catalyst for the cracking purpose and they all obtained good results with saccharose. As made clear above there is an optimum range in every analytical condition and, therefore, one mistake in selecting these ranges would bring unsatisfactory results.

(2) *Blank experiments*: The reduction of Ni-thoria catalyst prepared by the ignition of mixed nitrates requires 3 days at 400°C. and 12–15 hours at 500°C. after which the reduction water would be less than 1 mg.. Even though the catalyst tube was left overnight under hydrogen pressure, a little above the atmospheric pressure, 7–16 mg. of water were always caught in the first blank run of the next morning, and, therefore, it was necessary to reduce the catalyst half an hour at 450–500°C. and to make one blank run at 350°C. every morning. When the catalyst was sufficiently reduced for use, and if we streamed hydrogen through catalyst tube without opening the end of the tube for 1 hour at

Table 3. Effects of Blank Value.

Analytical condition: Pt-silica gel temp. 950°C., Ni-catalyst temp. 350°C., hydrogen streaming velocity 5 l/hr., time required for these runs 60 min.

Expt. No.	Analytical order	Sample		Water obtained g.	Blank value mg.	Oxygen found %	Error %	Note
		Kinds	Wt. g.					
(1) Case in which the Ni-catalyst was not yet completely reduced								
55	1	Saccharose	0.1089	0.0659	3.5	51.19	−0.24	
56	2	(0% = 51.43)	0.1282	0.0772	3.0	51.40	−0.03	
57	3		0.1121	0.0670	2.2	51.34	−0.09	
58	4		0.1072	0.0642	2.2	51.50	+0.07	
104	1	β-Naphthalic	0.1113	0.0259	2.5	18.67	+0.07	
105	2	Acid	0.1027	0.0237	2.2	18.59	−0.01	
106	3	(0% = 18.60)	0.1148	0.0262	2.2	18.56	−0.04	
(2) Cases in which the Ni-catalyst was almost completely reduced								
75	1	Benzoic	0.0913	0.0259	0.6	24.61	−1.61	too low
76	2	Acid	0.1144	0.0346	0.6	26.39	+0.17	
77	3	(0% = 26.22)	0.0869	0.0264	0.6	26.35	+0.12	
86	1	Saccharose	0.1042	0.0610	1.7	50.55	−0.88	too low
87	2	(0% = 51.43)	0.2007	0.1176	1.7	51.29	−0.14	
88	3		0.2510	0.1442	1.7	50.42	−1.01	sample excess
89	1	Saccharose	0.2147	0.1241	1.6	50.67	−0.76	(K = 12.9) too low
90	2	(0% = 51.43)	0.2449	0.1450	1.6	50.96	−0.47	sample excess
91	3		0.2211	0.1295	1.6	51.37	−0.06	(K = 12.8)

the rate of 5 l./hr., we would obtain about 1 mg./hr. of water. If, however, we followed the procedure just as in the actual analysis, that is, opening the end of the tube and streaming out the air in the reverse direction for 10 minutes, we always obtained about 2-3 mg./hr. of water. Strictly speaking we should apply these values to the analysis as corrections of the blank experiments, and so we have adopted this way of correction throughout this paper and obtained satisfactory results.

When the Ni-catalyst was reduced completely, the blank water value would be 0.6~1.7 mg./hr. and in these cases the first run used to give somewhat low results as clearly shown in Table 3. This means that the over-dried catalyst surface retained very tenaciously some water produced during the analysis and therefore, did not recover the original surface conditions within the limited experimental period. Thus we should make three successive runs of which the first might be looked upon as preliminary and the last as the check.

(3) In this hydrogenation analysis the sample should be very slowly vaporized or cracked so as not to cause a rapid decomposition of the sample, accordingly not to raise too high the partial pressure of carbon monoxide or carbon dioxide; otherwise the reduction equilibrium of reaction (1) or (2) becomes unfavourable for the complete reduction of carbon oxides and would give the analyses low results. From these standpoints we should make the preliminary run and should find the suitable heating rate for unknown sample to be analysed. These points will be discussed in details in the next paper.

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Studies on the Derivatives of Biphenylene Oxide. V. Bromo-derivatives of Biphenylene Oxide.

By Seishi YAMASHIRO.

(Received November 24, 1940.)

Among the bromo-derivatives of biphenylene oxide, although all isomers of the monobromo-compounds and three dibromo-compounds (2,3-,⁽¹⁾ 2,6-⁽²⁾ and 3,6⁽³⁾-dibromobiphenylene oxides) are already prepared by many investigators, yet nothing has been reported to this day about the tri- and tetra-bromo compounds.

(1) K. Tatematsu and B. Kubota, this Bulletin, **9** (1934), 456.

(2) H. McCombie, W. G. Macmillan and H. A. Scarborough, *J. Chem. Soc.*, **1913**, 536.

(3) O. Hoffmeister, *Ann.*, **159** (1871), 215; H. McCombie, W. G. Macmillan and H. A. Scarborough, *J. Chem. Soc.*, **1913**, 536; N. M. Cullinane, H. G. Davey and H. J. H. Padfield, *J. Chem. Soc.*, **1934**, 719; H. Gilman, H. B. Willis and J. Swislowsky, *J. Am. Chem. Soc.*, **61** (1939), 1372.

The present author obtained recently one tribromo- and two tetrabromo-biphenylene oxides, by isolating them from the bromination products of 3,6-dibromobiphenylene oxide. He inferred, from his experiment on the nitration of 3,6-dinitrobiphenylene oxide, that each of these newly obtained compounds might be respectively 2,3,6-tri- and 1,3,6,7- and 2,3,6,7-tetra-bromo compounds (I, II and III), because in that experiment 3,6-dinitrobiphenylene oxide gave mainly the 2,3,6-trinitro-compound (together with the 1,3,6-trinitro-compound by the bye) which converted into 1,3,6,7- and 2,3,6,7-tetranitrobiphenylene oxides. In order to confirm this inference, the bromination of biphenylene oxide and its bromo derivatives was again examined systematically, and in that experiment a new dibromobiphenylene oxide was also obtained. Its result may be described here in order.

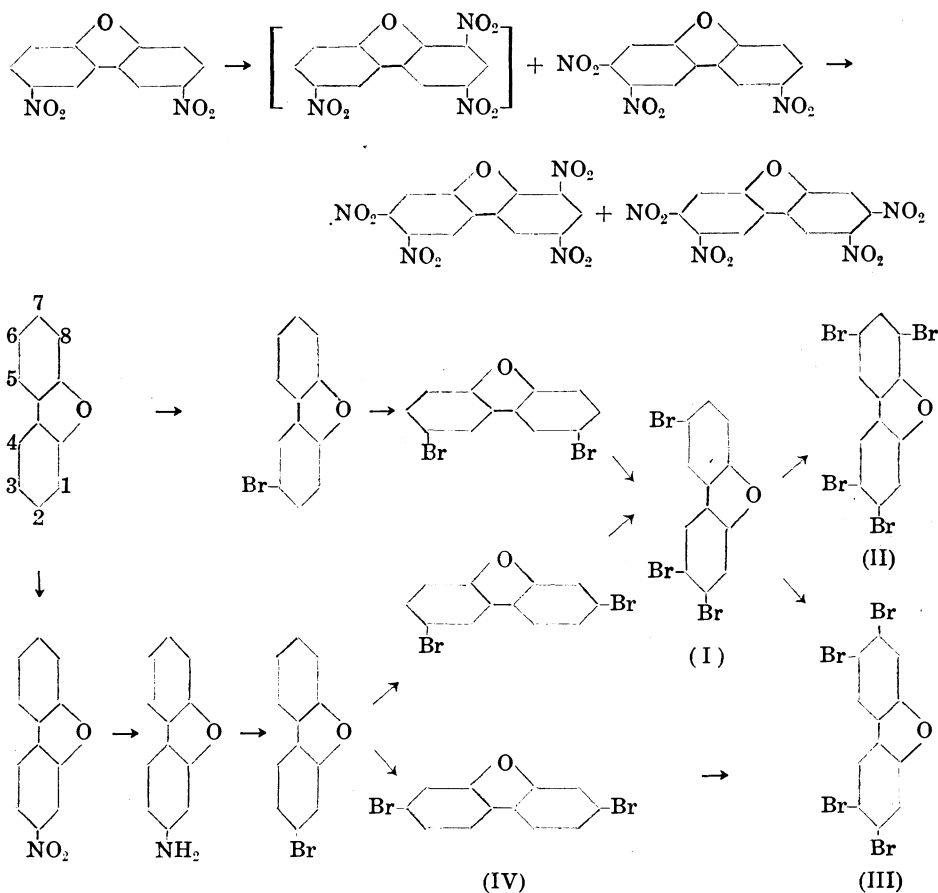
First, biphenylene oxide and 2-bromobiphenylene oxide were brominated and it was found that the former substance gives mainly the 3-bromo- and 3,6-dibromo-derivatives; none of the 2-bromo- and 2,6-dibromo derivatives being obtained so much as can be isolated from the reaction mixture, while the latter, mainly 2,6-dibromobiphenylene oxide and, along with it, a new dibromobiphenylene oxide melting at 199–200° (corr.). Now, in general, negative atoms or negative groups replace the hydrogen atoms of biphenylene oxide more freely at the positions 3(6) and 2(7) than at 1(8) and 4(5), and in the case of bromination, especially, the substitution takes place most freely at the position 3(6), as is shown by the above-mentioned experimental results. The tendency of the substitution of hydrogen atoms of biphenylene oxide by bromine, therefore, can be represented in the order of positions 3(6) > 2(7) > 1(8), 4(5)– and probably 1(8) > 4(5)–, and, as a consequence, the by-product obtained from 2-bromobiphenylene oxide should be 2,7-dibromobiphenylene oxide.

Next, 3,6-dibromobiphenylene oxide was brominated and a tribromo- and a tetrabromo-compounds were obtained this time. This tribromo-compound, which melts at 202–203° (corr.), is proved to be 2,3,6-tribromobiphenylene oxide, because it is identical with the corresponding compound which was obtained from 2,6-dibromobiphenylene oxide. The last compound gave on bromination two tetrabromo compounds besides the 2,3,6-tribromo-compound. The tetrabromo compounds isolated in these experiments are identical with the corresponding compounds which can be obtained from 2,3,6-tribromobiphenylene oxide.

When 2,3,6-tribromobiphenylene oxide was brominated, it converted into two tetrabromo-compounds, one of which, melting at 306–307° (corr.), is the main product, while the other melting at 248–249° (corr.), a by-product. Judging from this experimental result and the above-mentioned tendency of the substitution by bromine, it is rather reasonable to conclude that the higher melting one is 2,3,6,7-tetrabromobiphenylene oxide, and the lower, 1,3,6,7-tetrabromobiphenylene oxide. Further support for this conclusion can be found in the result of bromination of the 2,7-dibromo-compound mentioned above, because this compound converts into a tetrabromo-compound which is identical with the higher melting tetrabromobiphenylene oxide.

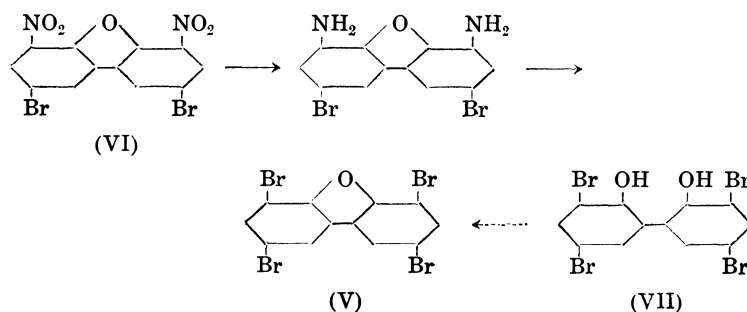
In summary, the processes of the reactions, which were utilized to

establish the constitutions of the new bromo derivatives of biphenylene oxide, therefore, may be represented by the following schemes:

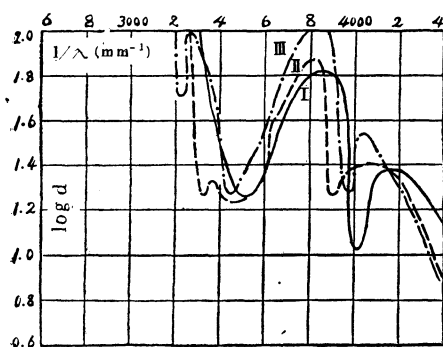


For the purpose of comparing with one another the possible isomers of the tetrabromobiphenylene oxides which would be found in the bromination products of 3,6-dibromobiphenylene oxide, 1,3,6,8-tetrabromobiphenylene oxide (V) was prepared from 3,6-dibromo-1,8-dinitrobiphenylene oxide (VI) which will be described in Part VII. The process of the reactions in that case is represented by the real-lined arrows in the scheme shown below. It was tried in vain, however, to prepare the same tetrabromo compound from 3,3',5,5'-tetrabromo-2,2'-dihydroxydiphenyl (VII) by heating it in a sealed tube, for 5 hours at about 195–200°, in the presence of hydrobromic acid and a small quantity of red phosphorus, or by melting its acetyl derivative in mixing with dry carbonate of sodium or of barium.

The physical properties and the absorption curves of biphenylene oxide and its bromo-derivatives were compared as in Table 1 and Figs. 1–4, which will be utilized for the benefit of isolation and identification of these compounds.

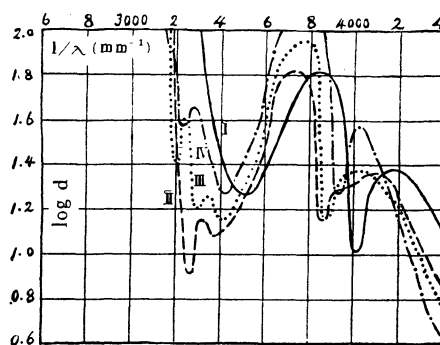


Comparison of the absorption curves of biphenylene oxide and its bromo derivatives.



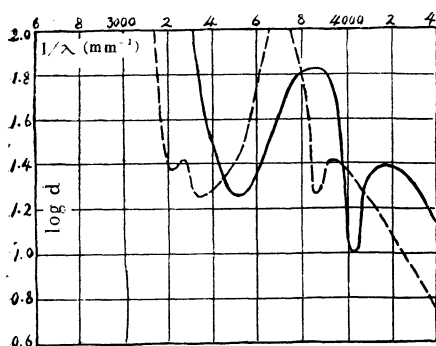
I (—) Biphenylene oxide.
 II (---) 2-Bromobiphenylene oxide.
 III (-.-) 3-Bromobiphenylene oxide.

Fig. 1. Monobromobiphenylene oxides,
 M/10000 alcoholic solutions.



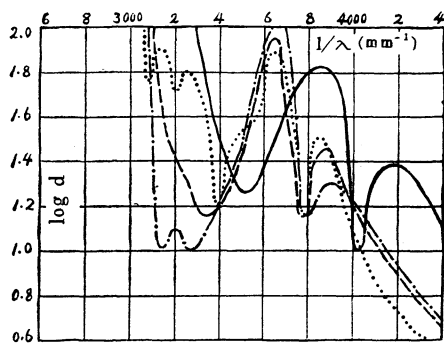
I (—) Biphenylene oxide.
 II (---) 2,7-Dibromobiphenylene oxide.
 III (....) 2,6-Dibromobiphenylene oxide.
 IV (-.-) 3,6-Dibromobiphenylene oxide.

Fig. 2. Dibromobiphenylene oxides,
 M/10000 alcoholic solutions.



I (—) Biphenylene oxide.
 II (---) 2,3,6-Tribromobiphenylene oxide.

Fig. 3. Tribromobiphenylene oxide,
 M/10000 alcoholic solution.



I (—) Biphenylene oxide.
 II (---) 1,3,6,7-Tetrabromobiphenylene oxide.
 III (....) 1,3,6,8-Tetrabromo- " " "
 IV (-.-) 2,3,6,7-Tetrabromo- " " "

Fig. 4. Tetrabromobiphenylene oxides,
 M/10000 alcoholic solutions.

Table 1. Comparison of the physical properties of biphenylene oxide and its bromo derivatives.

Compound	M.p. (corr.)	Crystalline form (crystallizing solvent)	Solubility (e : easily soluble, e-m : less easily soluble, m : moderately soluble, d-m : less difficultly soluble, d : difficultly soluble ; e > e-m > m > d-m > d.)										
			Ligroin	Ether	Carbon tetra- chloride	Chloro- form	Benzene	Ethyl acetate	Methanol	Ethanol	Acetone	Acetic acid	Toluene
Biphenylene oxide	86-87°	Colorless thin blades (ethanol)	e	e	e	e	e	e	e	e	e	e	e
2-Bromo- biphenylene oxide	121-122°	Colorless hexagonal plates (ethanol)	e	e	e	e	e	e	m	m	e	e	e
3-Bromo- biphenylene oxide	109-110°	Colorless thin blades (ethanol)	m	e	e	e	e	e	m	m	e	e	e
2,6-Dibromo- biphenylene oxide	178-179°	Colorless needles (acetone)	d	e-m	e	e	e	e	d	d	e-m	m	e
2,7-Dibromo- biphenylene oxide	199-200°	Colorless needles (acetone)	d	e-m	e	e	e	e	d	d	e-m	m	e
3,6-Dibromo- biphenylene oxide	199-200°	Colorless rectangular plates (acetic acid)	d	m	e	e	e-m	e	d	d	e	m	e-m
2,3,6-Tribromo- biphenylene oxide	202-203°	Colorless needles (acetone)	d	d	m	m	e-m	m	d	d	d-m	d	e-m
1,3,6,8-Tetrabromo- biphenylene oxide	237-238°	Pale yellow small needles (carbon tetrachloride)	d	d	e-m	e-m	e-m	e-m	d	d	d-m	d-m	e-m
1,3,6,7-Tetrabromo- biphenylene oxide	248-249°	Colorless needles (toluene)	d	d	m	m	m	d-m	d	d	d-m	d-m	m
2,3,6,7-Tetrabromo- biphenylene oxide	306-307°	Colorless large needles (toluene)	d	d	d	d	d-m	d	d	d	d	d	m

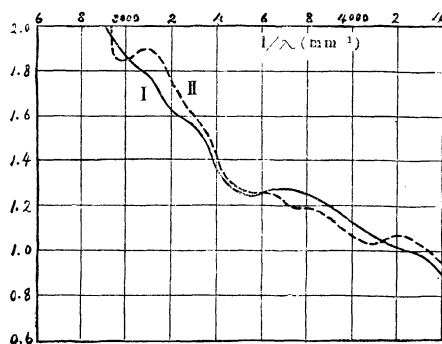
From the comparison of these absorption curves in Figs. 1-4, it may be found that the introduction of bromine into biphenylene oxide shifts always bathochromically the absorption bands of the parent compound, and in many cases gives rise to some new characteristic absorption bands. With regard to the strength of absorption, however, the effect exerted by bromine depends on the position of bromine introduced and the order of the absorption bands of biphenylene oxide.

The introduction of a bromine atom into the position 2 of biphenylene oxide (Fig. 1, Curve II) exerts an effect somewhat hyperchromically on the first less refrangible band of the parent compound, but hypochromically on the second more refrangible one, and moreover gives rise to a small characteristic band at $1/\lambda$ (mm^{-1}) 4330, whereas the introduction of a bromine atom into the position 3 (Fig. 1, Curve III) exerts no effect upon the strength of absorption in the first band of the parent compound, but it shows a hypochromic effect on the second one and moreover gives rise to a selective absorption band at 3220.

Among the absorption spectra of the dibromobiphenylene oxides compared in Fig. 2, those of 2,7- and 3,6-dibromobiphenylene oxides (Curves II and IV) have each three bands which are similar to a series of bands of 2- and 3-bromobiphenylene oxides respectively except for the strength of absorption, this being increased—especially so in the case of the 2,7-dibromo-compound—owing to the symmetrical constitutions of these two dibromo compounds; on the contrary, that of the unsymmetrical 2,6-dibromobiphenylene oxide (Curve III) has four bands, of which the bands located at $1/\lambda$ 4420 and 4890 correspond to the two characteristic bands of biphenylene oxide, and those at 3220 and 3300 are the characteristic bands of the bromine atoms introduced. These latter two bands are to be attributed to the presence of bromine at the positions 6 and 2 respectively. Therefore, so far as it goes at least, the additivity of the characteristic absorption bands may be detected in this case.

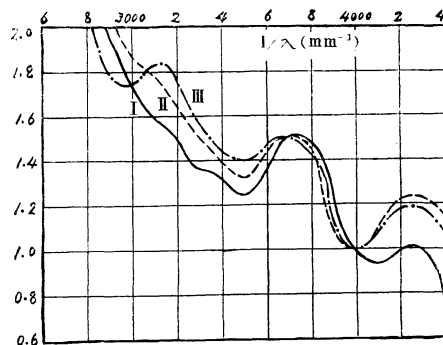
As will be seen from the curves in Figs. 3 and 4, however, the characteristic bands of the bromine atoms in a polybromobiphenylene oxide are not always developed separately, but rather partly or perfectly overlap one another in many cases, the curve of the polybromo-compound being often simpler than those of the lower bromo-compounds. In the 2,3,6-tribromo- and 2,3,6,7-tetrabromo-compounds (Fig. 3, Curve II and Fig. 4, Curve II), for example, though the characteristic band of the bromine atom at the position 2 or 7 can be found, the same at 3 and 6 can not be perceived in their curves, and in the 1,3,6,7-tetrabromo-compound (Fig. 4, Curve III) even none of them comes out in its curve. 1,3,6,8-Tetrabromobiphenylene oxide, however, gives a special curve (Fig. 4, Curve IV), and it possesses two characteristic bands at $1/\lambda$ 3100 and 3220 besides those at 3400 and 3780 which characterize the parent compound. As the band at 3220 of the former two corresponds to the characteristic band of the bromine atom at the position 3 or 6, the band at 3100 must be attributed to the same atom at 1 or 8.

A support for this view may be found in the comparisons between the absorption spectra of 1,3,6-trinitro- and 8-bromo-1,3,6-trinitro-biphenylene oxides (Fig. 5, Curves I and II) on the one hand and also among those of 1,6-dinitro-, 3-bromo-1,6-dinitro- and 3,8-dibromo-1,6-dinitro-bipheny-



I 1,3,6-Trinitro-biphenylene oxide.
II 8-Bromo-1,3,6-trinitro- „ „ .

Fig. 5. M/10000 alcoholic solutions.



I 1,6-Dinitro-biphenylene oxide.
II 3-Bromo-1,6-dinitro- „ „ .
III 3,8-Dibromo-1,6-dinitro- „ „ .

Fig. 6. M/10000 alcoholic solutions.

lene oxides (Fig. 6, Curves I, II, and III) on the other hand, because the compounds alone that have bromine at the position 8 give a distinct selective absorption band respectively in the neighbourhood of $1/\lambda$ 3000.

Experimental.

(1) *1,3,6- and 2,3,6-Trinitrobiphenylene oxides from 3,6-Dinitrobiphenylene oxide.* 3,6-Dinitrobiphenylene oxide (5.16 g.) was dissolved in fuming nitric acid (d 1.52; 20 c.c.) at room temperature and after being kept for 10 minutes at this temperature the reaction mixture was poured into water, when the reaction product separated as yellow precipitates. The trinitrobiphenylene oxides thus obtained (Yield almost theoretical) were extracted with a mixture of acetone and alcohol, and the residue was recrystallized from a small quantity of acetone, colourless rectangular plates melting at 311–312° (corr.) (Yield 0.28 g., 4.6% of the theoretical. Found: N, 13.92. Calc. for $C_{12}H_5O(NO_2)_3$: N, 13.87%). The acetone-alcoholic extract was evaporated and the crystals separated on cooling were recrystallized from acetic acid, colourless needles melting at 236–237° (corr.) (Yield 3.61 g., 60% of the theoretical. Found: N, 12.82. Calc. for $C_{12}H_5O(NO_2)_3$: N, 13.87%). No depression of the melting point was observed each time when the former trinitro-compound was mixed with 1,3,6-trinitrobiphenylene oxide⁽⁴⁾ obtained from 1,6-dinitrobiphenylene oxide, and the latter one, with 2,3,6-trinitrobiphenylene oxide⁽⁵⁾ obtained from 2,6-dinitrobiphenylene oxide.

(2) *1,3,6,7- and 2,3,6,7-Tetranitrobiphenylene oxides from 2,3,6-trinitrobiphenylene oxide.* 2,3,6-Trinitrobiphenylene oxide (3.01 g.) was heated for one hour with fuming nitric acid (d 1.52; 15 c.c.) on the water bath and the reaction mixture was poured into water, giving pale yellow precipitates. The reaction product was recrystallized from acetic acid, colourless rectangular plates melting at 285–286° (corr.) (Yield 1.83 g., 53% of the theoretical. Found: N, 16.23. Calc. for $C_{12}H_4O(NO_2)_4$: N, 16.10%). The mother-liquor was concentrated and then diluted with water precipitating the other component of the nitration product. The precipitates were extracted with much alcohol to remove the contaminated sparingly soluble component and the extract was evaporated to dryness and then recrystallized repeatedly from benzene, colourless needles melting at 249–250° (corr.) (Yield 0.35 g., 10% of the theoretical. Found: N, 15.98. Calc. for $C_{12}H_4O(NO_2)_4$: N, 16.10%). No depression was observed

(4) S. Yamashiro, *J. Chem. Soc. Japan*, **59** (1938), 449.

(5) S. Yamashiro, *ibid.*, **59** (1938), 450.

in the mixed melting points of these nitration products when the higher melting one was mixed with 2,3,6,7-tetranitrobiphenylene oxide obtained from 2,3,7-trinitrobiphenylene oxide, and the lower melting one, with 1,3,6,7-tetranitrobiphenylene oxide obtained from 1,3,6-trinitrobiphenylene oxide.

(3) *3-Bromo- and 3,6-dibromobiphenylene oxides from biphenylene oxide.* In the hope of obtaining the theoretical quantity of dibromobiphenylene oxides, biphenylene oxide (84 g.) was heated for 60 hours with bromine (160 g.) in boiling carbon tetrachloride (500 c.c.), but the bromination was incomplete. After the remaining bromine and the solvent had been distilled off, the reaction product (144.6 g.) was washed with hot water and recrystallized from acetic acid, colourless rectangular plates, m.p. 199–200° (corr.) (Yield 41 g. Found: Br, 49.12. Calc. for $C_{12}H_6OBr_2$: Br, 49.03%). The more soluble part was recovered from the mother-liquor and extracted with much hot alcohol to remove the sparingly soluble (in alcohol) dibromo-compound. The monobromo-compound was obtained on concentrating the alcoholic extract and recrystallized from the same solvent, colourless plates, m.p. 109–110° (corr.) (Yield 15 g. Found: Br, 32.31. Calc. for $C_{12}H_7OBr$: Br, 32.36%). Judging from the literature on the bromo derivatives of biphenylene oxide, this monobromo-compound must be 3-bromobiphenylene oxide and the dibromo-compound obtained above, 3,6-dibromobiphenylene oxide. The alcoholic mother-liquor was evaporated to dryness and the residue was extracted with cold ligroin, 3-bromobiphenylene oxide being almost removed. The ligroin extract was again evaporated to dryness and the residue was recrystallized from alcohol in the hope of isolating 2-bromobiphenylene oxide, but in vain.

(4) *2,6- and 2,7-Dibromobiphenylene oxides from 2-bromobiphenylene oxide.* 2-Bromobiphenylene oxide was prepared from 2-aminobiphenylene oxide by means of the Sandmeyer's diazo-reaction described by E. Noelting and his co-workers⁽⁶⁾ and purified by sublimation and recrystallization from alcohol, colourless hexagonal plates, m.p. 121–122° (corr.) (Yield 56%). 2-Hydroxybiphenylene oxide described by K. Tatematsu and B. Kubota⁽⁷⁾, m.p. 139–139.5° (corr.), was also obtained as a by-product, yield 5%.

2-Bromobiphenylene oxide (15 g.) was heated for 48 hours with bromine (10 g.) in boiling carbon tetrachloride (50 c.c.) and after addition of acetic acid (50 c.c.), heating was continued until the colour of bromine disappeared. When the solvents were almost recovered by distillation from the reaction mixture, the residue was diluted with water. The reaction product thus separated (Yield 21.5 g.) was repeatedly extracted with hot alcohol and the residue was recrystallized from a small quantity of acetone, colourless needles, m.p. 178–179° (corr.) (Yield 9.2 g., 46.5%. Found: Br, 49.20. Calc. for $C_{12}H_6OBr_2$: Br, 49.03%). The crystals separated on cooling from the alcoholic extracts were repeatedly recrystallized from a mixture of acetone and alcohol, colourless needles, m.p. 199–200° (corr.) (Yield 0.4 g., 2.2%. Found: Br, 49.15. Calc. for $C_{12}H_6OBr_2$: Br, 49.03%). It was found very difficult to gather more crop of the last crystals, owing to the resemblance between the solubilities of those isomers. Judging from the literature on the dibromobiphenylene oxides (2,3-dibromo compound, m.p. 150–150.5°⁽¹⁾ and 2,6-dibromo compound, m.p. 176°⁽²⁾) and also from the orientation of bromine which has been mentioned in the introductory part of this paper, the lower melting isomer of those reaction products must be 2,6-dibromobiphenylene oxide, and the higher melting one, 2,7-dibromobiphenylene oxide.

(5) *2,3,6-Tribromo- and 2,3,6,7-tetrabromo-biphenylene oxides from 3,6-dibromobiphenylene oxide.* 3,6-Dibromobiphenylene oxide (16.3 g.) was heated for 12 hours with a large excess of bromine (30 g.) in boiling acetic acid (500 c.c.), when the colour of bromine disappeared. The reaction mixture was concentrated, diluted with water, and the reaction product thus separated was filtered and dried (Yield 22 g.). After extraction with carbon tetrachloride, the sparingly soluble part of the reaction product was recrystallized from toluene, large colourless needles, m.p. 306–307° (corr.) (Yield 4 g. Found: Br, 66.15. Calc. for $C_{12}H_4OBr_4$: Br, 66.05%). The carbon tetrachloride extract was evaporated to dryness, the residue was fractionally extracted

(6) E. Noelting, A. Braun and G. Thesmar, *Ber.* **34** (1901), 2253.

(7) K. Tatematsu and B. Kubota, this Bulletin, **9** (1934), 452.

with acetone, and the fraction melting at 193–198° (uncorr.) was recrystallized from acetone, colourless needles, m.p. 202–203° (corr.) (Yield 8.6 g. Found: Br, 59.34. Calc. for $C_{12}H_5OBr_3$: Br, 59.20%). Both of those bromination products gave no depression of their melting points when the tribromo compound was mixed with the corresponding compound obtained from 2,6-dibromobiphenylene oxide, and the tetrabromo-compound, with the corresponding compound obtained from 2,7-dibromobiphenylene oxide. Those products, therefore, were evidently identified respectively as 2,3,6-tribromobiphenylene oxide and 2,3,6,7-tetrabromobiphenylene oxide.

(6) *2,3,6,7-Tetrabromobiphenylene oxide from 2,7-dibromobiphenylene oxide.* 2,7-Dibromobiphenylene oxide (0.2 g.) was heated for 4 hours with a large excess of bromine (2 g.) in boiling glacial acetic acid (40 c.c.), when the colour of bromine disappeared. The crystals separated on cooling from the reaction mixture were recrystallized from toluene, colourless needles, m.p. 306–307° (corr.) (Yield 0.21 g., 71%). The good yield of this 2,3,6,7-tetrabromo-compound from 2,7-dibromobiphenylene oxide owes to the fact that the most favourable positions 3 and 6 for the introduction of bromine remains free in the last compound.

(7) *2,3,6-Tribromo- and 1,3,6,7- and 2,3,6,7-tetrabromo-biphenylene oxides from 2,6-dibromobiphenylene oxide.* 2,6-Dibromobiphenylene oxide (3.26 g.) was heated for 12 hours with bromine (6 g.) in boiling glacial acetic acid (100 c.c.), when the colour of bromine disappeared. After distillation of the solvent, the reaction mixture was diluted with water to the precipitation of a white crystalline mass, which was filtered, dried (Yield 4.4 g.) and then extracted with hot benzene. From the sparingly soluble residue, 2,3,6,7-tetrabromobiphenylene oxide was isolated by recrystallization from toluene in large colourless needles, m.p. 306–307° (corr.) (Yield 1.6 g.). The benzene extract was evaporated to dryness and fractionated into 10 parts by means of the fractional extraction of the residue with acetone. Of these fractions the part melting at 238–240° (uncorr.) was recrystallized from toluene, colourless needles, m.p. 248–249° (corr.) (Yield 0.3 g. Found: Br, 66.08. Calc. for $C_{12}H_4OBr_4$: Br, 66.05%) and the part melting at 196–198° (uncorr.) was recrystallized from acetone to the isolation of 2,3,6-tribromobiphenylene oxide, colourless needles, m.p. 202–203° (corr.) (Yield 0.8 g.). The lower melting tetrabromo-compound obtained here was identical with the corresponding compound which was obtained as a by-product from 2,3,6-tribromobiphenylene oxide and consequently concluded to be 1,3,6,7-tetrabromobiphenylene oxide.

(8) *1,3,6,7- and 2,3,6,7-Tetrabromobiphenylene oxides from 2,3,6-tribromobiphenylene oxide.* 2,3,6-Tribromobiphenylene oxide (1 g.) was heated for 12 hours with a large excess of bromine in boiling acetic acid (200 c.c.), the solvent was distilled off and the residue was then diluted with water. The reaction product thus separated was filtered, dried, and after extraction with benzene, recrystallized from toluene, colourless needles of 2,3,6,7-tetrabromobiphenylene oxide, m.p. 306–307° (corr.) (Yield 0.6 g.). The benzene extract was evaporated to dryness, the residue was repeatedly extracted with ligroin, and the sparingly soluble part was recrystallized from toluene, colourless needles of 1,3,6,7-tetrabromobiphenylene oxide, m.p. 248–249° (corr.) (Yield 0.06 g.). 2,3,6-Tribromobiphenylene oxide was recovered from the ligroin extract.

(9) *1,3,6,8-Tetrabromobiphenylene oxide from 3,6-dibromo-1,8-dinitrobiphenylene oxide.* (i) 1,8-Diamino-3,6-dibromobiphenylene oxide. 3,6-Dibromo-1,8-dinitrobiphenylene oxide (2.08 g.) was heated with stannous chloride (10 g.) and concentrated hydrochloric acid (10 c.c.) in boiling acetone (300 c.c.), when the colourless needle crystals of 1,8-diamino-3,6-dibromobiphenylene oxide dihydrochloride separated; which were filtered on cooling and washed successively with hydrochloric acid, water and then with acetone. The filtrate was distilled to the recovery of acetone, dilute hydrochloric acid was added and the second crop of the dihydrochloride thus separated was treated as before (Yield 2.07 g., 97%). The dihydrochloride was converted into the free base by treating it with an excess of sodium acetate solution, and was recrystallized from chloroform, small colourless needles which take blue colour on standing in the wet air, m.p. 276.5–277.5° (corr.) (Found: N, 7.94. Calc. for $C_{12}H_4OBr_2(NH_2)_2$: N, 7.87%). 1,8-Diamino-3,6-dibromobiphenylene oxide is soluble easily in acetone and ethyl acetate, moderately in benzene and chloroform, but difficultly in alcohol, ether, ligroin, and carbon tetrachloride. The dihydrobromide of this base was obtained by

treating the base with hydrobromic acid in acetone solution, colourless needles (Found: Br, 61.58. Calc. for $C_{12}H_4OBr_2(NH_2)_2 \cdot 2HBr$: Br, 61.77%).

(ii) 1,8-Biacetamino-3,6-dibromobiphenylene oxide, 1,8-Diamino-3,6-dibromobiphenylene oxide (0.178 g.) was heated with a mixture of glacial acetic acid (2 g.) and acetic anhydride (0.1 g.), and diluted with water, when a white crystalline mass separated. The reaction product (Yield 0.222 g.) was recrystallized from alcohol, small colourless needles, m.p. 358–360° (corr.) (Found: N, 6.42. Calc. for $C_{12}H_4OBr_2(NHCOCH_3)_2$: N, 6.36%). It is soluble fairly in acetone, alcohol, and acetic acid, but sparingly in the other ordinary organic solvents.

(iii) 1,3,6,8-Tetrabromobiphenylene oxide. Finely powdered 1,8-diamino-3,6-dibromobiphenylene oxide (1.39 g.) was suspended in 10% hydrobromic acid, and was diazotized with sodium nitrite (0.46 g.) under ice cooling, when the base changed slowly into the yellow diazo-compound. Cuprous bromide, on the other hand, was prepared by heating a mixture of crystalline copper sulphate (1.8 g.), copper bronze (0.7 g.), potassium bromide (3 g.), concentrated sulphuric acid (0.8 g.) and water (12 c.c.) until the blue colour of the cupric salt disappeared. After being washed with cold air-free water, cuprous bromide was added to the above-mentioned ice-cold suspension of the diazo-compound. This mixture was allowed to stand overnight under cooling and then gradually heated on the water bath to complete the decomposition of the diazo-compound, when the brown solid separated out. The reaction product was filtered, washed well with hot water, dried and extracted with benzene. The extracted was evaporated to dryness and, after being extracted again with acetone to the removal of the easily soluble impurity, the residue was recrystallized from carbon tetrachloride, pale yellow small needles, m.p. 237–238° (corr.) (Yield 0.51 g. Found: Br, 65.01. Calc. for $C_{12}H_4OBr_4$: Br, 65.05%).

Summary.

For the purpose of confirming the constitution of the polybromo-compounds obtained directly from biphenylene oxide by bromination, the following experiments were performed by the present author:

(1) Verification of the formation of 2,3,6-trinitro- and 1,3,6,7- and 2,3,6,7-tetranitro-biphenylene oxides from 3,6-dinitrobiphenylene oxide and of the formation of 2,3,6-tribromo- and 1,3,6,7- and 2,3,6,7-tetrabromo-biphenylene oxides from 3,6-dibromobiphenylene oxide.

(2) Isolation of 2,7-dibromobiphenylene oxide from the bromination products of 2-bromobiphenylene oxide, and preparation of 1,3,6,8-tetrabromobiphenylene oxide from 3,6-dibromo-1,8-dinitrobiphenylene oxide.

(3) Comparative studies on the characteristics and the absorption spectra of biphenylene oxide and its bromoderivatives.

In conclusion, the author wishes to express his hearty thanks to Prof. R. Majima of the Osaka Imperial University and Shigemi Ôba, the principal of the Yonezawa Higher Technical School, for their kind advices and encouragements. A part of the expense of this investigation has been defrayed from the grant of the Nippon Gakuzyutu Sinko-kwai (the Japan Society for the Promotion of Scientific Research) for which also the author wishes to record his thanks.

Yonezawa Higher Technical School.

Polymerisation of Tung Oil, IV. Effects of Various Natural Fatty Oils upon the Gelation of Tung Oil.

By Monzi TATIMORI.

(Received November 28, 1940.)

It is well known that the gelation of tung oil on heating may be delayed or prevented by the addition of certain substances. Considerable amount of works have been done along this line,⁽¹⁾ but as to the quantitative relation between gelation time and the amount of substances added to tung oil, only a few informations have been published.

There are known various types for curves of the gelation time and the amount of added substances, but as for the nature of the curve nothing is said. The work described in this article was undertaken for the purpose of determining the comparative effects of various fatty oils in preventing the gelation of tung oil on heating, with a hope to throw light on the explanation of gelation phenomenon of tung oil.

Experimentals. The apparatus consists of an oil bath (the diameter being 20 cm., height 17 cm.) which was maintained at a required constant temperature. The cover of the bath is provided with four openings through which the ordinary test tube, whose size was predetermined by measuring the height of 5 c.c. of alcohol taken in it (expressed in cm. unit), was dipped in bath so that the lower 9 cm. of the test tube was immersed in the oil. Five c.c. of a mixture, containing known proportion of tung oil and added substances, was put in a test tube, a glass rod (its diameter being 3 mm., length 16 cm.) was inserted in, and the test tube was put into the oil bath. The time required for the oil to gelatinize was then measured and noted. The determination was repeated for the same mixture a few times and the mean value was calculated.

The samples used have the following constants (Table 1).

Table 1.

Kind of oils	d_{15}^{15}	n_D^{20}	Iodine value	Acid value
Tung oil (A)	0.942	1.518	164.5	3.17
Tung oil (C)	0.941	1.517	166.8	4.64
Japanese wood oil	0.935	1.501	168.2	1.44
Perilla oil	0.935	1.483	199.3	5.71

(1) R. Birstinbinder, *Farben Ztg.*, **23** (1917), 243; *Chem. Umschau Fette, Oele Wachse*, **36** (1929), 36; Krumbhaar, *Chem. Abstrs.*, **9** (1915), 2155; J. Marcusson, *Zt. deut. Oele Fette Ind.*, **43** (1923), 162; H. Hardert, *Farbe und Lack*, 1928, 558; H. Brendel, *ibid.*, 1932, 145; L. A. Jordan, *J. Oil Colour Chem. Assoc.*, **17** (1934), 47.

Table 1.—(Concluded)

Kind of oils	d_{15}^{15}	n_D^{20}	Iodine value	Acid value
Linseed oil	0.934	1.480	171.1	4.31
Hemp seed oil	0.927	1.479	162.7	2.08
Soya bean oil	0.922	1.475	131.4	1.12
Maize oil	0.923	1.475	122.1	0.94
Sesame oil	0.923	1.474	115.2	1.19
Rape oil	0.917	1.473	99.4	1.90
Olive oil	0.918	1.470	83.0	4.37
Camellia oil	0.917	1.469	80.9	3.43
Castor oil	0.975	1.479	84.8	1.79
Sardine oil	0.934	1.483	194.4	4.66
Hardened fish oil	—	—	17.1	2.24
Liquid paraffin	0.882	1.479	—	—

From the preliminary experiments it was found that the gelation time is affected by the heating temperature, by the size of the test tube as well as by the kind of tung oils.

One of the examples is shown in Table 2, in which the gelation time of tung oil (A) were measured at 290°C. in three kinds of test tubes, widely different in size.

Table 2.

% of linseed oil added to tung oil	Gelation time in sec. Size of test tube (height of 5 c.c. in cm.)		
	3.1 cm.	3.5 cm.	4.5 cm.
0	485	478	465
10.00	565	559	549
15.01	633	623	620
20.04	701	699	685

The absolute value of the gelation time is affected remarkably by the size of test tube. The relation between the reciprocals of the gelation time (t) and percentage of linseed oil (x) are shown in Fig. 1.

It is a very important new fact that in all cases $1/t$ and x are in linear relations and the limiting value of x at $t = \infty$ (hereafter denoted as x_∞) converge on one point, in spite of wide differences in dimension of test tubes.

(1) Gelation time for the system of Japanese wood oil and tung oil (A).

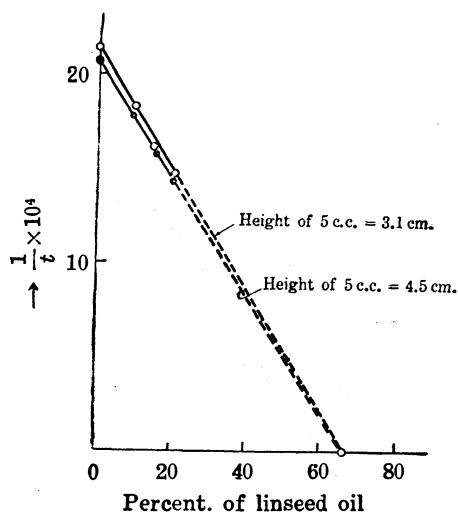


Fig. 1.

Results at 290°C. in test tubes of 3.7 cm. are given in Table 3.

Table 3.

Percent. of Japanese wood oil added to tung oil.	Gelation time (sec.)
0	467
10	513
20	555
30	640
40	730
50	862
60	1033
70	1237
100	3848

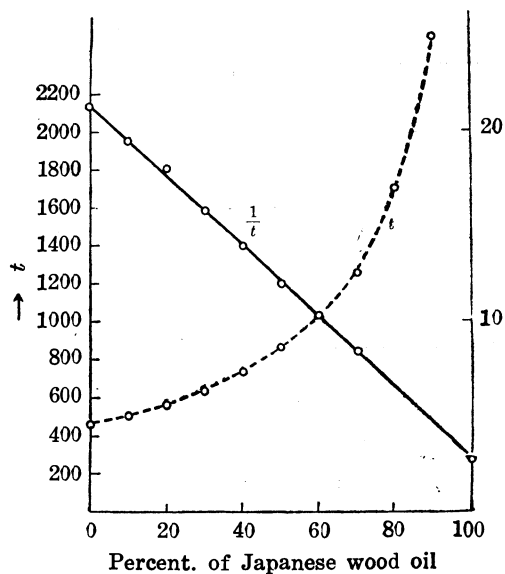


Fig. 2.

The relations of $t-x$ and $1/t-x$ are shown in Fig. 2. x and $1/t$ form a straight line in the whole range of Japanese wood oil.

(2) *The gelation time of the system of tung oil and linseed oil.* From the preliminary experiments it was noticed that the amount of

added substance necessary to make the gelation time of tung oil be infinitely long, increases a little, when the heating temperature falls from 290 to 280°C., so the gelation time of the system of tung oil and linseed oil was measured in wide temperature range. It was found that the temperature of 270°C. is most suitable to determine the relation between $1/t$ and x .

The results are shown graphically in Fig. 3.

From Fig. 3 it was found that below 280°C. lines of $1/t-x$ converge

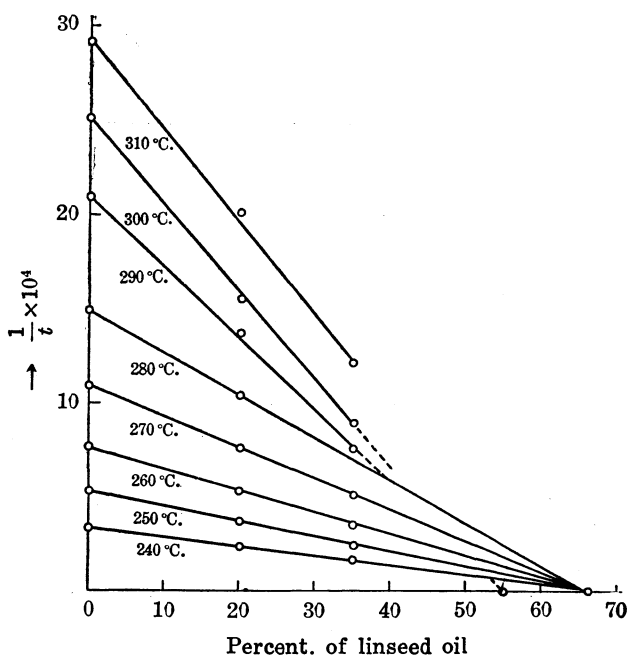


Fig. 3.

on one point of 67% and above 290°C. they shift gradually to the origin according as temperature increases: above 310°C. the rectilinear relationship is no more formed. The temperature of 270°C. is the most suitable for measuring the time of gelation by reason that above this temperature relation of $1/t-x$ is unstable and below this temperature the gelation time becomes too great.

The values of x at $\frac{1}{t}=0$ (x_{∞}) obtained from graphs are shown in Table 4.

Table 4.

Temperature (°C.)	x_{∞} (%)
305	52.0
300	54.0
295	56.5
290	61.5
280	67.0
270	67.0
260	67.0
250	66.5
240	67.5

(3) *Effects of temperature upon the gelation time.* The gelation time of tung oil is prolonged by lowering the heating temperature. L. A. Jordan and W. E. Wornum⁽²⁾ measured the gelation time of many kinds of tung oils. F. T. Walker⁽³⁾ treated their results and stated that the relation of the gelation time and temperature can be expressed by a hyperbola, whose equation is $(T-m) \times t = k$, where m and k denote constants, T the temperature, t the gelation time.

If the above be true, $1/t$ and T should be in linear relation.

From Fig. 4. neither from the case of tung oil only, nor from that added by 20% linseed oil straight lines can be obtained.

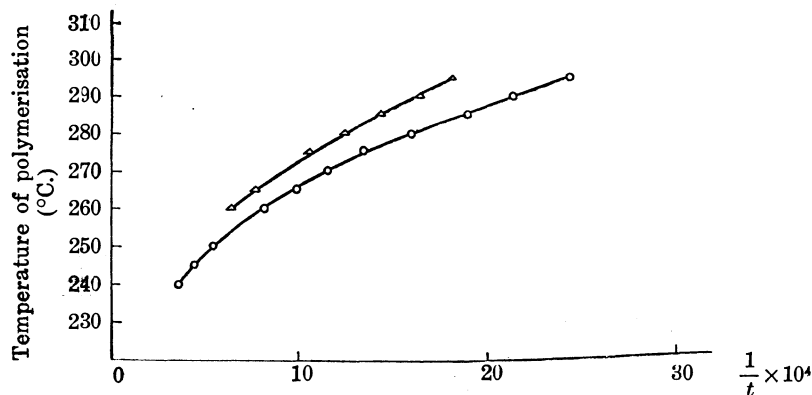


Fig. 4. Upper curve: 80% Tung oil+20% linseed oil.
Lower curve: Tung oil.

The relation between gelation time and temperature is shown in Fig. 5. It is seen that the gelation time of tung oil decreases according

(2) *J. Soc. Chem. Ind.*, **53** (1934), 1.

(3) *Ibid.*, **53** (1934), 104.

to increasing degree of temperature, but at temperature higher than 300°C. the decreasing amounts become less and less, and at last the gelation time of the system containing 20% linseed oil reaches a minimum value at 330°C., then again it increases.

It is known that the acidic substance prevents the gelation and also that when the fatty oil is heated at high temperature the cracking of glycerine radical occurs,⁽⁴⁾ so it is reasonable that at high temperature the gelation of tung oil is prolonged.

(4) *Effects of various fatty oils.* The gelation time of various fatty oils mixed in tung oil (C) was measured at 270 and 280°C. and the results are shown in Table 5.

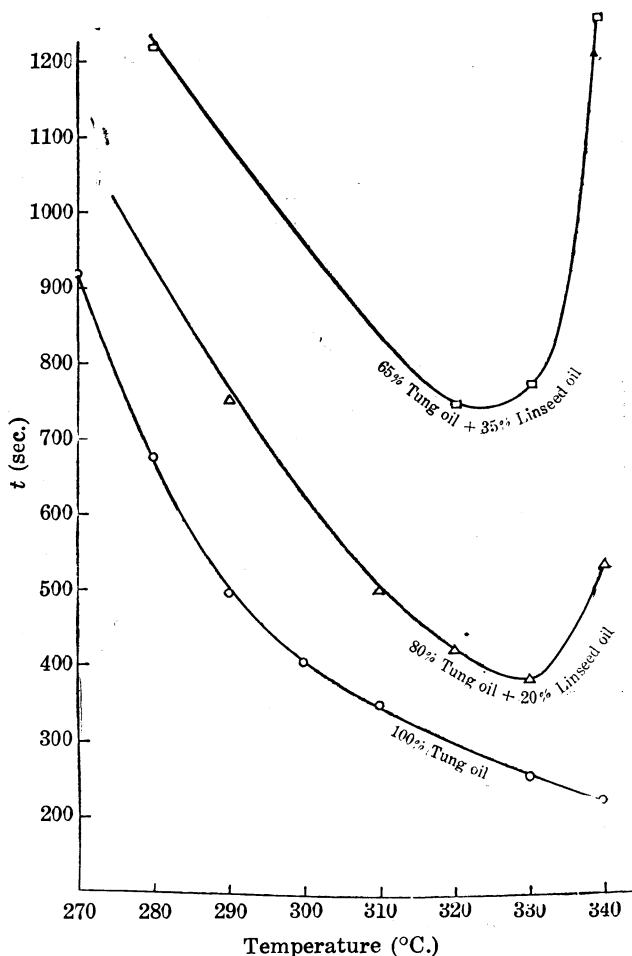


Fig. 5.

Table 5.

Kind of oils	Temperature (°C.)	Gelation time	
		% added to tung oil	
		20%	30%
Perilla oil	270	1298	1534
Hemp seed oil	270	1324	1710
	280	952	1216
Soya bean oil	270	1325	1727
	280	1023	1309
Maize oil	270	1353	1742
	280	1001	1293

(4) R. Sändig, Dissertation, Leipzig (1934), 26; Kürz, *Zt. angew. Chem.*, **49** (1936), 235.

Table 5.—(Concluded)

Kind of oils	Temperature (°C.)	Gelation time	
		% added to tung oil	
		20%	30%
Rape oil	270	1396	1823
	280	959	1364
Camellia oil	270	1434	1879
	280	1044	1408
Sesame oil	270	1485	2079
	280	1120	1638
Castor oil	270	1393	1815
Sardine oil	270	1483	1983
	280	1075	1440
Hardened fish oil	270	1351	1745
	280	957	1213
Liquid paraffin	270	1397	1873
	280	982	1355

For any oil $1/t$ and x are in linear relation and the lines of 270 and 280°C. converge on one point.

Discussion of Results. The gelation time of tung oil within the limit of experiments is prolonged by the addition of other fatty oil without exception. The retarding nature of any fatty oils are similar to that of Japanese wood oil (Fig. 2). For any kind of added oils $1/t$ and x show linear relation when measured in test tubes of the same dimension. This relation is expressed by

$$\frac{1}{t} = \frac{1}{t_0} - ax = b - ax, \quad (1)$$

where a denotes a constant, t_0 the gelation time of tung oil. a and b vary widely according to experimental conditions, but the value of x when $t = \infty$, i.e. the amount of added substance necessary to make the gelation time of the mixture to be infinitely great, is fixed, not affected by the dimension of test tubes. It is therefore considered that x_∞ is a specific property of the substance in gelation phenomenon of tung oil.

x_∞ of various oils at 270 and 280°C. are shown in Table 6.

From the above table it is concluded that drying oils such as perilla, linseed, hempseed are less effective and for the perfect prevention of gelation the amount of more than 67% of them should be added, while semi- and non-drying oils are more effective. This is expected from the fact that at high temperature the drying oils have themselves the tendency of polymerisation and gel-formation.

Table 6— x_{∞} (%).

Kind of oils	270°C.	280°C.
Perilla oil	75.5	—
Linseed oil	67.0	67.0
Hemp seed oil	67.0	69.0
Maize oil	64.5	64.5
Soya bean oil	63.0	63.5
Rape oil	63.0	63.5
Camellia oil	59.0	59.0
Sesame oil	53.0	54.5
Sardine oil	58.0	59.0
Hardened fish oil	65.0	66.5
Castor oil	62.0	—
Liquid paraffin	60.4	60.7

As a general idea x_{∞} of common fatty oils increases according to increase of iodine values. The effects of castor oil, hardened fish oil and liquid paraffin were measured for the purpose of comparison, they have specific effects respectively.

Summary.

(1) The gelation time of the system of tung oil and linseed oil was measured at 240–310°C. In the range of 240–280°C. the lines of $1/t-x$ converge on one point.

(2) The relation between gelation time and the amount of addition of any fatty oil is expressed by $1/t=1/t_0-ax$, and the value of x at $t=\infty$ is considered as a characteristic constant of added fatty oil.

(3) Gelation preventing effects of various natural fatty oils were measured at 270 and 280°C. Drying oils are less effective than non-drying oils due to their tendency of polymerisation.

(4) The temperature dependance of gelation time was discussed.

In conclusion, the author wishes to express his sincere thanks to Dr. K. Baba, Dr. T. Yosioka, and Mr. K. Yokota for their kind guidance.

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Hitachi Ltd.*

The Nature of the Complex Formation between Boric Acid and Organic Polyoxy Compounds.

By Yojiro TSUZUKI.

(Received December 21st, 1940.)

It is a well-known fact that complex compounds are formed between boric acid and polyoxy compounds. The compositions have been estimated by means of various methods, and even definite compounds have been isolated.⁽¹⁾ It has not been elucidated, however, under what conditions the complexes are formed. The author has previously shown that free boric acid forms complexes only in little quantity with diols such as ethyl tartrate, while alkali borates combine with it to a large extent.⁽²⁾ Thus the author has stated that only borate ion combines with diols, but free boric acid does not, since it gives in aqueous solution only a small quantity of BO_2' , and it has been suggested that complexes (similar to boric acid complex) can be formed in general between polyoxy compounds, only when one reactant is in ionic state.

The present work deals with the polarimetric studies on the complex formation between boric acid and polyoxy compounds of various types (mannitol, glucose, tartaric acid, tartrates, gluconate) carried out in order to elucidate the nature of the complex formation.

The experimental results will be described and discussed with each polyoxy organic compound.

Mannitol. It is known that mannitol shows a very feeble laevorotation, which is scarcely changed by the addition of free boric acid,⁽³⁾ but in the presence of alkali borate, the solution shows strong dextro-rotation.⁽⁴⁾ It was shown several years ago by Böeseken and Vermaas⁽⁵⁾ that, in the solutions of mannitol in water with NaBO_2 , there exist complex ions of the formula BD' and BD_2' , where D represents a molecule of a polyhydric alcohol. The author has now observed the variation in the optical rotation of mannitol with the change of BO_2' concentration in the mannitol-boric acid system. The results are shown in Fig. 1 and described in Table 1.

(1) Lowry, *J. Chem. Soc.*, **1929**, 2853; Bancroft and Davis, *J. Phys. Chem.*, **34** (1930), 2479; Lowry, "Optical Rotatory Power," 290, London (1935).

(2) Y. Tsuzuki, this Bulletin, **13** (1938), 337 (by distribution method); Y. Tsuzuki and Y. Kimura, this Bulletin, **15** (1940), 27 (by polarimetric method).

(3) J. M. Braham, *J. Am. Chem. Soc.*, **41** (1919), 1707; F. B. Marti, *Bull. Soc. chim. Belg.*, **39** (1930), 590.

(4) Vignon, *Compt. rend.*, **77** (1873), 1191; *Ann. chim. phys.*, [5], **2** (1874), 440; E. Fischer, *Ber.*, **23** (1890), 385.

(5) J. Böeseken and N. Vermaas, *Rec. trav. chim.*, **54** (1935), 853.

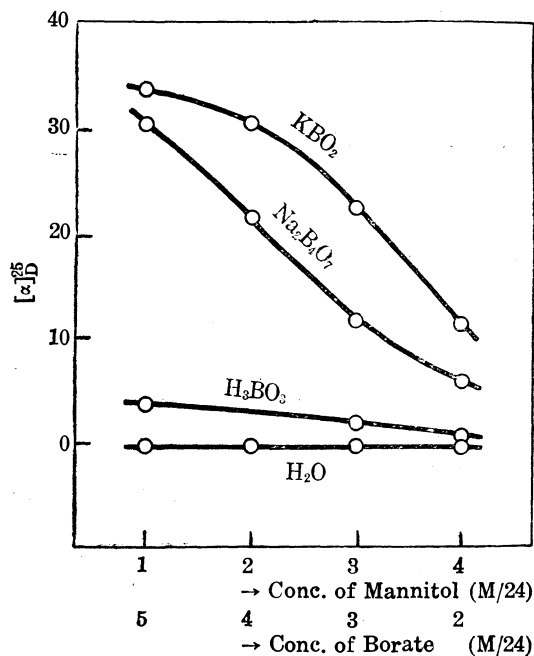
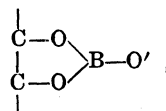
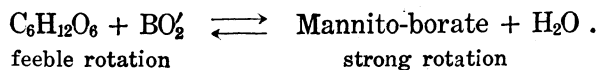


Fig. 1. Effect of Borates on the Optical Rotation of Mannitol.

The experiments indicate that complex formation proceeds with the increase of the concentration of borate ion. Borate ion enhances the rotation of mannitol because it gives a complex with the cyclic



structure, which is assumed to have a large optical rotation, since the free rotation of the OH groups in the molecule is inhibited. The quantity of this complex compound will be increased if the concentration of BO_2' becomes greater, inasmuch as equilibrium exists between these substances.



It is, therefore, due to the greater concentration of BO_2' that KBO_2 has a stronger effect than borax of the same molar concentration with respect to B-atom.

Mention should be made here to the well-known fact that boric acid can be titrated with alkali in the presence of mannitol (as well as glycerol), although it is in itself a very weak acid. It appears, therefore, that free boric acid can form complex compounds of a strongly acidic character with these polyhydric alcohols, but this fact is to be explained in the following way. In the titration of boric acid in the presence of mannitol, mannito-boric acid is formed from mannitol and borate ion. This complex which has a strongly acidic character can be formed in a measurable quantity, only after adding a certain amount of alkali, and the quantity of this complex is gradually increased with the progress of titration, thus in the presence of excess mannitol, all the boric acid can be titrated, since it can then be totally converted into strongly acidic complex acid.

Glucose. Darmois and Peyroux⁽⁶⁾ have shown that H_3BO_3 even at saturation is without effect on the rotation of glucose, but that sodium borates have a large effect. Murgier and Darmois⁽⁷⁾ came to the con-

(6) Darmois and Peyroux, *Compt. rend.*, **193** (1931), 1182.

(7) Murgier and Darmois, *Angew. Chem.*, **51** (1938), 753, X International Congress for Chemistry in Rome, May 1938.

clusion by examining optical rotation that H_3BO_3 gives with hexoses a very small amount of complexes, while NaBO_2 gives a well characterized compound.

The author has examined the effects of boric acid and its alkali salts on the rotation of glucose by varying the ratio Borate/Glucose (Fig. 2 and Table 2) as in the case of mannitol.

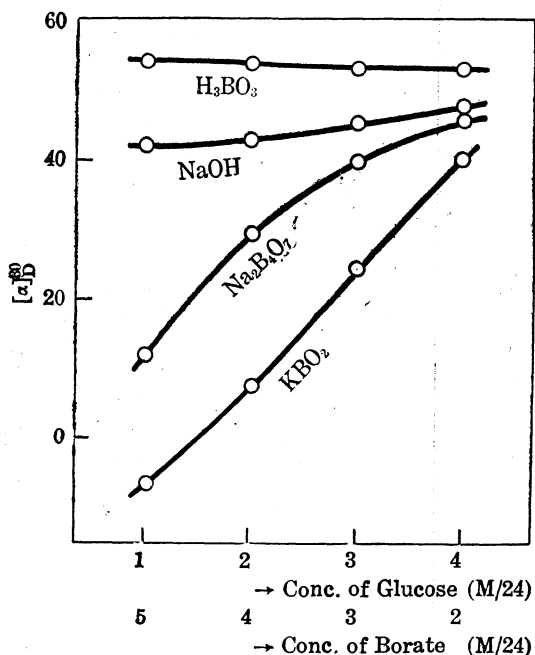


Fig. 2. Effect of Borates on the Optical Rotation of Glucose.

The experiment is in harmony with the statement of Darmois and his collaborators⁽⁸⁾. The specific rotation of glucose, whose large value is due to the cyclic structure of glucoside formula, suffers great changes in the presence of alkali borates, and indeed even negative rotation appears with the increase of the concentration of alkali borate. It is not improbable that the cyclic structure of glucose suffers some modifications by the alkalinity of borate salts, thus the strong dextro-rotation being depressed, but the actual effect of weak alkali on the rotation of glucose is very small (Table 2) and even stronger alkali such as NaOH does not exercise a remarkable influence (Fig. 2). We should, therefore,

assign the radical change of the rotation to the complex formation between borate ion and glucose. The cyclic nature of the complex is responsible to the depression of the specific rotation of glucose. The general behaviours of glucose with respect to the change of optical rotation are very similar to that of mannitol, although it is in the opposite direction. This is, no doubt, due to the lack of carboxyl group.

Tartaric Acid and Alkali Tartrates. In these cases free boric acid has remarkable influence, in contrast to polyhydric alcohols. The complex formation between boric acid and tartaric acid and alkali tartrates, is due to the union of COO' and $\text{B}(\text{OH})_3$. Here the latter does not act as an ion, but as an undissociated polyoxy compound.

The reaction of these complex formations has been already examined, thus Darmois⁽⁹⁾ has concluded from his polarimetric measurements that

(8) The author could not confirm the observation of P. S. Tang and P. N. Sung with regard to the effect of boric acid on glucose that the rotation of glucose shows the minimum value of $[\alpha]_D = +47^\circ$ in the region of 0.2M H_3BO_3 . *Nature*, **137** (1936), 275.

(9) Darmois, *J. Chim. phys.*, **23** (1926), 649.

a complex $B(OH)_3 \cdot 2C_4H_6O_6$ exists in the mixture of tartaric-boric acid. On the other hand he observed that in strong alkaline solution boric acid gives a laevo-rotatory complex salt.

The present author's observations on the effects of boric acid and borates on the rotation of tartaric acid are shown in Fig. 3 and Table 3.

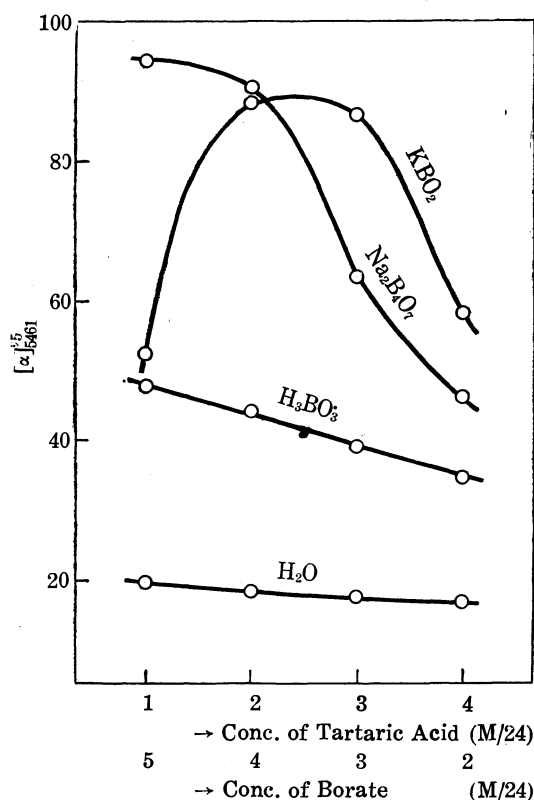
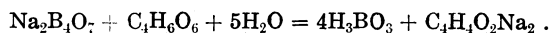


Fig. 3. Effect of Borates on the Optical Rotation of Tartaric Acid.

partial rotation originating in the OH group predominates. Now the actions of borax on the rotation of tartaric acid (Table 3) are in fact similar to those of H_3BO_3 on sodium tartrate (Table 4). Of course this is due to the circumstances that in aqueous solution there takes place the following exchange reaction between these substances:



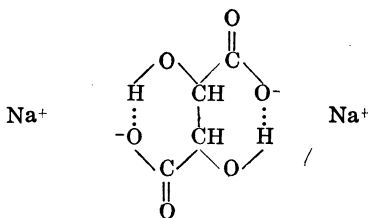
Since these mixtures are always acidic, undissociable OH group is present in an appreciable quantity either in tartaric or in boric acid, and thus combination occurs between anion and OH group, leading to the formation of complexes, similar in structure to those of the free tartaric-boric acid system, but these complexes dissociate more strongly than the latter, so

The results are apparently complicated, hence one must be cautious to draw from these figures some conclusions with respect to complex formation. It is noticed, however, that dextro-rotation is elevated as the ratio $H_3BO_3/C_4H_6O_6$ increases. This phenomenon is to be explained as follows. Boric acid combines with the COO' group of tartaric acid, giving a complex with a cyclic structure. Since all the cyclic derivatives of tartaric acid formed by fixing its carboxyl groups are strongly dextro-rotatory, borotartaric acid now under consideration is expected to show enhanced dextro-rotation. According to the author's view⁽¹⁰⁾ the COOH group of *d*-tartaric acid is a contributor of its laevo-partial rotation, and its characteristic (i.e. partial rotatory contribution) is enfeebled when it forms a cyclic structure, hence the dextro-

(10) Y. Tsuzuki, *Sci. Pap. Inst. Phys. Chem. Res.*, **35** (1939), 425.

that the complex formation proceeds further, and thus strong dextro-rotation appears. With the increase of the ratio Borax/Tartrate, the concentration of alkali becomes greater. Hence the concentration of borate ion will be raised with the result that dextro-rotation is enhanced.

It is known that alkali tartrates show none of the optical anomalies of the acid⁽¹¹⁾ and exhibit considerably high specific rotation (Tables 4 and 5). This may be due to the formation of a somewhat fixed cyclic structure:



As already shown by the author⁽¹⁰⁾ the (negative) partial rotation of the COOH group is enfeebled in a ring compound of this sort, and the (positive) partial rotation of the OH group becomes predominant; consequently the molecule shows strong dextro-rotation.

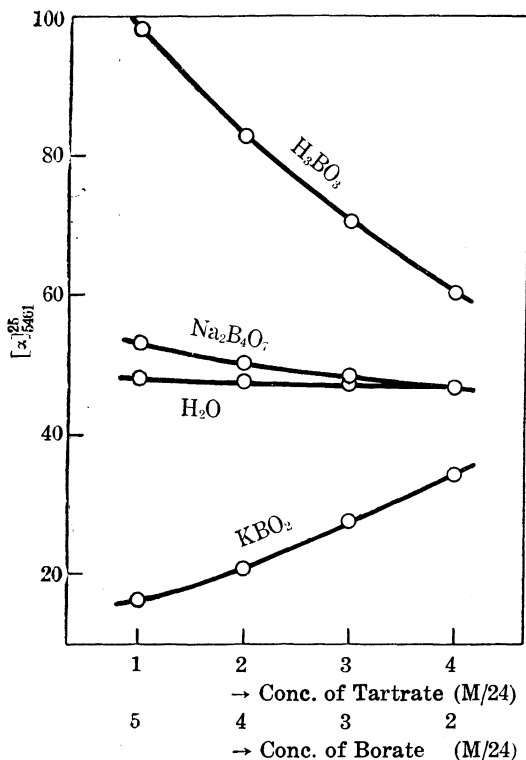


Fig. 4. Effect of Borates on the Optical Rotation of Sodium Tartrate.

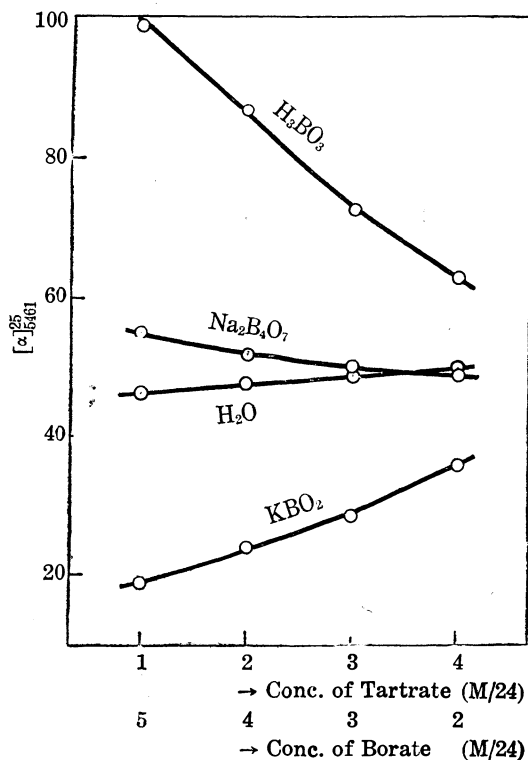
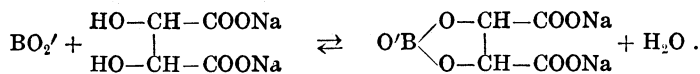


Fig. 5. Effect of Borates on the Optical Rotation of Potassium Tartrate.

(11) Lowry and Austin, Bakerian Lecture, *Phil. Trans. A*, **222** (1922), 249.

The action of KBO_2 on alkali tartrates depresses the high dextro-rotations of these salts, and indeed the effect becomes stronger as the concentration of BO_2' increases. (Fig. 4 and 5, Tables 4 and 5). This can be explained in the following way. Since BO_2' can not unite with the COO' group of tartrates, it combines with their OH groups, the reaction being represented as follows:



Seeing that cyclic compounds of the type $\text{R} \begin{array}{c} \text{O}-\text{CH}-\text{COOR}' \\ | \\ \text{O}-\text{CH}-\text{COOR}' \end{array}$ show strong laevo-rotation,⁽¹²⁾ it will be understood that, with increasing concentration of KBO_2 , the concentration of the complex with laevo-rotatory character will be raised, and hence the system becomes less dextro-rotatory. Thus in the system, $\text{KBO}_2 : \text{C}_4\text{H}_6\text{O}_6 = 20 : 10$ (Fig. 3, Table 3), which is equivalent to the system, $\text{H}_3\text{BO}_3 : \text{C}_4\text{H}_4\text{O}_6\text{K}_2 = 20 : 10$ (Fig. 5, Table 5) the specific rotation reaches the maximum value $[\alpha]_{5461}^{25} = +87.84^\circ$ at this point, and by adding BO_2' further to this mixture, the high dextro-rotation of this system will be lowered.

Borax is nearly without effect on the rotation of alkali tartrates (Fig. 4 and 5, Tables 4 and 5). This phenomenon appears rather curious, but the author considers that borax reacts with tartaric ion in

two ways: on one hand the portion of undissociated boric acid $\text{B}(\text{OH})_3$ in borax combines with the COO' group of the tartrate forming a strongly dextro-rotatory complex, and on the other hand the dissociable portion in borax (BO_2') forms a rather laevo-rotatory complex. The two opposite effects cancel each other, so that the total rotation remains almost unaffected.

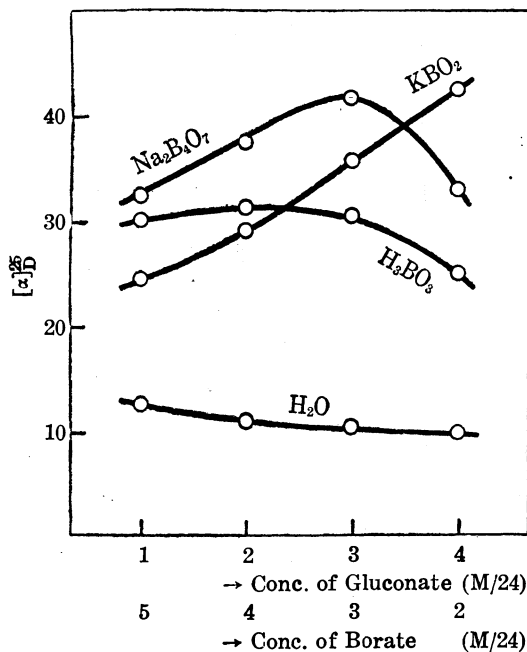


Fig. 6. Effect of Borates on the Rotation of Calcium Gluconate.

Calcium Gluconate. Although free boric acid shows a very feeble ability for complex formation with polyhydric alcohols, such as mannitol and glucose, it exerts a remarkable influence on polyoxy compounds with carboxyl group. This is well illustrated with gluconic acid (Fig. 6 and Table 6).

(12) Y. Tsuzuki, this Bulletin, **15** (1940), 27; *Sci. Pap. Inst. Phys. Chem. Res.*, **35** (1939), 425, 466; **36** (1939), 31.

As will be easily understood from the examples of tartrates, this phenomenon must be attributed to the presence of complexes formed between COO' and H_3BO_3 . Calcium gluconate also shows somewhat complicated behaviours with alkali borates as in the cases of tartaric acid and its salts. It is remarkable that the dextro-rotation is lowered with the increase of KBO_2 concentration. This may, however, be explained as follows. In alkaline medium BO_2' unites no more with COO' , but reacts with alcoholic hydroxyl groups, so that it is natural that the rotation suffers alteration in the other direction.

In conclusion it should be remarked that these reactions of complex formation arrive at equilibrium almost instantaneously. This is probably due to exchange reaction. In this connexion mention should be made further that heteropoly acids as well as isopoly acids in inorganic field are perhaps of the nature similar to the present cases, thus they may be explained from the point of view above stated.

Experimental Part.

Polarimetric measurements were made on the mixtures of the following compositions:

	No. 1	No. 2	No. 3	No. 4
M/4-Optically active compound c.c.	5	10	15	20
M/4- H_3BO_3 , $\frac{\text{Na}_2\text{B}_4\text{O}_7}{4}$ or KBO_2 c.c.	25	20	15	10

Hence the concentrations in the mixtures are:

	No. 1	No. 2	No. 3	No. 4
Optically active compound M/24	1	2	3	4
Borate or other substances M/24	5	4	3	2

The numerical values are given in the following tables. The length of the observation tube is 2.2 dm. The specific rotation of tartaric acid and its salts is given for tartrate ion $\text{C}_4\text{H}_4\text{O}_6''$, and that of gluconate for gluconate ion $\text{C}_6\text{H}_{11}\text{O}_7'$.

Table 1. Mannitol.

No.	α				$[\alpha]_D^{25}$			
	H_2O	H_3BO_3	$\text{Na}_2\text{B}_4\text{O}_7$	KBO_2	H_2O	H_3BO_3	$\text{Na}_2\text{B}_4\text{O}_7$	KBO_2
1	-0.001	+0.06	+0.510	+0.564	-0.06	+3.59	+30.55	+33.78
2	-0.003		+0.722	+1.02	-0.09		+21.62	+30.54
3	-0.009	+0.09	+0.583	+1.13	-0.18	+1.80	+11.64	+22.56
4	-0.012	+0.05	+0.387	+0.746	-0.24	+0.60	+ 5.79	+11.17 ₄

Table 2. Glucose.

No.	α					$[\alpha]_{\text{D}}^{30}$				
	H ₃ BO ₃	Na ₂ B ₄ O ₇	KBO ₂	K ₂ CO ₃	NaOH	H ₃ BO ₃	Na ₂ B ₄ O ₇	KBO ₂	K ₂ CO ₃	NaOH
1	+0.888	+0.196	-0.107	+0.833	+0.696	+53.77	+11.87	- 6.48	+50.74	+42.14
2	+1.782	+0.979	+0.249	+1.683	+1.421	+53.94	+29.64	+ 7.54	+50.94	+43.02
3	+2.611	+1.97	+1.405	+2.528	+2.235	+52.70	+39.76	+24.36	+51.02	+45.10
4	+3.49	+3.002	+2.683	+3.385	+3.132	+52.83	+45.45	+40.25	+51.25	+47.41

Table 3. Tartaric Acid.

No.	α				$[\alpha]_{5461}^{25}$			
	H ₂ O	H ₃ BO ₃	Na ₂ B ₄ O ₇	KBO ₂	H ₂ O	H ₃ BO ₃	Na ₂ B ₄ O ₇	KBO ₂
1	+0.271	+0.652	+1.28	+0.711	+19.97	+48.03	+94.32	+52.38
2	+0.501	+1.20	+2.45	+2.385	+18.45	+44.19	+90.24	+87.84
3	+0.719	+1.59	+2.58	+3.50	+17.66	+39.04	+63.36	+85.94
4	+0.898	+1.88	+2.50	+3.16	+16.55	+34.62	+46.05	+58.20

Table 4. Sodium Tartrate.

No.	α				$[\alpha]_{5461}^{25}$			
	H ₂ O	H ₃ BO ₃	Na ₂ B ₄ O ₇	KBO ₂	H ₂ O	H ₃ BO ₃	Na ₂ B ₄ O ₇	KBO ₂
1	+0.650	+1.35	+0.72	+0.22	+47.89	+98.0	+53.1	+16.2
2	+1.295	+2.25	+1.36	+0.57	+47.70	+82.9	+50.1	+21.0
3	+1.927	+2.88	+1.96	+1.14	+47.32	+70.8	+48.2	+28.0
4	+2.562	+3.28	+2.43	+1.88	+47.19	+60.5	+46.6	+34.6

Table 5. Potassium Tartrate.

No.	α				$[\alpha]_{5461}^{25}$			
	H ₂ O	H ₃ BO ₃	Na ₂ B ₄ O ₇	KBO ₂	H ₂ O	H ₃ BO ₃	Na ₂ B ₄ O ₇	KBO ₂
1	+0.625	+1.34	+0.75	+0.26	+46.04	+99.0	+55.3	+19.1
2	+1.280	+2.36	+1.40	+0.66	+47.16	+86.9	+51.6	+24.3
3	+1.989	+2.94	+2.04	+1.17	+48.84	+72.2	+50.0	+28.8
4	+2.722	+3.40	+2.65	+1.96	+50.13	+62.7	+48.8	+36.2

Table 6. Calcium Gluconate.

No.	α				$[\alpha]_D^{25}$			
	H ₂ O	H ₃ BO ₃	Na ₂ B ₄ O ₇	KBO ₂	H ₂ O	H ₃ BO ₃	Na ₂ B ₄ O ₇	KBO ₂
1	+0.226	+0.544	+0.580	+0.44	+12.64	+30.42	+32.44	+24.61
2	+0.394	+1.13	+1.34	+1.05	+11.02	+31.59	+37.47	+29.36
3	+0.555	+1.64	+2.24	+1.92	+10.35	+30.56	+41.76	+35.80
4	+0.706	+1.99	+2.37	+3.04	+ 9.87	+24.82	+33.09	+42.50

Summary.

By polarimetric observations with regard to the effects of H₃BO₃, Na₂B₄O₇ and KBO₂ on various polyoxy compounds the following results and conclusion were obtained.

Boric acid has a very feeble ability for complex formation with non-ionizable polyoxy compounds, such as mannitol and glucose, while alkali borates show strong activity upon them. The order of the strengths is H₃BO₃ $\ll$ Na₂B₄O₇ $<$ KBO₂. Complex is formed between borate ion and polyhydric alcohols. Its quantity increases with increasing BO₂'.

The effects of boric acid and alkali borates on ionizable polyoxy compounds, like tartaric acid and its salts, appear somewhat complicated. In this case complex formation is possible to a large extent between free boric acid and free tartaric acid (complex I). Complexes are also formed between alkali borate and alkali tartrates (complex II), but they (II) are different in structure from those formed in acidic medium (I). The complex I is formed by the action between BO₂' and alcoholic OH groups, but complex II between B(OH)₃ molecule and COO' ion.

Calcium gluconate behaves toward boric acid and borates like alkali tartrates. H₃BO₃ combines with the COO' group of the gluconate, while BO₂' reacts with its alcoholic OH groups.

Thus it has been shown that the complex formation is in general based upon the reaction between molecule and ion, and not between neutral molecules nor between ions.

The author wishes to express his hearty thanks to Mr. Y. Kimura and Mr. T. Yamana for assistance with the experiments and to the Department of Education for a grant.

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Direct Determination of Oxygen in the Organic Compounds by the Hydrogenation. II. Cracking Mechanism on the Pt-silica Gel Catalyst.

By Kiyoshi MORIKAWA, Toraki KIMOTO, and Ryonosuke ABE.

(Received November 21, 1940.)

In the previous paper the optimum analytical conditions were searched and found to lie within the definite ranges out of which the experimental values obtained were always lower than the calculated ones. We are going to explain the reasons for these by the experimental results and theoretical considerations.

I. Heating Rate of the Sample. When the rates of heating the sample are different the mean partial pressures of carbon oxides produced in the cracking zone will be also different; and slower the heating rate, more favourable it is for the complete reduction of carbon oxides. The temperature of the small outlet tube, on the inside wall of which the reduction water is condensed, is estimated to be around 40°–50°C. and, therefore, the mean partial pressure of water vapour produced and then the mean ratios of hydrogen to carbon monoxide and carbon dioxide are estimated to be around 14 and 25 respectively.

II. Cracking on the Pt-silica Gel Catalyst. (1) *Experimental Procedure.* The vapours produced from the sampling boat are normally heated to 950°C. on the Pt-silica gel catalyst and are completely decomposed to carbon monoxide, carbon dioxide and water vapour. The nickel catalyst which reduces the carbon oxides thus produced is removed from the reaction tube, intending to see the reaction course in the cracking zone. The water produced is caught by calcium chloride and the carbon dioxide by 50% potassium hydroxide solution.

(2) *Influence of Cracking Temperature.* The results on saccharose are given in Table 4.

Table 4. The influence of cracking temperature on the distribution of oxygen in the various products.

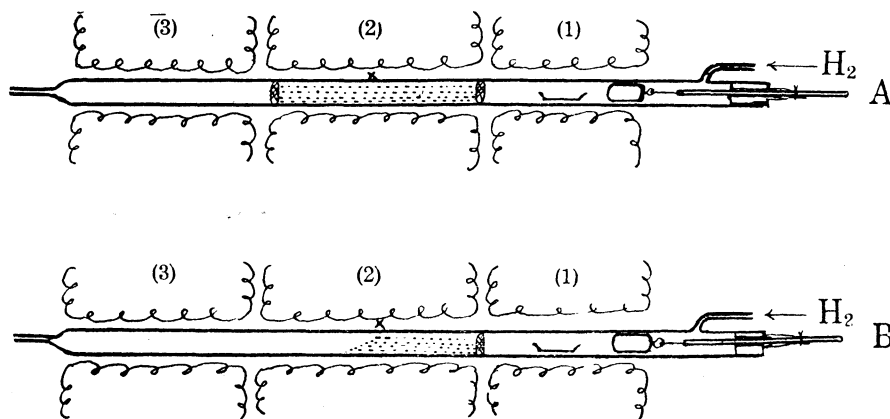
Sample saccharose (Oxygen % = 51.43), heating temp. of sample saccharose 950°C., hydrogen velocity 4 l./hr., analytical period, 60 min. .

Expt. No.	Temp. of Pt-silica gel °C.	Sample g.	H ₂ O produced %	CO ₂ produced %	Oxygen balance, %			
					to H ₂ O	to CO ₂	to CO	Unde-composed
C-18	800	0.1526	30.34	5.77	52.38	8.17	37.04	2.41
C-32	850	0.1777	28.19	5.46	48.69	7.72	41.63	1.96
C-15	860	0.1668	27.04	4.98	46.68	7.04	44.32	1.96
C-16	860	0.1486	27.05	5.18	46.70	7.33	44.01	1.96

Table 4.—(Concluded)

Expt. No.	Temp. of Pt-silica gel °C.	Sample g.	H ₂ O produced %	CO ₂ produced %	Oxygen balance, %			
					to H ₂ O	to CO ₂	to CO	Undecomposed
C-21	880	0.1423	25.37	4.36	43.81	6.16	48.48	1.55
C-20	900	0.1676	24.82	3.58	42.85	5.06	50.54	1.55
C-22	950	0.1487	21.59	2.96	37.27	4.18	58.55	0
C-24	950	0.1332	21.25	2.78	36.69	3.93	59.38	0
C-3	* 950	0.1328	24.92	3.61	43.04	5.10	51.86	0
C-2	* 950	0.1154	25.41	3.47	43.87	4.91	51.22	0

* The cracking Pt-silica gel catalyst was inserted in the reaction tube as shown in Fig. 6-A, the other as in Fig. 6-B.



x : The position, at which the temperature was measured.

Fig. 6. Modes of Charging Pt-silica Gel Catalyst.

In the previous paper the percentage decompositions of oxygen of saccharose as a function of cracking temperatures were ascertained, and, therefore, percentage of carbon monoxide and that of oxygen remained undecomposed may be calculated, combining with the data here obtained.

The results of Table 4 show that the oxygen of saccharose is largely decomposed into water vapour and carbon monoxide, and the higher the cracking temperature, the more carbon monoxide and the less water vapour and carbon dioxide are produced. The different results of C-2, C-3 from those of C-22, and C-24 are easily explained through the different temperature distributions of cracking catalyst.

(3) *Influence of Streaming Velocity of Hydrogen.* The cracking catalyst was inserted as shown in Fig. 6-B and the influence of streaming velocity of hydrogen was examined and the results obtained were shown in Table 5.

Table 5. The influence of streaming velocity of hydrogen.

Sample saccharose, temp. of Pt-silica gel catalyst 950°C., analytical period 60 min..

Expt. No.	H ₂ Vel. l./hr.	Sample g.	H ₂ O produced %	CO ₂ produced %	CO (diff.) %	Oxygen balance		
						to H ₂ O	to CO ₂	to CO
C-27	2.2	0.1641	22.48	4.20	28.09	38.81	5.93	55.26
C-25	3.0	0.1423	21.64	3.51	29.64	37.37	4.96	57.67
C-24	4.0	0.1332	21.25	2.78	30.52	36.69	3.93	59.38
C-28	4.8	0.1391	22.14	1.94	30.34	38.23	2.74	59.03

The rapid flow of hydrogen produced the decreased production of carbon dioxide and the increased production of carbon monoxide, while the amount of water approximately remaining constant.

(4) *Cracking of Other Several Organic Compounds.* Succinic acid, benzoic acid, and anthraquinone were examined for their cracking behaviour in the same way as in the case of saccharose. The results of Table 6 indicate that the sample which contained large amount of oxygen tends to give large amount of carbon dioxide, particularly at lower temperatures.

Table 6. The cracking of several organic compounds at various temperature.

Streaming velocity of H₂ 4 l./hr., analytical period 60 min..

Expt. No.	Sample	Temp. of Pt-silica gel Catalyst °C.	Sample g.	H ₂ O produced %	CO ₂ produced %	Oxygen balance		
						to H ₂ O	to CO ₂	to CO
C-40	Succinic acid (0% = 54.22)	850	0.1405	15.94	18.93	26.11	25.40	—
C-41		860	0.2274	12.01	17.15	19.67	23.00	—
C-39		900	0.1809	10.17	10.06	16.65	13.50	—
C-38		950	0.1828	6.35	3.83	10.40	5.15	84.45
C 36	Benzoic acid (0% = 26.22)	800	0.1213	0.99	1.32	3.36	3.36	—
C-34		850	0.1240	0.56	1.29	1.90	3.55	—
C-35		900	0.1492	0.47	1.00	1.60	2.78	—
C-33		950	0.1317	0.30	0.68	1.03	1.87	97.10
C 42	Anthraquinone (0% = 15.37)	950	0.2757	0.22	0.22	1.27	1.04	97.69

(5) Discussion of Results. *Calculation of Oxygen Distribution Balance.* At the high temperatures as 800–950°C. all the organic compounds containing oxygen decompose and liberate their oxygen as carbon monoxide, carbon dioxide, and water vapour, and, therefore, the following several reactions have to be considered in the discussion of the results.

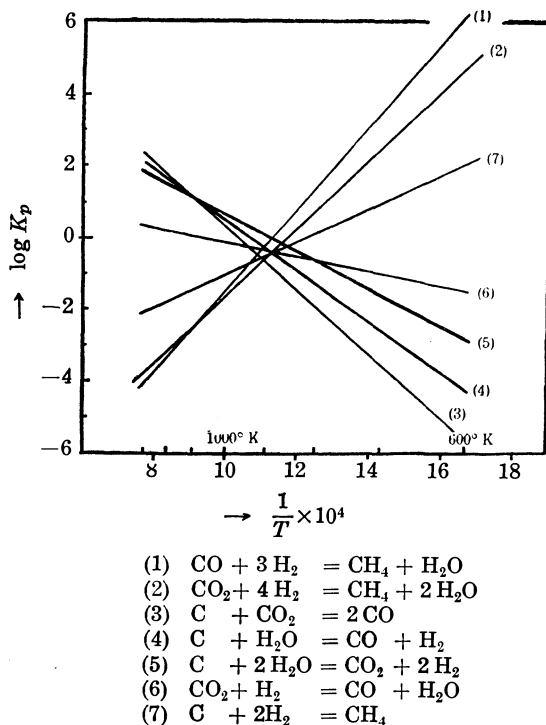


Fig. 7. Relation between Equilibrium Constants and Reaction Temperatures.

The dependence of equilibrium constants K_p on the temperatures of these reactions are represented in Fig. 7. Reaction (5) is the combination of reaction (4) and (6) and is not necessary to be considered here. The K_p of reaction (3), (4), and (6) increase with temperature and, therefore, produce more carbon monoxide. The percentage distributions of oxygen in the products of reactions are calculated and plotted in Fig. 8–11 as a function of temperatures.

The reaction (3) occurs under approximately 1/10 atmosphere in our analytical conditions and consequently ought to give at equilibrium about 1% of carbon dioxide at 950°C. (Fig. 8). H_2/CO_2 being 10~20, the reaction (6) may produce 3–6% of

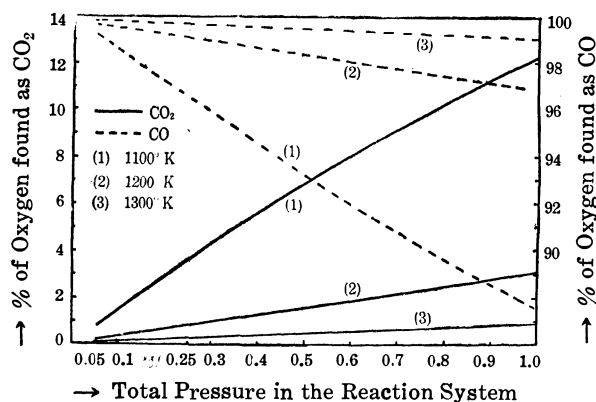
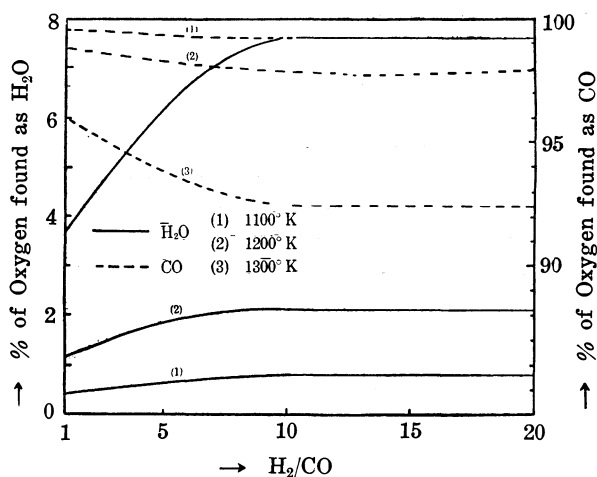
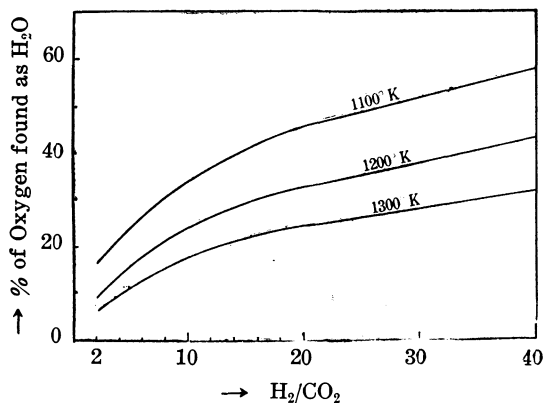
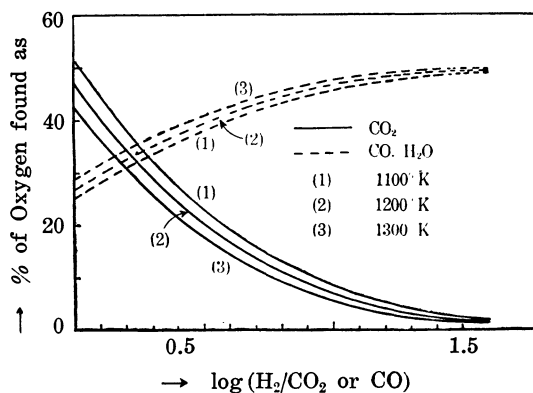


Fig. 8. Oxygen Balance in $\text{C} + \text{CO}_2 = 2\text{CO}$.

Fig. 9. Oxygen Balance in $C + H_2O = CO + H_2$.Fig. 10. Oxygen Balance in $C + 2H_2O = CO_2 + 2H_2$ Fig. 11. Oxygen Balance in $CO_2 + H_2 = CO + H_2O$.

carbon dioxide at 950°C. and the large proportion of oxygen in the sample will appear as carbon monoxide and water vapour. These estimations are quite concordant with our experimental results.

(6) *Reaction of Free Carbon with Carbon Dioxide.* The aromatic compounds produce on decomposition quite considerable amount of free carbon. The increase of streaming velocity of hydrogen reduces the mean partial pressures of carbon oxide and, therefore, drive the equilibrium point of reaction (3) toward the carbon monoxide side and reduces the carbon dioxide formation. On the contrary the decrease of hydrogen velocity favours the carbon dioxide formation. These considerations show good agreement with the experimental results given in Table 5. Succinic acid and saccharose give at 950°C. 3-4% of carbon dioxide and these are more than the equilibrium figures and, therefore, it is concluded that the cracked gases from the compounds which contain large amount

of oxygen pass through the cracking zone without reaching the equilibrium point.

(7) *Reaction of Free Carbon with Steam.* The water produced by the cracking reaction of the sample will react with the free carbon deposited in the cracking zone of reaction tube. The Fig. 9 indicates that 97% of water may decompose at 950°C. through the reaction (4). Succinic acid and saccharose which deposit only small amount of carbon give large amount of water and small amount of carbon monoxide. On the contrary the aromatic compounds like benzoic acid and anthraquinone which produce a considerable amount of carbon give nearly calculated amount of carbon monoxide and water (Table 6). Planning to prove these conclusion more definitely the surface of Pt-silica gel catalyst was purposely covered with free carbon and its behaviour was compared with that of the clean surface.

Table 7. Reaction of free carbon with H₂O or CO₂

Temp. of Pt-silica gel catalyst 950°C., H₂ velocity 4 l./hr.,

A cases, the catalyst was clean

B cases, the catalyst was covered with free carbon

Sample		Condition of catalyst	H ₂ O produced %	CO ₂ produced %	Oxygen balance, %		
Kinds	g.				to H ₂ O	to CO ₂	to CO
H ₂ O	0.1441	A	99.39	0	99.39	0	0.61
	0.0428	B	2.10	1.64	2.10	1.34	96.56
NaHCO ₃ *	0.2830	A	16.86 (10.72)	5.9 (26.19)	52.41 (33.34)	15.01 (66.66)	32.58 (0)
	0.2199	B	0.79 (10.72)	0.79 (26.19)	2.46 (33.34)	1.99 (69.66)	95.55 (0)

* The sample bicarbonate, on heating to 300°C. decomposed stoichiometrically, $2\text{NaHCO}_3 = \text{Na}_2\text{CO}_3 + \text{CO}_2 + \text{H}_2\text{O}$, and gave the products of figures in brackets.

The results of Table 7 prove quite conclusively the deduction discussed above. These data, furthermore, indicate that the presence of sufficient amount of free carbon produces the equilibrium mixture of cracked gases after the reaction (4).

(8) *Water-gas Reaction.* In order to decide whether the reaction (6) participates or not in the formation of water in the cracking zone, the behaviour of sodium oxalate which produces only carbon monoxide and carbon dioxide and no water was examined and the results obtained were given in Table 8. The degree of decomposition of sodium oxalate at 950°C. was found to be about 90.0% by the blank experiments. It is clear that the reaction (6) is also responsible for the formation of water and also that the reaction (6) does not reach the equilibrium point of these cases in which the initial concentration of carbon dioxide is exceedingly high.

Table 8. Cracking of sodium oxalate.



Expt. No.	Sample g.	Temp. of Pt-silica gel catalyst °C.	H ₂ Vel. l./hr.	Oxygen balance, %		
				to H ₂ O	to CO ₂	to CO (diff.)
C-53	0.2037	800	3.8	27.66	21.68	50.66
C-52	0.2901	900	3.0	22.53	21.28	56.19
C-51	0.3183	950	4.0	22.93	19.56	57.51
C-50	0.2654	1000	3.5	22.44	10.41	67.15

(9) *Reaction of Free Carbon with Hydrogen.* The free carbon produced in the cracking zone may combine with hydrogen and disappear as methane; however, at such a high temperature as 950°C. the equilibrium of reaction (7) is unfavorable for the production of methane and, furthermore, the free carbon formed may be transformed into a stable form and loses its activity toward hydrogen; thus resulting in the accumulation of free carbon on Pt-silica gel catalyst in the cracking zone. It is, therefore, necessary to burn off the free carbon with air from time to time, usually after 7–10 analyses.

In conclusion, the mechanism of reaction in the cracking zone is satisfactorily explained by the occurrence of reactions (3), (4), and (6); the higher the cracking temperature the more carbon monoxide forms, and the rapid heating of the sample in the boat or high content of oxygen of the sample favours the increasing amount of carbon dioxide, thus exceeding equilibrium amount of carbon dioxide at the cracking temperatures. The mechanism of reduction of carbon monoxide and carbon dioxide thus formed will be discussed in the next paper.

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The Formation of Polyhydroxy-dialdehydes. I. Xylo-tri-hydroxy-glutaric Dialdehyde and its Derivatives.

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(Received December 27, 1940.)

Among the onoses, namely, sugars which have two carbonyl groups in separated positions, those with one aldehydic and one ketonic groups have been reported by some investigators.⁽¹⁾ While, very little is known about the onoses with two aldehydic groups;⁽²⁾ and nothing seems to have been reported about dialdo-pentonoses, that is, trihydroxy-glutaric dialdehydes, where it should exist theoretically four such dialdehydes. So attempts were made to obtain these series of sugars, and xylo-trihydroxy-glutaric dialdehyde and *d*-lyxo-trihydroxy-glutaric dialdehyde (xylo- and lyxo-dialdo-pentonose) and their derivatives were now prepared.⁽³⁾ This communication concerns with the formation of xylo-derivatives.

For this purpose, 1,2-monoacetone-*d*-glucofuranose is oxidized by lead tetracetate⁽⁴⁾ in benzene solution. The mixture is filtered, the filtrate evaporated under diminished pressure, and 1,2-monoacetone-*d*-xylo-trihydroxy-glutaric dialdehyde is obtained by distilling the remaining sirup. It distills at 132°–136° in 0.01–0.02 mm pressure. It is a colourless hygroscopic sirup, although it can be made powdery. It is not sweet, but bitter. $[\alpha]_D^{20} = 20^\circ \pm 3^\circ$.

The phenylhydrazone of 1,2-monoacetone-*d*-xylo-trihydroxy-glutaric dialdehyde is prepared by boiling the alcoholic solution of dialdehyde with phenylhydrazine. It is recrystallized first from the mixture of benzene and petroleum ether and then from dilute alcohol. It crystallizes in colourless needles or leaflets. Melting point, 140.5°–141° (corrected). $[\alpha]_D^{20} = -41^\circ \pm 1^\circ$ in chloroform.

The semicarbazone of 1,2-monoacetone-*d*-xylo-trihydroxy-glutaric dialdehyde is prepared by adding semicarbazide hydrochloride and potassium acetate to the aqueous solution of the acetone derivative. It crystallizes in fine colourless leaflets. The melting point is 209°–209.5° (corrected, decomposing).

Xylo-trihydroxy-glutaric dialdehyde is obtained by hydrolizing the above acetone-derivative with 1% sulphuric acid in a boiling water bath. It does not crystallize, but its *bis*-phenylhydrazone and *bis-p*-nitrophenylhydrazone are obtained crystalline by adding phenylhydrazine or *p*-nitrophenylhydrazine to the acidic solution of xylo-trihydroxy-glutaric dialdehyde. Melting point of *bis*-phenylhydrazone of xylo-trihydroxy-

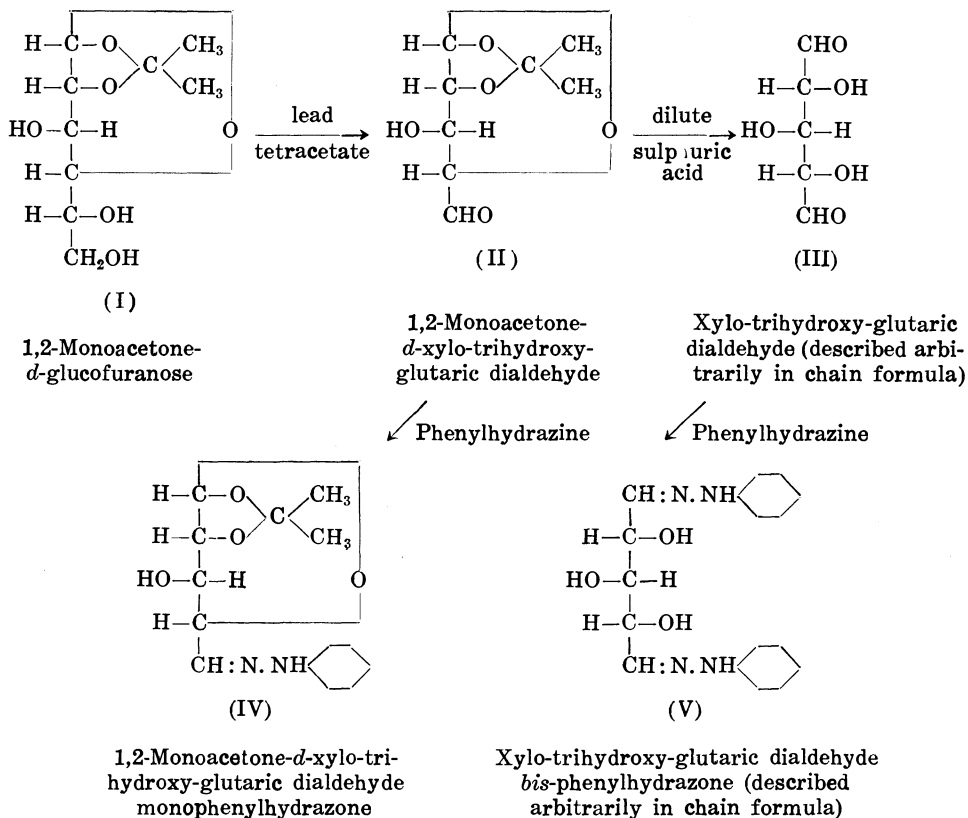
(1) For instance: B. Helferich and E. Himmen, *Ber.*, **62** (1929), 2136; B. Helferich and N. M. Bigelow, *Z. physiol. Chem.*, **200** (1931), 263.

(2) H. O. L. Fischer and H. Appel, *Helv. Chim. Acta*, **17** (1934), 1574.

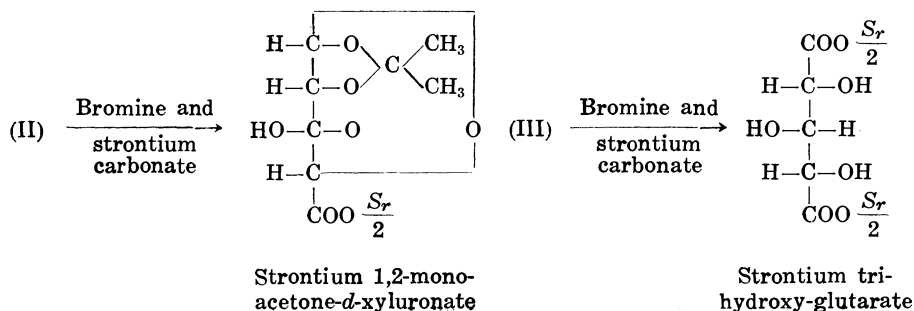
(3) The author reported on these on the annual meeting of the Chemical Society of Japan in July 1940 at Sapporo.

(4) Criegee, *Ann.* **507** (1933), 159.

glutaric dialdehyde is 126.5° – 127.5° (corrected), and that of its *bis-p*-nitrophenylhydrazone is 191° – 192° (corrected, decomposing).



By oxidizing the aldehyde groups of such dialdehyde derivatives with bromine, the corresponding carboxylic acids are obtained. Thus, strontium salt of 1,2-monoacetone-*d*-xyluronic acid is obtained by oxidizing 1,2-monoacetone-*d*-xylo-trihydroxy-glutaric dialdehyde with bromine, generated acids being neutralized by excess of strontium carbonate. And, by the same method, strontium salt of xylo-trihydroxy-glutaric acid is obtained from xylo-trihydroxy-glutaric dialdehyde.



Experimental.

1,2-Monoacetone-d-glucofuranose. For preparing this substance, 1,2,5,6-diacetone-*d*-glucofuranose was first prepared by the slight modification of usual method.⁽⁵⁾ That is, 700 c.c. of acetone containing 40 c.c. of concentrated sulphuric acid and a few grams of acetaldehyde were mechanically shaken with 35 g. of usual *α*-*d*-glucose. The colour of the mixture soon became brownish-yellow, and the greater part of *d*-glucose disappeared after a half hour, and all but coarse grains dissolved after an hour. The mixture was neutralized by adding 150 g. of anhydrous powder of sodium carbonate, and then filtered from inorganic substances. Filtrate, coloured in light lemon-yellow, was evaporated to sirup, which was dissolved in water. The water solution was shaken three times with benzene to remove resinous material, benzene extract thus obtained washed twice with water, and combined water solution was extracted six times with each 100 c.c. of chloroform. Chloroform extract, containing diacetone-*d*-glucose, was dried with anhydrous sodium sulphate, and evaporated. About 25 g. of raw diacetone-*d*-glucose was obtained. 1,2-Monoacetone-*d*-glucofuranose was prepared by partial hydrolysis⁽⁶⁾ of diacetone derivative. Namely, 20 g. of the latter was warmed in a water bath at 50° with 400 c.c. of water containing 0.8 g. of concentrated hydrochloric acid. After two hours the mixture was neutralized with excess of silver carbonate, and filtered. The filtrate was freed from silver ions by passing sulphuretted hydrogen, filtered, and evaporated under reduced pressure. The residue was recrystallized from ethyl acetate. Melting point. 160–160.5° (corrected).

1,2-Monoacetone-d-xylo-trihydroxy-glutaric dialdehyde. Ten grams of lead tetracetate were dissolved in 200 c.c. of benzene. To this, 5 g. of monoacetone-glucose were added, and the mixture was shaken and warmed in a water bath for a few minutes. After standing for a short while, the cooled mixture was filtered and the residue was thoroughly washed with 200 c.c. of acetone. Combined filtrate and washings were evaporated under reduced pressure, the temperature of the bath not being allowed to rise above 40°. The thick sirup thus obtained was dissolved in alcohol, filtered and again evaporated in vacuo. This procedure was twice repeated. The remaining sirup was now dissolved in ether, filtered from insoluble material and the solvent was removed under diminished pressure. This sirup was distilled in high vacuum. Boiling point, 132–136° at 0.01–0.02 mm. pressure. It is a colourless, glassy and very thick sirup which can be made powdery. It is also hygroscopic. It reduces Fehling's solution very slowly at room temperature, but at once when heated. (Found: C 51.26, H 6.80. Calc. for C₈H₁₂O₅: C 51.06, H 6.43%). $[\alpha]_D^{20} = 20 \pm 3^\circ$ in alcohol (c=0.65) thirty minutes after solution.

Monohydrazone of 1,2-monoacetone-d-xylo-trihydroxy-glutaric dialdehyde. 1,2-Monoacetone-*d*-xylo-trihydroxy-glutaric dialdehyde (0.5 g.) was dissolved in alcohol and 0.25 g. of phenylhydrazine added to it. The mixture was warmed on a water bath for about 5 minutes, and, after

(5) K. Freudenberg and K. Smeykal, *Ber.*, **59** (1926), 100; *Ber.*, **61** (1928), 1741.

(6) E. Fischer, *Ber.*, **28** (1895), 2496.

cooling, poured into water. The separated oil solidified on standing. It was recrystallized first from the mixture of benzene and petroleum ether, and then twice from dilute alcohol (the mixture of 2 parts of water and 1 part of alcohol). It is colourless needles or leaflets. It melts at 140.5° – 141° (corrected). (Found: C 60.74, H 6.39, N 10.15. Calc. for $C_{14}H_{18}O_4N_2$: C 60.42, H 6.52, N 10.07%). $[\alpha]_D^{20} = -41^{\circ} \pm 1^{\circ}$ (0.2071 g. was made up to 10 c.c. by chloroform, direct reading being -0.84°).

Monosemicarbazone of 1,2-monoacetone-d-xylo-trihydroxy-glutaric dialdehyde. 1,2-Monoacetone-d-xylo-trihydroxy-glutaric dialdehyde (0.2 g.) was dissolved in 4 c.c. of water, and 0.2 g. of semicarbazide hydrochloride and 0.3 g. of potassium acetate were added to it. After standing overnight, fine colourless leaflet separated from the solution. It was filtered and washed with a small quantity of water. Melting point, 209 – 209.5° (corrected, decomposing). (Found: N 17.21. Calc. for $C_9H_{15}O_5N_3$: N 17.14%).

Xylo-trihydroxy-glutaric dialdehyde. 1,2-Monoacetone-d-xylo-trihydroxy-glutaric dialdehyde (0.5 g.) was dissolved in 30 c.c. of 0.1 N sulphuric acid and heated in a boiling water bath for an hour. The solution was neutralized with excess of barium carbonate, small quantity of active charcoal added, and the mixture was filtered. Dialdehyde was obtained as sirup by evaporating the filtrate under reduced pressure. It reduces Fehling's solution after several minutes at room temperature, but at once reduces it strongly when heated.

Bis-phenylhydrazone of xylo-trihydroxy-glutaric dialdehyde. 1,2-Monoacetone-d-xylo-trihydroxy-glutaric dialdehyde (0.5 g.) was hydrolyzed with 30 c.c. of 0.1 N sulphuric acid, and to this mixture 0.5 g. of phenylhydrazine was added. The separated mobile oil was washed with the mixture of benzene and petroleum ether, and the residual oil solidified after standing overnight. It was partly dissolved in a very small quantity of acetone, and then petroleum ether was added to this mixture. The precipitated bis-phenylhydrazone was recrystallized from alcohol. It melts at 126.5° – 127.5° (corrected). It is colourless leaflet. (Found: C 62.05, H 6.53, N 16.86. Calc. for $C_{17}H_{20}O_3N_4$: C 62.18, H 6.17, N 17.06%).

Bis-p-nitro-phenylhydrazone of xylo-trihydroxy-glutaric dialdehyde. 1,2-Monoacetone-d-xylo-trihydroxy-glutaric dialdehyde (0.5 g.) was hydrolyzed with 30 c.c. of 0.1 N sulphuric acid, and to this mixture 0.8 g. of p-nitro-phenylhydrazine dissolved in dilute sulphuric acid was added. Bis-p-nitro-phenylhydrazone precipitated at once from the mixture. It was filtered and washed with water. And the precipitate was recrystallized from pyridine. Yellow needles. It is slightly soluble in alcohol, more in acetone. It melts at 191 – 192° (corrected, decomposing). (Found: N 19.82. Calc. for $C_{17}H_{18}O_7N_6$: N 20.09%).

Strontium 1,2-monoacetone-d-xylyluronate. 1,2-Monoacetone-d-xylo-trihydroxy-glutaric dialdehyde (1 g.) was dissolved in 50 c.c. of water and 8 g. of strontium carbonate and 1.5 g. of bromine were added to it. The mixture was frequently shaken for several hours and then kept standing for two days. It was filtered from strontium carbonate, and dissolved bromine was removed by airing under reduced pressure. Then the solution was stirred on adding silver carbonate to remove bromine ions and

filtered. Sulphuretted hydrogen was passed in the filtrate to eliminate silver ion and the mixture was again filtered. When the filtrate was evaporated under reduced pressure to a small volume, a considerable quantity of white precipitate appeared. Then the concentration was stopped, and alcohol was added to it. The mixture was filtered after standing for a short while. Strontium 1,2-monoacetone-*d*-xyluronate thus obtained is white crystalline powder and is slightly soluble in water. (Found: C 38.41, H 4.63, Sr 17.99. Calc. for $C_{16}H_{22}O_{12}Sr$: C 38.91, H 4.46, Sr 17.75%).

Strontium xylo-trihydroxy-glutarate. 1,2-Monoacetone-*d*-xylo-trihydroxy-glutaric dialdehyde (0.5 g.) was hydrolized with 30 c.c. of 0.1 N sulphuric acid and to this mixture 5 g. of strontium carbonate and 1.6 g. of bromine were added. After standing overnight it was filtered and the filtrate was treated just like above mentioned method for strontium 1,2-monoacetone-*d*-xyluronate. Strontium xylo-trihydroxy-glutarate is slightly soluble in water. (Found: Sr 33.46. Calc. for $C_5H_6O_7Sr$: Sr 32.98%).

Summary.

By the oxidation of 1,2-monoacetone-*d*-glucofuranose with lead tetraacetate, 1,2-monoacetone-*d*-xylo-trihydroxy-glutaric dialdehyde was obtained, which distils at 132–136° at 0.01–0.02 mm. pressure, and has specific rotatory power, $[\alpha]_D^{25}$, of $20^\circ \pm 3^\circ$ in alcohol. Its monophenylhydrazone melts at 140.5–141° and has specific rotatory power, $[\alpha]_D^{25}$, of $-41^\circ \pm 1^\circ$ in chloroform, and its monosemicarbazone melts at 209.5°. 1,2-Monoacetone-*d*-xylo-trihydroxy-glutaric dialdehyde was hydrolized to xylo-trihydroxy-glutaric dialdehyde and *bis*-phenylhydrazone and *bis-p*-nitrophenyl-hydrazone of the latter were obtained. Melting points of them are 126.5–127.5° and 191–192° respectively. 1,2-Monoacetone-*d*-xylo-trihydroxy-glutaric dialdehyde and xylo-trihydroxy-glutaric dialdehyde were oxidized by bromine in presence of strontium carbonate, and strontium 1,2-monoacetone-*d*-xyluronate and strontium xylo-trihydroxy-glutarate were obtained respectively.

In conclusion the author wishes to express his hearty thanks to Prof. B. Kubota for his kind advice for this experiment.

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Polymerisation of Tung Oil. V. Effects of Treated Fatty Oils upon the Gelation of Tung Oil.

By Monzi TATIMORI.

(Received November 28, 1940.)

As the nature of fatty oil is markedly affected by various treatments, the effect of several kinds of fatty oil treated by different ways upon the gelation time of tung oil is dealt in the present paper.

Cooked drying oils. Drying oils such as linseed or perilla oils are usually cooked and at the end of cooking they turn by oxidation or polymerisation into a gelatinous state, therefore the gelation preventing action of these oils upon tung oil should be affected by their cooking degree. To obtain the relation between x_{∞} and the cooking degree, the following experiments were done. The measurements of gelation times carried out at 270°C. were the same as in the previous report.

I. Oxidised and polymerised linseed oils. The cooked oils were obtained by oxidising linseed oil at 100°C. with oxygen, and by polymerising it at 287°C. in carbon dioxide atmosphere.

Table 1. Raw linseed oil.

(iodine value 172.4).

x (%)	t (270°C.)	t (280°C.)
10.40	1040	730
20.00	1228	841
30.15	1576	1075
x_{∞}	67%	66%

Table 2. Oxidised linseed oil No. 1.

(iodine value 140.8).

x (%)	t (270°C.)	t (280°C.)
10.22	989	691
20.21	1167	828
30.86	1367	950
x_{∞}	85%	86%

Table 3. Oxidised linseed oil No. 2.

(iodine value 124.1).

x (%)	t (270°C.)	t (280°C.)
10.40	944	688
20.71	1036	751
30.97	1165	843
x_{∞}	122%	122%

Table 4. Oxidised linseed oil No. 3.

(iodine value 115.9).

x (%)	t (270°C.)	t (280°C.)
15.0	971	719
30.6	1068	798
x_{∞}	196%	198%

Table 5. Polymerised linseed oil
No. 1.

(iodine value 161.0).

x (%)	t (270°C.)
0	882
5.23	942
15.1	1106
30.9	1595
x_{∞}	69%

Table 6. Polymerised linseed oil
No. 2.

(iodine value 140.3).

x (%)	t (270°C.)
7.73	947
10.00	1010
15.00	1067
30.00	1430
x_{∞}	73%

Table 7. Polymerised linseed oil
No. 3.

(iodine value 124.1),

x (%)	t (270°C.)
10.58	985
20.55	1146
29.28	1230
x_{∞}	87%

Table 8. Polymerised linseed oil
No. 4.

(iodine value 122.2).

x (%)	t (270°C.)
15.04	1085
30.40	1435
x_{∞}	88%

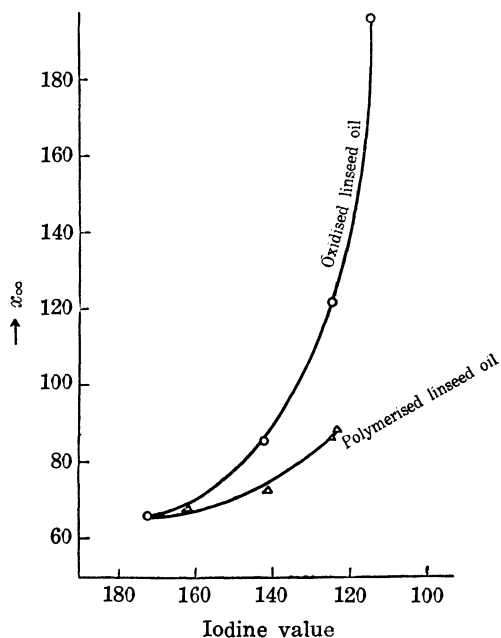


Fig. 1.

The relation of x_{∞} to the iodine value of cooked oils is shown in Fig. 1.

From Fig. 1 it is noticed that the value of x_{∞} increases with the increase of cooking degree; that is, the gelation-preventing action becomes weaker, as the cooked oil itself has the gelation tendency.

For the same cooking degree, the value of x_{∞} for the oxidised linseed oil is greater than that for the polymerised oil. This coincides with the fact that the drying power of oxidised oil is always greater than that of polymerised oil⁽¹⁾.

II. Oxidised perilla oil. The gelation retarding effect of the oxidised perilla oils oxidised at 100°C., 200°C. and 300°C. was measured.

(1) M. Tatimori, *Hitachi Hyoron*, **20** (1937), 43.

Perilla oil taken in 1l. beaker were oxidised, by air-blowing at temperatures of 100°C., 200°C. and 300°C. respectively. The oxidised oils then had the following constants.

Table 9.

Kind of oil		Abbreviation	Iodine value
Raw Perilla oil		200 (0)	210.0
Oxidised at	100°C.	170 (100)	175.5
„	200°C.	170 (200)	177.6
„	300°C.	170 (300)	177.5
„	100°C.	150 (100)	160.4
„	200°C.	150 (200)	156.5
„	300°C.	150 (300)	149.9
„	100 C.	140 (100)	140.7
„	200°C.	140 (200)	140.9
„	300°C.	140 (300)	137.5

Table 10.

Kind of oil and Remarks	Amount of addition (x %)	Gelation time (t, sec.)	Kind of oil and Remarks	Amount of addition (x %)	Gelation time (t, sec.)
200 (0) : The relation between $1/t$ and x is linear and the value of x_{∞} becomes 59.5%.	0 10 20 30 40 50	881 1040 1254 1622 2338 3899	150 (200) : A curved line is obtained, the estimated value of x_{∞} is 84%.	0 10 20 30 40 50	885 950 1050 1184 1375 1590
170 (100) : The relation of $1/t$ and x forms a convex curve, the estimated value of x_{∞} is 62%.	0 10 20 30 40 50	888 1017 1140 1409 1794 2695	150 (300) : A straight line is obtained, x_{∞} is 89%.	0 10 20 30 40 50	870 980 1120 1269 1498 1777
170 (200) : The relation of $1/t$ and x forms nearly a straight line and x_{∞} is 66%.	0 10 20 30 40 50	884 1057 1170 1524 1935 2842	140 (100) : A curved line is obtained.	0 10 20 30 40 50	886 899 940 982 1018 1086
170 (300) : The relation between $1/t$ and x is linear and x_{∞} is 66%.	0 10 20 30 40 50	885 1144 1348 1660 2197 3130	140 (200) :	0 10 20 30 40 50	884 910 983 1074 1177 1298
150 (100) : A curved line is obtained, the estimated value of x_{∞} is 67%.	0 10 20 30 40 50	886 942 1032 1200 1464 2040	140 (300) : The relation between $1/t$ and x is linear and x_{∞} is 110%.	0 10 20 30 40 50 100	884 930 1018 1101 1255 1422 5012

The relations between the reciprocals of gelation times and the amount of addition of oils are shown in Fig. 2.

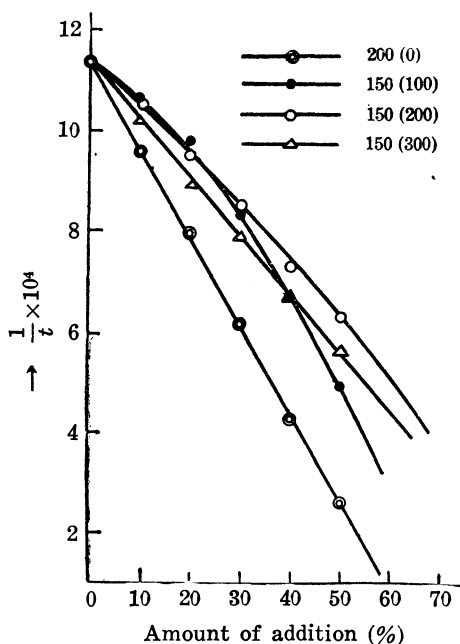


Fig. 2.

From the above results it is concluded that with the addition of oxidised oils at 300°C. the relation of $1/t$ and x are linear, on the contrary in the cases of oxidised oils at 100°C. curved lines are obtained and in the cases of oxidised oils at 200°C., those of the beginning of cooking, a straight line, but those of the increased degree of cooking curved lines are obtained.

It is supposed that oxidised fatty oil prepared at low temperature contains a substance which has special action upon the gelation of tung oil. M. Nakamura⁽²⁾ reported that oxidised fatty oil prepared at temperatures lower than 160°C. contains a peroxide, while high temperature oxidation oil does not contain it. The author conformed from a qualitative experiment that the oil oxidised at 100°C. contains peroxide, while that oil oxidised at 300°C. does not contain it.

Therefore the curved nature of the relation between $1/t$ and x is supposed to be due to the peroxide contained in the oil.

III. Effect of benzoyl peroxide. To verify the above presumption the effect of benzoyl peroxide were studied.

Table 11. Effect of perilla oil added with 5% of benzoyl peroxide.

x (%)	t (sec.)
0	885
10	1032
20	1168
30	1512
40	2111
50	3762

Table 12. Effect of perilla oil added with 10% of benzoyl peroxide.

x (%)	t (sec.)
0	878
10	981
20	1125
30	1353
40	1775
50	2911

(2) *J. Chem. Ind. Japan*, **40** (1937), 448.

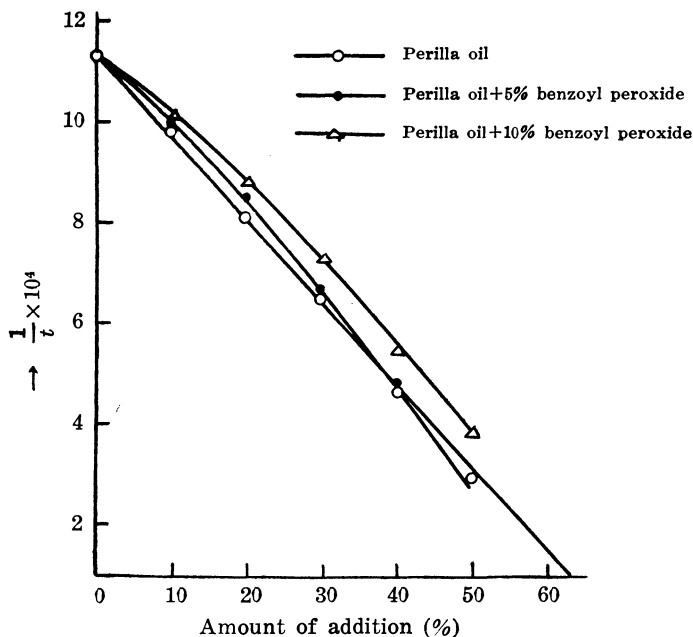


Fig. 3.

The nature of the curve is similar to that of oxidised perilla oil prepared at 100°C.

From the above results benzoyl peroxide has a great accelerating action upon the gelation of tung oil. It is a well known fact that peroxides have accelerating actions upon the polymerisation of butadiene and styrol. It is concluded that the curved nature of $1/t-x$ relation of oxidised perilla oil is due to the superposed effects of retarding action of oxidised perilla oil and of accelerating action of peroxide contained in it. The relation of x_{∞} to the degree of cooking of oxidised oil prepared at 300°C. is shown in Table 14.

Table 14.

Kind of oil	x_{∞} (%)	Iodine value
200 (0)	59.5	210.0
170 (300)	66.0	177.5
150 (300)	89.0	149.9
140 (300)	110.0	137.5

The value of x_{∞} increases according to the increase of cooking degree. This tendency is similar to that of the cooked linseed oil.

Table 13.

Effect of benzoyl peroxide.

x (%)	t (sec.)
0	883
0.1	860
0.3	837
0.5	810
0.8	760
1.0	730
10.0	349
20.0	148
30.0	23

Table 15. Brominated soya bean oil (Br content 31.3%).

x (%)	t (270°C.)
0	904
1.09	885
2.07	958
3.00	1410

The gelation preventing action is very strong and the value of x_{∞} is less than 6%.

Table 16. Brominated soya bean oil (Br content 16.4%)

x (%)	t (270°C.)
0	903
1.19	791
2.27	1088
3.00	3818

The value of x_{∞} is 3.5%.

Table 17. Brominated oleic acid (Br content 17.7%).

x (%)	t (270°C.)
0	1086
1.43	1291
2.00	1994

The value of x_{∞} is less than 3.0%.

IV. Brominated fatty oils.

Brominated fatty oils and fatty acids have a strong gelation—retarding action. On heating the brominated fatty oil the hydrogen bromide is evolved. It is supposed therefore that the gelation—preventing action of brominated oils is due to the isomerizing action of hydrogen bromide exerting on the conjugated double bond of the tung oil molecule.

Summary.

1. The gelation—preventing actions of oxidised and polymerised linseed oil were measured. The value of x_{∞} increases with the increasing degree of cooking and the value for oxidised oils is always greater than that for polymerised oils of the same cooking degree.

2. Perilla oil was oxidised at 100°C., 200°C. and 300°C. to the degrees of iodine values 170, 150, 140 and the effects upon the gelation were measured. In the cases of oxidised oil prepared at 300°C. the relation of $1/t \sim x$ was linear and the value of x_{∞} increase according to the increase of cooking degree. In the cases of oxidised at 100°C. and 200°C. curved lines were obtained. This tendency is supposed to be due to the peroxide contained in it.

3. The effect of benzoyl peroxide also was examined. Benzoyl peroxide has a strong gelation accelerating action. The effect of perilla oil added with benzoyl peroxide is similar to that of perilla oil oxidised at low temperature.

4. The gelation—preventing action of brominated oils is very strong and the value of x_{∞} is less than 4%. Therefore, these substances can be used as a strong gelation—preventing agent.

In conclusion, the author wishes to express his sincere thanks to Dr. K. Baba, Dr. T. Yosioka, and Mr. K. Yokota, for their kind guidance.

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Polymerisation of Tung Oil. VI. Effects of Fatty Acids, Fatty Alcohols and Several Organic Substances upon the Gelation of Tung Oil.

By Monzi TATIMORI.

(Received November 28, 1940.)

I. Fatty Acids. It is a well known fact that the addition of any acidic substance retards the gelation of tung oil when cooked⁽¹⁾, and the gelation time of tung oil increases in proportion to the increasing degree of acidity of the oil⁽²⁾. The interpretation of the mechanism for this retarding action has been attempted by some investigators⁽³⁾, but it is likely that there is not yet a definite theory hereabout.

The measuring methods of the gelation time etc. were the same as those described in the previous report.

(1) *Simple fatty acids.* The Merck's pure stearic, oleic and linolic acids were used. The gelation times measured in second are shown in Table 1 and 2.

Table 1.

	Temp. (°C.)	0%	5%	7.5%	10.0%	12.5%	15.0%
Stearic acid	260	1386	1626	—	1957	—	—
	270	940	1115	1250	1397	1501	1768
	280	682	819	928	1053	1199	1482
Linolic acid	260	1340	1526	—	1769	1959	2226
	270	937	1068	1160	1262	1380	1592
	280	682	782	869	956	1050	1334

Table 2. Oleic acid.

Temp. (°C.)	0%	5%	7.5%	10.0%	12.5%	15.0%	20.0%
320	282	378	—	1560	—	—	—
310	349	475	—	781	—	4980	—
300	405	520	580	722	1130	2988	—
290	532	643	—	830	—	1482	—
280	702	834	908	1036	1192	1476	9720
270	961	1132	1207	1327	1765	1892	2820
260	1320	1575	1727	1911	2132	2369	3588
250	1995	2253	—	2699	—	3420	—

(1) R. Bürstinbinder, *Farben Ztg.*, **23** (1917), 243; H. Rhodes, J. Potts, *Chem. Metall. Eng.*, **29** (1923), 533.

(2) H. A. Gardner, *Chem. Absts.*, **15** (1921), 1081.

(3) Krumbhaar, *ibid.*, **9** (1915), 2155; L. A. Jordan, *J. Chem. Ind.*, **53** (1934), 1.

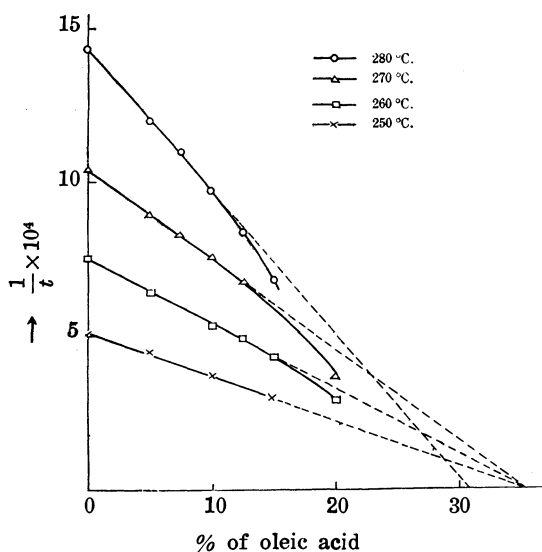


Fig. 1.

The relations between the reciprocals of gelation time ($1/t$) and the percentage of oleic acid (x) present are shown in Fig. 1.

(2) *Mixed fatty acids.* The fatty acids of tung, linseed, soyabean and sesame oils were prepared by the saponification of the respective oils by the usual methods. The gelation times are shown in the following tables.

Table 3. Tung oil acids.

Temp. (°C.)	6.9%	9.8%	14.4%	19.8%
270	1046	1150	1318	1570
280	730	808	945	1151

Table 4. Linseed oil acids.

Temp. (°C.)	5.07%	10.2%	15.0%	20.2%
270	1016	1196	1466	1948
280	726	884	1121	1677

Table 5. Soya bean oil acids.

Temp. (°C.)	5.09%	10.1%	14.7%	19.6%
270	1062	1278	1578	1771
280	775	938	1236	2269

Table 6. Sesame oil acids.

Temp. (°C.)	5.0%	10.9%	15.0%	20.3%
270	1152	1482	1764	2601
280	801	1063	1427	2361

The linear relations exist between $1/t$ and x , when x is less than 15%, beyond which curved lines are obtained. The values of x_{∞} can be

Table 7. α_{∞} (at 270°C.)

Stearic acid	32.0%
Oleic acid	33.5
Linolic acid	38.0
Fatty acids of sesame oil	33.3
Fatty acids of soya bean oil	34.0
Fatty acids of linseed oil	35.0
Fatty acids of tung oil	42.0

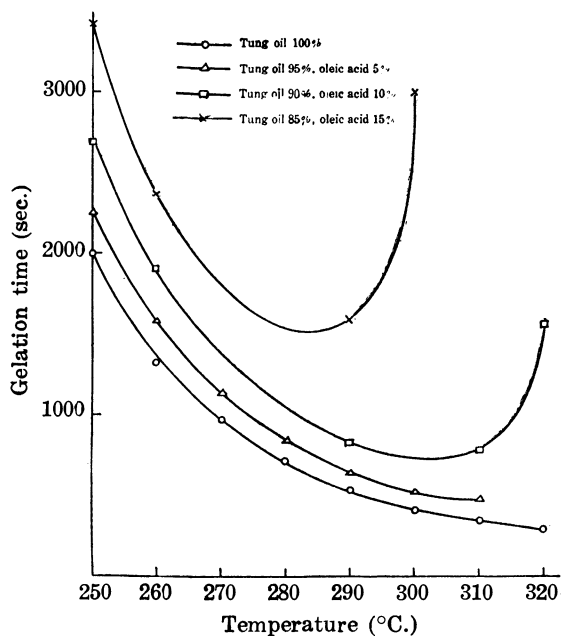


Fig. 2.

calculated from the initial inclination of the lines. The results thus obtained are summarized in the following table.

From the above results it is concluded that the value of α_{∞} becomes greater as the degree of unsaturation of fatty acid increases.

The temperature effect of the gelation time of the system added with oleic acid is shown in Figs. 2 and 3.

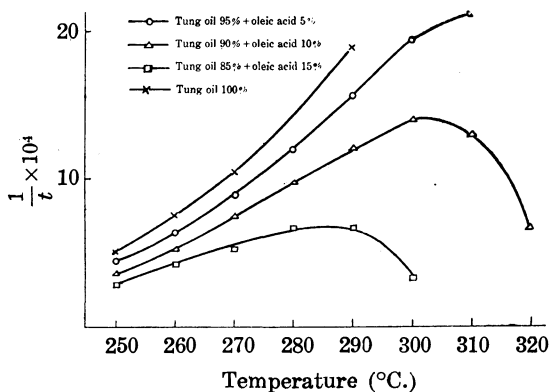


Fig. 3.

In general, oleic acid behaves like linseed oil.

II. Fatty Alcohols. Next, the effects of fatty alcohols which from the standpoint of esterification have the natures opposite to those of fatty acids, were measured. Numerical data are shown below.

(1) *Glycerine* (30° Be').

Table 8.

Temperature	Glycerine added x (%)	Gelation time t (sec.)	$\frac{1}{t} \times 10^4$
280°C.	0	674	14.84
	5.25	1589	6.29
	7.76	2731	3.66
	19.20	3650<	2.74>
290°C.	0	436	22.94
	5.11	620	16.13
	9.09	2794	3.58
	11.92	3484<	2.87>

As glycerine does not mix with tung oil, the measurement was carried out by weighing both materials into the test tubes, and the mixture was stirred with a glass rod during the first two minutes while the determination was carried on.

From the $1/t-x$ curve it is seen that the gelation-retarding action of glycerine becomes more intense as the amount of glycerine increases, than it could be expected from the linear relation of initial part. The results obtained without stirring the mixture are shown in Table 9.

Table 9.

Temperature	x (%)	t (sec.)	$\frac{1}{t} \times 10^4$
270°C.	0	885	11.30
	5.26	958	10.44
	10.08	1045	9.57
	13.50	1085	9.22
	20.60	1257	7.96

The gelation time is greatly affected by the mechanical stirring; and the value of x_∞ may be considered to be less than 10%, when the system of tung oil and glycerine is violently stirred.

(2) *Cetyl alcohol* $C_{16}H_{34}O$.

Table 10.

x (%)	t (280°C.)	t (270°C.)	t (260°C.)
0	671	919	1344
5	740	1054	1474
10	897	1309	1965
15	1159	1705	2486

The relation of $1/t$ to x is given by a curved line V, the value of x_∞ becoming 31% when estimated from the data with samples containing 10 to 15% of cetyl alcohol.

(3) *Oleyl alcohol* $C_{18}H_{36}O$.

Table 11.

x (%)	t (280°C.)	t (270°C.)	t (260°C.)
0	665	906	1346
5	763	1097	1542
10	902	1295	1844
15	1210	1619	2256

The general tendency is the same as that of cetyl alcohol and x_∞ becomes 32.5%.

(4) *Mono-glyceride of oleic acid.*

Table 12.

x (%)	t (280°C.)	t (270°C.)	t (260°C.)
0	660	902	1306
5	766	1035	1489
10	998	1388	1887
15	1731	2227	2879
20	3439	4182	4860

Mono-glyceride of oleic acid is prepared as usual by heating glycerine and an equivalent amount of oleic acid with 1% of sulphuric acid.

The relation of $1/t$ and x is nearly linear and the value of x_{∞} is 24.5% at 270°C. The gelation-preventing power is very intense.

(5) *Mono-glycol ester of oleic acid.*

Table 13.

x (%)	t (280°C.)	t (270°C.)	t (260°C.)
0	635	902	1300
5.43	724	1030	1512
10.00	863	1231	1728
15.73	1162	1502	2090
20.40	1684	2121	2712

The mono-glycol ester of oleic acid is synthesized in the same way as the case with mono-glyceride. The general tendency is the same as in mono-glyceride, the value of x_{∞} amounting to 35%.

Fig. 4 shows the results obtained for four systems of tung oils added respectively with 10, 20% of oleyl alcohol, and 9.7, 13.5% of mono-glyceride.

At elevated temperatures near 300°C. the gelation time reaches a minimum value and again it increases

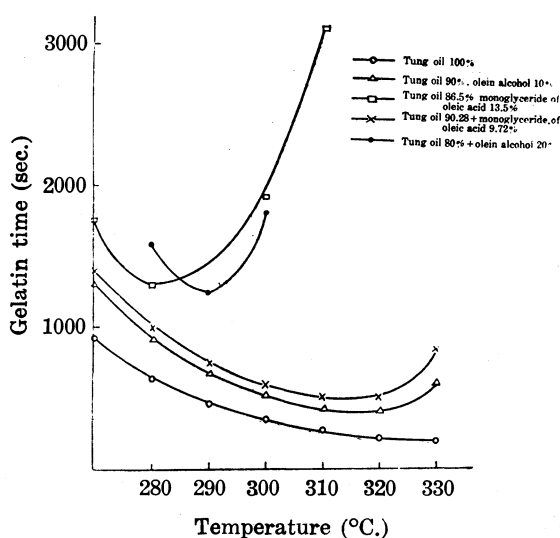


Fig. 4.

as the temperature increases. This tendency is the same as in fatty acids.

The fact that glycerine has a remarkable gelation-retarding action has been reported by Rhodes and Potts, but on the effect of mono-glyceride and fatty alcohols no report has been published.

In the cases of monovalent alcohol such as oleic, cetyl and mono-glycol ester, the values of x_{∞} become 33, 31 and 35% respectively. On the other hand in the polyvalent alcohols such as glycerine, glycerine mono-ester, x_{∞} amount to 10 and 14%. The peculiar behavior of glycerine is thus anticipated.

It is known that the exchange of glycerine radical occurs when fatty oil is heated with alcohols⁽⁴⁾. Therefore the exchange of alcohol radical plays a part in the gelation-retarding effect of glycerine.

From the results of author's experiments monovalent alcohols have the retarding effect comparable to that of fatty acids. It follows therefore that another consideration should be given for this case.

III. Several Organic Substances. (1) *Hydrocarbons.* (a) Solid paraffin (Solidifying point 53°C.).

Table 14.

Solid paraffin (%)	Gelation time (sec.)
0	1247
15	1719
20	1952

The percentage of solid paraffin added (x) behaves linearly to the reciprocals of the gelation time ($1/t$) and the value of x_{∞} is 56%.

(b) Mobile oil A (Boiling range 195~230°C. at 1 mmHg.).

The linear relation also exists in this case between $1/t$ and x , the value of x_{∞} being 53%.

Table 15.

x (%)	t (sec.)
10	1102
15	1226
20	1428

(2) *Organic acids.* (a) Aromatic acids. The gelation-retarding effects of benzoic acid, cinnamic acid and phthalic acid anhydride were tested and their results are shown in Fig. 5.

The gelation-retarding effects of benzoic acid and cinnamic acid are very remarkable and the value of x_{∞} become 18 and 25%, respectively. Phthalic acid anhydride has also retarding effect, but not so remarkable as the former two acids, probably on account of its less soluble nature in tung oil.

(b) Aliphatic polybasic acids. Succinic, malic, citric and tartaric acids were tested and their results are shown in Fig. 6.

Malic acid has a strong effect and the value of x_{∞} is 19% at 270°C. Succinic acid has a poor gelation retarding action and citric acid shows practically no effect. Tartaric acid has, on the other hand, an accelerating action.

(c) Miscellaneous acids. Tannic and gallic acids, and pyrogallol were tested and their results are shown in Fig. 7.

(4) H. H. Young, H. C. Black, *J. Am. Chem. Soc.*, **60** (1938), 2603.

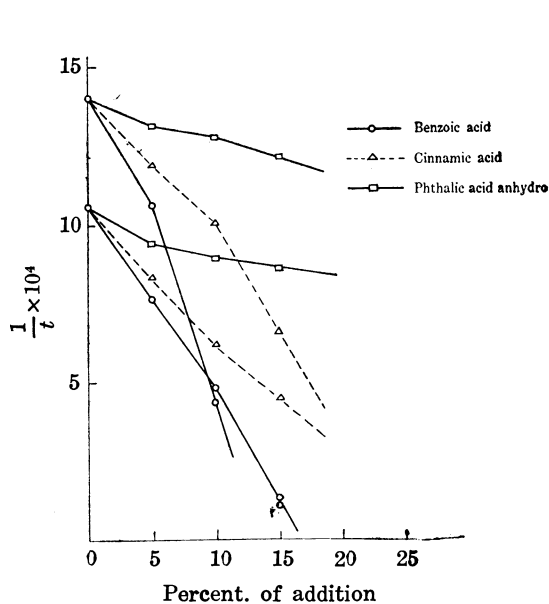


Fig. 5.

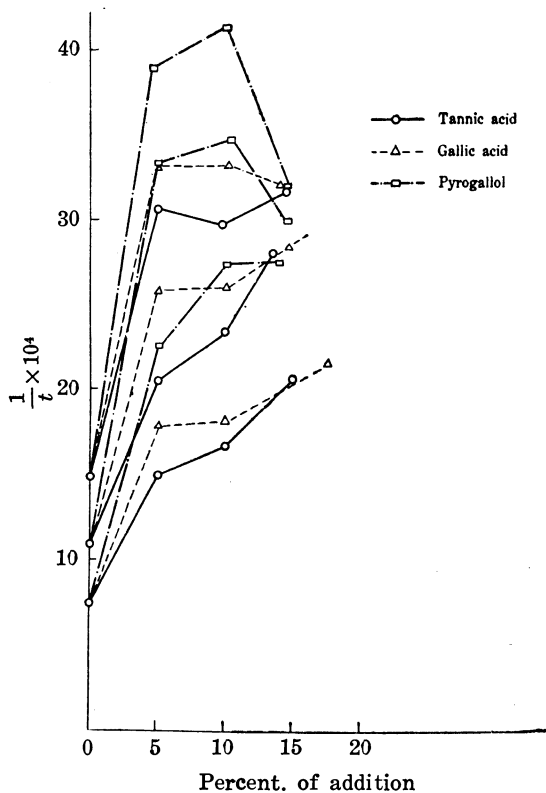


Fig. 7.

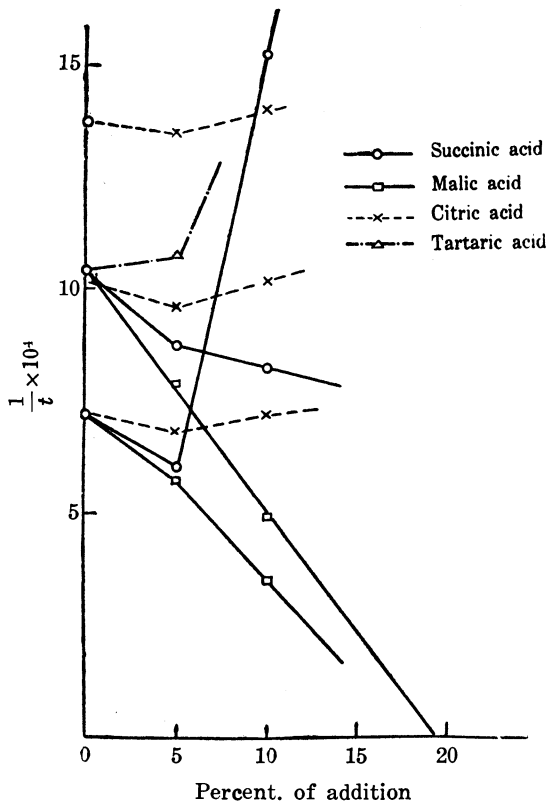


Fig. 6.

These acids have poor solubility in tung oil, but all of them have weak accelerating effects.

(3) *Aromatic substances.*

(a) *α -Naphthylamine.*

Table 16.

x (%)	t (sec.)
0	898
4.90	1015
9.98	1170
15.0	1381

The linear relation exists between $1/t$ and x and the value of x_{∞} becomes 42.3%.

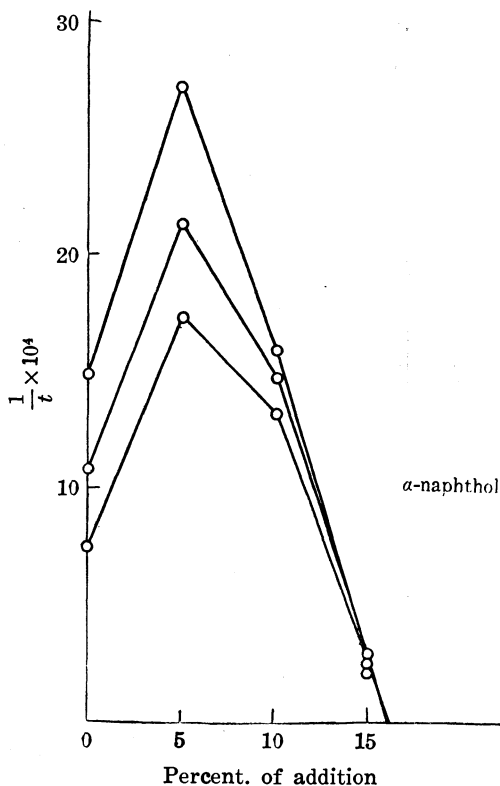


Fig. 8.

butyl stearate, tricresyl phosphate, triacetin and Sipalin AOM (methylcyclohexanol ester of adipic acid) were tested. They have also the gelation retarding effects and the linear relations are held between $1/t$ and x in each case. The value of x_{∞} at 270°C . are summarized in the following table.

Table 18.

Substances	x_{∞} (%)
Butyl stearate	44.8
Tricresyl phosphate	62.5
Triacetin	54.0
Sipalin AOM	57.0

Summary.

(1) The effects of fatty acids, fatty alcohols, and other several organic substances upon the gelation of tung oil were studied.

(2) As simple fatty acids, stearic, oleic and linolic acid, as mixed fatty acids, tung oil, linseed oil, soya bean oil and sesame oil acids were used. The gelation-preventing actions of these acids are stronger than that of fatty oils and the relation of $1/t-x$ are linear, when x is less than 15%, beyond which curved lines are obtained. The value of x_{∞} becomes greater as the degree of unsaturation of fatty acids increases.

(3) As fatty alcohols, glycerine, cetyl alcohol, oleyl alcohol, monoglyceride of oleyl acid, monoglycol ester of oleic acid were used. The

(b) Hydroquinone.

Table 17.

x (%)	t (sec.)
0	888
5	908
10	926
15	947

The linear relation exists between $1/t$ and x and the value of x_{∞} amounts to 236%.

(c) α -Naphthol. The results are shown in Fig. 8. Up to 10% addition it has an accelerating effect, but beyond this limit it acts inversely and prevents the gelation.

(d) β -Naphthol. The relation between $1/t$ and x appears to form a curved smooth line and in this case no inversion is observed.

(4) *Esters*. Of the plasticizers for cellulose ester lacquers,

gelation-preventing actions of these monovalent alcohols are strong and their order are similar to that of fatty acids.

Glycerine and monoglyceride of oleic acid have very strong gelation-preventing actions and their retarding nature is probably due to special chemical reaction such as exchange of glycerine radicals.

(4) Among the several organic substances tested by the author, neutral substances such as solid paraffin, mobile oil, butyl stearate, triacetin, tricresyl phosphate, Sipalin AOM, α -naphthylamine, hydroquinone, β -naphthol have the retarding effects and the linear relations exist between $1/t$ and x . Benzoic acid, phthalic acid anhydride and malic acid have remarkable retarding effects, but their relations between $1/t$ and x are irregular.

Tartaric, tannic and gallic acids and pyrogallol have accelerating actions. The behavior of α -naphthol is very noteworthy; that is, it accelerates the gelation of tung oil when the amount of addition is less than 10%, but beyond this limit it retards the gelation of tung oil.

In conclusion, the author wishes to express his sincere thanks to Dr. K. Baba, Dr. T. Yosioka, and Mr. K. Yokota for their kind guidance.

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Studies on the Derivatives of Biphenylene Oxide. VI.

4-Nitrobiphenylene Oxide and its Derivatives.

By Seishi YAMASHIRO.

(Received February 3, 1941.)

In the previous communication⁽¹⁾, it was shown by the present author that the mononitrobiphenylene oxide melting at about 91–93° (uncorr.), which was obtained from the nitration products of biphenylene oxide by fractional distillation and fractional crystallization, should be 4-nitrobiphenylene oxide, not being 1-nitrobiphenylene oxide. This conclusion, however, was nothing but an assumption based upon the tendency of substitution of the hydrogen atoms of biphenylene oxide by the nitro group, because till that time 1-nitrobiphenylene oxide had not yet been prepared by anyone. In the recent investigation⁽²⁾ 1-nitrobiphenylene oxide was prepared, and lately a pure mononitrobiphenylene oxide melting at 126–126.5° (corr.) was isolated by the same author from the above-mentioned fraction melting at 91–93°, by means of repeated recrystallization from glacial acetic acid for the removal of contaminated 2- and 3-nitrobiphenylene oxides. This newly isolated nitro compound was ascertained to be 4-nitrobiphenylene oxide by the depression of its melting point then occurred when mixed with 1-, 2- or 3-nitrobiphenylene oxide. Judging from the yields of 2-nitro (71%), 3-nitro (10%), 4-nitro (crude product, 5%; purified product, 1%) and 1-nitro (none was isolated) compounds, the tendency of the introduction of the nitro group in the formation of the mononitrobiphenylene oxides must be in the order of the positions 2>3>4>1.

Amido-, acetamido-, dinitro-, trinitro-, tetranitro-, and bromonitrobiphenylene oxides were derived from 4-nitrobiphenylene oxide in confirmation of the last compound. The constitutions of those derivatives were determined, and then the physical properties and the absorption spectra of the four mononitrobiphenylene oxides and their corresponding derivatives were compared one another as in Tables 1–7 and Figs. 1–5 respectively, which will be utilized for the benefit of isolation and identification of those compounds.

The compounds obtained newly by the present author are asterisked in the above tables. Of those compounds, 6-bromo-1-nitro-, 6-bromo-3-nitro- and 6-bromo-4-nitro-biphenylene oxides were prepared from the corresponding nitro compounds by bromination in glacial acetic acid, and 4,6-dinitro-, 2,4,6-trinitro-, and 2,4,6,7-tetranitro-biphenylene oxides, from 4-nitrobiphenylene oxide by successive nitrations. The constitution of those new compounds were established as follows.

(1) S. Yamashiro, *J. Chem. Soc. Japan*, **57** (1936), 715.

(2) S. Yamashiro, *ibid.*, **59** (1938), 950.

Comparison of the physical properties.

Table 1. Mononitrobiphenylene oxides.

Compound	M.p.(corr.)	Crystal (Crystallizing solvent)	Solubility (e : easily soluble, m : moderately soluble, d : difficultly soluble ; e>m>d.)									
			Ligroin	Ether	Carbon tetra-chloride	Chloro-form	Benzene	Methanol	Ethanol	Actone	Acetic acid	Ethyl acetate
1-Nitro	138 -139°	Pale yellow needle (Ethanol)	d	e	e	e	e	m	m	e	m	e
2-Nitro	186 -186.5°	Pale yellow needle (Acetic acid)	d	d	m	m	m	d	d	m	m	m
3-Nitro	158.5-159.5°	Pale yellow needle (Ethanol)	d	d	m	e	e	m	m	e	m	e
*4-Nitro	126 -126.5°	Pale yellow needle (Acetic acid)	m	e	e	e	e	m	m	e	m	e

Table 2. Amidobiphenylene oxides.

1-Amido	118 -119°	Colourless needle (Ethanol)	e	e	e	e	e	e	e	e	e	e
2-Amido	99°	Colourless needle (Ethanol-water)	d	e	e	e	e	e	e	e	e	e
3-Amido	125 -125.5°	Colourless needle (Ethanol-water)	m	e	e	e	e	e	e	e	e	e
*4-Amido	113.5-114.5°	Colourless needle (Ligroin)	m	e	e	e	e	e	e	e	e	e

Table 3. Acetamidobiphenylene oxides.

1-Acetamido	235 -236°	Colourless short needle (Ethanol-water)	d	d	e	e	e	e	e	e	e	e
2-Acetamido	182°	Colourless needle (Ethanol-water)	d	e	m	e	e	e	e	e	e	e
3-Acetamido	166 -166.5°	Colourless needle (Ethanol)	d	d	m	m	m	m	m	e	e	e
*4-Acetamido	259 -260°	Colourless long needle (Ethanol)	d	d	d	e	m	m	m	e	m	e

Table 4. Dinitrobiphenylene oxides.

Compound	M.p. (corr)	Crystal (Crystallizing solvent)	Solubility (e : easily soluble, m : moderately soluble, d : difficultly soluble ; e>m>d.)									
			Ligroin	Ether	Carbon tetra-chloride	Chloro-form	Benzene	Methanol	Ethanol	Actone	Acetic acid	Ethyl acetate
1,6-Dinitro	263 -264°	Colourless needle (Acetic acid)	d	d	d	m	m	d	d	m	m	m
2,6-Dinitro	255 -256°	Pale yellow needle (Benzene)	d	d	d	m	m	d	d	m	m	m
3,6-Dinitro	329 -330°	Colourless needle (Acetone)	d	d	d	m	m	d	d	m	m	m
*4,6-Dinitro	241 -242°	Colourless needle (Acetic acid)	d	d	d	e	m	d	d	m	m	m
1,8-Dinitro	351 -352°	Pale yellow needle (Ethanol)	d	d	d	d	d	d	d	d	d	d
2,7-Dinitro	326 -327°	Colourless needle (Acetic acid)	d	d	d	d	d	d	d	d	d	d

Table 5. Trinitrobiphenylene oxides.

1,3,6-Trinitro	312 -313°	Small colourless rhombic plate (Benzene)	d	d	d	d	m	d	d	m	m	m
1,3,8-Trinitro	260 -261°	Pale yellow hexagonal plate (Acetone-ethanol)	d	d	d	e	e	d	d	e	e	e
2,3,6-Trinitro	237 -238°	Pale yellow hexagonal plate (Benzene)	d	d	d	d	m	d	d	e	m	e
2,3,7-Trinitro	276.5-277.5°	Pale yellow needle (Benzene)	d	d	d	e	m	d	d	e	e	e
*2,4,6-Trinitro	207 -208°	Pale yellow needle (Ethanol)	d	d	d	e	e	m	m	e	e	e

Table 6. Tetranitrobiphenylene oxides.

Compound	M.p. (corr.)	Crystal (Crystallizing solvent)	Solubility (e : easily soluble, m : moderately soluble, d : difficultly soluble; e>m>d.)									
			Ligroin	Ether	Carbon tetra-chloride	Chloro-form	Benzene	Methanol	Ethanol	Acetone	Acetic acid	Ethyl acetate
1,3,6,8-Tetranitro	262 -263°	Colourless prism (Acetic acid)	d	d	d	d	m	d	d	e	m	e
1,3,6,7-Tetranitro	249 -250°	Colourless needle (Benzene)	d	d	d	d	m	m	m	e	e	e
2,3,6,7-Tetranitro	285 -286°	Colourless needle (Benzene)	d	d	d	d	m	d	d	e	m	e
*2,4,6,7-Tetranitro	253 -254°	Colourless rectangular plate (Benzene)	d	d	d	d	m	d	d	e	m	m

Table 7. Bromonitrobiphenylene oxides.

6-Bromo-1-nitro	231 -232°	Small colourless needle (Carbon tetrachloride)	d	d	m	e	e	d	m	e	m	e
6-Bromo-2-nitro	258 -259°	Colourless needle (Acetic acid)	d	d	m	m	m	d	d	m	m	m
*6-Bromo-3-nitro	226 -227°	Colourless rhombic plate (Acetone)	d	d	m	e	e	d	d	m	m	m
*6-Bromo-4-nitro	189.5-190.5°	Yellow long needle (Acetic acid)	m	e	e	e	e	m	m	e	m	e

The bromination of biphenylene oxide in glacial acetic acid takes place, as shown in Part V⁽³⁾, smoothly at the position 3, not at 1, 2, and 4. This directive action in one phenylene residue of biphenylene oxide must be strengthened by the introduction of a negative nitro group in the other phenylene residue. On the other hand, the bromination of mononitro- and dinitro-biphenylene oxides were examined by the author to be found that no bromine atom can be introduced smoothly into the phenylene residue, in which a nitro group is present. That is to say, the mononitro compounds gave only monobromo derivatives in good yield, whereas the dinitro compounds which have each of the nitro groups in both phenylene residues of a molecule, as in 1,8-, 2,6-, 2,7-, and 3,6-dinitro compounds, gave no bromo derivatives. From those experimental results, it can be concluded that the bromination of *x*-nitrobiphenylene oxide (*x*=1, 2, 3, or 4) gives 6-bromo-*x*-nitrobiphenylene oxide as a main product. A support of this view can be found in the paper communicated by H. Gilman and his co-workers⁽⁴⁾, who had obtained 6-bromo-2-nitrobiphenylene oxide from 2-nitrobiphenylene oxide.

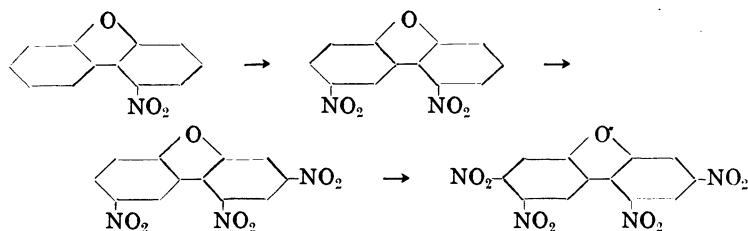
The dinitrobiphenylene oxide derived from 4-nitrobiphenylene oxide must have each of the nitro groups in both phenylene residues separately, forming 4,6-dinitrobiphenylene oxide, because this dinitro compound gave no bromo derivative by bromination. Among the positions (2, 3, and 7) which are free and more active to be taken in the nitration of the 4,6-dinitro compound, 2 and 3 are more favourable than 7 for the introduction of the third nitro group owing to the meta-directive influence of the nitro groups already present in the molecule, because either of the nitro groups of 4,6-dinitrobiphenylene oxide exerts a favourable directive influence to the position 2 or 3, while neither of them exerts a similar influence to the position 7. Of the positions 2 and 3 again, the former is more favourable than the latter for the introduction of the third nitro group, as in the case of nitration of biphenylene oxide, even if the directive influence of the nitro group at the position 4 causing the nitration at the position 2 is equal to that of the nitro group at the position 6 which causes the nitration at 3. From these considerations, it can be concluded that the trinitro compound obtained from 4,6-dinitrobiphenylene oxide is 2,4,6-trinitrobiphenylene oxide. The tetranitro compound obtained as a main product from the last compound must be 2,4,6,7-tetranitrobiphenylene oxide (along with it 2,4,6,8-tetranitrobiphenylene oxide may be formed, by the bye), because it gave no higher polynitro compound, as in the case of nitration of 1,3,6,8-, 1,3,6,7-, and 2,3,6,7-tetranitrobiphenylene oxides, even when it was heated for a long time with a large excess of fuming nitric acid (d 1.52). On the contrary, if the tetranitro compound were 2,3,4,6-tetranitro-biphenylene oxide, it would give 2,3,4,6,7- and 2,3,4,6,8-pentanitrobiphenylene oxides, as in the case of nitration of 1,3,6- and 2,3,6-trinitrobiphenylene oxides⁽⁵⁾, the former of which gave 1,3,6,7- and 1,3,6,8-tetranitro compounds and the latter, 2,3,6,7- and 2,3,6,8-tetranitro

(3) S. Yamashiro, this Bulletin, **15** (1941), 6.

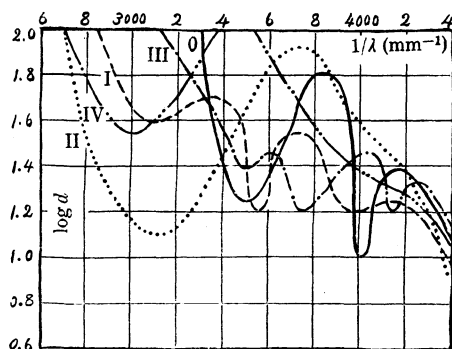
(4) H. Gilman, G. E. Brown, W. B. Bywater and W. H. Kirkpatrick, *J. Am. Chem. Soc.*, **56** (1934), 2476.

(5) S. Yamashiro, *J. Chem. Soc. Japan*, **59** (1938), 448, 450.

compounds. Judging from the reasoning given above, the main reactions of the successive nitrations of 4-nitrobiphenylene oxide may proceed as follows:

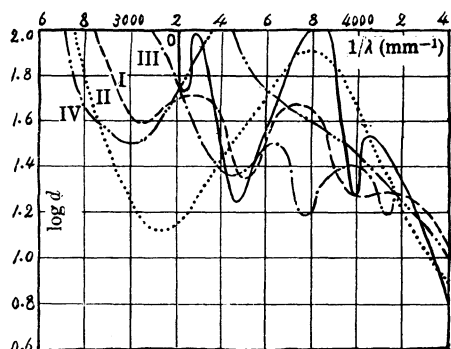


Comparison of the absorption curves.



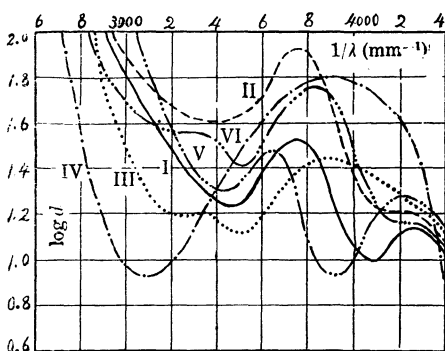
0 (—) Biphenylene oxide.
 I (---) 1-Nitrobiphenylene oxide.
 II (....) 2- " " "
 III (-.-) 3- " " "
 IV (-.-.-) 4- " " "

Fig. 1. Mononitrobiphenylene oxides.
 M/10000 alcoholic solutions.



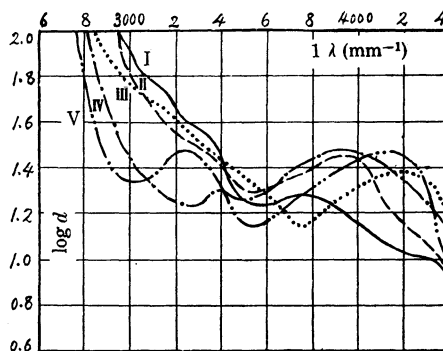
0 (—) 3-Bromobiphenylene oxide.
 I (---) 6-Bromo-1-nitrobiphenylene oxide.
 II (....) 6- " -2- " " "
 III (-.-) 6- " -3- " " "
 IV (-.-.-) 6- " -4- " " "

Fig. 2. Bromonitrobiphenylene oxides.
 M/10000 alcoholic solutions.



I (—) 1,6-Dinitrobiphenylene oxide.
 II (---) 1,8- " " "
 III (....) 2,6- " " "
 IV (-.-) 2,7- " " "
 V (-.-.-) 3,6- " " "
 VI (-.-.-) 4,6- " " "

Fig. 3. Dinitrobiphenylene oxides.
 M/10000 alcoholic solutions.



I (—) 1,3,6-Trinitrobiphenylene oxide.
 II (---) 1,3,8- " " "
 III (....) 2,3,6- " " "
 IV (-.-) 2,3,7- " " "
 V (-.-.-) 2,4,6- " " "

Fig. 4. Trinitrobiphenylene oxides.
 M/10000 alcoholic solutions.

Among the mononitrobiphenylene oxides, the 1- and 3-nitro compounds having a nitro group at the *o*- and *p*-positions respectively to the ring-forming oxygen atom of biphenylene oxide give two resembling absorption curves, which have three characteristic absorption bands in each other (Fig. 1, Curves I and III), whereas the 2- and 4-nitro compounds, which have both a nitro group at the *m*-position to the ring-forming oxygen atom, give also two resembling curves which have both only one wide characteristic absorption band respectively (Fig. 1, Curves II and IV). The absorption bands of the 1- and 4-nitro compounds are more bathochromic than the corresponding bands of the 3- and 2-nitro isomerides.

As seen from the comparison between the absorption curve of the *x*-nitrobiphenylene oxide ($x=1, 2, 3$ or 4) and that of the corresponding 6-bromo-*x*-nitro compound (Fig. 1, Curves I-IV and Fig. 2, Curves I-IV), the introduction of a bromine atom into the position 6 of the *x*-nitro compound exerts no remarkable influence upon the absorption spectrum of the parent compound.

Similarity of the absorption curves can be found also in the case of dinitrobiphenylene oxides, namely, among the 1,6-, 1,8-, and 3,6-dinitro compounds on one hand (the compounds having nitro groups at the *o,p'*-, *o,o'*- and *p,p'*-positions respectively to the ring-forming oxygen atom; Fig. 3, Curves I, II, and V), and between the 2,6-, and 4,6-dinitro compounds on the other (the compounds substituted at the *m,p'*-positions to the ring-forming oxygen atom; Fig. 3, Curves III and VI). But the 2,7-dinitro compound (the *m,m'*-substituted compound; Fig. 3, Curve IV) gives a curve of special type which is analogous to that of 2-nitrobiphenylene oxide.

In the curves of the trinitro- and tetranitro-biphenylene oxides, no analogy can be found among them, except for those of the 2,4,6-trinitro and 2,4,6,7-tetranitro compounds, both of which give a characteristic absorption band at about $1/\lambda$ (mm^{-1}) 3000, owing to the presence of a nitro group at the position 4 of them.

Experimental.

4-Nitrobiphenylene oxide. As shown in Part I,⁽¹⁾ the reaction products obtained by treating biphenylene oxide (100 g.) with fuming nitric acid (d 1.52; 300 c.c.) in glacial acetic acid (100 c.c.) were recrystallized from acetic acid, when 2-nitrobiphenylene oxide (Yield 71%) was isolated. The mother-liquor was diluted with water precipitating the other components which were fractionated by repeated crystallizations from alcohol and by fractional distillations under the reduced pressure. The fraction distilled out at about the temperature $180-185^\circ/3$ mm was again recrystallized

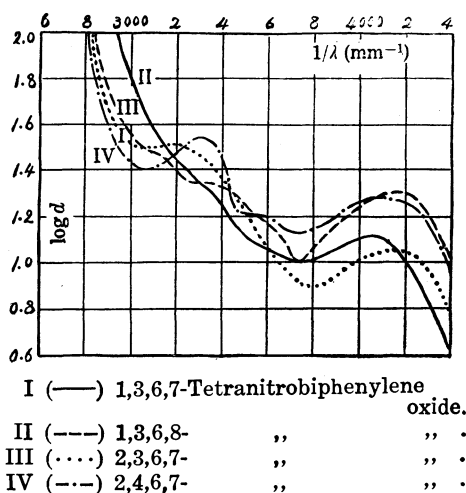


Fig. 5. Tetranitrobiphenylene oxides.
M/10000.

from alcohol, when 3-nitrobiphenylene oxide was isolated (Yield 10%). Next, the fraction distilled out up to the temperature 180°/3 mm was repeatedly recrystallized from glacial acetic acid, pale yellow needles melting at 126–126.5° (corr.) (Yield 1%. Found: N, 6.64. Calc. for $C_{12}H_7ON_2$: N, 6.57%). The last compound is 4-nitrobiphenylene oxide.

4-Amidobiphenylene oxide. 4-Nitrobiphenylene oxide (2 g.) was reduced by heating it with stannous chloride (8 g.) and concentrated hydrochloric acid (40 c.c.) in alcohol (300 c.c.). The reaction mixture was evaporated, diluted with water and made strongly alkaline with caustic soda solution precipitating the reduced substance. The base thus separated out was dried quickly, extracted with benzene and the extract was evaporated to dryness. The residue was then recrystallized from ligroin, colourless needles, m.p. 113.5–114.5° (corr.) (Yield 1.86 g., 97.5%. Found: N, 7.70. Calc. for $C_{12}H_7ONH_2$: N, 7.69%).

4-Acetamidobiphenylene oxide. 4-Amidobiphenylene oxide (1 g.) was warmed for a short time with a mixture of acetic anhydride (1 c.c.) and acetic acid (5 c.c.), and then diluted with water precipitating the reaction product, which was recrystallized from alcohol, colourless needles, m.p. 259–260° (corr.) (Yield 1.2 g., 97.6%. Found: N, 6.32. Calc. for $C_{12}H_7ONHCOCH_3$: N, 6.23%).

6-Bromo-1-nitrobiphenylene oxide. 1-Nitrobiphenylene oxide (1 g.) was heated for 5 hours with a large excess of bromine (3. g.) in boiling glacial acetic acid (30 c.c.). After dilution with water, the reaction product separated out was recrystallized from alcohol, colourless needles, m.p. 231–232° (corr.) (Yield 1.28 g., 93.4%. Found: N, 4.81; Br, 27.34. Calc. for $C_{12}H_6OBrNO_2$: N, 4.79; Br, 27.36%).

6-Bromo-2-nitrobiphenylene oxide. 2-Nitrobiphenylene oxide (1 g.) was brominated by the method described by H. Gilman and his co-workers⁽³⁾ and the reaction product was recrystallized from glacial acetic acid, colourless needles, m.p. 258–259° (corr.) (Yield 1.15 g., 84%. Found: N, 4.82; Br, 27.30. Calc. for $C_{12}H_6OBrNO_2$: N, 4.79; Br, 27.36%).

6-Bromo-3-nitrobiphenylene oxide. 3-Nitrobiphenylene oxide (1 g.) was brominated as in the case of bromination of 1-nitrobiphenylene oxide and the reaction product was recrystallized from acetone, colourless rhombic plates, m.p. 226–227° (corr.) (Yield 1.33 g., 97%. Found: N, 4.86. Br, 27.29. Calc. for $C_{12}H_6OBrNO_2$: N, 4.79; Br, 27.36%).

6-Bromo-4-nitrobiphenylene oxide. 4-Nitrobiphenylene oxide (1 g.) was also brominated as in the case of bromination of 1-nitrobiphenylene oxide and the reaction product obtained was recrystallized from glacial acetic acid, long yellow needles, m.p. 189.5–190.5° (corr.) (Yield 1.20 g., 87.5%. Found: N, 4.84; Br, 27.41. Calc. for $C_{12}H_6OBrNO_2$: N, 4.79; Br, 27.36%).

4,6(or 3,5)-Dinitrobiphenylene oxide. 4-Nitrobiphenylene oxide (2.13 g.) was treated with fuming nitric acid (d 1.45; 20 c.c.) at the room temperature. After 20 minutes, the reaction mixture was poured into water and the reaction product thus separated out (2.5 g.) was recrystallized from glacial acetic acid, colourless needles, m.p. 241–242° (corr.) (Yield 1.70 g., 66%. Found: N, 10.71. Calc. for $C_{12}H_6O(NO_2)_2$: N, 10.85%). This compound gave no brominated product even when it was heated for a long time with a large excess of bromine in boiling acetic acid.

2,4,6-Trinitro- and 2,4,6,7-tetranitro-biphenylene oxides. 4,6-Dinitrobiphenylene oxide (1.29 g.) was heated for 30 minutes with fuming nitric acid (d 1.52; 13 c.c.) and then diluted with water, separating out white precipitates. The reaction products were filtered, dried (Yield 1.58 g.) and extracted with chloroform. The residue was recrystallized from benzene, colourless rectangular plates, m.p. 253–254° (corr.) (Yield 0.196 g., 15.2%. Found: N, 16.12. Calc. for $C_{12}H_4O(NO_2)_4$: N, 16.10%). The chloroform extract was evaporated to dryness and, after being extracted with 1% hot caustic soda solution to remove the contaminated tetranitro compound, the residue was recrystallized from acetone-alcohol, pale yellow needles, m.p. 207–208° (corr.) (Yield 0.294 g., 22.8%. Found: N, 13.93. Calc. for $C_{12}H_5O(NO_2)_3$: N, 13.87%). The last trinitro compound was heated for 3 hours with a large excess of fuming nitric acid (d 1.52), when the foregoing tetranitro compound was obtained, but none of the pentanitro compound was isolated. The trinitro and tetranitro compounds obtained here are, as is made clear by the reasoning given above, 2,4,6-trinitro- and 2,4,6,7-tetranitrobiphenylene oxides respectively.

Summary.

(1) 4-Nitrobiphenylene oxide was isolated in a pure state from the nitration products of biphenylene oxide and the amido, acetamido, dinitro, trinitro, tetranitro and bromonitro derivatives were prepared from it. The constitutions of the latter four derivatives were established.

(2) The physical properties, especially the absorption spectra, of those newly obtained compounds and the corresponding compounds derived from 1-, 2- and 3-nitrobiphenylene oxides were comparatively studied.

In conclusion, the author wishes to express his hearty thanks to Prof. R. Majima of the Osaka Imperial University and Shigemi Oba, the principal of the Yonezawa Higher Technical School, for their kind advices and encouragements. A part of the expense of this investigation has been defrayed from the grant of the Nippon Gakujutsu Shinko-kwai (the Japan Society for the Promotion of Scientific Research) for which also the author wishes to record his thanks.

Yonezawa Higher Technical School.

**The Copper Content of the Hot Springs of Yunohanazawa,
Hakone, Kanagawa Prefecture, and that of the Hot Springs of
Osoreyama, Aomori Prefecture.**

By **Kazuo KURODA.**

(Received February 22, 1941.)

In a previous paper⁽¹⁾, the author gave the results obtained, up to the time of publication, on the copper content of Japanese mineral springs. The copper content of a number of mineral springs was estimated by H. Fischer's diphenylthiocarbazone (dithizone) method⁽²⁾. The writer's recent work, the results of which are given in this paper, concerns the determination of this element by the polarographic method.

(1) Determination of Copper by the Polarographic Method. For the polarographic determination of copper, the method of M. Shikata,

(1) K. Kuroda, this Bulletin, **15** (1940), 439.

(2) H. Fischer, *Angew. Chem.*, **47** (1934), 685; **50** (1937), 919.

I. Tachi, and N. Hozaki⁽³⁾ was at first tried, but the writer failed to detect the presence of copper in the hot springs by this method. The second method adopted was that of K. Heller, G. Kuhla, and F. Machek⁽⁴⁾, in which the copper in mineral waters is extracted with a carbon tetrachloride solution of dithizone. Notwithstanding the most scrupulous care exercised, the search ended in failure. The chief cause of failure probably lay in the presence of a large amount of iron in the mineral waters. After several trials, the following procedure, in which the large excess of iron is removed by ammonia prior to the extraction of copper by the carbon tetrachloride solution of dithizone, was found to be satisfactory for determining the minute traces of copper in acid alum-vitriol springs:

Add nitric acid to 500 c.c. of the mineral water and boil in order to oxidize the iron to the ferric condition. Add ammonium hydroxide (1:1) in slight excess and 5 c.c. of saturated ammonium carbonate solution. Warm and filter. Wash the residue with a warm mixture of 10 c.c. of water, 1 c.c. of ammonium hydroxide (1:1), and 1 c.c. of saturated ammonium carbonate solution. Dissolve the precipitate in 5 c.c. of nitric acid (1:5) and precipitate as above. Combine the filtrates, and render them acid with nitric acid, and evaporate to dryness. Dissolve the residue in nitric acid, adjust to pH 3. Shake with successive 10 c.c. portions of the purified carbon tetrachloride solution of dithizone. Continue the extraction until the carbon tetrachloride layer remains green. Add 10 c.c. of conc. nitric acid and 10 mg. of sodium nitrate to the combined extracts and evaporate to dryness. Dissolve the residue in 10 c.c. of "Grundlösung A"⁽⁵⁾ (170 g. NaNO₃+200 c.c. of gelatine solution (2%)+1800 c.c. H₂O). The solution is transferred to a small electrolysis vessel and polarographically examined. Fig. 1 shows a calibration curve obtained from various heights of wave due to various amount of copper salt in "Grundlösung A".

The efficacy of the method was tested by adding known amounts of standard copper sulphate solution to 500 c.c. of water and submitting the solution to complete extraction, and polarographic determination with the following results:

Table 1.

No.	Height of wave (mm.)	Sensitivity
(1) 500 γ copper.	54	1/10
(2) Cu (500 γ) added to distilled water (500 c.c.). Extracted by dithizone.	53	1/10
(3) Cu (500 γ) added to the Yoemon-Yu spring water (500 c.c.). Extracted by dithizone.	54	1/10

(3) M. Shikata, I. Tachi and N. Hozaki, *Bull. Agr. Chem. Soc. Japan*, **3** (1927), 883.

(4) K. Heller, G. Kuhla and F. Machek, *Mikrochemie*, **23** (1937), 78.

(5) H. Hohn, "Chemische Analysen mit dem Polarographen," Berlin (1937), 41.

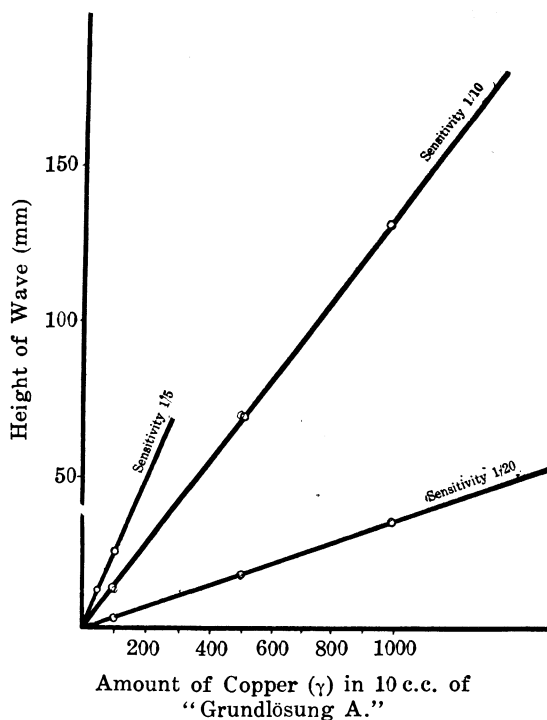
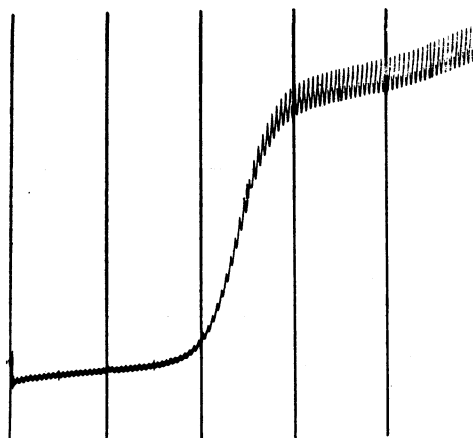
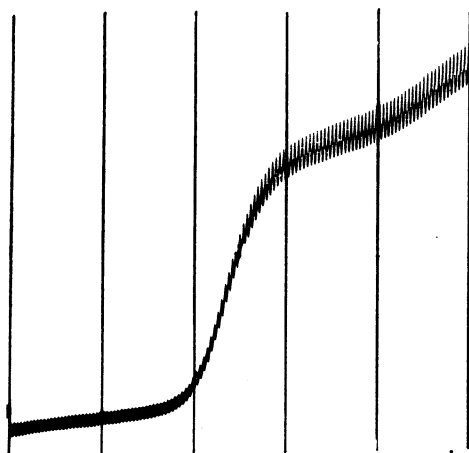
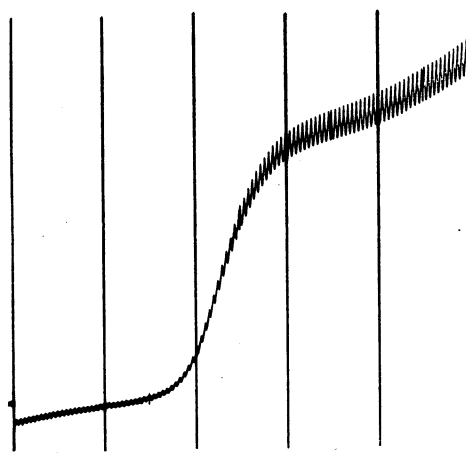


Fig. 1.

Fig. 2. Wave due to 500 γ of copper in "Grundlösung A". Sensitivity 1/10.Fig. 3. 500 γ of copper was added to 500 c.c. of water. Extracted with carbon tetrachloride solution of diphenylthiocarbazone. "Grundlösung A". Sensitivity 1/10.Fig. 4. 500 γ of copper was added to 500 c.c. of "Yoemon-Yu" spring. Extracted with carbon tetrachloride solution of diphenylthiocarbazone. "Grundlösung A". Sensitivity 1/10.

(2) **Copper Content of the Hot Springs of Yunohanazawa, Hakone, Kanagawa Prefecture.** The copper content of the Yoemon-Yu hot spring was polarographically estimated, with the result shown in Table 2, and

that of the hot springs of Yunohanazawa, estimated by H. Fischer's dithizone method⁽²⁾, shown in Table 3.

The relations between temperature, pH, and the copper content are shown in Figs. 5, 6. The copper content is greater, the higher the temperature and the smaller the pH value of the hot spring. Table 4. shows the chemical composition of the Yoemon-Yu spring.

Table 2.

Hot spring	Date	Temp. (°C)	pH	Copper content	
				γ/l.	% (total residue)
Yoemon-Yu	Feb. 19, 1939	74.5	2.2	45	0.0026

Table 3.

Hot spring	Date	Copper content	
		γ/l.	% (total residue)
(1) Gongen-Yu	Aug. 20, 1938	7.1	0.0009
(2) Gongen-Yu	Aug. 26, 1939	10	0.0008
(3) Kōbō-Yu	Aug. 20, 1938	5	0.0005
(4) Yoemon-Yu	Aug. 20, 1938	90	0.0045
(5) Yoemon-Yu	Feb. 19, 1939	45	0.0026
(6) Daruma-Zigoku	Aug. 20, 1938	163	0.0081

Table 4.

Yoemon-Yu. Dec. 11 (1938)	
Temp. 73.0°C. pH 2.3	
K ⁺	0.0029 g./l.
Na ⁺	0.0329
Ca ⁺⁺	0.1029
Mg ⁺⁺	0.0131
Fe ⁺⁺	0.0392
Al ⁺⁺⁺	0.1204
SO ₄ ⁻⁻	1.0366
Cl ⁻	0.0026
H ₂ SiO ₃	0.3674
H ₂ S	trace
	1.7180 g./l.

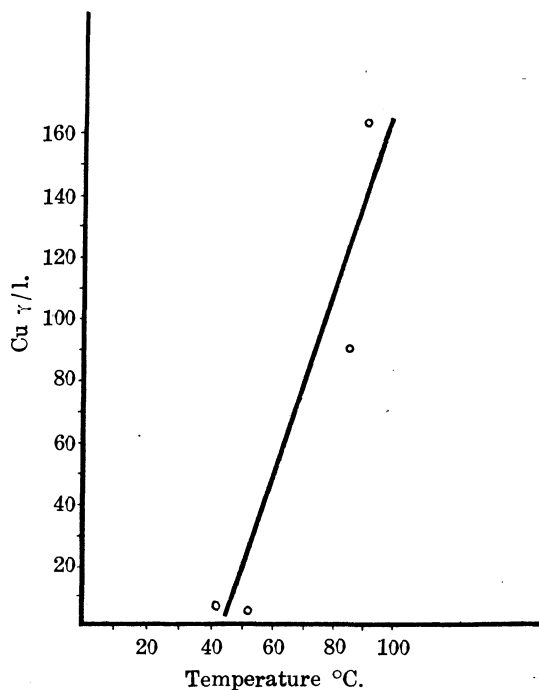


Fig. 5. Temperature and Copper Content.

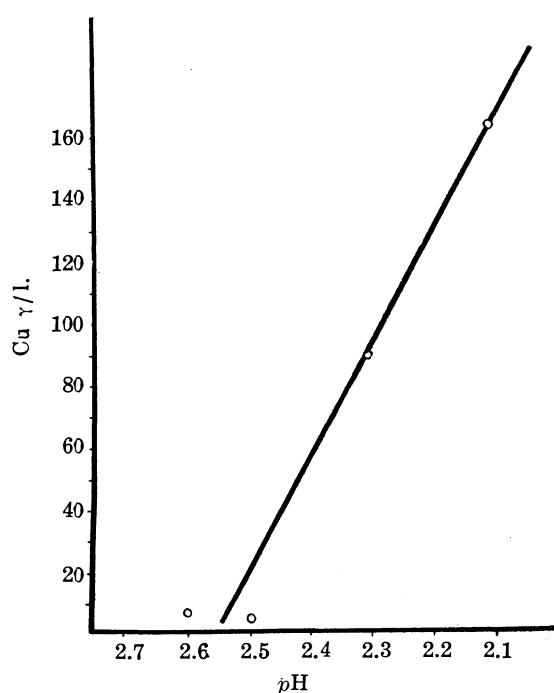


Fig. 6. pH and Copper Content.

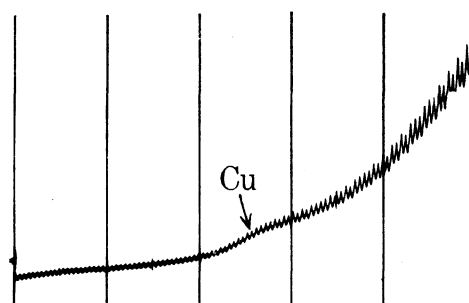


Fig. 7. Wave due to 45 γ of copper extracted from the "Yoemon-Yu" spring. "Grundlösung A". Sensitivity 1/10.

(3) **Copper Content of the Hot Springs of Osoreyama, Aomori Prefecture.** The temperature, pH, total residue, and the iron content of the hot springs of Osoreyama, Aomori prefecture, were measured in 1940. The copper content was also estimated polarographically, when it was found that it is very small compared with that of other acid springs in Japan, the reason for which is probably the presence of considerable hydrogen sulphide in these springs⁽⁶⁾.

Table 5. Hot Springs of Osoreyama.

No.	Hot spring	Temp. °C.	pH	Total residue (g./l.)	Iron content	
					g./l.	% (total residue)
1	Yakusi-Yu	70.0	1.8	3.2	0.025	0.78
2	Hie-no-Yu	89.5	1.9	5.25	0.018	0.34
3	Hurutaki-no-Yu	79.0	2.0	5.30	0.030	0.57
4	Hanazome-no-Yu	68.5	2.0	1.5	0.0013	0.087
5	Sintaki-no-Yu No. 1	83.0	2.2	4.2	0.0034	0.081
6	Sintaki-no-Yu No. 2	60.8	2.4	3.1	0.015	0.48

(6) As is shown in Table 2, the copper content of the Gongen-Yu spring and the Kōbō-Yu spring is very small compared with that of other hot springs in Yunohanazawa, the reason for which is also the presence of considerable hydrogen sulphide in these springs. The Gongen-Yu spring contains 51.9 mg. and the Kōbō-Yu spring 33.1 mg. per litre of hydrogen sulphide.

Table 5.—(Concluded)

No.	Hot spring	Temp. °C	pH	Total residue. (g./l.)	Iron content.	
					g./l.	% (total residue)
7	Tikusyo-Zigoku	23.5	2.2	0.4	0.0022	0.55
8	Sioya-no-Zigoku	98.5	2.4	6.05	0.0101	0.167
9	Zigokudani No. 1	97.5	2.4	2.2	0.0042	0.19
10	Zigokudani No. 2	95.5	2.4	2.6	0.0038	0.15
11	Zigokudani No. 3	93.8	2.5	1.6	0.0044	2.75
12	Zigokudani No. 4	75.5	2.4	4.8	0.0106	0.22
13	Bakutiuti-no-Zigoku	97.5	4.1	11.45	0.0017	0.015
14	Syurao-no-Zigoku	99.0	5.6	14.40	0.0001	0.007
15	Hokke-no-Zigoku	82.8	5.8	2.3	0.0001	0.004
16	Lake Osoreyama	22.0	3.0	0.1	0.0001	0.1
17	Drinking water	14.0	4.8	0.03	0.0001	0.3

Table 6. Copper Content of the Hot Springs
of Osoreyama.

	γ/l.	% (total residue)
No. 6	30	0.00026
No. 13	20	0.00065

Summary.

A method for the polarographic estimation of copper is described. The copper content of the hot springs of Yunohanazawa, Hakone, Kanagawa prefecture, and that of Osoreyama, Aomori prefecture, are polarographically estimated.

The writer expresses his hearty thanks to Prof. Kenjiro Kimura for his kind guidance in the course of this study. The expenses in connexion with this study were defrayed from a grant received by Prof. Kimura from the Japan Society for the Promotion of Scientific Research, to which last the writer's thanks are also due.

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Polymerisation of Tung Oil. VII. Effects of Various Inorganic Substances upon the Gelation of Tung Oil.

By Monzi TATIMORI.

(Received November 28, 1940.)

The effects of various inorganic substances upon the gelation of tung oil at elevated temperatures being little known, the author carried out this experiments to obtain the effects of inorganic substances upon the gelation time of tung oil.

Each of the reagents was added to tung oil with 10% by weight and the measurements were done at 273°C, and the results were compared with the blanc tests.

The reagents were pulverized as fine as possible and the sifted parts were used. The substances which affect the metallic net of the standard sieve, or which could not be pulverized were directly weighed into the test tube.

Experimentals. The results were shown in Tables 1 (substances having no or little effects), 2 (accelerating effects), 3 (retarding effects). The number in the Tables are the values calculated from $(t-t_0)/t_0$, where t and t_0 are the gelation times of tung oil added with reagents and that of the blanc test. Therefore the plus sign means the gelation retarding action and the minus sign, the gelation accelerating one.

Table 1.

$(t-t_0)/t_0$ (%)	Substances
0	Hg, Bi, $(\text{NH}_4)_2\text{Cr}_2\text{O}_7$.
0~+1.0	$\text{Ba}(\text{NO}_3)_2$, $\text{Co}(\text{NO}_3)_2$, K_2CrO_4 , $\text{Na}_2\text{C}_2\text{O}_4$, KBr.
+1.0~2.0	KNO_3 , $\text{NaHPO}_3 \cdot 3\text{H}_2\text{O}$, $\text{Na}_2\text{HPO}_4 \cdot 12\text{H}_2\text{O}$, $\text{Na}_2\text{SO}_3 \cdot 7\text{H}_2\text{O}$, NaBr , $\text{C}_2\text{O}_4\text{Ce}$.
+2.0~3.0	$\text{AlK}(\text{SO}_4)_2 \cdot 12\text{H}_2\text{O}$, NH_4Cl .
+3.0~4.0	Sb_2O_3 , PbCl_2 , KNO_2 , Cr_2O_3 , $\text{Al}_2(\text{SO}_4)_3 \cdot 18\text{H}_2\text{O}$.
+4.0~5.0	K_2SO_4 , $\text{CH}_3\text{COONa} \cdot 3\text{H}_2\text{O}$, BaSO_4 .
0~-1.0	Na_2SO_4 , KI, NaNO_3 , SnO_2 , Al_2O_3 , Sb.
-1.0~2.0	$\text{CaCl}_2 \cdot x\text{H}_2\text{O}$, BaCl_2 , Hg_2Cl_2 , $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$.
-2.0~3.0	$\text{MnCl}_2 \cdot 4\text{H}_2\text{O}$, KHSO_4 , $\text{Fe}_2(\text{SO}_4)_3$, $\text{MnSO}_4 \cdot 4\text{H}_2\text{O}$, $\text{C}_2\text{O}_4\text{Pb}$, Lead Arsenate.
-3.0~4.0	Ni (plate), CaSO_4 , ZnS , $(\text{NH}_4)\text{ClO}_4$.
-4.0~5.0	$\text{Sr}(\text{NO}_3)_2$, Cd, NaCl, $\text{Cr}(\text{NO}_3)_3$.

Table 2.

$(t-t_0)/t_0$ (%)	Substances
- 5~ 10	$\text{Fe}(\text{NH}_4)_2(\text{SO}_4)_2 \cdot 6\text{H}_2\text{O}$, $\text{CdSO}_4 \cdot 8\text{H}_2\text{O}$, $(\text{NH}_4)_2\text{SO}_4$, $\text{K}_2\text{Cr}_2\text{O}_7$, CuCl_2 , Cu_2Cl_2 , $\text{CrCl}_3 \cdot x\text{H}_2\text{O}$.
-10~ 20	$\text{Fe}(\text{NH}_4)_2(\text{SO}_4)_2 \cdot 12\text{H}_2\text{O}$, Zn , HgSO_4 , MgSO_4 , $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$, $(\text{Hg})_2\text{CrO}_4$.
-20~ 30	NH_4NO_3 , KClO_3 , $(\text{CH}_3\text{COO})_2\text{Cu} \cdot \text{H}_2\text{O}$.
-30~ 40	CuO , Cu_2O , $\text{Ni}(\text{NO}_3)_2$, $\text{Hg}(\text{NO}_3)_2$, CH_3COOHg .
-40~ 50	$\text{Th}(\text{NO}_3)_4 \cdot 4\text{H}_2\text{O}$, HgO , $\text{UO}_2(\text{NO}_3)_2$, $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$.
-50~ 60	$\text{Bi}(\text{NO}_3)_3$.
-70~ 80	Na .
-80~ 90	HgCl_2 .
-90~100	ZnCl_2 , ICl_3 , $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$, AlCl_3 , I_2 , SnCl_4 , POCl_3 .

Generally halides have very strong gelation accelerating actions.

Table 3.

$(t-t_0)/t_0$ (%)	Substances
+ 5~ 10	$(\text{NH}_4)_2\text{S}_2\text{O}_8$, $\text{CuCO}_3 \cdot \text{Cu}(\text{OH})_2$, NaHPO_4 , Uranium acetate, KCNS , Fe , Cu , AgNO_3 , Sn .
+10~ 20	LiCl , CoO , NaOCl , $\text{Mn}(\text{OH})_2$, Mn-Borate .
+20~ 30	ZnO , Al .
+40~ 50	$(\text{HCOO})_2\text{Pb}$, Mg , KCN , Na-Oleate , Al-Stearate .
+50~ 60	$\text{Ca}(\text{NO}_3)_2$, NaHCO_3 , KMnO_4 .
+90~100	SbCl_3 .
+100~200	$\text{Mg}(\text{NO}_3)_2 \cdot x\text{H}_2\text{O}$, $\text{Pb}(\text{NO}_3)_2$, $\text{H}_3\text{AsO}_4 \cdot 1/2\text{H}_2\text{O}$, Animal Charcoal.
+100	No gelation MgO , PbO , PbO_2 , Pb_3O_4 , P (red), $(\text{CH}_3\text{COO})_2\text{Mn}$, $(\text{CH}_3\text{COO})_2\text{Pb}$, Se , NaOH , KOH .
+300	No gelation MnO , Na_2O_2 , Na_2HASO_3 , NaHSO_3 , NaNO_2 , As_2O_3 , S_2Cl_4 , Na_2S , $\text{Na}_2\text{S}_2\text{O}_3 \cdot 5\text{H}_2\text{O}$, $\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$.

Generally basic substances have strong gelation retarding actions.

Next, about the effects of sulphur and selenium, experiments were carried out in more detail. It is known that sulphur and selenium have special chemical action (a kind of isomerisation) upon the drying oil⁽¹⁾, but no report has been published about the effects upon the gelation of tung oil.

I. Effect of Sulphur. As it was difficult to mix sulphur in tung oil uniformly, the carbon disulphide solution of sulphur was added and after

(1) T. P. Hilditch and H. Jasperson, *J. Soc. Chem. Ind.* London, **58** (1939), 233; H. I. Waterman, C. Van Vlodrop, F. Althuisius, *ibid.*, **57** (1938), 87; J. Rinse, *Rec. trav. Chim.*, **51** (1932), 529.

Table 4.

Time lapsed from addition of sulphur (min.)	Gelation time (sec.)
30	1337
60	1366
90	1411
150	1426
210	1454
270	1478

evaporating the solvent the measurements were carried out at 270°C. by usual method.

In Table 4 the results of gelation times of tung oil added with 0.013% of sulphur were given. The gelation time increases with the lapse of time from addition of sulphur.

In the following experiments the measurements were done at 30 min. after addition of sulphur.

Table 5. (Tung oil 100%).

Amount of S (%)	Gelation time (t)	$\frac{1}{t} \times 10^4$	log t
0	830	12.05	2.919
0.005	1032	9.69	3.014
0.010	1212	8.25	3.084
0.015	1404	7.12	3.147
0.020	1586	6.32	3.200
0.025	1793	5.58	3.254
0.030	2018	4.97	3.305

Table 6. (Tung oil 95%, Soya bean oil 5%).

S (%)	t	$\frac{1}{t} \times 10^4$	log t
0	855	11.69	2.932
0.005	1139	8.77	3.057
0.010	1379	7.24	3.139
0.015	1680	5.95	3.225
0.020	1896	5.29	3.278
0.025	2311	4.32	3.364
0.030	2567	3.90	3.409

Table 7. (Tung oil 90%, Soya bean oil 10%).

S (%)	t	$\frac{1}{t} \times 10^4$	log t
0	1125	8.89	3.051
0.005	1307	7.62	3.116
0.010	1671	5.95	3.223
0.015	1970	5.06	3.295
0.020	2446	4.00	3.388
0.025	2838	3.52	3.453
0.030	3436	2.90	3.536

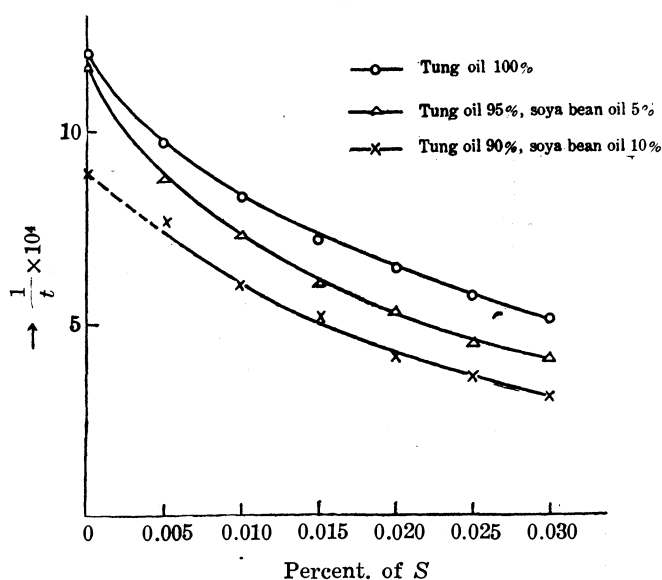


Fig. 1.

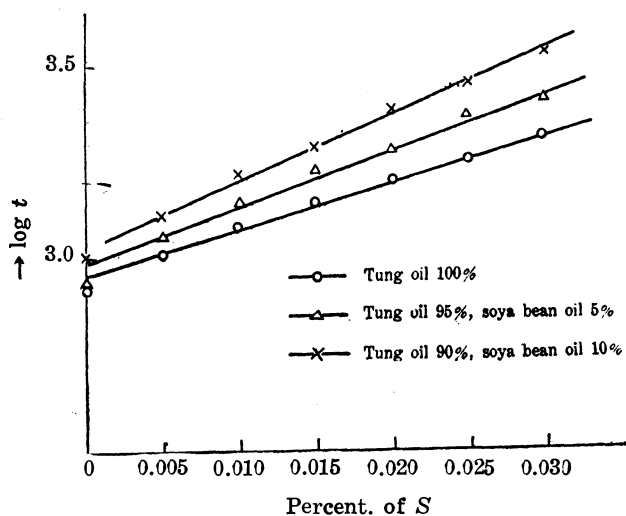


Fig. 2.

As shown in Fig. 1, from the relations between $1/t$ and x curved lines were obtained. In Fig. 2 relations of $\log t$ - x were shown. Except the initial points linear relations were obtained.

II. Effect of Selenium. The experiments were conducted as same as that of sulphur. In this case the solvent was not evaporated off, but the blanc test was done (Table 8).

Table 8. Effect of carbon disulphide.

Amount of carbon disulphide (g./5 g. tung oil)	%	<i>t</i>
0	0	1024
0.1	2	1090
0.2	4	1155
0.3	6	1200
0.4	8	1220
0.5	10	1245
0.6	12	1280
0.7	14	1310
0.8	16	1335
0.9	18	1352

The solvent has a little gelation retarding action.

Table 9. (Tung oil 100%).

Amount of solution added (g.)	Se (%)	<i>t</i>	$\frac{1}{t} \times 10^4$	$\log t$
0	0	1018	9.82	3.008
0.5	0.0139	1646	6.08	3.216
0.6	0.0167	1860	5.38	3.270
0.7	0.0195	1980	5.05	3.297
0.8	0.0222	2165	4.62	3.336
0.9	0.0250	2397	4.17	3.380
1.0	0.0278	2640	3.99	3.422
2.0	0.0556	5400<	1.85>	3.73<

Table 10. (Tung oil 95%, Soya bean oil 5%).

Amount of solution added (g.)	Se (%)	<i>t</i>	$\frac{1}{t} \times 10^4$	$\log t$
0	0	1130	8.85	3.053
0.1	0.0027	1355	7.38	3.131
0.3	0.0082	1718	5.82	3.235
0.4	0.0110	2052	4.87	3.312
0.5	0.0137	2240	4.46	3.351
0.7	0.0192	3090	3.24	3.481
0.9	0.0247	4170	2.40	3.620

Table 11. (Tung oil 90%, Soya bean oil 10%).

Amount of solution added (g.)	Se (%)	<i>t</i>	$\frac{1}{t} \times 10^4$	$\log t$
0	0	1300	7.69	3.114
0.1	0.0028	1695	5.89	3.229
0.2	0.0056	2122	4.71	3.328
0.3	0.0083	2430	4.12	3.386
0.5	0.0140	3275	3.05	3.515
0.6	0.0168	3780	2.65	3.578
0.7	0.0196	4565	2.19	3.659

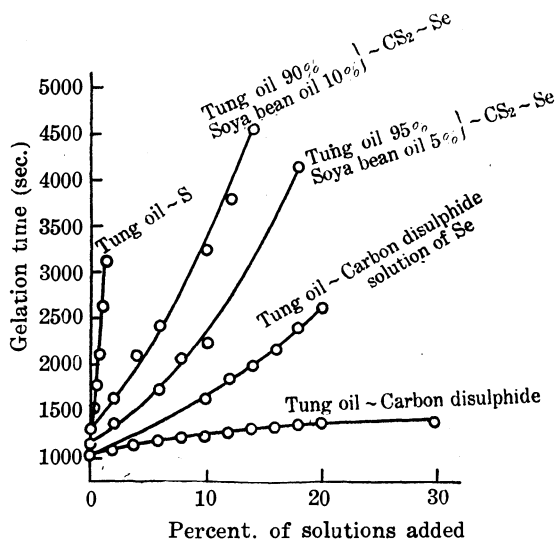


Fig. 3.

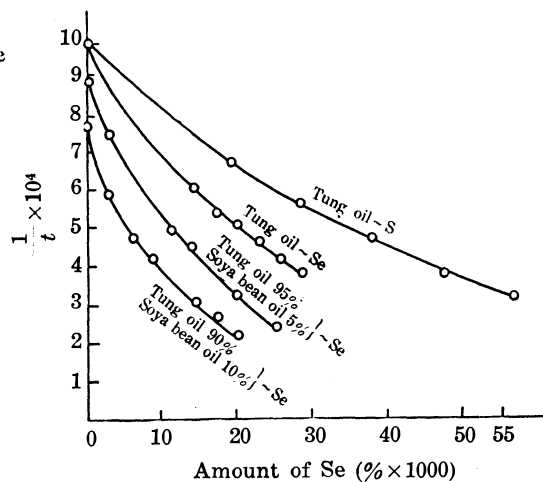


Fig. 4.

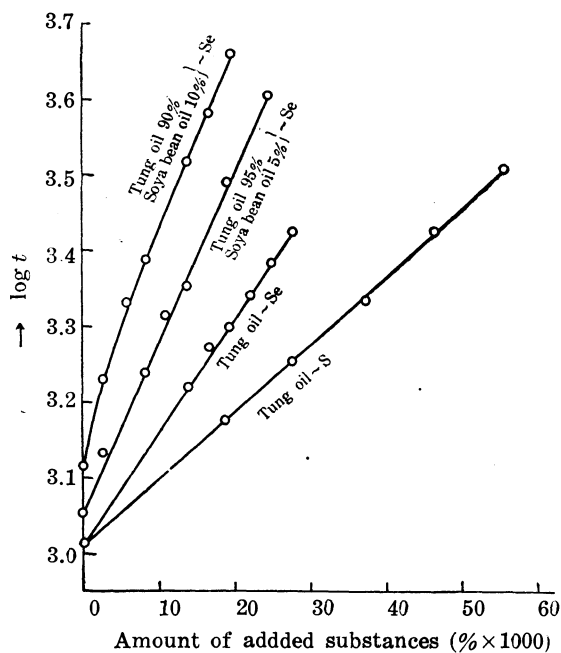


Fig. 5.

The comparison of the effects of sulphur and selenium with the same conditions was shown in Fig. 4. Selenium has stronger gelation retarding action than sulphur.

III. Isomerisation. Isomerisation of tung oil by S, Se and I_2 were examined. 10 g. of tung oil was taken in a glass dish (80, 15h) and irradiated by a ultraviolet lamp (100–110 V, 4 A.), distance of lamp and sample being 35 cm.

The photographs of tung oil added with 0.05% of reagents, after irradiation of 10 hours, were shown in Fig. 6.

Iodine has the strongest isomerisation power and the next is selenium.

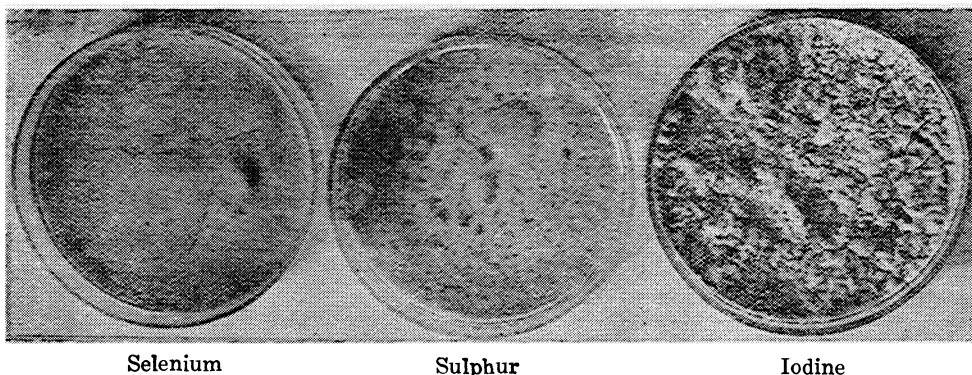


Fig. 6.

Summary.

(1) As inorganic reagent besides sulphur and selenium, 16 kinds of elements, 28 of halides, 18 of nitrates, 23 of sulphates, 17 of oxides and 29 of other miscellaneous substances were used. Many of the halides have strong gelation accelerating actions and magnesium compounds have strong gelation retarding actions.

Metallic sodium acts gelation accelerating and manganese, compounds which are used as oxidation catalysers in paint industry, act as gelation retarding catalysers. Generally speaking acidic substances have gelation accelerating and basic substances have gelation retarding action.

(2) Gelation retarding power of S and Se are very strong and the gelation time of tung oil becomes infinitely long when added with 0.05% of reagents. At the same concentration the gelation retarding action of Se is stronger than that of S.

(3) The relation between the logarithm of gelation time and the amount of S added is linear. These results can be applied also to the systems of mixture of tung oil and soya bean oil.

(4) S, Se and I_2 have isomerisation action upon tung oil at room temperature when irradiated by ultraviolet light.

(5) The gelation time of tung oil increases with the lapse of time from addition of S, so there is an intimate connection between the isomerisation and the gelation retarding action.

In conclusion, the author wishes to express his sincere thanks to Dr. K. Baba, Dr. T. Yosioka, and Mr. K. Yokota for their kind guidance.

Laboratory of Hitachi Works, Hitachi Ltd.

Polymerisation of Tung Oil. VIII. Effects of Various Bitumens and Resins upon the Gelation of Tung Oil.

By Monzi TATIMORI.

(Received November 28, 1940.)

The insulating varnishes are made by cooking the mixture of drying oils, bitumens and resins, and their properties are affected eminently by the cooking process. As drying oils, tung oil is one of the most preferable. This paper deals with the results of the effects of various bitumens and resins upon the gelation of tung oil.

(I) **Effects of Bitumens.** The samples used have the following constants (Tables 1, 2).

Table 1.

Constants of petroleum asphalts.

Kind of Asphalts	Penetration degree (25°C., 100g., 5 sec.)	Softening point (°C.) (Ball & ring method)
S-1	6.0	72.5
S-2	40.7	52.0
S-3	70.0	51.0
B-1	7.0	126.5
B-2	29.0	69.0
B-3	33.5	66.0

S: Straight asphalt

B: Blown asphalt

Table 2.

Softening point of bitumens.

Names of bitumens	Softening point (°C.)
Gilsonite	150.5
Petroleum pitch	108.5
Stearin pitch	82.5
Mineral rubber	137.0
Coal tar pitch	121.0

The measuring methods were the same as those described in the previous reports, the determinations being carried out at 270°C. The relation between gelation time and percentage of petroleum asphalt added to tung oil is shown in Table 3.

Fig. 1 and Fig. 2 show the relation between reciprocals of gelation times ($1/t$) and percentages (x) of straight and blown asphalts added to tung oil.

As shown in these figures, the gelation of tung oil is promoted, when petroleum asphalt is added in an amount less than 10 percent.; but an addition of a larger amount of asphalt tends to prevent the gelation. This sort of inversion is a newly recognized fact. It seems that petroleum asphalt which has a lower softening point has somewhat greater retarding effect on the gelation.

Results with various bitumens are shown in the following.

The inversion was observed at 10% with samples containing gilsonite, mineral rubber, tar pitch, petroleum pitch, and at 25% with those containing stearin pitch.

Table 3. Gelation time of tung oil containing petroleum asphalts.

Kind of asphalts	Percent. of asphalt added (x)	Gelation time (sec.) (t)	$\frac{1}{t} \times 10^4$
S-1	0	938	10.66
	4.96	875	11.43
	9.96	866	11.55
	20.00	944	10.59
	29.82	1101	9.08
	39.90	1585	6.31
S-2	0	939	10.65
	5.00	881	11.35
	9.94	871	11.42
	19.96	973	10.28
	29.50	1228	8.14
	40.00	2398	4.17
S-3	0	937	10.67
	5.00	891	11.22
	9.82	907	11.03
	20.00	1014	9.86
	30.00	1208	8.28
	39.95	1766	5.66
	50.00	>3499	2.86 >
B-1	0	938	10.66
	10	754	13.26
	20	799	12.52
	30	992	10.08
B-2	0	933	10.72
	10	798	12.53
	20	861	11.61
	30	1037	9.64
B-3	0	938	10.66
	10	861	11.62
	20	922	10.85
	30	1238	8.08

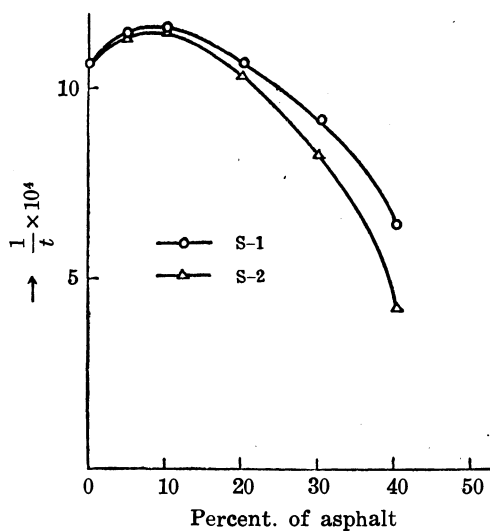


Fig. 1.

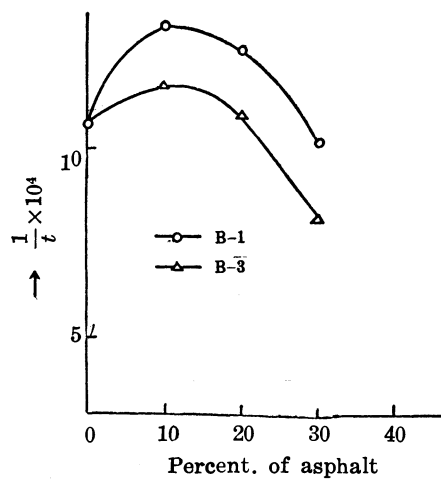


Fig. 2.

Table 4. Gelation time of tung oil containing bitumens.

Kind of bitumens	x (%)	t (sec.)	Kind of bitumens	x (%)	t (sec.)
Gilsonite	0	782	Coal tar pitch	0	904
	4.96	752		5.0	870
	10.80	771		10.0	810
	15.31	781		14.9	836
	25.00	792		25.1	969
	35.30	849		35.1	1148
	45.10	958	Stearin pitch	0	776
	54.80	1108		4.96	618
Mineral rubber	0	785		9.95	551
	5.16	723		14.97	546
	9.94	734		24.85	543
	15.56	773		35.0	566
	24.00	814		44.9	649
	35.18	940		54.5	771
	45.00	1056	Petroleum pitch	0	920
	55.00	1447		5.0	764
				10.0	736
				15.0	755
				25.0	761
				35.0	947

The relation between components of asphalt and the inversion. As shown above, every bitumen added in small amount to tung oil promotes the gelation, where when the added amount increases the effect is reversed, and it retards the gelation. This is a phenomenon which is not found in cases of fatty oils, fatty acids, hydrocarbons, etc.

In order to study the relation between components of asphalt and the inversion, following two experiments were undertaken.

(1) The measurements were made with 15°- blown asphalt, which was separated into two parts, soluble and insoluble in hot alcohol.

For the purpose of separation, asphalt was heated with 94% alcohol for 5 hours at 120–130° under 7 atmospheric pressure, followed with renewal of alcohol, and heated again under the same conditions. By repeating this treatment four times, the asphalt was separated into soluble and insoluble parts.

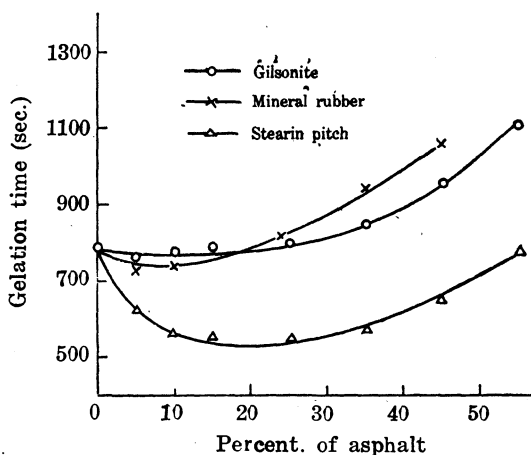


Fig. 3.

Results obtained with soluble and insoluble parts are shown in Table 5.

Table 5. Gelation time of tung oil containing 15°-blown asphalt.

15°-Blown asphalt	x (%)	t (sec.)	15°-Blown asphalt	x (%)	t (sec.)
Alcohol-insoluble part	0	871	Alcohol-soluble part	0	897
	5.0	843		5.0	810
	9.97	809		10.0	800
	14.97	870		14.75	799
	20.0	919		23.60	833
	25.0	998		26.10	894
	30.0	1117		30.00	997

The inversion occurs at 10% with tung oil containing alcohol-insoluble part of blown asphalt and at 15% with that containing alcohol-soluble part.

(2) The components of asphalt are not well known at present, but it is generally accepted that asphalt is composed of petrolen and asphalten. A solution of 5 g. of 5°-blown asphalt in 25 c.c. benzene was poured into 200 c.c. benzine. The precipitate thus obtained was collected and dried to give asphalten, and the filtrate was evaporated to an oily substance, petrolen.

Effects of the petrolen and asphalten upon gelation of tung oil were studied. Results with petrolen are given in Table 6.

Table 6. Gelation time of petrolen of 5°-blown asphalt.

x (%)	t (sec.)	$\frac{1}{t} \times 10^4$
0	917	10.91
5.0	1004	9.96
10.13	1181	8.47
15.0	1392	7.18
20.0	1826	5.48
24.93	2538	3.94
29.94	3671	2.72

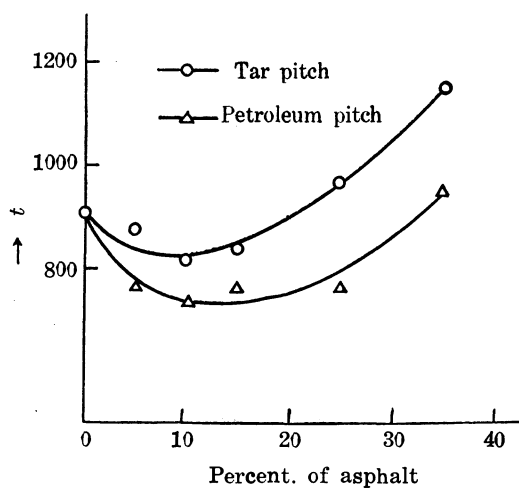


Fig. 4.

The inversion was not found in the experiments with petrolen. As in the case of fatty oils, $1/t$ and x were in a linear relation, and x_{∞} was 38.0%.

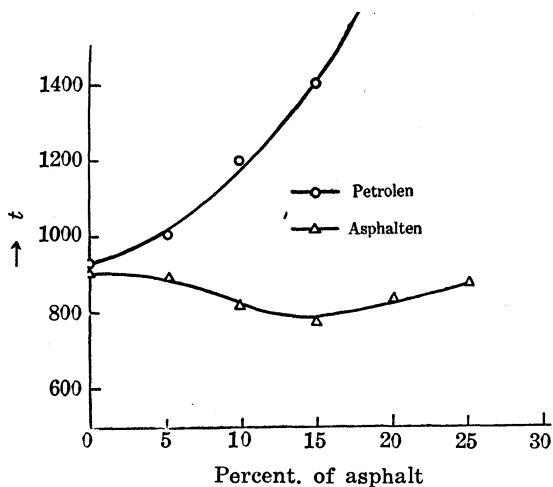


Fig. 5.

Table 7. Gelation time of tung oil containing asphalt-en of 5°-blown asphalt.

x (%)	t (sec.)
0	899
4.99	886
9.98	801
15.0	768
20.0	827
24.95	861

Results with asphalt-en are shown in Table 7. In this case the inversion occurred at 15%.

Of the substances reported only α -naphthol indicated the inversion. It can be anticipated that asphalt-en contains some substances giving a peculiar effect on tung oil.

(II) **Effects of Various Resins.** Next the effect of various natural and synthetic resins on gelation time of tung oil were examined. Acid values and iodine values of these resins are shown in Table 8.

Table 8.

Resin	Acid value	Iodine value
Copal	134	120.7
Dammar	31.2	83.5
Amber	20.5	61.4
Mastic gum	56.7	124.0
Sandarac gum	134	101.9
Rosin	132.4	130.9
Ester rosin	35.0	115.8
Tamanol No. 125 L	17.8	80.1
Super becacite	28.1	52.7
Bakelite resin No. 254	47.5	66.3
Leuchtol	4.7	55.1
Phthalate resin	7.6	80.4
Coumarone resin	0.5	31.8
Hitachi oil soluble resin	21.4	79.8

Each of these resins was pulverized, weighed, and put into test tubes and suitable quantities of tung oil were added; measurement was carried out at 270°C. in every case.

The gelation times in second were shown in Table 9.

Table 9.

Kind of Resins and Remarks	Addition x (%)	t (sec.)	$\frac{1}{t} \times 10^4$
(1) Copal: An approximately linear relation is found between $1/t$ and x and the value of x_∞ is 91.5%.	0	803	12.45
	4.98	891	11.22
	10.0	936	10.68
	15.1	999	10.00
	20.1	1073	9.32
	25.1	1142	8.75
	30.0	1254	7.97
(2) Dammar: The result is similar to that of copal and the value of x_∞ is 67%.	0	791	12.64
	4.99	857	11.67
	9.95	928	10.77
	14.9	1019	9.81
	19.9	1120	8.98
	24.95	1265	7.91
	30.0	1445	6.92
(3) Amber: The general tendency is the same as the above two resins and x_∞ is 62.5%.	0	882	11.34
	4.97	935	10.70
	10.0	1029	9.27
	15.0	1141	8.76
	19.9	1313	7.62
	24.9	1503	6.65
	29.9	1658	6.03
(4) Mastic gum: A slightly curved line is obtained, x_∞ being 62.5%.	0	879	11.38
	5.36	954	10.48
	10.3	1016	9.84
	14.9	1111	9.00
	19.9	1259	7.94
	24.9	1430	6.99
	30.0	1693	5.91
(5) Sandarac gum: The value of x_∞ is approximately estimated to 87%.	0	892	11.21
	5.0	952	10.51
	10.0	988	10.12
	15.0	1084	9.22
	20.0	1118	8.95
	25.0	1228	8.14
	30.0	1394	7.17
(6) Coumarone resin: A straight line is obtained, x_∞ being 64.5%.	0	843	11.86
	4.99	924	10.82
	10.53	1004	9.96
	14.94	1088	9.19
	19.89	1173	8.52
	25.15	1382	7.23
	31.2	1661	6.02
(7) Ester rosin: A curved line is obtained and x_∞ is 42%.	0	889	11.25
	4.98	947	10.56
	9.96	1002	9.98
	15.0	1114	8.98
	20.0	1358	7.36
	25.0	1661	6.02
	30.0	2742	3.65

Table 9.—(Concluded)

Kind of Resins and Remarks	Addition x (%)	t (sec.)	$\frac{1}{t} \times 10^4$
(8) Tamanol 125 L: $1/t$ and x bear an irregular relation, this may be probably due to the less soluble nature of the resin in tung oil and the value of x_∞ estimated is 120%.	0	917	10.91
	5.11	927	10.79
	10.0	956	10.46
	13.88	972	10.29
	20.0	1060	9.43
	25.0	1120	8.93
	30.0	1265	8.58
(9) Super beckacite: A slightly gelation-accelerating action is observed.	4.98	909	10.98
	9.90	953	10.49
	14.94	932	10.74
	19.84	904	11.06
	23.97	866	11.55
	29.46	798	12.53
(10) Fththalate resin: A curved line is obtained and the value of x_∞ is less than 60%.	4.90	923	10.83
	10.0	948	10.55
	14.59	978	10.22
	19.92	1034	9.67
	25.00	1055	9.48
	29.64	1128	8.87
(11) Leuchtol: The gelation-preventing action is very strong and the value of x_∞ is approximately 22%.	5.0	928	10.78
	9.83	1062	9.42
	14.74	1554	6.43
	20.0	3642	2.74
(12) Bakelite resin No. 254: An irregular relation, probably due to its less soluble nature in tung oil, is obtained.	0	848	
	5.0	809	
	9.84	751	
	14.76	742	
	19.92	728	
	24.5	761	
	30.0	848	
(13) Oil soluble phenol-formaldehyde resin made by Hitachi Works: The result is the same as above.	0	882	
	4.6	866	
	9.8	889	
	14.9	938	
	19.7	922	
	24.0	942	
	29.7	988	

(14) Rosin:

In order to find the gelation-retarding effect of rosin the following experiments were carried out.

Table 10. Gelation time at 250°C.

x (%)	t (sec.)	$\frac{1}{t} \times 10^4$	$\frac{1}{x} \left(\frac{1}{t_0} - \frac{1}{t} \right) \times 10^4$
0	1910 (t_0)	5.236	—
5	1954	5.118	0.0256
10	2095	4.773	0.0463
15	2301	4.346	0.0593
20	2582	3.873	0.0682
25	3120	3.205	0.0812

Table 11. Gelation time at 260°C.

x (%)	t (sec.)	$\frac{1}{t} \times 10^4$	$\frac{1}{x} \left(\frac{1}{t_0} - \frac{1}{t} \right) \times 10^4$
0	1324	7.553	—
5	1366	7.321	0.0044
10	1460	6.849	0.0704
15	1563	6.277	0.0857
20	2039	4.904	0.1325
25	3030	3.300	0.1701

Table 12. Gelation time at 270°C.

x (%)	t (sec.)	$\frac{1}{t} \times 10^4$	$\frac{1}{x} \left(\frac{1}{t_0} - \frac{1}{t} \right) \times 10^4$
0	955	10.47	—
5	985	10.17	0.060
10	1066	9.38	0.109
15	1250	8.00	0.164
20	1598	6.26	0.210
25	3025<	—	—

Table 13. Gelation time at 290°C.

x (%)	t (sec.)	$\frac{1}{t} \times 10^4$	$\frac{1}{x} \left(\frac{1}{t_0} - \frac{1}{t} \right) \times 10^4$
0	441	22.68	—
5	491	20.37	0.462
10	574	17.42	0.526
15	753	13.28	0.621
20	1371	7.29	0.769
25	3720<	2.69>	0.800<

Table 14. Gelation time at 300°C.

x (%)	t (sec.)	$\frac{1}{t} \times 10^4$	$\frac{1}{x} \left(\frac{1}{t_0} - \frac{1}{t} \right) \times 10^4$
0	365	27.4	—
5	397	25.2	0.442
10	510	19.6	0.779
15	703	14.2	0.878
20	2203	4.54	1.143
25	4800<	2.08	—

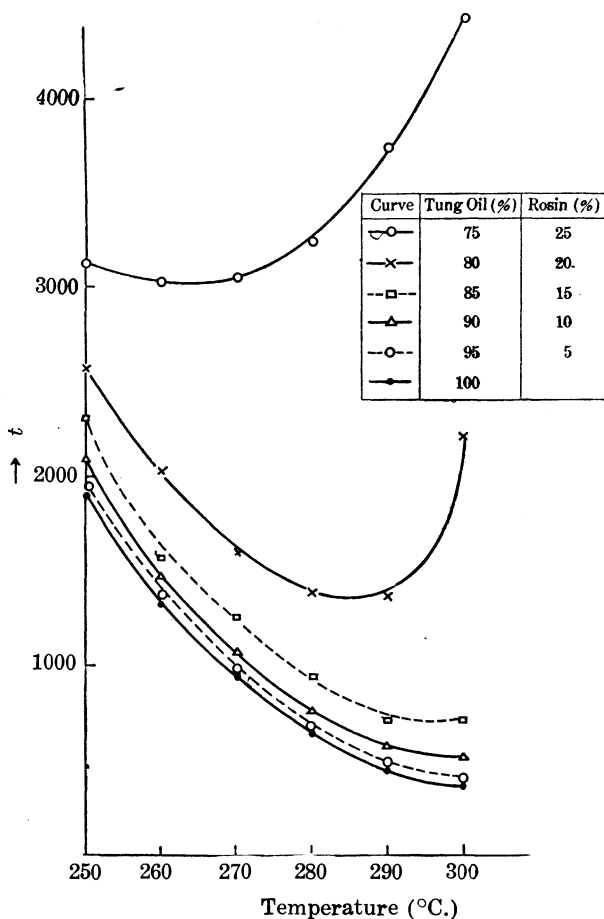


Fig. 6. Relation between Gelation-time and Temperature

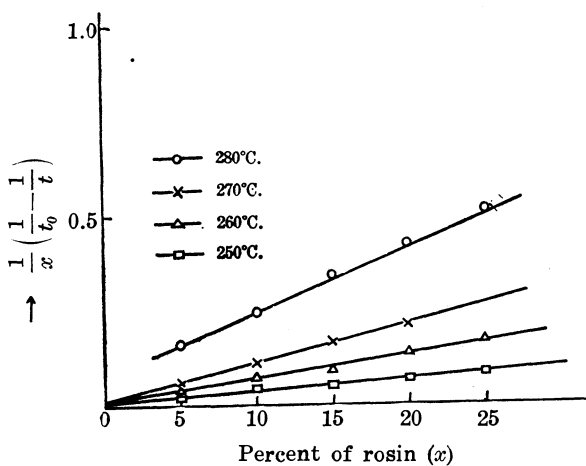


Fig. 7.

The relations between gelation time and temperature are shown in Fig. 6.

The general tendency is the same as that of fatty acid.

The relations between $\frac{1}{x} \left(\frac{1}{t_0} - \frac{1}{t} \right)$ and x are shown in Fig. 7.

From Fig. 7 it is noticed that the reciprocals of gelation time ($1/t$) may be expressed by the quadratic equation of x .

Summary.

(1) Studies on the effects of straight asphalts, blown asphalts, gilsonite, petroleum pitch, stearin pitch, mineral rubber, coaltar pitch, etc. on the gelation time of tung oil lead to the conclusions that the gelation is promoted with bitumen added in an amount less than 10–15 percent., but is prevented with an addition of larger amount of bitumen. The inversion was noticed as the amount of substances added increase.

(2) Petroleum asphalt with a lower softening point has a somewhat greater gelation preventing effect.

(3) 15° blown asphalt was separated into alcohol soluble and insoluble parts. As in the case of the original asphalt, the inversion was found in the experiments with the soluble and insoluble parts.

(4) 5° blown asphalt was separated into asphalten and petrolen, and effects on gelation were studied. As in the case of ordinary neutral substances, the linear relation of $1/t$ and x was observed in the experiments with petrolen, but as in the case with original asphalt, the inversion was noticed when asphalten was used.

(5) The gelation-retarding effects of various natural and synthetic resins were observed. Among them copal, dammar, amber, coumarone resin have retarding effects, and $1/t$ and x bear a linear relation.

The relation $1/t$ and x for mastic, leuchtol, phthalate resin, ester rosin, sandarac, tamanol are not linear.

Generally speaking, the relations of $1/t$ and x for neutral and soluble resins are linear, but those of the less soluble resins are not linear.

About the effect of rosin upon gelation of tung oil, many measurements were carried out and the relation of $1/t$ and x are shown to be expressed by a quadratic equation. The influence of temperature on the gelation times of tung oil mixed with rosin is similar to that of fatty acid.

In conclusion, the author wishes to express his sincere thanks to Dr. K. Baba, Dr. T. Yosioka, and Mr. Yokota for their kind guidance.

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Studies on Reactions between Gas and Solid. VII. Nitrogenation of Calcium Carbide and Its Kinetic Discussion.

By Takeo AONO.

(Received February 24, 1941.)

Introduction. The velocity of nitrogenation of calcium carbide had been experimentally determined as functions of pressure, temperature, size of grain and catalysers, and was formerly reported.^{(1) (2) (3) (4)} Some theoretical discussions upon this reaction kinetics will be given here.

Gas-Solid Reaction. The carbide which was used in these experiments* did not melt or sinter till about 1100°C when heated in vacuum for some time. When the carbide was subjected to the reaction with nitrogen the product sintered very slightly at the furnace temperature above 950°C; and the local melting was perceived above 1150°. At 870°C of the furnace temperature even slight sintering was not perceived.

(1) T. Aono, this Bulletin, **7** (1932), 143-154.

(2) T. Aono, *ibid.*, 247-255.

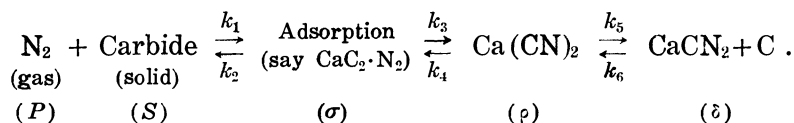
(3) T. Aono, *ibid.*, 274-280.

(4) T. Aono, *ibid.*, 287-297.

* Technical carbide powder of the composition 68.2% CaC_2 , 1% CaF_2 .

Therefore, beneath the furnace temperature of about 950°C, it can be thought that nitrogen is acting upon solid carbide to form solid products. In this range of temperature the reaction mechanism can be considered as follows.

The first step of the reaction will be the adsorption of nitrogen on some active spots of the carbide. Being higher temperatures the adsorption will chiefly be of chemical or activated nature and an adsorption compound, say $\text{CaC}_2 \cdot \text{N}_2$, will be formed temporarily. Some of such a compound, with an energy larger than the heat of activation, will change to $\text{Ca}(\text{CN})_2$; others will break up again into carbide and nitrogen. The $\text{Ca}(\text{CN})_2$, thus formed, can exist also temporarily, because at such temperatures the cyanide is very unstable and goes into CaCN_2 and C.⁽⁵⁾ The reaction scheme is given as follows.



Equations of the reaction velocity. Let us use the following notations:

- S : the total (effective) active spots capable of formation of the adsorption compound, at time t ,
- σ : position occupied by the adsorption compound, say $\text{CaC}_2 \cdot \text{N}_2$,
- ρ : quantity of effective $\text{Ca}(\text{CN})_2$,
- δ : quantity of effective CaCN_2 ,
- k_1 : velocity constant of condensation of nitrogen,
- k_2 : velocity constant of evaporation of nitrogen,
- k_3 : velocity constant of $\text{Ca}(\text{CN})_2$ -formation from adsorption compound,
- k_4 : velocity constant of back formation of adsorption compound from $\text{Ca}(\text{CN})_2$,
- k_5 : velocity constant of formation of $\text{CaCN}_2 + \text{C}$ from $\text{Ca}(\text{CN})_2$,
- k_6 : velocity constant of formation of $\text{Ca}(\text{CN})_2$ from $\text{CaCN}_2 + \text{C}$,

all being taken in proper units. Assuming the law, which resembles that of mass-action, to hold in this case, the following equations can be written down:

$$-\frac{dN}{dt} = k_1 P(S - \sigma) - k_2 \sigma \quad (1),$$

$$\frac{d\sigma}{dt} = -\frac{dN}{dt} - k_3 \sigma + k_4 \rho \quad (2),$$

$$\frac{d\rho}{dt} = k_3 \sigma - k_4 \rho - k_5 \rho + k_6 \delta \quad (3),$$

(5) The formation of $\text{Ca}(\text{CN})_2$ was varified by the author experimentally, and this will be discussed later. It was also reported by H. H. Franck and his co-workers in *Z. Elektrochem.* **45** (1939), 541.

$$\frac{d\delta}{dt} = k_5\rho - k_6\delta \quad (4),$$

and

$$-\frac{dN}{dt} = \frac{d\sigma}{dt} + \frac{d\rho}{dt} + \frac{d\delta}{dt} \quad (5),$$

where $-\frac{dN}{dt}$ means the rate of decrease of the gaseous nitrogen by means of the above change, and P means the pressure of nitrogen. Adsorption other than the above chemical one must also be existing, but owing to the high temperature the quantity of such will be small, and moreover, the velocity of condensation and evaporation of such kind of adsorption will be very fast, and we can consider that this kind of adsorption is always in a stationary state. Therefore the decrease of gaseous nitrogen will practically be due to the above change.

From Equations (1) and (2) we have

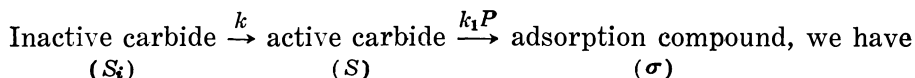
$$\frac{d\sigma}{dt} = (k_1PS + k_4\rho) - (k_1P + k_2 + k_3)\sigma \quad (6),$$

and then

$$\begin{aligned} \sigma &= e^{-\int (k_1P + k_2 + k_3) dt} \left\{ \int (k_1PS + k_4\rho) e^{\int (k_1P + k_2 + k_3) dt} dt + \text{const.} \right\} \\ &= e^{-Kt} \left\{ \int (k_1PS + k_4\rho) e^{Kt} dt + \text{const.} \right\} \end{aligned} \quad (7),$$

where $K = k_1P + k_2 + k_3$.

At constant temperature and pressure k_1 , k_2 , k_3 , k_4 , k_5 , k_6 and P must all be constant. S is, of course, a function of time. From the experimental evidence reported formerly by the author⁽²⁾⁽³⁾⁽⁴⁾, this change seems to be of a kind of auto-catalysis, and if we assume the following scheme:



$$-\frac{dS_i}{dt} = kS_i; \quad S_i = S_{i0}e^{-kt} \quad (8),$$

where $S_{i0} = S_i$ at $t = 0$.

(6) The "Active and inactive" have two meanings:

- a) in case of reaction with nitrogen and solid carbide, the ordinary position is inactive, while the position adjacent to the produced nascent carbon and cyanamide or the activator, and which has the properties of fixing the nitrogen in active. The reaction will proceed principally along the contact places, that is, the active position.
- b) in case of reaction with nitrogen and carbide at higher temperatures, the carbide dissolves into the products and becomes easier to react with the nitrogen. Therefore in this case the "active" means the dissolved and activated carbide.

$$\frac{dS}{dt} = kS_i - k_1PS \quad (9),$$

from which

$$S = \frac{S_{i0}}{k_1P - k} \cdot e^{-kt} - \left(\frac{S_{i0}}{k_1P - k} - S_0 \right) e^{-k_1Pt} \quad (10),$$

or

$$S = S'_0 e^{-kt} - (S'_0 - S_0) e^{-k_1Pt} \quad (10'),$$

where

$$S'_0 \equiv S_{i0} / (k_1P - k).$$

From (10) and (7) we have

$$\sigma = \sigma_0 e^{-Kt} + k_1P \left\{ \frac{S'_0}{K - k} (e^{-kt} - e^{-Kt}) - \frac{S'_0 - S_0}{K - k_1P} (e^{-k_1Pt} - e^{-Kt}) \right\} \quad (11),$$

because, at the earlier stage of the reaction, where the change is proceeding from the left to the right, $k_4\rho$ must be very much smaller than k_1PS and can be neglected.

S_0 and σ_0 represent the values of S and σ at $t=0$. (See Fig. 1).

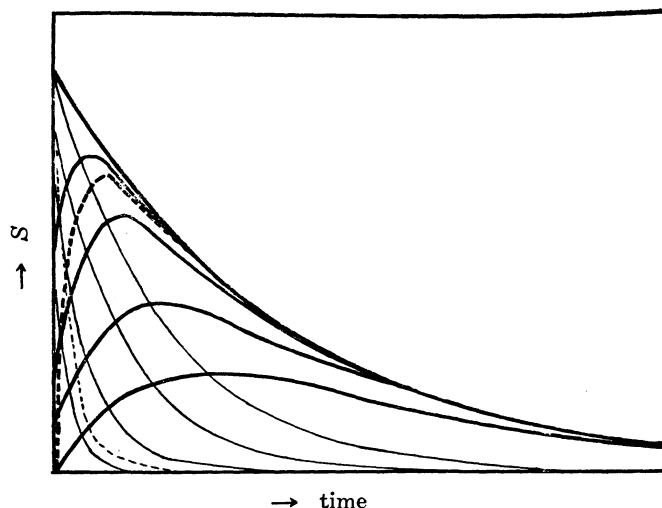


Fig. 1. Curves for "S."

Introducing Eq. (11) into (1) we have

$$\begin{aligned} -\frac{dN}{dt} = & \frac{k_1(k_3 - k)PS'_0}{K - k} e^{-kt} - \frac{k_1P(k_3 - k_1P)(S'_0 - S_0)}{k_2 + k_3} e^{-k_1Pt} \\ & - (k_1P + k_2) \left\{ \frac{S'_0}{K - k} - \frac{S'_0 - S_0}{k_2 + k_3} \right\} e^{-Kt} \end{aligned} \quad (12).$$

This equation (12) gives the rate of nitrogen fixation provided that the reaction products affecting no retarding effect to the reacting sub-

stances. The characteristics of the reaction velocity-time curves found by the experiments coincide with this Eq. (11)⁽²⁾⁽³⁾.

Effect of pressure. By studying the reaction in its comparatively earlier stage, whereby the influence of the layer of the product was small, it was also found by the author⁽¹⁾ that at a constant temperature the velocity of this reaction is not directly proportional to the pressure of nitrogen but the following relation exists.

$$-\frac{dP}{dt} = \kappa \frac{P}{1 + aP} \equiv \frac{P}{aP + b} \quad (13),$$

where κ and a or a and b being constants. This relation can also be derived from the above equations.

During a short time of measurement at such a lower temperature of nitrogenation as in those experiments, S can be taken as constant and $k_4\rho$ can be neglected against k_1PS , then from Eq. (7) we have

$$\sigma = \sigma_0 e^{-Kt} + \frac{k_1}{K} PS \{1 - e^{-Kt}\} \quad (14),$$

After a sufficient time e^{-Kt} becomes sufficiently small and then we have

$$\sigma_\infty = \frac{k_1}{K} PS = \frac{k_1 PS}{k_1 P + k_2 + k_3} \quad (15),$$

and from (1).

$$-\frac{dN}{dt} = \frac{k_1 k_3 PS}{k_1 P + k_2 + k_3} \quad (16).$$

This relation is also obtained by putting

$$-\frac{dN}{dt} = k_1 P(S - \sigma_\infty) - k_2 \sigma_\infty = k_3 \sigma_\infty \quad (17),$$

which means that the decrease of gaseous nitrogen is merely due to the chemical change, that is, $\frac{d\sigma}{dt} = 0$.

For a constant gaseous space (v) the decrease of nitrogen is proportional to the decrease of pressure and we have from (16)

$$\begin{aligned} -\frac{dN}{dt} &= -v \frac{dP}{dt} = \frac{k_1 k_3 PS}{k_1 P + k_2 + k_3}, \\ \therefore -\frac{dP}{dt} &= \frac{P}{\left(\frac{v}{k_3 S}\right)P + \left(\frac{k_2 + k_3}{k_1 k_3 S}\right)v} \equiv \frac{P}{aP + b} \end{aligned} \quad (18)$$

(1), (2), (3): *loc. cit.*

or

$$-\frac{dP}{dt} = \frac{k_1 k_3 S}{(k_2 + k_3)v} \cdot \frac{P}{\left(\frac{k_1}{k_2 + k_3}\right)P + 1} \equiv \kappa \frac{P}{aP + 1} \quad (18')$$

where

$$\left. \begin{aligned} \kappa &= \frac{k_1 k_3 S}{(k_2 + k_3)v}, & a &= \frac{k_1}{k_2 + k_3} = \frac{a}{b} \\ \alpha &= \frac{v}{k_3 S}, & b &= \left(\frac{k_2 + k_3}{k_1 k_3 S}\right)v \end{aligned} \right\} \quad (19).$$

The relations (18), (18') coincide with (13) which was experimentally obtained.

Heat of Activation. From Equation (19) we have

$$\frac{1}{a} = \frac{S}{v} k_3 \quad (20),$$

and as k_3 represents the reaction velocity between adsorbed nitrogen and carbide, its temperature function will be given as

$$k_3 = A \cdot e^{-\frac{E}{RT}} \quad (21),$$

and then for constant S we have

$$\frac{1}{a} = A' \cdot e^{-\frac{E}{RT}} \quad (22).$$

Therefore, if the above postulations are not wrong, $\log \left(\frac{1}{a}\right)$ will stand in linear relation with $\frac{1}{T}$ and the inclination of this line to the $1/T$ axis will give the value of $(-E/R)$, from which the temperature increment E can be calculated. From the experimental data reported in the former paper⁽¹⁾ we have Table 1 and Fig. 2.

Table 1.

Temp. °C	790	869	946	1008
a	4.07	1.36	0.125	0.022
$\frac{1}{T} \times 10^3$	0.940	0.876	0.820	0.781
$\log_{10} \left(\frac{1}{a}\right)$	-0.609	-0.133	0.903	1.657

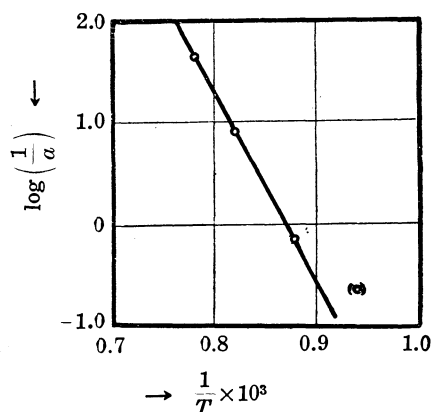


Fig. 2. Temperature increment.

Points except at the temperature of 790°C fall in a straight line, which proves the above postulation to be plausible. (The point of 790°C cannot be compared with the others, because this was taken from the measurement just at the beginning of the reaction, and which, as was formerly reported,⁽²⁾⁽³⁾ is a period of very abnormal). From the inclination of the line we have $E \approx 86$ Cal./mol., which must be the heat of activation for the reaction of adsorbed nitrogen and calcium carbide to form calcium cyanide.

Other reaction formulae. The equations derived above are to be available for the fixation of nitrogen by very fine powder of carbide, the reaction products affecting no retarding effect to the contact between the reacting substances.

When the grain of carbide is larger, or when the temperature is high enough to make the product sinter or melt, the reaction must occur between the carbide and nitrogen which has come through the product layers. Some of the velocity formulae were already derived and discussed in the preceding papers; and was also mentioned there that it is commonly difficult to represent the complete velocity course, experimentally found, with a single equation. This will partly be due to elevation of the local temperature by dint of the reaction heat, which changes the velocity constants during the course of the reaction, and partly because the products change their physical properties during the process due to the change of temperature.

Summary.

(1) From the experimental study of the nitrogenation of calcium carbide the author concluded its mechanism to be as follows:

- (a) adsorptions of nitrogen on the carbide,
- (b) formation of intermediate compound $\text{Ca}(\text{CN})_2$ temporarily,
- (c) breaking of $\text{Ca}(\text{CN})_2$ into CaCN_2 and C.

(2) Equations for this (gas-solid) reaction velocity were derived from the above view. For constant temperature and pressure

$$-\frac{dN}{dt} = \frac{k_1 P(k_3 - k) S'_0}{K - k} e^{-kt} - \frac{k_1 P(k_3 - k_1 P)(S'_0 - S_0)}{k_2 + k_3} e^{-k_1 P t} \\ - (k_1 P + k_2) \left\{ \sigma_0 - k_1 P \left(\frac{S'_0}{K - k} - \frac{S'_0 - S_0}{k_2 + k_3} \right) \right\} e^{-kt}$$

and for changing pressure

$$-\frac{dN}{dt} = \frac{k_1 k_3 P S}{k_1 P + (k_2 + k_3)} \\ -\frac{dP}{dt} = \frac{P}{aP + b}$$

(3) The coincidence of these equations with the experimental results were discussed.

(4) The heat of activation for the reaction of the adsorbed nitrogen and carbide to form calcium cyanide was calculated to be approximately 86 Cal./mol.

Studies on Luminescent Materials. III. On the Photoconductivity and the Molecular Vibration Structure of Fluorescence Spectra of the Zinc Sulphide Crystal Phosphors.*

By Yasuo UEHARA.

(Received February 24, 1941.)

Theory of Photoconductivity of ZnS phosphors. Pure ZnS phosphor containing no activator impurities as well as ZnS phosphors activated by Cu or Ag can emit a remarkable fluorescence by the excitation of ultraviolet ray or cathode ray.

It was pointed out by the author^{(1),(2)} that the resonance radiation, in its wide meaning, in the activation centre is responsible for the fluorescence of these phosphors.

Fig. 1 shows the energy level diagram of the pure ZnS and ZnS/Cu phosphors schematically.

If the ZnS phosphors absorb the excitation energy, an electron of the impurity atom such as Zn atom or Cu⁺ ion in the activation centre makes a transition from the ground state to excited states. When this electron in an excited state absorbs the heat energy from the crystal lattice, it can make a transition to the conduction band and be free to move in the crystal phosphor.

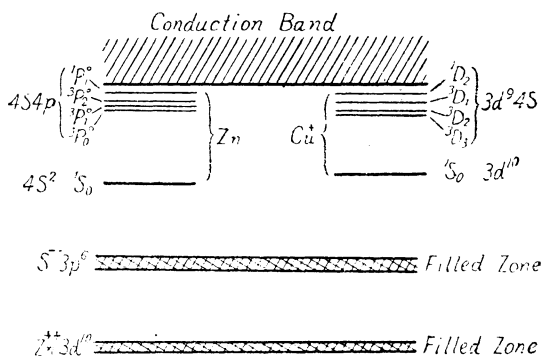


Fig. 1. Energy level diagram of the pure ZnS and the ZnS/Cu phosphor.

When the temperature is so low that the electron in the excited states cannot make a transition to the conduction band by absorbing heat energy, photoconductivity should disappear.

We wish to calculate the temperature dependence of photoconductivity of ZnS phosphors by the similar method as the theory of photoconductivity of F-centre of the alkali halide crystals, proposed by N. F. Mott.^{(3),(4)}

As quoted above, an electron in the levels of $^1D_2$, $^3D_1$, $^3D_2$, $^3D_3$ of Cu⁺ ion or $^1P_1$, $^3P_2$, $^3P_1$, $^3P_0$ of Zn Atom in the activation centre can make

* Read before at the Monthly Meeting of the J. Chem. Soc. Japan, September, 16, 1939 and reported on the *J. Chem. Soc. Japan*, **60**, (1939), 1293.

(1) Y. Uehara, *This Bulletin*, **14** (1939), 539.

(2) Y. Uehara, *ibid.*, **15** (1939), 214.

(3) N.F. Mott, *Proc. Roy. Soc., (London)*, **50** (1938), 196.

(4) N.F. Mott, *Trans. Faraday Soc.*, **34** (1938), 506.

a transition to the conduction band by absorbing elastic (or molecular) vibration energy.⁽¹⁾

For the sake of simplicity, we assume only one energy level of excited state which represents all four levels of excited states.

Suppose that the activation energy necessary to free the electron from this excited state is ΔE , then the probability per unit time that the electron is released, will be approximately

$$A e^{-\Delta E/kT} \quad (1)$$

k = Boltzmann's constant,
 T = Absolute temperature,

with A of the order of magnitude of the elastic vibrations which is about 3.66×10^{12} sec.⁻¹, as we shall see in the following sections. Let B be the probability per unit time that an electron in the excited state drops back into the ground state, either with the emission of fluorescence or by giving up its energy as elastic vibration energy to the lattice. Then the quantum yield η that an electron in the excited state makes a transition to the conduction band is given by

$$\eta = \frac{A e^{-\Delta E/kT}}{A e^{-\Delta E/kT} + B} = \frac{1}{1 + B/A e^{\Delta E/kT}} \quad (2)$$

We can express the electric conductivity in the crystal as follows,

$$J = Ne\omega$$

with e = electronic charge,
 N = total number of the electrons in the unit volume,
 ω = mobility of the electrons.

The mobility of the electrons in the polar crystals is given as follows, by the theory of Fröhlich and Mott,⁽⁵⁾

$$\omega = 2\sqrt{\frac{3}{\pi m k \Theta}} \cdot e \cdot a_0 \cdot (e^{\Theta/T} - 1) \cdot \frac{\epsilon - \epsilon_0 + 1}{\epsilon - \epsilon_0} \quad (4)$$

$$\equiv C(e^{\Theta/T} - 1)$$

$$C \equiv 2\sqrt{\frac{3}{\pi m k \Theta}} \cdot e \cdot a_0 \cdot \frac{\epsilon - \epsilon_0 + 1}{\epsilon - \epsilon_0}$$

with m = mass of the electron,
 Θ = characteristic temperature of the crystal,
 a_0 = radius of the Bohr orbit of hydrogen,
 ϵ = dielectric constant in the static field,
 ϵ_0 = contribution to the dielectric constant for the polarisability of the ions.

(5) H. Fröhlich, N. F. Mott, *Proc. Roy. Soc.*, (London), **171** (1939), 496.

Then the photoconductivity σ is given as follows

$$\begin{aligned}\sigma &= Ne\omega\eta \\ &= NeC(e^{\Theta/T}-1) \cdot \frac{1}{1+B/A e^{\Delta E/kT}} \\ &\equiv K \cdot \frac{1}{1+B/A e^{\Delta E/kT}} \cdot (e^{\Theta/T}-1)\end{aligned}\quad (6)$$

$$K \equiv NeC = 2N\sqrt{\frac{3}{\pi m k \Theta}} \cdot e^2 \cdot a_0 \cdot \frac{\varepsilon - \varepsilon_0 + 1}{\varepsilon - \varepsilon_0} \quad (7)$$

$$\text{or} \quad \log \sigma = \log K + \log \left\{ \frac{1}{1+B/A e^{\Delta E/kT}} (e^{\Theta/kT}-1) \right\} \quad (8)$$

With $\Theta = 175$ for Zincblende,⁽⁶⁾ we get the following values, to obtain a good fit between the calculated values from eq. (9) and the observed values by Lentz⁽⁷⁾ for Zincblende,

$$\left. \begin{aligned} B/A &= 2.13 \times 10^{-3}, \quad (A = 3.66 \times 10^{12} \text{ sec}^{-1}) \\ \Delta E &= 0.081 \text{ eV} \end{aligned} \right\} \quad (10)$$

We can now get $1/B = 1.28 \times 10^{-10}$ sec. This value obtained above is reasonable for the mean time in the excited state.**

Fig. 2 shows the photoconductivity curve *vis a* temperature calculated from eq. (9) with the values of (10) and also the observed values by Lentz. The coincidence between these two values is satisfactory.

As the results, we can say that the resonance radiation, in the wide meaning, in the activation centre is responsible for the fluorescence of ZnS phosphors. If it is the case, we can expect that the molecular vibration structure should be observed in the fluorescence spectra of ZnS phosphors.

In facts, the author could observe the molecular vibration structure in the fluorescence spectra, as we shall see in the following sections.

Observation of the fluorescence spectra. The fluorescence of ZnS phosphors excited by Hg 3650 Å line was photographed by means of Zeiss three glass prism spectrograph.

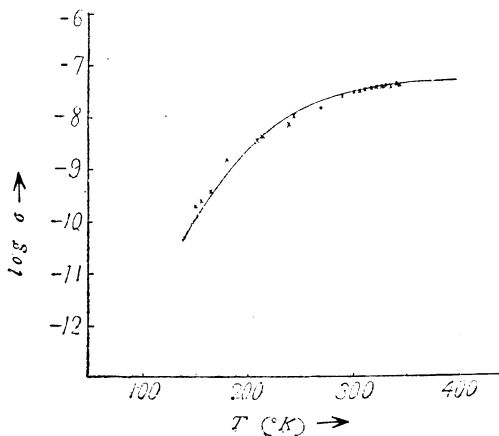


Fig. 2. Temperature dependence of the photoconductivity of ZnS phosphor; thick line (theoretical curve), cross (observed value).

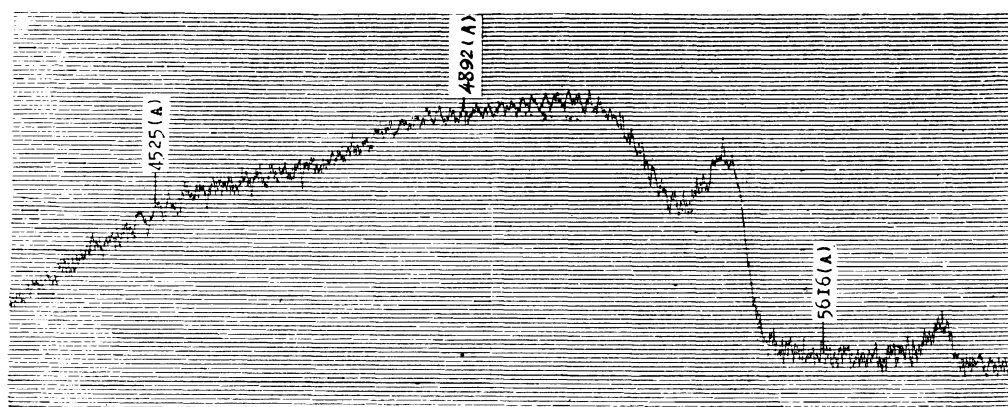
(6) K. Försterling, *Z. Physik*, **8** (1922), 251; **3** (1920), 9.

(7) H. Lentz, *Ann. Physik*, **77** (1925), 449.

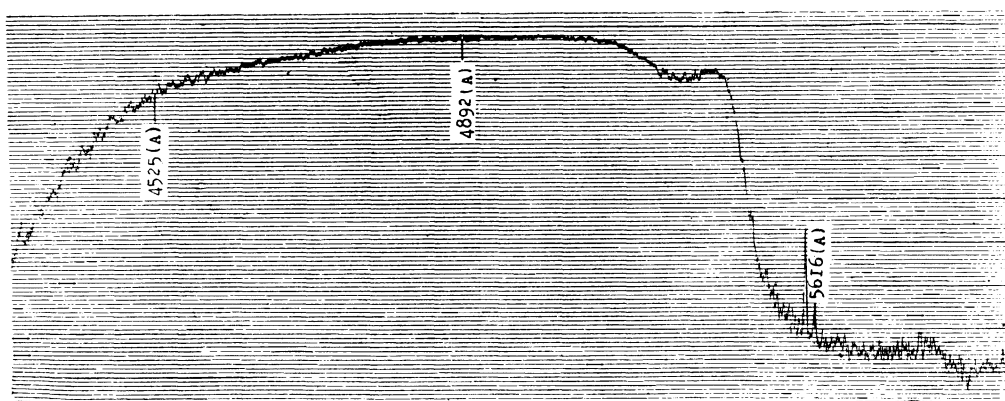
** Mott got the values for the quantities for the colour centre of NaCl, $E=0.075$ eV, $1/B=0.7 \times 10^{-10}$ sec.



Fig. 3. Fluorescence spectra of (1) pure ZnS and (2) ZnS/Cu at $+150^{\circ}\text{C}$.



(1)



(2)

Fig. 4. Microphotometer curves of fluorescence spectra of (1) pure ZnS and (2) ZnS/Cu at $+150^{\circ}\text{C}$.

The same apparatus and methods as that reported in the previous paper⁽²⁾ were used in the present measurements. The measurements of fluorescence spectra were carried out at the temperature covering a range from -185°C to $+300^{\circ}\text{C}$. We could observe the molecular vibration structure of the fluorescence spectra most obviously at the temperature about $+150^{\circ}\text{C}$. The fluorescence spectra of the pure ZnS phosphor and the ZnS phosphor containing 1×10^{-5} g. atom/mol. Cu as an activator were shown in the figures (1) and (2) of Fig. 3 respectively. The microphotometer curves for the fluorescence spectra of the pure ZnS and ZnS/Cu phosphors were given in the curves (1) and (2) of Fig. 4 respectively. Also the (mean) energy distribution curves of the fluorescence spectra of both phosphors were given in the curves (I) and (II) of Fig. 5 respectively. The each fluorescence band given by the curves (I) and (II) in Fig. 5 are caused from the transition ${}^3\text{P}_1 \rightarrow {}^1\text{S}_0$ in the pure ZnS phosphor and ${}^3\text{D}_3 \rightarrow {}^1\text{S}_0$ in the ZnS/Cu phosphor respectively, as already shown in the previous paper.⁽¹⁾

The fluorescence spectra for both the pure ZnS phosphor and the ZnS/Cu phosphor have the identical structure, within the range of error, consisting of many diffused lines.

The observed values of the wave length and wave number of these spectra were shown in Table 1.

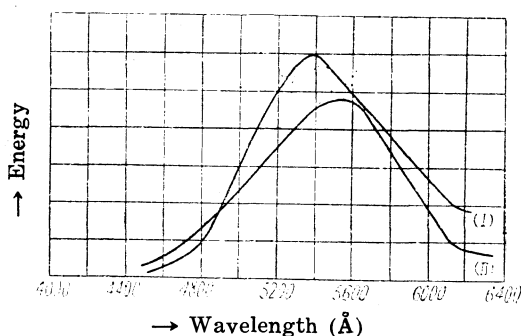


Fig. 5. Fluorescence spectra of (1) pure ZnS and (2) ZnS/Cu at $+150^{\circ}\text{C}$.

Theoretical interpretations for the experimental results. The properties of the molecular and elastic vibrations in the polar crystals have been extensively investigated by Born, Kármán, and many other investigators. According to their theory, we can distinguish the molecular vibrations and elastic vibrations in the diatomic crystals, so far as the masses of atoms or ions constituting the binary crystals are not identical each other. Although the molecular vibration frequency of Zincblende crystal has not yet been known experimentally, its theoretical value has been obtained as follows,

from the Madelung-Einstein formula⁽⁸⁾

$$\lambda_M = 44.8\mu \quad \nu_M = 223.2 \text{ cm}^{-1},$$

and from the Lindemann formula⁽⁹⁾

$$\lambda_L = 36.9\mu \quad \nu_L = 271.0 \text{ cm}^{-1}.$$

On the other hand, F. Seitz⁽⁹⁾ gave the following formula for the cubic crystal, from the viewpoint of quantum mechanics,

(8) C. Schaefer, F. Mottossi "Das ultrarote Spectrum," 285, Berlin (1930).

(9) R. B. Barnes, R. R. Brattain, F. Seitz, *Phys. Rev.*, **48** (1935), 582.

$$\tilde{\nu} = \frac{1}{\sqrt{2\pi}} \left(\frac{f}{M} \right)^{1/2} \quad (11),$$

$$\text{with } f = (C_{11} + C_{44}) \times r, \quad M = \frac{m_1 m_2}{m_1 + m_2}$$

C_{11}, C_{44} = elastic constant in the terms of Voigt,

r = the shortest distance between two unlike atoms,

m_1, m_2 = mass of each unlike atom.

For Zincblende these quantities have following values,⁽⁶⁾

$$C_{11} = 9.43 \times 10^{10},$$

$$C_{44} = 4.34 \times 10^{11},$$

$$r = 2.35 \text{ \AA}.$$

With these results, we can get from eq. (11)

$$\nu_s = 226 \text{ cm}^{-1}, \quad \lambda_s = 44.2 \mu.$$

It has been known that Zincblende shows Reststrahlen at 31μ and the characteristic temperature of this crystal is 175 .⁽⁶⁾

The maximum frequency $\tilde{\nu}_m$ and the corresponding wave number of the elastic vibrations are expected as

$$\tilde{\nu} = 3.66 \times 10^{12} \text{ sec}^{-1}$$

$$\nu_m = 122 \text{ cm}^{-1}.$$

We can see that the maximum frequency of the elastic vibrations is almost equal to one half of the fundamental frequency of the molecular vibrations.

By assuming the usual formula for the diatomic molecule in this case, we can analyze the observed fluorescence spectra as follows,

$$\nu = 1805 + 315(v' + 1/2) - 236(v'' + 1/2) + \dots \quad (12)$$

with v' = vibration quantum number for the excited state,

v'' = vibration quantum number for the ground state.

The calculated values from eq. (12) were given in Table 1 together with the wave number difference ($\Delta\nu$) between the calculated values and the observed values. The molecular vibration structure of ZnS phosphor activated by Cu is identical with that of pure ZnS, as mentioned above. This fact can be explained as follows. The molecular vibration will be influenced by the presence of atoms of other kinds only in the magnitude of second order.⁽¹⁰⁾ Since Cu atom has almost the same mass as Zn atom especially in our case, the variation of the frequency of the molecular vibrations caused by the substitution of Zn atom by minute amount of Cu atom (of the order of 10^{-5}) is very small, as we can evaluate it from the Madelung-Einstein, Lindemann or Seitz formula.

(10) J. Frenkel, *Rhys. Rev.*, **37** (1931), 17.

Table 1. Fluorescence spectra of the pure ZnS phosphor (at +150°C).

$\lambda_{\text{obs.}} (\text{\AA})$	$\nu_{\text{obs.}} (\text{cm}^{-1})$	$\nu_{\text{calc.}} (\text{cm}^{-1})$	(ν'/ν'')	$\Delta\nu$	$\lambda_{\text{obs.}} (\text{\AA})$	$\nu_{\text{obs.}} (\text{cm}^{-1})$	$\nu_{\text{calc.}} (\text{cm}^{-1})$	(ν'/ν'')	$\Delta\nu$
5754	17379	17392	(0 5)	-13	5103	19596	19593	(4 1)	0
5731	17449	17471	(1 6)	-22	5083	19673	19675	(5 2)	- 2
5705	17523	17550	(2 7)	-22	5062	19755	19754	(6 3)	+ 1
5675	17621	17628	(0 4)	- 7	5041	19837	19832	(4 0)	+ 5
5654	17687	17707	(1 5)	-20	5021	19916	19911	(5 1)	+ 5
5625	17778	17786	(2 6)	- 8	5001	19996	19990	(6 2)	+ 6
5600	17857	17864	(0 3)	- 7	4982	20072	20069	(7 3)	+ 3
5574	17940	17943	(1 4)	- 3	4965	20141	20147	(5 0)	- 6
5551	18015	18022	(2 5)	- 7	4946	20213	20226	(6 1)	- 8
5527	18095	18100	(0 2)	- 5	4924	20309	20305	(7 2)	+ 4
5502	18175	18179	(1 3)	- 4	4903	20396	20384	(8 3)	+12
5479	18252	18258	(2 4)	- 6	4886	20467	20463	(9 4)	+ 4
5453	18339	18336	(0 1)	+ 3	4868	20542	20541	(7 1)	+ 1
5429	18420	18415	(1 2)	+ 5	4849	20623	20620	(8 2)	+ 3
5406	18498	18494	(2 3)	+ 4	4831	20700	20699	(9 3)	+ 1
5384	18574	18572	(0 0)	+ 2	4813	20777	20778	(10 4)	- 1
5360	18657	18651	(1 1)	+ 6	4794	20859	20857	(11 5)	+ 2
5339	18730	18730	(2 2)	0	4776	20938	20936	(12 6)	+ 2
5318	18804	18809	(3 3)	- 5	4759	21013	21014	(10 3)	- 1
5292	18896	18887	(1 0)	+ 9	4742	21088	21093	(11 4)	- 5
5270	18975	18966	(2 1)	+ 9	4725	21164	21172	(12 5)	- 8
5250	19048	19045	(3 2)	+ 3	4707	21245	21251	(13 6)	- 6
5230	19120	19124	(4 3)	- 4	4690	21322	21329	(11 3)	- 7
5209	19198	19202	(2 0)	- 4	4672	21404	21408	(12 4)	- 4
5188	19275	19281	(3 1)	- 6	4655	21482	21487	(13 5)	- 5
5167	19354	19360	(4 2)	- 6	4638	21561	21566	(14 6)	- 5
5142	19448	19439	(5 3)	+ 9	4621	21640	21644	(12 3)	- 4
5122	19524	19517	(3 0)	+ 7	4605	21716	21723	(13 4)	- 7

Thus we can confirm that the resonance radiation in the activation centre is responsible for the fluorescence of ZnS phosphors and the breadth of the fluorescence bands of ZnS phosphors is caused by the molecular vibration structure of the fluorescence spectra.

In conclusion, the author wishes to express his sincere thanks to Vice-Director B. Imamura of this institute for his generous help, and also to Prof. S. Mizushima of Tokyo Imperial University for his kind advices and encouragement.

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Studies on Reactions Between Gas and Solid. VIII. The Mechanism of Nitrogenation of Calcium Carbide.

By Takeo AONO.

(Received February 24, 1941.)

Introduction. The chemical process of the nitrogenation of calcium carbide to calcium cyanamide, $\text{CaC}_2 + \text{N}_2 = \text{CaCN}_2 + \text{C}$, is very much interesting not only for its technical importance but also for its complicity of chemical change itself. For the explanation of the mechanism of cyanamide formation and the action of its catalysts, many hypothetical theories have been proposed and discussed. The author intends here to review those theories and discuss this problem from his experimental results and reaction-dynamical considerations.

Reaction Velocity. It was found by the author,^{(1),(2),(3),(4),(5)} and also by H. H. Franck and his co-workers⁽⁶⁾ that, when calcium carbide was heated in vacuo at high temperature and nitrogen was suddenly introduced, the fixation of nitrogen by the carbide starts with very small velocity, which increases with the proceeding of the reaction to a maximum point. (See Fig. 1). This means that, for this reaction something like an initial activation is necessary either in side of carbide or in side of nitrogen.

The fact that the velocity increases with the proceeding of the reaction was explained by the author formerly⁽³⁾ as the results of (1) liberation of heat of reaction, (2) liberation of nascent carbon, which activates the reaction, (3) formation of new crystal germs of CaCN_2 , the boundary between which and CaC_2 will also favors the reaction.

It was also found by the author⁽²⁾ that the velocity of nitrogenation is not directly proportional to the pressure of nitrogen, but follows the equation $-(dP/dt) = P/(aP+b)$. The temperature relations and the effect of size of grain of carbide and additional substances on the velocity were also determined experimentally and computed kinetically.⁽³⁾⁽⁴⁾⁽⁵⁾

Activation of Nitrogen. In 1933 J. Gelhaar⁽⁷⁾ investigated that this reaction proceeded in nickel tubes twice as fast as in quartz tubes. It was said to be shown that the reaction velocity is directly proportional to the degree of ionization of the nitrogen, the values obtained being in close agreement with mathematical computations that are outlined. Because

(1) T. Aono, This Bulletin, **7** (1932), 143.

(2) T. Aono, *ibid.*, 247.

(3) T. Aono, *ibid.*, 274.

(4) T. Aono, *ibid.*, 287.

(5) T. Aono, *ibid.*, **16** (1941),

(6) Frank, Hochwald, Hoffman, *Z. physik. Chem. Bodenstein-Festband*, (1931), 895.

(7) J. Gelhaar, *Teknisk Tidskrift Uppl. C. Kemi*, **63** (1933), 25, 37, 41, *Chem.-Ztg.*, **57** (1933) 242; *ibid.*, **57** (1933) 506; *C. A.* **27** (1933) 811, 4751.

of lack of the original paper of Gelhaar, the author cannot discuss his work, but these conclusions were said by Birger⁽⁸⁾ to be based on misinterpreted observations, and the ionization theory invalid. According to Birger the true degree of ionization at 1000° C is normally about 10^{-32} , and in a Ni-tube it is even less, 10^{-34} . The increase in the reaction velocity with nickel tube is to be attributed to the ability of this metal to remove CO from the reaction chamber either by direct absorption or formation of $\text{Ni}(\text{CO})_4$.

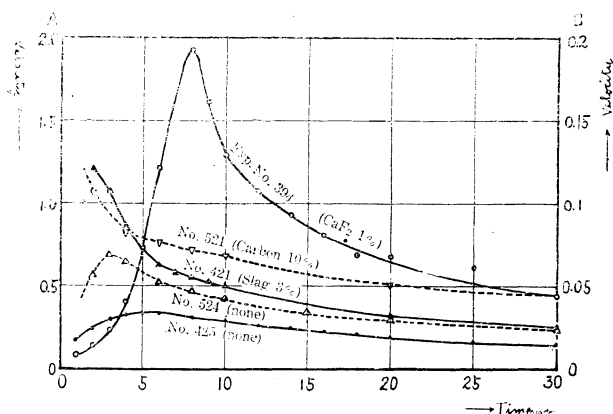


Fig. 1. Effect of catalysts on the velocity of nitrogenation.

Use scale A for full lines (at 1000°C)

and scale B for dotted lines (at 870°C).

The action of CO on calcium carbide at elevated temperatures was experimentally discussed by the author.⁽⁹⁾ And the action of nickel on the nitrogen, containing CO as impurities, was also studied by the author,⁽¹⁰⁾ the conclusion of which did not agree with that of Birger. Indeed carbon monoxide reacts with nickel at high temperature, but the nickel carbonyl, then formed, can not exist as such at these high temperatures; it breaks up instantly into Ni and CO again.

Nickel and iron have the action of decomposing acetylene, which is liberated from carbide and calcium hydroxide into its elements, C and H, at high temperatures.⁽⁹⁾ This nature will play some rôle on the nitrogenation process.

Activation by Adsorption. Now we come to the second problem "adsorption theory" of the author. At the beginning of nitrogenation, it was found that the reaction velocity is commonly very small. This can be attributed to lack of reacting or adsorptive position on the side of carbide. Such state of carbide can be called "inactive". The assumption of the author that the formation of cyanamide and separation of fresh carbon will favor the reaction, and if an active carbon is previously added to the carbide, the reaction will begin with a greater velocity, have all been proved to be true by the author with the experiments.⁽²⁾⁽³⁾⁽⁴⁾ (See Fig. 1.). Bredig's experiments⁽¹¹⁾⁽¹²⁾ that sugar charcoal accelerates the

(8) Birger W, *Nordlander Tek. Tid. Uppl. C. Kemi*, **64** (1934), 9.

(9) T. Aono, *J. Electrochem. Assoc. Japan*, **9** (1941), 81, 83.

(10) T. Aono, Unpublished.

(11) G. Bredig, *Z. Elektrochem.* **13** (1907), 69.

(12) G. Bredig, W. Fraenkel, E. Wilke, *ibid*, **13** (1907), 605.

reaction, while powder of cokes has no effect, will also support this hypothesis, because the adsorptive power and activity of cokes is commonly very small compared with sugar charcoal.

The famous experiment of Moissan,⁽¹³⁾ that pure CaC_2 does not react with nitrogen, can be attributed to lack of the initial adsorptive positions, which is necessary to introduce the reaction. Technical carbide contains always about 2% of free carbon, and beside this, the $\text{Ca}(\text{OH})_2$, which is always found in varying quantities by absorption of atmospheric moisture by the carbide, reacts with carbide at elevated temperatures, separating carbon as a very fine powder on the surface of carbide.⁽¹⁴⁾ $\text{Ca}(\text{OH})_2 = \text{CaO} + \text{H}_2\text{O}$, $\text{CaC}_2 + \text{H}_2\text{O}(\text{vap.}) = \text{CaO} + \text{C}_2\text{H}_2$, $\text{C}_2\text{H}_2 = 2\text{C} + \text{H}_2$. Le Blanc and Eschmann⁽¹⁴⁾ attributed this decomposition of carbide by heating to the catalytic action of nickel used in their experiments as the container of carbide. Their conclusion is not true, because the decomposition always occurs even in the absence of nickel. This unnecessary of nickel was also pointed out by P. Dolch,⁽¹⁵⁾ V. Ehrlich⁽¹⁶⁾ and also by Ruff and Förster.⁽¹⁷⁾

These carbon must always be acting an important rôle in starting the reaction.

An analogous example is the formation of nitride of alkali-earth metals from their elements, in case of which argon in the nitrogen forms a layer on the metals, and retards the reaction velocity remarkably.⁽¹⁸⁾

Another example, which support this adsorption hypothesis is that which was already reported and discussed in the former papers.^{(1),(5)} The adsorption of nitrogen on carbon and carbide at these high temperatures will chiefly be of chemical nature or activated adsorption. This nitrogen will form an intermediate compound with carbide, say $\text{CaC}_2\cdot\text{N}_2$, which, being very unstable, will rapidly liberate off nitrogen again or change to the second compound $\text{Ca}(\text{CN})_2$. This $\text{Ca}(\text{CN})_2$ is also unstable at the nitrogenation temperature and changes to CaCN_2 and C, which will again act as catalysts.

Formation of Cyanide. The formation of calcium cyanide as an intermediate product was verified by the author with the following experiment.

5.0372 g. of carbide ($\text{CaC}_2=80.0\%$, without any catalyst), contained in a nickel tube was subjected to nitrogenation at 1000°C for 55 minutes by the method previously reported. It was then suddenly taken out and rapidly cooled in cold water. The results of analyses were: increase in weight= $0.4236\text{g}=8.40\%$, residual CaC_2 in the product= 55.5% , total N= 7.40% , cyanamide N= 5.96% , cyanide N= 0.74% , insoluble N= 0.23% .

The presence of cyanide in the cyanamide in small quantities had already been reported by Bredig.⁽¹¹⁾ H. Franck and his co-workers discussed the equilibrium $\text{Ca}(\text{CN})_2 \rightleftharpoons \text{CaCN}_2 + \text{C}$ with their close experiments.⁽¹⁹⁾ According to them $\text{Ca}(\text{CN})_2$ is stable, when it is side by side with CaCN_2 , only at above the melting temperature of the system (ordinarily about 1150°C in case of technical cyanamide), or under 400°C . At the intermediate temperatures $\text{Ca}(\text{CN})_2$ soon decomposes into CaCN_2

(13) Moissan, C. r., **118** (1894), 501.

(14) M. Le Blanc and M. Eschmann, *Z. Elektrochem.* **17** (1911), 20.

(15) P. Dolch, *Z. Elektrochem.* **26** (1920), 455.

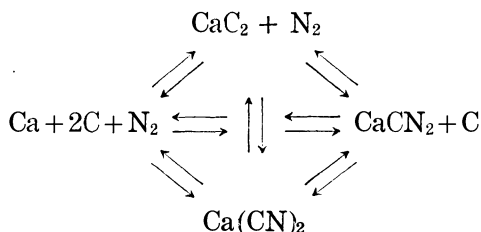
(16) V. Ehrlich, *Z. Elektrochem.* **28** (1922), 529.

(17) O. Ruff and E. Förster, *Z. anorg. allgem. Chem.*, **131** (1923), 321, 332.

(18) A. v. Antropoff, *Z. angew. Chem.* **44** (1931), 921; *Chem. Ztg.* **56** (1932), 424.

(19) H. H. Franck, W. Makkus and F. Janke, „Der Kalkstickstoff in Wissenschaft, Technik und Wirtschaft,“ Stuttgart (1931).

and C. Many other works have been reported on this problem^{(20) (21) (22) (23) (24) (25)}, and H. H. Frank and Kendler⁽²⁶⁾ proposed the following scheme for the nitrogenation equilibrium:



The formation of $\text{Ca}(\text{CN})_2$ as the intermediate compound is thus a matter of no question.

Action of Catalysts. In 1909 G. Bredig⁽¹¹⁾ and his co-workers⁽¹²⁾ studied the action of various substances on this nitrogenation, and objected to many explanatory hypotheses which had been offered by many persons at their time, such as "Oxydbildungstheorie", "Initialzündungstheorie", "auflockernde Wirkungstheorie" and "Abdissoziationstheorie". They left however "Verflüssigungstheorie" as a plausible one. Ehrlich⁽¹⁶⁾ reported that the system ($\text{CaCN}_2 = 75\%$, $\text{CaO} = 10\%$, $\text{CaCl}_2 = 15\%$) began to melt at about $820\text{--}900^\circ\text{C}$, while calcium cyanamide, prepared without any additions, sintered slightly at about 1100°C and became viscous fluid at $1200\text{--}1250^\circ\text{C}$. He concluded from his research that the catalytic action of CaCl_2 is to be attributed to the lowering of the melting point and depression of the vapour pressure and decomposition pressure of CaCN_2 . H. Franck and Heimann⁽²⁷⁾ also measured the melting points of CaCN_2 with additional substances. According to them the melting point of CaCN_2 is 1180°C , the lowest eutectic point of $\text{CaCN}_2\text{--CaC}_2\text{--CaO}$ system is 1146°C , and when CaF_2 is added to this system, the melting point lowers down to 953°C with 20% CaF_2 , while the lowest melting point of $\text{CaC}_2\text{--CaO--CaF}_2$ system is 1070°C . They also came to the same conclusion with Ehrlich. J. Gelhaar,⁽⁷⁾ on the contrary, reported that the melting point lowering of the mixtures due to additions has no relation to the reaction velocity.

The author has also perceived the lowering action of these salts, although CaF_2 has smaller effect on this point. Indeed their catalytic action can be attributed greatly to those lowering actions, but as those lowering powers are not parallel to their catalytic powers, there must be something more left to consider.

Chemical explanations have also been given. Polzenius⁽²⁸⁾ tried

(20) O. Kühling and O. Berkold, *Z. angew. Chem.*, **22** (1909), 193.

(21) H. Ewan and T. Napier, *J. Soc. Chem. Ind.*, **32** (1913), 467.

(22) P. Askenasy and F. Grude, *Z. Elektrochem.*, **28** (1922), 131.

(23) H. H. Franck and C. Bodea, *Z. angew. Chem.*, **44** (1931), 379.

(24) H. H. Franck and R. Neubner, *Z. Elektrochem.*, **40** (1934), 693.

(25) G. Petersen and H. H. Franck, *Z. anorg. allgem. Chem.*, **237** (1938), 1.

(26) H. H. Franck and W. Kendler, *Z. Elektrochem.*, **45** (1939), 541.

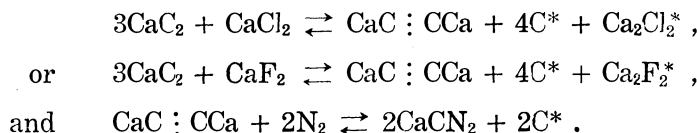
(27) H. H. Franck and Heimann, *Z. Elektrochem.*, **33** (1927), 469.

(28) Polzenius, *Chem. Ztg.*, **31** (1907), 958.

to explain the action of salts, such as CaCl_2 and NaF , with their low melting points and high ionization constants, which favor the formation of his so-called intermediate compound Ca_3N_2 . The formation of calcium nitride by this reaction was also supported by Krase and Yee,⁽²⁹⁾ who thought that CaC_2 dissociates to Ca and C , and this dissociated Ca combines with nitrogen to Ca_3N_2 , which quickly changes to CaCN_2 by the action of C and N_2 . The dissociation of CaC_2 into Ca and 2C had already been reported by Briner and Kühne,⁽³⁰⁾ while Erlwein and his co-workers⁽³¹⁾ said that CaC_2 dissociates to their so-called "subcarbides" and carbon. Ehrlich⁽¹⁶⁾ supported this and said that their subcarbide will be CaC , being the primary dissociation product of CaC_2 and CaCN_2 . This "subcarbide theory" was denied by Ruff and Förster.⁽¹⁷⁾ The existence of $(\text{CaC})_x$ is thus a matter yet undetermined.

The fact that the catalysts for nitrogenation of carbide have an action of decomposing CaC_2 and make it easy to combine with nitrogen was perceived by Erlwein and his co-workers.⁽³¹⁾ Although their conclusion was objected by Ruff and Förster,⁽¹⁷⁾ but Ehrlich and also Krase and Yee reported that CaCl_2 greatly accelerate the decomposition of CaC_2 by heating. The author⁽³²⁾ recognized the decomposition of CaC_2 when a piece of carbide was thrown into molten CaCl_2 or NaCl . One of the decomposition products was determined as carbon, while others are left yet as a matter of interesting problem to study. Of course it is difficult to say that this decomposition might not have been due to presence of traces of water remaining in the molten salts, though it was heated for a longer time.

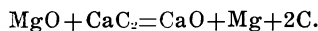
It is known that calcium tends to monovalent at elevated temperatures. The action of CaF_2 and CaCl_2 on CaC_2 at their melting temperatures might be considered conveniently as follows:



Of course this is only an hypothetical explanation of the author and has no experimental proof. But we are able to say surely that the action of CaCl_2 or CaF_2 is not equal to that of active carbon and phosphorus slag, because the latter affect the reaction at the starting point, while the former accelerate the reaction only after it has begun. (Compare the curves in Fig. 1.)

This postulation has another support.

The reduction of metals from their oxides with calcium carbide was experimentally studied by the author. For example, magnesia was reduced with carbide by heating the mixture at $1000\sim 1300^\circ \text{C}$ in vacuum. Mg metal was distilled off, and carbon was set free.



(29) H. J. Krase and J. Y. Yee: *J. Am. Chem. Soc.*, **46** (1924), 1358.

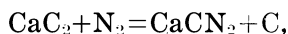
(30) Briner and Kühne, *J. du four Electr.* **1913**, 137, *C. r.* **156** (1913), 620.

(31) Erlwein, Warth and Beutner, *Z. Elektrochem.* **17** (1911), 177.

(32) T. Aono, Reported before the meeting of Chemical Society of Japan in Feb. (1932).

For this reaction, which occurs between the two solids, addition of CaF_2 in 10–30% shows favorite action.⁽³²⁾ Matsuno, Uchino and Tsuda also obtained the same results.⁽³³⁾ They tested many other additions such as $\text{AlF}_3 \cdot 3\text{NaF}$, CoS , CuS , Fe_2S_3 , $\text{Ca}(\text{BO}_2)_2$, but CaF_2 was recognized to be the only favorite catalyst in this reaction, all the others having negative effect. The effect of CaF_2 in this case must be attributed to its physical, such as melting point lowering, rather than chemical action upon the CaC_2 - MgO system; it facilitates the reaction just like the nitrogenation of carbide.

Heat of Activation and Catalytic Power. From the velocity constants and their thermal relations, the apparent heat of activation for the reaction,

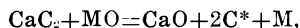


was determined by the author to be 58.6 Cal./mol. at 1000–1060°C. Above 1080°C, where the reaction proceeds very rapidly, the heat of activation decreases to 33 Cal./mol. in case of powdered carbide containing CaF_2 in 1%.⁽²⁾ These values coincide with those which were determined recently by H. Franck and Endler⁽³⁴⁾ fairly well. They found the heat (at 950–1000°C) to be about 54 Cal./mol. for pure carbide (crystal structure I, II, III), 54 Cal./mol. for carbide containing sulphur, 40 Cal./mol. for carbide containing cyanamide nitrogen (melted together with CaCN_2) and 33 Cal./mol. for carbide containing CaF_2 .

From the above figures we can recognize certainly the fact that the effective catalysts depress the heat of activation at temperatures where the catalysts play their rôle effectively.

Action of Carbon. In the earlier section of this paper, it was stated that the nascent carbon, liberated by the reaction, may act as a catalyser. It was found that addition of active carbon not only affects the reaction velocity, but also changes the character of the velocity curves of nitrogenation. (See Fig. 1.)

It was also pointed out by the author⁽⁴⁾ that the slag of phosphorus furnace, having the composition $\text{P}_2\text{O}_5=1.29$, $\text{SiO}_2=18.3$, $\text{Fe}_2\text{O}_3=1.75$, $\text{Al}_2\text{O}_3=16.55$, total $\text{CaO}=49.40\%$, had also catalytic action. It is very interesting that the slag has the same character as the active carbon (See Fig. I.). This can be explained by the fact that the slag, being oxides of metals, decomposes carbide as follows:



Some kind of metals thus liberated, also with the nascent C^* , may accelerate the reaction.

At temperatures of the nitrogenation CaC_2 and C will not react with each other, therefore the influence of C on the activity of CaC_2 must be of physical nature, such as adsorbing property due to the boundary surface action. The freshly separated carbon will not only sorbs nitrogen on its own surface, but also will give CaC_2 an active boundary, and thus the nitrogen will be activated to form $\text{Ca}(\text{CN})_2$ with these surrounding carbide.

(32) G. Harada, T. Aono, I. Kobayashi, Report in the *Denki-Kagaku-Kogyo*. K. K. (1938).

(33) Matsuno, Uchino and Tsuda, *J. Soc. Chem. Ind. Japan*, **42** (1939), 597.

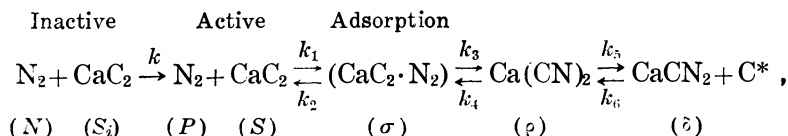
(2) T. Aono, *loc. cit.* see also Landolt-Börnstein's *Physikalische-Chemische Tabellen*, Eg. III C. (1936), 2892.

(34) H. H. Franck and H. Endler, *Z. physik. Chem.* **184** (1939), 127.

It is known that in case of "case-hardening" of steel, presence of nitrogen is effective for the carburization of iron with charcoal. Comparing this with the effectiveness of CN-compounds as carbonizers, it can be thought that nitrogen will be adsorbed by the carbon chemically and acts as a CN-compound to the surface of adjacent iron, giving carbon to it and setting nitrogen free again.

Analogous mechanism could be given in our case. Some of the nitrogen, which is adsorbed by carbon at these high temperatures, may react with CaC_2 (or its dissociated product, if there is any of such) to form $\text{Ca}(\text{CN})_2$ or CaCN_2 and C.

Mathematical considerations. With the reaction scheme proposed by the author:



the following equations were deduced previously,⁽⁵⁾

$$\begin{aligned}
 S &= \frac{S_{i0}}{k_1 P - k} \cdot e^{-kt} - \left(\frac{S_{i0}}{k_1 P - k} - S_0 \right) \cdot e^{-k_1 P t} \quad \text{and} \\
 -\frac{dN}{dt} &= \frac{k_1(k_3 - k)PS'_0}{K - k} \cdot e^{-kt} - \frac{k_1 P(k_3 - k_1 P)(S'_0 - S_0)}{k_2 + k_3} \cdot e^{-k_1 P t} \\
 &\quad - (k_1 P + k_2) \left\{ \sigma_0 - k_1 P \left(\frac{S'_0}{K - k} - \frac{S'_0 - S_0}{k_2 + k_3} \right) \right\} e^{-Kt}
 \end{aligned}$$

Comparing the curves represented by these equations and those of experimentally found, we can find that the physical meanings of these equations give us fair agreement with the above considerations.

For example, the active carbon and phosphorus slag give considerably large values for S_0 , which means that they are initial activators, and in presence of them the reaction begins with a larger velocity at once, while calcium fluoride gives no influence upon S_0 . In the latter case S_0 is nearly equal to zero, and the reaction starts with nearly zero velocity.

On the contrary, calcium fluoride increases the velocity constants k_3 and k_5 and also the stability of CaCN_2 , which means that it makes k_4 small and shifts the equilibrium to the right hand. Calcium chloride and sodium chloride increase k_3 , k_5 , k_6 simultaneously. These halogenides are not mere catalysts in this reaction.

As it was stated, the above equations represent mainly the earlier stage of the nitrogenation of powdered carbide at comparatively lower temperatures. For granular carbide, in case of which the reaction velocity is chiefly determined by penetration of nitrogen into the inner part from the surface, as was formerly studied by the author⁽³⁾, the action of carbon

is negligible, while CaCl_2 and CaF_2 play an important rôle, depressing the melting points and reducing the chemical resistance of the reaction.

Classification of the Catalysts. Conclusively the author considers the action of catalysts to be quite different with each other. Active carbon and phosphorus slag favor the first stage of the nitrogenation, i. e. adsorption and activation of nitrogen, and makes the start of the reaction easy, (Class I.), while calcium fluoride favors chiefly the third stage, diminishing the resistance in the CaCN_2 formation, both chemically and physically, and also it keeps the cyanamide stable. (Class IV.).

The second stage, i. e. the formation of $\text{Ca}(\text{CN})_2$ is favored by adding alkali- and alkali-earth-chlorides such as NaCl and CaCl_2 . (Class II.). Of course these additions are not welcomed in industry, because they increase the contents of cyanide in the cyanamide, which is dangerous to our health.

$\text{Ca}(\text{CN})_2$ and CaCN_2 formed by the reaction or co-melted previously with carbide, facilitate the cyanamide formation by activating the carbide (Class III), while CaS hinders the reaction by inactivation.

Some of the catalysts, mentioned above, have combined actions, affecting on two or three stages simultaneously, and cannot be confined to a definite class.

Summary.

In this paper the theories of nitrogenation of calcium carbide were summarized and discussed, and the mechanism of these catalytic action was explained.

1. The mechanism of nitrogenation was ascertained as follows:
 - I. activated adsorption of nitrogen on active positions of carbide, (at comparatively lower temperatures);
 - II. formation of an intermediate compound, $\text{Ca}(\text{CN})_2$, temporarily,
 - III. breaking up of $\text{Ca}(\text{CN})_2$ into CaCN_2 and C ,
 - IV. further propagation of the CaCN_2 -formation.
2. The action of catalysts can be classified also in four kinds:
 - I. catalysts which affect the adsorption of nitrogen on the carbide surface and make the start of the reaction easy, (active carbon or nascent carbon and carbon separating material such as phosphate-slag,)
 - II. catalysts which favor the cyanide formation as well as the procession of cyanamide formation, (alkali and alkali-earth chlorides), they also affect the equilibrium $\text{Ca}(\text{CN})_2 \rightleftharpoons \text{CaCN}_2 + \text{C}$,
 - III. catalysts which activate the carbide and facilitate the cyanamide formation, ($\text{Ca}(\text{CN})_2$ and CaCN_2 formed by the reaction or co-melted previously with the carbide; CaS being a negative catalyst in this class,)
 - IV. catalysts which accelerate the propagation of the reaction diminishing chemical resistance physically as well as chemically, (CaF_2 , CaCl_2 etc.)

Of course some of these catalysts have combined actions affecting on two or three stages simultaneously.

3. The depression of melting points, heat of activation, dissociation pressure of the cyanamide and the CaC_2 - CaCN_2 system by these catalysts were also discussed.
4. Some chemical interpretations for the action of some catalysts were also proposed, (hypothetically).

The Denki-Kagaku-Kogyo Kabushiki Kaisha.

Polymerisation of Tung Oil. IX. Comparison of Gelation Phenomena of Tung Oil and Oiticica Oil.

By Monzi TATIMORI.

(Received November 28, 1940.)

The main constituent of tung oil which is one of the most rapidly drying fatty oils, is the glyceride of α -eleostearic acid, and has three double bonds in conjugated form. Recently oiticica oil produced in South America has been found to have powerful drying nature as comparable to that of tung oil. The main constituent of oiticica oil is licanic acid and its constitution is believed to be $\text{CH}_3(\text{CH}_2)_3\text{CH}=\text{CH}\text{CH}=\text{CH}\text{CH}=\text{CH}(\text{CH}_2)_4\text{CO}(\text{CH}_2)_2\text{COOH}$, and its unsaturated nature is considered similar to α -eleostearic acid, therefore the gelation tendency of oiticica oil also is supposed to be similar to tung oil. The author reported formerly about the results of gelation of tung oil and it is interesting to ascertain that the conclusion obtained from the study of tung oil concerning gelation

may be applied to oiticica oil which has the similar constitution as tung oil.

Table 1. Constants of oiticica oil.

Density (15/15)	0.9771
Iodine value	148.9
Refractive index (20°C.)	1.5130
Acid value	4.93
Saponification value	183.7

Experimentals. In this experiment the following oiticica oil was used.

The characteristic constants of the fatty oils used are shown in Table 2.

Table 2.

Kind of oil	Density (15°C.)	Refractive index (20°C.)	Iodine value	Saponification value	Acid value
Japanese wood oil	0.9347	1.5037	155.4	196.0	3.2
Tung oil	0.9422	1.5185	168.5	180.0	6.9
Linseed oil	0.9329	1.4818	182.2	190.6	11.1
Soya bean oil	0.9247	1.4750	134.8	195.7	1.4
Camellia oil	—	1.4694	79.8	191.9	5.0

The method of determining the gelation times is the same as in the previous reports and the experiment was carried out at 270°C.

Table 3.

Added Substances (%)	Gelation time (t) (sec.)	$\frac{1}{t} \times 10^4$
(1) Tung oil*		
0	1291	7.75
20	1218	8.21
40	1138	8.79
60	1082	9.24
80	1030	9.71
100	970	10.31
(2) Linseed oil		
0	1290	7.75
5	1442	6.94
10	1639	6.10
15	1921	5.21
20	2260	4.43
(3) Soya bean oil		
0	1415	7.07
5	1630	6.13
10	1890	5.29
15	2258	4.43
20	2849	3.51
25	3960	2.53
(4) Camellia oil		
0	1199	8.34
5	1368	7.31
10	1620	6.17
15	1982	5.05
20	2497	4.01
(5) Stearic acid		
0	1209	8.27
2.5	1459	6.85
5.0	1877	5.33
7.5	2690	3.72
10.0	3889	2.52
(6) Cetyl alcohol		
0	1200	8.33
2.5	1470	6.80
5.0	1996	5.02
7.5	3295	3.05
10.0	4700	2.13
(7) Rosin		
0	1209	8.27
2.5	1250	8.00
5.0	1285	7.78
7.5	1344	7.44
10.0	1403	7.13

* The relations between gelation times and percent. of tung oil are shown in Fig. 1.

Table 3.—(Concluded)

Added Substances (%)	Gelation time (t) (sec.)	$\frac{1}{t} \times 10^4$
(8) 5° blown asphalt**		
0	1200	8.33
5	1132	8.83
10	1260	7.94
15	1609	6.21
(9) Japanese wood oil		
0	1120	8.93
20	1221	8.15
40	1350	7.41
60	1500	6.67
80	1697	5.89
100	1928	5.18

** The results are shown in Fig. 2.

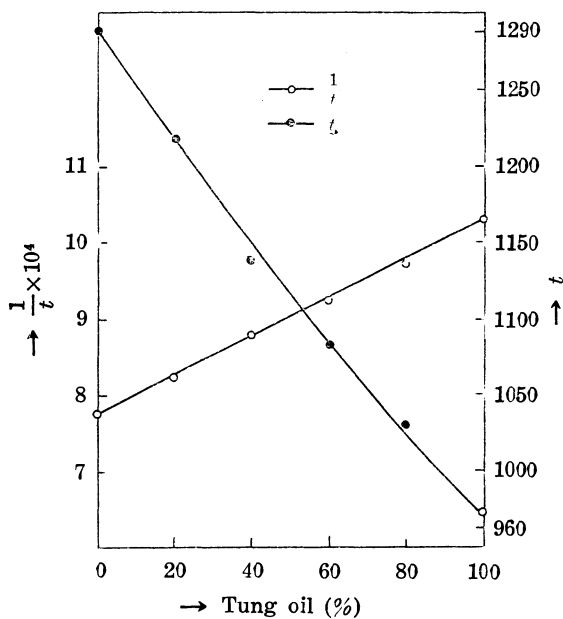


Fig. 1. The relation between gelation time and percentage of tung oil added.

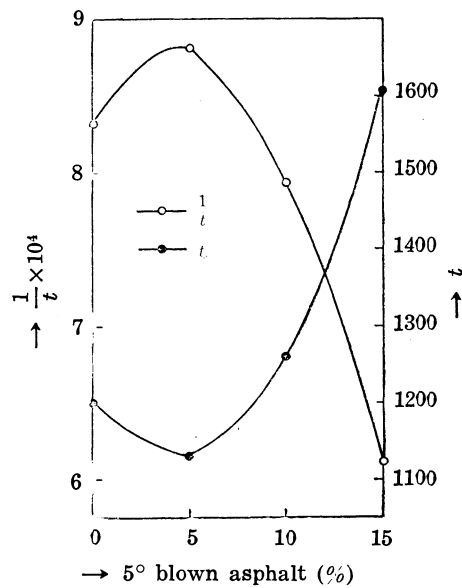


Fig. 2. The relation between gelation time and percentage of 5° blown asphalt added.

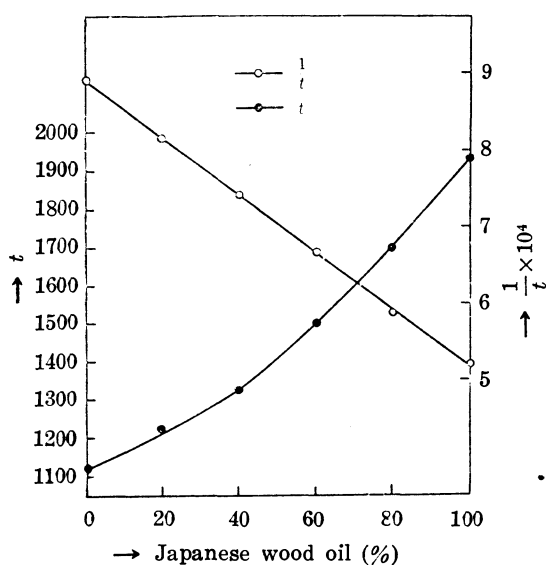


Fig. 3.

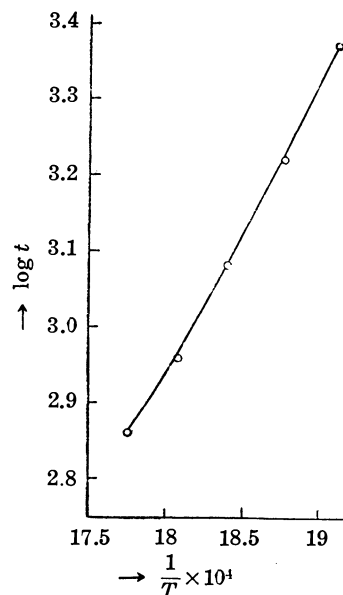


Fig. 4.

Relation between gelation times and temperatures. The gelation times of oiticica oil are shown in Table 4.

Table 4. Gelation time of oiticica oil.

Temp. (°C.)	Gelation time	$\frac{1}{t} \times 10^4$	$\log t$
250	2358	4.24	3.373
260	1660	6.02	3.220
270	1207	8.28	3.082
280	914	10.94	2.961
290	730	13.70	2.863

The relation between $\log t$ and $1/T$ is shown in Fig. 4.

The gelation times of the mixture of 50% of oiticica oil and 50% of tung oil are shown in Table 5.

Table 5.

Temp. (°C.)	Gelation time
250	2105
260	1383
270	989
280	745
290	595

The relations between gelation times and temperatures are shown in Fig. 5.

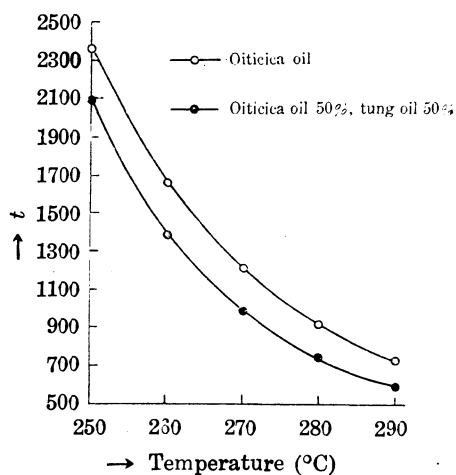


Fig. 5.

Discussion of Results. The general tendency of the gelation phenomena of oiticica oil is similar to that of tung oil.

Table 6.

Substances	x_{∞} at 270°C. (%)
Japanese wood oil	236
Linseed oil	46
Soya bean oil	39
Camellia oil	37.5
Stearic acid	14.5
Cetyl alcohol	12.7

The gelation time is prolonged by the addition of fatty oils and the relations between the reciprocals of gelation times and the percentage of added fatty oils are linear, and the values of x_{∞} were obtained by extrapolation.

The value of x_{∞} increases according to the increasing degree of the unsaturation of fatty oil.

The gelation preventing action of stearic acid and cetyl alcohol are very strong as compared to fatty oils.

The temperature dependence of the gelation time of oiticica oil is similar to that of tung oil.

In conclusion, the author wishes to express his sincere thank to Dr. K. Baba, Dr. T. Yosioka, and Mr. K. Yokota for their kind guidance.

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Polymerisation of Tung Oil. X. Gelation of Tung Oil at High Temperature (Summarized Report).

By Monzi TATIMORI.

(Received November 28, 1940.)

In the previous reports⁽¹⁾ the author informed about the gelation preventing effects of various materials, such as fatty oils, fatty acids, fatty alcohols, several organic and inorganic reagents, bitumens, cooked drying oils, brominated fatty oils, and natural and synthetic resins etc., and interesting results were obtained. In this paper the summarised conclusions are reported.

I. Classification by the Type of Relation of $1/t-x$. The gelation times of the samples were measured by the method of test tube similar to that of A.S.T.M. and the numerical results were reported in the previous reports.

(1) M. Tatimori, *J. Soc. Chem. Ind., Japan*, Suppl. Bd., **41** (1938) 39-41B; 100-102B; **42** (1939) 162-163B; **43** (1940) 102-104B; **43** (1940) 136-140B; 161-162B; 194-196B; This Bulletin, **13** (1938) 142; **15** (1940) 315, 474; **16** (1941) 16, 45, 51, 75, 82, 114.

The various types of relation of $1/t-x$ are shown in Fig. 1 and these could be classified in the next 8 classes:

(1) *Substances whose relations of $1/t-x$ are linear.* Greater part of the samples are included in this class. This class is noteworthy both from theoretical and industrial view point and the further discussion shall be given later.

Example: fatty oils, oxidised and polymerised linseed oil, oxidised perilla oil, fatty acids, fatty alcohols, paraffines, coumarone resin.

(2) *Substances which have no effect.*

Example: neutral salts and oxides, e.g. BaCl_2 , NaCl , KCl , ZnO .

(3) *Substances of which gelation times increase more rapidly than the linear relation.* It is supposed that these materials have special actions upon tung oil, of which reaction products have gelation retarding action. At higher

temperature than 300°C . many substances belonging to class (1) convert to this class.

Example: glycerine, oleic acid monoglyceride, rosin.

(4) *Reverse of class (3).* The gelation retarding action of the substance decreases with the lapse of heating time, by the decomposition or vaporisation.

Example: β -naphthol, camphor, naphthalene.

(5) *Substances having very strong gelation retarding actions.* These substances act catalytically upon tung oil.

Example: sulphur, selenium, brominated fatty oils.

(6) *Substances having gelation accelerating actions.* These substances act catalytically upon tung oil.

Example: benzoyl peroxyde, tannic acid, gallic acid, pyrogallol, tartaric acid, metallic sodium.

(7) *Substances which act gelation retarding at little addition, but convert to gelation accelerating at increased addition.*

Example: succinic acid, citric acid.

(8) *Reverse of class (7).*

Example: α -naphthol, various bitumens.

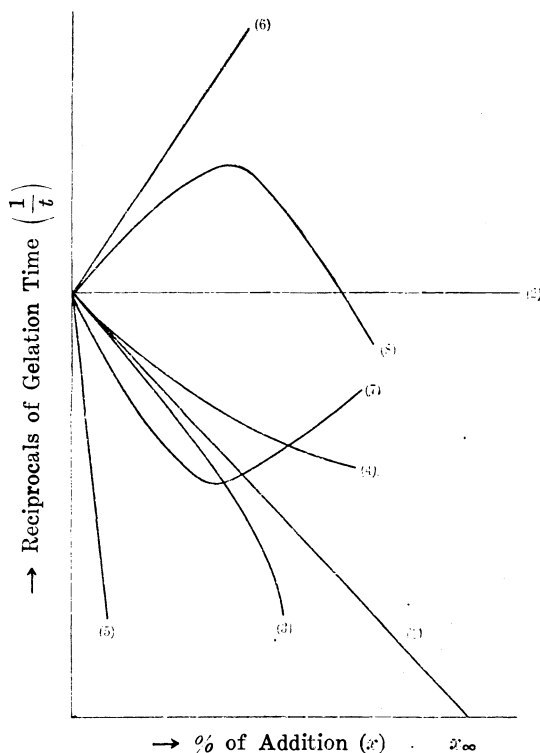


Fig. 1.

II. General Consideration. Of the retarding nature of all substances the next could be concluded in common.

(1) *Effect of unsaturation.* In the addition of fatty oils and fatty acids, the values of x_{∞} increase as the degree of unsaturation increases. This is anticipated from the fact that the unsaturated compound has the tendency to polymerise itself, and co-polymerise with the tung oil.

(2) *Effect of cooking degree.* Similarly the values of x_{∞} of cooked drying oils increase according to the degree of cooking. This coincides with the fact when drying oils were cooked, they turned into gelatinous state at last. From this fact the gelation tendency of cooked drying oil could be estimated and these have wide application in industrial field.

(3) *Effect of secondary reaction at high temperature.* It is supposed that at higher temperature than 300°C. the secondary reactions occur during the measurement, because the relation of $1/t-x$ becomes irregular at high temperature. The gelation time shows a minimum value above 300 °C. and further it increases.

From the next experiment it is concluded that the cracking of glycerine radical occurs. The increased of acid value is shown in Table 1, when the mixture of 100 g. of tung oil and 100 g. of linseed oil was heated in a glass bottle at 310 °C. Acid value increased as proportion to the heating time.

Table 1.

Time of polymerisation (min.)	Acid value
0	4.56
5	6.21
10	6.93
15	7.32
20	7.93
25	8.34

The cracking products have gelation preventing action, therefore the gelation time of the system increases.

When fatty acids and alcohols were added, the minimum of gelation time was found at lower temperature than in the case of addition of fatty oils, and the temperature of minimum gelation time becomes lower as the amount of addition increases.

When fatty oils were heated at temperature higher than 200 °C. with fatty alcohols, fatty acids and esters the exchange of ester part occurred.⁽²⁾ Thus the strong gelation preventing action of glycerine and oleic acid monoglyceride can be explained.

Beside these reactions the isomerisation of α -eleostearic acid by S, Se and brominated fatty oils is considered as the cause of strong gelation retarding action of the substances.

(4) *Solubility.* The irregularity of relation of $1/t-x$ was observed when tung oil was heated by addition of less soluble substances such as polybasic acids. At the limiting case the added reagent often crystalysed out when the polymerisation of tung oil proceeded considerably.

III. Effect of Molecular Weight. The values of x_{∞} of several substances which was considered not to react with tung oil are shown in Table 2.

(2) Norman, *Chem. Umschau*, **30** (1923) 250; Krumbhaar, "The Chemistry of Synthetic Coating Materials;" R. Oda, *J. Soc. Chem. Ind. Japan*, Suppl. Bd., **36** (1938) 755, 945.

Table 2.

Substances	Molecular weight	x_{∞} (weight %)	x_{∞} (mol %)
Tristearin	890	61.0	60.5
Camellia oil (triolein)	884	59.0	58.5
Stearic acid	284	33.0	59.2
Oleic acid	282	34.5	62.2
Olein alcohol	266	32.5	61.4
Cetyl alcohol	242	31.0	61.6
Oleic acid monoglycol	326	35.0	59.3
Oleic acid monoglyceride	356	24.0	40.8
Glycerine	92	10.5	52.5
Perilla oil	(878)	75.5	75.5

The values of x_{∞} of first group, substances from tristearin to oleic acid monoglycol, are about 60%. The cause of gelation preventing action of these substances are considered as mechanical dilution.

Hitherto the special degelating action was considered as the nature of strong gelation preventing action of fatty acid, but from the author's opinion there is no special difference observed between fatty acid and oil, except their molecular weight. The molecular weight of fatty acid was 1/3 of that of fatty oil, therefore the gelation preventing action of fatty acid apparently is great when expressed by weight percentage.

Substance such as glycerine, whose value of x_{∞} is less than 60%, has special chemical action, of which the reaction products have strong gelation preventing action; on the other hand substances whose value of x_{∞} are greater than 60%, promote the gelation of tung oil due to co-polymerisation.

IV. Examination of Measured Gelation Time. As the gelation times of tung oil were measured by heating the sample taken in test tubes, they are affected by the conditions of measurement such as the dimensions of the apparatus, the volume of sample taken etc. The fatty oil itself is a complex mixture of glycerides of various fatty acids, therefore the absolute values obtained have no important meaning, but the results obtained in the same conditions can be used for the comparison of gelation preventing or accelerating actions of various substances.

As remarked above, in the case where the neutral substances soluble in tung oil were added to the oil, the relation between the reciprocals of gelation time and the amount of addition are linear. The value of x_{∞} extrapolated, was experimentally shown to be a characteristic constant of the added substance and it is not affected by the measuring conditions. In order to ascertain this fact the measurements were carried out at 270°C. in the case of addition of linseed oil, by using two test tubes, one

being the ordinary, with length of 15.5 cm., diameter of 4.0 cm., the other being the specially made, its length 13.9 cm. and its diameter 0.8 cm. (this is very small as compared to the ordinary one), and the linear relations were observed and the values of x_{∞} were 67%, in the both measurements.

But strictly speaking the gelation time thus observed contains some errors apparently; that is, it takes about two minutes for the sample taken in the measuring apparatus to attain the measuring temperature.

The temperature of the sample was measured by inserting the pyrometer junction in the sample and it was observed that within the first one minute the temperature rose rapidly above 200°C., but after this time the elevation of temperature became very slow. Strictly, the gelation time must be measured at constant temperature, therefore the correction term (α minutes), the ineffectual time during the rise of the temperature of the sample to the measuring temperature, should be subtracted from the apparent gelation time.

Now denoting the apparent gelation times of tung oil and of that added with other gelation preventing substance as t_0 and t'_0 , it was established from the observations that the next equation holds.

$$\frac{1}{t'} = \frac{1}{t'_0} - \frac{x}{C} \quad (1)$$

As C equals $t'_0 \times x_{\infty}$, so it can be expressed as follows.

$$\frac{1}{t'} = \frac{1}{t'_0} \left(1 - \frac{x}{x_{\infty}}\right) \quad (2)$$

Taking t_0 and t , as the theoretical gelation time then $t'_0 = t_0 + \alpha$, $t' = t + \alpha$ and

$$\frac{1}{t + \alpha} = \frac{1}{t_0 + \alpha} \left(1 - \frac{x}{x_{\infty}}\right) \quad (3)$$

That is,

$$\begin{aligned} \frac{1}{t} \left(1 - \frac{\alpha}{t}\right) &= \frac{1}{t_0} \left(1 - \frac{\alpha}{t_0}\right) \left(1 - \frac{x}{x_{\infty}}\right). \\ \frac{1}{t} &= \frac{1}{t_0} \left\{1 + \alpha \left(\frac{1}{t} - \frac{1}{t_0}\right)\right\} \left(1 - \frac{x}{x_{\infty}}\right) \\ &= \frac{1}{t_0} \left(1 - \frac{\alpha x}{t_0 x_{\infty}}\right) \left(1 - \frac{x}{x_{\infty}}\right) \end{aligned} \quad (4)$$

If we neglect the term $\frac{\alpha}{t} \frac{x}{x_{\infty}}$, the both equations (4) and (2) coincide.

Assuming $t_0 = 15$, $\alpha = 1$, $x_{\infty} = 0.5$, then the value of $\frac{\alpha}{t_0} \frac{x}{x_{\infty}}$ becomes as follows.

The error increases as x increases, but the maximum value is about 5%. The term $\alpha x / t_0 x_{\infty}$ can be neglected, and by

Table 3.

x	$\alpha x / t_0 x_{\infty}$	Error (%)
0	0	0
0.1	1/75	1.3
0.2	2/75	2.6
0.3	3/75	4.0
0.4	4/75	5.3
0.5	0	—

using the theoretical gelation times we obtain the next formula.

$$\frac{1}{t} = \frac{1}{t_0} \left(1 - \frac{x}{x_\infty} \right) \quad (5)$$

Thus it is noticed that the above formula should have theoretical meaning.

V. Theoretical Deduction of Linear Relation of $1/t$ and x . For this purpose the content of polymerides in the tung oil gel should be known. From the result of Bolton⁽³⁾ the next relation was obtained, $G = G_0 (1 - \alpha x)$, where G denotes the content of polymerised tung oil in the gel, G_0 , that of 100% tung oil gel, x is the percent. of added substance, α is a constant.

From the study of the author⁽⁴⁾ the polymerisation of tung oil proceeds as a bimolecular reaction.

$$\frac{dx}{dt} = K(a-x)^2$$

Now integrating the above formula, we have

$$\frac{G}{a(a-G)} = Kt \quad (6)$$

Generally, when other substances were added to tung oil, then the value of a , K , G were changed, and consequently it results in various types of relation of $1/t$ and x .

Now we consider the case where the neutral substance was added. Assuming the amount of addition to be x , then $a=1-x$, and $G=G_0(1-\alpha x)$, $K=K_0(1-\beta x)$, then

$$\begin{aligned} \frac{1}{t} = \frac{K_0}{G_0} & \left[(1-G_0) - \{A-\alpha+(1+\beta)(1-G_0)\}x + \{(1+\beta)(1-\alpha) \right. \\ & \left. -\alpha(1-G_0\alpha) + (1-G_0)\beta\} \right] x^2 + \dots \end{aligned} \quad (7)$$

By neglecting the higher term of x , we have

$$\frac{1}{t} = \frac{1}{t_0} - \frac{K_0}{G_0} \{2+\beta-\alpha-G_0(1+\beta)\}x \quad (8)$$

Thus the linear relation of (5) can be deduced theoretically.

VI. Polymeric Functionality and Gelation of Tung Oil. Carothers⁽⁵⁾ and Bradley⁽⁶⁾ classified the chemical reactions in the types of (m, n) , from the number of reactive radicals of interacting molecules (functionality). In the reaction of (1, 1), (1, 2) and (2, 2) no gelation

(3) Bolton, *Analyst*, **51** (1926) 335.

(4) M. Tatimori, this Bulletin, **13** (1938) 142.

(5) Carothers, *Trans. Faraday Soc.*, **32** (1936) 39.

(6) Bradley, *Ind. Eng. Chem.*, **30** (1938) 689.

occurs, and the gelation occurs only in the reactions of (2, 3) or higher order reaction.

According to Carothers a general equation relating degrees of reaction (P), average degree of polymerisation (x) and functionality can be developed.

Let f =degree of functionality

N_0 =number of monomer molecules initially present

Then N_0f =number of functions initially present

N =number of molecules after reaction has occurred.

$2(N_0-N)$ =number of functions lost

$\frac{2(N_0-N)}{N_0f}$ =fraction of functions lost = P = extent of reaction

obviously, N_0/N =average degree of polymerisation= x .

Hence,

$$P = \frac{2}{f} \left(1 - \frac{1}{x} \right) \quad (9)$$

This equation has interesting application in the gelation of tung oil.

Referring again to formula (9), if x is very large the second term disappears, and we have $P_\infty = 2/f$, which tells us at what degree of reaction the molecular weight will become infinite (gelation occur), or where, in polyfunctional reactions, gelation will occur and inter molecular reaction cease.

It is supposed that the number of functionality f of α -eleostearic acid triglyceride is 6, but in the case of tung oil $f=5.1$ (6×0.85), then the value of P_∞ equals 0.40. That is, when tung oil turns to gelatinous state, at least 40% of the oil must be polymerised.⁽⁷⁾ This fact coincides with the above experimental results which require for preventing the gelation of tung oil, 60% of other neutral substance should be added.

Summary.

(1) The summarized conclusions about the gelation of tung oil at elevated temperature are reported.

(2) The various types of relation of $1/t \sim x$ of added substances can be classified into 8 classes and the general consideration of gelation-retarding nature are given.

(3) The measuring method of gelation time are discussed and the formula of $1/t = 1/t_0 - ax$ is deduced from the polymerisation mechanism.

(4) The gelation phenomena of tung oil are considered from the theory of polyfunctionality and the value of x_∞ can be obtained from the formula $x_\infty = (1 - p_\infty) = \left\{ 1 - \lim_{x \rightarrow \infty} \frac{2}{f} \left(1 - \frac{1}{x} \right) \right\}$ as 60%. This value coincides with the experimental fact.

(7) P_∞ can be obtained also by the following method,

$$\frac{5.1(100 - x_\infty) + 0 \times x_\infty}{100} = 2$$

In conclusions, the author wishes to expresses his sincere thanks to Prof. J. Samesima of the Tokyo Imperial University and to Dr. K. Baba, Dr. T. Yosioka and Mr. K. Yokota of this Works for their kind guidance.

Tung oil is one of the most important product of Chinese continent and hitherto was exported about 65,000 tons per year. Tung oil is the most unsaturated and quick drying fatty oils in the world, and the varnishes made from it have many excellent properties such as water proofness, acid and alkali proofness, and used for the important machines, such as arms, motor-cars and electric machines.

The Japanese industry nowadays has a tendency to mass production with the development of the Japanese economical block from the standpoint of "autarkie" of the East Asia, and the demand of the quick-drying varnishes increases more and more.

Therefore the study of tung oil will be increased in its importance.

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Polymerisation von Styrol in schwerem Alkohol.⁽¹⁾
(Ein Beitrag zum Mechanismus der Kettenpolymerisation
von Styrol in Lösungen.)

Von Tohiti YOSIDA und Toshizo TITANI.

(Eingegangen am 6. März 1941.)

Inhaltsübersicht. Das Styrol wird in Lösung von schwerem Alkohol d.h. D-haltigem Alkohol thermisch polymerisiert und der Gehalt des dabei gebildeten Polystyrols an D dadurch bestimmt, dass man das Polymerisat, nachdem es entweder durch mehrmaliges Auswaschen mit Toluol oder durch langstündige Erwärmung (300°) im Vakuum vom anhaftenden Lösungsmittel d.h. vom Alkohol so weit wie möglich befreit worden ist, im Sauerstoffstrom bis zu Wasser verbrannt und der Gehalt des so gewonnenen Wassers an D genau bestimmt. Die Versuche werden unter Benutzung zweier Arten von schwerem Alkohol zweireihig ausgeführt. Die eine Art schwerer Alkohol enthält (praktisch) sämtliche D-Atome im Hydroxylradikal d.h. in direkt austauschbarer Form die andere dagegen im Äthylradikal also in nicht direkt austauschbarer Form. Der Gehalt des Wassers an D, das unter Verwendung dieser beiden Arten der schweren Alkohole gewonnen wurde, blieb aber innerhalb des Messfehlerbereiches immer derselbe, mindestens so lange als die D-Konzentration in den gesamten H-Atomen des verwendeten Alkohols dieselbe bleibt und der Versuch unter den gleichen Bedingungen ausgeführt wird. Aus diesem Versuche wird deshalb geschlossen, dass erstens praktisch keine H-Atome des Styrolmoleküls während seines Polymerisationsprozesses genügend frei bis zur Austauschreaktion gegen die des Lösungsmittels gelockert werden und zweitens dass das Polymerisat einige Moleküle Alkohol an sich bzw. in sich ziemlich fest enthält. Auf Grund dieser Befunde wird der Mechanismus der Kettenpolymerisation des Styrols in Lösungen diskutiert.

(1) Vorläufig mitgeteilt in *Proc. Imp. Acad. Tokyo*, **16** (1940), 33.

Einleitung. Die Polymerisation von Styrol kann nicht nur in Gasphase sondern auch in rein flüssiger Phase bzw. in Lösung von verschiedenen Arten des Lösungsmittels verlaufen. Die Reaktion kann weiter nichtkatalytisch als auch katalytisch ausgeführt werden. Aber in jedem Fall wird die Reaktion als eine Art Kettenreaktion aufgefasst. Der ganze Prozess der Kettenpolymerisation des Styrols kann deshalb gemeinsam mit der allgemeinen einfachen Kettenreaktion in drei Teilprozesse geteilt werden: ⁽²⁾

- (1) Kettenstart bzw. Keimbildungsprozess,
- (2) eigentliche Polymerisation bzw. Kettenwachstumsprozess,
- (3) Desaktivierung bzw. Kettenabbruchsprozess.

Obwohl jede Einzelheit dieser drei Teilprozesse noch nicht ganz einwandfrei aufgeklärt worden ist, liegt doch die Vermutung nahe, dass möglicherweise eine Lockerung der H-Atome in einem Styrolmolekül (beim Keimbildungsprozess) oder eine intra- bzw. intermolekulare Wanderung der H-Atome (beim Wachstums- und Abbruchsprozess) stattfinden kann. Falls dies wirklich der Fall wäre, dann liegt weiter die Möglichkeit vor, dass während der Polymerisation des Styrols die H-Atome des letzteren gegen die des Lösungsmittels ausgetauscht werden, wenn man die Reaktion in solch einem Lösungsmittel ausführt, das ein bzw. einige austauschbare H-Atome enthält. Unter dieser Voraussetzung wird die Reaktion von Koizumi und Titani⁽³⁾ beim Vorhandensein von verdünntem schwerem Wasser sowie in Lösung von verdünntem schwerem Alkohol untersucht. Der Versuch wird dabei so ausgeführt, dass man den Gehalt des schweren Wassers bzw. schweren Alkohols an D vor und nach dem Versuch bestimmt und dadurch die eventuell wegen der Austauschreaktion zwischen dem Styrol und Wasser bzw. Alkohol stattfindende Veränderung der D-Konzentration im letzteren ausfindig zu machen versucht. Bei diesem Versuch stellt sich aber heraus, dass der Gehalt des Wassers bzw. des Alkohols an D durch die darin stattfindende Polymerisation von Styrol kaum beeinflusst wird. Deshalb die Schlussfolgerung, dass praktisch keine H-Atome im Styrolmolekül bis zur Austauschreaktion gegen die des Lösungsmittels gelockert werden, wenigstens so lange als es sich um einen Keimbildungsprozess und daran folgenden Kettenwachstumsprozess handelt. Doch allein aus den damals gewonnenen Versuchsergebnissen können wir nicht ohne weiteres zu dem Schluss kommen, dass dieselbe auch beim zuletzt verlaufenden Kettenabbruchsprozess auftritt, weil bei diesem letzten Prozess jedes Styrolmolekül schon bis zu einem sehr grossen Kettenmolekül angewachsen ist und deshalb die eventuell durch den Austausch der H-Atome hervorgerufene minimale Veränderung der D-Konzentration im Lösungsmittel durch den Vergleich seines Gehaltes an D vor und nach dem Versuch sehr schwer ausfindig zu machen ist. Um auf diese letzt genannte Möglichkeit einzugehen, wird bei dem vorliegenden Versuche das Styrol in Lösung von möglichst konzentriertem schwerem Alkohol polymerisiert und nicht der Gehalt des Lösungsmittels d.h. des Alkohols

(2) Vgl. z.B. H. Mark, *Naturwiss.*, **25** (1937), 753. A. Springer, *Kautschuk*, 1938, 3. G. V. Schulz, *Ergeb. exakt. Naturwiss.*, **17** (1938), 367.

(3) M. Koizumi und T. Titani, *Bull. Chem. Soc. Japan*, **13** (1938), 304.

sondern der des gebildeten Polystyrols an D genau gemessen, indem man das letztere bis zu Wasser verbrennt und dessen Gehalt an D schwebemetricisch bestimmt. Dabei bedienten wir uns zweier Arten der schweren Alkohole zum Versuch. Die eine Art schwerer Alkohol enthält alle seine D-Atome im Hydroxylradikal d.h. in direkt austauschbarer Form die andere dagegen im Äthylradikal also in nicht direkt austauschbarer Form. Die Herstellungsmethode jeder dieser Arten der Alkohole soll weiter unten bei jedem einzelnen Versuche beschrieben werden.

Versuchsmethode. Das zum Versuch verwendete Styrol wird durch die Trockendestillation der Zimmtsäure hergestellt. Etwa 2 ccm des so frisch hergestellten Styrols wird zusammen mit etwa 1 ccm schwerem Alkohol in einem Glasrohr eingeschmolzen⁽⁴⁾ und bei $130^{\circ} \pm 1$ etwa 22 Stunden lang stehen gelassen. Dann wird das Reaktionsgefäß bis zu Zimmertemperatur abgekühlt und das dabei abgeschiedene Polymerisationsprodukt, nachdem es auf die weiter unten zu beschriebene Weise möglichst vollständig vom Alkohol befreit worden ist, in einem Verbrennungsrohr unter Durchleitung von Sauerstoffgas bis zu Wasser verbrannt. Das so gewonnene Wasser, dessen Volumen durchschnittlich 0.5 ccm beträgt, wird nun, nachdem es unter Zusatz von KMnO_4 und Na_2O_2 bei 100° mehr als fünf Stunden lang erwärmt worden ist, durch viermalige Destillation im Vakuum gereinigt. Da aber alle diese Destillationen in einem abgeschlossenen Glasrohrsystem durchgeführt werden, geht fast kein Tropfen Wasser während dieses Destillationsprozesses verloren. Die Dichte und folglich der Gehalt dieses Wassers an D wird mit Hilfe eines kleinen Glasschwimmers bestimmt. Die Messgenauigkeit des Schwimmers liegt innerhalb $\pm 1 \gamma$.

Der mittlere Polymerisationsgrad des in dem vorliegenden Versuche gewonnenen Polymers. Da jeder Polymerisationsversuch immer unter den möglichst gleich beibehaltenen Versuchsbedingungen durchgeführt wurde, darf der Polymerisationsgrad des Polymers während der ganzen Versuchsreihe als praktisch konstant angesehen werden. Aus diesem Grunde wird er deshalb durch einige Vorversuche von vornherein bestimmt. Die Messmethode beruht wie üblich auf der Beziehung (1) zwischen dem mittleren Molekulargewicht $\bar{M}$ des Polymers und der spezifischen Zähigkeit η_{sp} seiner Lösung in Benzol bei 25° :⁽⁵⁾

$$\bar{M} = \frac{1}{K_m} \frac{\eta_{sp}}{C} \quad (1)$$

In dieser Gl. (1) stellt K_m eine Konstante⁽⁶⁾ und C das sogenannte Grundmol des Styrols pro Liter dar. Einige Messresultate, die nach dieser Methode von dem unter den schon oben angegebenen Versuchsbedingungen gebildeten Polystyrol gewonnen wurden, geben wir in Tabelle 1 wieder.

(4) Dabei wird dass beladene Glasrohr nicht evakuiert; die Polymerisation wird also beim Vorhandensein von Luft ausgeführt.

(5) H. Staudinger, Ber., **63** (1930), 222.

(6) Nach dem neueren Versuch von G. V. Schulz (Z. phys. Chem., B **44** (1939), 227) wird gefunden, dass die Grösse der Konstante K_m in Gl. (1) bis zu einem gewissen Grad durch den Verzweigungs- und folglich Polymerisationsgrad des Polymers beeinflusst wird. Aber wenn es sich um die grobe Abschätzung des Molekulargewichts des Polymers handelt und besonders wenn dies wie beim vorliegenden Fall nicht allzu gross ist, darf die Konstante K_m unabhängig von der Molekulargrösse des Polymers als genügend konstant angesehen werden.

Tabelle 1. Das mittlere Molekulargewicht $\bar{M}$ des in Alkohol bei 130° gebildeten Polystyrols.

Versuchsnr.	γ_{sp}	C	K_m	$\bar{M}$
1	2.719	0.2521	0.00025	43140
2	2.760	0.2500	0.00025	44160

Der Polymerisationsgrad des in Rede kommenden Polymers beträgt also ungefähr 400 und enthält durchschnittlich 32000 Stück H-Atome in einem Molekül. Falls deshalb das eine H-Atom in einem Polystyrolmolekül gegen ein D-Atom des Lösungsmittels ausgetauscht würde, müsste das aus der Verbrennung dieses Polystyrols entstehende Wasser um 33 γ dichter als gewöhnliches Wasser sein.

Polymerisationsversuch in gewöhnlichem Alkohol. Um über den Fehlerbereich der vorliegenden Versuchsmethode Kenntnis zu gewinnen, wird der Versuch zunächst unter Verwendung von gewöhnlichem Alkohol ausgeführt. Das in der Lösung von gewöhnlichem Alkohol aber unter den sonst genau gleichen Versuchsbedingungen wie bei dem Hauptversuche polymerisiert gebildete Polystyrol wird sorgfältig bis zu Wasser verbrannt. Die Dichte des so gewonnen Wassers wird dann, nachdem es ebenfalls auf genau dieselbe Weise wie bei dem Hauptversuche (d.h. auf die schon oben beschriebene Weise) gereinigt worden ist, mit Hilfe eines kleinen Glasschwimmers bestimmt. Das so gewonnene und gereinigte Wasser zeigt sich aber immer um etwa 10 γ dichter als gewöhnliches Wasser, wie man dies aus Tabelle 2 ersieht. In dieser Tabelle bedeutet Polystyrol (g) die Gewichtsmenge des gebildeten Polystyrols in Gramm, H_2O (g) die des aus der Verbrennung dieser Menge des Polystyrols gebildeten und dann gereinigten Wassers und $\Delta s(\gamma)$ der in γ -Einheit gemessene Dichteüberschuss dieses Wassers gewöhnlichem Wasser gegenüber.

Tabelle 2. Polymerisationsversuch in C_2H_5OH .

Versuchsnr.	Polystyrol (g)	H_2O (g)	$\Delta s(\gamma)$	Mittelwert von $\Delta s(\gamma)$
1	0.632	0.444	7.7	9.7
2	0.520	0.351	10.5	
3	0.861	0.599	11.0	

Die Annahme, dass diese Dichtezunahme des Wassers, das aus dem Versuch mit gewöhnlichem Alkohol gewonnen wird, von irgendwelchen flüchtigen Verunreinigungen herrührt, die während der Vakuumdestillation des Wassers bei seinem Reinigungsprozess hauptsächlich aus der Glaswand

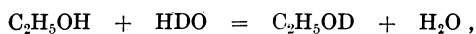
der Destillationsapparatur hineingekommen sind, konnte u.a. aus dem in Tabelle 3 wiedergegebenen Kontrollversuch überzeugend wirken. Bei diesem Versuch wird nämlich etwa 0.5 ccm, d.h. das gleiche Volumen gewöhnliches Wasser wie das beim eigentlichen Polymerisationsversuch gewonnene genau wie dies, nachdem es unter Zusatz von KMnO_4 und Na_2O_2 fünf Stunden lang erwärmt worden ist, im Vakuum vier Mal nacheinander abdestilliert und dann die Dichte des so behandelten Wassers mit Hilfe des oben beschriebenen Glasschwimmers bestimmt. Sie war aber, wie in Tabelle 3 gezeigt wird, immer um etwa 5 bis 11 γ , durchschnittlich um 9 γ , dichter als gewöhnliches Wasser.

Tabelle 3. Dichteüberschuss der kleinen Mengen Wassers, das durch das Glasrohr im Vakuum vier Mal abdestilliert worden ist.

Versuchsnr.	1	2	3	4	5	6	7	Mittel
$\Delta s (\gamma)$	11.0	7.7	11.0	4.4	5.5	9.9	8.8	8.8

Wir haben deshalb beim eigentlichen Polymerisationsversuch, der offensichtlich unter Verwendung des schweren Alkohols durchgeführt wurde, den direkt gefundenen Dichteüberschuss $\Delta s (\gamma)$ des aus der Verbrennung des Polymerisationsprodukts entstandene Wassers dadurch korrigiert, dass man aus diesem immer 9 γ abzieht. Der so korrigierte Wert von $\Delta s (\gamma)$ wird in folgenden Tabellen mit dem Buchstaben $\Delta s_0 (\gamma)$ ausgedrückt.

Polymerisationsversuch in 3.6%— $\text{C}_2\text{H}_5\text{OD}$. Der schwere Alkohol $\text{C}_2\text{H}_5\text{OD}$ wird unter Benutzung der Austauschreaktion zwischen gewöhnlichem Alkohol und schwerem Wasser hergestellt:



und mit Hilfe von gebranntem Kalk und metallischem Calcium von zugleich vorhandenem Wasser vollständig abgetrennt. Die atomare Konzentration von D im Wasser, das aus der Verbrennung des so hergestellten schweren Alkohols gewonnen wird, beträgt 3.6%. Da aber alle diese D-Atome, wie aus der oben angegebenen Herstellungsmethode ohne weiteres ersichtlich ist, lediglich im Hydroxylradikal enthalten sind, muss die D-Konzentration im Hydroxylwasserstoff des betreffenden schweren Alkohols um sechsmal so gross wie die oben angegebene d.h. 21.6% sein. Das Polymerisat, das in dieser Art schwerem Alkohol gebildet und davon grob abgetrennt worden ist, wird durch paarmaliges Auswaschen mit Toluol vom anhaftenden Alkohol möglichst vollständig befreit. Zu diesem Zweck wird das Polymerisat in eine Menge von Toluol ausgelöst und aus dieser Lösung wird das Toluol durch die Destillation im Vakuum abgetrennt. In der Praxis wird dieser Prozess drei bis fünfzehn Mal wiederholt und erst dann wird das Polymerisat bis zu Wasser verbrannt. Die Anzahl n in der

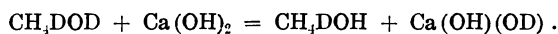
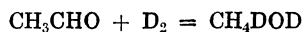
vierten Spalte der Tabelle 4 gibt diese Anzahl des Auswaschens mit Toluol an.

Tabelle 4. Polymerisationsversuch in 3.5%-C₂H₅OD.

Versuchsnr.	Polystyrol (g)	HDO (g)	<i>n</i>	Δs_0 (γ)	Mittel von Δs_0 (γ)
1	0.896	—	3	12	13
2	0.924	0.634	5	2	
6	0.501	0.327	5	23	
3	0.676	0.451	7	2	
5	0.552	0.382	7	19	
4	0.488	0.325	15	19	

Das so gewonnene und dann gereinigte Wasser, dessen Gewichtsmenge mit HDO(g) in der dritten Spalte der Tabelle 4 angegeben ist, zeigt sich durchschnittlich um 13 γ dichter als gewöhnliches Wasser, wie aus der zweitletzten und letzten Spalte der Tabelle ersichtlich ist, wo Δs_0 (γ) den auf die schon angegebene Weise korrigierten Wert des Dichteüberschusses anzeigt. Falls nun dieser Gehalt des Wassers an D tatsächlich von der Austauschreaktion herrührt, entspricht er etwa zwei Stück H-Atome in einem Polystyrolmolekül, die gegen die D-Atome des Alkohols ausgetauscht werden. Aber bevor wir zu diesem Schluss kommen, müssen wir noch auf die Ergebnisse der anderen Reihen der Versuche eingehen, die unter Benutzung von solch einer Art schwerem Alkohol durchgeführt wurden, dessen sämtliche D-Atome im Äthylradikal d.h. in nicht direkt austauschbarer Form enthalten sind.

Polymerisationsversuch in 11.5%-C₂H₄DOH. Der in diesem Versuch benutzte, sämtliche D-Atome lediglich im Äthylradikal enthaltende schwere Alkohol C₂H₄DOH wird dadurch hergestellt, dass man zunächst das gewöhnliche Acetaldehyd mit schwerem Wasserstoff unter Benutzung des Nickelkatalysators bis zum Alkohol reduziert und den Hydroxylwasserstoff des so gewonnenen schweren Alkohols CH₄DOD mit Hilfe der Austauschreaktion gegen gelöschten Kalk möglichst vollständig von D befreit:



Die atomare Konzentration von D im Wasser, das aus der Verbrennung des so hergestellten schweren Alkohols entsteht, beträgt 11.5% aber dieselbe im Hydroxylwasserstoff allein wird unterhalb 0.3% geschätzt. Die Versuchsergebnisse, die unter Verwendung dieser Art von schwerem Alkohol gewonnen wurden, sind in Tabelle 5 wiedergegeben, wo die letzte Spalte die Methode angibt, durch welche das gebildete Polymerisat von daran anhaftendem Alkohol befreit worden ist.

Tabelle 5. Polymerisationsversuch in 11.5%-C₂H₄DOH.

Versuchs-nr.	Polystyrol (g)	HDO (g)	Δs_0 (γ)	Bemerkung
1	0.996	0.669	50	Das gebildete Polystyrol wird mit Toluol dreimal gewaschen.
2	1.018	0.669	63	„ fünfmal „
3	0.708	0.487	48	„ zehnmal „
4	0.671	0.450	66	Nach dreimaligem Auswaschen mit Toluol wird das Polystyrol im Vakuum bei 150° sechs Stdn. lang erwärmt.
5	0.815	0.559	16	Nach fünfmaligem Auswaschen mit Toluol wird das Polystyrol im Vakuum bei 300° drei Stdn. lang erwärmt.

Die Versuche Nr. 1 bis 3 in Tabelle 5 zeigen an, dass das Polymerisat, das in dieser Art von schwerem Alkohol gebildet wird, sogar nach zehnmaligem Auswaschen mit Toluol noch einen nennenswerten Gehalt an D besitzt. Dies weist deutlich darauf hin, wie schwer die letzten Moleküle des an dem Polymerisat anhaftenden Alkohols durch blosses Auswaschen mit Toluol zu befreien sind. Bei dem nächsten Versuch Nr. 4 wird deshalb das gebildete Polymerisat, nachdem es mit Toluol dreimal ausgewaschen worden ist, im Vakuum bei 150° sechs Stunden lang erwärmt. Da aber der Gehalt des resultierten Wassers an D dadurch kaum abnimmt, wird beim letzten Versuch Nr. 5 die Erwärmungstemperatur bis auf 300° erhöht. Durch diese ziemlich gewaltsame Behandlung wird der D-Gehalt des Polymerisats erst bis zu etwa ein Drittel des oben gefundenen vermindert. Aber zugleich bemerkte man, wie das Polymerisat während der Erwärmung schon ziemlich schnell zu depolymerisieren begann.

Nach all diesem liegt die Vermutung nahe, dass die letzten paar Moleküle Alkohole ziemlich stark an dem gebildeten Polymerelement angehäftet bzw. darin eingeschlossen sind. Eine einfache Rechnung zeigt, dass der oben bei Versuchen Nr. 1 bis 4 gefundene Wert von Δs_0 (γ) etwa zwei bis drei Stück Alkoholmolekülen entspricht, die an bzw. in einem Polystyrolmolekül angehäftet sind. Wir haben beim letzten Versuch mit 3.6%-C₂H₅OD gefunden, dass das Wasser aus diesem Versuch durchschnittlich um 13 γ dichter als gewöhnliches Wasser ist (vgl. Tabelle 4). Rechnet man diesen Wert von Δs_0 (γ) zu dem Fall um, wo die D-Konzentration im verwendeten Alkohol ebenso wie beim vorliegenden Versuch 11.5% beträgt, so ergibt sich ein Wert von 42 γ . Dieser stimmt aber mit dem beim vorliegenden Versuch Nr. 1 bis 4 unter Verwendung von 11.5%-C₂H₄DOH gewonnenen Wert von Δs_0 (γ) befriedigend überein. Daraus darf wohl geschlossen werden, dass praktisch keine H-Atome des Styrols während seines Polymerisationsprozesses gegen die des Alkohols ausgetauscht werden. Dieser Schluss wird weiter durch die unten angegebenen zwei Reihen der Versuche bestätigt, die ebenfalls unter Verwendung von zwei Arten der schweren Alkohole C₂H₅OD und C₂H₄DOH durch-

geführt wurden, doch der Gehalt dieser Arten der Alkohole an D war miteinander praktisch gleich und grösser als die oben benutzten.

Polymerisationsversuch in 10.4%—C₂H₅OD und in 9.8%—C₂H₄DOH.
Der zu diesem Versuch benutzte 10.4%—C₂H₅OD wird, genau so wie schon oben angegeben wurde, durch die Austauschreaktion gewöhnlichen Alkohols gegen schweres Wasser während 9.8%—C₂H₄DOH durch die Verdünnung von reinem Äthyl-*d*-ol C₂D₅OH unter Zusatz von gewöhnlichem Alkohol hergestellt. Deshalb handelt es sich bei diesem letzteren Fall um ein Gemisch aus C₂D₅OH und C₂H₅OH, dessen gesamter Gehalt an D, d.h. die atomare Konzentration von D im daraus durch Verbrennung entstehenden Wasser, 9.8% beträgt. Der zur Bereitung dieses Gemisches verwendete reine Äthyl-*d*-ol C₂D₅OH wird aus dem von Norsk Hydroelektrisk bezogenen 99.6%—C₂D₅OD durch die Austauschreaktion gegen gelöschten Kalk gewonnen. Das Polymerisationsprodukt, das in diesen beiden Arten der schweren Alkohole gebildet wird, wird immer ohne weiteres, d.h. ohne es mit Toluol auszuwaschen, direkt im Vakuum bei 300° sechs Stunden lang erwärmt. Das auf diese Weise unter den möglichst gleich bleibenden Bedingungen vom Alkohol so weit wie möglich befreite Produkt wird im Strom von reinem Sauerstoff sorgfältig bis zu Wasser verbrannt und die Dichte des so gewonnenen Wassers, nachdem es nach der schon oben angegebenen Methode gereinigt worden ist, schwebemetrisch bestimmt. Die letzten Spalten der Tabellen 6 und 7 geben den korrigierten (vgl. oben) Dichteüberschuss $\Delta s_0(\gamma)$ des so gewonnenen und gereinigten Wassers gewöhnlichem Wasser gegenüber an.

Tabelle 6. Polymerisationsversuch in 10.4%—C₂H₅OD.

Versuchs-nr.	Polystyrol (g)	HDO (g)	$\Delta s_0(\gamma)$	Versuchs-nr.	Polystyrol (g)	HDO (g)	$\Delta s_0(\gamma)$
1	0.833	0.570	8	5	0.399	0.277	20
2	0.977	0.680	16	6	0.681	0.471	23
3	0.679	0.474	9	7	1.077	0.743	10
4	0.701	0.487	20	8	0.991	0.683	23

Mittelwert von $\Delta s_0(\gamma) = 14.8 \pm 1.7$.

Tabelle 7. Polymerisationsversuch in 9.8%—C₂H₄DOH.

Versuchs-nr.	Polystyrol (g)	HDO (g)	$\Delta s_0(\gamma)$	Versuchs-nr.	Polystyrol (g)	HDO (g)	$\Delta s_0(\gamma)$
1	0.578	0.405	16	9	0.984	—	31
2	0.668	0.462	13	10	0.926	0.650	14
3	0.864	0.601	11	11	1.002	0.703	27
4	0.888	0.615	13	12	0.803	0.565	12
5	0.808	0.564	27	13	0.875	0.611	9
6	0.634	0.442	15	14	0.561	0.388	15
7	0.641	0.441	17	15	0.923	0.644	6
8	0.516	0.364	11	16	1.061	0.736	6

Mittelwert von $\Delta s_0(\gamma) = 15.1 \pm 1.2 \gamma$.

Rechnet man den unterhalb jeder Tabelle angegebenen direkt gefundenen Mittelwert von $\Delta s_0(\gamma)$ zu dem Fall um, wo der Gehalt des benutzten Alkohols an D gerade 10% betragt, so ergibt er bei dem Versuch in Tabelle 6 $\Delta s_0(\gamma)$ (10% $-C_2H_5OD$) $=14.2 \pm 2 \gamma$ und bei dem Versuch in Tabelle 7 $\Delta s_0(\gamma)$ (10% $-C_2H_5DOH$) $=15.4 \pm 2 \gamma$. Diese beiden Werte von $\Delta s_0(\gamma)$ stimmen aber innerhalb des Messfehlerbereiches ganz uberein. Dadurch wird namlich die oben angegebene Annahme weiter bestatigt, dass praktisch keine H-Atome im Styrolmolekul wahrend seines Polymerisationsprozesses nicht genugend bis zur Austauschreaktion gegen die des Alkohols oder allgemein gesagt gegen die des Losungsmittels gelockert werden. Der Dichteuberschuss von 2 γ des resultierten Wassers, der wohl innerhalb des Messfehlerbereiches der vorliegenden Versuche liegt, entspricht etwa einem in 32000 H-Atome, das gegen die des schweren Alkohols ausgetauscht wird. Da aber das bei dem vorliegenden Versuche gebildete Polystyrol, wie schon oben angegeben, durchschnittlich etwa 3200 H-Atome in einem Molekul enthalt, kann die Anzahl der austauschbaren H-Atome nicht mehr als eins pro zehn Stuck Polystyrolmolekule sein.

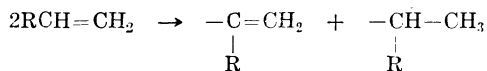
Diskussion der Ergebnisse. Nach dem Versuch von Walters⁽⁷⁾ wird gefunden, dass bei der Kettenpolymerisation von Formaldehyd in schwerem Wasser D_2O keine D-Atome im gebildeten α -Polyoxymethylen eingebaut werden. Dieses Ergebnis wird von dem Verfasser durch die wahrscheinlichste Annahme gedeutet, dass keine H-Atome im Formaldehydmolekul wahrend seines Polymerisationsprozesses ihre Bindung zu C-Atome aufgeben. Dieselbe Annahme liegt auch sehr nahe beim vorliegenden Fall fur die Kettenpolymerisation von Styrol, weil wir keinen Austausch der H-Atome des Styrols bzw. Polystyrols gegen die des Alkohols gefunden haben. Auf Grund dieser Annahme wollen wir deshalb den Mechanismus der Kettenpolymerisation des Styrols naher bei Licht betrachten.

I. Keimbildungsprozess. Als den plausiblen Mechanismus fur diesen ersten Schritt der Polymerisation kommen mindestens vier Moglichkeiten in Betracht:⁽⁸⁾

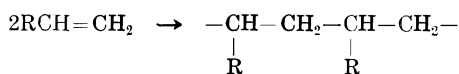
(1) Ein Monomermolekul wird in zwei Teile wie z.B. in ein freies Radikal und ein H-Atom gespalten:



(2) Aus zwei Monomermolekulen entstehen durch die Wanderung eines H-Atoms zwei freie Radikale:



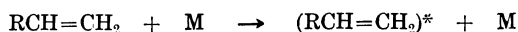
(3) Durch die Vereinigung zweier Monomermolekule entsteht ein freies Radikal:



(7) W. D. Walters, *Z. phys. Chem.*, A **182** (1938), 275.

(8) G. V. Schulz, A. Dinglinger und E. Husemann, *Z. phys. Chem.*, B **43** (1939), 385. P. G. Flory, *J. Am. Chem. Soc.*, **59** (1937), 241.

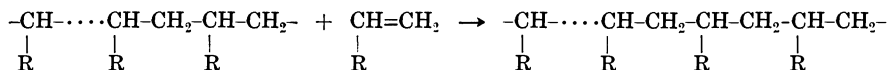
(4) Durch das Zusammenstossen gegen das andere dritte Molekül M wird das Styrolmolekül angeregt und dadurch wird ein Polymerisationsfähiges angeregtes Monomermolekül ($\text{RCH}=\text{CH}_2$)* gebildet:



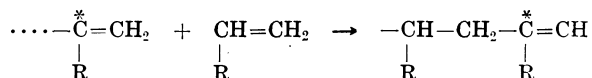
Unter diesen vier Möglichkeiten sind die ersteren zwei (1) und (2) im Lichte der vorliegenden Versuchsergebnisse nicht so wahrscheinlich wie die anderen, weil nach diesen beiden Mechanismen eventuell die Austauschreaktion der H-Atome des Styrols gegen die des Lösungsmittels stattfinden kann. Als ebenso wenig wahrscheinlich kommt der dritte Mechanismus (3) aus dem energetischen Grund in Wegfall,⁽⁸⁾ obwohl dieser Mechanismus keine Aufhebung der C-H-Bindung braucht und allein in diesem Punkt mit dem vorliegenden Befund der Nichtaustauschbarkeit der H-Atome des Styrols in Widerspruch steht. Auf diese Weise bleibt nur noch der zuletzt angegebene Mechanismus (4) als der wahrscheinlichste für den Keimbildungsprozess übrig. Danach wird nämlich die Polymerisationskette der Styrols durch die Bildung eines angeregten Monomermoleküls abgelöst.

II. Kettenwachstumsprozess. Als den Mechanismus dieses eigentlichen Polymerisationsprozesses sind mindestens zwei Möglichkeiten denkbar:⁽⁸⁾

(1) Das wachsende Polymermolekül ist eine Art freies Radikal. Es wächst dank seiner freien Valenzen nach dem Schema an:



(2) Die andere Möglichkeit des Kettenwachstumsprozesses besteht darin, dass der wachsende Polymer an seinem einen Ende immer angeregt ist und an diesem angeregten Ende das weitere Monomermolekül verbindet:



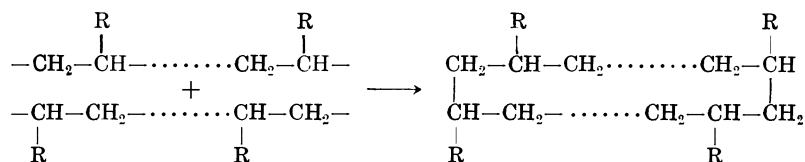
Da aber bei diesem letzteren Mechanismus (2) ein H-Atom von dem zu verbindenden Monomermolekül zu dem wachsenden Polymermolekül transportiert werden muss, erscheint er im Lichte der vorliegenden Versuchsergebnisse noch weniger wahrscheinlich als der erstere (1). Zu derselben Ansicht sind auch alle anderen Autoren durch ihre eigenen Versuche gekommen.⁽⁸⁾

III. Kettenabbruchprozess. Unter den drei Teilprozessen der Kettenpolymerisation von Styrol ist dieser zuletzt verlaufende Abbruchprozess am schwierigsten zu verstehen. Wir wollen deshalb unter den ziemlich vielen denkbaren Möglichkeiten nur folgende zwei in Betracht ziehen:

(1) Die freien Valenzen des wachsenden Polymers, falls er als eine Art freies Radikal aufgefasst werden kann, werden durch irgendeinen der

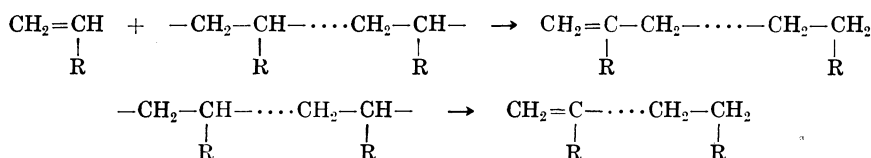
unten angegebenen Mechanismen abgesättigt und dadurch die Polymerisationskette abgebrochen.

(a) Ringschliessung. Diese kann entweder intermolekular, d.h. zwischen mehr als zwei Molekülen, etwa nach dem Schema:



oder intramolekular, d.h. zwischen der beiden Enden eines Riesenpolymermoleküls stattfinden.⁽⁹⁾

(b) Inter- bzw. intramolekulare Wanderung der H-Atome, wie etwa nach dem Schema:



Falls aber dieser letztere Prozess (b) wirklich massgebend ist, dürfte diese Wanderung der H-Atome, genau so wie dies Fredenhagen und Bonhoeffer⁽¹⁰⁾ bei ihrem Studium über die Canizzarosche Reaktion angenommen haben, durch die Bildung einer lockeren Zwischenverbindung stattfinden,⁽¹¹⁾ weil sonst die in dem vorliegenden Versuch bestätigte Nichtaustauschbarkeit der H-Atome des wachsenden Polymers gegen die des Lösungsmittels schwer zu erklären ist.

(2) Das Wachstum des Kettenmoleküls kann aber auch bloss durch die immer weiter fortlaufende Polymerisationsreaktion verhindert werden, weil dadurch erstens der sterische Faktor des wachsenden Polymers d.h. die Aktivierungsentropie der Reaktion und zweitens die Konzentration des zurückbleibenden Monomers immer weiter abnimmt. Infolge dieser beiden Einflüsse nimmt die Geschwindigkeit der Reaktion nach und nach ab und zum Schluss kann sie fast unmessbar so klein werden. Über den Endzustand des dabei resultierenden Polymerisationsprodukts können wir bis auf weiteres nichts Genaueres sagen. Aber unter den vielen denkbaren Mechanismen mag auch die Möglichkeit bestehen, dass das Polymerisationsprodukt bis zu einem gewissen Grad die Natur des freien Radikals behält. Diese Annahme, für deren Bestätigung offensichtlich noch weitere experimentelle Versuche erforderlich sind und dafür u.a. die thermochemische Untersuchung aussichtsreich sein dürfte, kann aber auch aus dem heutigen Zustand der Valenztheorie vielleicht nicht ohne weiteres ausgeschlossen werden, wenn man u.a. die Tatsache ins Auge fasst, dass das Polymerisationsprodukt eine ungeheuer grosse Anzahl von π -Elekt-

(9) H. Dostal und H. Mark, *Angew. Chem.*, **50** (1937), 348.

(10) H. Fredenhagen und K. F. Bonhoeffer, *Z. phys. Chem.*, A **181** (1938), 379.

(11) Dasselbe können wir auch von dem unter (2) beim Keimbildungsprozess und unter (2) beim Kettenwachstumsprozess hingewiesenen Mechanismus sagen.

ronen bzw. „Elektronen zweiter Art“⁽¹²⁾ in einem Molekül enthält. Dank der von dieser grossen Anzahl Elektronen zweiter Art bewirkten Mesomerie kann das Polymermolekül trotz seiner ungesättigten Natur doch eventuell in einem befriedigend stabilen Zustand existieren.

Wie schon oben gefunden wurde, hält das in Alkohol polymerisiert gebildete Polystyrolmolekül einige Molekül Alkohol so fest an bzw. in sich, dass sie durch blosses Auswaschen mit Toluol oder milde Erwärmung nicht vollständig zu entfernen sind. Über den Mechanismus dieser festen Anlagerung der Alkoholmoleküle an dem Polymerisationsprodukt kommen zwei Möglichkeiten in Betracht: entweder sind die Alkoholmoleküle im knäueiförmigen Riesenmolekül des Polymers mechanisch eingeschlossen oder sie sind an irgendwelchen Stellen des Polymermoleküls durch seine Residualvalenz halbchemisch verbunden. Mit jeder dieser Annahmen können wir die gefundene Tatsache wohl erklären, dass der Gehalt des Polymerisationsprodukts an Alkohol durch starke Erwärmung des ersteren beträchtlich verringert wird. Falls nämlich nach der ersteren Annahme die Alkoholmoleküle im knäueiförmigen Riesenmolekül des Polymerisats eingeschlossen sind, nimmt wegen der bei hohen Temperaturen immer heftiger werdenden „intramolekularen Brownschen Bewegung“⁽¹³⁾ des Kettenmoleküls des Polymers die Gelegenheit zu, dass die darin eingeschlossenen Alkoholmoleküle ausgeschleudert werden. Wenn dagegen, wie zweitens angenommen wird, die Alkoholmoleküle an dem Polystyrolmolekül halbchemisch verbunden sind, muss die Anzahl der Alkoholmoleküle mit steigender Temperatur stark zunehmen, die dank ihrer thermischen Schwingung vom Polystyrolmolekül abgerissen werden. Um zwischen diesen beiden Möglichkeiten zu unterscheiden, ist weiterhin noch eine eingehende Untersuchung über die Beziehung zwischen dem Polymerisationsgrad des gebildeten Polymers und dessen Gehalt an (schwerem) Alkohol erforderlich.

Zum Schluss möchten wir der Nippon Gakuzyutu-Sinkohkai (der Japanischen Gesellschaft zur Förderung der wissenschaftlichen Arbeit) sowie der Hattori Hohkohkai (der Hattori-Stiftung) für ihre finanzielle Unterstützung bei der Durchführung der vorliegenden Arbeit unseren wärmsten Dank aussprechen.

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(12) E. Hückel, *Z. Elektrochem.*, **43** (1937), 752, 827.

(13) Vgl. E. Jenkel, *Z. Elektrochem.*, **45** (1939), 206.

A Rapid Determination of Potassium with Hexanitrodiphenylamine (Dipicrylamine) Reagent.

By Hideo SUEDA and Motomi KANEKO.

(Received March 6, 1941.)

During the past few years, the feasibility of the use of Hexanitrodiphenylamine or dipicrylamine as a reagent in the quantitative determination of potassium has been reported from several sources. Most of the reports give procedures for the gravimetric method, in which the potassium is precipitated and weighed as the potassium salt of dipicrylamine, expressed as H_K . The drying at a certain temperature, cooling in a dessicator and weighing of the H_K are all quite time consuming. Colorimetric methods such as those of Kielland⁽¹⁾ and of Kolthoff and Bendix⁽²⁾ are particularly suitable for the determination of microquantities of potassium, and a potentiometric titration method is reported by T. Kiba⁽³⁾, but these methods require elaborate apparatus and are not particularly suited for rapid, simple application.

Perhaps the quickest, simplest, and in general the most satisfactory method is the direct titration of the H_K with standard acid. Kolthoff and Bendix give an acidimetric method, in which the potassium salt, H_K , (after being precipitated and washed as for the gravimetric method) is dissolved in acetone, converted to the amine with a measured excess of standard acid, and after evaporating off the acetone and then removing the precipitated amine by filtering through a glass filter, the excess acid is back titrated with standard sodium hydroxide using bromothymol blue as indicator.

After studying the above methods, the authors found that when acid is added to the acetone solution of the H_K , the reddish solution becomes yellow with the precipitation of the amine. On measuring the volume of acid added until the disappearance of the reddish color, it was found that the titration was quantitative. The addition of an excess amount of the acid followed by the back titration with sodium hydroxide until the permanent appearance of the reddish color of the H_K did not affect the accuracy of the titration. Working with sample solutions of KCl containing approximately 20 mg. of potassium, the results for a series of twelve determinations checked satisfactorily as shown in Table I. The KCl solution was calculated to be 0.252% in K_2O , and the relative errors ranged from -1.98% to +1.19%, corresponding to an average of 0.87%.

Experimental Materials: Magnesium Dipicrylamine, H_{Mg} . A 3% solution H_{Mg} was prepared by dissolving 12 g. of dipicrylamine with 5 g. of MgO in 400 c.c. of distilled water. After stirring the solution well, it

(1) Kielland, *Ber.*, **71** B (1938), 220.

(2) Kolthoff and Bendix, *Ind. Eng. Chem., Anal. Ed.*, **11** (1939), 94.

(3) T. Kiba, *J. Chem. Soc. Japan*, **60** (1939), 1073.

Table 1. Titration of H_K with $N/10$ H_2SO_4 .

Sample No.	0.1102 N H_2SO_4 (c.c.)	0.09378 N NaOH (c.c.)	Corrected Vol. H_2SO_4 (c.c.)	K_2O % Present	K_2O % Found	Relative Error (%)
1	6.85	2.54	4.79	0.252	0.250	-0.79
2	8.75	4.60	4.84	„	0.252	0.00
3	5.68	0.95	4.87	„	0.253	+0.40
4	5.55	0.96	4.73	„	0.247	-1.98
5	5.85	1.20	4.83	„	0.251	-0.40
6	5.70	1.00	4.85	„	0.253	+0.40
7	7.50	3.10	4.86	„	0.254	+0.79
8	6.10	1.60	4.74	„	0.247	-1.98
9	5.53	0.92	4.77	„	0.249	-1.19
10	8.00	3.70	4.85	„	0.253	+0.40
11	6.00	1.40	4.81	„	0.250	-0.79
12	6.60	2.00	4.90	„	0.255	+1.19

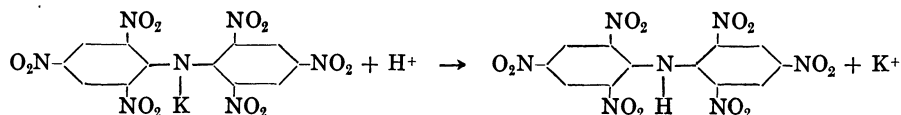
was allowed to stand overnight and was then filtered through a No. 1 G 4 glass filter.

Washing Solution A. Distilled water was cooled to $0^\circ C$. in a 100 c.c. wash bottle placed in an ice bath.

Washing Solution B. A solution of potassium dipicrylamine saturated at $0^\circ C$. was prepared by dissolving an excess of the H_K (about 0.5 g. per 500 c.c.) in distilled water and then filtering the solution after cooling to $0^\circ C$. The solution was then kept at that temperature in a 100 c.c. wash bottle placed in an ice bath.

Standard Potassium Chloride Solution. A solution of potassium chloride was prepared by dissolving 0.9977 g. of dried KCl (Takeda, "zur Analyse") in 250 c.c. of distilled water. This solution was calculated to be 0.252% in K_2O and to contain 20.65 mg. of potassium per 10 c.c.

Experimental Procedure. 10 c.c. of the standard KCl solution were pipetted into a 100 c.c. beaker. With constant stirring, 10 c.c. of the H_{Mg} solution, corresponding to an excess of 20%, were added dropwise to precipitate the potassium as H_K . After cooling for about 15 minutes over an ice bath, the precipitate was filtered with a No. 1 G 4 glass filter, washed with about 1 c.c. of washing solution A, then with 3 or 4 c.c. of washing solution B and finally with about $1/2$ c.c. of washing solution A. The H_K was then dissolved with a minimum of acetone. If more than 5 c.c. of the latter are required, the excess must be evaporated off, because it prevents a sharp color change at the titration end point. Before each titration, the acetone solution was diluted to about 15 or 20 c.c. with distilled water. It was found that the color change of from yellow to red was shaper than that of from red to yellow, so as shown in Table I, a slight excess of acid was added, and the latter was then back titrated with standard sodium hydroxide. The reaction of the H_K conversion to the amine is as follows:



Conclusion. By revising the methods reported by Kolthoff and Bendix and by T. Kiba, a simple, rapid determination of potassium with Hexanitrodiphenylamine as the reagent was found. The potassium, after being precipitated as the potassium salt of dipicrylamine, is dissolved in acetone, and the resulting solution is directly titrated with standard acid. By taking advantage of the color change of the solution from the red of the potassium salt to the yellow of the precipitated amine, no indicator is necessary in the titration. The relative errors ranged from -1.98 to $+1.19\%$, and the average for a series of twelve determinations was 0.87% . However, it is believed that the simplicity and rapidity of the method justify its application in routine analyses, where the accuracy of more sensitive methods may be sacrificed.

Acknowledgment is hereby made to the head of the Oi Research Laboratory of the privilege of performing the above experiments and of the permission to present this report.

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Oi Research Laboratory Tokyo.

Über die unregelmässige Reihe der kolloiden Lösungen durch Elektrolyten. III-Mitteilung: Untersuchung an HgS-Solen aus verschiedenen Ausgangsmaterialien.⁽¹⁾

Von Naoyasu SATA und Koziro MÔRI.

(Eingegangen am 22. März 1941.)

(1) **Einleitung.** Zur Untersuchung unregelmässiger Koagulationsreihe von HgS-Sol haben wir zuerst, wie gewöhnlich, das Sol nach Winssinger benutzt, welches aus HgCl_2 und H_2S hergestellt wird⁽²⁾. Dadurch wurde erklärt, dass diese Erscheinung stark abhängig ist, nicht nur nach den Herstellungsbedingungen des Sols, sondern auch nach kleiner Menge beigemischter Fremdsubstanzen. So ist z.B. in obengenanntem Fall bestätigt, dass Cl-Ionen des HgCl_2 eine wichtige Rolle spielen.

(1) N. Sata u. Y. Niwase, *Kolloid-Z.*, **84** (1938), 314; N. Sata u. S. Itô, dieses Bulletin, **15** (1940), 271.

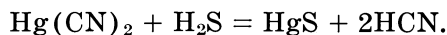
(2) C. Winssinger, *Bull. Acad. roy. Belgique*, Cl. Sci. (3), **15** (1888), 390; *Bull. Soc. Chim. France*, (2), **49** (1888), 452; H. Freundlich u. K. Schacht, *Z. physik. Chem.*, **85** (1913), 647: Das Sol ist dadurch gekennzeichnet, dass das HgS aus HgCl_2 -Lösung mit H_2S gefällt, ausgewaschen und durch wiederholtes H_2S -Durchleiten peptisiert wird.

Nachstehend haben wir untersucht die unregelmässige Reihe an HgS-Solen welche aus verschiedenen Ausgangsmaterialien hergestellt sind, unter der Meinung, die Bedeutung oder die Wirkung der beigemischten Fremdstoffen auf unregelmässigen Reihe zu klären.

(2) **Versuch an HgS-Sol aus $\text{Hg}(\text{CN})_2$.** Prinzipiel ist die Darstellungsmethode nach Winssinger nicht anders als eine Peptisation eines chemisch niedergeschlagenes Sulfides durch wiederholtes H_2S -Durchleiten.

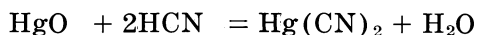
Das HgCl_2 ist dabei als Ausgangsmaterial ausgewählt, weil es leicht erhältlich und verhältnismässig leicht löslich ist. Aus allen Hg-Salzen sollte das HgS-Sol in gleicher Weise erhalten werden können, wenn das Salz so löslich ist, dass man daraus das HgS chemisch niederschlagen könnte. Von Hg-Salzen hat das $\text{Hg}(\text{CN})_2$ die grösste Löslichkeit, an welchem wir demnächst Untersuchung angestellt haben.

A. Lottermoser⁽³⁾ hat schon das HgS-Sol aus $\text{Hg}(\text{CN})_2$ dargestellt, indem er in $\text{Hg}(\text{CN})_2$ -Lösung den H_2S , in der Wärme unter vermindertem Druck, durchleitete. Die Reaktion verläuft nach der Gleichung:



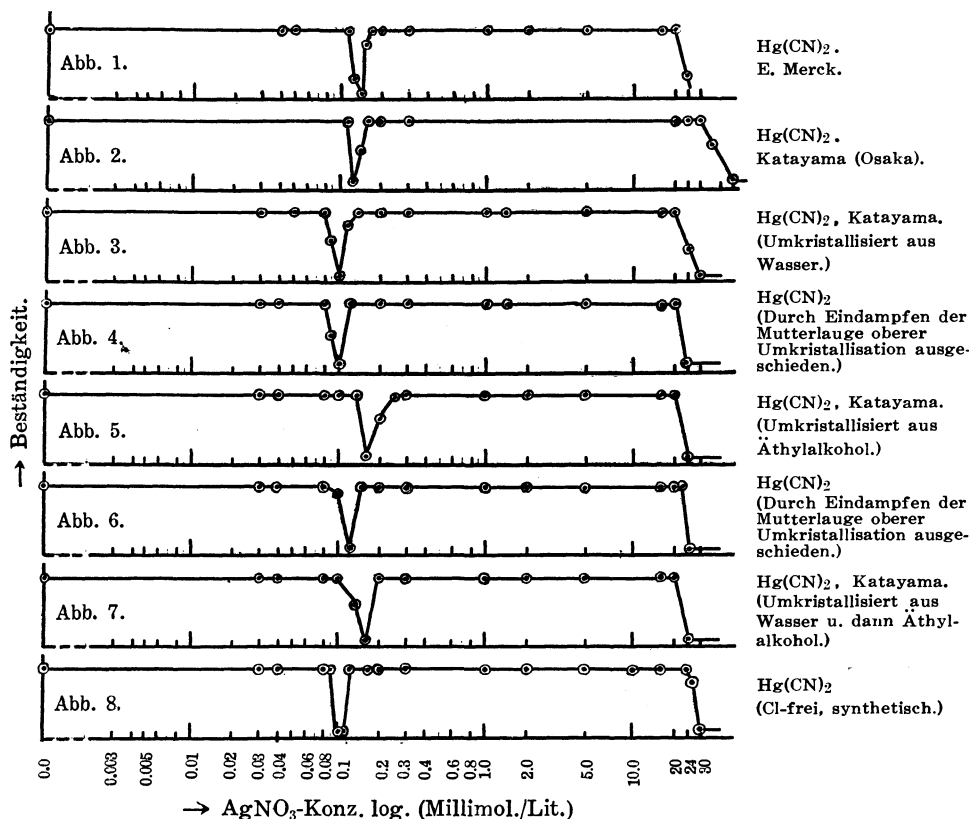
Das Nebenprodukt ist der gasförmige Cyanwasserstoff, der grösstenteils während der Reaktion mit überschüssigem H_2S ausgetrieben wird. Nun aus 2%-iger $\text{Hg}(\text{CN})_2$ -Lösung haben wir nach dieser Methode das Sol hergestellt. Überschüssiger H_2S und HCN wurde durch 30-minütiges H_2 -Durchleiten ausgetrieben. Das Sol ist schwarz ganz undurchsichtig, riecht vollkommen nicht nach H_2S und sehr beständig. Der Koagulationsversuch an diesem Sol, mit AgNO_3 als Elektrolyt, wurde wie gewöhnlich vorgeführt. Wie aus Abb. 1 und 2 zu ersehen sind, ergeben die Koagulationskurven ausgesprochene unregelmässige Reihe. Zur Kontrolle haben wir den gleichen Versuch ausgeführt mit $\text{Hg}(\text{CN})_2$, welches durch Umkristallisieren aus Wasser bzw. Äthylalkohol gereinigt ist. Die Resultate, welche in Abb. 3–7 ersichtlich sind, zeigen fast keinen Unterschied wie vorhergehender Versuche. (Abb. 1–2).

Inzwischen haben wir erfahren, dass das käufliche $\text{Hg}(\text{CN})_2$ nach folgender Reaktion hergestellt worden ist.

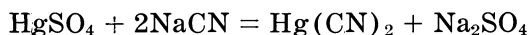


Also das $\text{Hg}(\text{CN})_2$ hat auch das HgCl_2 als Ausgangsmaterial. Dann kann man nicht garantieren, dass wie obenerwähnt hergestelltes $\text{Hg}(\text{CN})_2$ absolut Cl-frei ist: denn obwohl es wiederholt auf gewöhnlichem chemischem Sinne vorsichtig gereinigt ist, könnten noch die Cl-Ionen vom HgCl_2 (Ausgangsmaterial) durch Adsorption und andere Ursache in $\text{Hg}(\text{CN})_2$ zurückbleiben, welche auf der unregelmässigen Koagulation des aus diesem $\text{Hg}(\text{CN})_2$ hergestellten HgS-Sols etwaigen Einfluss ausüben

(3) A. Lottermoser, *J. prakt. Chem.* (2), **57** (1898), 484: The Svedberg, „Herstellung kolloider Lösungen anorganischer Stoffe“, S. 300, Dresden u. Leipzig (1922).



würden. Von diesem Grunde, haben wir noch einen Versuch angestellt mit absolut Cl-freiem Hg(CN)_2 , welches folgendermassen zubereitet ist⁽⁴⁾.



Das Produkt wurde durch Umkristallisieren aus Äthylalkohol gereinigt. Die Koagulationskurve des HgS -Sols, welches aus diesem Hg(CN)_2 hergestellt ist, ist in Abb. 2 übergetragen. Die unregelmässige Reihe ist immer noch deutlich zu erkennen.

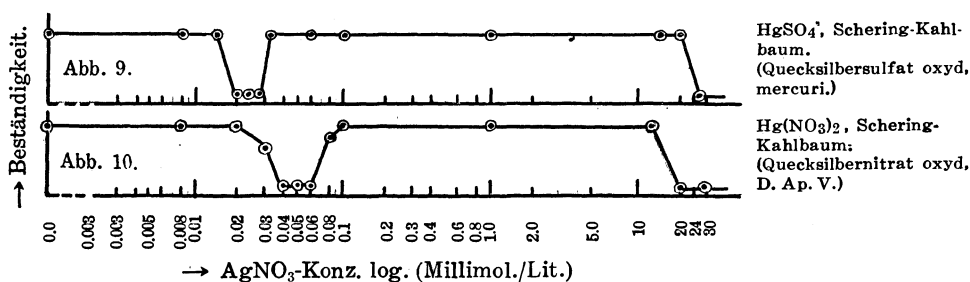
Jetzt ist es uns allmählich klar, dass zur unregelmässigen Reihe das Cl-Ion nicht einzige verantwortliche Fremdstbstanz ist.

(3) **Versuch mit HgSO_4 und $\text{Hg(NO}_3)_2$.** Noch gibt es HgSO_4 und $\text{Hg(NO}_3)_2$ als gewöhnlich käufliche Hg-Salze vor uns. Trotzdem sie beide schwer löslich sind, unter Anwendung grosser Menge gesättigter Lösungen, könnte man mit H_2S das HgS niederschlagen. Von diesem HgS haben wir in gleicher Weise das Sol hergestellt. Die Sole aus HgSO_4 bzw. $\text{Hg(NO}_3)_2$ sind manchmal so unbeständig, dass sie schon sich koagulieren, wenn man ihnen H_2 -Gas durchleitet, um überschüssigen H_2S auszutreiben. Die Sol-Beständigkeit kann man aber sehr einfach erhöhen durch die Beschallung von Ultraschallwellen, worüber bei uns eingehend untersucht wurde⁽⁵⁾.

(4) L. Vanino, „Präparative Chemie“, Bd. I, S. 584, Stuttgart (1925).

(5) N. Sata u. Y. Niwase, *Kolloid-Z.*, **81** (1937), 294.

Die Koagulationskurven dieser Sole sind in Abb. 9 und Abb. 10 angezeigt.



Die Kurven zeigen in allen Fällen die unregelmässige Reihe vor sich. Es ist dabei zu beachten, dass der 1-Koagulationspunkt die Tendenz zeigt, zur Stelle kleinerer Elektrolytkonzentration sich schieben, im Vergleich mit den Resultaten vorstehender Versuche. (Siehe Abb. 1–8.) Solche Verschiebung des 1-Koagulationspunktes haben wir auch mit dem Sol aus hochgereinigtem $\text{HgS}^{(6)}$ gemerkt, die vermutlich mit der Sol-Beständigkeit oder Sol-Konzentration zu abhängen ist.

(4) Schlussbemerkung. In voriger Untersuchung an HgS -Sol aus HgCl_2 , haben wir die Rolle von Cl -Ionen als sehr wichtig gefunden. Durch obenausgeführte Versuche wurde bestätigt, dass die unregelmässige Reihe, bei allen HgS -Solen aus verschiedenen Ausgangsmaterialien, d.h. unabhängig der beigemischten Nebenprodukten, immer zu erkennen ist. Daraus muss man schliessen, dass es nicht allein an Cl -Ionen begrenzt, sondern alle beigemischte Fremdionen sich ähnlich verhalten würden. Wie erwähnt, vermuten wir, dass sie hauptsächlich mit der Beständigkeit bzw. Konzentration des Sols, höchstens mit der Verschiebung des 1-Koagulationspunktes zu tun haben. Die Sol-Eigenschaft die die unregelmässige Reihe zu ergeben, scheint doch immer auf HgS -Teilchen aufbehalten zu sein.

Dann könnte man es zuerst als eine einfache Umladungserscheinung durch Ionen-Adsorption verstehen. Aber die Frage, dass die unregelmässige Reihe warum nur mit bestimmten Kombinationen der Sole und Elektrolyte zu geschehen ist, wird dadurch nicht aufgelöst. Dass die Umladung der Grenzflächen, im allgemeinen, durch Adsorption hochwertiger Ionen vor sich geht, wurde schon oft, theoretisch als auch experimentell, studiert⁽⁷⁾. Dabei handelt es sich nur um die Ladung und Umladung reiner, neutraler Grenzfläche durch Ionen-Adsorption aus einzigem Elektrolyt. Die Sache verhält sich ganz anders und zwar sehr kompliziert, wenn die Grenzfläche anfangs nicht neutral, sondern schon Ladung trägt, worüber noch kaum untersucht worden ist⁽⁸⁾. Wir möchten hier darauf aufmerksam

(6) Noch unveröffentlicher Versuch von uns. Das HgS wurde gereinigt durch Kochen und Dekantieren im Quarzgefäss über 300 Tage. [Siehe auch (4)].

(7) E. A. Hauser, "Colloidal Phenomena", S. 98, New York and London (1939): "Hydrophobic Colloids", S. 58, 83. Amsterdam (1938): H. Freundlich, E. Ettisch u. P. Rona, *Z. physik. Chem.*, **116** (1925), 401.

(8) "Colloidal Phenomena", S. 107: E. J. W. Verwey, *Kolloid-Z.*, **72** (1935), 187.

machen, dass die Erscheinung der unregelmässigen Reihe gerade auf diesem Problem auffällt. Ausserdem sind von dieser Erscheinung scheinbar ganz unabhängige zwei Kategorien bekannt, namentlich die von Mastix-, Platin-Sol usw. durch hochwertigen Elektrolyt, wie FeCl_3 bzw. AlCl_3 ⁽⁹⁾ und die von HgS-Sol durch einwertiges AgNO_3 . Vorderer Fall wurde so erklärt, dass er durch Adsorption der hochwertigen Ionen, oder der von diesen Elektrolyten hydrolytisch entstandenen Kolloidteilchen zurückzuführen ist, was aber zum letzten Fall von HgS-Sol gar nicht gültig ist. Mit Mastix-Sol⁽¹⁾ haben wir auch schon einigen Versuche durchgeführt. Dabei wurde gezeigt, dass zur unregelmässigen Reihe nicht nur der zugefügte Elektrolyt, sondern die im Sol vorhandenen dialysierbaren Substanzen auch verantwortlich sein können.

Aus den bisherigen Untersuchungen ist es nur soweit klar, dass die unregelmässige Reihe sich stattfindet, wenn die Kolloidteilchen die Eigenschaft besitzen, sich umzuladen durch Zufügen variierender Konzentrationen geeignetes Elektrolyts. Aber welche Sorten der Kolloidteilchen, unter welchen Bedingungen diese Eigenschaft bekommen würden, bleibt fast noch unberührt. Die bekannte Regel der Umladung durch Adsorption hochwertiger Ionen hat zur Erklärung unregelmässiger Reihe keine Allgemeinheit; denn, wie erwähnt, kennen wir schon die Beispiele derselben durch einwertiges AgNO_3 und dreiwertiges FeCl_3 .

Weitere Untersuchung wird fortgesetzt nach der Richtung genannten Fragestellen, die Spezifität dieser Erscheinung in erster Linie, zu klären.

Zusammenfassung.

(1) Es wurde die unregelmässige Koagulationsreihe des HgS-Sols aus verschiedenen Ausgangsmaterialien ausser HgCl_2 untersucht.

(2) Alle Sole, welche aus $\text{Hg}(\text{CN})_2$, HgSO_4 bzw. $\text{Hg}(\text{NO}_3)_2$ als Ausgangsmaterial hergestellt sind, zeigen immer die unregelmässige Reihe vor sich.

(3) Daraus wurde konstatiert, dass zu dieser Erscheinung, im Sol beigemischte Fremdsubstanzen(-ionen) keine grosse Bedeutung hat.

(4) Es scheint, dass sie hauptsächlich die Sol-Beständigkeit, Sol-Konzentration und höchstens die kleine Formänderung der Koagulationskurve verursacht, während die Sol-Eigenschaft die unregelmässige Reihe zu ergeben unverändert bleibt.

(5) Es wurde darauf aufmerksam gemacht, dass diese Erscheinung, aber, nicht als eine Umladungserscheinung durch Adsorption hochwertiger Ionen zu betrachten ist, weil es zwei ganz unabhängige Beispiele vorhanden sind; bei dem einen durch einwertigen, während beim anderen durch dreiwertigen Elektrolyt die unregelmässige Reihe hervorgerufen wird.

*Chemisches Institut der Kaiserlichen Universität
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und chemische Forschung.*

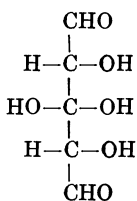
(9) H. Bechold, *Z. physik. Chem.*, **48** (1904), 418; H. Buxton u. P. Schaffer, *ibid.*, **57** (1907), 58; H. Buxton u. O. Teague, *ibid.*, **57** (1907), 72; H. Mayanagi, *Kolloid-Z.*, **39** (1926), 319.

The Formation of Polyhydroxy-dialdehydes. II.⁽¹⁾ *d*-Lyxo-tri-hydroxy-glutaric Dialdehyde and its Derivatives.

By Koichi IWADARE.

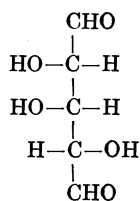
(Received April 7, 1941.)

Theoretically there should exist four dialdo-pentonoses, that is, trihydroxy-glutaric dialdehydes, and, among them, it was reported in the first paper about xylo-trihydroxy-glutaric dialdehyde (I). This communication concerns with the formation of *d*-lyxo-derivatives⁽²⁾ (or *d*-arabo-derivatives) (II).



(I)

Xylo-trihydroxy-glutaric
dialdehyde (described arbi-
trarily in chain formula)



(II)

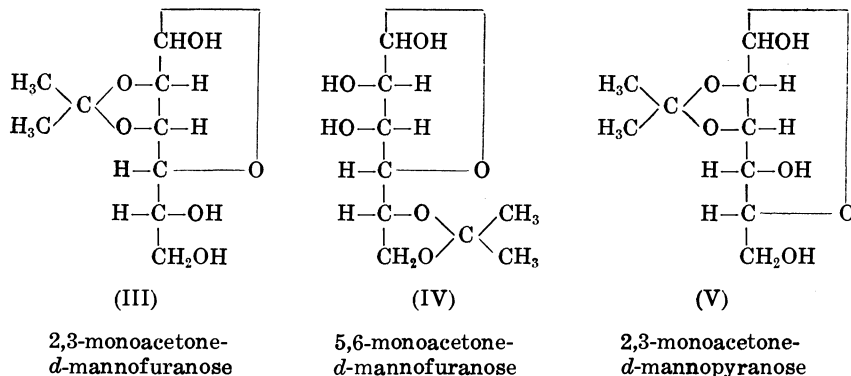
d-Lyxo-trihydroxy-glutaric
dialdehyde (described arbi-
trarily in chain formula)

For obtaining xylo-trihydroxy-glutaric dialdehyde, 1,2-monoacetone-*d*-glucofuranose was used as the starting substance, and so monoacetone-*d*-mannose, whose constitution had not yet been ultimately determined, was analogically used for obtaining *d*-lyxo-trihydroxy-glutaric dialdehyde and was proved to be suitable for its formation. And the constitution of monoacetone-*d*-mannose was decided at the same time. This compound was first obtained as impure sirup by K. Freudenberg⁽³⁾ by the partial hydrolysis of 2,3,5,6-diacetone-*d*-mannofuranose which has no substituent at 1 position. And it was identified as crystalline triacetyl-monoacetone-*d*-mannose by acetylating it with pyridine and acetic anhydride, and assumed to be 2,3-monoacetone-*d*-mannofuranose (III). It might, however, be 5,6-monoacetone-*d*-mannofuranose (IV), or, although less probable, 2,3-monoacetone-*d*-mannopyranose (V). But it was now proved to be 2,3-monoacetone-*d*-mannofuranose as supposed before. For formaldehyde was obtained by oxidizing it with lead tetracetate, and this certificated the presence of $-\text{C}(\text{OH})-\text{CH}_2\text{OH}$ linkage. And the fact that the derivative of trihydroxy-glutaric dialdehyde was obtained by oxidizing monoacetone-*d*-mannose with lead tetraacetate was another evidence of its structure.

(1) This Bulletin, **16** (1941), 40.

(2) The author reported briefly on these on the annual meeting of the Chemical Society of Japan in July 1940 at Sapporo.

(3) K. Freudenberg, W. Durr, and H. v. Hochstetter, *Ber.*, **61** (1928), 1740.

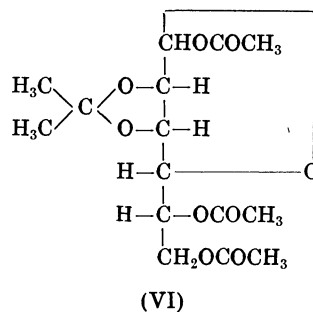


2,3,5,6-Diacetone-*d*-mannose is dissolved in biphthalate buffer solution (pH 4.4), and the solution is distilled by heating in an oil bath at $140-150^\circ$ for 1.5 hours, the necessary quantity of water being added during the time to keep the volume of the solution constant⁽³⁾. Then the buffer solution containing diacetone-*d*-mannose and monoacetone-*d*-mannose which is obtained by partial hydrolysis of diacetone-derivative is neutralized (phenolphthalein) and evaporated to small volume under diminished pressure, and extracted with ether for 48 hours. The ether extract is evaporated to sirup and thoroughly washed with boiling petroleum benzine to remove diacetone-mannose. The remaining sirup of monoacetone-mannose crystallizes spontaneously on standing. It is recrystallized from ether. It crystallizes in fine colourless needles. Melting point, $80.5-82^\circ$ (corrected). $[\alpha]_D^{15} = +4.5^\circ$ in water (5 minutes after solution). $[\alpha]_D^{15} = -3.7^\circ$ (40 hours after solution). It is soluble in ether, glacial acetic acid, ethyl acetate, acetone, etc. It does not reduce Fehling's solution, or, if does, quite feebly.

Monoacetone-mannose is dissolved in glacial acetic acid, equivalent quantity of lead tetracetate is added and the mixture is warmed on a water bath at $60-65^\circ$ for half an hour⁽⁴⁾. The evolved formaldehyde is water-distilled under diminished pressure and estimated as formaldehyde. About 70% of the theoretical quantity of formaldehyde is obtained. Thus the structure of monoacetone-*d*-mannose (III) is now established.

The crystalline 2,3-monoacetone-*d*-mannose is acetylated by pyridine and acetic anhydride in usual manner, and the same triacetyl-derivative ($58.5-59^\circ$) is obtained as from sirupy one⁽³⁾. And so this derivative is ascertained to be 1,5,6-triacetyl-2,3-monoacetone-*d*-mannofuranose (VI).

2,3-Monoacetone-*d*-mannofuranose is dissolved in benzene and oxidized with lead tetraacetate. The mixture is filtered, filtrate evapo-

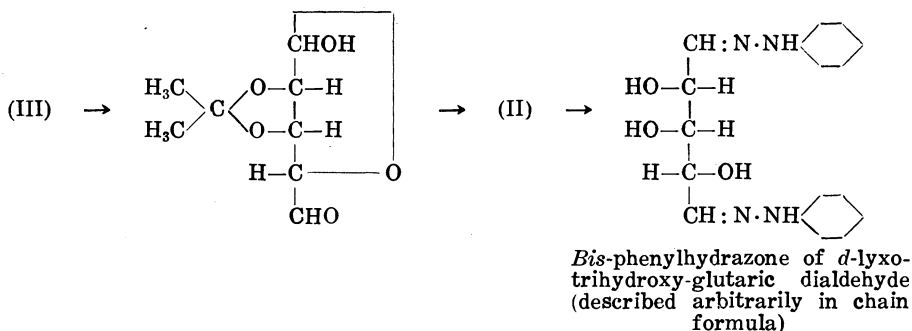


1,5,6-triacetyl-2,3-mono-
acetone-*d*-mannofuranose

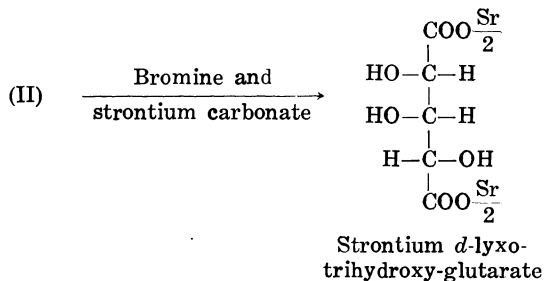
(4) Criegee, *Ann.*, **495** (1932), 211.

rated under diminished pressure, and the remaining sirup is hydrolized by warming with dilute sulphuric acid. Phenylhydrazine is added to the solution and *bis*-phenylhydrazone of *d*-lyxo-trihydroxy-glutaric dialdehyde soon precipitates on standing. It is recrystallized from acetone and petroleum ether, and then from alcohol. It crystallizes in fine needles. $[\alpha]_D^{15} = -72^\circ$ in pyridine. Melting point, $168.5-169^\circ$ (corrected, decomposing). *d*-Lyxo-trihydroxy-glutaric dialdehyde is obtained as sirup by decomposing its *bis*-phenylhydrazone with benzaldehyde, phenylhydrazine groups being removed as benzaldehyde-phenylhydrazone. The specific rotation of this dialdehyde is calculated by directly measuring the rotation of its water solution, which is obtained by decomposing the known quantity of its *bis*-phenylhydrazone, on the assumption that the conversion is quantitative. Thus, the specific rotatory power of *d*-lyxo-trihydroxy-glutaric dialdehyde, $[\alpha]_D^{15}$, is found to be $+5^\circ$.

Bis-p-nitro-phenylhydrazone of *d*-lyxo-trihydroxy-glutaric dialdehyde is obtained by adding acidic aqueous solution of *p*-nitro-phenylhydrazine to the aqueous solution of the dialdehyde. Orange leaflets. Melting point, $207-207.5^\circ$ (decomposing, corrected).



By oxidizing the aldehyde groups of *d*-lyxo-trihydroxy-glutaric dialdehyde with bromine, the corresponding carboxylic acid is obtained. Thus, strontium salt of *d*-lyxo-trihydroxy-glutaric acid is obtained by oxidizing the dialdehyde with bromine, generated acids being neutralized by excess of strontium carbonate.



Experimental.

2,3-Monoacetone-d-mannofuranose. For preparing this substance, *2,3,5,6-diacetone-d-mannofuranose* was first obtained by the slight modi-

fication of the usual method⁽⁵⁾. That is, 15 g. of *d*-mannose were mechanically shaken with 600 c.c. of acetone containing 10.5 c.c. of concentrated sulphuric acid. The greater part of *d*-mannose disappeared after half an hour, and all but coarse grains dissolved after an hour. The mixture was shaken for two hours, and then the colour of the solution was orange. It was neutralized with excess of anhydrous sodium carbonate after two hours standing, and then filtered from inorganic substances. Filtrate, now coloured in light lemon-yellow, was boiled on a water bath with a few grams of sodium carbonate and active charcoal. It was filtered after an hour, and the filtrate was concentrated first at ordinary pressure to a small volume and then evaporated to dryness under diminished pressure. The crystalline residue was recrystallized from benzine. Yield, 16 g. Ten grams of diacetone-*d*-mannose were dissolved in 250 c.c. of biphthalate buffer solution of pH 4.4, and the mixture was distilled in an oil bath at 140–150° for about two hours, adding water from time to time to maintain the initial volume. The distillate, received in an ice-cooled receiver, was made up to 250 c.c. with water. The acetone-content of the solution was measured by iodine-method⁽⁶⁾, and it was found that 51% of acetone (calculated from the initial quantity of diacetone-*d*-mannose) had come to the distillate. The cooled buffer solution, which contained *d*-mannose and monoacetone- and diacetone-*d*-mannose, was neutralized to phenolphthalein, evaporated to about 25 c.c. under diminished pressure, and extracted with ether for 48 hours. The ether extract was concentrated to sirup. In order to remove diacetone-derivative completely from the sirup, 70 c.c. of petroleum benzine (70–90°) were added to it, and the mixture was heated on a boiling water bath, and stirred mechanically for one or two hours. Benzine extract was removed by decantation, and the remaining sirup was again extracted with benzine just like above-mentioned method. This procedure was repeated ten times and then the remaining sirup crystallized slowly on standing. It was recrystallized from ether. Fine colourless Needles. Melting point, 80.5–82°. (Found: C 48.64, H 7.49. Calc. for $C_9H_{16}O_6$: C 49.09, H 7.33%). $[\alpha]_D^{15} = +4.5$ in water (5 minutes after solution). $\rightarrow -1^\circ$ (30 minutes) $\rightarrow -2^\circ$ (one hour) $\rightarrow -3.7^\circ$ (40 hours) ($c=2.42$).

The oxidation of monoacetone-d-mannose. Monoacetone-*d*-mannose (46.3 mg.) was dissolved in 3 c.c. of glacial acetic acid, 95.1 mg. of lead tetracetate were added to it, and the mixture was warmed for 30 minutes on a water bath at 60–65°. Then it was steam-distilled at 55° under reduced pressure (50 mm.), and 120 c.c., of distillate were obtained in an ice-cooled receiver. The alkaline solution of 0.5 g. of dimethylcyclohexandion-1,3 (dimedon) was added to the distillate, and the mixture was made slightly acidic by adding acetic acid. Then the colourless crystalline needles appeared at once. It was filtered after standing overnight in a refrigerator. Thus, 46.8 mg. of formal-dimedon was obtained. Melting point, 189–190° (corr.). This corresponds to 74% of the theoretical yield of formaldehyde from 2,3-monoacetone-*d*-mannofuranose.

(5) K. Freudenberg and A. Wolf, *Ber.*, **60** (1927), 232.

(6) K. Freudenberg, *Ber.*, **60** (1927), 241.

Bis-phenylhydrazone of d-lyxo-trihydroxy-glutaric dialdehyde. Mono-acetone-*d*-mannose (1.2 g.) was dissolved in 60 c.c. of benzene and lead tetracetate (2.4 g.) was added. The mixture was warmed on a water bath at 70° for ten minutes, cooled and then filtered. The precipitate was washed with acetone, and combined filtrate and washings were evaporated in vacuo to sirup, the temperature of the bath being kept below 30°. The sirup was dissolved in 50 c.c. of N/20-sulphuric acid, and warmed on a water bath for half an hour. It was warmed in vacuo to remove the isolated acetone, and phenylhydrazine (1.5 g.) was added to it. Light yellow precipitate soon appeared from the mixture. It was filtered, dried, and dissolved in acetone. Acetone solution was filtered, if necessary, and *bis*-phenylhydrazone was precipitated by adding petroleum ether. It was recrystallized from alcohol. Fine colourless needles. $[\alpha]_D^{15} = -72^\circ$ in pyridine. Melting point, 168.5–169°. (Found: N 17.36. Calc. for $C_{17}H_{20}O_3N_4$: N 17.06%).

d-Lyxo-trihydroxy-glutaric dialdehyde. *Bis*-phenylhydrazone of *d*-lyxo-trihydroxy-glutaric dialdehyde (1 g.) was suspended in 30 c.c. of water, 1 g. of benzaldehyde added, and the mixture was mechanically stirred for an hour, heating on a water bath at 90°. After cooling, it was extracted with ether and the aqueous solution was filtered with charcoal and evaporated in vacuo to sirup. *d*-Lyxo-trihydroxy-glutaric dialdehyde thus obtained reduces Fehling's solution after several minutes at room temperature, but at once reduces it strongly when heated. The equilibrium rotatory power of *d*-lyxo-trihydroxy-glutaric dialdehyde was calculated from the rotatory power of its aqueous solution obtained by decomposition of the known quantity of its *bis*-phenylhydrazone. That is, 0.418 g. of *bis*-phenylhydrazone was suspended in 6 c.c. of water and decomposed by benzaldehyde as mentioned above. The aqueous solution was made up to 10 c.c. by adding water and its rotatory power was measured with 1 dm. tube. $\alpha_D^{15} = +0.10^\circ$. As 0.188 g. of free dialdehyde should be obtained from 0.418 g. of its *bis*-phenylhydrazone, the specific rotatory power, $[\alpha]_D^{15}$, of *d*-lyxo-trihydroxy-glutaric dialdehyde is about $+5^\circ$.

Bis-p-nitro-phenylhydrazone of d-lyxo-trihydroxy-glutaric dialdehyde. To the aqueous solution of *d*-lyxo-trihydroxy-glutaric dialdehyde, obtained as mentioned above, acidic solution of *p*-nitro-phenylhydrazine was added. Fine orange yellow precipitate soon appeared. It was filtered, and recrystallized from alcohol containing a small quantity of pyridine. Melting point, 207–207.5° (decomposing, corrected). (Found: N, 20.06. Calc. for $C_{17}H_{18}O_7N_6$: N, 20.09%).

Strontium d-lyxo-trihydroxy-glutarate. To the aqueous solution of *d*-lyxo-trihydroxy-glutaric dialdehyde (containing about 0.2 g. of it), 4 g. of strontium carbonate and 0.7 g. of bromine were added. The mixture was frequently shaken for several hours and then kept standing for two days. Excess bromine was removed by airing under reduced pressure, and the mixture was filtered from strontium carbonate. Then the solution was stirred on adding silver carbonate to remove bromine ion, and filtered. Sulphuretted hydrogen was passed in the filtrate to eliminate silver ion and the mixture was again filtered. The filtrate was evaporated under

reduced pressure to a small volume, and white precipitate of strontium *d*-lyxo-trihydroxy-glutarate was obtained on adding alcohol to it. (Found: Sr, 33.28. Calc. for $C_5H_6O_7Sr$: Sr, 32.98%).

1,5,6-triacetyl-2,3-monoacetone-d-mannofuranose. Crystalline 2,3-monoacetone-*d*-mannofuranose (0.4 g.) was dissolved in 2 c.c. of pyridine and 1 g. of acetic anhydride was added to it. The mixture was evaporated in vacuum desiccator with soda-lime and sulphuric acid, and a small quantity of dilute methyl alcohol was added to the remaining sirup, which solidified spontaneously on standing. It was recrystallized from dilute methyl alcohol. Melting point, 58.5–59°.

Summary.

(1) Monoacetone-*d*-mannose was now obtained as colourless crystalline needles and its structure was established as 2,3-monoacetone-*d*-mannofuranose (III). Melting point, 80.5–82°. $[\alpha]_D^{15} = +4.5^\circ$ (5 minutes) $\rightarrow -3.7^\circ$ (40 hours) in water. And triacetyl-monoacetone-*d*-mannose⁽³⁾ was ascertained to have the constitution (VI).

(2) *Bis*-phenylhydrazone of *d*-lyxo-trihydroxy-glutaric dialdehyde was obtained as colourless needles, starting from 2,3-monoacetone-*d*-mannofuranose. Melting point, 168.5–169°. $[\alpha]_D^{15} = -72^\circ$ in pyridine. Equilibrium rotation of *d*-lyxo-trihydroxy-glutaric dialdehyde was measured. $[\alpha]_D^{15} = +5^\circ$ in water. *Bis-p*-nitrophenylhydrazone of *d*-lyxo-trihydroxy-glutaric dialdehyde was obtained as orange-yellow leaflets. Melting point, 207–207.5°.

Strontium salt of *d*-lyxo-trihydroxy-glutaric acid was obtained by oxidizing the dialdehyde with bromine in presence of strontium carbonate.

In conclusion the author wishes to express his hearty thanks to Prof. B. Kubota for his kind advice for this experiment.

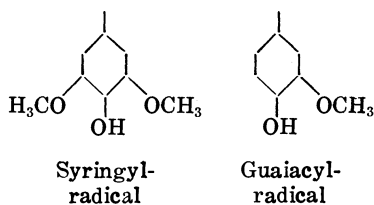
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Studies on Lignin. III.⁽¹⁾ On the Lignin of *Paulownia imperialis*.

By Koichi IWADARE.

(Received April 7, 1941.)

It was recently discovered that, according to the species of woods, lignins contained in them are classified into two series.^{(2) (3)} Namely, the one contains syringyl and guaiacyl radicals as building units, while the other consists mainly of guaiacyl radicals. Among the lignins of woods which have hitherto been studied, those of birch, maple, and beech contain both syringyl and guaiacyl radicals, and those of spruce and fir contain merely guaiacyl radicals. Japanese pine and cryptomeria belong to the latter. Thus, broad-leaved trees or hard woods contain syringyl radical,



while needle-leaved trees or soft woods do not. The wood of Japanese paulownia, however, is very soft, but it belongs to broad-leaved trees. So it is not clear to which series the paulownia wood belongs. This communication concerns with this point.

The lignin content of paulownia wood is measured by sulphuric acid method.⁽⁴⁾ That is, fine saw-dust (80 mesh) of paulownia is dried at 105°, and extracted with alcohol-benzene mixture for 4 hours. Then it is added to 72% sulphuric acid to remove cellulose, hemicellulose, and other materials by hydrolysis. Water is added to the mixture to make 3% sulphuric acid solution and the solution is boiled for 4 hours and filtered. The obtained lignin is weighed and the lignin content is found to be 19.3% of dried wood. While the lignin contents of soft woods as spruce or fir are 25 to 28%, and those of hard woods as maple or birch are about 20%.

Lignin is isolated from paulownia wood by method of Harris.⁽⁵⁾ That is, fine saw-dusts of paulownia wood, extracted first with alcohol-benzene mixture, then with alcohol, and finally with hot water, are treated with 70% sulphuric acid for 20 hours at 10°. Then the mixture is diluted with water to make 3% sulphuric acid solution, boiled, and then filtered. The methoxyl-value of the lignin thus obtained is 20.7%, and is same as that of the lignin of maple wood obtained by Harris. As the methoxyl-contents of the lignin of needle-leaved trees such as spruce, fir, or cryptomeria are

(1) K. Iwadare, *J. Chem. Soc. Japan*, **62** (1941), 186.

(2) K. Freudenberg and H. Fr. Müller, *Ber.*, **71** (1938), 1821.

(3) Hibbert et. al., *J. Am. Chem. Soc.*, **61** (1939), 509, 516, 868, 2198; **62** (1940), 986, 2149; **63** (1941), 312.

(4) C. J. Ritter, R. M. Seborg, and R. L. Mitchell, *Ind. Eng. Chem., Anal. Ed.*, **4** (1932), 202.

(5) E. C. Sherrard and E. E. Harris, *Ind. Eng. Chem.*, **24** (1932), 103; E. E. Harris, E. C. Sherrard, and R. L. Mitchell, *J. Am. Chem. Soc.*, **56** (1934), 889; E. E. Harris, *J. Am. Chem. Soc.*, **58** (1936), 894.

15–17%, the paulownia belongs apparently to the series of so-called hard-wood lignin.

Paulownia wood is ethanolised by usual method. Dry saw-dust, the resinous materials of which have been removed as mentioned above, is heated for 48 hours with absolute alcohol containing hydrogen chloride. The experimental data are as follows. (Table 1).

Table 1.⁽⁶⁾

		Weight (g.)	Percentage (%)	
			Calc. for wood-meal	Calc. for lignin
Starting substance	Paulownia wood-meal dried at 100–105°	70		
	Lignin content of the wood-meal (by 72% sulphuric acid method ⁽⁴⁾)	13.5	19.3	
Reaction products	Residual wood-meal	38	54	
	Lignin content of the residual wood-meal	2.8	7.4	21
	Lignin removed by ethanolysis	10.7		79
	Ethanol lignin	2.5		18
	Materials extracted with benzene { From aqueous solution	5.5		41
	{ From ethanol lignin	3.5		26
	Total	9.0		67

The methoxyl-content of the ethanol lignin is 26.9%, calculating ethoxyl as methoxyl.

The benzene solution of the extracted materials is shaken with aqueous solutions of sodium bisulphite, sodium bicarbonate and sodium hydroxide respectively and fractionated into aldehydic, acidic, phenolic, and neutral materials. (Table 2).

Table 2.⁽⁶⁾

	Weight (g.)	Percentage (Calc. for total lignin) (%)
Materials extracted with benzene	9	67
Aldehydic	0.8	6
Acidic	0.2	1.5
Phenolic	3.7	27
Neutral	0.4	3
Total	5.1	37.5%

(6) Some of the percentages in table 1 and 2 should be corrected by the factor $L/(L+OC_2H_5)$ owing to the ethoxyl group added to lignin. (L is the molecular weight of the building unit of lignin.)

The aldehydic fraction is dissolved in ethyl alcohol, and saturated ethyl alcohol solution of anhydrous potassium acetate and 2% potassium hydroxide-ethyl alcohol solution are added to it. Orange-yellow needles appear within half an hour. Adding semicarbazide hydrochloride to this precipitate, colourless crystals melting at 210.5–211.5° are obtained. This melting point agrees with that of monosemicarbazone of syringoylmethylketone (210–210.5°) obtained by Hibbert from maple wood, and so this compound obtained from paulownia lignin is identified as syringoylmethylketone. It is therefore established that paulownia lignin contains syringyl radicals, and belongs to so-called hard wood lignin.

Recently, it was reported by K. Freudenberg,⁽⁷⁾ that vanilline was obtained by oxidation of spruce wood-meal with nitrobenzene, and now paulownia wood-meal was oxidized by the same method. That is, paulownia wood-meal is heated in an autoclave at 160° with nitrobenzene and aqueous alkaline solution. From the reaction mixture nitrobenzene is removed by water-distillation. The residual solution is filtered, made slightly alkaline with sodium bicarbonate, and extracted continuously with benzene for 72 hours. Benzene extract corresponds to about 14% of the initial wood-meal and therefore to 70% of the lignin contained in it. A small portion of the benzene extract is suspended in water and acidic aqueous solution of 2,4-dinitrophenylhydrazine is added. The precipitated 2,4-dinitrophenylhydrazone is weighed, and the whole quantity of the aldehydes in the benzene extract is calculated from it. It corresponds to about 38% (by weight) of the lignin existing in the initial wood-meal, assuming the aldehydes as vanilline, and to about 43%, assuming them as syringylaldehyde.

Another portion of the benzene extract is dissolved in alcohol, filtered if necessary, and alcohol which contains dry ammonia is added. Yellow crystals appear immediately on standing. 2,4-Dinitrophenylhydrazone melting at 234.5–235° is obtained from it, so it is identified as the syringaldehyde derivative.

Experimental.

Lignin content of paulownia wood-meal. Paulownia wood-meal (80 mesh) was dried at 105°, and 1.971 g. of it were extracted with benzene-alcohol mixture in Soxlet-apparatus for 4 hours. It was filtered, washed with alcohol, and heated with 400 c.c. of water in a boiling water bath for 3 hours. It was filtered, dried and mixed with 25 c.c. of 72% sulphuric acid. After 2 hours, it was diluted with water to make 3% sulphuric acid solution and boiled for 4 hours. Insoluble lignin was weighed by filtering the solution with a tared glass-filter. Brown lignin (0.380 g.) was obtained. This corresponds to 19.3% of the initial wood-meal.

The methoxyl-value of paulownia lignin. Paulownia wood-meal (24 g.) was mixed with 240 c.c. of 70% sulphuric acid, and stirred for 3 hours at 10°. After standing overnight in a refrigerator at 10°, it was poured in 9 l. of water and boiled for 4 hours. It was filtered and air-dried.

(7) K. Freudenberg, W. Lautsch, and K. Engler, *Ber.*, **73** (1940), 167.

Yield, 5 g. The methoxyl-value of the lignin dried at 100° in vacuo over phosphorous pentoxide is 20.7%.

The ethanolysis of paulownia wood-meal. Paulownia wood-meal (70 g.), freed from resinous materials by extracting with alcohol-benzene mixture, alcohol, and then with hot water, was boiled for 48 hours with 850 c.c. of absolute ethyl alcohol containing 2% of hydrogen chloride. It was filtered, washed well with alcohol, and the combined filtrate and washings were neutralized with sodium ethylate, and evaporated under reduced pressure to 150 c.c. It was poured into 1.2 l. of water, and filtered. The precipitate was dried and extracted ten times by shaking mechanically with benzene (50 c.c.). The filtrate was evaporated to 200 c.c. and extracted continuously with benzene for 48 hours. Both benzene extracts were evaporated, and 3.5 g. and 5.5 g. of sirups were obtained respectively. The sirups were dissolved in benzene and the combined benzene solution was extracted many times with aqueous solution of sodium bisulphite, sodium bicarbonate and sodium hydroxide to fractionate it into aldehydic, acidic, phenolic and neutral materials. The sodium bisulphite extract was made acidic by sulphuric acid, isolated sulphurous acid being removed under diminished pressure, and extracted continuously with benzene. The benzene extract was evaporated to sirup (0.8 g.) and dissolved in absolute ethanol (25 c.c.). The ethyl alcoholic solution of sodium acetate was added to it, and 2% alcoholic solution of sodium hydroxide was added to the mixture to make it slightly alkaline. Orange-yellow needles precipitated within half an hour. It was filtered, and 20 mg. of the precipitate were dissolved in 1 c.c. of water, and 14 mg. of semicarbazide hydrochloride and 20 mg. of potassium acetate were added. It was filtered after 2 hours. Melting point, 210.5–211.5° (corrected). This corresponds to monosemicarbazone of syringoylmethylketone.

The methoxyl-value of ethanol lignin is 26.9%, and that of the lignin isolated from the residual wood-meal by 70% sulphuric acid method is 21.0%, which is almost equal to the methoxyl-value of the lignin from initial wood-meal. Other experimental data are given in tables 1 and 2.

The oxidation of paulownia wood-meal with nitrobenzene. Paulownia wood-meal (35 g.) was heated for five hours in an autoclave with 400 c.c. of 10% sodium hydroxide solution and 20 c.c. of nitrobenzene. The mixture was water-distilled, and remaining solution was filtered. The filtrate was made slightly acidic by adding hydrochloric acid, and then made slightly alkaline by sodium bicarbonate. It was continuously extracted with benzene for 72 hours, and the benzene solution was evaporated in vacuo. The residual sirup was 5.0 g. It was dissolved in 100 c.c. of benzene, and 1 c.c. of it was evaporated and acidic aqueous solution of 2,4-dinitrophenylhydrazine was added to it. Calculating from the weight (58.2 mg.) of 2,4-dinitrophenylhydrazone obtained, 2.66 g. or 2.92 g. of aldehydes should exist in the benzene extract, if the aldehydes are assumed to consist only of vanilline or syringaldehyde respectively. They correspond to about 38% or 43% (by weight) of the lignin existing in the initial wood-meal.

Benzene extract (0.7 g.) was dissolved in 5 c.c. of alcohol, filtered, and alcohol which contained dry ammonia was added. Yellow crystals

were obtained. It was dissolved in ethanol containing a few drops of concentrated hydrochloric acid, and 2,4-dinitrophenylhydrazine was added. Red crystals melting at 234.5–235° were obtained. This melting point agrees with that of 2,4-dinitrophenylhydrazone of syringaldehyde.

The residual aqueous solution, which had been extracted with benzene, was made acidic by adding hydrochloric acid and extracted continuously with benzene. Thus, 1.2 g. of acidic fraction were obtained.

Summary.

Although paulownia wood is very soft, its lignin belongs to so-called hard-wood lignin, and it contains both syringyl and guaiacyl radicals. These facts are established by the measurements of the lignin content and of the methoxyl value of the paulownia wood lignin, and by the ethanolysis and oxidation with nitrobenzene.

In conclusion, the author wishes to express his hearty thanks to Prof. B. Kubota for his kind advice for this experiment.

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Synthese einiger Glykoside.

Von Kazutosi NISIZAWA.

(Eingegangen am 9. April 1941.)

Seit einigen Jahren habe ich mich als einer der Mitarbeiter von Herrn Prof. Dr. T. Miwa mit dem Spezifitätsproblem der Glykosidasen beschäftigt⁽¹⁾. Die Substrate, die zu dieser Fermentforschung nötig sind, haben wir meist synthetisch dargestellt. Im folgenden soll über die Synthese einiger neuen und wichtigen Glykoside kurz berichtet werden.

Zu diesem Zwecke kam in erster Linie eine ausgezeichnete Methode von B. Helferich und Mitarbeitern⁽²⁾ zur Anwendung, worin das Zinkchlorid bei der Synthese der α -Glykoside und die *p*-Toluolsulfonsäure bei der der β -Glykoside je als spezifischer Katalysator wirken.

Bei den vorliegenden Versuchen liess sich dieses Verfahren meist mit dem befriedigenden Erfolg durchführen, jedoch ergaben sich bei einigen Fällen, wie es auch Helferich selbst nicht selten angetroffen waren, abweichende Resultate. So wurden bei der Darstellung des β -Galaktosids von *p*-Oxyacetophenon, Guajakol und *m*-Kresol unter Anwendung von *p*-Toluolsulfonsäure als Katalysator stets ein Gemisch von α - und β -Form erzeugt. Wenn man anstatt der *p*-Toluolsulfonsäure das Zinkchlorid anwendete, so bildete sich bei dem *p*-Oxyacetophenon- und Guajakolgalaktosid auch dasselbe Gemisch, aber mit einem geringen Überschuss von α -Form. Daraus konnte ich das *p*-Oxyacetophenon- α - und - β -galaktosid sowie das Guajakol- α - und - β -galaktosid kristallisiert erhalten. Die so gewonnenen β -Formen dieser Galaktoside haben sich mit denjenigen, welche aus Acetobromgalaktose dargestellt wurden, als identisch erwiesen. Hingegen soll das Gemisch von α - und β -Form, das bei der Synthese des *m*-Kresolgalaktosids mit *p*-Toluolsulfonsäure gebildet wurde, als wahres Mischkristall betrachtet werden. Dafür spricht der Befund: (1) dass der Schmelzpunkt dieses Produktes (175–8°), welcher sich durch Umkristallisieren nicht ändert, höher als jeder der beiden Formen (α -Form 150–2°, β -Form 166–7°) liegt, und (2) dass die Trennung der beiden Komponenten voneinander nicht erzielt werden konnte, trotzdem ich unter verschiedenen Reaktionsbedingungen verarbeitet hatte, was jedoch bei den gewöhnlichen Gemischen, wie *p*-Oxyacetophenon- oder Guajakolgalaktosid, ohne grosse Schwierigkeit erreicht wurde. Während es B. Helferich⁽³⁾ gelungen war, reines *m*-Kresol- β -*d*-galaktosid mit *p*-Toluolsulfonsäure als Katalysator herzustellen, konnte ich doch es nicht erhalten, obschon ich unter genau denselben Bedingungen wie Helferich versucht hatte. Führt man aber diese Synthese mit Zinkchlorid und bei einer Temperatur von 100° aus, so gewinnt man glatt das reine *m*-Kresol- α -*d*-galaktosid, dagegen wiederum dasselbe Mischkristall von α - und β -Form, wenn die Reaktions-

(1) *Acta Phytochim.* (Japan), **10** (1937), 155; *Hattori-Hôkôkai Kenkyû Shôroku*, **7** (1939), 155.

(2) *Ber.*, **66** (1933), 378.

(3) *Ann.*, **514** (1934), 228.

temperatur auf 125–128° gesteigert wird. Zur Synthese des β -Galaktosids von Salicylaldehyd, Methylsalicylat, 1:3:5-Xylenol und Isoeugenol sowie auch *n*-Butanol diene ausschliesslich die klassische Methode, indem Acetobromgalaktose und Phenole bzw. *n*-Butanol mit Hilfe von Alkali oder von Silberoxyd bzw. Silbercarbonat kondensiert wurden.

Beschreibung der Versuche.

(1) *Guajakol- β -d-galaktosid*. 50 g β -Pentacetyl-*d*-galaktose (1 Mol) wurden mit 38 g Guajakol (2.5 Mol) und 0.65 g *p*-Toluolsulfonsäure in einem Ölbad von 125–128° 120 Min. unter dauerndem Rühren erhitzt. Die dunkelbraune Schmelze wurde nach dem Erkalten in etwa 300 ccm Benzol aufgenommen, die Lösung wurde 2 mal mit Wasser, dann mehrmals mit etwa 8-proz. Natronlauge und wieder mit Wasser gewaschen, mit Chlorcalcium getrocknet und zur Trockne verdampft. Der Rückstand wurde in Äthanol aufgenommen und in Eisschrank gestellt. Die ausgeschiedenen Kristalle wurden ferner 3 mal aus 40 ccm Äthanol umkristallisiert. Ausbeute 6.4g, d.i. 11.0% d. Th. Schmp. 65–69° (nicht scharf). $[\alpha]_D^{20} = +0.63^\circ \times 7.3949/0.0409 \times 1.478 \times 1 = +77.0^\circ$ (in Chloroform). Gefunden: C, 55.34, 55.53; H, 6.02, 5.98. Berechnet für $C_{21}H_{26}O_{11}$: C, 55.47; H, 5.68%.

Das erhaltene Produkt ist aber nicht einheitlich, sondern es stellt ein Gemisch von α - und β -Form dar, so dass die Trennung der beiden Formen folgendermassen vorgenommen wurden. 9.5g Tetracetat in 40 ccm absolutem Methanol wurden mit 2 ccm N/5-Natriummethylat 60 Min. unter Rückfluss gelinde erhitzt. Danach wurde die Lösung mit etwas Tierkohle behandelt, auf etwa 15 ccm eingedampft und übernacht im Eisschrank aufbewahrt. Die ausgeschiedenen Kristalle wurden von der Mutterlauge, die vornehmlich α -Form enthielt, abfiltriert und durch 2 maliges Umkristallisieren aus Methanol gereinigt. Ausbeute 1.0g. Schmp. 203–204°. $[\alpha]_D^{20} = -0.42^\circ \times 8.8880/0.0424 \times 0.9875 \times 2 = -44.64^\circ$ (in Wasser).

Dass dieses Produkt die β -Verbindung ist, ist daraus zu ersehen dass sein Drehungsvermögen sowie sein Schmelzpunkt mit denjenigen des aus Acetobromgalaktose folgendermassen hergestellten Galaktosids übereinstimmen. 25g Acetobromgalaktose und 15g Guajakol wurden in Aceton gelöst und mit 5g Natriumhydroxyd in wenig Wasser versetzt. Die Lösung wurde 2 Tage bei Zimmertemperatur stehen gelassen und unter vermindertem Druck eingedampft. Der ölige Rückstand wurde zuerst mit verdünnter Natronlauge, dann mehrmals mit Wasser gewaschen und schliesslich in etwa 30 ccm heissem Methanol aufgenommen und die nach dem Abkühlen sofort ausgeschiedenen Kristalle wurden aus wenig Methanol umkristallisiert. Ausbeute 9.5g (34.4% d. Th.). Schmp. 100–102°, $[\alpha]_D^{20} = -0.30^\circ \times 13.3285/0.0807 \times 1.481 \times 2 = -16.71^\circ$ (in Chloroform). Gefunden: C, 55.21, 55.04; H, 6.09, 5.75. Berechnet für $C_{21}H_{26}O_{11}$: C, 55.47; H, 5.68%.

Durch Verseifen von 8.0g Tetracetat in 50 ccm wasserfreiem Methanol mit 2 ccm N/5-Natriummethylat erhält man 3.2g Guajakol- β -d-galaktosid. Es wurde aus Methanol umkristallisiert. Schmp. 203–204°. $[\alpha]_D^{20} = -0.45^\circ \times 5.0261/0.0506 \times 1.005 \times 1 = -44.48^\circ$ (in Wasser). Gefunden: C, 54.66, 54.85; H, 6.60, 6.59. Berechnet für $C_{21}H_{26}O_{11}$: C, 54.54; H, 6.30%.

(2) *Guajakol- α -d-galaktosid*. Die methanolische Mutterlauge (etwa 15 ccm), die bei dem voranstehenden Versuch nach Entfernung von Guajakol- β -d-galaktosid zurückblieb, wurde eingedampft, der Rückstand in wenig Wasser gelöst und mit Tierkohle entfärbt. Beim Aufbewahren im Eisschrank schieden sich allmählich Kristalle aus, die nach einigen Tagen abgesaugt und mehrmals aus Wasser umkristallisiert wurden. Aus 9.5g Tetracetat wurde etwa 1g Produkt mit $[\alpha]_D$ von etwa +200° gewonnen. Die erhaltene Substanz ist aber noch mit einer geringen Menge von β -Form beigemengt. Weitere Reinigung gelingt man am besten über Acetylderivat. 1.2g Substanz wurden mit 10 ccm Pyridin und 7 ccm Essigsäureanhydrid 5 Min. auf dem siedenden Wasserbad erhitzt und das Reaktionsprodukt in Eiswasser gegossen. Das ausgeschiedene Acetat wurde nach Aufgewahren übernacht im Eisschrank zweimal aus Äthanol umkristallisiert, woraus man 1.6g reines Tetracetylguajakol- α -d-galaktosid erhielt. Schmp. 82–84°. $[\alpha]_D^{20} = +2.28^\circ \times 13.2187/0.0587 \times 1.4688 \times 2 = +227.6^\circ$ (in Chloroform). Gefunden: C, 55.18; H, 5.74. Berechnet für $C_{21}H_{26}O_{11}$: C, 55.47; H, 5.68%.

Durch Verseifen wurden aus 1g Acetat 0.35g reines Guajakol- α -*d*-galaktosid gewonnen. Schmp. 140–142°, $[\alpha]_D^{20} = +2.01^\circ \times 8.9520/0.0478 \times 0.9947 \times 2 = +211.4^\circ$ (in Wasser). Gefunden: C, 54.13, 54.24; H, 6.64, 6.77. Berechnet für $C_{17}H_{18}O_7$: C, 54.54; H, 6.30%.

Zur Darstellung von Guajakol- α -*d*-galaktosid, ist es vorteilhaft, das Zinkchlorid anstelle der *p*-Toluolsulfonsäure als Katalysator anzuwenden, denn die α -Form wird hierbei mit etwas verbesserter Ausbeute gebildet. 30g β -Pentacetyl-*d*-galaktose (1 Mol) wurden mit 22.5g Guajakol (2.5 Mol) und 1.6g Chlorzink 120 Min. auf dem siedenden Wasserbad erhitzt. Weitere Aufarbeitung erfolgte wie bei (1). Der nach dem Verdampfen des Benzols zurückbleibende Sirup wurde in etwa 30 ccm heissem Äthanol gelöst, der beim Erkalten kristallinisch erstarrte. Das Produkt wurde solange aus Äthanol umkristallisiert bis das Reduktionsvermögen gegen Fehlingsche Lösung völlig verschwindet. Ausbeute 4.2g (12.0% d. Th.). Schmp. 65–69° (nicht scharf). $[\alpha]_D^{18} = +0.97^\circ \times 7.4883/0.0573 \times 1.4976 \times 1 = +84.7^\circ$ (in Chloroform). Gefunden: C, 55.25, 55.26; H, 5.98, 5.84. Berechnet für $C_{21}H_{20}O_{11}$: C, 55.47; H, 5.68%.

Aus dem Drehungswert der erhaltenen Substanz erweist sich dieses Produkt wiederum als ein Gemisch beider Komponenten. Liess man diese Reaktion bei 125° während 90 Min. vor sich gehen, so wurde ebenfalls dasselbe Gemisch erzeugt wie bei dem eben beschriebenen Verfahren, aber mit etwas schlechterer Ausbeute.

(3) *m*-Kresol- α -*d*-galaktosid. 30g β -Pentacetyl-*d*-galaktose (1 Mol), 24g *m*-Kresol (3 Mol) und 1.2g Chlorzink wurden 120 Min. auf dem siedenden Wasserbad erhitzt. Nachdem die Schmelze in gleicher Weise wie bei (1) aufgearbeitet wurde, erhielt man daraus nach dem Umkristallisieren aus 30 ccm Äthanol 5.5g reines Tetracetat (16.3% d. Th.). Schmp. 75–76°. $[\alpha]_D^{17} = +2.77^\circ \times 13.3257/0.0700 \times 1.4806 \times 2 = +178.0^\circ$ (in Chloroform). Gefunden: C, 57.39, 57.79; H, 6.11, 5.94. Berechnet für $C_{21}H_{20}O_{10}$: C, 57.50; H, 5.93%.

Das durch Verseifen mit Natriummethylat gewonnene *m*-Kresol- α -*d*-galaktosid schmolz nach 3.5-stündigem Trocknen in Vakuum über Phosphorpentoxyd bei 100° bei 150–152°. $[\alpha]_D^{19} = +1.61^\circ \times 8.9400/0.035 \times 0.9933 \times 2 = +207.0^\circ$ (in Wasser). Gefunden: C, 57.20, 57.00; H, 6.72, 7.04. Berechnet für $C_{17}H_{18}O_6$: C, 57.77; H, 6.67%.

Wenn man aber diese Synthese bei 125–128° ausführt, so wird ein Gemisch gewonnen, welches aus gleicher Menge von α - und β -Form besteht. Dabei ist zu bemerken, dass man immer dasselbe Gemisch erhält, gleichgültig ob man als Katalysator Zinkchlorid oder *p*-Toluolsulfonsäure anwendet. Dagegen gewannen B. Helferich und Mitarbeiter⁽³⁾ das β -Derivat, indem sie die Reaktion bei 100° mit *p*-Toluolsulfonsäure durchführten und zur Verseifung anstatt des Natriummethylats *N*-Natronlauge anwandten. Zur Darstellung von β -Form habe ich auch genau nach ihrer Vorschrift verarbeitet, jedoch konnte ich nicht die β -Form sondern immer dieselbe Mischung von α - und β -Derivat erhalten. $[\alpha]_D^{13} = +0.72^\circ \times 100/0.4444 \times 2 = +81.0^\circ$ (in Wasser). Aus diesem Drehungswert ergibt sich, dass das erhaltene Produkt ein Gemisch von gleicher Menge der α - und β -Form darstellt (α -Form: +207.0°, β -Form: –44.3°). Der Schmelzpunkt des Produktes liegt bei 175–178°. Also ist er höher als der Schmelzpunkt von beiden Formen (α -Form: 150–152°, β -Form: 166–167°). Präparat dargestellt mit Chlorzink als Katalysator. Gefunden: C, 57.94, 58.05; H, 6.88, 6.69%. Präparat dargestellt mit *p*-Toluolsulfonsäure als Katalysator. Gefunden: C, 58.27, 58.05; H, 6.82, 6.88. Berechnet für $C_{18}H_{18}O_6$: C, 57.77; H, 6.67%.

Dieser Mischkristall kann man auch erhalten, wenn man die gleiche Menge von reinen α - und β -Derivaten zusammen in Wasser löst und daraus auskristallisieren lässt.

(4) *p*-Oxyacetophenon- β -*d*-galaktosid. 28g Acetobromgalaktose (1 Mol), 18g *p*-Oxyacetophenon (2 Mol) und 5.5g Natriumhydroxyd (2 Mol) wurden in verdünntem Aceton gelöst. Nach 4 Tagen wurde das Aceton abgedampft, der sirupöse Rückstand mehrmals zuerst mit 1-proz. Natronlauge dann mit Wasser gewaschen und schliesslich in wenig Methanol gelöst. Die beim Abkühlen ausgeschiedenen Kristalle wurden durch Umkristallisieren aus Methanol gereinigt. Erhalten 16.5g (52.0% d. Th.). Schmp. 146–147°. $[\alpha]_D^{20} = -0.52^\circ \times 4.3724/0.0503 \times 0.8745 \times 1 = -51.69^\circ$ (in Benzol). Gefunden: C, 56.46, 56.60; H, 5.91, 5.89. Berechnet für $C_{22}H_{20}O_{11}$: C, 56.63; H, 5.56%.

Weiter habe ich versucht, dieses Galaktosid mit *p*-Toluolsulfonsäure als Katalysator herzustellen. Unter den folgenden Reaktionsbedingungen wurde unerwarteterweise nur das α -Derivat erzeugt. 10g β -Pentacetyl-*d*-galaktose (1 Mol), 8.3g *p*-Oxyacetophenon (2.5 Mol) und 0.13g *p*-Toluolsulfonsäure wurden 90-minutenlang bei 128°

erhitzt. Aufarbeitung wie bei 1). Erhalten etwa 1g Tetracetat. Schmp. 155–157°. $[\alpha]_D^{25} = +2.56^\circ \times 13.2730 / 0.055 \times 1.475 \times 2 = +209.0^\circ$ (in Chloroform). Gefunden: C, 56.51, 56.74; H, 5.70, 5.68. Berechnet für $C_{22}H_{26}O_{11}$: C, 56.63; H, 5.56%.

(5) *p*-Oxyacetophenon- α -*d*-galaktosid. 14.3g β -Tetracetyl-*d*-galaktose (1 Mol), 7.5g *p*-Oxyacetophenon (2 Mol) und 1.5g Zinkchlorid wurden 90 minutenlang bei 127–128° erhitzt. Nach der Aufarbeitung wie bei 1), erhielt man 1.6g reines Tetracetat. Ausbeute 9.4% d. Th. Schmp. 155–157°. $[\alpha]_D^{25} = +0.90^\circ \times 7.2925 / 0.0215 \times 1.4585 \times 1 = +209.0^\circ$ (in Chloroform). Gefunden: C, 56.65, 56.33; H, 5.52, 5.73. Berechnet für $C_{22}H_{26}O_{11}$: C, 56.63; H, 5.56%.

Aus 2.8g Tetracetat wurden 0.9g *p*-Oxyacetophenon- α -*d*-galaktosid nach der Verseifung mit Natriummethylat gewonnen. Schmp. 158–160°. $[\alpha]_D^{25} = +0.87^\circ \times 4.9945 / 0.0192 \times 1 = +226.2^\circ$ (in Wasser). Gefunden: C, 56.51, 56.64; H, 6.19, 5.98. Berechnet für $C_{14}H_{18}O_7$: C, 56.37; H, 6.04%.

(6) *o*-Oxybenzaldehyd- β -*d*-galaktosid. 1.5g Salicylaldehyd (1 Mol) und 11g Acetobromgalaktose (2 Mol) wurden in 10 ccm Chinolin gelöst, mit 6g frisch hergestelltem Silberoxyd (2 Mol) versetzt (Kühlen in Wasser). Die beim Reiben mit Glasstab erstarrende Masse wurde zuerst mit etwa 500 ccm 25-proz. Essigsäure mehrmals in Portionen gewaschen, von der Waschflüssigkeit durch Dekantieren und Zentrifugieren völlig abgetrennt, und der Rückstand mit etwa 50 ccm heissem Methanol extrahiert. Nachdem das Silbersalz abfiltriert worden war, wurde die methanolische Lösung stark eingeeengt und übernacht in Eisschrank aufbewahrt. Die ausgeschiedenen Kristalle wurden 2 mal aus Methanol umkristallisiert. Ausbeute 1.2g (21.6% d. Th.). Nach dem Trocknen bei 78° im Vakuum über Phosphorpentoxyd, schmolz das Produkt bei 107–109°. $[\alpha]_D^{25} = -0.30^\circ \times 13.2650 / 0.101 \times 1.474 \times 2 = -13.74^\circ$ (in Chloroform). Gefunden: C, 55.80; H, 5.58. Berechnet für $C_{21}H_{24}O_{11}$: C, 55.74; H, 5.31%.

Nach dem Verseifen erhielt man das freie Galaktosid. Es ist in Wasser sowie in Äthanol sehr schwer löslich. Das Umkristallisieren erfolgte aus etwa 500 facher Menge Wasser. Schmp. 237–239°. $[\alpha]_D^{30} = -0.08^\circ \times 100 / 0.1667 \times 2 = -23.6^\circ$ (in Wasser). Gefunden: C, 54.87, 54.68; H, 5.78, 5.58. Berechnet für $C_{13}H_{18}O_7$: C, 64.92; H, 5.63%.

(7) *Methylsalicylat*- β -*d*-galaktosid. 3.7g Methylsalicylat (1 Mol) und 20g Acetobromgalaktose (2 Mol) wurden in 20 ccm Chinolin gelöst, mit 12g Silberoxyd (2 Mol) unter Wasserkühlung versetzt, wobei das Gemisch zur teigartigen Masse erstarrte. Daraus wurde nach der Aufarbeitung wie bei (6) 4.8g Tetracetat gewonnen, das durch Umkristallisieren aus Äthanol gereinigt wurde. Ausbeute etwa 40% d. Th. Schmp. 116–117°. $[\alpha]_D^{25} = -0.22^\circ \times 13.2752 / 0.0752 \times 1.475 \times 2 = -13.16^\circ$ (in Chloroform). Gefunden: C 54.85, 54.88; H, 5.49, 5.28. Berechnet für $C_{22}H_{26}O_{12}$: C, 54.77; H, 5.39%.

Durch Verseifen mit Natriummethylat wurde das freie Galaktosid erhalten, das aus Äthanol umkristallisiert wurde. Schmp. 171–172°. $[\alpha]_D^{25} = -0.45^\circ \times 8.9622 / 0.0500 \times 0.9958 \times 2 = -40.1^\circ$ (in Wasser). Gefunden: C, 53.61, 53.33; H, 5.74, 5.60. Berechnet für $C_{14}H_{18}O_8$: C, 53.50; H, 5.73%.

(8) 1:3:5-Xylenol- β -*d*-galaktosid. 25g Acetobromgalaktose (1 Mol), 14.9g Xylenol (2 Mol) und 5g Natriumhydroxyd (2 Mol) wurden in verdünntem Aceton gelöst und 4 tagelang bei Zimmertemperatur aufbewahrt. Nach dem Verdampfen des Acetons wurde der sirupöse Rückstand, nachdem man ihn mehrmals mit Natronlauge und Wasser gewaschen hatte, in etwa 40 ccm Äthanol gelöst, woraus das Tetracetat durch vorsichtigen Wasserzusatz kristallin ausgeschieden und aus wenig Methanol umkristallisiert wurde. Ausbeute 8.6g, d. i. 24.6% d. Th. Schmp. 116–117°. $[\alpha]_D^{25} = -0.17^\circ \times 7.8805 / 0.0400 \times 0.8756 \times 2 = -19.0^\circ$ (in Benzol). Gefunden: C, 58.54, 58.45; H, 6.34, 6.31. Berechnet für $C_{22}H_{28}O_{10}$: C, 58.41; H, 6.19%.

Durch Verseifen des so erhaltenen Tetracetyl-xylenol- β -*d*-galaktosids wurde das freie Galaktosid gewonnen, das aus etwa 17 facher Menge 30-proz. Äthanol umkristallisiert wurde. Aus 7.6g Tetracetat wurden 2.2g reines Galaktosid gewonnen. Schmp. 193–194°. $[\alpha]_D^{25} = -0.74^\circ \times 9.0480 / 0.0775 \times 1.00 \times 2 = -43.0^\circ$ (in Wasser). Gefunden: C, 59.13, 58.97; H, 7.14, 7.12. Berechnet für $C_{14}H_{20}O_6$: C, 59.15; H, 7.04%.

(9) *Isoeugenol*- β -*d*-galaktosid. 19.0g Acetobromgalaktose (1 Mol), 15.0g Isoeugenol (2 Mol) und 4.0g Natriumhydroxyd (2 Mol) wurden in verdünntem Aceton gelöst und 4 tagelang bei Zimmertemperatur stehen gelassen. Der nach dem Verdampfen des Acetons zurückbleibende Sirup wurde mehrmals mit Natronlauge und Wasser gewaschen und in etwa 40ccm Äthanol gelöst. Durch vorsichtigen Wasser-

zusatz bis zur bleibenden Trübung erhielt man daraus das Tetracetat, das aus Methanol umkristallisiert wurde. Ausbeute 6.5g (etwa 20% d. Th.). Schmp. 140–141°. $[\alpha]_D^{20} = -0.70^\circ \times 7.8925/0.0600 \times 0.8769 \times 2 = -52.5^\circ$ (in Benzol). Gefunden: C, 58.43, 58.43; H, 6.12, 5.86. Berechnet für $C_{21}H_{30}O_{11}$: C, 58.29; H, 6.07%.

Das durch Verseifen mit Natriummethylat gewonnene Isoeugenol- β -*d*-galaktosid ist in Wasser und Alkohol schwer löslich und scheidet sich aus Alkohollösung als gallertartige Masse aus. Zur Analyse wurde die aus Wasser mehrmals umkristallisierte Substanz 3-stundenlang bei 100° im Vakuum über Phosphorpentoxyd getrocknet. Schmp. 196–198°. $[\alpha]_D^{20} = -0.29^\circ \times 9.2361/0.219 \times 1.0262 \times 2 = -59.6^\circ$ (in 1.78 N-Natronlauge). Gefunden: C, 58.68, 58.85; H, 6.81, 6.48. Berechnet für $C_{16}H_{22}O_7$: C, 58.87; H, 6.72%.

(10) *Phenol- α -*d*-galaktosid*. Das Tetracetat wurde nach Vorschrift von B. Helferich und Mitarbeitern⁽²⁾ mit Zinkchlorid als Katalysator dargestellt. Sie schmolz bei 131–132° und zeigte eine spezifische Drehung von +175.5° (in Chloroform). Durch Verseifen mit Natriummethylat wurde das freie Galaktosid gewonnen. Aus 50-Proz. Äthanol umkristallisiert, enthielt es noch 1 Mol Kristallwasser und schmolz bei 88–90°. $[\alpha]_D^{17} = +2.70^\circ \times 8.7580/0.061 \times 0.9730 \times 2 = +199.2^\circ$ (in Wasser). Gefunden: C, 52.40, 52.45; H, 6.53, 6.59. Berechnet für $C_{12}H_{16}O_6 \cdot H_2O$: C, 52.55; H, 6.57%.

Das Kristallwasser kann durch 4 stündiges Trocknen bei 110° im Vakuum über Phosphorpentoxyd weggeschaffen werden und so gewonnene Substanz schmilzt unscharf bei 138–142°.

(11) *Butanol- β -*d*-galaktosid*. Man liess 30g Acetobromgalaktose (1 Mol) und 28g Silbercarbonat (1.4 Mol) in 300 ccm wasserfreiem Butylalkohol unter dauerndem Rühren bei 60° reagieren, bis die Bromreaktion mit Silbernitrat aus der Lösung völlig verschwunden ist (etwa 80 Min.). Nachdem der Niederschlag von Bromsilber abfiltriert war, wurde das Filtrat unter vermindertem Druck eingedunstet und in etwa 200 ccm Äther aufgenommen. Die ätherische Lösung wurde zuerst mit 5-proz. Sodalösung dann mit Wasser mehrmals gewaschen, mit Chlorcalcium getrocknet und zur Trockne verdampft. Der Rückstand wurde in etwa 30 ccm. Äthanol gelöst und mit Wasser zur beginnenden Trübung versetzt. Durch Reiben und Kühlen erhielt man ein kristallines Produkt. Ausbeute 13.5g, d.i. (45% d. Th.). Aus wenig absolutem Alkohol umkristallisiert, schmolz das Tetracetat bei 60–62°. $[\alpha]_D^{20} = -0.60^\circ \times 7.6022/0.2172 \times 1.520 \times 1 = -13.8^\circ$ (in Chloroform). Gefunden: C, 53.63, 53.94; H, 6.85, 6.93. Berechnet für $C_{18}H_{25}O_{10}$: C, 53.46; H, 6.93%.

12g Acetylverbindung wurden durch Kochen mit 10 ccm 0.1 N-Natriummethylat in 50 ccm. Methanol verseift. Nach Verdampfen des Methanols wurde der Rückstand in etwa 30 ccm Aceton gelöst und vorsichtig mit Petroläther bis zur bleibenden Trübung versetzt. Beim Abkühlen im Eisschrank kristallisierte das freie Galaktosid aus. Ausbeute 5.0g. Das Produkt wurde durch Lösen in Aceton und Füllen mit Petroläther gereinigt. Schmp. 99–100°. $[\alpha]_D^{15} = -0.42^\circ \times 9.1117/0.2500 \times 1.0124 \times 2 = -8.4^\circ$ (in Wasser). Gefunden: C, 50.22, 50.48; H, 8.57, 8.29. Berechnet für $C_{10}H_{20}O_6$: C, 50.84; H, 8.47%.

(12) *p*-Kresol- α -*d*-glucosid. Eine Mischung von 20g β -Pentacetyl-*d*-glucose (1 Mol), 17g *p*-Kresol (3 Mol) und 1.4g Zinchlorid wurde 90 Min. auf 128–130° erhitzt. Das stark dunkelbraun gefärbte Reaktionsprodukt wurde in Benzol aufgenommen, mit Natronlauge und Wasser gewaschen, wobei die farbige Substanz im Gegensatz zu den anderen Fällen nicht in Natronlauge überging. Die Benzollösung wurde zur Trockenheit verdampft und der Rückstand in Äthanol gelöst. Da das Tetracetyl-glucosid daraus nicht zur Kristallisation gebracht werden konnte, wurde es ohne weiteres verseift. Dazu wurde die äthanolische Lösung verdampft, mit 100 ccm Methanol und 10 ccm 0.1 N-Natriummethylatlösung versetzt und 3 stundenlang gekocht. Danach wurde die Lösung zur Trockne verdampft und der Rückstand aus 50-proz. Äthanol umkristallisiert. Ausbeute 2.0g. Schmp. 190–191°. $[\alpha]_D^{18} = +1.20^\circ \times 4.9840/0.0335 \times 0.997 \times 1 = +178.0$ (in Wasser). Gefunden: C, 57.78, 57.84; H, 6.86, 6.63. Berechnet für $C_{17}H_{18}O_6$: C, 57.75; H, 6.71%.

Ein Teil des so erhaltenen Glucosids wurde in Tetracetat zurückgewandelt. 0.80g Glucosid wurden mit 12 ccm Essigsäureanhydrid und 7 ccm Pyridin 2 stundenlang bei 75–80° erhitzt. Das Reaktionsprodukt wurde in etwa 300 ccm Eiswasser gegossen,

wobei sich das Tetracetat, nach dem Stehen übernacht, teils kristallinisch, teils amorph ausschied. Es wurde aus Äthanol umkristallisiert. Ausbeute 0.95g (73% d. Th.). $[\alpha]_D^{25} = +4.59^\circ \times 13.2405 / 0.1275 \times 1.4712 \times 2 = +162.0^\circ$ (in Chloroform). Gefunden: C, 57.34, 57.54; H, 5.87, 5.83. Berechnet für $C_{21}H_{30}O_{10}$: C, 57.50; H, 5.93%.

(13) *Guajakol- α -d-glucosid*. 50g β -Pentacetyl-*d*-glucose (1 Mol), 48g Guajakol (3 Mol) und 4g Chlorzink wurden unter mechanischem Rühren 3.5 Stdn. auf 130–132° erhitzt. Weitere Aufarbeitung wurde wie bei (1) durchgeführt. Das Reaktionsprodukt liess sich aber, wie bei dem *p*-Kresol-glucosid, dabei nicht kristallinisch erhalten, so wurde es ohne weiteres mittels Natriummethylats verseift. Nach dem Verseifen wurde die stark braune Flüssigkeit zur Trockne verdampft, der Rückstand in etwa 15 ccm 50-proz. Äthanol aufgenommen und im Eisschrank gestellt. Nach einigen Tagen schieden sich allmählich Kristalle von Guajakol- α -*d*-glucosid beim häufigen Reiben mit Glasstab aus. Sie wurden durch starkes Absaugen von der sirupösen Mutterlauge getrennt und mit Äthanol nachgewaschen. Ausbeute 3.6g. Durch 3 maliges Umkristallisieren aus etwa 50-proz. Äthanol erhielt man ein Produkt, dessen Schmelzpunkt und Drehungsvermögen sich durch weitere Umkristallisation nicht änderte. Die im Vakuum-Exsikator getrocknete Substanz enthält noch 1 Mol Kristallwasser, das beim 4-stündigen Trocknen bei 110° im Vakuum über Phosphorpentoxyd entweicht. Das kristallwasserfreie Glucosid zeigt den Schmelzpunkt von 150–153° und das Drehungsvermögen von $[\alpha]_D^{18} = +156.4^\circ$. Ausbeute 1.0g. Gefunden: C, 51.58, 51.36; H, 6.67, 6.74. Berechnet für $C_{13}H_{18}O_7 \cdot H_2O$: C, 51.31; H, 6.57%. $[\alpha]_D^{18} = +1.21^\circ \times 4.9802 / 0.0387 \times 0.9960 \times 1 = +156.4^\circ$ (in Wasser).

Es wurde versucht, aus diesem Glucosid mit Pyridin und Essigsäureanhydrid das Tetracetat zu gewinnen, jedoch gelang es mir nicht, trotzdem man unter verschiedenen Reaktionsbedingungen ausprobiert hatte, das kristallisierte Produkt zu erhalten. Die amorphe, aus Eisessiglösung mit Wasser umgefällte Substanz zeigte die spezifische Drehung von $[\alpha]_D^{15} = +1.69^\circ \times 13.2929 / 0.0446 \times 1.477 \times 2 = +170.5^\circ$ (in Chloroform).

Zum Schluss sei es mir gestattet, meinem verehrten Lehrer, Herrn Prof. Dr. T. Miwa, für seine stete Leitung und wohlwollende Unterstützung meinen besten Dank auszusprechen. Auch bin ich dem Iwata-Institut für Pflanzenbiochemie für die Freundlichkeit in der Durchführung einiger Elementaranalysen zu Dank verbunden.

Der Hattori-Hôkô-Gesellschaft dankt Prof. Miwa für die finanzielle Unterstützung zu dieser Arbeit.

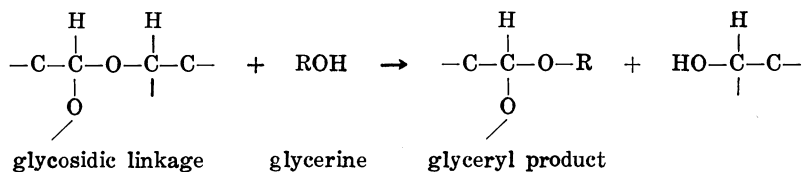
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Glycerolysis of Starch and the Molecular Weight and the Viscosity of the Products.

By Yojiro TSUZUKI.

(Received May 5, 1941.)

Zulkowski in 1880 obtained degraded starch, soluble in water, by heating starch in glycerine at 190° and by pouring the products into alcohol.⁽¹⁾ Pictet and his collaborators made extensive studies of the glycerolysis of starch and obtained a number of intermediate products (so-called hexosanes).⁽²⁾ It was, however, shown by Berner and Petersen⁽³⁾ that these hexosanes are not definite degradation products, containing a certain amount of alcohol and glycerine as impurities, so that the individuality of these products is doubtful. Later Berner and Melhus⁽⁴⁾ showed with clearness that glycerine is not only contained as impurity, but also as a constituent of the reaction products, the reaction being represented as follows:



H. Pringsheim gave a detailed description of the products of glycerolysis of starch.⁽⁵⁾

The author has preliminarily examined the procedure of glycerolysis of some varieties of starch changing two conditions, namely time and temperature of the reaction, and has determined the quantity of combined glycerine in the degradation products for the purpose of finding the relation between the glycerine content and the degree of glycerolysis, seeing that Berner and Melhus obtained glyceryl-*d*-glucoside by the total glycerolysis of starch at 180°.

Glycerolysis of Starch. As Zulkowski already noticed, potato starch can be dispersed with ease in hot glycerine, while rice starch does not dissolve so easily. When 8.00 g. dried starch is heated in 60.00 g. distilled glycerine at 180° the appearances of the mixtures were found to change with the progress of time as follows:

(1) K. Zulkowski, *Ber.*, **13** (1880), 1395; **23** (1890), 3295.

(2) A. Pictet and R. Jahn, *Helv. Chim. Acta*, **5** (1922), 640; P. Castan and A. Pictet, *ibid.*, **8** (1925), 946; A. Pictet, *ibid.*, **9** (1926), 33; A. Pictet and H. Vogel, *ibid.*, **12** (1929), 1220. M. Samec and M. Blinc, *Kolloid-Beihfte*, **48** (1939), 249.

(3) E. Berner and R. Petersen, *Ber.*, **65** (1932), 687.

(4) E. Berner and F. Melhus, *Ber.*, **66** (1933), 1333.

(5) "Die Polysaccharide", Berlin (1931); "The Chemistry of the Monosaccharides and Polysaccharides", New York (1932); Cf. Tollens-Elsner, "Kurzes Handbuch der Kohlenhydrate", 4 Aufl., 570, Leipzig (1935).

Duration of time (hrs.)	Potato starch	Wheat starch	Rice starch
2	Fairly clear	Not transparent	Not soluble
4	Completely clear	"	"
8	"	"	"
16	"	Clear	"

This shows that at this concentration wheat starch does not easily dissolve in glycerine and that rice starch is more difficultly soluble and the latter was found to get coloured strongly brown. These differences in dispersion of starches according to the nature of plants may probably be due to the difference of the sizes and formes as well as of the inorganic constituent⁽⁶⁾ of the grain.

Optical Rotation and Viscosity of the Degradation Products. Optical rotation could not be observed with wheat and rice starches, as clear solution was not obtained from the above products. In the case of potato starch the aqueous solution could be made transparent by mixing the reaction product with potassium hydroxide and its optical rotation was measured. The solution thus prepared contained 0.645% starch and 5.05% glycerine, and the concentration of KOH in the solution was 1/8 normal.

The specific viscosity was measured at 30° with the solution of 5.00 g. reaction product in 45 c.c. H₂O. Both the specific rotation and the specific viscosity diminishes with the duration of glycerolysis, showing that the degradation of the potato starch advances with the time.

Table 1.

Duration of glycerolysis (hrs.)	$[\alpha]_D^{30}$	η_{sp}
2	+165.7°	0.430
4	+162.7°	0.345
8	+148.7°	0.311
16	+145.5°	0.298

In the cases of wheat and rice starches more glycerine is needed to effect dissolution of them. In these cases 5.00 g. dried starch was heated at 180° in 60.00 g. distilled glycerine. The solution for measurement of optical rotation contained 0.422% starch and 6.8% glycerine, and the concentration of KOH in the solution was 1/6 normal. The solution for the measurement of viscosity was made by dissolving 5.00 g. reaction mixture in 40 c.c. H₂O.

The rotation and the viscosity in Table 2 show that the degradation of wheat starch proceeds more slowly than rice starch.

The optical rotation of the acetates of glyceryl potato starch was observed in chloroform at 25°, the results being shown in Table 3.

(6) See M. Samec, M. Minaeff and N. Rouzin, *Kolloid-Beihefte*. **19** (1924), 203; Th. Posternak, *Helv. Chim. Acta*, **18** (1935), 1351.

Table 2.

Duration of glycerolysis (hrs.)	$[\alpha]_D^{25}$		γ_{sp}	
	Wheat starch	Rice starch	Wheat starch	Rice starch
2			1.131	0.819
4	+178.2°	+162.5°	0.911	0.746
8	+176.7°	+148.3°	0.764	0.498
16	+142.0°	+124.6°	0.506	0.498

Table 3.

Glycerolysis		$[\alpha]_D^{25}$	p
Temp.	Time (hrs.)		
170°	6	+163.0°	1.14%
180°	6	+156.8°	1.36 „
180°	15	+114.9°	1.14 „
180°	29	+103.3°	1.68 „

As may be seen from Table 3 the specific rotation of the products falls with higher temperature and with longer duration of glycerolysis.

The Glycerine Content and the Molecular Weight of Glyceryl Starch. The author has prepared various products of glycerolysis of starch and measured their glycerine contents. The preparation of glyceryl starch was carried out as follows: 25 g. wheat starch dried in vacuum at 100° is heated at 180° with mechanical stirring in 100 g. glycerine dried by distilling in vacuum. The reaction product is poured into 80 g. alcohol, the separated glyceryl starch being powdered by rubbing, and filtered through a glass filter by suction. A part of this powder is dissolved in a small amount of water and again precipitated by pouring into alcohol. The precipitate is washed well with alcohol, and dried by heating 10 hours in vacuum at 80°. The rest of glyceryl wheat starch (ca 2.5 g.) is used for acetylation. The glycerolysis product is acetylated at room temperature with 30 c.c. pyridine and 50 c.c. acetic anhydride. After standing over night the reaction product is poured into water, the precipitate dried and purified by precipitating twice from chloroform-alcohol solution. The glycerolysis product obtained by heating for so long as 32 hours is energetically degraded and coloured deeply brown. In this case the glycerine is for the most part distilled off under reduced pressure, the residue is poured into alcohol and then treated as above.

The determination of glycerine was carried out according to the method of Zeisel-Fanto⁽⁷⁾. Instead of concentrated solution of hydrogen iodide of $d=1.90$, the author used the acid of ordinary concentration ($d=1.70$). This method really gives values a little lower than the theoretical, but the author has confirmed that it is practically useful. It has been found that glycerolysis products of starch contain a certain amount of combined glycerine even if it is moderately glycerolysed. The glycerine content of the products is shown in Tables 4 and 5.

(7) *Chem. Zeitg.*, **26** (1902), 173; Cf. Schulze, *Chem. Zeitg.*, **29** (1905), 976.

Table 4. Glycerine Content of Glyceryl Wheat Starch.

Product No.	Condition of Glycerolysis		Determination of Glycerine		
	Temp.	Duration (hrs.)	Substance (g.)	AgI (g.)	Glycerine content %
1	180°	4	0.6103	0.0201	1.32
2	180°	8	0.2985	0.0173	2.27
3	180°	16	0.3023	0.0272	3.53
4	180°	32	0.1012	0.1194	7.52

Table 5. Glycerine Content of Acetylated Glyceryl Wheat Starch.

Product No.	Condition of Glycerolysis		Determination of Glycerine		
	Temp.	Duration (hrs.)	Substance (g.)	AgI (g.)	Glycerine Content %
5	180°	4	0.5988	0.0148	0.97
6	180°	8	0.4014	0.0162	1.58
7	180°	16	0.3024	0.0187	2.43
8	180°	32	0.3024	0.0437	5.67

Potato starch is treated in a similar manner, the results of glycerine determination being shown in Tables 6 and 7.

Table 6. Glycerine Content of Glyceryl Potato Starch.

Product No.	Condition of Glycerolysis		Determination of Glycerine		
	Temp.	Duration (hrs.)	Substance (g.)	AgI (g.)	Glycerine Content %
9	180°	4	0.3974	0.0184	1.82
10	180°	6	0.3063	0.0317	4.06
11	180°	8	0.2208	0.0366	6.72
12	200°	10	0.2390	0.0892	14.6

Table 7. Glycerine Content of Acetylated Glyceryl Potato Starch.

Product No.	Condition of Glycerolysis		Determination of Glycerine		
	Temp.	Duration (hrs.)	Substance (g.)	AgI (g.)	Glycerine Content %
13	170°	6	0.5412	0.0160	1.16
14	180°	6	0.3122	0.0100	1.26
15	180°	8	0.2607	0.0170	2.56
16	180°	15	0.1793	0.343	7.47

As may be seen from Tables 4-7 the glycerine content of the degradation products increases with the rise of temperature as well as with the duration of glycerolysis. This is probably due to the circumstances that by glycerolysis the huge molecule of starch is gradually divided into smaller pieces, a glycerine molecule being attached to the end of a chain molecule. By comparing Tables 4 and 5 with Table 6 and 7 it is seen that the degree of glycerolysis is greater in potato starch than in wheat starch which may be expected from the rotation as well as the viscosity data (Tables 1 and 2).

Now if we assume that the degradation product of starch has a structure, to which end a glyceryl group is attached, we may be able to calculate the chain length of the glyceryl starch by determining the content of glycerine in the degradation product. On the other hand the author has determined the molecular weight of the glyceryl starches by cryoscopy and compared the cryoscopic molecular weight with that determined by the end group method. The results are shown in Tables 8-11, from which it is seen that the molecular sizes determined by the two methods are for the most part in good harmony. For the solvent in cryoscopy water is used with glyceryl starch, and ethylene dibromide C_2H_4Br with its acetylated products. Since water has a small molecular depression and is not a good cryoscopic solvent for starch of large molecular weight, the data in water are in general not very reliable, but ethylene dibromide has proved to be a suitable solvent for cryoscopy of high molecular substances, since it has a very large dissolving power for high molecular substances and is not so sensitive to moisture.⁽⁸⁾

Table 8. Molecular Weight in Glyceryl Wheat Starch.

Product No.	Glycerine Content (%)	<i>M</i>	Cryoscopy			
			Subst. (g.)	Water (g.)	ΔT	<i>M</i>
1	1.32	6990	0.3013	12	0.011°	4250
2	2.27	4050	0.2996	10	0.018°	3100
3	3.53	2610	0.1782	10	0.027°	1230
4	7.52	1224	0.1946	17	0.026°	819

Table 9. Molecular Weight in the Acetates of Glyceryl Wheat Starch.

Product No.	Glycerine Content (%)	<i>M</i>	Cryoscopy			
			Subst. (g.)	C_2H_4Br (g.)	ΔT	<i>M</i>
5	0.97	9500	0.1968	15.26	0.014°	11000
6	1.58	5810	0.1708	16.35	0.027°	6320
7	2.43	3790	0.1500	15.26	0.032°	3690
8	5.67	1620	0.0789	17.05	0.029°	1930

(8) Cf. Y. Tsuzuki, this Bulletin, 3 (1928), 276.

Table 10. Molecular Weight in Glyceryl Potato Starch.

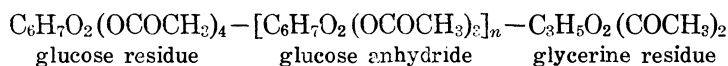
Product No.	Glycerine Content (%)	<i>M</i>	Cryoscopy			
			Subst. (g.)	Water (g.)	ΔT	<i>M</i>
9	1.12	5070	0.3500	16	0.010°	4060
10	4.06	2268	0.5947	10	0.040°	2760
11	6.72	1460	0.1000	11.5	0.013°	1600
12	14.6	629	0.3932	10	0.120°	609

Table 11. Molecular Weight in the Acetates of Glyceryl Potato Starch.

Product No.	Glycerine Content (%)	<i>M</i>	Cryoscopy			
			Subst. (g.)	C ₂ H ₅ Br (g.)	ΔT	<i>M</i>
13	1.16	7940	0.7000	26.0	0.045°	7180
14	1.26	7330	0.3029	15.26	0.040°	5960
15	2.56	3590	0.2668	14.75	0.070°	3100
16	7.47	1230	0.2833	16.22	0.158°	1240

The Acetyl Value and the Chain Length. The acetyl value was determined in the following manner:⁽⁹⁾ the substance is dissolved in 10 c.c. warm acetone, 15 c.c. N/4-KOH are added, and after standing for 30 minutes, the excess alkali is titrated with N/10-HCl.

The acetyl value thus determined diminishes with the increasing molecular weight of the acetyl starch. This observation is significant with respect to the structure of these products, and indeed the results are to be explained from the idea that a glycerine rest is standing at one end of the chain molecule as follows:



Some typical results will be shown in Table 12, from which it is seen that the observed value of the acetyl content is in good harmony with the value calculated from the above developed formula.

Table 12.

Product No.	Observed			Calculated		
	Mol. wt. by Glycerine Content	Mol. wt. by Cryoscopy	CH ₃ CO (%)	CH ₃ CO (%)	<i>n</i>	Mol. wt.
5	9500	11000	45.2	45.10	35	10590
14	7330	5900	45.3	45.26	23	7133
15	3590	3100	45.8	45.73	10	3387
16	1230	1240	47.6	47.64	2	1355

(9) Cf. Y. Tsuzuki, this Bulletin, 3 (1923), 278; 4 (1929), 154.

The Viscosity of the Glyceryl Starch. The author has measured the viscosity of glyceryl starch in water and that of acetylated glyceryl starch in dioxan at 25°, some ones at 20°. The results are shown in Tables 13–16, where p is the concentration, the specific viscosity η_{sp} is equal to the relative viscosity minus one, and C is the concentration in moles of recurring unit per litre. The values of molecular weight determined by the end group method as well as by cryoscopy are quoted in the tables for reference.

Table 13. Viscosity of Glyceryl Wheat Starch.

Product No.	Measurement of viscosity				Molecular weight	
	p (%)	η_{sp}	η_{sp}/p	η_{sp}/C	from Glycerine content	Cryoscopy
1	0.5930	0.0875	0.1476	2.396	6990	4250
2	0.6013	0.0526	0.0875	1.417	4050	3100
3	0.7327	0.0496	0.0677	1.097	2610	1230
4	0.8494	0.0342	0.0403	0.652	1224	819

Table 14. Viscosity of Acetylated Glyceryl Wheat Starch.

Product No.	Measurement of viscosity				Molecular weight	
	p (%)	η_{sp}	η_{sp}/p	η_{sp}/C	from Glycerine content	Cryoscopy
5	0.3844	0.0721	0.1876	5.251	9500	11000
6	0.4054	0.0572	0.1411	3.950	5810	6320
7	0.6206	0.0460	0.0741	2.135	3790	3690
8	0.6368	0.0319	0.0501	1.443	1620	1930

Table 15. Viscosity of Glyceryl Potato Starch.

Product No.	Measurement of viscosity				Molecular weight	
	p (%)	η_{sp}	η_{sp}/p	η_{sp}/C	from Glycerine content	Cryoscopy
9	0.333	0.0786	0.2361	3.735	5070	4060
10	0.489	0.0525	0.1073	1.742	2268	2760
11	0.648	0.0462	0.0712	1.155	1460	1600
12	0.934	0.0360	0.0385	0.626	629	609

Table 16. Viscosity of Acetylated Glyceryl Potato Starch.

Product No.	Measurement of viscosity				Molecular weight	
	p (%)	η_{sp}	η_{sp}/p	η_{sp}/C	from Glycerine content	Cryoscopy
13	0.6277	0.1290	0.2055	5.834	7940	7180
14	0.5593	0.0823	0.1472	4.096	7330	5960
15	0.638	0.0576	0.0903	2.601	3590	3100
16	0.607	0.0223	0.0371	1.069	1230	1240

As may be seen from Tables 13–16, the viscosity of the glyceryl starch η_{sp}/p falls with progressing degradation, i.e. it is in parallel relation with the glycerine content and the cryoscopic molecular weights. In the lower members of these glyceryl starches the molecular weight estimated with the Staudinger's viscosity equation.

$$\eta_{sp}/C = K_m M \quad (1)$$

coincides with the values of the molecular weight determined by the other two methods, if we assume $K_m = 8.0 \times 10^{-4}$, both in wheat and potato starches. But in the higher members we see that K_m must fall to $3\text{--}5 \times 10^{-4}$. Several years ago Haworth⁽¹⁰⁾ already observed with dextrans obtained by heating potato starch in glycerine that the molecular weight from viscosity with $K_m = 10 \times 10^{-4}$ is somewhat smaller than that obtained by his end group method. On the contrary he observed in the following cases that the molecular weight from viscosity is several times higher than that determined by his own chemical assay, namely in the cases of waxy maize starch⁽¹¹⁾ both in acetylated and methylated states and of the potato starch treated with alcoholic hydrochloric acid in the acetylated form, while in the methylated state the two methods gave identical values of molecular weight (26–30 α -glucopyranose units)⁽¹²⁾. Staudinger⁽¹³⁾ found such a small value of K_m as 1×10^{-4} by comparing the values of osmotic pressure of disaggregated starch measured by Biltz⁽¹⁴⁾ with his own viscosity measurements. He obtained a still smaller value, $K_m = 0.63 \times 10^{-4}$, in formamide with starch degraded with 2 n -HCl.⁽¹⁵⁾ Staudinger and Husemann⁽¹⁶⁾ obtained $K_m = 0.64 \times 10^{-4}$ in formamide at 20° by studying similarly with wheat starch. In the cases of its triacetyl derivative having the polymerisation degree 600, they found K_m be 1.02×10^{-4} in chloroform. Hirst and Young⁽¹⁷⁾ used $K_m = 1.0 \times 10^{-4}$ in evaluating the molecular weight of acetates of native wheat and rice starches. This value was provisionally obtained from the data of the osmotic-pressure measurements provided by Carter and Record⁽¹⁸⁾ with methylated starches.

Now the author's results appear to be partly in harmony with the results of Haworth and partly with those of Staudinger.

It appears to the author that K_m is not independent on the chain length, as Staudinger has already suggested.⁽¹⁶⁾ It tends to decrease with increasing molecular weight, and indeed in the acetates of glucose and of cellobiose K_m is greater than 10×10^{-4} , but in tetrasaccharide acetate K_m shows a smaller value as 9.0×10^{-4} (in dioxan)⁽¹⁹⁾.

The present investigation concerns with the starch derivatives with

(10) W. N. Haworth, E. L. Hirst and M. M. T. Plant, *J. Chem. Soc.*, **1935**, 1214.

(11) W. N. Haworth, E. L. Hirst and M. D. Woolgar, *J. Chem. Soc.*, **1935**, 177.

(12) D. K. Baird, W. N. Haworth, E. L. Hirst, *J. Chem. Soc.*, **1935**, 1201.

(13) H. Staudinger and E. Eilers, *Ber.*, **69** (1936), 819.

(14) W. Biltz, *Ber.*, **46** (1913), 1532; *Z. physik. Chem.*, **83** (1913), 683.

(15) H. Staudinger and E. Husemann, *Ann.*, **527** (1937), 195; H. Staudinger, *Naturw.* **25** (1937), 673.

(16) H. Staudinger and E. Husemann, *Ber.*, **71** (1938), 1057.

(17) E. L. Hirst and G. T. Young, *J. Chem. Soc.*, **1939**, 951, 1471.

(18) S. R. Carter and B. R. Record, *J. Chem. Soc.*, **1939**, 664.

(19) H. Staudinger and A. E. Werner, *Ber.*, **71** (1937), 2140.

comparatively lower molecular weight, so that it is comprehensible that K_m shows a relatively high value. To cover the whole range of widely distributed molecular weight the Staudinger's simple equation does not suffice. The author has, therefore, applied an equation of the modified form:

$$\eta_{sp}/C = K_m M + k \quad (2)$$

which has already been presented by K. H. Meyer and van der Wyk⁽²⁰⁾ to express the viscosity of relatively simple high molecular compounds, namely normal paraffines in the range C_{17} – C_{34} . The present author's viscosity data can be expressed fairly well by this equation, the constants K_m and k being shown in Table 17.

It is probable that in the present case a correction term k becomes necessary, since the chain of glyceryl starch is not of uniform constitution, a glyceryl group standing at one end of chain. The higher the molecular weight of the chain the end group becomes less important, so that the correction term k ought to become negligible with higher polymer-homologues and the simple Staudinger equation holds. It has, however, been remarked that Staudinger's equation requires that the weight average molecular weight be used when it is applied to non-homogeneous polymers,⁽²¹⁾ and indeed Flory⁽²²⁾ in recent times derived an equation $[\ln \eta_r/C]_0 = K_w M_w + I$, a modified form of the equation (2), in order to express the relationship between the viscosity-concentration and the weight average molecular weight of nonhomogeneous linear polymers. But the author's glyceryl starch is improved in homogeneity by fractionation and as a matter of fact the ratio M_w/M_n is nearly constant within a given polymer series. Hence the equation (2) is considered to hold in the present case.

Table 17. The Constants K_m and k of Glyceryl Starches.

Glyceryl starch	K_m	k
wheat	4×10^{-4}	0.2
potato	7×10^{-4}	0.2
wheat, acetylated	5×10^{-4}	0.5
potato, acetylated	7×10^{-4}	0.4

The author is indebted to Mr. H. Suzuki and Mr. Y. Kimura for assistance in the experiments and to the Department of Education and to the Japan Society for the Promotion of Scientific Research for grants.

Summary.

(1) Glycerolysis of some varieties of starch has been studied, the progress of which being shown by observing the transparency, the optical rotation and the viscosity of the products. Potato starch is glycerolysed most easily, but wheat starch somewhat difficulty.

(2) With the duration of time the glycerine content of the products of glycerolysis increases, and this content is in parallel relation with the

(20) *Helv. Chim. Acta*, **18** (1935), 1067.

(21) E. O. Kraemer and W. D. Lansing, *J. phys. Chem.*, **39** (1935), 153.

(22) P. J. Flory, *J. Amer. Chem. Soc.*, **62** (1940), 3032.

cryoscopic molecular weight as well as with the acetyl value. Thus it has been shown that a glyceryl group probably stands at one end of the molecular chain of disaggregated starch.

(3) The viscosity measurements of these glyceryl starches indicate that K_m of the Staudinger's equation decreases with increasing molecular weight, and it has been shown that an equation $\eta_{sp}/C = K_m M + k$ expressing the relationship between viscosity-concentration and molecular weight, holds. In this respect wheat starch and potato starch behave a little different from each other.

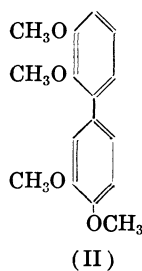
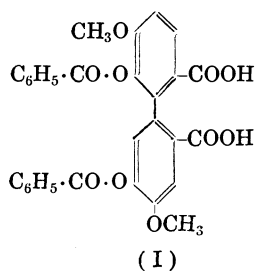
Musashi Higher School, Itabashiku, Tokyo.

Abbau von Dibenzoyl-sinomenol-chinon zu 2,3,3',4'-Tetramethoxy-diphenyl⁽¹⁾.

Von Kakuji GOTO und Hideo SHISHIDO.

(Eingegangen am 5. Mai, 1941.)

Dibenzoyl-sinomenol-chinon⁽²⁾ wurde in Eisessig mit Perhydrol (30%) zu 5,4'-Dimethoxy-6, 5'-dibenzoyloxy-diphenssäure (I) oxydiert. Diese Säure wurde debenzoyliert und mit Diazomethan zu 5, 6, 4', 5'-Tetramethoxy-diphenssäure methyliert. Beim Decarboxylieren,⁽³⁾ hat die letztere Säure 2, 3, 3', 4'-Tetramethoxy-diphenyl (II) gegeben.



Die Versuche, die oben genannten Tetramethoxy-diphenssäure in die aktiven Komponenten über Strychnin-, Brucin- oder Cinchonin-Salze abzuspalten, wurde gescheitert.

Wir danken herzlichst Herrn Hiroshi Hara für seine wertvolle Hilfe in Bereitung der Ausgangsmaterialien.

(1) 48. Mitteilung über Sinomenin.

(2) Dies Bull. **4** (1929), 169.

(3) Vergleiche, Shepard u. a., *J. Am. Chem. Soc.*, **52** (1930), 2083.

Versuche.

(1) 5,4'-Dimethoxy-6,5'-dibenzoyloxy-diphensäure. Dibenzoyl-sinomenol-chinon wurde in Eisessig mit etwas mehr als der berechneten Menge von Perhydrol langsam erhitzt. Wenn die rote Farbe vom Chinon verschwunden ist, wurde die Essigsäure i.V. abdestilliert und der Rückstand in Soda aufgenommen. Die mit Essigsäure gefällte Diphensäure wurde in Äthanol gelöst und der Äthanol unter wiederholtem Zusatz von Benzol abgedampft. Beim Stehenlassen, krystallisierte die Diphensäure in Rosetten, die mit Benzol+wenig Äthanol gut gewaschen wurde. Schmp. 233~235° (Aufblasen).

Anal.: Subst.=4.513; CO₂=10.815; H₂O=1.87 mg
 Subst.=2.105; AgJ=1.705 mg
 Gef.: C=65.36; H=4.60; CH₃O—=10.70%
 Ber. für C₃₀H₂₂O₁₀+½H₂O (551): C=65.34;
 H=4.17; CH₃O—=11.25%

Dimethyl-ester. Bereitet mit Diazomethan auf die freie Säure. Umgelöst aus Methanol. Schmp. 170~173°.

Anal.: Subst.=4.926; CO₂=11.670; H₂O=2.42 mg
 Subst.=1.469; AgJ=3.300 mg
 Gef.: C=64.61; H=5.42; CH₃O—=29.67%
 Ber. für C₃₂H₂₆O₁₀+2 CH₃OH (634): C=64.35;
 H=5.36; CH₃O—=29.34%

(2) 5,6,4',5'-Tetramethoxy-diphensäure. 0.5 g von 5,4'-Dimethoxy-6,5'-dibenzoyloxy-diphensäure wurde in 15 ccm Methanol gelöst und unter Wasserstoff-leitung mit 10 ccm 10 proc. Kalilauge bei 100° 3 Stunden lang hydrolysiert. Dann wurde das Gemisch mit 10 ccm Dimethylsulfat und 10 proc. Kalilauge dreimal behandelt. Die mit Wasser verdünnte Lösung wurde abfiltriert, mit Salzsäure angesäuert und mit Äther viermal geschüttelt. Beim Abdampfen des Äthers krystallisierte die Tetramethoxy-diphensäure in Prismen. Ausbeute 0.15 g. Umlösbar aus Wasser. Schmp. 206~208°.

Anal.: Subst.=3.301; CO₂=7.250; H₂O=1.51 mg
 Subst.=1.537; AgJ=3.980 mg
 Gef.: C=59.90; H=5.08; CH₃O—=34.18%
 Ber. für C₁₈H₁₈O₈ (362): C=59.66; H=4.97; CH₃O—=34.25%

Titration: 0.0452 g Subst., gelöst in 20 ccm Äthanol, Phenolphthalein als Indikator, verbrauchte 2.49 ccm N/10 NaOH.

Gef.: —COOH 24.78% Ber. 24.86%.

Dimethyl-ester. Bereitet mit Diazomethan. Umgelöst aus Methanol. Schmp. 132° (Sintern an 124°).

Anal.: Subst.=5.670; CO₂=12.965; H₂O=2.96 mg
 Gef.: C=61.39; H=5.71%
 Ber. für C₂₀H₂₂O₈ (390): C=61.54; H=5.64%.

(3) 2,3,3',4'-Tetramethoxy-diphenyl.

0.2 g 5,6,4',5'-Tetramethoxy-diphensäure wurde in 10 g Chinolin gelöst und mit 0.55 g Naturkupfer C unter Luftkühler zuerst zehn Minuten bei $190\sim 200^{\circ}$, dann eine halbe Stunde bei $240\sim 250^{\circ}$ gekocht. Nach Abkühlen, wurde es mit viel Äther versetzt und durch 10 maliges Waschen mit 10 proc. Salzsäure von Chinolin befreit. Der Äther wurde noch zweimal mit Alkali, zweimal mit Wasser gewaschen und dann abdestilliert. Aus dem Äther-rückstand krystallisierte 2,3,3',4'-Tetramethoxy-diphenyl-beim Stehenlassen mit wenig Methanol. Tafeln. Schmp. $96\sim 100^{\circ}$.

Anal.: Subst.=4.582; $\text{CO}_2=11.680$; $\text{H}_2\text{O}=2.69$ mg.

Gef.: C=69.52; H=6.52%

Ber. für $\text{C}_{16}\text{H}_{18}\text{O}_4$ (274) : C=69.34; H=6.57%.

Kitasato Institut, Tokio.

Untersuchungen der chemischen Eigenschaften der Kohlenhydrate mit Hilfe des schweren Sauerstoffs. I. Austauschreaktion der Sauerstoffatome zwischen einigen Monosen und Wasser (Auszug).⁽¹⁾

Von Kokiti GOTO und Toshizo TITANI.

(Eingegangen am 6. Mai, 1941.)

Inhaltsübersicht. Die Austauschreaktion der O-Atome zwischen Glucose, Fructose, Galaktose, Xylose bzw. Arabinose und Wasser wird in neutraler Lösung unter Benutzung des an schwerem Sauerstoff angereicherten Wassers untersucht. Jede der untersuchten Arten der Monosen tauscht eines ihrer O-Atome gegen die des Wassers aus, wenn die neutrale Lösung des Zuckers in Wasser bei 55°C 100 Stdn. bzw. bei 100°C 15 bis 10 Stdn. lang erwärmt wird. Die Reaktion wird durch die Annahme erklärt, dass ein Hydrat durch die Anlagerung eines Wassermoleküls an einem Zuckermolekül gebildet und dieses Hydratmolekül reversibel wieder gespalten wird.

Einleitung. Koizumi und Titani⁽²⁾ haben unter Benutzung des an schwerem Sauerstoff angereicherten Wassers festgestellt, dass die Glucose eines ihrer O-Atome verhältnismässig leicht gegen die des Wassers austauscht, wenn ihre wässrige Lösung auf 100°C 2 bis 48 Stdn. lang erwärmt wird. In dem vorliegenden Versuche werden dieselben Versuche unter Verwendung nicht nur von Glucose sondern auch anderer Arten der Monosen, nämlich Fructose, Galaktose, Xylose und Arabinose, ausgeführt.

Versuchsmethode und Ergebnisse. Das zum vorliegenden Versuche benutzte an schwerem Sauerstoff angereicherte Wasser wird durch die

(1) K. Goto, *J. Chem. Soc. Japan*, **61** (1940), 1283. Vorläufig mitgeteilt in T. Titani und K. Goto, *Proc. Imp. Acad. Tokyo*, **15** (1939), 298.

(2) M. Koizumi und T. Titani, dies Bulletin, **13** (1938), 463, 607.

fraktionierte Destillation des gewöhnlichen Wassers hergestellt. Da aber bei der fraktionierten Destillation des Wassers nicht nur der schwere Sauerstoff sondern auch schwerer Wasserstoff im zurückgebliebenen Wasser bis zu einem gewissen Grad angereichert wird, wird das Wasser, das direkt aus der Destillation gewonnen wurde, zuerst unter Zusatz eines passenden Elektrolyts elektrolytisch gespalten und das daraus entwickelte (schwere) Sauerstoffgas zusammen mit elektrolytischem Wasserstoff aus gewöhnlichem Wasser wieder bis zu Wasser rekombiniert. Der kleine Mangel des so gewonnenen Wassers an schwerem Wasserstoff (der Gehalt des aus der Elektrolyse des gewöhnlichen Wassers entwickelten Wasserstoffs an schwerem Wasserstoff ist bis zu einem gewissen Grad geringer als der des gewöhnlichen Wassers!) wird unter Zusatz einer passenden Menge des direkt aus der fraktionierten Destillation des Wassers gewonnenen und folglich an beiden Arten der schweren Isotope des Sauerstoffs und Wasserstoffs angereicherten Wassers ersetzt.⁽³⁾ Der Dichteüberschuss des so bereiteten Wassers gewöhnlichem Wasser gegenüber, der etwa 24 bis 32 γ beträgt, kann deshalb ausschliesslich auf die Anreicherung an schwerem Sauerstoff zurückgeführt werden. Eine Menge dieses schweren Wassers wird zusammen mit einer passenden Menge von Zucker in einem Glasrohr eingewogen und, nachdem es unter Luftabschluss zugeschmolzen worden ist, wird das Rohr in einem elektrisch geheizten Luftthermostat bei einer bestimmten Temperatur während einer bestimmten Zeitlänge erwärmt.⁽⁴⁾ Nach der Beendigung der Erwärmung wird das Glasrohr zu einem Glasrohrsystem zugeschmolzen und das schwere Wasser durch die Destillation im Vakuum in einem anderen Glasrohr abgeschieden. Dabei wird das die Lösung enthaltende Rohr gegen Ende der Destillation bis auf eine um einige Grade unterhalb der eigenen Reaktionstemperatur liegende Temperatur erwärmt, um das schwere Wasser so weit wie möglich vom Zucker abzutrennen. Auf diese Weise konnten wir mehr als 95% der verwendeten Menge des schweren Wassers wieder bekommen. Der Gehalt des so abgeschiedenen schweren Wassers an schwerem Sauerstoff und folglich der Dichteüberschuss des betreffenden Wassers gewöhnlichem Wasser gegenüber wird, nachdem das schwere Wasser sorgfältig gereinigt worden ist, mit Hilfe eines Quarzschwimmers bestimmt. Die Anzahl n der O-Atome in einem Zuckermolekül, die unter den angegebenen Versuchsbedingungen gegen die des Wassers ausgetauscht worden sind, wird unter Benutzung des so gemessenen endlichen (Δs_e) sowie des anfänglichen (Δs_a) d.h. vor dem Versuch bestehenden Dichteüberschusses des schweren Wassers mit Hilfe der Gl. (1) berechnet:

$$n = \frac{M_w}{M_z} \frac{\Delta s_a - \Delta s_e}{\Delta s_e} \quad (2),$$

wo M_w und M_z resp. die Molzahl des zum Versuch verwendeten schweren Wassers und Zuckers bedeutet.

(3) Dieses Wasser wird von Dr. N. Morita hergestellt, dem wir unseren besten Dank aussprechen möchten.

(4) Höchstwahrscheinlich mag die vorliegende Reaktion durch H-Ionen und besonders aus der Glaswand abgelösten OH-Ionen katalysiert werden, obwohl das in demselben Glasrohr längere Zeit erwärmte Wasser gegen Phenolphthalein sich ganz neutral verhielt.

Die auf diese Weise unter Verwendung von fünf Arten der Monosen erhaltenen Versuchsergebnisse sind in Tabellen 1 bis 5 zusammengestellt, wo die Versuchsnummer die zeitliche Reihenfolge der einzelnen Versuche und Versuch K einen Kontrollversuch darstellt, der statt schweren Wassers unter Verwendung des gewöhnlichen Wassers ausgeführt wurde.

Tabelle 1. Glucose.

Versuchs-nr.	M_z	M_w	Δs_a in γ	Δs_e in γ	Versuchs-temp. °C	Versuchsdauer in Stdn.	n
5	0.1099	0.5556	31.4	25.6	55	100	1.15
4	0.1944	0.6667	31.4	22.8	100	15	1.29
1	0.1222	0.8889	32.3	28.4	100	20	1.00
2	0.0890	0.6667	32.3	27.5	100	20	1.31
3	0.1110	0.8333	31.4	27.1	100	20	1.19
K	0.1222	0.8889	0	-1.3	100	20	—

Tabelle 2. Fructose.

Versuchs-nr.	M_z	M_w	Δs_a in γ	Δs_e in γ	Versuchs-temp. °C	Versuchsdauer in Stdn.	n
5	0.1110	0.6667	32.3	29.9	55	20	0.48
3	0.1270	0.6667	31.4	25.5	55	100	1.21
2	0.1469	0.8333	31.4	26.8	100	9	0.97
1	0.1231	0.6667	31.4	25.9	100	20	1.15
K	0.1231	0.6667	0	-1.5	100	20	—

Tabelle 3. Galaktose.

Versuchs-nr.	M_z	M_w	Δs_a in γ	Δs_e in γ	Versuchs-temp. °C	Versuchsdauer in Stdn.	n
4	0.0556	0.6667	31.4	29.9	55	20	0.60
3	0.1222	0.7778	31.4	27.1	55	100	1.01
5	0.1112	0.7222	31.4	26.3	55	100	1.26
2	0.0777	0.6667	31.4	29.4	100	10	0.58
1	0.0777	0.6611	32.3	28.8	100	20	1.03

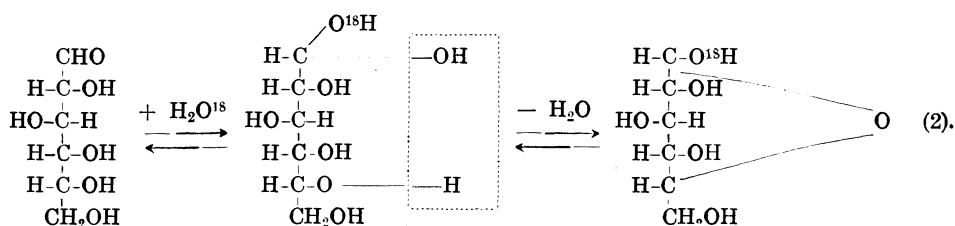
Tabelle 4. Xylose.

Versuchs-nr.	M_z	M_w	Δs_a in γ	Δs_e in γ	Versuchs-temp. °C	Versuchsdauer in Stdn.	n
4	0.1333	0.6667	31.4	28.4	55	20	0.53
3	0.1469	0.6667	31.4	24.9	55	100	1.18
2	0.1469	0.6667	31.4	23.1	55	100	1.60?
1	0.2132	0.7778	31.4	24.8	100	20	0.97

Tabelle 5. Arabinose.

Versuchs- nr.	M_z	M_w	Δs_a in γ	Δs_e in γ	Versuchs- temp. °C	Versuchs- dauer in Stdn.	n
1	0.0666	0.6667	24.2	23.5	55	20	0.30
2	0.0666	0.6667	24.2	21.5	55	100	1.26
3	0.1133	0.6667	24.2	20.8	100	20	0.96

Diskussion der Ergebnisse. Aus oben in Tabellen 1 bis 5 angegebenen Versuchsergebnissen erwies sich ohne weiteres, dass jede der untersuchten Arten der Monosen eines ihrer O-Atome verhältnismässig leicht gegen die des Wassers austauscht, wenn man ihre wässrige Lösung bei 55°C mehr als etwa 100 Stdn. bzw. bei 100°C 15 bis 20 Stdn. lang erwärmt, obwohl ein kleiner Unterschied zwischen der Austauschbarkeit der O-Atome bei einigen Zuckerarten deutlich erkennbar ist. So wird z.B. ein O-Atome in einem Glucosemolekül nach dem schon oben zitierten Versuch von Koizumi und Titani bereits durch eine zwei bis fünf stündige Erwärmung bei 100°C sehr leicht gegen die des Wassers ausgetauscht. Dagegen ergibt sich die Anzahl n der Galaktose, wie aus der oben angegebenen Tabelle 3 ersichtlich ist, sogar nach zehnstündiger Erwärmung bei 100°C noch deutlich kleiner als eins. Dieser Unterschied der Austauschbarkeit der O-Atome kann auf den Unterschied der räumlichen Struktur der einzelnen Zuckerarten zurückgeführt werden. In Bezug auf die Natur bzw. die Art dieses leicht austauschbaren O-Atoms im Monosenmolekül haben Koizumi und Titani die wahrscheinlichste Annahme geäußert, dass es sich um den Carbonylsauerstoff handelt. Unter dieser Annahme kann die vorliegende Austauschreaktion durch die Zwischenbildung eines Hydratmoleküls gedeutet werden; der Mechanismus der Reaktion wird z.B. bei Glucose durch das Schema angegeben:



Ein (schweres) Wassermolekül wird zunächst an dem Carbonylkohlenstoffatom des Zuckers angelagert, indem das erstere in ein H-Atom und ein Hydroxylradikal gespalten wird. Wird ein Wassermolekül aus dem so gebildeten Hydratmolekül wieder abgespalten, so findet eventuell die Austauschreaktion der O-Atome zwischen Zucker und Wasser statt. Aber für diese Wasserabspaltung aus dem hydratisierten Zuckermolekül sind zwei Möglichkeiten denkbar: entweder wird das abzuspaltende Wassermolekül aus dem H-Atom der Hydroxylgruppe an dem Carbonylkohlen-

stoffatom und aus dem alkoholischen OH-Radikal an dem fünften Kohlenstoffatom gebildet oder es geschieht, wie in Gl. (2) gezeigt wird, aus dem OH-Radikal an dem Carbonylkohlenstoffatom und dem H-Atom der alkoholischen Hydroxylgruppe an dem fünften Kohlenstoffatom. Falls diese beiden Mechanismen mit gleicher Wahrscheinlichkeit nebeneinander stattfinden würden, müssten offensichtlich zwei O-Atome in einem Zuckermolekül gleich leicht austauschbar sein. Da aber in Wirklichkeit sich nur ein O-Atom in einem Zuckermolekül leicht austauschbar erwies, müssen wir annehmen, dass die wirkliche Austauschreaktion ausschliesslich nach irgend einem dieser beiden Mechanismen vor sich geht. Als solcher kommt nun der letzt genannte d.h. in Gl. (2) angegebene Mechanismus mit grösserer Wahrscheinlichkeit in Frage als der erstere, weil nach den vielen bisher durchgeführten Versuchen fast ausnahmslos sichergestellt wurde, dass das Carbonylsauerstoffatom verhältnismässig leicht, dagegen das Alkoholsauerstoffatom äusserst schwer austauschbar ist.⁽⁵⁾ Diese Annahme, dass die Wasserabspaltung aus dem hydratisierten Zuckermolekül aus dem Hydroxylradikal der hydratisierten Carbonylgruppe und dem Wasserstoffatom der alkoholischen Hydroxylgruppe stattfindet, steht weiter mit der ebenfalls unter Benutzung des schweren Sauerstoffs sichergestellten Tatsache im Einklang, dass bei der Esterbildung das Wassermolekül stets aus dem Hydroxylradikal der Säure und dem Wasserstoffatom des Alkohols gebildet wird.⁽⁶⁾ Aus demselben Grund gibt bei der Hydrolyse des Esters das Brückensauerstoffatom immer seine Bindung zu dem Alkyloxyradikal aber nicht zu dem Alkylradikal auf. Dasselbe muss aber auch bei der hydrolytischen Eröffnung des Pyranrings des Zuckermoleküls geschehen; das Pyranringsauerstoffatom gibt immer seine Bindung zu dem Carbonylkohlenstoffatom auf.⁽⁷⁾ Auf diese Weise können wir den vorliegenden Befund befriedigend erklären, dass nur ein O-Atom in einem Zuckermolekül verhältnismässig leicht gegen die des Wassers ausgetauscht wird.

Es bleibt noch die Frage übrig, ob mehrere O-Atome des Zuckermoleküls gegen die des Wassers ausgetauscht werden können, wenn die Lösung eventuell unter Zusatz von Säuren bzw. Basen noch längere Zeit erwärmt wird. Ein vorläufiger Versuch zeigte, dass dies wirklich der Fall zu sein scheint, obwohl der Zucker durch solch eine verhältnismässig gewaltsame Behandlung sich schon ziemlich beträchtlich zu zersetzen beginnt.

Zum Schluss möchten wir Herrn Prof. Akabori sowie Herrn Prof. Urushibara für ihre wertvollen Ratschläge bei der Durchführung der vorliegenden Versuche unseren wärmsten Dank aussprechen. Der Nippon

(5) M. Koizumi und T. Titani, dies Bulletin, **13** (1938), 463, 607. J. B. M. Herbert und I. Lauder, *Trans. Faraday Soc.*, **34** (1938), 432. M. Cohn und H. C. Urey, *J. Am. Chem. Soc.*, **60** (1938), 679; *J. Chem. Phys.*, **6** (1938), 175. M. Senkus und W. G. Brown, *J. Org. Chem.*, **2** (1938), 569.

(6) M. Polanyi, A. L. Szabo, *Trans. Faraday Soc.*, **30** (1934), 508. S. C. Datta, J. N. E. Day und C. K. Ingold, *J. Chem. Soc.*, **1939**, 838. J. B. M. Herbert und E. Blumenthal, *Nature*, **144** (1939), 248. I. Roberts und H. C. Urey, *J. Am. Chem. Soc.*, **60** (1938), 2391. J. B. M. Herbert und I. Lauder, *Nature*, **142** (1938), 954.

(7) Unter dieser Annahme können wir auch umgekehrt aus der Ringformel des Zuckers ausgehend die vorliegende Austauschreaktion erklären.

Gakujutsu Shinkohkai (der Japanischen Gesellschaft zur Förderung der Wissenschaft) und der Hattori Hohkohkai (der Hattori Stiftung) sind wir für ihre finanzielle Unterstützung zu bestem Dank verpflichtet.

Siomi Rikagaku Kenkyu-sho
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und chemische Forschung)
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Osaka Teikoku Daigaku
Rigaku-bu
Kagaku Kyositsu
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der Kaiserlichen Universität Osaka).

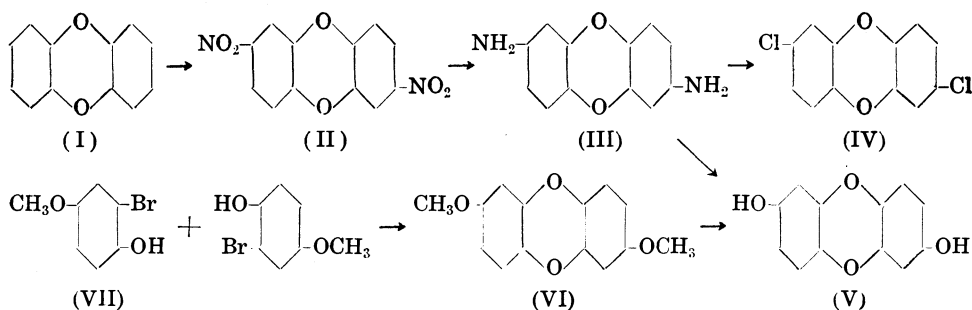
Über 2.6-Dichlor-diphenylendioxyd.

Von Shojiro UYEO.

(Eingegangen am 15. Mai 1941.)

Im Zusammenhang mit einer Arbeit über den räumlichen Bau des Diphenylendioxyds, war es erwünscht, das elektrische Dipolmoment auch über einen symmetrisch substituierten Halogenabkömmling zu ermitteln, um dadurch einen weiteren Anhaltspunkt zu liefern für die Annahme von K. Higasi, dass das Diphenylendioxyd-Molekül nicht in einer Ebene liegt, sondern mehr oder weniger im gefalteten Zustand ist, wie es z.B. bei Thianthren oder Selenanthren der Fall ist.

Zu diesem Zwecke habe ich nun das noch unbeschriebene 2.6-Dichlor-diphenylendioxyd nach folgendem Schema hergestellt.



Früher gelang es M. Tomita⁽¹⁾ durch Nitrierung von Diphenylendioxyd unter bestimmter Bedingung ein Dinitroderivat vom Schmp. 256° in ziemlich guter Ausbeute zu erhalten. Durch Reduktion derselben mit

(1) *J. Pharmac. Soc. Japan*, **55** (1935), 205.

Zinn und Salzsäure wurde dann Diaminoverbindung vom Schmp. 249° gewonnen, die tetrazotiert und durch Aufkochen in schwefelsaurer Lösung in das Dioxy-diphenylendioxyd vom Schmp. 269° übergeführt wurde.

Da diese Verbindung sich in jeder Hinsicht mit dem 2.6-Dioxy-diphenylendioxyd (V), das, vom Brom-hydrochinon-monomethyläther (VII) ausgehend, über die Verbindung VI auf vollkommen durchsichtigem Wege dargestellt worden war, als identisch erwies, sind das Dinitro-diphenylendioxyd vom Schmp. 256° und die daraus abgeleitete Diaminoverbindung eindeutig als 2.6-Disubstitutionsprodukte anerkannt worden.

Nun wurde 2.6-Diamino-diphenylendioxyd (III), das man jetzt bequemer durch katalytische Hydrierung des Dinitroderivates in Eisessig mit Palladium-Kohle als Katalysator in fast quantitativer Ausbeute bereiten kann, tetrazotiert und mittels der Sandmeyerschen Reaktion in die Dichlorverbindung umgewandelt. Das so erhaltene 2.6-Dichlordiphenylendioxyd (IV) bildet hellgelbe Nadeln vom Schmp. 207° und lieferte die richtigen Analysenzahlen.

Der Wert des Dipolmomentes für diesen Stoff beträgt, wie Herr Dr. Higasi freundlicherweise gemessen hat, 0.62 D, was wohl für die gefaltete Struktur des Diphenylendioxyds zu sprechen scheint. Nähere Beschreibung und Diskussion über diesen Gegenstand werden bald von ihm an anderer Stelle veröffentlicht.

Nur sei es hier erwähnt, dass das Moment des 2.6-Dichlorderivates etwas kleiner ist als das des Diphenylendioxyd selbst (0.64 D). Dieses Ergebnis ist vielleicht so zu deuten, dass die entgegengesetzte Richtung der Momente der C-Cl-Bindung einerseits und der C-O-Bindung andererseits hierbei eine Rolle spielt. Ähnliche Verhältnisse liegen bei Thianthren und 2.6-Dichlor-thianthren⁽²⁾ vor.

Für die freundliche Unterstützung dieser Arbeit bin ich Herrn Prof. M. Tomita zu grossen Dank verpflichtet. Besonderer Dank gilt auch Herrn Dr. K. Higasi für die Dipolmessung und viele Ratschläge.

Beschreibung der Versuche. *2.6-Diamino-diphenylendioxyd*: 4.5 g 2.6-Dinitro-diphenylendioxyd (II) (gelbe Nadeln aus Dioxan, Schmp. 262°) wurden in 150 ccm Eisessig suspendiert und in einer Schüttelente mit Palladium-Kohle (0.1 g PdCl₂+0.5 g Tierkohle) in Wasserstoffatmosphäre geschüttelt, wobei 2410 ccm Wasserstoff aufgenommen wurden. Die Reaktionslösung wurde dann vom Katalysator abfiltriert und im Vakuum zur Trockne eingedampft. Das zurückgebliebene essigsäure Diamino-diphenylendioxyd erstarrte sofort zu einer Krystallmasse, die ohne weiteres zur folgenden Reaktion verwendet werden konnte.

Eine kleine Probe davon wurde in Wasser gelöst, mit Natronlauge alkalisch gemacht, das ausgeschiedene Niederschlag wurde abgenutscht und aus Alkohol umgelöst. Freies Diamin bildet derbe Krystalle vom Schmp. 249°. Leicht löslich in Aceton, schwer in Äther, Chloroform und Benzol.

2.6-Dichlor-diphenylendioxyd: Das oben gewonnene essigsäure Diamin wurde in 80 ccm 28-proz. Salzsäure gelöst und unter Eiskühlung mit einer Lösung von 2.3 g NaNO₂ in 20 ccm Wasser diazotiert. Nach

(2) Bergmann und Weismann, *Chem. & Ind.*, **16** (1938), 364.

einigem Stehen wurde dann mit einer Suspension von 10 g Cu_2Cl_2 in 70 ccm 15-proz. Salzsäure versetzt und vorsichtig auf dem Wasserbade erwärmt. Nach dem Absetzen der Stickstoffentwicklung wurde das Reaktionsprodukt mit Benzol geschüttelt, die Benzolauszüge wurden getrocknet und eingedampft, wobei sich Krystalle ausschieden, die mit wenig Äther versetzt und abfiltriert wurden. Ausbeute 3.0 g. Nach zweimaligem Umlösen aus Benzol-Methanol wurden hellgelbe feine Nadeln vom konstanten Schmp. 207° erhalten. Leicht löslich in Benzol, mässig in Äther und schwer in Methanol. Gefunden C 56.84, H 2.53, Cl 27.95. Berechnet für $\text{C}_{12}\text{H}_6\text{O}_2\text{Cl}_2$ C 56.92, H 2.39, Cl 28.03.

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α -Oestradiol Dimethyl Ether, 17-Monomethyl Ether, and Related Compounds.

By Yoshiyuki URUSHIBARA and Takesi NITTA.

(Received May 21, 1941.)

Neither α -oestradiol dimethyl ether nor 17-monomethyl ether has been described. In order to fill up the vacancies in the literature the authors prepared these ethers and some related compounds. In view of the remarkably prolonged oestrogenic action of the dimethyl ether of diethylstilboestrol,⁽¹⁾ a similar physiological action of α -oestradiol dimethyl ether was expected.

α -Oestradiol dimethyl ether was prepared in a good yield by the action of dimethyl sulphate on the sodium compound from α -oestradiol 3-monomethyl ether and metallic sodium. The same substance was obtained in a smaller yield by the action of the methylating agent on the product from oestrone methyl ether and metallic sodium. The mechanism of the latter reaction is unknown. α -Oestradiol dimethyl ether forms colourless fine needles melting at 161–162° (corr.). It produced a prolonged oestrus in ovariectomized rats lasting 60 days by a single injection of 1 mg.

α -Oestradiol 3-monobenzoate failed to react with metallic sodium, and defied the attempt to methylate it through a sodium derivative. α -Oestradiol 17-monomethyl ether was prepared in a good yield by a partial demethylation of the dimethyl ether with hydroiodic acid and glacial acetic acid, while α -oestradiol was given by a more drastic demethylation. The 17-monomethyl ether forms colourless fine needles melting at 213.5–214.5° (corr.). It is insoluble in cold and even hot 5% aqueous caustic alkali

(1) E. C. Dodds, L. Golberg, W. Lawson, and R. Robinson, *Proc. Roy. Soc. (London)*, B, **127** (1939), 140.

in spite of the free phenolic hydroxyl group. It gives a 3-benzoate forming fine prisms melting at 165.5–166.5° (corr.), and a 3-*p*-toluene-sulphonate melting at 124.5–125.5° (corr.). In rat tests the 17-monomethyl ether showed a threshold value (less than 2.5 γ) approximating to that of oestrone (2 γ), and caused a duration of oestrus comparable to that caused by oestrone methyl ether.

Further the following derivatives of α -oestradiol were prepared: α -oestradiol 3-methyl ether 17-acetate, m.p. 103.5–104.5° (corr.); α -oestradiol 3-methyl ether 17-benzoate, m.p. 131–132° (corr.); α -oestradiol 3-methyl ether 17-*p*-toluene-sulphonate, m.p. 160–161° (corr.); α -oestradiol 3-benzoate 17-*p*-toluene-sulphonate, m.p. 184.5–185.5° (corr.); α -oestradiol 17-mono-*p*-toluene-sulphonate, m.p. 171–172° (corr.); and α -oestradiol di-*p*-toluene-sulphonate, difficultly crystallizable.

The new ethers of α -oestradiol were compared with some known substances in the physiological activity for ovariectomized rats.⁽²⁾ Table 1 shows the minimum active doses obtained by single subcutaneous injections in oil solution. Table 2 records the duration of oestrus caused by single subcutaneous injections of 1 mg. and of 50 γ in oil solution.

Table 1. The Minimum Doses to Produce Oestrus in Ovariectomized Rats by Single Subcutaneous Injections.

Substance	Minimum active dose (γ)
α -Oestradiol	0.4
α -Oestradiol 3-monomethyl ether	4~5
α -Oestradiol 17-monomethyl ether	< 2.5
α -Oestradiol dimethyl ether	<10*
α -Oestradiol 17-mono- <i>p</i> -toluene-sulphonate	ca. 100
Oestrone	2
Oestrone methyl ether	15
Diethylstilboestrol	0.5
Diethylstilboestrol dimethyl ether	5

* No response with 5 γ .

Table 2. The Duration of Oestrus in Ovariectomized Rats Caused by Single Subcutaneous Injections.

Substance	Duration of Oestrus (Days)	
	1 mg.	50 γ
α -Oestradiol 3-monobenzoate		18
α -Oestradiol 3-monomethyl ether		5
α -Oestradiol 17-monomethyl ether	18	5~6
α -Oestradiol dimethyl ether	60	24
α -Oestradiol 17-mono- <i>p</i> -toluene-sulphonate	4~5	no response
Oestrone		6
Oestrone benzoate		10
Oestrone methyl ether	17	5
Diethylstilboestrol		3
Diethylstilboestrol dimethyl ether	26,52**	38

** Two animals died on the 26th day of oestrus and one on the 52nd day.

(2) For biological tests the authors thank Dr. M. Ito and Dr. F. Ueno.

Experimental.

α -Oestradiol Dimethyl Ether. A solution of α -oestradiol 3-monomethyl ether (m.p. 95–97°, corr.) in a small volume of pure ether was added to an excess of finely granulated metallic sodium. A white deposit separated out gradually with evolution of hydrogen gas. The mixture was left to stand overnight with exclusion of moisture. Dimethyl sulphate was added in a slight excess to sodium and the mixture was heated for an hour under a reflux condenser. To make sure that the reaction was complete, ether was distilled off and the residue was heated in benzene for an hour. The benzene solution was filtered from insoluble matters and evaporated. A light-yellow oil remained and solidified to a crystalline mass in a short time. It was repeatedly recrystallized from acetone. α -Oestradiol dimethyl ether thus obtained forms colourless fine needles melting at 161–162° (corr.). The yield of a pure substance about 60% of the 3-monomethyl ether. (Found: C, 80.3, 80.4; H, 9.4, 9.4. Calculated for $C_{20}H_{28}O_2$: C, 79.96; H, 9.39%.)

A large excess (400 mg.) of finely granulated metallic sodium was added to a solution of oestrone methyl ether (m.p. 168–169°, corr.) (1 g.) in anhydrous benzene (10 c.c.). No change was noticed to occur in the cold. When the mixture was boiled for five hours it became orange-red. On adding dimethyl sulphate (3 c.c.) an active reaction took place and the liquid became light-yellow. After boiled for an hour, the benzene solution was filtered, washed with water, 5% caustic soda, and again with water, dried, and evaporated. A reddish brown oil was obtained. When it was dissolved in a small amount of acetone and the resulting solution was left to stand for a day or two, a crystalline substance (100 mg.) separated out. It was collected and recrystallized twice from acetone. The substance thus obtained melted at 158–159° (corr.) and showed no depression of the melting point in admixture with a specimen (m.p. 159–160°) of oestradiol dimethyl ether obtained from oestradiol 3-monomethyl ether.

α -Oestradiol 17-Monomethyl Ether. A mixture of a glacial acetic acid solution of the dimethyl ether from oestradiol 3-monomethyl ether and hydroiodic acid (specific gravity 1.7) in a quantity equal to that of acetic acid was heated for 30 minutes on a boiling water bath, poured into water, and extracted with ether. The ethereal solution was washed successively with water, 5% aqueous soda, 5% sodium thiosulphate, and again with water, dried, and evaporated. The oily residue solidified to a crystalline mass. It was repeatedly recrystallized from methanol. Fine needles melting at 213.5–214.5° (corr.). Yield 60% of the dimethyl ether. The 17-monomethyl ether is insoluble in cold and hot 5% aqueous alkali.

The specimen of the dimethyl ether obtained from oestrone methyl ether could be demethylated to the same 17-monomethyl ether.

α -Oestradiol 17-Methyl Ether 3-Benzoylate. The 17-monomethyl ether was dissolved in pyridine and benzoyl chloride was added. The mixture was left to stand for a week and poured into cold water. An oily precipitate separated out and crystallized immediately. Recrystallization from acetone gave fine prisms melting at 165.5–166.5° (corr.).

α -Oestradiol 17-Methyl Ether 3-*p*-Toluene-sulphonate. The 17-monomethyl ether was dissolved in pyridine and *p*-toluene-sulphonyl chloride was added. After standing for a day or two water was added and the mixture was well stirred to crystallization. The crystalline substance was collected and recrystallized from acetone. Melting point 124.5–125.5° (corr.).

α -Oestradiol 3-Methyl Ether 17-Acetate. Prepared from oestradiol 3-monomethyl ether and acetic anhydride in pyridine. Glittering scaly crystals melting at 103.5–104.5° (corr.).

α -Oestradiol 3-Methyl Ether 17-Benzoylate. Oestradiol 3-monomethyl ether was dissolved in pure pyridine and benzoyl chloride was added with cooling. The mixture was left to stand at room temperature for a week and poured into ice water. An orange-coloured oil separated out and crystallized slowly. It could be crystallized completely by stirring with a small quantity of methanol. Recrystallization from acetone gave small prisms melting at 131–132° (corr.).

α -Oestradiol 3-Methyl Ether 17-*p*-Toluene-sulphonate. Prepared from oestradiol 3-monomethyl ether and *p*-toluene-sulphonyl chloride in pyridine. Melting point 160–161° (corr.).

α -Oestradiol 3-Benzate 17-*p*-Toluene-sulphonate. Oestradiol 3-monobenzoate (m.p. 193–194°, corr.) was dissolved in pure pyridine and *p*-toluene-sulphonyl chloride was added. After standing for a day or two water was added to the mixture. The precipitate was recrystallized from acetone. Melting point 184.5–185.5° (corr.). Yield nearly theoretical.

α -Oestradiol 17-Mono-*p*-toluene-sulphonate. The above 3-benzoate 17-*p*-toluene-sulphonate was saponified partially with alcoholic potash, and the product was recrystallized from methanol. The substance melts at 171–172° (corr.) to a deep red liquid. It is difficultly soluble in 5% aqueous alkali. On acylation with *p*-toluene-sulphonyl chloride and pyridine it yielded the difficultly crystallizable di-*p*-toluene-sulphonate.

α -Oestradiol Di-*p*-toluene-sulphonate. Oestradiol was treated with *p*-toluene-sulphonyl chloride in pyridine. The product crystallized very slowly. On saponification by boiling with alcoholic potash it gave oestradiol 17-mono-*p*-toluene-sulphonate melting at 172–173° (corr.) alone and in admixture with the above specimen.

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The Configurations of Cholesterol Oxides, Δ^4 -Cholestenediols-(3,6), and Cholestenediols-(3,6).

By Yoshiyuki URUSHIBARA.

(Received May 26, 1941.)

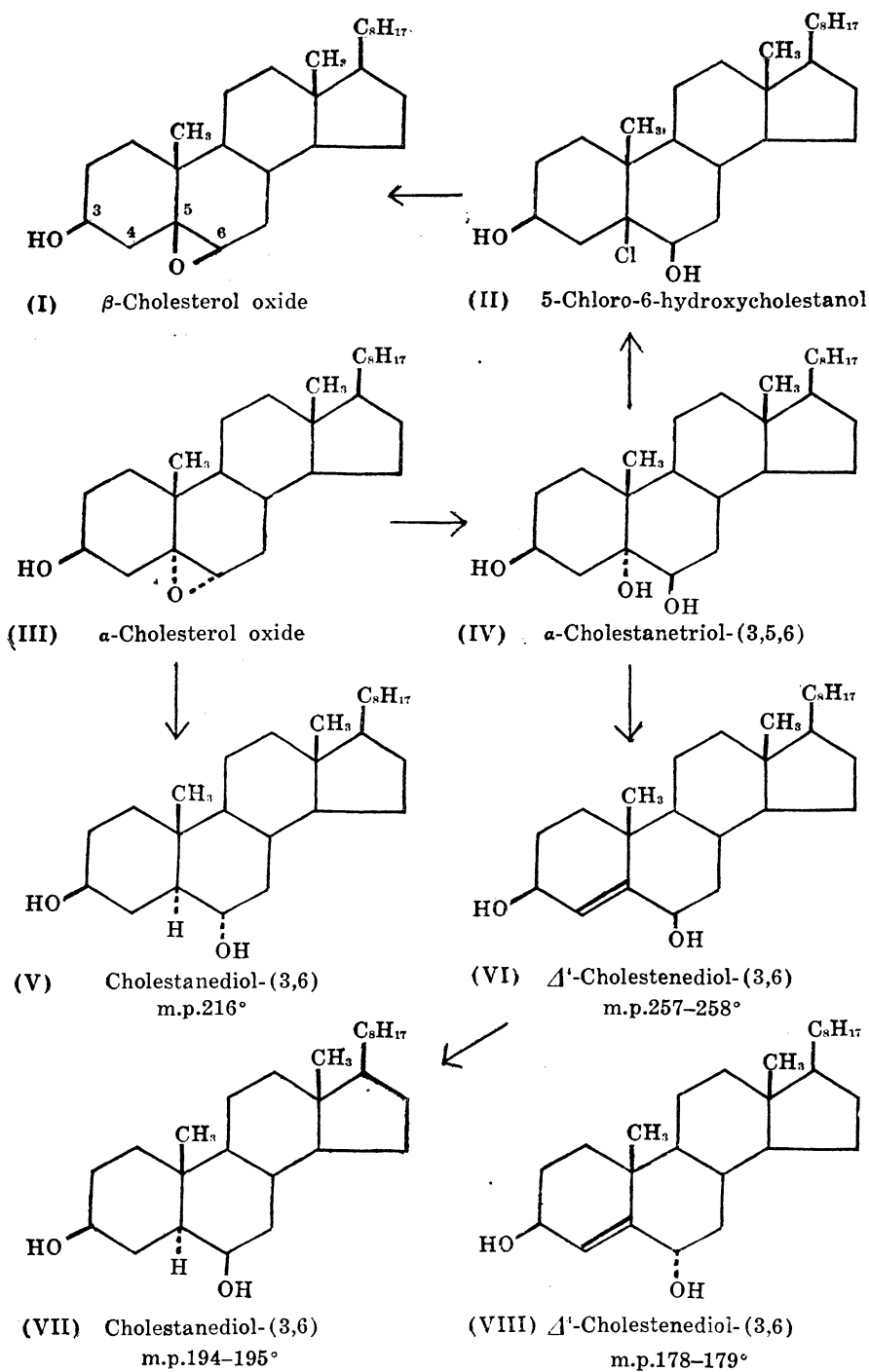
The action of perbenzoic acid on cholesterol in chloroform solution yields two isomeric cholesterol oxides.⁽¹⁾⁽²⁾ α -Cholesterol oxide (m.p. 140–141°) is the less soluble and can be obtained in a pure state, while β -cholesterol oxide has not yet been isolated in a pure state. A similar treatment of cholesteryl acetate is reported to give mainly the acetate of β -cholesterol oxide,⁽²⁾ but the homogeneity of the product thus obtained seems doubtful.⁽³⁾ The α -oxide is hydrated to α -cholestanetriol-(3,5,6) when heated with water in a tube⁽¹⁾; α -cholestanetriol is converted into "5-chloro-6-hydroxycholestanol" when treated with methanol-hydrochloric acid; and action of alcoholic potash on this chlorohydrin produces β -cholesterol oxide.⁽⁴⁾⁽³⁾ The β -oxide (m.p. 136°) obtained by this process is supposed to be pure.⁽³⁾ Thus a complete inversion of α -oxide into β -oxide seems to occur during this transformation.

(1) T. Westphalen, *Ber.*, **48** (1915), 1064.

(2) L. Ruzicka and W. Bosshard, *Helv. Chim. Acta*, **20** (1937), 244.

(3) J. Hattori, *J. Pharm. Soc. Japan*, **60** (1940), 334.

(4) A. Windaus, *Z. physiol. Chem.*, **117** (1921), 146.



Formulas I and III have to be assigned to cholesterol oxides, but the configurations of the oxide rings in these stereoisomeric compounds have not yet been determined. Recently Ellis and Petrow⁽⁵⁾ established the configurations of α - and β -cholestanetriols-(3,5,6), and showed the α -triol is cholestanetriol-(3 β ,5 α ,6 β) (IV). Now, the transformation of α -cholesterol oxide into β -oxide through α -cholestanetriol and the known configuration of α -cholestanetriol enable the author to infer the configurations of cholesterol oxides.

The elimination of hydrogen chloride from the "5-chloro-6-hydroxy-cholestanol" by the above-mentioned process yields neither a Δ^4 -cholestenediol nor 6-ketocholestanol through Δ^5 -cholestenediol,⁽⁶⁾ but gives a cholesterol oxide. Hence, it must be assumed that the chlorine atom at carbon atom 5 forms hydrogen chloride with the hydrogen atom attached to the hydroxyl group at carbon atom 6. Such an elimination may be easy if the chlorine atom is situated at a *cis* position to the hydroxyl group. If so, the substitution of a chlorine atom for the hydroxyl group at carbon atom 5 in α -cholestanetriol is accompanied by a Walden inversion, and the "5-chloro-6-hydroxycholestanol" is 5(β)-chloro-6 β -hydroxycoprostanol-(3 β) (II). An alternative is that a Walden inversion occurs at carbon atom 5, not when the chlorohydrin is formed from the triol, but when hydrogen chloride is eliminated from the chlorohydrin. In any case, β -cholesterol oxide should be 5,6-epoxy-coprostanol-(3 β) (I), and consequently α -cholesterol oxide should be 5,6-epoxy-cholestanol-(3 β) (III). It is fortunate that cholesterol oxides have been correctly designated as α and β , but the Greek letters may be more appropriately prefixed to the word "oxide," thus cholesterol α -oxide and cholesterol β -oxide.

Further, the configurations of Δ^4 -cholestenediols-(3,6) and cholestane-diols-(3,6) can be inferred from that of α -cholestanetriol. A Δ^4 -cholestenediol-(3,6) melting at 257–258° is formed by the action of sodium acetate on cholesterol dibromide⁽⁷⁾ or by the action of selenium dioxide on cholesterol acetate or benzoate.^{(8) (9)} As this cholestenediol is also obtained by a Darzens dehydration of α -cholestanetriol diacetate followed by saponification,⁽¹⁰⁾ it should be Δ^4 -cholestenediol-(3 β ,6 β) (VI). Another Δ^4 -cholestenediol-(3,6) melting at 178–179° is obtained from 6-ketocholestanol through 5-bromo-6-ketocholestanol (acetate) and 6-keto- Δ^4 -cholestenol-(3).⁽¹¹⁾ The latter cholestenediol differs from the cholestenediol melting at 257–258° only in the configuration of the hydroxyl group at carbon atom 6, because both are prepared from cholesterol as the starting substance and no change liable to cause an inversion of the hydroxyl group at carbon atom 3 is involved. Thus it is shown that the cholestenediol melting at 178–179° is Δ^4 -cholestenediol-(3 β ,6 α) (VIII).

(5) B. Ellis and V. A. Petrow, *J. Chem. Soc.*, **1939**, 1078.

(6) H. Lettré and M. Müller, *Ber.*, **70** (1937), 1947, obtained a cholestenediol dibenzoate by eliminating hydrogen chloride from the dibenzoate of the same chlorohydrin but the product from hydrolysis of the cholestenediol dibenzoate proved to be 6-ketocholestanol.⁽¹⁰⁾

(7) J. Lifschütz, *Z. physiol. Chem.*, **106** (1919), 271; also compare foot-notes (8) and (9).

(8) O. Rosenheim, W. W. Starling, *J. Chem. Soc.*, **1937**, 377.

(9) A. Butenandt and E. Hausmann, *Ber.*, **70** (1937), 1154.

(10) V. A. Petrow, O. Rosenheim, W. W. Starling, *J. Chem. Soc.*, **1938**, 677.

(11) I. M. Heilbron, E. R. H. Jones, and F. S. Spring, *J. Chem. Soc.*, **1937**, 801.

The higher melting Δ^4 -cholestenediol-(3,6) gives a saturated diol melting at 194–195° by a catalytic reduction with platinum oxide in acetic acid.⁽⁸⁾ That the reduction product belongs to the cholestane series has not been proved but is highly probable because it is formed along with cholestane and cholestanol.⁽¹²⁾ Then the constitution of the saturated diol should be cholestenediol-(3 β ,6 β) (VII). Another cholestenediol-(3,6) melting at 216° is obtained by reducing 6-ketocholestanol with sodium and alcohol.⁽¹³⁾ This diol is derived from cholestane because it was transformed into cholestane through dichlorocholestanol,⁽¹³⁾ and differs from the cholestenediol melting at 194–195° only in the configuration of the hydroxyl group at carbon atom 6. Thus the cholestenediol melting at 216° is cholestenediol-(3 β ,6 α) (V).

Now, the experimental linking of α -cholesterol oxide to cholestenediol-(3 β ,6 α) has been accomplished in this laboratory: Reduction of α -cholesterol oxide with sodium and amyl alcohol yields the same cholestenediol-(3,6) as obtained by the similar reduction of 6-ketocholestanol.⁽¹⁴⁾ The establishment of this relationship affords a strong support to the configurations inferred from other evidences.

The author expresses his hearty thanks to the Department of Education for grants.

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(12) R. E. Marker and J. Krueger, *J. Am. Chem. Soc.*, **62** (1940), 79, obtained a cholestenediol-(3,6) melting at 190° by reducing 6-ketocholestanol with platinum oxide in alcohol. It is probably identical with the cholestenediol melting at 194–196° prepared by Rosenheim and Starling.⁽⁹⁾ If so, this is surely a cholestane derivative.

(13) A. Windaus, *Ber.*, **50** (1917), 133.

(14) Experimental details will be reported by Dr. M. Chuman.

Researches on Camphor, Borneol and Their Allied Substances.

By Seiichi YAMADA.

(Received May 6, 1941.)

(1) **Catalytic Reduction and Oxidation of Camphor, Borneol and Their allied Substances.** According to the researches by Aloy and Brustier⁽¹⁾ camphor is obtained quantitatively by passing borneol over copper heated to 300°C, and Neave⁽²⁾ under the reaction condition akin to that of Aloy and others, obtained *d*-camphor from *d*-borneol but camphene from isoborneol. Later, Masumoto⁽³⁾ observed that catalytic oxidations of borneol into camphor by reduced copper differ according to the manufacturing process of the latter.

A sample of copper (1) was obtained by reducing copper oxide which was gained from copper nitrate and sodium hydroxide. When this copper was used as a catalyser, the yield of camphor from borneol was at its best at 200°C amounting to 80%, while at 300°C the yield decreased to its half. On the other hand when copper (2) obtained by reducing copper oxide which was gained by using ammonium hydroxide instead of sodium hydroxide was used as a catalyser, the yield of camphor hardly reached 10% even under the best condition. Copper (3) was made according to Sabatier's process by reducing copper oxide which was gained by heating copper nitrate. When this catalyser was used, the results were generally satisfactory, the yield of camphor amounting to 75%. Ikeda⁽⁴⁾ reports that when isoborneol was passed over reduced copper prepared by Sabatier's process, only dehydration occurred, and at 130°–140°C, 90% of the isoborneol was changed to camphene.

Isoborneol, inspite of its being a secondary alcohol, is promoted to dehydrate under the catalytic reaction of metals, and thus behaves unlike borneol. In order to investigate more closely the behaviour of the two isomers, the writer, just as Masumoto did, used the three kinds of copper and examined its catalytic reaction upon borneol at 400°C. The result showed that copper (1) yielded camphor quantitatively, copper (2) yielded camphor and camphene in the proportion of 80:20, and copper (3) of 87:13. It seems, therefore, that copper (1) promotes only oxidation of borneol, while coppers (2) and (3), not only oxidation but to some extent dehydration. On the other hand, isoborneol under the catalytic reaction of copper (1) at 150°C and also at 300°C yielded camphor as a reaction product in each case, and with copper (2) at 150°C all of the isoborneol was changed to camphene, and at 300°C camphor and camphene were formed in the proportion of 24:76. In short, copper (1) acts against isoborneol as to promote oxidation independent of the reaction tempera-

(1) *Bull. Soc. Chim.*, [4] **9** (1911), 733.

(2) *J. Chem. Soc.*, **101**, 513.

(3) *Memoirs Coll. Sci. Kyoto Imp. Univ. A.* **9** (1925), 219.

(4) *Bull. Institute Phys. Chem. Research*, **4** (1925), 343.

ture, while copper (2) promotes dehydration at low temperatures, but oxidation as the temperature is raised. Therefore, for the purpose of synthesising camphor from borneol and isoborneol copper (1) seems to be the most appropriate catalyser.

The fact that nickel as a catalyser plays an analogous role as copper does has often been pointed out, and according to two patents⁽⁵⁾ regarding the action of reduced nickel toward borneol and isoborneol, reduced nickel is almost or completely defective of the power to promote oxidation, but when small quantity of either caustic soda, sodium nitrate or sodium sulphate is added, the oxidation is very strongly promoted. The writer examined the catalytic action of reduced nickel toward borneol and isoborneol and found that though oxidation is promoted, there is some difference in the reaction conditions compared with those in the case of reduced copper.

With respect to the catalytic reduction from camphor to borneol and isoborneol, Komatsu and Masumoto⁽⁶⁾ obtained isocamphane besides small quantity of borneol by reducing camphor in the stream of hydrogen at 180°C under the catalytic reaction of reduced nickel,⁽⁷⁾ and Ipatiev,⁽⁸⁾ using nickel oxide as a catalyser, tried the reduction in an atmosphere of hydrogen under the pressure of 129 atms. and at 200°C, and obtained borneol and isocamphane. Further, Kubota and Hayashi⁽⁹⁾ reported that using reduced copper as a catalyser, camphor was reduced under high pressure of hydrogen and at high temperatures to borneol and isoborneol in the range of proportion from 29:71% to 21:79%. Vavon⁽¹⁰⁾ inferred that by the reduction of camphor isoborneol is formed at first and then this undergoes a rearrangement to form borneol.

The writer using reduced nickel as a catalyser submitted camphor to the catalytic reduction with hydrogen at high temperature and high pressure and found that at about 180°C the proportions of borneol and isoborneol formed were 51:49, 50:50, 47:53 when the pressure of hydrogen were 23, 49, 85 atms. respectively; and when the reaction temperatures were 140–160°C, and 170–190°C the proportions of formation of both of the isomers were 51:49 and 47:53 respectively (cf. Fig. 1–5). When the temperature of reaction is raised above 200°C, hydrogen is absorbed more than 1 mole, and it seems that the alcohol formed at first is subsequently dehydrated and reduced successively, and as a matter of fact isocamphane and a small quantity of water were formed as reaction products (cf. Fig. 6–7). This fact can be explained by deciding experimentally the temperatures of dehydration of borneol and isoborneol; the writer's experiment shows that borneol is dehydrated at 220–260°C and isoborneol

(5) Schering, D.R.P., 219043 (1908); cf. D.R.P. 219044 (1908).

„ D.R.P., 211147 (1908); cf. D.R.P. 271157 (1909).

(6) *Mem. Coll. Sci. Kyoto Imp. Univ.*, **5** (1922), 225.

(7) O. Aschan, "Naphth. Therp. Campherarten" p. 152, 1929; D.R.P. 213154 (1907); *Chem. Zentr.*, **1909**, II, 1025.

(8) *J. Russ. Phys. Chem. Soc.*, **38** (1906); *Chem. Zentr.*, **1906**, II, 87; *Ber.*, **45** (1912), 3212.

(9) *Bull. Chem. Soc. Japan*, **1** (1926), 69.

(10) G. Vavon and P. Peignier, *Bull. soc. chim.*, **39** (1926), 924; *Compt. rend.*, **181** (1925) 183; P. Lipp, *Ber.*, **68** (1935), 1029.

at 160–190°C. From this it is to be seen that the dehydration temperature of isoborneol being in close vicinity of the temperature adequate to the reduction of camphor, the reduction is usually accompanied by the dehydration (cf. Fig. 8–10).

In order to investigate how the yield of catalytic reduction is influenced by the introduction of solvents, cyclohexane as a non-polar substance on the one hand, and absolute alcohol, acetic acid and pyridine as polar substances on the other hand, were used, and the proportions of borneol and isoborneol formed were 23:77, 12:88, 37:63, 36:64 respectively (cf. Fig. 11–15). In the above case, the introduction of solvents increased remarkably the yield of isoborneol, but any relation between this increase and the polarity of solvents is barely recognisable. The addition of absolute alcohol raised the yield of isoborneol, and yield of some 90% was gained.

When camphor (I) is reduced with metallic sodium and ethyl alcohol, borneol is formed mainly, and when camphor is catalytically reduced with metallic catalyser and hydrogen in alcoholic solution the main product is isoborneol. Epi-camphor (II), when reduced with metallic sodium and alcohol gives epi-borneol only, and when catalytically reduced with platinum black and hydrogen in acetic acid solution it gives epi-isoborneol.⁽¹¹⁾ Nor-camphor (III) gives nor-isoborneol when reduced either with metallic sodium and alcohol or with palladium chloride, platinum colloid and hydrogen in alcoholic solution.⁽¹²⁾ This may be due to the fact that the molecular construction of nor-camphor differ from those of camphor and epi-camphor, and a mobile hydrogen is linked with the α -carbon adjacent to C=O group. Then as the chemical constitution of dimethylcamphor, (IV) differs from that of nor-camphor, having in the α -position CH_3 substituted for the mobile hydrogen, under the expectation that dimethylcamphor unlike nor-camphor may form a derivative of borneol as the reduction product, the writer synthesised, according to Haller's process,⁽³⁾ α , α' -dimethylcamphor from camphor and then reduced it with metallic sodium and alcohol. Thus two kinds of alcoholic compounds A and B were gained in the proportion 88:12, as shown in the following table.

As to the stereochemical configuration of the two alcohols formed, just like in the case of borneol and isoborneol, the less easily dehydrated was defined as dimethylborneol and the easily dehydrated as dimethylisoborneol. Now, dimethylcamphor was heated in hydrogen under 60 atms. at 220–230°C in the presence of reduced nickel and it was found that this reduction was much more difficult than that of camphor, the yield of alcohol being only 19% even after about 27 hours. The proportion of dimethylborneol and dimethylisoborneol formed being 85:15, it was almost the same as when the reduction was done with metallic sodium and alcohol (cf. Fig. 16). When the catalytic reduction was done by adding absolute

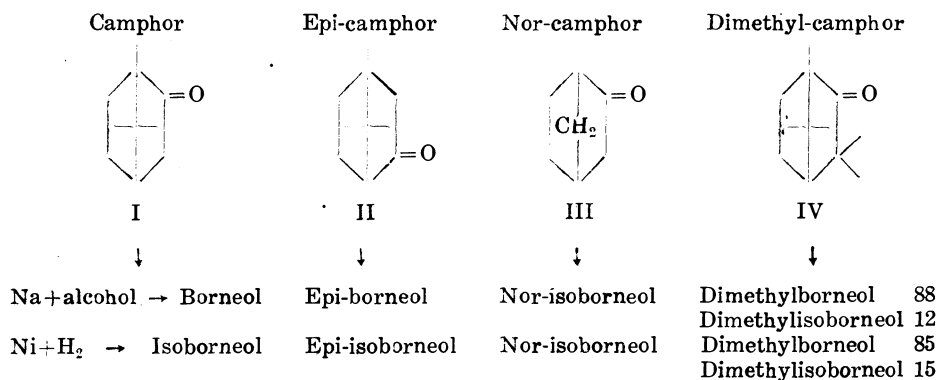
(11) M. Lipp geb. Bredt Savelsbery, E. Bund. Ber., **68** (1935), 249; cf. Bredt and Perkin, *J. prakt. Chem.*, [2] **89** (1914), 254.

(12) Komppa and Beckmann, *Ann.*, **512** (1934), 174; Alder and Stein, *Ann.*, **514** (1934), 220.

(13) *Compt. rend.*, **148** (1909), 1645.

Substance	A	B
B. p. M. p. [α] _D	90.5~93/5 mm 57°C +50.72° (in alcohol) at 26° +53.76° (in toluene) at 26°	82~83/3 mm 47~49°C +36.47° (in alcohol) at 15° +42.71° (in toluene) at 15°
Phenylurethane	112–113°C	116–117°C
<i>p</i> -Nitrobenzoate	Needle crystal of silky luster and of faintly greenish white colour. 115–115.8°C	Nearly colourless and lustrous needle crystal. 114.5–115°C
Phthalic acid monoester	Fine, white needle crystal 177–178°C	Lustrous, fine scaly crystal 173–174°C
Magnesium phthalate	Lustrous white scaly crystal 175–176.2°C	Crystalline white powder 180–182°C
Reacting with ZnCl ₂ or with phthalic anhydride	Not dehydrated	Dehydrated

alcohol or a little acetic acid, the proportions of both of the isomers produced were 66:34 and 86:14 respectively, and the use of absolute alcohol as a solvent increased the yield of iso-compound as in the case of camphor (cf. Fig. 17). When the reduction temperature was raised to 260°–280°C, more than 1 mole hydrogen was absorbed dehydration occurred, and hydrocarbon was formed (cf. Fig. 18).



(2) **Isomeric Change between Borneol and Isoborneol.** Applying the aforesaid method of separation⁽¹⁴⁾ of borneol and isoborneol to the crude isoborneol (90%), gained by the catalytic reduction of camphor in alcoholic solution, isoborneol which may be considered pure was obtained, and its properties were compared with those of its isomer, borneol.

(14) *J. Chem. Soc. Japan*, **53** (1932), 807.

	M.p.	$[\alpha]_D$	$[\alpha]_D^{15}$		
Borneol	204–204.5°C (in a sealed tube)	+38.10°C = 3.57 (in alcohol, at 11°)	+38.44°C = 3.92 (in toluene)		
Isoborneol	212–213°C (in a sealed tube)	–34.42°C = 3.35 (in alcohol, at 7°)	–19.59°C = 5.17 (in toluene)		
	Acetate				
	Combustion heat	B.p.	d_4^{20}	n_D^{20}	$[\alpha]_D$
Borneol	Kcal/mol 1489.3	98/11 mm	0.9864	1.4655	+42.75° at 11°
Isoborneol	1472.5	76–77/3 mm	0.9867	1.4623	–51.98° at 18°
	Magnesium phthalate			Methoxy value after etherification with HCl–methyl alcohol	
	M.p.	$[\alpha]_D^{15}$			
Borneol	103–104°C	+31.9°C = 1.99 (in alcohol)	0.42		
Isoborneol	95–97°C	–29.46°C = 4.0 (in alcohol)	12.5		

Borneol and isoborneol being stereoisomers of *cis*- and *trans*-form,⁽¹⁵⁾ a transformation from one into the other may be possible as we expect from heats of combustion of the two isomers. And hitherto the transformation of isoborneol into borneol was accomplished by adding alkaline metal to the solution of isoborneol in alcohol, in xylene or in ligroin and then it was heated under pressure;⁽¹⁶⁾ otherwise the solution in cyclohexane was heated to about 200°C in the presence of nickel catalyser with hydrogen under 30 atmos.⁽¹⁷⁾ When isoborneol was heated for about 4 hours in the presence of reduced nickel under 50 atm. hydrogen at 130–150°C and 140–165°C, 16% and 51% of the sample was changed to borneol in each case; conversely it was seen that only 1% of borneol was transformed to isoborneol, when heated for about 20 hours in the presence of reduced nickel under 70 atm. hydrogen at 170–190°C (cf. Fig. 19). Further, when each of the solutions of borneol and isoborneol in absolute alcohol was heated for 20 hours in the presence of reduced nickel under 70 atms. hydrogen at 150–160°C and 130–140°C respectively, 10% of borneol was transformed to isoborneol and 11% of isoborneol to borneol (cf. Fig. 20–21).

(3) **Dehydration of Borneol and Its allied Substances.** Formerly dehydrating agents used for the dehydration of borneol and isoborneol

(15) Vavon and Peignier, *Bull. soc. chim.*, [4] **39** (1926), 666, 924; Hüchel, *Ann.*, **477** (1930), 157.

(16) Wagner and Brickner; *Chem. Zentr.*, **1909**, II, 25; Schmitz & Co., D.R.P., 212, 908; *Chem. Zentr.*, **1909**, II, 1392.

(17) H. Sandkuhl, Rhein. Kampf. Fabr. Düsseldorf–Oberkassel. D.R.P., 408666, *Chem. Zentr.*, **1925**, I, 1809.

were zinc chloride, phosphorus pentoxide, potassium bisulphate, sulphuric acid, oxalic acid, glacial acetic acid, phthalic anhydride and active carbon; and although isoborneol forms easily camphene, the dehydration of borneol is very difficult, and therefore the reaction has been utilized to distinguish these two isomers. But, if an adequate reagent is found, the dehydration of borneol may be executed. Therefore, for the dehydration of borneol and isoborneol the writer used $\text{H}_2\text{SO}_4 \cdot 3\text{H}_2\text{O}$, which Sendrens⁽¹⁸⁾ recommended as a good dehydrating agent for alcohol. When 0.07 mol of $\text{H}_2\text{SO}_4 \cdot 3\text{H}_2\text{O}$ was added to 1 mol of isoborneol and the mixture was heated at 140–145°C for 10 hours, dehydration occurred easily and 56% camphene and 18% ether compound of high boiling point were obtained; borneol, under the same condition, gave 63% camphene and 12% ether.

No.	Substances	Method of preparation	M.p. °C	B.p. °C	d_4	n_D	$[\alpha]_D$
1	Di- <i>d</i> -bornyl-ether ⁽¹⁹⁾	Dehydration with ZnCl_2	43–44	317/753 mm	—	45°C 1.4810	18°C +65.6°
2	Di- <i>l</i> -bornyl-ether ⁽²⁰⁾	Dehydration with conc. H_2SO_4	liquid	312–314	18°C 0.9600	24°C 1.4940	—88.56°
3	Di- <i>d, l</i> -isobornylether ⁽²¹⁾	Action of conc. H_2SO_4 to camphene	90–91	322	—	—	—
4	Di- <i>d</i> -bornyl-ether	Dehydration with $\text{H}_2\text{SO}_4 \cdot 3\text{H}_2\text{O}$	liquid	134–137/2 mm	20°C 0.9564	20°C 1.4927	27°C +41.68°
5	Di- <i>d, l</i> -isobornylether	„	„	134–145/2 mm	20°C 0.9672	20°C 1.5010	—

In addition, when dry alumina is acted on borneol at 350°C dehydration occurs and a good yield of racemic camphene is obtained.

By dehydrating borneol $[\alpha]_D + 18.62^\circ$ and isoborneol $[\alpha]_D - 15.72^\circ$ with $\text{H}_2\text{SO}_4 \cdot 3\text{H}_2\text{O}$, there were obtained solid camphenes $[\alpha]_D + 3.3^\circ$ and $[\alpha]_D + 4.35^\circ$ respectively; and by dehydrating isoborneols $[\alpha]_D - 15.72^\circ$ and $[\alpha]_D - 34.42$ with phthalic anhydride, solid camphenes $[\alpha]_D + 25.25$ and $+49.33$ were obtained respectively. The rotatory powers of camphenes thus formed were seen to be influenced both by the time and temperature of reaction. And, in order to find out the cause of this change in the rotatory power of camphene, active camphene was directly treated with alumina, phthalic anhydride, hydrochloric acid, $\text{H}_2\text{SO}_4 \cdot 3\text{H}_2\text{O}$, 50% H_2SO_4 and acetic acid, and in each case the rotatory power decreased gradually and it was recognised that the velocity of racemisation was affected not only by the time and temperature of reaction but also by the kind, concentration, and quantity of the acid itself. When bornyl acetate was set to reaction of $\text{H}_2\text{SO}_4 \cdot 3\text{H}_2\text{O}$ for 10 hours at 140–145°C, both isomerisation and dehydration occurred and 0.5 mol % isobornyl acetate and 3 mol % camphene were obtained; again when treated under the same conditions, 75 mol % isobornyl acetate

(18) Sendrens, *Compt. rend.*, **154** (1912), 1168; *ibid.*, **177** (1923), 1183.

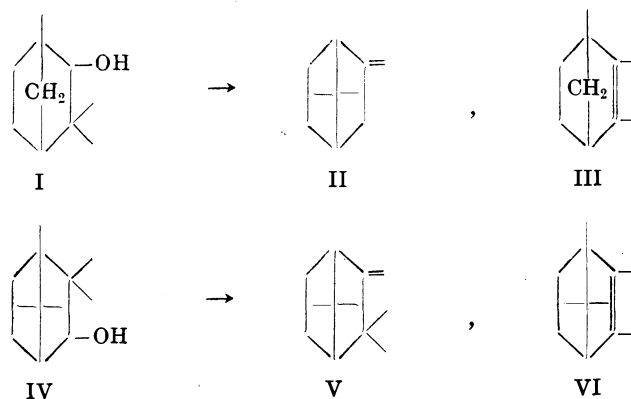
(19) Tetsusaku Ikeda, *J. Chem. Soc. Japan*, **48** (1927), 491.

(20) Gulbew, *Chem. Zentr.*, **1913**, I, 24.

(21) Bouchardat and Lafont, *Bull. soc. chim.*, [3] **11**, 902.

changed into camphene. Camphene in acetic acid solution changed as much as 50 mol % into isoboryl acetate, when treated under the same conditions.

Some time ago, Toivonen and Tikkanen⁽²²⁾ obtained a mixture of α -fenchene (II) and methylsantane (III) by dehydrating fenchyl alcohol (I) with aluminium phosphate. Hence, it is suspected that the hydrocarbons obtained by dehydrating dimethylborneol (IV), which has a chemical constitution similar to that of fenchyl alcohol, may be camphene form (V) and bornylene form (VI), as will be shown below:



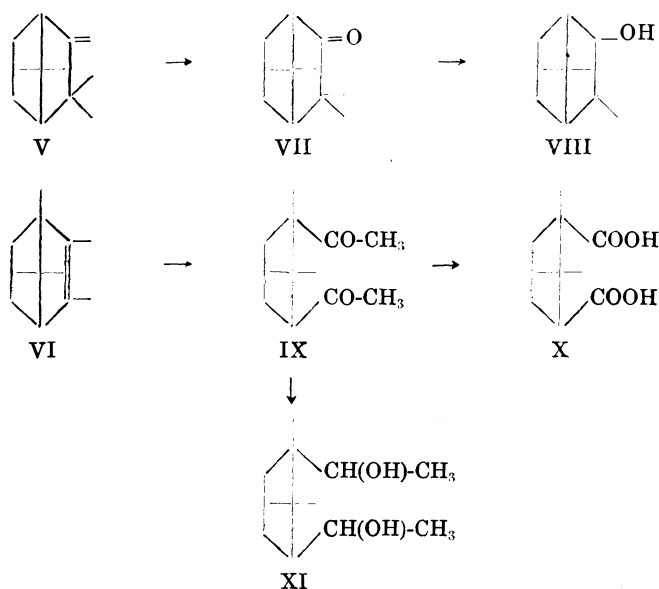
When dimethylborneol was heated with $\text{H}_2\text{SO}_4 \cdot 3\text{H}_2\text{O}$ at $140\sim 145^\circ\text{C}$ for over 10 hours, a mixture of hydrocarbons (B.p. $48\sim 82^\circ/5\text{ mm.}$) was obtained, the yield being 71%. When dehydrated with phosphorus pentoxide, a single hydrocarbon (VI) (b.p. $192\sim 193^\circ\text{C}$, $d_4^{25} 0.8754$, $n_D^{25} 1.4765$, $[\alpha]_D^{19} -5.76^\circ$) was obtained; and when dehydrated with phthalic anhydride, a product to be suspected as a mixture of hydrocarbons was obtained, but as the sample was too scanty, further study could not be executed. The hydrocarbons obtained by dehydrating with $\text{H}_2\text{SO}_4 \cdot 3\text{H}_2\text{O}$ were most probably a mixture of two hydrocarbons; but as it was impossible to separate it into its components even after eight fractional distillations, the writer tried anew to separate it in the form of oxidised compound, by submitting its chloroform solution to ozone oxidation. As its result, two compounds were obtained:

Subs.	B.p.	d_4^{25}	n_D^{25}	$[\alpha]_D$	Remarks
A	72-73/6 mm	0.9473	1.4712	$+27.06^\circ$ at 9°C	Colourless
B	120-123/6 mm	1.0087	1.4746	$- 6.87^\circ$	Yellowish green, viscous, easily decomposes during distillation.

Substance A, as it forms semicarbazone (M.p. $243.6\sim 243.9^\circ\text{C}$), and gives a product to be considered as alcohol VIII (B.p. $82\sim 86^\circ/5\text{ mm.}$, d_4^{25}

(22) *Chem. Zentr.*, 1931, II, 2150.

0.9581, n_D^{25} 1.4831, $[\alpha]_D^{+1.5}$) when reduced with metallic sodium and alcohol, might be a monoketone (further confirmation was desirable, but as the sample run short we postponed it to the future.) Substance B was inferred to be a diketone (IX), as it is changed to camphoric acid (X) by the oxidation with nitric acid of sp. gr. 1.29 or by decomposition during distillation, and also as it gives three kinds of what may be considered as glycol isomers (XI) when reduced with metallic sodium and alcohol. The reactions are shown by the following scheme:



In addition, when the mixture of hydrocarbons was oxidised with ozone in a solution of benzene, the following substance of the physical constants, to be considered as a dextro-rotatory diketone, was obtained.

B.p. 112–114°/4 mm	d_4^{25} 1.0166	n_D^{25} 1.4749	$[\alpha]_D^{+38.91^\circ}$

The content of the A- and B-compounds in the product of ozone oxidation was determined to be in the proportion of 43:57. Borneol and isoborneol, when dehydrated, give chiefly camphene alone; while dimethyl-borneol, a substitution product of methyl radical in place of α -hydrogen, forms hydrocarbons of both camphene and bornylene forms after dehydration.

(4) **Hydration of Camphene.** Camphene, by the hydration with a mixture of 50% H_2SO_4 and glacial acetic acid, gives in addition to isoborneol about 10% of borneol. Camphene $[\alpha]_D^{+72.69^\circ}$, obtained by the process of A. Reychler,⁽²³⁾ was hydrated with 50% sulphuric acid and glacial acetic acid for 1/3 hour, and there was formed isoborneol $[\alpha]_D^{+10.56^\circ}$. During this reaction, as the time of reaction was prolonged, the

(23) A. Reychler, *Ber.*, **29** (1896), 696.

rotatory power decreased gradually; and after the elapse of 110 hours the isoborneol obtained was quite inactive.

Camphene $[\alpha]_D + 8.28^\circ$ when treated separately with 50% sulphuric acid and glacial acetic acid, gave camphene of $[\alpha]_D + 5.20^\circ$ in the former case and of $[\alpha]_D + 6.22^\circ$ in the latter; while isoborneol $[\alpha]_D \pm 0^\circ$ was formed when treated with the mixture of the two acids. Further, isobornyl acetate $[\alpha]_D - 47.81^\circ$ was treated with 50% sulphuric acid, glacial acetic acid, and their mixture. When each of the acids was used separately, no appreciable change in the rotatory power of the ester was seen although the reaction was continued for 3 hours; however, when the acid mixture was used, even after the reaction of only 1/3 hour, there was seen appreciable change in the rotatory power of the ester, and the longer the time of reaction, the more remarkable was the change.

Conclusion.

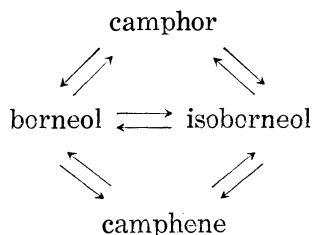
Camphor, when reduced, forms borneol and isoborneol, and both of them change into camphor when oxidised. Camphor and epicamphor form mainly borneol and alcohol of borneol type respectively when reduced with metallic sodium and alcohol, and mainly isomeric alcohol corresponding to it when reduced with metallic catalyser and hydrogen, while nor-camphor in these cases gives constantly alcohol of isoborneol type as a main product. On the other hand, dimethylcamphor always forms alcohol of borneol type as a reduction product due to the asymmetric synthesis.⁽²⁴⁾

Vavon⁽²⁵⁾ has inferred that by the reduction of camphor, isoborneol is formed, which is soon transformed into borneol. This inference of Vavon that isoborneol is transformed into borneol was confirmed by the writer's experiment, and it was also recognized, conversely, that borneol may be transformed into isoborneol. This fact that isoborneol is as well transformed to borneol as it is formed from borneol, is also explained by the result of determination of the heats of combustion of both of these compounds. However, from these values of heat of combustion, it will be considered that borneol 1489.3 Kcal is at first formed which changes into isoborneol 1472.5 Kcal. The proportion of diastereoisomers of alcohol thus formed by the reduction of camphor depends on the mobility of hydrogen in α -position caused by the process and condition of the reduction. It was observed that the velocity of the isomeric change was greatly influenced in the presence of alcohol. The intramolecular change between borneol and isoborneol was also seen, when their acetates were treated with sulphuric acid. Although borneol which was considered very difficult to convert into camphene, the transformation was easily effected by using dehydrating agent such as alumina or $\text{H}_2\text{SO}_4 \cdot 3\text{H}_2\text{O}$. Bornyl acetate forms camphene as well as isobornyl acetate by the action of $\text{H}_2\text{SO}_4 \cdot 3\text{H}_2\text{O}$, and it is an interesting phenomenon that dimethylborneol, when dehydrated, forms hydrocarbons of not only the camphene form but also the bornylene form.

(24) J. H. Van't Hoff, *Die Lagerung d. Atome in Raum*, 1894, 30.

(25) Vavon and Peignier, *Bull. soc. chim.*, [4] **39** (1926), 666, 924.

When camphene is treated with 50% H_2SO_4 and glacial acetic acid, borneol as well as isoborneol is formed. Therefore, it is supposed⁽²⁶⁾ that there is the following chemical relation between camphor, borneol, isoborneol, and camphene.



The fact that in the course of the dehydration of borneol and isoborneol inactive camphene was formed, was explained by some investigators⁽²⁷⁾ that when borneol and isoborneol are changed to camphene, an isomer, named camphene hydrate, is formed which converts itself to the racemic compound. That, during the change from camphene to isoborneol by hydration, camphene hydrate is formed as an intermediate product is quite acceptable, but with regard to the racemisation of camphene hydrate, it is rather inconceivable from the standpoint of stereochemistry and only a future investigation will explain it. (*To be continued*).

(26) cf. Meerwein and Van Ernster, *Ber.*, **53** (1920), 1815; *ibid.*, **55** (1922), 2500.

(27) J. Bredt, *J. prakt. Chem.*, **131** (1931), 137; J. Houben and E. Pfankuch, *Ann.*, **489** (1931), 193.

On the Catalytic Action of Japanese Acid Earth. XI*. The Isomerisation of Aldehydes to Ketones and the Explanation of the Migration of the Radicals from the Standpoint of the Electronic Theory.

By Koshiro ISHIMURA.

(Received May 14, 1941.)

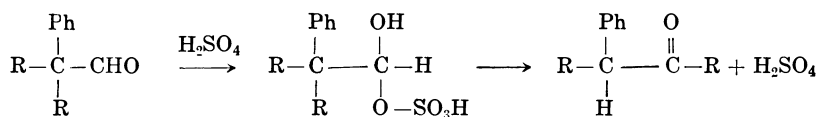
Introduction. S. Daniloff⁽¹⁾ first observed that di- or trisubstituted acetaldehydes are partly transformed into the corresponding ketones, when warmed with acidic substances such as dilute sulphuric acid or a mixture of hydrochloric and acetic acids, or when treated with phosphorus pentachloride at ordinary temperature, while they are completely changed

* X., this Bulletin, **10** (1935), 1

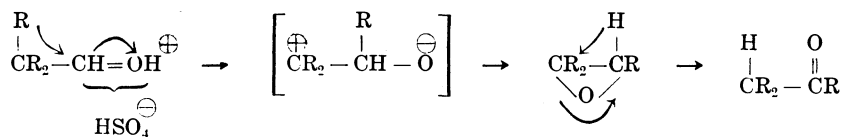
(1) *J. Russ. Phys. Chem. Soc.*, **49** (1917), 282; *ibid.*, **51** (1919), 97; *ibid.*, **57** (1925), 428; *Ber.*, **59** (1926), 377; *ibid.*, **60** (1927), 2390; S. Daniloff and E. Venus Danilova, *Ber.*, **59** (1926), 1032; *ibid.*, **60** (1927), 1050; *ibid.*, **62** (1929), 2653; *ibid.*, **63** (1930), 2269, 2765; E. Venus Danilova, *Ber.*, **61** (1928), 1954.

into ketones by the action of concentrated sulphuric acid at about -10°C . The oximes of the aldehydes also yield ketones on heating with dilute sulphuric acid, but in this case the reaction product contains a certain quantity of the original aldehydes. Similar facts were observed by A. Orekhoff and M. Tiffeneau.⁽²⁾ Later M. Tiffeneau⁽³⁾ has studied extensively with his collaborators along this line, aiming to explain the relation between the "migratory tendency" and "capacity of affinity" of various organic radicals. They seem to hold the view that the migratory tendency as well as the capacity of affinity of organic radicals is a certain definite property of each radical and they concluded that a parallel relation does not always exist between these two properties. M. Migita⁽⁴⁾ studied the pinacolinic rearrangement as a method of determining the relative electronegativities of organic radicals. He explained lucidly the facts observed by himself and others from the standpoint of the electronic theory of valency, which have previously been regarded apparently contradictory and not interpreted satisfactorily.

It appears, as J. W. Baker⁽⁵⁾ suggested, that the rearrangement of the aldehydes mentioned above results from the actual interaction between the aldehydes and the strong acidic substances, giving rise to certain intermediate compounds, which are subsequently decomposed into the ketones isomeric to the original aldehydes. Thus in the presence of sulphuric acid the initial stage of the isomerisation may be the addition of a molecule of sulphuric acid to the aldehyde and the resulting sulphuric ester of the glycol may then undergo an ordinary pinacolinic rearrangement so as to give the ketones.



Another explanation was given by C. W. Shoppee⁽⁶⁾ who suggested that sulphuric acid may function in the conversion of the carbonyl oxygen into the type of an oxonium salt, the attraction of positive charge so formed initiating the necessary electronic displacements resulting in the formation of an ethylene oxide, which then undergo a further pinacolinic change.



Different mode of combination may be possible, however, between aldehydes and the acidic reagents according to the nature of the latter.

(2) *Compt. rend.*, **182** (1926), 67.

(3) *Bull. soc. chim.*, **49** (1931), 1595-1860 (twenty-two papers).

(4) *This Bulletin*, **3** (1928), 308; *ibid.*, **4** (1929), 57, 225; *ibid.*, **7** (1932), 334, 341, 377, 382; *ibid.*, **8** (1933), 22, 27.

(5) Baker, "Tautomerism", (1934), 292.

(6) Thesis, London, 1929; (Baker, "Tautomerism", 1934, 292).

Consequently the intermediate compounds thus formed may have different intramolecular structures and show different chemical behaviours. It is clear that the subsequent decomposition of such an intermediate compound may take a different course giving rise sometimes to one and sometimes to other ketone, isomeric to each other, depending on the reagent as well as on the experimental conditions.

There is another type of reaction leading to the same isomerisation, i.e., isomerisation by thermal effect in the presence of catalysts. It was observed for the first time by Ramart-Lucas⁽⁷⁾ and her collaborators. They distilled polysubstituted ethylene glycols, ethylene oxides and acetaldehydes over diatomaceous earth at different temperatures ranging from 200 to 600°C. under the reduced pressure of about 10 mm., and obtained various types of ketone, aldehyde, and hydrocarbon. The kinds and structures of these reaction products were found to depend chiefly upon the reaction temperature. They used the ultraviolet absorption spectra of these compounds for the study of the molecular rearrangement, and found that the "ascending branch" of the absorption curve of the more stable substance lies always nearer to the visible part than that of the less stable, when a rearrangement of a less stable substance into a more stable one takes place, preceded or followed by the elimination of a molecule of water, acid or salt. Thus the "ascending branch" of the absorption curve of glycol is placed farthest and that of the corresponding ketone nearest to the visible part, while that of aldehyde lies in an intermediate position; and hydrocarbon of the related structure, if produced, will exhibit its absorption curve with an "ascending branch" lying nearest to the visible part. Of the two isomeric ketones the one more stable at higher temperature always shows deeper absorption than the less stable. Thus it is a natural course, according to their opinion, that glycols are converted by thermal effect successively into aldehydes, ketones, and hydrocarbons. They further supposed that the study of the absorption spectra in the ultraviolet region would, therefore, enable them to predict which ketone will be produced from a certain aldehyde when there is a possibility of obtaining two isomeric ketones. No actual example of isomerisation of this type was, however, given by them so far as the author knows.

S. Daniloff⁽⁸⁾ also observed the same type of isomerisation in the cases of substituted acetaldehydes, which were easily transformed into the isomeric ketones by thermal effect; thus by passing aldehydes over anhydrous aluminium sulphate heated at about 350°C. he obtained ketones isomeric to the aldehydes, and reasonably remarked⁽⁹⁾ that it is natural that the less stable aldehydes may isomerise into the more stable ketones, that is to say, a substance with greater heat of combustion isomerises into that with the smaller.

In the present research a number of disubstituted acetaldehydes have been newly synthesised and subjected to isomerisation into the corresponding ketones in order to find which ketone of the two possible isomers

(7) *Compt. rend.*, **186** (1928), 1301; *ibid.*, **186** (1928), 1626, 1848; *ibid.*, **188** (1929), 638, 1301; *Bull. soc. chim.*, **45** (1929), 478, 718; *ibid.*, **49** (1931), 1860.

(8) *J. Russ. Phys. Chem. Soc.*, **62** (1929), 723.

(9) *Ber.*, **60** (1927), 1056.

will thereby be produced, and the results have been explained from the standpoint of the electronic theory of organic compounds.

The isomerisation was carried out in the presence of Japanese acid earth. Its catalytic action at high temperatures has already been investigated by Dr. H. Inoue and the present author⁽¹⁰⁾ on various organic compounds, and has been shown to be far stronger than those of alumina and silica, the chief components of the acid earth. It was also confirmed by the present author* that the existence of water in addition to the two components is indispensable for the characteristic catalytic action of the earth, and was suggested that these three components must be suitably oriented on the surface of the earth in order to form the catalytically "active centres." When a molecule of an organic compound is adsorbed on the "active centre" thus formed, it must also be oriented suitably on this centre in order to get activated. The interatomic bonds of a molecule thus adsorbed on an active centre, will consequently be weakened and the atoms will rearrange themselves within the molecule so as to gain a more stable structure, leading to the observed transformation.

Experimental Procedure. *Conditions of the Experiment and Manipulation.* The middle part converging 33 cm. of a Jena glass tube with an inner diameter of 1.5 cm. was filled with granules of Japanese acid earth with diameters from 1.5 to 3.0 mm.. The tube was heated at 300°C. and maintained at that temperature during the experiment in a horizontal electric furnace slightly inclined, and then the aldehyde was passed into it drop by drop with a rate from 3 to 4 g. per hour. A slow flow of carbon dioxide through the tube served to prevent the oxidation of the aldehyde by atmospheric oxygen and to carry away the reaction products. A receiver connected with the end of the tube was cooled with ice water to collect the reaction products. When all of the aldehyde was passed in and no more reaction product (i) was observed to come out of the tube, the receiver was changed and the whole reaction system was evacuated, the temperature being maintained at 300°C. meanwhile, and some more product (ii) was obtained. The receiver was again changed and the temperature was raised to 350°C. under the reduced pressure and a further portion of the product (iii) was obtained. The product (i) usually consisted of an easily flowing colourless liquid (mainly hydrocarbon) mixed with water drops, while the products (ii) and (iii) were for the most part colourless or yellowish fragrant viscous oils which solidified on cooling to crystalline masses. In some cases the temperature of the reaction tube was finally raised to 450°C. under the reduced pressure and a reddish brown viscous oil mixed with a small quantity of crystals was obtained. Each product was separately subjected to suitable treatments to isolate and identify the individual substances contained in it, and to estimate their relative quantities.

Confirmation and Analysis of the Reaction Products. In every case no trace of the aldehyde unchanged was found to exist in the reaction

(10) H. Inoue, this Bulletin, **1** (1926), 157, 177, 197, 219; H. Inoue and K. Ishimura, *ibid.*, **9** (1934), 423, 431; K. Ishimura, *ibid.*, **9** (1934), 493, 522; *ibid.*, **10** (1935), 1.

* *Loc. cit.*

products. The ketones produced by the isomerisation were mostly obtained as solid crystalline mass. Their constitutions were confirmed by the Beckmann rearrangement of their oximes on one hand and by synthesis on the other, as described below.

When two isomeric ketones were formed simultaneously by the isomerisation of one aldehyde, the exact analysis of the experimental results became sometimes very difficult, for the isolation of both the ketones followed by the estimation of their relative quantities was not an easy work. A simple thermal analysis carried out beforehand proved very useful in such cases. Equilibrium diagrams of the systems of phenyl-*p*-methylbenzyl ketone and *p*-tolylbenzyl ketone and of *p*-chlorophenyl-*p*-methylbenzyl ketone and *p*-tolyl-*p*-chlorobenzyl ketone were drawn, which much helped to determine the compositions of the reaction mixtures. Rheinboldt's method⁽¹¹⁾ was modified for this purpose; definite quantities of the two compounds synthesised and purified by appropriate methods were intimately mixed, molten, crushed and pulverised after cooling and put in small capillaries of about 40 mm. in length and from 1 to 2 mm. in diameter. The determination of the thawing as well as melting points was carried out in the same manner as the molecular weight determination by Rast's method. Reliable results were obtained as well without stirring the content of the capillary with a slender glass rod inserted into it, as proposed by Rheinboldt. Thus a very small quantity of materials was enough to complete one series of experiment and the time required for the determination was considerably shortened.

As shown in Fig. 1 and 2 it has been found by the author that a eutectic point exists in the system of phenyl-*p*-methylbenzyl ketone and

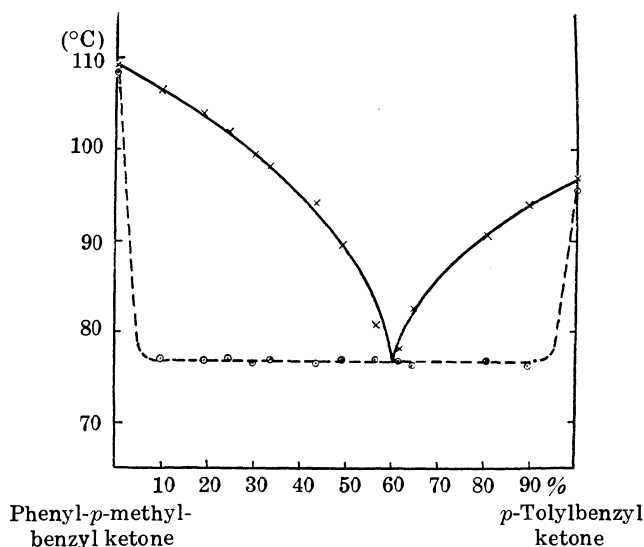


Fig. 1. Equilibrium diagram of the system: phenyl *p*-methylbenzyl ketone and *p*-tolylbenzyl ketone.

(11) *J. prakt. Chem.*, [2] **111** (1925), 242; *ibid.*, **112** (1926), 187; *ibid.*, **113** (1926), 199. Pfeiffer, "Organische Molekülverbindungen", (1927) 66-85.

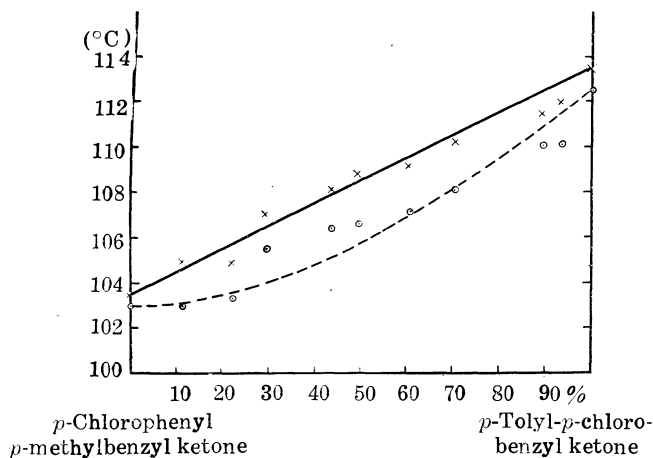
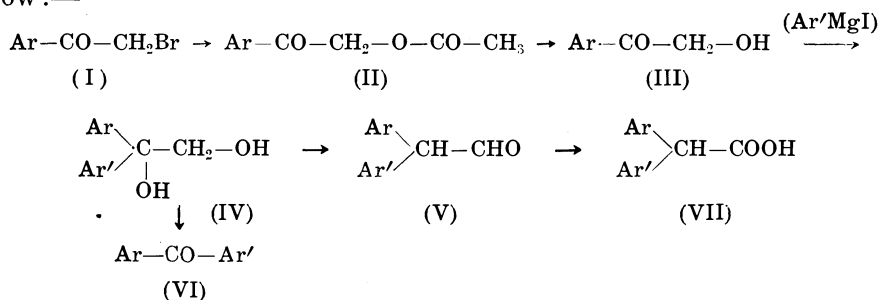


Fig. 2. Equilibrium diagram of the system: *p*-chlorophenyl-*p*-methylbenzyl ketone and *p*-tolyl-*p*-chlorobenzyl ketone.

p-tolylbenzyl ketone, while in that of *p*-chlorophenyl-*p*-methylbenzyl ketone and *p*-tolyl-*p*-chlorobenzyl ketone a diagram characteristic to solid solution has been obtained.

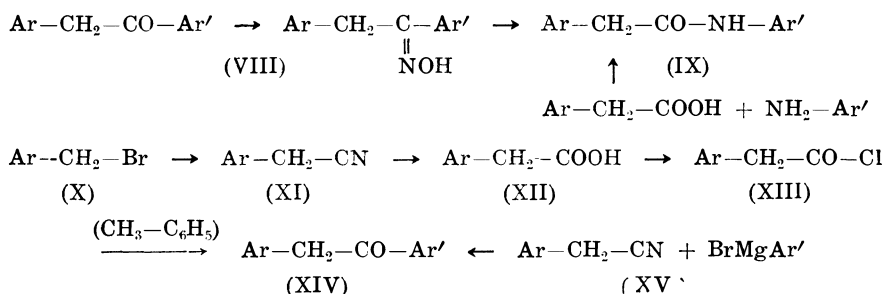
Materials and Products. The aldehydes employed in the present experiment were synthesised according to the general scheme shown below:—



ω -Bromacetophenone and ω -bromo-*p*-methylacetophenone (I) were interacted with potassium acetate in alcoholic solution giving the corresponding acetates (II), which on hydrolysis by boiling with barium carbonate were changed respectively to benzoyl carbinol and *p*-methylbenzoyl carbinol (III). By Grignard reaction with aryl magnesium iodide they gave α , α' -diaryethylene glycols (IV) which suffered intramolecular rearrangement accompanied by the splitting of a molecule of water, when heated at about 115°C. with crystalline oxalic acid mixed with a small quantity of water for three hours, or when heated at about 180°C. for several hours, with a mixture of water and a few drops of concentrated sulphuric acid in a sealed tube, resulting in the formation of the required aldehydes (V).

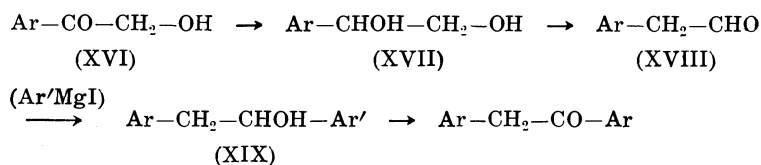
The constitutions of the glycols and the aldehydes were confirmed by oxidising them to diaryl ketones (VI) and diarylacetic acids (VII) respectively.

The ketones produced by the isomerisation of the aldehydes were identified by the Beckmann rearrangement of their oximes on one hand and by synthesis on the other, as schematically shown below:—



The oxime (VIII) of the ketone was dissolved in dry ether and phosphorus pentachloride was added little by little, and the reaction product was poured into ice water, and the solid mass separated was purified by recrystallisation from alcohol, which was identified with the product (IX) obtained by the interaction between arylacetic acid and arylamine.

Tolyl and xylyl bromides (X) were converted successively into cyanides (XI), carboxylic acids (XII) and acid chlorides (XIII) which were condensed with toluene in the presence of anhydrous aluminium chloride, thus the required ketone (XIV) were synthesised. The ketones were also obtained from arylacetoneitriles (XV) by the action of aryl magnesium iodide. A third method of obtaining the same ketone is the oxidation of diarylcarbinol (XIX) produced from arylacetaldehyde (XVIII) by the Grignard reaction, which was in its turn produced by heating aryethylene glycol (XVII) at about 180°C for four hours in a sealed tube with water and a few drops of concentrated hydrochloric acid.



The aryethylene glycol (XVII) was obtained by the catalytic hydrogenation of aroylcarbinol (XVI) under the ordinary pressure with colloidal platinum as catalyst.

Purification of m-Tolyl-p-Tolyl Acetaldehyde. It has been observed by the present author that a large quantity of *m*-tolyl-*p*-tolyl ketone was sometimes produced when the purification of *m*-tolyl-*p*-tolyl acetaldehyde was carried out through its addition compound with sodium bisulphite or when it was oxidised to the corresponding acid with moist silver oxide. Similar facts have been also observed in the case of *p*-tolyl-*p*-chlorophenyl acetaldehyde. The mechanism of the reaction is for the time left open. F. W. Semmler⁽¹²⁾ observed that enolacetates of aldehydes of the types

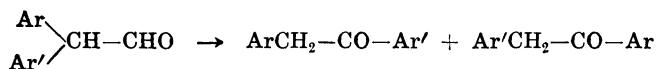
(12) *Ber.*, **42** (1909), 588, 962; *ibid.*, **43** (1910), 1724, 1890.

RCH_2CHO and $RRCHCHO$ are changed to the acid RCO_2H and the ketone $RCOR$ respectively when oxidised with ozone or permanganate.

Separation of o- and p-Isomers of Xylyl Derivatives. As the starting materials for the synthesis of ketones of the type $ArCH_2COAr'$ the three isomers of xylene were used as mentioned above (p. 202), each of which usually contains small quantities of its isomers as impurities. According to P. Hill and W. F. Short⁽¹³⁾ the pairs of *o*- and *p*-isomers of xylyl chlorides, alcohols, acetates as well as cyanides boil at the same temperature and cannot be separated by fractional distillation, whilst *o*- and *p*-tolylacetic acids form a continuous series of solid solutions. On the contrary, the present author has found that the corresponding acid amides can be easily separated from each other by fractional crystallisation from boiling water and the purification of the related substances was always carried out quite well at this stage of preparation.

Autoxidation of Ketones of the Type $ArCH_2COAr'$. The ketones of the type $ArCH_2COAr'$ such as *o*-tolyl-*p*-methylbenzyl, *m*-tolyl-*p*-methylbenzyl, *p*-chlorophenyl-*p*-methylbenzyl and *p*-tolyl-*p*-chlorobenzyl ketones have been found to be converted largely into the mixtures of the corresponding arylacetic acids, on standing in the presence of light and air for several months. Similar facts were observed by E. C. Fortey⁽¹⁴⁾ and by S. S. Jenkins.⁽¹⁵⁾

Results of Isomerisation Experiments. Four diarylacetaldehydes were employed in the present work. They were subjected to the intramolecular rearrangement in the presence of Japanese acid earth under the conditions stated above and all gave the corresponding ketones.



(1) Phenyl-*p*-tolyl acetaldehyde has given phenyl-*p*-methylbenzyl ketone exclusively, in other words, only the phenyl group has migrated.

(2) *m*-Tolyl-*p*-tolyl acetaldehyde has given *m*-tolyl-*p*-methylbenzyl ketone exclusively, that is only the *m*-tolyl group has migrated.

(3) *o*-Tolyl-*p*-tolyl acetaldehyde has given a mixture of *o*-tolyl-*p*-methylbenzyl and *p*-tolyl-*o*-methylbenzyl ketones. The ratio of the yield in the former ketone to that in the latter was found to be about 4:1, showing that in this case the *o*-tolyl group has a migratory tendency about four times as large as that of the *p*-tolyl group.

(4) *p*-Tolyl-*p*-chlorophenyl acetaldehyde has been changed mainly to *p*-chlorophenyl-*p*-methylbenzyl ketone accompanied by a small quantity (about one tenth of the foregoing ketone) of *p*-tolyl-*p*-chlorobenzyl ketone, showing that the *p*-chlorophenyl group has a very large migratory tendency in comparison with the *p*-tolyl group in this case.

Thus these results clearly show that the order of the migratory tendency of the aryl groups is as follows:—

Phenyl, *m*-tolyl > *p*-chlorophenyl > *o*-tolyl > *p*-tolyl.

(13) *J. Chem. Soc.*, **1935**, 1126.

(14) *J. Chem. Soc.*, **75** (1899), 871.

(15) *J. Am. Chem. Soc.*, **57** (1935), 2733.

Discussion of the Results. *Nature of the Catalyst in the Isomerisation.* Japanese acid earth employed as catalyst in the present experiment is a kind of clay abundantly produced in many districts in Japan. It resembles Fuller's earth and Florida earth in many respects and is essentially a certain type of hydrated aluminium silicate mixed with colloidal silica⁽¹⁶⁾ and small amounts of many other metallic oxides. Its average composition is as follows:—

SiO₂, 60–72; Al₂O₃, 13–20; Fe₂O₃, 2–4; CaO, 0.5–2; MgO, 1–5; K₂O+Na₂O, 0.5–1.8; ignition loss, 7–15%.

The earth is designated "acid" because it turns a blue litmus paper red when placed on the paper and moistened with a few drops of water. But the colour change is restricted only to the neighbourhood of that part of the paper which is directly in contact with the earth. This phenomenon was explained as due to its characteristic selective adsorptive power for hydroxyl ion.⁽¹⁷⁾ The earth also manifests various oxydase-like colour reactions, e.g. the reactions for indophenol, potassium iodide, leuco-base of malachite green and benzidine.⁽¹⁸⁾ When suspended in the water solution of pyrogallol the earth oxidizes it gradually.⁽¹⁹⁾ Cane sugar and starch are hydrolysed into invert sugar⁽²⁰⁾ and maltose⁽²¹⁾ respectively, when their water solutions are shaken with the earth. All these reactions also, the author believes, may be ascribed to the hydrogen ion generated as the result of the selective adsorption mentioned above.

In dry state, especially when dehydrated at 200–300°C., the earth adsorbes ammonia, vapours of water, alcohols, ketones, ethers, etc.. The adsorption of these vapours takes place very strongly, sometimes with the evolution of considerable quantity of heat, the adsorbates being retained tenaciously on it.⁽²²⁾ At high temperature, water or ammonia is eliminated from the organic adsorbates when the organic molecules contain hydroxyl or amino group, and the dehydration or deamination is accompanied very often by intramolecular rearrangements. Thus cyclohexanol and their methyl derivatives have been found to produce cyclohexene and its methyl derivatives together with methylcyclopentane and dimethylcyclopentanes respectively,⁽²³⁾ when passed on the earth heated at 300–350°C. Cyclohexylamine and its methyl derivatives have similarly given cyclopentane series,⁽²⁴⁾ showing that the six-membered carbon ring was converted into the five-membered one.

The elimination of water or ammonia may be induced by the initial attraction of hydroxyl or amino group towards the earth, and these negative groups tend to be ionized and will be splitted as anions. If the remain-

(16) K. Yamamoto, *J. Soc. Chem. Ind. Japan*, **34** (1931), 244B; *ibid.*, **36** (1933), 38B, 460B.

(17) Y. Tanaka and T. Kuwata, *J. Soc. Chem. Ind. Japan*, **32** (1929), 290B; Y. Tanaka, T. Kuwata and S. Furuta, *ibid.*, **35** (1932), 224B.

(18) K. Kobayashi and K. Yamamoto, *ibid.*, **26** (1923), 23B.

(19) H. Kaneko, *J. Chem. Soc. Japan*, **45** (1924), 189.

(20) T. Okuno, *J. Soc. Chem. Ind. Japan*, **28** (1925), 54B.

(21) B. Kato, *J. Zymurgy* (in Japanese), **2** (1924), 1023.

(22) K. Ishimura, *this Bulletin*, **10** (1935), 2.

(23) H. Inoue, *loc. cit.*

(24) K. Ishimura, *loc. cit.*

anion is very unstable, and one of the aryl groups, therefore, will be separated. Which of the two aryl groups, then, will be separated first is, determined by the magnitude of their capacity for electron-attraction; the more electron-attracting group will more easily be separated. When the capacities for electron-attraction of the two groups are not greatly different, there is the possibility of the simultaneous separation of the two groups, giving rise to a mixture of two isomeric ketones, their relative yields depending upon the relative capacity for electron-attraction of the migrating groups.

If the proton and the anion thus successively separated pass outside the force field of the rearranging molecule, they may combine directly to give rise to the formation of hydrocarbons. Thus benzene and toluene have been actually confirmed to exist in the reaction products of the present experiment in considerable quantities.

According to J. W. Baker's⁽²⁸⁾ opinion the initial stage of the rearrangement of the aldehyde by the action of sulphuric acid is possibly the addition of a molecule of the acid to the aldehyde and the sulphuric acid ester of the glycol so formed may then undergo an ordinary pinacolinic electron displacement with hydrogen migration to give the ketone. C. W. Shoppee⁽²⁸⁾ has explained the conversion, as above stated, by assuming the intermediate formation of an ethylene oxide. But in the case of the present work the mechanism involving the actual formation of either glycol or ethylene oxide as intermediates seems untenable. R. Lagrave⁽²⁹⁾ distilled under the reduced pressure a series of ethylene

oxides of the general formula $(\text{Ph})_2\overset{\text{O}}{\underset{\text{O}}{\text{C}}}-\text{CHR}$ and obtained as the major product the ketone $(\text{Ph})_2\text{CH}-\text{CO}-\text{R}$ but found that the considerable quantity of the aldehyde $(\text{Ph})_2\text{CR}-\text{CHO}$ was also produced, where Ph and R represent phenyl and alkyl groups respectively. Therefore, if the transformation of an aldehyde into an isomeric ketone be effected through the intermediate formation of an ethylene oxide, there should exist an equilibrium between the aldehyde and the ethylene oxide under such conditions. No trace of either aldehyde or ethylene oxide, however, was found in the reaction product.

The experimental results obtained by Ramart-Lucas and Jean-Pierre Guerlain⁽³⁰⁾ are in good accordance with those of the present experiment. They passed aldehyde of the type ArRCHCHO over diatomaceous earth heated at 500–600°C. as above stated and obtained ketones of the type ArCH_2COR as the main product together with some quantity of the unchanged original aldehydes. It is natural in the light of the consideration above given that the alkyl group R migrates in preference to the aryl group Ar, since it has a smaller capacity for electron-release. The reaction temperature was, however, by far higher than in the case of the present experiment and yet there remained a portion of aldehyde unchanged. These facts may be explained by the weaker activity of the catalyst, in other words, by the smaller capacity for electron-attraction of diatomace-

(28) "Tautomerism", (1934), 292.

(29) *Ann. chim.*, [X], **8** (1927), 363.

(30) *Bull. soc. chim.*, **45** (1929), 478, 718; *ibid.*, **49** (1931), 1860.

ous earth in comparison with Japanese acid earth. The far weaker catalytic activity of the former than that of the latter has been shown by the present author⁽³¹⁾ by comparing the activity for producing β , β' -dinaphthyl from naphthalene.

Comparison of the Capacity for Electron-release of the o- and p-Tolyl Groups. As above stated, in the author's experiment, when diarylacet-aldehydes rearrange into the corresponding ketones, phenyl-, o-tolyl-, m-tolyl and p-chlorophenyl radicals migrate in preference to the p-tolyl radical, showing that the last mentioned possesses the greatest capacity for electron-release.

Since the methyl group tends to produce an effect of electron-release relative to hydrogen, when it is attached to the benzene nucleus, it loses electrons to the ring; they go mainly to the ortho and para carbon atoms. This capacity of the methyl group to repel electrons has been regarded as due to its inductive effect only and the tautomeric effect of the methyl group is inconceivable from the standpoint of ordinary organic chemical theory. J. W. Baker and W. S. Nathan⁽³²⁾ suggested, however, that the methyl group, when directly attached to a conjugated system, is capable of permitting electron-release by a mechanism which is assumed to function in addition to the inductive effect and in essentials is of the type of tautomeric effect $\text{H}-\text{CH}_2-\text{C}=\text{C}-\text{C}-$ much as if the electrons were unshared as in chlorine. The inductive effect of the methyl group will thus be greatly reinforced. By applying the new idea the English authors gave a satisfactory explanation to various points till then obscure in organic chemistry and found furthermore, together with C. W. Shoppee,⁽³³⁾ that the new postulated mechanism is of not an electromeric but of a mesomeric (permanent) type. The definite demonstration of the reality of the tautomeric electron displacements of the electrons of nonionizing CH_2 -groups was then made by the study of E. D. Hughes, C. K. Ingold, N. A. Taher and L. C. Bateman.⁽³⁴⁾ Recently Y. Tsuzuki, T. Uemura and N. Hirasawa⁽³⁵⁾ found that the absorption bands of o- and p-nitrosotoluenes are shifted to a longer wave length relative to that of nitrosobenzene. They ascribed the fact to the tautomeric but not inductive effect of the methyl group situated in the ortho and para positions with regard to nitroso group. They showed moreover that the methyl group in the para position exerts a much stronger effect than those in the ortho and meta positions. The results of the present work lead also to the same conclusion. Thus the o-tolyl group migrated to a larger degree than the p-tolyl group as already stated (p. 203). These results apparently contradict with the facts that in the aromatic substitution the methyl group appears to be more nearly ortho-orienting than any other.⁽³⁶⁾ It is tentatively suggested here that the smaller effect of the methyl in the ortho position or the greater ease with which the o-tolyl group separates as anion may be

(31) This Bulletin, **9** (1934), 498.

(32) *J. Chem. Soc.*, **1935**, 1844.

(33) *Ibid.*, **1935**, 1847.

(34) *J. Chem. Soc.*, **1940**, 949, and subsequent papers.

(35) *J. Chem., Soc., Japan*, **61** (1940), 1063.

(36) J. B. Rease, *Chem. Reviews*, **14** (1934), 77.

ascribed to the formation of hydrogen bond between hydrogen in the methyl and carbonyl (or nitroso) oxygen: it is very probable that an alkyl group can form a hydrogen bond, provided that an electron-donating atom is suitably placed with respect to it.

*Comparison of the *p*-Tolyl and *p*-Chlorophenyl Radicals.* A greater resistance of the *p*-tolyl (and *o*-tolyl) group to ionisation in comparison with the *p*-chlorophenyl group, indicated by its smaller tendency to migration, can be explained by taking into consideration the inductive effect (+I) in the methyl group as above visualised on one hand and the well known inductive effect (-I) in chlorine atom superimposed on the electromeric effect of the opposite sign (+T) on the other. The action of the electromeric effect (+T) in chlorine atom is diminished by the inductive effect of its own, if not totally suppressed, by the flow of electrons towards it from α -carbon atom.

Quite recently Y. Tsuzuki, T. Uemura and N. Hirasawa⁽³⁷⁾ reached to the conclusion that the *p*-tolyl group has a greater capacity for electron-release than the *p*-chlorophenyl group by studying the effect of para-substituents to shift the absorption band of nitrosobenzene to a longer wave length. Their results accord well with that of the present work.

*Comparison of the *m*-Tolyl and Phenyl Groups.* The methyl group in the meta position exhibits a simple inductive effect but not a mesomeric effect as in the cases of para and ortho derivatives. The *m*-tolyl group shows therefore a much smaller tendency to migration, as clearly shown by the non-existence of *p*-methylbenzyl-*m*-tolyl ketone in the reaction product.

The phenyl group is capable of drawing an electric charge of either sign ($\pm$), as generally admitted, by an electromeric electron displacements of either sign ($\pm T$), when promoted by the requirement of the system. In the present case it may easily be ionised by absorbing electrons which will flow from the adjacent *p*-tolyl group. Thus the greater separability and the subsequent migration of the phenyl group may be expected in preference to the *p*-tolyl group, which actually took place.

Though the actual comparison of the relative mobility of the phenyl and *m*-tolyl groups has not been made, it is very probable that the phenyl group would be separated to a greater degree than the *m*-tolyl group owing to the inductive effect of an electron-release of the methyl group on one hand and to the inherent dual electronic character of the phenyl on the other. (*To be continued*).

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(37) *Ber.*, **74** (1941), 616.

The Synthesis of 1,4-Diphenyl-1,4-di-*p*-tolylbutatriene and 1,4-Diphenyl-1,4-di-*p*-chlorophenylbutatriene.⁽¹⁾

By Osamu SIMAMURA.

(Received May 27, 1941.)

Kuhn and Wallenfels⁽²⁾ synthesized tetraphenylbutatriene, which had been obtained by Brand⁽³⁾ and by Salkind and Kruglow,⁽⁴⁾ by treating tetraphenylbutynediol with phosphorus diiodide and accomplished the preparation of tetraarylhexapentaenes from hexaarylhexadiyne-(2, 4)-diols by the same procedure and later by an improved method of reducing with chromous chloride in the presence of hydrogen chloride.⁽⁵⁾ The chemistry of these compounds, cumulenes, as Kuhn and Wallenfels call them, is of interest not only because of chemical behaviours which a system of cumulated double bonds displays. Extending van't Hoff's model which pictures double-bonded carbon atoms by two tetrahedra sharing one edge in common, Kuhn and Wallenfels suggested that asymmetrically substituted cumulenes with an odd number of double bonds such as $R_1R_2C=C=C=CR_3R_4$ should exist in cis and trans isomerides and those with an even number of double bonds should be resolved into optical antipodes. Although the syntheses of allene derivatives in enantiomorphic isomerides⁽⁶⁾ were verifications of van't Hoff's prediction, it may be questioned whether the model would be applicable as well to a system of many cumulated double bonds, in view of the electronic concept of valency and the mesomerism in a system of conjugated multiple bonds. A carbon atom which is bound to two neighbouring atoms by two double bonds is of the acetylene type in that it has as atomic orbitals involved in bond formation two derived from *sp*-hybridization⁽⁷⁾ lying in a straight line extending in the opposite directions and two *pπ* orbitals perpendicular to the former two, the former entering into σ bonds with σ orbitals and the latter into π bonds with *pπ* orbitals of the two adjacent atoms. Thus the molecular structure of cumulenes may be assumed to be such that the double-bonded carbon atoms lie in a single straight line just as is the case with carbon suboxide.⁽⁸⁾ Then, the question is to what extent the energy of the molecule depends upon the relative orientation of the substituents at one end with respect to those at the other end of the carbon atom chain. In the ethylenic linkage the single π bond makes the energy susceptible to the perturbation by the substituent groups yielding cis and trans positions of the substituents

(1) Presented on April 4, 1941, at the 63rd Annual Meeting of the Chemical Society of Japan in Tokyo.

(2) R. Kuhn and K. Wallenfels, *Ber.*, **71** (1938), 783.

(3) K. Brand, *ibid.*, **54** (1921), 1987.

(4) J. Salkind and K. Kruglow, *ibid.*, **61** (1928), 2306.

(5) R. Kuhn and K. Wallenfels, *ibid.*, **71** (1938), 1510.

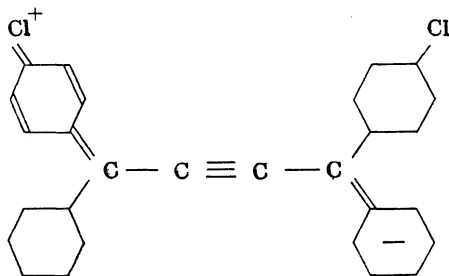
(6) P. Maitland and W. H. Mills, *Nature*, **135**, (1935) 994; *J. Chem. Soc.*, **1936**, 987; E. P. Kohler, J. T. Walker, and M. Tischler, *J. Am. Chem. Soc.*, **57** (1935), 1743.

(7) Cf. J. H. Van Vleck and A. Sherman, *Rev. Modern Phys.*, **7** (1935), 205.

(8) L. O. Brockway and L. Pauling, *Proc. Natl. Acad. Sci.*, **19** (1933), 860.

H. Boersch, *Monatsh.*, **65** (1935), 314.

as stable minima;⁽⁹⁾ but in cumulenes, two *p* orbitals of each carbon atom being involved in bond formation, the electronic density of the bonds in the middle part of the chain may presumably be more or less symmetric with respect to the rotation around the axis of the chain and the energy



less dependent on the relative orientation of the terminal groups. Further, the intense colour of cumulenes suggests⁽¹⁰⁾ a large contribution of dipolar mesomeric structures such as for example shown by the accompanying formula, and thus the double bonds acquire a single or a triple bond character considerably. It will be inferred from these considerations that the two pairs of terminal groups may rotate around the axis of the carbon atom chain with some freedom and may not be fixed in one plane contrary to the expectation from the van't Hoff model. With a view to settling this point experimentally a synthesis of cumulenes having a set of substituents which, according to the van't Hoff model, makes possible the existence of geometrical isomerides was undertaken.

The meso and racemic forms of 1,4-diphenyl-1,4-di-*p*-tolylbutynediol and 1,4-diphenyl-1,4-di-*p*-chlorophenylbutynediol were synthesized from acetylene dimagnesium bromide and *p*-methylbenzophenone and *p*-chlorobenzophenone respectively. Treatment with phosphorus diiodide converted these butynediols into desired 1,4-diphenyl-1,4-di-*p*-tolylbutatriene and 1,4-diphenyl-1,4-di-*p*-chlorophenylbutatriene. From both meso and racemic forms of each butynediol only one butatriene was obtained. If *cis* and *trans* isomerides were formed the synthetic procedure, which involved the use of phosphorus diiodide and hence the liberation of iodine in its course, may have caused the isomerization into the stabler form. By chromatographic analysis with activated alumina no identifiable compounds other than those described above were obtained. As it is a well established fact that the *trans* isomeride of ethylenic compounds is usually converted into the *cis* isomeride by irradiation with ultraviolet light, a benzene or petroleum ether solution of 1,4-diphenyl-1,4-di-*p*-tolylbutatriene was exposed to ultraviolet or sun light. It was found that decomposition of the compound took place and that when the decomposition was slight only the starting material was recovered by chromatographic separation.

Although the evidence obtained so far is not conclusive to decide between the two possibilities discussed above—which will be possible by dipole moment measurement—the synthesis may be worth reporting in

(9) E. Hückel, *Z. Physik*, **60** (1930), 423.

(10) L. Pauling, Gilman's "Organic Chemistry", 1888, New York (1938).

view of the attempted synthesis by Kuhn and Platzer,⁽¹¹⁾ who could obtain no asymmetrically substituted cumulenes in crystalline state by means of exactly the same procedure that proved successful in the case of symmetrically substituted ones.

Experimental.

1,4-Diphenyl-1,4-di-*p*-tolylbutynediols. To an ethyl magnesium bromide solution prepared from 2.4 g. of magnesium and 11 g. of ethyl bromide in 100 c.c. of ether dry acetylene was passed until no further increase of the viscous oily precipitate was observed. A solution of 15 g. of *p*-methylbenzophenone in 50 c.c. of ether was added to the acetylene dimagnesium bromide so prepared and the mixture was heated on a water bath with stirring for six hours. The reaction mixture was decomposed with dilute sulphuric acid and ice water. The ether layer was washed with aqueous sodium bicarbonate and after drying with anhydrous sodium sulphate the ether was evaporated. The remaining brown oil was brought to crystallization by rubbing with a small quantity of petroleum ether. Repeated crystallization from methanol effected the separation into two apparently pure crystalline products, one melting at 154–155.5° and the other at 145.5–151.5°, in the yields of 2.3 g. and 1.4 g. respectively. A mixture melted at 134–140°. They correspond to the theoretically expected meso and racemic forms of 1,4-diphenyl-1,4-di-*p*-tolylbutynediol. They effloresced on keeping and, as the presence of methanol of crystallization was suspected, they were recrystallized from benzene—petroleum ether mixture up to the melting points of 156–157° and 151.5° respectively. The di-*p*-chlorophenyl derivative described below was demonstrated to crystallize with one molecule of ethanol. Found for the higher melting butynediol: C, 85.9; H, 6.5; for the lower melting one: C, 86.3; H, 6.6. Calculated for C₃₀H₂₆O₂: C, 86.09; H, 6.20%.

Salkind and Martinsson⁽¹²⁾ reported the synthesis of 1,4-diphenyl-1,4-di-*p*-tolylbutynediol melting at 146°. It appears to have been a mixture of the two isomerides or, if it was crystallized from alcohol, the lower melting point may be attributed to alcohol of crystallization.

1,4-Diphenyl-1,4-di-*p*-tolylbutatriene. To a solution of 1 g. of the higher melting 1,4-diphenyl-1,4-di-*p*-tolylbutynediol in 15 c.c. of dry ether was added about 1 g. of phosphorus diiodide dissolved in carbon bisulphide. The colour of the solution grew darker and suddenly yellow needles precipitated. The mixture was shaken with an aqueous solution of sodium thiosulphate and sodium hydroxide, and the crystals were collected on a filter, washed with water, and dried in a vacuum desiccator. Repeated precipitation from a hot chloroform solution by adding methanol gave lemon yellow needles melting at 236° with decomposition, yield 23% of the theory. The lower melting butynediol yielded the identical product, the mixed melting point having not been depressed. The products were combined, recrystallized from chloroform—methanol and analyzed. Found: C, 94.1; H, 6.4. Calculated for C₃₀H₂₄: C, 93.71; H, 6.29%.

(11) R. Kuhn and G. Platzer, *Ber.*, **73** (1940), 1410.

(12) J. Salkind and E. E. Martinsson, *Chem. Zentr.*, **1938**, II, 3678.

1,4-Diphenyl-1,4-di-*p*-chlorophenylbutynediols. The synthetic procedure was the same as described above for the di-*p*-tolyl derivatives. Two isomerides corresponding to the meso and racemic forms were obtained, m.p. 133–134° and 148–148.5°. Found for the higher melting butynediol: C, 73.5; H, 4.5; Cl, 15.5; for the lower melting one: C, 73.0; H, 4.4; Cl, 15.4. Calculated for $C_{28}H_{20}O_2Cl_2$: C, 73.21; H, 4.39; Cl, 15.44%.

1,4-Diphenyl-1,4-di-*p*-chlorophenylbutatriene. On treatment with phosphorus diiodide in the same manner as described for the di-*p*-tolyl derivative the above butynediols gave in the yield of 13% of the theory the corresponding butatriene melting at 246–247° with decomposition, orange yellow needles. Found: C, 79.0; H, 4.5; Cl, 16.7. Calculated for $C_{28}H_{18}Cl_2$: C, 79.06; H, 4.27; Cl, 16.67%.

The author wishes to express sincere thanks to Prof. Y. Urushibara for his kind guidance and encouragement throughout this work.

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Physico-Chemical Investigations on Catalytic Mechanism. II. Note on The Fischer-Tropsch Synthesis of Hydrocarbons with Special Reference to its Reaction Mechanism.

By Senzo HAMAI.

(Received May 30, 1941.)

Introduction. With increasing demands for technological products, as well as from the theoretical interest in hydrocarbon chemistry in general, the synthesis of suitable hydrocarbons, especially in the line of fuel industry in the country where the sources of natural oil are lacking has become one of the most vital importance in the present time, especially, since the first publication of Fischer and Tropsch⁽¹⁾ was announced.

Fischer and his coworkers ever since have contributed much in establishing this into industrial scale, and besides many reports have been contributed from Professor Kita's laboratory in our country, but as far as its reaction kinetics and mechanism are concerned, the existing literatures is practically none, or at least very meagre.⁽²⁾

(1) *Ber.*, **56** (1923), 2428.

Brenn.-Chem., **4** (1923), 276, **5** (1924), 201 (Synthol); *Brenn.-Chem.*, **7** (1926), 97, 299; *Ber.*, **59** (1926), 830, 832, 923.

(2) (a) S. R. Craxford, *Trans. Faraday Soc.*, **35** (1939), 946.

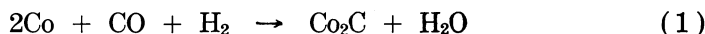
(b) E. F. G. Herington and L. A. Woodward. *Trans. Faraday Soc.*, **35** (1939), 958.

Considering such a status, we have undertaken some aspect of this investigation so as to discuss the reaction mechanism of Fischer-Tropsch synthesis of hydrocarbons and also to select good and suitable catalyst to proceed the above mentioned synthesis very effectively.

Especially the fact that the word "Catalysis" according to Schönbein, is a "Synonym" for ignorance, truly points out the exact status of the field of catalytic investigations; however, at present some noticeable progress has been made by various workers. We are not yet to be satisfied with the present condition, and we feel that there should be much done among experimentalists as well as theoreticians in this field of vital importance.

These in mind, we have carried out our experiments; the present purpose of this paper is to discuss briefly the various mechanisms so far proposed especially in reference to the recent papers of Craxford, of Herington and Woodward, and of Kodama in connection with our new mechanism recently proposed⁽³⁾ in detail.

According to Craxford^(2a), the primary step in this synthesis is the alternate formation and reduction of cobalt carbide to give CH_2 group, as:



and with the chemisorbed hydrogen, these methylene groups are being hydrogenated into CH_4 ; if the formation of carbide is more rapid than its reduction, there will be very little chemisorbed hydrogen on the surface, and the CH_2 group will link to form long chains. Furthermore, the products formed are broken off as long chains on the surface by the action of the chemisorbed hydrogen. When CO is adsorbed in the outer adsorption layers and not in direct contact with the catalytic surface, its reduction leads to compounds containing oxygen, rather than hydrocarbons.

While Herington and Woodward^(2b) proposed that there are two types of catalytic surfaces, namely Type A (probably cobalt carbide) which is responsible for the formation of the CH_2 groups which polymerize to the long chain hydrocarbons and Type B (probably bare cobalt metal) which through the agency of hydrogen, is responsible for the liberation of the observed products from the catalyst surface. During the reaction when (besides water) only gaseous products are formed, the centers of Type B predominate over those of Type A whereas, when liquid and solid products are produced the reverse is true.

A recent paper by Kodama and his coworkers^(2c), proposed the mechanism of benzine synthesis as follows:

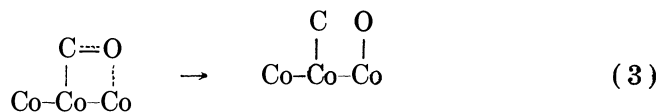
Firstly,



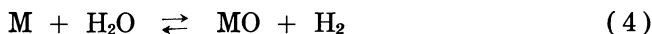
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- (2) (c) S. Matsumura, K. Tarama and S. Kodama, *Sci. Paper of Inst. Phys.-Chem. Research* **37** (1940), 302.
 (d) B. Jerofejew, A. Runtzo and A. Walkowa, *Acta Physicochim.* **12** (1940), 111.
 (e) F. Fischer and H. A. Bahr, *Gesamm. Abh. Kennt. Kohle*, **8** (1929), 255; O. C. Elvins and A. W. Nash, *Fuel*, **5** (1926), 263; *Nature*, **118** (1926), 154; O. C. Elvins, *J. Soc. Chem. Ind.*, **46** (1927), 473; D. F. Smith, C. O. Hawk and P. C. Golden, *J. Am. Chem. Soc.*, **52** (1930), 3221.
 (3) S. Hamai, *J. Chem. Soc. Japan*, **62** (1941), 516.

and then atomic hydrogen acting on M_2C to give CH_2 and finally the longer chain hydrocarbons. As far as CO is considered it seemed quite improbable i.e., CO at the surface of catalyst with excess of H_2 , Co is practically in reduced state for complete reduction of Co below $200^\circ C$. and if CO is present, reduction temperature is even lower⁽⁴⁾.

Such reaction mechanism as Eq.(2) is another way of stating that carbon monoxide, at the surface of metal, is ruptured, and one of the components, the carbon remains as Co-C linked together (cobalt carbide) and the other component, oxygen, linked to the adjacent metal surface forming oxide of the metal which is quite improbable to be existing in such condition as,



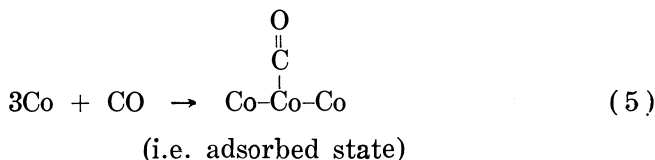
Furthermore,



is a reversible process, and the reaction from right to left takes place more rapidly at lower temperatures (such as $190^\circ-200^\circ C$.); the reverse process at higher temperatures. $CO+3Co=Co_2C+CoO$ cannot be obtained in the experimental conditions of ordinary Fischer synthesis. The heat of formation of links for CO is 235.5 Kcal. while those of Co_3-C and $Co-O$ are 9.33 Kcal. and 57.5 Kcal., respectively, so that the heat of rupture for CO molecules is enormously large as compared to those of Co_3-C and $Co-O$; consequently, the reaction is very improbable from the energetic consideration.

A New Mechanism Proposed. We have proposed a probable mechanism (3) of Fischer-Tropsch synthesis reaction, which we shall now elucidate in a more detailed manner.

In the case of Co type catalyst, when a $(CO+2H_2)$ mixture is passed over the catalyst, after it is thoroughly reduced by H_2 stream, the reaction is



which in turn act as the active center of the said reaction; then

— (4) (a) Ephraim, "Inorganic Chemistry", p 357.

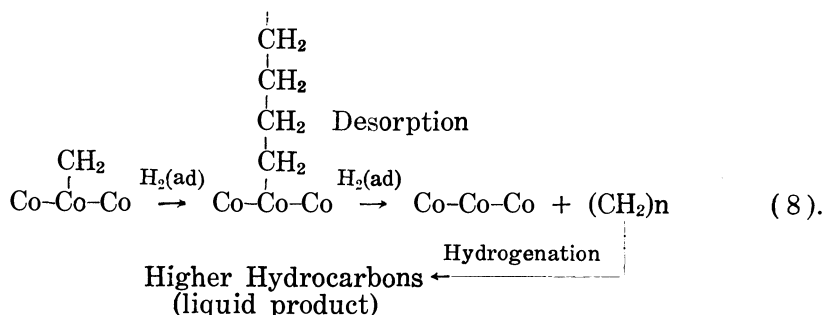
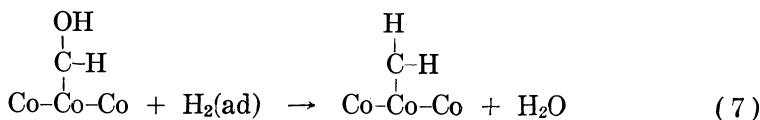
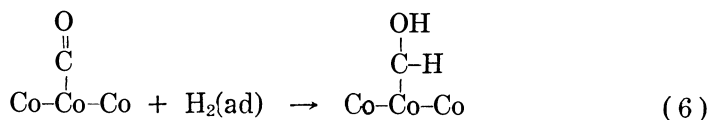
— (b) Watanabe, *Sci. Report Tohoku Imp. Univ.* Ser. I, **22** (1933), 892.

Reported the study of $CoO+CO \rightleftharpoons Co+CO_2$ of which the equilibrium is practically shifted to the CO_2 side even at $563^\circ C$. and it should be completely shifted to the CO_2 side at the temperature as low as $200^\circ C$.;

$\Delta F_{200}^\circ = -10344 \text{ cal.}$

$CO_2\% = 99.43\%$ at $563^\circ C$.

$CO_2\% = 95.87\%$ at $861^\circ C$.



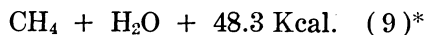
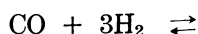
Thus, CH_2 in adsorbed state polymerize to long chain hydrocarbons on the surface of catalyst; then the desorption in presence of $\text{H}_2(\text{ad})$ takes place; and finally with hydrogenation reaction, the observed liquid hydrocarbons are produced.

Table 1.

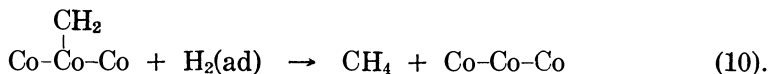
Temp. °C.	ΔF_t° cal./mol.	
25°C	-34547 ⁽⁵⁾	-34356 ⁽⁶⁾
100°	-30332	-30496
200°	-24712	-25123
300°	-19092	-19568
400°	-13472	-13890
500°	-7852	-8123

Discussion of the Mechanism.

At the initial stage of the experiment, CH_4 formation predominates, this is probably due mainly to the following reaction,



for which the free energy changes are tabulated in Table 1, but not through



$\begin{array}{c} \text{CH}_2 \\ | \\ \text{Co}-\text{Co}-\text{Co} \end{array}$ exists comparatively in a small amount as compared with that of H_2 in the beginning of the experiment, which shows that CH_4 formation predominates through reaction (9) rather than (10). More-

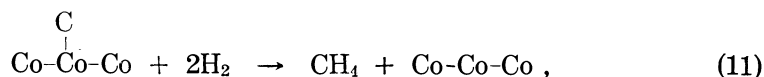
(5) C. Ellis, "The Chemistry of Petroleum Derivatives" Vol. II, (1937), 1225.

(G. S. Parks and Huffman, "The Free Energies of Some organic Compounds", (1932).

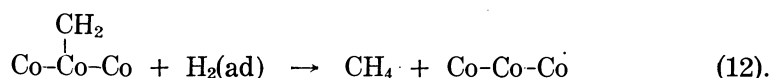
(6) J. Chipman, *Ind. Eng. Chem.*, **24** (1932), 1013.

(*) The fact that if the ratio $\text{CO}:\text{H}_2 = 1:3$ or over, CH_4 formation is very active, indicates that this reaction is very reasonable. (We also confirmed this fact (2b).)

over, the fact that CH_4 formation is mainly through (9) at the initial stage is quite clearly demonstrated in our experiment, i.e., when we pumped out completely the mixed gases after a regular synthesis, and only H_2 gas was passed at 200°C . (Reaction temperature), then we confirmed that there was no formation of CH_4 , contrary to what had been claimed by Craxford^(2a); but when a similar experiment was done at 300°C ., we observed CH_4 formation as shown in Table 2 and Fig. 2. ($\text{CO}:\text{H}_2=1:3.18$). According to the various "Carbide theory," it is explained that CH_4 formation in such a case is due to the following reaction.



but in our case, as there is definitely no CH_4 , it is obviously explained as:



The reaction (12) is kinetically not observed at a temperature near 200°C ., but at higher temperature (for example near 300°C .) it took place, as had been stated in our previous note⁽³⁾. This is definitely confirmed as shown in Table 2 and Fig. 2.

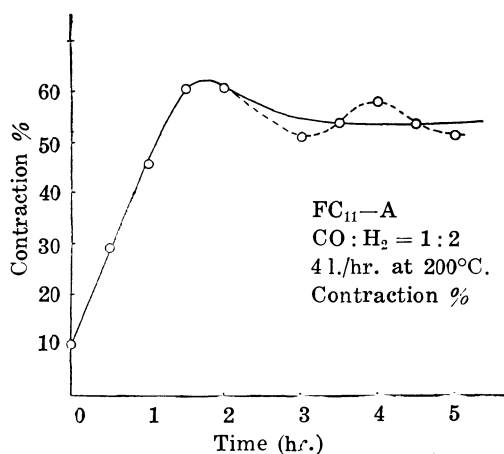


Fig. 1.

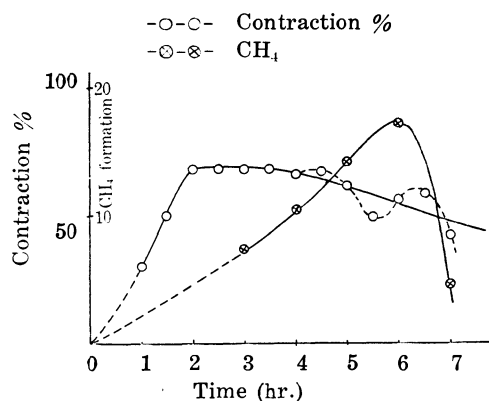


Fig. 2. FC₁₁-B CO:H₂ = 1:3.18, 4 l./hr. at 200°C
Oil yield 67.5 c.c./m³

Furthermore, when we pretreated the catalyst with CO at 200°C . for 6–8 hours, and all the gases evacuated from the catalyst zone, and then only H_2 was passed, (4 l./hr.) in our desorption experiment, we observed that after certain period, CH_4 formation took place as shown in Fig. 3. (Of course, a certain time is spent for the gas to pass through the reaction vessel to the sampling part.) This time lag for CH_4 formation is probably due to the fact that CO must be desorbed before it reacts with H_2 as in Eq. (9); this in turn means that the reaction of CH_4 formation as in Eq. (9) is taking place in the gaseous phase and not on the

Table 2. Gas Analysis Data

After the regular synthesis, all the gas mixtures evacuated, and H₂ only was passed 4 l./hr. at 200°C. and 300°C.

Exp. No.	FC ₁₁ -A/(200°)	FC ₁₁ -B/(200°)	FC ₁₁ -I/(200°)	FC ₁₁ -N/(300°)
CO ₂	0.2	0.2	0.2	0.1
C ₂ H ₂	0.2	0.0	0.0	0.1
C ₂ H ₄	0.2	0.0	0.0	0.0
CnH _{2n}	0.0	0.0	0.0	0.3
O ₂	0.2	0.4	0.1	0.1
CO	0.7	0.2	0.6	0.3
H ₂	96.8	96.9	96.4	93.1
CH ₄	0.0	0.0	0.0	3.0
C ₂ H ₆	0.0	0.0	0.0	0.5
N ₂	1.7	2.3	2.7	2.5
Total	100.0	100.0	100.0	100.0

Table 3. Gas Analysis Data

The effect of CO : H₂ ratio on the CH₄ formation in the regular synthesis at 200°C. 4 l./hr.

Exp. No.	FC ₁₁ -A(CO : H ₂ = 1 : 2) Contraction 59%	FC ₁₁ -B(CO : H ₂ = 1 : 3.18) Contraction 68%
CO ₂	1.8	3.8
C ₂ H ₂	0.1	0.0
C ₂ H ₄	0.1	0.0
CnH _{2n}	0.4	0.5
O ₂	0.2	0.8
CO	29.6	5.6
H ₂	56.2	58.1
CH ₄	6.6(*)	17.1
C ₂ H ₆	1.4	4.2
H ₂	3.6	9.9
Total	100.0	100.0

catalyst surface. When H₂ streaming velocity was 8 l./hr. instead of 4 l./hr. and other conditions being the same, we observed that the above mentioned time lag for CH₄ formation was shortened, as expected. Hence, we may safely say that the reaction such as Eq.(9) is not occurring on the catalytic surface. A similar pretreatment was done with H₂ instead of CO, and CO only was passed after evacuation; then we found no CH₄ formation as shown in Fig. 4.

(*) CH₄ formation at the initial stage.

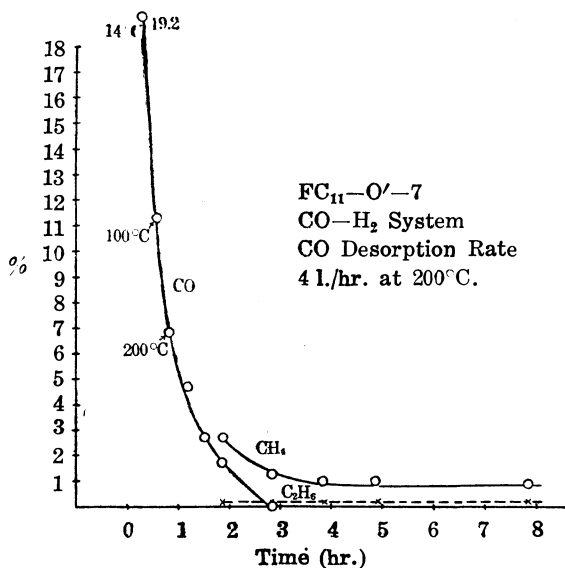


Fig. 3.

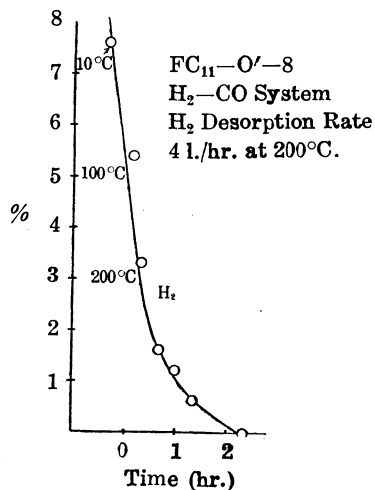
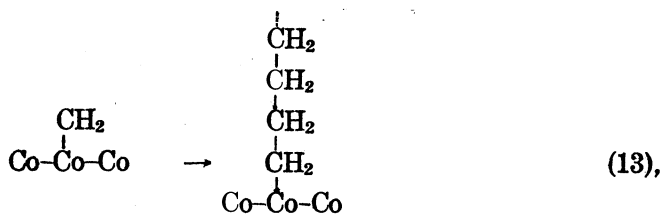


Fig. 4.

As time proceeds, the regular synthesis,



gradually becomes vigorous in parallel with the increase of $\text{Co}-\overset{\text{CH}_2}{\text{Co}}-\text{Co}$. This is quite consistent with our observation that during certain initial period practically only H_2O and CH_4 formations were recognized and no liquid hydrocarbon was observed, but after certain period (at least 5–8 hrs.), the catalytic surface might possibly have rearranged in such a way as we had conceived in our mechanism, $\text{CH}_2(\text{ad})$ molecules gradually increased, and the desired liquid hydrocarbon was formed.

With regard to CH_2 of which carbon is said to be in divalent state⁽⁷⁾ and itself shows the nature of a molecule rather than a radical, and a divalent carbon quite easily passes into a trivalent state. Some of its molecular characteristics are:

Life period	5.0×10^{-3} sec. (Thermal)
	6.4×10^{-3} sec. (Photochem.)

CH_2 "Bent molecule" for which the following constants are assigned:

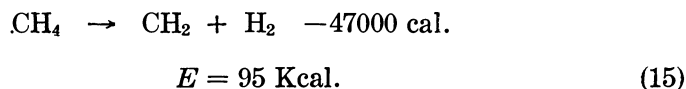
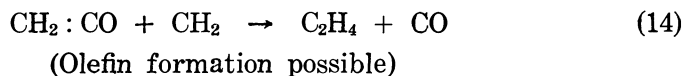
(7) R. F. Barrow, T. G. Person, and R. H. Purcell, *Trans Faraday Soc.*, **35** (1935), 880.

$$\nu(\sigma) = 3060 \text{ cm.}^{-1} \text{ (8)}$$

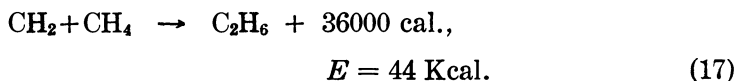
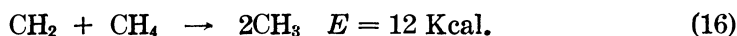
$$\nu(\pi) = 3980 \text{ cm.}^{-1}$$

$$\delta(\pi) = 1450 \text{ cm.}^{-1}$$

The occurrence of CH_2 is without doubt as far as hydrocarbon chemistry is concerned as:

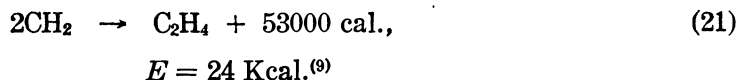
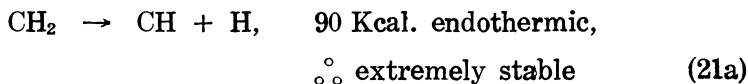
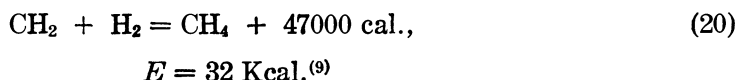


where E = activation energy,
if CH_2 , then



$$E = 77 \text{ Kcal. (Kassel)}^{(9)}$$

$$E = 150 \text{ Kcal. (Rice)}^{(10)}$$



Voge⁽¹¹⁾ has calculated, from the Heitler-London-Pauling-Slater theory, the relative energies of formation of CH , CH_2 , CH_3 and CH_4 as 4.0 e.v.

(8) Mecke, *Leipziger Vorträge*, (1931), 46.

R. F. Barrow, T. G. Person and R. H. Purcell, *Trans. Faraday Soc.*, **35** (1939), 880.

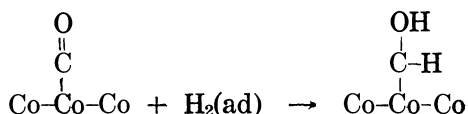
(9) L. Kassel, *J. Am. Chem. Soc.*, **54** (1932), 3949.

(10) F. O. Rice and K. K. Rice, "The Aliphatic Free Radicals" (1935).

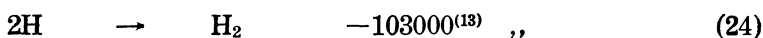
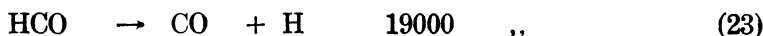
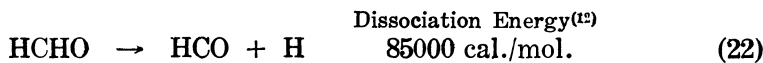
(11) (a) H. H. Voge, *J. Chem. Phys.*, **4** (1936), 581,

(b) G. Nordheim-Pöschl, *Ann. Physik*, **26** (1936), 258, 281 also gives estimates for the relative energies of CH_4 , CH_3 , CH_2 and CH based on the Heitler-London theory, and the results are in good agreement with those of H. H. Voge's calculation.

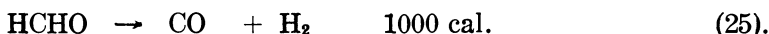
(92 Kcal.), 8.0 e.v. (184 Kcal.), 12.1 e.v. (279 Kcal.) and 17.0 e.v. (392 Kcal.) respectively. The value of 184 Kcal. for CH_2 is reasonable since it is practically twice the energy of C-H molecule (91 Kcal.) which is known from the spectroscopic data. The possibility that $\text{CH}_2 + \text{H}_2 \rightarrow \text{CH}_4$ occurs at the surface of the vessel cannot be excluded at present; from the thermochemical evidence, the high reactivity with hydrogen is predictable. $\text{CH}_2 + \text{H}_2 \rightarrow \text{CH}_4$ would be 80 Kcal.^(*) exothermic whereas from Voge's data for CH_3 the alternative reaction, $\text{CH}_2 + \text{H}_2 \rightarrow \text{CH}_3 + \text{H}$, is 19 Kcal.^(*) endothermic. The activation energy will be at least equal to the endothermicity and this is probably much greater than the activation energy of the highly exothermic reaction $\text{CH}_2 + \text{H}_2 \rightarrow \text{CH}_4$ as pointed out by Bawn and Milsted;^(11c) therefore $\text{CH}_2 + \text{H}_2 \rightarrow \text{CH}_4$ is more probable, but as we already stated, during the normal synthesis, this reaction is found inhibited, i.e. $\text{CH}_2(\text{ad})$ interact much effectively with adjacent $\text{CH}_2(\text{ad})$ as seen in Eqs. (20) and (21) through migration on the surface; concerning such possibility we will discuss a little later. Concerning the reaction (6)



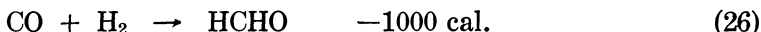
we can approximately estimate the activation energy, for we know that



by combining these (22), (23) and (24) we get

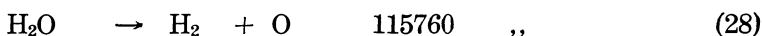
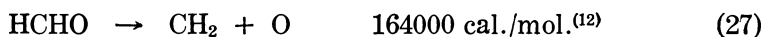


Therefore



Hence we can say that at least the activation energy for (26) is 1000 cal/mol; consequently if we consider HCHO is formed from the adsorbed CO and H_2 molecules the value of the activation barrier would be reduced to the extent of the respective heats of adsorption.

Furthermore, similarly we know that,



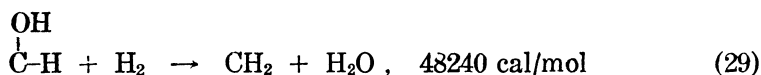
combining these (27) and (28) as before we get

(*) After correcting Voge's data for zero point energy.

(11) (c) C. E. H. Bawn and J. Milsted, *Trans. Faraday Soc.*, **35** (1939), 889.

(12) H. Zeise, *Z. Elektrochem.*, **47** (1941), 238.

(13) Sidgwick, "Covalent Links in Chemistry" p. 119.



therefore at least the activation energy is 48240 cal./mol., so that if this

type of reaction is proceeded through the molecules such as $\begin{array}{c} \text{OH} \\ | \\ \text{C}-\text{H} \\ | \\ \text{Co}-\text{Co}-\text{Co} \end{array}$ and $\text{H}_2(\text{ad})$ the reaction rate would be much accelerated to the extent of the heats of adsorption since

$$k' = z_0 e^{-\frac{E-Q_1-Q_2}{kT}} \quad \text{i.e.}$$

the activation energy will be lowered by the amount of Q_1 and Q_2 where OH

Q_1 is the heat of adsorption of $\begin{array}{c} \text{OH} \\ | \\ \text{C}-\text{H} \end{array}$ on the catalyst surface and Q_2 is the heat of adsorption for H_2 . Adopting the heat of adsorption for H_2 on Co practically the same as that of H_2 on Ni for which Beebe and Taylor⁽¹⁴⁾ have given (12600–14600), 48240 cal/mol will be reduced by at least 13000 cal./mol. which means E is about 35000 cal./mol. Of course, further reduction will be possible by the heat of adsorption for HCHO on Co for which at present the value is not known.

The rôle played by CH_2 during the normal synthesis of the Fischer-Tropsch reaction are no longer doubtful as it is evidenced by various accumulated facts in hydrocarbon chemistry in general⁽¹⁵⁾.

Starting from CH_2 , if polymerized to C_2H_4 , various reactions including polymerization and hydrogenation leading to higher hydrocarbons are quite easily attained as pointed out by Egloff, Schaad and Lowry⁽¹⁶⁾, furthermore, Egloff and Wilson⁽¹⁷⁾ pointed out that C_2H_4 acts as the key substance in hydrocarbon chemistry. Considering these, we have a very rational basis for our mechanism of the synthesis for which CH_2 plays the fundamental role in the formation of liquid hydrocarbons.

Egloff and Parrish⁽¹⁸⁾ stated that the activation energies of the polymerization reaction of the olefins are about 38–40 Kcal. This is much less than the energy required to break the bonds, hence the polymerization predominates at lower temperature for all the olefins.

The activation energies of some of the polymerization reactions are shown in Table 4.

In connection with the polymerization of the adsorbed CH_2 molecules on the catalyst surface, we must conceive that these molecules migrate freely to interact with each other, i.e.,

(14) Beebe and Taylor, *J. Am. Chem. Soc.*, **46** (1924), 43.

(15) (a) R. G. W. Norrish, *Proc. Roy. Soc. (London) A*, **150** (1925), 36.

(b) L. S. Kassel, *J. Am. Chem. Soc.*, **54** (1932), 3949.

(c) C. E. H. Bawn, *Trans. Faraday Soc.*, **34** (1938), 598.

(d) E. W. R. Steacie, *Chem. Rev.*, **22** (1938), 311.

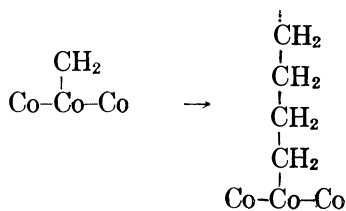
(16) Egloff, Schaad and Lowry, *J. Phys. Chem.*, **35** (1931), 1825.

(17) Egloff and Wilson, *Ind. Eng. Chem.*, **27** (1935), 917.

(18) Egloff and Parrish, *Chem. Rev.*, **19** (1936), 145.

Table 4. The Polymerization of the Olefins.⁽¹⁹⁾

Reactions	<i>E</i> cal./mol.
2CH ₂ → C ₂ H ₄	24000(*)
2C ₃ H ₄ → C ₄ H ₆	37700(**)
2C ₃ H ₆ → C ₄ H ₁₀	37400(**)
2C ₄ H ₆ → C ₈ H ₁₆	38000
2-iso C ₄ H ₈ → C ₈ H ₁₆	43000
2C ₅ H ₁₀ → C ₁₀ H ₂₀	38000



the above reaction is controlled by the freedom of migration. Fortunately, there are very good evidences that under certain condition, the adsorbed molecules are capable of moving laterally over the surface. These are principally connected with the metal atoms and molecules of organic compounds, of these compound movement, for various reasons migrations are easier to follow but we can draw by analogy certain conclusions as to the probable behavior of the adsorbed gas molecules. Volmer⁽²⁰⁾ has shown that when mercury atoms are condensed from the vapor on a suitably cooled surface, the crystals which form grow nearly 1000 times as fast as in some direction as in others. This can only be due to the migration of the condensed atoms over the surface of the growing crystal until they reach the position of the maximum stability. Estermann⁽²¹⁾ has found the similar evidence in case of cadmium condensed from the vapor, and for crystal growth of benzophenone by Adhikari⁽²²⁾. That Ba atoms can migrate in the same way over a tungsten surface has been demonstrated by Becker⁽²³⁾. This fact is beautifully shown by measuring the variation of thermoionic emission. Adsorbed Caesium⁽²⁴⁾ has also been shown to migrate in the same way. Thus in the mechanism which the author proposed, the way of migration of CH₂ on the catalytic surface cannot be far from these definite evidences.

With regard to adsorption, we must remember that while adsorption is necessary for catalytic action, the maximum adsorption does not necessarily coincide with the maximum catalytic activity⁽²⁵⁾, as often erroneously stated by some investigators. The amount of adsorption increases with the decrease of temperature; the rate of adsorption and the rate of chemical reaction both decreases; there is, however, an optimum temperature depending on these factors. Taylor and Burns^(25b) have definitely demonstrated that the maximum catalytic activity does not occur at the temperature at which the maximum adsorption in their experiment of

(*) Taken from L. Kassel (15b).

(**) *E* = 38400 and 38000, respectively, given in a later paper.

(Krauze, Nemtsov and Soskina, *J. Gen. Chem. (U.S.S.R.)*, **5** (1935), 382.

(19) Tabulated in: F. W. R. Steacie, *Chem. Rev.*, **22** (1938), 311.

(20) Volmer, *Trans. Faraday Soc.*, **28** (1932), 359.

(21) Estermann, *Z. Elektrochem.*, **31** (1925), 441; *Z. Physik*, **33** (1925), 320.

(22) Adhikari, *Z. Physik*, **35** (1925) 170.

(23) Becker, *Trans. Faraday Soc.*, **28** (1932), 148.

(24) Taylor and Langmuir, *Phys. Rev.*, **44** (1933), 423.

(25) (a) Smithells, "Gases and Metals", (1938), p. 69.

(b) H. S. Taylor and R. M. Burns, *J. Am. Chem. Soc.*, **43** (1921), 1273.

hydrogenation of ethylene, and similar observations may be made with respect to a cobalt catalyst with carbon monoxide and hydrogen, and with nickel in the case of carbon dioxide and hydrogen. Considering these, again, we may say that Kodama's interpretation with regard to this phenomenon, i.e., the necessary coincidence of maximum catalytic activity and maximum adsorption is quite improbable (if there is, a happy coincidence). Of course, the magnitude of the heat of adsorption is definitely related to the catalytic activity by the relation already stated.

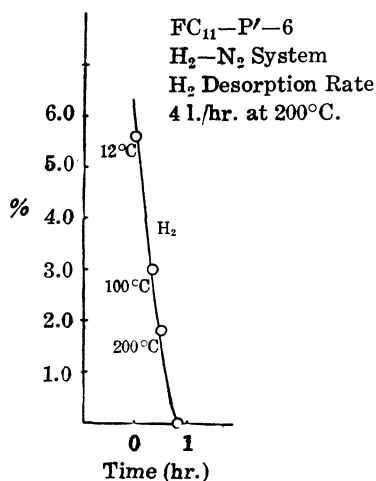


Fig. 5.

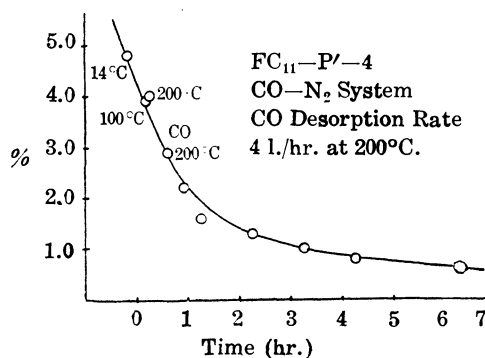


Fig. 6.

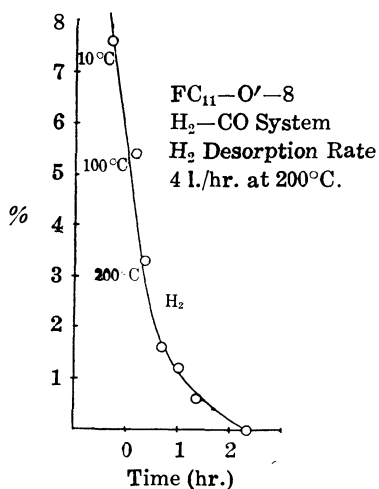


Fig. 7.

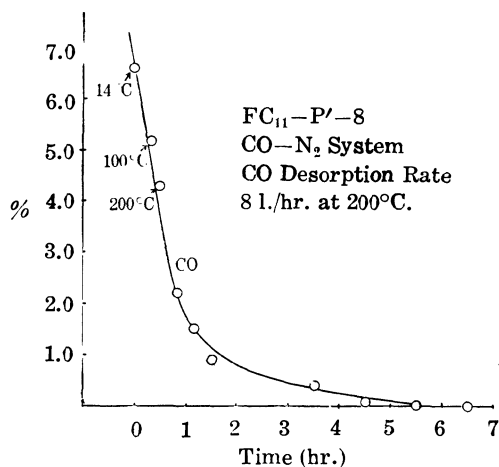
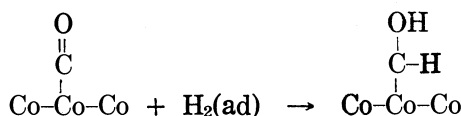


Fig. 8.

Furthermore, Taylor has demonstrated that carbon monoxide is very firmly adsorbed by metals and that at moderate partial pressure, it probably covers the metal surface completely. Thus, in such a case, H₂ in the

presence of CO can be adsorbed only on the surface of carbon monoxide and not on the metal surface.

With regard to this point that carbon monoxide is more firmly adsorbed on the surface of the catalyst has also been demonstrated in our desorption experiments of CO, H₂ and N₂ from the catalysts. The details of the experiments will be published in our subsequent paper. Figs. 5—8 show some of the adsorptive characteristics for H₂ and CO at 200°C.. The point that H₂ in the presence of CO can be adsorbed only on the surface of CO and not on the metal may be conceivable and furthermore, it is quite concordant with our mechanism, that is, in the Fischer-Tropsch reaction. When the catalyst at first is reduced by streaming H₂, such reduced catalyst is covered by adsorbed hydrogen. At the beginning, as a (CO+2H₂) mixture is passed, since CO is more strongly and easily adsorbed than H₂, it is quite reasonable to assume that some of the already adsorbed hydrogen is replaced by CO and some hydrogen remains, and the replaced hydrogen may immediately be attached to CO(ad), as shown in our mechanism, i.e., through the migration of the adsorbed molecule



This is quite reasonable from our approximate values of its activation energy which is 1000 cal./mol.^(*); hence the above reaction is quite rapid. This value may correspond to the potential barrier for the process of surface migration⁽²⁶⁾.

J. K. Roberts⁽²⁷⁾ has also demonstrated that in his experiment of the adsorption of oxygen on a tungsten surface already covered with H₂, when an oxygen molecule is adsorbed, a hydrogen molecule is thrown off; every oxygen molecule adsorbed throws off a molecule of H₂. Moreover, he concluded that the hydrogen must be thrown off as molecule, not as separate atoms from his direct measurement of the heat of adsorption.

Considering the surface partially covered by oxygen, it is stated that the activated adsorption of hydrogen is connected with the interaction between hydrogen (thrown off hydrogen) and surface oxygen in the adsorbed state or that forming a integral part of the solid lattice.

This is quite analogous to our case of H₂ covered catalyst surface, once, it is partially replaced by CO and the fraction of H₂ is thrown off by CO, and immediately, through the surface migration, H₂ interacts with the adsorbed CO as shown in our theory.

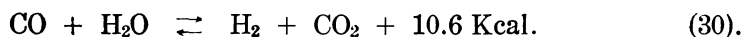
Thus by applying our proposed mechanism to the Fischer-Tropsch reaction, all the facts of experimental observations are practically explained quite satisfactorily.

(26) Lennard-Jones, *Trans. Faraday Soc.*, **28** (1932), 333. From the point of view of wave mechanics the question of surface migration has been considered by: Lennard-Jones and Strachan, *Proc. Roy. Soc. (London)*, A **150** (1935), 442.

(27) J. K. Roberts, *Proc. Roy. Soc. (London)*, A **152** (1935), 477.

(*) E. K. Rideal, *Trans. Faraday Soc.*, **28** (1932), 139, cites $E = 1000$ cal./mol. for the potential barrier for the process of surface migration in H₂ adsorbed on Ni from the experiment of Davisson and Germer, *Phys. Rev.* **2** (1927), 35, 705.

If the catalyst is of Fe type, our mechanism is equally satisfactory; the reactions (5) (6) (7) and (8) should proceed equally as well and in the presence of Fe catalyst, H₂O produced reacts as



This reaction is quite fast over the Fe catalyst. The equilibrium is quite shifted to the CO₂ side as shown in the values of ΔF° .

Table 5.

Temp. °C.	ΔF° cal./mol.	
25°	-7241 ⁽²⁸⁾	-6810 ⁽²⁹⁾
100°	-6484	-6057
200°	-5494	-5115
300°	-4536	-4209
400°	-3611	-3340
500°	-2721	-2500

As observed experimentally, no H₂O formation but only CO₂, (of course, even in the case of Co and Ni type catalyst this water gas reaction is occurring) hence we observe a very slight amount of CO₂ formation as seen in the gas analysis data.

However, in the case of Fe catalyst usually the experiment is proceeded at above 250°C., and in such experimental conditions the reaction is quite rapid. If this is carried on at near 200°C., even in the Fe type catalyst, we have observed the formation of H₂O. This is quite obviously due to the fact that the H₂O formed during the synthesis is not used up rapidly enough in the water gas reaction to give CO₂, so that the CO₂ formation in the Fe catalyst is considered as secondary.

Table 6. Gas Analysis Data.

Types of catalyst	Co Type		Fe Type		(Co+Fe) Type	
Exp. No.	F ₄₅ -H	F ₄₅ -B(*)	F ₂₈ -A	F ₅₇ -C	F ₅₃ -D	F ₅₄ -C
CO ₂	0.6	12.4	20.4	3.8	1.9	1.0
C ₂ H ₂	0.0	0.0	0.0	0.0	0.0	0.2
C ₂ H ₄	0.4	0.3	0.8	0.2	0.2	0.0
C _n H _{2n}	0.0	0.0	0.5	0.2	0.0	0.0
O ₂	0.5	1.5	0.3	0.5	0.1	0.2
CO	30.5	1.6	26.2	45.2	33.1	30.0
H ₂	63.9	30.1	50.3	46.6	60.0	65.5
CH ₄	0.0	45.8	0.0	0.0	0.0	0.0
C ₂ H ₆	0.0	0.0	0.0	0.0	0.0	0.0
N ₂	4.1	8.3	1.5	3.5	4.7	3.1
Total	100.0	100.0	100.0	100.0	100.0	100.0

In the case of (Co+Fe) type catalyst, in which the experiment proceeded at 200°C., we demonstrated that the formation of H₂O is the same as in the case of Co catalyst.

(28) Lewis and Randall, "Thermodynamics", (1923) 575.

(29) J. Chipman, *Ind. Eng. Chem.*, **24** (1932), 1013.

(*) Initial stage of the reaction where CH₄ formation is predominating.

Thus we can safely say that our proposed mechanism explains very concordantly the experimental observations not only for Co and Ni type catalysts but also for Fe type catalyst for which, so far, it has been considered that an entirely different mechanism should play.

The inhibitive action of CO on the occlusive power of palladium for hydrogen was recognized by von Hemptinne.⁽³⁰⁾ This is similar to our results in that, when CO pretreatment at 350°C. was done for the catalyst, it destroyed the activity, i.e., when the CO treatment is made, the entire surface is covered by CO which may prevent the adsorption of H₂. This is necessary for obtaining the activated hydrogen which reacts with the

adsorbed $\begin{array}{c} \text{O} \\ \parallel \\ \text{C} \\ | \\ \text{Co}-\text{Co}-\text{Co} \end{array}$ to give CH₂ molecule (ad) for the regular synthesis

of CH₂ (ad) → polymerization → desorption → hydrogenation → higher hydrocarbon. The Pd case seemed to be applicable also in the case of Co surface in the Fischer synthesis. This fact is very concordant with that when CO is used in the reduction of the catalyst at 350°C. instead of H₂ for the preparation of the catalyst, it does not show as good catalytic activity as when H₂ is used in the reduction. However, after the catalyst is being normally reduced by H₂ and then CO pretreatment was done at the temperature of reaction (190°–200°C.), then the activity is quite as good.

This is clearly shown in our experiment.

Table 7.

Various pretreatments for Co catalyst (XII ₁₆ –1)					
Subs.	Temp. °C.	React. Temp.	Activity	Exp. No.	Contraction (%)
CO	350°	200°	Activity destroyed. No oil formation.	FC ₁₁ –C	13
CO	200°	200°	Good.	FC ₁₁ –D	14
				FC ₁₁ –L	30
				FC ₁₁ –M	34
N ₂	200°	200°	Not so good.	FC ₁₁ –J	28
				FC ₁₁ –H	31
H ₂	200°	200°	Good.	FC ₁₁ –I	40
H ₂	350°	200°	Not so good as at 200°C. with respect to its oil formation.	FC ₁₁ –F	21

The explanation for this is very clear as already discussed in connection with Roberts' experimental evidence and our desorption experiments.

The experimental data for the series of this investigation will be given in our subsequent papers to be published elsewhere.

(30) von Hemptinne, *Z. phys. Chem.*, **27** (1898), 429.

Summary.

(1) Introductory remarks for the Fischer-Tropsch reaction in connection with various mechanisms so far proposed are presented briefly.

(2) Our proposed mechanism is presented and discussed in detail.

(3) The role of CH_2 in hydrocarbon chemistry in general is stressed especially in connection with the Fischer-Tropsch reaction mechanism.

(4) Approximate values of the activation energies for the reactions involved in the synthesis are presented and discussed in correlation with adsorption.

(5) The aspect of polymerization process is discussed, and the question of surface migration is correlated with the polymerization reaction.

(6) Adsorption and catalytic activity involved in the synthesis are discussed in the light of our desorption experiment.

(7) The proposed mechanism is also applied to Fe type catalyst and discussed.

(8) Various pretreatment effects on the catalytic activity are discussed in the light of our experimental evidences.

In conclusion, the author expresses his hearty thanks to Dr. T. Marusawa, Former Director of the Institute, and Dr. S. Sato, Director of the Institute, for their interests and constant encouragement for carrying on this investigation and for the permission for this publication. Also the author takes this occasion to extend his thanks to Dr. R. Negishi who willingly has criticized and discussed the problem throughout this investigation—also to his colleagues; and to Messrs. S. Hayashi, Shimamura, Igarashi, Fujiwara and Kuwabara who were willing to assist in our experimental part of this investigation; and to Messrs. Kataoka, Inaba, Kodama and Nakano who have helped with their part in the analytic work.

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Direct Determination of Oxygen in the Organic Compounds by the Hydrogenation. III. Reduction Mechanism on the Ni-Thoria Catalyst.

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(Received November 21, 1940.)

In the previous paper the cracking mechanism on the Pt-silica gel catalyst was elucidated. We are going to examine the reducing reactions which occur on the Ni-thoria catalyst. Experimental details are found in the previous papers.

I. Reduction on the Ni-Thoria Catalyst. The CO and CO₂ which are produced in the cracking zone at 950°C are reduced on the Ni-thoria catalyst in the hydrogen stream of about 5 l/hr.



The high partial pressure of water vapour may prefer the reaction (2'), but in our analytical condition the situation is opposite and, therefore, this reaction may be duly discarded.

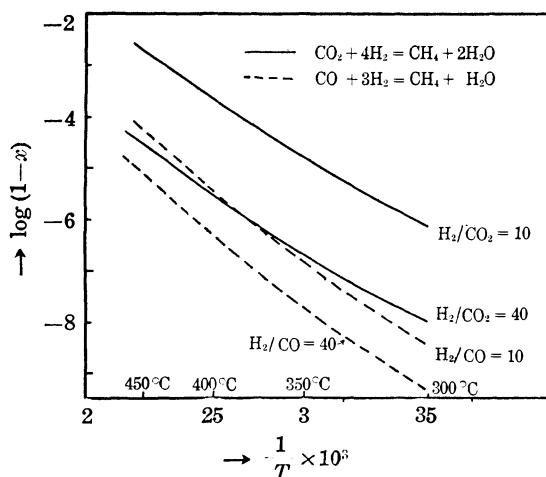


Fig. 12. Relation between Reaction Temperature and Rate of Reaction.

(1) *Reaction Temperature and Equilibrium Constants.* The equilibrium constants of reaction (1) and (2) decrease as the reaction temperatures are raised; therefore, the higher the reduction temperatures on Ni-thoria catalyst, the less favourable the equilibrium condition and the temperature of 350°C was found best suited for our purpose.

(2) *Calculation of Unreacted Carbon Oxides.* The relations between the reaction temperatures and unreacted carbon oxides are shown in Fig. 12 for the various ratios of H₂ to CO

or CO₂.

In our analytical conditions the ratio of H₂ to CO may be around 7.2–12.8 and that of H₂ to CO₂ 14.4–25.6 as already been discussed in the

previous paper. Fig. 12 definitely shows that above 400°C, even if the equilibrium state is nearly reached, the reduction of CO₂ may complete with difficulty.

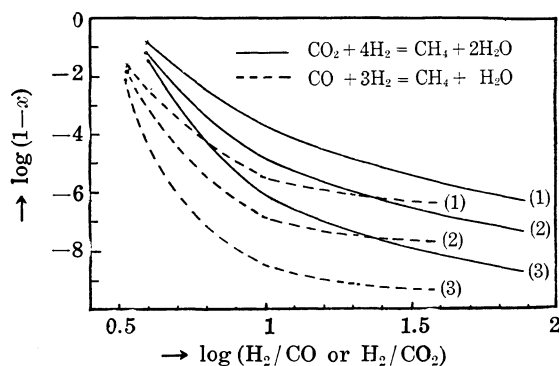


Fig. 13. Relation between reaction temperatures and ratio of concentration of reactants.

pressures of carbon oxides and, therefore, brings the unsatisfactory results. The slow evaporation or decomposition of the sample is the key of success in this analysis.

(3) *Activity of Ni-Thoria Catalyst.* The Ni-catalyst was prepared after the method of H. S. Taylor and W. W. Russel⁽⁵⁾ and contained 2% of thoria. The activity of this catalyst was examined by reducing CO₂ which was evolved from NaHCO₃. The production of CO₂ exactly followed the reaction,



The results of table 9 proved that the activity of Ni-catalyst was quite satisfactory.

Table 9. Reducing activity of Ni-Catalyst.

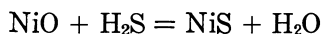
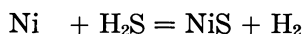
Sample pure NaHCO₃, Hydrogen streaming velocity 41/hr.
Calculated: residue 63.19%, H₂O 10.72%, CO₂ 26.19% (as H₂O, 21.45%) Total H₂O 32.17%

Exp. No.	Catalyst temp. °C	Sample gr.	Found				cal-Expt. ΔH ₂ O %
			H ₂ O %	CO ₂ (as H ₂ O)		Residue. %	
				%	%		
C-61	295	0.1962	31.96	0	0	63.20	-0.21
C-60	315	0.2669	32.22	0.11	0.09	63.58	+0.05
C-58	350	0.2393	32.05	0	0	63.23	-0.12
C-59	350	0.2166	31.90	0.28	0.23	63.02	-0.27
C-62	400	0.2227	31.61	—	—	63.45	-0.56
C-63	400	0.3335	31.66	0.33	0.27	63.13	-0.51

(5) H. S. Taylor and W. W. Russel, *J. Phys. Chem.*, **29** (1925), 1325.

(4) *Hydrogenation Decomposition of Ethane and Ethylene.* The hydrocarbons higher than methane, i.e. ethane and ethylene, are easily and completely hydrogenated and decomposed to methane on the Ni-thoria catalyst⁽⁶⁾ and, therefore, we are not concerned with the behaviour of these higher hydrocarbons which may be produced in the cracking reaction zone.

(5) *Effects of Water Vapour and Hydrogen Sulphide.* The oxidation of Ni-catalyst by the water vapour produced is impossible under the conditions employed.



Poisoning effect of H_2S on Ni-catalyst is well known and, furthermore, water vapour produced in this reaction is the source of error in this analysis and, therefore, some device for the removal of H_2S prior to the reduction of carbon oxides is essential and will be discussed in the following paper.

II. Decomposition of Native High Molecular Compounds in the Hydrogen Stream.

Saccharose, cellulose, lignin and brown coal of Jarahinohi mine (Manchoukuo) are decomposed at several temperatures in the hydrogen stream and the % of oxygen evolved as the volatile oxygen compound is measured by the method developed above. The variation of heating time of the sample between 10–30 minutes changed the % of oxygen found very little. Fig. 14 shows that the higher the polymerisation degree of the sample the more difficult it is to expel the oxygen from the sample

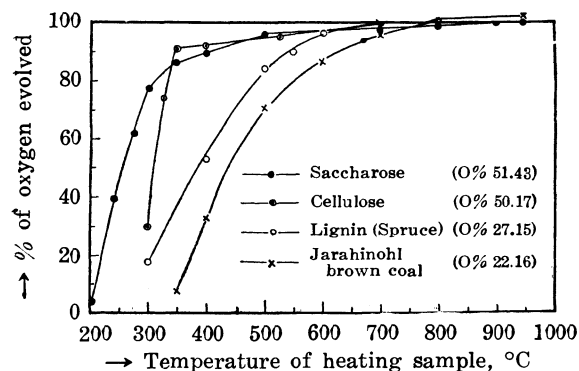


Fig. 14. Relation between the Temperature of Heating Sample and % of Oxygen Evolved from the High Molecular Compounds.

and needs the higher temperature.

Table 10 is the classification of oxygen bonds in these samples and is compared with the results shown in Fig. 14.

It is well known that the initial decomposition of saccharose and cellulose is the liberation of water and, therefore, hydroxyl bond of alcoholic type is considered to be most unstable. Stabilities of pyran and furan rings or oxygen bonds of ether type placed between pyran and pyran or furan rings coming next; methoxyl bond and benzopyran or benzofuran ring seem to be most stable. Thus this analytical methods of oxygen in the organic compounds may be well employed for the study of thermal behaviour of high molecular compounds.

(6) Kiyoshi Morikawa, W. S. Benedict and H. S. Taylor, *J. Am. Chem. Soc.*, **58** (1936), 1795; Kiyoshi Morikawa, N. R. Trenner, and H. S. Taylor, *ibid.*, **59** (1937), 1103.

Table 10. Classification of Oxygen Bonds.

Sample	O found %	Classification of Oxygen bonds.					
		Alcoholic OH %	Pyran or furan %	Etheric* %	Methoxy %	Benzo- pyran or Benzo- furan %	Dime- thylene Oxide %
Saccharose ⁽⁷⁾	51.43	72.73	18.18	9.09	0	0	0
Cellulose ⁽⁸⁾	50.17	60.00	20.00	20.00	0	0	0
Lignin ⁽⁹⁾ (spruce)	27.15	33.10	0	0	30.9	30.1	5.9
Brown coal (Jarahinohl)	22.16	—	—	—	—	—	—

* Oxygen bond placed between pyran and pyran or furan rings in cellulose or saccharose.

The authors wish to express their sincere thanks to Mr. Junichi Uchida, chief chemist of the Fiber Section of this Laboratory, who kindly gave much valuable informations on the native high molecular compounds.

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(7) Tollens-Elsner, "Kurzes Handbuch der Kohlenhydrate", 4 Ed., 477, (1935).

(8) W. N. Haworth and H. Machemer, *J. Chem. Soc.*, **1932**, 2270.

(9) K. Freuderberg, M. Meister, and E. Flickinger, *Ber.*, **70** (1937), 500; K. Freudenberg, F. Sohns and A. Janson, *Ann.*, **518** (1935), 62.

Thermal Diffusion of Binary Salt Solutions. A Note on the Paper of Gillespie and Breck.

By Kozo HIROTA.

(Received June 17, 1941.)

Introduction. In previous two papers (printed in Japanese), accepted by the Chemical Society of Japan on April 17 and May 27, the present author reported the method on the determination of thermal diffusion coefficient of solutions, using an apparatus of Clusius and Dickel,⁽¹⁾ and discussed the data thereby obtained and also reported preliminarily an "inverse" effect found in the binary solution of NaCl-HCl.

While these papers were being translated, a journal containing a paper of Gillespie and Breck, where the similar effect (in their FeCl₃-HCl

(1) K. Clusius and G. Dickel: *Naturwissenschaften*, **26** (1938), 546.

system) to that given in the author's second paper was described, came into his hand on the 3rd of June. For the purpose of comparing his result with theirs, his second paper is now translated with additional data for the $\text{HCl-NH}_4\text{Cl}$ and a few remarks before the detailed experimental descriptions are published.

Experiments. The column consisted of two concentric boron glass tubes, having reservoirs of capacities 28 and 23 c.c. at the top and bottom ends, respectively. Width, length and volume of the annular space of the column were 1.5 mm. 94 cm. and 89 c.c., respectively. The higher temperature of the inner tube was maintained by the boiling point of carbon tetrachloride ($76^\circ\text{C}.$) which was heated electrically, while the lower one of the outer tube by running water which was kept constant at $20^\circ\text{C}.$ at the entrance and at $30^\circ\text{C}.$ at the exit of the column, mean temperature difference thus being $51^\circ\text{C}.$ The top reservoir was cooled as much as possible to protect the solution from evaporation and to circulate the solution freely.

At a fixed time after the experiment was begun, the content of each reservoirs was taken out, and the concentrations of the H^+ and Cl^- ions were analysed volumetrically, while those of the other ions were determined by the difference. The experimental results are summarised in Table 1 and 2, where every value is the mean of at least two measure-

Table 1.

Separation Ratio $\left(= \frac{\text{Concentration at the bottom reservoir}}{\text{Concentration at the top reservoir}} \right)$ of $\text{HCl-H}_2\text{SO}_4$.

Hours Elapsed	1			2			Infinite		
Ions	H^+	Cl^-	SO_4^{--}	H^+	Cl^-	SO_4^{--}	H^+	Cl^-	SO^{--}
1 N HCl	1.19 ₅	1.19 ₅	—	1.22	1.22	—	1.25	1.25	—
0.5 N HCl 0.5 N H_2SO_4 }	1.19	1.21	1.18	1.23	1.23	1.22	—	—	—
1 N H_2SO_4	1.21	—	1.21	1.23	—	1.23	1.23	—	1.23

Table 2.

Separation Ratios of HCl-NaCl and $\text{HCl-NH}_4\text{Cl}$.

Hours Elapsed	1			2			Infinite		
Ions	H^+	Cl^-	Na^+ or NH_4^+	H^+	Cl^-	Na^+ or NH_4^+	H^+	Cl^-	Na^+ or NH_4^+
1 N NaCl	—	1.04 ₃	1.04 ₃	1 —	1.04 ₇	1.04 ₇	—	1.04 ₈	1.04 ₈
0.5 N HCl 0.5 N NaCl }	1.30 ₅	1.12	0.96	1.34	1.26	0.97	—	—	—
1 N HCl	1.19 ₅	1.19 ₅	—	1.22	1.22	—	1.25	1.25	—
0.5 N HCl 0.5 N NH_4Cl }	1.35	1.12	0.90	1.42	1.22	0.89	—	—	—
1 N NH_4Cl	—	1.00 ₈	1.00 ₈	—	1.01 ₀	1.01 ₀	—	1.01 ₀	1.01 ₀

ments, and those of the infinite hours were estimated by extrapolation, according to the theory of Debye. It was thus observed that in the system of $\text{HCl-H}_2\text{SO}_4$, the separation took place additively for the component salts, and that in the systems of HCl-NaCl and $\text{HCl-NH}_4\text{Cl}$, the concentration of H^+ ion became larger than that in system of HCl alone, while Na^+ and NH_4^+ ions were concentrated in the top reservoir. Such an "inverse" effect occurred especially more markedly in the $\text{HCl-NH}_4\text{Cl}$ system.

Remarks. Because the annular space was constructed larger,^(*) in order to shorten the time of attainment of the stationary state, the observed effect was small when it was compared to that of Korsching and Wirtz⁽²⁾ or to that of Gillespie and Breck, who used an apparatus with the annular space of 0.75 mm. and needed about one day for the attainment of the stationary state. But, as both the experimental conditions and the solutions were selected so as to be free from the ambiguity effected by creeping and hydrolysis of the solute, the "negative"⁽³⁾ effect in the solutions, which contained H^+ and Cl^- ions, was confirmed without doubt.

In conclusion the author wishes to express his sincere thanks to Dr. R. Yoshimura, Director of the Department, for his interest and encouragement in carrying out this research.

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(*) The details of the reason was described in the first paper which will be translated shortly.

(2) H. Korsching and K. Wirtz: *Naturwissenschaften*, **27** (1939), 367.

(3) L. J. Gillespie and S. Breck: *J. Chem. Phys.*, **9** (1941), 370.

Analyse des Mineralwassers von Kinkei in der Provinz Totigi.

Von Kazuo KURODA.

(Eingegangen am 30. Juni 1941.)

Die Mineralquellen von Kinkei, in der Nähe des Berggipfels Keityo (Provinz Totigi), welcher ungefähr 1700 m. über dem Meeresspiegel liegt, wurden von T. Misawa vom therapeutischen Standpunkt aus genau untersucht. T. Misawa hat gefunden, dass das Trinken dieses Mineralwassers, wegen seines Kupferreichtums, Blutarmut heilt. Dieses Mineralwasser wurde im Jahre 1932 vom chemisch- hygienischem Laboratorium analysiert und im letzten Jahre von K. Kimura mit spektroskopischer Methode untersucht. Die Existenz folgender Elemente im Mineralwasser war mit spektroskopischer Methode gefunden (s. Tabelle 1).

Tabelle 1. Resultat der spektroskopischen Analyse (K. Kimura).

Li(?)	Na	Cu	Ag(?)	Mg	Ca	Zn(?)	B(?)	Al	Si
Ti	Sn(?)	Pb	V	Bi	Cr	Mn	Fe	Co	Ni

Die Analyse geringer Quantität obengenannter Elemente im Mineralwasser ist sowohl therapeutisch wie auch geochemisch sehr interessant. Deshalb haben wir dieses Mineralwasser nach verschiedenen Methoden, d.h. spektroskopisch, polarographisch, colorimetrisch und gravimetrisch genau analysiert.

Das Kinkei-Wasser hat infolge seines hohen Ferrisulfatgehalts eine braun-gelbe Farbe. Durch Einwirkung der Luft setzen sich allmählich Niederschläge des Eisens ab. Thermometrische Beobachtungen und pH Messungen, welche am 5. Mai 1940 und am 2. Juni 1941 versucht worden, ergaben folgendes Resultat. (s. Tabelle 2).

Tabelle 2.

Datum	Temp. der Quelle °C.	pH-Wert
5. Mai 1940	10.0	2.4
2. Juni 1941	8.8	2.4

Das spezifische Gewicht des Mineralwassers verglichen mit destilliertem Wasser von 25°C. ist 1,003.

Kupfer, Blei, Kadmium, Nickel, Zink und Kobalt wurde durch Dithizon- Methode oder dithizon-polarographische Methode analysiert.⁽¹⁾ Vanadin, Chrom und Molybdän wurde nach der E. B. Sandellschen colorimetrischen Methode bestimmt.⁽²⁾ Titan war nach der Wasserstoffperoxyd Methode,⁽³⁾ Gallium und Beryllium war mit einer spektroskopischen Methode bestimmt.⁽⁴⁾ Für die Bestimmung des Radons wurde ein I. M. Fontaktoskop von Dr. S. Iimori angewandt. Bei Ausführung der Analyse von übrigen Bestandteilen hielten wir uns an den gewöhnlichen Gang der Mineralwasseranalyse. Die vorgenommenen Bestimmungen ergaben die in nachfolgender Tabelle verzeichneten Resultate (s. Tabelle 3).

Wie man aus Tabelle 3 ersieht, ist der Hauptbestandteil dieses Mineralwassers Schwefelsäure, Eisensulfat, Aluminiumsulfat und Kieselsäure. Dieses Mineralwasser ist also eine vorbildlich saure Alaun-Vitriolquelle.

- (1) Heller, Kuhla und Machek, *Mikrochem* **23** (1937). 78.
Stout, Levy und Williams, *Collection Czechoslov. Chem. Commun.* **10** (1938), 129.
Kuroda, dies Bulletin, **15** (1940), 88, 439.
- (2) Sandell, *Ind. Eng. Chem. Anal. Ed.*, **8** (1936), 336.
Kuroda, dies Bulletin, **14** (1936), 307.
- (3) Snell, "Colorimetric Methods of Analysis", 1936 (New York) 355.
- (4) Kuroda, dies Bulletin, **14** (1939), 305; *ibid.*, **15** (1940), 234-237.

Tabelle 3.

H ⁺	0.0033	g./l.	Zn	0.00011
K	0.000		Ti	0.0001
Na	0.001		Cr	0.000073
Ca	0.0150		Ni	0.000066
Mg	0.0032		V	0.000051
Fe ⁺⁺	0.2836		Mo	0.000002
Fe ⁺⁺⁺	0.2346		Ga	0.0000005 ~0.000001
Al	0.1067		Be	0.0000005 ~0.000001
Cl	0.0180		Rn	0.00~0.05 (Mache)
SO ₄ ⁻⁻	1.6897		Pb	< 0.000010
HSO ₄ ⁻	0.3686		Cd	< 0.000010
H ₂ SiO ₃	0.1339		Co	< 0.000010
Cu	0.001033			
As	0.0010			
Mn	0.00030			2.8658 ₃₅₁

Die Bestimmung des Abdampfdruckstandes ergaben die in nachfolgender Tabelle verzeichneten Resultate (Tabelle 4).

Tabelle 4.

110 °C.	3.62 g./l.
140 °C.	3.49
> 1 00°C.	1.125

Dieses Mineralwasser wurde im Jahre 1932 zweimal vom chemisch-hygienischem Laboratorium analysiert. In Tabelle 5 haben wir unser Analysenresultat mit dem Resultat des chemisch-hygienischen Laboratoriums verglichen.

Tabelle 5 zeigt eine bedeutende Zunahme des Eisens; Aluminium und

Kieselsäure hatten jedoch etwas abgenommen. Das Sulphat hat sich ungeheuer vermehrt, im gegensatz dazu hat sich die freie Schwefelsäure fast nicht verändert.

Tabelle 5.

	Chemisch-hygienischer Laboratorium zu Tokyo		Kuroda
	Mai 1932	Oktober 1932	Juni 1941
H ⁺	0.0033	0.004507	0.0038
K	0.0023	0.002056	0.000
Na	0.0117	0.0152	0.001
Ca	0.0036	0.002997	0 0150
Mg	0.0026	0.002793	0.0032
Fe ⁺⁺	0.0043	0.0312	0.2836
Fe ⁺⁺⁺	0.1643	0.1457	0.2346
Al	0.1324	0 1444	0.1067
Cu	—	0.0006	—

Tabelle 5. (*Fortsetzung*)

	Chemisch-hygienischer Laboratorium zu Tokyo		Kuroda
	Mai 1932	Oktober 1932	Juni 1941
Cl	0.0190	0.002965	0.0180
HSO ₄ ⁻	0.3169	0.4375	0.3686
SO ₄ ⁻⁻	1.1599	1.245	1.6897
HBO ₂	0.1153	—	—
H ₂ SiO ₃	—	0.1562	0.1389
	1.9371	2.191	2.8641
Spezifische Gewicht	1.0004	1.001	1.003
pH-Wert	2.39	2.26	2.4

Ich möchte hiermit Herrn Prof. Kenjiro Kimura für seine freundliche Anleitung und steten Ratschläge, die mir bei der Ausführung dieser Arbeit zuteil gewordn sind, meinen herzlichsten Dank aussprechen. Herrn Prof. Yuji Shibata möchte ich für sein warmes Interesse an dieser Arbeit ergebenst danken. Der Kaiserlichen Akademie der Wissenschaft sowie der Notgemeinschaft der japanischen Wissenschaft sind wir wegen ihrer finanziellen Unterstützung zu grossem Dank verpflichtet.

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Researches on Camphor, Borneol and Their Allied Substances (Continued).

By Seichi YAMADA.

(Received, May 6, 1941.)

I. Catalytic Oxidation of Borneol and Isoborneol. Borneol (m.p. 204.2°C, $[\alpha]_D^{16} +21.34$ in alcoholic solution) was prepared by the reduction of camphor.

Isoborneol (m.p. 208°C in a sealed tube, $[\alpha]_D^{16} -1.3$ in alcoholic solution) was synthesised by the hydration of camphene, and recrystallised for several times from its solution in petroleum ether. Reduced copper which was used as catalyser was prepared by the method described by Mr. Masumoto,⁽²⁸⁾ and reduced nickel was prepared by Sabatier's method by first igniting nickel nitrate and then reducing the nickel oxide thus obtained at 300°C.

As the experimental apparatus, combustion furnace of common type was used, and camphor of the reaction product was estimated by the semicarbazone process,⁽²⁹⁾ and borneol and isoborneol by ester value after acetylation under the following conditions. During the acetylation, as the camphene itself is esterified by 13%, the content of borneol and isoborneol underwent some adjustments accordingly.

(1) borneol

Number	Weight (g.)	Saponification hours	Ester value after acetylation	isoborneol
1	2	2	266.4	93.3 %
2	1	4	283	99.1

(2) isoborneol

Number	Weight (g.)	Saponification hours	Ester value after acetylation	isoborneol
1	1	5	283	99.1 %

(1) Catalytic oxidation of borneol by reduced copper.

Catalyser	Borneol (g.)	Reaction temp. °C	Reaction time	Reaction products		
				Yield (g.)	M.p.	$[\alpha]_D^{14}$
Cu (1)	11.9	400	2 h. 07 min.	11.7	177.8-178.1	+41.8
Cu (2)	11.9	400	1 55	11.6	161-163.5	+40.8
Cu (3)	11.5	400	1 55	11.1	178.8-182	+40.3

(28) Loc. cit.

(29) Yamada, *J. Chem. Soc. Japan*, **48** (1927), 341.

(1)—*Concluded.*

Catalyser	Reaction products				
	Camphor (%)	Borneol (%)	Camphene (%)	Camphor (%)	Camphene (%)
Cu (1)	96.3	3.5	0.2	99.8	0.2
Cu (2)	57	29	14	80	20
Cu (3)	58	33	9	87	13

(2) Catalytic oxidation of isoborneol by reduced copper.

Catalyser	Isoborneol (g.)	Reaction temp. °C	Reaction time	Reaction products		
				Yield (g.)	M.p.	$[\alpha]_D^{25}$
Cu (1)	11.2	150	2 05 ^{h. min.}	10.7	166-171.8	±0
Cu (1)	9.3	300	2 00	8.2	165.5-169.1	±0
Cu (2)	10.5	150	2 15	9.6	204.4-207.9	±0
Cu (2)	10.1	300	1 55	8.1	72.5-84.0	±0

Catalyser	Reaction products				
	Camphor (%)	Isoborneol (%)	Camphene (%)	Camphor (%)	Camphene (%)
Cu (1)	56	37	7	89	11
Cu (1)	86	10	4	96	4
Cu (2)	0	96	4	0	100
Cu (2)	22	9	69	24	76

(3) Catalytic oxidation of borneol by reduced nickel.

No.	Borneol (g.)	React. temp. °C	React. time (hr.)	Reaction products							
				Yield (g.)	M.p.	$[\alpha]_D^{16}$	Camphor (%)	Borneol (%)	Camphene (%)	Camphor (%)	Camphene (%)
1	10.6	200	3 25 ^{h. min.}	10.1	177-178.3	+43.1	86	8	6	94	6
2	8.7	300	2 20	8.0	174.2-175.9	+42.5	90	7	3	97	3
3	11.9	400	1 30	11.6	176.5-178.8	+41.3	82	13	5	95	5

(4) Catalytic oxidation of isoborneol by reduced nickel.

No.	Isoborneol (g.)	React. temp. °C	React. time (hr.)	Reaction products							
				Yield (g.)	M.p.	$[\alpha]_D^{18}$	Camphor (%)	Isoborneol (%)	Camphene (%)	Camphor (%)	Camphene (%)
1	11.8	200	3 40 ^{h. min.}	11.1	173.5-175.3	±0	81	19	0	100	0
2	12.1	300	2 40	11.1	167-168.8	±0	89	7	4	96	4
3	10.7	400	1 50	10.2	168.5-171.3	±0	75	16	9	89	11

II. Catalytic Reduction and Rearrangement of Camphor, Borneol and Isoborneol under High Pressures and High Temperatures.

Camphor—Refined camphor manufactured by the Nippon Camphor Company; m.p. 176.4°C, $[\alpha]_D^{24}+44.13$.

Borneol—By reducing the purified camphor with metallic sodium and alcohol, some borneol was obtained, which, according to the writer's own method,⁽³⁰⁾ was treated with 2 moles of phthalic anhydride under 140–145°C for 20 hours and then immediately by steam distillation volatile substances were distilled off and the residue was treated with some warm water to remove the excess of phthalic acid. The ester was purified by recrystallisation; m.p. 158–159°C, $[\alpha]_D^{15}+52.41$ (C=4 in alcohol).⁽³¹⁾ The ester was saponified and the borneol thus obtained was recrystallised from its solution in petroleum ether; m.p. 204–204.5°C (in sealed tube), $[\alpha]_D^{15}+38.44$ (C=3.92 in toluene).

Isoborneol—Some camphor was dissolved in absolute alcohol and then was reduced by the catalytic reaction of reduced nickel under high temperature and pressure. To the isoborneol thus obtained, 2 moles of phthalic anhydride and some toluene were added, esterified by heating at 110°C for 5 hours, distilled out the volatile matter with steam, and to the residue warm water was added to remove the excess of phthalic acid. Borneol ester which contaminated the product was, as it is easily saponifiable, taken away by hydrolysis,⁽³²⁾ and the ester was recrystallised from its alcoholic solution, m.p. 168–168.2°C, $[\alpha]_D^{15}-83.07$ (C=3.7 in alcohol),⁽³³⁾ isoborneol obtained by saponifying the ester was recrystallised from petroleum ether, m.p. 212–213°C, $[\alpha]_D^{15}-34.42$ (C=3.35 in alcohol) $[\alpha]_D^{15}-19.59$ (C=5.17 in toluene).

Nickel—Nickel nitrate was ignited to produce nickel oxide, which was reduced with hydrogen at 300°C.

The reaction product was separated from nickel, camphor was quantitatively estimated by the semicarbazone process, and borneol and isoborneol were calculated from the specific rotation of their respective solutions in alcohol and toluene, the mean number being adopted.

In cases of samples 5–9, among the reaction products some water was present, which clearly indicated that dehydration had occurred. Therefore, after the estimation of camphor, the sample was distilled over sodium and isocamphane⁽³⁴⁾ (b.p. 164.5–165°C, m.p. 66–67°C, $[\alpha]_D \pm 0$) was obtained. Found: C, 86.60; H, 13.22. Calculated for $C_{10}H_{18}$: C, 86.86; H, 13.14%.

With regard to sample 17 and 18, to prove the presence of borneol 2 moles of phthalic anhydride were added in each case and the mixture was heated to 140–145°C for 20 hours. Thus all of the isoborneol was converted to camphene, and borneol was separated in the form of phthalic ester.

(30) *J. Chem. Soc. Japan*, **53** (1932), 807.

(31) Pickard and Littlebury, *J. Chem. Soc.*, **91**, 1978.

(32) Vavon and Peignier, *Bull. soc. chim.*, **39** (1926), 924.

(33) Kenyon and Picard, *J. Chem. Soc.*, **107**, 59.

(34) P. Lipp, *Ann.*, **382** (1911), 279; Komatsu and Masumoto, *Mem. Coll. Sci. Kyoto Imp. Univ.*, **5** (1922), 225.

No.	Sample	(g.)	Initial press. (atm.)	React. temp. °C.	Temp. at the begin- ning of ab- sorp. °C.	React. time (hr.)	H ₂ absorbed (mol.)
1	camphor	50	23.3	170~190	170	7 $\frac{1}{2}$	1.1
2	camphor	50	49.4	170~200	150	6 $\frac{1}{3}$	1.0
3	camphor	50	84.5	170~190	140	5 $\frac{5}{6}$	1.0
4	camphor	50	79.5	140~160	150	20 $\frac{1}{2}$	0.7
5	camphor	50	91.6	200~280	—	8 $\frac{5}{6}$	2.0
6	camphor	50	51	190~220	160	3	1.5
7	borneol	25	49.5	130~250	210	7 $\frac{1}{2}$	1.0
8	isoborneol	15	67	170~190	—	15	0.7
9	borneol	25	50.5	120~256	150	16	1.1
	isoborneol	25			220		
10	camphor	50	55.5	170~190	150	21	1.0
11	camphor	50	78.2	140~170	—	7 $\frac{1}{2}$	1.4
	cyclohexane	60					
12	camphor	50	90.7	140~160	130	5 $\frac{1}{2}$	1.4
	abs. alcohol	60					
13	camphor	50	61.8	170~200	—	8	1.0
	acetic acid	0.5					
14	camphor	50	85.4	180~200	—	8 $\frac{1}{2}$	0.7
	pyridine	0.5					
15	camphor	50	58.2	160~170	150	9 $\frac{1}{2}$	1.2
	cyclohexane	60					
	metallic Na	1					

No.	Reaction product					
	Yield (g.)	M.p. °C.	$[\alpha]_D^{25}$ at °C	Camphor %	Borneol %	Isoborneol %
1	49.0	195—196	+11.2 ²⁰	20.0	51	49
2	48.0	190—194	+10.6 ²⁴	20.0	50	50
3	49.3	187—191	+ 4.8 ³²	12.0	47	53
4	48.5	194—195	+12.1 ³²	21.5	51	49
5	40.5 H ₂ O 1.6	80—103	± 0	7.0	—	—
6	48.0 H ₂ O	119—125	+ 8.3 ¹³	5.0	—	—
7	12.0 H ₂ O	100—110	+ 3.7 ²⁰	—	—	—
8	7.0 H ₂ O	78—79	— 0.7 ¹⁰	—	—	—
9	25.0 H ₂ O	78—81	± 0	—	—	—
10	49.0	197—198	+11.8 ²⁶	23.0	50	50
11	48.0	203—204	— 8.2 ¹¹	21.0	23	77
12	47.2	208—210	—24.7 ¹⁴	2.5	12	88
13	48.5	196—198	+ 1.6 ²³	21.5	37	63
14	49.0	199—200	+ 5.5 ¹⁴	32.0	36	64
15	49.0	206	— 7.4 ²²	8.0	33	67

* determined in alcohol.

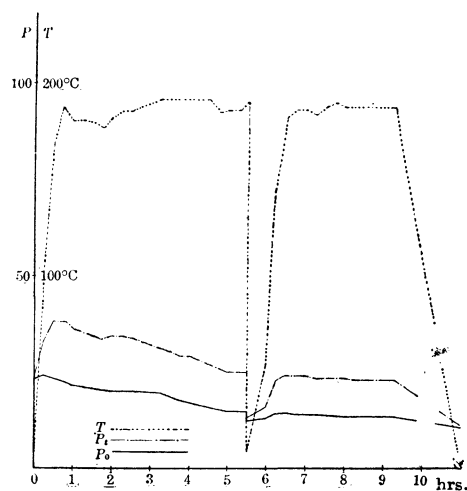


Fig. 1.

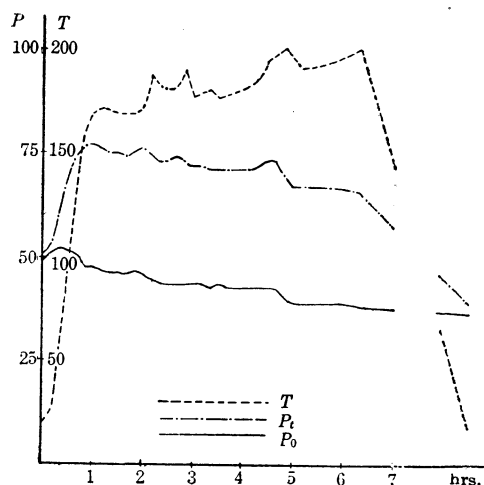


Fig. 2.

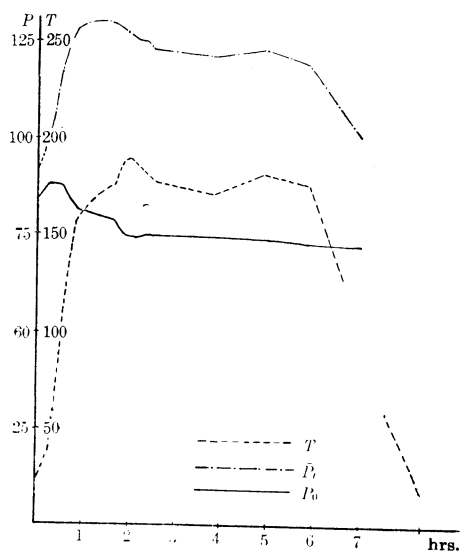


Fig. 3.

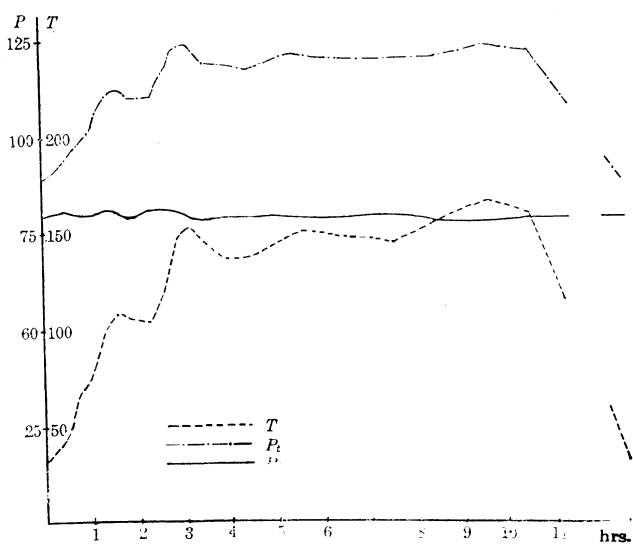


Fig. 4. (1)

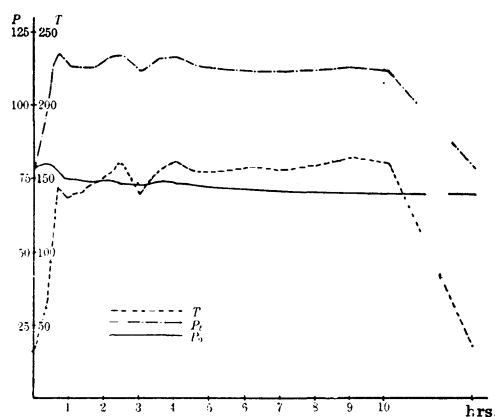


Fig. 4. (2)

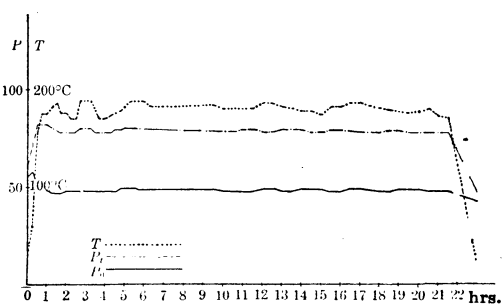


Fig. 5.

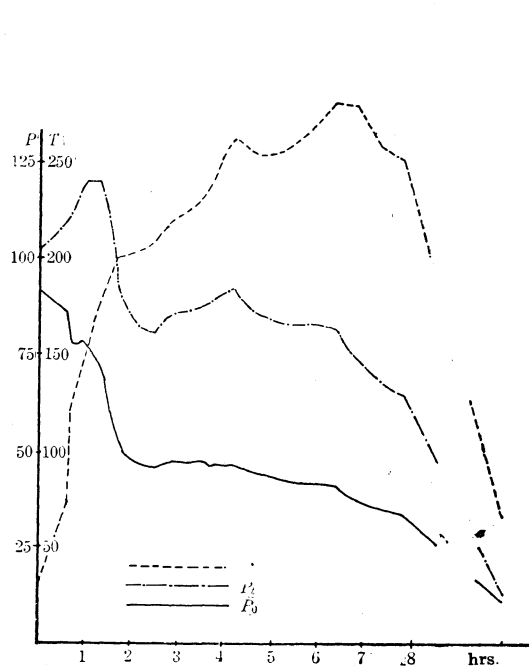


Fig. 6.

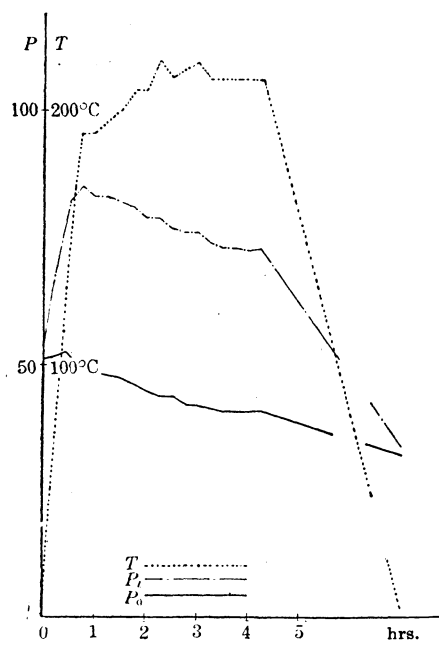


Fig. 7.

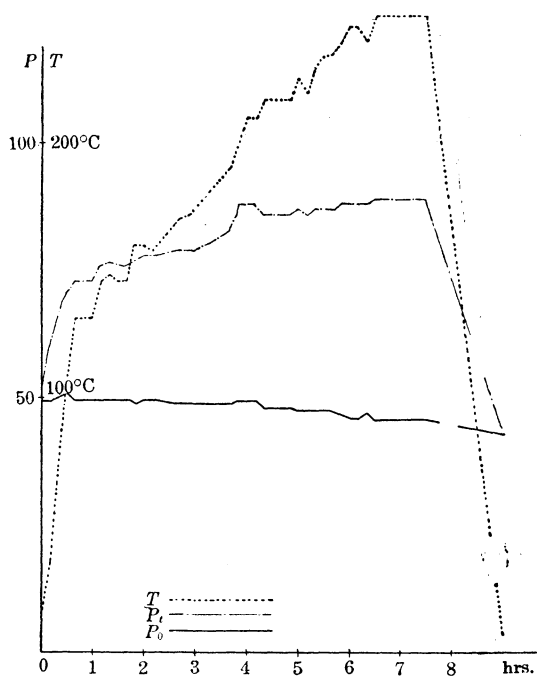


Fig. 8. Dehydration of Borneol.

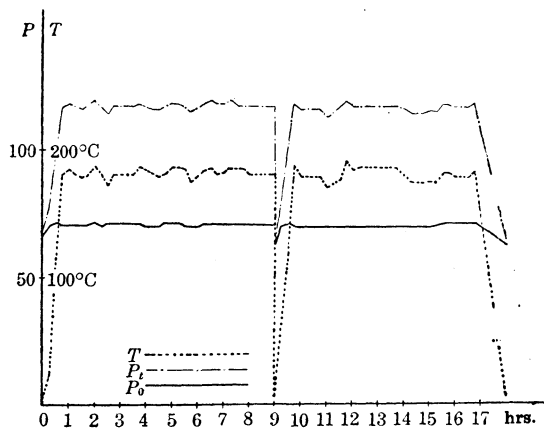


Fig. 9. Dehydration of Isoborneol.

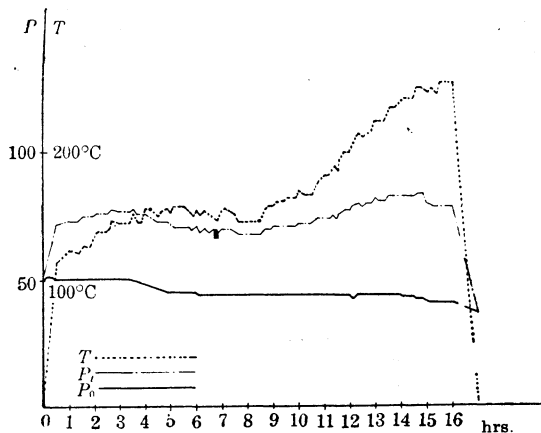


Fig. 10. Dehydration of Mixture of Borneol and Isoborneol.

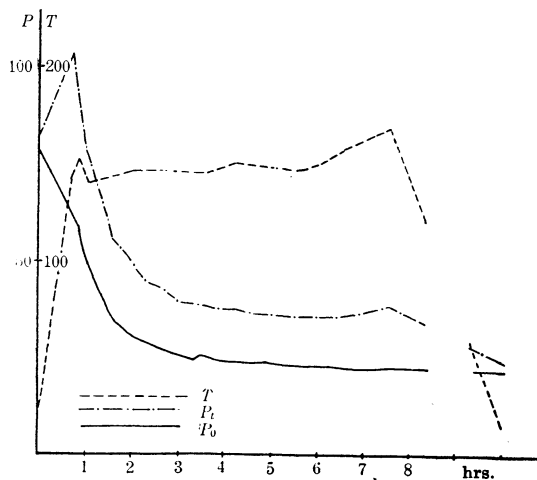


Fig. 11. Camphor+Cyclohexane.

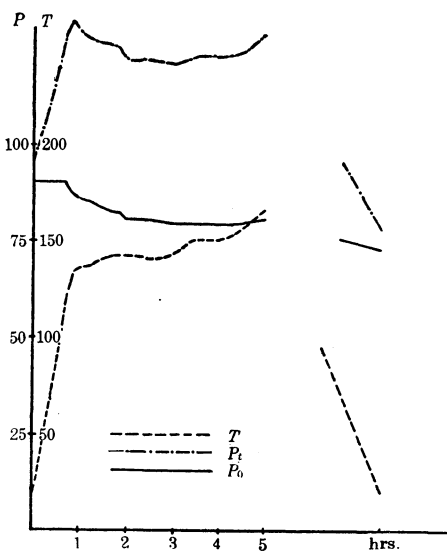


Fig. 12. Camphor+Abso. Alcohol.

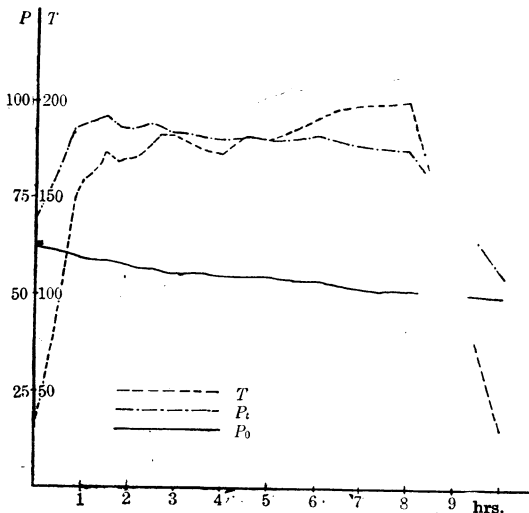


Fig. 13. Camphor+Acetic acid.

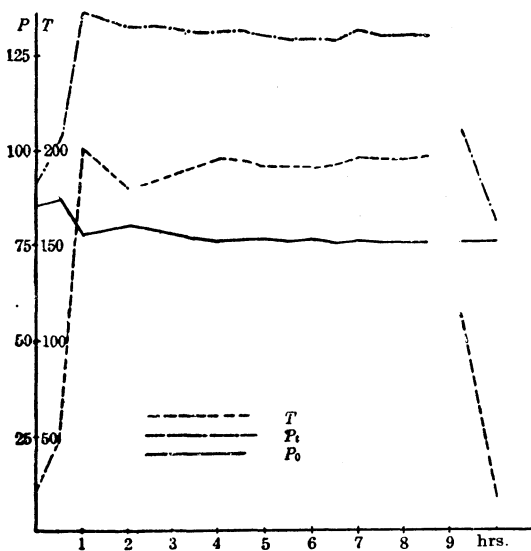


Fig. 14. Camphor+Pyridine.

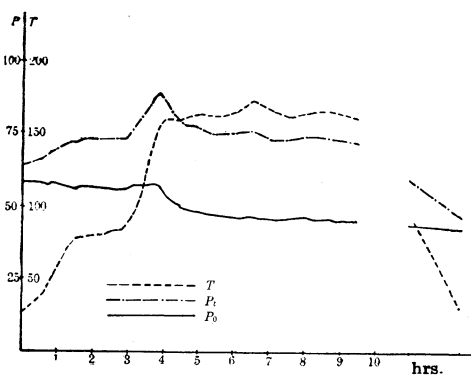


Fig. 15. Camphor+Cyclohexane+Na.

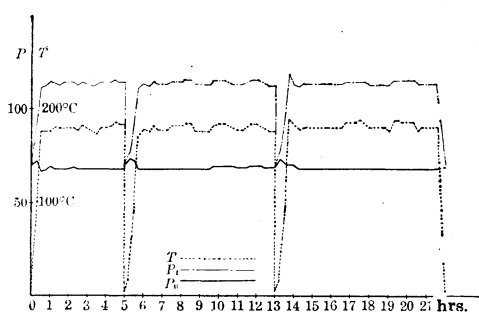


Fig. 16. Borneol.

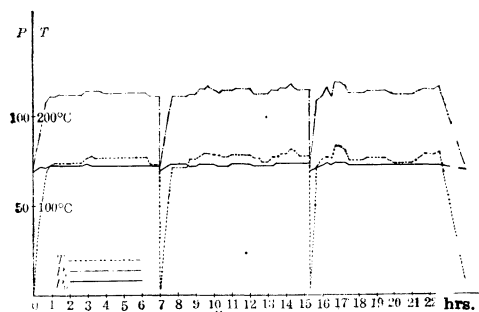


Fig. 17. Borneol-Abs. alcohol.

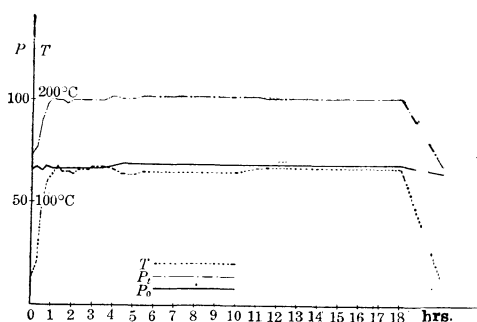


Fig. 18. Isoborneol-Abs. alcohol.

No.	Sample	(g.)	Initial press. (atm.)	React. temp. (°C)	React. time (hrs.)	H ₂ absorbed (mol)
16	borneol	15	71	170—190	19.5	0.3
17	isoborneol	25	53	130—150	4	0
18	isoborneol	35	47	140—165	4	0
19	borneol alcohol	15 20	70	150—160	20.5	0
20	isoborneol alcohol	15 20	66	130—140	16.3	0.3

No.	Reaction product							
	Yield (g.)	M.p. °C	[α] _D alc. °C	[α] _D toluene °C	Methoxy value after ether. by HCl+CH ₃ OH	Camphor %	Borneol %	Isoborneol %
16	13	201—202	+37.1 ¹⁰	+38.0 ¹³	0.5	0.6	99	1
17	23	193—202	—22.2 ¹⁶	—10.3 ¹⁶	10.1	0.6	16	84
18	30	199—200	+ 6.1 ³³	+10.1 ³³		0.5	51	49
19	13	199—199.5	+31.2 ²⁰	+33.7 ¹³	1.5	0.2	90	10
20	13.5	209—210	—25.9 ³¹	—12.6 ³¹	10.3	0.6	11	89

Esters	M.p. °C	[α] _D	Borneol obtained by saponification	
			M.p. °C	[α] _D
Acidic ester	153.5–159	+33.89	203–204	+29.68
Neutral ester	99–100	+25.05	201–202	+11.94

The esters and borneol were confirmed to be pure by the mixed fusion method. In one half of sample 19, for the purpose of proving the presence of isoborneol, it was tried to separate it as a Mg salt of phthalic acid ester, but due to the scarcity of sample, the experiment was not successful. The other half was dehydrated with phthalic anhydride and successfully confirmed as camphene. In sample 20, borneol was separated in the form of acidic ester of phthalic acid (m.p. 158–159°C.), as before. The borneol obtained by saponification; m.p. 201–202°C., [α]_D+14.52.

III. Reduction of Dimethylcamphor with Metallic Sodium and Alcohol.

(1) *α,α' -Dimethylcamphor*. According to the method of Haller,⁽³⁵⁾ by treating camphor with NaNH₂ and ICH₃ monomethylcamphor was obtained quantitatively. Moreover, this monomethylcamphor was repeatedly methylated; to remove the remaining camphor and monomethylcamphor, they were changed into oximes by heating at 100°C for 49 hours with 2 moles of NH₂OH.ZnCl₂ and after fractionally distilling 8 times, pure dimethylcamphor [b.p. 85–85.5°/8 mm, d_4^{25} 0.9460, n_D^{25} 1.4725, [α]_D²⁵+91.27, M.R. (obs.) 53.25, (calc.) 53.23] was obtained in a yield of 63%. Found: C, 79.86; H, 11.31. Calculated for C₁₂H₂₀O: C, 80.00; H, 11.11%.

(2) *Dimethylborneol*. Dimethylcamphor was reduced with metallic sodium and alcohol, and a crystalline matter (d_4^{25} 0.954, n_D^{25} 1.481, [α]_D²⁵+46 in alcohol) mixed with oily substance was obtained 96.5%.

This reaction product was separated into 75% crystal and 25% oil; by recrystallising the crystal with petroleum ether for several times, a white needle crystal of borneol-like odour was obtained, b.p. 90.5–93°/5 mm., m.p. 57°C, [α]_D²⁵+50.72 (C=2.11 in alcohol), [α]_D²⁵+53.76 (C=1.71 in toluene). Found: C, 78.83; H, 12.15. Calculated for C₁₂H₂₂O: C, 79.12; H, 12.09%.

This substance makes a beautiful white short needle crystal of phenylurethane (m.p. 112–113°C.), and, by reacting with p-nitrobenzoic acid, forms a needle crystal of silky lustre and of faintly greenish white colour. This crystal (m.p. 115–115.8°C. [α]_D²⁵+50.94 (C=0.53 in alcohol) or +70.78 (C=0.367 in chloroform) is soluble in ether, petroleum ether, or warm alcohol, but sparingly soluble in cold alcohol. Further, it reacts with phthalic anhydride and forms monoester quantitatively.

Sample (g.)	Phthalic anhydride (moles)	React. temp. °C	React. time (hrs)	Monoester	
				Yield (g.)	%
4	2	110–115	10	7.2	99.4
5	2	140–145	20	9.1	99.6

(35) *Compt. rend.*, **148** (1909), 1645.

The monoester crystallises in beautiful white needles (m.p. 177–178°C., $[\alpha]_D^{27} + 16.32$ ($C=0.42$ in alcohol), $[\alpha]_D^{19} + 19.12$ ($C=0.471$ in chloroform)), and is soluble in ether, alcohol, or chloroform, but insoluble in petroleum ether and water.

The Mg salt of phthalic acid ester is white lustrous crystals of scale shape, the m.p. being 175–176.2°C. The solution of dimethylborneol in benzene was boiled with zinc chloride for 3 hours, and yet no change occurred.⁽³⁶⁾

(3) *Dimethylisoborneol*. The oily matter (d_4^{25} 0.953, n_D^{25} 1.485, $[\alpha]_D^{29} + 38$ in alcohol) separated from the crystal already mentioned was fractionally distilled under a reduced pressure, and the following three fractions were obtained.

Fraction	B.p. 5mm	Yield (%)	d_4^{25}	n_D^{25}	$[\alpha]_D^{27}$ in alc.
1	81–87	10.6	0.9422	1.4780	+48.5
2	87–95	13.4	0.9483	1.4809	+52.3
3	95–103	71.2	0.9522	1.4831	+52.4

Each fraction was cooled with common salt and ice; from fractions (1) and (2) no crystal was obtained, and fraction (3) solidified entirely. Further, when the fraction (2) was treated with phthalic anhydride at 140–145°C. for 10 hours, unsaturated hydrocarbon was obtained as well as ester. From this experimental fact, the presence of an isomer to be easily dehydrated was suspected. Then it was tried in vain to obtain this isomer as *p*-nitrobenzoic ester by fractional crystallization. The isomer was treated with phthalic anhydride at 110–115°C. for 10 hours, the monoester thus obtained being changed to a Mg salt. Utilising the difference in the solubility in alcohol, an easily soluble crystalline powder (m.p. 180–182°C.) was obtained abundantly. This was further changed to an acidic ester, and recrystallising it from its solution in acetic acid, a lustrous beautiful crystal of scale shape (m.p. 173–174°C.) was obtained. By saponifying it, a compound $C_{12}H_{22}O$ to be considered as dimethylisoborneol was obtained, b.p. 82–84°/3 mm, m.p. 47–49°C, d_4^{25} 0.9406, n_D^{25} 1.4748, M.R. (obs.) 54.5, (calc.) 54.8, $[\alpha]_D^{15} + 36.47$ ($C=1.70$ in alcohol), $[\alpha]_D^{15} + 42.71$ ($C=1.43$ in toluene). Found: C, 78.79; H, 12.06. Calculated for $C_{12}H_{22}O$: C, 79.12; H, 12.09%.

Phenylurethane is a lustrous, colourless needle crystal (m.p. 116–117°C.), and *p*-nitrobenzoic ester is also a lustrous, colourless needle crystal, but its m.p. is 114.5–115°C and $[\alpha]_D^{19} + 24.90$ ($C=0.321$ in alcohol), $[\alpha]_D^{19} + 44.11$ ($C=0.317$ in chloroform). When heated with 2 moles of phthalic anhydride at 110–115°C. for 10 hours, monoester is obtained in yield of 90%, and when the temperature was raised to 140–145°C. and

(36) Piccard and Littlebury, *J. Chem. Soc.*, **91**, 1977; Tetsusaku-Ikeda, *Proc. Sci. Inst. Japan*, **7**, 257.

the reaction was continued for about 10 hours, dehydration was complete and no ester was formed at all. And by the reaction with zinc chloride dehydration occurs.

Further, to find out the proportion of dimethylborneol and dimethylisoborneol in the reduction product which was obtained by reducing dimethylcamphor with metallic sodium and alcohol, 2 moles of phthalic anhydride was added, and, after the reaction at 110–115°C. for 10 hours, there were obtained 93% ester and 4% unesterified oil. The alcoholic part separated from the ester was again treated with phthalic anhydride at 140–145°C., and the product was separated into a substance (90%) to be considered as dimethylborneol and another (10%) to be considered as dimethylisoborneol. Unesterified oil, as it forms no phenylurethane by all means, was assumed to be a mixture of unsaturated hydrocarbons formed by dehydrating dimethylisoborneol and dimethylcamphor, and, from the bromine absorption,⁽³⁷⁾ the content of unsaturated hydrocarbons in the unesterified oil was found to be 34%.

Sample (g.)	1/5 N Br ₂ sol. (c.c.)	React. time (hors)	Na ₂ S ₂ O ₃ c.c.			Unsat. hydrocarbon (%)
			Total Br absorbed	Br substituted	Br added	
0.2050	15	8	9.5	4.2	5.3	34.2
0.1649	15	8	7.7	3.4	4.3	34.8

As a result, the proportion of dimethylborneol and dimethylisoborneol formed was calculated to be 88:12.

IV. Catalytic Reduction of Dimethylcamphor at High Temperatures and under High Pressures. By catalytically reducing dimethylcamphor at 220–230°C. in hydrogen of 60 atmospheres pressure in the presence of reduced nickel, the following results were obtained.

No.	Sample	(g.)	Initial press. (atm.)	React. temp. °C	React. time (hrs)	H ₂ absorbed (mol)
1	dimethylcamphor	30	57	220–230	27½	1.1
2	dimethylcamphor abs. alcohol	30 40	60	200	20	1.1
3	dimethylcamphor acetic acid	30 0.3	60	220–230	25	1.1
4	dimethylcampbor	30	49	280	10	2.1

(37) H. Meyer, *Org. Chem. Method.*, Bd., I, 1126, 4. Aufl.

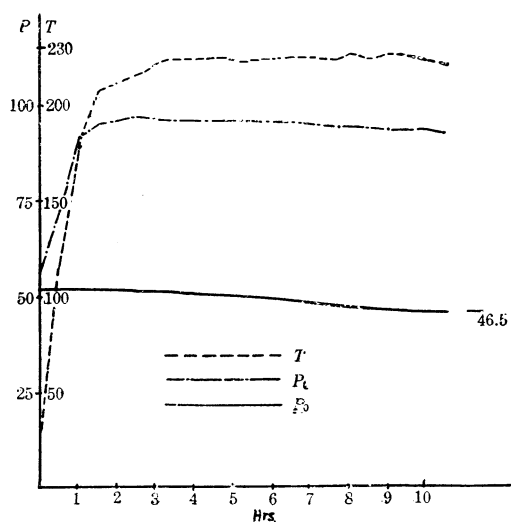


Fig. 19. (1). Dimethylcamphor.

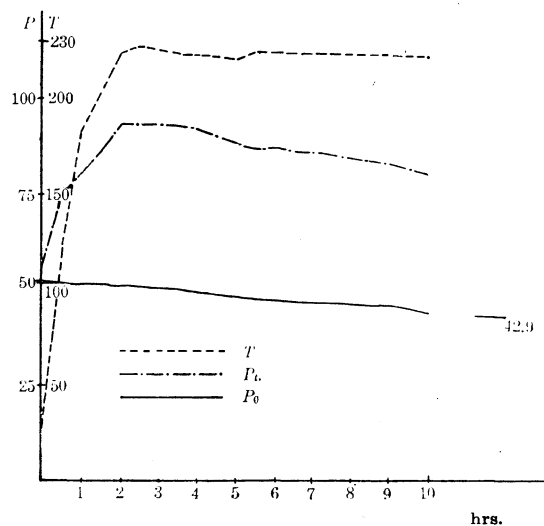


Fig. 19. (2).

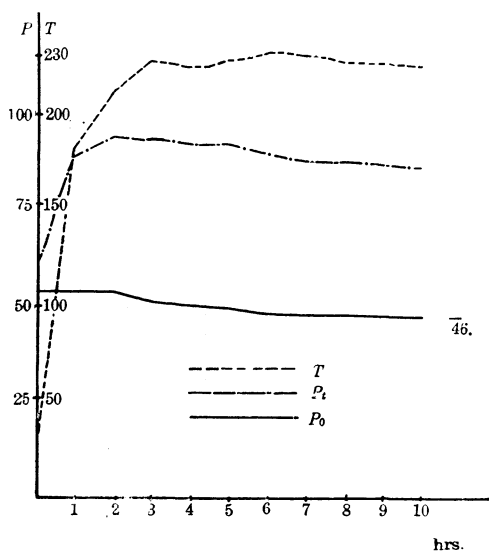


Fig. 20. (1). Dimethylcamphor + Acetic acid.

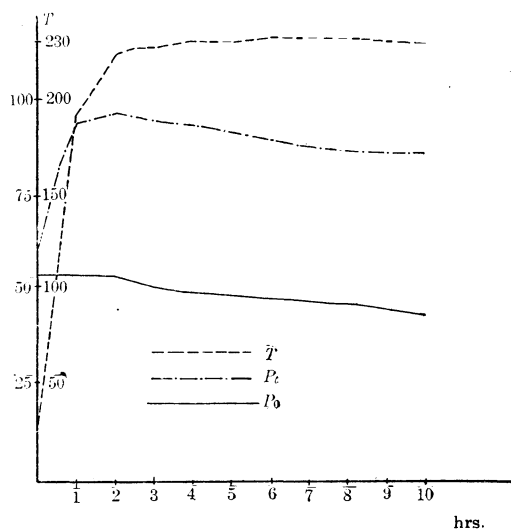


Fig. 20. (2)

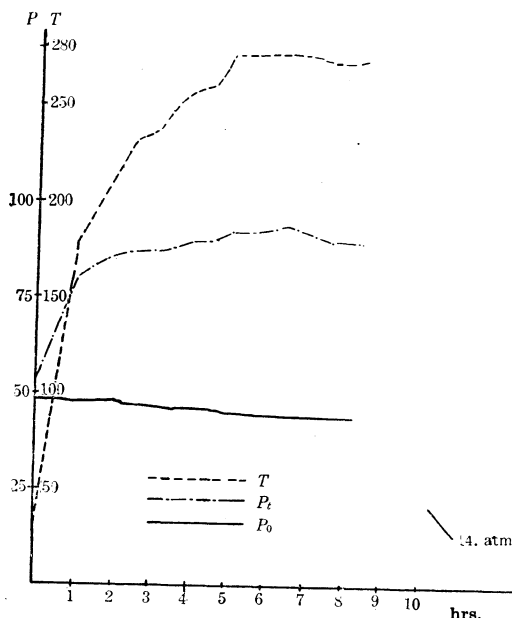


Fig. 21. Dehydration of Dimethylcamphor.

No.	Reaction product						
	Yield (g.)	d_4^{25}	n_D^{25}	$[\alpha]_D$ in alcohol	Dimethylcamphor (%)	Dimethylborneol (%)	Dimethylisoborneol (%)
1	26	0.927	1.474	+48	80	85	15
2	24	0.948	1.475	+77	63	66	34
3	26	0.949	1.479	+59	51	86	14
4	26	0.876	1.470	-26			

In the case of sample (4), some water being mixed in the reaction product, dehydration had occurred undoubtedly. After distilling several times at ordinary pressure, the following two fractions were separated.

Fraction	B.p. °C	Yield (g.)	d_4^{25}	n_D^{25}	$[\alpha]_D$ (in alcohol)	M. R.	
						obs.	calc. for $C_{12}H_{22}$
(1)	197-200	1.9	—	—	—	—	—
(2)	200-203	20.6	0.8706	1.4695	-28.07	53.17	53.22

The elementary analysis of fraction (2) is; Found: C, 86.39; H, 13.51. Calculated for $C_{12}H_{22}$: C, 86.75; H, 13.25%.

(To be continued.)

On the Catalytic Action of Japanese Acid Earth. XI. The Isomerisation of Aldehydes to Ketones and the Explanation of the Migration of the Radicals from the Standpoint of the Electronic Theory (Continued).

By Koshiro ISHIMURA.

(Received May 14, 1941.)

Experimental. *Benzoyl carbinol.* Various methods of obtaining benzoyl carbinol have been tried by the author. Acetophenone was brominated by R. Möhlaus⁽³⁸⁾ method in glacial acetic acid. Interaction of the resulting ω -bromacetophenone with potassium acetate was carried out more smoothly by R. Stroemer's⁽³⁹⁾ method than by W. L. Evans'⁽⁴⁰⁾ method, while the hydrolysis of the acetate according to the latter's information gave a better result. But I. Fischer and M. Busch's⁽⁴¹⁾ method of hydrolysing it by boiling with the excess of barium carbonate in hot water about fifty times as much as the amount of the acetate gave the best. Benzoyl carbinol thus obtained has one molecule of water of crystallisation when recrystallised from hot water, m.p. 73–74°C. On standing it in a desiccator under the reduced pressure for about five hours the water of crystallisation was set free, giving anhydrous crystal, m.p. 86–87°C. Evans gave the m.p. 85–86°C., while J. Plöchl and F. Blümlein⁽⁴²⁾ 86–87°C.

α -Phenyl α -p-tolyl ethylene glycol. Anhydrous benzoyl carbinol (27 g.) dissolved in ether was added into the Grignard reagent prepared from *p*-tolyl iodide (110 g.) and magnesium ribbon (10 g.). As the solubility of the carbinol in ether is not so great, it was put in Soxlet's apparatus connected with the flask containing the reagent. The content of the flask was gently boiled so that the carbinol was gradually extracted by hot ether and the solution flowed down into the flask. When all the carbinol was dissolved the reaction mixture was left to stand overnight. It was treated with a mixture of ice water (500 g.) and glacial acetic acid (25 c.c.). The ethereal layer was separated from the water layer which was extracted with ether several times. The combined ethereal solution was washed with dilute solution of sodium hydroxide, with water and then with a saturated solution of sodium bisulphite in order to remove the remaining carbinol. It was again washed with dilute solution of sodium hydroxide and water, concentrated by distillation till about 100 c.c. of the solution remained. On cooling a large amount of *pp'*-ditolyl produced by the side reaction crystallised out. The solution freed from the solid matter was distilled in steam and a considerable quantity of *pp'*-ditolyl, iodotoluene and toluene came over thereby. Without the previous

(38) *Ber.*, **15** (1882), 2465.

(39) *Ber.*, **39** (1906), 2294.

(40) *Am. Chem. J.*, **35** (1906), 120.

(41) *Ber.*, **24** (1894), 2680.

(42) *Ber.*, **16** (1883), 1292.

removal of these impurities, the purification of the required glycol often became very difficult. The contents of the distilling flask were extracted with ether. The ethereal solution was dried over anhydrous sodium sulphate and the solvent was removed. The required glycol was solidified on cooling. Yield about 26 g. It was recrystallised from petroleum benzine in colourless fine needles, m.p. 84.5–85.5°C. (Found: C, 78.9; H, 7.3. $C_{15}H_{16}O_2$ requires C, 78.9; H, 7.0%).

The benzoyl derivative was obtained by dissolving the glycol (0.8 g.) in ether (10 c.c.) and adding benzoyl chloride (3 g.) and sodium hydroxide (3 g.) dissolved in water (20 c.c.) and by shaking the mixture vigorously. The reaction heat evolved thereby was removed away by cooling with water intermittently. The ethereal layer was washed with water, dried over anhydrous sodium sulphate and the ether removed, leaving colourless syrup which on the addition of a small quantity of alcohol solidified immediately. It did not tend to crystallise for several days, if not treated as stated above. It formed colourless plates from dilute alcohol, m.p. 136°C. (corr.). (Found: C, 79.0; H, 6.2. $C_{22}H_{20}O_3$, monobenzoyl derivative requires C, 79.5; H, 6.0; $C_{29}H_{24}O_4$, dibenzoyl derivative, C, 79.8; H, 5.5%). Mol. wt., found (Rast), 344. $C_{22}H_{20}O_3$ requires 332 whereas $C_{29}H_{24}O_4$ 436. The substance was therefore the monobenzoyl derivative.

Oxidation of α -phenyl α -p-tolyl ethylene glycol to phenyl p-tolyl ketone. The glycol (0.5 g.) was added by portions into the solution of chromic oxide (0.55 g.) dissolved in 80% acetic acid (30 c.c.), and the mixture was left to stand overnight. It was heated for 30 minutes on the water bath, cooled and poured into water (400 c.c.) and then cooled with ice and salt. White crystals (0.37 g.) were thrown down which when washed with water and recrystallised from dilute alcohol melted at 57–57.5°C. (uncorr.) alone or mixed with the specimen of phenyl p-tolyl ketone which was obtained from toluene and benzoyl chloride and melted at the same temperature. (Found: C, 85.9; H, 6.7. $C_{14}H_{12}O$ requires C, 85.7; H, 6.1%). According to Th. Zinke⁽⁴³⁾ the stable modification of the ketone melted at 59–60°C. and the metastable at 55°C, while K. Schaum, K. Schäling and F. Klausling⁽⁴⁴⁾ gave the m.p. 55 and 52°C. respectively.

Phenyl p-tolyl acetaldehyde. The mixture of α -phenyl α -p-tolyl ethylene glycol (16 g.), water (40 c.c.) and 9 drops of concentrated sulphuric acid was heated in a sealed tube at 180–185°C. for 3 hours. When cooled down the contents were extracted with ether, washed with dilute solution of sodium carbonate, shaken with saturated solution of sodium bisulphite, the addition compound of which with the required aldehyde, white crystalline powder, was collected. Yield, 19 g. The addition compound (15 g.) was decomposed by 15% sodium hydroxide solution (50 c.c.), the aldehyde set free was extracted with ether and distilled under reduced pressure after separated from the solvent. The pure aldehyde (6.7 g.) thus obtained boiled at 176°C. (corr.) under 7 mm. It formed a colourless and almost odourless oil, tinged fuchsin sulphurous acid with pink colour when pure, while the specimen mixed with a trace of impurity prussian blue. d_4^{25} , 1.0785; n_D^{25} , 1.5844; M. R., 65.20; calculated (Eisen-

(43) Cited by C. Bodewig, *Ann. d. Physik*, **153** (1876), 234.

(44) *Ann.*, **411** (1911), 188.

lohr), 64.28. (Found: C, 85.9; H, 6.7. $C_{15}H_{14}O$ requires C, 85.7; H, 6.6%). On long standing its analytical data showed gradual decreases in the contents of both carbon and hydrogen suggesting the autoxidation of the aldehyde with atmospheric oxygen. The oxime of the aldehyde formed oil at the ordinary temperature. The semicarbazone was obtained by standing overnight a mixture of the aldehyde (2 g.), potassium acetate (2 g.), semicarbazide hydrochloride (2 g.), dissolved in hot 95% alcohol (20 c.c.) diluted with water (10 c.c.). It crystallised from dilute alcohol in colourless columns (3.0 g.) m.p. 158–159°C. (corr.) (Found: N, 16.0. $C_{16}H_{17}ON_3$ requires N, 15.7%). M. Tiffeneau and J. Lévy⁽⁴⁵⁾ obtained the same aldehyde by the isomerisation of α -phenyl β -tolyl ethylene oxide and gave the following data: b.p., 180–185°C./10 mm.; n_D^{20} , 1.582; m.p. of the semi-carbazone, 157–158°C.

Oxidation of phenyl p-tolyl acetaldehyde. Silver nitrate (1.2 g. in 1 c.c. water) was added to the alcoholic solution of the aldehyde (0.8 g. in 15 c.c.) and then potassium hydroxide (0.9 g. in 10 c.c. water) was added gradually, the mixture was shaken for 3 hours and left to stand overnight. It was filtered, the filtrate was concentrated on the water bath, and acidified with dilute sulphuric acid. An oily substance separated out which solidified on cooling. Yield, 0.5 g. Phenyl p-tolyl acetic acid thus obtained was recrystallised from dilute alcohol with the addition of active charcoal forming colourless plates, m.p. 115° (Found: C, 79.1; H, 6.6. $C_{15}H_{14}O_2$ requires C, 79.6, H, 6.2%). M. Tiffeneau and J. Lévy⁽⁴⁵⁾ gave the m.p. 112–115°C.

Isomerisation of phenyl p-tolyl acetaldehyde. The isomerisation was carried out as stated above (p. 199*). The aldehyde (12.0 g.) was passed over Japanese acid earth (25 g) drop by drop with a rate of 3.5 g. per hour. The reaction products consisted of (i) colourless easily-flowing liquid (2.0 g.) with a faint fluorescence mixed with water drops, (ii) colourless fragrant viscous oil (5.0 g.) which flowed out of the tube when the temperature of the furnace was raised to 350°C. after the total aldehyde was passed into it, and solidified to colourless crystalline mass, and (iii) a reddish brown viscous liquid (2.0 g.) mixed with a small quantity of crystals, obtained when the temperature was raised to 450°C.

The product (i) was separated from water drops and distilled over metallic sodium giving colourless liquid (1.0 g.), b.p. 80–112°C, d_4^{24} 0.8690, n_D^{18} 1.4997. It proved to be a mixture of about 20% benzene and about 80% toluene, when calculated from the specific gravity or from the refractive index. The product (ii) consisted of almost pure phenyl p-methylbenzyl ketone. (Found: C, 85.9; H, 6.7. $C_{15}H_{14}O$ requires C, 85.7; H, 6.6%). After recrystallised from dilute alcohol several times it melted at 97°C. alone or mixed with the authentic specimen synthesised from ω -bromacetophenone and toluene by Friedel-Crafts' reaction. A. McKenzie, A. K. Mill and J. R. Myles⁽⁴⁶⁾ gave the m.p. 95–96°C., while M. Tiffeneau⁽⁴⁷⁾

(45) *Bull. soc. chim.*, **49** (1931), 1744.

* All the samples of the acid earth used throughout this series of experiments were taken from one and the same stock, and the electric furnace as well as the reaction tube were also the same ones. This Bulletin, **16** (1941), 199.

(46) *Ber.*, **63** (1930), 908.

(47) *Compt. rend.*, **139** (1904), 1507.

94–95°C. The oxime of the ketone obtained by K. Auers' ⁽⁴⁸⁾ method formed colourless needles melting sharply at 101°C. after recrystallisation several times from either dilute alcohol or from ligroin. H. Strassmann ⁽⁴⁹⁾ gave the m.p. 109°C. and A. McKenzie, A. K. Mill and J. R. Myles ⁽⁵⁰⁾ 108–109°C. (Found: N, 6.7. $C_{15}H_{15}ON$ requires N, 6.2%).

p-Tolyl benzyl ketone, isomeric to the above one, was not found to be present in the reaction product of the present experiment. The specimen synthesised from acetyl chloride and toluene melted at 110–110.5°C. H. Strassmann ⁽⁵¹⁾ gave the m.p. 109°C., while M. Tiffeneau ⁽⁵²⁾ 108–109°C. Its semicarbazone was obtained by heating a mixture of the ketone (0.2 g.), semicarbazide hydrochloride (0.2 g.) and potassium acetate (0.2 g.), dissolved in dilute alcohol (3 c.c.). After three day's standing long glittering needles (0.3 g.) crystallised out, which melted at 166.5°C. (corr.) after recrystallised from dilute alcohol. (Found: N, 15.4. $C_{16}H_{17}ON_3$ requires N, 15.7%). Kipping ⁽⁵³⁾ obtained only azine melting at 170–173°C. by prolonged heating of the ketone with semicarbazide hydrochloride and sodium acetate and E. E. Turner ⁽⁵⁴⁾ obtained the same product melting at 181°C. by heating the ketone with semicarbazide hydrochloride dissolved in dilute alcohol, in a sealed tube heated at 180°C. for three hours. Both the English authors reported that they could not obtain the semicarbazone. The oxime melts at 131°C. H. Strassmann ⁽⁴⁹⁾ gave the same melting point.

Phenyl *p*-methylbenzyl ketone dissolves in concentrated sulphuric acid with a tint of canary yellow while *p*-tolyl benzyl ketone thereby develops at first dirty green which gradually changes into greenish yellow colour.

α,β-Dibenzoyl ethane. When phenyl *p*-methylbenzyl ketone was synthesised from *ω*-bromacetophenone and toluene by the Friedel and Crafts' reaction, a small quantity of colourless microcrystalline columns, m.p. 145–146°C. (uncorr.), was also obtained. It was confirmed to be *α, β*-dibenzoyl ethane produced undoubtedly by the condensation of two molecules of *ω*-bromacetophenone. (Found: C, 81.0; H, 5.8; Mol. wt., (Rast), 289. $C_{16}H_{14}O_2$ requires C, 80.7; H, 5.9%; Mol. wt., 238). S. Kape and C. Paal ⁽⁵⁵⁾ gave it a melting point 144–145°C. and G. Dupont ⁽⁵⁶⁾ 144°C.

p-Methylbenzoyl carbinol. *p*-Methylbenzoyl methyl acetate (30 g.) was hydrolysed by boiling with barium carbonate (30 g.) in hot water (1500 c.c.) for two hours. The solution was filtered hot. On cooling *p*-methylbenzoyl carbinol (15 g.) crystallised out, which was recrystallised from ligroin in colourless prisms, m.p. 89–90°C. (Found: C, 75.9; H, 5.4. $C_{16}H_{14}O_3$ requires C, 75.6; H, 5.5%). K. Auers ⁽⁵⁷⁾ described it as light yellow prisms melting at 89–89.5°C., and J. Boëseken, L. W. Hansen and S. H. Bertram ⁽⁵⁸⁾ gave a melting point 90°C. It dissolved in concentrated

(48) *Ber.*, **22** (1889), 604.

(49) *Ber.*, **22** (1889), 1231.

(50) *Loc. cit.*

(51) *Loc. cit.*

(52) *Compt. rend.*, **134** (1902), 1507.

(53) Proceeding of the Chemical Society, No. 220.

(54) *J. Chem. Soc.*, **107** (1915), 1462.

(55) *Ber.*, **21** (1888), 3056.

(56) *Compt. rend.*, **158** (1914), 1350; *Bull. soc. chim.*, (4) **15** (1914), 606.

(57) *Ber.*, **39** (1906), 3761.

(58) *Rec. trav. chim. Pays-Bas*, **35** (1916), 311.

sulphuric acid with canary yellow colour which faded away on dilution with water.

α-m-Tolyl α-p-tolyl ethylene glycol. *p*-Methylbenzoyl carbinol (28 g.) dissolved in ether was gradually added to the Grignard reagent prepared from *m*-iodotoluene (140 g.) and magnesium ribbon (14 g.) and the solution was boiled for 5 hours. As the solubility of the carbinol in ether is relatively small, a Soxhlet's flask was very useful to carry out the reaction as in the case of the preparation of *α*-phenyl *α-p*-tolyl ethylene glycol. The contents of the reaction flask formed two layers which became one on concentration on the water bath. It was treated with a solution of glacial acetic acid (28 g.) in ice water (800 c.c.). Two layers again appeared, the upper layer was combined with the ethereal extract of the lower one, washed with dilute sodium carbonate solution and with water, shaken mechanically with saturated solution of sodium bisulphite for 10 hours to remove the remaining *p*-methylbenzoyl carbinol. It was washed with dilute aqueous sodium hydroxide and with water, the ether was removed by distillation and the residue was subjected to steam distillation for about 35 hours until no more oily substance came over. The contents of the distilling flask turned turbid white with amber coloured oil at the bottom. On cooling to -15°C . white powder was thrown down from the solution and the amber coloured oil became viscous mass (39 g.). Both were recrystallised from a large amount of hot water and then from petroleum ether giving colourless powder of *α-m*-tolyl *α-p*-tolyl ethylene glycol, m.p. $59-60^{\circ}\text{C}$. (Found: C, 79.0, 79.6; H, 7.2, 7.5. $\text{C}_{16}\text{H}_{18}\text{O}_2$ requires C, 79.3, H, 7.4%). Monobenzoyl derivative was obtained by Schotten-Baumann's method. It crystallised from 95% alcohol in colourless columns with one molecule of water of crystallisation, m.p. $173-174^{\circ}\text{C}$. (corr.) (decomp.). (Found: C, 75.6, 75.9; H, 6.7, 6.2%; Mol. wt. (Rast), 370. $\text{C}_{23}\text{H}_{22}\text{O}_3 \cdot \text{H}_2\text{O}$ requires C, 75.8; H, 6.6%; Mol. wt., 364). The water of crystallisation was not set free by heating at 57°C . under the reduced pressure of 7 mm. for 1 hour or at 120°C . under 760 mm. for 2 hours.

Oxidation of α-m-tolyl α-p-tolyl ethylene glycol. The glycol (0.14 g.) was dissolved in 80% acetic acid (10 c.c.) and chromic oxide (0.15 g) was added by portions into the solution, the solution was heated on the water bath for 20 minutes, diluted with water and cooled to -5°C . when white granules of *m*-tolyl *p*-tolyl ketone were obtained. It crystallised from dilute alcohol in long blades or prisms, m.p. 72°C . Yield 0.1 g.

m-Tolyl p-tolyl acetaldehyde. *α-m*-Tolyl *α-p*-tolyl ethylene glycol (50 g.) was boiled gently with a mixture of crystalline oxalic acid (125 g.) and water (50 c.c.) in an oil bath for $\frac{3}{4}$ hours. The temperature of the boiling mixture was maintained at $115-120^{\circ}\text{C}$. while that of the bath showed $150-160^{\circ}\text{C}$. After cooling, it was extracted with ether, the ethereal extract was washed with dilute aqueous solution of potassium hydroxide and with water, dried over anhydrous sodium sulphate. The ether was removed and the residue was distilled in vacuo. 29.1 g. of the raw aldehyde came over boiling between 160°C . and 180°C . under 5 mm. It was purified through the addition compound with sodium bisulphite. *m*-Tolyl *p*-tolyl acetaldehyde thus obtained boiled at 182°C . (corr.) under 7 mm., d_4^{20} , 1.0684; n_D^{20} , 1.5803; M.R., 69.81; calculated (Eisenlohr), 68.90. (Found: C, 85.2; H, 7.6. $\text{C}_{16}\text{H}_{16}\text{O}$ requires C, 85.7; H, 7.1%). The semicarbazone

was produced by adding the aldehyde (1 g.) to a mixture of potassium acetate (1 g.) and semicarbazide hydrochloride (1 g.) dissolved in dilute alcohol (10 c.c. of 95% alcohol and 6 c.c. of water) and heating to make a clear solution. On cooling white crystals (1.1 g.) were formed. It was recrystallised from dilute alcohol in long prisms, m.p. 179–180°C. (corr.) (decomp.) (Found: N, 15.0. $C_{17}H_{19}ON_3$ requires N, 14.9%).

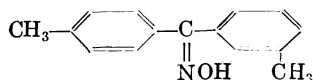
m-Tolyl p-tolyl acetic acid. Silver nitrate (10 g. in 10 c.c. water) was added to *m*-tolyl *p*-tolyl acetaldehyde (5 g.) dissolved in 95% alcohol (100 c.c.), followed by potassium hydroxide (7.5 g. in 70 c.c. water). 5 c.c. of the potash solution were added at a time every 10 minutes and the vessel was well shaken after each addition. After all the potash was added shaking was continued for further 3 hours, the reaction mixture was filtered and the filtrate was saturated with carbon dioxide and concentrated on the water bath. An oily substance separated out and floated on the surface, which solidified on cooling and confirmed to be *m*-tolyl *p*-tolyl ketone. The solution removed from the above ketone was neutralised with dilute sulphuric acid. Impure *m*-tolyl *p*-tolyl acetic acid separated thereby as an oily substance which on cooling turned to semi-solid mass. It was dissolved in alkali leaving a small quantity of *m*-tolyl *p*-tolyl ketone as an insoluble oil, and the solution again neutralised by the mineral acid. These steps of purification were repeated several times and finally *m*-tolyl *p*-tolyl acetic acid (0.2 g.) was recrystallised from hot water in pure state. It formed long prisms, m.p. 93–94°C. (Found: C, 79.5; H, 7.3%. Equiv. wt. (by titrating with 1/20 N NaOH), 240.1. $C_{16}H_{16}O_2$ requires C, 80.0; H, 6.7%; Equiv. wt., 240.1).

m-Tolyl p-tolyl ketone. As stated above, a considerable quantity of this ketone was produced when *m*-tolyl *p*-tolyl acetaldehyde was oxidized by moist silver oxide. It was also found to be present as less reactive substance with sodium bisulphite than *m*-tolyl *p*-tolyl acetaldehyde when the latter was purified through the addition product, and likewise obtained by the oxidation of *α*-*m*-tolyl *α*-*p*-tolyl ethylene glycol by chromic acid in acetic acid as mentioned above. The Friedel Crafts' reaction between *m*-toluyl chloride and toluene also gave the same ketone. All these specimens melted at 72°C. alone or mixed with one another, and gave the analytical data conforming with the formula. (Found: C, 85.2; H, 7.2%. Mol. wt. (Rast), 226, (cryoscopic in benzene), 218. $C_{15}H_{14}O$ requires C, 85.7; H, 6.6%. Mol. wt., 210). J. Lavaux⁽⁵⁹⁾ obtained the ketone by the oxidation of *m,p*-ditolylmethane finding the melting point 70.5°C, while W. Scharivin and Schorygin⁽⁶⁰⁾ gave 82°C., probably a typographical error for 72°C. The semicarbazone was obtained by standing the hot solution of the ketone (0.2 g.), semicarbazide hydrochloride (0.2 g.) and potassium acetate (0.2 g.) dissolved in dilute alcohol (2 c.c.) for 22 days. The solution of the mixture had been heated and shaken every morning and on the 22nd day the content of the flask was first found solidifying to a semi-solid mass. It crystallised from dilute alcohol in flat prisms, m.p. 177–179°C. (corr.). Lavaux⁽⁵⁹⁾ gave the melting point 180°C. The oxime of the ketone was obtained by adding aqueous sodium hydroxide (0.7 g. in 2 c.c.

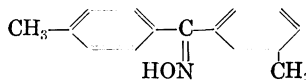
(59) *Chem. Zentr.*, **1910 II**, 1386.

(60) *Ber.*, **36** (1903), 2027.

water) into the alcoholic solution of the ketone (0.4 g. in 7 c.c. alcohol) mixed with hydroxylamine hydrochloride (0.4 g. in 2 c.c. water) and by the subsequent heating of the mixture for a while. The reaction mixture was left to stand overnight and neutralised with dilute hydrochloric acid. An oil separated which soon solidified. It melted at 119–129° when recrystallised once from dilute alcohol. By the fractional crystallisation over twenty times from dilute alcohol two fractions melting at 119–121°C. (A) and 133–134°C. (B) were obtained. J. Lavaux⁽⁵⁹⁾ obtained the oxime melting at 128–129°C. and W. Scharivin and Schorygin⁽⁶⁰⁾ two isomers melting at 118–119°C. and 143°C. respectively. Both (A) and (B) were subjected to the Beckmann rearrangement by the action of phosphorus pentachloride in ether solution giving two isomeric toluytoluidides melting at 104°C. (glittering scales from dilute alcohol) and 111–112°C. (silky needles from the same solvent) respectively. (Found: N, 6.8 for the former, 6.1 for the latter. $C_{15}H_{15}ON$ requires N, 6.2%). The former (m.p. 104°C.) was confirmed to be *p*-toluytoluidide by the mixed melting point with the specimen synthesised from *p*-toluic acid and *m*-toluidine, while the latter (m.p. 111–112°C.) *m*-toluytoluidide, the same product as that from *m*-toluic acid and *p*-toluidine. The configurations of the oximes, therefore, are as follows:—



(A) (m.p. 119–121°C.)



(B) (m.p. 133–134°C.)

p-Tolyl *m*-methylbenzyl ketone. As one of the starting materials for the preparation of the above ketone *m*-xylene was taken. It was first brominated and then interacted with potassium cyanide following the informations given by E. F. J. Atkinson and J. F. Thorpe⁽⁶¹⁾ and A. F. Titley⁽⁶²⁾ respectively. *m*-Xylyl cyanide thus obtained was converted to *m*-tolyl acetamide by Br. Radziszewski and P. Wispek's method,⁽⁶³⁾ which (5 g.) on boiling with concentrated hydrochloric acid (15 c.c.) gave *m*-tolyl acetic acid (3.5 g.). The acid (5 g.) was boiled with thionyl chloride (20 c.c.) on the water bath for 2 hours, the excess thionyl chloride was driven by evacuation and the residue distilled in vacuo giving pure *m*-tolyl acetyl chloride (5 g.). At every step of the above preparation the fractional distillation or fractional crystallization was carried out in order to remove the isomeric impurities as far as possible. The most effective separation from isomers was now found to be performed by the fractional crystallization of the acid amides from hot water. P. Hill and W. F. Short⁽⁶⁴⁾ reported the inseparability of the mixture of ortho and para isomers of xylyl bromides, chlorides, cyanides, acetates or alcohols and tolyl acetic acids by fractionations as already stated.

m-Tolyl acetyl chloride (5 g.) thus obtained was added drop by drop to toluene (30 c.c.) mixed with anhydrous aluminium chloride (5 g.). After 4 hour's standing all the aluminium chloride was dissolved. The

(61) *J. Chem. Soc.*, **91** (1907), 1699.(62) *J. Chem. Soc.*, **1926**, 514.(63) *Ber.*, **18** (1885), 1282.(64) *J. Chem. Soc.*, **1935**, 1126.

reaction mixture was poured into ice water (150 c.c.), the upper layer was separated, combined with the toluene extract of the lower layer, washed with dilute caustic potash and with water, dried over anhydrous sodium sulphate. On distilling off the toluene a blackish brown mass (8 g.) was obtained, which was recrystallised from dilute alcohol several times with the addition of active charcoal and gave the required ketone which formed colourless long flat needles (3.1 g.), m.p. 68°C. (Found: C, 85.8; H, 7.4. $C_{16}H_{16}O$ requires C, 85.7; H, 7.1%). The ketone dissolves in concentrated sulphuric acid tinging it with a canary yellow colour. The semicarbazone crystallised in colourless needles from dilute alcohol, m.p. 192–194°C. (uncorr.) (with slight decomp.). (Found: N, 14.8. $C_{17}H_{19}ON_3$ requires N, 14.9%).

The oxime formed also colourless needles when recrystallised from dilute alcohol, m.p. 108–109°C. (Found: N, 6.3. $C_{16}H_{17}ON$ requires 5.9%).

m-Tolyl p-methylbenzyl ketone. The ketone was synthesised in two ways.

(a) *p*-Tolyl acetonitrile (6 g.) dissolved in ether (50 c.c.) was added to the Grignard reagent prepared from *m*-iodotoluene (40 g.) and magnesium ribbon (4.4 g.), the reaction mixture was boiled for 10 hours, treated with cold dilute sulphuric acid (20 g. conc. acid in 800 c.c. ice water). The required ketone was produced as ketimine sulphate dissolved in the water layer, which was separated, washed with ether and heated gently on the water bath. The ketone was liberated as a reddish oil floating on the surface. It was extracted with ether, washed with water, dried over anhydrous sodium sulphate and the ether was driven off. A brownish oil (1.4 g.) thus obtained solidified on cooling to –15°C., which crystallised from dilute alcohol in colourless fine needles, m.p. 40–41°C. (Found: C, 85.4; H, 7.4. $C_{16}H_{16}O$ requires C, 85.7; H, 7.1%).

(b) The ketone was obtained by the oxidation of the corresponding alcohol, which was in its turn obtained by the interaction of *p*-tolyl acetaldehyde with *m*-tolyl magnesium iodide. The *p*-tolyl acetaldehyde was prepared by dehydration of *p*-tolyl ethylene glycol produced by the catalytic hydrogenation of *p*-methylbenzoyl carbinol in the following way.

A colloidal solution of platinum was obtained by passing hydrogen into the solution of chloroplatinic acid (1.5 g., calc. as Pt) and gum arabic (1 g.) in dilute acetic acid (50 c.c. acid in 120 c.c. water) with platinum black (0.03 g.) suspended in the solution. *p*-Methylbenzoyl carbinol (13.1 g. dissolved in 80 c.c. glacial acetic acid) was added to the above colloidal solution and the mixture was shaken in the atmosphere of hydrogen at the ordinary temperature and pressure. 1800 c.c. (22°C, 761 mm.) of hydrogen were absorbed in 60 minutes. Caustic soda (85 g. dissolved in a small quantity of water) was added to the solution. Care must be taken not to make the solution alkaline, as otherwise the next step i.e. the extraction with ether would become difficult. It was extracted with a large amount of ether, the ethereal extract washed with dilute alkali and with water, dried over anhydrous sodium sulphate and the ether was removed by distillation. The residue (11 g.) solidified on standing. The raw *p*-tolyl ethylene glycol thus obtained crystallised from petroleum benzine in glittering scales, m.p. 76.5–77.5°C. (Found: C, 70.5; H, 8.0. $C_9H_{12}O_2$ requires C, 71.1; H, 7.9%). The remaining *p*-methylbenzoyl car-

binol could thereby be easily removed, as it is more soluble in the solvent than the glycol though its melting point is higher than that of the glycol by about 15°. E. Späth⁽⁶⁵⁾ obtained diethyl ether of the glycol. No description of the free glycol was however given by him.

The raw product of *p*-tolyl ethylene glycol (8 g.) was sealed in a glass tube mixed with water (20 c.c.) and 4 drops of concentrated hydrochloric acid, heated at 180–185°C. for 4 hours. The contents of the tube were then extracted with ether, washed with water, dried over anhydrous sodium sulphate and distilled in vacuo. *p*-Tolyl acetaldehyde (2 g.) thus obtained passed over at 92–93°C. under the reduced pressure of 8 mm. which on further purification boiled at 97°C. under 10 mm., d_4^{20} , 1.0052; n_D^{20} , 1.5255; M. R. found: 40.86; calc. (Eisenlohr) 40.17. K. Kling⁽⁶⁶⁾ gave the boiling point 109°C./17 mm. while E. Späth⁽⁶⁷⁾ 96°C./10 mm.

p-Tolyl acetaldehyde (2 g. dissolved in 2 c.c. ether), synthesised as stated above, was added to the Grignard reagent prepared from *m*-iodotoluene (3.5 g.) and magnesium ribbon (0.36 g.). The reaction mixture was boiled for 2 hours and left to stand overnight. It was decomposed by dilute hydrochloric acid (1.2 c.c. conc. acid in 50 c.c. ice water) and extracted with ether, the ethereal extract was washed with dilute solution of potassium carbonate, dried over anhydrous sodium sulphate and the ether was removed by distillation. The residue was distilled in steam leaving in the flask a thick oil (0.85 g.), the raw *p*-methylbenzyl *m*-tolyl carbinol, which without further purification was oxidized to the corresponding ketone; the oil was dissolved in 80% acetic acid (60 c.c.) and chromic oxide (0.28 g. in 1 c.c. water) was added to it. The mixture turned at once blackish, and then green when heated on the water bath for 30 minutes. It was poured into ice water (600 c.c.). A resinous matter thus produced stuck to the bottom of the vessel, which was extracted with ether, the ethereal extract was washed with dilute caustic potash and with saturated solution of sodium chloride, dried over calcium chloride, and the ether was removed leaving viscous matter (0.53 g.). It solidified on long standing at –15°C. It was recrystallised from dilute alcohol giving a small quantity of the required ketone melting at 40–41°C.

The semicarbazone was not obtained even after 140 days' standing of the solution of the ketone (0.2 g.), semicarbazide hydrochloride (0.2 g.) and potassium acetate (0.2 g.) in dilute alcohol, only a small quantity of white powder being thereby produced which decomposed at about 250°C.

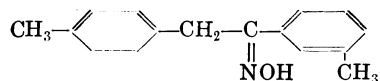
The oxime was obtained in the usual way; the ketone (0.08 g.) and hydroxylamine hydrochloride (0.14 g.) were dissolved in hot dilute alcohol (2 c.c.), the solution was left to stand overnight and neutralized with dilute sulphuric acid. An oil (0.06 g.) was thrown down which on cooling solidified. It crystallised from dilute alcohol in colourless needles, m.p. 88.5°C. It was subjected to the Beckmann rearrangement; phosphorus pentachloride (0.05 g.) was added to the ether solution of the oxime (0.05 g. in 2 c.c. ether), which was shaken for 15 minutes and poured into ice water. White granules separated and was recrystallised from dilute

(65) *Monatsh.*, **37** (1916), 9.

(66) *Chem. Zentr.*, **1908**, **I**, 951.

(67) *Ber.*, **47** (1914), 767; *Monatsh.*, **37** (1916), 9.

alcohol in colourless plates or from ligroin in needles, m.p. 123–124°C., which was not depressed by the mixing of [*p*-tolyl-acetyl]-*m*-toluidide synthesised from *p*-tolyl acetic acid and *m*-toluidine, showing that the original oxime was of the following anti-*p*-methylbenzyl configuration:—



(Found: N, 5.9. $\text{C}_{16}\text{H}_{17}\text{ON}$ requires N, 5.9%). *m*-Toluyyl *p*-methylbenzylamine, the compound isomeric to [*p*-tolyl-acetyl]-*m*-toluidide, was obtained by the condensation of *m*-toluic acid and *p*-methylbenzylamine, colourless leaflets from dilute alcohol, m.p. 116°C. (Found: N, 6.3, $\text{C}_{16}\text{H}_{17}\text{ON}$ requires N, 5.9%). *m*-Tolyl *p*-methylbenzyl ketone was oxidized slowly by atmospheric oxygen giving *p*- and *m*-toluic acids; on long standing white granules deposited on the wall of the vessel containing the ketone, which were separated into the above mentioned two isomeric acids by the fractional crystallisation from hot water, melting at 179°C. and 110°C. respectively alone or mixed with the authentic specimens.

Isomerization of m-tolyl p-tolyl acetaldehyde. The aldehyde (13.5 g.) was passed on the Japanese acid earth (25 g.) heated at 300°C. at a rate of 3.8 g. per hour, being accompanied by the slow current of carbon dioxide. A heavy yellowish brown oil covered by the thin layer of toluene (7.5 g. in total) was collected in the receiver during the passing of the aldehyde and the lapse of 1 hour after it. The temperature of the tube was then raised to 350°C. under the reduced pressure of 30 mm. and a thick brownish red oil (0.7 g.) was obtained. Both the products showed no colour reaction characteristic to aldehydes. They were combined, washed with dilute aqueous potassium hydroxide, with the saturated solution of sodium chloride and dried over calcium chloride. The calcium chloride was washed with ether to remove the absorbed reaction products, the ether was evaporated up and the residue was combined with the main part, which was distilled under the reduced pressure of 5 mm. giving the following fractions:—

Table 1.

Fraction	B.p. (°C)	Yields (g.)	Remarks
(1)	140–167	1.1	Light yellow oil with aromatic odour.
(2)	167–175	1.3	Light yellow oil, almost odourless.
(3)	175–180	4.0	Almost all amount came over constantly at 177°C. Odourless, yellow viscous oil.
(4)	Above 180	0.7	Very viscous, reddish brown oil.
		Total 7.1	

The alkaline washing liquid of the reaction product before subjected to the distillation was concentrated on the water bath and neutralised by dilute sulphuric acid. Oil drops were thrown down which crystallised on

cooling (0.01 g.). They were recrystallised from hot water and found to be a mixture of *p*- and *m*-toluic acids.

The third fraction in Table I (b.p. 175–180°C./5 mm.) made the main part of the reaction products. It did not tend to solidify when cooled. 0.5 g. of it gave the solid oxime (0.4 g.), colourless needles, m.p. 86.5–87.5°C., which was confirmed to consist of *m*-tolyl *p*-methylbenzyl ketoxime exclusively. The oxime was identified by the mixed melting point with the authentic specimen as well as by the formation of [*p*-tolyl-acetyl]-*m*-toluidide by the Beckmann rearrangement. *p*-Tolyl *m*-methylbenzyl ketoxime was not found to exist in it, the fact which was also confirmed in the cases of the other fractions in Table 1. It may, therefore, safely be mentioned that in the molecule of *m*-tolyl *p*-tolyl acetaldehyde the migration of *m*-tolyl radical exclusively took place under the experimental condition given above.

In one run of the experiment carried out under the same condition, the reaction product was left to stand for just three months. A considerable quantity of white deposit was formed in the vessel containing the oily product, which revealed itself as a mixture of *m*- and *p*-toluic acids melting at 110 and 179°C. respectively when separated by the fractional crystallisation from hot water. The acids were most probably formed by the oxidation of *m*-tolyl *p*-methylbenzyl ketone with atmospheric oxygen.

(To be continued.)

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Studien über Oxydationszersetzung des Methans.

Von Toyoziro OGURA.

(Eingegangen am 6. Juni, 1941.)

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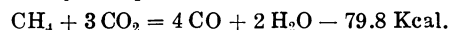
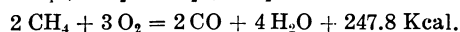
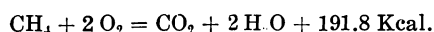
VIII. Zusammenfassung. Schlusswort.

I. Einleitung und Literatur. Die Oxydation des Methans kann man, von dem Gesichtspunkte der Reaktionsprodukte aus, in folgende drei Klassen einteilen. Die Erste ist die sogenannte Verbrennung, wobei Wasser, Kohlendioxyd oder Kohlenoxyd durch die Einwirkung des Sauerstoffs entstehen. Die Zweite ist die Oxydationszersetzung, in welcher sich Wasserstoff, Kohlendioxyd oder Kohlenoxyd bilden. Die Dritte ist die unvollkommene Oxydation; es werden dabei sauerstoffhaltige Verbindungen niederer Klasse, z.B. Methanol, Formaldehyd, Ameisensäure, Essigsäure, Azeton u.s.w. gebildet.

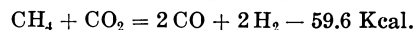
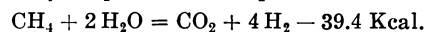
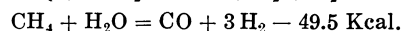
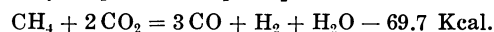
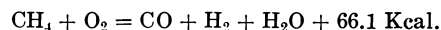
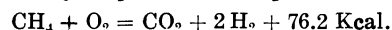
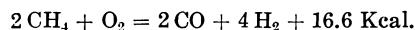
Tafel 1 veranschaulicht die oben erwähnten Verhältnisse.

Tafel 1.

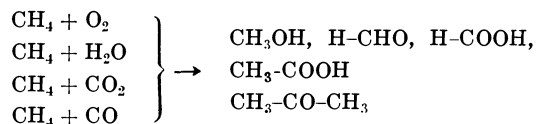
A. Verbrennung.



B. Oxydationszersetzung.



C. Unvollkommene Oxydation.



Diese Reaktionen sind bereits einigermaßen studiert: als Oxydationsmittel hat man sich einiger Gase, z.B. Sauerstoff, Wasserdampf, Kohlendioxyd und Stickstoffoxyd, bedient, ausserdem sind anorganische Oxydationsmittel, Chromsäure, Permangansäure und Bichromsäure und Metalloxyde verwendet worden.

Die Literatur darüber liegt in ziemlich grosser Menge vor, wovon ich einige Beispiele in der folgenden Tafel übersichtlich zusammengefasst habe.

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Methan-Sauerstoff-Reaktion.

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- (16) Pearl, Brown, *Ind. Eng. Chem.*, **28** (1936), 1058.
- (17) Fujimoto, *dies Bulletin*, **13** (1938), 281.
- (18) Kafuku, Ogura, *J. Chem. Soc. Japan*, **50** (1934), 1445.

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- (20) Sabatier, Senderens, *Compt. rend.*, **134** (1902), 514.
- (21) Mayer, Henseling, Altmayer, Jacoby, *J. Gasbeleuchtung*, **52** (1909), 166, 194, 238, 282, 305.
- (22) Neuman, Jacob, *Z. Elektrochem.*, **30** (1924), 557.
- (23) Pease, Chesebro, *J. Am. Chem. Soc.*, **50** (1928), 1464.
- (24) Fischer, Tropsch, *Brennstoffchem.*, **9** (1928), 39.
- (25) Stanley, Nash, *J. Soc. Chem. Ind.*, **48** (1929), 1 T.
- (26) Eastman, *U. S. Bur. Mines. Information Circ.*, **1929**, 6125.
- (27) Kubota, Yamanaka, *dies Bulletin*, **4** (1929), 211.
- (28) Gluud, Keller, Klempt, *Ber. Ges. Kohlentechnik*, **3** (1930), 211.
- (29) Klykvin, Klykvina, *J. Chem. Ind. Russia*, **7** (1930), 743, 877.
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- (31) Hawk, Golden, Storch, Fiedner, *Ind. Eng. Chem.*, **24** (1932), 23.
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- (43) Ogura, *J. Soc. Chem. Ind. Japan*, **43** (1940), 395.
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Methan-Kohlendioxyd-Reaktion

- (45) Lang, *Z. physik. Chem.*, **2** (1888), 161.
- (46) Mayer, Altmayer, *J. Gasbeleuchtung*, **52** (1909), 326.
- (47) Fischer, Tropsch, *Brennstoffchem.*, **9** (1928), 39.

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- (53) Ogura, Huzimura, *J. Chem. Soc. Japan*, **2** (1938), 139.
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Vorliegende Abhandlung ist eine Zusammenstellung meiner Arbeiten über Oxydationszersetzung des Methans, welche sich mit den notwendigen Bedingungen und den Katalysatoren befasst und die Reaktionen des Methans mit Sauerstoff, Wasserdampf und Kohlendioxyd in Klarheit gebracht haben.

Roh Methan aus Naturgas von Kinsui, Sintiku, Formosa wurde zum Experiment verwendet. Das Naturgas von Kinsui kommt aus 1000–1500 m Tiefe unter der Erde und wird nach Entfernung des Benzins durch Kerosenausspülung, in einer eisernen Leitungsröhre nach der Stadt Sintiku geleitet. Dasselbe hat folgende Komponenten.

CO_2 1.0%, C_nH_m 0.5%, Luft 1.0%, CH_4 95.0%, C_2H_6 2.5%.

Als Darstellungsmethode des Methans in Laboratorien sind folgende drei oder vier Weisen in der Literatur⁽¹⁾ angegeben.

- 1) Essigsäuresnatrium, Kalk und Aetznatron.
- 2) Aluminiumkarbid und Wasser.
- 3) Zersetzung des Jodmethyl.

Diese Methoden reichen aber zur Darstellung reines Methans nicht aus. Letzteres kann man nur durch wiederholtes Destillieren unter niedrigerer Temperatur erhalten.

Zum Experiment bediente ich mich gewöhnlicher Strömungsmethode. Die Veränderungen in der Anordnung des Apparates, die ich vorgenommen habe, sind in Abb. 1 schematisch dargestellt.

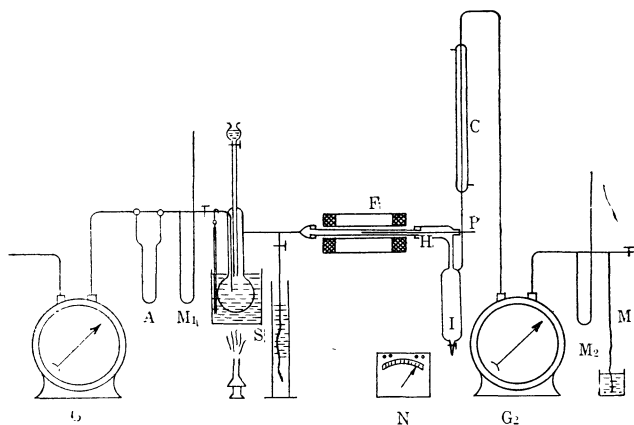


Abbildung 1. Schematische Anordnung des Apparates.

-
- (1) L. Moser, "Reindarstellung von Gasen", 1920.
 A. Klemenc, "Die Behandlung u. Reindarstellung von Gasen", 1938.
 A. Farkas u. H. W. Melville, "Experimental Methods in Gas Reactions", 1939.

Reaktionsröhre sind aus Porzellan oder Quartz, von 15–20 mm. Durchmesser und 500 mm. Länge und mit passenden Katalysatoren versehen. Ich gebrauchte Gasometer zur Messung der Gase und Kapillar-Strömungsmesser zur Bestimmung des Sauerstoffs und Kohlendioxyds. Der Wasserdampf wurde durch die Regulierung der Badetemperatur, den Kapillar-Strömungsmesser und die Menge des kondensierten Wassers kontrolliert. Dabei wurde zur Vermeidung der Kondensation des Dampfes die Leitungsröhre mittels Nichromdrahts erwärmt.

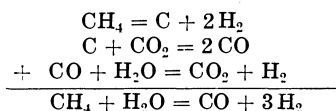
Die Gasproben, die man an beliebigen Stellen entnahm, wurde nach der Hempelschen Methode analysiert.

II. Gleichgewichtskonstanten. Die Gleichgewichtskonstanten der Reaktionen des Methans auf Wasserdampf, Sauerstoff und Kohlendioxyd sind von einigen Autoren angegeben. Diese Werte weichen aber ziemlich von einander ab.

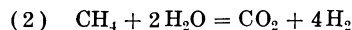
Setzt man die Gleichgewichtskonstanten der folgenden 1–10 Reaktionen als $Kp_1, Kp_2, Kp_3, Kp_4, Kp_5, Kp_6, Kp_7, Kp_8, Kp_9, Kp_{10}$ und die der Reaktionen 11–14 als Kp_A, Kp_B, Kp_C, Kp_D , so kann man die ersteren Werte $Kp_1 \dots Kp_{10}$ aus der Benutzung der letzteren Werte $Kp_A \dots Kp_D$, die genau festgestellt sind, berechnen. Die Werte $\log Kp_A \dots Kp_D$ wurden nach folgenden Formeln berechnet. Tafel 2 zeigt diese Werte, Tafel 3 die Werte $\log Kp_1 \dots \log Kp_{10}$. Abb. 2 zeigt die Kurven des $\log Kp$ und der Temperatur.



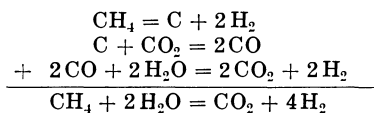
$$Kp_1 = \frac{p\text{CH}_4 \cdot p\text{H}_2\text{O}}{p^3\text{H}_2 \cdot p\text{CO}} = \frac{p\text{CH}_4 \cdot p\text{CO}_2 \cdot p\text{CO} \cdot p\text{H}_2\text{O}}{p^2\text{H}_2 \cdot p^2\text{CO} \cdot p\text{CO}_2 \cdot p\text{H}_2} = \frac{Kp_A}{Kp_B \cdot Kp_C}$$



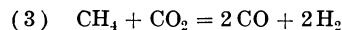
$$\log Kp_1 = \log Kp_A - \log Kp_B - \log Kp_C$$



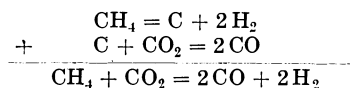
$$Kp_2 = \frac{p\text{CH}_4 \cdot p^2\text{H}_2\text{O}}{p\text{CO}_2 \cdot p^4\text{H}_2} = \frac{p\text{CH}_4 \cdot p^2\text{H}_2\text{O} \cdot p\text{CO}_2 \cdot p^2\text{CO}}{p^2\text{H}_2 \cdot p^2\text{CO} \cdot p^2\text{CO}_2 \cdot p^2\text{H}_2} = \frac{Kp_A}{Kp_B \cdot K^2p_C}$$



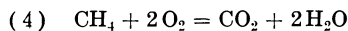
$$\log Kp_2 = \log Kp_A - \log Kp_B - 2 \log Kp_C$$



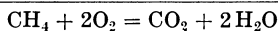
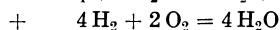
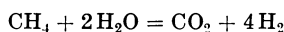
$$Kp_3 = \frac{p\text{CH}_4 \cdot p\text{CO}_2}{p^2\text{CO} \cdot p\text{H}_2} = \frac{Kp_A}{Kp_B}$$



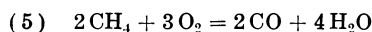
$$\log Kp_3 = \log Kp_A - \log Kp_B$$



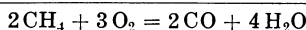
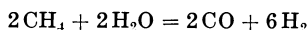
$$Kp_4 = \frac{p\text{CH}_4 \cdot p^2\text{O}_2}{p\text{CO}_2 \cdot p^2\text{H}_2\text{O}} = \frac{p\text{CH}_4 \cdot p^2\text{H}_2\text{O} \cdot p^4\text{H}_2 \cdot p^2\text{O}_2}{p\text{CO}_2 \cdot p^4\text{H}_2 \cdot p^4\text{H}_2\text{O}} = \frac{Kp_2}{K^2p_D}$$



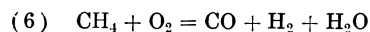
$$\log Kp_4 = \log Kp_2 - 2 \log Kp_D$$



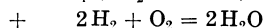
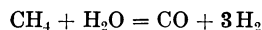
$$Kp_5 = \frac{p^2\text{CH}_4 \cdot p^3\text{O}_2}{p^2\text{CO} \cdot p^4\text{H}_2\text{O}} = \frac{p^2\text{CH}_4 \cdot p^2\text{H}_2\text{O} \cdot p^6\text{H}_2 \cdot p^3\text{O}_2}{p^2\text{CO} \cdot p^6\text{H}_2 \cdot p^6\text{H}_2\text{O}} = \frac{K^2p_1}{K^3p_D}$$



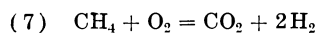
$$\log Kp_5 = 2 \log Kp_1 - 3 \log Kp_D$$



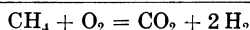
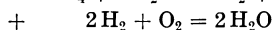
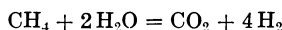
$$Kp_6 = \frac{p\text{CH}_4 \cdot p\text{O}_2}{p\text{CO} \cdot p\text{H}_2 \cdot p\text{H}_2\text{O}} = \frac{p\text{CH}_4 \cdot p\text{H}_2\text{O} \cdot p^2\text{H}_2 \cdot p\text{O}_2}{p\text{CO} \cdot p^3\text{H}_2 \cdot p^2\text{H}_2\text{O}} = \frac{Kp_1}{Kp_D}$$



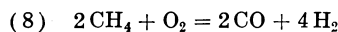
$$\log Kp_6 = \log Kp_1 - \log Kp_D$$



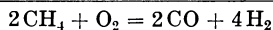
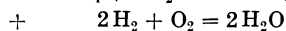
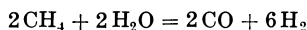
$$Kp_7 = \frac{p\text{CH}_4 \cdot p\text{O}_2}{p\text{CO}_2 \cdot p^2\text{H}_2} = \frac{p\text{CH}_4 \cdot p^2\text{H}_2\text{O} \cdot p^2\text{H}_2 \cdot p\text{O}_2}{p\text{CO}_2 \cdot p^4\text{H}_2 \cdot p^2\text{H}_2\text{O}} = \frac{Kp_2}{Kp_D}$$



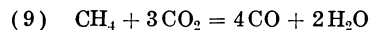
$$\log Kp_7 = \log Kp_2 - \log Kp_D$$



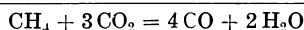
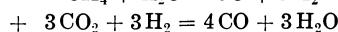
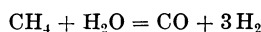
$$Kp_8 = \frac{p^2\text{CH}_4 \cdot p\text{O}_2}{p^2\text{CO} \cdot p^4\text{H}_2} = \frac{p^2\text{CH}_4 \cdot p^2\text{H}_2\text{O} \cdot p^2\text{H}_2 \cdot p\text{O}_2}{p^2\text{CO} \cdot p^6\text{H}_2 \cdot p^2\text{H}_2\text{O}} = \frac{K^2p_1}{Kp_D}$$



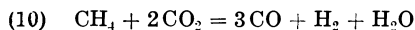
$$\log Kp_8 = 2 \log Kp_1 - \log Kp_D$$



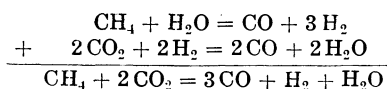
$$Kp_9 = \frac{p\text{CH}_4 \cdot p^3\text{CO}_2}{p^4\text{CO} \cdot p^2\text{H}_2\text{O}} = \frac{p\text{CH}_4 \cdot p\text{H}_2\text{O} \cdot p^3\text{CO}_2 \cdot p^3\text{H}_2}{p\text{CO} \cdot p^3\text{H}_2 \cdot p^4\text{CO} \cdot p^3\text{H}_2\text{O}} = Kp_1 \cdot K^3p_C$$



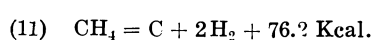
$$\log Kp_9 = \log Kp_1 + 3 \log Kp_C$$



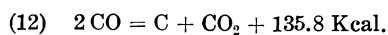
$$Kp_{10} = \frac{p\text{CH}_4 \cdot p^2\text{CO}_2}{p^3\text{CO} \cdot p\text{H}_2 \cdot p\text{H}_2\text{O}} = \frac{p\text{CH}_4 \cdot p\text{H}_2\text{O} \cdot p^2\text{CO}_2 \cdot p^2\text{H}_2}{p\text{CO} \cdot p^3\text{H}_2 \cdot p^2\text{CO} \cdot p^2\text{H}_2\text{O}} = Kp_1 \cdot K^2p_C$$



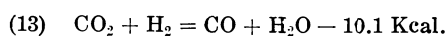
$$\log Kp_{10} = \log Kp_1 + 2 \log Kp_C$$



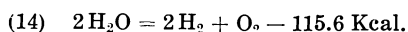
$$Kp_A = \frac{p\text{CH}_4}{p^2\text{H}_2}$$



$$Kp_B = \frac{p^2\text{CO}}{p\text{CO}_2}$$



$$Kp_C = \frac{p\text{CO}_2 \cdot p\text{H}_2}{p\text{CO} \cdot p\text{H}_2\text{O}}$$



$$Kp_D = \frac{p^2\text{H}_2\text{O}}{p^2\text{H}_2 \cdot p\text{O}_2}$$

Die Werte $\log Kp_A$, $\log Kp_B$, $\log Kp_C$, $\log Kp_D$, wurden nach folgenden Formeln berechnet.

$$\log Kp_A = \frac{3.798}{T} - 3.958 \log T - 1.039 \cdot 10^{-5} T + 4.76 \cdot 10^{-7} T^2 - 4.795 \cdot 10^{-11} T^3 + 7.04$$

$$\log Kp_B = \frac{-8.742}{T} + 3.731 \log T - 2.248 \cdot 10^{-3} T + 4.76 \cdot 10^{-7} T^2 - 4.795 \cdot 10^{-11} T^3 + 0.496$$

$$\log Kp_C = \frac{-9.360}{4.571 T} - \frac{1}{2} \log T + \frac{1}{4.571} \frac{dT}{T^2} \left[R \frac{5000}{T} + 2R \frac{90}{T} + 2R \frac{3500}{T} - R \frac{3100}{T} \right. \\ \left. - R \frac{2300}{T} - 2R \frac{5800}{T} \right] dT - 0.789$$

$$\log Kp_D = \frac{25119}{T} - 0.95 \log T - 0.72 \cdot 10^{-3} T + 1.62 \cdot 10^{-7} T^2 - 1.601$$

Tafel 2. Die Werte $\log Kp_A$, $\log Kp_B$, $\log Kp_C$ und $\log Kp_D$.

°C	°TK	$\log Kp_A$	$\log Kp_B$	$\log Kp_C$	$\log Kp_D$
400	673	1.481	-4.246	1.096	32.623
450	723	0.941	-3.315	0.889	29.989
500	773	0.675	-2.505	0.720	27.690
550	823	0.284	-1.795	0.571	25.667
600	873	-0.064	-1.168	0.441	23.873
650	923	-0.378	-0.611	0.326	22.269
700	973	-0.661	-0.112	0.224	20.828
750	1023	-0.919	-0.335	0.135	19.527
800	1073	-1.155	0.741	0.047	18.344
850	1123	-1.371	1.108	-0.025	17.263
900	1173	-1.569	1.444	-0.089	16.276
950	1223	-1.751	1.750	-0.149	15.366
1000	1273	-1.921	2.032	-0.205	14.527
1050	1323	-2.050	2.291	-0.254	13.749
1100	1373	-2.223	2.530	-0.297	13.029
1150	1423	-2.356	2.756	-0.342	12.358
1200	1473	-2.486	2.958	-0.381	11.733

Tafel 3. Die Werte $\log K_{p_1} \dots \log K_{p_{10}}$.

°C	°T _K	$\log K_{p_1}$	$\log K_{p_2}$	$\log K_{p_3}$	$\log K_{p_4}$	$\log K_{p_5}$
400	673	4.637	3.547	5.727	-61.699	-88.595
450	723	3.367	2.478	4.429	-57.500	-83.233
500	773	2.460	1.740	3.180	-53.640	-78.150
550	823	1.508	0.937	2.076	-50.397	-73.985
600	873	0.663	0.222	1.104	-47.524	-70.293
650	923	-0.093	-0.419	0.233	-44.957	-66.993
700	973	-0.773	-0.997	-0.549	-42.653	-64.030
750	1023	-1.339	-1.524	-1.254	-40.578	-61.359
800	1073	-1.943	-1.990	-1.896	-38.678	-58.918
850	1123	-2.454	-2.429	-2.479	-36.955	-56.697
900	1173	-2.924	-2.835	-3.013	-35.387	-54.676
950	1223	-3.352	-3.203	-3.501	-33.597	-52.802
1000	1273	-3.748	-3.543	-3.953	-32.597	-51.077
1050	1323	-4.087	-3.833	-4.341	-31.331	-49.477
1100	1373	-4.456	-4.159	-4.753	-30.217	-47.999
1150	1423	-4.773	-4.431	-5.115	-29.147	-46.620
1200	1473	-5.063	-4.682	-5.444	-28.148	-45.325

°C	°T _K	$\log K_{p_6}$	$\log K_{p_7}$	$\log K_{p_8}$	$\log K_{p_9}$	$\log K_{p_{10}}$
400	673	-27.986	-29.076	-23.349	7.925	6.829
450	723	-26.622	-27.511	-23.255	6.034	5.145
500	773	-25.230	-25.950	-22.770	4.620	3.900
550	823	-24.159	-24.730	-22.651	3.221	2.650
600	873	-23.332	-23.651	-22.547	1.986	1.545
650	923	-22.362	-22.688	-22.455	0.885	0.559
700	973	-21.601	-21.825	-22.374	-0.101	-0.325
750	1023	-20.916	-21.051	-22.305	-0.984	-1.119
800	1073	-20.287	-20.334	-22.230	-1.802	-1.849
850	1123	-19.717	-19.692	-22.171	-2.529	-2.504
900	1173	-19.200	-19.111	-22.124	-3.191	-3.102
950	1223	-18.718	-18.569	-22.070	-3.799	-3.650
1000	1273	-18.275	-18.070	-22.023	-4.363	-4.158
1050	1323	-17.864	-17.582	-21.979	-4.849	-4.595
1100	1373	-17.485	-17.188	-21.941	-5.347	-5.050
1150	1423	-17.131	-16.789	-21.904	-5.799	-5.457
1200	1473	-16.796	-16.415	-21.859	-6.206	-5.825

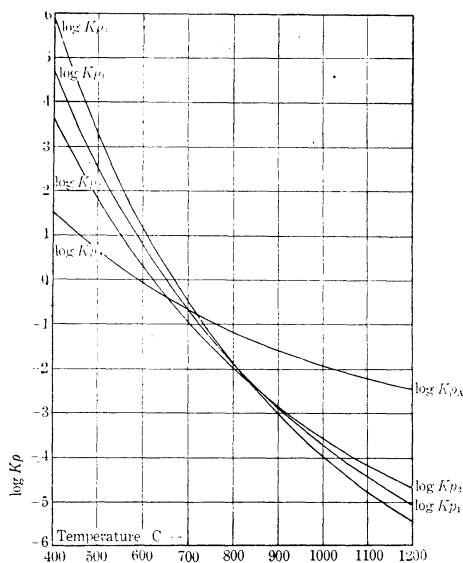


Abbildung 2.
Die Kurve $\log Kp_1$, $\log Kp_2$, $\log Kp_3$
und $\log Kp_A$.

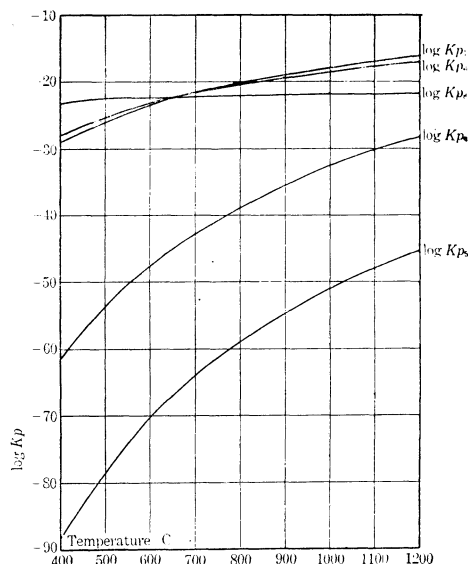


Abbildung 3.
Die Kurve $\log Kp_4$, $\log Kp_5$, $\log Kp_6$,
 $\log Kp_7$ und $\log Kp_8$.

Die Reaktion des Methans auf Wasserdampf wird durch die Menge des Wasserdampfes wesentlich beeinflusst.

Lässt man 100 VT Methan mit $n \cdot 100$ VT Wasser nach der Gleichung $\text{CH}_4 + \text{H}_2\text{O} = \text{CO} + 3 \text{H}_2$ auf einander reagieren, und setzt die verwandelte Menge des Methans gleich x , so betragen die Volumen nach Gleichungseinstellung $(100-x) \text{CH}_4$, $(n \cdot 100 - x) \text{H}_2\text{O}$, $x \text{CO}$ und $3x \text{H}_2$. So ergibt sich das Kp nach folgender Formel.

$$Kp_1 = \frac{(100-x)(n \cdot 100 - x)[100(n+1) + 2x]^2}{27x^4}$$

$$\log Kp_1 = \log(100-x) + \log(n \cdot 100 - x) + 2 \log[100(n+1) + 2x] - 4 \log x - 1.43$$

Wenn man 100 VT Methan mit $2n \cdot 100$ VT Wasser nach der Gleichung $\text{CH}_4 + 2\text{H}_2\text{O} = \text{CO}_2 + 4\text{H}_2$ auf einander reagieren lässt und die verwandelte Menge des Methans x stellt, so betragen die Volumen nach der Gleichungseinstellung $(100-x) \text{CH}_4$, $2(n \cdot 100 - x) \text{H}_2\text{O}$, $x \text{CO}_2$ und $4x \text{H}_2$. So ergibt sich Kp , wie in der Formel gezeigt,

$$Kp_2 = \frac{(100-x)(n \cdot 100 - x)^2[100(2n+1) + 2x]^2}{64x^5}$$

$$\log Kp_2 = \log(100-x) + 2 \log(n \cdot 100 - x) + 2 \log[100(2n+1) + 2x] - 5 \log x - 1.806$$

Wenn man die Werte $n=1,2,3$ annimmt, so ergeben sich die Komponenten des Reaktionsendgases wie in Tafel 4 und 5 dargestellt. Abb. 4 und 5 zeigen die Verhältnisse zwischen dem Verwandlungsgrad des

Methans und $\log Kp$ als $n=1,2,3$..Ein im Ueberschuss vorhandene Wasserdampf bewirkt eine Steigerung des Methanumsatzes. Man kann durch Verwendung der Abb. 2 und Abb. 4 oder Abb. 5 das Gleichgewicht des Methans unter allen Bedingungen berechnen.

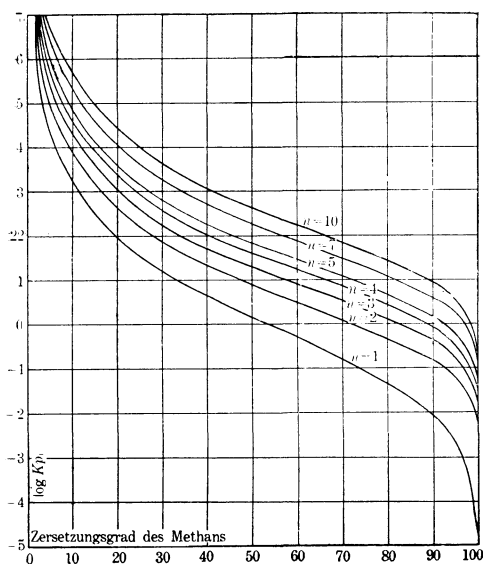


Abbildung 4.
 $\log Kp_1$ und Wassermenge.

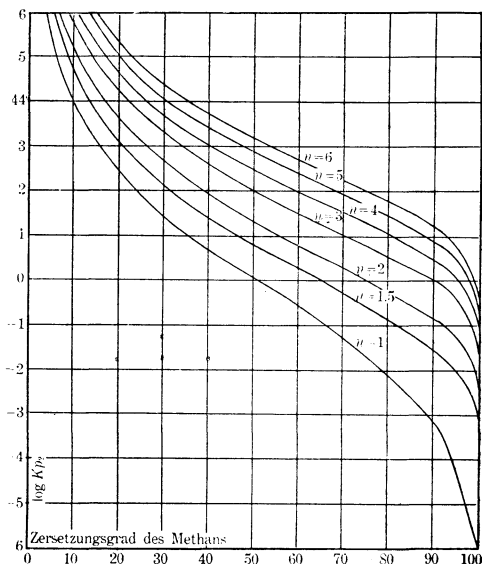


Abbildung 5.
 $\log Kp_2$ und Wassermenge.

Beispiel 1. Die Temperatur, die zur 70% Veränderung des Methans mit dreimal soviel Wasserdampf der theoretischen Menge nötig ist, ergibt sich aus der Gleichung $\text{CH}_4 + 2\text{H}_2\text{O} = \text{CO}_2 + 4\text{H}_2$.

Mann kann aus dem Schnittpunkt der Kurve $n=3$ und der Kurve 70% in Abb. 5 $\log Kp_2=1.05$ feststellen. Dann erhält aus $\log Kp_2$ Kurve $t^\circ\text{C}=545^\circ$. Es ist die erforderliche Temperatur. Abb. 5 veranschaulicht, dass 6 facher Wasserdampf der theoretische Menge bei 545°C . 92.0% Verwandlung bewirkt.

Beispiel 2. zeigt das Verhältnis zwischen dem Verwandlungsgrade und der Wassermenge nach der Gleichung $\text{CH}_4 + \text{H}_2\text{O} = \text{CO} + 3\text{H}_2$ bei 800°C .

Man findet zuerst aus Abb. 2 die Werte $\log Kp=-1.90$ bei 800°C , dann aus Abb. 4 den Verwandlungsgrad 99.0% bei $n=2$, 88.5% bei $n=1$. Tafel 4 und 5 zeigen die Komponenten der Reaktionsgase bei Temperatur- und Wasserdampf-veränderung.

Tafel 4. $\log Kp_1$ und Wassermenge.

°C	$\log Kp_1$	$n = 1$			$n = 2$			$n = 3$		
		CO	H ₂	CH ₄	CO	H ₂	CH ₂	CO	H ₂	CH ₄
400	4.637	3.89	11.67	84.44	5.37	16.11	78.52	6.38	19.14	74.48
450	3.367	7.09	21.27	71.64	9.35	28.05	62.60	10.95	32.85	56.20
500	2.460	10.25	30.75	59.00	12.93	33.79	48.28	16.75	50.25	33.00
550	1.508	14.38	43.14	42.48	17.30	51.90	30.80	19.00	57.00	24.00
600	0.663	17.96	53.88	28.16	20.86	62.58	16.56	22.07	66.21	11.72
650	-0.093	20.73	62.19	17.08	23.00	69.00	8.00	24.06	72.18	3.76
700	-0.773	22.57	67.71	9.72	24.24	72.72	3.04	24.67	74.01	1.32
750	-1.339	23.65	70.95	5.40	24.75	74.25	1.00	24.92	74.76	0.32
800	-1.943	24.20	72.60	3.20	24.91	74.73	0.36	24.95	74.85	0.20
850	-2.454	24.55	73.65	1.80	24.97	74.91	0.14			
900	-2.924	24.73	74.19	1.08						
950	-3.352	24.82	74.46	0.72						
1000	-3.748	24.83	74.49	0.68						
1050	-4.087	24.93	74.79	0.23						
1100	-4.456	24.96	74.88	0.16						
1150	-4.773	24.97	74.91	0.14						

Tafel 5. $\log Kp_2$ und Wassermenge.

°C	$\log Kp_2$	$n = 1$			$n = 1.5$			$n = 2$		
		CO ₂	H ₂	CH ₄	CO ₂	H ₂	CH ₂	CO ₂	H ₂	CH ₄
400	3.547	8.39	33.56	58.06	9.93	39.92	50.10	11.20	44.80	44.00
450	2.478	11.12	44.48	44.40	12.80	51.20	36.00	13.95	55.80	30.25
500	1.740	12.93	51.72	35.35	14.62	58.48	26.90	15.75	63.00	21.25
550	0.937	14.82	59.28	25.90	16.40	65.60	18.00	17.40	69.60	13.00
600	0.222	16.17	64.68	19.15	17.65	70.60	11.75	18.50	74.00	7.50
650	-0.419	17.35	69.40	13.25	18.58	74.32	7.10	19.23	76.92	3.85
700	-0.997	18.12	72.48	9.40	19.17	76.68	4.15	19.67	78.68	1.65
750	-1.524	18.62	74.48	6.90	19.58	78.32	2.10	19.87	79.48	0.65
800	-1.990	18.95	75.80	5.25	19.80	79.20	1.00	19.93	79.72	0.35
850	-2.429	19.24	76.96	3.80	19.90	79.60	0.50	19.97	79.88	0.15
900	-2.835	19.43	77.72	2.85	19.95	79.95	0.25			
950	-3.203	19.58	78.32	2.10						
1000	-3.543	19.66	78.64	1.70						
1050	-3.833	19.75	79.00	1.25						
1100	-4.159	19.76	79.04	1.20						
1150	-4.431	19.88	79.52	0.60						

Tafel 4.—(Fort.)

$n = 4$			$n = 5$			$n = 7$			$n = 10$		
CO	H ₂	CH ₄	CO	H ₂	CH ₄	CO	H ₂	CH ₄	CO	H ₂	CH ₄
7.52	22.56	69.92	8.21	24.63	67.16	10.00	30.00	60.00	11.43	34.29	54.28
12.25	36.75	49.00	13.37	40.11	46.52	15.30	45.90	38.80	16.83	50.49	32.68
16.22	48.66	35.12	17.38	52.14	30.48	19.13	57.39	23.48	20.62	61.86	17.52
20.27	60.81	18.92	21.16	15.36	15.36	22.53	67.59	9.88	23.54	70.62	5.84
22.24	66.72	11.04	23.43	70.29	6.28	24.23	72.69	3.08	24.58	73.74	1.68
24.33	72.99	2.68	24.55	73.65	1.80	24.84	74.52	0.64	24.90	74.70	0.40
24.88	74.64	0.48	24.90	74.70	0.40	24.96	74.88	0.16	24.98	74.94	0.08
24.96	74.88	0.16	24.97	74.91	0.14						

Tafel 5.—(Fort.)

$n = 3$			$n = 4$			$n = 5$			$n = 6$		
CO ₂	H ₂	CH ₄	CO ₂	H ₂	CH ₂	CO ₂	H ₂	CH ₄	CO ₂	H ₂	CH ₄
12.98	51.92	35.10	14.17	56.68	29.15	15.13	60.52	24.35	17.68	70.72	11.60
15.63	62.52	21.85	16.72	66.88	16.40	17.45	69.80	12.75	18.00	72.00	10.00
17.18	68.72	14.10	18.05	72.20	9.75	18.64	74.56	6.80	19.00	76.00	5.00
18.53	74.12	7.35	19.17	76.68	4.15	19.52	78.08	2.40	19.78	79.12	1.10
19.35	77.40	3.25	19.72	78.88	1.40	19.87	79.48	0.65	19.94	79.76	0.30
19.77	79.08	1.15	19.90	79.60	0.50	19.97	79.88	0.15	19.98	79.92	0.10
19.92	79.68	0.40	19.97	79.88	0.15						
19.97	79.88	0.15									

(Fortsetzung folgt.)

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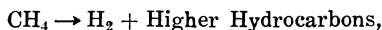
Researches on the Chemical Reaction by Use of the Thermal Diffusion Apparatus of Clusius and Dickel. I. Thermal Polymerisation of Methane.*

By Kozo HIROTA.

(Received June 12, 1941.)

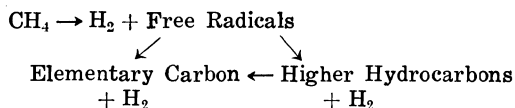
Introduction. Separation of gases by thermal diffusion method is much improved by the application of an apparatus⁽¹⁾, sometimes called thermal diffusion column, by means of which many researches are going on in order to separate isotopes such as those of chlorine, xenon, mercury and carbon⁽²⁾, while the author has used the apparatus as a rectifying column and discussed its efficiency⁽³⁾. The author also tried to use the apparatus as a reaction vessel, intending to perform a chemical reaction smoothly and completely as well as to separate the reactants at the same time by the action of thermosyphone found by Clusius and Dickel.

Object of the Research. On the first trial, the thermal polymerisation (or cracking-polymerisation) of methane,



which was found in nineteenth century and was extensively studied by F. Fischer⁽⁴⁾ in 1928, was carried out, because the effect would be remarkable in this reaction for the following reason, and on the other hand this reaction is important from the industrial point of view.

The elementary process of the above reaction is considered, at present,⁽⁴⁾⁽⁵⁾ though not yet definitely determined in detail, to consist in two stages: the first stage in which methane is cracked in hydrogen and some free radicals* and the second stage in which these free radicals polymerise into higher hydrocarbons, such as benzene and naphtalene. At high temperatures at which the reaction takes place with a measurable speed, both free radicals and hydrocarbons produced are very unstable and decompose easily into hydrogen and elementary carbon.



* Main part of this paper was read at the annual meeting of the Chemical Society of Japan (April 5, 1941).

(1) K. Clusius and G. Dickel, *Naturwissenschaften*, **26** (1938), 546.

(2) For instance, a) Cl, K. Clusius and G. Dickel, *ibid.*, **27** (1939), 148, 487; b) Xe, W. Groth, *ibid.*, 260; c) Hg, W. Groth and P. Harteck, *ibid.*, 584; d) C, H. S. Taylor, *Nature*, **144** (1939), 8.

(3) K. Hirota, *J. Soc. Chem. Ind. Japan*, **44** (1941), 391.

(4) F. Fischer, *Brennstoff Chem.*, **9** (1928), 308.

(5) H. M. Stanley and W. Nash, *J. Chem. Soc. Ind.*, **48** (1928), 1.

* The kind of free radicals is considered as CH_3 , CH_2 or CH , according to the different theory, but is not the main point of the argument.

So the important condition in getting a yield of hydrocarbons is to prevent the decomposition of free radicals in the hot region and to make those polymerise in the cold region. To meet this, Fischer passed methane very rapidly through a porcelain or quartz tube laid horizontally and heated at 900°C. or above, but his maximum yield of condensed hydrocarbons is 0.126 g. per liter of methane^{(4) (6)}, i.e., the conversion of 18% of the original methane. Kobayashi and others⁽⁷⁾ modified the method so as to pass the cracked methane through a slightly colder tube in order to acceralate the polymerisation of the free radicals. Dilution of the methane with nitrogen, hydrogen, chlorine, water steam or other gases⁽⁸⁾ cannot alter the yield considerably better and rather unfavourably in some cases. Hessel and others⁽⁹⁾ used a vertical tube and mixed some gaseous hydrocarbons or chlorine gas into the original methane. All these results obtained with a quartz and a porcelain tube, however, are of the same degree as some of these are shown in Table 1, while it was found that metallic tubes are not suitable on account of its catalytic power of accerelating the decomposition into carbon and hydrogen.

Table 1. Maximum Yield of Condensed Hydrocarbons in the Reaction, $\text{CH}_4 \rightarrow \text{H}_2 + \text{Higher Hydrocarbons.}^*$

Investigators	Vol. % of CH_4 in original gas	Conditions		Condensed Hydrocarbons		
		Temp. (°C.)	Contact Time(sec.)	Light Oil (g./l.)	Tar (g./l.)	Total (g./l.)
Fischer ⁽⁴⁾	93	1050	—	0.009	0.0045	0.014
Stanley, Nasch ⁽⁵⁾	93	1150	0.6	0.028	0.035	0.063
Fischer, Pichler ⁽⁶⁾	—	1300	0.016	0.050 (0.110)	0.076 (0.082)	0.126 (0.192)
Oda ⁽¹⁰⁾	82	1200	0.23	0.026 c.c./l.	0.023	—
Kobayashi, etc. ⁽⁷⁾	76	1100	0.45	0.091	0.022	0.113
Hessel, etc. ⁽⁹⁾	—	1190	0.29	0.031 (0.117)	0.029 (0.115)	0.050 (0.232)

Now if the reaction is carried on in the thermal diffusion column, we can consider that it will proceed as follows:—

Methane gas, introduced in from the bottom of the column, is cracked into hydrogen gas and free radicals at the electrically heated wire, placed in the central axis of the column. By the action of thermosyphone, the hydrogen molecules, the molecular weight of which is small, rise up along the heated wire and flow out from the top of the column, while the free

(6) F. Fischer and H. Pickler, *Brennstoff Chem.*, **13** (1932), 381.

(7) K. Kobayashi, K. Yamamoto, H. Ishikawa and S. Hinonishi, *J. Soc. Chem. Ind. Japan*, **37** (1937), 785.

(8) G. Egloff, "The Reaction of Pure Hydrocarbons", 64 (1937).

(9) W. Hessels, D. W. von Krevelen and H. I. Waterman, *J. Soc. Chem. Ind.*, **58** (1939), 321.

* Values in parentheses are obtained by repeated treatment of the gas for four times.

radicals go down along the cold wall, polymerising into higher hydrocarbons. Then we can expect in this process (i) that the decomposition of free radicals and higher hydrocarbons diminishes and (ii) that the reaction takes place completely, because the unreacted methane remains in the column, repeatedly colliding with the wire.

Experiment. The experiments were carried out at one atmospheric pressure. The column was a boron-glass (terex glass) tube of 1.01 meter in length and of 2.0 cm. in diameter with a tungsten wire of 0.75 mm. in diameter and 70 cm. in length and with a cooling glass tube of running water. Methane gas was prepared from sodium acetate and soda lime in an ordinary way. A gas interferometer was used constantly throughout the experiments for the check of gas analysis. Other details of the experimental procedures have been described in another journal⁽¹¹⁾, so only the summarised results are shown in Table 2 and 3.

Table 2. Summarised Experimental Results I.

No. of Exp.	Original Gas		Experimental Conditions				
	Vol. % of CH ₄	Vol. % of H.H.C.*	Gas Vol. Used (l.)	Flow Velocity (l./hr.)	Maximum† Temp. of the Wire °C.	Temp. of the Cold Wall °C.	Drying Substance
A	90	0.0	2.3	1.3	1200	34	} Soda lime
B	89	0.2	7.6	6.8	1300	42	
C**	89	1.2	4.5	6.3	1200	28	
D	93	1.2	1.8	1.3	1300	30	} One normal sodium hydroxide
E	93	1.2	3.0	1.2	1200	31	
F	93	1.2	1.9	0.4	1300	44	
G	93	1.2	2.2	0.8	1200	30	
H***	93	1.2	5	3.0	1300	35	

† Maximum Temp. of the Wire was obtained pyroptically. This value was probably too low on account of the disturbance caused by a brown product deposited on the cold glass wall.

* H. H. C. means heavy hydrocarbons.

** Part of the reacted gas was let to flow out from the bottom of the column too with the flow velocity of 0.2 liter per hour, and had the composition as follows: CH₄, 91%, H₂, 2%, etc.

*** Tungsten wire coated with sodium silicate was used.

(10) R. Oda, *J. Soc. Chem. Ind. Japan*, **37** (1934), B 630.

(11) K. Hirota, *J. Chem. Soc. Japan*, (Printed in Japanese) **62**, (1941), 392.

In the course of these experiments upper part of the wire was observed to be less bright than the lower part, probably owing to the higher concentration of hydrogen as would be expected.

Table 3. Summarised Experimental Results II.

No. of Exp.	Produced Gas				Produced Hydrocarbons			
	Flow Velocity l./hr.	Ex-pansion Ratio	Vol. % of H ₂	Vol. % of CH ₄	Liquid (g./l.)	Solid (g./l.)	Total (g./l.)	Ratio
A	0.6	0.5	77	11	0.12	0.04	0.16	3
B	3.7	0.5	79	11	0.03	0.02	0.05	1.5
C	4	0.6	33	59	0.09	>0.005	0.09	< 20
D	1.6	1.2	87	6	0.22	0.08	0.30	3
E	1.6	1.3	82	12	0.14	0.01	0.15	14
F	0.4	1.0	80	14	0.10	0.05	0.15	2
G	0.3	0.4	85*	—	0.17	0.07	0.24	3
H	2.0	0.6	60*	—	0.00	0.08	0.08	∞

* These values were estimated from the refractive index of the gas produced.

Discussion. I. The maximum yield of condensed hydrocarbons was 0.30 g. per liter of the original methane used, i.e., the conversion of 42%, and the concentration of hydrogen in the reacted gas amounted to 87% in the same experiment. This results are much superior to those of the researches of other investigators, and, moreover, to those obtained after the treatment of four times^{(6) (8)}.

II. Experiment H seems to show that a surface covered with non-metallic substance favours the undesirable decomposition to carbon and hydrogen, in spite of the reversed result of other investigators, but this might be due to the fact that contact plane of the wire to gas could not be heated fully.

III.(*) From the above experiments the following relations could be deduced easily:—

(i) Comparing A and B to D, E, F and G, small degree of drying seems to act to prevent the decomposition into carbon and hydrogen as indicated in the expansion ratio.

(ii) Comparing D to E, higher temperature seems to act to decrease the ratio of the liquid to the solid product and to increase the total yield.

(iii) The effect of flow velocity exists, if D to F is compared.

But as the number of the experiments is small, it must be examined carefully by later researches if these relations really hold.

IV. The liquid and solid products had the odour of toluene and naphthalene respectively. Both were insoluble in water and liquid paraffine and were hardly soluble in ethyl alcohol but soluble in benzene. These materials could be considered to be higher aromatic hydrocarbons. This conforms with the previous researches in connecton with this point.

* Content of this paragraph is slightly different from that in ref. (11) on account of the addition of new data.

As it has been shown very effective to use a thermal diffusion apparatus of Clusius and Dickel as a reaction vessel, the author is going not only to study the reaction expensively, but also to apply the method to other reactions.

Summary.

(1) A method of thermal polymerisation of methane proceeding in a thermal diffusion column of Clusius and Dickel has been described and discussed.

(2) By this method a good yield of condensed hydrocarbons and highly concentrated hydrogen gas have been obtained.

(3) Effects of the experimental conditions have been obtained.

In conclusion the author wishes to express his sincere thanks to Dr. R. Yoshimura, Director of the Department, for his interest and encouragement in carrying out this research.

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The Separation of Iso- and Normal Butyl Alcohols from Hydrocarbons by Azeotropic Distillation.

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(Received June 17, 1941.)

Two of the promising methods of the synthesis of iso- and normal butyl alcohols are first, the reaction of a mixture of hydrogen and carbon monoxide⁽¹⁻⁵⁾ under pressure in the presence of a suitable catalyst and, second, dehydration and polymerization of the lower alcohols⁽⁶⁻⁸⁾ under ordinary or elevated pressures in the presence of a catalyst. By either method, the products are not pure iso- and normal alcohols, but contain

(1) G. T. Morgan, R. Taylor, and T. J. Hedley, *J. Soc. Chem. Ind.*, **47** (1928), 117T; R. Taylor, *J. Chem. Soc.*, **1934**, 1429; G. T. Morgan, Hardy, and Proctor, *J. Soc. Chem. Ind.*, **51** (1932), 1T; G. T. Morgan and R. Taylor, *Proc. Roy. Soc., A* **131** (1931), 533.

(2) G. Natta, *Osterr. chem. Zeitg.*, **40** (1937), 162.

(3) E. M. Bocharova, B. N. Dolgov, and Z. M. Prokhorova, *Khim. Tverdogo Topliva*, **6** (1935), 665; *Chem. Abst.*, **30** (1936), 2171.

(4) I. G. Farbenind., A. G., G. P. 625757 (1936).

(5) H. Tahara, Y. Tatuki, and J. Simizu, *J. Soc. Chem. Ind., Japan* (Supp. Binding), **43** (1940), 82.

(6) Neuman, Brit. P. 326812 (1923).

(7) O. Fuchs and W. Querfurth, G. P. 594672; U. S. 205078.

(8) Deutsche Gold- und Silber-Scheideanstalt vormals Roessler, G. P. 674751 (1939); Brit. P. 478141 (1938).

a large number of hydrocarbons. Ordinarily, the alcohols are separated by distillation because of convenience and simplicity. However, owing to the circumstance that the alcohols are susceptible to the formation of azeotropic mixtures with a large number of hydrocarbons, straight forward distillation cannot be expected to give accurate results. Because of the fact that the alcohols form also azeotropic mixtures with water, distillation method can be so modified, taking advantage of the fact, to give a convenient and accurate separation of the alcohols from the hydrocarbons.

The purpose of this paper is to describe this method in some detail and to give the experimental results obtained from the measurements of alcohol-toluene and alcohol-gasoline mixtures. We have assumed in our case that the only water soluble substances are the alcohols. The separation of the alcohols from the mixtures containing such oxygenated compounds as the lower alcohols, aldehydes, and ketones, besides hydrocarbons will be the subject of a subsequent report, which will appear later in this bulletin.

In the present method, the following properties of the alcohols have been taken advantage of:

(1) The alcohols dissolve appreciably⁽⁹⁾ (at 20°C. the normal dissolves 7.8% and the iso- 8.5% by weight) in water, while hydrocarbons do not⁽¹⁰⁾.

(2) The alcohols dissolve completely in ether, while water does not but slightly.

(3) The alcohols form azeotropic mixtures with water, but not with ether.

Experimental Details.

A) Purification. *Normal Butyl Alcohol.* It was purified by a method similar to that given by Weissberger and Proskauer⁽¹¹⁾. It was washed with dilute sulphuric acid and then with sodium bisulphite. Then it was boiled with an aqueous KOH solution. A boiling fraction, 116.5–118°C., was first collected, and the final distillation was made over CaO. A fraction boiling at 117–118°C. was used.

Iso-Butyl Alcohol. A commercial product was first treated with quick lime and then distilled. A fraction boiling between 106.9–108.5 was collected.⁽¹²⁾

Toluene. It was purified⁽¹³⁾ by washing with concentrated H₂SO₄ and with water. It was then dried over CaCl₂, and the final distillation was made over metallic sodium. A fraction boiling at 110–112°C. was collected.

Gasoline. Commercial gasoline^(*) was purified by treating it with con-

(9) A. Seidell, "Solubility of Inorganic and Organic Compounds," D. Van Nostrand Co., Vol. II, 1121 (1928).

(10) Int. Crit. Tables, III, 387 (1928). Dissolves but slightly.

(11) A. Weissberger and E. Proskauer, "Organic Solvents," Oxford Press, 126 (1935).

(12) Kuwada, "Solvents," Maruzen, 219 (1940). In Japanese.

(13) G. L. Lewis and C. P. Smyth, *J. Chem. Phys.*, **7** (1939), 1087.

* "Rising Sun," brand, straight-run.

centrated H_2SO_4 , KOH, H_2O , dried with CaCl_2 , and finally distilled over metallic sodium. Fractions boiling from 50 to 130°C . were used.

Ether. It was first treated⁽¹⁴⁾ with concentrated sulphuric acid and then washed with KOH and water. It was then distilled over metallic sodium. A fraction, 36.0 – 37.0°C . was used.

B) Method. No special apparatus was used. 500 c.c. and 100 c.c. (for ether extractions) separatory flasks; calibrated 30 c.c. graduated cylinders, which were graduated to 0.1 c.c., with well-fitting ground glass stoppers; and a distillation set-up made of Terex glass with interchangeable ground glass joints were used. The distillation column was insulated by an annular space of air formed by fitting a glass tube over its whole length. The column was about 60 cm. in length and contained a Terex glass spiral. Heating was made either electrically or by gas. The temperature was measured by means of an alumel-chromel thermocouple connected to a potentiometer whose scale readings could be estimated to about 0.2°C .

The alcohols were first separated from the hydrocarbons by adding water 20 times⁽¹⁵⁾ the volume of the sample and shaken and left alone until all the alcohols had separated out from the hydrocarbon phase. It was shown by the results of Table 1 that 1.5 hours were sufficient to separate toluene completely (and also the alcohols; compare the results of Table 2) from the mixture. In order to break up the last traces of the emulsion formed by the system, the mixture was heated at 60°C . As it was indicated by the Table, 50°C . seemed not sufficient, and at this temperature the time of heating had to be longer. One shaking was adequate to remove practically all of the alcohols. The non-dissolving fraction was considered hydrocarbons. The validity of this assumption is justified, as shown by the results of Tables 1, 2, and 3.

To extract and concentrate the alcohols from such dilute aqueous solutions by means of some selective solvent appears unnecessarily tedious and wasteful in view of the fact that iso- and normal butyl alcohols form azeotropic mixtures with water in the respective proportions⁽¹⁶⁾ (by weight of alcohol), 67% and 57.6%, at the constant boiling points⁽¹⁶⁾, 90.0 and 92.6°C ., respectively.

Distillations were carried out in the apparatus, which has been mentioned above. Until the last traces of the alcohol had disappeared, the boiling point was constant; moreover, the distillation could be made quite rapidly and roughly without fear of introducing serious errors. It was continued until 100°C .⁽¹⁷⁾ When it was completed, the distillates, which had separated out into two layers, were shaken to bring about an equilibrium between alcohol and water, and the respective amounts of the alcohol in the water and the water in the alcoholic phase were corrected for at the experimental temperature. The above method was sufficient to determine accurately the amounts of the alcohols in their binary systems

(14) C. W. Porter, T. D. Stewart, and G. E. K. Branch, "Methods of Organic Chemistry," Ginn and Co., 70 (1927).

(15) V. G. Shaposhnikov and S. E. Pinchuk, *Chem. Abst.*, **30** (1936), 4787. They have suggested 35 fold addition in a similar separation.

(16) T. H. Durrans, "Solvents," Chapman and Hall, 102, 103 (1938).

(17) By 95°C practically all of the alcohols had been distilled out.

Table 1. Effects on Separation of Toluene of Time and Temperature.

Toluene-Iso alcohol Systems.*

Time left alone after shaking (hr.)	Conditions of aqueous layer	Temp. °C. of destroying emulsion	Time of heating (min.)	Toluene (c.c.)	Recovery %
1.0	Not quite clear	70	6	9.66	3.4
1.5	Clear	60	8	9.76	2.4
2.0	Clear	60	7	9.73	2.7
3.0	Clear	50	16*	9.71	2.9
4.0	Clear	60	6	9.75	2.5

* Break-up appeared not quite complete.

Toluene-Normal alcohol Systems.**

Time left alone after shaking (hr.)	Conditions of aqueous layer	Temp. °C. of destroying emulsion	Time of heating (min.)	Toluene (c.c.)	Recovery %
1.0	Not quite clear	60	9	9.64	3.6
1.5	Clear	60	7	9.72	2.8
2.0	Clear	60	6	9.80	2.0
3.0	Clear	60	5	9.79	2.1

** Conditions: toluene 10 c.c.; alcohol 10 c.c.; water 400 c.c.; time of shaking 5 minutes.

with hydrocarbons. If, however, a system contains both alcohols and hydrocarbons simultaneously, several additional steps must be made in order to separate the respective alcohols from each other. These additional operations involve, first, the extraction with ether⁽⁵⁾ of the alcohols from the aqueous phase and, second, the separation of the alcohols by distillation.

Results. The simpler method has been used for the separation of iso- and normal alcohols from their respective binary systems with toluene, and the results obtained at 15°C. (unless otherwise stated) are shown in Table 2. The actual amounts of toluene and the alcohols lost are independent of the amounts of the respective components in the system. What this means is, among others, that the loss is mainly operational. The results of our measurements indicate that the method is quite simple and fairly accurate. At present, we do not have a suitable explanation of the fact that the loss of toluene in the normal system is consistently smaller than that in the iso- system.

For the mixtures consisting of iso-, normal butyl alcohols, and commercial gasoline, the more involved method was used. The alcohols were separated from the gasoline and concentrated as in the simpler method.

Then to the distillates a sufficient amount of CaCl_2 was added to saturate the aqueous phase. Then by four separate additions of the same volume as that of the distillates of ether, the alcohols were completely extracted from water. Ether and the alcohols were, then, separated from each other by distillation which presented no difficulty.

Table 2.

Normal Butyl Alcohol-Toluene Systems at 15°C.

Vol. c.c.		Toluene c.c.		Alcohol recovered c.c.				% Alcohol Loss
Alcohol	Toluene	Recov.	Loss	Alc. phase	Aqueous phase	Total	Loss	
5*	15	14.83	0.17	4.04	0.67	4.71	0.29	5.8
5*	15	14.83	0.17	3.54	1.21	4.76	0.24	4.8
10	10	9.72	0.28	8.73	1.13	9.86	0.14	1.4
10	10	9.77	0.23	9.04	0.79	9.83	0.17	1.7
15*	5	4.76	0.24	12.64	2.03	14.71	0.29	1.9
15*	5	4.83	0.17	12.37	2.35	14.72	0.28	1.9

* At 10°C.

Iso-butyl Alcohol-Toluene Systems.

Component c.c.		Toluene c.c.		Alcohol Recovered c.c.				% Alcohol Loss
Alcohol	Toluene	Recov.	Loss	Alc. phase	Aqueous phase	Total	Loss	
5	15	14.75	0.25	4.66	0.33	4.99	0.01	0.2
5	15	14.77	0.23	4.49	0.45	4.94	0.06	1.2
10	10	9.72	0.28	8.65	1.08	9.82	0.28	2.8
10	10	9.73	0.27	8.85	0.84	9.68	0.32	3.2
15	5	4.78	0.22	14.29	0.68	14.97	0.03	0.2
15	5	4.73	0.27	13.95	0.89	14.84	0.16	1.1

The iso-butyl alcohol range was taken from 100 to 111°C., and what had been left over undistilled was considered all normal alcohol. As indicated by Fig. 1 and Table 3, the separation of iso-butyl alcohol is complete, and although a range from 100 to 111°C. has been taken, in reality, practically all has come out at a constant temperature, 108.4°C. The range of temperature, 100 to 108°C., is due to the time lag in bringing the thermocouple to the proper temperature.

As can be seen from Table 3, the actual loss in c.c. of the gasoline is about the same in each run, but it is larger than that of toluene. This is probably due to a higher volatility of the gasoline. Regardless of the amounts of the individual alcohols, the loss in each run is about the same; moreover, it is of the same order of magnitude as that in the toluene-alcohol systems. This indicates that the loss is, as it has been already

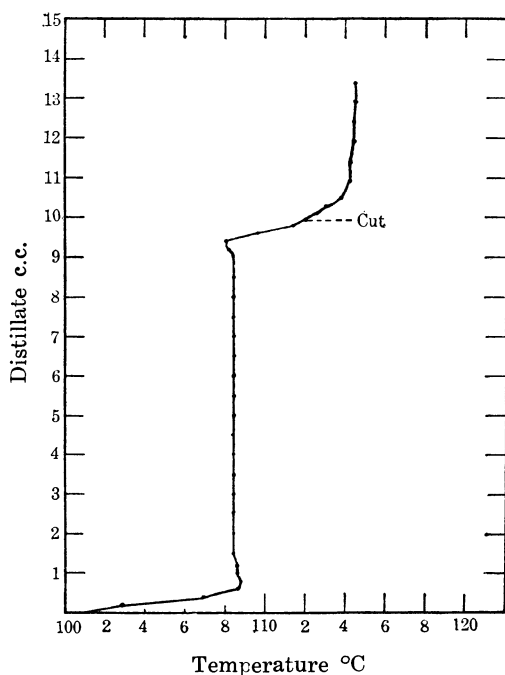


Fig. 1.

mentioned, chiefly mechanical. When the results of the two tables are compared, some information as to the sources of error involved in the present method may be gained. In Table 3 the amounts of iso- and of normal alcohols finally separated are always less than the original amounts and they are about the same as those in Table 2. What it means is that during the ether extractions and the final distillation the loss is negligible, and the main source of error seems either in the extraction by water of the alcohols or in the distillation of the azeotropic mixtures. By a number of preliminary runs the latter has been shown to give negligible error; therefore the chief source must be the former. The same inference can be drawn

Table 3.

Iso- and Normal Butyl Alcohols-Gasoline Systems at 15°C.

Components c.c.			Gasoline c.c.			Iso-Alcohol c.c.			Normal Alcohol c.c.		
Gasoline	Iso-	Normal	Recov.	Loss	% loss	Recov.	Loss	% loss	Recov.	Loss	% loss
10	10	10	9.64	0.36	3.6	9.70	0.3	3.0	9.67	0.33	3.3
10	10	10	9.67	0.33	3.3	9.75	0.25	2.5	9.73	0.27	2.7
10	10	10	9.64	0.36	3.6	9.80	0.20	2.0	9.68	0.32	3.2
10	5	15	9.60	0.40	4.0	4.83	0.17	3.4	14.91	0.09	0.6
10	15	5	9.52	0.48	4.8	14.78	0.22	1.4	4.75	0.25	5.0

from the fact that some difficulties, which have been already referred to, are encountered with in connection with the extraction.

Finally, a word may be mentioned of the accuracy of the method. Since the actual loss is independent of the total amount of each component in the system, the larger the amount of the component, the smaller will be its percentage error. If the alcohol to be separated is about 5 c.c., the percentage error is about 5; for 10 c.c., it is about 3%; and for over 15 c.c., it can be reduced to about 1%.

Summary.

A new method has been devised, employing the principle of azeotropic distillation, to separate iso- and normal butyl alcohols from hydrocarbons.

This method has been applied to the binary systems of iso- and normal alcohols with toluene. It has also been tried with the mixtures of the alcohols and gasoline. The individual components have been separated, and it has been shown that this method is accurate within 5% when the amount of the component to be separated is about 5 c.c.; 3% when it is 10 c.c.; and about 1% or less for the amount larger than 15 c.c.

The authors are grateful to Dr. Sato, the director of the institute, for permitting us to publish this paper.

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Über die Bildung der partiellen Acetate von Flavonen, Flavanonen, Anthrachinonen und dergleichen Verbindungen.

Von Masami SIMOKORIYAMA.

(Eingegangen am 2. Juli 1941.)

Bei der Methylierung von Flavonen, Flavanonen, Anthrachinonen und dergleichen Verbindungen, namentlich im Falle mit Diazomethan, stiessen wir gewöhnlich auf nicht kleinen Widerstand des der Carbonylgruppe ortho-ständigen Hydroxyls. Dies sollte, wie allgemein anerkannt, auf der Chelatbildung zwischen der letzteren Gruppe mit der ersteren beruhen. Falls diese von vielen Seiten vertretene Ansicht zutrifft, so müsste sich die Reaktionsträgheit der betreffenden Hydroxylgruppe auch bei Acetylierung geltend machen. In dieser Hinsicht untersuchte ich über das Verhalten von Substanzen oben genannter Stoffklasse in dem unter milden Bedingungen ausgeführten Acetylierungsverfahren, und fand, dass sie Acetate gaben, welche gegen Eisen(III)chlorid ausgezeichnete purpurbraune Farbreaktion zeigten. Wider Erwarten bildeten dabei jedoch *o*-Oxybenzoesäuren Ausnahmen, welche ohne Schwierigkeit vollständig acetylierte Derivate lieferten. Was die Ursache hierfür sei, ist mir zur Zeit unbekannt. Wohl ist die Chelatbildung in diesen Fällen viel lockerer.

Um den Essigsäurerest einzuführen, kann man sich natürlich über verschiedene Acetylierungsmethoden verfügen. Man acetyliert bisweilen in Gegenwart etwaigen indifferenten Verdünnungsmittels oder meistens ohne Verdünnungsmittel, d. h. durch unmittelbares Zusammenbringen der zu acetylierenden Substanz mit dem Acetyliermittel, z. B. Essigsäureanhydrid, ausführen, wobei die Reaktion in der Kälte nur langsam vor

sich geht. So ist dazu meist mehrstündiges Erwärmen in Anspruch genommen. Natürlich verläuft die Acetylierung glatt, wenn man eine kleine Menge Reaktionsbeschleuniger, wie z. B. konzentrierte Schwefelsäure⁽¹⁾, Natriumacetat⁽²⁾ oder Pyridin⁽³⁾, u. a. hinzufügt.

Den Zusatz von Pyridin bei Acetylierungen mittels Essigsäureanhydrids haben R. Behrend und P. Roth⁽³⁾ im Jahre 1904 zuerst für die Herstellung von Zuckeracetaten vorgeschlagen und diese Methode wurde nachher von E. Fischer und M. Bergmann⁽⁴⁾ als den mildesten Weg der Acetylierung empfohlen.

Ich bediente mich in vorliegender Untersuchung auch der oben erwähnten Pyridinmethode, in welcher aber das Pyridin nur im Sinne eines Katalysators⁽⁵⁾, nämlich in sehr kleiner Menge, verwendet wird.

Zur Untersuchung dienten einfache *o*-Oxyphenyl-aldehyde, -ketone u. -säuren, *o*-Oxy-flavone, -flavanone und -anthrachinone. Alle zur Untersuchung verwendeten Substanzen wurden in einem kleinen Röhrchen, den Zahlen der Hydroxylgruppen entsprechend, mit ca. 5–10 Mol. Essigsäureanhydrid gemischt, mit 2–3 Tropfen Pyridin versetzt und das Gemisch mit Glasstab gut umgerührt, wobei die Reaktion, mit schwacher Wärmeentwicklung begleitet, spontan vor sich geht, indem es sich entweder eine klare Lösung bildet oder Krystalle des Acetates sich ausscheiden und der Inhalt eventuell zu einer breiigen Masse erstarrt, je nachdem das gebildete Acetat in Essigsäureanhydrid leicht löslich ist oder schwer bzw. unlöslich ist. Im grossen und ganzen vollzieht sich die Reaktion innerhalb 2–3 Minuten. Dann wird das Gemisch mit Wasser versetzt und die abgeschiedene Reaktionsmasse abfiltriert, mit Wasser gut gewaschen und aus geeignetem Lösungsmittel umkrystallisiert. Auf diesem Wege kann man schon hinreichend reines Acetat in krystallisierter Form gewinnen. Durch diese Methode erhielt ich bei Verbindungen, welche nicht dem Carbonyl *o*-ständige Hydroxylgruppe tragen, Peracetate (Phloroglucin, Pyrogallol, Fisetin und ausnahmsweise Salicylsäure, β -Resorcyssäure, Brenzcatechin- und Pyrogallol-*o*-carbonsäure) und von solcher, welche u. a. dem Carbonyl *o*-ständige Hydroxylgruppe trägt, Acetat, in welchem die betreffende Hydroxylgruppe frei bleibt, worüber die purpurbraune Eisenchloridreaktion schon kundgibt.

Die so erhaltenen Acetylverbindungen werden im Vergleich mit Peracetaten in der folgenden Tabelle übersichtlich zusammengestellt.

1. Phloroglucin	Triacetat	103–104° (104–106° ⁽⁶⁾).
2. Pyrogallol	Triacetat	162–163° (165° ⁽⁷⁾).
3. Fisetin	Tetracetat	198–200° (196–199° ⁽⁸⁾ , 200–201° ⁽⁹⁾).

(1) A. P. N. Franchimont, *Ber.*, **12** (1879), 1941, **14** (1881), 1284, 1290; *Zd. H. Skraup, Monatsh. Chem.*, **19** (1898), 458.

(2) C. Liebermann u. O. Hörmann, *Ber.*, **11** (1878), 1619.

(3) R. Behrend u. P. Roth, *Ann.*, **331** (1904), 362; A. Verley u. Fr. Bülsing, *Ber.*, **34** (1901), 3354.

(4) E. Fischer u. M. Bergmann, *Ber.*, **50** (1917), 1048.

(5) R. Robinson u. K. Venkataraman, *J. Chem. Soc.*, **1926**, 2347.

(6) J. Herzig, *Monatsh. Chem.*, **6** (1885), 888.

(7) Knoll & Co., *Chem. Zentr.*, **1900** I, 270.

(8) J. Herzig, *Monatsh. Chem.*, **12** (1891), 178; J. Allan u. R. Robinson, *J. Chem. Soc.*, **1926**, 2335.

(9) J. Schmid, *Ber.*, **19** (1886), 1742; A. G. Perkin u. O. Gunnell, *J. Chem. Soc.*, **69** (1893), 1305.

4. Phloreoglucinaldehyd	Triacetat	122–123° ⁽¹⁰⁾ ,	Diacetat	93–94°.
5. Resacetophenon	Diacetat	38° ⁽¹¹⁾ ,	Monoacetat	72–73° (72° ⁽¹²⁾ , 74° ⁽¹³⁾).
6. Gallacetophenon	Triacetat	83° ⁽¹⁴⁾ , 85° ⁽¹⁵⁾ ,	Diacetat	78–81°.
7. Isosakuranetin	Diacetat	138–140°,	Monoacetat	173–175°.
8. Hesperetin	Triacetat	80–82° ⁽¹⁶⁾ ,	Diacetat	103–105°.
9. Chrysin	Diacetat	185° ⁽¹⁷⁾ , 192° ⁽¹⁸⁾ , 192–194° ⁽¹⁹⁾ ,	Monoacetat	160–165°.
10. Apigenin	Triacetat	181–182° ⁽²⁰⁾ ,	Diacetat	192–193°.
11. Acacetin	Diacetat	198–200° ⁽²¹⁾ , 203° ⁽²²⁾ ,	Monoacetat	203–208°.
12. Baicalein	Triacetat	191–192° ⁽²³⁾ ,	Diacetat	194°.
13. Wogonin	Diacetat	152–153° ⁽²⁴⁾ ,	Monoacetat	159–161°.
14. Kämpferol	Tetracetat	181–182° ⁽²⁵⁾ ,	Triacetat	177°.
15. Quercetin	Pentacetat	193–194° ⁽²⁶⁾ ,	Tetracetat	160–162°.
16. Myricetin	Hexacetat	214–216° ⁽²⁷⁾ ,	Pentacetat	189–190°.
17. Purpurin	Triacetat	200–201° ⁽²⁸⁾ ,	Diacetat	175–178°.
18. Salicylsäure	Monoacetat	134–135° (135° ⁽²⁹⁾ , 136–137° ⁽³⁰⁾).		
19. Brenzcatechin- <i>o</i> -carbonsäure	Diacetat	146–170° (148–150° ⁽³¹⁾).		
20. β -Resorcylsäure	Diacetat	136–137° (136–138° ⁽³²⁾).		
21. Pyrogallol- <i>o</i> -carbonsäure	Triacetat	163–164° (164° ⁽³³⁾).		

An dieser Stelle spreche ich meinem verehrten Lehrer, Herrn Prof. Dr. Sh. Hattori, meinen besten Dank für seine stetige Belehrung aus. Auch Herrn Dr. K. Hayashi des Iwata Institutes für Pflanzenbiochemie sage ich meinen besten Dank für sein lebenswürdiges Entgegenkommen zu dieser Arbeit aus.

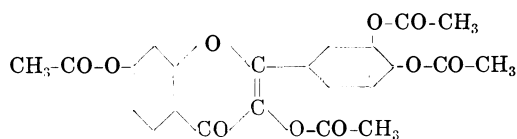
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Experimenteller Teil.

1. **Phloroglucin-triacetat**, $C_6H_3(O \cdot CO \cdot CH_3)_3^{1,3,5}$. 0.5 g. Phloroglucin werden mit 2 ccm (5 Mol.) Essigsäure-anhydrid und 2–3 Tropfen Pyridin versetzt. Nach ca. 1 Min. entsteht eine klare Lösung unter spontaner Temperaturerhöhung. Bald erstarrt das Ganze zu einer Krystallmasse. Phloroglucin-triacetat bildet lange weisse Nadeln aus 90-proz. Alkohol. Leicht löslich in heissem 90-proz. Alkohol. Schmp. 103–104°C. Ausbeute ca. 0.9 g.

2. **Pyrogallol-triacetat**, $C_6H_3(O \cdot CO \cdot CH_3)_3^{1,2,3}$. 0.5 g Pyrogallol werden in 2 ccm (5 Mol.) Essigsäure-anhydrid gelöst und dazu 2–3 Tropfen Pyridin hinzugesetzt. Nach starker Wärmeentwicklung erstarrt die Reaktionsmasse zu einem Krystallbrei, welcher nach ca. 10 Min. Stehenlassen mit Wasser versetzt wird. Das ausgeschiedene wird abfiltriert und aus 90-proz. Alkohol umkrystallisiert. Farblose kurze Prismen vom Schmp. 162–163°C. Ausbeute ca. 0.9 g.

3. **Fisetin-3.7.3'.4'-tetracetat**, $C_{23}H_{18}O_{10}$. 0.2 g (1 Mol.) Fisetin werden mit 0.6 ccm. (10 Mol.) Essigsäureanhydrid und 2–3 Tropfen Pyridin versetzt und mit Glasstab



gut umgerührt. Nach ca. 1.5–2 Minuten beginnt die Reaktion mit schwacher Wärmeentwicklung und beendigt sich in ca. 5 Minuten. Die nun farblos gewordene Reaktionsmasse wird mit Wasser versetzt, die weisse Acetylverbindung abgesaugt,

mit Wasser gewaschen und aus 90-proz. Alkohol umgelöst. Farblose Nadeln vom Schmp. 198–200°C. Schwer löslich in kaltem Alkohol, nicht so leicht löslich in heissem Alkohol. Ausbeute etwa 0.25 g.

4. **Phloroglucinaldehyd-2.4-diacetat**, $C_6H_3(OH)(O \cdot CO \cdot CH_3)_2 \cdot CHO^{1,3,5,2}$. 0.2 g Phloroglucinaldehyd (1 Mol.) werden mit 0.65 ccm. (5 Mol.) Essigsäure-anhydrid und 2–3 Tropfen Pyridin versetzt. In ca. 1–1.5 Min. kommt die Reaktion zum Abschluss, um unter Wärmeentwicklung klare Lösung zu geben. Man versetzt mit Wasser und krystallisiert den bald erstarrenden Niederschlag aus 90-proz. Alkohol um. Weisse Nadeln vom Schmp. 93–94°C. Ausbeute ca. 0.2 g.

Gef.: C 55.43, 55.88; H 4.27, 4.53. Ber. für $C_{11}H_{10}O_6$: C 55.48; H 4.23%.

5. **Resacetophenon-4-monoacetat**, $C_6H_3(OH)(O \cdot CO \cdot CH_3) \cdot CO \cdot CH_3^{1,3,6}$. Man erhält diese Verbindung, welche schon 1881 von M. Nencki und N. Sieber⁽¹²⁾ und A. Michael und G. M. Palmer⁽¹³⁾ aus Resacetophenon (1 Gew.-Tl.) durch eine Stunde langes Kochen am Rückflusskühler mit Essigsäure-anhydrid (3 Gew.-Tl.) und darauffolgende Destillation (Sdp. 303°C.) in der Vorlage krystallinisch (Schmp. 72°C.) erhalten wurde, wenn man 0.2 g. Resacetophenon (1 Mol.) in einem kleinen Röhrchen mit 0.7 ccm. Essigsäure-anhydrid (10 Mol.) und 2–3 Tropfen Pyridin versetzt und mit Glasstab umrührt. Mit schwacher Wärmeentwicklung beendigt sich die Reaktion in 2–3 Minuten. Dann versetzt man die Lösung mit Wasser und krystallisiert die entstehende farblose Krystallmasse aus verd. Alkohol um. Schmp 72–73°C. Ausbeute 0.15 g. Die alkoholische Lösung gibt mit Ferrichlorid eine purpurbraune Färbung.

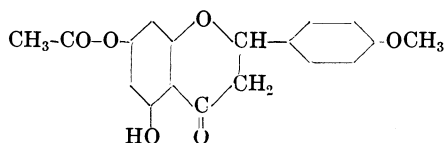
Gef.: C 61.72; H 5.36. Ber. für $C_{10}H_{10}O_4$: C 61.84; H 5.19%.

6. **Gallacetophenon-3.4-diacetat**, $C_6H_2(OH)(O \cdot CO \cdot CH_3)_2 \cdot CO \cdot CH_3^{1,2,3,6}$. Man versetzt 0.2 g. (1 Mol.) Gallacetophenon, gelöst in 0.6 ccm. Essigsäure-anhydrid (5 Mol.), mit 2–3 Tropfen Pyridin in einem kleinen Röhrchen und rührt mit Glasstab um. In 0.5–1 Min. ist die Reaktion beendigt und eine klare gelbe Lösung ergibt sich. Nach ca. 5–10 Min. Stehengelassen, versetzt man mit Wasser und krystallisiert die schwierig erstarrende gelbbraune Reaktionsmasse aus verd. Alkohol um. Schmp.

78–81°C. Die alkoholische Lösung gibt mit Ferrichlorid eine purpurbraune Färbung. Diese Substanz ist nicht mit der Verbindung identisch, welche von G. Heller⁽³⁴⁾ aus Pyrogallol-triacetat durch halbstündiges Erhitzen mit ZnCl_2 auf 130–135°C. erhalten wurde. Sie zeigte nach dem Umkrystallisieren aus Eisessig den Schmp. 217–219°C. und gab mit Ferrichlorid eine dunkelrote Färbung.

Gef.: C 56.68; H 4.37. Ber. für $\text{C}_{12}\text{H}_{12}\text{O}_6$: C 57.14; H 4.76%.

7. **Isosakuranetin-7-monoacetat**, $\text{C}_{18}\text{H}_{16}\text{O}_6$. Versetzt man 0.1 g. (1 Mol.) Isosakuranetin mit 0.35 ccm. (10 Mol.) Essigsäure-anhydrid und 2–3 Tropfen Pyridin in kleinem Proberröhrchen, so lösen sich die Krystalle von Isosakuranetin allmählich auf und es entsteht in 5 bis 6 Minuten eine klare Lösung.



Dann wird diese Lösung mit Wasser versetzt, die abgeschiedene Acetylverbindung abfiltriert und aus 80–90-proz. Alkohol umkrystallisiert. Weisse Nadeln von Schmp. 173–175°C.

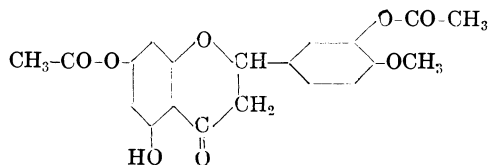
In alkoholischer Lösung gibt die Substanz mit Ferrichlorid eine purpurbraune Reaktion und bei der Reduktion mit Mg und konz. Salzsäure zeigt sie eine kirschrote Färbung. Ausbeute 0.1 g.

Gef.: C 59.32; H 5.44. Ber. für $\text{C}_{18}\text{H}_{16}\text{O}_6 \cdot 2\text{H}_2\text{O}$: C 59.34; H 5.53%.

8. **Isosakuranetin-5,7-diacetat**, $\text{C}_{20}\text{H}_{18}\text{O}_7$. 0.1 g Isosakuranetin wird mit 0.35 ccm. Essigsäure-anhydrid (10 Mol.) und 2–3 Tropfen Pyridin versetzt und auf dem siedenden Wasserbade 30 Minuten lang erhitzt. Das Produkt wird aus 90-proz. Alkohol umgelöst und erwies sich als schwer krystallisierbar. Schliesslich schieden sich farblose Nadeln vom Schmp. 138–140°C. Sehr leicht löslich in Alkohol. Eisenchloridreaktion negativ. Farbreaktion bei der Reduktion mit Mg und konz. Salzsäure stark positiv. Ausbeute ca. 0.05 g.

Gef.: C 59.09; H 5.25. Ber. für $\text{C}_{20}\text{H}_{18}\text{O}_7 \cdot 2\text{H}_2\text{O}$: C 59.11; H 5.46%.

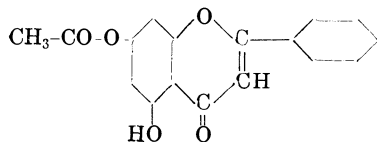
9. **Hesperetin-7,3'-diacetat**, $\text{C}_{20}\text{H}_{18}\text{O}_8$. Versetzt man 0.2 g (1 Mol.) Hesperetin mit 0.7 ccm. (10 Mol.) Essigsäure-anhydrid und 2–3 Tropfen Pyridin, so gehen die Krystalle von Hesperetin unter Wärmeentwicklung allmählich in Lösung innerhalb ca. 0.5–1 Minuten.



Versetzt man diese Lösung mit Wasser, so entsteht schwer erstarrende harzige Masse. Diese Verbindung krystallisiert aus Alkohol in Nadeln oder prismatischen Krystallen vom Schmp. 103–105°C. Die alkoholische Lösung zeigt mit Ferrichlorid eine purpurbraune Färbung.

Gef.: C 62.00; H 5.03. Ber. für $\text{C}_{20}\text{H}_{18}\text{O}_8$: C 62.18; H 4.70%.

10. **Chrysin-7-monoacetat**, $\text{C}_{17}\text{H}_{12}\text{O}_5$. 0.15 g. Chrysin werden in einem kleinen Röhrchen mit 0.6 ccm. (10 Mol.) Essigsäure-anhydrid und 2–3 Tropfen Pyridin gemischt und mit Glasstab umgerührt, so dass sich nach 1–1.5 Min. das Gemisch verflüssigt und dann zu einer Krystallmasse erstarrt.



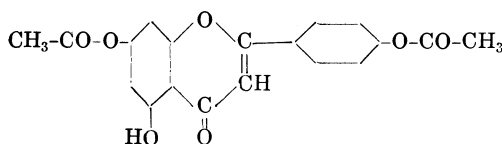
Nach Ablauf weiterer 2–3 Minuten versetzt man die Reaktionsmasse mit Wasser. Die ausfallende Krystallmasse wird abgesaugt und aus 90-proz. Alkohol umkrystallisiert. Die so erhaltene Monoacetylverbindung schmilzt bei 160–165°C.

Leicht löslich in heissem Alkohol. Die alkoholische Lösung gibt mit Ferrichlorid purpurbraune Färbung. Ausbeute ca. 0.15 g.

Gef.: C 69.20; H 3.99. Ber. für $\text{C}_{17}\text{H}_{12}\text{O}_5$: C 68.91; H 4.08%.

(34) G. Heller, *Eer.*, **45** (1912), 2389.

11. **Apigenin-7,4'-diacetat**, $C_{19}H_{14}O_7$. 0.1 g. Apigenin (1 Mol.) wird mit 0.4 ccm. (10

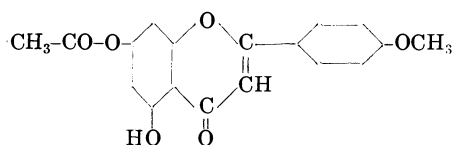


Mol.) Essigsäure-anhydrid und 2 Tropfen Pyridin versetzt. In ca. 3 Minuten ist die Reaktion beendet. Schwache Wärmeentwicklung und Verflüssigung der Reaktionsmasse. Nach dem Versetzen mit Wasser wird die Acetylverbindung abgesaugt und aus 90-proz. Alkohol um-

krystallisiert. Weisse Nadeln vom Schmp. 192-193°C. Purpurbraune Eisenchloridreaktion. Ausbeute ca. 0.1 g.

Gef.: C 64.47; H 3.96. Ber. für $C_{19}H_{14}O_7$: C 64.40; H 3.98%.

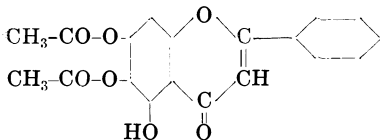
12. **Acacetin-7-monoacetat**, $C_{18}H_{14}O_6$. 0.1 g. (1 Mol.) Acacetin wird mit 0.35 ccm. (10 Mol.) Essigsäure-anhydrid und 2 Tropfen



Pyridin versetzt. Die Reaktion wird nach ca. 2-3 Minuten beendet. Wie üblich mit Wasser versetzt und die abgeschiedene Kristalle aus 90-proz. Alkohol umkrystallisiert. Weisse kurze Nadeln vom Schmp. 203-208°C. Die alkoholische Lösung gibt mit Ferrichlorid

eine purpurbraune Färbung. Ausbeute ca. 0.1 g.

13. **Baicalein-6,7-diacetat**, $C_{19}H_{14}O_7$. 0.2 g. (1 Mol.) Baicalein werden mit 0.8 ccm. (10 Mol.) Essigsäure-anhydrid und 2-3 Tropfen Pyridin versetzt und mit Glasstab vermischt. In 2-3

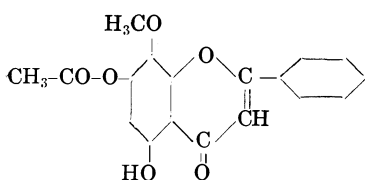


Minuten ist die Reaktion beendet, mit Wasser versetzt und abfiltrierte Acetylverbindung aus 90-proz. Alkohol umkrystallisiert. Weisse Nadeln vom Schmp. 194°C. Die alkoholische Lösung zeigt mit Eisenchlorid eine purpurbraune Färbung. Leicht

löslich in heissem Alkohol. Ausbeute ca. 0.2 g.

Gef.: C 64.34; H 3.91. Ber. für $C_{19}H_{14}O_7$: C 64.40; H 3.98%.

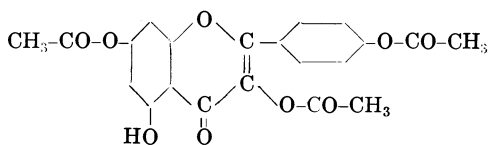
14. **Wogonin-7-monoacetat**, $C_{18}H_{14}O_6$. 0.15 g. Wogonin werden mit 0.55 ccm. (10 Mol.) Essigsäure-anhydrid und 2-3 Tropfen Pyridin versetzt. Nach 1 Minuten Umrühren endet die Reaktion. Goldgelbe Wogoninkristalle verwandelt sich



zu schwach gelben Nadeln. Mit Wasser versetzt, abfiltriert, aus 90-proz. Alkohol umkrystallisiert, bildet das Acetylwogonin lange hellgelbe Nadeln vom Schmp. 159-161°C. Eisenchloridreaktion in alkoholischer Lösung purpurbraun (olivengrünlich). Ausbeute ca. 0.15 g.

Gef.: C 66.37; H 4.37. Ber. für $C_{18}H_{14}O_6$: C 66.26; H 4.32%.

15. **Kämpferol-3,7,4'-triacetat**, $C_{21}H_{16}O_9$. Zur Gewinnung des Triacetyl-kämpferols werden 0.2 g. (1 Mol.) Kämpferol mit 0.7

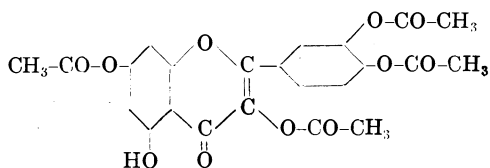


ccm. (10 Mol.) Essigsäure-anhydrid und 2-3 Tropfen Pyridin versetzt und mit Glasstab gut umgerührt. In 1.5 Minuten wird die Acetylierung vollendet. Die Reaktionsmasse wird dann mit Wasser versetzt, das Acetylderivat abgesaugt, mit Wasser gewaschen und aus 90-proz.

Alkohol umkrystallisiert. Weisse Nadeln vom Schmp. 177°C. Leicht löslich in heissem Alkohol, aber schwer löslich in kaltem Alkohol. Eisenchloridreaktion purpurbraun. Ausbeute 0.2 g.

Gef.: C 61.40; H 4.14. Ber. für $C_{21}H_{16}O_9$: C 61.17; H 3.91%.

16. Quercetin-3.7.3.'4'-tetracetat, $C_{27}H_{18}O_{11}$. 0.3 g. (1 Mol.) lufttrocknes Quercetin werden in ein kleines Röhrchen von etwa 5 ccm Inhalt eingeführt, mit 1 ccm. (10 Mol.)

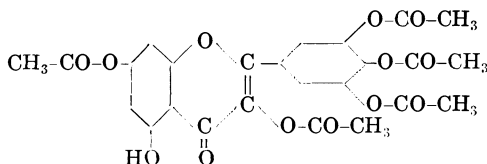


Essigsäure-anhydrid und 2-3 Tropfen Pyridin versetzt und mit Glasstab bei Zimmertemperatur umgerührt, wobei sich gelbe Krystalle von Quercetin nach und nach in weissen Nadeln von Acetylverbindung umwandeln. Unter Wärmetönung ist die Reaktion nach 4-5 Minuten beendet. Nach 10 Minuten Stehenlassen wird die Reaktionsmasse mit Wasser gewa-

schen und aus 90-proz. Alkohol umkrystallisiert. Farblose Nadeln. Das Tetracetatderivat schmilzt bei 160-162° und zeigt in alkoholischer Lösung mit Ferrichlorid eine purpurbraune Färbung. Ausbeute etwa 0.3 g.

Gef.: C 58.73; H 4.05. Ber. für $C_{27}H_{18}O_{11}$: C 58.70; H 3.86%.

17. Myricetin-3.7.3'.4'.5'-pentacetat, $C_{25}H_{20}O_{13}$. 0.2 g. Myricetin werden mit 0.65 ccm. (10 Mol.) Essigsäureanhydrid und 2-3

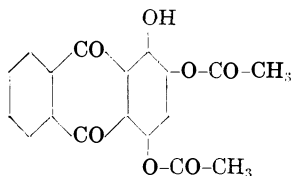


Tropfen Pyridin versetzt. In ca. 1 Min. verflüssigt sich das Gemisch, nach einer weiteren Minuten Umrühren beginnt die Reaktion unter schwacher Wärmeentwicklung und Erstarrung der Reaktionsmasse. Aus 90-proz. Alkohol scheidet sich das Acetat in langen Nadeln vom Schmp.

189-190°C. ab. Schwer löslich in kaltem, aber leicht löslich in heissem Alkohol. Eisenchloridreaktion purpurbraun. Ausbeute ca. 0.2 g.

Gef.: C 57.23; H 3.81. Ber. für $C_{25}H_{20}O_{13}$: C 56.84; H 3.82%.

18. Purpurin-2.4-diacetat, $C_{18}H_{12}O_7$. 0.2 g. (1 Mol.) Purpurin werden mit 0.8 ccm. (10 Mol.) Essigsäure-anhydrid und 2-3 Tropfen Pyridin ver-



setzt. Nach ca. 1 Min. Umrühren mit Glasstab beginnt die Reaktion und nach 5-6 Minuten bleibt kein rotes Purpurinkryställchen mehr. Die orangefelbe Reaktionsmasse wird mit Wasser versetzt, abfiltriert und aus 90-proz. Alkohol umkrystallisiert. Orangefelbe Krystalle vom Schmp. 175-178°C. In alkoholischer Lösung zeigt die Acetylverbindung eine jodbraune Eisenchloridreaktion. Ausbeute ca. 0.2 g.

Gef.: C 63.29; H 3.52. Ber. für $C_{18}H_{12}O_7$: C 63.53; H 3.56%.

19. Salicylsäure-acetat, $C_6H_4(O\cdot CO\cdot CH_3)\cdot COOH^{1,2}$. 0.5 g. Salicylsäure werden mit 1.85 ccm. (5 Mol.) Essigsäure-anhydrid und 2-3 Tropfen Pyridin versetzt, wodurch bald klare Lösung entsteht. Versetzt man diese Lösung mit Wasser, so entsteht schwer erstarrende ölige Masse. Das Produkt erstarrt, bald krystallinisch und wird aus verd. Alkohol umkrystallisiert. Farblose Nadeln oder Prismen vom Schmp. 134-135°C. Eisenchloridreaktion völlig negativ.

20. Brenzcatechin-o-carbonsäure-diacetat, $C_6H_3(O\cdot CO\cdot CH_3)_2\cdot COOH^{1,2,3}$. 0.2 g. Brenzcatechin-o-carbonsäure werden mit 0.66 ccm. (5 Mol.) Essigsäure-anhydrid und 2-3 Tropfen Pyridin versetzt. In ca. 1-2 Min. entsteht klare Lösung. Versetzt man diese Lösung mit Wasser, so entsteht schwer erstarrende ölige Masse. Diese Verbindung krystallisiert aus verd. Alkohol in farblosen Nadeln vom Schmp. 146-170°C. Eisenchloridreaktion ganz negativ.

21. β -Resorcylsäure diacetat, $C_6H_3(O\cdot CO\cdot CH_3)_2\cdot COOH^{1,2,3}$. 0.2 g. β -Resorcylsäure werden mit 0.66 ccm. Essigsäure-anhydrid und 2-3 Tropfen Pyridin versetzt. In ca. 1-2 Min. entsteht klare Lösung. Beim Versetzen mit Wasser entsteht öliges Reaktionsprodukt, welches im Kühlraum bald krystallinisch erstarrt und aus wenigem Alkohol in

prismatischen Nadeln krystallisiert. Die alkoholische Lösung zeigt mit Ferrichlorid keine Färbung. Schmp. 136–137°C.

22. **Pyrogallol-o-carbonsäure-triacetat**, $C_6H_2(O \cdot CO \cdot CH_3)_3 \cdot COOH^{1,2,3,4}$. Die Herstellung des Triacetats erfolgt durch unmittelbares Zusammenbringen von Pyrogallol-o-carbonsäure (0.2 g.) mit 0.6 ccm. (5 Mol.) Essigsäure-anhydrid und 2–3 Tropfen Pyridin. In ca. 1 Min. entsteht braune Lösung unter Temperaturerhöhung. Diese Verbindung krystallisiert aus verd. Alkohol in farblosen Nadeln vom Schmp. 163–164°. Prismatische Nadeln aus Xylol⁽³³⁾. In alkoholischer Lösung gibt die Substanz mit Eisenchlorid keine Färbung.

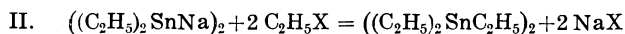
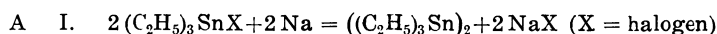
*Biochemisches Laboratorium, Botanisches Institut,
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A Note to the Paper "On the Metallo-organic Compounds. X. Electroisomerism in the Triethyltin Group."

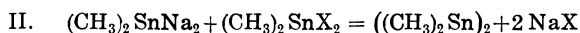
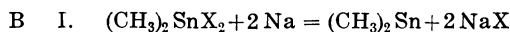
By Taichi HARADA.

(Received July 4, 1941.)

In the paper "on the metallo-organic compounds. X. Electroisomerism in the triethyltin group,"⁽¹⁾ the author reported a difference between the rates of oxidation of two preparations of the triethyltin group in a polymerized form prepared in liquid ammonia by the following two methods:



Kraus and Greer⁽²⁾ also observed that a similar behavior exists between the following two dimethyltin preparations:



that is, the latter (B II) preparation is much more sensitive to oxygen than that of the former (B I). In accounting for the difference between the rates of oxidation of the preparations (A I) and (A II), the present author believed that an explanation may be found by assuming the cause to be due to the method of preparation or the difference in their electronic constitutions (electroisomers). However, such assumption must now be withdrawn since it is not only hasty but is inconceivable that the triethyltin group can exist in two isomeric forms with present knowledge. The different rates of oxidation in question can not be explained satisfactorily at present but it may be correct to assume that the difference might be due to some contaminating trace of impurity in the preparation. Further investigation on this point was not carried out because it is not within the scope of this original investigation.⁽³⁾

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(1) T. Harada, this Bulletin, **15** (1940), 481.

(2) Kraus and Greer, *J. Am. Chem. Soc.*, **47** (1925), 2568.

(3) Kraus and T. Harada, *ibid.*, **47** (1925), 2416; T. Harada, *Sc. Pap. I. P. C. R.*, **38** (1940), 146.

On the Catalytic Action of Japanese Acid Earth. XI. The Isomerisation of Aldehydes to Ketones and the Explanation of the Migration of the Radicals from the Standpoint of the Electronic Theory (*Continued and concluded*).

By Koshiro ISHIMURA.

(Received May 14, 1941.)

α-o-Tolyl α-p-tolyl ethylene glycol. *p*-Methylbenzoyl carbinol (9.5 g) was added to the Grignard reagent (44 g. *o*-iodotoluene and 4.8 g. magnesium). After all of the carbinol was added the reaction mixture was boiled for 3 hours. It was cooled and treated with acetic acid (15 g. glacial acetic acid in 300 c.c. ice water). The upper ethereal solution was washed with dilute caustic soda, saturated solution of sodium chloride, and sodium bisulphite and again with brine. The ether was removed and the residue was subjected to the steam distillation for 5 hours. The contents of the flask were left to stand overnight. The main part (14.5 g.) of the required glycol settled down to the bottom forming yellowish solid mass, while a small portion (0.9 g.) of it was found to be suspending in water forming colourless needles, which crystallised from dilute alcohol in colourless needles, m.p. 115–116°C. (Found: C, 78.5; H, 7.7. $C_{16}H_{18}O_2$ requires C, 78.3; H, 7.4%).

The benzoyl derivative was obtained by Schotten-Baumann's method. It crystallised from 95% alcohol in colourless columns or needles, m.p. 164–165°C. (to a yellow melt). It has one molecule of water of crystallisation alike benzoyl *m*-tolyl *p*-tolyl ethylene glycol. (Found: C, 76.1; H, 6.0%; Mol. wt., (Rast), 325. $C_{23}H_{22}O_3 \cdot H_2O$ requires C, 75.8; H, 6.6%; Mol. wt., 364).

Oxidation of α-o-tolyl α-p-tolyl ethylene glycol. The glycol (0.83 g.) was added by portions to chromic oxide (1.2 g.) dissolved in 80% acetic acid (50 c.c.) and heated to boiling for a short time and left to stand overnight. It was neutralised with dilute caustic soda, extracted with ether, the ethereal extract washed with a solution of sodium chloride, dried over calcium chloride, the ether distilled off leaving an oil (0.55 g.), the crude *o*-tolyl *p*-tolyl ketone. The oxime produced from the ketone crystallised from dilute alcohol in colourless needles, m.p. 120°C. W. Scharwin and Schorygin⁽⁶⁸⁾ described the ketone as an oil boiling at 316–318°C./760 mm., characterised by an oxime melting at 122°C. The oxime was converted to *o*-toluyl *p*-toluidide through the Beckmann rearrangement, m.p. 144°C. (Found: N, 6.6. $C_{15}H_{15}ON$ requires N, 6.2%), which has also been given by the above-mentioned Russian authors.

o-Tolyl p-tolyl actaldehyde. A mixture of *α-o*-tolyl *α-p*-tolyl ethylene glycol (30 g.), crystalline oxalic acid (75 g.) and water (30 c.c.) was gently boiled for 3 hours, carbon dioxide being meanwhile passed into

(68) *Ber.*, **36** (1903), 2025.

the reaction vessel in order to prevent the oxidation of the product with atmospheric oxygen. The upper layer of the contents of the vessel was extracted with ether, the ethereal extract washed with dilute caustic soda and with water, dried over anhydrous sodium sulphate and the ether was removed by distillation. The residue was distilled in the

reduced pressure of 9 mm. giving the fractions shown in Table 2.

Table 2.

Fractions	B.p. (°C.)	Yield (g.)
(1)	140-165	1.1
(2)	165-175	3.0
(3)	175-180	3.0
(4)	180-182	5.4
(5)	182-205	3.5
(6)	Residue	—

The fraction (1) consists chiefly of *p*-methylbenzoyl carbinol still remaining. The fraction (4) is the required aldehyde, d_4^{20} , 1.0669; n_D^{20} , 1.5812; M.R., found, 69.96; calc. (Eisenlohr), 68.90. (Found: C, 85.4; H, 7.5. $C_{16}H_{16}O$ requires C, 85.7; H, 7.1%).

The aldehyde unites with sodium bisulphite very difficultly obviously owing to the steric hindrance of the methyl group attached to the carbon atom next to the carbonyl. A small quantity of *o*-tolyl *p*-tolyl ketone, which is still more difficult than the foregoing ketone to produce the addition compound with bisulphite, was found to be produced thereby. Its existence was confirmed by the production of *o*-toluyl *p*-toluidide, m.p. 143-144°C., (Found: N, 6.5. $C_{15}H_{15}ON$ requires N, 6.2%), from the oxime through the Beckmann rearrangement. The melting point did not depress by mixing it with the condensation product of *o*-toluic acid and *p*-toluidine.

o-Tolyl *p*-tolyl acetaldehyde forms a faintly yellow, viscous oil, and turns blue when brought to contact with Fuchsin-bisulphite solution. The semicarbazone crystallised from dilute alcohol in thick prisms, m.p. 154-155°C. (to a yellow melt). (Found: N, 15.2. $C_{17}H_{19}ON_3$ requires N, 14.9%).

o-Tolyl *p*-tolyl acetic acid. Potassium hydroxide (5 g. dissolved in 50 c.c. water) was added by portions (5 c.c. at a time every ten minutes) to the mixture of *o*-tolyl *p*-tolyl acetaldehyde (3 g. dissolved in 60 c.c. alcohol) and silver nitrate (7 g. dissolved in 7 c.c. water), and the mixture was shaken vigorously meanwhile. It was filtered, the filtrate saturated with carbon dioxide, concentrated on the water bath. The remaining aldehyde was thereby thrown down as oil drops, which were separated on filter paper. The filtrate was neutralised with dilute sulphuric acid. An oily substance separated, and solidified on cooling and crystallised from hot water in glittering plates (0.8 g.), m.p. 115-116°C. (Found: C, 80.2; H, 7.0%; Equiv. wt. (by titration with 1/20 N alkali solution), 239.8. $C_{16}H_{16}O_2$ requires C, 80.0; H, 6.7%; Equiv. wt., 240.1).

o-Tolyl *p*-methylbenzyl ketone. Attempts to prepare the above ketone by the condensation of *o*-brom-*o*-methylacetophenone with toluene in the presence of anhydrous aluminium chloride failed, while the oxidation of *o*-tolyl *p*-methylbenzyl carbinol resulted in the formation of the impure ketone difficult to be purified. The pure ketone was obtained only by the isomerization of *o*-tolyl *p*-tolyl acetaldehyde. It melts at 26°C.

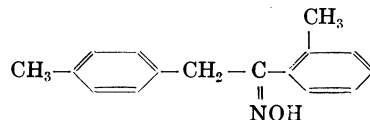
The preparation of the ketone from *o*-tolyl *p*-methylbenzyl carbinol was carried out in the following way. *p*-Tolyl acetaldehyde (2 g. dissolved in 2 c.c. ether) was added to the Grignard reagent (3.26 g. of *o*-tolyl iodide and 0.36 g. of magnesium), the reaction mixture was boiled for 2 hours and left to stand overnight. A small quantity of ice water was added to the product, followed by 36% hydrochloric acid (1.2 c.c.). It was then treated as usual and a yellow thick oil (1.3 g.) was obtained, which showed no tendency to solidify when cooled. The raw *o*-tolyl *p*-methylbenzyl carbinol (0.80 g.) thus obtained was dissolved in 80% acetic acid (30 c.c.) and chromic oxide (0.15 g.) was added to the solution little by little. The solution was boiled for 30 minutes, cooled and poured into ice water (400 c.c.), the water solution extracted with ether, the ethereal extract was washed with aqueous sodium hydroxide and with a solution of sodium chloride, dried over calcium chloride and the ether removed. A semi-solid yellow mass (0.37 g.) with aromatic odour was obtained, which did not solidify when cooled at -15°C . for 12 hours. Attempts to obtain the oxime from the ketone considered to have thus been produced resulted in the formation of viscous oil which again did not solidify when cooled at -5°C . It was dissolved in ether and treated with phosphorus pentachloride and the well defined crystals of [*p*-tolyl acetyl]-*o*-toluidide (0.05 g.), m.p. 163°C . (uncorr.), was finally obtained showing that the required ketone has actually been synthesised. The melting point was not depressed by mixing it with the authentic specimen mentioned below.

As mentioned above and will be described below in detail *o*-tolyl *p*-methylbenzyl ketone was produced by the isomerization of *o*-tolyl *p*-tolyl acetaldehyde and melted at 26°C . when recrystallised from dilute alcohol. (Found: C, 85.8; H, 7.1. $\text{C}_{16}\text{H}_{16}\text{O}$ requires C, 85.7; H, 7.1%). It is slowly oxidised with atmospheric oxygen to *o*- and *p*-toluic acids.

The oxime (0.19 g.) was obtained from the ketone (0.3 g.) by Auers' method, which melted at $96\text{--}103^{\circ}\text{C}$. after recrystallisation three times from dilute alcohol. It was subjected to the fractional crystallisation and gave the following fractions:—

Fractions	M.p. ($^{\circ}\text{C}$.)	Yields (in g.)
(1)	109–115	0.06
(2)	77– 84	0.05
(3)	75– 80	0.02

The first fraction (m.p. $109\text{--}115^{\circ}\text{C}$.) gave [*p*-tolyl acetyl]-*o*-toluidide by the Beckmann rearrangement indicating the configuration of the oxime as follows:—



[*p*-Tolyl acetyl]-*o*-toluidide was also obtained by the condensation of *p*-tolyl acetic acid and *o*-toluidide in flat needles, m.p. 165°C . (corr.) (Found: N, 5.8. $\text{C}_{10}\text{H}_{17}\text{ON}$ requires N, 5.9%), and the isomeric compound

o-toluyl *p*-methylbenzylamine by the condensation of *o*-toluic acid and *p*-methylbenzylamine in leaflets, m.p. 114°C. (Found: N, 6.1. $C_{16}H_{17}ON$ requires N, 5.9%).

The semicarbazone of *o*-toluyl *p*-methylbenzyl ketone was obtained in the usual way. It crystallised from dilute alcohol in colourless needles, m.p. 172°C. (corr.) (decomp.).

p-Tolyl *o*-methylbenzyl ketone. The ketone (7.5 g.) was obtained by the condensation of *o*-toluyl acetyl chloride (6.5 g.) with toluene (30 c.c.) in the presence of anhydrous aluminium chloride (6 g.) It was recrystallised from dilute alcohol forming colourless scales, 86–87°C. (Found: C, 85.4; H, 7.5. $C_{16}H_{16}O$ requires C, 85.7; H, 7.1%).

o-Tolyl acetyl chloride, obtained from the corresponding acid and thionyl chloride, boiled at 175°C under 28 mm. with slight decomposition. According to P. Hill and W. F. Short⁽⁶⁹⁾ it boils at 106–107°C. under 10 mm. and A. E. Bradfield, B. H. Hedge, B. S. Rao, J. L. Simonsen and A. E. Gillam gave the boiling point 111–112°C. under 16 mm.

The semicarbazone crystallised in bundled needles on the 54th day of standing of the solution of the ketone (0.9 g.), semicarbazide hydrochloride (0.9 g.) and potassium acetate (0.9 g.) in dilute alcohol (10 c.c. of 95% alcohol mixed with 4 c.c. of water). It was recrystallised from dilute alcohol in colourless needles, m.p. 185–186°C. (corr.) (decomp.) (Found: N, 6.3. $C_{16}H_{17}ON$ requires N, 5.9%).

Isomerization of o-tolyl p-tolyl acetaldehyde. The aldehyde (15.0 g.) was passed on the Japanese acid earth (25 g.) heated at 300°C. at a rate of 3.3 g. per hour being accompanied by the slow flow of carbon dioxide. A heavy yellowish oil (a) mixed with drops of water (8.8 g. in total) was collected in the receiver in the course of the passing and during the lapse of 1 hour after the passing of all of the aldehyde into the reaction tube. The tube was then evacuated at 300°C. and 0.9 g. of a yellow oil (b) were obtained. When the temperature was raised to 350°C. under the reduced pressure, 0.1 g. of a reddish viscous oil (c) came out. All (a), (b) and (c) showed no colour reaction characteristic to aldehydes.

The product (a) was freed from the water drops with anhydrous sodium sulphate and distilled, giving a fraction (0.9 g.) which boiled at 100–115°C. obviously consisting of mainly toluene. The residue (7.3 g.) was distilled under the reduced pressure of 4 mm. giving the fractions shown in Table 3.

Table 3.

Fractions	B.p. (°C.)	Yields (g.)	Remarks
(1)	145–165	1.3	Yellow oil with aromatic odour.
(2)	165–172	0.9	„
(3)	172–180	3.6	Yellow viscous oil, odourless.
(4)	Residue	1.5	„

(69) *J. Chem. Soc.*, 1935, 1125.(70) *Ibid.*, 1936, 675.

The fractions (1) and (2) in Table 3 manifested no apparent change when cooled at -15°C . for 21 hours. The fraction (3) was converted to a mush when similarly treated, which melted on touching with the hand. It was recrystallised from dilute alcohol in colourless columns, m.p. 26°C ., and confirmed to be *o*-tolyl *p*-methylbenzyl ketone through the Beckmann rearrangement of its oxime as described above.

The fraction (4) was changed to a mush by standing at the ordinary temperature for several days and a small amount of *p*-tolyl *o*-methylbenzyl ketone, m.p. $86-89^{\circ}\text{C}$., was obtained from it, which was identified by the mixed melting point with the sample synthesised as stated above.

The ratio of the amount of *o*-tolyl *p*-methylbenzyl ketone to that of *p*-tolyl *o*-methylbenzyl ketone, both produced by the isomerisation of *o*-tolyl *p*-tolyl acetaldehyde, was estimated about 4:1.

p-Chlorobenzoyl methyl acetate. Potassium acetate (200 g.) dissolved in alcohol (300 c.c.) was added to *p*-chlor- ω -bromacetophenone (170 g.) dissolved in hot alcohol (500 c.c.) and the mixture was heated for a while and left to stand. On the next day a large amount of potassium bromide was found thrown down, which was filtered and the filtrate concentrated on the water bath and left to cool down to the ordinary temperature: *p*-Chlorobenzoyl methyl acetate (102 g.) separated forming glittering scales, m.p. $71.5-72.5^{\circ}\text{C}$., when recrystallised from ligroin (b.p. $80-120^{\circ}\text{C}$.). (Found: Cl, 16.8. $\text{C}_{10}\text{H}_9\text{O}_3\text{Cl}$ requires Cl, 16.7%).

p-Chlorobenzoyl carbinol. Barium carbonate (50 g.) was added to the boiling water (200 c.c.) followed by *p*-chlorobenzoyl methyl acetate (40 g.) and the mixture was boiled for 1 hour. It was filtered hot and the insoluble matter remaining on the filter paper was extracted with hot water, the extract combined with the filtrate. On cooling the combined liquid, *p*-chlorobenzoyl carbinol (28 g.) separated. It was recrystallised from ligroin in colourless needles, m.p. $123-126^{\circ}\text{C}$. (uncorr.) (decomp.) (Found: Cl, 20.7. $\text{C}_8\text{H}_7\text{O}_2\text{Cl}$ requires Cl, 20.8%).

α -*p*-Chlorophenyl α -*p*-tolyl ethylene glycol. *p*-Chlorobenzoyl carbinol (11 g.) was added little by little in the form of crystalline powder to the Grignard reagent prepared from *p*-iodotoluene (50 g.) and magnesium. A vigorous reaction occurred. The reaction mixture was boiled for 2 hours and left to stand overnight. It was treated with cold dilute acetic acid (12 g. of glacial acetic acid in 200 c.c. of ice water). The upper ethereal solution was washed with dilute caustic soda and then with water and the ether was removed. The residue solidified on cooling. It was subjected to the steam distillation, toluene and other volatile impurities being thereby removed. The required glycol remained in the distilling flask, which on cooling solidified to a yellowish mass. It was recrystallised from ligroin in colourless needles (17 g.), m.p. $132-133^{\circ}\text{C}$. (uncorr.) (Found: Cl, 13.4. $\text{C}_{15}\text{H}_{15}\text{O}_2\text{Cl}$ requires Cl, 13.5%).

The benzoyl derivative obtained by the usual method crystallised from dilute alcohol in fine needles, m.p. $145-146^{\circ}\text{C}$. Mol. wt. (Rast), 358.2. $\text{C}_{22}\text{H}_{19}\text{O}_3\text{Cl}$ requires 366.5.

p-Chlorophenyl *p*-tolyl acetaldehyde. A mixture of α -*p*-chlorophenyl α -*p*-tolyl ethylene glycol (40 g.), crystalline oxalic acid (100 g.) and water (40 c.c.) was heated in an oil bath for 3 hours, the slow flow of carbon dioxide being passed into the mixture meanwhile. The tempera-

ture was maintained at 115°C. while that of the oil bath showed 140°C. After cooling the content of the vessel was extracted with ether, the ethereal solution washed with dilute caustic alkali, saturated solution of sodium chloride and with water, dried over calcium chloride. The residual oil (38 g.) obtained by removal of the ether was distilled under the reduced pressure of 6 mm. giving the results shown in Table 4.

Table 4.

Fractions	B.p. (°C.)	Yields (g.)
(1)	150-197	2.2
(2)	197-200	20.9
(3)	Residue	11.0

The fraction (2) was purified through the addition compound of sodium bisulphite and pure *p*-chlorophenyl *p*-tolyl acetaldehyde was obtained as a faintly yellow oil, b.p. 195-197°C./5 mm.; d_4^{22} , 1.1805; n_D^{22} , 1.5896 M.R., found, 69.85, calc. (Eisenlohr), 69.15. (Found; Cl. 14.4. $C_{15}H_{13}OCl$ requires Cl, 14.5%). It tinges

fuchsin-sulphurous-acid solution with blue colour. It is oxidized slowly in the presence of air and light at the ordinary temperature to produce *p*-chlorophenyl acetic acid. The semicarbazone prepared in the usual way dissolved difficultly in dilute alcohol; it was recrystallised from a mixture of toluene and ligroin (1:1) in white powder, m.p. 159-160°C. (uncorr.) (to a yellow melt). (Found: N, 14.1. $C_{16}H_{16}ON_3Cl$ requires N, 13.9%).

p-Chlorophenyl *p*-tolyl acetic acid. The acid (1.3 g.) was obtained from *p*-chlorophenyl *p*-tolyl acetaldehyde (4.0 g.) by the method similar to that employed for the oxidation of *o*-tolyl *p*-tolyl acetaldehyde. It was recrystallised from ligroin in clustered needles in stellar form, m.p. 145.5°C. (uncorr.). (Found: Cl, 13.4; Mol. wt. (by titration with 1/20 N sodium hydroxide), 261.5. $C_{15}H_{13}O_2Cl$ requires Cl, 13.6%; Mol. wt., 260.5).

p-Chlorophenyl *p*-tolyl ketone. (a) *α*-*p*-Chlorophenyl *α*-*p*-tolyl ethylene glycol (0.30 g.) was dissolved in 80% acetic acid (20 c.c.) and chromic oxide (0.32 g. dissolved in a small quantity of water) was added to the solution and the mixture was left to stand overnight. It was heated on the water bath for 20 minutes and cooled. Glittering scales (0.25 g.) crystallised out, of which the amount increased on the addition of water. It was separated by filtration, washed with water and recrystallised from dilute alcohol in colourless scales, m.p. 128-129°C. (uncorr.) (Found: Cl, 15.3. $C_{14}H_{11}OCl$ requires Cl, 15.4%).

(b) *p*-Tolyl acetyl chloride (4.0 g.) was condensed with chlorobenzene in the presence of anhydrous aluminium chloride and the required ketone (0.36 g.) thus obtained was recrystallised from dilute alcohol in faintly reddish scales.

(c) When *p*-chlorophenyl *p*-tolyl acetaldehyde was purified through the addition compound of sodium bisulphite a small amount of a substance very difficult to react with the bisulphite was obtained which was confirmed to be *p*-chlorophenyl *p*-tolyl ketone.

(d) On long standing *p*-chlorophenyl *p*-tolyl acetaldehyde was partly changed to *p*-chlorophenyl *p*-tolyl ketone.

All the four specimens described above showed the same melting point which was not depressed when mixed with one another. W. D.

Cohen⁽⁷¹⁾ obtained the same ketone by the condensation of *p*-chlorobenzoyl chloride and toluene and gave the melting point 118°C. (very probably a typographical error for 128°C.).

p-Tolyl p-chlorobenzyl ketone. Phenyl acetic acid (22 g.) was nitrated following the information given by W. Borsche⁽⁷²⁾ resulting in *p*-nitrophenyl acetic acid (15 g.) which on reduction by the method described in "Organic Syntheses"⁽⁷³⁾ gave *p*-aminophenyl acetic acid (10.4 g.). The amino acid was changed to *p*-chlorophenyl acetic acid (4.0 g.) and then to *p*-chlorophenyl acetyl chloride (4.0 g.) which was condensed with toluene (20 c.c.) in the presence of anhydrous aluminium chloride (6 g.). The reaction mixture was treated with ice water and the crystals thereby separating (6.0 g.) were recrystallised from dilute alcohol in colourless glittering plates, m.p. 113.5°C. (uncorr.). (Found: Cl, 14.4. C₁₅H₁₃OCl requires Cl, 14.5%). L. Szëgo and P. Ostinelli⁽⁷⁴⁾ gave the melting point 113°C. Attempts to obtain the ketone from *p*-methyl ω -bromacetophenone and chlorobenzene resulted in no good result.

The semicarbazone prepared in the usual way formed colourless needles m.p. 191–192°C. (uncorr.) (decomp.). (Found: N, 5.5. C₁₅H₁₄ONCl requires N, 5.4%). The oxime was prepared in the usual way. It was recrystallised from dilute alcohol in glittering plates, m.p. 136–137°C (uncorr.). (Found: N, 5.5. C₁₅H₁₄ONCl requires N, 5.4%).

p-Chlorophenyl p-methylbenzyl ketone. The raw *p*-tolyl acetyl chloride prepared from *p*-tolyl acetic acid (4 g.) and thionyl chloride (12 g.) was added drop by drop to chlorobenzene (20 c.c.) mixed with anhydrous aluminium chloride (6 g.), the mixture being cooled with ice water meanwhile. After 4 hours' standing, it was treated with ice water, washed with dilute alkali and then with water, dried over calcium chloride and the excess chlorobenzene was removed leaving resinous brown mass (4 g.), which was recrystallised from dilute alcohol in colourless scales (1.2 g.), m.p. 103.5°C. (Found: Cl, 14.6. C₁₅H₁₃OCl requires Cl, 14.5%). L. Szëgo and P. Ostinelli⁽⁷⁵⁾ gave the melting point 123°C.

The semicarbazone crystallised from dilute alcohol in colourless needles, m.p. 151–152°C. (Found: N, 13.9. C₁₆H₁₆ON₃Cl requires N, 13.9%). The oxime crystallised from dilute alcohol in colourless needles, m.p. 106–107°C. (Found: N, 5.7. C₁₅H₁₄ONCl requires N, 5.4%).

Isomerization of p-chlorophenyl p-tolyl acetaldehyde. The aldehyde (18.0 g.) was passed on the Japanese acid earth (25 g.) heated at 300°C at a rate of 4.5 g. per hour, being accompanied by the slow current of carbon dioxide. A yellow oil (a) mixed with a small amount of crystals (1.6 g. in total) was first collected and then a viscous yellow oil (b) (4.5 g.) came out which soon solidified on cooling. By evacuating the reaction tube at the same temperature a blackish oil (c) (4.5 g.) was obtained which likewise solidified at once. The product (b) was separated into two parts by fractional crystallisation from ligroin, i.e., (i) (3.0 g.) less soluble in the solvent and (ii) (1.5 g.) more soluble in it. The product

(71) *Rec. Trav. Chim. Pays-Bas.*, **38** (1919), 117.

(72) *Ber.*, **42** (1909), 3596.

(73) *Coll. Vol. I*, (1932), 44.

(74) *Gazz. chim. ital.*, **60** (1930), 677; *Chem., Abst.*, **25** (1931), 1524.

(75) *Loc. cit.*

(i) was recrystallised once more from ligroin forming colourless scales (2.7 g.) melting at 104–105.5°, from which the following fractions were obtained by fractional crystallisation three times from ligroin:—

Table 5.

Fractions	Yields (g.)	M.p. (°C.)	Thawing point (°C.)	Remarks
(1)	2.31	105.6	103	Colourless scales.
(2)	0.20	104	101	„ „
(3)	0.15	95–98	—	Yellowish scales.
(4)	0.02	170–195	—	Colourless powder.

The fraction (1) in Table 5 may safely be stated to consist of *p*-chlorophenyl *p*-methylbenzyl ketone (ca. 80%) and *p*-tolyl *p*-chlorobenzyl ketone (ca. 20%) by referring it to Fig. 1. (p. 201). The fraction (1) melted at 103.5–104°C. when mixed with the former ketone (m.p. 103.5°C.) and at 108°C. with the latter (m.p. 113.5°C.). The fraction (2) is richer in *p*-chlorophenyl *p*-methylbenzyl ketone than the fraction (1). The fraction (3) is obviously very impure, and the fraction (4) was not further studied of which the melting point was found much higher than those of both the above ketones.

The product (ii) mainly consisted of oily substance mixed with a small quantity of solid matter which was recrystallised several times from dilute alcohol forming colourless glittering scales (0.15 g.), m.p. 101°C.; thawing point, ca. 85°C, probably *p*-chlorophenyl *p*-methylbenzyl ketone mixed with a small quantity of impurities.

The product (c) was treated similarly to (b); it was first separated into two parts, i.e., (i) (3.0 g.) less soluble in ligroin, m.p. 100–104°C. and (ii) (1.5 g.) more soluble in it. The part (i) was once more recrystallised from ligroin forming light yellow scales which melted at 106.5–107.5°C. alone, and at 105–106°C. when mixed with pure *p*-chlorophenyl *p*-methylbenzyl ketone (m.p. 103.5°C.), revealing the composition of 59% of this ketone and 41% of *p*-tolyl *p*-chlorobenzyl ketone. It was recrystallised several times from dilute alcohol giving the following fractions:—

Table 6.

Fractions	Yields (g.)	M.p. (°C.)	Thawing point (°C.)	Remarks
(1)	0.02	107.5	106.7	—
(2)	1.34	108.0	107.1	Yellowish scales.
(3)	0.31	107.0	106.0	Colorless scales.
(4)	6.27	104.3	102.0	Yellow scales.
(5)	0.09	95–99.5	—	—

0.4 g. of the fraction (2) in Table 6 gave the oxime (0.3 g.) which was fractionated over ten times affording colourless needles (0.09 g.), m.p. 106–107°C. alone or mixed with *p*-chlorophenyl *p*-methylbenzyl ketoxime, and a small quantity of needles which melted alone at 122–126°C., and at 128–134°C. when mixed with *p*-tolyl *p*-chlorobenzyl ketoxime (m.p. 136–137°C.). By the repeated fractional crystallisation of the semicarbazone obtained from the fraction (2) in Table 6, a small quantity of a fraction was obtained which melted at 187–189°C. alone, and at 188–189°C. when mixed with the semicarbazone of *p*-tolyl *p*-chlorobenzyl ketone (m.p. 191–192°C.).

More soluble part of the product (c), (p. 300) was recrystallised several times from dilute alcohol and gave 0.62 g. of yellowish scales melting at about 96°C. and 0.04 g. of yellowish scales melting at about 95°C. Both may very probably be impure *p*-chlorophenyl *p*-methylbenzyl ketone.

Summary.

(1) All the phenomena hitherto ascribed to the characteristic catalytic action of Japanese acid earth can be explained by taking its strong electron-seeking property into consideration. Thus its ability to promote the hydrolysis of cane sugar or starch and the oxidation of pyrogallol and its property to give various oxidase-like colour reactions are all due to its selective adsorptive power for hydroxyl ion. The facts can similarly be explained that the dehydration or deamination of various organic compounds takes place through its catalytic action followed by the intramolecular rearrangement, as observed in the reaction of producing cyclopentane derivatives from cyclohexanol, cyclohexylamine or their methyl derivatives.

The initial step of the formation of β,β' -dinaphthyl from naphthalene in the presence of the earth is the polarisation of the naphthalene molecule promoted by its electron-seeking property.

(2) Several diarylacetaldehydes have been newly synthesised and found to rearrange themselves to give the corresponding ketones, when heated at 300°C. in the presence of the earth. Thus phenyl *p*-tolyl and *m*-tolyl *p*-tolyl acetaldehydes gave phenyl *p*-methylbenzyl and *m*-tolyl *p*-methylbenzyl ketones respectively, while *o*-tolyl *p*-tolyl and *p*-tolyl *p*-chlorophenyl acetaldehydes gave the respective mixtures of *o*-tolyl *p*-methylbenzyl and *p*-tolyl *o*-methylbenzyl ketones and of *p*-chlorophenyl *p*-methylbenzyl and *p*-tolyl *p*-chlorobenzyl ketones.

(3) By comparing the yields in the isomeric ketones thus produced the order of the facility of separation of the different aryl groups was determined as follows:—

Phenyl, *m*-tolyl > *p*-chlorophenyl > *o*-tolyl > *p*-tolyl.

The phenyl group may most probably have the greater migratory tendency than the *m*-tolyl.

(4) The mechanism of the conversion of the aldehydes to the ketones has been discussed. It has been postulated that an electromeric displacement of electrons in the carbonyl group $\overset{\curvearrowright}{\text{C}}=\text{O}$ is promoted by the

action of the earth, and one of the aryl groups migrates with its valency electrons from the adjacent α -carbon atom to the depleted carbonyl carbon. A proton is then splitted from the carbonyl carbon and unites with the carbonyl oxygen to give the enolic form of the ketone, isomeric to the aldehyde. The conclusion has been reached that the more electron-attracting of the two aryl groups must be first separated as anion.

(5) It was confirmed that the capacity of the *p*-tolyl group for electron-release is much larger than those of *o*-tolyl, *m*-tolyl, phenyl and *p*-chlorophenyl groups. By these results a new chemical evidence has been given for the tautomeric effect of the methyl group.

(6) Following compounds have been newly synthesised and their constitutions were confirmed:— *a*-phenyl *a*-*p*-tolyl, *a*-*m*-tolyl *a*-*p*-tolyl, *a*-*o*-tolyl *a*-*p*-tolyl and *a*-*p*-chlorophenyl *a*-*p*-tolyl ethylene glycols and their benzoyl derivatives; *p*-tolyl *m*-methylbenzyl, *m*-tolyl *p*-methylbenzyl, *o*-tolyl *p*-methylbenzyl, *p*-tolyl *o*-methylbenzyl, *p*-chlorophenyl *p*-methylbenzyl and *p*-tolyl *p*-chlorobenzyl ketones and their oximes and semicarbazones; *m*-tolyl *p*-tolyl, *o*-tolyl *p*-tolyl and *p*-tolyl *p*-chlorophenyl acetic acids; *p*-methylbenzoyl carbinol, *p*-chlorobenzoyl methyl acetate and *p*-chlorobenzoyl carbinol.

(7) *o*-Tolyl *p*-methylbenzyl and *m*-tolyl *p*-methylbenzyl ketones have been found to be oxidised slowly by the action of atmospheric oxygen on long standing, giving the mixtures of *o*-toluic and *p*-toluic acids and of *m*-toluic and *p*-toluic acids respectively, while the isomeric ketones, *p*-tolyl *o*-methylbenzyl and *p*-tolyl *m*-methylbenzyl ketones remained unchanged.

(8) The stereo-isomers of the oximes of the following ketones were isolated and their configurations were determined by carrying out the Beckmann rearrangement:— *m*-tolyl *p*-tolyl, *m*-tolyl *p*-methylbenzyl and *o*-tolyl *p*-methylbenzyl ketones.

For the identification of the products of the rearrangement the following compounds were newly synthesised:— *p*-toluyl *m*-toluidide, *m*-toluyl *p*-toluidide, [*p*-tolyl acetyl]-*m*-toluidide, *m*-toluyl *p*-methylbenzylamine, [*p*-tolyl acetyl]-*o*-toluidide and *o*-toluyl *p*-methylbenzylamine.

(9) α , β -Dibenzoyl ethane was confirmed to occur in the reaction product when ω -bromacetophenone was condensed with toluene by the Friedel and Crafts' reaction. The anticipated phenyl *p*-methylbenzyl ketone has not been isolated from the reaction product.

(10) It was found that the considerable quantity of *m*-tolyl *p*-tolyl ketone was produced when *m*-tolyl *p*-tolyl acetaldehyde is purified through its bisulphite compound or oxidised with moist silver oxide.

Similar facts have been observed in the cases of *o*-tolyl *p*-tolyl and *p*-chlorophenyl *p*-tolyl ketones. They were produced in the course of the purification of *o*-tolyl *p*-tolyl and *p*-chlorophenyl *p*-tolyl acetaldehydes respectively through the addition compounds of sodium bisulphite and by the autoxidation of the above-mentioned aldehydes on long standing in the presence of light and air.

(11) The semicarbazones of several above-mentioned ketones have been found very difficult to be produced. Thus the semicarbazone of *m*-tolyl *p*-tolyl ketone was formed after 22 days' standing of the dilute alcoholic solution of the ketone mixed with semicarbazide hydrochloride and potassium hydroxide and that of *p*-tolyl *o*-methylbenzyl ketone only

after 54 days. The semicarbazone of *m*-tolyl *p*-methylbenzyl ketone was not confirmed to produce even after 140 days' standing of the reaction mixture.

(12) Equilibrium diagrams of the systems of phenyl *p*-methylbenzyl and *p*-tolyl benzyl ketones and of *p*-chlorophenyl *p*-methylbenzyl and *p*-tolyl *p*-chlorobenzyl ketones have been drawn by applying the modified Rheinboldt's method. It was found that an eutectic point exists in the former system while a solid solution is formed in the latter. (*Concluded*).

The author wishes to express his gratitude to Dr. H. Inoue for his unfailing interest and encouragement.

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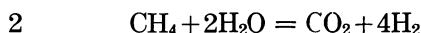
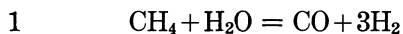
Studien über Oxydationszersetzung des Methans (*Fortsetzung*).

Von Toyoziro OGURA.

(Eingegangen am 6. Juni 1941.)

III. Methan-Wasserdampf-Reaktionen.

Die Methan-Wasserdampf-Reaktion ist die wesentliche Reaktion des Oxydationszersetzung des Methans und hat zwei Reaktionsformen.



Diese Reaktionen sind endothermisch. Die erste Reaktion tritt unter höherer Temperatur, die Zweite unter niedriger Temperatur ein. Unter den vielen Verfahren, aus Methan Wasserstoff zu gewinnen sind diese Reaktionen die ergebnisreichsten, d.h. sie geben die grösste Menge Wasserstoff aus einem Volum Methan.

Zur Zersetzung des Methans wurde bei den Untersuchungen die Wärmeenergie benutzt, man kann aber auch mit Elektrizität, Hochspannung im Vakuum, arbeiten.

Da der Katalysator bei der Oxydationszersetzung eine wichtige Rolle spielt, habe ich die katalytischen Eigenschaften einiger Materien studiert. Die erhaltenen Resultate passen gleichfalls auf andere Oxydationszersetzungen, wie Methan-Sauerstoff- oder Kohlendioxyd-Reaktionen.

Andere physikalischen und chemischen Eigenschaften des Katalysators, wie die Oberflächenbeschaffenheit, Aktivierung, Krystallstruktur usw. sowie der Reaktionsmechanismus, kommen hier nicht in Frage.

a) *Verfolgung der Katalysatoren.* Bei den Methan-Wasserdampf-Reaktionen spielt der Katalysator, wie oben erwähnt, eine wichtige Rolle. Man kann behaupten, dass die Qualität des Katalysators das wichtigste ist, was die Reaktionen beherrscht. Tafel 6 zeigt die Komponenten der Reaktionsgase ohne Katalysator. Bei 1000°C. ist der Zersetzungsgrad nur 16.2 und bei 1200°C. bleiben noch 12% des Methans unverändert.

Zersetzungsgrad wird nach der Formel $100(\text{CO}_2 + \text{CO}) / \text{CO}_2 + \text{CO} + \text{CH}_4$.

Aber bei Anwendung passender Katalysatoren erfolgt die Zersetzung schon besser, woraus die Wichtigkeit des Katalysators klar wird, wie in Tafel 7 erwähnt. Ich habe die Katalysatoren, die Nickel-Alumina-Kaolin Reihe, erst bei 500°C. kalziniert, bei 300°C. reduziert und dann gebraucht. $\text{H}_2\text{O}/\text{CH}_4=2.0$ bedeutet, dass das molare Verhältnis des Wasserdampfes und des Methans 2:1 ist.

Tafel 6.

Exp. Nr. b 105, ohne Kat. $\text{H}_2\text{O}/\text{CH}_4 = 2.5$, Gas. Ges. 5 lt/St.

Reakt. Temp. °C.	CO ₂	C _n H _m	CO	H ₂	CH ₄	Z.G.
800	1.6	3.4	1.4	10.0	83.6	3.5
900	1.8	2.0	5.8	23.2	67.2	10.1
1000	2.0	1.4	8.7	32.2	55.7	16.1
1100	3.0	1.6	10.4	52.0 ¹⁾	33.0	28.4
1200	5.0	1.0	11.6	69.6 ²⁾	12.8	56.5

Z.G. = Zersetzungsgrad des Methans

od. Z. G. a. $\frac{\text{CO}_2 + \text{CO}}{\text{CO}_2 + \text{CO} + \text{CH}_4} \times 100$

1) theo. Wert 43.2 2) theo. Wert 54.8

Tafel 7.

Exp. Nr. b 102.103, Kat. Nr. B 47., $\text{H}_2\text{O}/\text{CH}_4 = 2.5$, Gas. Ges. 5 lt/St.

Reakt. Temp. °C.	CO ₂	CO	H ₂	CH ₄	Z.G. a
500	6.2	3.8	37.1	52.9	15.9
600	8.2	10.7	65.0	16.1	54.0
700	5.3	17.2	71.8	5.7	79.8
800	4.0	19.5	74.5	2.0	92.2
900	3.6	20.1	74.8	1.5	94.0
1000	2.2	22.7	74.3	0.8	96.8

Die Differenz zwischen den beiden oben beschriebenen Reaktionen besteht nicht nur im Zersetzungsgrad, sondern auch in der Art der Reaktionen. Ohne Katalysatoren bilden sich ungesättigter Kohlenwasserstoff und wenn die Erhitzung 1000°C. übersteigt so bildet sich eine Menge freien Kohlenstoffs (Russ). Das zeigt die Thermozerersetzung des Methans nach der Gleichung $\text{CH}_4 = \text{C} + 2\text{H}_2$. Aus der Tafel 8 ersieht man, dass das Wasserstoffprozent im Reaktionsgase bei 1100°C. und 1200°C. resp. 52.0 und 69.6 sind, trotz der theoretischen Werte, die nach der Formel $4\text{CO}_2 + 3\text{CO}$ resp. 43.2 und 54.8% sein sollen. Bei höherer Temperatur über 1000°C. ist die Thermozerersetzung bedeutender, als die Wasserdampfzerersetzung des Methans, wie Gleichgewichtskonstanten zeigen. Die Verwendung passender Gruppen des Katalysators aber hemmt die Thermozerersetzung und befördert die Wasserzerersetzung.

Nickel wird im allgemeinen als die beste Katalysator für Methan-Wasserdampf-Reaktionen betrachtet. Bei vorliegender Arbeit kamen ausser Nickel, auch Kobalt, Kupfer und Eisen sowie Metalloxyde zur Verwendung.

Die Resultate sind in Tafel 8 zusammengestellt. Diese reduzierten Metalle sind alle wirksam; nächst Nickel ist Kobalt am wirksamsten. Von den Metalloxyden wurden Aluminiumoxyd, Chromoxyd, Wolframoxyd, Magnesiumoxyd, Kalziumoxyd, Uranoxyd, Kieselsäure, Thoriumoxyd, Zinnoxid, Manganoxyd, Zinkoxyd, Vanadinoxid, Bariumoxyd, benutzt. Die Oxyde haben meistens nur geringes katalytisches Vermögen für Methan-Wasserdampf-Reaktionen, ausserdem sind sie noch unbequem zu handhaben, da sie bei höherer Temperatur schmelzen und durch Methan leicht reduziert werden. Reine Kahlbaumsche Präparate wurden verwendet, u. zw. in Menge von 20–30 g.

Tafel 8.

Exp. Nr. a 25-a 66, Kat. Nr. A 1–A 41, Reak. Temp. 970°C.,
 $\text{H}_2\text{O}/\text{CH}_4 = 2.0$, Gas. Ges. 5 lt/St.

Kat. Nr.	Bestandteil des Katalysators.	CO ₂	CO	H ₂	CH ₄	Z.G.a.	Z.G.b.
A 1	Ni	2.0	21.3	72.3	4.4	84.2	94.5
A 2	Co	1.8	20.5	69.0	8.7	72.0	89.7
A 3	Fe	2.5	18.2	66.0	13.3	60.7	84.5
A 4	Cu	4.2	15.3	65.1	15.4	55.8	82.0
A 24	Cr ₂ O ₃	1.7	18.7	70.1	9.5	68.0	88.2
A 25	Cr ₂ O ₃	1.7	17.9	71.7	8.7	69.2	89.2
A 34	WO ₃	4.0	11.9	52.3	31.8	33.4	62.2
A 37	Coks	3.8	11.5	51.1	33.6	31.2	61.3
A 29	MgO	3.8	9.5	44.9	41.8	24.2	53.5
A 31	CaO	6.4	9.6	53.4	30.6	34.4	63.5
A 32	U ₃ O ₈	5.6	8.3	46.1	40.0	24.9	57.7
A 27	SiO ₂	5.1	5.9	40.6	48.4	18.5	46.2
A 28	ThO ₂	2.8	4.0	34.1	59.1	10.3	36.6
A 35	ZnO	4.7	3.6	35.1	56.6	12.8	38.3
A 38	MnO ₂	4.2	3.0	42.4	50.4	14.9	45.7
A 33	V ₂ O ₅	4.4	2.0	34.9	58.7	9.8	37.3
A 23	Al ₂ O ₃	0.8	0.8	65.2	33.2	4.6	64.3
A 30	BaO	2.4	0.4	41.2	56.0	4.8	42.7
A 36	ZnCrO ₄	3.6	2.8	41.4	52.2	10.9	44.2

Chromoxyd hat besondere Eigenschaften als andere Oxyde. Katalysator A 24 in Tafel 8, der aus Ammoniumbichromat durch Rösten hergestellt wird, und Katalysator A 25, der aus Natriumbichromat und Schwefel hergestellt wird, haben eine mässige Wirksamkeit und weisen verschiedene Eigenschaften auf, als andere schwer reduzierbare Oxyde. Zersetzungsgrad a ist der für Kohlenstoff und wird mit der Formel $(\text{CO}_2 + \text{CO})100/\text{CO}_2 + \text{CO} + \text{CH}_4$ gezeigt und Zersetzungsgrad b ist der für Wasserstoff und wird mit der Formel $\text{H}_2 \cdot 100/\text{H}_2 + \text{CH}_4$ gezeigt. Zersetzungsgrad a und b gehen meist mit einander parallel, allein Aluminiumoxyd und Bariumoxyd haben einen niederen Zersetzungsgrad a und einen höheren Zersetzungsgrad b. Daraus geht hervor, dass sie gute Katalysatoren für Thermozerersetzung abgeben, aber für Wasserdampfzerersetzung versagen.

Katalysator A 23 in Tafel 10 Quarzsand, 0.5–1.0 mm. Durchmesser, wird nach kurzer Zeit mit einem glänzenden Film Kohlenstoffs bedeckt. Bei Verwendung eines Katalysators mit geringem Zersetzungsvermögen a bildet sich geringe Menge eines teerartigen Stoffs, der hauptsächlich aus aromatischem Kohlenwasserstoff besteht.

Ich habe die oben erwähnten Katalysatoren allein jeden für sich verwendet. Durch Zusatz von schwer reduzierbaren Oxyden z.B. Silika, feuerfester Ziegel, Kaolin und Bimsstein wird die Wirksamkeit erhöht, wovon unten die Rede sein wird.

b) *Einfluss der Wasserdampfmenge.* Wie oben erwähnt, spielt die Wassermenge bei Methan-Wasserdampf-Reaktionen eine grosse Rolle. Grosse Menge Wasserdampf beschleunigt die Reaktion und gibt Kohlendioxyd in Menge, während kleine Menge Wasserdampf Kohlenoxyd vermehrt. Die Resultate der Reaktion mit grosser Menge Wasserdampf und ohne Katalysator, sind in Tafel 9 dargestellt. Die Zersetzung des Methans ist etwas besser als in Tafel 6, welche die Reaktionsresultate mit geringer Menge Wasserdampf zeigt. Aber es bilden sich schon freier Kohlenstoff und ungesättigter Kohlenwasserstoff.

Tafel 9.

Exp. Nr. b 59, $\text{H}_2\text{O}/\text{CH}_4 = 10$, ohne Kat., Gas. Ges. 5 lt/St.

Reak. Temp. °C.	CO ₂	C _n H _m	CO	H ₂	CH ₄	Z.G.
500	1.2	0.5	0.2	0.0	98.1	1.4
600	1.2	0.4	0.3	0.0	98.1	1.5
700	1.2	0.5	0.6	0.0	97.7	1.8
800	1.4	0.3	3.0	14.9	80.4	5.2
900	2.2	0.2	6.2	27.7	63.7	11.6
1000	4.6	0.2	8.8	47.5	38.7	25.6

Tafel 10 zeigt die Wirkung guter Katalysatoren unter Zuführung grösserer Menge Wasserdampf wie in Tafel 7. Gasgeschwindigkeit ist 5.0 lt/St. Wenn man diese zwei Reaktionen mit einander vergleicht, so kann man den Einfluss der Katalysatoren auf einen Blick erkennen.

Tafel 10.

Exp. Nr. b 67, Kat. Nr. B 57, Gas. Ges. 5 lt/St., $\text{H}_2\text{O}/\text{CH}_4 = 10$.

Reak. Temp. °C.	CO ₂	CO	H ₂	CH ₄	Z.G.	Volum- zunahme; Mal.
500	18.6	1.4	76.6	3.4	85.4	3.5
600	18.6	3.0	77.7	0.7	96.4	4.4
700	18.2	3.2	78.1	0.5	97.7	4.3
800	17.2	4.4	77.9	0.5	97.7	4.3
900	16.8	5.4	77.4	0.4	98.2	4.4
1000	16.0	6.0	78.0	0.0	100.0	4.2

Abbildung 6 zeigt die Verhältnisse zwischen dem Zersetzungsgrad α des Methans und der Reaktionstemperatur in den Fällen, in denen man bald mit Katalysator, bald ohne ihn, sowie bald mit mehr, bald mit weniger Menge Wasserdampf gearbeitet hat.

Die Kurve in Abbildung 6 bedeutet:

- A ohne Katalysator mit wenig Wasserdampf (Tafel 6)
- B ohne Katalysator mit viel Wasserdampf (Tafel 9)
- C mit Katalysator und wenig Wasserdampf (Tafel 7)
- D mit Katalysator und viel Wasserdampf (Tafel 10)
- E mit Nickel allein und viel Wasserdampf (Tafel 14)
- F Vermögenskurve des Nickels.

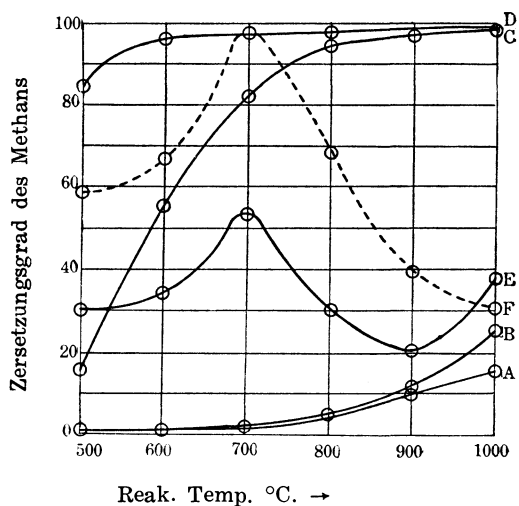


Abb. 6. Die Kurve Zersetzungsgrad des Methans.

Tafel 11 und 12 zeigen die Resultate der Experimente, die ich zur genaueren Verfolgung der Einflüsse des Wasserdampfs auf Methan-

Wasserdampf-Reaktionen bei 600°C. vorgenommen habe. In Tafel 11 ist die Methangeschwindigkeit konstant und die Menge des Wasserdampfes verändert, so dass die Geschwindigkeit des letzteren sich verändert. In Tafel 12 ändert sich die Geschwindigkeit des Wasserdampf und ist die gesamt Geschwindigkeit des Ganzen konstant. Als Katalysatoren wurde Nickel, Alumina und Porzellan verwendet.

Tafel 11.

Exp. Nr. b 49, Kat. Nr. B 39, Reak. Temp. 600°C. Gas. Ges. 5 lt/St.

$\text{H}_2\text{O}/\text{CH}_4$	CO_2	H_2	CH_4	CO	Z.G.
17.5	19.8	79.2	0.0	1.0	100.0
10.5	19.2	78.9	0.1	1.8	99.5
7.5	18.5	77.8	0.5	3.2	96.5
5.1	17.2	76.9	0.9	5.0	96.1
3.3	16.6	75.7	2.2	5.5	91.0
2.0	12.3	69.0	11.7	7.0	62.2
0.5	2.0	48.4	47.8	1.8	7.5

Tafel 12.

Exp. Nr. b 47, Kat. Nr. B 39, Reak. Temp. 600°C.

CH_4 lt/St.	$\text{H}_2\text{O}/\text{CH}_4$	CO_2	CO	H_2	CH_4	Z.G.
2.0	20.0	19.2	1.4	79.4	0.0	100.0
3.6	11.0	19.3	2.4	78.2	0.1	99.5
5.0	7.5	18.7	2.6	78.1	0.6	97.2
6.6	5.3	16.2	5.3	77.8	0.7	96.9
11.0	3.6	14.3	8.2	75.9	1.6	93.3

c) *Einfluss der Temperatur und des Drucks auf die Reaktionen.* Die Wirkung der Temperatur auf die Reaktionen ist, theoretisch und experimentel, aus der oben angegebenen Tafel der Gleichgewichtskonstanten zu ersehen.

Wenn der Reaktionsdruck annimmt, so fällt die Reaktionstemperatur, da bei der Reaktion eine Vergrößerung des Volumens entsteht.

Tafel 13 zeigt die Resultate der Experimente unter dem Druck resp. 760, 400, 200, 100 und 50 mm. der Quecksilbersäule. Einfluss des Drucks wird unter 200 mm. Quecksilbersäule sichtbar. Unter 500°C. zersetzt sich Methan in Kohlenoxyd und Wasserstoff. Abbildung 7 zeigt die Verhältnisse zwischen Druck und Zersetzungsgrad a des Methans. Gasgeschwindigkeit ist 5.0 lt/St. $\text{H}_2\text{O}/\text{CH}_4 = 2.0$. Als Katalysator wurde Nickel-Alumina verwendet. Da dieser Katalysator nur mittelmässiges Beschleunigungsvermögen hat, so sind die Resultate verhältnismässig schlecht, bei Verwendung besserer Katalysatoren aber kann man schon auf bessere Resultate rechnen.

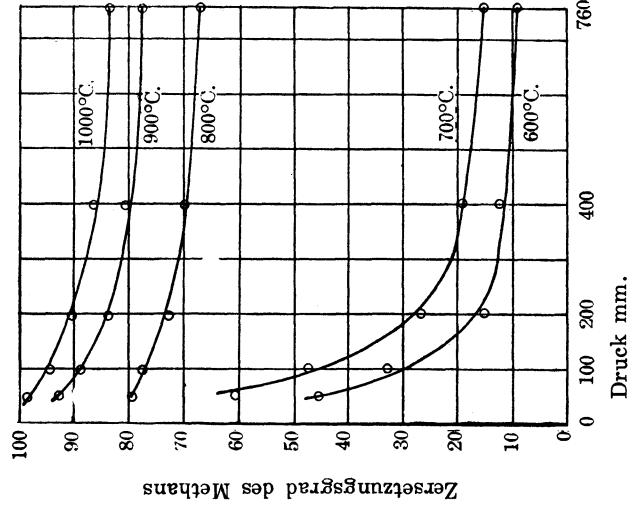


Abb. 7. Druck und Zersetzungsgrad.

Tafel 13.

Exp. Nr. a 101-a 150, Kat. Nr. A 47, Gas. Ges. 5 lt/St., $H_2O/CH_4 = 2.0$.

Reak. Temp. °C	Druck mm. Hg	CO ₂	CO	H ₂	CH ₄	Z. G.
600	50	5.0	13.5	59.5	22.0	45.7
"	100	5.0	10.4	53.3	31.3	33.6
"	200	4.4	5.0	34.2	56.4	14.8
"	400	4.2	4.7	30.7	60.4	12.8
"	760	3.6	3.4	22.7	70.3	9.1
700	50	1.7	19.8	64.6	13.9	60.7
"	100	1.0	18.3	57.2	23.5	45.5
"	200	3.0	10.7	45.3	41.0	25.0
"	400	3.7	7.8	40.5	48.0	19.3
"	760	4.2	5.6	34.3	55.8	14.9
800	50	2.0	21.0	71.1	5.9	79.5
"	100	2.0	22.0	69.0	7.0	77.3
"	200	1.7	20.8	68.8	8.7	72.2
"	400	1.0	21.0	68.5	9.5	69.8
"	760	1.9	20.0	67.1	11.0	66.5
900	50	0.3	24.5	73.5	1.8	93.3
"	100	0.3	24.4	72.1	3.2	88.5
"	200	0.0	24.0	71.5	4.5	84.3
"	400	0.0	22.8	71.7	5.5	80.5
"	760	0.0	22.6	70.9	6.5	77.7
1000	50	0.0	24.8	75.0	0.2	99.0
"	100	0.0	24.2	74.5	1.3	95.0
"	200	0.0	24.0	73.6	2.4	91.0
"	400	0.0	23.2	73.3	3.5	86.7
"	760	0.0	22.0	73.4	4.4	83.5

d) *Nickel-Katalysator*. Unter den ausgeführten vielen Experimenten, hat sich das Nickel als der beste Katalysator bewährt, und welches ich im folgenden gedenke, u. zw.

1. Nickel allein. 2. Promotor und Träger 3. Katalysator aus zwei Elementen. 4. Beifügungsmenge des Promotors, Konzentration und Korngrösse des Katalysators. 5. Kontaktdauer. 6. Röstungs- und Reduktions-Temperatur. 7. Haltbarkeit des Katalysators. 8. Katalysator mit Alkalien.

1. Anwendung des Nickels allein. Wenn man Nickel allein gebraucht, so sinkt die Wirkung des Katalysators bedeutend durch Semisinterung herab. Da die Reaktion eine endothermische und oberfläche ist, so ist die Wirkung eine ganz andere als die der Reaktionswärme.

Die Resultate bei Anwendung des Nickels ohne Träger und Promotor, sind in Tafel 14 zusammengestellt. Das Nickel wurde hierbei aus Nickel-nitrat und Alkali hergestellt, indem das so erhaltene Nickelhydroxyd bei 500°C. geröstet und bei 300°C. mit Wasserstoff reduziert wurde.

Tafel 14.

Exp. Nr. b 23, Kat. Nr. B 16, Gas. Ges. 5 lt/St., $\text{H}_2\text{O}/\text{CH}_4 = 10.0$.

Reakt. Temp. °C	CO ₂	CO	H ₂	CH ₄	Z.G.
500	14.0	0.8	51.0	34.2	30.2
600	13.5	0.6	58.4	27.5	33.9
700	16.5	1.4	66.4	15.7	53.3
800	11.4	3.8	57.0	27.8	35.3
900	8.8	3.0	41.1	47.1	20.0
1000	10.7	5.4	57.6	26.3	37.9

Zersetzungsgrad des Methans steigt mit Temperaturerhöhung, aber bei 800°C. sinkt er plötzlich, bei 900°C. hat er die niedrigsten Werte und über 1000°C. steigt er wieder langsam auf. Diese Erscheinung die auf den ersten Blick unregelmässig erscheint, führt sich, bei genauerer Beobachtung, auf folgenden Ursachen zurück.

Die Reaktion schreitet mit der Steigerung der Temperatur fort, aber an einem Punkt vermindert sich das katalytische Vermögen des Katalysators plötzlich und der Zersetzungsgrad sinkt herab, obgleich die Temperatur immer höher steigert, bleibt das katalytische Vermögen am niedrigsten. Die langsame Steigerung des Zersetzungsgrades ist der Wirkung der Wärme, nicht der des Katalysators, zuzuschreiben. Das katalytische Vermögen hat bei 700°C. den maximalen Wert und sinkt mit der Steigerung der Temperatur wieder herab. Abbildung 6 zeigt graphisch dieses Verhältnis. Kurve E zeigt den Zersetzungsgrad der oben erwähnten Reaktion, Tafel 14 mit Nickel Katalysator. Kurve A das Resultat ohne Katalysator, Tafel 6, Kurve F Vermögenskurve des Katalysators, die sich aus Kurve E und A ergibt. Man kann die Ergebnisse des Experimentes aus Kurve A, E, F erklären.

Verminderung der Oberfläche durch Halbsinterung verursacht

schnelle Verminderung des katalytischen Vermögens des Nickels. Diese Tatsache ist aus folgenden Experimenten deutlich zu ersehen. Wenn man die Verwandlung des Katalysators in einem durchsichtigen Quarzrohr beobachtet: das reduzierte Nickel zeigt bei 300°C. eine schwarze Farbe, bei 500°C. eine graue, bei 600°C. koaguliert es allmählich zu grauen Körnern, welche metallisch glänzende Partikeln haben. Diese Erscheinung schreitet mit der Temperatursteigerung fort. Bei 1000°C. tritt das Nickel als grosskörniges Metall hervor. Dieses hat ziemlich gleiches Vermögen wie das marktmässige körnige Nickel. Die Temperatur, wo reduziertes Pulver des Nickels zur Koagulierung und Halbsinterung kommt, ist verhältnismässig niedrig, schon bei 600°C. vermindert sich das Vermögen des Katalysators, der Zersetzungsgrad des Methans aber erst nach längerer Zeit.

Tafel 15 und Abbildung 8 erklären die Tatsache.

Tafel 15.

Exp. Nr. b 24, Kat. Nr. B 16, Gas. Ges. 5 lt/St., Reak. Temp. 600°C., $\text{H}_2\text{O}/\text{CH}_4 = 10.0$.

Verlauf (Min.)	CO_2	CO	H_2	CH_4	Z.G.
60	15.0	1.2	60.8	23.0	41.3
90	15.0	1.0	59.5	24.5	39.8
120	14.4	1.0	56.2	28.4	35.1
150	14.8	1.0	58.3	25.9	37.9
180	14.8	1.1	60.0	24.1	39.9
210	13.8	1.0	52.6	32.6	31.2
240	12.5	1.0	55.2	31.3	30.1
270	12.6	0.8	51.2	35.4	27.4
300	13.1	1.0	54.9	31.0	31.2
330	11.0	0.8	49.9	38.3	23.5
360	11.8	1.1	49.4	37.7	25.5
420	12.6	1.0	51.7	34.7	28.2

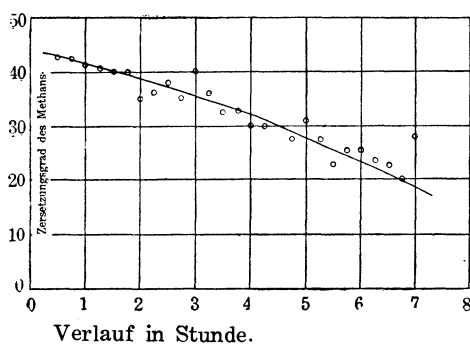


Abb. 8. Verminderung des katalytischen-Vermögens des Nickels.

Katalysator mit geringem Vermögen gibt schwankende und unbestimmte Resultate (Tafel 15). Wenn man Nickel allein gebraucht, kann man eine Verminderung des katalytischen Vermögens infolge einer langdauernden Temperatursteigerung nicht vermeiden. Um einer Verminderung des katalytischen Vermögens vorzubeugen, versuchte ich die Anwendung des Promotors und Trägers. Der Zusatz dieser Materien hat ge-

wissermassen meiner Erwartung entsprochen.

2. Promotor und Träger. Die Wirkung des Promotors auf den Katalysator ist eine günstige; insbesondere Magnesiumoxyd, Aluminiumoxyd, Kieselsäure und Chromoxyd u.s.w. haben in zweckmässiger Menge einen wichtigen Einfluss entfaltet. Tafel 16 zeigt die Resultate, die sich bei Gebrauch des Nickelkatalysators, und der schwer reduzierbaren Oxyde in verschiedenen Mengen-Verhältnisse ergeben haben; Reaktionstemperatur, 970°C ., $\text{CH}_4/\text{H}_2\text{O}=2.0$. Dabei wurde Nickeloxyd Pulver mit dem anderen Oxyd Pulver vermischt, das Ergebnis war aber besser als mit Nickel allein.

Tafel 16.

Exp. Nr. a 70-a 100, Kat. Nr. A 45-A 67, Reak. Temp. 970°C ., Gas. 5 lt/St., $\text{H}_2\text{O}/\text{CH} = 2.0$.

Kat. Nr.	Bestandteil des Katalysators $\text{Ni}+\text{Al}_2\text{O}_3$ (Mol)	CO_2	CO	H_2	CH_4	Z.G.
A 45	0.9 : 0.1	2.8	20.2	75.3	1.7	93.0
A 46	0.7 : 0.3	0.8	24.6	73.5	1.1	95.8
A 47	0.5 : 0.5	4.4	20.1	73.6	1.9	92.8
A 48	0.3 : 0.7	0.7	23.4	74.0	1.9	92.8
A 49	0.1 : 0.9	0.6	23.5	74.2	1.7	93.5
Ni : MgO						
A 51	0.9 : 0.1	1.1	22.1	75.3	1.5	94.0
A 52	0.7 : 0.3	0.6	23.7	75.2	0.5	94.0
A 53	0.5 : 0.5	2.0	21.5	73.3	3.2	91.2
A 54	0.3 : 0.7	0.4	23.0	74.3	2.3	91.0
A 55	0.1 : 0.9	1.6	23.1	73.3	2.0	92.5
Ni : SiO_2						
A 60	0.1 : 0.9	0.8	22.1	73.3	3.8	85.2
Ni : Cr_2O_3						
A 65	0.1 : 0.9	1.6	21.8	72.0	4.6	83.5
Ni :						
A 67	10% Ni	2.8	22.4	73.3	1.5	94.5

Die Anwendung eines richtigen Trägers befördert ferner die leichte Formgebung des Katalysators, Verhütung der Halbsinterung und so kann man feuerfestere und bequemere dauerhaftere Katalysatoren gewinnen. Als Träger muss man feuerfeste und poröse Materien, wie Bimsstein, Porzellan, Kaolin, feuerfesten Ziegel usw. erwähnen. Da aber diese Materie in ihren Eigenschaften und Komponenten sehr verschieden sind, so lässt sich etwas Allgemeingültiges darüber nicht sagen. Bimsstein ist poröse aber nicht feuerfest und kann deshalb nur bei niederer Temperatur in Betracht kommen, bei einer höheren Temperatur versagt er ganz und gar. Porzellanscherben und feuerfester Ziegel kommen in Frage, aber sie passen nicht zu Formgebung und Anhaften des Nickels. Die Mazerationsmethode in Salzlösung ist nicht am Platz, weil bei der Trocknung die Konzentration der Oberfläche des Katalysators zu gross wird und ein Film der Metalle sich bildet. Der Katalysator mit Kaolin und Nickelhydroxyd unter Mischung mit Wasser und Formgebung

ist der wirksamste unter den Niederschlagskatalysatoren. Dagegen von den Röstungskatalysatoren entfaltet der aus Nickel und Chromoxyd die beste Wirkung.

Andere Materien z.B. Alumina, Kieselsäure, Magnesia können in Frage kommen, nur die Formgebung ist bei ihnen etwas schwierig. Tafel 17 zeigt die Resultate der Experimente, in denen ich dem Nickel als Katalysator Alumina, Magnesia, Kieselsäure und Chromoxyd als Promotor und Bimsstein als Träger beigegeben habe. Diese bilden zusammen mit Lösungsgemischen der Nitraten Niederschläge.

Tafel 17.

Ges. Gas. 5 lt/St., $H_2O/CH_4 = 10-7$, Ni-Katalysator.

Exp. Nr.	Kat. Nr.	Träger	Promotor	Reak. Temp. °C	CO ₂	CO	H ₂	CH ₄	Z.G.
b 22	B 15	Bimsstein	Al ₂ O ₃	500	18.2	3.1	75.9	2.8	88.3
				600	18.0	4.0	76.9	1.1	95.8
				700	17.1	4.5	78.0	0.4	98.0
b 38	B 30	Feuerfester Ziegel	Al ₂ O ₃	500	19.2	0.9	76.4	3.5	85.3
				600	17.6	3.1	76.5	2.8	88.0
				700	18.6	2.6	77.8	1.0	95.5
b 43	B 37	Porzellan	Al ₂ O ₃	500	19.4	1.8	76.7	2.1	90.8
				600	18.2	3.1	77.5	1.2	94.7
				700	19.2	3.0	77.3	0.5	98.5
b 66	B 58	Kaolin	Al ₂ O ₃	500	19.2	1.2	76.2	3.4	89.3
				600	18.9	3.0	77.3	0.8	96.5
				700	18.2	3.0	78.3	0.5	97.7
				800	17.2	4.2	78.4	0.2	99.0
				900	15.5	6.0	78.5	0.0	100.0
				1000	15.5	7.4	77.1	0.0	100.0
b 72	B 55	Kaolin	MgO	500	19.5	1.4	74.4	4.7	81.5
				600	19.6	1.8	77.3	1.3	94.2
				700	19.3	2.0	77.8	0.9	96.0
				800	18.8	2.0	78.5	0.8	96.3
				900	18.3	2.8	78.1	0.8	96.5
				1000	18.2	4.1	76.9	0.7	97.0
b 76	B 40	Kaolin	Cr ₂ O ₃	500	18.7	1.0	75.6	4.7	80.8
				600	18.8	2.1	77.8	1.3	94.0
				700	18.6	2.9	77.7	0.8	96.5
				800	16.6	5.1	77.6	0.7	96.8
				900	15.5	6.9	77.1	0.5	98.0
				1000	15.0	7.6	76.9	0.5	98.0
b 14	B 9	Bimsstein	Fe ₂ O ₃	500	17.4	1.8	68.7	12.1	61.3
				600	16.7	4.4	76.1	2.8	88.3
				700	13.6	7.0	76.8	2.6	88.8

3. Katalysator besteht aus zwei Metallen. Weiter studierte ich die Wirkung Nickel-Katalysators mit Kupfer, Eisen, Silber, Kobalt, Mangan und Chrom auf Methan-Wasserdampf-Reaktion. Doch konnte ich keinen bedeutenden Einfluss beobachten. Die erhaltenen Resultate sind in Tafel 18 zusammengestellt. Dabei fand ich aber einen feuerbeständigen Katalysator, der, wie unten erwähnt wird, durch Röstungs- und Reduktions-Temperatur wenig beeinträchtigt wird, Reaktionstemperatur 1000–1100°C. Methangeschwindigkeit 100 lt/St. Verhältnis Methans zu Wasser ist 2.0.

4. Menge des Promotors, Konzentration und Korngrösse des Katalysators. Wenn man die Menge der Alumina des Katalysators in Alumina-Nickel Reihe verändert, so ergeben sich interessante Resultate. Es stellte sich nämlich heraus, dass es eine optimale Beifügungsmenge des Promotors gibt, Tafel 19. Der Katalysator wird folgendermassen hergestellt; die Lösung der Nitrate des Nickels und Aluminiums wird in gewissem Verhältniss vom feuerfesten Ziegel absorbiert und getrocknet und geröstet und mit Wasserstoff sorgfältig reduziert.

Tafel 18.

Gas. Ges. 70 lt/St., Reak. Temp. 1000°C., $\text{H}_2\text{O}/\text{CH}_4 = 2.0$, Ni-Katalysator.

Exp. Nr.	Kat. Nr.	Träger	Promotor	Reak. Temp. °C	CO ₂	CO	H ₂	CH ₄	Z G.
g 25	G 1	Kaolin	Al ₂ O ₃	880	3.8	20.5	74.6	1.1	95.8
g 22	G 2	Kaolin	Bauxite	990	5.5	17.6	73.1	3.8	86.0
g 40	G 3	Kaolin	Fe ₂ O ₃	800	5.2	16.2	71.7	6.7	76.0
g 34	G 5	Kaolin	Ag	1000	3.8	18.6	72.6	0.9	96.2
g 37	G 6	Kaolin	MnO ₂	950	4.4	17.4	71.0	7.2	75.2
g 36	G 8	Kaolin	Cu	1100	8.2	17.4	64.8	9.3	73.5
g 33	G 12	Kaolin	Co	990	7.3	15.9	76.0	0.8	96.5
g 19	G 13	ohne	Bauxite	1000	4.6	20.0	74.4	1.0	95.0

Tafel 19.

Gas. Ges. 5 lt/St., $\text{H}_2\text{O}/\text{CH}_4 = 7$.

Exp. Nr.	Kat. Nr.	Katalysator Ni : Al ₂ O ₃ mol.	Reak. Temp. °C	CO ₂	CO	H ₂	CH ₄	Z.G.
b 41	B 32	1 : 0.500	500	17.2	1.4	68.1	13.3	58.3
b 36	B 28	1 : 0.250	500	16.7	2.1	71.4	9.8	65.7
b 35	B 27	1 : 0.100	500	16.6	0.8	73.5	9.1	65.7
b 34	B 26	1 : 0.050	500	17.8	1.3	71.9	9.0	68.0
b 38	B 30	1 : 0.025	500	19.2	0.9	76.4	3.5	85.2

Tafel 19.—(fort.)

Exp. Nr.	Kat. Nr.	Katalysator Ni : Al ₂ O ₃ mol.	Reak. Temp. °C	CO ₂	CO	H ₂	CH ₄	Z.G.
b 40	B 33	1 : 0.010	500	17.4	1.8	72.7	8.1	70.0
b 37	B 29	1 : 0.005	500	15.8	0.8	69.7	13.7	54.7
b 39	B 31	1 : 0.000	500	17.2	1.5	69.6	11.7	61.4
b 41	B 32	1 : 0.500	600	18.8	1.7	74.8	4.7	81.3
b 36	B 28	1 : 0.250	600	18.6	1.4	73.6	6.4	75.7
b 35	B 27	1 : 0.100	600	18.9	1.2	74.7	5.2	79.5
b 34	B 26	1 : 0.050	600	18.7	1.6	73.9	5.8	78.0
b 38	B 30	1 : 0.025	600	17.7	3.1	76.7	2.5	89.2
b 40	B 33	1 : 0.010	600	18.9	1.8	75.8	3.5	85.5
b 37	B 29	1 : 0.005	600	18.2	1.7	73.4	6.7	74.8
b 39	B 31	1 : 0.000	600	17.6	1.8	69.6	11.0	63.8
b 41	B 32	1 : 0.500	700	19.6	2.2	75.6	2.6	89.3
b 36	B 28	1 : 0.250	700	18.6	2.0	76.6	2.8	88.0
b 35	B 27	1 : 0.100	700	18.6	2.0	77.5	1.9	91.5
b 34	B 26	1 : 0.050	700	18.7	3.0	76.5	1.8	92.1
b 38	B 30	1 : 0.025	700	18.6	2.6	77.8	1.0	95.5
b 40	B 33	1 : 0.010	700	18.9	2.6	76.7	1.8	92.3
b 37	B 29	1 : 0.005	700	18.2	2.1	74.7	5.0	80.2
b 39	B 31	1 : 0.000	700	17.1	3.4	73.8	5.7	78.2

Zur Bestimmung der optimalen Konzentration des Katalysators auf dem Träger habe ich Experimente angestellt, die in der Tafel 20 angegeben sind. Bei Konzentration des Nickels über 7–8% der Gewichte des Trägers, hat der Katalysator ein sehr wirksames Vermögen, aber unter 7% sinkt das Vermögen deutlich herab, während bei einer Konzentration über 10% er in seiner Wirkung kaum beeinflusst wird. So befindet sich die optimale Konzentration des Katalysators in der Nähe von 10%: Grosse Konzentration bei Bimsstein, ferner feuerfestem Ziegel, hat einen schlechten Einfluss, auf den Träger, da eine Sinterung des Metalls leicht auf der Oberfläche des Katalysators geschieht. Die optimale Konzentration bei Porzellan ist 7% und die bei Kaolin ist 10%. Bei Porzellan ist, je nach der Darstellungsweise des Katalysators, die Konzentration an der Oberfläche grösser als im Innern. Der Oberflächenzustand des Trägers spielt hierbei eine wichtige Rolle, so dass man die optimale Konzentration des Katalysators nicht so einfach bestimmen kann.

Tafel 20.

Gas. Ges. 5 lt/St., $\text{H}_2\text{O}/\text{CH}_4 = 7$.

Exp. Nr.	Kat. Nr.	Konzentration %	Reakt. Temp. °C	CO ₂	CO	H ₂	CH ₄	Z.G.
Träger : Bimsstein.								
b 45	B 35	1.6	500	17.5	1.5	72.2	8.8	68.0
b 42	B 34	3.0	500	18.4	1.4	72.3	7.9	71.5
b 43	B 37	7.0	500	19.4	1.8	77.2	1.6	93.0
b 44	B 38	16.0	500	20.1	1.5	76.6	1.8	92.0
b 45	B 35	1.6	600	18.0	2.8	73.4	5.8	78.1
b 42	B 34	3.0	600	18.2	2.3	73.9	5.6	78.5
b 43	B 37	7.0	600	18.2	3.1	77.8	0.9	95.9
b 44	B 38	16.0	600	19.0	2.2	78.2	0.6	97.0
b 45	B 35	1.6	700	18.0	3.7	73.9	4.4	83.1
b 42	B 34	3.0	700	17.6	2.7	76.3	3.4	85.7
b 43	B 37	7.0	700	19.0	3.0	77.7	0.3	98.7
b 44	B 38	16.0	700	18.2	3.6	78.2	0.0	100.0
Träger : Feuerfester Ziegel.								
b 54	B 59	5.0	500	18.4	1.6	72.4	7.6	72.4
b 55	B 60	8.0	500	18.7	1.5	77.2	2.6	83.5
b 57	B 58	9.8	500	19.8	1.2	77.9	1.1	95.0
b 56	B 61	12.2	500	19.4	1.1	78.5	1.0	95.5
b 54	B 59	5.0	600	18.0	2.0	78.8	11.2	94.7
b 55	B 60	8.0	600	19.0	1.8	78.2	1.0	95.5
b 57	B 58	9.8	600	19.6	2.2	77.6	0.6	97.4
b 56	B 61	12.2	600	19.4	1.8	78.3	0.5	97.7
b 54	B 59	5.0	700	18.7	3.3	77.0	1.0	95.7
b 55	B 60	8.0	700	18.0	2.2	79.2	0.6	97.0
b 57	B 58	9.8	700	18.2	2.8	78.7	0.3	98.5
b 56	B 61	12.2	700	18.5	2.7	78.6	0.2	99.0

Der Katalysator durch Niederschlagsmethode hat homogene Struktur an der Oberfläche und im Innern, so dass die Konzentration leicht bestimmt wird. Je kleiner die Körner des Katalysators ist, desto grösser ist deren Oberfläche, desto besser die Wirkung, zugleich wird aber Widerstand gegen den Gaszug grösser. Tafel 21 zeigt die Resultate mit verschiedener Körngrösse des Katalysators.

Tafel 21.

Gas. Ges. 5 lt/St., $\text{H}_2\text{O}/\text{CH}_4 = 10$.

Exp. Nr.	Kat. Nr.	Reak. Temp. °C.	CO_2	CO	H_2	CH_4	Z.G.
b 75	B 58	500	18.7	1.5	73.9	5.9	77.5
b 74	B' 58	500	19.0	1.6	76.4	3.0	86.9
b 65	B'' 58	500	18.8	1.9	76.4	2.9	87.7
b 75	B 58	600	19.1	1.9	77.4	1.6	92.8
b 74	B' 58	600	19.0	2.6	78.5	0.7	96.7
b 65	B'' 58	600	18.6	2.6	78.3	0.5	97.7
b 75	B 58	700	17.8	2.8	78.0	1.4	93.5
b 65	B' 58	700	18.3	3.0	78.3	0.4	98.5
b 65	B'' 58	700	18.4	3.6	77.7	0.3	98.7

Korngrösse B 58 10 mm / 10 mm Zylinder.
 B' 58 3 mm / 4 mm „
 B'' 58 2 mm / 3 mm „

5. *Kontakt d a u e r*. Sie ist ein sehr wichtiger Faktor für den Fortgang der Reaktion, und wird durch vielen Bedingungen z.B. Katalysator, Temperatur und Gasgeschwindigkeit usw. bedingt. Zur Aufklärung dieser Punkte habe ich folgende zwei Experimente ausgeführt. Einmal veränderte ich die Menge der Katalysatoren, die zu Kaolin-Alumina-Nickel Reihe gehören, wobei die Geschwindigkeit des Gases konstant blieb. Das zweite Mal versuchte ich die Experimente bei gleicher Menge des Katalysators und verschiedener Menge der Wasserdämpfe. Nachfolgende Formel zeigt die Kontaktdauer.

$$\text{Kontaktdauer (Sek.)} = \frac{\text{Volum des Katalysators in c.c.}}{\text{Methan Volum pro Stunde in c.c.}} \times 3600$$

Bei 700°C. beträgt sie, nach der Gleichung $\text{CH}_4 + 2\text{H}_2\text{O} = \text{CO}_2 + 4\text{H}_2$, 25–20 Sekunde und 10–15 Sekunde bei 900°C. nach der Gleichung $\text{CH}_4 + \text{H}_2\text{O} = \text{CO} + 3\text{H}_2$.

Tafel 22 und 23 sind die Resultate, und Abbildung 9 zeigt die Verhältnisse zwischen Kontaktdauer und unverändertem Methan im Reaktionsgas.

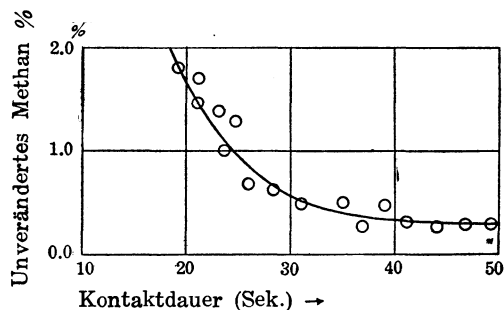


Abbildung 9. Kontaktdauer und unverändertes Methan.

Tafel 22.

Kat. Nr. B 58., Gas Ges. 5 lt/St., $\text{H}_2\text{O}/\text{CH}_4 = 10$.

Exp. Nr.	Kat. Gewicht g.	Kontakt-Dauer (Sek.)	Reaktions-Temp. °C.	CO ₂	CO	H ₂	CH ₄	Z.G.
b 68	10	12.3	500	17.4	1.4	68.0	13.2	58.8
			600	17.8	2.4	71.7	8.1	71.2
			700	17.0	4.0	73.4	5.5	79.2
b 69	20	24.6	500	19.5	1.1	73.2	6.2	75.5
			600	18.4	2.4	77.7	1.5	93.2
			700	17.6	4.4	76.7	1.3	94.5
b 66	30	37.0	500	19.3	0.8	76.9	3.0	87.0
			600	18.9	3.0	77.3	0.8	96.5
			700	18.3	3.0	78.1	0.5	97.7
b 70	40	49.3	500	19.4	2.1	76.9	1.6	91.0
			600	19.1	2.2	78.1	0.6	97.2
			700	18.5	3.4	77.8	0.3	98.5

Tafel 23.

Exp. Nr. b 73, Kat. Nr. B 58, Reak. Temp. 600°C., $\text{H}_2\text{O}/\text{CH}_4 = 7$.

Gas Geschwindigkeit (Lt/St)	Kontakt Dauer (Sek.)	CO ₂	CO	H ₂	CH ₄	Z.G.
4.2	44	17.5	5.0	77.1	0.4	98.0
4.8	39	18.2	3.3	78.0	0.5	97.7
5.3	35	17.8	4.1	77.4	0.7	96.7
6.0	31	17.9	3.8	77.6	0.7	96.7
7.2	26	17.4	4.4	77.3	0.9	96.0
8.0	23	18.0	3.6	76.7	1.7	92.7
8.9	21	17.8	3.5	76.5	2.2	90.6
9.9	19	17.9	3.6	76.5	2.2	90.6

6. Röstungs- und Reduktions-Temperatur des Katalysators. Im allgemeinen ist die Röstungs- und Reduktions-Temperatur des Katalysators bei der Nickel-Kaolin-Alumina Reihe sehr wichtig. Diese Tatsache ist aus der Tafel 24 deutlich zu ersehen. Der bei 400, 500 resp. 600°C. geröstete Katalysator wird bei 300°C. durch Wasserstoff reduziert, bei 350°C. ist er schon wirksam; bei 600°C. beträgt der Zersetzungsgrad 97.7. Die Erhöhung der Röstungstemperatur steigert die Reduktionstemperatur und setzt das Vermögen herab.

Der Katalysator, geröstet bei 900–1000°C., kann nicht unter 600–700°C. reduziert werden. Er verliert auch unter niedriger Temperatur die katalytische Wirkung. Diese Erscheinung beruht auf der Bildung inaktiver Verbindungen (Silikat und Aluminat) infolge einer Wirkung des Nickels auf den Träger. Zur Aufklärung dieser Vorgänge machte ich die Experimente, wie in Tafel 25 gezeigt, durch Gebrauch von Nickel Silikat (meta) und Aluminat (meta) als Katalysator. Diese Katalysatoren sind unter niedriger Temperatur unwirksam, bei höher Tempe-

rature aber sind sie wirksam. Abbildung 10 zeigt die Verhältnisse zwischen der Temperatur und dem Zersetungsgrad des Katalysators bei verschiedener Röstungstemperatur.

Tafel 24.

Gas. Ges. 5 lt/St., $H_2O/CH_4 = 10$, Katalysator 30 g.

Exp. Nr.	Kat. Nr.	Röst- Temp.	Reduk. Temp.	Reak. Temp.	CO ₂	CO	H ₂	CH ₄	Z. G.
b 83	B 46	400	300	300	1.2	0.8	2.7	95.3	2.1
				350	10.6	1.3	35.7	52.4	18.3
				400	16.8	0.9	61.9	20.4	45.1
				500	19.1	1.3	74.1	5.5	79.3
				600	19.0	3.4	77.1	0.5	97.8
				700	17.7	4.5	77.6	0.2	98.9
				800	16.3	5.5	78.0	0.2	99.3
				900	15.9	6.4	77.7	0.0	100.0
				1000	14.8	7.2	78.0	0.0	100.0
b 84	B 47	500	300	350	8.5	0.8	33.7	57.0	16.3
				400	11.1	1.0	40.9	47.0	20.5
				500	18.4	1.4	76.8	3.4	85.5
				600	18.5	2.8	77.0	1.7	92.6
				700	17.8	3.8	77.3	1.1	95.2
				800	16.0	5.4	77.7	0.9	96.0
				900	15.9	6.1	77.4	0.6	97.3
				1000	13.0	9.4	77.4	0.4	98.2
b 92	B 48	600	300	350	7.2	0.8	30.9	61.1	10.8
				400	15.1	1.0	58.5	25.4	38.8
				500	18.9	2.3	73.9	4.9	81.2
				600	18.7	2.8	76.9	1.6	93.0
				700	17.7	3.4	78.2	0.7	97.0
				800	17.1	5.4	77.1	0.4	98.2
				900	15.8	5.7	78.1	0.4	98.2
				1000	15.5	6.3	78.2	0.0	100.0
b 87	B 49	700	300	350	2.4	1.4	6.5	89.7	4.1
				400	7.6	1.2	28.4	63.4	11.9
				500	18.3	1.2	69.3	11.2	63.5
				600	18.2	3.0	77.0	1.8	92.2
				700	18.0	3.5	77.4	1.1	95.0
				800	16.4	4.8	78.1	0.7	96.7
				900	16.2	5.5	77.8	0.5	97.5
				1000	15.4	6.8	77.5	0.3	98.5
b 86	B 50	800	400	400	5.7	0.8	23.6	69.9	8.5
				500	14.2	1.0	56.7	28.1	35.1
				600	17.4	1.7	69.6	11.3	62.8
				700	17.1	3.8	78.0	1.1	94.8
				800	16.9	4.6	77.8	0.7	96.8
				900	16.7	5.0	77.8	0.5	97.7
				1000	14.0	8.0	77.7	0.3	98.5
b 94	B 51	900	600	600	10.5	1.0	38.4	50.1	18.6
				700	16.0	2.6	73.3	8.1	68.2
				800	17.4	3.7	77.1	1.8	92.2
				900	15.3	7.5	76.2	1.0	95.7
				1000	16.3	4.9	77.9	0.9	95.9
b 88	B 52	1000	700	700	16.3	2.5	68.3	12.9	59.3
				800	16.0	5.4	76.8	1.8	92.2
				900	15.6	5.5	78.0	0.9	96.0
				1000	14.7	6.4	78.2	0.7	96.8

Tafel 25.

Gas. Ges. 5 lt/St., $H_2O/CH_4 = 7$.

Exp. Nr.	Katalysator.	Reak. Temp. °C.	CO ₂	CO	H ₂	CH ₄	Z.G.
f 17	Nickel- + meta- Silikat F 11	600	1.0	0.5	0.0	96.5	1.5
		700	3.0	0.0	1.3	95.7	3.0
		800	13.5	1.5	35.0	50.0	23.1
		900	14.2	3.1	49.3	35.5	32.8
		1000	14.6	7.4	73.7	4.3	83.8
f 13	Nickel- Aluminat F 13	610	7.2	0.6	27.7	65.0	10.7
		700	10.2	2.4	50.1	36.3	25.8
		800	12.1	5.8	68.7	13.4	57.3
		900	12.8	7.2	74.4	5.6	78.3
		990	12.6	7.8	75.6	4.0	83.8

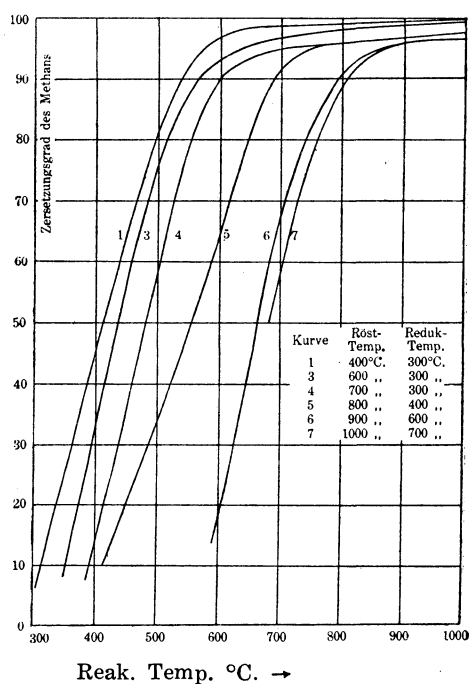


Abb. 10. Röstungstemperatur und Zersetungsgrad des Methans.

Metalloxyde, die kein Wirkungsvermögen haben, werden aktiv, wenn sie bei über 800°C. durch Methan reduziert werden. Es gibt auch Katalysatoren, welche durch Röstungstemperature nicht beeinflusst werden, z.B. derjenige, der aus Nickelbichromat durch Hitzezersetzung hergestellt wird. Seine Wirksamkeit ist zwar etwas geringer aber sie sind feuerfest. Tafel 26 zeigt diese Verhältnisse.

Tafel 26.

Gas. Ges. 5 lt/St., $H_2O/CH_4 = 10$.

Exp. Nr.	Kat. Nr.	Röst-Temp. °C.	Reak. Temp. °C.	CO ₂	CO	H ₂	CH ₄	Z.G.
b 80	B 52	1000	800	1.2	0.8	2.5	95.5	2.1
			900	1.8	4.4	15.6	78.2	7.4
			1000	16.0	5.8	75.5	2.7	88.9
			1100	15.9	5.7	77.6	0.7	96.8
b 81	B 51	900	600	1.2	1.0	2.5	95.3	2.3
			700	1.2	0.8	6.9	91.1	21.6
			800	1.6	1.0	6.7	90.7	26.0
			900	1.6	4.0	12.4	82.0	63.8
			1000	17.0	5.0	75.3	2.7	89.0

7. Lebensdauer und Vergiftung des Katalysators. Bestimmung der Lebensdauer, eine wichtige Eigenschaft des Katalysators, ist sehr schwer. Ich habe sie durch Gebrauch des Katalysators in Nickel-Alumina-Kaolin Reihe durch längere Zeit versucht. Die Resultate sind in Tafel 27 gezeigt. Katalysator B 58 ist unter verschiedenen Katalysatoren der wirksamste. Er wird unter Rücksicht der oben erwähnten Faktoren hergestellt und kann lange gebraucht werden.

Tafel 27.

Exp. Nr. b 52, Reak. Temp. 600°C., Kat. Nr. B 58, $H_2O/CH_4 = 10.0$, Gas. Ges. 5 lt/St.

Verlauf Stunde	CO ₂	CO	H ₂	CH ₄	Z.G.	Volum-zunahme Mal.
1	19.2	1.8	78.0	1.0	95.5	5.2
10	19.1	1.8	78.9	0.2	99.0	5.2
20	18.5	2.1	79.4	0.1	100.0	5.2
30	19.1	2.6	78.2	0.1	99.5	5.2
40	19.6	1.6	78.4	0.4	98.5	5.2
50	19.5	2.9	77.2	0.6	98.2	5.2
60	19.1	2.0	78.9	0.0	100.0	5.0
70	19.1	1.7	78.5	0.7	96.7	5.1
80	19.1	2.6	77.3	1.0	95.5	5.0
90	19.2	3.2	77.0	0.6	97.5	4.9
100	19.6	2.0	78.3	0.1	99.5	5.1
110	18.9	2.4	78.3	0.4	98.2	5.2
120	18.4	2.9	78.6	0.1	99.5	5.2
130	19.4	2.4	77.4	0.8	96.5	5.1
140	19.3	2.0	78.5	0.2	99.0	5.2
150	19.3	1.5	78.6	0.6	97.2	5.2

Die Vergiftung des Katalysators beruht hauptsächlich auf der oben erwähnten Ursache. Schwefel und Arsen unter 0.004 g. in NM Gas beeinträchtigt bei höherer Temperatur das Vermögen nicht. Der aus Nickelsulfat hergestellte Katalysator hat nachfolgendes Vermögen, wie in Tafel 28. Schwefel hat wenig Einfluss auf die Reaktionen.

Tafel 28.

Exp. Nr. f 25, Kat. Nr. F 25, Gas. Ges., 5 lt/St., $H_2O/CH_4 = 10$.

Reakt. Temp. °C.	CO ₂	O ₂	CO	CH ₄	H ₂
600	10.6	0.4	1.0	44.8	43.2
700	12.8	0.2	4.8	10.6	71.5
800	12.6	0.2	8.6	2.4	76.2
900	10.4	0.2	10.2	0.8	78.4
1000	13.0	0.2	7.8	0.0	79.0

Herstellungsweise des Katalysators ist sehr wichtig, so hat der aus Alumina und Nickelhydroxyd durch Mischung hergestellte Katalysator gutes Vermögen, aber der aus kolloidalem aktiven Alumina Gel oder Natriumaluminat Lösung mit überschüssigem Alkali hergestellte Katalysator zeigt kein Vermögen, auch wenn durch wiederholtes Auswaschen das Alkali entfernt ist.

Zwischen Silika und kolloidalem aktiven Silikagel besteht das gleiche Verhältnis. Gemisch aus Magnesia oder Kalk und Nickelhydroxyd in trockenem Zustand zeigt gutes Vermögen, aber das in feuchtem Zustand hergestellte zeigt kein Vermögen. Diese Resultate sind in Tafel 29 gezeigt.

Tafel 29.

Gas. Ges. 5 lt/St., $H_2O/CH_4 = 10$.

Exp. Nr.	Katalysator.	Reak. Temp. °C.	CO ₂	CO	H ₂	CH ₄	Z.G.
b 95	Nickel + Magnesia (10%) F 1—F 5	600	1.2	1.2	0.0	96.4	1.2
		700	1.2	1.0	0.0	96.0	1.2
		800	1.4	1.6	2.0	93.2	3.1
		900	3.1	2.4	11.7	82.7	6.7
		1000	7.5	4.8	39.2	48.2	20.9
f 18	Nickel + Kalk	590	0.0	0.0	0.0	99.8	
		680	4.4	0.0	0.0	95.4	
		800	9.8	0.4	29.6	60.0	
	F 18	890	12.7	2.0	54.8	30.5	
		1000	13.8	6.4	68.8	11.0	

Tafel 29.—(fort.)

Exp. Nr.	Katalysator.	Reak. Temp. °C.	CO ₂	CO	H ₄	CH ₄	Z.G.
b 01	Nickel + aktiv Alumina	600	0.8	0.0	0.0	99.2	
		700	0.6	0.0	0.0	99.4	
		800	0.8	1.8	1.0	98.2	
		900	2.8	1.8	1.0	94.4	
		1000	3.3	3.0	11.0	83.6	

8. Katalysator mit Alkalizusatz. Es wird gesagt, dass Katalysator mit kleiner Menge Alkali vortreffliches Vermögen hat. Zur Feststellung habe ich folgende Experimente vorgenommen. Tafel 30 ist ein Teil der Resultate. Ich kann es nicht beweisen, bin aber der Meinung, dass der Zusatz einer kleinen Menge Alkali unter 0.01 Mol das katalytische Vermögen nicht herabdrücke. Er macht aber das Leben des Katalysators kürzer.

Diese Resultate sind in Tafel 31 gezeigt.

Tafel 30.

Gas. Ges. 5 lt/St., H₂O/CH₄ = 10.

Exp. Nr.	Kat. Nr.	Bestandteil Kom des Katalysators.	Träger	Reak. Temp.	CO ₂	CO	H ₂	CH ₄	Z.G.
b 4	B 3	Nickel	Feuerfester Ziegel	500	17.7	2.5	65.6	14.2	58.7
				600	17.6	2.0	70.6	9.8	66.7
				700	16.9	3.5	69.2	10.4	66.2
b 1	B 1	Ni-K ₂ CO ₃		500	16.2	1.2	65.4	17.2	50.1
				600	16.1	4.4	70.0	9.5	68.2
				700	14.1	5.8	67.2	12.9	60.7
b 25	B 17	Ni-Al ₂ O ₃		500	19.8	1.3	72.7	6.2	77.2
				600	18.1	2.4	74.7	4.8	81.0
b 2	B 2	Ni-Al ₂ O ₃ -K ₂ CO ₃		500	18.9	3.0	71.2	6.9	76.2
				600	17.4	3.2	74.2	5.2	79.8
				700	17.0	4.3	76.7	2.0	91.4
				800	17.7	3.6	75.7	3.0	87.6
				900	16.9	4.9	75.5	2.8	88.5
				1000	14.8	7.3	75.6	2.3	90.6
b 22	B 15	Ni-Al ₂ O ₃	Bimsstein	500	18.1	3.1	76.9	1.9	91.7
				600	17.9	4.0	77.1	1.0	95.4
				700	17.2	4.5	78.3	0.0	100.0
b 7	B 4	Ni-Al ₂ O ₃ -K ₂ CO ₃		500	18.8	2.1	74.2	4.9	81.0
				600	18.8	2.4	77.8	1.0	95.5
				700	18.8	2.6	77.4	1.2	94.7
				800	18.4	3.2	77.5	0.9	96.0
				900	17.1	3.6	78.5	0.8	96.5
				1000	16.4	5.4	77.6	0.6	97.2

Tafel 31.

Exp. Nr. b 19, Kat. Nr. B 10, Gas. Ges. 5 lt/St., $\text{H}_2\text{O}/\text{CH}_4 = 7$, Reak. Temp. 600°C .

Verlauf Stunde	CO_2	CO	H_2	CH_4	Z.G.
1	17.8	4.0	77.2	1.0	95.5
5	16.9	3.6	78.5	1.0	95.4
10	17.3	3.8	78.5	0.5	97.7
20	18.0	1.8	79.4	0.8	96.0
28	16.4	4.3	78.8	0.5	97.5
30	16.9	2.2	71.4	9.5	66.7
31	11.2	2.3	42.4	44.1	23.2

(Fortsetzung folgt)

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von Taiwan.*

Direct Determination of Oxygen in the Organic Compounds by the Hydrogenation. IV. Analyses of the Sulphur-Containing Compounds, Coals.

By Toraki KIMOTO, Kiyoshi MORIKAWA and Ryonosuke ABE.

(Received July 4, 1941.)

The method so far developed can not successfully be applied to the sulphur-containing compounds.

Coals contain 0.3–3% of sulphur and give on heating hydrogen sulphide which poisons and reduces the activity of nickel catalyst. We have tried to fix the sulphur as copper sulphide, placing the reduced copper between the Pt-silica gel catalyst and the nickel catalyst in the reaction tube.

Experimental Details. *The apparatus* used and the procedure employed are described in the previous papers.⁽¹⁾⁽²⁾

The desulphuring agent. Copper oxide is easily and completely reduced by hydrogen at moderate temperature, and therefore, the unfavorable reaction of hydrogen sulphide with copper oxide is excluded.

(1) K. Morikawa, T. Kimoto and R. Abe, this Bulletin, **16** (1941) 1.

(2) K. Morikawa, T. Kimoto and R. Abe, *ibid*, **16** (1941) 33.

Furthermore copper combines with sulphur very tenaciously and is difficultly reduced by hydrogen under ordinary conditions. These properties of copper were thought to be very suitable for fixing sulphur from the hydrogen stream in this analytical procedure. Kieselguhr is impregnated with copper nitrate solution and the resultant dried mass was ignited.

The 15 g. of copper oxide-kieselguhr mixture thus prepared were inserted between Pt-silica gel catalyst and Ni-thoria catalyst and completely reduced in situ before the analysis.

The time required for analysis. As the amount of kieselguhr was increased the time required for analysis was prolonged to 70 minutes.

Sample: coal. Three kinds of coal of different ranks were used and their analytical data were given in Table 6.

Table 6. Ultimate analyses of sample coals.

Kinds	Ash %	C %	H %	N %	S %	O %	O (pure coal)
Jarahinol.	4.43	67.52	4.54	1.17	0.18	22.16	23.18
Fushun	2.38	76.63	5.30	1.25	0.48	13.96	14.30
Tatong A	2.94	81.99	4.41	0.89	0.37	9.40	9.68
Tatong B	5.18	79.65	4.24	0.78	0.50	9.65	10.18
Tatong C	8.48	76.04	4.78	0.89	0.35	9.46	10.34

Experimental Results. *Examination of Absorbents.* Coals contain nitrogen and, therefore, give ammonia in the process of this analytical method. Inaba and Abe proved that coal which contained 1–2% of nitrogen gave appreciable amount of ammonia, i.e., 2.0 mg. in this procedure. They caught ammonia, by 0.02 N sulphuric acid solution and water by calcium chloride. In the experiments shown in Table 7. We found that copper catalyst not only caught sulphur and extended the life of Ni-catalyst but also decomposed ammonia to its elements and decreased partial pressure of ammonia to the negligible extent; therefore, calcium chloride could be more conveniently used than caustic soda as the absorbent for water.

Table 7. Examination of CaCl_2 as the absorbent for water. Analytical condition; Pt-silica gel temp. 950°C ., Ni-catalyst temp. 350°C ., hydrogen streaming velocity 5 l./hr., time for analysis 70 min., Sample; mixture of saccharose and dimethylglyoxime.

Expt. No.	Sample (g.)	N % in sample	Formed NH_3 (mg.)	O % (Found)	O % (Calculated)	Error %	absorbent
D-3	0.1510	2.23	0.30	48.78	49.15	−0.37	0.02 NH_2SO_4 + CaCl_2
D-6	0.2914	1.51	0.45	49.95	49.90	+0.05	
D-5	0.1977	1.47	0.30	48.94	48.83	+0.11	
D-9	0.1487	3.02	—	48.62	48.41	+0.21	CaCl_2
D-7	0.1897	2.12	—	49.05	49.34	−0.29	
D-8	0.2134	1.45	—	50.20	49.96	+0.24	

Effects of coal ash. We are accustomed to determine the inorganic substances in coal by burning the coal in air and weighing the calcined residue, that is, the ash of coal. It is clear that we deal not with the real inorganic substances as present in coals, but with the oxidized forms. Here on the contrary, in this procedure we are concerned with the reduced forms instead of the real inorganic substances. Considering the nature and composition of inorganic substances which occur in coals, we expect, in general, but not necessarily always, higher values of oxygen by hydrogenation than ordinary oxidation method. The results given in Table 8 may be taken as a good example.

Table 8. Results of direct determination of oxygen in the coals. Analytical condition; Pt-silica gel temp. 950°C., Ni-catalyst temp. 350°C., hydrogen streaming velocity 5 l./hr., analytical period 70 min., absorbent: granules of caustic soda.

Expt. No.	Kind of samples	Heating temp. of the sample	Sample (g.)	Oxygen %	Difference between hydrogenation and oxidation methods.
D-32	Jarahinol	950°C.	0.2125	24.02	+0.84
D-33	"	800	0.2050	23.62	+0.44
D-28	Fushun	950	0.2177	14.79	+0.49
D-29	"	950	0.2508	14.86	+0.56
D-35	"	900	0.2372	14.91	+0.61
D-39	"	800	0.2287	14.88	+0.58
D-45	Tatong A	950	0.1934	10.22	+0.54
D-43	Tatong B	950	0.2354	10.47	+0.29
D-44	Tatong C	950	0.1999	10.77	+0.43

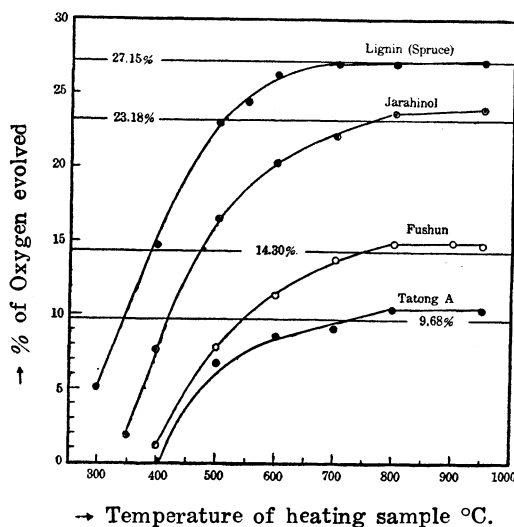


Fig. 15. Relation between the temperature of heating sample and % of oxygen evolved from the various coals.

Effects of coal ranks. The relations between the temperatures of heating samples and the amounts of oxygen caught as water were plotted in Fig. 15.

Degree of polymerisation increases in the order of lignin, Jarahinol, Fushun, and Tatong coals. Extrapolating the curves to the abscissa we know the decomposition temperature of each sample and found that the higher the polymerisation degree the higher the decomposition temperature. Above 800°C. all the three coals gave constant amounts of oxygen which were 0.5% higher than the values obtained by usual combustion method. The presence of copper

extended the life of Ni-thoria catalyst and it was actually possible to repeat the analysis 18–20 times with coal samples. Pt-silica gel catalyst was so stable that we could recover the activity by burning the free carbon deposited on the catalyst and found not necessary to replace it during year's experiments.

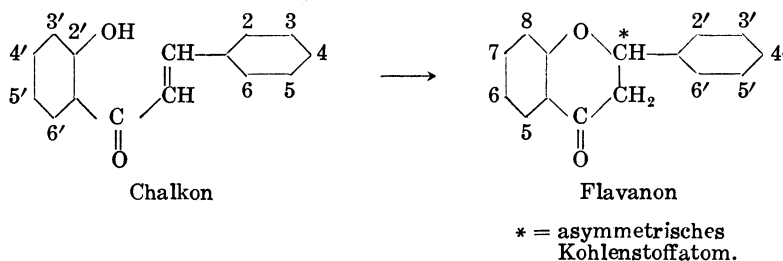
*Coal Section of Fuel Department, Central Laboratory
South Manchuria Railway Co., Dairen Japan.*

Asymmetrische Synthese. II. Asymmetrische Synthese von Oxy-flavanon aus Oxy-chalkon⁽¹⁾.

Von Haruo TATSUTA.

(Eingegangen am 18. Juli 1941.)

In einer früheren Mitteilung berichten S. Fujise und H. Sasaki⁽²⁾ über die asymmetrische Synthese von *d*-Diacetyl-matteucinol (6,8-Dimethyl-5,7-diacetoxy-4'-methoxy-flavanon) aus 2', 4', 6'-Triacetoxy 3', 5'-dimethyl-4-methoxy-chalkon. In der vorliegenden Mitteilung möchte ich über die Resultate der asymmetrischen Synthesen von 7-Oxyflavanon, 5,7-Dioxy-flavanon und Homoeriodictyol (5, 7, 4'-Trioxy-3'-methoxy-flavanon) aus dem entsprechenden Oxy-chalkon (bzw. Acetoxy-chalkon) berichten.



Über die Bedingungen der Umwandlung von Oxy-chalkon in optisch-aktives Oxy-flavanon spielten die Zusatzmenge der optisch-aktiven Säure (*d*-Camphersulfonsäure), die Reaktionstemperatur und die Dauer der Erhitzung eine wichtige Rolle.

Glücklicherweise ist mir die Isolierung der optisch-aktiven Oxyflavanone aus den entsprechenden Oxy-chalkonen gelungen.

S. Fujise und A. Nagasaki⁽³⁾ haben schon über die Spaltung von

(1) Diese Mitteilung wurde schon auf Japanisch berichtet. *J. Chem. Soc. Japan*, **61** (1940), 1048.

(2) S. Fujise und H. Sasaki, *J. Chem. Soc. Japan*, **59** (1938), 440; *Ber.*, **71** (1933), 341.

(3) S. Fujise und A. Nagasaki, *J. Chem. Soc. Japan*, **57** (1936), 1245; *Ber.*, **69** (1936), 1893.

d,l-7-Oxy-flavanon in die Antipoden mittels *l*-Methoxy-acetylchlorids berichtet. Sie erhielten *d*-7-Oxy-flavanon vom Schmp. 181–182°C., $[\alpha]_D^{15} + 33.3^\circ$. Der Drehungswert meiner Substanz ist nahezu der gleiche, daher tritt wahrscheinlich bei meinem Versuche eine fast 100%ige asymmetrische Synthese ein.

Die niedrige Drehungswert von *d*-5,7-Dioxy-flavanon und *d*-Homooriodictyol verursacht die Mischentstehung der Racematen. Aus der Tabelle ist zu ersehen, dass die asymmetrische Synthese vielmehr von der Reaktionstemperatur und der Zeitdauer abhängig ist, als von der Menge der *d*-Camphersulfonsäure.

opt.-aktiv. Oxy- flavanone	Chalkon g.	Alkohol c.c.	<i>d</i> -Cam- pher- sulfon- säure g.	Temper- ature °C.	Zeit (Std.)	Schmp. °C.	$[\alpha]_D$ (in Dioxan)
<i>d</i> -7-Oxy- flavanon	2',4'-Dioxy- chalkon						
Nr. 1	1.0	12	0.30	115–120°	66	180–181°	$[\alpha]_D^{10} + 29.3^\circ$
Nr. 2	1.2	14	0.30	93–100° 115–120°	48 24	187°	$[\alpha]_D^{15} + 5.6^\circ$
Nr. 3	1.0	12	0.06	113–117°	48	186.5–187°	$[\alpha]_D^{15} + 0.9^\circ$
<i>d</i> -5,7-Oxy- flavanon	2',4',6'-Tri- acetoxy- chalkon						
Nr. 1	1.0	18	0.30	115–120°	66	190°	$[\alpha]_D^{10} + 9.8^\circ$
Nr. 2	1.0	18	0.037	112–119°	40	193.5–194°	$[\alpha]_D^{16} + 4.4^\circ$
Nr. 3	1.2	21	0.24	98–100°	48	190°	$[\alpha]_D \doteq 0$
<i>d</i> -Homoorio- dictyol	Acetoxy- chalkon (Schmp. 158°) ⁽⁴⁾						
Nr. 1	0.8	32	0.05	113–117°	48	224°	$[\alpha]_D^{15} + 8.0^\circ$
Nr. 2	0.6	24	0.12	98–100°	48	221°	$[\alpha]_D^{15} + 6.3^\circ$

Beschreibung der Versuche. (1) *d*-7-Oxy-flavanon. 2', 4'-Dioxy-chalkon und Alkohol wurden nach Zusatz von *d*-Camphersulfonsäure im Einschlussrohr mittels Ölbad erhitzt. Die Substanzmenge usw. wurden in der Tabelle angegeben. Die Farbe der Lösung wandelte sich von gelb zu hellrot um. Nach dem Erkalten wurde die Hauptmenge des Alkohols im Vacuum verjagt, die abgeschiedenen Krystalle wurden einmal mit wenig Alkohol und dann mehrmals mit Wasser gut gewaschen.

Die Krystalle zeigen nach dem Umlösen aus Alkohol (unter Zusatz von Entfärbungskohle) einen Schmp. von 180–181°C. (Schmp. des *dl*-7-Oxy-flavanons ist 189°C.). $[\alpha]_D^{10} + 29.3^\circ$ (in Dioxan). Gefunden: C, 74.74; H, 5.10. Berechnet für $C_{15}H_{12}O_3$: C, 75.0; H, 5.0%.

(2) *d*-5, 7-Dioxy-flavanon. 2', 4', 6'-Triacetoxy-chalkon (Schmp. 116°C.) wurde durch Acetylierung von 5, 7-Dioxy-flavanon mittels Essigsäureanhydrids und wasserfreien Natriumacetats gewonnen. Die Aufarbeitung des Reaktionsansatzes geschah wie bei (1). Nach Beendigung der Reaktion roch die Lösung stark nach Essigester. Die rohen Krystalle wurden zuerst mit wenig Petroleumäther und Alkohol, dann mit viel Wasser gut gewaschen, sie wurden aus Alkohol umkrystallisiert und schmolzen bei 190°C. (*d,l*-5, 7-Dioxy-flavanon schmolz bei 203–204°C.) $[\alpha]_D^{10} + 9.8^\circ$ (in Dioxan). Gefunden: C, 70.29; H, 4.79. Berechnet für $C_{15}H_{12}O_4$: C, 70.3; H, 4.7%.

(3) *d*-Homoeriodictyol. Das Acetoxy-chalkon (Schmp. 158°C.)⁽⁴⁾ wurde aus Homoeriodictyol dargestellt. Die Aufarbeitung geschah wie bei (1) und (2).

Die gereinigten Krystalle schmolzen bei 224°C. (Das Racemat schmolz bei 224–225°C.). $[\alpha]_D^{16} + 8.0^\circ$ (in Dioxan). Gefunden: C, 63.38; H, 4.94. Berechnet für $C_{16}H_{14}O_6$: C, 63.6; H, 4.7%.

Es sei mir erlaubt, Herrn Prof. Dr. S. Fujise für seine lebenswürdige Anleitung zu dieser Arbeit meinen herzlichen Dank auszusprechen.

*Chemisches Institut, Wissenschaftl. Fakultät,
Tohoku Kaiserl. Universität, Sendai.*

(4) Der Verf. benutzte etwas unreinen Krystall.

Die reinste Krystalle schmolzen bei 163–164°C., vgl. Shinoda und Sato, *J. Pharm. Soc. Japan*, **49** (1929), 64.

Synthese von rac. 3,6-Dimethoxy-5-äthoxy-N-äthyl-nor-aporphin⁽¹⁾.

Von Kakuji GOTO, Reikichi INABA und Hideo SHISHIDO.

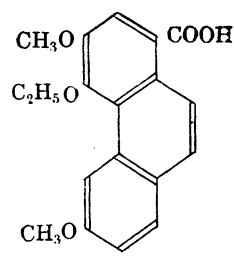
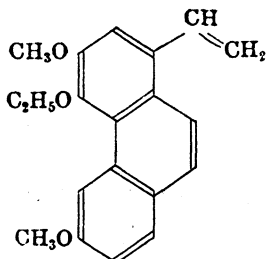
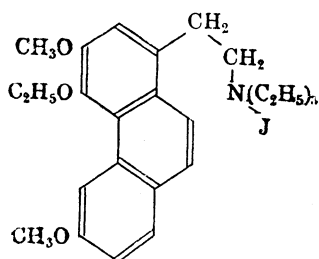
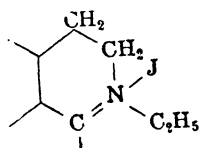
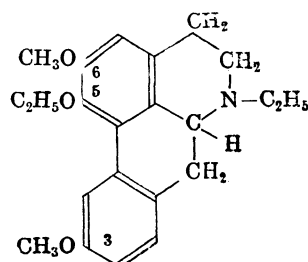
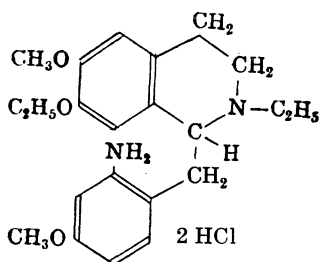
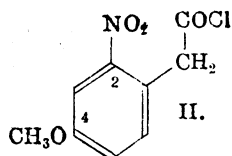
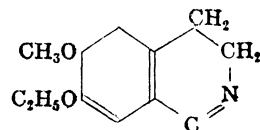
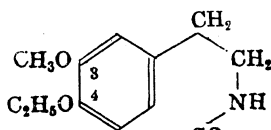
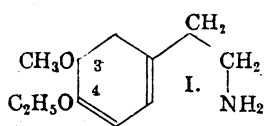
(Eingegangen am 19. Juli 1941.)

Bei der Konstitutionbestimmung von Tuduranin auf synthetischem Wege⁽²⁾ haben wir auch die Gelegenheit gehabt, rac. 3,6-Dimethoxy-5-äthoxy-N-äthyl-nor-aporphin aufzubauen. Diese Substanz wurde zuerst zum Zwecke von Vergleich mit dem N-Aethyl-tuduranin-äthyl-äther synthetisiert, aber bei ihrem Abbau zu Vinyl-phenanthren ergab sich, dass sie nur eine isomere Substanz darstellt. Da der Gang der Synthese ganz

(1) 49. Mitteilung über Sinomenin.

(2) K. Goto und H. Shishido, *Ann.*, **539** (1939), 262; Goto u.a., *Ann.*, **530** (1937), 142.

gleich mit demjenigen des rac. *N*-Aethyl-tuduranin-äthyl-äthers ist, möchten wir ihn nur schematisch unten abbilden und die Beschreibung der einzelnen Substanzen sollen möglichst kurz angegeben werden.



Versuche. β - (3 - Methoxy-4-äthoxy-phenyl) - äthyl-2'-nitro-4'-methoxy-phenacetamid (III). Aus 3 - Methoxy-4-äthoxy-phenyl - äthyl-amin (I)⁽³⁾ und 2-Nitro-4-methoxy-phenyl-essigsäure-chlorid (II)⁽⁴⁾. Weisse,

(3) Die hierzu nötige 4-Aethoxy-3-methoxy-phenyl-essigsäure wurde durch Kondensation von Aethyl-vanillin mit Essigsäure und darauffolgende Reduktion dargestellt. Die Säure wurde zuerst ins Chlorid und dann Amid nach Perkin (*J. Chem. Soc.*, **125**, 1679.) umgewandelt, daraus das Amin (I) durch NaOCl bereitet wurde.

(4) *J. Chem. Soc.*, **119**, 1630; *Helv. Chim. Acta*, **15** (1932), 398.

haarige Nadeln aus Methanol. Schmp. 132°C. Gefunden: C, 61.56; H, 6.08. Berechnet für $C_{20}H_{29}N_2O_6$ (388): C, 61.86; H, 6.19%.

2'-Nitro-4'-methoxy-1-benzyl-β-(6-methoxy-7-äthoxy)-3, 4-dihydro-isochinolin (IV). Bereitet durch die Einwirkung von P_2O_5 auf dem Phenacetamid (III) in getrocknetem Toluol bei der Siedehitze. Das Dihydro-isochinolin wurde aus verdünnter salzsaurer Lösung mit Alkali befreit und durch Aether aufgenommen. Der Aether-rückstand wurde aus Methanol umkrystallisiert. Prismen. Schmp. 139–141°C. (verschwärzt; sintern ab 134°C.). Gefunden: C, 64.96; H, 6.07. Berechnet für $C_{20}H_{22}N_2O_5$ (370): C, 64.86; H, 5.95%.

Jodäthylat. Durch Erhitzen der freien Base bei 100°C. mit überschussigem Aethyljodid im Druckflasche. Gelbe Prismen aus 95 proc. Aethanol. Schmp. 206–207°C. (zers.). Gefunden: C, 50.05; H, 5.26. Berechnet für $C_{22}H_{27}N_2O_5J$ (526): C, 50.19; H, 5.13%.

2'-Amino-4'-methoxy-β-(6-methoxy-7-äthoxy)-1-benzyl-2-äthyl-tetrahydro-isochinolin-dichlorhydrat (V). Das obige Jodäthylat wurde in konz. Salzsäure mit Zinkpulver reduziert. Nach Filtrieren und Alkalisieren wurde das entstandene Tetrahydro-isochinolin in Aether aufgenommen. Das Dichlorhydrat krystallisierte beim Zusatz von wenig 10 proc. Salzsäure zum Aether-rückstand. Weisse Prismen aus Wasser. Schmp. 185–188°C. (zers.; sintern ab 178°C.). Gefunden: C, 57.94; H, 7.47. Berechnet für $C_{22}H_{32}N_2O_3Cl_2 + \frac{1}{2}H_2O$ (452): C, 58.41; H, 7.30%.

Racem. 3, 6 - Dimethoxy-5-äthoxy-N-äthyl-nor-aporphin (VI+ HCl). Das Dichlorhydrat (V) wurde in Methanol gelöst und mit 2 N Schwefelsäure und berechneter Menge $NaNO_2$ diazotiert. Nach dem Zersetzen der Diazonium-gruppe durch Erhitzen bei 100°C., wurde die Lösung mit Salzsäure und Zinkpulver entfärbt. Die mit Aether gewaschene Lösung wurde alkalisiert und mit Aether extrahiert. Durch Versetzen mit Salzsäure zum Aether-rückstand das racem. Aporphin als Chlorhydrat isoliert. Prismen aus Wasser. Schmp. 256–262°C. (zers.). Gefunden: C, 67.41; H, 7.35. Berechnet für $C_{22}H_{27}NO_3 \cdot HCl$ (389,5): C, 67.78; H, 7.19%.

Die racem. freie Base (VI) krystallisiert aus Aether in grossen Tafeln. Schmp. 105–107°C. Gefunden: C, 74.77; H, 7.64; N, 4.06. Berechnet für $C_{22}H_{27}NO_3$ (353): C, 74.79; H, 7.65; N, 3.97%.

Des-N-diäthyl-3,6-dimethoxy-5-äthoxy-nor-aporphin-jodäthylat (VII). Das Jodäthylat (Schmp. 184–186°C. (zers.)) vom obigen Aporphin (VI) wurde durch Kochen mit 11% NaOH in die des-N-Diäthyl-base umgewandelt. Da die letztere keine Neigung zur Krystallisation zeigte, wurde sie als Jodäthylat (Schmp. 160–164°C.) analysiert. Gefunden: C, 56.96; H, 6.82; N, 2.20. Berechnet für $C_{26}H_{36}NO_3J + \frac{1}{2}H_2O$ (546): C, 57.14; H, 6.78; N, 2.56%.

3,6-Dimethoxy-5-äthoxy-8-vinyl-phenanthren (VIII). Das oben genannte Jodäthylat (VII) wurde durch Kochen mit methanolischem Natron desaminiert. Der Vinyl-Körper wurde mit Aether gesammelt und aus Aethanol umkrystallisiert. Prismen. Schmp. 79–81°C.⁽⁵⁾ Gefunden: C, 77.48; H, 6.44. Berechnet für $C_{20}H_{20}O_3$ (308): C, 77.92; H, 6.49%.

(5) Das Dimethoxy-äthoxy-vinyl-phenanthren aus Tuduranin schmilzt bei 108°C. (loc. cit., S. 263 Anm.)

Die Vinyl-seitenkette wurde durch Oxydation mit Kalium-permanganat in Aceton (bei 40–45°C.) ins Carboxyl verwandelt. Die 3,6-Dimethoxy-5-äthoxy-phenanthren-carbonsäure (IX) krystallisierte in Prismen und schmolz bei 185–187.5°C., also um etwa 7°C. höher als die 3-Aethoxy-5,6-dimethoxy-phenanthren-8-carbonsäure, bereitet aus Tuduranin.

Alle Analysen wurden von Firma Takeda in Osaka ausgeführt, dafür sprechen wir unseren besten Dank aus.

An Electron Diffraction Study of the Protective Coating on Metals and Alloys (*Continued*): the Acid-Proof Surface of Ferrosilicon (Duriron).

By Shigeto YAMAGUCHI.

(Received June 27, 1941.)

Introduction. It is well-known that an alloy⁽¹⁾ of Fe and Si containing about 14% Si is one of the few alloys capable of resisting the corrosive action of sulphuric acid, but the state of this acid-proof surface as well as the surface substance produced here inhibiting the corrosive action of the acid have escaped study, because it is very difficult to detect such thin films by the usual methods except the electron diffraction method. The present study by the latter method can successfully produce the entity of the protective coating obtained over the silicon-iron alloy immersed in sulphuric acid solutions.

When aluminium bronze was heated in the air, electron diffraction analyses only γ -Al₂O₃ over the surfaces of these alloys.⁽²⁾ The mechanism of this "selective oxidation" is at present being discussed by many investigators throughout the world, but no interpretation regarding this phenomenon can be held as conclusive.^{(3) (4) (5)} A selective oxidation by sulphuric acid solution, not by air, was found through the present study, and consequently this phenomenon can be considered from a point of view other than those assumed by the above investigators.

-
- (1) Woldman and Dornblatt, "Engineering alloys," 1936.
 - (2) I. Iitaka and S. Miyake, *Nature*, **136** (1935), 437; **137** (1936), 457.
 - (3) G. D. Preston and L. L. Bircumshaw. *Phil. Mag.*, **20** (1935), 706.
 - (4) S. Dobinski, *Nature*, **141** (1938), 81; **144** (1939), 510.
 - (5) H. Bienfait, *Nature*, **145** (1940), 190.

Electron Diffraction Experiments. A piece of ferrosilicon ("Duriron") (Si: ca. 15%), whose macro-structure as seen through the microscope consists mainly of Fe-Si solid solution intermixed with a small quantity of Fe_2Si_3 , was adopted as a specimen. The corrosive reagent was sulphuric acid at various concentrations (5~20 N); the experimental results obtained were always the same.

Experiment 1. On immersing the specimen in the sulphuric acid solution, a faint generation of gas bubbles (H_2) was observed for 5~10 minutes, and then this phenomenon ceased. The surface of the specimen in this state has a gray colour and possesses a practically perfect acid-proof nature. An electron diffraction analysis was made on this surface. The four spacings corresponding to the four weak rings observed in the diffraction pattern here obtained were determined by repeating the experiment about twenty times.* However, since it was difficult to determine the entity of the substance giving these four rings on the basis of these four spacings alone, further experiment was carried out.

Table

d	d_{obs}	$d_{\text{x-ray}}$	$h \ k \ l$	I_{obs}
—	—	4.90	1 1 0	—
3.60	3.60	3.58	2 0 0	m
—	3.00	2.99	2 1 1	s
2.15	2.16	2.20	3 1 0	s
1.84	1.84	1.87	3 2 1	s
—	1.53	1.56	4 2 0	f
1.35	1.36	1.37	4 3 1	s
—	1.26	1.28	5 2 1	s
—	1.08	1.13	5 3 2	f

d : Spacings characteristic of the surface of the sample.

d_{obs} : Spacings of α -cristobalite crystal.

$d_{\text{x-ray}}$: Spacings of α -cristobalite observed by x-ray.

$h \ k \ l$: Miller Indices.

I_{obs} : Intensity of the rings observed here.

Experiment 2. As may be suggested in Experiment 1, the crystals producing the above four spacings must be a weak electron scatterer, i.e., the existence of silica (SiO_2) on the acid-resisting surface of Duriron is suspected. According to our physical and chemical studies the following modifications of SiO_2 are known:

* It was vain to expect that the diffraction rings from α -Fe (body-centred structure) will be observed here. This fact suggests the formation of some protective coating over the specimen, since a heavy metal Fe diffracts intense electron beam.

α - and β -Cristobalite

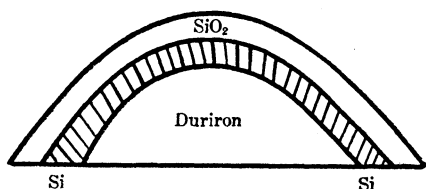
α - and β -Tridymite

α - and β -Quartz.

Of these six modifications the existence of α -cristobalite is not only the most probable, but also it is the form appearing at low (room) temperature.⁽⁶⁾ The present author carried out an experiment here: pure α -cristobalite was chemically prepared and the diffraction pattern, consisting of many obvious rings, from α -cristobalite was directly compared with that from the surface of Duriron passive to sulphuric acid.

The thin film of α -cristobalite for the experiment was produced by making beforehand a film of water-glass over a platinum wire-gauze and then by dropping hydrochloric acid upon it.* The values of spacings determined with the rings from pure α -cristobalite were, as listed in the table, in accordance with those of α -cristobalite by X-ray study. As may be seen in the table, the values of d agree with those of d_{obs} satisfactorily, and therefore there is no room for doubt that the acid-proof surface of ferrosilicon (Duriron) is coated with small crystals of α -cristobalite.

Discussion. Under the same conditions, not only Fe but also Si in the solid solution of the iron silicon alloy must be attacked by the corrosive molecule or ion; but the reaction product of the former is easily soluble in water,** whereas that from the latter is insoluble in water. It is chemically well-known that pure silicon is practically unattacked by common mineral acids (HCl, H_2SO_4 , HNO_3 , etc.). However, the present study concludes that the silicon surface immersed in acid is coated with SiO_2 (α -cristobalite) small crystals. Since the surface or the superficial



layer of Duriron immersed in acid is α -cristobalite small crystals, the second layer lying below the SiO_2 layer should be chiefly silicon or the silicon-rich layer, and below this layer lies the alloy substrate. A picture of the condition of the layers imparting the acid resistant property is shown in the figure.

The iron in the alloy is coated with Si and SiO_2 which are both resistant toward acid; as it were, "a protective double layer" exists on the iron alloy. It is due to this double layer that the iron silicon alloy is able to resist satisfactorily the attack of sulphuric acid.

(6) T. F. W. Barth, *Am. J. Sci.*, **23** (1932), 350; **24** (1932), 97.

* The platinum wire-gauze used here has been explained many times in my previous papers; e.g., *Sci. Papers Inst. Phys. Chem. Research (Tokyo)*.

The NaCl solution produced over the wire-gauze was removed with a small piece of clean filter paper.

** Fe in the solid solution exists in the same state as in metallic iron, because the ferrosilicon used here contains no compound between Fe and Si.

As a matter of fact, the corrosive solution (sulphuric acid) altered the colour of ferricyanide solution to blue.

When Fe in the solid solution is removed by the acid and Si remains adhering to the metal substrate, many small protuberances consisting of Si possessing free bond are produced on the surface of this alloy. This silicon atom has a large chemical affinity and can give SiO_2 more easily than ordinary silicon. Although the gaps are partly packed with SiO_2 crystals, the recrystallization of the active silicon, i.e., the metallic bond formation of Si helps partly the packing of the gaps.

The phenomenon of formation of SiO_2 over the ferrosilicon is doubtlessly selective oxidation of the alloy taking place in solution. The "selective oxidation" which has been often discussed only with the oxide obtained in air can here be considered from another point of view.

The selective oxidation of Duriron by sulphuric acid is realized as a result of the following chemical and physical processes:

(1) Fe, a component weak towards acid is removed from the metal surface,

(2) Si, a component strong towards acid remains over the metal surface, becoming a protective coating of SiO_2 , and recrystallization of Si and SiO_2 occurs in order to stretch over the surface and covering the metal substrate. If the analogy between this selective oxidation in solution and that in air is permitted, in the latter environment also the processes (1) and (2) should take place. When on the surface of aluminium bronze oxidation by air takes place, process (1) results in that the CuO produced on the surface exfoliates, because it is produced comparatively coarse and does not adhere strongly to the metals substrate, while the $\gamma\text{-Al}_2\text{O}_3$ produced over the alloy adheres strongly to the ground metal, for both of these oxide coatings are very thin, compact and strong as were verified in the previous study of the present author.⁽⁷⁾

In conclusion, I wish to express my deep thanks to Dr. Ichiro Iitaka, under whose direction this work has been undertaken, for his many important suggestions, to Prof. S. Mizushima for his sincere interest. I also take this opportunity in thanking the Nippon Gakuzyutsu Shinkokwai for the financial grant through the auspices of its Corrosion Committee.

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Research, Tokyo.*

(7) S. Yamaguchi: *Sci. Papers Inst. Phys. Chem. Research (Tokyo)*, **36** (1939), 463; I. Iitaka and S. Yamaguchi: *Nature*, **144**, (1939), 1090.

Researches on Camphor, Borneol and Their Allied Substances (Continued and Concluded).

By Seichi YAMADA.

(Received May 6, 1941.)

V. The Dehydration of Borneol and Isoborneol. (1) *The dehydration of borneol and isoborneol with $\text{H}_2\text{SO}_4 \cdot 3\text{H}_2\text{O}$.* Borneol (m.p. 205°C ., $[\alpha]_D +18.62$) and isoborneol (m.p. $209\text{--}210^\circ\text{C}$. in a sealed tube $[\alpha]_D -15.72$) 10 g. of each was taken in a distilling flask, to which 0.4 c.c. of $\text{H}_2\text{SO}_4 \cdot 3\text{H}_2\text{O}$ (in volume 4%) was added; and being heated at $140\text{--}145^\circ\text{C}$. for a definite time the water formed by the reaction accompanying a small quantity of camphene was distilled out. The reaction product was put into some water to be extracted with ether; and the ether solution was washed with a dilute solution of sodium carbonate and was dried to distil off the ether, and then it was fractionally distilled.

No.	Sample	Heat. hours	Yield %	Main fraction (camphene)				Fraction of higher boiling point			
				Yield %	B.p. $^\circ\text{C}$.	M.p. $^\circ\text{C}$.	$[\alpha]_D$	Yield %	B.p.	d_4^{20}	n_D^{20}
1	borneol	5	90	62	155–161	42–45	+3.3	13	150–167 ¹⁰ mm		
2	„	10	93	63	155–166	43–45	+1.8	12	147–173 ¹¹ „		
3	„	15	87	58	155–161	42–44	0	10	148–168 ¹¹ „		
4	iso-borneol	2	95	47	152–160	43–52	+4.4	20	120–147 ⁵ „		
5	„	10	89	56	154–163	47–48	+0.5	18	120–153 ⁵ „	0.955	1.493
6	„	15	91	50	152–161	42–45	0	11	120–148 ⁵ „	0.956	1.493

The mixture of fractions (1), (2), (3) of higher boiling points was fractionally distilled, and a colourless viscous compound to be considered as di-*d*-bornyl ether was obtained:—

B.p.	d_4^{20}	n_D^{20}	$[\alpha]_D^{27}$ (in alcohol)	M.R.	
				obs.	calc. for $\text{C}_{20}\text{H}_{34}\text{O}$
134–137 ² mm	0.9564	1.4927	+41.68	88.15	87.40

Found: C, 82.93, H, 11.73. Calculated for $\text{C}_{20}\text{H}_{34}\text{O}$: C, 82.67; H, 11.81%.

This fraction was treated with hydrogen iodide (b.p. $125\text{--}127^\circ\text{C}$.) at 130°C . for an hour; and from the reaction product, crystal of borneol (its phenylurethane m.p. $135\text{--}137^\circ\text{C}$.) was obtained.

On the other hand, this fraction manifested no colour reaction when conc. nitric acid was added to it; and when it was heated, a yellow precipitation of camphor-like odour issued.

Next, fractions (4), (5), (6) of higher boiling points were collected

and fractionally distilled, and compounds to be considered as di-*d,l*-isobornylether were obtained:—

B.p.	d_4^{20}	n_D^{20}	M.R.
136—145 ^{2.5} mm	0.9672	1.5010	90.29

Found: C, 82.22, H, 11.37. Calculated for $C_{20}H_{34}O$: C, 82.67, H, 11.81%.

By treating this with hydrogen iodide, alcohol was obtained, from which phenylurethane (m.p. 139—139.5°C.) was obtained.

By treating with conc. nitric acid, it changed to a green colour, which grew reddish brown when heated. Again, when it was diluted, a yellow precipitation of camphor-like odour was obtained.

(2) *The Dehydration of Borneol with Alumina.* Borneol (m.p. 205°C., $[\alpha]_D + 18.62$) was passed over alumina (Merk) heated at 350°C. at the rate of about 5 g. per hour; and the reaction product, accompanying a trace of water, was fractionally distilled. The result was as follows:—

Fraction	B.p. °C.	Yield (g.)	d_4^{20}	n_D^{20}	M.R.	$[\alpha]_D^{12}$ in alcohol
1	33—100	2.4	—	—	—	—
2	100—145	7.1	0.8356 ²⁰	1.4690 ²⁰	45.37	0
3	145—155	38.8	0.8312 ⁴⁰	1.4596 ⁴⁰	44.82	+0.23
4	155—155.5	36.6	0.8286 ⁴⁰	1.4627 ⁴⁰	45.22	+0.58
5	155.5—161	6.4	0.8459 ²⁰	1.4730 ²⁰	45.14	+2.31
6	161—	5.5	—	—	—	—

From the main fractions (3) and (4), solid camphene (m.p. 52—53°C., $[\alpha]_D + 0$) was obtained.

(3) *The action of $H_2SO_4 \cdot 3H_2O$ on bornyl acetate.* When borneol (m.p. 204°C., $[\alpha]_D + 38.44$) was heated with glacial acetic acid and potassium acetate, the following acetic ester⁽³³⁾ was obtained:

B.p.	d_4^{20}	n_D^{20}	$[\alpha]_D^{11}$
98 ¹¹ mm	0.9864	1.4655	+42.75

To 20 g. of this ester, 0.8 c.c. of $H_2SO_4 \cdot 3H_2O$ was added; and, after a reaction of 10 hours at 140—145°C., the reaction product was fractionally distilled to separate it into camphene and the ester as completely as possible:

Fraction	B.p.	Yield %	d_4^{20}	n_D^{20}	$[\alpha]_D^{12}$ in alcohol
1	30 - 82 ⁵ mm	8.8	0.9511	1.4727	—
2	82—84	77.0	0.9813	1.4657	+39.13
3	residue	12.1	—	—	—

(33) Bertram, *Ann.*, **231**, 304.

Of the reaction products, to the estimation of camphene, the bromine absorption was adopted, and to that of borneol and isoborneol, the phthalic anhydride method; and it was found that the reaction products were 96.5 moles% bornylester, 0.5 mole% isobornylester, and 3 moles% camphene.

(4) *Conversion of isobornylacetate to camphene by the action of $\text{H}_2\text{SO}_4 \cdot 3\text{H}_2\text{O}$.* Inactive isobornylacetate (b.p. $79.5\text{--}81.5^{3.5\text{mm}}$, d_4^{20} 0.9848, n_D^{20} 1.4640, saponification value (obs.) 285.8, (calc.) 286) was reacted with $\text{H}_2\text{SO}_4 \cdot 3\text{H}_2\text{O}$. From the saponification value 103.2 of the reaction product, it was calculated out that the proportions of the ester and camphene were 22 moles% and 78 moles%.

(5) *The Conversion of camphene to isoborneol by the action of $\text{H}_2\text{SO}_4 \cdot 3\text{H}_2\text{O}$.* Camphene (5 g.) was dissolved in glacial acetic acid (2.5 g.), and the solution was treated with $\text{H}_2\text{SO}_4 \cdot 3\text{H}_2\text{O}$ (0.2 c.c.). From the saponification value 168.2 of the reaction product, the proportions of isobornylester and camphene were calculated out to be 50 moles% and 50 moles%.

(6) *The dehydration of isoborneol with phthalic anhydride.* Isoborneol (m.p. $209\text{--}210^\circ\text{C}$., in a sealed tube, $[\alpha]_D^{15}$ -15.72 in alcohol) 20 g. and phthalic anhydride (2 moles) were reacted under the following conditions:

No.	React. temp. $^\circ\text{C}$.	React. hours h	Reaction product		Camphene obtained from the dehydrated oil		
			Ester (g.)	Dehydrated oil (g.)	B.p. $^\circ\text{C}$.	M.p. $^\circ\text{C}$.	$[\alpha]_D$
1	140–145	11	19	6.5	153–163	48–52	+ 1.34 ¹³
2	110–115	13	29.5	3.5	150–157	45–47	+25.25 ¹⁴
3	80–85	46	35.2	1.3			

The ester No. 1 was separated into 10 g. of acid ester (m.p. 164°C ., $[\alpha]_D^{25}$ $+43.10$, $C=0.99$ in alcohol), 10 g. of borneol and 6.3 g. of neutral ester (m.p. $100\text{--}101^\circ\text{C}$., $[\alpha]_D^{25}$ $+27.93$, $C=0.806$ in alcohol). By the saponification of the ester, borneol (m.p. $205\text{--}206^\circ\text{C}$) was isolated; and when the mixture of it and other borneol was put to a mixed fusion, no depression of the melting point was seen. The ester No. 2 was separated into 10 g. of acid ester (m.p. 152°C ., $[\alpha]_D$ -20) and 3 g. of neutral ester (m.p. 92°C ., $[\alpha]_D$ -22). These esters were saponified, and isoborneol of m.p. 207°C ., in a sealed tube and $[\alpha]_D$ -2 was obtained from the former ester, and isoborneol of m.p. 203°C . in a sealed tube and $[\alpha]_D$ -7 from the latter. Moreover, to isoborneol (m.p. $212\text{--}213^\circ\text{C}$. in a sealed tube $[\alpha]_D$ -34.42) 2 moles of phthalic anhydride was added; and after a reaction at $110\text{--}115^\circ\text{C}$., camphene $[\alpha]_D^{25}$ $+49.33$) was obtained.

(7) *Hydration of camphene.* From bornyl chloride (m.p. 131°C ., $[\alpha]_D$ $+31.29$), by means of the following method, diverse camphenes were obtained.

(i) By the reaction of aniline⁽³⁹⁾ for over 10 hours, the camphene produced was of m.p. 49–52°C. and $[\alpha]_D^{20}$ 0.

(ii) Yellow lead oxide⁽⁴⁰⁾ was heated at about 250°C., and bornyl chloride was acted on it. The camphene thus produced was of m.p. 49.5°C. and $[\alpha]_D^{19} + 12.86$.

(iii) Camphene produced by the reaction of phenol⁽⁴¹⁾ was of m.p. 48–50°C. and $[\alpha]_D^{18.5} + 72.69$.

The specific rotation of the isoborneols obtained by the hydration of the 3 kinds of camphenes shown above is as follows:

(i) The isoborneol obtained from the camphene $[\alpha]_D^{19}$ 0: m.p. 209 (in a sealed tube), $[\alpha]_D^{19}$ 0.

(ii) The isoborneol obtained from the camphene $[\alpha]_D^{19} + 12.86$: m.p. 210°C. (in a sealed tube): $[\alpha]_D^{19} - 0.54$.

(iii) The isoborneol obtained from the camphene $[\alpha]_D^{18.5} + 72.69$: m.p. 208°C. (in a sealed tube), $[\alpha]_D^{19} - 5.13$.

The content of borneol in the isoborneol, obtained as above, estimated by means of the phthalic anhydride method, was 10%.

Further, the influence of the time to the hydration of camphene $[\alpha] + 72.69$ was investigated to be as follows:

No.	React. hours	Isoborneol ester				Isoborneol	
		B.p.	d_4^{20}	n_D^{20}	$[\alpha]_D$ °C.	M.p.* °C.	$[\alpha]_D$ in alc. °C.
1	1/3	74–77 ^{3.5} mm	—	—	–11.47 ²⁰	207–208	–10.56 ¹⁹
2	4 1/3	86 ⁷	0.9825	1.4656	– 7.83 ⁹	208.3	– 5.13 ⁹
3	27 1/2	88 ⁶	0.9825	1.4652	– 4.14 ⁹	—	—
4	118	85 ⁴	0.9813	1.4650	– 0.78 ⁹	206	± 0 ⁹

* Measured in a sealed tube.

From No. 1 unreacted camphene (m.p. 51–53°C., $[\alpha]_D^{22} + 14.01$ was separated.

(i) By the reaction between bornyl chloride and phenol, a camphene $[\alpha]_D + 72.69$ was obtained, which was colourless even after hydration, and there was no change of colouration.

(ii) By the reaction between bornyl chloride and yellow lead oxide or aniline, a camphene $[\alpha] + 12.86$ was obtained, which became yellow when hydrated.

(iii) By the dehydration of borneol with alumina, a camphene $[\alpha]_D$ 0 was obtained, which, when hydrated, became faintly brown at first and changed to blackish green afterwards. Further, it became crimson red when thrown into water. This colour reaction is a phenomenon also seen in the case of hydrocarbons formed when dimethylborneol is dehydrated with $H_2SO_4 \cdot 3H_2O$.

(39) Ullmann and Schmidt, *Ber.*, **43** (1910), 3202.

(40) Tetsusaku Ikeda, *Proc. Sci. Inst. Japan*, **4** (1925), 503.

(41) A. Reychler, *Ber.*, **29** (1896), 696.

(iv) When borneol is dehydrated with $\text{H}_2\text{SO}_4 \cdot 3\text{H}_2\text{O}$, a camphene $[\alpha]_{\text{D}} 0$ is obtained, which, in the course of hydration, becomes to a faint purple red colour at first and then changes to a faint reddish brown colour afterwards. When thrown into water, it becomes to a faint yellowish brown colour. As has been described above, according as the preparation differs, camphenes behave differently in the colour reaction by hydration. This is to be considered due to the accompanying impurities.

(8) *Racemisation of camphene by $\text{H}_2\text{SO}_4 \cdot 3\text{H}_2\text{O}$.* By the reaction between bornyl chloride and yellow lead oxide, a camphene (m.p. $52.2\text{--}52.9^\circ\text{C}$. $[\alpha]_{\text{D}}^{25} +8.28$) was obtained, to 10 g. of which, 0.4 c.c. of $\text{H}_2\text{SO}_4 \cdot 3\text{H}_2\text{O}$ (0.05 mol) was added and it was heated at $140\text{--}145^\circ\text{C}$. Afterwards the camphene was collected and its rotatory power was examined.

No.	React. hours h	React. product			Camphene			Oily part			
		B.p. $^\circ\text{C}$.	Yield %	$[\alpha]_{\text{D}}$ $^\circ\text{C}$.	M.p. $^\circ\text{C}$.	Yield %	$[\alpha]_{\text{D}}$	Yield %	d_4^{25}	n_{D}^{25}	$[\alpha]_{\text{D}}$
1	12	154–158	72	—	52–52.4	58	0	14	0.847	1.470	+0.6
2	1	153–158	72	+1.76 ²³	53–54	25	+0.3	23	0.853	1.469	+1.6
3	1/6	153–155	71	+5.8	53–54	51	+5.2	2	—	1.470	—

To investigate the influence upon the racemisation of camphene at the temperature of $10\text{--}20^\circ\text{C}$., 13 g. (2.3 moles) $\text{H}_2\text{SO}_4 \cdot 3\text{H}_2\text{O}$ was added to 5 g. camphene, and, after an elapse of 400 hours, it was recognised that racemisation had occurred.

No.	React. hours	React. product		Camphene	
		B.p. $^\circ\text{C}$.	Yield %	M.p. $^\circ\text{C}$.	$[\alpha]_{\text{D}}$
1	20	154–157	50	52–54	+4.8
2	412	155–170	40	48–50	+1.6

(9) *The racemisation of camphene with 50% sulphuric acid.* 5 g. camphene was treated with 0.5 g. of 50% (0.05 moles) sulphuric acid at $50\text{--}60^\circ\text{C}$.

No.	React. hours	Reaction product		Camphene	
		B.p. $^\circ\text{C}$.	Yield %	M.p. $^\circ\text{C}$.	$[\alpha]_{\text{D}}$
1	3	153–155	98	49–50	+5.2
2	24	155–159	80	52	+3.8

(10) *The racemisation of camphene with hydrochloric acid.* 10 g. camphene was treated with 0.4 c.c. $\text{HCl} \cdot 3\text{H}_2\text{O}$ at $140\text{--}145^\circ\text{C}$. Although the rate of reaction was rather slow, it was found that racemisation had occurred to some extent.

No.	React. hours	Reaction product		Camphene	
		B.p. °C.	Yield %	M.p. °C.	$[\alpha]_D$
1	1	155–162	58	51–53	+8.5
2	12	155–162	70	43–53	+5.4

(11) *The racemisation of camphene with acetic acid.* 5 g. camphene was treated with 12.5 g. (5 moles) glacial acetic acid at 50–60°C., and some evidence of racemisation was recognised.

No.	React. hours	Reaction product		Camphene	
		B.p. °C.	Yield %	M.p. °C.	$[\alpha]_D$
1	3	155–156	50	49–53	+6.2
2	12	155–156	60	49–53	+6.0

(12) *The racemisation of camphene with phthalic anhydride.* To 10 g. camphene (m.p. 47–50°C., $[\alpha]_D^{18.5} + 49.33$), a well dried 19 g. (2 moles) phthalic anhydride was added, and the mixture was heated at 140–145°C. for 11 hours. To separate out camphene from the reaction product, the extraction by petroleum ether was adopted instead of steam distillation, and the yield of camphene (b.p. 153–160°C., m.p. 46.5–47.5°C., $[\alpha]_D^{22} + 1.9$) was 50%. Although great precautions were taken not to admit the entrance of any drop of water during the reaction, there was seen at the end of the reaction neutral and acid esters of isoborneol, both insoluble in petroleum ether. When the neutral ester $C_{28}H_{34}O_4$ was recrystallised from its solution in methyl alcohol, the following substance was obtained: Neutral ester, m.p. 99–100.5°C., $[\alpha]_D^{22} - 3.32$ (C=1.8 in alcohol). Found: C, 76.65; H, 8.62. Calculated for $C_{28}H_{38}O_4$: C, 76.66; H, 8.73%.

When the acid ester $C_{18}H_{22}O_4$ was recrystallised from its solution in methyl alcohol, the following substance was obtained: Acid ester, m.p. 169–170.5°C., $[\alpha]_D^{25} - 1.57$ (C=1.91 in alcohol). Found: C, 71.47; H, 7.66; Calculated for $C_{18}H_{22}O_4$: C, 71.48; H, 7.34%.

(13) *The racemisation of camphene with alumina.* 12 g. camphene (m.p. 42–45°C., $[\alpha]_D^{18} + 9.28$) together with a small quantity of steam was passed over alumina heated to 350°C. for 7 hours, and 49% camphene (b.p. 145–156°C., m.p. 46–51°C., $[\alpha]_D^{19} + 1.8$) was obtained.

(14) *The racemisation of camphene by the application of heat.* The above camphene was passed alone through a glass tube heated to 350°C., and the camphene thus obtained was of b.p. 154–158.5°C., m.p. 45.5–46.5°C., $[\alpha]_D^{18} + 9.9$. Therefore, no change was seen.

(15) *The racemisation of isobornyl acetate by the Bertram Walbaum's method of hydration.* The writer, dissolving camphene $[\alpha]_D^{18.5} + 64.40$ in

absolute alcohol after Kachler and Spitzer's method⁽⁴²⁾ and passing hydrogen chloride through the solution cooled with ice, obtained isobornyl chloride (m.p. 146–148°C., $[\alpha]_D^{25} -27.08$ ($C=3.46$ in alcohol) in yield of 85%. It was heated to 70°C. with silver acetate in a sealed tube and there was obtained, in addition to a great quantity of camphene ($[\alpha] +58.29$), an extremely small quantity of ester ($[\alpha]_D^{25} -5.71$). On the other hand, isborneol (m.p. 212–213°C., in a sealed tube) was treated both with acetic anhydride and potassium acetate for indefinite hours, and the following ester of isborneol was obtained:

No.	React. hours	Ester of isborneol				
		Yield (g.)	B.p.	$[\alpha]_D$	d_4^{20}	n_D^{20}
1	3	11	97–99 ¹¹ mm	–46.73 ¹⁸ $C = 4.46$ in alcohol	0.9882	1.4649
2	2	11	80–82 ¹	–50.29 ¹⁸ $C = 4.23$ „	0.9867	1.4659
3	1	10.5	76–77 ³	–51.98 ¹⁸ $C = 5.05$ „	0.9867	1.4623

By saponifying the esters 2 and 3, isborneols $[\alpha]_D -33.18$ and $[\alpha]_D -34.10$ were obtained respectively.

To isobornyl acetate (b.p. 76–77°C.^{3mm}, d_4^{20} 0.9876, n_D^{20} 1.4649, $[\alpha]_D^{20} -47.81$), each of the 50% sulphuric acid, acetic acid, and the mixture of the two was added separately, and the reaction was excited at 50–60°C. As to the specific rotation of the ester, there was no change whatever in the former two cases, while a decrement was observed in the case of the acid mixture, the detail being as follows:

No.	Sample (g.)	Catalyser (g.)	React. hours	Reaction product				
				Yield (g.)	d_4^{20}	n_D^{20}	$[\alpha]_D^{23}$	Br ₂ test
1	4	acetic acid 10	3	4	0.9884	1.4644	–47.80	—
2	4	50% H ₂ SO ₄ 0.4	3	4	0.9840	1.4644	–47.51	—
3	4	acetic acid 10 50% H ₂ SO ₄ 0.4	1/3	4	0.9833	1.4649	–45.62	+
4	15	acetic acid 33 50% H ₂ SO ₄ 1.5	4	15	0.9813	1.4631	–17.08	+

No.	Isobornyl acetate				
	Yield (g.)	B.p.	d_4^{20}	n_D^{20}	$[\alpha]_D$
1	3.5	71–72 ^{2.5} mm	0.9856	1.4648	–47.89
2	3.2	70–71 ^{2.5}	0.9856	1.4648	–47.43
3	3.2	71–73 ^{2.5}	0.9852	1.4648	–45.58
4	11.5	115–116 ³	0.9813	1.4651	–19.01

(42) *Ann.*, **200**, 345.

Of the reaction products of sample No. 4, camphene was estimated by the bromine absorption to be 1.3%.

Accordingly, the reaction products were distilled, and, using the earlier distillate after Balbiano's method,⁽⁴³⁾ formed a needle-shaped addition product (m.p. 185.5–186°C.) composed of mercuric acetate and camphene, and thus the presence of camphene was confirmed. When the reaction product was once more distilled after the elapse of a whole day, a distillate b.p. 80–91°C.^{3mm}, d_4^{20} 0.9832, n_D^{20} 1.4653 was obtained; while when the distillation was tried after the elapse of 20 days, the distillate was of b.p. 81–83.5°C.^{3.5mm}, d_4^{20} 0.9863, n_D^{20} 1.4651. Thus an extraordinary variation⁽⁴⁴⁾ in the boiling point was shown. The ester, which was distilled out in the rear, was saponified; and it was found that the isoborneol thus obtained had the following properties and had accompanied neither camphenhydrate nor camphene and others.

M.p.	$[\alpha]_D^{25}$ in alcohol	$[\alpha]_D^{25}$ in toluene	M.p. of <i>p</i> -Nitrobenzoate	Methoxy value of what was methylated with HCl and CH ₃ OH
211–212°C. (in a sealed tube)	–16.74	–8.79	129°C.	10.9

No trace of water was generated even when isoborneol was heated to 220°C. for half an hour, and no decolourisation of bromine water was observed.

VI. The Dehydration of Dimethylborneol. (1) *The dehydration of dimethylborneol with H₂SO₄·3H₂O.* Dimethylcamphor was reduced with metallic sodium and alcohol and then treated with phthalic anhydride at 110–115°C. To 50 g. of the dimethylborneol (m.p. 45–50.8°C., $[\alpha]_D^{25}$ +49.05) thus obtained, 2.5 c.c. of H₂SO₄·3H₂O was added, and the mixture was heated at 140–145°C. for 15 hours. The reaction product obtained was 43.4 g. It was fractionally distilled under reduced pressure and separated into the 1.5 g. unchanged alcohol (b.p. 82–95°C.^{5mm}) and 32 g. hydrocarbons (b.p. 48–82°C.^{5mm}). The hydrocarbons were again fractionally distilled under the normal pressure over metallic sodium 8 times repeatedly.

No.	B.P. °C.	yield %	d_4^{25}	n_D^{25}	$[\alpha]_D$	M.R.		
						obs.	calc. C ₁₂ H ₂₀ F ₁	<i>d</i>
1	177–182	1	0.8510	1.4681	+14.17	53.51	52.75	0.76
2	182–185	5	0.8557	1.4702	+15.45	53.49	„	0.74
3	185–186	11	0.8570	1.4715	+17.51	53.53	„	0.78
4	186–187	17	0.8567	1.4721	+15.51	53.61	„	0.86
5	187–188	24	0.8557	1.4731	+15.03	53.77	„	1.02
6	188–190	6	0.8553	1.4744	+14.01	53.93	„	1.18
7	190–191	8	0.8543	1.4760	+12.74	54.16	„	1.41

(43) Balbiano and Paolini, *Ber.*, **35** (1902), 2994; **36** (1903), 3575; **48** (1915), 394.

(44) Tetsusaku Ikeda, *Proc. Sci. Inst. Japan*, **7** (1928), 269; Yasuzi Fujita, *ibid.*, **7**, 1.

No.	Sample B.p. °C.	Wt. g.	Volatile neutral substance
1	177—187	29	21
2	188—191	35	25

Hydrocarbons were put to ozone oxidation in a chloroform solution.

The volatile neutral substances were separated from each other by fractional distillation.

No.	B. p. °C.	yield g.	d_4^{25}	n_D^{25}	Remarks
1	55— 87 ^{7mm}	3.3	0.9320	1.4690	colourless
	87— 96	1.8	0.9614	1.4710	faint yellowish green
	96—120	9.0	0.9951	1.4736	faint yellowish green, viscous
2	48— 86	7.0	0.9026	1.4699	colourless
	86— 96	0.5	—	1.4714	faint yellowish green
	96—130	10.6	0.9881	1.4723	faint yellowish green, viscous

Fractions of similar properties were collected together and the mixture was fractionally distilled three times more.

Frac- tion	B. p. °C.	yield g.	d_4^{25}	n_D^{25}	M. R.		Appearance	Analyses obs.	
					obs.	calc.		C %	H %
1	51— 56 ^{7mm}	2.0	0.8803	1.4677	51.75	$C_{12}H_{20}F_1$ 52.75	colourless	84.77	11.67
2	56— 74	0.9	—	—	—	—	"	—	—
3	74— 79	4.5	0.9290	1.4706	49.90	$C_{11}H_{18}O$ 48.61	"	82.25	11.11
4	79— 90	3.3	0.9525	1.4727	48.85		"	78.18	11.51
5	90—120	2.9	0.9772	1.4756		$C_{12}H_{20}O_2$ 55.41	yellowish green	75.67	10.24
6	120—126	9.2	1.0124	1.4749	54.52		"	73.65	10.31
7	126—129	1.6	1.0124	1.4740	54.18		"	71.55	10.66

Calc. for $C_{12}H_{20}$: C, 87.80; H, 12.20%.
 $C_{11}H_{18}O$: C, 79.52; H, 10.84%.
 $C_{12}H_{20}O_2$: C, 73.47; H, 10.21%.

Each of the fractions 5–7 decomposed by every distillation and an abundant quantity of acid remained every time. About these acids, some references will be made later. It is considered that fraction 1 is mainly composed of hydrocarbons, fraction 3 contains about 60% of the compound $C_{11}H_{18}O$, fraction 4 is mainly composed of the compound $C_{11}H_{18}O$, fraction 5 contains about 50% of the compound $C_{12}H_{20}O_2$ and the fraction 6 and 7 are both mainly composed of the compound $C_{12}H_{20}O_2$.

Fractions 3 and 4 were mixed together, and the mixture was fraction-

ally distilled repeatedly to separate out a principal component as follows:

B.p.	d_4^{25}	n_D^{25}	$[\alpha]_D^{19}$	M. R.	
				obs.	Calc. for $C_{11}H_{18}O$
72–73°C. 6 mm	0.9473	1.4712	+27.06	48.87	48.61
(C=2.62 in alcohol)					

Found: C, 79.94; H, 11.26. Calculated for $C_{11}H_{18}O$; C, 79.52; H, 10.84%.

Semicarbazone is formed with a great difficulty and it decomposes at 243.6–243.9°C. 2 g. of the oxygen compound described above was reduced with metallic sodium and alcohol, and a reaction product having the following properties was obtained.

B.g.	d_4^{25}	n_D^{25}	$[\alpha]_D^{25}$	M. R.	
				obs.	Calc. for $C_{11}H_{20}O$
82–86°C 6 mm	0.9581	1.4831	+1.5	50.07	50.12
(C=1.373 in alcohol)					

Found: C, 78.25; H, 12.05. Calculated for $C_{11}H_{20}O$; 78.57; H, 11.90%.

The phenylurethane of this substance is a white needle which melts at 147.6–148.7°C.

Fraction 6 was purified by carefully distilling it, and a yellowish green viscous liquid was obtained.

B.p.	d_4^{25}	n_D^{25}	$[\alpha]_D^{10}$	M. R.		Δ
				obs.	Calc. for $C_{12}H_{20}O_2$	
120–123°C 6 mm	1.0087	1.4746	–6.87	54.60	55.44	–0.84
(C=1.455 in alcohol)						

Found: C, 73.39; H, 10.41. Calculated for $C_{12}H_{20}O_2$; C, 73.47; H, 10.21%.

Moreover, the hydrocarbons described above was put to ozone oxidation in its solution in benzene, and the oxidation product thus obtained was distilled under reduced pressure. There was obtained a yellowish green and viscous compound $C_{12}H_{20}O_2$, whose rotatory power was of opposite sign as follows:

B.p.	d_4^{25}	n_D^{25}	$[\alpha]_D$	M. R.		Δ
				obs.	Calc. for $C_{12}H_{20}O_2$	
112–114°C. 4 mm	1.0166	1.4749	+38.91	54.27	55.44	–1.17

To 2 g. of the compound $C_{12}H_{20}O_2$, 20 c.c. of nitric acid of 1.29 specific gravity was added. The mixture was heated for 15 hours over a hot water bath and 0.8 g. of an acidic substance was obtained. When it was left alone for a long time, crystals of camphoric acid (m.p. 183°C.) was obtained; and after an analysis made on its silver salt, the following results were obtained: Found: Ag, 52.84. Calculated for $C_{10}H_{14}O_4Ag_2$: Ag, 52.15%.

A reaction product was obtained by reducing 10 g. of the compound $C_{12}H_{20}O_2$ with metallic sodium and alcohol. The reaction product was

separated by steam distillation into a 3.7 g. volatile substance and a 3.4 g. unvolatile substance; and, by fractionally distilling the former, there was obtained a principal component of the following properties:

B.p.	d_4^{25}	n_D^{25}	$[\alpha]_D^{15}$	M.R.		appearance
				obs.	Calc. for $C_{12}H_{24}O_2$	
140—143°C. 6 mm	0.9907	1.4833	—13.31 (C=1.578 in alcohol)	57.71	58.47	faint yellow, viscous

Found: C, 72.18; H, 11.58. Calculated for $C_{12}H_{24}O_2$: C, 72.00; H, 12.00%.

As crystals precipitated out from the latter, they were recrystallised from ether and petroleum ether, and two different compounds were obtained. One of them, a colourless needle crystal (m.p. 82–83°C.), was insoluble in petroleum ether but soluble in both ether and alcohol. The other, a colourless needle (m.p. 114–115°C.) assembled in an asterisk form, was insoluble in petroleum ether and less soluble in ether than the former crystal. Crystal (I) (m.p. 82–83°C.). Found: C, 66.38; H, 11.62. Crystal (II) (m.p. 114–115°C.) C, 65.82; H, 11.63. Calculated for $C_{12}H_{24}O_2 \cdot H_2O$: C, 66.06; H, 11.93%.

These two kinds of crystals were dried at 80°C. under a reduced pressure and put anew to elementary analysis.

	Decrement of wt. by drying	Theoretical number	M.P. after drying
Crystal I (M.P. 82–83°C.)	7.95 %	8.26 %	83–84°C.
Crystal II (M.P. 114–115°C.)	8.41 %	„	115.8–116.8°C

Crystal (I) Found: C, 71.95; H, 11.99. Crystal (II) C, 71.63; H, 12.41. Calc. for $C_{12}H_{24}O_2$ C, 72.00; H, 12.00%.

To the hydrocarbons (b.p. 185–190.5°C., d_4^{25} 0.8562, n_D^{25} 1.4726, $[\alpha]_D^{15}$ +12.66) described above, some 50% sulphuric acid and glacial acetic acid were added and the mixture was heated at 70–80°C. for 25 hours. A great majority was recovered as unreacted hydrocarbons, and, in addition to these, a small quantity of a polymerisation product was obtained as follows:

B.p.	n_D^{25}	$[\alpha]_D^{24}$	M. R.			
			obs.	Calc. for $C_{12}H_{20}F_1$	obs.	Calc. for $C_{24}H_{38}F_2$
161–162°C 5 mm	1.4966	+14.83	106.6	105.5	106.1	103.3

Found: C, 87.95; H, 12.56. Calc. for $(C_{12}H_{20})_2$: C, 87.80; H, 12.20. Calc. for $C_{24}H_{38}$ C, 88.34; H, 11.66%.

The determination of molecular weight (by Rast's method)

obs.	$(C_{12}H_{20})_2$	$C_{24}H_{38}$
329.5	328	326

(2) *The dehydration of dimethylborneol with phosphorus pentoxide.* 10 g. dimethylborneol was taken drop by drop into a flask, which had

already contained 13 g. phosphorus pentoxide and 30 c.c. petroleum ether. When the generation of hydrogen chloride ceased, the content was left alone for several hours. Then it was thrown into ice water and the reaction product was extracted by the aid of ether. The ether was distilled off and the reaction product was fractionally distilled for several times, and there was obtained the following hydrocarbon.

B. p.	d_4^{25}	n_D^{25}	$[\alpha]_D^{25}$	M. R.	
				obs.	Calc. for $C_{12}H_{20}F_1$
192—193°C./2 mm	0.8754	1.4765	—5.76	52.38	52.75

Found: C, 87.66; H, 12.13. Calculated for $C_{12}H_{20}$: C, 87.80; H, 12.20%.

When this hydrocarbon was put to ozone oxidation, a single oxidation compound $C_{12}H_{20}O_2$ was obtained as follows:

B. p.	d_4^{25}	n_D^{25}	$[\alpha]_D^{25}$	M. R.	
				obs.	Calc. for $C_{12}H_{20}O_2$
100—105°C./2 mm	1.0026	1.4765	—17.78	55.20	55.44

Found: C, 73.34; H, 10.49. Calculated for $C_{12}H_{20}O_2$: C, 73.47; H, 10.21%.

This compound, to be considered as a diketone, has decomposed during distillation, forming an acidic substance, which gave trans-camphoric acid (m.p. 174°C.) when recrystallised by the aid of ether and petroleum ether. Found: C, 29.29 H, 3.39 Ag, 52.96. Calculated for $C_{10}H_{14}O_4Ag_2$: C, 29.00; H, 3.38; Ag, 52.15%.

(3) *The dehydration of dimethylborneol with phthalic anhydride.* Dimethylborneol was dehydrated, heating it with phthalic anhydride, and the following hydrocarbon was obtained.

B. p.	d_4^{25}	n_D^{25}	$[\alpha]_D^{18}$	M. R.	
				obs.	Calc. for $C_{10}H_{20}F_1$
179—196°C./3 mm	0.8556	1.4710	+7.13	53.44	52.75

Found: C, 87.69; H, 12.50. Calculated for $C_{12}H_{20}$: C, 87.80; H, 12.20%.

To our regret, the quantity of the sample being very small, we could not continue the research further.

In conclusion let me express my sincere gratitude to Prof. Dr. Shigeru Komatsu, my benefactor, Mr. Motoe Hagiwara in the class of Prof. Komatsu of Kyoto Imperial Univ., and Messrs. the late Hiroshi Ogata, Yukio Nomura, Kiyoshi Yamada of the chemical laboratory of the Nippon Camphor & Co., without whose encouragement, advice, help of experiments and loving friendship, these experiments would have never been completed.

On the Catalytic Action of Japanese Acid Earth. XII. The Relation between the Catalytic Activity and Adsorption. II. The Adsorption Isotherms of Water and Acetonitrile for the Earth.

By Koshiro ISHIMURA.

(Received May 14, 1941.)

Naphthalene produces β,β' -dinaphthyl when mixed with dry powdered Japanese acid earth and heated at about 300°C.⁽¹⁾ In this catalytic action, neutral substances containing oxygen such as water, alcohols, ethers and ketones exert a distinct promoting action, while nitrogen-containing substances such as ammonia, amines and nitriles behave as strong poisons. Carbon tetrachloride, chloroform and various hydrocarbons are indifferent to this catalytic action.⁽²⁾

In a previous paper it was reported by the present author⁽³⁾ that with various specimens of the earth a parallel relation holds between the catalytic activity and the adsorptive powers for water, benzene and naphthalene.

It was thought that a promoter and a poison might show different behaviours, when they are adsorbed on the surface of the earth. An investigation was therefore made on the isothermal adsorption of the vapours of water and acetonitrile, one of which is a typical promoter and the other a typical poison.

Apparatus and Procedure. The essential part of the apparatus consists of McBain's sorption balance⁽⁴⁾ suspended in a transparent silica tube which is installed in a thermostat of 25°C. ($\pm 0.01^\circ\text{C}.$) and connected with the reservoir of water or acetonitrile in another thermostat whose temperature may be varied from 0° to 25°C. ($\pm 0.01^\circ\text{C}.$). The spring of the sorption balance is made of a fine fused silica fibre, 0.14 mm in diameter. The diameter of the coils of the spring is 7 mm, the number of the coil is 49 and the total length of the spring without load is 77.16 mm. Previous to the employment the fibre is carefully annealed at 300°C. for 1 hour with the load of 0.3 g. The balance is calibrated throughout the working range by observing the deflections caused by known weights. A small platinum bucket (0.0238 g.) is suspended from the lower end of the spring and known weights are placed on it and the respective elongations of the spring are measured by a cathetometer. The instrument used is capable of giving readings accurate to 0.01 mm. The equation expressing the relation between the load (y in centigramme) and the elongation (x in mm.) is obtained by the method of least square as follows:—

$$y = x/0.9564.$$

(1) H. Inoue and K. Ishimura, this Bulletin, **9** (1934), 431.

(2) K. Ishimura, *Ibid.*, **9** (1934), 521.

(3) K. Ishimura, *Ibid.*, **9** (1934), 493.

(4) J. W. McBain and A. M. Baker, *J. Am. Chem. Soc.*, **48** (1926), 690.

The total weight of a sample weighing 0.2 g. can be determined within the experimental error of 0.1 per cent.

The Japanese acid earth designated D in the previous paper⁽⁵⁾ is dried in a desiccator of sulphuric acid, pulverised and sifted by a sieve of 200 mesh. It is kneaded with a small quantity of water to small balls, about 2 mm. in diameter. Eight balls thus formed are placed on the platinum bucket. The bucket is hung from the lower end of the silica spring and the whole is enclosed in a silica tube, and then heated gradually to 200°C. in an electric furnace and maintained at that temperature for 4 hours under the high vacuum of 0.001 mm., effected by a Cenco Hyvac pump. Then it is cooled and put in the first thermostat (25°C.). The weight of the dry earth is calculated from elongation of the spring.

In order to expel the gas dissolved in the liquid, the vapour of which is to be adsorbed, its reservoir is first cooled with ice and salt and evacuated and then the temperature is raised to the room temperature allowing any gas which has been dissolved to get free. It is again cooled and evacuated. This process of outgassing the liquid and evacuation is repeated until the dissolved gases are completely expelled. Then the reservoir is put in the second thermostat of the required temperature. Now the cock connecting the reservoir and the silica tube is opened and the adsorption experiment is commenced. The elongation of the spring is measured at intervals, until no increase is observed for 3 hours and thus the equilibrium is considered to be attained. Then the cock is closed and the temperature of the second thermostat is raised by some degrees, and the cock is again opened and the second adsorption experiment is carried out. Thus the velocity of adsorption as well as the amount of the substance adsorbed at equilibrium can be measured under varying vapour pressures of the adsorbate. Directly after a series of adsorption experiments is finished, desorption is carried out, which is followed by the second series of adsorption and desorption and so on.

To carry out the desorption the reservoir of the adsorbate is cooled for a while with ice water, or with a mixture of ice and salt. The vapour pressure in the system is thereby depressed and a portion of the adsorbed substance is set free. The cock between the reservoir and the balance room is closed and the system is left to attain the equilibrium. When no more change of the length of the spring is observed and the reading of the manometer become constant for 2 hours the desorption experiment is ended. After the vapour pressure is lowered considerably, the system is evacuated by the pump instead of cooling the reservoir, and the final desorption is carried out by working the pump for 5 hours or more under 0.001 mm. For the measurement of the pressures a McLeod's gauge is used. The values of vapour pressure of water at various temperatures are adopted from Landolt's "Physikalisch-Chemische Tabellen", while those of acetonitrile are calculated by applying Dühring's rule.⁽⁶⁾

Dühling expressed the relationship between the boiling points of two pure substances as follows:—

(5) H. Inoue and K. Ishimura, this Bulletin, **9** (1934), 431.

(6) R. Lorenz, *Z. anorg. allg. Chem.*, **138** (1924), 104; E. H. Leslie and A. R. Carr, *Ind. Eng. Chem.*, **17** (1925), 810; A. R. Carr and D. W. Murphy, *J. Amer. Chem. Soc.*, **51** (1929), 116. A. M. White, *Ind. Eng. Chem.*, **22** (1930), 230.

$$\frac{T_1 - T_2}{\theta_1 - \theta_2} = K$$

in which T_1 and T_2 are the boiling points of one substance at two different pressures, θ_1 and θ_2 the boiling points of the other at the same two pressures, K a constant. Vapour pressures of acetonitrile at 0°, 10° and 15°C. were measured by using the apparatus of the present experiment, varying the temperature of the reservoir of acetonitrile and it was confirmed that the Dühling's rule holds very well in this case too. Values of the observed vapour pressure together with that at 760 mm. are given below and the corresponding Dühling's line in Figure 1.

B. p. (°C.)	0	10	15	81.6
Vapour pressure (mm.)	25.2	41.9	55.5	760

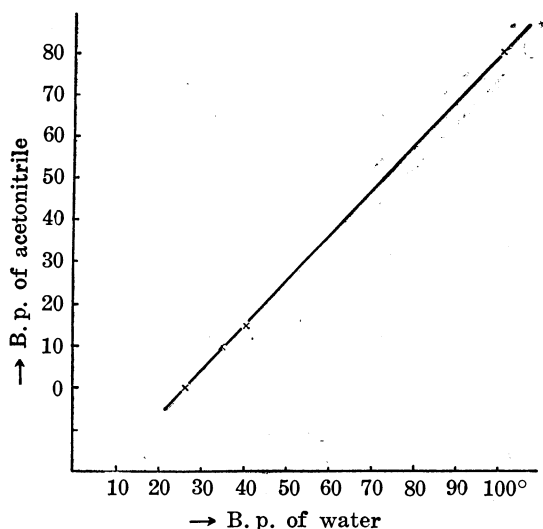


Fig. 1. Dühling's line of acetonitrile

From the above data the vapour pressures at various temperatures are obtained as follows:—

B. p. (°C.)	17.0	20.0	22.0	24.0	24.6	25.0
Vapour pressure (mm.)	58.0	67.6	74.5	82.1	84.6	86.3

In the case of water the experiment was extended to the third desorption, while in the case of acetonitrile to the fourth desorption which was immediately followed by the adsorption and desorption of water vapour.

Results of Experiments. (1) In every case a marked hysteresis has been observed, which is shown in Figures 2 and 3.

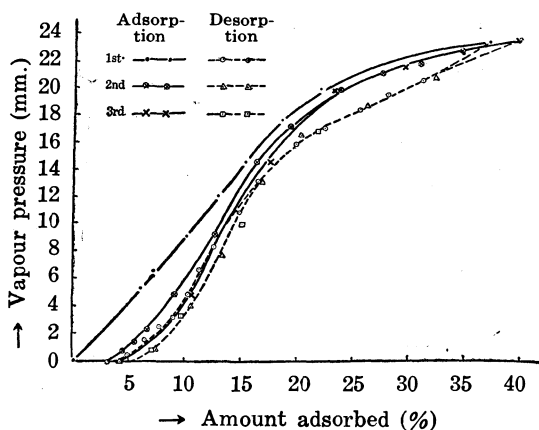


Fig. 2. Isotherm of water

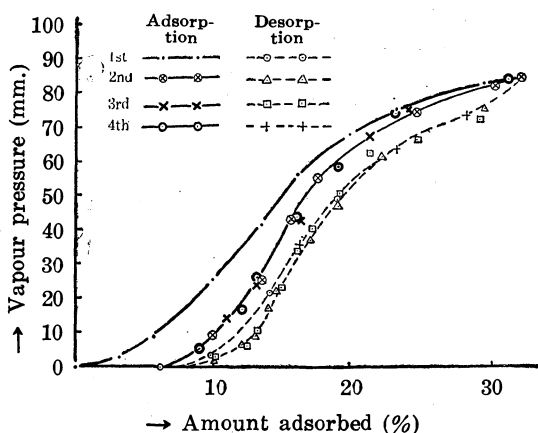


Fig. 3. Isotherm of acetonitrile

tion curves are practically the same as those without the retained acetonitrile. The retained amount thereby decreased from 6.31 to 3.26%, the value very near to 3.15% ("retained" water on the earth without acetonitrile).

(5) The rate of adsorption increases as the process of adsorption and desorption is repeated. Figure 4 shows the amount of adsorbed water plotted against time in the first, second and third adsorption experiments under the pressure of 14.53 mm. (saturated vapour pressure at 17°C.).

The initial points of the three curves are made superimposed in order to render the comparison easy.

Similarly Figures 5 and 6 show the rate of adsorption of water under 4.58 mm. (saturated vapour pressure at 0°C.) and those of acetonitrile

(2) It is clearly seen from Figures 2 and 3 that the vapour pressures corresponding to the definite quantities of the adsorbed substances are greater in the first adsorption than in the second and the subsequent adsorptions.

(3) A small proportion of the adsorbed substance is very difficult to be expelled by evacuation; water remains undesorbed in the amount of 3.15% even after 5 or more hours' evacuation at 0.001 mm. and acetonitrile in the amount of 6.31% under the same condition. This very tenaciously held water or acetonitrile is that which has been designated by the present author "retained", and has been noticed to play an important rôle in the promotion and poisoning of the catalytic action of the earth.⁽⁷⁾

(4) It has been found that the first adsorption as well as desorption curves of water vapour in the presence of the "retained" acetonitrile considerably deviate from those without it, but the second adsorption and desorp-

(7) K. Ishimura, this Bulletin, 9 (1934), 522.

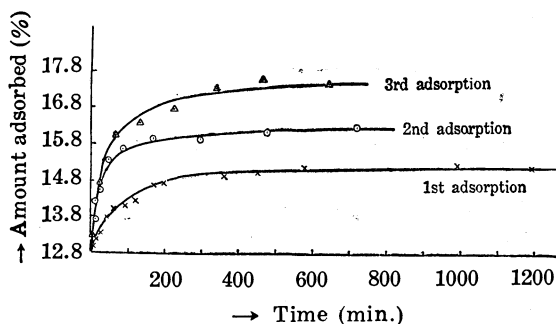


Fig. 4. Rate of adsorption of water at 17°C.

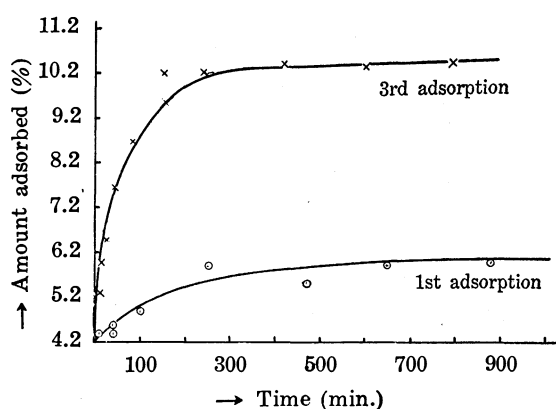


Fig. 5. Rate of adsorption of water at 0°C.

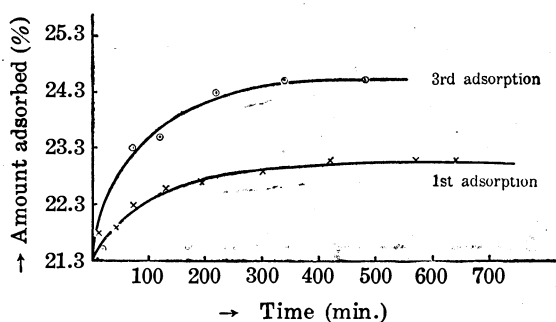


Fig. 6. Rate of adsorption of acetonitrile at 22°C.

under 74.5 mm. (saturated vapour pressure at 22°C.) respectively.

(6) It may be seen from Figures 4, 5 and 6 that not only the rate of adsorption but also the amount the substance adsorbed at equilibrium increase as the adsorption and desorption are repeated.

(7) The rate of desorption could not be accurately measured under the condition of the present experiment. It can only be stated here that the time required for desorption is relatively short and shows little variation from one experiment to the other, usually about 1-2 hours' standing is enough to obtain the constant elongation of the spring and the constant reading of the manometer.

Discussion of Results.

It is well established that adsorbed films cannot be completely removed by evacuation, but that the treatment with a high pressure of gas at high temperature is much more efficient. For example, as H. S. Harned⁽⁸⁾ observed, simply heating charcoal up to 1200°C. in a vacuum will not suffice to produce an absolutely gas-free surface. When, however, charcoal is heated to over 700°C. in a vacuum, cooled in

a vacuum, exposed to the gas until considerable quantities are adsorbed, and then again heated to above 700°C. in a gas, the surface of the charcoal seems to be first cleaned up, as the velocity of adsorption on the charcoal gives a reproducible value. Such process of "washing out" has most probably been effected on Japanese acid earth in the case of the present

(8) *J. Amer. Chem. Soc.*, **42** (1920), 372.

experiment at ordinary temperature. Thus as the process of adsorption and desorption of water or acetonitrile is repeated, the surface is successively washed out by these substances and consequently the adsorptive power of the earth gradually increase. The effect of the washing out process is clearly recognized from the increases in both the rate of adsorption and the amount of the adsorbed substances at equilibria, as shown in Figures 4, 5 and 6.

Though acetonitrile is capable of washing out the adsorbed foreign gas it hinders in its turn the adsorption of water vapour. It can however easily be flushed by the water vapour, as may be understood from the facts that the earth with "retained" acetonitrile adsorbs water vapour more slowly than the case without it, but after the first adsorption and desorption is finished the original rate of adsorption recurs and the upper region of the subsequent isotherm falls completely on the preceding one. At the same time the "retained amount" (6.31%) was found to be reduced to 3.26%, the value very near to the amount of retained water (3.15%) on the earth without acetonitrile. These facts suggest that water has a most strong affinity to the earth and capable of replacing acetonitrile from the surface.

The molecules of "retained water" visualized as above are those which are put in their original positions from where they were liberated when heated. As the present author⁽⁹⁾ has previously suggested, the active centres for the catalysis, which are formed when the three components, Al_2O_3 , SiO_2 and water are suitably oriented, become inactive by loss of water, but recover their ability by regaining it in the original position. The "retained water" is not therefore that simply adsorbed on the surface; it is much more strongly held, it may be said quasi-chemically combined with other components of the earth.

The hysteresis observed in the isotherms above shown may be partly explained by taking the "washing out" process into consideration. The first adsorption lags more or less on account of the hindering effect of the foreign adsorbed substances. These are, however, more easily liberated than water vapour when desorption is commenced, giving rise to the observed "washing out" action of water vapour. The first isotherm shows therefore a marked hysteresis from the very initial stage of adsorption i.e. layer adsorption. An example of such hysteresis phenomenon due to the existence of the foreign adsorbed substance was given by R. Fricke and H. Marquardt.⁽¹⁰⁾ They reported that a marked hysteresis was observed in the adsorption of water vapour on human hair in the presence of air, while in the high vacuum of 0.0001 mm. no such hysteresis appeared.

Now in the case of the present experiment, most part of the foreign adsorbed substances are washed out by the first series of adsorption and desorption and hysteresis areas greatly decrease in the subsequent series. With acetonitrile curves of the second and the subsequent series overlap completely and the hysteresis covers the whole range, while with water the lower portion of the isotherm tends gradually to be reversible and accordingly the hysteresis tends to be restricted only to the upper region of the curve. This difference of the behaviours of the two substances may also

(9) K. Ishimura, this Bulletin, **9** (1932), 527.

(10) *Kolloid Z.*, **60** (1932), 124.

be attributed to the greater power of water vapour for the washing out process. By acetonitrile the foreign adsorbed substances cannot be removed by only repeating the process of adsorption and desorption and persist to stay on the surface.

The upper region of the hysteresis area, however, does not tend to decrease in both cases. Different mechanisms may, therefore, govern the hysteresis in the lower and the upper regions of the isotherms. The former, which tends to disappear, is most probably due to the existence of the foreign adsorbed substances as stated above, and in this region layer adsorption mainly takes place. The latter is associated with capillary condensation process which follows the layer adsorption. The boundary between the two types of adsorption can be ascertained, by the narrow part existing in the middle of the hysteresis area.

According to R. Zsigmondy,⁽¹¹⁾ during addition of vapour walls of pores are wetted incompletely and very slowly and therefore the radius of curvature of the meniscus is greater than that during desorption. Hence the vapour pressure of a definite quantity of liquid held in pores is greater during adsorption than during desorption. A. G. Foster⁽¹²⁾ studied equilibria between dehydrated gels (silica gel, and ferric oxide gel) and condensible vapours (water, benzene and ethyl alcohol). He attributed the higher pressures observed during adsorption to the liquid which is held in an unstable state on the walls of these pores in which the meniscus has not formed, the pressure of which masks the progress of the condensation process. During desorption all the adsorbed liquid is bound by the meniscus (with the exception of the strongly adsorbed layer which remains on the walls), and therefore show smaller vapour pressures.

The adsorption will come to an end when the pores of the adsorbent are all filled by liquid. This will occur under the vapour pressure of adsorbates, saturated at the temperature of adsorbents, that is, when the temperatures of the two thermostats are the same. If the temperature of the adsorbate is raised over that of adsorbent, wetting process will begin to take place. At the end of the adsorption in the present experiment carried out under the saturated vapour pressure of adsorbate at 24.6°C., the temperature very near to that (25°C.) of the first thermostat in which the tube holding the silica spring with the earth is immersed, the adsorbed quantities of water and acetonitrile amounted to 39.82 and 32.16% of the weight of the earth respectively. Volumes of the two liquids at 25°C. to be adsorbed by 100 g. of the earth are therefore 39.8 c.c. of water and 40.7 c.c. of acetonitrile. The two values are very near. The difference between them will become smaller if the amounts adsorbed at the same humidity are taken instead of those at the same temperature. It is very probable therefore that the above values approximately represent the total volume of pores of 100 g. of the earth.

Summary.

Adsorption isotherms of water and acetonitrile for Japanese acid earth have been studied by using a McBain's sorption balance. A marked

(11) "Kolloidchemie," Leipzig, (1918), 214.

(12) *Trans. Faraday Soc.*, **28** (1932), 653.

hysteresis phenomenon has been observed in both cases. It has been found that as the process of adsorption and desorption is repeated, the lower region of the hysteresis area tends to be reversible in the case of water, while in the case of acetonitrile hysteresis covers the whole range of the isotherms even after the fourth series of adsorption and desorption. In both cases the upper region of the hysteresis area remains unchanged. The first type of the hysteresis, which tends to disappear, has been explained as due to the existence of the adsorbed foreign substances on the surface of the earth, while the second type is associated with capillary condensation process. The difference between the behaviours of water and acetonitrile can be attributed to the difference of affinity of the two substances to the earth. The total volume of pores of the earth has been calculated from the adsorbed amounts of the two substances and found about 40 c.c. for 100 g. earth.

The author's thanks are due to Dr. H. Inoue for his encouragement and advice.

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Studien über Oxydationszersetzung des Methans (Fortsetzung und Schluss).

Von Toyoziro OGURA.

(Eingegangen am 6. Juni 1941.)

IV. Methan-Sauerstoff Reaktionen. Man kann die Zersetzungsreaktionen des Methans durch Sauerstoff nach folgender Formel in fünf Klassen einteilen. Diese Reaktionen sind alle exothermische und das Reaktionsprodukt sind Wasser, Kohlendioxyd und Kohlenoxyd. Reaktionen nach der Gleichung 1 und 2 sind sogenannte Verbrennung unter niederer oder höherer Temperatur und finden bei genügender Versorgung mit Sauerstoff statt. Reaktionen nach der Gleichung 3, 4 und 5 gehen bei mangelhafter Versorgung mit Sauerstoff vor sich. Reaktion 3 findet unter Explosion statt und Reaktionen 4 und 5 bei höherer Temperatur. Wenn die Menge des Sauerstoffs nicht genügend ist, so ist die Zersetzung des Methans eine unvollkommene und die Kohlenstoffpartikeln (Russ) werden frei.

Der Autor hat die oben erwähnte Reaktionen nach der Strömungs- und Explosionsmethode studiert. Die Apparate für die Strömungsmethode sind in Abbildung 8 veranschaulicht.

Methan bildet nach längerer Wirkung des Sauerstoffs, sauerstoffhaltige Verbindungen, wie Formaldehyd, Methylalkohol usw. der Oxy-

dationsmechanismus ist ein komplizierter, wovon aber in diesem Berichte abgesehen wird.

	Volum Veränderung (%)
$2 \text{CH}_4 + \text{O}_2 = 2 \text{CO} + 4 \text{H}_2 + 16.6 \text{ Kcal.}$	200
$\text{CH}_4 + \text{O}_2 = \text{CO} + \text{H}_2\text{O} + \text{H}_2 + 66.1 \text{ Kcal.}$	100
$\text{CH}_2 + 2 \text{O}_2 = \text{CO}_2 + 2 \text{H}_2\text{O} + 191.8 \text{ Kcal.}$	33
$2 \text{CH}_4 + 3 \text{O}_2 = 2 \text{CO} + 4 \text{H}_2\text{O} + 247.8 \text{ Kcal.}$	40
$\text{CH}_4 + \text{O}_2 = \text{CO}_2 + 2 \text{H}_2 + 76.2 \text{ Kcal.}$	66

a) *Verfolgung des Katalysators.* Diese Reaktionen haben verschiedene Reaktionsformen, je nach den Mischungsverhältnissen des Rohgases, aber sie werden durch Gebrauch des Katalysators sehr beschleunigt. Die Versuche ohne Katalysator gehen nur langsam vor sich, wie in Tafel 32 gezeigt. Einige Beispiele unter den verschiedenen Mengenverhältnissen des Methans und Sauerstoffs sind in Tafel 32 angeführt. Wenn die Menge des Sauerstoffs grösser ist, so findet die Explosion etwa bei 600°C. statt.

Tafel 32.

ohne Kat. $\text{CH}_4 : \text{O}_2 = 3 : 1$ Gas Ges. 10 l./St.

Reak. Temp. °C	CO_2	C_nH_m	O_2	CO	H_2	CH_4	Z.G.	Vol.-Veränderung (%)
600	1.0	0.8	25.0	1.4	0.0	71.8	3.2	85.2
700	5.6	2.5	12.8	5.5	2.7	70.9	13.5	76.0
800	7.4	3.4	6.4	9.3	5.4	68.0	19.7	71.5
900	8.0	3.6	1.4	13.4	5.4	68.1	26.5	68.5
1000	6.1	2.6	1.0	16.2	12.2	61.9	27.5	72.5

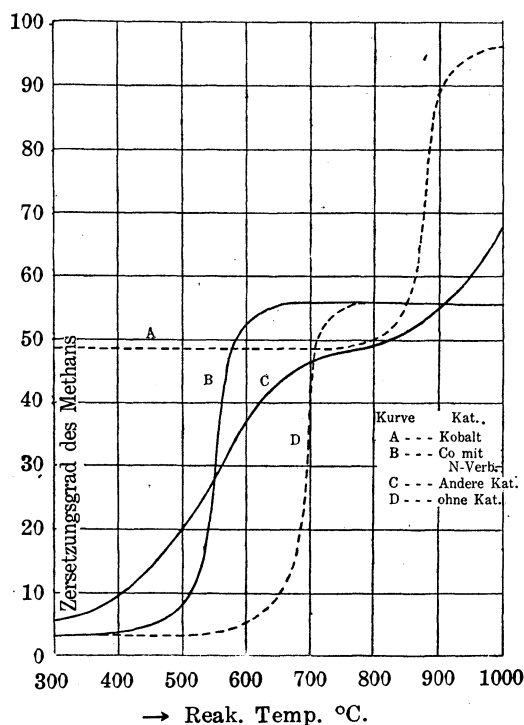
$$\text{Z. G.} = \frac{\text{CO}_2 + \text{CO}}{\text{CO}_2 + \text{CO} + \text{CH}_4} \times 100$$

Die Metalloxyde mit Kaolin als Katalysator. Die Metalloxyde sind Nickeloxyd, Kobaltoxyd, Kupferoxyd, Eisenoxyd, Chromoxyd usw. Kobalt ist am wirksamsten, aber bei höherer Temperatur entfaltet Nickel ähnliches Vermögen. Die Oxyde sind aus Hydroxyden hergestellt, die aus Nitrat durch Alkali niedergeschlagen wurden. Hopcalit II enthält Kobalt, aber Hopcalit I besteht aus Kupfer und Mangan. Tafel 33 zeigt die Resultate des Versuchs mit gleichem Volum des Methans und Sauerstoffs. Sie zeigt die Temperatur, bei welcher der Prozent des Sauerstoffs im erhaltenen Reaktionsgas gleich eins ist. Gasgeschwindigkeit ist 5 l. pro Stunde. Abbildung 11 zeigt die Beziehung zwischen Temperatur und Zersetzungsgrad der verschiedenen Katalysatoren. Die Zersetzungskurve liegt zwischen beiden Resultaten mit Kobalt als Katalysator und ohne einen solchen.

Tafel 33.

Exp. Nr. d 40—d 47, Gas. Ges. 5 lt/St. $\text{CH}_4:\text{O}_2 = 7:3$, Kat. Nr. D 1-D 8.

Katalysator.	Reak. Temp. °C	CO_2	C_nH_m	O_2	CO	H_2	CH_4	Z.G.
Kobalt	300	24.6	0.4	1.3	0.4	1.0	72.3	25.7
Kupfer	500	24.6	0.4	1.6	0.0	0.0	73.4	25.2
Hopcalit II ⁽¹⁾	500	22.2	0.4	1.8	0.2	0.0	75.4	22.9
Hopcalit I ⁽²⁾	600	21.5	0.5	1.6	0.7	0.0	75.7	22.7
Silber	600	24.2	0.5	1.3	0.8	0.9	72.3	25.6
Nickel	800	21.6	0.5	1.4	4.1	2.0	70.4	26.7

Abb. 11. Zersetzungsgrad und Temperatur $\text{CH}_4:\text{O}_2 = 1:1$.

Bei Anwesenheit des Katalysators geht die Reaktion nach der Gleichung 3 vor sich, bei höherer Temperatur und mit kleiner Menge des Sauerstoffs schreitet sie nach der Gleichung 2 fort. Auf Tafel 34 sind die Resultate bei dem Gebrauch von Kobalt und Equivolum Gemisch des Methans und Sauerstoffs gezeigt. Schon bei 300°C. reagiert ein halbes Volum Methan mit einem Volum Sauerstoff und bildet Kohlendioxyd, bei

- (1) 50 % MnO_2 , 30 % CuO , 15 % Co_2O_3 und 5 % Ag_2O .
 (2) 60 % MnO_2 ; 40 % CuO .

900°C. reagiert ein Volum Methan mit einem Volum Sauerstoff und bildet Wasserstoff-Kohlenoxyd-Gasgemisch. Gasgeschwindigkeit ist 5 l. pro Stunde.

Tafel 34.

Exp. Nr. d 53, Kat. Nr. D 3, Gas. Ges. 5 l./St., $\text{CH}_4/\text{O}_2 = 1$.

Reak. Temp. °C	CO_2	C_nH_m	O_2	CO	H_2	CH_4	Z.G.	Vol.-veränderung (%)
500	44.8	1.8	1.1	1.1	2.8	49.4	48.0	56.2
600	43.6	0.7	0.7	0.6	4.2	49.9	47.0	56.2
700	44.4	0.7	1.0	1.0	3.0	49.8	47.7	57.0
800	40.8	1.2	1.0	3.1	5.6	48.3	47.5	58.3
900	11.7	0.6	0.7	30.4	53.0	3.6	92.2	140.0
1000	11.0	0.5	0.6	30.9	54.2	2.4	94.6	134.0

b) *Einfluss des Mischungsverhältnisses des Methans und des Sauerstoffs.* Mischungsverhältnis des Methans und Sauerstoffs beherrscht die Reaktion. Der Versuch ohne Katalysator gibt nur unvollkommene Resultate, und Gasgemische mit überschüssigem Sauerstoff explodiert bei 600°–700°C. Tafel 35 ist ein Teil der Resultate ohne Katalysator und unter Veränderung des Mischungsverhältnisses, wobei die Menge des Kohlendioxyds grösser ist als die des Wasserstoffs.

Tafel 35.

Exp. Nr.: d 1–d 13, ohne Kat., Reak. Temp. 900°C, Gas. Ges. 5 l./St.

$\text{CH}_4:\text{O}_2$	CO_2	C_nH_m	O_2	CO	H_2	CH_4	Z.G.	Vol.-veränderung (%)
9 : 1	1.2	2.4	0.6	9.3	1.6	68.5	14.2	75.8
3 : 1	6.1	2.6	1.0	16.2	12.2	61.9	26.5	72.7
2 : 1	6.8	2.5	0.7	22.9	18.0	49.8	37.3	73.6
1 : 1	15.2	0.9	13.6	26.2	15.4	28.6	65.0	65.0

Tafel 36 zeigt den Einfluss des Mischungsverhältnisses beim Gebrauch des Kobalt-Katalysators, dabei geht die Reaktion glatt ohne Explosion vor sich und man kann die Einflüsse verschiedener Verhältnisse deutlich beobachten. Wenn die Menge des Sauerstoffs eine kleine ist, da bildet sich grössere Menge Wasserstoff infolge einer Thermozersetzung bei mässiger Temperatursteigerung, im Gegensatz zu dem Fall ohne Katalysator, wo grössere Menge des Methans unverändert bleibt. Kobalt hat also katalytisches Vermögen durch Thermozersetzung. Je grösser die Menge des Sauerstoffs ist, desto grösser ist die Menge des Wasserstoffs und Kohlenoxyds. Ein Gasgemisch aus zwei Volumen Sauerstoff und einem Volum Methan gibt nur Kohlendioxyd.

Tafel 36.

Exp. Nr. d 29–d 63, Kat. Nr. D 3, Reak. Temp. 300°C.

CH ₄ :O ₂	CO ₂	C _n H _m	O ₂	CO	H ₂	CH ₄	Z.G.	Vol.-Veränderung (%)
9 : 1	7.5	0.7	0.6	1.6	2.6	86.9	9.9	89.0
4 : 1	15.1	1.0	1.1	1.1	2.2	79.5	16.9	82.5
7 : 3	24.1	0.4	1.3	0.4	1.0	72.8	25.2	69.0
1 : 1	44.2	0.5	2.5	0.9	3.4	48.5	48.2	68.7
1 : 1.3	65.1	0.3	1.4	0.1	1.9	31.2	67.5	46.2
1 : 2	90.2	0.4	3.2	0.0	0.0	6.2	93.5	40.0

c) *Einfluss des Zusatzes von Stickstoffhaltigen Verbindungen.* Der Zusatz einer geringen Menge der stickstoffhaltigen Verbindungen z.B. Salpetersäure, Ammoniak und Salmiak beschleunigt die Methan-Sauerstoff-Reaktion, andere Reaktionen werden dagegen verhindert. Man erhält nämlich eine ausserordentlich grössere Menge des Kohlendioxyds als die des Wasserstoffs. Tafel 37 ist die Resultate mit einigen Stickstoffhaltigen Verbindungen. Diese Materien wirken ziemlich gut als Hemmungsmittel gegen Explosion.

Tafel 37.

Exp. Nr. d 70–d 90, Kat. D 3, Gas. Ges. 5 l./St.

CH ₄ :O ₂	N-Verb.	CO ₂	C _n H _m	O ₂	CO	H ₂	CH ₄	Reak. Temp. °C	Z.G.
9 : 1	HNO ₃	1.8	1.4	1.2	6.0	2.9	86.7	600	8.2
8 : 2	NH ₄ Cl	2.8	1.6	1.6	14.2	3.6	76.1	600	18.3
3 : 1	NH ₄ Cl	9.2	2.2	0.4	16.1	5.6	66.5	700	27.5
1 : 1	NH ₄ Cl	19.4	0.8	1.0	32.0	5.0	41.8	700	55.0
1 : 1	NH ₃	21.4	0.8	2.4	30.4	1.2	43.8	600	54.3

d) *Explosionsreaktion.* Bone und andere Forscher haben explosive Reaktionen des Methan-Sauerstoffs untersucht und festgestellt, dass die Bestandteile des Reaktionsgasmisch mit dem Mischungsverhältnis ändert. Nach der Explosion mit gewöhnlicher Hempelschen Pipette habe ich die Bestandteile und deren Volume bestimmt.

Tafel 38 zeigt die Resultate. Wenn die Sauerstoffmenge klein ist, so tritt keine Explosion ein, und die Veränderung des Volums ist nur eine geringe. Bei einem Sauerstoffgehalt von über 40% geschah die Explosion und die Reaktion erfolgte zunächst nach Gleichung $\text{CH}_4 + \text{O}_2 = \text{CO} + \text{H}_2\text{O} + \text{H}_2$, dann aber nach Gleichung $\text{CH}_4 + 2\text{O}_2 = \text{CO}_2 + 2\text{H}_2\text{O}$. Abbildung 12 zeigt die Beziehung zwischen Mischungsverhältnis, Reaktionsgasvolum und Veränderung der Bestandteile bei Explosionsreaktionen.

Die Explosion durch Wärme tritt nur bei einer Temperatur über

600°C. ein. Durch elektrische Funken usw. wird die Explosion aber leicht bei gewöhnlicher Temperatur hervorgerufen und ist häufig Ursache eines grossen Unglücks gewesen. Der Reaktionsmechanismus ist aber noch nicht völlig aufgeklärt.

Tafel 38.

Exp. Nr. k 1—k 24.

CH ₄ : O ₂	CO ₂	O ₂	CO	CH ₄	H ₂	Vol.-Veränderung (%)
87.7 : 12.3	0.0	11.4	1.4	86.8	0.0	103
80.0 : 20.0	0.9	18.0	0.7	79.0	1.1	103
74.5 : 27.5	0.9	23.9	1.8	71.8	1.6	103
62.2 : 37.7	0.5	34.0	2.4	57.0	5.6	102
53.6 : 46.4	4.0	1.5	38.0	6.7	48.8	125
50.1 : 49.9	5.8	1.0	38.8	3.1	51.3	113
44.0 : 56.0	14.6	1.2	42.6	5.7	36.2	81
40.6 : 59.4	20.0	2.0	41.4	2.7	33.9	70
29.3 : 70.7	70.5	21.2	0.0	0.4	7.9	42
19.8 : 80.2	42.2	57.8	0.0	0.0	0.0	58
10.0 : 90.0	14.4	85.6	0.0	0.0	0.0	80

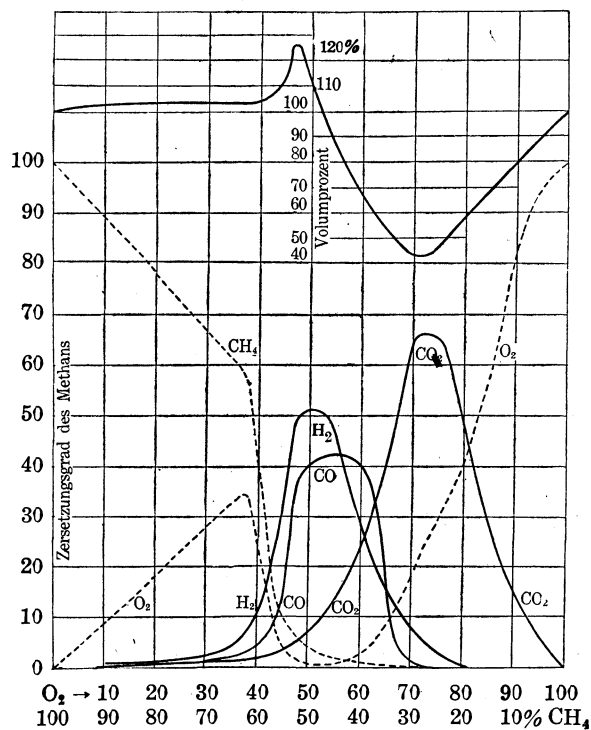


Abb. 12. Volumen- und Bestandteilen-Veränderung der explosiven Reaktionen.

V. Methan-Kohlendioxyd Reaktionen. Die Reaktionen zwischen Methan und Kohlendioxyd sind unter gewöhnlichem Druck sehr einfach, wie durch folgende Formel gezeigt wird. Die Reaktionsprodukte sind Wasserstoff und Kohlenoxyd. Dazu ist aber eine höhere Temperatur notwendig. Unter höherem Druck bilden sich aus Methan-Kohlendioxyd Gemisch Azetylen, Essigsäure usw.

Die Reaktion geht nur unter höherer Temperatur vor sich, indem die Kohlenstoffpartikeln (Russ) freigegeben werden. Man kann dies durch Zusatz der Wasserdämpfe in kleiner Menge vermeiden. Ich verfuhr nach Strömungsmethode und bediente mich des oben erwähnten Apparates. Dieselben Katalysatoren wie bei Methan-Sauerstoff-Reaktionen kamen in Betracht. Es wurde auf das katalytische Vermögen des Metalls und Metalloxydes, Einfluss des Temperatur und des Mischungsverhältnisses untersucht. Gasgeschwindigkeit war 5 l. pro Stunde.

	Vol.-Veränderung (%)
$\text{CH}_4 + 3 \text{CO}_2 = 4 \text{CO} + 2 \text{H}_2\text{O} - 79.8 \text{ Kcal.}$	100
$\text{CH}_4 + 2 \text{CO}_2 = 3 \text{CO} + \text{H}_2 + \text{H}_2\text{O} - 69.7 \text{ Kcal.}$	130
$\text{CH}_4 + \text{CO}_2 = 2 \text{CO} + 2 \text{H}_2 - 59.6 \text{ Kcal.}$	200

a) *Verfolgung des Katalysators.* Einfluss des Katalysators für die Methan-Kohlendioxyd Reaktionen war nicht so bedeutend, wie oben beschriebenen zwei Reaktionen, aber doch deutlich genug. Tafel 39 zeigt die Resultate der Reaktionen ohne Katalysator bei gleichem Volum Gasgemisch.

Anwendung des Katalysators beschleunigt die Reaktionen. Tafel 40 zeigt die Resultate der Reaktionen mit Oxyden oder Metallen, wie Nickel, Kobalt, Kupfer, Eisen, Silber und ihren Oxyde. Die Metalle, die mit Wasserstoff durch einige Stunden reduziert wurden, haben besseres Vermögen als Oxyde. Abbildung 13 zeigt das Verhältnis zwischen Zersetzungsvermögen der Metalle und der Temperatur. Kobalt ist am wirksamsten, aber bei höherer Temperatur entfaltet Nickel ähnliches Vermögen.

Tafel 39.

Exp. Nr. e 1, ohne Kat., $\text{CH}_4/\text{CO}_2 = 1$, Gas. Ges. 5 l./St.

Reak. Temp. C°	CO ₂	C _n H _m	O ₂	CO	H ₂	CH ₄	Z.G.	Vol.-Veränderung. (%)
400	49.4	0.2	0.9	0.0	0.0	49.4	—	
500	50.3	0.2	0.8	0.0	0.0	48.6	—	
600	48.2	0.2	0.7	0.0	0.0	50.8	—	
800	49.1	0.8	0.4	0.0	0.2	49.6	—	
900	49.0	0.7	0.5	2.9	0.7	46.2	7.3	115
1000	40.1	0.3	0.3	10.6	8.1	40.5	31.6	121

$$\text{Z. G.} = \frac{\text{CO} + \text{H}_2}{\text{CO} + \text{H}_2 + \text{CH}_4} \times 100$$

Tafel 40.

Exp. Nr. e 2-e 20, Kat. Nr. D 1-D 10, Reak. Temp. 1000°C, $\text{CH}_4/\text{CO}_2 = 1$.

Katalysator	CO_2	C_mH_m	O_2	CO	H_2	CH_4	Z.G.
Nickel	1.5	0.0	0.3	47.8	46.6	3.7	96.3
Nickeloxyd	0.9	0.0	0.3	48.7	44.8	5.3	94.5
Kobaltoxyd	3.3	0.0	0.4	46.2	44.2	7.0	92.7
Kobalt	2.3	0.0	0.3	46.7	41.2	9.5	90.2
Kupferoxyd	3.4	0.1	0.3	45.5	41.4	9.3	90.5
Chromoxyd	31.0	0.8	0.4	20.2	14.3	33.2	51.2
Hopcalit I	22.6	0.4	0.3	26.7	20.7	29.3	62.0
Hopcalit II	3.9	0.3	0.3	47.5	42.0	6.0	92.5
Silberoxyd	6.2	0.0	0.4	45.9	36.3	11.2	87.5
Silbermanganat manganat	36.8	1.3	0.3	15.7	10.6	35.5	41.0

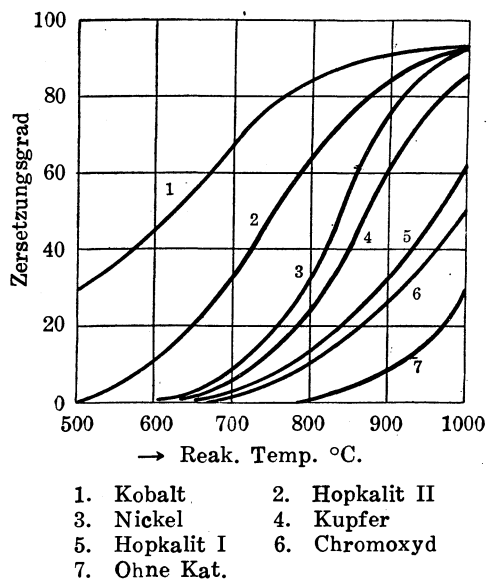


Abb. 13. Vermögen der Katalysatoren.

b) *Einfluss der Temperatur und des Mischungsverhältnisses.* Tafel 41 zeigt die Resultate der Versuche beim Gebrauch von Kobalt und Nickel als Katalysator und unter verschiedener Temperatur. Methan und Kohlendioxyd sind von gleichem Volum.

Wenn man das Verhältnis des Methans und Kohlendioxyds ändert, so verändert sich das Volum des Reaktionsgases, aber das Kohlendioxydvolum bleibt konstant und der Wasserstoffprozent steigert. Die Resultate des Experiments unter verändertem Mischungsverhältnis und gleicher Temperatur sind in Tafel 42 gezeigt. Kontaktdauer ist etwa 10 Sekunden.

Tafel 41.

Exp. e 16, e 19. $\text{CO}_2/\text{CH}_4 = 1:1.03$ Gas. Ges. 5.0 l./St.

Reak. Temp. °C.	Kat.	CO_2	C_nH_m	O_2	CO	H_2	CH_4	Z.G.
Roh Gas	—	49.2	0.7	1.2	0.6	0.0	48.3	—
500	Co	43.4	0.6	0.8	8.2	8.3	38.6	30.1
600	„	38.8	0.2	1.0	9.0	16.5	34.5	42.5
700	„	26.6	0.0	1.0	15.3	34.8	22.3	69.0
800	„	17.8	0.0	1.4	27.4	41.9	11.5	85.7
900	„	8.5	0.8	1.2	35.6	45.8	8.2	90.0
1000	„	3.7	0.8	2.2	43.7	44.7	4.8	94.7
Roh Gas	—	50.0	0.4	0.8	0.0	0.0	48.6	—
500	Ni.	51.2	0.5	0.4	0.0	0.0	48.0	—
600	„	49.0	0.5	0.4	0.0	0.0	50.1	—
700	„	50.0	0.5	0.5	0.0	0.0	48.0	—
800	„	43.2	0.4	0.3	7.3	2.8	45.9	18.0
900	„	17.0	0.1	0.5	34.8	27.1	20.4	75.3
1000	„	1.5	0.0	0.4	49.0	44.4	4.7	85.0

Tafel 42.

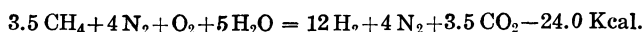
Exp. e 17- Exp. e 28. Katalysator Nr. D 3 (Kobalt) Gas. Ges. 5 l./St.

Reak. Temp. 1000°C.

$\text{CO}_2 : \text{CH}_4$	CO_2	C_nH_m	O_2	CO	H_2	CH_4	Kohlenstoff- abscheidung
22.8 : 76.3	3.0	0.4	1.4	16.5	65.2	13.2	+
33.0 : 65.7	4.8	0.4	2.0	23.4	54.8	14.4	+
40.7 : 58.4	6.8	0.4	1.0	32.5	47.9	11.4	+
49.5 : 48.7	3.7	0.8	2.2	43.7	44.7	4.8	
50.0 : 48.2	2.2	1.0	1.6	44.1	45.0	6.1	
59.2 : 39.1	10.5	0.2	0.4	47.3	35.5	6.1	
64.3 : 33.2	15.6	1.2	1.6	43.2	29.5	7.4	
72.4 : 25.0	19.8	0.4	1.3	46.6	23.9	1.1	

VI. Methan-Luft-Wasserdampf Reaktionen. Methan-Wasserdampf-Reaktion ist eine endothermische, Methan-Sauerstoff-Reaktionen dagegen eine exothermische. Wenn man diese zwei Reaktionen mit einander verbindet, so kann man tüchtige Reaktionsgase erhalten. Gebraucht man Luft statt des Sauerstoffs, so erfolgen nachfolgende endothermische Reaktionen. Tafel 43 zeigt die Resultate des Versuches mit Nickel-Katalysator. Rohgas hat folgende Bestandteile.

Bestanteile des Rohgases (%)	CH_4	O_2	N_2	CO_2
	42.3	11.5	46.0	0.2



Tafel 43.

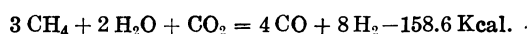
Exp. Nr. b33 Kat. Nr. B 25, Gas. Ges. 5 l./St., $\text{H}_2\text{O}/\text{CH}_4 = 10.0$.

Reak. Temp. °C.	CO ₂	O ₂	CO	H ₂	CH ₄	N ₂	Z.G.
600	16.8	0.8	1.3	61.7	0.5	18.8	97.3
650	17.8	0.4	1.2	60.4	0.5	19.7	97.3
650	17.5	0.4	1.2	60.6	0.5	19.8	97.3

$$\text{Z.G.} = \frac{\text{CO}_2}{\text{CO}_2 + \text{CH}_4} \times 100$$

VII. Methan-Kohlendioxyd-Wasserdampf Reaktionen. Methan-Kohlendioxyd- und Methan-Wasserdampf-Reaktionen sind endothermische. Man kann ein Gasgemisch des Kohlenoxyds und des Wasserstoffs in verschiedenen Verhältnissen durch Kombination dieser beiden Reaktionen erhalten. Tafel 44 zeigt die Resultate nach folgender Gleichung; selbstverständlich ist dabei höhere Temperatur notwendig. Reduziertes Nickel wird als Katalysator verwendet und Wassermenge ist zweimal so gross als Methanmenge, Gasgeschwindigkeit ist 5 l. pro Stunde. Rohgas hat Bestandteile, wie nachfolgende Tafel zeigt.

Reaktionsformel



$$\text{Z. G.} = \frac{\text{CO}_2}{\text{CO} + \text{CH}_4} \times 100$$

Bestandteile des Rohgases (%)	CO ₂	O ₂	CH ₄	N ₂
	27.8	0.4	71.1	0.7

Tafel 44.

Exp. Nr: b 104, Kat. Nr. B 8.

Reak. Temp. °C.	Gas. Ges. lt/St.	H ₂ O / CH ₄	CO ₂	O ₂	CO	H ₂	CH ₄	N ₂	Z.G.
800	7.0	2.0	13.0	0.1	15.7	68.0	1.6	1.6	90.7
800	7.2	1.0	5.3	0.4	26.5	64.6	1.3	1.9	95.3
800	6.4	0.5	4.4	0.4	30.6	59.4	4.5	0.7	87.0
850	8.0	0.5	0.9	1.0	30.6	60.0	3.8	3.8	89.0
900	5.0	1.5	8.4	0.8	21.5	66.2	0.7	2.2	96.7
900	8.0	1.0	4.2	0.4	27.6	64.9	0.9	1.6	96.5
900	7.0	0.5	0.8	0.2	32.0	63.4	1.8	1.8	94.6

VIII. Zusammenfassung und Schlusswort. Diese Abhandlung ist die Resultate der Untersuchungen über die Reaktionen des Methans, des Hauptbestandteils des formosaischen Naturgases, welche es mit Wasserdampf, Sauerstoff und Kohlendioxyd zur Gewinnung des Wasserstoffs durch Oxydationszersetzungen entfaltet. Gleichgewichtskonstanten dieser Reaktionen, insbesondere der Einfluss der Wasserdampfmenge auf Methan-Wasserdampf-Reaktionen und die Veränderung der Bestandteile des Reaktionsgases sind in Nomogram am Anfang der Abhandlung angegeben. Die oben erwähnten drei Reaktionen haben manches gemein an Reaktionsmechanismus und Katalysator. Zur Verfolgung des Katalysators habe ich verschiedene Experimente über Methan-Wasserdampf-Reaktionen angestellt. Ich bin der Meinung, dass die erhaltenen Resultate auch auf die Oxydationszersetzung des Methans verwenden lasse. Ausser Katalysator habe ich auch die Einflüsse von Temperatur, Druck und Mischungsverhältnis untersucht. Die Ergebnisse über Katalysatoren bei der Oxydationszersetzung lassen sich folgendermasser zusammenfassen.

(1) Katalysatoren sind notwendig zur Oxydationszersetzung des Methans durch Wasserdampf, Sauerstoff und Kohlendioxyd, Nickel ist bei Wasserdampf-Reaktionen am wirksamsten, aber für die Sauerstoff- und Kohlendioxyd Reaktionen bewährt sich Kobalt am besten.

(2) Zusatz einer passenden Menge von Promotor befördert die katalytische Wirkung. Als Promotor empfehle ich passende Menge Alumina.

(3) Vermögen des Katalysators wird durch Gebrauch eines Trägers gesteigert, wobei ein passender Konzentrationsgrad des Metalls eine Rolle spielt. Kaolin ist der beste Träger.

(4) Niederschlagskatalysator wird in seiner Wirkung durch Röstungs- und Reduktionstemperatur beherrscht. Niedrige Temperatur ist in beiden Fällen immer wünschenswert.

(5) Zusatz einer kleinen Menge Alkali beeinträchtigt zwar das Vermögen nicht, er verkürzt aber die Lebensdauer des Katalysators.

(6) Existenz einer kleinen Menge Schwefel hat keinen Einfluss auf das Vermögen. Die Bildung des Silikats und Aluminats beeinträchtigt bei niedriger Temperatur die Wirkung.

(7) Zusatz einer mässigen Menge Alkali und Alkalierde ist von schädlichem Einfluss.

(8) Kontaktdauer ist zwischen 10 und 30 Sekunden.

Verminderung des Drucks fördert die Reaktion. Als Beispiel habe ich Methan-Wasserdampf-Reaktion studiert. Steigerung der Reaktionstemperatur befördert die Reaktionen, sie verursacht aber eine Verwandlung der Reaktionsform. Die Bildung des Kohlenoxyd tritt natürlich bei höherer Temperatur ein, bei niedriger Temperatur kann man sie durch Zusatz von Stickstoffhaltige Verbindungen erzeugen. Veränderung im Mischungsverhältnis verwandelt auch Reaktionsarten. Ueberschuss vom Wasserdampf gibt Kohlendioxyd. Insbesondere sind Veränderungen im Mischungsverhältnis wesentliche Ursachen einer Verwandlung der Reaktionsarten bei Methan-Sauerstoff-Reaktionen. Wenn die Menge des Sauerstoffs grösser ist, so findet keine Oxydationszersetzung statt, sondern eine Verbrennungsreaktion.

Zum Schluss der Abhandlung habe ich die Resultate der Reaktionen des Methans mit Luft-Wasserdampf und Kohlendioxyd-Wasserdampf in

einigen Tafeln zusammengestellt, ohne weiter auf die technischen Fragen einzugehen.

Diese Experimente sind ein Teil der Untersuchungen, die im Zentral-Institut und Naturgasforschungsinstitut des Generalgouvernements von Formosa seit einigen Jahren unternommen wird. Ich gestatte mir den Herren Kollegen und Mitarbeitern meinen besten Dank für die freundlichen Anregungen und Hilfe auszusprechen.

Ein Teil der Experimente wurde durch freundliches Entgagen der Japanischen Gesellschaft für Förderung der Wissenschaften (Nippon Gakujutu Sinkokai) ausgeführt, wofür ich mich ganz besonders verbunden fühle.

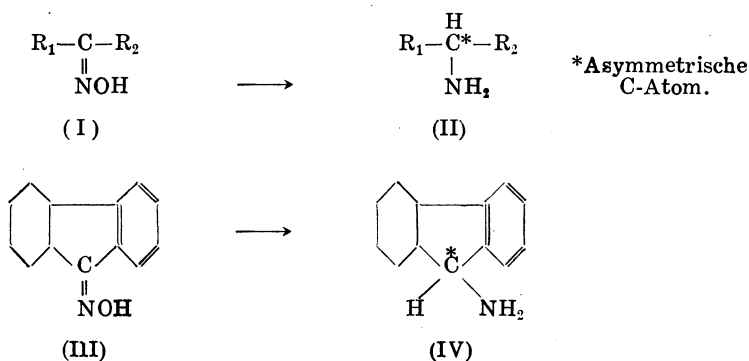
*Naturgasforschungsinstitut,
Sintiku, Formosa.*

Asymmetrische Synthese. III. Versuch zur Darstellung eines optisch-aktivenamins durch die Reduktion des Ketoxims beim Vorhandensein von optisch-aktiver Säure.⁽¹⁾⁽²⁾⁽³⁾

Von Yozo NAKAMURA.

(Eingegangen am 18. Juli 1941.)

Die Reduktion des asymmetrischen Ketoxims (I) ergab im allgemeinen ein Amin von Formel (II), welches ein asymmetrisches C-Atom enthält. Somit dürfen wir das Amin in seine opt. Antipoden zerlegen.



(1) Diese Mitteil. wurde schon auf Japanisch berichtet, *J. Chem. Soc. Japan*, **61** (1940), 1051.

(2) I. Mitteil., S. Fujise und H. Sasaki, *J. Chem. Soc. Japan*, **59** (1938), 440; *Ber.*, **71** (1938), 341.

(3) II. Mitteil., H. Tatsuta, *J. Chem. Soc. Japan*, **61** (1940), 1043.

Es fehlte noch eine Untersuchung darüber, ob die katalytische Hydrierung des Ketoxims bei Anwesenheit einer optisch-aktiven Substanz ein optischaktives Amin ergebe.

Wenn man eine Lösung des Ketoxims mit optisch-aktiven Säure versetzt, dann bildet sich aus den beiden Substanzen ein Salz oder eine salzartige Verbindung.

Die folgende Reaktion scheint dem Verfasser sehr wahrscheinlich zu sein: nämlich bei Anwesenheit der optisch-aktiven Säure verläuft die katalytische Hydrierung des Ketoxims selektiv und die optisch-aktiven Amine werden als Reduktionsprodukte gewonnen.

Die Erwartung des Verfassers erfüllte sich bei der katalytischen Hydrierung von Acetophenonoxim (I, $R_1=C_6H_5$, $R_2=CH_3$) und Hexahydrofluorenonoxim (III); als optisch-aktive Säure wurden *d*-Weinsäure und *l*-Menthoxo-essigsäure benutzt.

Zur Trennung des Amins aus den optisch-aktiven Säuren, wurden das Reduktionsprodukt stark alkalisch gemacht und mit Äther das freie Amin extrahiert; dann wurde das Amin mit Mineralsäure oder optisch-inaktiver organischer Säure in kristallisiertes Salz übergeführt.

(1) *Acetophenonoxim* wurde bei Anwesenheit von *d*-Weinsäure oder *l*-Menthoxo-essigsäure katalytisch hydriert. Die Resultate zeigt die folgende Tafel.

I. α -Phenyläthylamin-hydrochlorid

Opt. aktive-Säure	$[\alpha]_D$ in Wasser	Opt. Reinheitsgrad (%)
<i>l</i> -Menthoxo-essigsäure ..	+0.9° (c=9.22)	18
<i>d</i> -Weinsäure	+1.1° (c=24.7)	15

II. α -Phenyläthylamin-hydrochlorid⁽⁴⁾

Konzentration (%)	25.86	14.93	3.25
$[\alpha]_D^{25}$	+7.4°	+5.4°	+3.5°

(2) *Hexahydro-fluorenylamin aus Hexahydro-fluorenonoxim*. (III). Das Oxim wurde schon von J. Murai, S. Fujise und T. Okudera⁽⁵⁾ hergestellt. Trotz der verschiedenen Reinigungsversuche erhielten die Autoren ein Oxim vom Schmp. 105–115°, doch die katalytische Hydrierung ergab ein einheitliches Amin (β -Amin, das Acetat schmolz bei 172–173°). Die Erklärung der Beobachtung wies darauf hin, dass das Oxim aus einem Stereoisomerie-Gemisch der C=N-Doppelbindung bestand. Weiter bei der Reduktion des Oxims in Alkohol-Eisessig mit Natrium-amalgam wurden hauptsächlich das β -Isomer und wenig α -Isomer erhalten.

Das α -Isomer wandelt sich bei der Acylierung teilweise in das *N*-Acyl- β -isomer um; daher vermuten die Verfasser, dass sich beide isomeren Amine nur durch die *cis*- bzw. *trans*-Stellung der Aminogruppe gegenüber dem hydrierten Benzolring des Hexahydro-fluorens unterscheiden⁽⁶⁾ (vgl. IV).

(4) Wolfgang Leithe, *Monatsh*, **381** (1929), 51.

(5) J. Murai, S. Fujise u. T. Okudera, *J. Chem. Soc. Japan*, **60** (1939), 21.

(6) S. Fujise, K. Hori und J. Matsuzawa, *J. Chem. Soc. Japan*, **60** (1939), 25. Vgl. auch die zusammenfassende Mitteilung von S. Fujise, *Ber.*, **71** (1938), 2461.

Durch die katalytische Hydrierung des Ketoxims erhalte der Verfasser unter Zusatz von *l*-Menthox-essigsäure ein optisch-aktives Hexahydrofluorenylamin. Die optische Drehung des Aminacetats war $[\alpha]_D + 4.6 \sim +6.8^\circ$. Untersuchung zur Bestimmung des optischen Reinheitsgrades wird fortgesetzt.

Versuche. (+)-*a*-Phenyläthylamin. a) 6.47 g. (0.03 mol.) *l*-Menthox-essigsäure und 4.05 g. (0.03 mol.) Acetophenonoxim wurden in je 10 c.c. Essigester gelöst und vermischt. Die Lösung wurde nach Zusatz von 0.2 g. Pt.-schwarz und 25 c.c. Essigester unter Wasserstoff geschüttelt. Nach 25 Stdn. wurde die berechnete Menge Wasserstoff (2 mol.) aufgenommen. Das Reduktionsprodukt wurde vom Essigester befreit, mit Natronlauge versetzt, ausgeäthert und nach dem Trocknen des Lösungsmittels mit Kaliumhydroxyd, die Lösung filtriert.

Das Filtrat wurde mit der ätherischen Lösung der Oxalsäure versetzt. Aus der Lösung schied sich das saures Oxalat der Base aus. Ausbeute 2.47 g. (52.7%). Die Krystalle wurden aus Alkohol umkrystallisiert. Schmp. (unter Zersetzung) 135° .

Gefunden: N, 6.72. Berechnet für $C_{10}H_{13}O_4N$: N, 6.63%.

Das Oxalat wurde mittels Kalilauge zerlegt und ausgeäthert. Nach dem Trocknen des ätherischen Extrakts wurde der Äther mit ätherischer Chlorwasserstoffsäure versetzt, und das salzsaure Salz wurde filtriert. Schmp. 166.5° .⁽⁷⁾

$$[\alpha]_D^{14} = \frac{+0.08^\circ \times 100}{9.22 \times 1} = 0.9^\circ \quad (\text{Wasser})$$

b) 2.20 g. (0.0164 mol.) Acetophenonoxim wurde im 10 c.c. Alkohol gelöst und mit einer Lösung von *d*-Weinsäure (2.54 g. in 10 c.c. Wasser) versetzt. Zur Hydrierung wurde das Gemisch nach Zusatz von 0.2 g. Platinschwarz und Alkohol-Wasser (15 c.c. und 35 c.c.) unter Wasserstoff geschüttelt. Nach 23 Stdn. wurde die berechnete Menge Wasserstoff aufgenommen. Der vom Katalysator und wässrigem Alkohol im Vacuum befreite Rückstand wurde wie bei a) als saures Oxalat isoliert. Ausbeute 2.67 g. (76%). Zersetzungspunkt 118° .

$$[\alpha]_D^{14} = \frac{+0.12 \times 100}{3.22 \times 1} = 3.2^\circ \quad (\text{Wasser})$$

Das saure Oxalat wurde in Chlorhydrat übergeführt. Schmp. $154\text{--}155^\circ$

$$[\alpha]_D^{16.5} = \frac{+0.27^\circ \times 100}{24.7 \times 1} = +1.1^\circ \quad (\text{Wasser})$$

Hexahydro-fluorenylamin (IV). a) 2.01 g. Hexahydro-fluorennoxim (0.01 mol.) und 2.14 g. *l*-Menthox-essigsäure (0.01 mol.) wurden in Alkohol-Eisessig. (1:1) gelöst, mit 1.26 g. Platinoyd unter Wasserstoff geschüttelt. Nach $5\frac{1}{2}$ Stdn. wurde die berechnete Menge Wasserstoff aufgenommen. Der von Katalysator und Lösungsmittel befreite Rück-

(7) R. Paul, *Bull. soc. chim.*, [5] 4 (1937), 1121. Der angegebene Schmelzpunkt des *dl*- α -Phenyläthylaminchlorhydrats war $157\text{--}158^\circ$.

stand liess sich beim Anreiben mit Äther in Krystalle überführen. Ausbeute 1.60 g. (60%), Schmp. 176–177°.

Die wässrige Lösung des krystallisierten Acetats wurde mit Kalilauge versetzt, ausgeäthert und nach dem Trocknen des Lösungsmittels wieder mit Eisessig versetzt. Das ausgeschiedene Hexahydro-fluorenyl-amin-acetat wurde einmal aus Alkohol umkrystallisiert und schmolz unter teilweiser Zersetzung bei 177°. Ausbeute 0.9 g.

$$[\alpha]_D^{14} = + \frac{0.31^\circ \times 100}{0.823 \times 7.95} = +4.6^\circ \quad (\text{Alkohol})$$

b) Die Essigester-Lösung (50 c.c.) von Hexahydro-fluorenonoxim (2.01 g.) und *l*-Menthoxy-essigsäure (2.14 g.) wurde mit 0.5 g. Platin-Katalysator unter Wasserstoff geschüttelt. Am Ende der Hydrierung schieden sich einige Krystalle aus, die beim Erwärmen auf 50° wieder in Lösung gebracht und heiss filtriert wurden. Das Aminsatz wurde wie bei a) zuerst frei gemacht und dann im Acetat übergeführt. Die Ausbeute des Hexahydro-fluorenylamin-acetats betrug 1.25 g. (51.3%), Schmp. 180–181.5°.

$$[\alpha]_D^{17} = \frac{+0.28^\circ \times 100}{0.799 \times 4.12 \times 1} = +6.8^\circ \quad (\text{Alkohol})$$

Aus dem Acetat wurde Hexahydro-fluorenylamin frei gemacht, welches bei 30.5–31.5° schmolz.

$$[\alpha]_D^{17} = \frac{+0.16 \times 100}{4.60 \times 1} = +3.5^\circ \quad (\text{Alkohol})$$

Zum Schlusse möchte ich Herrn Prof. Dr. Shin-ichiro Fujise für seine Anleitung bei der Ausführung dieser Arbeit meinen herzlichsten Dank aussprechen.

*Chemisches Institut, Wissenschaftliche Fakultät,
Tohoku Kaiserliche Universität, Sendai.*

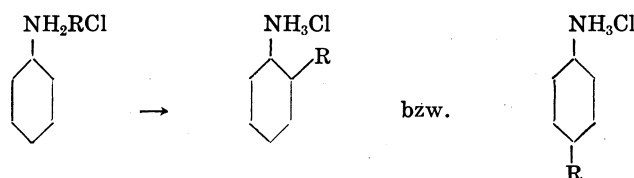
Austauschreaktion der Wasserstoffatome im festen Anilinchlorhydrat und seinen Derivaten. I. Anilinchlorhydrat (Auszug.)⁽¹⁾

Von Nobukazu OKAZAKI und Masao KOIZUMI.

(Eingegangen am 17. Juli 1941.)

Inhaltsübersicht. Erwärmt man das in der Ammoniumgruppe D-Atome enthaltende Anilinchlorhydrat, so tauschen diese D-Atome ihre Plätze gegen die H-Atome aus, die im Benzolkern befindlich sind. Dieser Platzwechsel der H-Atome findet nicht nur oberhalb des Schmelzpunktes des Anilinchlorhydrats (198°C.) in der Schmelzphase sondern auch unterhalb desselben in der mindestens mit bloßem Auge fest aussehenden Phase statt. Die Geschwindigkeit der Platzwechselreaktion wird durch die sorgfältige Trocknung des Präparates kaum beeinflusst aber sie nimmt mit steigender Temperatur ziemlich stark zu, bis schliesslich ganz nahe beim Schmelzpunkt oder noch wahrscheinlicher oberhalb desselben das Austauschgleichgewicht schnell (innerhalb einer Stunde) erreicht wird. Aus dem Versuche, der unter Benutzung des von vornherein in *o*-, *o'*- und *p*-Stellung des Benzolkerns D eingeführten Anilinchlorhydrats durchgeführt wird, ergibt sich, dass die sich an dieser Reaktion beteiligenden Kernwasserstoffatome gerade diese drei in *o*-, *o'* und *p*-Stellung befindlichen H-Atome sind.

Einleitung. Behandelt man das Chlorhydrat des *N*-Alkylanilins bei hoher Temperatur, so wandert das von vornherein an *N* gebundene Alkylradikal in die *o*- bzw. *p*-Stellung des Benzolkerns:



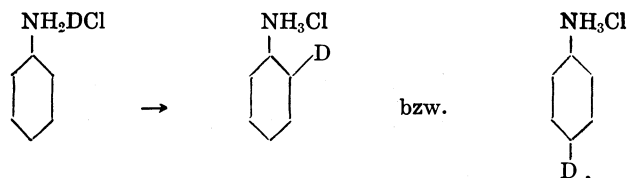
Diese zuerst von Hofmann und Martius⁽²⁾ entdeckte Umlagerung des Chlorhydrats des *N*-Alkylanilins hat später ein sehr weites Anwendungsgebiet gefunden und folglich von vielen Autoren eingehend untersucht worden.⁽³⁾ Kürzlich wurde aber von Harada und Titani⁽⁴⁾ festgestellt, dass das nicht substituierte einfache Anilinchlorhydrat die ähnliche Umlagerung ausführt. Sie fanden nämlich, dass die D-Atome, die zuerst in die Ammoniumgruppe des Anilinchlorhydrats eingeführt wurden, durch die Erwärmung des letzteren ihre Plätze gegen die Kernwasserstoffatome wechseln, die höchstwahrscheinlich in *o*-, *o'*- und *p*-Stellung befindlich sind:

(1) N. Okazaki, *J. Chem. Soc. Japan*, **62** (1941), 52.

(2) Hofmann und Martius, *Ber.*, **4** (1871), 742. Hofmann, *ebenda*, **5** (1872), 704, 720; *ebenda*, **7** (1874), 526; *ebenda*, **18** (1885), 1821.

(3) Benz, *Ber.*, **15** (1882), 1646. Nölting und Baumann, *ebenda*, **18** (1885), 1150. Nölting und Forel, *ebenda*, **18** (1885), 2681. Limpach, *ebenda*, **21** (1888), 640. Hodgkin und Limpach, *J. Chem. Soc.*, **61** (1892), 420. Reilly und Hickinbottom, *J. Chem. Soc.*, **117** (1920), 103.

(4) M. Harada und T. Titani, *dies Bulletin*, **11** (1936), 554.



Diese von Harada und Titani festgestellte Umlagerung des Anilinchlorhydrats ist in soweit für uns interessant, als sie nicht nur oberhalb des Schmelzpunktes d.h. in der Schmelzphase sondern auch unterhalb desselben in dem mindestens mit blossen Auge fest aussehenden Anilinchlorhydrat deutlich erkennbar ist. Da aber das von Harada und Titani verwendete Präparat des Anilinchlorhydrats in bezug auf seine Trocknung (über Chlorcalcium getrocknet!) nicht als ganz einwandfrei angesehen werden konnte, haben wir dieselben Versuche unter Benutzung des Anilinchlorhydrats wiederholt, das über Phosphorpentoxyd bzw. durch die Sublimation im Vakuum möglichst vollständig getrocknet worden ist.

Versuchsmethode. Die Versuchsmethode ist im grossen und ganzen dieselbe wie die früher von Harada und Titani benutzte.

Etwa 1 g. Anilinchlorhydrat,⁽⁵⁾ das von Kahlbaum für wissenschaftliche Zwecke bezogen und auf passendem Wege gereinigt worden ist,⁽⁶⁾ wird in etwa 1 ccm. 5%igen schweren Wassers aufgelöst. Da durch dieses Auflösen die H-Atome in der Ammoniumgruppe gegen die des Wassers sehr schnell ausgetauscht und bis zum Austauschgleichgewicht gebracht werden, wird das Wasser ohne weiteres durch die Destillation im Vakuum vom Anilinchlorhydrat abgetrennt. Diese dauerte aber etwa eine Nacht, um das Wasser möglichst vollständig vom Anilinchlorhydrat abzutrennen. Das so abgesonderte Wasser wird separat in einem zugeschmolzenen Glasrohr aufbewahrt.

Das auf diese Weise in die Ammoniumgruppe D eingeführte Anilinchlorhydrat wird dann, nachdem es durch Stehenlassen über Phosphorpentoxyd (dies dauerte zwei bis sechs Tage) bzw. durch die Sublimation im Hochvakuum (<0.001 mm. Hg) möglichst vollständig getrocknet worden ist, in einem Glasrohr unter Luftabschluss eingeschmolzen und während einer bestimmten Zeitlänge auf einer gewünschten Temperatur erwärmt. Nach der Erklattung wird das so erwärmte Anilinchlorhydrat im oben aufbewahrten, d.h. mit dem nicht erwärmten Anilinchlorhydrat im Austauschgleichgewicht befindlichen, schweren Wasser wieder aufgelöst. Da aber durch die Erwärmung ein Teil der D-Atome, die sich zuerst lediglich in der Ammoniumgruppe befanden, in den Benzolkern transportiert wird, werden weitere D-Atome aus dem schweren Wasser in die Ammoniumgruppe aufgenommen und der D-Gehalt des schweren Wassers nimmt dementsprechend weiter ab. Mit Hilfe der so gefundenen Abnahme des D-Gehaltes des schweren Wassers können wir deshalb den Grad des im Anilinchlorhydrat durch Erwärmung stattgefundenen Platzwechsels der H-Atome abschätzen.

Den Grad des Platzwechsels haben wir mittels des Austauschäquivalents⁽⁷⁾ nk quantitativ gemessen. Dies ist das Produkt aus der statistischen Anzahl n der Kernwasserstoffatome, die sich unter den angegebenen Versuchsbedingungen an diesem Platzwechsel beteiligen, und dem Verteilungsquotient k der D-Atome zwischen ihnen und den in der Ammonium-

(5) In Wirklichkeit werden zunächst auf einmal einige Gramm Anilinchlorhydrat gegen schweres Wasser ausgetauscht und aus dem so in Ammoniumgruppe D eingeführten Anilinchlorhydrat wird jedesmal etwa 1 g. aufgenommen, um dies auf dem weiter unten zu erwähnenden Wege separat zu behandeln (Erwärmung u.s.w.!).

(6) Das direkt von Kahlbaum bezogene Anilinchlorhydrat wird entweder durch die Sublimation bzw. durch die Umkristallisation aus Alkohol gereinigt.

(7) M. Koizumi und T. Titani, dies Bulletin, 13 (1938), 88.

gruppe befindlichen H-Atomen. Das so definierte Austauschäquivalent nk kann nun mittels der Gl. berechnet werden:

$$nk = \frac{3(3M_A k' + 2M_W)(D_a - D_e)}{3M_A k' D_e - 2M_W(D_a - D_e)} \quad (1).$$

In dieser Gl. drückt M_A und M_W die Molzahl des Anilinchlorhydrats und schweren Wassers, D_a den gewöhnlichem Wasser gegenüber gemessene Dichteüberschuss des schweren Wassers, das sich mit dem nicht erwärmten Anilinchlorhydrat im Austauschgleichgewicht befindet, D_e den des Wassers, das mit dem erwärmten Anilinchlorhydrat sich ebenfalls im Austauschgleichgewicht befindet und k' den Verteilungsquotient der D-Atome zwischen der Chlorammoniumgruppe des Anilinchlorhydrats und Wasser aus. Dieser letztere ergibt sich aus einem Vorversuche als etwa 1.2.⁽⁸⁾

Versuchsergebnisse. Die Versuchsergebnisse sind in Tabelle 1 zusammengestellt, wo die Versuchsnr. die zeitliche Reihenfolge der einzelnen Versuche darstellt.

Tabelle 1. Die Austauschreaktion des Anilinchlorhydrats in fester und geschmolzener Phase.

Versuchsnr.	Erwärmungs- temp. °C.	Erwärmungs- dauer in Stdn.	nk	Trocknung	Bemerkung
1-5	ohne Erwärmung		± 0.2	P_2O_5	fest
1'-3'	ohne Erwärmung		± 0.2	Sublimation	"
33	150	1	0.3	P_2O_5	"
31	155	1	0.2	P_2O_5	"
32	"	2	0.1	P_2O_5	"
30	160	1	0.2	P_2O_5	"
29	174	1	0.2	P_2O_5	"
28	180	1	0.4	P_2O_5	"
25-26	184	1	0.7	P_2O_5	"
9'	"	1	0.4	Sublimation	"
27	"	2	0.8	P_2O_5	"
22,23	190	1	0.7	P_2O_5	"
8'	"	1	1.0	Sublimation	"
24	"	2	1.1	P_2O_5	"
18,19	194	1	1.2	P_2O_5	"
7'	"	1	0.9	Sublimation	"
20	"	2	1.4	P_2O_5	"
21	"	3	2.2	P_2O_5	"
15,16	197	1	1.8	P_2O_5	zusammen- sintert
6'	"	1	2.0	Sublimation	"
17	"	2	2.8	P_2O_5	"
12-14	198	5-10 Min.	2.4	P_2O_5	Schmelzpkt.
5'	"	10 Min.	2.5	Sublimation	"
9,10	200	1	2.6	P_2O_5	flüssig
4'	"	1	3.0	Sublimation	"
11	"	2	3.4	P_2O_5	"
8	204	1	3.4	P_2O_5	"
6,7	210	1	3.2	P_2O_5	"

(8) Da bei der Bestimmung dieses Verteilungsquotienten k' das schwere Wasser durch die Destillation in Vakuum vom Anilinchlorhydrat abgetrennt wurde und dabei die D-Atome wegen der fraktionierten Destillation mehr oder weniger in der zurückbleibenden Lösung angereichert werden, muss der so bestimmte Verteilungsquotient k' bis zu einem gewissen Grad grösser als der wahre Verteilungsquotient sein.

Aus dieser Tabelle 1 ersieht man, dass keine regelmässigen Unterschiede zwischen den beiden Reihen der Versuche zu beobachten sind, wo bei dem einen Phosphorpentoxyd und bei dem anderen Sublimation im Hochvakuum als Trocknungsmittel benutzt wurde (vgl. dazu auch Abb. 1). Diese weist vielleicht darauf hin, dass die Reaktion in Lösung, die durch das Auflösen des einen Teils des Anilinchlorhydrats in dem in minimaler Menge zurückgebliebenen Feuchtigkeitwasser entstanden ist, mindestens kein Hauptteil der beobachteten Platzwechselreaktion sein kann. Wählt man nun aus der Tabelle 1 solche Daten aus, deren Erwärmungsdauer gerade eine Stunde beträgt und zeichnet man diese graphisch ein, so erhält man die nebenstehende Abb. 1, wo das nk gegen die Erwärmungstemperatur eingetragen ist.

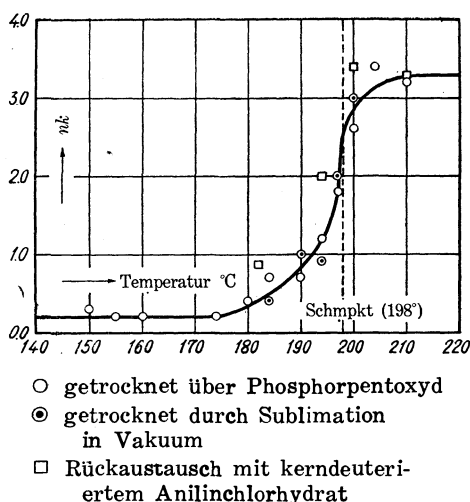


Abb. 1. Das Austauschäquivalent nk des Anilinchlorhydrats in Abhängigkeit von der Erwärmungsdauer.

Da das Austauschäquivalent nk das Produkt aus der statistischen Anzahl n der Kernwasserstoffatome, die sich an dieser Platzwechselreaktion beteiligen, und dem Verteilungsquotient k der D-Atome zwischen diesen und den in Chlorammoniumgruppe enthaltenen H-Atome ausdrückt und dieser letztere Quotient sehr nahe gleich eins angenommen werden darf, kann das nk in erster Annäherung als die statistische Anzahl n selbst angesehen werden. Diese Anzahl nimmt aber, wie Abb. 1 zeigt, bei konstant bleibender Erwärmungsdauer mit steigender Temperatur ziemlich stark zu und ganz nahe beim Schmelzpunkt oder noch genauer oberhalb desselben wird das Austauschgleichgewicht mit $n=3$ erreicht. Obwohl diese drei

H-Atome aus ihrer Anzahl zu beurteilen höchstwahrscheinlich die in *o*-, *o'*- und *p*-Stellung befindlichen drei Kernwasserstoffatome sein müssen, haben wir dies weiter durch einen besonderen Versuch sichergestellt.

Bei diesem Versuch wird nämlich das gewöhnliche Anilinchlorhydrat zuerst durch die längere Erwärmung zusammen mit 10%igem schweren Wasser ganz, d.h. nicht nur in der Ammoniumgruppe sondern auch im Benzolkern bis zum Austauschgleichgewicht deuteriert.⁽⁹⁾ Da aber durch diese Behandlung nur die in *o*-, *o'*- und *p*-Stellung befindlichen Kernwasserstoffatome durch D ersetzt werden,⁽¹⁰⁾ können wir, nachdem die in Ammoniumgruppe eingeführten D-Atome durch den Rückaustausch gegen gewöhnliches Wasser völlig ausgewaschen worden sind, solch ein schweres Anilinchlorhydrat gewinnen, das die D-Atome lediglich in *o*-, *o'*- und *p*-Stellung des Benzolkerns enthält.⁽¹¹⁾ Verfährt man mit diesem kern-

(9) M. Koizumi, dies Bulletin, **14** (1939), 530.

(10) A.P. Best und C.L. Wilson, *J. Chem. Soc.*, **1938**, 28.

(11) Das so hergestellte kerndeuterierte Anilinchlorhydrat wird durch die Fällung aus alkoholischer Lösung mittels Äthers gereinigt.

deutერიerten schweren Anilinchlorhydrat genau so wie oben und lässt das erwärmte schwere Anilinchlorhydrat gegen gewöhnliches Wasser austauschen, so kann man mit Hilfe der Gl. (1) ebenfalls das Austauschäquivalent nk ermitteln. Das so bestimmte nk geben wir in Tabelle 2 wieder.

Tabelle 2. Das unter Benutzung des schweren Anilinchlorhydrats bestimmte Austauschäquivalent nk .

Versuchsnr.	Erwärmungs- temp. °C.	Erwärmungs- dauer in Stdn.	nk	Trocknung	Bemerkung
7	182	1	0.9	P ₂ O ₅	fest
6	194	1	2.0	„	„
5	200	8 Min.	3.3	„	flüssig
3,4	200	1	3.4	„	„
1,2	210	2	3.3	„	„

Da diese Ergebnisse, die in Abb. 1 mit kleinen Vierecken eingezeichnet sind, mindestens oberhalb des Schmelzpunktes, wo das Austauschgleichgewicht eingestellt ist,⁽¹²⁾ gut mit denen übereinstimmen, die unter Verwendung des gewöhnlichen leichten Anilinchlorhydrats durchgeführt worden sind, wird nämlich festgestellt, dass wirklich die in *o*-, *o'*- und *p*-Stellung befindlichen Kernwasserstoffatome sich an dieser Reaktion beteiligen.

Diskussion der Ergebnisse. Über den Mechanismus der vorliegenden Platzwechselreaktion kommen drei Möglichkeiten in Betracht: (1) entweder findet die ganze Reaktion lediglich in der wässerigen Lösung statt, die durch das Auflösen des einen Teils des Anilinchlorhydrats in das Feuchtigkeitswasser entstanden ist, (2) oder die Reaktion findet unterhalb des Schmelzpunktes genau so wie oberhalb des Schmelzpunktes lediglich in der Schmelzphase statt, die unterhalb des Schmelzpunktes wie z.B. an den Ecken bzw. Kanten der Kriställchen in fein disperser Form gebildet wird, (3) oder es handelt sich schliesslich bei der Reaktion oberhalb des Schmelzpunktes um die Reaktion in der flüssigen Phase während unterhalb desselben von der Reaktion in der wahren festen Phase zu reden ist.

Bei dem früher von Harada und Titani⁽¹³⁾ ausgeführten Versuche, wo das Anilinchlorhydrat, das vom schweren Wasser abgetrennt worden war,

(12) Unterhalb des Schmelzpunktes, wo kein Gleichgewicht eingestellt ist, können wir keine strenge Übereinstimmung zwischen den beiden Arten der Versuchsergebnisse erwarten, weil die Geschwindigkeit der beiden Arten der Reaktion gegeneinander mehr oder weniger verschieden sein müssen. Bei den Versuchen mit dem in Ammoniumgruppe D enthaltenden Anilinchlorhydrat werden die D-Atome aus der Ammoniumgruppe in den Benzolkern transportiert, während mit dem kerndeutერიerten Anilinchlorhydrat gerade das entgegengesetzte der Fall ist. Aber die Geschwindigkeit dieser beiden Arten der Reaktion muss gegeneinander mehr oder weniger verschieden sein. Weiter müssen wir auch die Sachlage in Betracht ziehen, dass das kerndeutერიerte Anilinchlorhydrat wegen der Einfachheit des Reinigungsprozesses nicht so rein wie das in Ammoniumgruppe D eingeführte Anilinchlorhydrat war (vgl. dafür Fussnote (6) und (11)). Dieser Unterschied der Reinheit der Präparate übt offensichtlich auch gewisse Einflüsse auf die Reaktionsgeschwindigkeit aus.

(13) loc. cit.

über Chlorcalcium getrocknet wurde, wurde der Gleichgewichtswert des Austauschäquivalents nk ($=3$) durch einstündige Erwärmung schon um etwa vierzig Grad unterhalb des Schmelzpunktes erreicht. Dagegen wird dies bei dem vorliegenden Versuche, wo die Trocknung des vom schweren Wasser abgetrennten Anilinchlorhydrats mittels Phosphorpentoxyd bzw. durch die Sublimation im Hochvakuum durchgeführt wurde, ebenfalls durch einstündige Erwärmung erst ganz nahe beim Schmelzpunkt oder noch wahrscheinlicher erst oberhalb desselben erreicht. Diese Sachlage weist offensichtlich darauf hin, dass die erste der oben angegebenen Möglichkeiten auch nicht ganz ausgeschlossen werden kann, besonders wenn die Trocknung des Präparates nicht ganz einwandfrei ist. Aber mindestens bei dem vorliegenden Versuche, wo das vom Wasser abgetrennte Anilinchlorhydrat so weit wie möglich getrocknet worden war und weiter die Ergebnisse der beiden Reihen der Versuche, wo bei einer davon das Präparat über Phosphorpentoxyd und bei der anderen durch die Sublimation im Hochvakuum möglichst vollständig getrocknet worden war, miteinander sehr gut übereinstimmten, darf wohl geschlossen werden, dass die Reaktion in wässrigen Lösungen kein Hauptteil der beobachteten Reaktion sein dürfte. Wohl aber die zweite Möglichkeit, dass die Reaktion nicht nur oberhalb des Schmelzpunktes sondern auch unterhalb desselben, tatsächlich in der Schmelzphase stattfindet, die beim letzteren Fall wie z.B. an den Ecken bzw. Kanten der Kriställchen in dispersem und folglich nicht mit blossem Auge direkt beobachtbarer Form entsteht. Diese Möglichkeit liegt um so näher, als uns fast unmöglich wäre, eine absolut reine Substanz zu bereiten und gerade unter dem Einfluss dieser minimalen Menge der Verunreinigungen kann die disperse Schmelzphase in der mit blossem Auge fest aussehenden Substanz gebildet werden (Vorschmelzen!). Aber wäre dies wirklich der Fall, so müssen wir unbedingt annehmen, dass die Diffusion in fester Phase des Anilinchlorhydrats genügend schnell verläuft, um die beobachtete ziemlich grosse Geschwindigkeit der Bruttoreaktion befriedigend zu erklären. Aus diesem Grunde möchten wir augenblicklich lieber annehmen, dass die Reaktion unterhalb des Schmelzpunktes mindestens grössten Teils in der wahren festen Phase stattfindet, obwohl um diese Annahme zu bestätigen weitere sorgfältige Versuche ausgeführt werden müssen.

Hinsichtlich der Reaktion oberhalb des Schmelzpunktes ist durchaus möglich, dass es sich fast ausschliesslich um die Reaktion in geschmolzener flüssiger Phase handelt. In der geschmolzenen Phase des Anilinchlorhydrats sind fünf Arten der Moleküle und Ionen denkbar: nämlich $C_6H_5NH_3Cl$, $C_6H_5NH_3^+$, Cl^- , $C_6H_5NH_2$ und HCl . Da aber unter diesen fünf Arten der Moleküle und Ionen Cl^- keine direkte Beziehung zur Deuterierungsreaktion besitzt und weiter die Konzentration von $C_6H_5NH_2$ und HCl als sehr klein angesehen wird,⁽¹⁴⁾ kommen als Reaktionsteilnehmer hauptsächlich die nicht ionisierten Anilinchlorhydratmoleküle $C_6H_5NH_3Cl$ und Aniliniumionen $C_6H_5NH_3^+$ in Betracht. Falls aber diese beiden gerade in dieser Form als Protonakzeptor der Reaktion teilnähmen, würden die D-Atome in jedem Fall in *m*-Stellung eingeführt werden, weil die Chlorammoniumgruppe $-NH_3Cl$ und die Ammoniumgruppe $-NH_3^+$ den Kationoids substituenten immer zur *m*-Stellung diri-

(14) W.J. Kurbatow, *Chem. Zentr.*, **1902**, II, 89.

giert⁽¹⁵⁾ und die Deuterierungsreaktion als gerade diese Art der Reaktion aufgefasst werden muss.⁽¹⁶⁾ Um diese Diskrepanz zu vermeiden, müssen wir deshalb annehmen, dass die betreffenden beiden Molekülarten, mindestens so lange als sie als Protonakzeptor wirken, sich in einem fast dissoziierten Zutsand befinden, wie etwa durch die Formeln ausgedrückt wird:



Mit Hilfe dieser Annahme können die vorliegenden Versuchsergebnisse befriedigend erklärt werden, dass das Anilinchlorhydrat in Schmelzphase in *o*-, *o'*- und *p*-Stellung ziemlich leicht deuteriert wird, weil erstens die neutrale Aminogruppe den Kationoids substituenten immer zur *o*- und *p*-Stellung dirigiert und zweitens diese Kerndeuterierungsreaktion der neutralen Anilinmoleküle $\text{C}_6\text{H}_5\text{NH}_2$ im Vergleich mit den Aniliniumionen $\text{C}_6\text{H}_5\text{NH}_3^+$ viel leichter verläuft.⁽¹⁷⁾

Zum Schluss möchten wir Herrn Prof. T. Titani für seine Anregung zu dieser Arbeit und freundlichen Ratschläge herzlich danken. Der Nippon Gakujutu Sinkōkai (der Japanischen Gesellschaft zur Förderung der wissenschaftlichen Forschung) und der Hattori Kōkōkai (der Hattori Stiftung) sind wir auch für ihre finanzielle Unterstützung bei der Durchführung der vorliegenden Arbeit zu bestem Dank verpflichtet.

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chemische Forschung.)

(15) C.K. Ingold, C.G. Raisin und C.L. Wilson, *J. Chem. Soc.*, 1936, 1637.

(16) Vgl. z.B. M. Koizumi, dies Bulletin, 15 (1940), 37.

(17) M. Koizumi, dies Bulletin, 14 (1939), 530.

Influence of Sorption on the Electric Conductivity of Pulverized Metals. I.

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(Received July 18, 1941.)

Introduction. As the recent development of catalyst chemistry, it has become very important to make clear the state of sorbed hydrogen on metals, especially on transition elements, which are frequently used as catalyst. Generally speaking, from various experiments it is verified that above certain temperatures the sorbed hydrogen by metal is present in the atomic or in the ionic form. By the method of electron diffraction, Germer⁽¹⁾ has found that in some range of temperature and pressure, hydrogen exists in the atomic form on Ni surface and that the individual hydrogen atoms are so arranged around the lattice centers as to have twice the interatomic distances of the Ni atoms. On the other hand, the experiment of Coehn⁽²⁾ is sufficient to make us believe that the hydrogen is present in metal in the form of protons. Coehn has found that when electromotive force is applied to palladium wire, protons are concentrated toward cathodic side. Similar result has also been found by Hirota and Horiuti⁽³⁾. Moreover, according to the experimental data on the diffusion of hydrogen through metals, we can suggest that the hydrogen exists in the atomic form. These experiments elucidate the state of hydrogen on the surface or in the bulk of metal to some extent; there remains, however, some ambiguities. The present author has found that hydrogen has characteristic influence on the electric conductivity of various metal powders and attempted to make clear the state of sorbed hydrogen from these experimental data.

Experimental. The experiments were carried out on such metals as Ni, Co, Cu, Ag, Pt, and Au, of which Ni, Co, Cu, and Ag were prepared by ignition of nitrates and by reduction in hydrogen, while Pt and Au were prepared by reduction of chlorides in hydrogen. The conductivity was measured by current-voltage method. The hydrogen used was perfectly free from oxygen and water vapour, and its pressure can be controlled at will, while the conductivity is measured. Before measurements, the metals were thoroughly reduced again by hydrogen. Then the measurement of conductivity at constant temperature under various pressures of hydrogen shows that the influence of hydrogen pressure on the conductivity is characteristic for each metal. We can classify them in the three types as follow:

- (1) The conductivity increases as the hydrogen pressure rises:—Pt.

(1) L. Germer, *Z. Physik*, **54** (1929), 408.

(2) A. Coehn, *Z. Elektrochem.* **35** (1929), 676.

(3) K. Hirota and Horiuti, *Oyo Buturi*, **8** (1939), 266.

- (2) The conductivity decreases as the hydrogen pressure rises:—
Ni, Co, Ag, and Cu.
- (3) No effect:—Au.

Detailed observations will be described for each of these metals.

Nickel. It is well-known that the conductivity of nickel oxide increases with oxygen pressure, but no report is found on the effect of hydrogen on the conductivity of Ni powder.

When hydrogen is introduced on Ni oxide at temperatures higher than 200°C., the conductivity decreases as the reduction proceeds, the velocity of which is slower than that of reduction. The result of kinetic observation, which is carried out at 250°C., is shown in Fig. 1. In the reduction process, a stationary state is attained in 30 minutes, while in the oxidation process, it takes more than 5. hours to attain the stationary state.

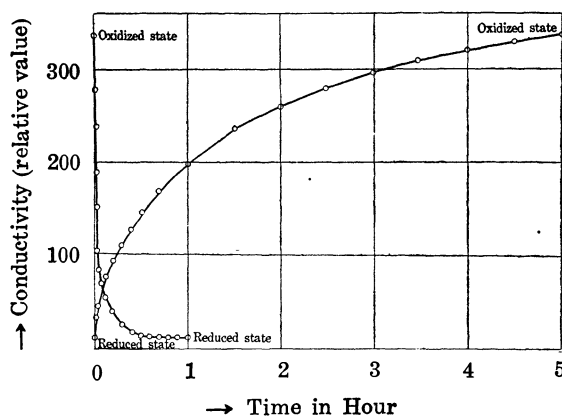


Fig. 1. Oxidation and reduction process for Ni at 250°C.

As the temperature coefficient of the conductivity is large, the conductivity-temperature relation is determined on oxidised and reduced states at constant oxygen and hydrogen pressures, respectively. The measurements show that conductivity increases with temperature and that the relation between the conductivity and the temperature is expressed exactly by the following exponential formula:

$$\sigma \propto e^{-E/RT},$$

in the oxidised as well as in the reduced state. The relation is shown in Fig. 2 and 3 by plotting the logarithm of σ against the reciprocal of the absolute temperature. The inclinations of these straight lines give the activation energies, and which are calculated to be 3.50 kcal and 6.98 kcal for oxidised and reduced states, respectively. The activation energy for reduced state is about twice that of the oxidised state.

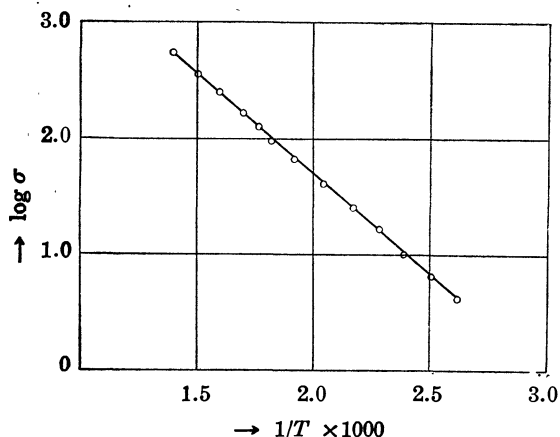


Fig. 2. Conductivity-temperature relation for oxidized Ni.

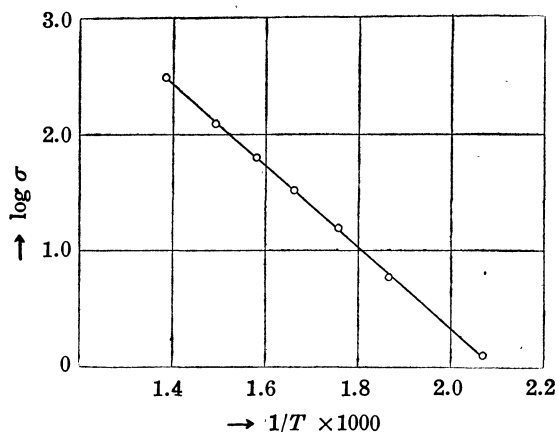


Fig. 3. Conductivity-temperature relation for reduced Ni.

In the determination of the conductivity, we must assume the Ohm's law. Here is checked the applicability of Ohm's law, both in the oxidized and the reduced Ni. The results of measurement are graphically shown in Fig. 4. In the figure, we see that the current-voltage relation is strictly linear, but the lines do not pass the origin. In both cases, the measurements were carried out after the specimen were electrolysed several hours. In the case of the oxide, $i=0$ at $V=0.24$ volt, and it shows negative current at $V=0$, while in the case of reduced Ni, $i=0$ at $V=0.1$ volt, and it also shows negative current at $V=0$. These results suggest that the electric current is at least partially conducted by the ions.

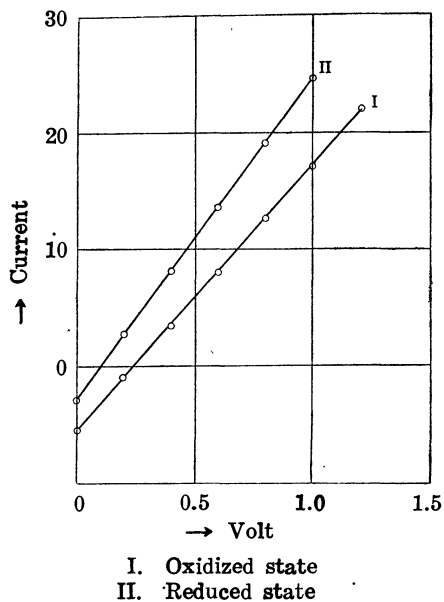


Fig. 4. Current-voltage relation.

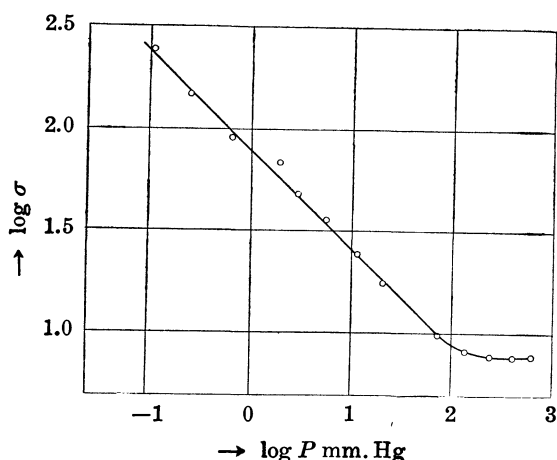


Fig. 5. Conductivity-pressure relation for Ni at 300°C.

Now, the relation between the conductivity and the hydrogen pressure will be described. As is mentioned above, the conductivity decreases as the hydrogen pressure increases. The relation between the conductivity and hydrogen pressure from 0.1 mm. Hg to 100 mm. Hg by the following formula:

$$\sigma \propto P^{-1/n},$$

where P is the pressure of hydrogen and n is a constant. The logarithm of σ and P is shown graphically in Fig. 5, which shows that the above relation holds from 0.1 mm. Hg to 100 mm. Hg, and above 100 mm. Hg the conductivity does not change any more. In the region where the above relation holds, n is found to be 2.0. This relation gives some hints as to the mechanism of conduction and the state of the sorbed hydrogen on nickel.

Summary.

(1) The electric conductivity of such pulverized metals as Pt, Au, Ni, Co, Cu, and Ag has been measured in the atmosphere of hydrogen.

(2) The effect of hydrogen on the conductivity is characteristic for each metal, and can be classified in three types:

- a) The conductivity increases as the hydrogen pressure rises:—Pt.
- b) The conductivity decreases as the hydrogen pressure rises:—Ni, Co, Cu, and Ag.
- c) No effect:—Au.

(3) In the case of nickel, more detailed observations were carried out as regards the oxidation and the reduction velocities, the relation between the conductivity and the temperature, the relation between the current and the voltage both in the cases of oxidized and reduced nickel, and finally the relation between the conductivity and the hydrogen pressure.

(4) A relation between the conductivity and the hydrogen pressure is expressed from 0.1 mm. Hg up to 100 mm. Hg by the following expression:

$$\sigma \propto P^{-1/n},$$

and above 100 mm. Hg a saturation in conductivity is attained.

In conclusion, the author wishes to express his sincere thanks to Dr. S. Sato, the director of the laboratory, for his kind guidance and also for the permission of the publication.

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Studies on Styrene Ozonide.

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(Received July 17, 1941.)

The writer's interest in the studies of ozone⁽¹⁾ particularly with respect to its preparation and its solubility in various solvents was directed by the suggestion of Prof. Komatsu toward the elucidation of the chemical state of ozonides which so far had not been definitely established.

As the first step the styrene ozonide has been studied. It has been found that this compound usually exists as polymers which will be described in the experimental part.

Experimental and Discussion.

I. Preparation of Styrene Ozonide. Purified styrene is dissolved in carbon tetrachloride, in benzene, in chloroform, or in ethyl ether. On cooling the above solutions in ice water about 2% ozonized air which has been washed with 5% potassium hydroxide solution is then passed through the solution at the speed of about 20 liter per hour. Immediately after the reaction is over petroleum ether is added to the reaction mixture and the styrene ozonide precipitate thus formed is filtered off. 20 g. of the dried ozonide precipitate is dissolved in 50 c.c. purified benzene. In case of ozonide prepared in carbon tetrachloride or in benzene, petroleum ether is added 3 times to the benzene solution using 5 c.c. at each time and shaking the solutions vigorously after each addition. Ozonide precipitate thus formed is indicated as Fraction A (F_A).

With the ozonide prepared in chloroform, its benzene solution is treated 6 times with petroleum ether using 5 c.c. at each time. The precipitate thus formed is indicated also as Fraction A (F_A). With ozonide prepared in ethyl ether its benzene solution is treated 16 times with petroleum ether using 5 c.c. at each time. The precipitate thus formed is indicated also as Fraction A (F_A).

To each mother liquor from which F_A has been separated is now added 5 c.c. petroleum ether and the precipitate formed is collected, thus repeating the same procedure until no more precipitate comes out. The precipitates obtained by this series of treatment are united and indicated as Fraction B (F_B). F_A and F_B are dried in a desiccator under reduced pressure, 5–6 mm. Hg.

All these precipitates have been subjected to the elementary analyses, the results of which are indicated in Table 1. It shows that all these ozonide precipitates have the same elementary composition within the limits of the experimental errors.

During the above experiment it has been found that these ozonide

(1) F. Kawamura, *J. Chem. Soc. Japan*, **53** (1932), 783; **54** (1933), 553; **55** (1934), 849.

Table 1. Results of Elementary Analysis of Styrene Ozonide Preparations.

Solvent	Yield		Material used (mg.)	C (%)	H (%)
	Fraction	(%)			
Carbon tetrachloride	A	62	1.375	63.91	5.32
	B	32	1.459	63.06	5.25
Benzene	A	66	1.520	64.01	5.33
	B	21	1.432	63.11	5.31
Chloroform	A	56	1.601	63.95	5.29
	B	32	1.386	63.17	5.23
Ethyl ether	A	45	1.474	63.65	5.32
	B	39	1.542	63.03	5.23
Calcd. for $C_8H_8O_3$				63.15	5.30

preparations decompose on being brought to contact with moisture into benzaldehyde, benzoic acid, formaldehyde, formic acid and hydrogen peroxide.

II. Effect of Styrene Ozonide upon Styrene Polymerization. During the ozonization it has been found that a part of styrene undergoes polymerization to produce a resinous substance, thus the yield of styrene ozonide being much reduced. With the purpose of finding out the cause of this styrene polymerization the reaction between monostyrene and styrene ozonide has been investigated by the methods described below. It has, thus, been found that the latter possesses no oxidative action upon the former but accelerates markedly the polymerization of the former.

a) *Effect of Styrene Ozonide Concentration.* To styrene is added the ozonide prepared in chloroform as indicated in Section I at the concentrations of 0, 0.04, 0.20, and 0.72 mole per liter, and the mixture is put in the Ostwald viscosimeter immersed in a thermostat at 40° and 50°. Its viscosity is measured at various intervals of time, from which the velocity of polymerization has been determined. The results are indicated in Figure 1. It shows that the ozonide promotes the polymerization, the effect of the ozonide concentration being marked when its concentration is small but becoming less marked as it increases.

For instance, the viscosity attained in 144 hours at 50° by styrene to which no ozonide has been added is attained in 42, 24, and 18 hours by those containing respectively 0.04, 0.2, and 0.72 mole per liter ozonide. This is in accord with the results obtained by Hantz and Adkins⁽²⁾ for styrene polymerization by di-isobutylene ozonide.

Figure 1 also shows that the reaction consists of two stages, Induction and Polymerization Stages. It is of interest to note that the increase in

(2) Hantz and Adkins, *J. Am. Chem. Soc.*, **53** (1931), 1058; **55** (1933), 1609.

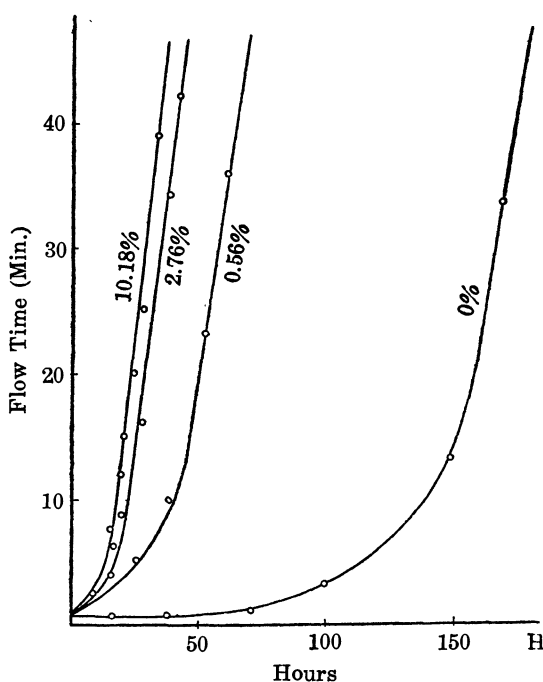


Fig. 1. Effect of Styrene Ozonide Concentration upon the Styrene Polymerization.

styrene ozonide concentration shortens the induction period, but has no effect upon the rate of polymerization.

b) *Effect of Temperature.* The styrene polymerization in the presence of varying amount of styrene ozonide has been studied at 30°, 40° and 50°, the results of which are plotted in Figure 2. It is seen from this figure that at 30° styrene containing 0.20 mole per liter of the ozonide attains a certain viscosity after 288 hours while at 40° the same viscosity is attained after 72 hours, and at 50° after 28 hours. Thus, the polymerization by the action of the ozonide is accelerated by the temperature rise. Like the effect of the concentration the temperature effect is also for the shortening of the induction period but not for the polymerization period. Figure 2 also shows that the lower the temperature, the more marked the effect of styrene ozonide concentration.

c) *Effect of the Decomposition Products.* As has been previously stated styrene ozonide decomposes by the action of water to benzaldehyde, formaldehyde, benzoic acid, and formic acid, also often this ozonide is mixed with some polystyrene. The effect of these decomposition products upon the styrene polymerization has, therefore, been investigated. That is, the velocity of the polymerization has been measured with pure styrene to which 0.20 mole per liter of each of these substances has been added separately. It has thus been found that benzaldehyde and polystyrene accelerate the polymerization although their effect is slight in comparison with that of styrene ozonide, whereas benzoic acid, formic acid, and formaldehyde retard the polymerization.

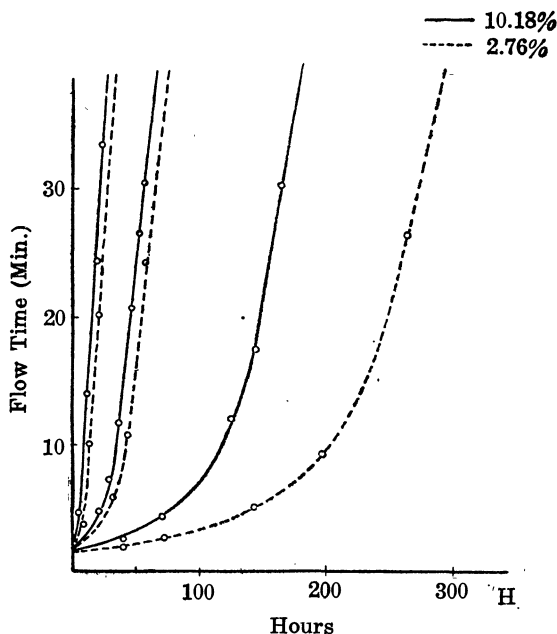


Fig. 2. Effect of Temperature upon the Styrene Polymerization.

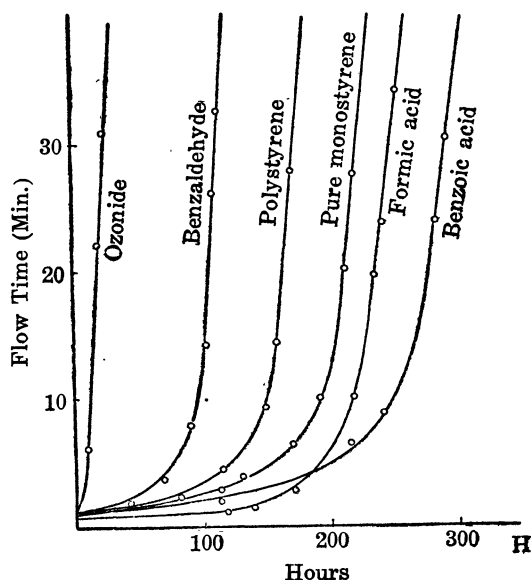


Fig. 3. Effect upon the Styrene Polymerization of the Decomposition Products of Styrene Ozonide, Benzaldehyde, Formaldehyde, Benzoic Acid, Formic Acid, and Polystyrene.

III. Polymerization of Styrene Ozonide. It has been stated in section I that styrene ozonide is prepared in various solvents. These ozonide preparations have been found to possess different viscosities. This is probably due to the fact that the ozonide is not a simple molecule as indicated by the formula, $\text{C}_6\text{H}_5\text{—CH—CH}_2$, but its polymers at different polymerization stages.

According to Harries⁽³⁾, Fonrobert⁽⁴⁾, and Wagner⁽⁵⁾ the molecular structure of styrene ozonide is of glycol type, i.e. $\text{C}_6\text{H}_5\text{—CH—CH}_2$. The production of benzaldehyde, hydrogen peroxide, and formaldehyde in the reaction of the ozonide and water supports this view. On the other hand, Baeyer⁽⁶⁾, Staudinger⁽⁷⁾, Rieche⁽⁸⁾ and Pummerer⁽⁹⁾ have proposed as the results of their studies the formula of acetal type, i.e. $\text{C}_6\text{H}_5\text{CH} \begin{matrix} \text{O—O} \\ \diagup \quad \diagdown \\ \text{O} \end{matrix} \text{CH}_2$. In fact, no glycol derivative is formed by the reduction of the ozonide.

(3) Harries, "Untersuchungen über Ozon und seine Einwirkung auf Organische Verbindungen," 48 (1916); *Ann.*, **410** (1915), 29.

(4) Fonrobert, "Das Ozon," 135 (1916).

(5) Wagner, *Ann.*, **410** (1915), 29.

(6) Baeyer and Villiger, *Ber.*, **32** (1899), 3625; **33** (1900), 858.

(7) Staudinger, *Ber.*, **58** (1925), 1088.

(8) Rieche, "Alkylperoxyd und Ozonid," (1913).

Z. angew. Chem., **43** (1930), 628; **44** (1931), 590; **45** (1932), 441.

(9) Pummerer, *Ann.*, **529** (1939), 33.

Z. angew. Chem., **47** (1934), 366.

However, the ozonide prepared at the present experiment is a highly viscous liquid of resinous consistency. Furthermore, the ozonide, like peroxides, induces polymerization for styrene but unlike the latter exerts no oxidizing action.

These chemical properties also support the view that the ozonide exists in polymerized form. It is then expected that the stage of polymerization, that is the number of monomer polymerized, depends upon the nature of the solvent used, particularly upon its dipole moment. With the purpose of confirming this view the benzene solutions of the ozonides prepared in the different solvents as mentioned in Section I, have been examined with respect to the viscosity and the freezing point.

The results have shown that they are in fact polymers and also that there is parallelism between the dipole moment of the solvent used for its preparation and the stage of the ozonide polymerization, e.g. the lower the dipole moment is, the higher the polymerization stage.

a) *Molecular Weight Determination by Cryoscopic Method.* As described in Section I styrene ozonide has been freshly prepared using the 4 different solvents and its benzene solution has been subjected to the determination of freezing point by the ordinary method and average molecular weight has been calculated from the results. They are shown in Table 2.

It is seen from the table that F_A and F_B of carbon tetrachloride, $\mu=0$, have different average molecular weight. That of the former, 882, may be approximated to 912, indicating the formula, $(C_8H_8O_3)_6$. That of the latter, 678, is roughly equal to 608 which corresponds to the composition,

Table 2. Molecular Weight of Styrene Ozonide by Cryoscopic Method.

a) Ozonide prepared in Carbon Tetrachloride; $\mu = 0$.

Fraction	Yield		Amount of material used g.	Δt °C.	Mol. Wt.	Formula
	g.	%				
$F_A \begin{cases} 1 \\ 2 \\ 3 \end{cases}$	$\begin{cases} 3.85 \\ 3.83 \\ 3.64 \end{cases}$	56	$\begin{cases} 0.4435 \\ 0.4264 \\ 0.4536 \end{cases}$	$\begin{cases} 0.140 \\ 0.108 \\ 0.117 \end{cases}$	$\begin{cases} 896 \\ 884 \\ 865 \end{cases}$	$\simeq 912 = (C_8H_8O_3)_6$
$F_B \begin{cases} 4 \\ 5 \end{cases}$	$\begin{cases} 3.36 \\ 3.33 \end{cases}$	33	$\begin{cases} 0.4665 \\ 0.4732 \end{cases}$	$\begin{cases} 0.112 \\ 0.155 \end{cases}$	$\begin{cases} 692 \\ 662 \end{cases}$	$\simeq 608 = (C_8H_8O_3)_4$
Total amount used	20.3)		0.4643	0.159	725	
Loss	2.30	11				

Fraction 1(F_1) has been precipitated by adding to 50 c.c. benzene solution 5 c.c. petroleum ether.

Fraction 2(F_2) Mother liquor of $F_1 + 5$ c.c. petroleum ether.

Fraction 3(F_3) " " " $F_2 + 5$ c.c. " "

Fraction 4(F_4) " " " $F_3 + 10$ c.c. " "

Fraction 5(F_5) " " " $F_4 + 15$ c.c. " "

$(C_8H_8O_3)_4$. Thus, styrene ozonide prepared in carbon tetrachloride, may be considered to consist of 56% $(C_8H_8O_3)_6$ and 33% $(C_8H_8O_3)_4$.

Similarly the ozonide prepared in benzene, $\mu=0$, consists of 56% hexamer (in F_A) and 29% tetramer (in F_B). The ozonide prepared in chloroform; $\mu=0.95 \times 10^{-18}$, contains 57% tetramer (in F_A) and 25% dimer (in F_B), but no hexamer. With the ozonide prepared in ethyl ether, $\mu=1.10 \times 10^{-18}$, 78% dimer only has been found. All these results are recorded in Table 2.

b) Ozonide prepared in Benzene, $\mu = 0$.

Fraction	Yield		Amount of material used g.	Δt °C.	Mol. Wt.	Formula
	g.	%				
$F_A \begin{Bmatrix} 1 \\ 2 \\ 3 \end{Bmatrix}$	$\begin{Bmatrix} 4.13 \\ 3.88 \\ 3.65 \end{Bmatrix}$	59	$\begin{Bmatrix} 0.3146 \\ 0.3364 \\ 0.3483 \end{Bmatrix}$	$\begin{Bmatrix} 0.082 \\ 0.089 \\ 0.095 \end{Bmatrix}$	$\begin{Bmatrix} 876 \\ 858 \\ 832 \end{Bmatrix}$	$\simeq 912 = (C_8H_8O_3)_6$
$F_B \begin{Bmatrix} 4 \\ 5 \end{Bmatrix}$	$\begin{Bmatrix} 2.95 \\ 2.88 \end{Bmatrix}$	29	$\begin{Bmatrix} 0.3567 \\ 0.3725 \end{Bmatrix}$	$\begin{Bmatrix} 0.121 \\ 0.132 \end{Bmatrix}$	$\begin{Bmatrix} 672 \\ 644 \end{Bmatrix}$	$\simeq 608 = (C_8H_8O_3)_4$
Total amount used	19.95		0.3426	0.109	715	
Loss	2.55	13				

Fractions 1, 2, 3, 4, and 5 have been obtained from benzene solution exactly in the same way as in Table 2 a.

c) Ozonide prepared in Chloroform, $\mu = 0.95 \times 10^{-18}$.

Fraction	Yield		Amount of material used g.	Δt °C.	Mol. Wt.	Formula
	g.	%				
$F_A \begin{Bmatrix} 1 \\ 2 \\ 3 \end{Bmatrix}$	$\begin{Bmatrix} 4.12 \\ 3.84 \\ 3.82 \end{Bmatrix}$	57	$\begin{Bmatrix} 0.3435 \\ 0.3628 \\ 0.3766 \end{Bmatrix}$	$\begin{Bmatrix} 0.133 \\ 0.146 \\ 0.155 \end{Bmatrix}$	$\begin{Bmatrix} 585 \\ 569 \\ 554 \end{Bmatrix}$	$\simeq 608 = (C_8H_8O_3)_4$
$F_B \begin{Bmatrix} 4 \\ 5 \end{Bmatrix}$	$\begin{Bmatrix} 3.66 \\ 3.61 \end{Bmatrix}$	35	$\begin{Bmatrix} 0.3845 \\ 0.3850 \end{Bmatrix}$	$\begin{Bmatrix} 0.226 \\ 0.253 \end{Bmatrix}$	$\begin{Bmatrix} 388 \\ 346 \end{Bmatrix}$	$\simeq 304 = (C_8H_8O_3)_2$
Total amount used	20.50		0.3762	0.176	486	
Loss	1.45	7				

Fraction 1(F_1) has been precipitated by adding to 50 c.c. benzene solution 10 c.c. petroleum ether.

Fraction 2(F_2) Mother liquor of $F_1 + 10$ c.c. petroleum ether.

Fraction 3(F_3) " " " $F_2 + 10$ c.c. " "

Fraction 4(F_4) " " " $F_3 + 20$ c.c. " "

Fraction 5(F_5) " " " $F_4 + 20$ c.c. " "

d) Ozonide prepared in Ethyl Ether, $\mu = 1.10 \times 10^{-18}$.

Fraction	Yield		Amount of material used g.	Δt °C.	Mol. Wt.	Formula
	g.	%				
F _A {	1 3.16	76	0.3674	0.290	288	} $\simeq 304 = (C_8H_8O_3)_2$
	2 3.28		0.3752	0.322	265	
	3 3.45		0.3566	0.320	254	
	4 3.06		0.3622	0.330	250	
	5 2.37		0.3455	0.325	242	
Total amount used	20.75		0.3865	0.341	289	
Loss	5.43	27				

Fraction 1 (F₁) has been precipitated by adding to 50 c.c. benzene solution 50 c.c. petroleum ether.

Fraction 2 (F₂) Mother liquor of F₁ + 15 c.c. petroleum ether.

Fraction 3 (F₃) " " " F₂ + 15 c.c. " "

Fraction 4 (F₄) " " " F₃ + 30 c.c. " "

Fraction 5 (F₅) " " " F₄ + 40 c.c. " "

b) *Molecular Weight Determination by Viscosity Measurement.* According to Staudinger⁽¹⁰⁾ molecular weight of a substance in colloidal solution, e. g. styrene ozonide in benzene, can be determined by viscosity measurement more accurately than by the freezing point method. With benzene solution of each fraction of the ozonide prepared in the previous experiment relative viscosity has been measured at 20° by means of the Ostwald viscosimeter. From this value the molecular weight as well as the number of monomer polymerized has been calculated according to the Staudinger equations:

$$\eta_{sp} / C_{gm} = K_m \cdot M \dots \dots (1) \quad \eta_{sp} / C = K_m \cdot n \dots \dots (2)$$

where η_{sp} , M , n , C_{gm} and C are respectively relative viscosity, molecular weight, number of monomer constituting a polymer, molar concentration, and concentration in grams per liter. K_m is viscosity-molecular weight constant and its value is taken as 8.3×10^{-4} .

The results thus obtained with the ozonide prepared in carbon tetrachloride, benzene, chloroform, and ethyl ether are shown in Table 3. It shows that the ozonide prepared in carbon tetrachloride contains 55% hexamer (F_A) and 34% tetramer (F_B).

The ozonide prepared in benzene contains 56% hexamer and 23% tetramer. This result is also in agreement with that obtained by freezing point method (Table 2) as well as with that of ozonide prepared in carbon tetrachloride. The ozonide prepared in chloroform contains 56% tetramer and 31% dimer, but no hexamer. In F_A and F_B from ethyl ether only dimer has been found by this method. All these results are in agreement with those obtained by the freezing point method which are shown in Table 2.

(10) Staudinger, *Z. angew. Chem.*, **49** (1936), 574.

Table 3. Molecular Weight of Styrene Ozonide by Viscosity Method.

a) Ozonide prepared in Carbon Tetrachloride

i. Molecular Weight

(calculated according to $\eta_{sp}/C_{gm} = K_m \cdot M$ $K_m = 8.3 \times 10^{-4}$)

Fraction	Yield		η_{sp}	C_{gm}	Mol. Wt. from η_{sp}	Mol. Wt. from F.P.	Formula
	g.	%					
F _A { 1	4.35	55	0.23	0.325	862 $\simeq$ 875	$\simeq$ 912 = (C ₈ H ₈ O ₃) ₆	(C ₈ H ₈ O ₃) ₆
2	5.38		0.21	0.298	855 $\simeq$ 860		
F _B 3	6.39	34	0.16	0.301	640 $\simeq$ 652		
Material used	18.85		0.21	0.300	850	855	
Loss	2.16	11					

ii. Number of Monomer polymerized

(calculated according to $\eta_{sp}/C = K_m \cdot n$)

Fraction	C	η_{sp}/C	n
F _A { 1	49.4	46.6 $\times 10^{-4}$	5.6
2	45.3	46.3 $\times$ „	5.6
F _B 3	45.7	35.0 $\times$ „	4.2 $\simeq$ 2
Total mixture	45.7	46.0 $\times$ „	5.6

F₁ has been precipitated by adding to 50 c.c. benzene solution 5 c.c. petroleum ether.F₂, Mother liquor of F₁ + 10 c.c. petroleum ether.F₃, „ „ „ „ F₂ + 25 c.c. „ „

b) Ozonide prepared in Benzene.

i. Molecular Weight

Fraction	Yield		η_{sp}	C_{gm}	Mol. Wt. from η_{sp}	Mol. Wt. from F.P.	Formula
	g.	%					
F _A { 1	5.38	65	0.23	0.322	850 $\simeq$ 865	$\simeq$ 912 = (C ₈ H ₈ O ₃) ₆	(C ₈ H ₈ O ₃) ₆
2	7.27		0.21	0.301	830 $\simeq$ 829		
F _B 3	4.63	23	0.15	0.300	600 $\simeq$ 658		
Material used	19.50		0.19	0.275	825	805	
Loss	2.22	11					

ii. Number of Monomer polymerized

Fraction	<i>C</i>	η_{sp}/C	<i>n</i>
$F_A \begin{cases} 1 \\ 2 \end{cases}$	49.0 45.9	46.9×10^{-4} $45.9 \times \text{,,}$	$\begin{cases} 5.1 \\ 5.5 \end{cases} \simeq 6$
$F_B \quad 3$	45.0	$33.3 \times \text{,,}$	$4.0 \simeq 4$
Total mixture	41.7	$41.6 \times \text{,,}$	5.5

F_1 has been precipitated by adding to 50 c.c. benzene solution 5 c.c. petroleum ether.

F_2 , Mother liquor of $F_1 + 10$ c.c. petroleum ether.

F_3 , " " " $F_2 + 25$ c.c. " "

c) Ozonide prepared in Chloroform.

i. Molecular Weight

Fraction	Yield		η_{sp}	C_{gm}	Mol. Wt. from η_{sp}	Mol. Wt. from F.P.	Formula
	g.	%					
F _A { 1 2	5.59 5.93	56	0.20 0.18	0.471 0.390	580 $\simeq$ 564 565 $\simeq$ 543 } $\simeq$ 608 = (C ₈ H ₈ O ₃) ₄		
F _B 3	6.19		31	0.11	0.387	333 $\simeq$ 364 $\simeq$ 304 = (C ₈ H ₈ O ₃) ₂	
Material used	20.10		0.13	0.280	560	505	
Loss	2.39	12					

ii. Number of Monomer polymerized

Fraction	<i>C</i>	η_{sp}/C	<i>n</i>
$F_A \begin{cases} 1 \\ 2 \end{cases}$	63.4 59.4	31.6×10^{-4} $30.3 \times \text{,,}$	$\begin{cases} 3.8 \\ 3.7 \end{cases} \simeq 4$
$F_B \quad 3$	58.8	$18.7 \times \text{,,}$	$2.3 \simeq 2$
Total mixture	42.6	$30.5 \times \text{,,}$	3.6

F_1 has been precipitated by adding to 50 c.c. benzene solution 15 c.c. petroleum ether.

F_2 , Mother liquor of $F_1 + 15$ c.c. petroleum ether.

F_3 , " " " $F_2 + 40$ c.c. " "

d) Ozonide prepared in Ethyl Ether.

i. Molecular Weight

Fraction	Yield		η_{sp}	C_{gm}	Mol. Wt. from η_{sp}	Mol. Wt. from F.P.	Formula
	g.	%					
$F_A \begin{cases} 1 \\ 2 \\ 3 \end{cases}$	$\begin{cases} 5.68 \\ 4.88 \\ 4.84 \end{cases}$	78	$\begin{cases} 0.14 \\ 0.13 \\ 0.13 \end{cases}$	$\begin{cases} 0.566 \\ 0.565 \\ 0.560 \end{cases}$	$\begin{cases} 300 \simeq 280 \\ 277 \simeq 264 \\ 258 \simeq 250 \end{cases}$		$\simeq 304 = (C_8H_8O_3)_2$
Material used	19.78		0.13	0.505	285	298	
Loss	4.38	22					

ii. Number of Monomer polymerized

Fraction	C	η_{sp} / C	n
$F_A \begin{cases} 1 \\ 2 \\ 3 \end{cases}$	$\begin{cases} 86.0 \\ 85.8 \\ 85.2 \end{cases}$	$\begin{cases} 16.3 \times 10^{-4} \\ 15.3 \times \text{,,} \\ 14.1 \times \text{,,} \end{cases}$	$\begin{cases} 2.0 \\ 1.8 \\ 1.7 \end{cases} \simeq 2$
Total mixture	76.7	$16.9 \times \text{,,}$	2.2

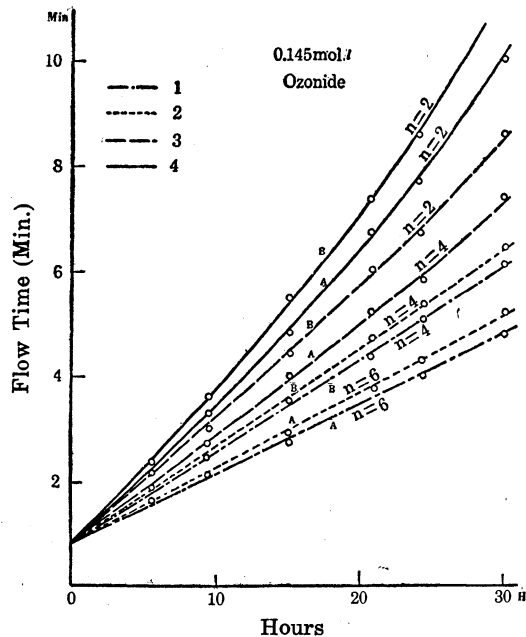
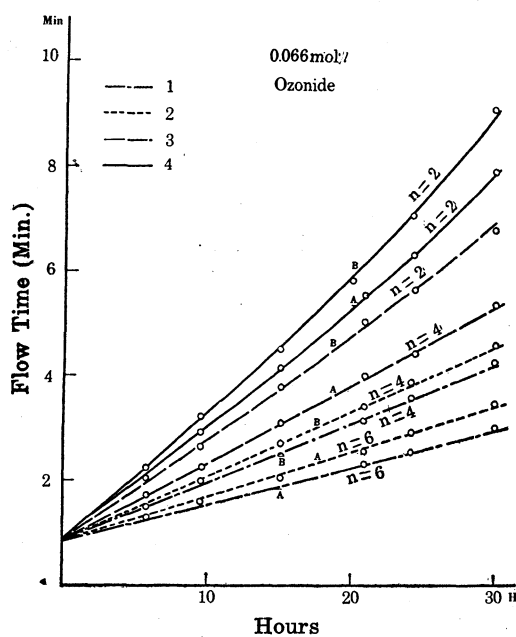
F_1 has been precipitated by adding to 50 c.c. benzene solution 65 c.c. petroleum ether.

F_2 , Mother liquor of F_1 + 25 c.c. petroleum ether.

F_3 , ,, ,, ,, F_2 + 70 c.c. ,, ,,

IV. Reactivity of Styrene Ozonide. As has been stated in Section II, styrene ozonide does not oxidise styrene but induces its polymerization. This fact may also be considered as supporting the conclusion of the previous experiments that the ozonide is a mixture of polymers. In order to see whether or not the reactivity of the polymers varies with the number of monomers polymerized the following experiments have been carried out.

a) *Promotion of Styrene Polymerization.* Each fraction of the ozonide obtained by fractional precipitation as described in Section I has been added to styrene so that the ozonide concentration may be 0.066 and 0.145 mole per liter (calculated as monomer). This mixture is put in the Ostwald viscosimeter immersed in a thermostat at 50°, and the viscosity is measured at various intervals of time. The results are shown in Table 4 and also in Figures 4 and 5. They indicate distinctly that each ozonide preparation accerelates the polymerization to different degree. Namely F_A of carbon tetrachloride and of benzene, both of which consist of the highest polymer, hexamer, as shown in Tables 4 a and b, accelerates the polymerization to the least extent, whereas F_B of chloroform and F_A and F_B of ethyl ether, all of which consist of the dimer, accelerate it to the



1. Ozonide prepared in carbon tetrachloride. 2. Ozonide prepared in benzene.
 3. Ozonide prepared in chloroform. 4. Ozonide prepared in ethyl ether.
 A. Fraction A (F_A). B. Fraction B (F_B).

Figs. 4 and 5. Acceleration of Styrene Polymerization by Styrene Ozonide.

Table 4. Acceleration of Styrene Polymerisation by Styrene Ozonide observed through Viscosity Change.

a) Ozonide prepared in Carbon Tetrachloride.

Time elapsed (hrs.)	Flow Time (min.: sec.)					
	Total ozonide		F_A (hexamer)		F_B (tetramer)	
	0.066 M	0.145 M	0.066 M	0.145 M	0.066 M	0.145 M
0	0 : 54	0 : 56	0 : 54	0 : 56	0 : 54	0 : 56
3	1 : 11	1 : 15	1 : 06	1 : 13	1 : 12	1 : 22
6	1 : 28	1 : 38	1 : 17	1 : 34	1 : 38	1 : 54
9	1 : 40	2 : 03	1 : 30	1 : 48	2 : 03	2 : 23
12	1 : 56	2 : 26	1 : 41	2 : 14	2 : 26	2 : 56
15	2 : 18	2 : 50	1 : 54	2 : 36	2 : 50	3 : 27
21	2 : 45	3 : 31	2 : 21	3 : 18	3 : 38	4 : 23
24	3 : 10	3 : 56	2 : 37	3 : 35	4 : 06	4 : 58
27	3 : 24	4 : 22	2 : 46	3 : 54	4 : 28	5 : 82
30	3 : 35	4 : 33	3 : 00	4 : 18	4 : 50	6 : 01

Total ozonide: Total ozonide precipitate obtained from CCl_4 solution by the addition of petroleum ether, yield 19.68 g.

F_A : Precipitate obtained by the addition of 15 c.c. petroleum ether to 50 c.c. benzene solution of the total ozonide precipitate, yield 11.22 g. (57%).

F_B : Precipitate obtained by the addition of 25 c.c. petroleum ether to the mother liquor of F_A , yield 7.12 g. (36%).

b) Ozonide prepared in Benzene

Time elapsed (hrs.)	Flow Time (min. : sec.)					
	Total ozonide		F _A (hexamer)		F _B (tetramer)	
	0.066 M	0.145 M	0.066 M	0.145 M	0.066 M	0.145 M
0	0 : 54	0 : 56	0 : 54	0 : 56	0 : 54	0 : 56
3	1 : 10	1 : 19	1 : 04	1 : 12	1 : 15	1 : 23
6	1 : 24	1 : 35	1 : 21	1 : 35	1 : 40	1 : 53
9	1 : 43	2 : 01	1 : 32	1 : 56	2 : 06	2 : 30
12	2 : 00	2 : 24	1 : 40	2 : 16	2 : 30	3 : 00
15	2 : 16	2 : 53	2 : 04	2 : 35	2 : 54	3 : 32
21	2 : 52	3 : 42	2 : 34	3 : 17	3 : 46	4 : 35
24	3 : 12	4 : 13	2 : 40	3 : 41	4 : 10	5 : 03
27	3 : 26	4 : 41	3 : 04	4 : 03	4 : 34	5 : 39
30	3 : 46	5 : 04	3 : 20	4 : 25	5 : 02	6 : 12

Total Ozonide: Total ozonide precipitate obtained from benzene solution by the addition of petroleum ether, yield 20.16 g.

F_A: Precipitate obtained by the addition of 15 c.c. petroleum ether to 50 c.c. benzene solution of the total ozonide precipitate, yield 12.43 g. (62%).

F_B: Precipitate obtained by the addition of 25 c.c. petroleum ether to the mother liquor of F_A, yield 5.05 g. (25%).

c) Ozonide prepared in Chloroform

Time elapsed (hrs.)	Flow Time (min. : sec.)					
	Total ozonide		F _A (tetramer)		F _B (dimer)	
	0.066 M	0.145 M	0.066 M	0.145 M	0.066 M	0.145 M
0	0 : 52	0 : 55	0 : 52	0 : 55	0 : 52	0 : 55
3	1 : 24	1 : 32	1 : 20	1 : 32	1 : 25	1 : 40
6	1 : 42	2 : 07	1 : 43	2 : 05	2 : 02	2 : 21
9	2 : 12	2 : 52	2 : 08	2 : 43	2 : 40	3 : 02
12	2 : 38	3 : 26	2 : 32	3 : 21	3 : 15	3 : 44
15	3 : 06	4 : 03	2 : 58	3 : 57	3 : 51	4 : 30
21	4 : 02	5 : 22	3 : 48	5 : 11	5 : 03	6 : 03
24	4 : 25	6 : 08	4 : 15	5 : 53	5 : 36	6 : 53
27	4 : 54	6 : 44	4 : 43	6 : 30	6 : 02	7 : 46
30	5 : 25	7 : 23	5 : 08	7 : 08	6 : 42	8 : 41

Total Ozonide: Total ozonide precipitate obtained from Chloroform solution by the addition of petroleum ether, yield 18.95 g.

F_A: Precipitate obtained by the addition of 30 c.c. petroleum ether to 50 c.c. benzene solution of the total ozonide yield 10.98 g. (58%).

F_B: Precipitate obtained by the addition of 40 c.c. petroleum ether to the mother liquor of F_A, yield 6.43 g. (34%).

d) Ozonide prepared in Ethyl Ether

Time elapsed (hrs.)	Flow Time (min. : sec.)					
	Total ozonide		F _A (dimer)		F _B (dimer)	
	0.066 M	0.145 M	0.066 M	0.145 M	0.066 M	0.145 M
0	0 : 52	0 : 55	0 : 52	0 : 55	0 : 52	0 : 55
3	1 : 32	1 : 50	1 : 30	1 : 45	1 : 32	1 : 50
6	2 : 15	2 : 40	2 : 13	2 : 33	2 : 21	2 : 45
9	3 : 00	3 : 34	2 : 56	3 : 28	3 : 03	3 : 51
12	3 : 38	4 : 24	3 : 36	4 : 18	3 : 37	4 : 42
15	4 : 21	5 : 21	4 : 14	5 : 10	4 : 32	5 : 38
21	5 : 46	7 : 20	5 : 36	7 : 02	6 : 00	7 : 45
24	6 : 32	8 : 23	6 : 12	8 : 03	6 : 47	8 : 53
27	7 : 17	9 : 32	6 : 57	9 : 05	7 : 31	10 : 05
30	8 : 00	10 : 43	7 : 40	10 : 08	9 : 16	11 : 35

Total Ozonide: Total ozonide precipitate obtained from ethyl ether solution by the addition of petroleum ether, yield 19.68 g.

F_A: Precipitate obtained by the addition of 80 c.c. petroleum ether to 50 c.c. benzene solution of the total ozonide, yield 8.31 g. (42%).

F_B: Precipitate obtained by the addition of 70 c.c. petroleum ether to the mother liquor of F_A, yield 7.90 g. (40%).

greatest extent that is approximately the same as the activity of the peroxide monomer. F_B of carbon tetrachloride and of benzene or F_A of chloroform which contain tetramer induce acceleration intermediate between hexamer and dimer. It may, therefore, be concluded that the activity decreases as the number of monomer polymerized increases.

b) *Reduction of Permanganate.* Fractions of the hexamer, tetramer and dimer used for the present experiment are the same as those employed in the previous one. Each fraction is added to 2×10^{-5} molar potassium permanganate in 1 N sulfuric acid so that the concentration of the polymers may be 6×10^{-4} molar when calculated as monomer. The time required for the just complete decolorization of the permanganate is determined, which can be taken as the measure of the reduction velocity.

Table 5. Time required for the Complete Reduction of Permanganate (room temperature)

Solvent	Dipole moment $\mu \times 10^{18}$	Total Ozonide		F _A		F _B	
		<i>n</i>	Time of reduction (sec.)	<i>n</i>	Time of reduction (sec.)	<i>n</i>	Time of reduction (sec.)
CCl ₄	0	6-4	105	6	135	4	64
C ₆ H ₆	0	6-4	92	6	123	4	56
CHCl ₃	0.95	4-2	26	4	25	2	10
C ₂ H ₅ OC ₂ H ₅	1.10	2	1	2	4	2	2

It has been found by this experiment that the hexamer fractions require for the reduction 125–135 sec., the tetramer fractions 35–64 sec., and the dimer fractions 2–10 sec. This shows that the reducing activity decreases as the number of monomer polymerized increases, which is in accord with the results of the previous experiment.

Summary.

Styrene ozonide has been prepared by introducing purified ozonized air into styrene dissolved in carbon tetrachloride, in benzene, in chloroform, and in ethyl ether.

The ozonide thus prepared does not oxidise styrene but promotes its polymerization. The increase of the ozonide concentration in styrene shortens the activation period but not the polymerization period. Temperature effect upon this polymerization is also seen to be exerted only upon the activation stage. Among the decomposition products of styrene ozonide, benzaldehyde and polystyrene slightly accelerate the styrene polymerization but benzoic acid, formic acid and formaldehyde are inactive in this respect.

The ozonides prepared in the four different solvents have been examined for their molecular weight by the measurements of freezing point and of viscosity. It has been found that they are not the simple ozonide but its polymers; those prepared in carbon tetrachloride and in benzene consist of hexamer and tetramer, that prepared in chloroform tetramer and dimer, and that prepared in ethyl ether only dimer. Thus, the solvent of higher dipole moment gives the lower polymer.

Both chemical and physical properties of the ozonide differ according to the stage of polymerization, higher polymer is less active for styrene polymerization and for permanganate reduction, the lower the stage of polymerization its chemical activity is more closely related to peroxide monomer. Higher polymer has higher viscosity than the lower.

This investigation was aided by a grant from the Nippon Gakuzitu Sinko Kai (Foundation for the Promotions of Science and Industrial Research of Japan) and the Department of Education.

The author wishes to acknowledge Dr. T. Tomiyama, the President of the Yokohama Technical College, for his kindness in enabling the former to take part in this work, and also the helpful advices of Prof. S. Komatsu of the Kyoto Imperial University and Prof. M. Yokoyama of the Yokohama Technical College throughout the course of this investigation.

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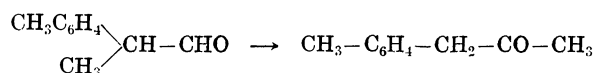
On the Catalytic Action of Japanese Acid Earth. XIII*. The Catalytic Action on Some Alkyl Aryl Acetaldehydes.

By Koshiro ISHIMURA.

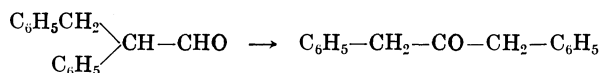
(Received May 14, 1941.)

In the previous papers it was reported that some diarylacetaldehydes were converted into the corresponding ketones when heated at about 300°C. in the presence of Japanese acid earth. When this rearrangement occurs there is a possibility of the formation of either one ketone or other as the result of the migration of one of the radicals, and the author has postulated that it separates as an anion and that the more electron-attracting radical always migrates in preference to the other less electron-attracting. When the migrating tendencies of the two radicals are not greatly different, both of the radicals migrate simultaneously, giving a mixture of two isomeric ketones. The yields in the two ketones depend upon the migrating tendencies of the two radicals, which are determined by their capacities for electron-attraction.

Now the methyl group is generally accepted as less electron-repelling than the *p*-tolyl group⁽¹⁾, therefore the methyl group will migrate in preference to the *p*-tolyl if methyl *p*-tolyl acetaldehyde is subjected to the above-mentioned rearrangement as shown below:—



Similarly, the benzyl group will be expected to migrate in preference to the phenyl group in the case of benzyl phenyl acetaldehyde. The facility of the separation of the benzyl anion must be increased, moreover, by the enhanced stability of this anion relative to phenyl.



It has been found, however, that the above mentioned two aldehydes are converted chiefly into hydrocarbons at 300°C. in the presence of the earth and the corresponding ketones have not been confirmed to exist in the reaction products. They must, therefore, be considerably more unstable than diarylacetaldehydes, described in the previous papers, and the condition of the present experiment is probably too drastic for them to undergo smoothly the usual rearrangement.

The reaction product from methyl *p*-tolyl acetaldehyde has been found to contain only about 3% of oxygen, but the aldehyde or ketones isomeric to it should contain 10.8%. Benzyl phenyl acetaldehyde gave products containing a still less quantity of oxygen. The reaction products

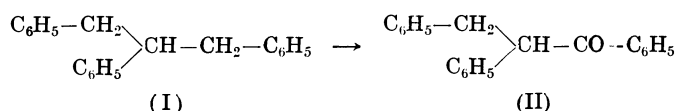
* This Bulletin **16** (1941), 349.

(1) H. Burton and C. K. Ingold: *J. Chem. Soc.* **1928**, 907.

from both of the aldehydes showed no colour reaction, characteristic to aldehyde. All attempts to obtain definite forms of oximes or semicarbazones of ketones from the reaction products failed. The main products were accordingly treated with metallic sodium in order to remove the oxygen-containing substances, and then fractionated, when a mixture of almost pure hydrocarbons was obtained.

Among the reaction products from methyl *p*-tolyl acetaldehyde, toluene and a compound $C_{10}H_{12}$, possibly $CH_3-C_6H_4-CH=CH-CH_3$ were confirmed to exist, while in the reaction products from benzyl phenyl acetaldehyde a solid crystalline substance of the composition $C_{15}H_{12}^{(2)}$ with a melting point $165-166^\circ C.$ was found.

It has been found that 1,2,3-triphenylpropane (I) is produced together with benzyl phenyl acetaldehyde when α -benzyl α -phenyl ethylene glycol is heated with a mixture of oxalic acid and water at $113^\circ C.$ 1,2,3-Triphenylpropane gave benzyl deoxybenzoin (II) on oxidation with chromic oxide. From this fact its constitution has been confirmed.



Experimental. *α -Benzyl α -phenyl ethylene glycol.* When magnesium is allowed to react with the calculated quantity of benzyl bromide, dissolved in dry ether, as has J. Marshall⁽³⁾ noticed, a large proportion of magnesium remains undissolved with the formation of a considerable quantity of dibenzyl. Pulverised benzoyl carbinol (20 g.) was added by portions to the solution of magnesium (16.4 g.) in benzyl bromide (193 g.) dissolved in ether, and the Grignard reagent thus formed was boiled for 30 hours. It was poured into acetic acid (50 g. glacial acetic acid in 300 c.c. ice water) and the upper layer of the reaction mixture was treated as usual, giving a yellowish liquid (ca. 300 c.c.), from which separated a large amount of dibenzyl. It was filtered and the filtrate was distilled in steam and further amount of dibenzyl (ca. 40 g. in total) passed over. The contents of the distilling flask were cooled and a part of α -benzyl α -phenyl ethylene glycol separated out in flocky precipitate while the main part of the glycol settled down at the bottom in viscous oily mass (30 g.).

The precipitate was recrystallised from ligroin into fine needles, m.p. $79-80^\circ C.$ (Found: C, 78.9; H, 7.3. $C_{15}H_{16}O_2$ requires C, 78.9; H, 7.0%). The viscous oil solidified only when inoculated with crystals of the glycol. The monobenzoyl derivative of the glycol was obtained by Schotten-Baumann's method. It formed a viscous matter, which solidified when rubbed with a glass rod with the addition of a small quantity of alcohol. It was recrystallised from dilute alcohol into fine needles, m.p. $100.5-$

(2) Ramart and F. Salmon-Legagneur (*Bull. soc. chim.*, **45** (1929), 478) obtained a substance of the composition $C_{15}H_{12}$ by passing α -benzyl α -phenyl ethylene glycol over diatomaceous earth heated at $500^\circ C.$ Though its chemical and physical properties are not described at all, it may probably be identical with the substance obtained by the present author.

(3) *J. Chem. Soc.*, **107** (1915), 520.

101.5°C. (Found: C, 79.6; H, 5.9%; Mol. wt. (Rast), 335.1. $C_{22}H_{20}O_3$ requires C, 79.5; H, 6.0%; Mol. wt., 332).

Oxidation of α -benzyl α -phenyl ethylene glycol to desoxybenzoin. Chromic oxide (0.31 g.) was added to the solution of the glycol (0.3 g.) dissolved in 70% acetic acid (50 c.c.) and the solution was heated on the water bath for 4 hours and poured into a large amount of water. White crystals separated out, which formed colourless scales (0.15 g.) from dilute alcohol. It melts at 57–58°C. alone or mixed with the authentic specimen of desoxybenzoin.

Benzyl phenyl acetaldehyde. A mixture of α -benzyl α -phenyl ethylene glycol (60 g.), crystalline oxalic acid (150 g.) and water (60 c.c.) was heated in an oil bath for 4 hours at 113°C. The reaction mixture was treated as usual and distilled under the reduced pressure of 4 mm., giving the following fractions:—

Table 1.

Fraction	B. p. (°C.)	Yields (in g.)	Remarks
(1)	Below 172	1.0	—
(2)	172–175	7.5	—
(3)	175–205	13.8	Boiling mainly at 202–205°C.
(4)	Residue	—	—

The fraction (2) in Table 1 consisted of the required aldehyde, d_4^{22} 1.0684; n_D^{22} 1.5861; M. R. found, 65.96; calc. (Eisenlohr), 64.28. The semicarbazone was produced with difficulty; after standing for 5 days the mixture of the aldehyde (1.0 g.), semicarbazide hydrochloride (1.0 g.) and potassium acetate (1.0 g.) dissolved in dilute alcohol, a large amount of water was added to the solution. The oil drops separated thereby solidified to the yellow powder (0.95 g.), which was recrystallised several times from dilute alcohol forming colourless fine needles, m.p. 123.4–124.4°C. (corr.). H. Burton and C. W. Shoppee⁽⁴⁾ obtained the same aldehyde by reducing the corresponding iminochloride with stannous chloride and then hydrolysing the resulting aldimine. It boiled, according to them, at 170°C./11 mm., and solidified after several weeks, and on recrystallisation formed colourless plates, m.p. 54°C. and its semicarbazone melted at 124–125°C. R. Stoermer, Cl. Thier and E. Laage⁽⁵⁾ described it as the monohydrate, m.p. 116°C., characterised by a semicarbazone, m.p. 189°C. (decomp.), which however was confirmed by H. Burton and C. W. Shoppee to be phenyl acetylphenyl carbinol. F. Kayser⁽⁶⁾ synthesised the aldehyde by treating 1,3-diphenylpropane-(1) with mercury oxide and iodine and gave the boiling point 179–180°C./18 mm.

(4) *J. Chem. Soc.*, **1937**, 546.

(5) *Ber.*, **58** (1925), 2607.

(6) *Ann. chim.*, [11] **6** (1936), 145.

1,2,3-Triphenylpropane. The fraction (3) in Table 1 tinged concentrated sulphuric acid with a deep red colour and contained a small proportion of oxygen. (Found: C, 91.3; H, 7.2%). It was treated with metallic sodium to remove the oxygen-containing substances, and a hydrocarbon $C_{21}H_{20}$ was obtained in colourless viscous oil, b.p. 204–205°C./8 mm.; $d_4^{20.4}$ 1.0254; $n_D^{20.4}$ 1.5864; M. R. found, 89.07, calc. (Eisenlohr), 88.38. (Found: C, 92.5; H, 7.5. $C_{21}H_{20}$ requires C, 92.7; H, 7.3%). It dissolves in concentrated sulphuric acid, developing brownish yellow colour with faint cobalt fluorescence. Its identity with 1,2,3-triphenylpropane was revealed by the formation of benzyl desoxybenzoin when oxidised with chromic oxide. E. Späth⁽⁷⁾ obtained the hydrocarbon by allowing benzyl halide to react with methyl- or ethylmagnesium halide and gave b.p. 225–230°C./10 mm. The hydrocarbon (1.1 g.) was dissolved in glacial acetic acid (30 c.c.), and chromic oxide (3.3 g. dissolved in 3 c.c. water) was added to the solution. After completing the reaction by heating the solution on the water bath for 1 hour, a small quantity of formic acid was added in order to decompose the excess chromic acid and the acetic acid was distilled off under the reduced pressure on the water bath. The residue was a deep green mud. It turned white on washing with water, and crystallised from dilute alcohol forming pure *ms*-benzyl desoxybenzoin in fine needles (0.25 g.), m.p. 120–121°C. (Found: C, 87.7; H, 6.5%; Mol. wt. (Rast), 289 295. $C_{21}H_{18}O$ requires C, 88.1; H, 6.3%; Mol. wt., 286). The oxime obtained by Auers' method formed colourless needles, apparently a pure substance, which however melted at 116–127°C. after recrystallisation 10 times from dilute alcohol and most probably consisted of a mixture of stereo-isomers. F. Klingemann⁽⁸⁾ obtained *ms*-benzyl desoxybenzoin by reducing *ms*-benzal desoxybenzoin and gave m.p. 120–122°C. A. McKenzie and E. R. Winton⁽⁹⁾ obtained it by interacting methyltropate with phenyl magnesium iodide, which melted at 120–121°C.

Attempted isomerisation of benzyl phenyl acetaldehyde. By passing 7.0 g. of the aldehyde on the Japanese acid earth (25 g.), heated at 300°C. at a rate of 3.2 g. per hour, accompanied by a slow current of carbon dioxide the following products were obtained: (a) 0.6 g. of easily-flowing oil with faint fluorescence and (b) 3.5 g. of a yellow solid mass moistened with oily substance. The product (a) consisted chiefly of toluene and benzene. The product (b) was separated into two parts, i.e., (i) crystalline mass (0.6 g.) and (ii) oily substance (2.3 g.), when it was pressed with a filter paper and the paper was extracted with ether. The product (i) crystallised from alcohol in colourless scales, m.p. 165–166°C. (Found: C, 93.5; H, 6.3%; Mol. wt. (Rast), 197, 206. $C_{15}H_{12}$ requires C, 93.8; H, 6.2%; Mol. wt., 192). Attempts to obtain any compound of a definite constitution by oxidising the foregoing hydrocarbon with chromic oxide failed and its constitution was for the time left open. Ramart and F. Salmon-Legagneur⁽¹⁰⁾ obtained a compound $C_{15}H_{13}$ by passing *a*-benzyl *a*-phenyl ethylene glycol on the diatomaceous earth heated at 500°C. How-

(7) *Monatschaft.*, **34** (1913), 1992.

(8) *Ann.*, **275** (1893), 65.

(9) *J. Chem. Soc.*, **1940**, 840.

(10) *Bull. soc. chim.*, **45** (1929), 478.

ever, no detailed description of properties of the compound has been given by them.

The portion (ii) was distilled under the reduced pressure of 10 mm. and 1.7 g. out of 2.3 g. passed over between 150–200°C, which contained 91.7% of carbon and 7.2% of hydrogen and may be considered to consist of 74% of $C_{15}H_{12}$ and 26% of $C_{15}H_{14}O$. It showed no colour reaction characteristic to aldehydes and formed neither semicarbazone nor oxime.

α-Methyl α-p-tolyl ethylene glycol. *p*-Methyl benzoyl carbinol (45 g.) was added by portions to the Grignard reagent prepared from methyl iodide (150 g.) and magnesium (24 g.) and left to stand for 2 days. It was treated with acetic acid (120 g. glacial acetic acid in 300 c.c. ice water), the ethereal layer was separated and combined with the ether extract of the water layer, the combined ethereal extract dried with anhydrous sodium bicarbonate, the ether removed and the residue was distilled in vacuo. 33 g. of the raw *α*-methyl *α*-*p*-tolyl ethylene glycol passed over between 150 and 158° under 33 mm. M. Tiffeneau⁽¹¹⁾ obtained the glycol by the same method and found that it melted at 36°C. and boiled at 175–180°C/15 mm. These data widely deviated from the present author's values.

p-Tolyl propionaldehyde. A mixture of raw *α*-methyl *α*-*p*-tolyl ethylene glycol (30 g.), crystalline oxalic acid (75 g.) and water (30 c.c.) was boiled gently in an oil bath for 3 hours, meanwhile a slow current of carbon dioxide was passed into the reaction flask. The reaction product was extracted with ether, washed with aqueous potassium carbonate and with water, dried over anhydrous sodium sulphate, the ether removed and the residue was distilled. 14 g. of the required aldehyde were obtained, b.p. 222–225°C.; d_4^{23} 0.9928; n_D^{23} 1.5173; M. R. found 45.12. $C_{10}H_{12}O$ (Eisenlohr) requires 44.79. W. v. Miller and G. Rohde⁽¹²⁾ gave b.p. 222–224°C./760 mm. (corr.), G. G. Henderson and W. Cameron⁽¹³⁾ b.p. 221–222°C./755 mm.; d_{20}^{20} 0.984; n_D^{20} 1.51436, and M. Tiffeneau,⁽¹⁴⁾ b.p. 219–221°C. The semicarbazone was synthesised by the usual way forming silky needles from dilute alcohol, m.p. 155.5–156.5°C. (uncorr.). G. Darzens⁽¹⁵⁾ gave m.p. 159–160°C. and G. G. Henderson⁽¹⁶⁾ m.p. 156–157°C., while M. Tiffeneau⁽¹⁷⁾ m.p. 152°C.

Attempted isomerisation of methyl p-tolyl acetaldehyde. The aldehyde (12 g.) was passed on the Japanese acid earth (25 g.) heated at 300°C. at a rate of 3.6 per hour, accompanied by a slow current of carbon dioxide and gave (a) a yellow oil (5.9 g.) mixed with a small amount of crystals and water (1.1 g.) which came out until the passing of the aldehyde ended and (b) a faint yellow resinous matter (0.5 g.). The product (a) was separated from water and distilled, giving the following fractions:—

(11) *Compt. rend.* **137** (1903), 1261; *Ann chim.*, [8] **10** (1907), 343.

(12) *Ber.*, **23** (1890), 1075.

(13) *J. Chem. Soc.*, **95** (1909), 969.

(14) *Compt. rend.*, **137** (1903), 126.

(15) *ibid.*, **139** (1904), 1216.

(16) *J. Chem. Soc.*, **91** (1907), 1874.

(17) *Loc. cit.*

Table 2.

Fraction	B. p. (°C.)	Yield (in g.)	Remarks
(1)	Below 200	2.1	Main part passed over above 180°C.
(2)	200-205	0.7	
(3)	205-230	0.9	The last 2 or 3 drops changed to mush on cooling.
(4)	Residue	1.1	Redish viscous oil containing crystals.

The fractions (1), (2) and (3) in Table 2 gave the following analytical data; C, 89.3, 88.0 and 86.7; H, 9.3, 9.2 and 8.2% respectively, suggesting that the higher the boiling point the richer in compounds which contain oxygen. The fractions (1) and (2) were combined and treated with metallic sodium in order to remove oxygen-containing substances and again fractionated as follows:—

Table 3.

Fraction	B. p. (°C.)	Yield (in g.)	Remarks
(1)	Below 110	0.6	Boiled almost constantly at 110°C.
(2)	110-180	0.4	Main part passed over above 150°C.
(3)	180-185	0.5	—
(4)	Residue	0.5	—

The fraction (1) in Table 3 consisted of almost pure toluene and the fraction (2) was found to be a compound $C_{10}H_{12}$; d_4^{26} 0.8615; n_D^{26} 1.4940; M. R. found, 44.61, calc. (Einsenlohr) for $C_{10}H_{12}$ 44.31. (Found: C, 90.4; H, 9.4. $C_{10}H_{12}$ requires C, 90.9; H, 9.1%).

The author's thanks are due to Dr. H. Inoue for his kind advice.

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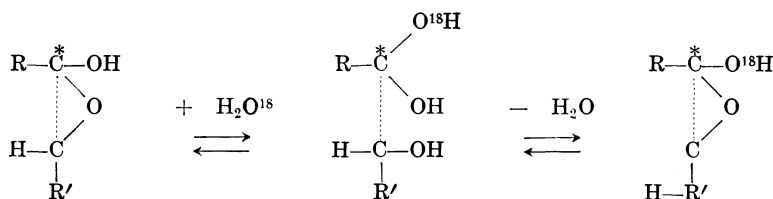
Untersuchungen der chemischen Eigenschaften der Kohlenhydrate mit Hilfe des schweren Sauerstoffs. II. Austauschreaktion und Mutarotation der Glucose und Fructose (Auszug).⁽¹⁾

Von Kokiti GOTO und Toshizo TITANI.

(Eingegangen am 23, Juli, 1941).

Inhaltsübersicht. Die Geschwindigkeit der Austauschreaktion der O-Atome zwischen der Glucose bzw. Fructose und Wasser sowie die der Mutarotation desselben Zuckers in wässriger Lösung wird unter den möglichst gleichen Versuchsbedingungen miteinander verglichen, indem man die neutrale Lösung des betreffenden Zuckers auf 30 bis 100°C., 0 bis 390 Min. lang erwärmt. Dabei wird festgestellt, dass bei 55°C. und 100°C. die Austauschreaktion fast ebenso schnell wie die Mutarotation verläuft, während bei 30°C. wo die Mutarotation noch mit wohl messbarer Geschwindigkeit ziemlich schnell stattfindet, die Geschwindigkeit der Austauschreaktion fast unmessbar so klein ist. Deshalb wird geschlossen, dass mindestens bei Zimmertemperatur der Mechanismus der Mutarotation ganz anders als der der Austauschreaktion angenommen werden muss. Als der wahrscheinlichste Mechanismus der Mutarotation bei Zimmertemperatur kommt die Prototropie in Betracht, obwohl bei hohen Temperaturen daneben noch die anderen Arten der Reaktionen, wie z. B. die Zwischenbildung der Hydrate als der mögliche Mechanismus der Umkehrung der räumlichen Struktur der Zuckermoleküle eintreten können.

Einleitung. Erwärmt man die wässrige Lösung der Glucose bzw. Fructose auf 55°C. 100 Stunden lang bzw. auf 100°C. 10 Stunden lang, so wird ein O-Atom in einem Zuckermolekül gegen die des Wassers ausgetauscht.⁽²⁾ Dieser Austausch der O-Atome zwischen Zucker und Wasser wird durch die Annahme gedeutet, dass ein Wassermolekül einem Zuckermolekül umkehrbar addiert und dadurch ein Hydratmolekül intermediär gebildet wird:



Findet aber solch eine Reaktion nach beiden Seiten mit messbarer Geschwindigkeit statt, so entsteht neben der Austauschreaktion der O-Atome auch die Möglichkeit, dass die räumliche Struktur des Zuckermoleküls um das mit * bezeichnete C-Atom während der Reaktion umgekehrt und dadurch die Mutarotation des Zuckers herbeigeführt wird. Dieser Mechanismus der Zwischenbildung der Hydrate wird in der Tat als ein möglicher Fall von Lowry⁽³⁾ angenommen. Wäre aber diese Reaktion

(1) K. Goto, *J. Chem. Soc. Japan*, **62** (1941), 408. Vorläufig mitgeteilt in T. Titani und K. Goto, *Proc. Imp. Acad. Tokyo*, **16** (1940), 398. I. Mittl.: dies Bulletin, **16** (1941), 172.

(2) K. Goto und T. Titani, dies Bulletin, **16** (1941), 172.

(3) M. Lowry, *Trans. Chem. Soc.* **83** (1903), 1314.

massgebend für die Mutarotation, so müsste zu gleicher Zeit der Mutarotation ein O-Atom in einem Zuckermolekül gegen die des Wassers ausgetauscht werden. Um das experimentell zu bestätigen, wird die Geschwindigkeit der Austauschreaktion und Mutarotation der Glucose und Fructose in wässrigen Lösungen unter den möglichst gleichen Versuchsbedingungen miteinander verglichen. Der Versuch ergab, dass die beiden Reaktionen bei hohen Temperaturen (mindestens oberhalb 55°C.) miteinander fast ebenso schnell stattfinden aber bei Zimmertemperatur die Geschwindigkeit der Austauschreaktion im Vergleich mit der Mutarotation unmessbar so klein ist.

Versuchsmethode und Ergebnisse. Die von Merck bezogene Glucose bzw. Fructose wird durch die Erwärmung auf 90°C. bis 100°C. in Vakuum möglichst vollständig getrocknet. Etwa 0.9 bis 1.6 g. des so getrockneten Zuckers wird in etwa 10 bis 13 ccm. an schwerem Sauerstoff angereicherten schweren Wassers aufgelöst und auf einer bestimmten Temperatur bestimmter Zeitlänge erwärmt. Das zu diesem Versuch benutzte an schwerem Sauerstoff angereicherte schwere Wasser wird mit Hilfe der fraktionierten Destillation des Wassers hergestellt und der zu gleicher Zeit angereicherte schwere Wasserstoff auf dem schon in I. Mittl. angegebenen Wege unter Benutzung der Elektrolyse beseitigt. Der Dichteüberschuss des verwendeten schweren Wassers, der gewöhnlichem Wasser gegenüber etwa 30 γ beträgt, kann deshalb lediglich auf die Anreicherung des schweren Sauerstoffs zurückgeführt werden. Nach der Beendigung der Erwärmung wird die Lösung, nachdem sie durch das Begiessen des kalten Wassers auf dem die Lösung enthaltende Glasrohr schnell abgekühlt worden ist, in zwei möglichst gleiche Teile abgetrennt, um die erste Hälfte zur Bestimmung der Austauschreaktion und die andere Hälfte zur Bestimmung der Mutarotation zu benutzen.

Um die Austauschreaktion zu bestimmen, wird das schwere Wasser zuerst durch die Vakuumdestillation vom Zucker abgetrennt. Dabei konnten wir etwa 80% der benutzten Menge des Wassers abdestilliert wiederbekommen.⁽⁴⁾ Der Dichteüberschuss des so abgetrennten Wassers wird, nachdem es auf passendem Wege gereinigt worden ist, genau so wie in I. Mittl. schwebemetrisch bestimmt. Die statistische Anzahl n der O-Atome in einem Zuckermolekül, die unter den angegebenen Versuchsbedingungen gegen die des Wassers ausgetauscht werden, wird dann mit Hilfe der Gl. berechnet:

$$n = \frac{M_w}{M_z} \frac{\Delta s_a - \Delta s_e}{\Delta s_e}$$

In dieser Gl. bedeutet M_w und M_z resp. die Molzahl des zum Versuch benutzten Wassers und Zuckers und Δs_a und Δs_e den gewöhnlichem

(4) Wird die Lösung gegen Ende der Destillation, wie dies bei den Versuchen in I. Mittl. der Fall war, mehr oder weniger erwärmt, so können wir mehr als 90% des verwendeten Wassers abdestilliert wiederbekommen. Da aber bei dem vorliegenden Versuche nicht nur bei erhöhter Temperatur sondern auch bei 30°C. gearbeitet werden sollte, wurde die Destillation immer bei Zimmertemperatur ohne Erwärmung durchgeführt. Die verhältnismässig kleine Ausbeute des abdestillierten Wassers wird darauf zurückgeführt.

Wasser gegenüber gemessene Dichteüberschuss des schweren Wassers vor und nach dem Versuch. Die so berechnete Anzahl n muss aber die obere Grenze von n ausdrücken, weil der schwere Sauerstoff bei der Abdestillation des schweren Wassers aus der Lösung mehr oder weniger im zurückgebliebenen Teil angereichert wird und dementsprechend der gefundene Wert von Δs_e bis zu einem gewissen Grad zu gross sein soll.

Zur Bestimmung der Geschwindigkeit der Mutarotation wird die oben angegebene andere Hälfte der erwärmten Lösung zunächst unter Zusatz des gewöhnlichen destillierten Wassers schnell bis zu 6 bis 12% ig verdünnt und das optische Drehungsvermögen der so verdünnten Lösung wird mittels eines Polarimeters bestimmt. Dabei gaben wir besonders darauf acht, dass alle diese Behandlungen so weit wie möglich schnell durchgeführt werden, um dadurch das unbekannte Fortschreiten der Mutarotation während dieser Manipulationen möglichst aufzuhalten. Das so bestimmte spezifische Drehungsvermögen $[\alpha]^D$ wird bei der Glucose ohne weiteres dagegen bei der Fructose erst nach der Korrektur für die Temperatur und Konzentration⁽⁵⁾ in der letzten Spalte der Tabelle 1 bis 4 wiedergegeben, wo die mit * bezeichneten Werte aus den veröffentlichten Daten aufgenommen wurden.⁽⁶⁾

Tabelle 1. Glucose bei 30°C.

Zeit in Min.	n	$[\alpha]^D$
0	0.4	+92.2
20	0.3	+78.3
45	0.3	+64.0
45	0.3	+63.7
130	0.1	+55.3
130	0.4	+56.4
300	0.4	+52.7
390	0.4	+51.8
390	0.3	+52.7
∞	(1.0)	+52.7*

Tabelle 2. Glucose bei 55°C.

Zeit in Min.	n	$[\alpha]^D$
5.5	(0.0)	+105.2*
60	0.7	+ 64.4
120	0.8	+ 57.5
∞	(1.0)	+ 52.7*

Tabelle 3. Glucose bei 100°C.

Zeit in Min.	n	$[\alpha]^D$
5.5	(0.0)	+105.2*
30	0.9	+ 52.3
45	0.9	+ 52.1
∞	(1.0)	+ 52.7*

Tabelle 4. Fructose bei 30°C.

Zeit in Min.	n	$[\alpha]^D$
0	0.2	-104*
15	0.1	-92.2
35	0.2	-91.8
60	0.1	-92.5
∞	(1.0)	-92.1*

Zieht man die oben hingewiesene Tatsache in Rechnung, dass das in Tabellen angegebene n die obere Grenze der Anzahl der ausgetauschten

(5) Um das direkt gemessene Drehungsvermögen der Fructose zum idealen Fall umzurechnen, wo die Temperatur $t = 20^\circ\text{C}$. und die Konzentration $c = 1$ beträgt, wird die Gl. benutzt (vgl. Jungfleisch und Grimbert, *Compt. rend.*, **107** (1888), 393):

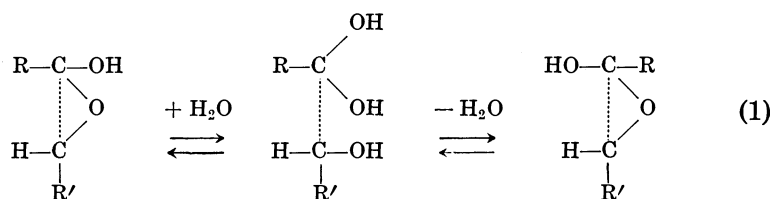
$$[\alpha]_{t,c}^D = -100.38^\circ + 0.56t - 0.108c$$

(6) E. Parcus und B. Tollens, *Ann.*, **257** (1890), 164.

O-Atome ausdrückt, so darf wohl geschlossen werden, dass bei 30°C. fast keine messbare Austauschreaktion der O-Atome zwischen jeder Art des Zuckers und Wasser stattfindet, obwohl die Mutarotation bei derselben Temperatur mit wohl messbarer Geschwindigkeit verläuft. Dagegen finden bei 55°C. und 100°C. die beiden Arten der Reaktionen der Glucose miteinander fast ebenso schnell statt.

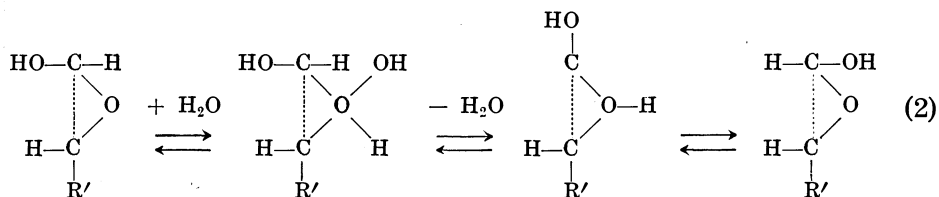
Diskussion der Ergebnisse. Als den möglichen Mechanismus der Mutarotation sind bisher mindestens drei Annahmen vorgeschlagen worden.

(i) Der erste Mechanismus, der von Lowry⁽⁷⁾ stammt, nimmt an, dass ein Wassermolekül an einem Zuckermolekül addiert und das dadurch gebildete Hydrat wieder in Wasser und Zucker gespalten wird:



Die Umkehrung der räumlichen Struktur des Zuckermoleküls wird durch diese umkehrbare Bildung und Spaltung des Hydratmoleküls herbeigeführt.

(ii) Der zweite Mechanismus, der von Armstrong⁽⁸⁾ vorgeschlagen wurde, nimmt ebenso wie der erste die Zwischenbildung eines Hydratmoleküls an. Aber in diesem Fall werden die OH-Gruppe und das H-Atom des addierenden Wassermoleküls beide am Pyranring-O-Atom angelagert und aus dem so gebildeten Hydratmolekül wird eine OH-Gruppe vom Pyranring-O-Atom, hingegen ein H-Atom vom Carbonylkohlenstoffatom abgerissen, um ein Wassermolekül zu bilden, so dass ein H-Atom am Pyranring-O-Atom zurückgelassen wird, das eigentlich vom Wassermolekül stammt. Wird dieses H-Atom zum Carbonylkohlenstoffatom transportiert, so wird das originale Zuckermolekül wieder gebildet und zugleich kann die Umkehrung der räumlichen Struktur des Zuckermoleküls stattfinden:



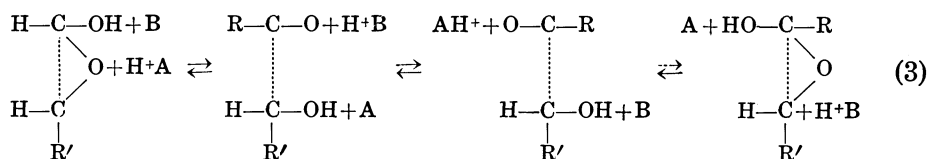
(iii) Der letzte Mechanismus, der von Lowry⁽⁹⁾ stammt und heute im allgemeinen angenommen wird, beruht auf der prototropischen Um-

(7) M. Lowry, *Trans. Chem. Soc.*, **83** (1903), 1314.

(8) E. F. Armstrong, *Trans. Chem. Soc.*, **83** (1903), 1309.

(9) M. Lowry, *J. Chem. Soc.*, **1925**, 1384.

wandlung des Zuckermoleküls, die mit Hilfe der Brönstedschen Säure H^+A und Base B herbeigeführt wird. Das Reaktionsschema ist aus der folgenden Gl. ohne weiteres klar:



Wäre Reaktion (1) massgebend für die Mutarotation des Zuckers, so müsste, wie darauf schon in Einleitung hingewiesen wurde, ein O-Atom in einem Zuckermolekül zu gleicher Zeit der Mutarotation gegen die des Wassers ausgetauscht werden. Da aber dies nach dem vorliegenden Versuche bei Zimmertemperatur sicherlich nicht der Fall ist, kann Reaktion (1) mindestens bei Zimmertemperatur kein Hauptteil des Mechanismus der Mutarotation sein. Ebenso wenig wahrscheinlich ist Reaktion (2) im Lichte der Versuche, die von Fredenhagen und Bonhoeffer⁽¹⁰⁾ durchgeführt wurde. Von diesen beiden Autoren wurde nämlich festgestellt, dass keine an C gebundenen H-Atome während der Mutarotation der Glucose bei Zimmertemperatur gegen die des Wassers ausgetauscht werden. Wäre aber Reaktion (2) der Hauptteil des Mechanismus der Mutarotation, so müsste offensichtlich ein an C (Carbonylkohlenstoffatom!) gebundenes H-Atom zu gleicher Zeit der räumlichen Umkehrung des Zuckermoleküls durch das des Wassers ersetzt werden.

So bleibt nur noch die letzte Reaktion (3) übrig. Nach diesem Mechanismus brauchen keine H- bzw. O-Atome im Zuckermolekül während seiner räumlichen Umkehrung gegen die des Wassers ausgetauscht werden. Weiter steht dieser Mechanismus mit der wohl bekannten Tatsache im Einklang, dass die Mutarotation des Zuckers eine typische säure-base-katalytische Reaktion ist. Auf diese Weise nehmen wir den letzten Mechanismus (iii) d.h. Reaktion (3) als den wahrscheinlichsten Mechanismus der Mutarotation des Zuckers an. Dabei müssen wir aber darauf aufmerksam machen, dass dieser Schluss nur bei Zimmertemperatur unbeschränkt gültig ist, nicht jedoch bei hohen Temperaturen. Die Nichtaustauschbarkeit der an C gebundenen H-Atome wurde nämlich von Fredenhagen und Bonhoeffer bei Zimmertemperatur bestätigt. Ebenso wird die Nichtaustauschbarkeit der O-Atome bei vorliegendem Versuche nur bei Zimmertemperatur festgestellt. Dagegen fanden wir bei erhöhten Temperaturen (bei 55°C. und 100°C.), dass ein O-Atom des Glucosemoleküls fast ebenso schnell wie die Mutarotation ausgetauscht wird. Dies weist ohne weiteres darauf hin, dass bei hohen Temperaturen der räumliche Struktur des Zuckermoleküls auch durch Reaktion (1) umgekehrt werden kann. So ist durchaus möglich, dass die Mutarotation des Zuckers bei niedrigen Temperaturen fast ausschliesslich nach dem prototropischen Mechanismus stattfindet aber bei erhöhten Temperaturen daneben noch andere Art der Reaktionen eintreten und mindestens ein Teil der Um-

(10) H. Fredenhagen und K. F. Bonhoeffer, *Z. phys. Chem.*, **A181** (1938), 392.

kehrung der räumlichen Struktur des Zuckermoleküls dadurch herbeigeführt wird.

Zum Schluss möchten wir Herrn Prof. Akabori für seine freundlichen Ratschläge herzlichst danken. Der Nippon Gakujutu-Sinkôkai (der Japanischen Gesellschaft zur Förderung der Wissenschaft) sowie der Hattori Hôkôkai (der Hattori Stiftung) sind wir für ihre finanzielle Unterstützung zu bestem Dank verpflichtet.

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Studies on the Derivatives of 3-Hydroxyflavanone (Dihydroflavonol). I. On the Action of Lead Tetraacetate on Flavanone and 4'-Methoxyflavanone.

By Taichiro OYAMADA.

(Received July 28, 1941.)

Several years ago, fustin⁽¹⁾, isolated from *Rhus succedanea* L., was confirmed by the present author to be a derivative of 3-hydroxyflavanone (dihydroflavonol), namely 3,7,3',4'-tetrahydroxyflavanone. Since then two new derivatives of this group, alpinon⁽²⁾ and ampeloptin⁽³⁾, have been isolated from plants by Japanese workers. Consequently, it is possible that many other new derivatives of this series may occur in nature. It would, therefore, be of great interest to synthesise many compounds of this new class and to investigate the behaviour of these compounds.

By the systematic studies of Criegee and others⁽⁴⁾, it has been shown that lead tetraacetate is an important reagent for the oxidative fission of α -glycols. However, only a few researches⁽⁵⁾ have been carried out as

(1) *J. Chem. Soc. Japan*, **55** (1935), 755-790; *Ann.*, **538** (1939), 44.

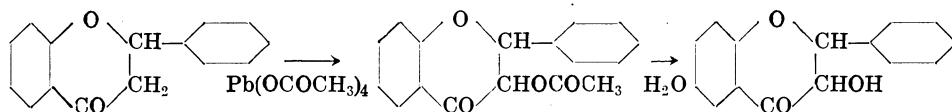
(2) Y. Kimura, *J. Pharm. Soc. Japan*, **57** (1937), 147.

(3) T. Kubota, *J. Chem. Soc. Japan*, **59** (1938), 1153.

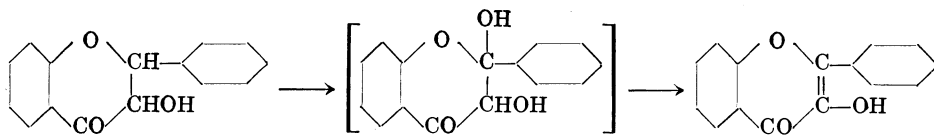
(4) R. Criegee, *Ber.*, **64** (1931), 260; *Ann.*, **507** (1933), 159; *Ber.*, **68** (1935), 665 etc.

(5) R. C. Morris, W. E. Hanfold and R. Adams, *J. Am. Chem. Soc.*, **57** (1935), 951; W. Hückel and K. Hartmann, *Ber.*, **70** (1937), 961; O. Dimroth and R. Schweizer, *Ber.*, **56** (1923), 1375; T. Reichstein and C. Montigel, *Helv. Chim. Acta*, **22** (1939), 1212 etc.

to the use of this reagent in substitution. The present author attempted to synthesise the derivatives of 3-hydroxyflavanone, in replacing the active hydrogen (position 3) in flavanones with an acetoxy-group by lead tetraacetate and the subsequent hydrolysis of the resulting esters, as shown in the following scheme:



The solution of flavanone (1 mol.) and lead tetraacetate (1 mol.) in glacial acetic acid was heated at 80–90°, until all unchanged tetraacetate disappeared, which was indicated by the absence of the formation of the brown colloidal lead peroxide on dilution of the solution with water. As the product thus obtained was viscous and difficult to purify, it was directly subjected to hydrolysis. The crude product was heated on the water-bath for a short time with alcohol containing concentrated hydrochloric acid and, on cooling, a colourless leaf-like crystalline compound, melting indefinitely at 140–175°, separated out. Even after several crystallisations from alcohol, the substance was still impure and melted indefinitely at 170–178°. However, it could be purified by converting it into the pure crystalline acetate by treatment with acetic anhydride and a drop of concentrated sulphuric acid, and then by hydrolysing it in an acidic medium in a current of carbon dioxide in order to prevent it from being oxidised. The compound thus purified melted at 183–184° and was very sensitive to oxygen, especially in the presence of alkali. It was partly soluble in hot alkali with the formation of a yellow solution. On acidifying the alkaline solution, a compound, melting at 170°, separated, which was proved to be flavonol by the method of the mixed melting point. For the explanation of the mechanism of this reaction, attention was directed to the fact that 7,3',4'-trimethoxy-3-hydroxyflavanone (trimethylfustin) yielded 7,3',4'-trimethoxy-3-hydroxyflavone (trimethylfisetin) when treated with alkali⁽⁶⁾. The formation of flavonol is obviously due to the oxidation of 3-hydroxyflavanone (dihydroflavonol), as probably indicated in the following scheme:



On the other hand, the present author tried to purify the hydrolysed product by the chromatographic method, using magnesia as an adsorbent, and observed that most of the product was adsorbed by magnesia, which became yellow, and that the substance adsorbed was regenerated as flavonol on dissolving the adsorbent in hydrochloric acid. This phenomenon was also observed in the pure compound, melting at 183–184°, and, moreover, in 4'-methoxy-3-hydroxyflavanone (4'-methoxydihydroflavonol)

(6) *J. Chem. Soc. Japan*, **55** (1935), 763 and 786; *Ann.*, **538** (1939), 46 and 51.

and trimethylfustin (trimethyldihydrofisetin). It is noteworthy that the derivatives of 3-hydroxyflavanone showed an extreme facility in forming the corresponding flavonols when they were adsorbed by magnesia or a similar weak basic substance. Furthermore, the author conducted the chromatographic adsorption in a current of hydrogen in order to avoid oxidation, but he could not obtain a good result, owing to the difficulty of securing the complete exclusion of oxygen during the whole operation.

From the part unadsorbed by magnesia, a new compound, melting at 132–133°, was obtained in a small quantity. This compound was very stable and did not change on heating at a comparatively high temperature with mineral acid in a sealed tube. Further study of this compound is now in progress.

The similar treatment was applied to 4'-methoxyflavanone with a view to synthesise 4'-methoxy-3-hydroxyflavanone. After a number of experiments, the expected compound was obtained together with a small quantity of an unknown compound, melting at 118–119°, by the procedure described in the experimental part. As the author had previously prepared the same compound in another way⁽⁷⁾, the compound obtained here was easily proved to be the expected one by direct comparison. The compound was also converted into the corresponding flavonol by adsorption with magnesia.

This investigation, both in the synthetic and the natural derivatives of flavanone, is now being extended at this laboratory.

Experimental. *Preparation of Lead Tetraacetate.* Lead tetraacetate was prepared according to the Dimroth method modified by Gattermann⁽⁸⁾. Red lead oxide (minium) (120 g.) was gradually added to glacial acetic acid (450 c.c.), containing acetic anhydride (12 c.c.), and thoroughly stirred while it was kept at 60–65°. Considerable amount of lead tetraacetate was deposited on cooling. On recrystallising from glacial acetic acid, it was obtained as colourless crystals. Although it is very unstable in the dry state, it can be kept for a long time by covering it with glacial acetic acid.

Action of Lead Tetraacetate on Flavanone. A solution of 24 g. of flavanone and 48 g. of lead tetraacetate in 400 c.c. of glacial acetic acid was heated in the water-bath at 80–90° for two hours. The completion of the reaction was proved by the absence of formation of brown colloidal lead peroxide on dilution of the solution with water. The solution was poured into water and extracted with ether. The ethereal extract was washed with water and then with sodium bicarbonate solution in order to remove acetic acid, dried over anhydrous sodium sulphate and evaporated. The residual oil was then distilled under a reduced pressure of 3 mm., and a viscous liquid, boiling at 198–200°, was obtained. The yield was 22 g. The viscous liquid was ascertained to be a mixture by further experiment.

Hydrolysis. The liquid thus obtained (13 g.) was heated with alcohol (150 c.c.) containing concentrated hydrochloric acid (30 c.c.) on the

(7) *J. Chem. Soc. Japan*, **56** (1936), 980.

(8) L. Gattermann, "Die Praxis des organischen Chemikers," (1936), 123.

water-bath for thirty minutes. On cooling, a leaf-like crystalline compound (6.2 g.), melting at 140–175°, was deposited. After several crystallisations from alcohol, it separated in crystals, sintering at 170° and melting completely at 178°. Although the purification by means of several recrystallisations from alcohol and other solvents was attempted, the substance remained impure and melted indefinitely. Therefore, the purification by recrystallisation was discarded and an adsorption method was then tried, but without success. Finally, it could be purified through its pure acetate in the way described in the following experiments.

Preparation of 3-Acetoxyflavanone. The acetylation of the hydrolysed product (4 g.), was effected by the action of acetic anhydride (20 g.) and a drop of concentrated sulphuric acid at room temperature. The acetylated product was poured into water, when an oil separated, and solidified on standing. After several crystallisations from alcohol, 3-acetoxyflavanone melted at 94–94.5°. The yield was 2.3 g. Found: C, 72.60; H, 5.21. Calc. for $C_{17}H_{14}O_4$: C, 72.34; H, 4.96%.

Preparation of 3-Hydroxyflavanone. The above acetate (2 g.) was heated with alcohol (40 c.c.), containing concentrated hydrochloric acid (20 c.c.), on the water-bath for an hour in a current of carbon dioxide. On cooling, a leaf-like crystalline compound separated out. After recrystallisation from alcohol, in an atmosphere of carbon dioxide in order to avoid the contact with oxygen, 3-hydroxyflavanone separated in crystals, melting at 183–184° when heated rapidly in the bath which had been previously heated to about 175°. However, it began to melt at lower temperature when heated from low temperature. The yield was 0.8 g. It is insoluble in cold alkali, but soluble in hot alkali with the formation of a yellow solution. On acidifying this alkaline solution, flavonol, melting at 170°, separated out. The 3-hydroxyflavanone was adsorbed by magnesia, which became yellow, and, on dissolving the magnesia in hydrochloric acid, flavonol was recovered. Further study of the 3-hydroxyflavanone is now in progress. Murakami and Irie⁽⁹⁾ had prepared the same compound by the action of hydrogen peroxide on 2'-hydroxychalkone in the presence of alkali and reported its melting point as 174–177°. Found: C, 75.28; H, 5.42. Calc. for $C_{15}H_{12}O_3$: C, 75.00; H, 5.00%.

Chromatographic Adsorption of the Hydrolysed Product. With the object of purifying the hydrolysed product, a chromatographic adsorption was tried, using magnesia as an adsorbent. When the colourless solution of the hydrolysed product (0.5 g.) in benzene (100 c.c.) was passed through the Tswett column, modified by Winterstein (22 cm. in height) and which was filled with magnesia (37 g.), the upper layer (3/4) of the magnesia became yellow, indicating an adsorption. On dissolving the yellow part of the magnesia in hydrochloric acid, a yellowish compound separated. It was collected and recrystallised from alcohol, when it separated in yellowish crystals, melting at 170°. No depression of the melting point was caused by admixture with an authentic specimen of flavonol. The yield was 0.3 g. The solution passed through magnesia was evaporated and a needle-like crystalline compound, melting at 132–133°, was obtained on recrystallising from alcohol. The yield was 0.08 g.

(9) M. Murakami and T. Irie, *Proc. Imp. Acad. (Tokyo)*, **11** (1935), 229.

No change was observed on heating this substance with a 20% alcoholic solution of hydrochloric acid in a sealed tube. Further study of this compound is now being carried out.

Hydrolysis of the Product formed in the Action of Lead Tetraacetate on Flavanone by means of Methyl-alcoholic Soda. The reaction product (2 g.) was dissolved in a 2.5% methyl-alcoholic soda (50 c.c.) and the solution was allowed to stand at room temperature for five days, when a dark yellow crystalline compound was deposited. On recrystallising it from alcohol, containing a small quantity of hydrochloric acid, a yellow compound, melting at 170°, was obtained and identified as flavonol by the method of the mixed melting point. The yield was 0.8 g.

Action of Lead Tetraacetate on 4'-Methoxyflavanone. A solution of 4'-methoxyflavanone (4 g.) and lead tetraacetate (7 g.) in glacial acetic acid (100 c.c.) was heated in the water-bath at 80–90° for two hours. After the removal of lead compound by the saturation with hydrogen sulphide, most of the acetic acid was distilled off under the reduced pressure, and the residue was poured into water and extracted with ether. The ethereal extract was washed with water, dried over anhydrous sodium sulphate and evaporated. On standing, the residue partly crystallised. The crystals were collected and recrystallised from ether, from which they separated in colourless crystals, melting at 118–119°. The yield was 0.7 g. Further study of this compound is now in progress.

The viscous filtrate from the above-mentioned crystalline compound was subjected to hydrolysis. The viscous liquid (3 g.) was heated with alcohol (40 c.c.), containing concentrated hydrochloric acid (4 g.) and water (2 c.c.), on a water-bath for an hour and, on cooling, a crystalline compound, melting at 143–153°, separated. This compound was purified by several crystallisations from alcohol and then from benzene. The compound thus purified melted at 172–174°. The yield was 0.5 g. This compound was proved to be identical with the 4'-methoxy-3-hydroxyflavanone, which had been previously prepared in another way by the present author. It was also converted into 4'-methoxy-3-hydroxyflavone (4'-methoxyflavonol), melting at 230–231°, by adsorption with magnesia.

In conclusion, the author wishes to express his sincere thanks to Mr. Shigemi Oba, the Director of the Yonezawa Higher Technical School, and to Prof. Tosaziro Yoshida of this school for their encouragements throughout this work. He also expresses his hearty thanks to the Department of Education for the Scientific Research Expenditure which has defrayed most of the cost of this research.

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Synthesis of *p*-Isopropyl- α -methylhydrocinnamic aldehyde.

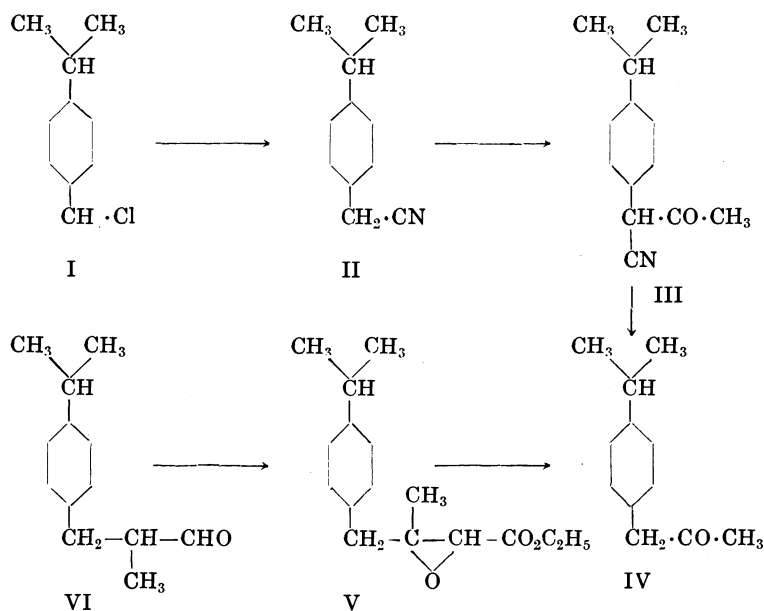
By Masataro YAMASHITA and Tokiyoshi MATSUMURA.

(Received July 28, 1941.)

Knorr and Weissenborn⁽¹⁾ synthesised *p*-isopropyl- α -methylhydrocinnamic aldehyde by condensing cuminaldehyde with propionaldehyde in the presence of alcoholic potash and then reducing the product with hydrogen, using nickel as a catalyser. Since then this compound has been used as perfume. More recently, the compound has been synthesised in the Société des Usines Chimiques⁽²⁾ by heating calcium *p*-isopropyl- α -methylhydrocinnamate with calcium formate or by heating *p*-isopropyl- α -methylhydrocinnamic acid with formic acid in the presence of metallic oxides, such as oxide of Ti, Mn, Al, Zn or Th. For this synthesis, *p*-isopropyl- α -methylhydrocinnamic acid was first synthesised by the condensation of cuminyl chloride with ethyl methylmalonate in the presence of sodium ethoxide and subsequent decomposition of the free acid liberated from the ester.

Two new methods, both starting from cuminyl chloride, of synthesising *p*-isopropyl- α -methylhydrocinnamic aldehyde have been devised by the present authors.

The first method. Cuminyl chloride (I) was first converted into *p*-isopropylbenzyl cyanide (II). The cyanide and ethyl acetate were condensed in the presence of sodium ethoxide to form α -*p*-isopropylphenyl-

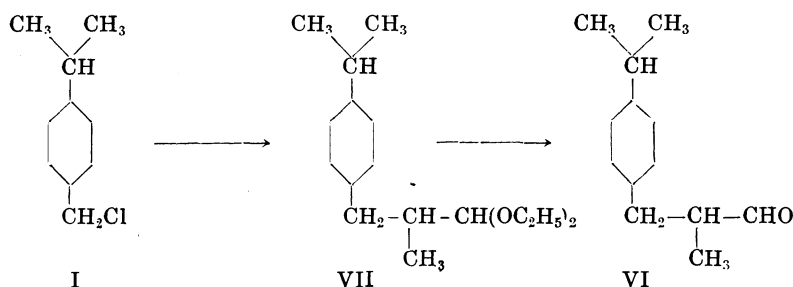


(1) A. Knorr and A. Weissenborn (Winthrop Chemical Co., Inc.), A.P. 1844013 (1932).

(2) F.P. 533644 (1938).

acetoacetonitrile (III), which was converted into *p*-isopropylbenzyl methyl ketone (IV). The ketone and ethyl monochloroacetate were again condensed to yield ethyl α,β -epoxy- γ -*p*-isopropylphenyl- β -methylbutyrate (V), which, on saponification, gave the desired *p*-isopropyl- α -methylhydrocinnamic aldehyde (VI) as shown in the accompanying scheme.

The second method. Cumyl chloride (I) was converted by the condensation with the diethylacetal of α -bromopropionaldehyde into the diethylacetal of *p*-isopropyl- α -methylhydrocinnamic aldehyde (VII). The acetal, on hydrolysis with dilute hydrochloric acid, yielded the desired *p*-isopropyl- α -methylhydrocinnamic aldehyde (VI), as shown in the following scheme:



Experimental. *p*-Isopropylbenzyl Cyanide (II). This compound was synthesised by Rossi⁽³⁾ and by Komppa⁽⁴⁾ by heating cumyl chloride with potassium cyanide in a sealed tube. However, the present authors were able to prepare it with an 85% yield in the following way: Cumyl chloride (170 g.) and alcohol (170 g.) were added to a solution of potassium cyanide (65 g.) in water (60 c.c.), and the mixture was boiled for 3 hours. On cooling, it separated potassium chloride, which was filtered off and washed with alcohol. The filtrate and the washings were combined and the alcohol evaporated. The residue was extracted with ether and the ethereal extract was washed with water and dried over calcium chloride. After the ether was evaporated, the residual oil was subjected to fractional distillation under reduced pressure, when an oil boiling at 125–128°/9 mm. passed over. The yield was 85% of the theoretical. The oil has n_D^{25} 1.5078, d_4^{25} 0.9619, $[\alpha]_D^{25}$ 49.28 (Calc. for $\text{C}_{11}\text{H}_{13}\text{N}$: 49.22).

o-*p*-Isopropylphenylacetoacetonitrile (III). A mixture of *p*-isopropylbenzyl cyanide (318 g.) and ethyl acetate (264 g.) was added to a solution of sodium (60 g.) in absolute alcohol (700 c.c.) and the whole was heated to boiling for about an hour on a water-bath, until it became a pasty mass. After being heated for an hour more, the mass solidified completely and was allowed to stand for 12 hours. Water (3 kg.) was then added, when unchanged *p*-isopropylbenzyl cyanide separated, which was removed by extraction with ether. The aqueous residue was acidified at about 10° with glacial acetic acid (100 c.c.). The yellow oil, thus obtained was extracted with ether and the ethereal extract was

(3) A. Rossi, *Ann., Suppl.*, **1** (1861), 139.

(4) G. Komppa, *Ber.*, **68** (1935), 1269.

washed successively with an aqueous solution of sodium carbonate and with water. After the ethereal extract was dried over calcium chloride, the ether was evaporated, and the residual oil solidified. The yield was 290 g. (72% of the theoretical). Although it was pure enough for the next preparation, it was recrystallised from methyl alcohol, from which it separated in colourless needles melting at 84–85°. Found: N, 7.26. Calc. for $C_{13}H_{15}ON$: N, 6.96%.

The semicarbazone crystallised from alcohol in colourless aggregated crystals melting at 156°. Found: N, 21.82. Calc. for $C_{18}H_{18}ON_4$: N, 21.70%.

p-Isopropylbenzyl Methyl Ketone (IV).—This compound has already been prepared by Bradfield, Pritchard and Simonsen⁽⁵⁾ by condensing cuminaldehyde with ethyl α -bromopropionate in the presence of sodium ethoxide, and then hydrolysing the condensation product, namely ethyl α,β -epoxy- β -cuminy- β -methylpropionate, with methyl alcoholic potassium hydroxide.

The present authors synthesised this compound in the following way: Powdered *o*-*p*-isopropylphenylacetoacetonitrile (120 g.) was added, with constant stirring, to concentrated sulphuric acid (170 c.c.), cooled at -10° . After all the nitrile was added, the mixture was warmed to 60° and a brown solution was obtained. After this was cooled to 0° , water (850 c.c.) was rapidly added and the whole was again heated, with constant stirring, for two hours on a water-bath. The green solution thus obtained was cooled, and the supernatant oil was separated. The aqueous solution was extracted several times with ether. The oil and ethereal extracts were combined, washed with water, dried over anhydrous sodium sulphate and evaporated. The residual oil was purified by distillation under diminished pressure, and a fraction, boiling at 125–128°/16 mm., was collected. This fraction has n_D^{25} 1.5033, d_4^{25} 0.9538, $[R_L]_D$ 54.33 (Calc. for $C_{12}H_{16}O$: 54.03).

The semicarbazone crystallised from alcohol in colourless prisms melting at 142–143°. Found: N, 18.20. Calc. for $C_{13}H_{19}ON$: N, 18.03%.

Ethyl α,β -Epoxy- γ -*p*-isopropylphenyl- β -methylbutyrate (V). Absolute alcohol (55 g.) was added to pieces of sodium (13.8 g.) covered with dry benzene (200 g.). After all the sodium dissolved, the solution was maintained at 0° , and, to this, *p*-isopropylbenzyl methyl ketone (88 g.) and ethyl monochloroacetate (62 g.) were added and stirred for two hours at 0° . The mixture was allowed to stand for 40 hours at the ordinary temperature, poured into ice-cold water (500 g.) and acidified with glacial acetic acid (5 c.c.). The supernatant oily layer was separated and the lower aqueous layer was extracted with benzene. The oil and benzene solution were combined, washed with water, dried over anhydrous sodium sulphate and evaporated. The residual oil was subjected to fractional distillation under reduced pressure of 11 mm., and a fraction distilling at 164–167°, was collected. The yield was 76 g. (58% of the theoretical). Found: C, 73.05; H, 8.62. Calc. for $C_{16}H_{22}O_3$: C, 73.23; H, 8.46%. It has n_D^{25} 1.4987 and d_4^{25} 1.0308.

p-Isopropyl- α -methylhydrocinnamic Aldehyde (VI). Ethyl α,β -epoxy-

(5) A. E. Bradfield, R. R. Pritchard and J. L. Simonsen, *J. Chem. Soc.*, 1937, 760.

γ -*p*-isopropylphenyl- β -methylbutyrate (60 g.) was stirred for two hours at 35° with a 10% solution of sodium hydroxide (100 g.), and a lustrous paste was obtained. After this was mixed with a 10% solution of oxalic acid (110 g.), the mixture was distilled in steam. The oil passed over with vigorous effervescence and was extracted with ether. The ethereal extract was dried over anhydrous sodium sulphate and evaporated. The residual oil was distilled under reduced pressure of 10 mm. in a current of carbon dioxide, and a fraction, boiling at 128–131°, was collected. The oil has n_D^{25} 1.5030, d_4^{25} 0.9529, $[R_L]_D$ 58.99 (Calc. for $C_{13}H_{16}OF_3$: 58.64).

The semicarbazone crystallised from alcohol in glazed colourless plates melting at 169–170°. Found: N, 16.24. Calc. for $C_{15}H_{21}ON_2$: N, 16.21%.

Diethylacetal of p-Isopropyl- α -methylhydrocinnamic Aldehyde (VII). A mixture of cuminyl chloride (115 g.) and diethylacetal of α -bromopropionaldehyde (140 g.) was gradually added, with constant stirring, to sodium (35 g.), cut into pieces and covered with ether. The stirring was continued, while the temperature rose gradually to boiling. The mixture was cooled with water and allowed to stand for five hours. After the reaction had subsided, the mixture was heated for 6 hours on a water-bath with a reflux condenser. The reaction product was then cooled and the oily part was removed by decantation. The residue left behind in the vessel was extracted with ether. The oily part and ethereal extract were combined, washed with water, dried over anhydrous sodium sulphate and evaporated. The residual oil was distilled under reduced pressure of 13 mm., and a fraction, boiling at 117–122°, was collected. Found: C, 77.01; H, 10.80; Calc. for $C_{17}H_{28}O_2$: C, 72.22; H, 10.92%.

It has n_D^{25} 1.4850, d_4^{25} 0.9376, $[R_L]_D$ 80.69 (Calc. for $C_{17}H_{28}O_2F_3$: 80.39).

The Conversion of the Acetal into p-Isopropyl- α -methylhydrocinnamic Aldehyde. The acetal (60 g.) was heated with a 3% solution of hydrochloric acid (600 c.c.) for fifty minutes under a reflux condenser. After the mixture was cooled, the supernatant oily layer was extracted with ether. The ethereal extract was washed with an aqueous solution of sodium carbonate and then with water. The extract was dried over anhydrous sodium sulphate and evaporated. The residual oil was subjected to fractional distillation under reduced pressure of 12 mm. in a current of carbon dioxide, when a colourless oil boiling at 133–135° passed over. The yield was 33 g. (77% of the theoretical). The melting point of the semicarbazone was not depressed by admixture with the specimen synthesised by the first method.

In conclusion, the authors wish to express their hearty thanks to Professor Eiichi Funakubo, Osaka Imperial University, for the assistance in the microanalyses of nitrogen of the substances described above.

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Austauschreaktion der Wasserstoffatome im festen Anilinchlorhydrat und seine Derivate. II. *p*-Toluidinchlorhydrat (Auszug).⁽¹⁾

Von Jisaku KURODA und Nobukazu OKAZAKI.

(Eingegangen am 8. September 1941.)

Inhaltsübersicht. Wird das in die Ammoniumgruppe D eingeführte *p*-Toluidinchlorhydrat unterhalb bzw. oberhalb seines Schmelzpunktes erwärmt, so tauschen die in die Ammoniumgruppe eingeführten D-Atome ihre Plätze gegen die der im Benzolkern befindlichen Kernwasserstoffatome aus. Die Anzahl der sich an dieser Austauschreaktion beteiligenden Kernwasserstoffatome ergibt unterhalb des Schmelzpunktes d.h. bei der Reaktion, die in der mit blossen Auge fest aussehenden Phase stattfindet, nur zwei. Dagegen wächst sie plötzlich bis auf vier an, so bald als die Erwärmungstemperatur den Schmelzpunkt überschreitet und das *p*-Toluidinchlorhydrat schmilzt. Dies deutet ohne weiteres darauf hin, dass der Mechanismus der Reaktion, die unterhalb des Schmelzpunktes in der festen Phase vor sich geht, ein ganz anderer ist als bei der Reaktion in der geschmolzenen Phase. Es liegt also die Annahme nahe, dass die erstere Reaktion wirklich in der echten festen Phase stattfindet und die Anzahl sowie die Lage der sich an der Reaktion beteiligenden Kernwasserstoffatome mit der geometrischen Ordnung des Kristallgitters in engem Zusammenhang steht.

Einleitung. Erwärmt man das in die Ammoniumgruppe D eingeführte Anilinchlorhydrat unterhalb bzw. oberhalb seines Schmelzpunktes, so tauschen diese D-Atome ihre Plätze gegen die H-Atome aus, die im Benzolkern befindlich sind. Diese von Harada und Titani⁽²⁾ gefundene eigenartige Platzwechselreaktion der H-Atome des Anilinchlorhydrats wurde von einem von uns und Koizumi⁽³⁾ eingehend untersucht. Dabei kamen wir zu dem Schluss, dass die oberhalb des Schmelzpunktes beobachtete Reaktion zweifellos in der flüssigen Phase vor sich geht. Aber über den Mechanismus der Reaktion, die unterhalb des Schmelzpunktes in der mit blossen Auge fest aussehenden Phase stattfindet, konnten wir bloss aus dem damals erhaltenen Versuchsergebnis keinen sicheren Schluss ziehen, ob es sich wirklich um die Reaktion in der echten festen Phase handelt oder die Reaktion hauptsächlich in der hochdispersen flüssigen Phase stattfindet, die unter dem Einfluss der Verunreinigungen insbesondere an den Kanten bzw. Ecken der Kriställchen entstehen.

Wäre die letztere Reaktion massgebend, so müsste die Anzahl der Kernwasserstoffatome, die sich an der Reaktion beteiligen, immer dieselbe Grösse besitzen, ohne Unterschied ob man die Reaktion unterhalb oder oberhalb des Schmelzpunktes untersucht, weil in diesem Fall der massgebende Mechanismus der Reaktion immer derselbe sein soll. Falls

(1) N. Okazaki und J. Kuroda, *J. Chem. Soc. Japan*, **62** (1941), 57. I. Mittl.: dies Bulletin, **16** (1941), 371.

(2) M. Harada und T. Titani, dies Bulletin, **11** (1936), 554.

(3) N. Okazaki und M. Koizumi, dies Bulletin, **16** (1941), 371.

dagegen die Reaktion oberhalb des Schmelzpunktes hauptsächlich in der flüssigen Phase vor sich geht während sie unterhalb desselben wirklich in der echten festen Phase stattfindet, ergibt sich die Möglichkeit, dass die oben angegebene Anzahl einen ganz verschiedenen Wert besitzt, je nachdem ob man die Reaktion oberhalb bzw. unterhalb des Schmelzpunktes untersucht. Die vorliegenden Versuche, die unter Verwendung des *p*-Toluidinchlorhydrats ausgeführt wurden, ergaben, dass dies wirklich der Fall ist; die Anzahl der Kernwasserstoffatome des *p*-Toluidinchlorhydrats, die sich an der Reaktion unterhalb des Schmelzpunktes beteiligen, ergibt zwei, während sie plötzlich bis auf vier anwächst, sobald als die Erwärmungstemperatur den Schmelzpunkt überschreitet und das *p*-Toluidinchlorhydrat schmilzt. Dies beweist ohne weiteres, dass der Mechanismus der Reaktion, die unterhalb des Schmelzpunktes in der mit blossen Auge fest aussehenden Phase stattfindet, ganz anders angenommen werden muss als die Reaktion, die oberhalb des Schmelzpunktes in der geschmolzenen Phase stattfindet.

Versuchsmethode und -ergebnisse. Die Versuchsmethode ist genau dieselbe wie die in der letzten Mitteilung beim Versuch mit dem Anilinchlorhydrat benutzt wurde.

Das *p*-Toluidinchlorhydrat wird durch die Vereinigung des reinen *p*-Toluidins mit der reinen Salzsäure hergestellt. Das so hergestellte *p*-Toluidinchlorhydrat wird dann durch die zweimalige Umkristallisation aus Alkohol sowie durch die zweimalige Fällung aus alkoholischer Lösung durch Äther gereinigt. Es schmilzt bei 242° bis 243.5°.

Die Versuchsergebnisse sind in Tabelle 1 zusammengestellt, wo die Versuchsnr. die zeitliche Reihenfolge der einzelnen Versuche zeigt und das Austauschäquivalent *nk* auf genau dieselbe Weise wie beim Anilinchlorhydrat mit Hilfe des D-Gehaltes des schweren Wassers ermittelt wird (vgl. Gl. (1) in I. Mittl.), das sich mit dem nicht erwärmten sowie erwärmten *p*-Toluidinchlorhydrat im Austauschgleichgewicht befindet. Die Bezeichnung „P₂O₅“ und „Sublimation“ in der zweiten letzten Spalte der Tabelle bedeutet, dass das *p*-Toluidinchlorhydrat vor der Erwärmung resp. über Phosphorpentoxyd bzw. durch die Sublimation im Hochvakuum getrocknet wurde.

Dass das *p*-Toluidinchlorhydrat auch nach der längeren Erwärmung auf hohen Temperaturen nicht so merklich zersetzt wurde, wird aus Tabelle 2 ohne weiteres ersichtlich, wo der Schmelzpunkt sowie die äussere Beschaffenheit einiger Proben des *p*-Toluidinchlorhydrats nach der Beendigung der Versuche wiedergegeben ist (vgl. Tabelle 1).

Zeichnet man die in Tabelle 1 angegebenen Daten graphisch ein, so erhält man Abb. 1, wo die Nummer bei jedem kleinen Kreis die Erwärmungsdauer angibt. Diese Abb. 1 zeigt, dass das Austauschäquivalent *nk*, das in erster Annäherung die statistische Anzahl *n* der Kernwasserstoffatome angibt, die sich an der Platzwechselreaktion beteiligen, mit steigender Temperatur (und bei konstant gehaltener Erwärmungsdauer) allmählich anwächst. Aber es wächst nur bis zu etwa zwei, so lange als die Erwärmungstemperatur unterhalb des Schmelzpunktes bleibt. Überschreitet dagegen die Erwärmungstemperatur den Schmelzpunkt, so wächst der Gleichgewichtswert von *nk* plötzlich bis auf etwa vier.

Tabelle 1. Die Austauschreaktion des *p*-Toluidinchlorhydrats in fester und geschmolzener Phase.

Versuchsnr.	Erwärmungs- temp. °C.	Erwärmungs- dauer in Stdn.	nk	Trocknung	Bemerkung
1-4	ohne Erwärmung		±0.2	P ₂ O ₅	fest
24	110	3.5	0.0	P ₂ O ₅	„
25	140	3.5	0.1	P ₂ O ₅	„
26	170	3.5	0.2	P ₂ O ₅	„
27	184	3.5	0.6	P ₂ O ₅	„
28	200	3.5	0.8	P ₂ O ₅	„
29	200	4	1.5	P ₂ O ₅	„
30	217	3.5	1.8	P ₂ O ₅	„
22	220	7	2.1	Sublimation	„
20	220	14	2.2	Sublimation	„
18	220-222	45	1.9	Sublimation	„
10	222-223	23	2.1	P ₂ O ₅	„
23	223.5	1	1.9	Sublimation	„
21	223.5	3.5	2.1	Sublimation	„
5	233-235	2	1.5	P ₂ O ₅	„
6	233-235	5	2.1	P ₂ O ₅	„
7	233-235	20	2.1	P ₂ O ₅	„
8,9	233-235	50	2.1	P ₂ O ₅	„
31	235	3.5	1.7	P ₂ O ₅	„
10	238-240	20	2.3	P ₂ O ₅	wenig zusammen- gesintert
32	243	3.5	3.1	P ₂ O ₅	Schmelzpkt.
11	246-249	2	2.6	P ₂ O ₅	flüssig
12	246-249	5	3.2	P ₂ O ₅	„
13	246-249	20	4.2	P ₂ O ₅	„
14	246-249	50	4.5	P ₂ O ₅	„
33	248	1/6	2.0	P ₂ O ₅	„
15	249	15	4.2	Sublimation	„
17	250	7	4.5	Sublimation	„
16	250	10	4.4	Sublimation	„

Tabelle 2. Schmelzpunkt und äussere Beschaffenheit des *p*-Toluidinchlorhydrats nach der Beendigung der Versuche.

Versuchsnr.	Erwärmungs- temp. °C.	Erwärmungs- dauer in Stdn.	Schmelzpunkt nach dem Versuch	äussere Beschaffen- heit nach dem Versuch
—	ohne Erwärmung		242-243.5°	farblos
14	246-249	50	—	braun gefärbt und ganz schwach nach Chinon gerochen
15	249	15	240-243° (von 232° ab zusammenge- sintert)	hell bräunlich gefärbt
16	250	10	239.5-241.5°	fast keine Färbung
17	250	7	239.5-242.5°	hell bräunlich gefärbt

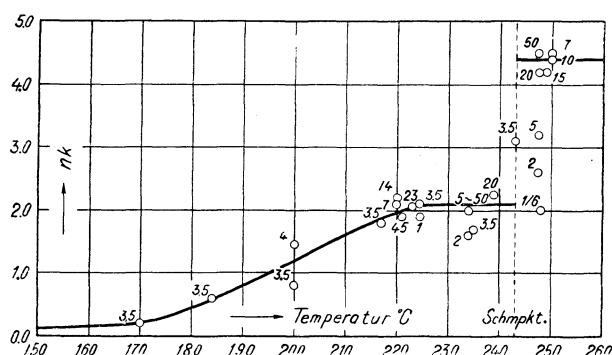


Abb. 1. Das Austauschäquivalent nk des p -Toluidinchlorhydrats in Abhängigkeit von der Erwärmungsdauer und -temperatur.

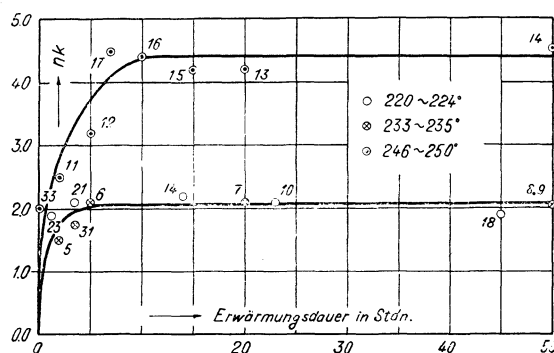


Abb. 2. Das Austauschäquivalent nk des p -Toluidinchlorhydrats in Abhängigkeit von der Erwärmungsdauer unterhalb bzw. oberhalb des Schmelzpunktes.

Diese sprungweise Zunahme des Gleichgewichtswertes von nk beim Schmelzpunkt kann weiter aus Abb. 2 deutlich ersehen werden, wo der Wert von nk , der dicht unterhalb (bei 220–224° sowie 233–235°) sowie oberhalb (bei 246–250°) des Schmelzpunktes beobachtet wird, beide in Abhängigkeit von der Erwärmungsdauer eingetragen ist. Obwohl der Wert von nk bei den Temperaturen, die unterhalb des Schmelzpunktes liegen, sogar nach 50 stündiger Erwärmung nur asymptotisch bis zu 2.1 anwächst, wächst er oberhalb des Schmelzpunktes schon nach einigen Stunden Erwärmung bis auf 4.4 an. Dies deutet ohne weiteres darauf hin, dass die Anzahl der Kernwasserstoffatome, die ihre Plätze unterhalb des Schmelzpunktes gegen die in der Ammoniumgruppe befindlichen H-Atome wechseln, nur zwei beträgt, während oberhalb des Schmelzpunktes alle vier H-Atome im Benzolkern sich an der Reaktion beteiligen.

Beim letzten Versuch mit dem Anilinchlorhydrat wird festgestellt, dass die drei in o -, o' - und p -Stellung befindlichen Kernwasserstoffatome ihre Plätze gegen die H-Atome in der Aminogruppe wechseln. Deshalb liegt die Annahme nahe, dass beim vorliegenden Versuch mit dem p -

Toluidinchlorhydrat die zwei Kernwasserstoffatome, die ihre Plätze zuerst d.h. schon unterhalb des Schmelzpunktes gegen die H-Atome in der Aminogruppe wechseln, die dieser Gruppe gegenüber in *o*- und *o'*-Stellung befindlichen beiden H-Atome sind. Sobald aber als das *p*-Toluidinchlorhydrat schmilzt, kommen dazu noch die anderen beiden d.h. in *m*- und *m'*-Stellung befindlichen nicht substituierten Kernwasserstoffatome ins Spiel, die unter dem Einfluss der in *p*-Stellung eingeführten Methylgruppe im Vergleich mit dem unsubstituierten Anilinchlorhydrat reaktionsfähiger werden.

Diskussion der Ergebnisse. Über den Mechanismus der vorliegenden Platzwechselreaktion der H-Atome gibt es, wie darauf schon in I. Mittl. hingewiesen wurde, zwei Möglichkeiten: entweder (1), dass die Reaktion nicht nur oberhalb sondern auch unterhalb des Schmelzpunktes immer in einer flüssigen Phase stattfindet, die unterhalb des Schmelzpunktes unter dem Einfluss der Verunreinigungen in hoch disperser Form gebildet wird, oder (2), dass die oberhalb des Schmelzpunktes beobachtete Reaktion in der flüssigen, während die unterhalb des Schmelzpunktes verlaufende Reaktion wirklich in der echten festen Phase stattfindet. Zwischen diesen beiden Möglichkeiten konnten wir aber beim letzten Versuch mit dem Anilinchlorhydrat keine eindeutige Entscheidung treffen, obwohl die letztere Möglichkeit wahrscheinlicher ist als die erstere.

Da aber beim vorliegenden Versuch festgestellt wurde, dass die Anzahl der Kernwasserstoffatome des *p*-Toluidinchlorhydrats, die sich an der Reaktion unterhalb des Schmelzpunktes beteiligen, einen ganz anderen Wert besitzt als oberhalb des Schmelzpunktes, darf wohl geschlossen werden, dass auch der Mechanismus der Reaktion in den beiden Fällen d.h. unterhalb und oberhalb des Schmelzpunktes voneinander ganz anders sein muss; die Reaktion, die unterhalb des Schmelzpunktes beobachtet wird, findet wirklich in der echten festen Phase statt, während die andere oberhalb desselben in der flüssigen Phase verläuft. Beim ersteren Fall können wir den Reaktionsmechanismus etwa so annehmen, dass die Kernwasserstoffatome durch die immer heftiger werdende thermische Schwingung so weit gelockert sind, bis schliesslich ihre Plätze gegen die ebenfalls gelockerten H-Atome in der Aminogruppe des eigenen bzw. der benachbarten Moleküle ausgetauscht werden. Dabei ist durchaus möglich, dass der intermolekulare Austausch der H-Atome durch die zugleich heftig werdende thermische Schwingung der einzelnen Moleküle bei weitem erleichtert wird. Für die Annahme, dass zu dieser Austauschreaktion nicht nur die Kernwasserstoffatome sondern auch die H-Atome in der Aminogruppe thermisch gelockert werden, spricht u.a. die experimentell gefundene Tatsache, dass der Zersetzungsdruck des Anilin- bzw. Toluidinchlorhydrats gerade beim Temperaturgebiet stark erhöht wird, wo die in Rede kommende Austauschreaktion merklich stattzufinden beginnt. Bei der Austauschreaktion im festen Zustand müssen wir weiter annehmen, dass die Anzahl und die Lage der sich an der Reaktion beteiligenden Kernwasserstoffatome hauptsächlich durch die geometrische Ordnung des Kristallgitters der betreffenden organischen Verbindungen bestimmt wird, weil sonst die beim vorliegenden Versuch festgestellte Tatsache kaum zu erklären ist, dass diese Anzahl des *p*-Toluidinchlorhydrats im

festen Zustand einen ganz anderen Wert besitzt als die Reaktion im geschmolzenen Zustand. Bei der Reaktion im geschmolzenen bzw. flüssigen Zustand, wo der Ordnungszustand des Kristallgitters ganz und gar verloren geht, wirkt für die Anzahl und die Lage der sich an der Reaktion beteiligenden Kernwasserstoffatome nur die Reaktionsfähigkeit der einzelnen H-Atome massgebend. So werden z.B. beim *p*-Toluidinchlorhydrat nicht nur die in *o*- und *o'*-Stellung befindlichen zwei H-Atome sondern auch die in *m*- und *m'*-Stellung befindlichen zwei H-Atome unter dem Einfluss der in *p*-Stellung befindlichen Methylgruppe in die Reaktion eingeführt. Dabei ist denkbar, dass die Reaktion oberhalb des Schmelzpunktes fast ausschliesslich intermolekular stattfindet, d.h. dass die Kernwasserstoffatome eines Moleküls gegen die H-Atome der Aminogruppe eines anderen Moleküls ausgetauscht werden, während bei der Reaktion, die unterhalb des Schmelzpunktes in der festen Phase stattfindet, ein Teil der Reaktion auch intramolekular stattfinden kann. So können z.B. das in *p*-Stellung befindliche Kernwasserstoffatome (des Anilinchlorhydrats) gegen das H-Atome der Aminogruppe des anderen benachbarten Moleküls, während die in *o*-Stellung befindlichen H-Atome gegen die H-Atome der Aminogruppe des eigenen Moleküls ausgetauscht werden.

Zum Schluss möchten wir Herrn Prof. T. Titani für seine freundlichen Ratschläge und seine Hilfe bei der vorliegenden Arbeit unseren herzlichsten Dank aussprechen. Der Nippon Gakujutsu-Shinkohkai (der Japanischen Gesellschaft für die Förderung der wissenschaftlichen Arbeit) sowie der Hattori Hohkohkai (der Hattori-Stiftung) für ihre finanzielle Unterstützung sind wir zu bestem Dank verpflichtet.

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Über die Reaktion von Grignardschen Reagenz auf α -Benzoyloxy-butyronitril.

Von Satoru KUWADA und Yosio SASAGAWA.

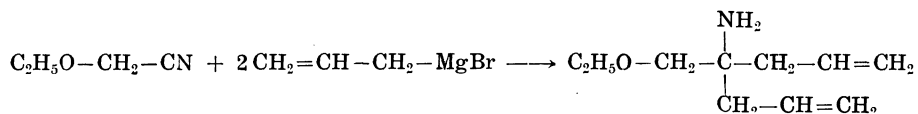
(Eingegangen am 8. September 1941.)

Im Anschluss an die Untersuchung über Stilben-Derivate haben wir⁽¹⁾ das Propioin durch Einwirkung von Überschuss Äthylmagnesiumbromid auf Propionaldehydecyanhydrin dargestellt. Es hat sich dabei gezeigt, dass die Ausbeute an Propioin durch den Reinheitsgrad des Cyanhydrins stark beeinflusst wird. Also haben wir als Ausgangsmaterial α -Benzoyloxy-butyronitril (I)⁽²⁾ gewählt, welches sich in reinerem Zustand erhalten lässt.

Lässt man nun Äthylmagnesiumbromid auf α -Benzoyloxy-butyronitril (I) einwirken, so erhält man kein zu erwartendes Benzoyl-propioin bzw. dessen Ketiminsalz, sondern ein krystallinisches Produkt $C_{15}H_{23}O_2N$ (II) vom Schmp. 134.5° ⁽³⁾, welches offenbar durch Zusammentreten von zwei Molen Äthylmagnesiumbromid auf einem Mol α -Benzoyloxy-butyronitril zustande kam. Dieses Produkt ist in verd. Mineralsäuren unlöslich und nimmt beim Acylieren eine Acyl-Gruppe auf. Sowohl in konz. Salzsäure als auch in konz. Schwefelsäure löst es sich leicht auf, scheidet sich aber beim Verdünnen mit Wasser nichts aus.

Im gleichem Sinne liefert α -Benzoyloxy-butyronitril durch Einwirkung vom Phenylmagnesiumbromid ein Produkt $C_{23}H_{23}O_2N$ vom Schmp. 128° (III), welches sich gegen Reagentien genau so wie (II) verhält.

Vor kurzem haben Allen und Henze⁽⁴⁾ berichtet, dass die Einwirkung von Allylmagnesiumbromid auf Äthoxy-acetonitril unter Bildung von einem Amin abnorm verläuft:



Zweifellos hat die Reaktion zwischen α -Benzoyloxy-butyronitril und Alkyl- bzw. Arylmagnesiumbromid in der ersten Phase, gleich wie die amerikanischen Forscher angaben, stattgefunden. Dass bei unserem Fall das Produkt keine basische Eigenschaft aufweist, ist darauf zurückzuführen, dass sich die Benzoyl-Gruppe am Hydroxyl zur benachbarten Amino-Gruppe umgelagert hat—eine schon häufig beobachtete Eigenschaft der Alkoholamine⁽⁵⁾. Erst durch Einwirkung von Säuren wird das neutrale N-Acylderivat unter Rückbildung von O-Acylderivat ins Aminsalz übergeführt. Also wollten wir die Einwirkung von Äthyl- bzw.

(1) *J. Pharm. Soc. Japan*, **60** (1940), 224.

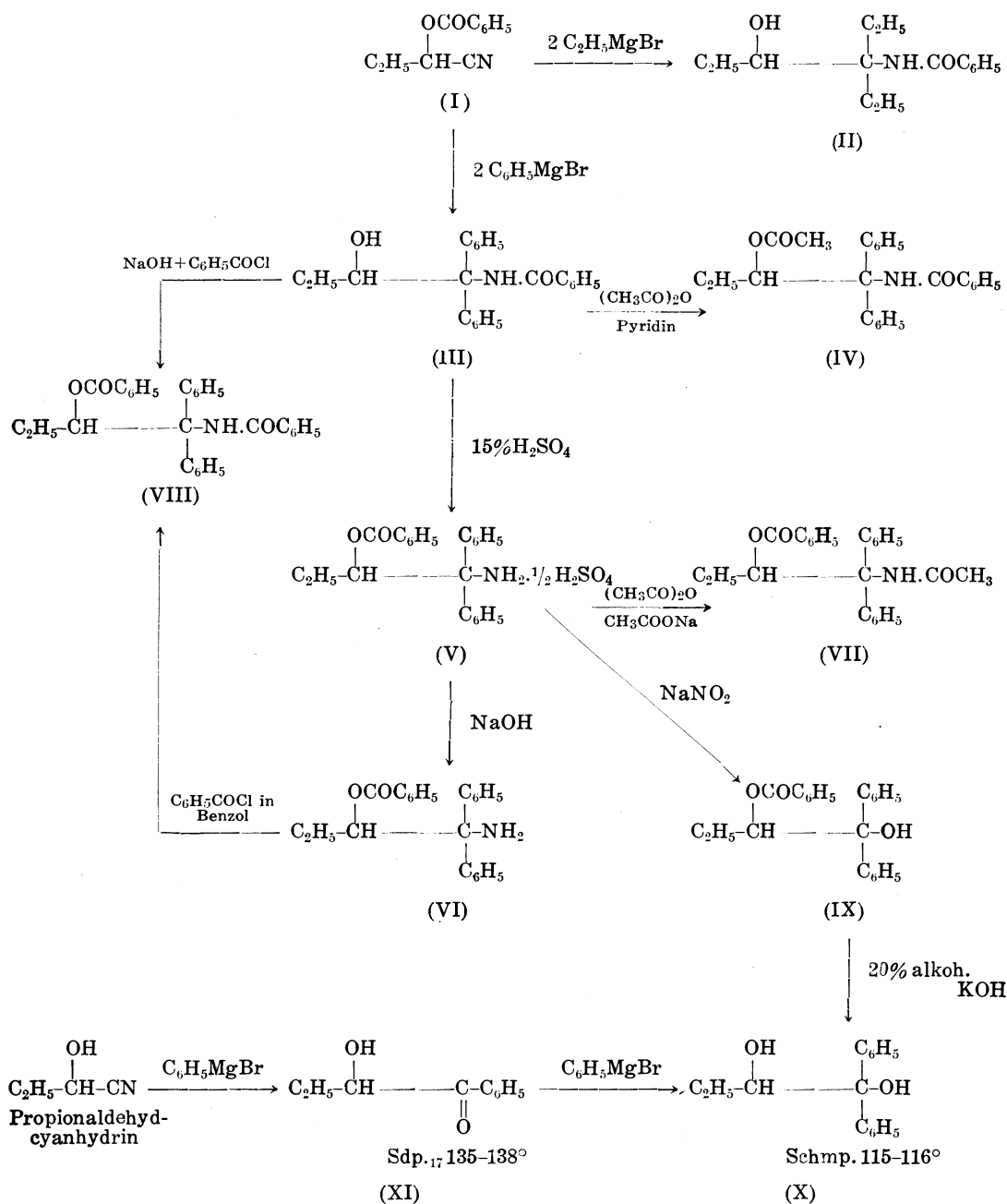
(2) Francis und Davis, *J. Chem. Soc.*, **95** (1909), 1403.

(3) Alle Schmp. und Sdp. sind unkorrigiert.

(4) *J. Am. Chem. Soc.*, **61** (1939), 1790.

(5) Takeda, *J. Pharm. Soc. Japan*, **426** (1917), 1; Vinkler und Bruckner, *J. prakt. Chem.*, [2] **151** (1938), 17.

Phenylmagnesiumbromid auf α -Benzoyloxy-butyronitril und die Umwandlungen des Reaktionsproduktes (III) durch die folgenden Schemata ausdrücken:



Das aus (V) durch Diazotierung dargestellte Monobenzoat des Diphenyläthylglykols (IX) liefert beim alkalischen Verseifen das Glykol (X) vom Schmp. 115–116°, welches sich als identisch mit racem. 2-Aethyl-

2-oxy-1, 1-diphenyläthanol-1 von Roger⁽⁶⁾ erwies. Derselbe Glykol(X) lässt sich auch aus Benzoyläthyl-carbinol(XI) vom Sdp.₁₇ 135–138° (aus Propionaldehydcyanhydrin und Phenylmagnesiumbromid⁽⁷⁾) und Phenylmagnesiumbromid darstellen. Da der Siedepunkt von (XI), im Gegensatz zum Benzoyläthylcarbinol (Sdp.₉ 143°) von Urion und Baum⁽⁸⁾ erheblich niedriger und eher zu dem des Umlagerungsproduktes (Phenylpropionylcarbinols, Sdp.₁₁ 124–128° nach Urion und Baum) näher lag, so wäre es anzunehmen, dass unsere Verbindung(XI) schon eine Umlagerung in Phenylpropionylcarbinol erlitten hätte. Dass es aber nicht der Fall ist, ist daraus ersichtlich, da das Phenylpropionylcarbinol von Urion und Baum durch Einwirkung von Phenylmagnesiumbromid das bei 105–106° schmelzende α -2-Phenyl-1, 1-äthylphenyl-glykol⁽⁹⁾ liefert. Auch haben wir durch Einwirkung des Äthylmagnesiumbromids auf Benzoin das β -2-Phenyl-1, 1-äthylphenyl-glykol⁽¹⁰⁾ dargestellt, welches trotz des sehr naheliegenden Schmp. 116–117° in der Mischschmp.-Bestimmung mit unserem 2-Äthyl-1, 1-diphenyl-glykol(X) eine deutliche Depression zeigte. Also liegt daran kein Zweifel mehr, dass die Verbindung(XI) bei der Darstellung keine Umlagerung erlitten hat.

Hiermit wurde es gezeigt, dass Aldehydcyanhydrine auf Grignardschen Reagentien normaler Weise unter Bildung von Ketoalkoholen reagieren⁽⁷⁾, während dessen O-Acyl-Verbindungen mit denselben Mitteln im Sinne der Allen-Henzeschen Reaktion N-Acyl-amine bilden.

Beschreibung der Versuche.

α -Benzoyloxy-butyronitril (I)⁽²⁾. 23.2 g. Propionaldehyd und 56 g. Benzoylchlorid wurden unter Umrührung in die eisgekühlten 250 c.c. Wasserlösung von 31.2 g. Cyankalium zugetropft und noch 4 Stdn. weiter umgerührt. Das Reaktionsprodukt wurde in Aether aufgenommen und der Aetherrückstand unter vermindertem Druck destilliert. Die Fraktion vom Sdp.₁₇ 157–158° beträgt 62.5 g. (82.7% d.Th.). Gefunden: C, 69.92; H, 5.72; N, 7.23. Berechnet für C₁₁H₁₁O₂N: C, 69.81; H, 5.86; N, 7.41%.

2-Äthyl-2-oxy-1,1-diäthyl-1-benzoylamino-äthan (II). In die Grignardschen Lösung, die aus 22 g. Äthylbromid, 5 g. Magnesiummetall und 150 c.c. abs. Aether dargestellt wurde, wurden 10 g. α -Benzoyloxy-butyronitril zugetropft und 5 Stdn. auf dem Wasserbade umgerührt. Nach der Spaltung der Mg-Verbindung mit 20%iger Ammoniumchlorid wurde das Reaktionsprodukt mit Chloroform extrahiert. Durch Umlösen des Chloroformrückstands wurden farblose Nadeln vom Schmp. 133–134.5° erhalten. Ausbeute 3.7 g. Die Verbindung ist in Alkohol, Methanol, Aceton und Chloroform leicht löslich, in Aether und Benzol löslich, in Ligroin, Hexan und Petroläther schwer löslich, in kalter Salz-

(6) *Helv. chim. Acta*, **12** (1929), 1063.

(7) Asahina und Terasaka, *J. Pharm. Soc. Japan*, **494** (1923), 19; *Chem. Zentr.*, **1923** III, 434.

(8) *Chem. Zentr.*, **1939**, II, 3041.

(9) Tiffenau und Lévy, *Bull. soc. chim.*, **41** (1927), 1351.

(10) Tiffenau und Dorlencourt, *Compt. rend.*, **143** (1906), 127, 1243, *Ann. chim. phys.*, [8] **16** (1909), 237.

säure unlöslich. Erhitzt man sie mit 20%iger Schwefelsäure 40 Min., so löst sie in die Säure, aber beim Erkalten scheidet sich keine Substanz aus. Durch Verseifen mit 10%iger Kalilauge liefert sie Benzoesäure. Gefunden: C, 72.11; H, 9.09; N, 5.47. Berechnet für $C_{15}H_{23}O_2N$: C, 72.23; H, 9.30; N, 5.62%. Molekulargewichtsbestimmung nach Barger: 250 ± 20 . Ber. Mol.-Gew. 249.

Acetat: Dargestellt durch Behandlung mit Essigsäureanhydrid in Pyridin. Aus verd. Alkohol wurde es in Nadeln vom Schmp. $88-89^\circ$ erhalten. Gefunden: C, 70.18; H, 8.42; N, 4.73. Berechnet für $C_{17}H_{25}O_3N$: C, 70.05; H, 8.65; N, 4.81%.

2-Äthyl-2-oxy-1,1-diphenyl-1-benzoylamino-äthan (III). In die Grignardschen Lösung, die aus 30 g. Brombenzol, 15 g. Magnesium und 50 c.c. abs. Aether dargestellt wurde, wurden 30 g. α -Benzoyloxybutyronitril eingetropft und gleich wie bei der Darstellung von (II) durchgeführt. Nach Umkrystallisieren aus Essigester-Petroläther des in Aether aufgenommenen Reaktionsprodukts erhielt man die farblose flache Nadeln vom Schmp. $127-128.5^\circ$. Ausbeute 48 g. (87.7% d.Th.). Die Verbindung ist in Aether, Methanol, Alkohol, Essigester, Aceton, Chloroform, Benzol und Dioxan leicht löslich, in Ligroin, Hexan und Petroläther schwer löslich. Gefunden: C, 79.76; H, 6.76; N, 4.19. Berechnet für $C_{23}H_{23}O_2N$: C, 79.96; H, 6.72; N, 4.06%.

Molekulargewichtsbestimmung nach Barger: 350 ± 25 . Ber. Mol.-Gew. 345.

Acetat (IV): Dargestellt durch Behandlung mit Essigsäureanhydrid in Pyridin. Farblose Tafeln vom Schmp. $149-152^\circ$ (aus Methanol). Gefunden: C, 77.31; H, 6.66; N, 3.78. Berechnet für $C_{25}H_{25}O_3N$: C, 77.48; H, 6.51; N, 3.62%.

Benzoat (VIII): Die Verbindung (III) wurde in ca. 23%iger Kalilauge suspendiert und in der Kälte mit 2.5 g. Benzoylchlorid versetzt, dann noch 5 Stdn. umgerührt. Die mit Aether extrahierte ölige Substanz scheidet nach einem Monate Krystalle, die aus verd. Alkohol in farblose Nadeln vom Schmp. $146.5-148^\circ$ bilden. Gefunden: C, 80.26; H, 5.88; N, 3.28. Berechnet für $C_{30}H_{27}O_3N$: C, 80.14; H, 6.06; N, 3.12%.

2-Äthyl-2-benzoyloxy-1,1-diphenyl-1-amino-äthan-schwefelsäuresalz (V). Die Verbindung (III) wurde mit 15%iger Schwefelsäure 2-3 Stdn. bis zur Auflösung erhitzt. Beim Stehenlassen scheiden sich daraus farblose Nadeln, die über 90° schmelzen, aber beim Waschen mit Wasser wird der Schmelzpunkt herabgedrückt.

2-Äthyl-2-benzoyloxy-1,1-diphenyl-1-acetylamino-äthan (VII). Das Schwefelsäuresalz (V) wurde mit Essigsäureanhydrid und Natriumacetat auf dem Wasserbad 3 Stdn. erwärmt. Das acetylierte Produkt wurde aus Ligroin umgelöst und die ausgeschiedene farblose feine Nadeln schmelzen bei $189-190^\circ$. Gefunden: C, 77.40; H, 6.81; N, 3.58. Berechnet für $C_{25}H_{25}O_3N$: C, 77.48; H, 6.51; N, 3.62%.

2-Äthyl-2-benzoyloxy-1,1-diphenyl-1-amino-äthan (VI). Das Schwefelsäuresalz (V) wurde mit 5%iger Natronlauge neutralisiert und die

ausgeschiedene krystallinische Substanz aus Alkohol umgelöst. Tafeln vom Schmp. 130–132°. Der Mischschmelzpunkt mit 2-Aethyl-2-oxy-1, 1-diphenyl-1-benzoylamino-äthan (III) (Schmp. 127–128.5°) liegt bei 109–117°. Gefunden: C, 79.82; H, 6.67; N, 4.47. Berechnet für $C_{23}H_{23}O_2N$: C, 79.96; H, 6.72; N, 4.06%.

Benzoat (VIII): 1 g. der Verbindung (VI) wurde mit 20 c.c. Benzol und 3 g. Benzoylchlorid 12 stundenlang auf dem Wasserbad erwärmt. Das gebildete Benzoat wurde in Aether aufgenommen. Erst nach monatlängem Stehen scheiden sich aus dem Aetherrückstand Krystalle, die aus verd. Alkohol farblose Nadeln vom Schmp. 146.5–148° bilden. Eine Mischprobe mit dem Benzoat aus der Verbindung (III) zeigt keine Erniedrigung. Gefunden: C, 80.10; H, 5.88; N, 3.19. Berechnet für $C_{30}H_{27}O_3N$: C, 80.14; H, 6.06; N, 3.12%.

2-Äthyl-2-benzoyloxy-1,1-diphenyl-äthanol-1 (2-Äthyl-1,1-diphenylglykol-monobenzoat-2) (IX). 10 g. 2-Aethyl-2-benzoyloxy-1, 1-diphenyl-1-amino-äthan-schwefelsäuresalz (V) wurden im Gemisch von 30 c.c. Eisessig und 50 c.c. Wasser unter Eiskühlung mit dem Ueberschuss von kryst. Natriumnitrit versetzt, dann 2 Stdn. weiter umgerührt. Nach dem Behandlung der Reaktionslösung mit Harnstoff wurde die Äthanverbindung in Aether aufgenommen und aus Benzol umkrystallisiert. Seidenartige Nadeln vom Schmp. 149–152.5°. Ausbeute 5 g. Gefunden: C, 79.49; H, 6.39. Berechnet für $C_{23}H_{22}O_3$: C, 79.73; H, 6.41%.

2-Äthyl-2-oxy-1,1-diphenyl-äthanol-1 (2-Äthyl-1,1-diphenylglykol) (X). a) 1 g. der Verbindung (IX) wurde mit alkoholischer Kalilauge, die 2 g. Kaliumhydroxyd in 2 c.c. Wasser und 10 c.c. Alkohol enthält, 4 Stdn. auf dem Wasserbad erwärmt. Das mit Aether extrahierte Verseifungsprodukt krystallisiert aus Benzol-Petroläther in Rosetten der Nadeln vom Schmp. 115–116°. Gefunden: C, 79.32; H, 7.45. Berechnet für $C_{16}H_{18}O_2$: C, 79.29; H, 7.49%.

b) In die Grignardschen Lösung, die aus 31 g. Brombenzol, 5 g. Magnesium und 50 c.c. abs. Aether dargestellt wurde, wurden 5 g. Propionaldehydcyanhydrin zugetropft und unter Umrührung 5 Stdn. auf dem Wasserbad erwärmt. Nach dem Stehenlassen über Nacht wurde die Lösung mit 5%iger Schwefelsäure behandelt. Das mit Aether ausgezogene Substanz (XI) besitzt Sdp.₁₇ 135–138°. Ausbeute 5.1 g. Dieses Öl wurde sofort mit Phenylmagnesiumbromid, das gleich wie oben dargestellt wurde, in Aether zur Grignardschen Reaktion gebracht, wodurch konnten wir farblose Nadeln vom Schmp. 115–116° aus Benzol-Petroläther, die mit obenerwähnten 2-Aethyl-2-oxy-1, 1-diphenyl-äthanol-1, d.h. racem. 2-Äthyl-2-oxy-1, 1-diphenyl-äthanol-1 von Roger⁽⁶⁾ identisch ist. Gefunden: C, 79.11; H, 7.66. Berechnet für $C_{16}H_{18}O_2$: C, 79.29; H, 7.49%.

β -Äthylhydrobenzoin (β -2-Phenyl-1,1-äthylphenylglykol). 10 g. Benzoin wurden portionsweise in die Grignardschen Lösung, die aus 22 g. Äthylbromid, 5 g. Magnesium und 200 c.c. abs. Aether dargestellt wurde, zugetropft und 4 Stdn. auf dem Wasserbad umgerührt. Nach dem

Spalten der Magnesiumverbindung mit 20%igem Ammoniumchlorid wurde das Reaktionsprodukt mit Aether extrahiert und aus Alkohol umgelöst. Seidenartige Nadeln vom Schmp. 116–117°. Ausbeute 10.3 g.

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Studies on the Reactions between Oxides in Solid State at Higher Temperatures. I. The Reaction between Magnesium Oxide and Titanium Oxide.*

By Yasuo TANAKA.

(Received September 16, 1941.)

Introduction. From an early date, reactions in solid state, especially those between certain oxides at relatively high temperatures, have widely been used practically in the ceramic or the silicate industry, in the production of catalysts and pigments as well as in the various branches of chemical industry. Nevertheless, there have been a rather few scientific researches in this branch of chemistry. Although these reactions have recently become the object of a number of investigators, it is still desirable that more experimental results will be accumulated. The author has been studying for several years the addition reactions with the powder mixtures between a group of basic and of acidic oxides in the solid state, and the results will be published in a series of forthcoming papers.

By the reaction in solid state, the product is at first in an amorphous state, from which the new compound crystallizes out easily, when the reaction temperature is sufficiently high. At the lower temperature, the crystal growth is difficult, and this amorphous state is particularly active as a solid catalyst.⁽¹⁾ But the main object of the present series of investigation is not to discuss about this amorphous state. The experiments have been carried on in the temperature range so high that the reaction products may be considered to crystallize out comparatively easily. The present paper deals with the reaction between magnesium oxide and titanium oxide.

The reaction between magnesium oxide and titanium oxide was first studied by Hautefeuille.⁽²⁾ He obtained magnesium ortho- and metatitanate ($2\text{MgO}\cdot\text{TiO}_2$ and $\text{MgO}\cdot\text{TiO}_2$) by fusing titanium oxide to-

* A summarized translation of the papers published in Japanese in *J. Chem. Soc. Japan*, **59** (1938), 1412 (preliminary report); **60** (1939), 212, 314, 949.

(1) Cf., for instance, J. A. Hedvall, "Reaktionsfähigkeit fester Stoffe," 146, Leipzig (1938); G. F. Hüttig, *Z. angew. Chem.* **49** (1936), 882.

(2) P. Hautefeuille, *Ann. chim. phys.*, [4], **4** (1865), 169.

gether with magnesium chloride, and their densities were mentioned as 3.52 and 3.91, respectively. Wartenberg and Prophet⁽³⁾ studied the fusion curve of the system magnesium oxide and titanium oxide and obtained two maxima, corresponding to the melting points of $2\text{MgO}\cdot\text{TiO}_2$ and $\text{MgO}\cdot 2\text{TiO}_2$ (dititanate). Bössem, Schusterius and Ungewiss⁽⁴⁾ studied röntgenographically the reaction products between magnesium oxide and titanium oxide at 1460° and confirmed the existence of the three titanates, $2\text{MgO}\cdot\text{TiO}_2$, $\text{MgO}\cdot\text{TiO}_2$ and $\text{MgO}\cdot 2\text{TiO}_2$. Tammann⁽⁵⁾ reported that the "reaction temperature" between magnesium oxide and titanium oxide in solid state was 725° . Jander⁽⁶⁾ suggested that, in the solid reaction, $2\text{MgO}\cdot\text{TiO}_2$ was formed most easily among the three titanates. However, in studying the effect of titanium oxide on the sintering of magnesite, the present author⁽⁷⁾ found that $\text{MgO}\cdot\text{TiO}_2$ was formed more readily than $2\text{MgO}\cdot\text{TiO}_2$ even in a mixture of $\text{MgO}:\text{TiO}_2=2:1$.

As it is a very interesting problem, which of the compounds is formed at first by a reaction between solid substances where two or more addition compounds can be present,⁽⁶⁾⁽⁸⁾ the present experiment has been commenced mainly to make clear the order of formation of the three titanates in this reaction. In the meanwhile, Jander and Bunde⁽⁹⁾ have studied the solid reaction of this system by the X-ray method and reported that $\text{MgO}\cdot\text{TiO}_2$ was formed at first, whatever the mixing ratio of the two components might be, and that, while $\text{MgO}\cdot 2\text{TiO}_2$ was formed comparatively easily, the formation of $2\text{MgO}\cdot\text{TiO}_2$ was very difficult. As for the fact that $2\text{MgO}\cdot\text{TiO}_2$ is difficult to be formed, the result of the following experiment agrees with that of Jander and Bunde, but as for the order of formation of $\text{MgO}\cdot\text{TiO}_2$ and $\text{MgO}\cdot 2\text{TiO}_2$, the conclusion of the two experiments are different.

Besides, it has been known that many solid reactions can be influenced by water vapour and other gases.⁽¹⁰⁾ Especially, as studied thoroughly by Tamaru and Andô,⁽¹¹⁾ the reaction between calcium oxide and stannic oxide is accelerated remarkably by the traces of reducing gases due to the reduction of stannic oxide. As titanium oxide is comparatively easily reduced into lower oxides,⁽¹²⁾ it is expected that a reducing atmosphere may also have an accelerating effect upon the present reaction, and the author has actually found this effect, qualitatively. However, this problem was not treated in the present research. The experiments were carried out in a current of dry air.

I. Reaction products at 1400° . In order to confirm the kinds of the addition compounds formed by the solid reaction between MgO and

(3) H. v. Wartenberg and E. Prophet, *Z. anorg. allgem. Chem.*, **208** (1932), 369.

(4) W. Bössem, C. Schusterius and A. Ungewiss, *Ber. deut. keram. Ges.*, **18** (1937), 433.

(5) G. Tammann, *Z. anorg. allgem. Chem.*, **149** (1925), 68.

(6) W. Jander, *Z. Angew. Chem.*, **49** (1936), 879.

(7) *J. Soc. Chem. Ind., Japan*, **42** (1939), 387, 202B.

(8) W. Jander, *Z. Angew. Chem.*, **47** (1934), 235.

(9) W. Jander and K. Bunde, *Z. anorg. allgem. Chem.*, **239** (1938), 418.

(10) Cf. J. A. Hedvall, *loc. cit.*, 157, 204, 211 etc.

(11) S. Tamaru and N. Ando, *Z. anorg. allgem. Chem.*, **184** (1929), 385; **195** (1931), 309; *J. Chem. Soc. Japan*, **52** (1931), 36, 107.

(12) N. Nasu, *Science Repts. Tohoku Imp. Univ. Ser. I*, **25** (1936), 510; *J. Chem. Soc. Japan*, **56** (1935), 542, 659.

TiO₂ and to know their properties, uniform mixtures of various proportions of MgO and TiO₂ were pressed into small cylindrical bodies and heated at 1400° for 10 hours in a platinum boat; the densities of the reaction products were measured, they were studied by the X-ray method, and the compositions of them were determined analytically. As the lowest eutectic point of this system has been reported as 1625°⁽¹³⁾, it might be sure that at 1400° the reaction proceeded in solid state without any formation of a liquid phase.

MgO used was the "Shika, extra pure", and TiO₂ was a "Kahlbaum" preparation; both of them were very fine powders. TiO₂ has three modifications, and it has been known that the preparation obtained from a solution is in anatase modification, and on heating, it changes irreversibly to rutile.⁽¹³⁾ Their densities are 3.840 and 4.239, respectively. The density of TiO₂ used here was 3.839, and it changed to 4.163 when heated at 1200° for 5 hours.

As shown in Table 1, the densities of the reaction products are always smaller than those of the mechanical mixtures of the corresponding composition, and as three singular points are found at MgO:TiO₂=2:1, 1:1 and 1:2, it is readily supposed that the three titanates corresponding to the above compositions are formed.

Table 1. Densities and compositions of the reaction products at 1400°. §

No. of sample	Mixing ratio MgO:TiO ₂	Density	Composition (%)				
			MgO	2MgO·TiO ₂	MgO·TiO ₂	MgO·2TiO ₂	TiO ₂
1	—	3.493	100.0				
2	20:1	3.494	82.5	16.1	0.9	0.5	0.0
3	6:1	3.511	50.9	47.2	1.1	0.9	0.0
4	3:1	3.532	21.7	76.5	0.9	1.5	0.0
5	2:1	3.541	3.0	89.0	6.5	1.4	0.0
6	3:2	3.656	2.4	54.3	35.2	8.1	0.0
7	1:1	3.856	1.9	2.0	84.7	11.3	0.0
8	2:3	3.682	1.9	1.6	21.2	77.3	0.0
9	1:2	3.610	2.0	0.2	2.4	85.3	10.1
10	1:5	3.915	1.9	0.4	0.3	34.7	62.7
11	—	4.225					100.0

§ Mixing of the components and calculation of the compositions were carried out under the assumption that the two preparations were completely pure (ignition losses being considered).

This was confirmed by the X-ray method. At the same time, it was proved that in the reaction products TiO₂ was in the rutile modification. It seemed that there existed no appreciable amount of solid solutions between these compounds. The lattice constants of 2MgO·TiO₂, MgO·TiO₂

(13) Cf. J. W. Mellor, "A Comprehensive Treatise on Inorganic and Theoretical Chemistry," Vol. VII, 37, London (1927).

and TiO_2 are shown in Table 2, which are all in good agreement with the data hitherto given. The interference lines of $\text{MgO} \cdot 2\text{TiO}_2$ are given in Table 3; the crystal structure of which is not certain.

Table 2. Lattice constants.

Crystal	Crystal form	Lattice constant	
		observed here	hitherto given
$2\text{MgO} \cdot \text{TiO}_2$	Cubic (Spinel str.)	$a = 8.42\text{\AA}$	$a = 8.41\text{\AA}$; ⁽¹⁴⁾ $8.413\text{\AA}$ ⁽⁴⁾
$\text{MgO} \cdot \text{TiO}_2$	Hexagonal (Rhombohedral)	$a = 5.46\text{\AA}$, $\alpha = 55.0^\circ$	$a = 5.40\text{\AA}$, $\alpha = 55^\circ 1'$ ⁽¹⁵⁾ ; $a = 5.54\text{\AA}$, $\alpha = 54^\circ 39'$ ⁽¹⁶⁾
TiO_2 (Rutile)	Tetragonal	$a = 4.58\text{\AA}$, $c = 2.95\text{\AA}$	$a = 4.58\text{\AA}$, $c/a = 0.66_1$ ⁽¹⁷⁾

Table 3. Interference lines of $\text{MgO} \cdot 2\text{TiO}_2$

Intensity §	$\sin \theta$ §§	Intensity §	$\sin \theta$ §§
w	0.195	vw	0.570
vw	0.248	w	0.582 _s
st	0.276 _s	m	0.628
vw	0.339	w	0.682
st	0.354	vw	0.737
w	0.401	w	0.771 _s
w	0.437	w	0.781
m	0.495	vw	0.876
m	0.519 _s		
w	0.556		

§ Roughly estimated as very strong, strong, medium, weak and very weak.

§§ For K_α and K_β lines of iron.

The determination of the compositions of the reaction products were carried out as follows:—To the finely pulverized sample was added 10 parts of a 20% ammonium chloride solution, and it was warmed on a water-bath for 40 minutes, while stirred constantly. The amount of MgO dissolved was regarded as free magnesium oxide. A 10% ammonium

(14) Tom. F. W. Barth and E. Posnjak, *Z. Krist.*, **82** (1932), 325.

(15) Wm. H. Zachariasen, *Skrifter Norske Videnskaps-Akad. i Oslo*, **1**, (1928), 7; *Chem. Abstracts*, **23** (1929), 1790.

(16) T. Barth and E. Posnjak, *Z. Krist.*, **88** (1934), 265, 271.

(17) Cf. R. Glocker, "Materialprüfung mit Röntgenstrahlen," 2. Aufl., 240, Berlin (1936).

chloride solution, used by Büsser and coworkers,⁽⁴⁾ was proved too dilute. By a similar treatment, it was proved that, $2\text{MgO}\cdot\text{TiO}_2$ was completely soluble in 4 N hydrochloric acid with a trace of $\text{MgO}\cdot\text{TiO}_2$, and that all the $\text{MgO}\cdot\text{TiO}_2$ with a small part of $\text{MgO}\cdot 2\text{TiO}_2$ was dissolved in 12 N hydrochloric acid, while the major part of $\text{MgO}\cdot 2\text{TiO}_2$ and free TiO_2 were insoluble even in concentrated hydrochloric acid. Therefore, by determining the solubility of each sample in these three reagents, it is possible to calculate the amounts of the three titanates formed and of free MgO and TiO_2 . The results are also given in Table 1.

From these experiments it is obvious that three titanates,

Magnesium orthotitanate	$2\text{MgO}\cdot\text{TiO}_2$
Magnesium metatitanate	$\text{MgO}\cdot\text{TiO}_2$,
Magnesium dititanate	$\text{MgO}\cdot 2\text{TiO}_2$,

are formed by the solid reaction between MgO and TiO_2 at 1400° ; the purity of each of the three titanates obtained from the equivalent mixtures is 85–90%.

II. Course of the reaction between 780° and 1200° . The pressed cylinders of the mixtures corresponding to the three titanates, i.e., $\text{MgO}:\text{TiO}_2=1:2$, $1:1$ and $2:1$, and, as a case of excess MgO , a mixture of $\text{MgO}:\text{TiO}_2=6:1$ were heated at 1000° and 1200° , and in some instances at 780° and 900° also, for various durations of time; the course of reaction was followed by determining the compositions of the products analytically,* and the results were checked by the X-ray method.

The mixtures used for the reactions at 1000° and 1200° were heated previously to 600° to remove possible traces of hydroxide and carbonate of magnesium and kept in a desiccator; those used at 780° and 900° were treated at 400° , (because it was proved that at 600° the reaction might somewhat take place). The experiments were carried out in a platinum furnace fitted with a potentiometric temperature regulator. As already mentioned, a constant current of air, carefully dried with phosphorus pentoxide, was passed through the reaction tube during the experiments.

The compositions of the reaction products are given in Tables 4–7, and in some instances, they are graphically plotted in Figures 1–3. (In acid treatment, the solubilities of $\text{MgO}\cdot\text{TiO}_2$ and $\text{MgO}\cdot 2\text{TiO}_2$ in 4 N and

Table 4. Course of the reaction, $\text{MgO}:\text{TiO}_2 = 1:2$.

Reaction temperature	Time (hrs.)	Composition of the products (%)			
		MgO	$\text{MgO}\cdot\text{TiO}_2$	$\text{MgO}\cdot 2\text{TiO}_2$	TiO_2
780°	0.5	15.1	4.8	16.8	63.2
	1	14.0	6.9	18.8	60.2
	3	12.0	11.6	20.8	55.6
	6	10.9	11.6	26.3	51.2
900°	0.5	7.8	13.7	38.2	40.3
	1	6.8	14.6	41.7	36.9
	3	4.7	15.8	50.6	29.0
	6	4.0	11.9	60.0	24.0

* There are only two or three instances of solid reaction whose courses have been studied analytically.

Table 4.—(Concluded)

Reaction temperature	Time (hrs.)	Composition of the products (%)			
		MgO	MgO·TiO ₂	MgO·2TiO ₂	TiO ₂
1000°	0.5	5.4	4.8	65.5	24.3
	1	4.3	5.3	69.9	20.6
	3	3.3	9.2	68.0	19.4
	6	3.3	7.8	70.4	18.5
1200°	0.5	3.7	0.3	80.9	15.1
	1	3.4	0.6	82.3	13.7
	3	3.1	0.6	83.5	12.8
	6	2.9	0.5	84.9	11.7
	12	2.4	0.6	87.1	10.0

Table 5. Course of the reaction, MgO:TiO₂ = 1:1.

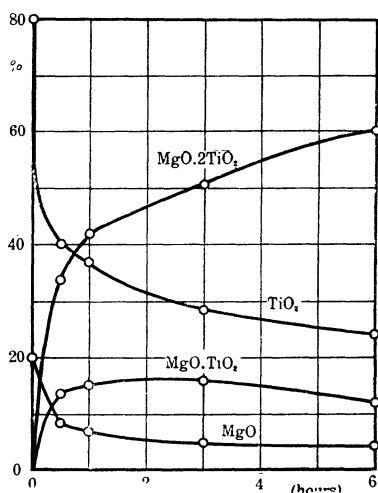
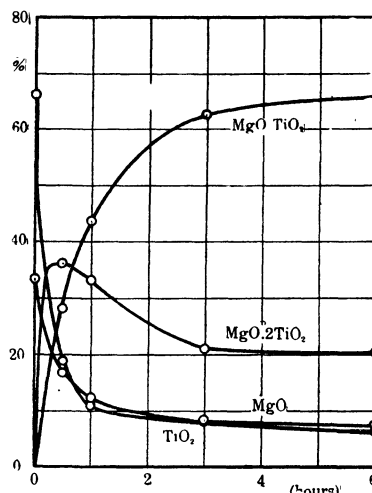
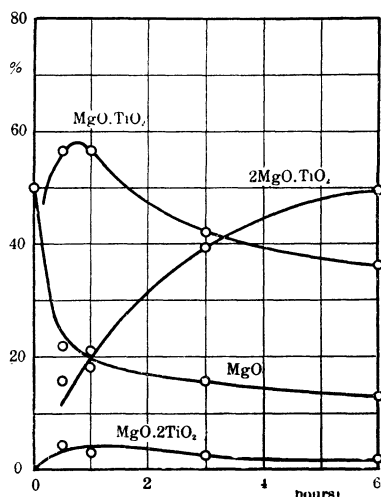
Reaction temperature	Time (hrs.)	Composition of the products (%)			
		MgO	MgO·TiO ₂	MgO·2TiO ₂	TiO ₂
780°	0.5	26.3	11.6	16.4	45.6
	1	25.3	13.7	18.4	42.6
	3	21.8	25.0	16.4	36.8
	6	19.3	33.1	15.4	32.2
900°	0.5	16.7	28.3	36.2	18.8
	1	12.2	43.5	33.3	11.0
	3	8.3	62.6	20.8	8.3
	6	7.4	65.8	20.3	6.6
1000°	0.5	10.4	36.5	53.2	0.0
	1	8.3	49.8	41.9	0.0
	3	4.8	71.1	24.1	0.0
	6	3.7	78.1	18.3	0.0
1200°	0.5	3.6	78.7	17.2	0.5
	1	3.7	80.2	14.3	1.8
	3	3.1	81.4	15.2	0.3
	6	2.8	83.5	13.8	0.0
	12	2.6	84.1	13.1	0.0

Table 6. Course of the reaction, MgO:TiO₂ = 2:1.

Reaction temperature	Time (hrs.)	Composition of the products (%)				
		MgO	2MgO·TiO ₂	MgO·TiO ₂	MgO·2TiO ₂	TiO ₂
1000°	0.5	28.5	0.0	54.3	17.5	0.0
	1	27.5	0.0	61.1	11.4	0.0
	3	27.1	0.0	62.7	10.2	0.0
	6	26.0	4.0	60.5	9.5	0.0
1200°	0.5	22.1	15.9	57.2	4.4	0.4
	1	21.3	18.2	57.3	3.0	0.2
	3	15.7	39.4	42.3	2.6	0.0
	6	12.8	49.7	36.1	1.4	0.0
	12	11.6	54.7	32.2	1.5	0.0

Table 7. Course of the reaction, $\text{MgO}:\text{TiO}_2 = 6:1$.

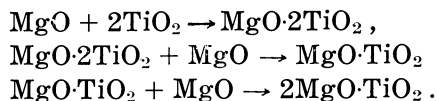
Reaction temperature	Time (hrs.)	Composition of the products (%)				
		MgO	$2\text{MgO}\cdot\text{TiO}_2$	$\text{MgO}\cdot\text{TiO}_2$	$\text{MgO}\cdot 2\text{TiO}_2$	TiO_2
1000°	0.5	63.8	0.0	30.4	5.8	0.0
	1	63.1	0.0	35.0	2.0	0.0
	3	63.1	0.0	34.9	2.0	0.0
	6	62.4	2.0	34.6	1.0	0.0
1200°	0.5	51.4	45.8	1.8	1.0	0.0
	1	50.9	46.7	2.4	0.0	0.0
	3	51.1	46.1	2.4	0.4	0.0
	6	50.6	47.9	1.5	0.0	0.0
	12	50.4	48.7	0.9	0.0	0.0

Fig. 1. Course of the reaction, $\text{MgO}:\text{TiO}_2 = 1:2$ at 900°.Fig. 2. Course of the reaction, $\text{MgO}:\text{TiO}_2 = 1:1$ at 900°.Fig. 3. Course of the reaction, $\text{MgO}:\text{TiO}_2 = 2:1$ at 1200°.

12 N HCl, respectively, were proved to increase with the decreasing reaction temperature. This might be attributed to the incompleteness of the crystal growth of the two titanates, i.e., to the existence of the amorphous reaction product, but the existence of the solid solutions might also be suspected.) With a mixture, $\text{MgO}:\text{TiO}_2=1:2$, it is obvious that the main reaction product is always $\text{MgO}\cdot 2\text{TiO}_2$; and it can be interpreted that some $\text{MgO}\cdot 2\text{TiO}_2$ accompanied is formed locally where MgO exists in excess, because the mixing of the components could never be completely homogeneous. In the case of $\text{MgO}:\text{TiO}_2=1:1$, while at the early stage

of the reaction there exists more $\text{MgO} \cdot 2\text{TiO}_2$ than $\text{MgO} \cdot \text{TiO}_2$, the ratio of the two titanates is reversed as the reaction proceeds, and finally $\text{MgO} \cdot \text{TiO}_2$ becomes the main reaction product. So it may easily be recognized that the initial reaction product in this case is also $\text{MgO} \cdot 2\text{TiO}_2$, and $\text{MgO} \cdot \text{TiO}_2$ is formed by the further reaction between $\text{MgO} \cdot 2\text{TiO}_2$ thus obtained and the excess MgO . $2\text{MgO} \cdot \text{TiO}_2$ is never found in this mixture. This compound is very difficult to be formed, and in a stoichiometric mixture it is formed at 1200° at length, but the reaction is hardly completed at this temperature. With the mixtures of a large excess of MgO , e.g., $\text{MgO}:\text{TiO}_2=6:1$, the formation is easily completed at 1200° . The results of the röntgenographic studies agree with these results.

From these results it could be concluded that, by the reaction between MgO and TiO_2 in solid state, the first reaction product is $\text{MgO} \cdot 2\text{TiO}_2$, whatever the mixing ratio of the two components might be; when an excess of MgO is present, $\text{MgO} \cdot \text{TiO}_2$ is formed gradually; and while $2\text{MgO} \cdot \text{TiO}_2$ is formed similarly, the velocity of its formation is very slow in the temperature range observed here. The reaction consists of the following three consecutive reactions:



III. Influence of the experimental conditions on the course of reaction. The conclusion about the order of the formations of $\text{MgO} \cdot \text{TiO}_2$ and $\text{MgO} \cdot 2\text{TiO}_2$ differs, as previously stated, in the above experiment and in the experiment of Jander and Bunde.⁽⁹⁾ As this may be due to the difference in some of the experimental conditions, the experiments were repeated under various conditions.

(1) *The reaction in loose powder form with TiO_2 in rutile modification:*— In the experiment of Jander Bunde, TiO_2 was heated to 800° before use, and they stated that the preparation thus obtained was in rutile modification*, and the reaction was carried out with powder mix-

Table 8. Reaction in powder form with rutile.

Mixture	Reaction temperature	Time (hrs.)	Composition of the products (%)			
			MgO	$\text{MgO} \cdot \text{TiO}_2$	$\text{MgO} \cdot 2\text{TiO}_2$	TiO_2
$\text{MgO}:\text{TiO}_2$ = 1:2	1000°	0.5	15.7	0.0	21.8	62.5
		3	12.0	1.5	37.7	48.8
	1200°	1	5.1	0.0	74.4	20.4
$\text{MgO}:\text{TiO}_2$ = 1:1	1000°	0.5	30.2	0.0	16.4	53.4
		3	28.5	0.9	23.3	47.2
	1200°	1	15.8	10.4	70.6	3.1

* Although 915° , given by A. Schröder [*Z. Krist.*, **66** (1928), 493], may be regarded as the most probable transition temperature of anatase into rutile, under certain conditions rutile seems to be obtained already at as low as 800° .

tures in loose form. To compare with their experiment, the reaction experiment in loose powder form was made at 1000° and 1200° by using the TiO_2 preparation previously heated to 1200° , i.e., rutile. MgO , too, was used after the same heat treatment. The results are given in Table 8, which lead to a conclusion, more distinctly than the results in the last paragraph; that $\text{MgO} \cdot 2\text{TiO}_2$ is the first reaction product. It goes without saying that the whole reaction proceeds slowly.

(2) *The reaction in loose powder form with anatase:*— The experiment in loose powder form with TiO_2 preparation used in the last paragraph, i.e., anatase, was also made. As shown in Table 9, although the reaction proceeds slowly, the course of the reaction is quite identical as before.

Table 9. Reaction in powder form with anatase, 1000° .

Mixture	Reaction time (hrs.)	Composition of the products (%)			
		MgO	MgO·TiO ₂	MgO·2TiO ₂	TiO ₂
MgO : TiO ₂ = 1 : 2	0.5	7.2	11.9	44.6	36.4
	3	4.4	8.6	63.9	23.2
MgO : TiO ₂ = 1 : 1	0.5	13.5	19.4	67.1	0.0
	3	8.3	50.7	41.0	0.0

(3) *Influence of water vapour:*— It has been already cited that, in some instances, the influence of water vapour on the solid reaction is remarkable.⁽¹⁰⁾ Although in the present experiment, this influence is always excluded carefully, Jander and Bunde touched nothing on this problem. Therefore, by way of precaution, an experiment to confirm this influence was carried out. A constant current of air was passed through a water reservoir at 98° and then into the reaction vessel; other experimental conditions were the same as in paragraph II. The results

Table 10. Influence of water vapour, 1000° .

Mixture	Reaction time (hrs.)	Composition of the products (%)			
		MgO	MgO·TiO ₂	MgO·2TiO ₂	TiO ₂
MgO : TiO ₂ = 1 : 2	0.5	5.6	6.4	61.5	26.5
	3	3.0	8.7	70.4	17.9
MgO : TiO ₂ = 1 : 1	0.5	8.2	50.7	41.1	0.0
	3	4.7	71.1	24.2	0.0

are given in Table 10; and it shows that, although the reaction seems to be slightly accelerated by the presence of water vapour, the course of the reaction in this case is also unchanged.

As seen from these experiments, the reaction proceeds, under various experimental conditions, in the same manner, and $\text{MgO} \cdot \text{TiO}_2$ could never

be regarded as the first reaction product. Therefore, it can be concluded that, in general cases or—if it is permitted to use the word “normal experimental condition” as Jander⁽¹⁸⁾ has previously used—under normal conditions, the course of the solid reaction between MgO and TiO₂ is as above mentioned, and even if MgO·TiO₂ happens to be formed at first, it must be under special conditions.

IV. The reaction MgO·TiO₂+TiO₂ and MgO·2TiO₂+MgO. The reactions between MgO·TiO₂ and TiO₂, and MgO·2TiO₂ and MgO at 900° were studied further. The results of the experiments together with the purities of the two titanates used are shown in Tables 11 and 12.

Table 11. The reaction MgO·TiO₂+TiO₂ at 900°.

Reaction time (hrs.)	Composition (%)			
	MgO	MgO·TiO ₂	MgO·2TiO ₂	TiO ₂
(sample)	2.9	81.8	15.3	0.0
0	1.7	48.9	9.1	40.3
1	1.8	28.6	43.1	26.5
3	1.6	14.7	67.4	16.4
6	1.7	13.7	68.9	15.8

Table 12. The reaction MgO·2TiO₂+MgO at 900°.

Reaction time (hrs.)	Composition (%)			
	MgO	MgO·TiO ₂	MgO·2TiO ₂	TiO ₂
(sample)	2.1	0.3	88.8	8.8
0	18.5	0.2	74.0	7.3
1	14.7	17.0	64.9	3.4
3	12.4	27.1	59.5	1.0
6	12.2	28.3	58.5	1.0

The reaction between MgO·TiO₂ and TiO₂ to form MgO·2TiO₂ proceeds more easily than the formation of MgO·TiO₂ from MgO·2TiO₂ and MgO. From these facts, too, it is readily anticipated that MgO·2TiO₂ is the first reaction product by the solid reaction between MgO and TiO₂.

V. Mechanism of the reaction. In order that a reaction takes place actually between solid substances, it is necessary first of all that a part of the atoms (or atom groups) of the components is in a deviated position from the normal crystal lattice, i.e., in a state of disorder.⁽¹⁹⁾

(18) W. Jander and E. Hoffmann, *Z. anorg. allgem. Chem.*, **218** (1934), 211.

(19) Cf. W. Jost, “Diffusion und chemische Reaktion in festen Stoffen,” 39, Dresden and Leipzig (1937).

Then, at the contact surface of the two components, these atoms may exchange with each other, forming an amorphous layer of the mixture of them, and from which a new reaction product crystallizes out easily so long as the reaction temperature is high enough.^{(1) (6)}

When a crystalline film of the reaction product is formed, further reaction is only possible by the diffusion of the two components through this film. Which of the components diffuses chiefly, depends on the nature of the reaction. By the reaction of silicate formation, it is believed that the basic oxide, e.g. MgO, diffuses^{(6) (18)}; by the spinel formation, Hild⁽²⁰⁾ has regarded that the basic oxide diffuses, while others⁽²¹⁾ have considered *vice versa*. Wagner⁽²²⁾ has suggested that in ion crystals the smaller cation diffuses generally, and this supposition was proved for the reaction: $2\text{AgI} + \text{HgI} = \text{Ag}_2\text{HgI}_4$ ⁽²³⁾, where equivalent quantities of Ag^+ and Hg^{++} ions are exchanged in Ag_2HgI_4 phase, and Ag_2HgI_4 is formed newly at the two boundaries, $\text{AgI}/\text{Ag}_2\text{HgI}_4$ and $\text{Ag}_2\text{HgI}_4/\text{HgI}_2$. He has presented analogous interpretation for the formation of spinels and silicates.⁽²²⁾

From these points of view, it may be admitted for the mechanism of the present reaction that, at the contact surface of magnesium oxide and titanium oxide, an amorphous layer of these mixtures is formed at first, the amount of which is not so much, within the temperature range observed here, from which the stable reaction product (in this case $\text{MgO} \cdot 2\text{TiO}_2$) crystallizes out easily; and further reaction proceeds by the diffusion of the two components—probably in the form of Mg^{++} and Ti^{+++} ions—through this phase. Further discussions about the amorphous layer at the early stage of the reaction and the diffusion component are abridged here.*

As repeatedly stated, the first reaction product in this reaction is always $\text{MgO} \cdot 2\text{TiO}_2$. About the problem which compound is formed at first by a reaction between solid substances in which many addition compounds can be formed, the relation is very complicated. For the formation of silicates, Jander^{(6) (18)} has considered that the relative difficulty of the formation depends chiefly on the crystal structure of the addition compounds, namely, as the crystal structure of orthosilicates with tetrahedral SiO_4 -group may be regarded as simple compared with the structure of metasilicates with long fibrous structure as $-\text{Si-O-Si}-$, the former crystallizes more readily from the amorphous layer and is formed at first. Contrary to Jander, Wagner⁽²²⁾ has considered that, as the diffusion in orthosilicates is easier than in metasilicates, even if both silicates are formed equally at the beginning of the reaction, metasilicate layer does not build up, and only the amount of orthosilicates increases; the relation is just as in the oxidation of metals where many oxide layers can be formed. At any rate, as it may be understood, the relative difficulty of

(20) K. Hild, *Z. physik. Chem.*, A, **161** (1936), 317.

(21) W. Jander and W. Stamm, *Z. anorg. allgem. Chem.*, **199** (1931), 165; G. Hüttig and E. Zeidler, *Kolloid-Z.*, **75** (1936), 170.

(22) C. Wagner, *Z. physik. Chem.*, B, **34** (1936), 309.

(23) E. Koch and C. Wagner, *ibid.*, **34** (1936), 317.

* Recently, W. Jander and G. Leuthner have studied about the amorphous reaction product between MgO and TiO_2 . [*Z. anorg. allgem. Chem.*, **241** (1939), 57.]

diffusion in crystals also depends upon their crystal structures—for instance, the diffusion in orthosilicates with simple constitution is easier than in metasilicates with complicated fibrous structure—, crystals of simple structure can be found from either argument at the early stage of the reaction.

In the present case, although the crystal structure of $\text{MgO} \cdot 2\text{TiO}_2$ is not certain, when it is permitted to assume that the crystal structure of $\text{MgO} \cdot 2\text{TiO}_2$ is more simple than that of $\text{MgO} \cdot \text{TiO}_2$ and of $2\text{MgO} \cdot \text{TiO}_2$, it may be considered that $\text{MgO} \cdot 2\text{TiO}_2$ crystallizes out most easily from the amorphous layer, and, even if other compounds are formed at the same time, they do not build up. Thus it is well interpreted that $\text{MgO} \cdot 2\text{TiO}_2$ is the first reaction product. As the reaction proceeds and the thickness of $\text{MgO} \cdot 2\text{TiO}_2$ layer increases, the diffusion in this layer becomes gradually difficult, and $\text{MgO} \cdot \text{TiO}_2$ begins to be formed at the contact surface of $\text{MgO} \cdot 2\text{TiO}_2$ and MgO . $2\text{MgO} \cdot \text{TiO}_2$ is formed also in the same way, but with great difficulty.

By the solid reaction, if the diffusion process takes place slowly enough compared with the surface reaction, which is just so in most cases, the rate of the whole reaction is controlled only by the diffusion,⁽²⁴⁾ and there exists an approximate relation between the thickness of the reaction product (ξ) and the reaction time (t):⁽²⁵⁾

$$d\xi/dt = k'/\xi \quad \text{or} \quad \xi^2 = 2k't + C'.$$

By the reaction with powder mixtures, it is impossible to determine directly the thickness of the layer of the product, and it is the amount of the product formed, or of the components reacted (x) which can be measured; therefore, in order to apply the above relation to this case, the relation between them should be known. Jander⁽²⁶⁾ has derived the following relation, by assuming that the reaction proceeds uniformly on a spherical substance with a radius of r :

$$1 - \sqrt[3]{1-x} = \xi/r, *$$

and so

$$\{1 - \sqrt[3]{1-x}\}^2 = 2kt + C.$$

Although this relation holds strictly for a substance in a small amount, through which another substance in large excess diffuses, it can also be applied approximately, at least in the early stage of the reaction, to a mixture of any mixing ratio, and it has been proved for the reactions between barium carbonate and silica, etc.^{(26) (6)}

It was tried to apply the relation to the result of the present experiment, and the relation between $\{1 - \sqrt[3]{1-x}\}^2$ and the reaction time was plotted for the mixture corresponding to the first reaction product,

(24) Cf. W. Jost, *loc. cit.*, 180.

(25) H. Braune, *Z. physik. Chem.*, **110** (1924), 147.

(26) W. Jander, *Z. anorg. allgem. Chem.*, **163** (1927), 1.

* x is expressed as the fraction of the original amount of the component.

i.e., $\text{MgO}:\text{TiO}_2=1:2$, in paragraph II. As the measured points fall on a straight line so long as the reaction temperature is not so high and the reaction proceeds not so far, it is recognized that the main part of the reaction is controlled by diffusion, but the line does not fall on the origin, showing that there exists a notable rapid initial reaction. It is natural that the above relation does not hold when the reaction proceeds too far.

For the rapid initial reaction, the following considerations may be given at present: as the reaction is exothermic,** at the beginning of the reaction, the true reaction temperature becomes inevitably higher than the furnace temperature, and, as the experiment has been carried out with pressed bodies of the mixtures of very fine powders, the surface reaction proceeds to a considerable amount. A similar initial reaction has been reported by Ward and Struthers⁽²⁷⁾ in the reaction between barium carbonate and ferric oxide.

The values of k for the diffusion process of $\text{MgO}\cdot 2\text{TiO}_2$ formation can be roughly represented in terms of

$$k = A e^{-Q/RT},$$

or

$$k = 3.9 \times 10^4 e^{-36,000/RT},$$

where Q may be regarded as the energy of activation in calories per mole of the diffusion.

As shown in Table 13, the value of Q is the same order as those which have been known in other solid reactions, and is also similar to those of the comparatively well studied diffusion processes between metals.⁽³¹⁾

Table 13. Energies of activation of the solid reactions.

Reaction	Mixing ratio	Product	Q (Kcal./mole)
$\text{BaCO}_3 + \text{SiO}_2$	1 : 10	Ba_2SiO_4 ?	50.2 ⁽²⁶⁾ , 40.7 ⁽²⁶⁾
"	1 : 1	"	42.6 ⁽²⁹⁾
$\text{CaO} + \text{SiO}_2$	1 : 1	Ca_2SiO_4	32.2 ⁽²⁹⁾
$\text{BaCO}_3 + \text{Fe}_2\text{O}_3$	1 : 1	$\text{BaO}\cdot\text{Fe}_2\text{O}_3$	25.0 (< 820°), 19.0 (> 820°) ⁽²⁷⁾
$\text{BaCO}_3 + \text{WO}_3$	1 : 10	BaWO_4	43.6 ⁽³⁰⁾
"	1 : 1	"	35.6 ⁽²⁹⁾
$\text{MgO} + \text{TiO}_2$	1 : 2	$\text{MgO}\cdot 2\text{TiO}_2$	36.0

** When a reaction between solid substances takes place smoothly, it must be an exothermic one.

(27) R. Ward and J. D. Struthers, *J. Am. Chem. Soc.*, **59** (1937), 1849.

(28) W. Jander and E. Hoffman, *Z. anorg. allgem. Chem.*, **200** (1931), 245.

(29) W. Jander and W. Stamm, *ibid.*, **190** (1930), 65.

(30) W. Jander, *ibid.*, **166** (1927), 31.

(31) Cf. W. Jost, *loc. cit.*, 131.

Summary.

(1) It has been confirmed that three titanates, i.e., magnesium orthotitanate ($2\text{MgO}\cdot\text{TiO}_2$), metatitanate ($\text{MgO}\cdot\text{TiO}_2$) and dititanate ($\text{MgO}\cdot 2\text{TiO}_2$), are formed by the solid reaction between MgO and TiO_2 ; $2\text{MgO}\cdot\text{TiO}_2$ is soluble in 4 N HCl and $\text{MgO}\cdot\text{TiO}_2$ in 12 N HCl, while $\text{MgO}\cdot 2\text{TiO}_2$ is scarcely soluble even in 12 N HCl.

(2) By following the course of the reaction analytically, it has been found that the first reaction product is $\text{MgO}\cdot 2\text{TiO}_2$, whatever the mixing ratio of the two components may be; $\text{MgO}\cdot\text{TiO}_2$ is formed gradually when an excess of MgO is present; and $2\text{MgO}\cdot\text{TiO}_2$ is formed similarly, but with difficulty.

(3) The reaction has been proved to proceed, under various experimental conditions, in the same manner, and $\text{MgO}\cdot\text{TiO}_2$ can never be regarded as the first reaction product.

(4) The reaction between $\text{MgO}\cdot\text{TiO}_2$ and TiO_2 to form $\text{MgO}\cdot 2\text{TiO}_2$ has taken place more easily than the formation of $\text{MgO}\cdot\text{TiO}_2$ from $\text{MgO}\cdot 2\text{TiO}_2$ and MgO .

(5) It has been concluded that, although there exists a notable rapid initial reaction, a further reaction is controlled by the diffusion of the two components through the reaction product. The energy of activation of the diffusion process of $\text{MgO}\cdot 2\text{TiO}_2$ formation has been estimated to be 36.0 Kilocalories per mole.

The author wishes to express his sincere thanks to Dr. R. Yoshimura, Director of the Department, for his generous help, and further to Prof. Y. Shibata of the Tokyo Imperial University for his kind advices and constant encouragement. X-ray photographs in this experiment were taken by the Physics Section of this Laboratory, to which author's thanks are also due.

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A Simple Procedure for Decolourisation of Organic Compounds.

By Koshiro ISHIMURA.

(Received May 14, 1941.)

In the course of the investigation on the molecular rearrangement of disubstituted acetaldehydes into the corresponding ketones, the author has prepared a number of aromatic compounds, namely, diaryl ketones, alkyl aryl ketones, their oximes and semicarbazones and benzoyl derivatives of diaryl ethylene glycols and of alkyl aryl ethylene glycols. They have usually been purified by recrystallisation from dilute alcohol, but in every case faintly yellowish or brownish colour could not be removed from the substances by the usual methods, such as changing the solvents, adding animal charcoal or dissolving them in hot alcohol and adding hot water to the solution till it becomes faintly turbid and subsequently leaving it to cool down.⁽¹⁾ In such cases the purification was accomplished with unexpected good results in the following way:—the substance to be purified is dissolved in hot alcohol, into which a large quantity of hot water is poured at a time. An almost colourless flocky precipitate is obtained. It is filtered and recrystallised from dilute alcohol once more in the usual way and thus a completely colourless substance with a well defined crystalline form is easily obtained.

The colouring matters may be some polymerisation or condensation products, possibly with large molecular weights, formed by the side reactions when the above-mentioned substances are synthesised. They are soluble in hot alcohol but not in cold alcohol and water. When hot water is poured into the hot alcoholic solution they may very probably be peptized, forming colloidal solutions, whereas the substances to be purified are precipitated, which are likewise insoluble in water but with much smaller molecular weights and existing in relatively large amount, and thus difficult to form colloidal solutions.

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(1) H. Meyer, "Analyse und Konstitutionsermittlung Organischer Verbindungen", 26, 1931.

Some Methods of Analysis of Commercial Methanol.

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(Received May 14, 1941.)

More than ten years ago, when the industry of synthetic methanol did not yet develop in this country, two samples of methanol were offered to the author for analysis from a certain factory of a small pilot-plant scale. The samples were produced while the investigations into the optimum conditions for manufacture were still busily going on, therefore they naturally contained a considerable quantity of various impurities.

Preliminary Examinations. The two samples were designated A and B respectively. They were colourless and their densities were d_4^{20} , 0.8084 and d_4^{20} , 0.7964 respectively.

On distillation, the fractions were obtained from 500 g. of each sample as reproduced in Tables 1 and 2.

Table 1.

Sample A.

Fraction	B. p. (°C.)	Yield		d_4^{20}
		g.	%	
1	Below 65	20.0	4.0	0.7737
2	65 — 67	160.0	32.0	0.7933
3	67 — 70	253.7	50.6	0.8050
4	Above 70	65.0	13.1	—

Table 2.

Sample B.

Fraction	B. p. (°C.)	Yield	
		g.	%
1	Below 63	11.2	2.2
2	63 — 65	101.6	20.3
3	65 — 67	322.7	64.5
4	67 — 70	49.1	9.8
5	Above 70	11.4	2.3

The residue, boiling above 70°C., separated into two layers in each case. The upper layer was light yellow oil (0.44 g. in the case of A),

while the lower one was light mobile liquid. 2.8 g. of the former oil and 79.8 g. of the latter liquid, both collected from several runs, were distilled, giving the fractions shown in Tables 3 and 4 respectively.

Table 3.

Fraction	B. p. (°C.)	Temperature of bath (°C.)	Yield (g.)	d_4^{20}
1	Below 102	250	0.1	0.8202
2	Residue	—	2.5	—

Table 4.

Fraction	B. p. (°C.)	Yield (g.)	d_4^{20}
1	70—75	40.0	0.8218
2	75—80	18.4	0.8429
3	80—92	8.8	0.8773
4	92—107	9.0	0.9794
5	107—117	3.6	0.9982
6	Residue	0.1	—

The residue in Table 3 was fractionated under reduced pressure of 38 mm. as shown in Table 5.

Table 5.

Fraction	B. p. (38 mm.) (°C.)	Yield (g.)	d_4^{20}	M. p. (°C.)
1	130—150	0.5	0.7908	2—6
2	150—160	0.5	0.7825	9—11
3	160—170	0.2	0.7803 d_4^{25}	13—16
4	170—180	0.5	0.7867 (d_4^{25})	19—22.5
		0.2	—	30—32.5
5	Residue	0.4	—	—

The fraction 4 in Table 5 was separated into two parts, i.e., one solidified at the ordinary temperature and the other did not solidify.

When the sample A was stocked in the cold place, a small quantity of colourless scales separated out and was proved to be *n*-docosane. It was recrystallised from methyl alcohol and melted at 44–45°C. Found: C, 85.70; H, 15.07. Calculated for $C_{22}H_{46}$: C, 85.62; H, 14.38%. It is very probable that the fraction 4 in Table 5 contains a considerable quantity of *n*-docosane.

Qualitative Analyses. *Higher Alcohols.* The colour reactions with salicyl aldehyde and sulphuric acid and with vanilline and sulphuric acid showed evidently the presence of higher alcohols in the samples, and the boiling points of the fractions in Table 4 suggest that alcohols higher than amyl alcohols may be present, if any, only in very small amounts. The fractions boiling above 70°C. in Tables 1 and 2 gave the colour reaction with vanilline and sulphuric acid, characteristic of propyl or amyl alcohols, when they were carried out according to the informations given by T. Higashi⁽¹⁾. Henville's test⁽²⁾ for isopropyl alcohol gave a positive result. The existence of ethyl alcohol could not be confirmed.

Aldehydes and Ketones. The samples did not reduce Fehling's solution. But the presence of aldehyde was confirmed by the colour reaction with fuchsin-sulphurous acid and by the formation of a silver mirror as well as of the insoluble compound with resorcin. Formaldehyde was confirmed to exist in the sample by two colour reactions, one with morphine hydrochloride and the other with phenylhydrazine hydrochloride, ferric chloride and concentrated hydrochloric acid. No ketone was found to exist.

Acids and Esters. The samples were neutral to litmus, but acidic to phenolphthaleine.

When the sample was subjected to hydrolysis with a sodium hydroxide solution for one hour on a water bath and then concentrated sulphuric acid was added to it, a gas was found to evolve. It was washed with alkali and passed into a solution of ammoniacal silver nitrate. A brown precipitate was thrown down indicating the evolution of carbon monoxide (Habermann's test⁽³⁾) and consequently the existence of formic acid or formic ester in the original sample.

Quantitative Analyses. *Methyl Alcohol.* A large number of methods for the estimation of methyl alcohol have been published; by counting only the principles underlying the methods ten or so will be pointed out, and moreover each method has been followed by its modifications. König's method⁽⁴⁾ has been modified by the present author and has been found to be the most suitable for the analysis of the commercial methanol. The principle of this method lies in the fact that methyl alcohol is completely oxidised to carbon dioxide and water by chromic acid mixture under the suitable condition, while the oxidation of the homologous alcohols remains incomplete, only aldehydes or acids being thereby produced.

The estimation of the evolved carbon dioxide will give the amount of methanol. The apparatus used in the present work is shown diagrammatically in Figure 1.

The determination proceeds as follows:— The air free from carbon dioxide is passed into the reaction flask to expel carbon dioxide present in it. The oxidising mixture (15 g. $K_2Cr_2O_7$, 25 c.c. conc. H_2SO_4 , 230 c.c. H_2O) is boiled for 15 minutes, cooled and rapidly poured into the flask,

(1) *Bull. Inst. Phys. Chem. Research* (Tokyo), **7** (1928), 527.

(2) *Analyst*, **53** (1928), 416.

(3) *Z. angew. Chem.*, **5** (1892), 324; F. C. Phillips, *Am. Chem. J.*, **16** (1894), 272.

(4) *Chem. Ztg.*, **36** (1912), 1025.

and then 10 c.c. of the sample are introduced, and meanwhile the air is gently passed in. The sample is prepared by diluting 10 c.c. of the original sample methanol to 100 c.c. The passing of the air is stopped and the mixture is left to stand for 30 minutes. Then it is boiled gently. Carbon dioxide thereby produced is washed with concentrated sulphuric acid, dried with calcium chloride (alkali-free) and absorbed by weighed soda lime. The ends of the two U-tubes containing soda lime are filled with a small quantity of calcium chloride in order to catch water which is to be produced by the reaction between soda lime and carbon dioxide. The boiling is continued for 1 hour and the air is passed for one hour and a half to expel the evolved carbon dioxide completely. The increase in the weight of U-tubes gives the amount of carbon dioxide, from which the amount of methyl alcohol can easily be calculated out. 3.5–4 hours are required for one run of the analysis.

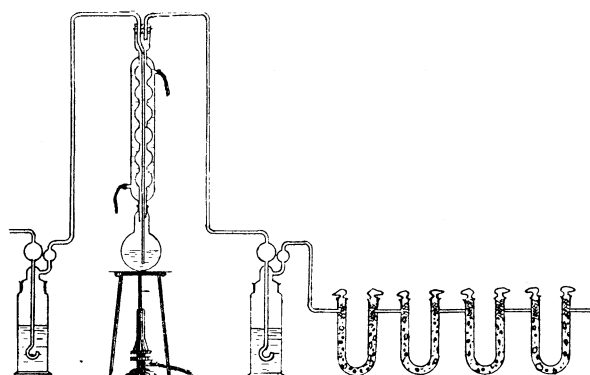


Fig. 1.

It has been found that the following corrections are necessary in the calculation.

(1) A correction for errors due to impurities contained in potassium bichromate, which must be determined by a blank test.

(2) Since some compounds other than methyl alcohol, e.g., formic acid, methyl formate or formaldehyde are also oxidised to carbon dioxide a correction is required.

The content of methyl alcohol was also determined by Zeisel's method of the determination of methoxyl group. The results, given by the two methods, were found to accord very well with each other as shown in Table 6.

Table 6.

Sample	Methyl alcohol (%)	
	By oxidation method	By Zeisel's method
A	89.63, 89.69	89.72
B	94.29	94.43

Acids and Esters. To determine the contents of acids the sample was diluted with equal volume of water and titrated with a 1/10 N sodium hydroxide solution with phenolphthaleine as indicator. It was treated with excess alkali on a water bath for 1 hour and then back-titrated with 1/10 N sulphuric acid in order to estimate the content of esters. Assuming that only formic acid and methyl formate were present, the values shown in Table 7 were obtained.

Table 7.

Sample	Formic acid (%)	Methyl formate (%)
A	0.009	0.13
B	0.08	0.25

Formaldehyde. According to B. H. Smith⁽⁵⁾, who has studied comparatively on various methods of the determination of formaldehyde, the method based on the complex formation with potassium cyanide is the most suitable, when formaldehyde is present in a mixture of several substances as in the case of the present experiment.

50 c.c. of the sample were brought into reaction with 20 c.c. of a 1/10 N silver nitrate solution in a 200 c.c. measuring flask, into which 5 drops of concentrated nitric acid were added. The reaction mixture was diluted with water just to 200 c.c., well shaken and filtered through a dry filter

Table 8.

Sample	Formaldehyde (%)
A	0.0021
B	0.0046

paper. 100 c.c. of the filtrate were titrated with a 1/10 N ammonium thiocyanate solution with iron alum as indicator. The required amount of formaldehyde (in g.) was given by twice the difference between the titres of the sample and a blank test, multiplied by a factor 0.0030016. The results are shown in Table 8.

Water. E. R. Weaver⁽⁶⁾ detected the presence of water in various organic solvents by allowing calcium carbide to react with water and by observing the red colour developed on the formation of copper acetylenide. He suggested that by this method it may be detected also in acetone. It has been found, however, by the present author that this is not the case. Hydroxylamine which is used to reduce cupric salt to cuprous salt, reacts with acetone to produce oxime which in its turn reacts with copper acetylenide and thus the red colour disappears. Ketones and aldehydes generally disturb the test; the presence of formaldehyde, benzaldehyde, acetophenone, menthone and furfurol has been found to be the disturbing factor. Besides the oxime-forming substances, acids dissolve copper acetylenide. E. R. Weaver⁽⁷⁾ afterwards

(5) *J. Am. Chem. Soc.*, **25** (1903), 1030.

(6) *J. Am. Chem. Soc.*, **36** (1914), 2462.

(7) *J. Am. Chem. Soc.*, **38** (1916), 352.

succeeded in applying the test to the colorimetric analysis of acetylene but not of water in organic solvents. Although H. Hartley and H. R. Raikes⁽⁸⁾ determined water contained in methyl alcohol by this method, no description of the experimental details was given.

According to the present author's experiment the formation of copper acetylenide does not seem to take place quantitatively. The amount of the precipitate of copper acetylenide was determined by R. Willstätter's method⁽⁹⁾ and it has been shown that only about 50% of water present in the sample can be detected. But it has been found, that water may be determined quantitatively as well by the colorimetry, if the taken standard solution contains the amount of water not so different from that in the sample.

Following the informations given by E. R. Weaver,⁽⁶⁾ grains of calcium carbide, about 3 mm. in diameter, were stocked in absolute alcohol. They were taken out immediately before the experiment and heated with 5 c.c. of absolute alcohol to dryness in order to expel the trace of the occluded acetylene. The sample and the standard methyl alcohol (5 c.c. each) were taken separately in two Erlenmeyer's flasks and two or three grains of the calcium carbide were added to each of them. The flasks were cooled with ice water for 30 minutes, meanwhile the acetylene remained dissolved in methyl alcohol. Cuprous chloride solution was prepared according to Hartley and Raikes' prescription:⁽⁸⁾ 1 c.c. each of the following two solutions were mixed immediately before use:—

A. 3 g. of cupric chloride and 6 g. of ammonium chloride dissolved in dilute ammonia (9 c.c. of ammonia, d, 0.88, diluted with 100 c.c. of water).

B. 12 g. of hydroxylamine hydrochloride dissolved in 100 c.c. of water.

The mixing was carried out in a glass tube, about 15 mm. in diameter and about 25 cm. in length, graduated to 0.1 c.c., and a few c.c. of 2% water solution of gum arabic were added to the mixture. Calcium carbide was separated from the sample and the standard solutions by rapid filtration on dry filter papers. According to the content of water, 0.3–1.0 c.c. of the filtrate were added to the cuprous solution. The red colour of the colloidal copper acetylenide developed immediately. Gum arabic served to keep the colloidal solution stable. The colours developed by the sample and the standard solutions were compared with each other

by a colorimeter and thus the water content can be calculated. As the standard methyl alcohol Merk's specimen "acetone free, extra pure" was used. The results are shown in Table 9.

Table 9.

Sample	Water content (%)
A	4.1
B	1.3

The reliability of the method above described is shown by the experimental results given in Table 10.

(8) *J. Chem. Soc.*, **127** (1925), 524.

(9) *Ber.*, **3** (1920), 939.

Table 10.

Water content in ethyl alcohol (vol. %)		Water content of the standards taken in colorimetry (vol. %)
By density determination	By colorimetry	
0.26	0.27	0.67
0.69	0.62	0.26
0.47	0.47	0.26
0.47	0.43	0.69
1.67	1.73	0.69
1.87	1.85	1.67

Higher Alcohols. Out of a number of methods for analysis of higher alcohols, two have been selected and investigated, i.e., Allen-Marquardt's method⁽¹⁰⁾ and that based on Komarowsky's colour reaction.⁽¹¹⁾

(1) Allen-Marquardt's method. This method consists in extracting higher alcohols with chloroform or carbon tetrachloride and subsequently oxidising to carboxylic acids which are then titrated after being distilled in steam. There are two difficulties in this method. Firstly propyl and butyl alcohols are not extracted quantitatively, and secondly the amount of inorganic acids to be distilled together with the carboxylic acids cannot be accurately known. In the present case the first difficulty need not be taken into account as extractions is unnecessary. The second difficulty can be avoided by carrying out a blank test.

25 g. of potassium bichromate dissolved in 100 c.c. of water were introduced into a 300 c.c. round flask and 2 c.c. of the sample was added to the solution. The flask was connected with a condenser with a ground joint. 30 c.c. of concentrated sulphuric acid was added drop by drop from the top of the condenser, and the reaction mixture was heated for 8 hours on a water bath. Carboxylic acids produced by the oxidation were then subjected to steam distillation. Inorganic acids, distilled out thereby, were determined by a blank test as stated above. When the progress of the distillation was adjusted so as to give 1 litre of distillate for 4 hours, the distillate in the blank test consumed 2.64 c.c. of a 1/10 N sodium hydroxide solution.

Preliminary tests, carried out with known amounts of butyl and amyl alcohol dissolved in methyl alcohol, gave satisfactory results as shown in Table 11.

(10) Allen and Chattaway, *Analyst*, **16** (1891), 102; Ph. Schidrowitch, *J. Soc. Chem. Ind.*, **21** (1902), 814; *Analyst*, **31** (1906), 181; *J. Am. Chem. Soc.*, **29** (1907), 561; E. A. Mann, *J. Soc. Chem. Ind.*, **25** (1906), 1125; W. L. Dudley, *J. Am. Chem. Soc.*, **30** (1908), 1271; Adams, *J. Assoc. Official Agr. Chem.*, **1** (1915), 143.

(11) Komarowsky, *Chem. Ztg.*, **27** (1903), 807; Th. von Fellenberg, *Mitt. Lebensm. Hyg.*, **1** (1910), 791; W. Müller, *ibid.*, **14** (1923), 105.

Table 11.

	Present in 2 c.c. of methyl alcohol (g.)	Found (g.)
Butyl alcohol (b.p., 104–110°)	0.07276	0.07408 0.07345 0.07104
Amyl alcohol (b.p., 128–131°)	0.08102	0.07911 0.08073

The results of the analysis of the methanol samples carried out under the same condition are shown in Table 12.

Table 12.

Sample	Higher alcohols (%) (calculated as butyl alcohol)
A	0.62, 0.57
B	1.20, 1.08

(2) *Colorimetric method.* Purple red colour is developed when higher alcohols are brought into contact with salicyl aldehyde. The colour reaction is known as Komarowsky's reaction. When applied to the quantitative analysis, it also has two disadvantages. First the depth of the colour depends upon the kind of alcohols and consequently the generally adoptable standard cannot be prepared, and secondly a linear relation does not always hold between the depth of the colour and the concentration of the alcohols and therefore the reaction can not be applied except when the concentrations of alcohols in samples and the standards are not greatly different. These disadvantages, however, can be turned into advantages, if they are appropriately treated. Thus it has been found by the present author that not only the total quantity of butyl and amyl alcohols but also the ratio between them can be determined at a time.

Standard solutions were prepared with the following reagents:—

(1) Butyl alcohol, b.p., 100–106°C.; d_4^{20} , 0.8084. Amyl alcohol, b.p., 125–131°C.; d_4^{20} , 0.8137. The two alcohols were Merk's "extra pure" quality, of which 0.0330 g. each was dissolved in 100 c.c. each of pure methyl alcohol (d_4^{20} , 0.7918).

(2) Salicyl aldehyde was synthesised by Reimer-Tiemann's method. It boiled at 196°C. It was confirmed to be pure enough for the purpose by Kreis' method⁽¹²⁾. 0.6767 g. of the aldehyde was dissolved in 100 c.c. of pure methyl alcohol.

The sample methanols were treated with silver oxide on the water

(12) *Chem. Ztg.*, **32** (1908), 149.

bath for 3 hours to remove any aldehyde completely according to Fellenberg's informations⁽¹³⁾, as the presence of aldehyde would interfere with the reaction.

The procedure of the analysis is as follows:— 1–4 c.c. of the sample solution is taken in a small glass cylinder, about 50 c.c. in volume, to which 1 c.c. of the salicyl aldehyde solution is added. If the total volume is less than 5 c.c., it is made just to 5 c.c. by adding pure methyl alcohol. Then 5 c.c. of distilled water is added, shaken, cooled with water and 20 c.c. of concentrated sulphuric acid is added drop by drop. Care must be taken not to allow the temperature of the mixture to rise unduly high. It is well shaken and left to stand for 20 hours. The red purple colour developed thereby is compared with that of the standard solution which has been similarly treated.

It has been found that not only the amount of higher alcohols but also that of salicyl aldehyde influences the depth of the colour as shown in Figure 2.

Now, the relation between the concentration of butyl or amyl alcohol (x , the unit of which is chosen arbitrarily as follows:— 0.0330 g. of the alcohol dissolved in 1 c.c. methyl alcohol) and height of the liquid column (y , expressed in mm., which should give the same depth of the colour as that of 5 mm. of the standard solution of the unit concentration) has been found to be capable of being expressed by the following equation:—

$$(5-y)^2 = p(x-1) \dots\dots\dots (1)$$

which represents parabola, p a parameter, being a constant depending upon the kind of alcohol.

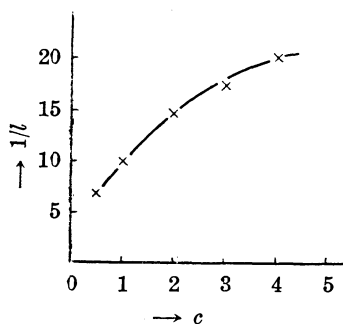


Fig. 2.

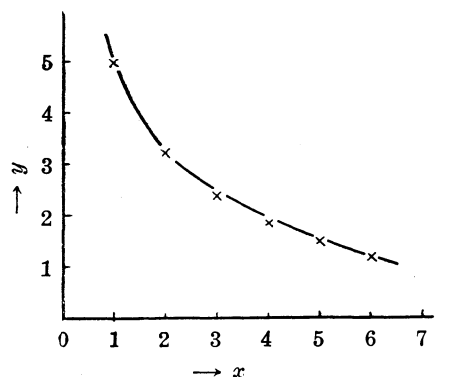


Fig. 3.

l : Height of liquid column,
 c : Concentration of salicyl aldehyde; 0.006767 g. of the aldehyde dissolved in 1 c.c. of methyl alcohol is taken arbitrarily as unit.
 Amount of butyl alcohol: 0.0660 g. dissolved in 1 c.c. of methyl alcohol, that is, $x = 2$.

In the case of butyl alcohol, p is 3.15 and the theoretical curve and the found values are shown in Figure 3.

(13) *Loc. cit.*

Similarly in the case of amyl alcohol 1.75 has been found as the value of the parameter and Figure 4 was obtained.

Next, the equal amount of the two alcohols were mixed and the mixed solution was examined similarly. The value of the parameter, in this case, must be the mean of the two values given to the two alcohols. The theoretical curve and the found values are shown in Figure 5.

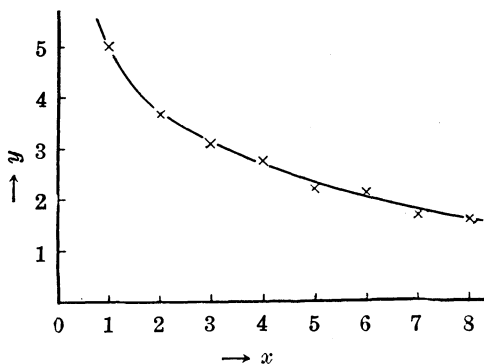


Fig. 4.

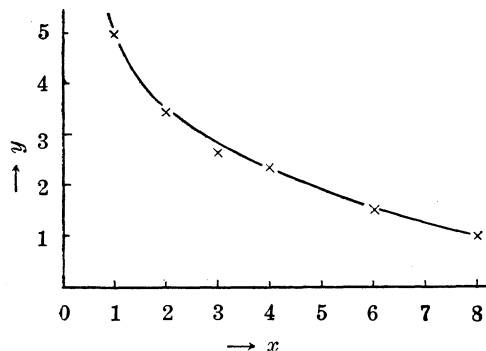


Fig. 5.

Thus the ratio of the amounts of the two alcohols and the corresponding value of the parameter can easily be calculated as shown in Table 13.

Table 13.

Butyl alc./Amyl alc. (g.)	10/0	9/1	8/2	7/3	6/4	5/5	4/6	3/7	2/8	1/9	0/10
p	3.15	2.99	2.84	2.69	2.54	2.40	2.26	2.13	2.00	1.87	1.75

The depth of the colour to be developed by the same concentration of butyl and amyl alcohols differs considerably. At the unit concentration the ratio of the depths was found to be 5.00/3.53. The ratio at any concentration will be obtained by a simple calculation by adopting this value and by applying it to equation 1. In Table 14 are shown the values of the ratio thus calculated together with the found values.

Table 14.

Concentration (x)		1	2	3	4
Ratio of depth of colour	Calculated	—	5.00/3.09	5.00/2.81	5.00/2.52
	Found	5.00/3.53	5.00/2.97	5.00/2.79	5.00/2.60

It is clear from the above consideration that the analysis of one of the two alcohols above mentioned, when it is present alone in methanol, may be carried out simply and accurately. When, however, both the alcohols co-exist, several standard solutions must be prepared and several curves must be described from the mixtures of the two alcohols in

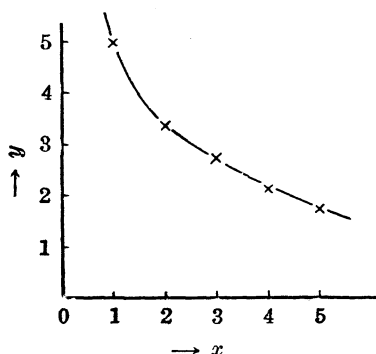


Fig. 6.

arbitrary proportions and it must be examined which of these curves accords with that of the sample. In the present case the state is more complicated. It is not known whether there are higher alcohols other than the above mentioned two or not. Even if only the two alcohols are present, our standards may not be used at once, as they are not prepared from pure substances but from mixtures of isomers.

A mixed standard was prepared from 7 parts of the butyl alcohol and 3 parts of the amyl alcohol, which gave the curve shown in Figure 6.

If the sample methanols contain only butyl and amyl alcohols which are identical with and in equal ratios to those of the mixed standard, the results of the colorimetry with the samples can be put in accordance with the curve given in Figure 6 by adopting the suitable concentrations of the samples to be analysed.

It has been found, in carrying out the experiment as stated above, that the samples actually contain the two alcohols in the proportion of 7:3. The values thus obtained are denoted by crossed marks in Figure 6. The total quantity of the two alcohols can easily be estimated, for the mixture can be thus treated as a single substance. The results are compared with those obtained by the oxidation method as shown in Table 15.

Table 15.

Sample	Higher alcohols (%)	
	By oxidation	By colorimetry
A	0.62, 0.57	0.53
B	1.20, 1.08	1.34

The results of the total analysis of the two sample methanols are summarised as shown in Table 16.

Table 16.

Sample	A (%)	B (%)	Sample	A (%)	B (%)
Methyl alcohol	89.68	94.34	Formic acid	0.009	0.08
Butyl alcohols	0.40	0.87	Methyl formate	0.13	0.25
Amyl alcohols	0.17	0.31	Formaldehyde	0.0021	0.0046
Water	4.1	1.3	Total	94.49	97.21

The rest may be considered as hydrocarbons, being calculated as 5.51 and 2.79% in A and B respectively.

The author's thanks are due to Dr. H. Inoue for his kind advice.

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Some Methods of Analysis of Commercial Methanol.

By Koshiro ISHIMURA.

(Received May 14, 1941.)

More than ten years ago, when the industry of synthetic methanol did not yet develop in this country, two samples of methanol were offered to the author for analysis from a certain factory of a small pilot-plant scale. The samples were produced while the investigations into the optimum conditions for manufacture were still busily going on, therefore they naturally contained a considerable quantity of various impurities.

Preliminary Examinations. The two samples were designated A and B respectively. They were colourless and their densities were d_4^{20} , 0.8084 and d_4^{20} , 0.7964 respectively.

On distillation, the fractions were obtained from 500 g. of each sample as reproduced in Tables 1 and 2.

Table 1.

Sample A.

Fraction	B. p. (°C.)	Yield		d_4^{20}
		g.	%	
1	Below 65	20.0	4.0	0.7737
2	65 — 67	160.0	32.0	0.7933
3	67 — 70	253.7	50.6	0.8050
4	Above 70	65.0	13.1	—

Table 2.

Sample B.

Fraction	B. p. (°C.)	Yield	
		g.	%
1	Below 63	11.2	2.2
2	63 — 65	101.6	20.3
3	65 — 67	322.7	64.5
4	67 — 70	49.1	9.8
5	Above 70	11.4	2.3

The residue, boiling above 70°C., separated into two layers in each case. The upper layer was light yellow oil (0.44 g. in the case of A),

while the lower one was light mobile liquid. 2.8 g. of the former oil and 79.8 g. of the latter liquid, both collected from several runs, were distilled, giving the fractions shown in Tables 3 and 4 respectively.

Table 3.

Fraction	B. p. (°C.)	Temperature of bath (°C.)	Yield (g.)	d_4^{20}
1	Below 102	250	0.1	0.8202
2	Residue	—	2.5	—

Table 4.

Fraction	B. p. (°C.)	Yield (g.)	d_4^{20}
1	70—75	40.0	0.8218
2	75—80	18.4	0.8429
3	80—92	8.8	0.8773
4	92—107	9.0	0.9794
5	107—117	3.6	0.9982
6	Residue	0.1	—

The residue in Table 3 was fractionated under reduced pressure of 38 mm. as shown in Table 5.

Table 5.

Fraction	B. p. (38 mm.) (°C.)	Yield (g.)	d_4^{20}	M. p. (°C.)
1	130—150	0.5	0.7908	2—6
2	150—160	0.5	0.7825	9—11
3	160—170	0.2	0.7803 d_4^{25}	13—16
4	170—180	0.5	0.7867 (d_4^{25})	19—22.5
		0.2	—	30—32.5
5	Residue	0.4	—	—

The fraction 4 in Table 5 was separated into two parts, i.e., one solidified at the ordinary temperature and the other did not solidify.

When the sample A was stocked in the cold place, a small quantity of colourless scales separated out and was proved to be *n*-docosane. It was recrystallised from methyl alcohol and melted at 44–45°C. Found: C, 85.70; H, 15.07. Calculated for $C_{22}H_{46}$: C, 85.62; H, 14.38%. It is very probable that the fraction 4 in Table 5 contains a considerable quantity of *n*-docosane.

Qualitative Analyses. *Higher Alcohols.* The colour reactions with salicyl aldehyde and sulphuric acid and with vanilline and sulphuric acid showed evidently the presence of higher alcohols in the samples, and the boiling points of the fractions in Table 4 suggest that alcohols higher than amyl alcohols may be present, if any, only in very small amounts. The fractions boiling above 70°C. in Tables 1 and 2 gave the colour reaction with vanilline and sulphuric acid, characteristic of propyl or amyl alcohols, when they were carried out according to the informations given by T. Higashi⁽¹⁾. Henville's test⁽²⁾ for isopropyl alcohol gave a positive result. The existence of ethyl alcohol could not be confirmed.

Aldehydes and Ketones. The samples did not reduce Fehling's solution. But the presence of aldehyde was confirmed by the colour reaction with fuchsine-sulphurous acid and by the formation of a silver mirror as well as of the insoluble compound with resorcline. Formaldehyde was confirmed to exist in the sample by two colour reactions, one with morphine hydrochloride and the other with phenylhydrazine hydrochloride, ferric chloride and concentrated hydrochloric acid. No ketone was found to exist.

Acids and Esters. The samples were neutral to litmus, but acidic to phenolphthaleine.

When the sample was subjected to hydrolysis with a sodium hydroxide solution for one hour on a water bath and then concentrated sulphuric acid was added to it, a gas was found to evolve. It was washed with alkali and passed into a solution of ammoniacal silver nitrate. A brown precipitate was thrown down indicating the evolution of carbon monoxide (Habermann's test⁽³⁾) and consequently the existence of formic acid or formic ester in the original sample.

Quantitative Analyses. *Methyl Alcohol.* A large number of methods for the estimation of methyl alcohol have been published; by counting only the principles underlying the methods ten or so will be pointed out, and moreover each method has been followed by its modifications. König's method⁽⁴⁾ has been modified by the present author and has been found to be the most suitable for the analysis of the commercial methanol. The principle of this method lies in the fact that methyl alcohol is completely oxidised to carbon dioxide and water by chromic acid mixture under the suitable condition, while the oxidation of the homologous alcohols remains incomplete, only aldehydes or acids being thereby produced.

The estimation of the evolved carbon dioxide will give the amount of methanol. The apparatus used in the present work is shown diagrammatically in Figure 1.

The determination proceeds as follows:— The air free from carbon dioxide is passed into the reaction flask to expel carbon dioxide present in it. The oxidising mixture (15 g. $K_2Cr_2O_7$, 25 c.c. conc. H_2SO_4 , 230 c.c. H_2O) is boiled for 15 minutes, cooled and rapidly poured into the flask,

(1) *Bull. Inst. Phys. Chem. Research* (Tokyo), **7** (1928), 527.

(2) *Analyst*, **53** (1928), 416.

(3) *Z. angew. Chem.*, **5** (1892), 324; F. C. Phillips, *Am. Chem. J.*, **16** (1894), 272.

(4) *Chem. Ztg.*, **36** (1912), 1025.

and then 10 c.c. of the sample are introduced, and meanwhile the air is gently passed in. The sample is prepared by diluting 10 c.c. of the original sample methanol to 100 c.c. The passing of the air is stopped and the mixture is left to stand for 30 minutes. Then it is boiled gently. Carbon dioxide thereby produced is washed with concentrated sulphuric acid, dried with calcium chloride (alkali-free) and absorbed by weighed soda lime. The ends of the two U-tubes containing soda lime are filled with a small quantity of calcium chloride in order to catch water which is to be produced by the reaction between soda lime and carbon dioxide. The boiling is continued for 1 hour and the air is passed for one hour and a half to expel the evolved carbon dioxide completely. The increase in the weight of U-tubes gives the amount of carbon dioxide, from which the amount of methyl alcohol can easily be calculated out. 3.5–4 hours are required for one run of the analysis.

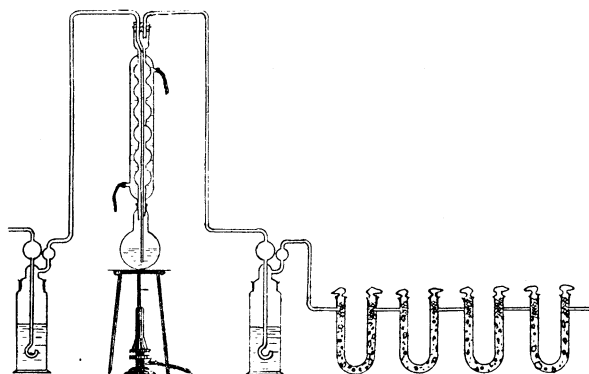


Fig. 1.

It has been found that the following corrections are necessary in the calculation.

(1) A correction for errors due to impurities contained in potassium bichromate, which must be determined by a blank test.

(2) Since some compounds other than methyl alcohol, e.g., formic acid, methyl formate or formaldehyde are also oxidised to carbon dioxide a correction is required.

The content of methyl alcohol was also determined by Zeisel's method of the determination of methoxyl group. The results, given by the two methods, were found to accord very well with each other as shown in Table 6.

Table 6.

Sample	Methyl alcohol (%)	
	By oxidation method	By Zeisel's method
A	89.63, 89.69	89.72
B	94.29	94.43

Acids and Esters. To determine the contents of acids the sample was diluted with equal volume of water and titrated with a 1/10 N sodium hydroxide solution with phenolphthaleine as indicator. It was treated with excess alkali on a water bath for 1 hour and then back-titrated with 1/10 N sulphuric acid in order to estimate the content of esters. Assuming that only formic acid and methyl formate were present, the values shown in Table 7 were obtained.

Table 7.

Sample	Formic acid (%)	Methyl formate (%)
A	0.009	0.13
B	0.08	0.25

Formaldehyde. According to B. H. Smith⁽⁵⁾, who has studied comparatively on various methods of the determination of formaldehyde, the method based on the complex formation with potassium cyanide is the most suitable, when formaldehyde is present in a mixture of several substances as in the case of the present experiment.

50 c.c. of the sample were brought into reaction with 20 c.c. of a 1/10 N silver nitrate solution in a 200 c.c. measuring flask, into which 5 drops of concentrated nitric acid were added. The reaction mixture was diluted with water just to 200 c.c. well shaken and filtered through a dry filter

Table 8.

Sample	Formaldehyde (%)
A	0.0021
B	0.0046

paper. 100 c.c. of the filtrate were titrated with a 1/10 N ammonium thiocyanate solution with iron alum as indicator. The required amount of formaldehyde (in g.) was given by twice the difference between the titres of the sample and a blank test, multiplied by a factor 0.0030016. The results are shown in Table 8.

Water. E. R. Weaver⁽⁶⁾ detected the presence of water in various organic solvents by allowing calcium carbide to react with water and by observing the red colour developed on the formation of copper acetylenide. He suggested that by this method it may be detected also in acetone. It has been found, however, by the present author that this is not the case. Hydroxylamine which is used to reduce cupric salt to cuprous salt, reacts with acetone to produce oxime which in its turn reacts with copper acetylenide and thus the red colour disappears. Ketones and aldehydes generally disturb the test; the presence of formaldehyde, benzaldehyde, acetophenone, menthone and furfural has been found to be the disturbing factor. Besides the oxime-forming substances, acids dissolve copper acetylenide. E. R. Weaver⁽⁷⁾ afterwards

(5) *J. Am. Chem. Soc.*, **25** (1903), 1030.

(6) *J. Am. Chem. Soc.*, **36** (1914), 2462.

(7) *J. Am. Chem. Soc.*, **38** (1916), 352.

succeeded in applying the test to the colorimetric analysis of acetylene but not of water in organic solvents. Although H. Hartley and H. R. Raikes⁽⁸⁾ determined water contained in methyl alcohol by this method, no description of the experimental details was given.

According to the present author's experiment the formation of copper acetylenide does not seem to take place quantitatively. The amount of the precipitate of copper acetylenide was determined by R. Willstätter's method⁽⁹⁾ and it has been shown that only about 50% of water present in the sample can be detected. But it has been found, that water may be determined quantitatively as well by the colorimetry, if the taken standard solution contains the amount of water not so different from that in the sample.

Following the informations given by E. R. Weaver,⁽⁶⁾ grains of calcium carbide, about 3 mm. in diameter, were stocked in absolute alcohol. They were taken out immediately before the experiment and heated with 5 c.c. of absolute alcohol to dryness in order to expel the trace of the occluded acetylene. The sample and the standard methyl alcohol (5 c.c. each) were taken separately in two Erlenmeyer's flasks and two or three grains of the calcium carbide were added to each of them. The flasks were cooled with ice water for 30 minutes, meanwhile the acetylene remained dissolved in methyl alcohol. Cuprous chloride solution was prepared according to Hartley and Raikes' prescription:⁽⁸⁾ 1 c.c. each of the following two solutions were mixed immediately before use:—

A. 3 g. of cupric chloride and 6 g. of ammonium chloride dissolved in dilute ammonia (9 c.c. of ammonia, d, 0.88, diluted with 100 c.c. of water).

B. 12 g. of hydroxylamine hydrochloride dissolved in 100 c.c. of water.

The mixing was carried out in a glass tube, about 15 mm. in diameter and about 25 cm. in length, graduated to 0.1 c.c., and a few c.c. of 2% water solution of gum arabic were added to the mixture. Calcium carbide was separated from the sample and the standard solutions by rapid filtration on dry filter papers. According to the content of water, 0.3–1.0 c.c. of the filtrate were added to the cuprous solution. The red colour of the colloidal copper acetylenide developed immediately. Gum arabic served to keep the colloidal solution stable. The colours developed by the sample and the standard solutions were compared with each other

by a colorimeter and thus the water content can be calculated. As the standard methyl alcohol Merk's specimen "acetone free, extra pure" was used. The results are shown in Table 9.

Table 9.

Sample	Water content (%)
A	4.1
B	1.3

The reliability of the method above described is shown by the experimental results given in Table 10.

(8) *J. Chem. Soc.*, **127** (1925), 524.

(9) *Ber.*, **3** (1920), 939.

Table 10.

Water content in ethyl alcohol (vol. %)		Water content of the standards taken in colorimetry (vol. %)
By density determination	By colorimetry	
0.26	0.27	0.67
0.69	0.62	0.26
0.47	0.47	0.26
0.47	0.43	0.69
1.67	1.73	0.69
1.87	1.85	1.67

Higher Alcohols. Out of a number of methods for analysis of higher alcohols, two have been selected and investigated, i.e., Allen-Marquardt's method⁽¹⁰⁾ and that based on Komarowsky's colour reaction.⁽¹¹⁾

(1) Allen-Marquardt's method. This method consists in extracting higher alcohols with chloroform or carbon tetrachloride and subsequently oxidising to carboxylic acids which are then titrated after being distilled in steam. There are two difficulties in this method. Firstly propyl and butyl alcohols are not extracted quantitatively, and secondly the amount of inorganic acids to be distilled together with the carboxylic acids cannot be accurately known. In the present case the first difficulty need not be taken into account as extractions is unnecessary. The second difficulty can be avoided by carrying out a blank test.

25 g. of potassium bichromate dissolved in 100 c.c. of water were introduced into a 300 c.c. round flask and 2 c.c. of the sample was added to the solution. The flask was connected with a condenser with a ground joint. 30 c.c. of concentrated sulphuric acid was added drop by drop from the top of the condenser, and the reaction mixture was heated for 8 hours on a water bath. Carboxylic acids produced by the oxidation were then subjected to steam distillation. Inorganic acids, distilled out thereby, were determined by a blank test as stated above. When the progress of the distillation was adjusted so as to give 1 litre of distillate for 4 hours, the distillate in the blank test consumed 2.64 c.c. of a 1/10 N sodium hydroxide solution.

Preliminary tests, carried out with known amounts of butyl and amyl alcohol dissolved in methyl alcohol, gave satisfactory results as shown in Table 11.

(10) Allen and Chattaway, *Analyst*, **16** (1891), 102; Ph. Schidrowitch, *J. Soc. Chem. Ind.*, **21** (1902), 814; *Analyst*, **31** (1906), 181; *J. Am. Chem. Soc.*, **29** (1907), 561; E. A. Mann, *J. Soc. Chem. Ind.*, **25** (1906), 1125; W. L. Dudley, *J. Am. Chem. Soc.*, **30** (1908), 1271; Adams, *J. Assoc. Official Agr. Chem.*, **1** (1915), 143.

(11) Komarowsky, *Chem. Ztg.*, **27** (1903), 807; Th. von Fellenberg, *Mitt. Lebensm. Hyg.*, **1** (1910), 791; W. Müller, *ibid.*, **14** (1923), 105.

Table 11.

	Present in 2 c.c. of methyl alcohol (g.)	Found (g.)
Butyl alcohol (b.p., 104–110°)	0.07276	0.07408 0.07345 0.07104
Amyl alcohol (b.p., 128–131°)	0.08102	0.07911 0.08073

The results of the analysis of the methanol samples carried out under the same condition are shown in Table 12.

Table 12.

Sample	Higher alcohols (%) (calculated as butyl alcohol)
A	0.62, 0.57
B	1.20, 1.08

(2) *Colorimetric method.* Purple red colour is developed when higher alcohols are brought into contact with salicyl aldehyde. The colour reaction is known as Komarowsky's reaction. When applied to the quantitative analysis, it also has two disadvantages. First the depth of the colour depends upon the kind of alcohols and consequently the generally adoptable standard cannot be prepared, and secondly a linear relation does not always hold between the depth of the colour and the concentration of the alcohols and therefore the reaction can not be applied except when the concentrations of alcohols in samples and the standards are not greatly different. These disadvantages, however, can be turned into advantages, if they are appropriately treated. Thus it has been found by the present author that not only the total quantity of butyl and amyl alcohols but also the ratio between them can be determined at a time.

Standard solutions were prepared with the following reagents:—

(1) Butyl alcohol, b.p., 100–106°C.; d_4^{20} , 0.8084. Amyl alcohol, b.p., 125–131°C.; d_4^{20} , 0.8137. The two alcohols were Merk's "extra pure" quality, of which 0.0330 g. each was dissolved in 100 c.c. each of pure methyl alcohol (d_4^{20} , 0.7918).

(2) Salicyl aldehyde was synthesised by Reimer-Tiemann's method. It boiled at 196°C. It was confirmed to be pure enough for the purpose by Kreis' method⁽¹²⁾. 0.6767 g. of the aldehyde was dissolved in 100 c.c. of pure methyl alcohol.

The sample methanols were treated with silver oxide on the water

(12) *Chem. Ztg.*, **32** (1908), 149.

bath for 3 hours to remove any aldehyde completely according to Fellenberg's informations⁽¹³⁾, as the presence of aldehyde would interfere with the reaction.

The procedure of the analysis is as follows:— 1–4 c.c. of the sample solution is taken in a small glass cylinder, about 50 c.c. in volume, to which 1 c.c. of the salicyl aldehyde solution is added. If the total volume is less than 5 c.c., it is made just to 5 c.c. by adding pure methyl alcohol. Then 5 c.c. of distilled water is added, shaken, cooled with water and 20 c.c. of concentrated sulphuric acid is added drop by drop. Care must be taken not to allow the temperature of the mixture to rise unduly high. It is well shaken and left to stand for 20 hours. The red purple colour developed thereby is compared with that of the standard solution which has been similarly treated.

It has been found that not only the amount of higher alcohols but also that of salicyl aldehyde influences the depth of the colour as shown in Figure 2.

Now, the relation between the concentration of butyl or amyl alcohol (x , the unit of which is chosen arbitrarily as follows:— 0.0330 g. of the alcohol dissolved in 1 c.c. methyl alcohol) and height of the liquid column (y , expressed in mm., which should give the same depth of the colour as that of 5 mm. of the standard solution of the unit concentration) has been found to be capable of being expressed by the following equation:—

$$(5-y)^2 = p(x-1) \dots\dots\dots (1)$$

which represents parabola, p a parameter, being a constant depending upon the kind of alcohol.

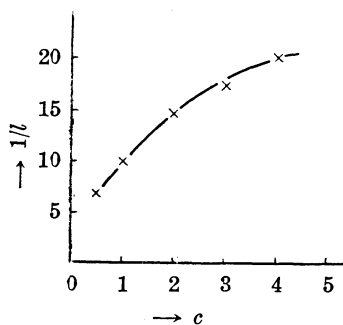


Fig. 2.

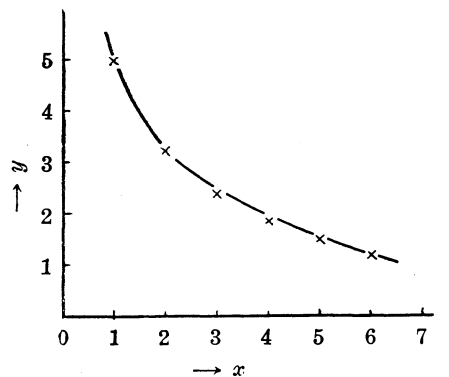


Fig. 3.

l : Height of liquid column,
 c : Concentration of salicyl aldehyde; 0.006767 g. of the aldehyde dissolved in 1 c.c. of methyl alcohol is taken arbitrarily as unit.
 Amount of butyl alcohol: 0.0660 g. dissolved in 1 c.c. of methyl alcohol, that is, $x = 2$.

In the case of butyl alcohol, p is 3.15 and the theoretical curve and the found values are shown in Figure 3.

(13) *Loc. cit.*

Similarly in the case of amyl alcohol 1.75 has been found as the value of the parameter and Figure 4 was obtained.

Next, the equal amount of the two alcohols were mixed and the mixed solution was examined similarly. The value of the parameter, in this case, must be the mean of the two values given to the two alcohols. The theoretical curve and the found values are shown in Figure 5.

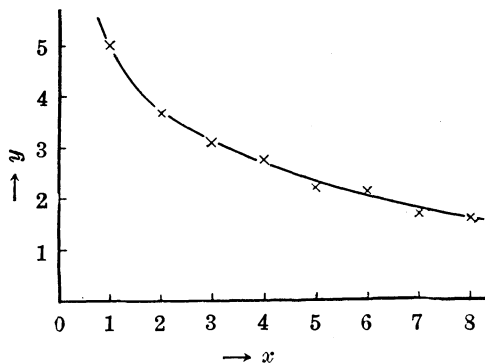


Fig. 4.

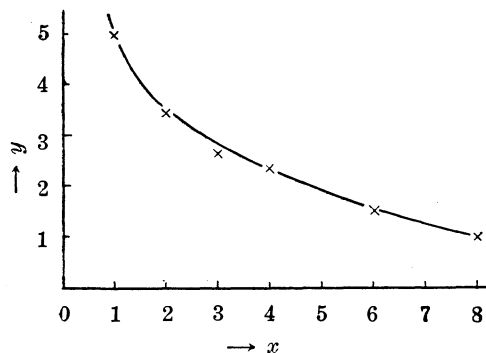


Fig. 5.

Thus the ratio of the amounts of the two alcohols and the corresponding value of the parameter can easily be calculated as shown in Table 13.

Table 13.

Butyl alc./Amyl alc. (g.)	10/0	9/1	8/2	7/3	6/4	5/5	4/6	3/7	2/8	1/9	0/10
p	3.15	2.99	2.84	2.69	2.54	2.40	2.26	2.13	2.00	1.87	1.75

The depth of the colour to be developed by the same concentration of butyl and amyl alcohols differs considerably. At the unit concentration the ratio of the depths was found to be 5.00/3.53. The ratio at any concentration will be obtained by a simple calculation by adopting this value and by applying it to equation 1. In Table 14 are shown the values of the ratio thus calculated together with the found values.

Table 14.

Concentration (x)		1	2	3	4
Ratio of depth of colour	Calculated	—	5.00/3.09	5.00/2.81	5.00/2.52
	Found	5.00/3.53	5.00/2.97	5.00/2.79	5.00/2.60

It is clear from the above consideration that the analysis of one of the two alcohols above mentioned, when it is present alone in methanol, may be carried out simply and accurately. When, however, both the alcohols co-exist, several standard solutions must be prepared and several curves must be described from the mixtures of the two alcohols in

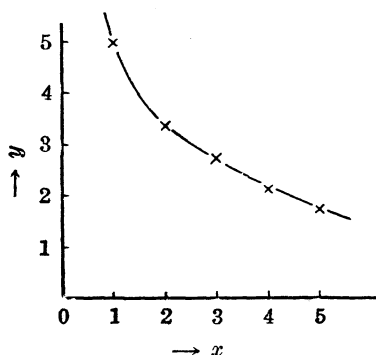


Fig. 6.

arbitrary proportions and it must be examined which of these curves accords with that of the sample. In the present case the state is more complicated. It is not known whether there are higher alcohols other than the above mentioned two or not. Even if only the two alcohols are present, our standards may not be used at once, as they are not prepared from pure substances but from mixtures of isomers.

A mixed standard was prepared from 7 parts of the butyl alcohol and 3 parts of the amyl alcohol, which gave the curve shown in Figure 6.

If the sample methanols contain only butyl and amyl alcohols which are identical with and in equal ratios to those of the mixed standard, the results of the colorimetry with the samples can be put in accordance with the curve given in Figure 6 by adopting the suitable concentrations of the samples to be analysed.

It has been found, in carrying out the experiment as stated above, that the samples actually contain the two alcohols in the proportion of 7:3. The values thus obtained are denoted by crossed marks in Figure 6. The total quantity of the two alcohols can easily be estimated, for the mixture can be thus treated as a single substance. The results are compared with those obtained by the oxidation method as shown in Table 15.

Table 15.

Sample	Higher alcohols (%)	
	By oxidation	By colorimetry
A	0.62, 0.57	0.53
B	1.20, 1.08	1.34

The results of the total analysis of the two sample methanols are summarised as shown in Table 16.

Table 16.

Sample	A (%)	B (%)	Sample	A (%)	B (%)
Methyl alcohol	89.68	94.34	Formic acid	0.009	0.08
Butyl alcohols	0.40	0.87	Methyl formate	0.13	0.25
Amyl alcohols	0.17	0.31	Formaldehyde	0.0021	0.0046
Water	4.1	1.3	Total	94.49	97.21

The rest may be considered as hydrocarbons, being calculated as 5.51 and 2.79% in A and B respectively.

The author's thanks are due to Dr. H. Inoue for his kind advice.

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Studies on the Reactions between Oxides in Solid State at Higher Temperatures. II.⁽¹⁾ The Reaction between Calcium Oxide and Titanium Oxide and the Photo-sensitivity of Calcium Titanate.⁽²⁾

By Yasuo TANAKA.

(Received September 16, 1941.)

Introduction. As a second example of the reaction between oxides in solid state, the reaction with powder mixtures between calcium oxide and titanium oxide was studied, and, as it was found that the reaction products were photo-sensitive, some observations in this respect were also made.

It has been known from an early date that the mineral perovskite consists of calcium metatitanate ($\text{CaO} \cdot \text{TiO}_2$).⁽³⁾ Ebelmen obtained the compound by fusing calcium carbonate and titanium oxide together with alkali carbonate, and there have been some reports on the synthesis of it by the use of fluxes.⁽³⁾ However, about the reaction between calcium oxide and titanium oxide in solid state, there was only one research by Tammann,⁽⁴⁾ in which he stated that the "reaction temperature" of this reaction was 675° .⁽⁵⁾ By studying the fusion curve of

(1) I, This Bulletin, **16** (1941), 428.

(2) A fuller communication has been published in Japanese in *J. Chem. Soc. Japan*, **61** (1940), 345.

(3) Cf. J. Mellor, "A Comprehensive Treatise on Inorganic and Theoretical Chemistry," Vol. VII, 52, London (1927).

(4) G. Tammann, *Z. anorg. allgem. Chem.*, **149** (1925), 68.

(5) Quite recently, J. A. Hedvall and K. Andersson [*Sci. Papers Inst. Phys. Chem. Research* (Tokyo), **38** (1941), 210] have reported their experiment on the solid reaction of this system, but the purpose of which was to compare the reactivity of the different preparations of TiO_2 .

this system, Wartenberg and co-worker⁽⁶⁾ supposed the existence of two other titanates besides $\text{CaO} \cdot \text{TiO}_2$, i.e., $2\text{CaO} \cdot \text{TiO}_2$ and $3\text{CaO} \cdot \text{TiO}_2$. The crystal structure of perovskite has been assigned as cubic, and the size of the unit cell has been given as $a=3.795\text{\AA}$ by Barth⁽⁷⁾ and $a=3.845\text{\AA}$ by Levi and Natta,⁽⁸⁾ but the latter authors reported that they could observe in their X-ray patterns some very faint lines which agreed with the size of the unit cell twice as great as the value above mentioned. Besides, natural perovskites have been reported in some instances as optically anisotropic. The density of natural perovskite lies between 4.037 and 3.974, and that of Ebelen's preparation has been reported as 4.10.⁽³⁾

In the present research, the kinds of the addition compounds which exist in this system were confirmed at first, and then the course of reaction was followed analytically. As described in the first report, it was expected that reducing atmosphere might also have an accelerating effect upon this reaction. To prevent this effect, the experiments were carried out throughout in a current of dry oxygen.

I. Reaction products at 1350° . Uniform mixtures of various proportions of CaCO_3 and TiO_2 were pressed to small cylindrical bodies, and heated at 1350° for 10 hours.⁽⁹⁾ The experimental procedure was almost the same as in the previous experiment. Both preparations used in the experiment were of Kahlbaum.⁽¹⁰⁾ The densities of the reaction products were measured, and free CaO was determined by the method of Lerch and Bogue.⁽¹¹⁾ The results are given in Table 1.⁽¹²⁾

Table 1. Densities and free CaO of the reaction products at 1350° .

No. of sample	Mixing ratio $\text{CaO} : \text{TiO}_2$	Density	Free CaO (%)	Combined CaO Total TiO_2
1	(CaO)	3.312		
2	6 : 1	3.492	60.73	1.49
3	3 : 1	3.620	36.20	1.38
4	2 : 1	3.721	17.86	1.39
5	3 : 2	3.907	3.69	1.39
6	1 : 1	4.056	0.00	1.00
7	1 : 2	4.086	0.00	(0.50)
8	(TiO)	4.233		

(6) H. v. Wartenberg, H. J. Reusch and E. Saran, *Z. anorg. allgem. Chem.*, **230** (1937), 257.

(7) T. Barth, *Norsk geologisk tidsskrift.*, **8** (1925), Sept.; *Chem. Zentr.*, **1926**, I, 11.

(8) G. Levi and G. Natta, *Rend. Acad. Lincei*, (1925), **39**; *Chem. Zentr.*, (1925), II, 2044.

(9) As it has been reported that the lowest eutectic point of this system is about 1450° , (6) it was considered that 1350° was the highest temperature at which the reaction might proceed with certainty in solid state.

(10) CaCO_3 : Calciumkarbonat gefällt, zur Analyse; TiO_2 : Titansäureanhydrid.

(11) W. Lerch and R. H. Bogue, *Ind. Eng. Chem.*, **18** (1926), 739.

(12) As CaO is very hygroscopic, the determination should be carried out immediately after ignition.

The densities of the reaction products were always smaller than the calculated values, assumed as mechanical mixtures, but no singular point could be observed in the relationship between the mixing ratios and the densities. The density of the sample⁽⁶⁾, i.e., $\text{CaO}:\text{TiO}_2=1:1$, was found to be 4.056, which agreed with the value given for $\text{CaO}\cdot\text{TiO}_2$.⁽³⁾

From the measurement of free CaO , too, it was anticipated that the sample (6) consisted of pure $\text{CaO}\cdot\text{TiO}_2$, because it contained no free CaO . By the mixtures with more CaO than this proportion, some free CaO was always found, but the molecular ratio of combined CaO to total TiO_2 became greater than 1, and in the sample (2) it reached approximately to a value of 1.5. Therefore, when it is assumed that the product consists of a pure compound, its empirical composition is to be $3\text{CaO}\cdot 2\text{TiO}_2$. However, as the product of any mixing ratio did not dissolve completely even in concentrated hydrochloric acid, it was in vain to ascertain the kinds of titanates formed by the difference in solubility.

The reaction products were studied further by the X-ray method. The data of the sample (6) are given in Table 2. As no interference lines belonging to CaO and TiO_2 could be detected, it was evident that the product consisted of pure $\text{CaO}\cdot\text{TiO}_2$. The data indicate that the crystal is cubic with a lattice constant of $a = 7.61_5\text{\AA}$, but the principal

Table 2. X-ray data of $\text{CaO}\cdot\text{TiO}_2$.

Intensity*	$\sin \theta^{**}$	hkl	a ($\text{\AA}$)
w	0.254	α 200	7.61
m	0.325 ₅	β 220	7.61
vw	0.346	β 300	7.60
vst	0.360	α 220	7.60
w	0.381 ₅	α 300	7.61
vw	0.422	α 311	7.61
w	0.440	α 222	7.62
w	0.460 ₅	β 400	7.61
vw	0.475	α 321	7.61
st	0.508	α 400	7.62
m	0.565	β 422	7.60
vw	0.583	α 421	7.60
vst	0.622	α 422	7.62
w	0.650	β 440	7.63
m	0.717	α 440	7.63
vw	0.730	β 620	7.59
st	0.802	α 620	7.63
vw	0.864	β 642	7.60
w	0.882	α 444	7.60
m	0.951	α 642	7.61
mean			7.61 ₅

* Roughly estimated as very strong, strong, medium, weak and very weak. Very weak lines are omitted for the calculation of the lattice constant.

** For K_α and K_β lines of iron.

lines are explained with half the value obtained here, which confirms the observation of Levi and Natta.^{(8) (13)}

By the sample (7), i.e., $\text{CaO}:\text{TiO}_2 = 1:2$, only the interference lines of perovskite and TiO_2 were observed, and by the samples with more CaO than the stoichiometric mixture of $\text{CaO}\cdot\text{TiO}_2$, too, no evidence was obtained which showed that any other addition compound than perovskite was formed.⁽¹⁴⁾ But the positions of the interference lines of perovskite were slightly different from each other, and, as shown in Table 3, the lattice constant calculated from the main lines (as a half value) increased from $3.80\text{\AA}$ to $3.83_5\text{\AA}$ with increasing the ratio of combined CaO to total TiO_2 from less than 1 to about 1.5. Therefore, it was concluded that there existed a solid solution between CaO and TiO_2 —perovskite solid solution—, and the range of its existence spreads approximately from a slight excess of TiO_2 than $\text{CaO}\cdot\text{TiO}_2$ to a molecular ratio of $\text{CaO}:\text{TiO}_2 = 3:2$. $3\text{CaO}\cdot 2\text{TiO}_2$ may be regarded as a member of the solid solution, rather than a new addition compound. It is a well known fact that the addition compound between certain oxides can take up an excess of either of the components to form a solid solution; for instance, $\text{MgO}\cdot\text{Al}_2\text{O}_3$ forms a solid solution with excess Al_2O_3 , and the range of its existence spreads from $\text{MgO}\cdot\text{Al}_2\text{O}_3$ to about $\text{MgO}\cdot 2\text{Al}_2\text{O}_3$.^{(15), (16)}

Table 3. Lattice constants.

No. of sample	2	3	4	7
$\frac{\text{Combined CaO}}{\text{Total TiO}_2}$	1.49	1.38	1.39	(0.50)
hkl	Lattice constant ($\text{\AA}$)			
α 110	3.84	3.82	3.81_5	3.79_5
α 200	3.80	3.79_5	3.81	3.80
α 211	3.84	3.83	3.82	3.80
α 220	3.85_5	3.84_5	3.83	3.81
α 310	3.83	3.82	3.81_5	3.81
α 321	3.83_5	3.83	3.82	3.80
mean	3.83_5	3.82_5	3.82	3.80

Further, by observing these results accurately, it is recognized that, while most of the interference lines of perovskite deviate and somewhat diffuse with the increase of the content of CaO, the position of 200 line

(13) As for the crystals of the perovskite type, it has been reported that, for PbZrO_3 , strictly speaking, a unit cell size of $a=12.38(=3\times 4.123)\text{\AA}$ should be given. [A. Hoffmann, *Z. physik. Chem.*, B, **28** (1935), 65.]

(14) Besides CaO lines, some $\text{Ca}(\text{OH})_2$ lines were detected.

(15) G. Hägg and G. Söderholm, *Z. physik. Chem.*, B, **29** (1935), 88.

(16) In these cases, whether the addition product of a simple molecular ratio, e.g., $\text{MgO}\cdot 2\text{Al}_2\text{O}_3$ or $3\text{CaO}\cdot 2\text{TiO}_2$, is really a member of the solid solution or an addition compound, can be decided rigorously only when the phase equilibrium in contact with the melt is made clear.

does not change within experimental errors. So it may be considered that perovskite solid solution deviates from the cubic structure gradually with the increase of the content of CaO; then it may also be explained that natural perovskites are sometimes optically anisotropic.

II. Fused products. To confirm the range of the existence of the perovskite solid solution and also of the possibility of the formations of $3\text{CaO}\cdot\text{TiO}_2$ and $2\text{CaO}\cdot\text{TiO}_2$, supposed by Wartenberg and coworkers,⁽⁶⁾ at still higher temperatures, the products obtained by the fusion of the components were studied.

Small sticks of the mixtures of CaCO_3 and TiO_2 corresponding to $\text{CaO}:\text{TiO}_2 = 3:1$, $2:1$ and $1:1$ were melted with oxy-acetylene flame and quenched in water; and then they were tempered at 1000° in a current of oxygen.⁽¹⁷⁾ Although it might be suspected that the components did not melt completely and also a part of the products was in glass state, the amounts of free CaO of these products were determined, which were, as shown in Table 4, nearly equal to those of the products of the corresponding mixtures at 1350° . The lattice constants of them were also almost the same as those obtained in the last paragraph.

Table 4. Free CaO of the fused products.

Mixing ratio $\text{CaO}:\text{TiO}_2$	Free CaO (%)	$\frac{\text{Combined CaO}}{\text{Total TiO}_2}$
3:1	36.63	1.38
2:1	17.15	1.41
1:1	0.00	1.00

With mixture $\text{CaO}:\text{TiO}_2 = 3:1$ and $2:1$, even by fusion, the ratio of CaO to TiO_2 in the solid solution could never reach to 1.5, the maximum values obtained with a mixture $\text{CaO}:\text{TiO}_2 = 6:1$ at 1350° . In order to reach this value, it seems necessary that a large excess of CaO must be present. From this experiment, too, the addition product, $3\text{CaO}\cdot 2\text{TiO}_2$, is more probably regarded as a member of the solid solution than a new compound, and, as the evidence of the formation of $3\text{CaO}\cdot\text{TiO}_2$ and $2\text{CaO}\cdot\text{TiO}_2$ could never be obtained in this experiment as well as in the products of the solid reaction, their existence could hardly be admitted at any temperature.

III. Course of the reaction. Mixtures of CaO and TiO_2 , corresponding approximately to $\text{CaO}:\text{TiO}_2 = 1:1$ and $3:1$,⁽¹⁸⁾ were heated at a certain temperature in the range between 900° and 1200° for various durations of time, and the course of reaction was followed by determining

(17) Perhaps, owing to the reduction of TiO_2 , the fused products were slightly black in colour, which were naturally turned white by tempering.

(18) Owing to hygroscopicity of CaO, it was impossible to prepare mixtures of accurate composition. The content of CaO was determined analytically after heating.

free CaO. The sample of CaO used was a Merck preparation,⁽¹⁹⁾ and was previously heated at 1100°; TiO₂ was used after the same heat treatment. Therefore, the crystals of the two preparations were evidently well developed compared with those of the preparations used in the first report (in paragraph II). As it has been ascertained in the previous paper that the reaction between MgO and TiO₂ in solid state proceeds in the same way under various experimental conditions, the present experiment was carried out only with pressed bodies. The results are given in Table 5.

Table 5. Free CaO (%) of the reaction products with a mixture CaO = 41.07%. (CaO : TiO₂ = 1 : 1).

Reaction time (hrs.)		0.5	1	3	6	10
Reaction temperature	920°	33.41	29.40	26.09	23.84	21.82
	950°	29.41	26.50	24.65	21.75	19.67
	1000°	24.97	22.83	21.33	17.77	—
	1050°	19.89	18.86	16.43	13.29	—
	1200°	16.84	15.73	13.73	12.91	—

Table 6. Free CaO (%) of the reaction products with a mixture CaO = 67.16%. (CaO : TiO₂ = 3 : 1).

Reaction time (hrs.)		0.5	1	3	6	10
Reaction temperature	920°	62.20	60.46	56.16	54.38	54.14
	1000°	57.64	56.14	54.46	53.45	—
	1200°	51.58	50.49	48.70	48.61	—

At 920° the reaction takes place already with a moderate rate, but it is never completed even at 1200°. By the reaction product with a mixture of CaO : TiO₂ = 3 : 1 at 1200° and 6 hours, the ratio of combined CaO to total TiO₂ becomes 0.81 : 1, which shows that a part of TiO₂ is also still in the free state.

X-ray photographs of some reaction products were taken. No other interference lines besides those belonging to perovskite, CaO (and Ca(OH)₂) and TiO₂ were detected. In all cases the lattice constant of perovskite was nearly equal to that of the sample (7) in the last paragraph, namely, the product might be considered to contain a slight excess of TiO₂ as solid solution, and the evidence of the formation of the solid solution with an excess of CaO was never found in the temperature range studied here.

IV. Mechanism of the reaction. The mechanism of the present reaction may be considered analogous to that of the reaction between

(19) CaO aus Marmor, zur Analyse.

magnesium oxide and titanium oxide which has been discussed in the previous report.

By the solid reaction between magnesium oxide and titanium oxide, $\text{MgO} \cdot 2\text{TiO}_2$ is formed most easily. In the present system, there exists only one addition compound, $\text{CaO} \cdot \text{TiO}_2$, but the compound has a range of solid solution, and at the beginning of the reaction the product is richest in titanium oxide, within the possible range of the solid solution, i.e., contains a slight excess of titanium oxide than the stoichiometric composition of $\text{CaO} \cdot \text{TiO}_2$. The tendency of the reaction product to be at first rich in titanium oxide is the same in the two reactions. It seems that, only with the mixtures containing an excess of calcium oxide, the solid solution rich in calcium oxide is formed, after the major part of titanium oxide has been reacted to form $\text{CaO} \cdot \text{TiO}_2$.

By plotting the relations between $\{1 - \sqrt[3]{1-x}\}^2$ ⁽²⁰⁾ and the reaction time for the mixture $\text{CaO}:\text{TiO}_2=1:1$, ⁽²¹⁾ it was proved that, although there was a rapid initial reaction, the later reaction was represented by the relation, ⁽²²⁾

$$\{1 - \sqrt[3]{1-x}\}^2 = 2kt + C,$$

between 920° and 1050° . (At 1200° the reaction had proceeded already too far within half an hour, so that the above relation did not hold.) The values of k thus obtained are expressed as,

$$k = 4.83 \times 10^2 e^{-30,300/RT}.$$

The energy of activation of the diffusion process, $Q = 30.3$ kilocalories per mole, is a little smaller than that of the formation of $\text{MgO} \cdot 2\text{TiO}_2$, but it is the same order as those of the solid reactions hitherto known. ⁽¹⁾ Thus it is concluded that the main part of the present reaction is also controlled by the diffusion of the two components through the layer of the reaction product.

The constant factor in the above equation, A , of the present experiment, $A = 4.83 \times 10^2$, is smaller than that of the formation of $\text{MgO} \cdot 2\text{TiO}_2$ in the first report, $A = 3.9 \times 10^4$. This constant is related chiefly to the particle size of the components, ⁽²²⁾ and, as already mentioned, the crystals of the preparations in the present experiment were well developed compared with those of the preparations used in the first report; therefore, the difference in A of the two experiments is easily understood.

V. Photo-sensitivity of calcium titanate. It was found that the reaction products kept in a glass tube turned to light red on the surface, and as the phenomenon was proved to be due to the action of light, some observations concerning this were carried out.

The results of the observations are summarized as follows:

(1) When the reaction products were left in the room, their surface turned to light red, and the colour change was more rapid when they were exposed to daylight, but the interior of the products remained white.

(20) The notations have been given in the first report.

(21) Calculated from the amounts of combined CaO.

(22) W. Jander, *Z. anorg. allgem. Chem.*, **163** (1927), 1.

By the action of X-ray and ultra-violet ray, a colour change occurred also. When the products were kept in the dark soon after heating, the colouration did not occur, but the colour, once turned, hardly faded when the products were again placed in the dark.

(2) With different preparations used in the experiment (CaO : CaCO_3 of Kahlbauh or CaO of Merck; TiO_2 : Kahlbaum or "Shika, extra pure") the change was observed equally well. But the phenomenon could not be observed by the magnesium titanates and also in the system zinc oxide and titanium oxide.

(3) Among the products obtained in the previous paragraphs, the products at 1200° were most sensitive, and those at 1350° were less sensitive; at 1350° , the samples (4) and (5) were comparatively sensitive, while pure $\text{CaO}\cdot\text{TiO}_2$ and especially the sample (7) coloured very faintly.

(4) In the presence of phosphorous pentoxide, even if the products were exposed to daylight for a long while, no colour change was observed. Therefore, it was obvious that the existence of moisture was necessary for the colouration.

(5) The coloured samples turned to white when they were heated to about 220° ; the phenomenon was, namely, thermo-reversible.

As the colour change could not be observed by magnesium and zinc titanates, the phenomenon may be assigned as characteristic for calcium titanate, but, perhaps, the minute impurities contained in the preparations may play an important rôle for the colouration. Further, as the traces of water is necessary for the colouration, it is supposed that some impurity decomposes water photo-chemically; the hydrogen formed thereby reduces TiO_2 to a lower oxide, the colour of which is red. However, the details of the mechanism is not yet clear.

The fact, that the products at 1200° are most sensitive, may easily be understood from the consideration that the titanate formed thereby is not yet crystallized well and is in a state of disorder, which is particularly reactive. At 1350° , the samples (4) and (5), which contain excess CaO as solid solution, are sensitive; it has been known that solid solutions turn readily into a state of disorder and are reactive in many respects.⁽²³⁾ On the other hand, the effect of the free CaO existing in these products may also be considered.

Recently, Williamson⁽²⁴⁾ has reported that some varieties of commercial TiO_2 and TiO_2 contaminated with iron showed reversible darkening in daylight. This is considered as a similar phenomenon obtained here, but the degree of colouration seems to be weaker than that of the present system.⁽²⁵⁾

Summary.

(1) It has been ascertained that there exists only one addition compound, perovskite ($\text{CaO}\cdot\text{TiO}_2$), in the system CaO and TiO_2 . As

(23) Cf. J. A. Hedvall, "Reaktionsfähigkeit fester Stoffe," 127, Leipzig (1938).

(24) W. O. Williamson, *Nature*, **140** (1937), 238; **143** (1939), 479.

(25) Afterwards, Williamson has reported his detailed observations in *Mineralog. Mag.*, **25** (1940), 513. T. Ogawa [Reports of the 17th General Meeting, *Elect. Soc. Japan*, **1940** (3). 10] has also reported on the darkening of the ceramic bodies containing TiO_2 .

for the unit cell size of pure perovskite, $a = 7.61_5 \text{ \AA}$ should be given as correct, which is twice as great as the value hitherto given.

(2) $\text{CaO} \cdot \text{TiO}_2$ has been proved to form a solid solution with the two components, the range of which spreads approximately from a slight excess of TiO_2 to $\text{CaO} : \text{TiO}_2 = 3 : 2$, and in which the lattice constant is enlarged and the crystal form deviates from cubic with the increase of the content of CaO .

(3) At the early stage of the solid reaction of this system, the product is richest in TiO_2 within the possible range of the solid solution; the solid solution rich in CaO may be formed gradually when an excess of CaO is present.

(4) It has been concluded that, although there exists a rapid initial reaction, a further reaction is controlled by the diffusion of the two components through the reaction product. The energy of activation of the diffusion process has been calculated as 30.3 kilocalories per mole.

(5) It has been found that the reaction products turn light red by the action of light; some observations thereon have been made.

In conclusion, the author expresses his hearty thanks to Prof. Y. Shibata of Tokyo Imperial University for his valuable advices and encouragement, and to Dr. R. Yoshimura, Director of the Department, for his sincere interest. He is also indebted to Mr. T. Takagi for his experimental assistance, and to the Physics Section of this Laboratory for taking the X-ray photographs.

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Katalytische Oxydation des Schwefeldioxyds mittels schweren Sauerstoffs an der Oberfläche des Platinschwamms (Auszug).⁽¹⁾

Von Sigeo NAKATA und Noriyoshi MORITA.

(Eingegangen am 27. September, 1941).

Inhaltsübersicht. Das Schwefeldioxyd wird mittels des an schwerem Sauerstoff angereicherten Sauerstoffgases an der Oberfläche des Platinschwamms katalytisch oxydiert. Aus den Versuchen, die unter Verwendung überschüssigen Sauerstoffgases bei verschiedenen Temperaturen durchgeführt wurde, ergab sich, dass das nicht reagiert zurückgebliebene überflüssige Sauerstoffgas genau dieselbe Isotopenzusammensetzung besitzt wie das von vorn herein zum Versuch benutzte, d.h. keine Austauschreaktion der O-Atome zwischen dem Sauerstoffgas und dem Schwefeldioxyd bzw. daraus gebildeten Schwefeltrioxyd stattfindet, so lange als die Reaktionstemperatur unterhalb etwa 400° bleibt. Sobald aber als die Versuchstemperatur 400°

(1) S. Nakata, *J. Chem. Soc. Japan*, **62** (1941), 519, 525. Vorläufig mitgeteilt von T. Titani und S. Nakata, *Proc. Imp. Acad. Tokyo*, **16** (1940), 184.

überschreitet, tritt die Austauschreaktion ein und der Gehalt des nicht reagiert übriggebliebenen Sauerstoffgases an schwerem Sauerstoff nimmt mit steigender Temperatur ziemlich rasch ab. Zugleich wurde gefunden, dass die Oxydation des Schwefeldioxyds, die bei diesem Temperaturbereich schon bis zum Gleichgewicht fortschreitet, von der eben erwähnten Temperatur ab nach und nach unvollständiger wird; das gebildete Schwefeltrioxyd bis zu einem gewissen Grad zu dissoziieren beginnt. Dasselbe Ergebnis wurde aber auch gewonnen, als der Schwefeltrioxyddampf zusammen mit schwerem Sauerstoffgas über denselben Platinkatalysator geleitet wurde; die Austauschreaktion zwischen dem Schwefeltrioxyddampf und dem schweren Sauerstoffgas zeigte genau denselben Verlauf wie die oben angegebene Reaktion zwischen dem Schwefeldioxyd und dem schweren Sauerstoffgas. Aus allen diesen Versuchsergebnissen wurde deshalb geschlossen, dass die beobachtete Austauschreaktion der O-Atome nicht zwischen dem Schwefeldioxyd und dem Sauerstoffgas sondern zwischen dem daraus gebildeten Schwefeltrioxyd und dem nicht reagiert übriggebliebenen Sauerstoffgas stattfindet. Als der geschwindigkeitsbestimmende Prozess für diese Austauschreaktion kommt die thermische Dissoziation des Schwefeldioxyds als der wahrscheinlichste in Betracht.

Um über den Mechanismus der katalytischen Oxydation des Schwefeldioxyds an der Oberfläche des Platinkatalysators Kenntnis zu gewinnen, wird die betreffende Reaktion unter Verwendung des an schwerem Sauerstoffisotope angereicherten Sauerstoffgases untersucht. Das aus der Elektrolyse des an schwerem Sauerstoff angereicherten schweren Wassers entwickelte schwere Sauerstoffgas wird mit dem gewöhnlichen Schwefeldioxyd aus der Stahlbombe im Mengenverhältnis von $\text{SO}_2:\text{O}_2 = 1:1$ vermischt und das so hergestellte Reaktionsgasgemisch mit der konstanten Strömungsgeschwindigkeit über den bis auf verschiedenen Temperaturen erhitzten Platinschwamm geleitet. Die Menge des benutzten Platinschwamms beträgt etwa 2 g. (vgl. weiter unten den experimentellen Teil) und die Strömungsgeschwindigkeit des Reaktionsgasgemisches (bei Zimmertemperatur gemessen) 48 ccm. pro Min. Das Schwefeldioxyd wird dadurch fast vollständig bis zu Schwefeltrioxyd umgesetzt. Hingegen bleibt mehr als die Hälfte der benutzten Mengen des Sauerstoffgases nicht reagiert übrig, weil seine Menge im verwendeten Reaktionsgasgemisch, wie aus der oben angegebenen Zusammensetzung des letzteren ohne weiteres ersichtlich ist, doppelt so viel wie die theoretische Menge beträgt. Dieses übriggebliebene Sauerstoffgas wird nun, nachdem es auf geeignetem Weg vom Schwefeltrioxyddampf und eventuell von nicht reagiert übriggebliebenen minimalen Mengen Schwefeldioxyd völlig befreit worden ist, unter Benutzung des Bombenwasserstoffs katalytisch bis zu Wasser verbrannt.

Der Gehalt des so rekombiert gewonnenen Wassers an schwerem Sauerstoff kann aber wegen des eventuell stattgefundenen Austausches der schweren O-Atome zwischen dem schweren Sauerstoffgas und dem Schwefeldioxyd (bzw. dem daraus gebildeten Schwefeltrioxyd) um einen gewissen Betrag kleiner als das Rekombinationswasser sein, das bei einem Kontrollversuch ohne Verwendung des Schwefeldioxyds (aber sonst unter denselben Versuchsbedingungen wie oben) gewonnen wird. Bezeichnet man deshalb mit Δs den gewöhnlichen Wasser gegenüber gemessenen Dichteüberschuss des bei einem beliebigen Oxydationsversuch gewonnenen Rekombinationswassers und mit Δs_0 den des beim Kontrollversuch gewonnenen, so wird der Grad der in Rede kommenden Austauschreaktion mit dem Ausdruck quantitativ gemessen:

$$\text{proz. Austausch} = \frac{(\Delta s_0 - \Delta s)}{(\Delta s_0 - \Delta s)_\infty} \times 100 \quad (1).$$

In dieser Gleichung drückt der Nenner $(\Delta s_0 - \Delta s)_\infty$ solch einen extremen Wert von $(\Delta s_0 - \Delta s)$ aus, der sich beim vollständigen Austausch ergeben würde und er kann entweder rechnerisch bzw. experimentell bestimmt werden, wie unten beim experimentellen Teil gezeigt wird. Der so bestimmte prozentuale Austausch zwischen dem Schwefeldioxyd und dem Sauerstoffgas ist in Abb. 1 mit Kurve I in Abhängigkeit von der Temperatur wiedergegeben. In derselben Abbildung geben wir weiter mit Kurve II den beim vorliegenden Versuch experimentell gefundenen prozentualen Umsatz d.h. den Oxydationsgrad des Schwefeldioxyds in Abhängigkeit von der Temperatur wieder, der wie üblich nach der Gleichung berechnet wird:

$$\text{proz. Umsatz} = \frac{\text{Menge des oxydierten SO}_2}{\text{Menge des verwendeten SO}_2} \times 100 \quad (2).$$

Kurve III in derselben Abbildung stellt den prozentualen Umsatz beim Oxydationsgleichgewicht dar, die mit Hilfe der von Bodenstein und Pohl⁽²⁾ angegebenen Gleichgewichtskonstante berechnet wurde. Oberhalb von etwa 400°C. fallen die beiden Kurven II und III aufeinander

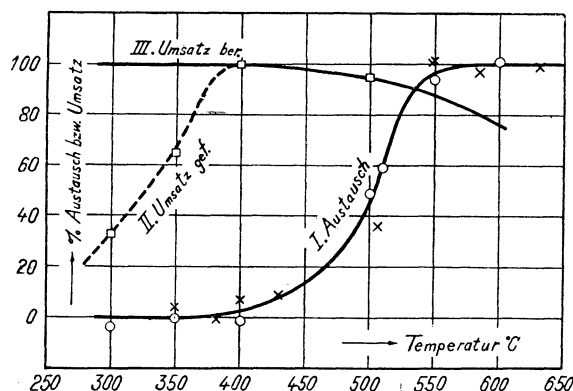


Abb. 1. Die Temperaturabhängigkeit des prozentualen Austausches (O) sowie des prozentualen Umsatzes (□) des Schwefeldioxyds und des prozentualen Austausches des Schwefeltrioxyds (x).

fast ganz zusammen. Der beim vorliegenden Versuch kinetisch gemessene prozentuale Umsatz (Kurve II) gibt deshalb bei diesem letzteren Temperaturbereich auch den Umsatz beim Gleichgewicht an. Aber zugleich wird bemerkt, dass die beiden Kurven II und III von der eben erwähnten Temperatur an allmählich abzustiegen beginnen. Dies weist offensichtlich darauf hin, dass der Umsatz des Schwefeldioxyds von dieser Temperatur an nach und nach unvollständiger wird; die thermische Dissoziation des Reaktionsproduktes, des Schwefeltrioxyds allmählich sich bemerkbar macht.

(2) M. Bodenstein und W. Pohl, Z. Elektrochem., 11 (1905), 373.

Vergleicht man diesen Verlauf der Oxydationskurve II bzw. III mit Kurve I, so bemerkt man ohne weiteres, dass die Austauschreaktion erst bei hohen Temperaturen merklich stattfindet, wo die Oxydationskurve sogar schon ziemlich deutlich absteigt, während bei niedrigen Temperaturen (unterhalb etwa $400^{\circ}\text{C}.$) fast keine nennenswerte Austauschreaktion auftritt, obwohl die Oxydation eventuell fast ganz bis zum Gleichgewicht fortschreitet (vgl. z.B. Kurve I und II bzw. III bei 400°). Deshalb liegt die Annahme nahe, dass die betreffende Austauschreaktion erst nach der vollständigen Oxydation des Schwefeldioxyd zwischen dem dadurch gebildeten Schwefeltrioxyd und dem nicht reagiert übriggebliebenen Sauerstoffgas stattfindet. Diese letztere Annahme wird weiter durch den Austauschversuch bestätigt, der zwischen dem Schwefeltrioxyddampf und dem schweren Sauerstoffgas ausgeführt wird.

Bei diesem letzteren Versuch wird das Gasgemisch von der Zusammensetzung $\text{SO}_3:\text{O}_2=2:3$ (d.h. in Bezug auf Sauerstoff von derselben Zusammensetzung wie das oben benutzte Gasgemisch $\text{SO}_2:\text{O}_2=1:1$) auf dem weiter unten beim experimentellen Teil ausführlich anzugebenden Weg aus dem gewöhnlichen Schwefeltrioxyd und dem elektrolytisch entwickelten schweren Sauerstoffgas hergestellt und dieses Gasgemisch bei verschiedenen Temperaturen über denselben Platinschwamm geleitet, der beim oben angegebenen Versuch mit Schwefeldioxyd benutzt wurde. Das aus dem Katalysatorrohr zusammen mit dem Schwefeltrioxyddampf hinausströmende Sauerstoffgas wird dann, nachdem es vom ersteren auf geeignetem Weg befreit worden ist, mit dem Bombenwasserstoff katalytisch bis zu Wasser rekombiniert. Mit Hilfe des Dichteüberschusses Δs des so gewonnenen Wassers sowie des Δs_0 des Wassers, das bei einem Kontrollversuch ohne Verwendung des Schwefeltrioxyds gewonnen wird, wird der prozentuale Austausch ebenfalls nach Gl. (1) berechnet. Der so gemessene prozentuale Austausch zwischen dem Schwefeltrioxyddampf und dem Sauerstoffgas zeigte aber genau dieselbe Temperaturabhängigkeit wie die oben angegebene Reaktion zwischen Schwefeldioxyd und Sauerstoff, wie aus Abb. 1 ersichtlich wird, wo die Versuchsergebnisse mit Schwefeltrioxyd durch kleine Kreuze eingezeichnet werden. Diese Kreuze liegen innerhalb des Messfehlerbereiches genau auf Kurve I, die aus dem Versuch mit Schwefeldioxyd gewonnen wurde. Deshalb folgt der schon oben angegebene Schluss, dass die Austauschreaktion zwischen dem Schwefeldioxyd und dem Sauerstoffgas in der Tat zwischen dem daraus entstandenen Schwefeltrioxyd und dem Sauerstoffgas stattfindet.

Die katalytische Oxydation des Schwefeldioxyds an der Oberfläche des Platins wurde von Bodenstein und Fink⁽³⁾ eingehend untersucht. Sie kamen dabei zu dem Ergebnis, dass die in Rede kommende Reaktion hauptsächlich an den aktiven Zentren bzw. Linien auf der Oberfläche des Katalysators stattfindet und die Geschwindigkeit der ganzen Reaktion durch die Geschwindigkeit der zweidimensionalen Diffusion bestimmt wird, die einer in wenigeren Mengen befindliche Bestandteil der Reaktionsteilnehmer, (das Schwefeldioxyd beim vorliegenden Versuch, wo die Menge des Sauerstoffgases im Reaktionsgasgemisch $\text{SO}_2:\text{O}_2=1:1$ im Vergleich mit dem Schwefeldioxyd überwiegend viel ist) durch die Adsorp-

(3) M. Bodenstein und C. G. Fink, *Z. phys. Chem.*, **60** (1907), 1; M. Bodenstein, *ebenda*, **B2** (1929), 345.

tionsschicht des Schwefeltrioxyds an der Oberfläche des Katalysators ausführt. Nach dieser Annahme muss deshalb an den aktiven Zentren bzw. Linien des Katalysators bei jeder betreffenden Temperatur das Oxydationsgleichgewicht eingestellt werden:



Nimmt man diesen Mechanismus der katalytischen Oxydation des Schwefeldioxyds als richtig an und weiter zieht man die oben angegebene Experimentalmethode in Betracht, dass der Verlauf der Austauschreaktion mit Hilfe der zeitlichen Änderung des Gehaltes des in der Gasphase befindlichen Sauerstoffgases an schwerem Sauerstoff gemessen wird, so kommen zwei Möglichkeiten als der plausible Mechanismus der vorliegenden Austauschreaktion in Frage: entweder (1) die Desorption des Sauerstoffgases, das aus der thermischen Dissoziation des Schwefeltrioxyds gebildet wird oder (2) die thermische Dissoziation des letzteren wirkt selbst massgebend.

(1) Nimmt man an, dass die Oxydationsreaktion (3) an den aktiven Zentren des Katalysators bei allen untersuchten Temperaturen nach beiden Seiten mit genügend grosser Geschwindigkeit stattfindet, so müssen die an diesen aktiven Zentren adsorbiert befindlichen Sauerstoffmoleküle bei jeder betreffenden Temperatur schnell bis zum Gleichgewicht (gegen Schwefeldioxyd bzw. Schwefeltrioxyd) ausgetauscht werden. In diesem Fall wird deshalb die Geschwindigkeit der beim vorliegenden Versuch beobachteten Austauschreaktion durch die Desorptionsgeschwindigkeit dieser bis zum Gleichgewicht ausgetauschten Sauerstoffmoleküle aus den aktiven Zentren bestimmt. Kurve I in Abb. 1 müsste dann die Temperaturabhängigkeit der Desorptionsgeschwindigkeit der Sauerstoffmoleküle aus der Oberfläche des Platinschwamms wiedergeben.

(2) Falls dagegen die Geschwindigkeit der Rückreaktion von (3) d.h. die Dissoziationsgeschwindigkeit des Schwefeltrioxyds an der Oberfläche des Katalysators im Vergleich mit der Desorptionsgeschwindigkeit der dadurch entstandenen Sauerstoffmoleküle viel kleiner ist, muss eben diese Dissoziationsgeschwindigkeit des Schwefeltrioxyds für die vorliegende Austauschreaktion massgebend sein. In diesem Fall gibt Kurve I in Abb. 1 die Temperaturabhängigkeit der Dissoziationsgeschwindigkeit des Schwefeltrioxyds an den aktiven Zentren wieder.

Zwischen diesen beiden Möglichkeiten können wir nicht ohne weiteres eindeutig zu einer Entscheidung kommen, bis der Gehalt des an der Oberfläche des Katalysators adsorbiert befindlichen Sauerstoffgases an schwerem Sauerstoff in Abhängigkeit von der Temperatur gemessen wird: beim Fall (1) würde dieser Gehalt fast unabhängig von der Temperatur konstant sein. Träfe hingegen die Annahme (2) zu, so würde der Gehalt des adsorbierten Sauerstoffgases an schwerem Sauerstoff genau dieselbe Temperaturabhängigkeit wie Kurve I in Abb. 1 zeigen. Obwohl solch ein Versuch nicht so leicht auszuführen ist, erscheint doch, bloss aus dem vorliegenden Versuchsergebnis zu urteilen, die Annahme (2) wahrscheinlicher als die Annahme (1). Wir haben oben in Abb. 1 gefunden, dass Kurve II und III, die die Umsatzmenge des Schwefeldioxyds in Abhängigkeit von der Temperatur wiedergeben,

agierende Schwefeldioxyd wird aus der käuflichen Stahlbombe SO_2 entnommen und, nachdem es nacheinander durch das gross Glasgefäss I, den Phosphorpenoxydbehälter G und den Strommesser F geleitet worden ist, durch die Glaskapillare E ebenfalls unter konstantem Überdruck ausgepresst, indem man das überflüssige Gas durch das mit Quecksilber gefüllte Sicherheitsventil H ausströmen lässt. Die Strömungsgeschwindigkeit der beiden Gase wird durch die geeignete Wahl der beiden Kapillaren D und E so kontrolliert, dass sie beide gleich 24 ccm. pro Min. betragen. Das so hergestellte Reaktionsgasgemisch von der Zusammensetzung $\text{SO}_2:\text{O}_2=1:1$ wird nun durch das Katalysatorrohr K von links nach rechts geleitet. Das Katalysatorrohr K enthält in seiner Mitte den Platinschwamm, der aus etwa 5 g. „Platinchlorid“ hergestellt worden ist, und wird von aussen elektrisch erwärmt. Die Temperatur des Katalysators wird mit Hilfe eines Thermoelements Th genau gemessen. Das gekrümmte Rohr J stellt das kleine Quecksilbermanometer dar.

Das aus dem Katalysatorrohr hinausströmende Gas enthält neben dem nicht reagiert übriggebliebenen Sauerstoffgas noch eine ebenso grosse Menge Schwefeltrioxyddampf sowie eine kleine Menge des nicht reagiert zurückgebliebenen Schwefeldioxyds. Dieses Gasgemisch wird zunächst durch das von aussen mit Wasser konstant bei 24°C . gehaltene Schlangenrohr L und dann durch das mit Kohlensäureschneegemisch bis unter zu -70°C . abgekühlte Rohr M geleitet und dort vom Schwefeltrioxyd- sowie dioxyddampf möglichst vollständig befreit. Das so gereinigte Sauerstoffgas wird zum Schluss, nachdem es mittels der in der Waschflasche N enthaltenen Schwefelsäure gewaschen worden ist, in den mit Wasser gefüllten Gasbehälter P eingesaugt. Die Apparatur O stellt die Anordnung dar, die das gereinigte Sauerstoffgas in den Behälter P unter konstantem Unterdruck einströmen lässt.

Das im Behälter P gesammelte Sauerstoffgas wird nun, nachdem der Oxydationsversuch beendet worden ist, mit dem gewöhnlichen Bombenwasserstoff bis zu Wasser katalytisch rekombiniert. Zu diesem Zweck wird das Gas im Behälter P nacheinander durch das Manometer R, den Strommesser S und das Chlorcalciumrohr T in das mit Platinschwamm beschickte Katalysatorrohr Y geschickt, indem man den Hahn Q sorgfältig öffnet, der während des Oxydationsversuches ganz geschlossen geblieben war. Der mit diesem Sauerstoffgas zu reagierende Wasserstoff wird aus der käuflichen Stahlbombe H_2 entnommen und nachdem er unter Benutzung des mit Platinschwamm gefüllten Rohrs U und des Chlorcalciumrohrs V vom beigemengten Sauerstoffgas befreit worden ist, durch den Strommesser W und das kleine Manometer X in die Rekombinationskammer Y eingeleitet. Das dort gebildete Wasser wird im mit Kohlensäureschneegemisch abgekühlten Gefäss Z ausgefroren. Der Dichteüberschuss Δs des so rekombinierten Wassers wird, nachdem es auf geeignetem Wege gereinigt worden ist, mittels eines kleinen Glaschwimmers im Vergleich mit dem gewöhnlichen Wasser gemessen.

Die Ergebnisse der Versuche, die unter Verwendung von zwei Arten des schweren Wassers von verschiedenem Gehalt an schwerem Sauerstoff zweireihig ausgeführt wurden, sind in Tabelle 1 zusammengestellt, wo Δs_0 den Dichteüberschuss des rekombinierten Wassers bei einem Kontrollversuch ausdrückt, der ohne Verwendung des Schwefeldioxyds ausge-

führt wird. Der extreme Wert $(\Delta s_0 - \Delta s)_\infty$, der sich beim vollständigen Austausch ergeben würde, wird rechnerisch ermittelt.

Das Rekombinationswasser, das bei I. Versuchsreihe ohne Verwendung des Schwefeldioxyds gewonnen wurde, besitzt den Dichteüberschuss $\Delta s_0 = 39.0 \gamma$ dem gewöhnlichen Wasser gegenüber. Dagegen besitzt das Wasser, das durch die Reduktion des zum Versuch benutzten Schwefeldioxyds gebildet wird,⁽⁴⁾ dieselbe Dichte wie das gewöhnliche Wasser. Da aber beim Versuch diese beiden Arten der Gase im Mengenverhältnis von $\text{SO}_2:\text{O}_2 = 1:1$ vermischt wurden, müsste die Abnahme des Dichteüberschusses $(\Delta s_0 - \Delta s)_\infty$ beim vollständigen Austausch $39.0 - (39.0 + 0.0)/2 = 19.5 \gamma$ betragen. Auf genau dieselbe Weise ergibt der Grenzwert $(\Delta s_0 - \Delta s)_\infty$ bei II. Versuchsreihe 17.7γ , wo das Rekombinationswasser beim Kontrollversuch den Dichteüberschuss von $\Delta s_0 = 35.3 \gamma$ besitzt.

Tabelle 1. Oxydations- und Austauschversuch mit Schwefeldioxyd.

I. Versuchsreihe. $(\Delta s_0 - \Delta s)_\infty = 19.5 \gamma$.

Temp. °C.	$(\Delta s_0 - \Delta s) \gamma$	Austausch %	Umsatz %
350	-0.1	-0.5	65
400	-0.3	-1.5	100
500	9.5	48.7	95

II. Versuchsreihe. $(\Delta s_0 - \Delta s)_\infty = 17.7 \gamma$.

Temp. °C.	$(\Delta s_0 - \Delta s) \gamma$	Austausch %	Umsatz %
300	-0.7	-4	33
510	10.4	59	—
550	16.7	94	—
600	18.0	101	—

Austauschversuch mit Schwefeltrioxyd. Der Strom des Reaktionsgemisches von der Zusammensetzung $\text{SO}_3:\text{O}_2 = 2:3$ wird dadurch gewonnen, dass man eine Menge des flüssigen Schwefeltrioxyds in einem Gefäß konstant bei 35°C . erwärmt und dadurch das aus der Elektrolyse des schweren Wassers entwickelte Sauerstoffgas mit der konstanten Geschwindigkeit von 20 ccm. pro Min. durchströmen lässt. Das aus dem Katalysatorrohr zusammen mit dem Schwefeltrioxyddampf hinausströmende Sauerstoffgas wird auf genau dieselbe Weise wie oben vom ersteren und eventuell von kleinen Mengen des Schwefeldioxyds befreit, das aus der thermischen Dissoziation des ersteren Gases entstanden ist, und dann mit dem gereinigten Bombenwasserstoff bis zu Wasser rekombiniert. Der prozentuale Austausch wird ebenfalls unter Benutzung des (gewöhnlichen Wasser gegenüber gemessenen) Dichteüberschusses des so rekombinierten Wassers (Δs) sowie des des Wassers (Δs_0), das bei einem Kontrollversuch

(4) Das Schwefeldioxyd wird unter Benutzung der Reaktion $\text{SO}_2 + 2\text{H}_2\text{S} = 3\text{S} + 2\text{H}_2\text{O}$ bis zu Wasser verwandelt.

ohne Verwendung des Schwefeltrioxyds gewonnen wird, nach Gl. (1) berechnet. Der zu dieser Berechnung notwendige extreme Wert $(\Delta s_0 - \Delta s)_\infty$ beim vollständigen Austausch wird diesmal bei jeder Reihe der Versuche experimentell ermittelt, indem der Mittelwert der bei den zwei höchsten untersuchten Temperaturen direkt beobachteten $(\Delta s_0 - \Delta s)$ als solcher angenommen wird, weil sie sich dort unabhängig von der Temperatur fast konstant ergaben.

Tabelle 2. Austauschversuch mit Schwefeltrioxyd.

I. Versuchsreihe. $(\Delta s_0 - \Delta s)_\infty = (19.9 + 19.7)/2 = 19.8 \gamma$.

Temp. °C.	$(\Delta s_0 - \Delta s) \gamma$	Austausch %
382	-0.2	-1
430	1.7	9
548	19.9	101
632	19.7	99

II. Versuchsreihe. $(\Delta s_0 - \Delta s)_\infty = (20.0 + 19.0)/2 = 19.5 \gamma$.

Temp. °C.	$(\Delta s_0 - \Delta s) \gamma$	Austausch %
350	0.7	4
400	1.3	7
507	7.0	36
550	20.0	102
585	19.0	97

Zum Schluss möchten wir Herrn Prof. T. Titani für seine Anregung zu dieser Arbeit und seine freundliche Hilfe herzlichst danken. Der Nippon Gakujutu Sinkôkai (der Japanischen Gesellschaft zur Förderung der wissenschaftlichen Arbeit) sowie der Hattori-Hôkôkai (der Hattori-Stiftung) sind wir für ihre finanzielle Unterstützung zu bestem Dank verpflichtet.

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Lösungsmittleffekt des Dipolmomentes disubstituierter Benzole.

Von Keniti HIGASI.

(Eingegangen am 30. September, 1941.)

Eine der erfolgreichsten Anwendungen des Dipolmomentes in der Chemie ist der wohlbekannte Versuch von Benzol nach hexagonaler Struktur. Da aber die meisten diesbezüglichen Studien⁽¹⁾ zu einer Zeit gemacht wurden, wo die Lösungsmittelwirkung bei dem Moment auf Null⁽²⁾ bewertet wurde, waren die damaligen Konklusionen nicht frei von Fehlern, die eben in diesen Lösungsmitteln ihren Ursprung hatten.

Im folgenden Artikel möchte ich deshalb eine erneute Untersuchung derselben anstellen. Da der Lösungsmittleffekt bei monosubstituierten Benzolen bereits früher gut dargestellt wurde,⁽³⁾ möchte ich mich einzig auf den Effekt bei disubstituierten Benzolen beschränken.

Dichlorbenzole: Die Dipolmomente der Dichlorbenzole sind bereits im Gaszustand von Groves und Sugden⁽⁴⁾ bestimmt worden. Ausserdem hat Müller⁽³⁾ den Lösungsmittleinfluss auf das Moment von ortho Isomern studiert. Ich habe neuerdings die Momente des *o*- und *m*-Isomers in Äthyl-äther, einem Lösungsmittel von grosser Dielektrizitätskonstante gemessen. (siehe Tabelle.)

Tabelle. Dipolmomente Chlor- und Dichlorbenzole.

Lösungsmittel	DK	<i>o</i> -C ₆ H ₄ Cl ₂	<i>m</i> -C ₆ H ₄ Cl ₂	C ₆ H ₅ Cl
Vakuum	1.00	(2.16)	1.67	1.72
Hexan	1.91	2.30	—	1.59
Dekalin	2.16	2.26	—	1.54
Benzol	2.28	2.26	1.46	1.51
Schwefelkohlenstoff	2.64	2.10	—	1.42
Äthyläther	4.37	2.00	1.33	1.30

Beim ersten Blick auf die Tabelle bemerkt man, dass die beiden Dichlorbenzole einen negativen Lösungsmittleffekt aufweisen. (Der geringe Gaswert des *o*-Dichlorbenzols ist augenscheinlich ungenau.)

(1) Errera: *Physik. Z.*, **27** (1926), 764; Smyth, Morgan, und Boyce: *J. Am. Chem. Soc.*, **50** (1928), 1936; Bergmann, Engel, und Sándor; *Z. physik. Chem.*, **B 10** (1930), 106; Tiganik: *ibid.*, **B 13** (1931), 425.

(2) Debye: "Polare Molekeln", Leipzig (1929) S. 53; Smyth: "Dielectric Constant and Molecular Structure," New York (1931), S. 32.

(3) Müller: *Physik. Z.*, **34** (1933), 689; Higasi: *Sc. Papers I.P.C.R. (Tokyo)*, **28** (1936), 284.

(4) Groves und Sugden: *J. Chem. Soc.*, **1937**, 1782.

Die Kurven der zwei Dichlorbenzole unterscheiden sich nicht wesentlich von der Kurven des Chlorbenzols und zeigen, dass die ersteren einen etwas geringeren Lösungsmittelleffekt als die letzteren besitzen. (Fig. 1).

Dinitrobenzol: Ich habe die Momente von Hexan-, Benzol- und Äthyläther-Lösungen gemessen und habe die Resultate mit denen des Nitrobenzols⁽³⁾ verglichen. (Fig. 2). Auch in diesem Falle läuft die Abnahme des Dipolmomentes parallel der Zunahme der Dielektrizitätskonstante, jedoch etwas weniger ausgesprochen als beim Nitrobenzol.

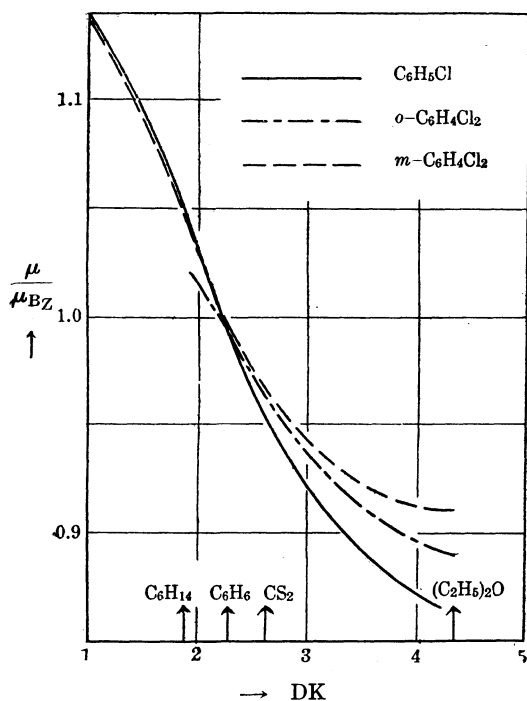


Fig. 1.

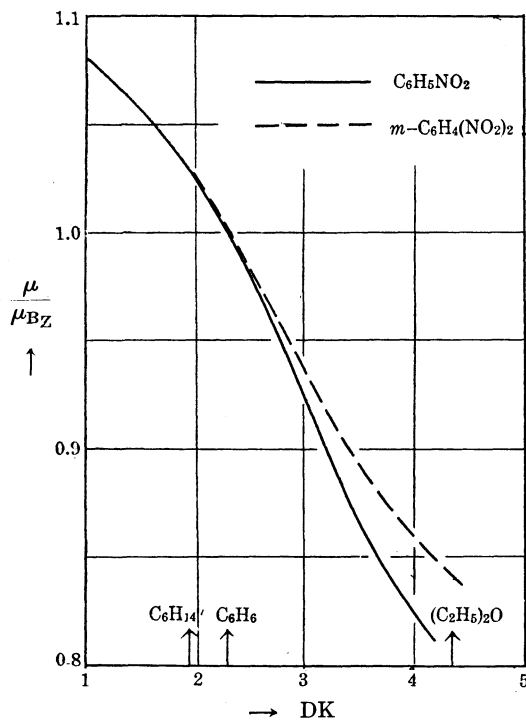


Fig. 2.

Ausserdem besitze ich bezüglich von 3 Isomeren nur Daten von Chlornitrobenzolen,⁽⁵⁾ welche alle einen negativen Lösungsmittelleffekt aufweisen.

Beim Berechnen der oben erwähnten Momente ist die Voraussetzung $P_A = 5\%$ von P_E gebraucht.⁽⁶⁾ Diese Voraussetzung lässt sich rechtfertigen aus der Tatsache, dass der Unterschied in der Wahl P_A die obige Konklusion ganz wenig ändert.

Aus obigem können wir schliessen, (1) dass sich der Lösungsmittelleffekt von disubstituierten Benzolen von denen der entsprechenden mono-

(5) Groves und Sugden: *loc. cit.* (4); "A Table of Dipole Moment," *Trans. Faraday Soc.*, **30** (1934), Appendix.

(6) Sugden: *Trans. Faraday Soc.*, **30** (1934), 734; Groves und Sugden: *J. Chem. Soc.*, **1937**, 1779.

substituierten nicht sehr unterscheidet und (2) dass die klassischen Werke von Errera, Smyth, und anderer⁽¹⁾ als Werke erster Annäherung betrachtet werden müssen, weil sie stets Benzol als Lösungsmittel benützt haben.

Demnächst werden wir den Unterschied der Lösungsmittelleffekte zwischen den Dipolmomenten der monosubstituierten Benzole und denen der disubstituierten besprechen. Sehr wesentlich für die Lösungsmittelleffekte sind die Raumerfüllung und die Dipolinduktion in der umgebenden Flüssigkeit. Im Lösungsmittel liegen um einen Dipol induzierte Dipole.

Wenn das Dipolmolekül kugelförmig ist, gleichen diese induzierten Momente sich aus, und nicht, bei nichtsphärischen Molekülen. Falls das Molekül ein grosses Radikal an der Dipolachse besitzt (z.B. Chlorbenzol, Nitrobenzol) bewirken die induzierten Dipole eine Herabsetzung des Dipolmomentes⁽³⁾; falls sie in einer Ebene senkrecht dazu liegen (z.B. Triäthylamin), so werden sie ein erhöhtes Dipolmoment verursachen.⁽⁷⁾ Diese Klassifikation von Molekülen nach geometrischen Typen findet in den Messungen allgemeine Bestätigung.⁽⁸⁾

Aus den Figuren ist ersichtlich, dass der Lösungsmittelleffekt bei para-disubstituiertem Benzol demjenigen bei monosubstituiertem Benzol

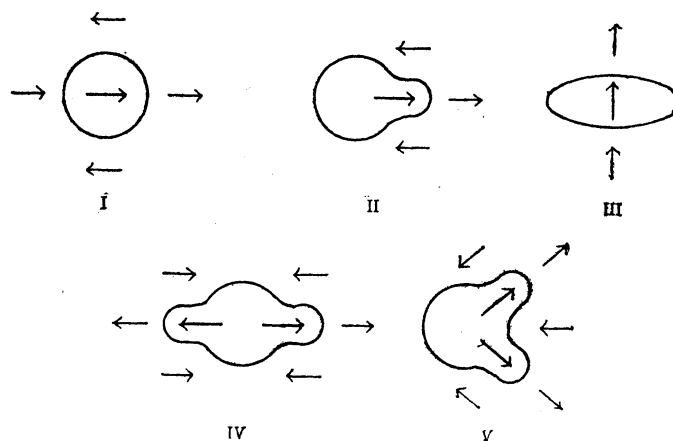


Fig. 3. — I. spärliches Molekül, II. Chlorbenzol (neg. L.E.), III. Triäthylamin (pos. L.E.), IV. *p*-Chlorbrombenzol (neg. L.E.), V. *o*- und *m*-Dichlorbenzole (neg. L.E.). L.E. = Lösungsmittelleffekt.

sehr ähnlich ist, jedoch derselbe Effekt bei ortho- bzw. meta-Verbindung von dem bei monosubstituiertem sich dagegen ziemlich unterscheidet. Vom geometrischen Standpunkt aus ist anzunehmen, dass die Lösungs-

(7) Cowley und Partington: *J. Chem. Soc.*, **1938**, 1598; Higasi: *Sc. Papers I.P.C.R.*, (Tokyo), **31** (1937), 311.

(8) Frank: *Proc. Roy. Soc., A* **152** (1935), 171; Cowley und Partington: *J. Chem. Soc.*, **1936**, 1184; **1937**, 130; **1938**, 1598; Glasstone: *Annual Reports*, **33** (1936), 117; Higasi: *Sc. Papers I.P.C.R.*, **28** (1936), 284; **31** (1937), 311, 317; *Bull. I.P.C.R.*, **13** (1934), 1167, **14** (1935), 146; **15** (1936), 776.

mittelwirkung dieser letzteren Verbindungen etwas geringer ist. (Fig. 3). Dies stimmt mit den oben erwähnten Kurven des Dipolmomentes (Fig. 1 u. Fig. 2) gut überein.

Es sei mir gestattet, Herrn Prof. Katayama und Herrn Prof. Mizushima für ihr Interesse an dieser Arbeit zu danken.

Anmerkung bei der Korrektur: Neulich hat Dr. Watanabe das Dipolmoment des *o*-Dichlorbenzols im Gaszustand gemessen und er fand ein verhältnissmässig grösseres Moment von 2.53D. Das ausführliche Ergebnis wird bald von ihm berichtet.

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Studies on the Thermal Diffusion of Solutions. I. Thermal Diffusion Coefficient of Some Inorganic Solutions.*

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(Received October 2, 1941.)

I. Introduction. Generally speaking, when a temperature gradient exists in a solution, a concentration gradient is also set up. This phenomenon, which is known as the thermal diffusion of solution, or as Ludwig-Soret effect after the discoverers,⁽¹⁾ has been studied by several workers. Analogous phenomenon in gaseous solutions, is also predicted from the detailed studies in gas-kinetic theory by Enskog⁽²⁾ and by Chapman,⁽³⁾ and later demonstrated experimentally by Chapman and Dootson.⁽⁴⁾

Concerning the phenomenon for gases many experimental as well as theoretical works have been carried out, and they have afforded an important basis to our knowledge of the repulsive potential of the molecules.⁽⁵⁾ Similarly, the studies on solutions might contribute to the elucidation of its constitution, but the systematic studies^{(6),(7),(8),(9)} in this field are comparatively rare until recently. These circumstances might have been due to such experimental difficulties as the effect produced is extremely small and as continuous measurements for many days are required.

* The main part of this paper has been published in Japanese [*J. Chem. Soc. Japan*, **62** (1941), 480].

(1) Ludwig: *Wien Akad. Ber.*, **20** (1856), 539; Soret: *Ann. chim. phys.*, (5), **22** (1881), 293.

(2) D. Enskog: *Phys. Zeit.*, **12** (1911), 533; *Ann. Phys.*, **38** (1912), 750.

(3) S. Chapman: *Proc. Roy. Soc.*, **A 93** (1916), 1; *Phil. Trans.*, **217** (1917), 157.

(4) S. Chapman and F. W. Dootson: *Phil. Mag.*, **33** (1917), 248.

(5) Chapman and Cowling: "The Mathematical Theory of Non Uniform Gases," Cambridge, (1939), 252-258.

(6) J. Chipman: *J. Am. Chem. Soc.*, **48** (1926), 2577.

(7) S. Arrhenius: *Z. phys. Chem.*, **26** (1898), 187.

(8) C. C. Tanner: *Trans. Faraday Soc.*, **23** (1927), 75.

(9) A. Eilert: *Z. anorg. Chem.*, **88** (1914), 1.

But in 1938 Clusius and Dickel⁽¹⁰⁾ devised an apparatus which could increase the small separation, caused by the effect in gaseous solutions, to such an extent as even chlorine isotopes could be separated perfectly. In the following year Clusius and Dickel,⁽¹¹⁾ as well as Korsching and Wirtz⁽¹²⁾ succeeded in an attempt to concentrate the liquid solutions with an apparatus constructed according to the same principle. This success opened out a new field of research in the study of the Ludwig-Soret effect.

The thermal diffusion phenomenon can be expressed quantitatively by the *thermal diffusion coefficient* D' which is defined by the equation: $f = D'n \frac{dT}{dx}$; f denotes the flow of diffusion caused by the temperature gradient $\frac{dT}{dx}$ in the solution of concentration n . It has been considered to be inconvenient to measure D' directly, on account of the ordinary diffusion phenomenon superposed on it; i.e., the concentration gradient set up is opposed by the process of diffusion, tending to equalise the composition. When a stationary state is reached, therefore, the next relation holds:

$$D \frac{dn}{dx} = -D'n \frac{dT}{dx},$$

or

$$d \ln n / dT = -D'/D,$$

D denotes the ordinary diffusion coefficient. As D'/D , or Soret constant (S.C.), can be obtained at once by the measurement of the concentration change and the temperature difference, there have been some measurement of D'/D in both, gaseous and liquid solutions, while those of D' have been scarcely done.

The object of the present paper is to devise an apparatus suitable for the direct determination of D' by the use of the thermal diffusion apparatus of Clusius and Dickel (II and III); to describe the experiments carried out for some inorganic solutions, using the apparatus devised (Art. 4 and 5); and to discuss the results thus obtained (Art. 6).

II. Theoretical Treatment of the Thermal Diffusion Apparatus.

Several papers,⁽¹³⁾ in which the actions of the thermal diffusion apparatus is treated mathematically, have been published up to the present. But most of these papers, except that of Debye,^(13a) treated the subject from the standpoint of applying the results to gaseous solutions, and the important problem in the case of liquid solution, i.e., the problem of the degree of separation against time, has been almost put aside.

(10) K. Clusius and G. Dickel: *Naturwiss.*, **26** (1938), 546.

(11) K. Clusius and G. Dickel: *ibid.*, **27** (1939), 148.

(12) K. Wirtz and H. Korsching: *ibid.*, **27** (1939), 110, 367.

(13) (a) W. H. Furry, R. C. Jones and L. C. Onsager: *Phys. Rev.*, **55** (1939), 1083.

(b) L. Waldman: *Naturwiss.*, **27** (1939), 230; *Z. Physik*, **114** (1939), 53.

(c) W. van der Grinten: *ibid.*, **27** (1939), 317.

(d) P. Debye: *Ann. Physik*, **36** (1939), 284.

(e) J. Bardeen: *Phys. Rev.*, **57** (1940), 35; **58** (1940), 94.

In the following paragraphs, therefore, the necessary conditions for the construction of the apparatus for measuring the thermal diffusion coefficient was discussed by the aid of the theory of Debye.

According to him, when the "equilibrium," or stationary state, is established in the solution, the concentration n' and n of the solute at the upper and the lower points, which lie apart from h vertically, are given, neglecting some small terms, by Eq. (1),

$$\ln\left(\frac{n'}{n}\right)_{t=\infty} = \frac{q/120}{1+q^2/10080} \cdot \frac{D'}{D} \tau \frac{h}{a}, \quad (1)$$

and

$$q = \frac{\beta g \rho \tau}{6\mu D} a^3 \quad (2)$$

g = acceleration of the gravity, β = coefficient of expansion of the solution, ρ = density, μ = viscosity, τ = temperature difference of the wall, and a = breadth between the equidistant walls.

At time t when the stationary state is not established, n'/n can be expressed, on the conditions that $n'/n \simeq 1$ and the apparatus has no reservoirs at either end, as:

$$\frac{n'}{n} = 1 + \frac{q/120}{1+q^2/10080} \cdot \frac{D'}{D} \tau \frac{h}{a} \left[1 - \frac{8}{\pi^2} \sum_{\nu=0}^{\infty} \frac{\exp\left\{-\frac{(2\nu+1)^2 t}{\Theta}\right\}}{(2\nu+1)^2} \right], \quad (3),$$

where Θ is defined by:

$$\Theta = \frac{h}{\pi^2 D} \frac{1}{1+q^2/10080}, \quad (4)$$

and is called "Time of relaxation", which gives the order of the time of attainment of the stationary state.⁽¹⁴⁾

In case of an apparatus with reservoirs, some approximate formulae^{(13b) (13e)} have been derived. In this paper it is assumed from the elementary consideration that, if the volume of the larger reservoir (V_l) is much larger than that of the solution flowing into the reservoir per unit time (F), Θ is enlarged by the factor V_l/F . If the relaxation time in the apparatus with reservoirs be denoted as Θ' , it is expressed by the above definition as:

$$\Theta' = \Theta \cdot V_l / F. \quad (5)$$

The flow velocity of the solution at a point x toward the vertical direction was given by Debye, as,

$$v = \frac{\beta g \rho \tau}{6\mu} a^2 \left(\frac{x}{a} - \frac{1}{2} \right) \left[\frac{1}{4} - \left(\frac{x}{a} - \frac{1}{2} \right)^2 \right], \quad (6)$$

where the co-ordinate was selected so that the walls of the higher and the lower temperatures were the planes of $x = 0$ and $x = a$, respectively.

(14) Numerically, Θ denotes the time when $[n'/n-1]$, attains to the value of 70.18% of $[(n'/n)-1]$ as it follows from the easy calculation.

Then F is given by the definition as,

$$F = \frac{s}{a} \int_{\frac{a}{2}}^a v dx = s \frac{\beta g \rho \tau}{6\mu} a^2 \frac{1}{64} \quad (7)$$

where s is the area of the horizontal cross section between the walls.

It should be borne in mind here that the important approximations included in the derivation of these equations are the constancy of β , μ , D' and D against the change of temperature and of concentration and that q is a dimensionless quantity.

III. On the Construction of the Thermal Diffusion Apparatus.

Among the quantities which are contained in Eqs. (1) and (4), ρ , μ and β , except D and D' , are all easily measurable and a and τ determinable from the apparatus used. Therefore, the measurement of Θ and of n'/n may give us both D and D' simultaneously in principle, though we must take account of the following difficulty in carrying out the above plan practically in case of a liquid solution.

It can be shown easily from Eqs. (1), (2) and (4) that n'/n becomes maximum, when $q \simeq 100$, and in case of a liquid solution Θ becomes very large, if n'/n takes its maximum value. For example, if we assume $D = 10^{-5}$ cm²/sec., and $h = 100$ cm., Θ will be 5.5×10^2 days (cf. Debye, *l.c.*). Moreover, if the apparatus with reservoirs is used, it requires more time to attain the stationary state. This conclusion was confirmed qualitatively by the experiments of Wirtz and Korsching.⁽¹²⁾ Such being the case, it seems practically impossible to measure D' by the use of the thermal diffusion apparatus of Clusius and Dickel, even if the concentration change produced be by no means small.⁽¹⁵⁾

We can also derive, however, from Eq. (4) that in case of large q , Θ becomes small, and that in such a case Eqs. (1) and (4) are modified into simpler forms as;

$$\ln\left(\frac{n'}{n}\right)_{t=\infty} = \frac{504}{\beta g \rho} \frac{\mu h}{a^4} D', \quad (1a)$$

$$\text{or} \quad \left(\frac{n'}{n}\right)_{t=\infty} = 1 + \frac{504}{\beta g \rho} \frac{\mu h}{a^4} D' \quad \text{if } n'/n \simeq 1, \quad (1a')$$

and

$$\Theta = \frac{h^2}{\pi^2 D} \frac{7680}{q^2} = \frac{h^2}{\pi^2 a^6} \times 7680 \left(\frac{6\mu}{\beta g \rho \tau}\right)^2 D. \quad (4a)$$

As it can be derived from Eqs. (1a), (4a), (6) and (5) that $\ln(n'/n)$, Θ and Θ' are proportional to $1/a^4$, $1/a^6$ and $1/a^8$,⁽¹⁶⁾ respectively, we can make Θ and especially Θ' very small without making n'/n small to the same degree, by increasing a slightly. Besides, we find the following

(15) In water solution and with temperature difference of 60°C., q takes the value of 100, when $a \simeq 0.1$ mm. Therefore, there exists a technical difficulty, besides, to use an apparatus which produces a large separation.

(16) It is assumed that s is constant.

three important advantages in making the wall distance of the apparatus small:

(a) As D' and D appear in Eqs. (1a) and (4a) separately, these can be determined independently from each other.

(b) As τ does not appear in Eq. (1a), only small errors arise in the D' values, even if the temperature of the solution at the walls cannot be measured accurately owing to the existence of the temperature gradient in the walls as well as the existence of a fluid film adhered to the wall surface.

(c) The small degree of separation, or $n'/n \approx 1$, favours the approximation included that β , μ , D and D' are constant against the concentration change.

From these reasons the author constructed an apparatus made of glass with a wall distance of 1.50 mm. and was able to measure the D' of liquid solutions directly, attaining the stationary state in a few hours.

IV. Performance of the Experiments. (a) Apparatus:—

Thermal diffusion column of the type, as shown in Fig. 1, was used. The column was made of Terex glass (Boron glass) except the cooling mantel. Carbon tetrachloride (b.p. 76°C .) put in the innermost tube was boiled by electrical heatings, so that the wall of the tube served as the hotter wall, while the outer tube was kept cool at 25°C . (the mean value) from outside, thus the temperature difference is 51°C . The temperatures in the cooling mantel are regulated so as to be 20°C . and 30°C . at the entrance and at the outlet of the mantel, respectively, by the adjustment of both, the flow velocity of cooling water and the degree of the heating. These temperatures could be made constant within $\pm 0.5^\circ\text{C}$.

The internal diameter of the outer tube and the outer one of the inner tube were 1.78 and is 2.08 cm., respectively; thus the annular breadth of the equidistant walls is 1.50 mm. The length of the walls which have the annular space (89 c.c.), is 94 cm., while the volumes of the reservoirs at the top and the bottom of the column were 100 and 23 c.c., respectively. In the experiments, the solution was introduced to the mark M, so that 28 c.c. of the solution was contained in the top reservoir.

The solution in the top reservoir was inclined to become warm and to interrupt the counter flow in the column there. This could be prevented by cooling it from the outside with tap water through a coil made of lead (not shown in the figure).

(b) *Samples*:—Materials, as described in Table 1, were diluted with, or dissolved in distilled water.

(c) *Procedures*:—After the sample was introduced to the mark of the

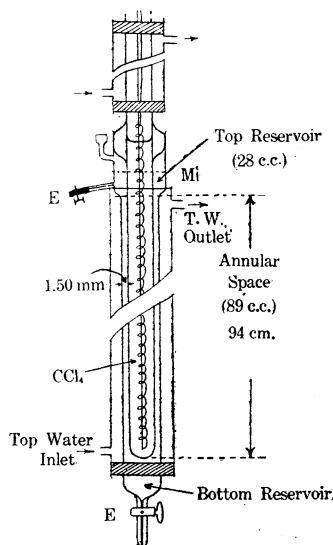


Fig. 1. Thermal Diffusion Apparatus.

apparatus, and the temperature of the cooling water was regulated at 20°C., the heating of carbon tetrachloride in the innermost tube was started; the temperature distribution in the apparatus became stationary in several minutes. At a fixed time from the beginning of heating, it was stopped, and the contents of the reservoirs were taken out from the outlets E' and E''. After they gained the room temperature, several c.c. of samples were pipetted out and were titrated or dried up to determine the concentration in accordance with the methods as described in Table 1.

(d) *Experimental Results*:— Observed values were expressed by the separation ratio n'/n , or a ratio of the concentration at the bottom reservoirs to that at the top. Plots of the measured $(n'/n-1)$ values against the hours elapsed and lines representing the theoretical ones which were determined according to the process as described in V (b), are all shown in Fig. 2, where the ordinate of NaOH is half scaled.

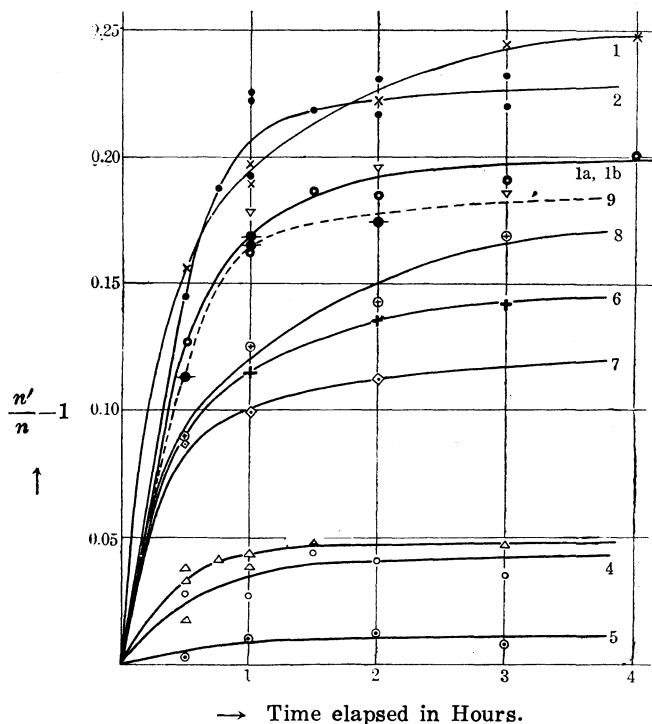
Table 1. Experimental Results.

No.	Solute (conc.)	Materials Used	Analytical Method	θ'_s (hr.)	$\left(\frac{n'}{n}\right)_{t=\infty}$	$D' \times 10^{-7}$ (cm ² /sec. deg.)
1	HCl (1 N)	Commercial pure subst. purified by destil.	Alkalimetry	0.75	1.24 ₈	1.7
1a 1b	HCl (0.1 N) " "	"de Häen" Fixanol	" "	0.7	1.19 ₈	1.5
2	H ₂ SO ₄ (1 N)	Commercial pure subst.	" "	0.5	1.23 ₀	1.7
3	NaCl (1 N)	"Shika" Extra pure	Precipitation Analysis	0.5	1.04 ₈	0.4
4	KCl (1 N)	"Shika" Extra pure	" "	0.9	1.04	0.3
5	NH ₄ Cl (1 N)	"Shika" Extra pure	" "	0.6	1.01 ₀	0.08
6	Na ₂ SO ₄ (1 N)	"Shika" Extra pure	Gravitation Analysis	0.75	1.14 ₅	1.1
7	CuSO ₄ (1 N)	"Merck" Extra pure	Iodimetry	0.5	1.12	0.7
8	Na ₂ CO ₃ (1 N)	"Shika" Extra pure	Acidimetry	1	1.17	1.2
9	NaOH ⁽¹⁷⁾ (1 N)	"Shika" Guaranteed	" "	0.5	1.3 ₇	2.6

(17) The accuracy of $(n'/n)_{t=\infty}$ is worse than that of the other solutes, but that of D' is not so, because of the large value of the separation. However, there is another source of errors, i.e., the existence of a small quantity of Na₂CO₃ (0.03N) mixed in the material used. The error thus produced may not be negligible [cf. ref. (21)].

V. Discussions. (a) It was observed that in every solutions, the stationary state was reached in such a short period of few hours, as was predicted theoretically in III. The separation ratios were, however, small comparing with that of Korsching and Wirtz⁽¹²⁾, who continued their experiment for one or two days using an apparatus with a wall distance of 0.25 mm., a wall length of 90 cm. and with no reservoirs. Although the values of n'/n were smaller in this experiments, they were large enough to determine the D' values. It was thus shown that the apparatus was suitably constructed for the object.

(b) We are now going to examine the experimental results obtained with respect to the systems of 1 N HCl, 0.1 N HCl and 1 N H₂SO₄ in details before D' values are calculated for every solution.



1 $\times$ HCl, 2 $\bullet$ H₂SO₄, 3 $\triangle$ NaCl, 4 $\circ$ KCl, 5 $\odot$ NH₄Cl, 6 $+$ Na₂SO₄,
7 $\diamond$ CuSO₄, 8 $\oplus$ Na₂CO₃, 9 $\bullet$ NaOH, 1a $\circ$ HCl (0.1 N), 1b ∇ HCl (0.1 N).
Concentrations are all one normal, if otherwise stated.

Fig. 2. Experimental Values.

To begin with, q 's which were defined by Eq. (2) were calculated by taking the viscosity of pure water as 0.00549 at 50°C. and by the use of the constants as described in Table 2, and was found to be much larger than 100 as shown in Table 3. So, by Eq. (4a) instead of Eq. (4), Θ 's, the time of relaxation in case of an apparatus without reservoirs, were calculated and found to be 90, 59, and 45 sec. for 1 N HCl, 0.1 N HCl and 1 N H₂SO₄, respectively. These were smaller by the factor 10^2 than the value observed, though it was natural to get such a result.

Then, F was calculated by Eq. (7), assuming that s equals to $2\pi r$ times a , where r is the mean of the outer radius of the inner tube and the inner radius of the outer one. As it was shown that F was smaller by the same factor than V_l , Θ' was calculated by Eq. (5), as shown in Table 3, i.e., 2.1×10^2 , 1.3×10^2 and 1.0×10^2 min., respectively. The agreement of Θ' with experiments was fairly good.

Table 2. Constants of Solutions (50°C.)
(Taken from Int. Crit. Tables and Landolt-Börnstein's Tables.)

No.	Solution	Specific Viscosity μ^*	Coefficient of Expansion β	Density	Diffusion ⁽¹⁸⁾ coefficient D
1	1 N HCl	1.10	4.5×10^{-4}	1.006	5.8×10^{-5}
1a, b	0.1 N HCl	1.00 *	4.5 *	1.002	4.6
2	1 N H ₂ SO ₄	1.19	5.0	1.019	3.2
3	1 N NaCl	1.01	4.8	1.03	—
4	1 N KCl	1.04 **	4.8	1.03	—
5	1 N NH ₄ Cl	1.02	4.5	1.00	—
6	1 N Na ₂ SO ₄	1.23	4.9	1.05	—
7	1 N CuSO ₄	1.40 **	4.2	1.08 **	—
8	1 N Na ₂ CO ₃	1.31 **	5.1	1.04 **	—
9	1 N NaOH	1.24	4.9	1.03	—

* The value of the pure water was substituted.

** Extrapolated values from the lower temperatures.

Table 3. Calculated Values.

	q	θ (sec.)	F (c.c.)	Θ' (min.)	D (cm ² /sec.)
Eqs. used in the calculation.	(2)	(4a)	(6)	(7)	(4a), (7)
1 N HCl	3.6×10^4	90	0.20	2.1×10^2	1.2×10^{-5}
0.1 N HCl	5.0	59	0.22	1.3	1.6
1 N H ₂ SO ₄	6.9	45	0.21	1.0	1.0

Then the thermal diffusion constant was calculated from the experimental data according to the following procedures, assuming that Θ' could be substituted for Θ : (i) to select Θ so as to give a straight line if n'/n were plotted against $\left\{1 - \frac{8}{\pi^2} \sum_{\nu=0}^{\infty} \frac{\exp.[-(2\nu+1)^2 t/\Theta]}{(2\nu+1)^2}\right\}$, (ii) to extrapolate the n'/n values at $t/\Theta = \infty$ from Eq. (3); (iii) to determine D' by Eq. (1). D' thus determined was shown in Table 1, together with the selected value of Θ' (denoted as Θ'_s).

As there exist no available data of D' for comparison at present, the calculated values of D'/D , or S.C., were compared with the ones calculated from the data of various workers^{(6),(7),(8)} in Table 4, where D values used for the calculation were extrapolated from the recent measurements of Gordon and co-workers⁽¹⁸⁾. Considering that temperatures are not perfectly coincident, the agreement can be said to be satisfactory.

(18) W. J. James and A. R. Gordon: *J. Chem. Phys.*, **7** (1939), 963 [HCl]; E. A. Hollinshead and A. R. Gordon: *ibid.*, **8** (1940), 423 [H₂SO₄].

Table 4. Soret Constants.

Solute	Concentration	Temperature		Soret Const. $\times 10^{-3} \left(\frac{1}{\text{deg.}} \right)$	Author
		Range	Mean		
HCl	1 N	23~30°C	25°C	2.94	Chipman
	"	27~67	47	2.3	Arrhenius
	"	26~41	33	5.6	Tanner
	"	25~76	50	2.9	The present author
HCl	0.1 N	23~30	25	2.1	Chipman
	"	25~76	50	3.3	The present author
H ₂ SO ₄	1 N	26~41	33	9.9	Tanher
	"	25~76	50	5.6	The present author

Experimentally, Θ' could also be determined by the time when $(n'/n - 1)$ was 70.18% of $(n'/n - 1)_{t \rightarrow \infty}$ ⁽¹⁹⁾. The values, denoted as Θ'_0 , were 0.7, 0.6 and 0.55 hour for 1 N HCl, 0.1 N HCl and 1 N H₂SO₄, respectively.

The ordinary diffusion coefficient could also be calculated from Eqs. (4a), (5) and from the selected Θ'_s (or Θ'_0 's), but it gave only the order of magnitude, as shown in Tables 2 and 3; this is perhaps due to the approximation included in Eq. (5). Notwithstanding, there is still some promise in applying this method, if we use an apparatus with no reservoirs, to the determination of D which is also difficult to be measured by the methods hitherto adopted.

It seems to be confirmed that the experimental results obtained are reasonable from both, the theoretical and the experimental points of view, but taking the several approximations included in consideration, this method might not give rigorously the absolutely correct values of D' , although it would give the relative ones.

(c) As q 's were also found to be much larger than 100 in case of other solutions, D' values were calculated according to the same procedure as described in (b), and were shown in the last column of Table 1. However, a comparison of the results in S.C. cannot be attempted, because there are no sufficiently accurate data of D at 50°C. for most of the salts at present.

Generally speaking, it was observed, (i) that a NaOH solution has very large D' , (ii) that the solutions (HCl and H₂SO₄) which contain H⁺ ion have comparatively larger D' values, and (iii) that the solutions (NaCl, KCl, and NH₄Cl) which contain Cl⁻ ion and univalent cation have smaller values. The above tendencies were known already by many workers^{(6),(7),(8)} with respect to the Soret effect. However, this coincidence is more or less to be expected, because the difference of D of inorganic substances is not so large as that of D' (from each other). Intermediate values were observed for sulphates and carbonates (Na₂CO₃, Na₂SO₄ and CuSO₄), while S.C. of CuSO₄ did not always accord so exactly to the measurement of some workers, e.g., an extraordinarily large value was observed by Arrhenius^{(7),(1)}.

(19) See the footnote at II.

While these results suggest, at least, that the thermal diffusion is a characteristic property of ions, an attempt to relate the degree of separation with the hydration of the ions in the solutions seems to be difficult, because the D' values of Na_2CO_3 is comparable to that of Na_2SO_4 , which is more hydrated. Similarly, Hiby and Wirtz,⁽²⁰⁾ who measured the S.C. by use of the thermal diffusion apparatus (wall distance: 0.25 mm.; wall length, 10 cm.) and indicated that their method also gave reasonable S.C. values in magnitude, pointed out the same difficulty from the experimental ground; S.C. of all lithium salts used was not large, though they were known to be much hydrated in the solution, and that the opposite result would be obtained, if there was any correspondence between S.C. and the degree of hydration.

Conspicuously large D' value of NaOH seems to be noteworthy, as acids are usually more anomalous than bases in the other properties, e.g., electrical conductivity.

Now, a series of measurements is being carried out in order to study the nature of the Ludwig-Soret effect further, and a part of the result with mixed electrolytes has been already published.⁽²¹⁾

Summary.

(1) It has been shown that the thermal diffusion apparatus of Clusions and Dickel with a comparatively large wall distance is suitable for the determination of the thermal diffusion coefficient of liquid solutions.

(2) The separations of some inorganic solutions (HCl , H_2SO_4 , NaCl , KCl , NH_4Cl , Na_2CO_3 , Na_2SO_4 , CuSO_4 and NaOH) have been carried out.

(3) The observed results have been shown to be in concordance with the theory of Debye and to give reasonable Soret constants if compared with those, hitherto, directly measured.

(4) The thermal diffusion coefficient of each solution has been determined, and from these values the nature of the thermal diffusion has been discussed to some extent.

In conclusion, the author wishes to express his hearty thanks to Dr. Y. Yoshimura, Director of the Department, for his encouragements and interest throughout this research.

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