BULLETIN OF THE
CHEMICAL SOCIETY OF JAPAN

The Absorption Spectra of Nitrocellulose.

By Kôiti MASAKI.

(Received October 30th, 1936.)

On account of the lack of a suitable solvent it has been hard to obtain the ultraviolet absorption spectra of nitrocellulose. B. Rassow and W. Aehnelt[1] used ether-alcohol as the solvent, but the maximum concentration was only 2 g. in 1000 c.c., namely, 7.94×10^{-3} mol as regards the dinitroglucose unit. Therefore, the characteristic absorption of nitrocellulose remains yet undiscovered, and the linear end-absorption has not been interpreted. Considered from the author's previous consideration, the selective absorption might be observed at a higher concentration or with a thicker layer. A good result has been obtained by using clear films of nitrocellulose prepared with a suitable solvent, instead of solutions, which appeared extremely difficultly to be raised to a concentration higher than Rassow's case. By the film method it was easy to obtain two absorptions (3300–2500 Å and below 2500 Å) which may be reasonably attributed to the nitro-groups as the case of nitroglycerine.[2]

Experimental. The preparation of good films depends chiefly on the selection of the solvent and on the technique of evaporation. Since the solvent remains in films in amounts of a few percent, it must not absorb above 2200 Å. The author used ether-alcohol (80 g. ether and 40 g. alcohol for 2 g. of nitrocellulose) or acetone as the solvent. The mixture of nitrocellulose and the solvent was frequently stirred or shaken so as to bring the suspended nitrocellulose into solution. After standing overnight, 10 c.c. of the filtered solution was spread over the surface of mercury. The liquid film was gradually evaporated to a clear solid film by evacuation in the course of a few days. Different numbers of films of about 1/100 mm. thickness were placed between two quartz plates. From the weight, the area, and the density (1.65), of the films, the thickness was computed. The experiments were carried out in the same way as in the case of nitroglycerine except that exposure time was 7 minutes. In the accompanying figure the logarithm of relative thickness is plotted against the wave number. From the figure, it is established that there are two absorptions.

(1) *Cellulosechem.*, **10** (1929), 163.
(2) This Bulletin, **11** (1936), 712.

Table 1 (Curve 1). Films prepared with acetone. Ilford Special Rapid Panchromatic Plates.

Thickness d (mm.)	log d	log of relative thickness* log D	Wave length (Å)	Wave number (mm.$^{-1}$)
0.245	$\bar{1}$.389	3.506	3185	3139
0.223	$\bar{1}$.348	3.465	3125	3199
0.200	$\bar{1}$.301	3.418	3075	3251
0.161	$\bar{1}$.207	3.324	3000	3332
0.104	$\bar{1}$.017	3.134	2869	3482
0.060	$\bar{2}$.778	2.895	2745	3642
0.051	$\bar{2}$.708	2.825	2647	3777
0.046	$\bar{2}$.663	2.780	2603	3841
0.023	$\bar{2}$.362	2.479	2460	4070

Table 2 (Curve 2). Films prepared with ether-alcohol. Ilford Special Rapid Panchromatic Plates.

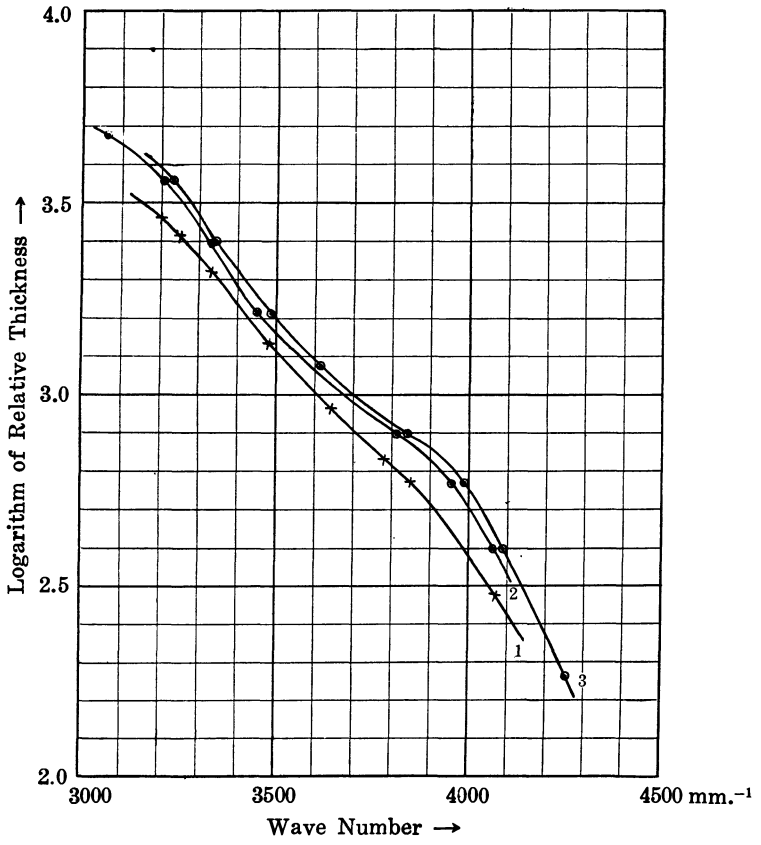
0.549	$\bar{1}$.740	3.857	—	—
0.450	$\bar{1}$.653	3.770	3754	2663
0.359	$\bar{1}$.555	3.672	3265	3062
0.273	$\bar{1}$.436	3.553	3101	3224
0.130	$\bar{1}$.279	3.396	2994	3339
0.124	$\bar{1}$.093	3.210	2891	3458
0.060	$\bar{2}$.778	2.895	2630	3816
0.030	$\bar{2}$.477	2.594	2459	4066

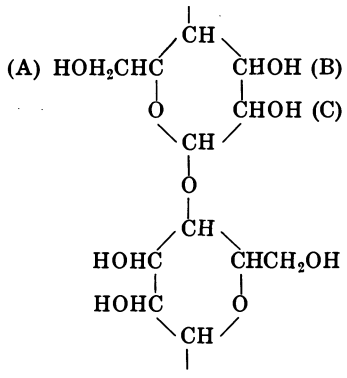
Table 3 (Curve 3). Films prepared with ether-alcohol. Ilford Schumann Plates.

0.273	$\bar{1}$.436	3.553	3089	3236
0.190	$\bar{1}$.279	3.396	2992	3341
0.124	$\bar{1}$.093	3.210	2867	3487
0.090	$\bar{2}$.954	3.072	2765	3616
0.060	$\bar{2}$.778	2.895	2600	3845
0.045	$\bar{2}$.653	2.771	2512	3980
0.030	$\bar{2}$.477	2.594	2444	4090
0.014	$\bar{2}$.146	2.263	2348	4258

* The equivalent thickness of N/2000 of the dinitroglucose unit, calculated from Beer's law. ($\log D = \log d + 4.117$)

Discussion. Considered from the molecular structure it is obvious that these absorptions of nitrocellulose must be attributed to the nitro-groups. When the molecular weight of nitroglucose unit in nitrocellulose divided by the number of nitro-groups is taken as one gram mol, the absorption intensity of nitrocellulose ($\log \varepsilon = 1.1$)[2] is very nearly coincident with the cases of the other nitro-esters and nitro-compounds. If the hydroxyl-groups in the glucose structure considered as the unit of cellulose are marked A, B, and C, as shown in the formula, the combination of AB or of AC may be the most possible for the positions of two nitro-groups in the case of nitrocellulose containing 11%





nitrogen, because a structure with a considerable distance between the two nitro-groups is probably more stable on account of a small interaction between them. It is, therefore, reasonable that the experiments are in excellent agreement with the values calculated for the absorption due to nitro-groups.

In the case of the nitrocellulose of a higher nitrogen content, the absorption seems to remain unchanged as in the case of nitroglycerine, because each of nitro-groups combines indirectly with a different carbon atom by a bridge of an oxygen atom and moreover may also maintain mutually a considerable distance in order to minimize the interaction.

The general discussion will be given later.

Synthetische Versuche in der Selenophen-Gruppe. III. β-Nitroselenophen und die Orientierung im Selenophen-Kern.

Von Sumio UMEZAWA.

(Eingegangen am 14, November 1936.)

Wenn in ein Monosubstitutionsprodukt des Selenophens ein zweiter Substituent eingeführt wird, so hängt es, wie beim Furan[1] und Thiophen[2], von der Konkurrenz zweier Faktoren ab, in welche Stelle der zweite Substituent dirigiert wird, d. h. einmal von der Natur des vorhandenen Substituenten, die auch in der Benzolreihe vorherrschend ist, dann aber auch von der grösseren Reaktionsfähigkeit der α- gegenüber den β-Wasserstoffatomen, mit anderen Worten von der nach den α-Stellen dirigierenden Kraft des Hetero-atoms.

Auf Grund dieses Satzes ist man imstande zu erschliessen, welche Isomeren sich als Haupt- und Nebenprodukte bilden müssen, wenn ein Substituent in ein mit einem solchen erster Ordnung substituiertes Selenophen eintritt. Wenn also ein 2-Halogenselenophen[3] weiter halogeniert oder nitriert wird, so entsteht 2,5-Dihalogenselenophen[3] oder 2-Halogen-5-nitroselenophen[4]; denn die Einflüsse des vorhandenen Halogen- und Selen-atoms liegen in derselben Richtung. Ebenso kann das 2-Halogen-3,5-dinitroselenophen[4] beim weiteren Nitrieren des 2-Halogen-5-nitroselenophens dargestellt werden. In demselben Sinne kann man die Bildung der 3,5-substituierten Selenophene eindeutig erschliessen, wenn an einer β-Stelle mit einem Substituenten zweiter Ordnung substituierte Selenophene weiter substituiert werden. Bei der weiteren Nitrierung des 3-Nitroselenophens entsteht also das 3,5-Dinitroselenophen (III) (siehe später).

Was aber die Orientierung des zweiten Substituenten betrifft, welcher in ein an einer α-Stelle mit einem Substituenten zweiter Ordnung besetztes Selenophen eingeführt ist, so muss man es experimentell nachweisen.

Ich habe mich deshalb mit Selenophen-2-sulfochlorid[4] und ihren Nitroprodukten weiter beschäftigt, einerseits um über die Substitutionsregeln in der Selenophenreihe klarer zu sehen, andererseits um die Konstitutionsbeweise klar zu stellen.

---

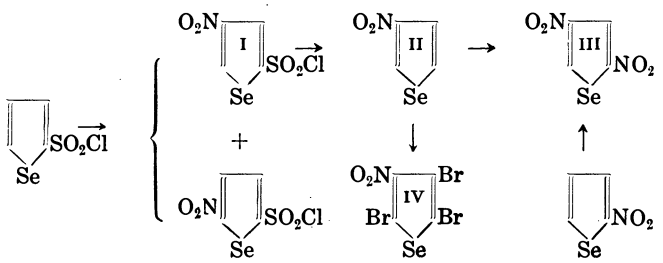
(1) H. Gilman und G. F. Wright, *Chem. Rev.*, **11** (1932), 323.

(2) W. Steinkopf und T. Höpner, *Ann.*, **501** (1933), 180; I. J. Rinks, *Rec. trav. chim.*, **53** (1934), 643.

(3) H. Suginome und S. Umezawa, dieses Bulletin, **11** (1936), 160.

(4) S. Umezawa, II. Mitteilung, dieses Bulletin, **11** (1936), 775.

Nitriert man bei tiefer Temperatur das Selenophen-2-sulfochlorid mit rauchender Salpetersäure, so entstehen Nitrosulfochloride, die aus zwei Ortsisomeren bestehen, von denen ich nur den höher schmelzenden einheitlich trennen konnte. Wenn man dann das letztere, 3-Nitroselenophen-5-sulfochlorid vom Schmelzp. 71–73.5° (I) nach der Spaltungsmethode, bei der Steinkopf und Höpner[2] in der Thiophenreihe schönen Erfolg hatten, in starker Schwefelsäurelösung bei 130–140° mit überhitzem Wasserdampf behandelt, so entsteht das β-Nitroselenophen vom Schmelzp. 77–78.5° (II) durch Abspaltung der α-Sulfonsäuregruppe. Bemerkenswert ist, dass, trotz der bisher bekannten Unbeständigkeit des Selenophenkerns gegenüber thermischer Behandlung, diese Reaktion sehr glatt verläuft und die Ausbeute 79 Proz. beträgt.



Beim Behandeln mit rauchender Salpetersäure lässt das β-Nitroselenophen sich zum 3,5-Dinitroselenophen nitrieren, welches mit dem bei weiterer Nitrierung aus α-Nitroselenophen entstandenen Dinitroderivat identisch ist.

Auf Grund der oben beschriebenen Tatsachen ist man imstande, für Substituenten zweiter Ordnung folgende Substitutionsregel beim Selenophen anzugeben: Wenn in einem an 2-Stelle besetzten Selenophen ein zweiter Substituent eingeführt wird, so tritt der letztere überwiegend in die 4-Stelle ein. Dabei entsteht keine oder nur in sehr geringer Menge eine 2,5-Verbindung. Infolgedessen ist durchaus wahrscheinlich, dass in der Selenophendisulfonsäure[4], die durch direkte Sulfonierung aus Selenophen erhalten ist, die Sulfonsäuregruppen die 2- und 4-Stellen einnehmen.

Es scheint hier von Interesse, die Orientierungseinflüsse der Heteroatome in Furan, Thiophen und Selenophen zu vergleichen. Nach Gilman und Wright[1] führt die direkte Kernsubstitution eines Mono-α-derivats des Furans zur Bildung eines α,α-Derivats, anscheinend unter Ausschluss eines α,β-Derivats. In Bezug auf die Substitutionsregeln beim Thiophen haben Steinkopf und Höpner[2] für Substituenten zweiter Ordnung geschlossen, dass bei besetzter 2-Stelle ein neuer Substituent in 4- und 5-Stelle eintritt, wobei 2,4-Verbindung meist an Menge überwiegt. Beim Selenophen tritt, wie schon erwähnt, der zweite Substituent hauptsächlich in die 4-Stelle ein. Dabei

kann man die 2,5-Verbindung nicht oder nur in sehr geringer Menge finden. Besonders entsteht kein 2,5-Dinitroselenophen beim Nitrieren von 2-Nitroselenophen. Es ist also bemerkenswert, dass eine Neigung über die Grösse der Orientierungseinflüsse von Hetero-atomen: Furan $\gg$ Thiophen $>$ Selenophen, in Übereinstimmung mit periodischer Beziehung, beobachtet wird[6].

Das β-Nitroselenophen ist der einzige β-substituierte Selenophenkörper, der weitaus beständiger als das α-Nitroselenophen ist und sich am Lichte nicht färbt. Mit Alkohol und Alkali zeigt es keine Farbenreaktion wie das α-Nitroselenophen. Daraus folgt, dass diese Farbenreaktion nicht von der Stelle der Nitrogruppe, sondern von der Zahl abhängt. Das β-Nitroselenophen lässt sich zum 2,3,5-Tribrom-4-nitroselenophen vom Schmelzp. 100.5–102° (IV) erschöpfend bromieren, beim α-Nitroselenophen aber gelang es mir infolge seiner Unbeständigkeit nicht.

Beim Reduzieren der 2,4-Disulfonsäure mit Natriumamalgam—eine von Steinkopf[5] in der Thiophenreihe ausgeführte Reaktion—wurde die α-ständige SO_3H-Gruppe nicht eliminiert, es fand nur Zersetzung statt.

Was das α-Nitroselenophen anbelangt, so habe ich schon in der zweiten Mitteilung[4] mitgeteilt, dass durch direkte Nitrierung des Selenophens Rohnitroselenophen vom Schmelzp. 38–42° gewonnen wurde. Bei der Behandlung des letzteren mit überschüssigem Brom wurde das 2,3,5-Tribrom-4-nitroselenophen (IV) isoliert. Infolgedessen zeigt es sich, dass wie beim Thiophen[2] der erste Substituent zweiter Ordnung nicht nur überwiegend in einer α-Stelle, sondern auch in geringer Menge in einer β-Stelle zu finden ist.

Es sei mir an dieser Stelle erlaubt, Herrn Prof. H. Suginome für die Überlassung dieser Arbeit, sowie für Anregungen und Ratschläge meinen verbindlichsten Dank auszusprechen. Gleichzeitig bin ich für Unterstützung der Kaiserlichen Akademie zu Dank verpflichtet.

Beschreibung der Versuche.

4-Nitroselenophen-2-sulfochlorid (I). 6 g. Selenophen-2-sulfochlorid werden in 20 c.c. rauchender Salpetersäure unter Umschütteln im Eiswasser nach und nach eingetragen. Die klare Reaktionslösung wird bei Zimmertemperatur etwa 20 Minuten stehen gelassen und dann in Eiswasser gegossen, wobei das Rohprodukt zu einem halbfesten Zustande erstarrt. Abgesaugt, mit Wasser gewaschen und getrocknet. Ausbeute 6.6 g. Schmp. 35–59°. Vor dem Umkrystallisieren wurden es analysiert. (Gef.: N, 5.25. Ber. für $C_4H_2O_4NClSSe$: N, 5.10%.) Es wurde dabei klar, dass in dieser Reaktion das 4-Nitroselenophen-2-sulfochlorid mit einem Ortsisomer, 5-Nitroselenophen-2-sulfochlorid beigemengt entsteht.

(5) W. Steinkopf, H. Jacob und H. Penz, *Ann.*, **512** (1934), 149.

(6) Siehe auch Suter, McKenzie und Maxwell, *J. Am. Chem. Soc.*, **58** (1936), 717.

3 g. des Präparats wurden aus Schwefelkohlenstoff viermal umkrystallisiert und nochmals analysiert. Prächtige, schwach-gelbe, säulenförmige Kryställchen. Schmp. 71-73.5°. Ausbeute 0.6 g. (Gef.: C, 17.45; H. 0.98; N, 5.19. Ber. für $C_4H_2O_4NClSSe$: C, 17.49; H, 0.73; N, 5.10%.)

Das 4-Nitroselenophen-2-sulfochlorid ist schwer löslich sogar auf dem Siedepunkte in Petroläther (40–60°), wie in Tetrachlorkohlenstoff in der Kälte. Am Lichte ist es ganz beständig und lässt sich im Exsikkator über Chlorcalzium ohne Zersetzung aufbewahren.

β-Nitroselenophen (II). (Konstitutionsermittlung des 4-Nitroselenophen-2-sulfochlorids). 5 g. 4-Nitroselenophen-2-sulfochlorid werden mit 25 c.c. Wasser durch Kochen unter Rückfluss hydrolysiert, was etwa eine Stunde in Anspruch nimmt. Die Lösung der freien 4-Nitroselenophen-2-sulfonsäure wird mit einer Mischung von 35 c.c. konzentrierter Schwefelsäure und 20 c.c. Wasser versetzt, zum Sieden erhitzt, dann mit überhitzem Wasserdampf destilliert. Die Reaktionslösung färbt sich allmählich dunkelbraun und bei 130-140° (in der siedenden Flüssigkeit) scheidet sich allmählich eine grosse Menge von schönen, farblosen Nädelchen im Kühler aus. Diese Spaltung durch überhitzen Wasserdampf nimmt etwa eine Stunde in Anspruch. Man saugt diese Kryställchen ab, wäscht sie mit Wasser und trocknet sie über Chlorcalzium. Schmp. 74–78°. Ausbeute 2.5 g., 79% der Theorie. Umkrystallisiert aus Alkohol. Farblose, aufgeschichtete Täfelchen. Schmp. 77–78.5°. (Gef.: N, 8.01; Se, 45.06. Ber. für $C_4H_3O_2NSe$: N, 7.95, Se, 44.89%.)

Krystallisiert man aus Petroläther (40–60°) um, so scheiden sich Nädelchen aus. β-Nitroselenophen färbt sich nicht am Lichte und ist im allgemeinen weitaus beständiger als α-Nitroselenophen. Mit Isatin und Schwefelsäure zeigt es keine Indopheninreaktion. Wird es mit wässerigen Alkalien gekocht, die es in der Kälte nicht lösen, so löst es sich mit braunroter Färbung auf. Mit Methanol und Kalilauge zeigt es keine Färbung.

2,4-Dinitroselenophen (III) aus 3-Nitroselenophen. 0.7 g. 3-Nitroselenophen werden in 2 c.c. rauchender Salpetersäure unter Umschütteln im Kältegemisch portionsweise eingetragen, wobei eine heftige Reaktion eintritt. Man lässt das Reaktionsgemisch sich auf Zimmertemperatur erwärmen und giesst es dann in Eiswasser ein. Bei richtiger Nitrierung scheiden sich dabei schwach-gelbe Nädelchen aus. Ausbeute 0.5 g. Schmp. 58–68°. Umkrystallisiert 4-malig aus Ligroin. Schmp. 76–78°. (Gef.: N, 12.83. Ber. für $C_4H_2O_4N_2Se$: N, 12.67%.)

Mischschmelzpunkt mit dem Präparate, das durch weitere Nitrierung aus α-Nitroselenophen erhalten wurde, zeigte keine Depression.

Dinitroselenophen verbindet sich wie Dinitrobenzol oder Dinitrothiophen mit aromatischen Kohlenwasserstoffen. Lässt man eine Lösung molekularer Mengen von Naphthalin und Dinitroselenophen in Benzol langsam verdunsten, so scheidet sich ein in schönen, gelben Nadeln krystallisierter Körper aus. Schmp. 50–53°. Er wurde in kaltem Alkohol gelöst und mit Wasser ausgefällt. Der Körper konnte unter Zusatz von Naphthalin aus Alkohol ohne Zersetzung umkrystallisiert werden und wurde in einen mit Chlorcalzium und Naphthalin beschickten Exsikkator gebracht. Schmp. 53–55°. (Gef.: N, 8.20. Ber. für $C_{14}H_{10}O_4N_2Se$: 8.0_%.) Mit Methanol und Kalilauge zeigt sich sofort schöne Rotfärbung.

2,3,5-Tribrom-4-nitroselenophen (IV). β-Nitroselenophen wird ohne Lösungsmittel mit überschüssigem Brom unter Umschütteln in Eiswasser nach und nach versetzt, wobei sich sehr heftig Bromwasserstoff entwickelt. Lässt man das Reaktionsgemisch unter Ausschluss von Feuchtigkeit einige Tage stehen, so scheidet es gelbe, säulenförmige Krystalle aus. Nach Abpressen auf die Tonplatte werden sie in Schwefelkohlenstoff

aufgelöst, mit sehr verdünntem Natriumcarbonat gewaschen, über Glaubersalz getrocknet und im Vakuum eingedunstet. Ausbeute ist fast quantitativ. Umkrystallisiert aus Alkohol. Schwach-gelbe Fadenbüschel. Schmp. 100.5–102°. (Gef.: N, 3.47; Br, 58.24. Ber. für $C_4O_2NBr_3Se$: N, 3.39; Br, 58.08%.)

Dies erwies sich im Lichte beständig und zeigte keine Farbenreaktion mit Methanol und Alkali.

Chemisches Institut
der Kaiserlichen Hokkaido-Universität,
Sapporo.

Electrolytic Reduction of Maleimide and Pyrroline.

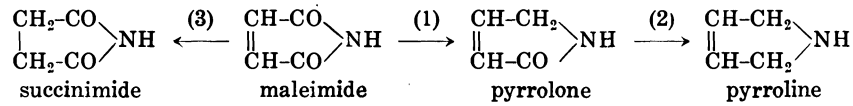
By Buhei SAKURAI.

(Received November 16th, 1936.)

In his recent researches on the electrolytic reduction of succinimide[1] and its derivatives, the present writer observed the remarkable reducing power of zinc amalgam which, when used as the cathode in a strong sulphuric acid solution, could well reduce both carbonyl groups into methylene.

In the electrolysis of pyrrol[2], however, conjugate double bonds were found not to be reduced by zinc amalgam, while the same reduction could easily be brought about by an addition of nickel. With the object of confirming whether such different behaviours of carbonyls and unsaturated carbon atoms towards the cathode are also observable in the radicals contained in a molecule, the electrolytic reduction of maleimide has been attempted.

If the above holds good, maleimide should be reduced in either one of the following ways according to the kind of cathode:



That is to say, if zinc amalgam is used as cathode, pyrroline will be obtained according to (1) and (2) and if reduced nickel is used instead, succinimide must be produced according to (3).

As the result of the experiments it was found that the reaction (3) took place quite smoothly, proceeding quantitatively at lead or copper cathode in dilute sulphuric acid solution, in which reduced nickel was suspended. With

(1) This Bulletin, **10** (1935), 311; **11** (1936), 41.
(2) This Bulletin, **11** (1936), 374.

zinc amalgam cathode, however, no such reaction could be observed, the material having been decomposed into succinic acid and ammonia. For the problem how succinic acid was produced in the above electrolysis two solutions are conceivable:

(1) First maleimide is reduced to succinimide and then decomposed into succinic acid and ammonia in alkaline electrolyte.

(2) Maleimide is first decomposed into maleic acid and ammonia and maleic acid thus produced is then reduced to succinic acid.

If solution (1) be right, pyrrolidone and pyrrolidine must have been produced from succinimide according to the result previously obtained by the present writer. This is, however, contrary to the facts.

Thus solution (2) may be regarded as the more probable, that is, may be taken to occur according to the following scheme:

$$\begin{matrix}\mathrm{CH\text{-}CO}\\ \|\\ \mathrm{CH\text{-}CO}\end{matrix}\!\!>\!\mathrm{NH} \xrightarrow{+2H_2O} \mathrm{NH_3} + \begin{matrix}\mathrm{CH\text{-}COOH}\\ \|\\ \mathrm{CH\text{-}COOH}\end{matrix} \xrightarrow{+2H} \begin{matrix}\mathrm{CH_2\text{-}COOH}\\ |\\ \mathrm{CH_2\text{-}COOH}\end{matrix}$$

As the decomposition was considered to be dependent upon the concentration of sulphuric acid, experiments were repeated with 10% as well as with 30% sulphuric acid. But in no case reduction of carbonyl groups was attained.

Experimental.

Maleimide[3] was prepared by oxidising pyrrol with potassium bichromate and sulphuric acid, and obtained as sublimable brown crystals melting at 93°.

Pyrroline[4] was prepared by reducing pyrrol with zinc dust and hydrochloric acid. It was a colourless liquid with ammonia smell, boiling at 90°.

Nickel catalyser was prepared from nickel hydroxide precipitated by carefully adding a sodium hydroxide solution to nickel sulphate solution, which was first ignited and then reduced at a temperature between 320° and 330° in pure hydrogen gas.

Zinc amalgam electrode was the same that was used in the electrolysis of succinimide.

I. **Reduction of Maleimide with Reduced Nickel.** The electrolysis was undertaken under the conditions as follows: Cathode: lead tube (50 sq. cm.). Catholyte: 100 c.c. of 10% sulphuric acid and 2 g. of maleimide and 0.5 g. of reduced nickel. Anode: lead plate. Anolyte: 10% sulphuric acid. Current density: 12 amp per 100 sq. cm. Current quantity: 38.0 F per mol. Temperature: 28°.

The imide dissolved gradually in the catholyte giving a yellow solution. From time to time the nickel catalyser in the form of finest dust was added to the catholyte. The catholyte and anolyte were separated by a cylindrical vessel of biscuit, and through the cathode tube a rapid current of water was made to pass. Thus the apparatus was well cooled with water from inside and outside and the cathodic solution was stirred vigorously throughout the electrolysis. After 3.5 hours' electrolysis, the catalyser was filtered off

(3) G. Plaucher and F. Cattadori, *Atti. accad. Lincei*, (5), **13** (1904), 489.
(4) Knorr, *Ber.* **34** (1907), 3497.

from the cathodic solution. Extracting the filtrate with ether several times 1.8 g. of colourless amorphous crystals were obtained. Recrystallized from alcohol, the substance melted at 125° alone and in admixture with succinimide. Thus, the reduction product was inferred to be succinimide.

The green mother liquid was made alkaline with caustic soda, and extracted with ether. But no basic substance was obtained. This experiment shows, therefore, that succinimide was the only reduction product in the electrolysis. With copper electrode succinimide was also obtained with a yield of 80%.

II. **Reduction of Maleimide with Zinc Amalgam.** The conditions of the electrolysis were as follows: Cathode: zinc amalgam (15.8 sq. cm.). Cathodic solution: mixture of 100 c.c. of 50% sulphuric acid, 10 c.c. of alcohol, and 2 g. of maleimide. Anode: lead plate. Anodic solution: 50% sulphuric acid solution. Current density: 113.5 amp per 100 sq. cm. Current quantity: 195.8 F per mol. Temperature: 30°.

During the electrolysis, the solution was prevented from foaming by adding a small portion of alcohol, and to prevent the rise of temperature a spiral lead tube, through which cold water was rapidly running, was inserted into the catholyte. The apparatus was kept cool in water, and the catholyte was stirred vigorously throughout the electrolysis. The yellow colour of the catholyte gradually faded away as the electrolysis went on. After 6 hours the electrolysis was stopped, and the colourless cathodic solution was extracted with ether. On evaporating ether about 1.2 g. of colourless substance was obtained. When recrystallized from alcohol, this substance became prismatic crystals, which melted at 183° alone and in admixture with succinic acid. The substance, therefore, undoubtedly was succinic acid. The mother liquer, when made alkaline with a sodium hydroxide solution, emitted a distinct smell of ammonia. It was therefore subjected to steam distillation, and the distillate was acidified with hydrochloric acid, and evaporated to dryness, whereupon a colourless crystalline salt weighing about one gram was produced. The gold double salt of it did not melt at a temperature higher than 250°. Found: Au, 54.55. Calculated for $NH_4Cl \cdot AuCl_3$: Au, 55.18%. This shows that the substance was nothing but ammonium chloride, containing neither pyrrolidone nor pyrrolidine. Two more electrolyses were repeated with 10 and with 30% sulphuric acid with different results.

III. **Reduction of Maleic Acid.** As a subsidiary means of finding the cause of the production of succinic acid in the preceding experiment, maleic acid was electrolysed under the same conditions. From 2 g. of maleic acid, 1.8 g. of prismatic crystals were produced in 4 hours' electrolysis (current quantity: 130.3 F per mol). The crystals melted at 183°, the melting point of succinic acid. The yield was 83% of the theoretical.

IV. **Reduction of Pyrroline.** The electrolysis was carried out under the following conditions: Cathode: lead tube of 50 sq. cm. Cathodic solution: 2 g. of pyrroline dissolved in 100 c.c. of 10% sulphuric acid to which about 0.5 g. of reduced nickel was added from time to time. Anode: lead plate. Anodic solution: 10% sulphuric acid solution. Current density: 7 amp. per 100 sq. cm. Current quantity: 10.3 F per mol. Temperature: 29°. The electrolysis was conducted in the same manner as in I.

When the electrolysis was over, the greenish cathodic solution was taken out and made alkaline with a sodium hydroxide solution, when a strong ammonia-like smell was evolved. The solution was then subjected to steam distillation, and the distillate was evaporated after having been acidified with hydrochloric acid. Colourless needles weighing 1.5 g. were obtained. The auric double salt was produced as yellow needles,

melting at 203° with partial decomposition. Found: Au, 47.89. Calculated for $C_4H_9N \cdot HCl \cdot AuCl_3$: Au, 47.95%. It is beyond doubt that the substance was the gold salt of pyrrolidine.

The writer expresses his heartfelt thanks to Dr. Motooki Matsui, President of the Kyoto Imperial University, at whose suggestion the present work was carried out.

Osaka Women's College, Osaka.

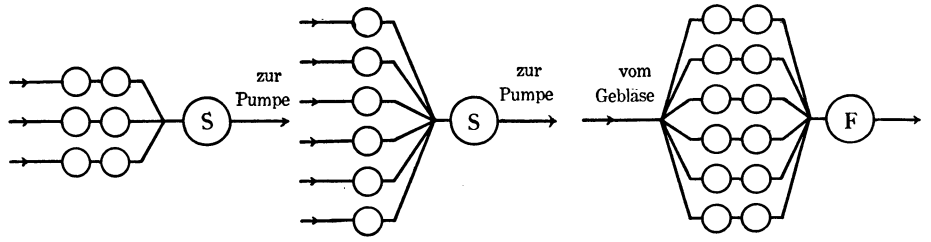
Über den Gehalt der atmosphärischen Feuchtigkeit an schwerem Wasser.

Von **Kenzo OKABE** und **Toshizo TITANI.**

(Eingegangen am 24. November 1936.)

Wir haben das spezifische Gewicht bzw. den Gehalt des durch vollständige Kondensation der atmosphärischen Feuchtigkeit unter verschiedenen Bedingungen gewonnenen Wassers an schwerem Wasser festgestellt und dieses Feuchtigkeitswasser hinsichtlich dieser Eigenschaften mit gewöhnlichem Wasser verglichen. Die Messergebnisse sind zusammen mit den Bedingungen bei der Sammlung der Proben in der beiliegenden Tabelle wiedergegeben.

Sammlung des Feuchtigkeitswassers. Bei den Versuchen von Nr. 1 bis 16 wurde die ausserhalb des Laboratoriums aufgenommene atmosphärische Luft mittels einer Wasserstrahlpumpe in mit Kohlensäureschnee-Petroleumäther-Gemisch abgekühlte leere Waschflaschen eingesaugt. Dazu wurden sechs Waschflaschen von je 15 cm. Höhe und 3 cm. l. W. benutzt, die bei den Versuchen von Nr. 1 bis 13, wie Schema Abb. a zeigt, in drei Reihen von je zwei nebeneinander angeordnet wurden. Dagegen wurden bei den Versuchen Nr. 14 bis 16 alle sechs Flaschen in einer Reihe nebeneinander gestellt (vgl. Abb. b).



a. Nr. 1 bis 13 b. Nr. 14 bis 16 c. Nr. 17 bis 22

Abb. Die Anordnung der Flasche zur Sammlung des Feuchtigkeitswassers.

Tabelle

1	2	3	4	5	6	7	8	9
Versuchsnr.	Datum	Temp. °C.	relative Feuchtigkeit in %	Barometerstand in mm. Hg	Wetter	Versuchsdauer in Stdn.	Menge des gesammelten Wassers in g.	ΔS gegen Osaka-Leitungswasser in γ
1	1935, 20/IX	23.5	64	763.5	leichter Regenfall	5.0	ca. 50	−6.8
2	,, , 21/IX	23.0	77	762	Regenwetter	4.5		
3	,, , 23/IX	22.5	77	758	,,	5.5		
4	,, , 11/X	21.0	73	761	,,	5.5		
5	1935, 25/IX	25.5	72	748	trübes Wetter	6.0	ca. 50	−4.8
6	,, , 26/IX	23.0	57	753	,, ,,	9.0		
7	1935, 10/X	22.0	47	767	schönes Wetter	4.5	ca. 50	−3.8
8	,, , 12/X	24.0	54	764	,, ,,	3.5		
9	,, , 16/X	22.5	58	764	trübes Wetter	7.0		
10	,, , 21/X	22.0	47	768	sehr schönes W.	7.0		
11	1935, 30/X	21.0	48	763	schönes Wetter	5.0	ca. 50	−4.6
12	,, , 31/X	20.0	43	766	sehr schönes W.	6.0		
13	,, , 2/XI	19.0	52	769	,, ,, ,,	7.5		
14	1936, 29/I	7.0	63	761	trübes Wetter	6.0	ca. 50	−3.6
15	,, , 14/II	9.0	57	764	,, ,,	7.0		
16	,, , 17/II	9.0	65	762	,, ,,	7.0		
17	1936, 22/VI	30.0	64	759	trübes Wetter	3.5	125	−0.8
18	1936, 27/VI	28.0	58	762	trübes Wetter von Zeit zu Zeit kleiner Regenfall	5.0	130	−2.8
19	1936, 29/VI	28.0	76	ca. 760	trübes Wetter mit leichtem Regenfall	4.5	100	−1.8
20	1936, 2/VII	20.0	88	ca. 760	Regenwetter	5.0	135	−3.0
21	1936, 6/VII	20.0	87	760	Regenwetter	ca. 3.0	90	−4.4
22	1936, 8/VII	23.0	85	764	Regenwetter	ca. 3.0	80	−3.8
							Mittel	−3.7

Zwischen diesem Flaschensystem und der Wasserstrahlpumpe wurde immer eine mit konzentrierter Schwefelsäure beschickte grosse Waschflasche (S in den Abb. a und b) eingeschaltet, um die Rückdiffusion der Feuchtigkeit aus der Pumpe in die Flaschen zu verhindern. Beim Versuch Nr. 1 setzten wir in der Praxis jeder Reihe noch eine Flasche hinzu, so dass nun jede dieser drei Reihen aus drei Flaschen bestand. Da aber in diesen zugesetzten dritten Flaschen fast kein Wasser kondensiert gefunden wurde, haben wir sie in den späteren Versuchen Nr. 2 bis 13 fortgelassen. In den Versuchen Nr. 14 bis 16, wo die Strömungsgeschwindigkeit sehr klein war, konnten wir ohne Gefährdung des Resultates von der Anordnung mit zwei hintereinander verbundenen Flaschen absehen. Auf diese Weise gelang es uns, die atmosphärische Feuchtigkeit vollständig kondensiert im Flaschensystem anzusammeln. Aber da die Menge des kondensierten Feuchtigkeitswassers bei einem Versuch, der durchschnittlich einige Stunden dauerte (vgl. 7. Reihe der Tabelle) nur 10 bis 15 c.c. betrug, wurden einige Proben, die unter den fast gleichen Bedingungen gesammelt worden, vereinigt, das Gemenge gereinigt und zur Dichtemessung verwendet.

Bei den späteren Versuchen Nr. 17 bis 22 wurde dagegen bei jedem einzelnen Experiment eine zur Dichtemessung genügende Menge des Feuchtigkeitswassers gesammelt, indem wir doppelt so viele Kondensationsflaschen wie früher benutzten und die Strömungsgeschwindigkeit der Luft so gross wie möglich machten. Zwölf Flaschen wurden, wie Schema Abb. c zeigt, in sechs parallelen Reihen von je untereinander verbundenen Flaschen angeordnet und von aussen mit Eis gekühlt. Durch diese Flaschen wurde die ausserhalb des Zimmers durch ein kleines Flügelgebläse eingesaugte atmosphärische Luft geleitet. Die aus diesen Flaschen strömende Luft leiteten wir noch durch eine grosse 25 cm. hohe und 5 cm. weite Glasflasche (F in der Abb. c), die von aussen mit einem Kohlensäureschnee-Gemisch gekühlt wurde. Mittels dieser Anordnung gewannen wir bei mehrstündiger Durchströmung der Luft durchschnittlich 100 g. Feuchtigkeitswasser (vgl. 7. und 8. Reihe der Tabelle). Von dieser Wassermenge wurden 60 bis 70% in der vorderen Abteilung 20 bis 30% in der hinteren des mit Eis gekühlten Flaschensystems und der Rest von 10% in der letzten mit Kohlensäure gekühlten Flasche F gefunden. Eventuell schalteten wir zu allerletzt noch eine mit Kohlensäure gekühlte Flasche ein. Doch fanden wir in dieser Flasche selbst nach halbstündiger Durchleitung von Luft kein Kondensat. Dies überzeugte uns, dass die atmosphärische Feuchtigkeit durch unsere Anordnung fast vollständig kondensiert wurde. Eine minimale Fraktionierung des Feuchtigkeitswassers, zu der es eventuell durch unvollständige Kondensation kommen kann, übt

wegen des kleinen Dichteunterschiedes zwischen Feuchtigkeits- und gewöhnlichem Wasser keinen merklichen Einfluss auf das Endresultat aus.

Reinigung und Dichtemessung des Feuchtigkeitswassers. Das auf die obenangegebene Weise gesammelte Feuchtigkeitswasser wurde zunächst entweder durch Destillation (bei Nr. 1 bis 16) oder durch Filtration (bei Nr. 17 bis 22) von beigemengten Stäubchen befreit und dann unter Zusatz von Kaliumpermanganat und Ätzkali drei bis fünf Stunden lang sieden lassen. Dann wurde das Wasser aus dieser Lösung vollständig abdestilliert. Das abdestillierte Wasser wurde durch weitere dreimalige Destillation völlig gereinigt, und zwar wurde die erste Destillation unter Zusatz einer geringen Menge Phosphorpentoxyd, die zweite unter Zusatz von Bariumhydroxyd in kohlensäurefreiem Luftstrom und die letzte ebenfalls in kohlensäurefreier Luft ohne jeden Zusatz aber unter Verwendung eines Quarzkühlers durchgeführt. Das spezifische Gewicht des so gereinigten Feuchtigkeitswassers wurde nach der Schwebemethode mittels eines Quarzschwimmers mit dem des Osaka-Leitungswassers bei 9.5°C. verglichen. Die Messgenauigkeit dürfte $\pm 0.5\,\gamma$ betragen. Den dabei gefundenen Dichteunterschied ΔS zwischen dem Feuchtigkeitswasser und dem Osaka-Leitungswasser haben wir in der 9. Vertikalreihe der Tabelle wiedergegeben. Danach ist das Feuchtigkeitswasser um 1 bis 7 γ, durchschnittlich um $4\,\gamma$ leichter als gewöhnliches Wasser.

Diskussion. Nimmt man an, dass die atmosphärische Feuchtigkeit durch die Verdampfung des Wassers auf der Erdoberfläche entsteht, so ist ohne weiteres zu erwarten, dass das Feuchtigkeitswasser spezifisch leichter als gewöhnliches Wasser sein muss. Was aber den quantitativen Dichteunterschied zwischen beiden anbetrifft, so ist die Sache insofern kompliziert, als die Dichte des Feuchtigkeitswassers bzw. dessen Gehalt an schwerem Wasser von vielen Faktoren abhängt. Dabei kommen zunächst die Bedingungen bei der Entstehung der Feuchtigkeit in Frage. Wenn z.B. gewöhnliches Süsswasser bei gewöhnlichen Temperaturen (5–35°C.) verdampft, muss die Dichte der ersten Fraktion um 3 bis $4\,\gamma$ kleiner als gewöhnliches Wasser sein, das entsprechende Destillat aus Meerwasser dagegen um 2 bis $3\,\gamma$, weil bekanntlich Meerwasser durchschnittlich um $1.5\,\gamma$ schwerer als Süsswasser ist.[1] Es handelt sich dabei aber um einen idealen Fall, wo die Verdampfung genügend langsam isothermisch verläuft. Nimmt die Verdampfungsgeschwindigkeit zu, so muss sich die resultierende Dichteabnahme des Destillats dementsprechend verändern.[2] Mit der Erhöhung der Temperatur bei der Ver-

(1) H. E. Wirth, T. G. Thompson und C. L. Utterback, *J. Am. Chem. Soc.*, **57** (1935), 400; *Nature*, **135** (1935), 662.

(2) Darüber, ob es sich dabei um die Vergrösserung oder Verminderung der Grösse der Dichteabnahme des Destillats handelt, kann man a priori nichts Bestimmtes sagen.

dampfung verringert sich offenbar die Dichteabnahme des Destillats und vice versa. Ausser den ebengeschilderten bei der Entstehung des Wassers in Frage kommenden Bedingungen kann auch folgender Umstand, auf den schon Eucken und Schäfer[3] hingewiesen haben, den Gehalt des Feuchtigkeitswassers an schwerem Wasser beeinflussen. Wenn z.B. ein Teil der Feuchtigkeit durch Regenfall abscheidet, muss der zurückbleibende Teil infolge fraktionierter Kondensation ärmer an schwerem Wasser, d.h. leichter werden. Durch das Zusammenwirken aller der ebenangegebenen Faktoren wird die Dichte des Feuchtigkeitswassers bestimmt. Die bei unseren Versuchen gefundene Grösse und Variation der Dichteabnahme des Feuchtigkeitswassers dem gewöhnlichen Wasser gegenüber lässt sich mit Hilfe der obenangeführten Faktoren genügend erklären.

Einige Autoren fanden bei ihren Versuchen[4] das *frisch* gefallene Schneewasser durchschnittlich um 2 bis 3 γ leichter als gewöhnliches Wasser, und es liegen für diese Erscheinung bereits einige Erklärungsversuche vor.[5] Aber bei unseren Versuchen ist ohne weiteres zu erwarten, dass das Schneewasser eine um einige γ kleinere Dichte als gewöhnliches Wasser besitzen muss, falls man annimmt, dass Schnee dadurch entsteht, dass atmosphärische Luft aus irgendeiner Ursache plötzlich abgekühlt und infolgedessen das Feuchtigkeitswasser, das sie enthält, fast restlos abgeschieden wird.

Der Nippon Gakujutsu-Schinkohkai (der Gesellschaft zur Förderung der japanischen Wissenschaft) sowie der Hattori-Hohkohkai (der Hattori-Stiftung) sind wir für ihre finanzielle Unterstützung zu herzlichstem Dank verpflichtet.

Physikalisch-chemisches Laboratorium
der Kaiserlichen Universität zu Osaka
und
Schiomi Institut für physikalische
und chemische Forschung.

---

(3) A. Eucken und K. Schäfer, *Göttinger Nachrichten, neue Folge*, **1935**, 137.

(4) E. Baroni und A. Fink, *Monatsh.*, **65** (1935), 386; *ibid.*, **67** (1936), 131, 193; A. Eucken und K. Schäfer, *Göttinger Nachrichten, neue Folge*, **1935**, 109, 137; W. A Alexander und L. A. Munro, *Can. J. Research*, B, **14** (1936), 47; M. Harada und T. Titani, dieses Bulletin, **10** (1935), 206, 263.

(5) Vgl. die Mitteilungen von A. Eucken und K. Schäfer in Fussnote (3) sowie die von M. Harada und T. Titani in Fussnote (4).

The Viscosity of Mixed Salt Solutions.

By Tetsuya ISHIKAWA.

(Received November 25th, 1936.)

From the extensive work on the viscosity of binary liquid mixtures and of solutions of solids in liquids for these ten years[1], the author has come to the conclusion that his fundamental formula defines an ideal mixture law or a physical mixture law. The formula runs:

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

where η_1, η_2, and η are the viscosities of component 1, 2, and the mixture; z_m a formal molar fraction of component 2 in the mixture; and K the characteristic constant for the mixture or, precisely saying, the ratio of the characteristic constant of component 2 to that of component 1.

Since this formula represents the true viscosity on mixing two chemically indifferent liquids for the whole range of concentration, and that on dissolving a non-reactive solid in a liquid up to its saturation, one may easily arrive at the precognition that the same law will hold for the viscosity of mixed salt solutions, provided that the component solutions which do not react have a common solvent and the composition of the mixture has a constant total concentration throughout the admixture. If we take c_1 and c_2 the concentrations of two solutions in the mixture, e.g. in gram-mole per 1000 g. of solvent respectively in order to make this sum c, total concentration, to keep a constant by mixing appropriate weights of primary solutions of concentration c, $(1-z_m)$ and z_m in the above formula may be replaced by c_1/c and c_2/c respectively, since the quantity of solvent is unchanged before and after mixing. Naturally, K which means here the ratio of the characteristic constants of two solutions of a common solvent may take a value not so much differing from unity especially for dilute salt solutions.

---

(1) This Bulletin, **4** (1929), 5, 25, 149, 288; **5** (1930), 47, 117; **8** (1933), 280, 293; **9** (1934), 155; **10** (1935), 153, 248; **11** (1936), 8, 64.

There have been a few measurements on the viscosity on mixing salt solutions under the above precaution. Stearn[2] first measured the relative viscosities of the aqueous solution pairs of NaCl—KCl and NaI—KI; Ruby and Kawai[3] made careful measurements, their precision being not less than one part in two thousand, on the relative viscosities of binary and ternary mixtures of HCl, KCl, and NaCl at the concentrations of 0.5, 1.0, 2.0, and 4.0 gram-mole per 1000 g. of water, and pointed out that the viscosities of binary mixtures of these electrolytes are consistently less than values computed by the rule of mixtures (additivity with respect to molar concentration), save in the cases of the most dilute mixtures; Tollert[4] measured the viscosities of similar pairs of electrolyte solutions at only one composition and tested with fair success his own formula, $\eta = \sqrt{\eta_1\eta_2}(1+A'\sqrt{\gamma_1\gamma_2})$, in which γ_1 and γ_2 denote the concentrations of components in val/litre, and A' a specific constant of the mixture depending on temperature alone; and recently Banchetti[5] examined, with the data of his own for the solution pairs of K_2SO_4—$ZnSO_4$ and urethane—urea and of those of others cited above, the formulas of Kendall, Bingham, and Tollert, and found that they all failed to represent the actual viscosities of mixtures at concentrated salt solutions. He referred the present author's paper on the viscosity of aqueous solutions of electrolytes[6], but unfortunately he did not attempt to test the latter's fundamental formula given above. The present paper is, therefore, contributed to the study in this line as an appendix to the author's foregoing papers on the viscosity of binary mixtures.

The data employed in the following verification of the author's formula are adopted from the values observed by Banchetti and by Ruby and Kawai.

As seen from Tables 1, 2, 3, 4, and 5, in which z_m denotes a fractional concentration of the second salt solution in each pair of total concentration c in gram-mole per 1000 g. of water, the divergences of the calculated values from the observed values are all less than 2×10^{-3} and lie within the experimental error limit, so that the coincidence is said to be extremely satisfactory. For closer investigation of K in these pairs, however, we must have more accurate measurements.

(2) A. E. Stearn, *J. Am. Chem. Soc.*, **44** (1922), 670.
(3) C. E. Ruby and J. Kawai, *J. Am. Chem. Soc.*, **48** (1926), 1120.
(4) H. Tollert, *Z. physik. Chem.*, A, **172** (1935), 129.
(5) A. Banchetti, *Gazz. chim. ital.*, **64** (1934), 229; **65** (1935), 159; **66** (1936), 446.
(6) This Bulletin, **10** (1935), 153.

Table 1. Urethane aq. (1)—Urea aq. (2), 25°C. (Banchetti).

z_m	$c = 0.5$			$c = 1.0$		
	$\eta_{obs.}$	$\eta_{calc.}$	Difference $\times 10^4$	$\eta_{obs.}$	$\eta_{calc.}$	Difference $\times 10^4$
0.00	1.0890	—		1.1755	—	
0.25	1.0713	1.0712	1	1.1416	1.1412	4
0.50	1.0536	1.0537	−1	1.1071	1.1071	0
0.75	1.0363	1.0363	0	1.0731	1.0731	0
1.00	1.0191	—		1.0393	—	
	$K = 1.021$			$K = 1.009$		

Table 2. $ZnSO_4$ aq. (1)—K_2SO_4 aq. (2), 25°C. (Banchetti).

z_m	$c = 0.1$			$c = 0.5$		
	$\eta_{obs.}$	$\eta_{calc.}$	Difference $\times 10^4$	$\eta_{obs.}$	$\eta_{calc.}$	Difference $\times 10^4$
0.00	1.0662	—		1.3656	—	
0.25	1.0548	1.0550	−2	1.2932	1.2930	2
0.50	1.0442	1.0441	1	1.2267	1.2269	−2
0.75	1.0337	1.0336	1	1.1662	1.1668	−6
1.00	1.0234	—		1.1115	—	
	$K = 1.067$			$K = 1.201$		

Table 3$_1$. HCl aq. (1)—KCl aq. (2), 25°C. (Ruby and Kawai).

z_m	$c = 0.5$			$c = 1.0$		
	$\eta_{obs.}$	$\eta_{calc.}$	Difference $\times 10^4$	$\eta_{obs.}$	$\eta_{calc.}$	Difference $\times 10^4$
0.0	1.0317	—		1.0617	—	
0.2	1.0250	1.0248	2	1.0483	1.0481	2
0.4	1.0182	1.0180	2	1.0351	1.0350	1
0.6	1.0112	1.0114	−2	1.0221	1.0224	−3
0.8	1.0048	1.0048	0	1.0102	1.0102	0
1.0	0.9983	—		0.9985	—	
	$K = 1.037$			$K = 1.096$		

Table 3_2. HCl aq. (1)—KCl aq. (2), 25°C. (Ruby and Kawai).

z_m	$c = 2.0$ $\eta_{obs.}$	$\eta_{calc.}$	Difference $\times 10^4$	$c = 4.0$ $\eta_{obs.}$	$\eta_{calc.}$	Difference $\times 10^4$
0.0	1.1210	—		1.2378	—	
0.2	1.0972	1.0968	4	1.2068	1.2052	16
0.4	1.0735	1.0734	1	1.1713	1.1709	4
0.6	1.0506	1.0508	−2	1.1341	1.1349	− 8
0.8	1.0285	1.0288	−3	1.0954	1.0970	−16
1.0	1.0076	—		1.0570	—	
	$K = 1.085$			$K = 0.881$		

Table 4_1. KCl aq. (1)—NaCl aq. (2), 25°C. (Ruby and Kawai).

z_m	$c = 0.5$ $\eta_{obs.}$	$\eta_{calc.}$	Difference $\times 10^4$	$c = 1.0$ $\eta_{obs.}$	$\eta_{calc.}$	Difference $\times 10^4$
0.0	0.9983	—		0.9985	—	
0.2	—			1.0166	1.0166	0
0.4	1.0169	1.0169	0	1.0352	1.0351	1
0.6	1.0264	1.0264	0	1.0537	1.0541	−4
0.8	—			1.0736	1.0736	0
1.0	1.0456	—		1.0936	—	
	$K = 0.974$			$K = 0.940$		

Table 4_2. KCl aq. (1)—NaCl aq. (2), 25°C. (Ruby and Kawai).

z_m	$c = 2.0$ $\eta_{obs.}$	$\eta_{calc.}$	Difference $\times 10^4$	$c = 4.0$ $\eta_{obs.}$	$\eta_{calc.}$	Difference $\times 10^4$
0.0	1.0076	—		1.0570	—	
0.2	1.0431	1.0435	−4	1.1309	1.1308	1
0.4	1.0811	1.0812	−1	1.2118	1.2121	−3
0.6	1.1209	1.1209	0	1.3022	1.3019	3
0.8	1.1632	1.1626	6	1.4030	1.4019	11
1.0	1.2065	—		1.5136	—	
	$K = 0.882$			$K = 0.771$		

Table 5_1. HCl aq. (1)—NaCl aq. (2), 25°C. (Ruby and Kawai).

z_m	$c = 0.5$			$c = 1.0$		
	$\eta_{obs.}$	$\eta_{calc.}$	Difference $\times 10^4$	$\eta_{obs.}$	$\eta_{calc.}$	Difference $\times 10^4$
0.0	1.0317	—		1.0936	—	
0.2	—			1.0862	1.0866	−4
0.4	1.0369	1.0370	−1	1.0797	1.0799	−2
0.6	1.0398	1.0397	1	1.0736	1.0736	0
0.8	—			1.0676	1.0675	1
1.0	1.0456	—		1.0617	—	
	$K = 0.914$			$K = 0.888$		

Table 5_2. HCl aq. (1)—NaCl aq. (2), 25°C. (Ruby and Kawai).

z_m	$c = 2.0$			$c = 4.0$		
	$\eta_{obs.}$	$\eta_{calc.}$	Difference $\times 10^4$	$\eta_{obs.}$	$\eta_{calc.}$	Difference $\times 10^4$
0.0	1.2065	—		1.5136	—	
0.2	1.1870	1.1865	5	1.4484	1.4474	10
0.4	1.1684	1.1681	3	1.3877	1.3875	2
0.6	1.1509	1.1512	−3	1.3329	1.3331	−2
0.8	1.1350	1.1355	−5	1.2834	1.2834	0
1.0	1.1210	—		1.2378	—	
	$K = 0.818$			$K = 0.792$		

The comparison among the results with other formulas which were given by Banchetti is reproduced here. In Tables 6 signify Δ_M, Δ_K, Δ_B, Δ_L, Δ_S, and Δ_I the average divergences of the observed and calculated viscosities by use of the formulas of viscosity linearity, Kendall's cube-root, Bingham, and Kendall's logarithmic, Banchetti, and Ishikawa.

Besides the formulas quoted above there have been proposed more than ten formulas. For the aid of further comparison, therefore, I will give severe tests for the validity of the hitherto existing formulas with two typical ideal mixtures in the classical meaning (mixtures in which there occurs no volume change on mixing), C_2H_5OH—i-C_3H_7OH[7] and $C_2H_4Br_2$—$C_2H_4Cl_2$[8].

(7) G. S. Parks and K. K. Kelley, *J. Phys. Chem.*, **29** (1925), 727.
(8) W. MacFarlane and R. Wright, *J. Chem. Soc.*, **(1933)**, 114.

Table 6. The Validity of Various Formulas for Solution Pairs.

Pair	Deviations × 10^3					
	Δ_M	Δ_K	Δ_B	Δ_L	Δ_S	Δ_I
$c = 0.5$						
HCl — KCl	−0.5	−0.4	−0.2	−0.3	−1.6	0.1
KCl — NaCl	−0.3	−0.1	0.2	−0.1	0.6	0.0
HCl — NaCl	−0.3	−0.3	−0.3	−0.3	−1.2	0.0
$c = 1.0$						
HCl — KCl	−1.7	−1.4	−0.8	−1.2	−1.7	0.0
KCl — NaCl	−1.3	−0.6	0.7	−0.3	0.7	−0.1
HCl — NaCl	−0.7	−0.7	−0.6	−0.7	−0.5	−0.1
$c = 2.$						
HCl — KCl	−2.3	−1.3	0.5	−0.4	1.3	0.0
KCl — NaCl	−5.6	−3.0	2.2	−1.7	7.0	0.0
HCl — NaCl	−3.7	−3.3	−2.4	−3.0	2.9	0.0
$c = 4.0$						
HCl — KCl	4.0	6.3	10.0	7.2	19.7	−0.1
KCl — NaCl	−23.0	−12.2	8.0	−7.7	33.5	0.3
HCl — NaCl	−11.4	−8.2	−1.6	−6.5	22.6	0.2

(1) Bingham[9] (1906): $\varphi = \varphi_1(1-z_v)+\varphi_2 z_v$.

(2) Drucker and Kassel[10] (1911): $\varphi = \varphi_1(1-z)+\varphi_2 z$.

(3) Dolezalek[11] (1913): $\eta^{\frac{1}{2}} = \eta_1^{\frac{1}{2}}(1-z_v)+\eta_2^{\frac{1}{2}} z_v$.

(4) Kendall[12] (1913): $\log \eta = (1-z_m)\log \eta_1 + z_m \log \eta_2$.

(5) Ssachanov and Rjachowski[13] (1914):

$$\eta = \eta_1(1-z_m)^2+\eta_2 z_m^2+n\sqrt{\eta_1\eta_2}(1-z_m)z_m .$$

(6) Ssachanov and Rjachowski[14] (1915):

$$\eta = \eta_1(1-z_m)+\eta_2 z_m - k(1-z_m)z_m , \quad k = \eta_1+\eta_2-n\sqrt{\eta_1\eta_2} .$$

(9) E. C. Bingham, *Am. Chem. J.*, **35** (1906), 195.
(10) K. Drucker and R. Kassel, *Z. physik. Chem.*, **76** (1911), 367.
(11) F. Dolezalek and A. Schulze, *Z. physik. Chem.*, **83** (1913), 45.
(12) J. Kendall, *Medd. Vetenskapzakad. Nobelinst.*, **2** (1913), No. 25, 1.
(13) A. Ssachanov and N. Rjachowski, *Z. physik. Chem.*, **86** (1914), 529.
(14) A. Ssachanov and N. Rjachowski, *J. Russ. Phys.-Chem. Soc.*, **47** (1915), 113.

(7) Kendall[15] (1917): $\eta^{\frac{1}{3}} = \eta_1^{\frac{1}{3}}(1-z_m)+\eta_2^{\frac{1}{3}}z_m$.

(8) Drucker[16] (1918): $\varphi d = \varphi_1 d_1(1-z_m)+\varphi_2 d_2 z_m$.

(9) Meyer and Mylius[17] (1920): $\varphi = \varphi_1\frac{b_1}{b}(1-z)+\varphi_2\frac{b_2}{b}z$.

(10) Macleod[18] (1924):

$$\eta = \eta_1\frac{x_1}{x}(1-z_m)+\eta_2\frac{x_2}{x}z_m,\quad x = x_1(1-z_v)+x_2z_v.$$

(11) Bateman and Baechler[19] (1926): $\eta^{(1-z_v)+kz_v} = \eta_1^{(1-z_v)}+\eta_2^{kz_v}$.

(12) Ishikawa[20] (1929): $$\eta = \frac{\eta_1}{1+K\frac{z_m}{1-z_m}}+\frac{\eta_2}{1+\frac{1}{K}\frac{1-z_m}{z_m}}.$$

(13) Bingham and Brown[21] (1932):

$$\varphi = \varphi_1(1-z_v)+\varphi_2 z_v-K(z-z_v)(v_1-v_2).$$

(14) Cragoe[22] (1933): $\eta v = Ae^{\frac{B}{L'}}$, $L' = L_1'(1-z)+L_2'z$.

(15) Lautié[23] (1935): $\eta^{\frac{1}{2}} = \eta_1^{\frac{1}{2}}(1-z_m)+\eta_2^{\frac{1}{2}}z_m$.

In these formulas, η and φ and those with suffixes 1 and 2 are the viscosities and fluidities of the mixture and components 1 and 2 respectively; v and d and those with suffixes the specific volumes and densities of the mixture and the components respectively; and z, z_v, and z_m a weight, volume, and molar fraction of component 2 respectively. For an explanation of the other symbols used the reader is referred to the original papers.

---

(15) J. Kendall and K.P. Monroe, *J. Am. Chem. Soc.*, **39** (1917), 1787.
(16) C. Drucker, *Z. physik. Chem.*, **92** (1918), 287.
(17) J. Meyer and B. Mylius, *Z. physik. Chem.*, **95** (1920), 349.
(18) D. B. Macleod, *Trans. Faraday Soc.*, **20** (1924), 348.
(19) E. Bateman and R. Baechler, *Proc. Am. Wood-Preserver's Assoc.*, (**1926**), 89.
(20) T. Ishikawa, this Bulletin, **4**, (1929), 5.
(21) E. C. Bingham and D. F. Brown, *J. Rheol.* **3** (1932), 95.
(22) C. S. Cragoe, *Proc. World Petroleum Congr., London F*, (**1933**), 529.
(23) R. Lautié, *Bull. soc. chim.*, [5], **2** (1935), 2187.

Table 7. The Validity of Various Formulas for the Pair of C_2H_5OH (1)—i-C_3H_7OH (2), 25°C. (Parks and Kelley).

Formula	$\begin{cases} z = 0.1639 \\ z_v = 0.1646 \\ z_m = 0.131 \end{cases}$ $\begin{cases} z = 0.3311 \\ z_v = 0.3321 \\ z_m = 0.275 \end{cases}$ $\begin{cases} z = 0.5013 \\ z_v = 0.5025 \\ z_m = 0.435 \end{cases}$ $\begin{cases} z = 0.6640 \\ z_v = 0.6649 \\ z_m = 0.607 \end{cases}$ $\begin{cases} z = 0.8277 \\ z_v = 0.8285 \\ z_m = 0.786 \end{cases}$ Deviations $\times 10^5$ (with respect to η)					Constants used
(1)	11	18	29	32	21	
(2)	11	19	29	33	22	
(3)	—37	—68	—83	—80	—62	
(4)	8	11	19	19	10	
(5)	2	1	3	—3	—4	$n = 1.942$
(6)	2	1	3	—3	—4	$k = 0.00241$
(7)	—2	—7	—5	—7	—10	
(8)	30	58	87	94	79	
(9)	—4	0	4	0	—23	$\begin{cases} b_1/b = 0.989 \\ b_2/b = 0.970 \end{cases}$
(10)	—	—	—	—	—	
(11)	3	2	5	5	—1	$k = 0.807$
(12)	0	—1	3	—1	—1	$K = 0.777$
(13)	2	—2	—1	—1	—5	
(14)	—5	1	4	7	—6	$K = 1.65 \times 10^5$
(15)	—8	—16	—19	—24	—18	

Table 8. The Validity of Various formulas for the Pair of $C_2H_4Br_2$ (1)—$C_2H_4Cl_2$ (2), 25°C. (MacFarlane and Wright).

Formula	$z=0.1005$, $z_v=0.1636$, $z_m=0.1750$	$z=0.2404$, $z_v=0.3686$, $z_m=0.3875$	$z=0.3510$, $z_v=0.4860$, $z_m=0.5059$	$z=0.4997$, $z_v=0.6365$, $z_m=0.6550$	$z=0.6504$, $z_v=0.7659$, $z_m=0.7791$	$z=0.7492$, $z_v=0.8396$, $z_m=0.8501$	Constants used
	Deviations $\times 10^5$ (with respect to η)						
(1)	47	57	53	43	29	12	
(2)	−37	−66	−57	−47	−36	−32	
(3)	−36	−46	−53	−42	−31	−30	
(4)	1	−1	−1	3	1	−6	
(5)	−4	−6	0	5	4	−3	$n=1.867$
(6)	−4	−6	0	5	4	−3	$k=0.00299$
(7)	−15	−26	−25	−19	−13	−17	
(8)	−32	−54	−52	−45	−33	−32	
(9)	58	2	0	−3	0	−4	$b_1/b=1.08$, $b_2/b=1.02$
(10)	−1	−6	−7	−3	−3	−6	$x_1=0.0628$, $x_2=0.0911$
(11)	0	−2	−1	2	2	−6	$k=1.08$
(12)	2	−2	−1	1	−1	−7	$K=1.43$
(13)	−51	−86	−83	−70	−48	−46	
(14)	7	−1	2	1	−1	−10	$K=92.7$
(15)	−24	−39	−39	−29	−21	−22	

The superiority of the Ishikawa formula above the rest is readily accepted from the strict coincidences equably obtained in these examples as shown in Tables 6, 7, and 8.

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

On the End-Point Voltage of the Lead-Acid Storage Cell.

By Kyôji KINOSHITA.

(Received November 27th, 1936.)

The terminal voltage of a lead-acid storage cell falls, gradually, in the course of discharge and finally the discharge must be terminated at the proper value of the voltage, which is called the end-point voltage of the cell. Abolition of the end-point voltage is said to result in the formation of crystalline lead sulphate in the active material of the plates, and reduces the capacity and life of the electrodes.

Vinal[1], Lyndon[2], and Nakamura[3] studied the relations between the end-point voltage and the discharge hour rate of the cell. The following experiments have been undertaken on this subject.

Table 1.

t_0-t (min.)	e (volt)	C (%)
$t_0 = 275$	2.038	100
274	1.960	99.6
273	1.962	99.3
272	1.966	98.8
269	1.968	97.8
264	1.968	96.1
259	1.968	94.2
254	1.970	92.4
249	1.966	90.6
234	1.962	85.2
219	1.960	79.6
199	1.958	72.4
179	1.948	65.2
149	1.940	54.2
119	1.928	43.3
89	1.920	32.2
59	1.900	21.4
29	1.866	10.6
14	1.838	5.1
9	1.816	3.3
4	1.770	1.5
3	1.756	1.1
2	1.722	0.7
1	1.642	0.4
0	1.480	

Experimental. The cells under examination were connected in series and several cycles of charge and discharge were made by the constant currents of 1.5 amp., 2.0 amp., 2.5 amp., and 3.0 amp. The end-point voltage was taken at about 1.3 volts, while that specified by the maker of the cells was 1.8 volts. As such discharge will cause the formation of crystalline lead sulphate in the active material, the cell was charged as soon as possible after the discharge had been terminated.

One example of change of the terminal voltage with time is tabulated in Table 1. In this table t_0 denotes the total time of discharge and t the time at which the terminal voltage is e. The values of C is defined as follow:

$$C = \frac{t_0-t}{t_0} \times 100 .$$

(1) Vinal, "Storage batteries," (1924), 177.
(2) Lyndon, "Storage battery engineering," (1911), 91.
(3) Nakamura, *Bull. Dept. Railways, Govt. Japan*, **18** (1930), 1-26.

The values of t_0-t in the table will be proportional to the remaining capacity of the cell provided the discharge is undertaken at a constant current. Consequently, the value of C indicates the percentage ratio of the remaining capacity to the total capacity of the cell.

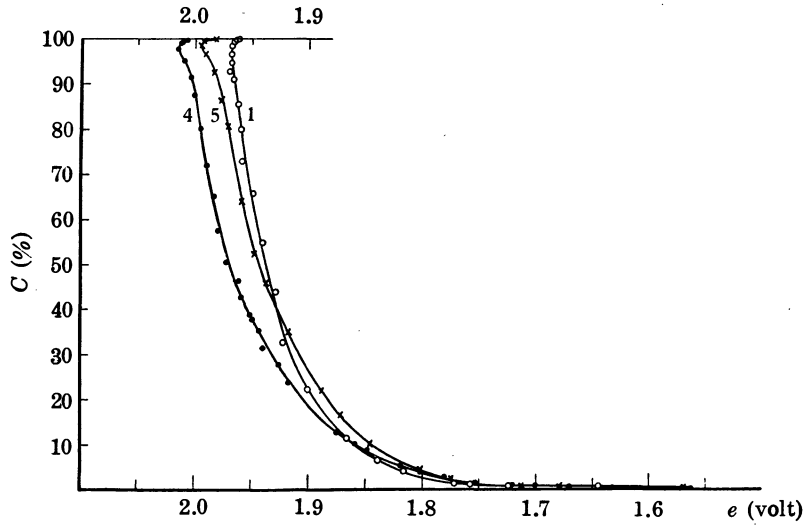


Fig. 1.

The relation between C and e on the three different types of the cells are represented in Fig. 1. As seen from Fig. 1, the terminal voltage of the cell No. 4 is higher than the others in the early stage of the discharge but it falls rather quickly. The terminal voltage of the cell No. 1 is lower at first but it falls slowly and finally takes the highest value among the three, when C falls to about 10. The cell No. 5 shows an intermediate value until C falls to about 40, and becomes the lowest when it falls under 40.

The discharge capacities of these three cells are shown in Table 2.

Table 2. (2.0 amp. discharge)

Cell No.	Discharge hours	Discharge capacity
1	4 h. 36 m.	9.2 a.h.
4	6 41	13.4
5	4 18	8.6

From the above results we see that the terminal voltage e of the cell having the larger capacity is not always higher than that of the cell having the smaller capacity, the value of C being the same. It may be an interesting fact that the C-e curve shows some characteristic nature of the cell.

The C-e curves obtained by different discharge currents on the cells of

the same type are shown in Fig. 2. The curves correspond to the discharge current of 1.5 and 3 amp. As is seen from this figure the terminal voltage is higher in the case of a weaker discharge current than the case of stronger

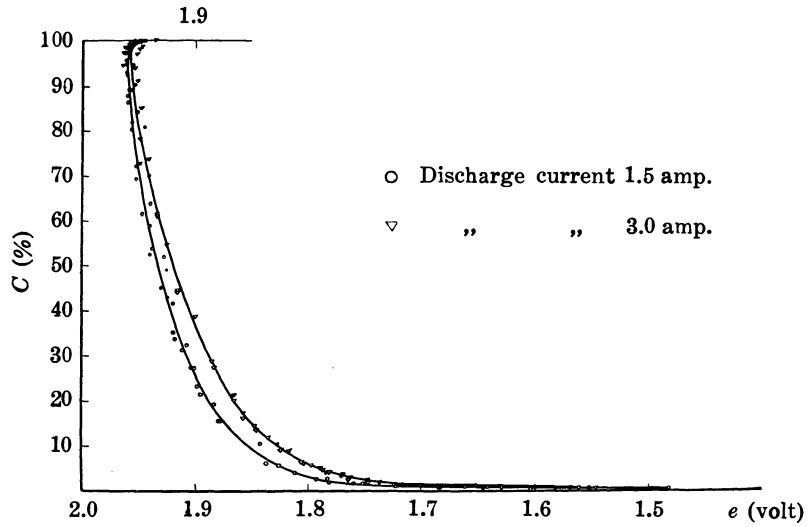


Fig. 2.

discharge current provided the value of C is the same. Consequently, if there be a definite value of C at which the formation of the crystalline lead sulphate occurs, the end-point voltage in the case of a smaller discharge current must be taken higher than in the case of a larger discharge current.

Now the values of $\log C$ and $\log e$ are delineated in Fig. 3, Fig. 4, Fig. 5, and Fig. 6. These figures correspond to the data obtained by the discharge currents of 1.5, 2.0, 2.5, and 3.0 amperes, respectively.

As seen from these figures the relation between $\log C$ and $\log e$ is almost linear in the upper part of the figures, while the curves are concave to the C axis at the lower part. We see, moreover, that the linear part becomes the more predominate in the case of the higher discharge current. The linear part of the curves may be represented by the following formula:

$$\log C = m \log e + \log k \qquad (1),$$

where m and k are the constants. This equation can be transformed into the following forms:

$$C = k\, e^m \quad (2) \qquad \text{or} \qquad e = K\, C^n \quad (3), \qquad \text{where} \quad n = 1/m.$$

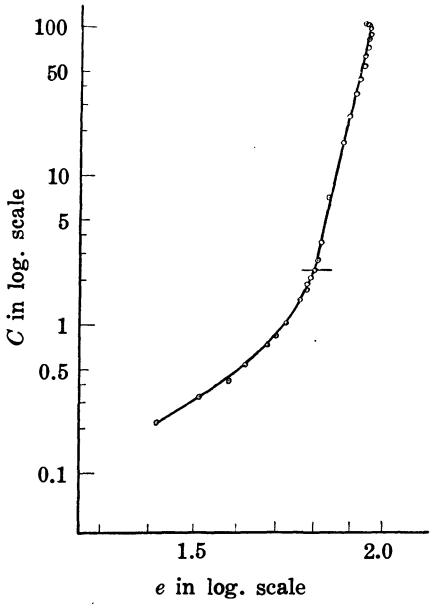


Fig. 3. Discharge current 1.5 amp.

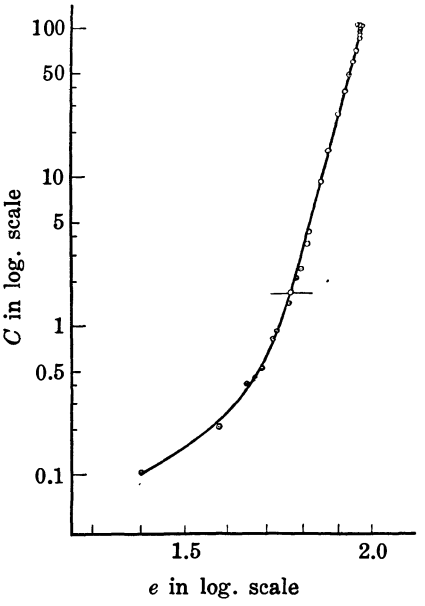


Fig. 4. Discharge current 2.0 amp.

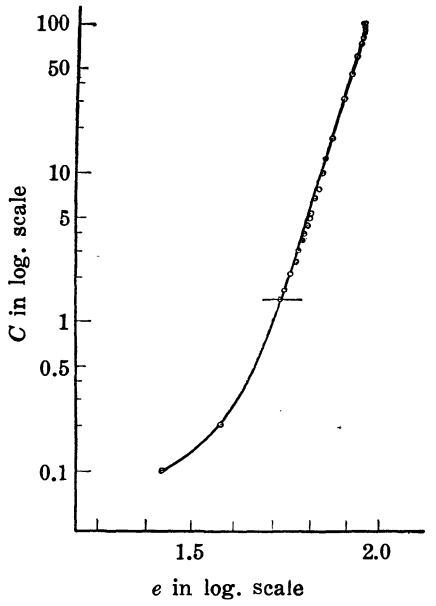


Fig. 5. Discharge current 2.5 amp.

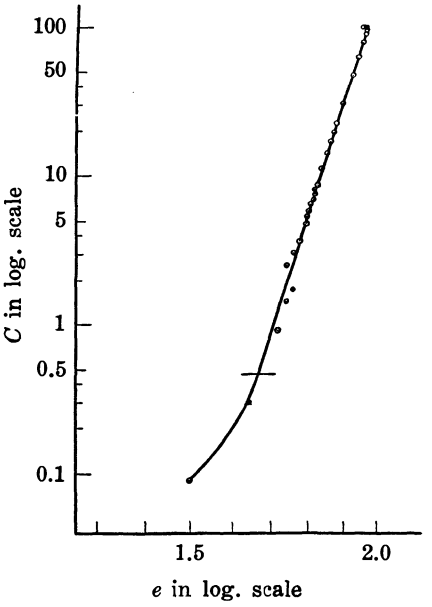


Fig. 6. Discharge current 3.0 amp.

From equation (3) it follows that the terminal voltage e of the cell is proportional to the n-th power of the percentage of the remaining active material out of the total active material, which should be consumed at the end of the discharge. Namely, the terminal voltage of the cell may be said to be proportional to the n-th power of the concentration of remaining active material in the plate.

It was known that the terminal voltage of the cell can be represented by the following equations:

$$e = E+IW \quad \text{in charge}; \quad \text{and} \quad e = E-IW \quad \text{in discharge},$$

where E is the electromotive force of the cell in volts, I the charge and discharge current in amperes, and W the internal resistance in ohms. The internal resistance of the cell is said to be very small except at the end of the discharge. It follows that the variation of the terminal voltage of the cell in the discharging state is mainly due to the variation of E by polarization. The polarization caused by the variation of the concentration of sulphuric acid at the electrode will be the most important factor. But the existence of the relation (3) shows that the variation of the value of C has some relation to the variation of e. The examination of the nature of the cell in the course of discharge may be made from this point of view.

As soon as the discharge is begun, the consumption of sulphuric acid at the electrodes is expected, and there occurs the reduction of the concentration of acid in the pores of the electrodes. The change of concentration of the acid will bring about the fall of terminal voltage by polarization. After a while sulphuric acid will diffuse into the pores from outside the electrodes, until finally the supply and the consumption of the acid become stationary. At this stage the chief cause which effects the fall of terminal voltage may be considered to be the variation of C within the active material of the plates. At the end of the discharge the pores of the plates are clogged by the lead sulphate which has formed during the course of discharge. Consequently, the supply of the acid into the pores may be interrupted and there occurs a sudden fall of the terminal voltage. The linear relation between $\log C$ and $\log e$ can no more be seen in this stage of the discharge. The fact that the curvature of the lower part of the $\log C$-$\log e$ curve becomes more gradual as the discharge current becomes large is the result of the gradual fall of the terminal voltage due to the steep concentration gradient between the electrolytes in and out of the pores produced by the superficial functioning of the plate.

From the above considerations, the ranges where the relation (3) holds between C and e may be the most favourable condition of the plates, for the

value of e varies according to the polarization due to the variation of the strength of acid and that of the value of C, these two being in equilibrium.

It follows that the value of e, where the relation (1) does no more hold between C and e may be the most reasonable end-point voltage of the cell.

Table 3.

No. of the cell	Discharge current 1.5 amp.		Discharge current 2.0 amp.		Discharge current 2.5 amp.		Discharge current 3.0 amp.	
	C (%)	e (volt.)	C (%)	e (volt.)	C (%)	e (volt.)	C (%)	e (volt.)
No. 1	1.55	1.785	1.30	1.752	1.00	1.720	1.03	1.708
No. 2	1.91	1.784	1.47	1.757	1.50	1.745	1.20	1.715
No. 3	1.46	1.758	1.45	1.753	1.25	1.734	0.77	1.689
Mean	1.64	1.776	1.41	1.754	1.25	1.733	1.00	1.704

The values of C and e thus obtained by the diagrams, Fig. 3—Fig. 6 as examples, are tabulated in Table 3. The values of C and e tabulatad here are the mean values of nine discharges for one value of discharge current. In Fig. 7 these values of e are plotted against the discharge hour rate of the cell. The reasonable end-point voltage of the cell at 6-hour rate of discharge may be considered to be 1.784 volts.

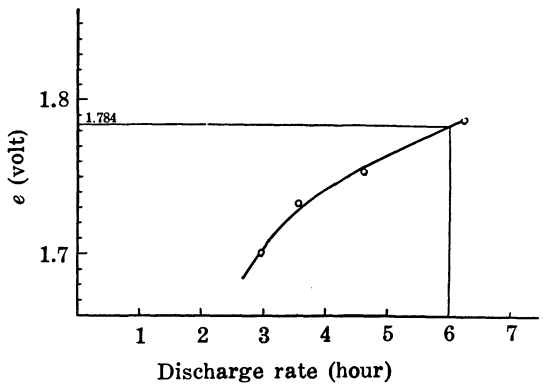


Fig. 7.

The equation (3) is analogous in form to Freundlich's formula for adsorption: $x = \alpha D^{\frac{1}{a}}$, where x denotes the amount of the solute adsorbed by 1 gram of the adsorbent, D the concentration of the solution in equilibrium with the adsorbent, and α and a are constants. If it be an ideal solution this formula coincides with Henry's partition law, and the value a becomes unity. By analogy the value of n in equation (3) may be considered to indicate the state of dispersion of the active material in the plate. If the active material of the plate forms a homogeneous solid solution with $PbSO_4$ the value of n in the equation (3) may become unity. In this case (3) will be transformed into the following form: $e = KC$. Namely, the terminal voltage of the cell is directly proportional to the concentration of the remaining active material in the plate. If the active material of the plate be colloidally dispersed into $PbSO_4$, e will be proportional to the n-th power of C. And if the active material of the plate behaves as a mere mass of PbO_2 or Pb, the value of n in the equation (3) will become naught, and the equation will takes the form: $e = \text{const.}$ In this case the terminal voltage of the cell only depends upon the active material used in the plate and will become quite independent of the concentration of the remaining active material.

As the results of above-mentioned analogy between the equation (3) and Freundlich's formula, the value of n in the equation (3) may be considered to represent the structural features of the plate.

In conclusion the author wishes to express his hearty thanks to Prof. J. Sameshima of the Tokyo Imperial University for his kind advice throughout this experiments.

Toyoda Research Laboratory, Imperial Invention Society, Shimomeguro, Tokyo.

A Theory of Surface Tension of Debye-Hückel Electrolyte.

By Kyozo ARIYAMA.

(Received June 1st, 1936.)

The present writer has recently proposed a comprehensible theory of adsorption of Debye-Hückel electrolyte.[1] It was found that a similar theory could be advanced to calculate the surface tension of Debye-Hückel electrolyte. Wagner's very elaborate mathematical theory of surface tension[2] which was later simplified by Onsager and Samaras[3] uses the theory of images near the boundary between water and air. Aside from a great mathematical difficulty, the use of theory of images in the atomic realm without justification is rather objectionable. Oka[4] recently formulated a very reasonable theory of surface tension of dilute solution of strong electrolyte and obtained an explicit expression for the change of surface tension with concentration of the solution in the liquid. The present paper[5] gives a very simple yet a quite reasonable methed of calculating the surface tension. The explicit formula is derived and compared with experiment quite satisfactory. The difference between Oka's value and the value that is given here is that Oka's value is exactly twice as large as that of the present author.

Consider a liquid which is in thermodynamic equilibrium with a vapor. We shall apply the thermographic principle to this system, then we obtain

$$dU = Td\eta + \sigma ds - pdV, \tag{1}$$

where U is the internal energy, η the entropy of the total system, σ the surface tension, and T, S, V and p stand for the usual meanings. Since U, the internal energy, is a function of T the temperature, V the volume, and S the surface of the liquid, we obtain

$$Td\eta = \frac{\partial U}{\partial T}dT + \left(\frac{\partial U}{\partial S} - \sigma\right)dS + \left(\frac{\partial U}{\partial V} + p\right)dV.$$

(1) This Bulletin, **11** (1936), 687.
(2) *Phys. Z.*, **25** (1924), 474.
(3) Onsager and Samaras, *J. Chem. Physics*, **2** (1934), 529.
(4) S. Oka, *Proc. Phys.-Math. Soc. Japan*, [3], **14** (1932), 649.
(5) The author was unaware of the Oka's paper at the time when he proposed a theory of adsorption of Debye-Hückel electrolyte. Oka's theory contains an integral which seems only approximately estimated, so it may change the result by a factor 2 or 3 if rigorously calculated.

The condition that $d\eta$ is an exact differential gives

$$\frac{\partial}{\partial S}\left(\frac{1}{T}\frac{\partial U}{\partial T}\right)=\frac{\partial}{\partial T}\left[\frac{1}{T}\left(\frac{\partial U}{\partial S}-\sigma\right)\right]$$

or
$$U_s=\sigma-T\frac{d\sigma}{dT}, \tag{2}$$

where
$$U_s=\frac{\partial U}{\partial S},$$

If we consider a solution of strong electrolyte, we obtain for small change in the surface energy U_s the following equation

$$\Delta U_s=\Delta\sigma-T\frac{d}{dT}\Delta\sigma, \tag{3}$$

where $\Delta\sigma$ is corresponding small change in the surface tension. Solving equation (3) for $\Delta\sigma$, we get

$$\Delta\sigma=-T\int_{\infty}^{T}\frac{\Delta U_s}{T^2}dT. \tag{4}$$

Here the intergration constant is determined so as to make $\Delta\sigma/T$ vanish at $T=\infty$.

We shall now apply the kinetic theory for the calculation of ΔU_s. If we consider a special case, that is, a dilute solution of univalent ions, the average number of ions in cm.^{3} at a distance between r and $r+dr$ from the free surface of the liquid is given by

$$C_r=C_\infty e^{-\frac{\epsilon^2}{2DkTa}\left(1-\frac{r}{a}\right)}dr \tag{5}$$

as it was shown in the previous paper.[1] In equation (5) $m=\frac{1}{a}=\sqrt{\frac{8\pi C_\infty\epsilon^2}{DkT}}$, where C_∞ is the average number of ions in cm.^{3} at a distance sufficiently far away from the surface, D the dielectric constant of the solution, k the Boltzmann constant, ϵ the charge of the ions.

The surface energy ΔU_s per unit area of the surface of the liquid, therefore, will be given by

$$\Delta U_s = \int_0^a C_r \frac{\epsilon^2}{2aD}\left(1-\frac{r}{a}\right)dr$$

$$= \int_0^a C_\infty \frac{\epsilon^2}{2Da}\left(1-\frac{r}{a}\right)e^{-\frac{\epsilon^2}{2DakT}\left(1-\frac{r}{a}\right)}dr. \qquad (6)$$

If we let $y=\left(1-\frac{r}{a}\right)$, $b=\frac{\epsilon^2}{2DakT}$, the above integral becomes $\frac{C_\infty \epsilon^2}{2D}\int_0^1 ye^{-by}dy$.

Since by the fundamental assumption of Debye-Hückel theory $b<1$, we can calculate the above integral and obtain

$$\Delta U_s = \frac{\epsilon^2 C_\infty}{4D}\left(1-\frac{2b}{3}\right). \qquad (7)$$

Since b is small compared with 1 for very dilute solutions, we shall neglect it entirely, and write

$$\Delta U_s = \frac{\epsilon^2 C_\infty}{4D}.$$

Substituting this in equation (4), we get

$$\Delta\sigma = -\frac{\epsilon^2 C_\infty}{4D} T\int_\infty^T \frac{dT}{T^2} = \frac{\epsilon^2 C_\infty}{4D}. \qquad (8)$$

If we use molar concentration c per c.c. instead of number of ions in cm.^{3} we get

$$\Delta\sigma = \frac{\epsilon^2 cN}{2D} \qquad (9)$$

where N is the Avogadro's number. This agrees except a factor 1/2 with the value found by Oka by a more elaborate yet possibly not much more rigorous calculations. The detailed comparison between the value of $\Delta\sigma/c$ found by experiments and the theoretical value of $\epsilon^2 N/2D$ was made in the previous theory of the present author[1]. There the agreement between the theory and the experiment was shown to be satisfactory.

Now according to the theory of Debye and Hückel for concentrated solutions of strong electrolyte, the potential energy of an ion due to its ion atmosphere is given by $-\frac{\epsilon^2 m}{D(1+md)}$ where d is the diameter of ions. Therefore the equation (7) is accordingly modified, and given in the first approximation by

$$\Delta U_s = \frac{\epsilon^2 C_\infty}{4D(1+md)}\left(1+\frac{2b'}{3}\right), \tag{10}$$

where $$b' = -\frac{\epsilon^2}{2aDkT(1+md)}.$$

Corresponding to equation (9), we get for the increase in surface tension

$$\frac{\Delta\sigma}{c} = \frac{\epsilon^2 N}{2D(1+md)}\left(1+\frac{2b'}{3}\right). \tag{11}$$

More general case. It is easy to extend the above theory to a more general case in which kinds of ions are homogeneously distributed in the solution. Let us suppose that the charges for S kinds of ions are represented by $z_1\epsilon, z_2\epsilon, \ldots, z_i\epsilon, \ldots, z_s\epsilon$ and the concentrations (no. in cm.^{3}) by $C_1, C_2, \ldots C_i, \ldots, C_s$ respectively. The potential energy of the i th ion species due to its ion atmosphere is $-(z_i\epsilon)^2\frac{m}{D}$, where

$$m^2 = \frac{4\pi\epsilon^2}{DkT}\sum_{i=1}^{s} C_i z_i^2.$$

Therefore the increase in the surface tension is given by

$$\Delta\sigma = \frac{\epsilon^2}{4D}\sum_{i=1}^{s} C_i z_i^2.$$

Therefore if we had solutions of the same molar concentration of, for example, KCl and Na_2SO_4, the change of surface tension should be in the ratio 2 to 6. If we take 1/2 molar concentration for solutions of binary mixture of uni- and bi-valent ions, and the molar concentration for solutions of univalent ions, the ratio of change of surface tension is 6 to 4 respectively. Table 1 gives data for a few solutions of dilute concentrations taken from Heydweiller's paper. As we see in the table, the theoretical prediction is satisfied approximately in the case of K_2SO_4, $SrCl_2$, and $BaCl_2$, however, for $MgCl_2$ and Na_2SO_4 the ratio is about 4 to 4. Considering the experimental difficulty in obtaining accurate result, the agreement here obtained may be considered quite satisfactory.

(6) Heydweiller, *Ann. Physik*, (4), **33** (1910), 145.

Table 1.* Increase of Surface Tension of Strong Electrolyte.

σ: the surface tension of solution; σ_0: the surface tension of pure water; c: the molar concentration; $\Delta = 100\ \frac{\sigma-\sigma_0}{c\sigma_0}$

NaCl		KCl		1/2 $MgCl_2$		1/2 Na_2SO_4	
c	Δ	c	Δ	c	Δ	c	Δ
0.020	2.61	0.025	2.55	0.269	2.00	0.210	2.46
0.059	2.33						
0.093	2.30	0.090	2.38	0.336	1.97	0.321	2.16
0.123	2.30	0.114	2.34	0.539	1.84	0.330	2.37
0.251	2.13						
0.290	2.11	0.225	2.26	0.808	1.74	0.428	2.16

1/2 K_2SO_4		1/2 $SrCl_2$		1/2 $BaCl_2$	
c	Δ	c	Δ	c	Δ
0.031	2.39	0.036	3.16	0.103	2.68
0.052	2.38	0.071	2.99	0.131	2.49
0.093	2.37	0.107	2.89	0.247	2.28
0.124	2.16	0.132	2 88	0.306	2.24
0.150	2.13	0.192	2.78	0.353	2.25
0.208	2.08	0.203	2.71		
0.217	2.11				

* Data taken from Heydweiller's paper, *loc. cit.*

Interfacial tension. The interfacial tension between two liquids is affected, in general, more or less by a third component which is added to this system. In the system of water and hydro-carbon oil each component has actually no mutual solubility and the added inorganic salt is only soluble in the water phase. Therefore, the change of the interfacial tension caused by the concentration change of the salt solution should run parallel to that of the surface tension of the salt solution.

But an unexpected result was obtained in the experiment of McLewis[7] on the interfacial tension of hydro-carbon oil against aqueous solution of metallic salt, namely, the lowering of the interfacial tension occurred by the addition of $CuCl_2$, $AgNO_3$, KCl. Since each of these substances raises the

(7) McLewis, *Phil. Mag.*, (6), **17** (1909), 466.

surface tension of water against air, and does not influence that of organic liquid, so that the interfacial tension might be expected to be raised. McLewis used a dynamical method for the measurement of interfacial tension. M. Kidokoro[8] recently repeated the experiment using both dynamical and statical method, and found that the interfacial tension is raised by the addition of inorganic salt in the water phase. The increase in the interfacial tension between normal hexane from petroleum and water by the addition of inorganic salt run parallel to that of the surface tension of the salt solution, as is expected from the theoretical anticipation. However, the magnitude of rise in the interfacial tension was about 2/3 of the rise in the surface tension of the salt solution for the same concentration.

The decrease in the rise of interfacial tension between hexane and water from that of water and air would possibly be accounted for by the consideration that there exists an electric force acting on the layer of hexane molecules due to the incomplete neutralization of the charge of any ion by the ion atmosphere of opposite charge at the vicinity of the surface. The molecules of hydro-carbon oil may orient themselves in such a way as to decrease the interfacial tension between the two phases. To attempt quantitative account for this effect will be too speculative since we have not yet any experimental evidence of molecular reorientation of hexane at the interface when inorganic salt is added.

In conclusion, the author wishes to express his thanks to Professor H. Erikson for his kind encouragement.

Summary.

A very comprehensible theory of surface tension of Debye-Hückel electrolyte is proposed. An explicit formula for surface tension is derived and compared with experiment very satisfactorily. A qualitative explanation of Heydweiller effect is given. Interfacial tension is also discussed very briefly.

(8) This Bulletin, **7** (1932), 280.

A Theory of Surface Tension of Ternary Solutions.

By Kyozo ARIYAMA.

(Received June 20th, 1936.)

Since Heydweiller and his co-workers[1] discovered that the surface tension of the solution of inorganic salts in water increases as the solute is increased, various attempts have been made to explain the phenomenon. The theories so far advanced may be divided into two main groups; one which is based on the assumption of the existence of the 'image force' near the boundary between water and air, and the other based on the calculation of surface energy caused by the electrostatic force of the ions. Theories of Wagner,[2] Shiba,[3] and Oneager and Samaras[4] belong to the former, while theories of Oka[5] and Ariyama[6] (present author) belong to the latter category. Aside from a great mathematical difficulty involved in the theories of the former category, the use of the theory of images in the atomic realm without justification was rather objectionable. However, until very recently there was not any experimental evidence to decide which theory is right. It seems that the experiment of Belton[7] conclusively favours the theories of latter category. The present author intends to show a reason for it in the following discussions.

The amount of ions negatively adsorbed at the surface of the solution of an aqueous salt is given by the Gibbs equation

$$-\frac{1}{2RT}\left(\frac{\partial\sigma}{\partial c}\right)=\,_0\Gamma\left(\frac{1}{c}+\frac{\partial \log f}{\partial c}\right). \qquad (1)$$

Where f is the activity coefficient of the salt and $_0\Gamma$ its negative adsorption. When a non-electrolyte is added to the system this simple relation does not apply, but becomes, when the surface concentration of one of the components is put equal to zero,

$$\begin{aligned} d\sigma &= -\Gamma_1 d\mu_1 - \Gamma_2 d\mu_2 \\ &= -\Gamma_1 2RTd \log f_1C_1 - \Gamma_2 RTd \log f_2C_2, \end{aligned}$$

(1) Heydweiller, *Ann. Physik*, (4), **33** (1910), 145.
(2) Wagner, *Phys. Z.*, **25** (1924), 474.
(3) Shiba, *Bull. Inst. Phys. Chem. Research*, (Tokyo), **13** (1934), 190.
(4) Onsager and Samaras, *J. Chem. Physics*, **2** (1934), 529.
(5) Oka, *Proc. Phys.-Math. Soc. Japan*, [3], **14** (1932), 649.
(6) Ariyama, this Bulletin, **11** (1936), 687.
(7) Belton, *Trans. Faraday Soc.*, **31** (1935), 1420.

where μ_1 and μ_2 are the chemical potentials, f_1 and f_2 the activity coefficients of electrolyte and non-electrolyte respectively. Γ_1 and Γ_2 are their corresponding adsorption and C_1 and C_2 are their molal concentrations. If the concentration of the non-electrolyte is kept constant, this may be written

$$-\left(\frac{\partial\sigma_{12}}{\partial c_1}\right)_{c_2} = 2RT\Gamma_1\left[\frac{1}{c_1}+\left(\frac{\partial \log f_1}{\partial c_1}\right)_{c_2}\right]+RT\Gamma_2\left(\frac{\partial \log f_2}{\partial c_1}\right)_{c_2}. \tag{2}$$

Now for dilute solution of Debye-Hückel electrolyte the surface tension was experimentally found to be given by

$$\rho-\sigma_0 = K_1C_1, \tag{3}$$

where σ_0 is the surface tention of water, K_1 a constant, C_1 the molal concentration of the salt.

If the change of activity of the salt is unaffected by the non-electrolyte,[8] (1), (2), and (3) may be combined to give

$$\left(\frac{\partial\sigma}{\partial c_1}\right)_{c_2} = K\frac{\Gamma_1}{{}_0\Gamma_1}-RT\Gamma_2\left(\frac{\partial \log f_2}{\partial c_1}\right)_{c_2}. \tag{4}$$

Since $\log f_2$ is given by Debye-McAaulay,[9] it is possible to calculate $\Gamma_1/{}_0\Gamma_1$ if we determine $(\partial\sigma/\partial c_1)c_2$ experimentally. Such an experiment was carried out by Belton[10] for systems of ethyl alcohol-water salt and acetic acid-water-salt. He discovered that 2 % of ethyl-alcohol mixed in water lowers the surface tension of the solution when the concentration of salt is increased, and that acetic acid-water-salt system increases the surface tension of the solution as the concentration of salt is increased. The calculated values of Γ_1/Γ_0 showed values always less than one for salts like KBr, K_2SO_4, $KClO_2$, and KNO_3. For NH_4Cl the value was about 1.2 for dilute concentration.

These results are difficult to be accounted for by the theories of surface tension based on the theory of images, but are easily accounted for by the theories of Oka[5] and Ariyama.[6]

It is well known that non-electrolyte are positively adsorbed at the free surface of the solution. Therefore let us assume, for simplicity of discussion, that the adsorption layer has thickness d, and the dielectric constant of this layer is D'_a. The dielectric constant of electrolyte solution is represented by D, and the dielectric constant of mixture of electrolyte and non-electrolyte solution sufficiently far away from the surface is represented by D'.

(8) Theoretical proof of this assumption will be given in this Bulletin shortly by the present author.

(9) Debye and McAaulay, *Physik. Z.*, **26** (1925), 22.

(10) See (7).

Then the repulsive force acting on the ions of charge $+\epsilon$ at a distance r from the surface of the electrolyte solution is given by $j\epsilon^2/4r^2D$ if we assume the image force at the boundary of water and air. In the above expression $j=D-1/D+1$. If non-electrolyte like ethyl-alcohol, which has much smaller dielectric constant than water, is added, D' will be in general smaller than D. The repulsive force for the ion in the mixture becomes $j'\epsilon^2/4r^2D'$. Now $j'=D'-1/D'+1$ will be smaller than j but D' in the denominator becomes smaller in the same order, the repulsive force outside of the adsorption layer remains almost unchanged. This can be seen very clearly if we take a specific example, and calculate each quantity specifically. Now in the adsorption layer D'_a will be very small compared with D for alcohol. Therefore $j'_a\epsilon^2/4r^2D'_a$ becomes larger than $j\epsilon^2/4r_2D$ since increase in $1/D'_a$ outweighs the decrease in j'_a. Therefore it is apparent that the addition of non-electrolyte tends to increase the negative adsorption of ions: or in any case will not decrease the negative adsorption except for those substances which have higher dielectric constants than water. This entirely contradicts the experimental fact that $\Gamma_1/{}_0\Gamma_1$ is much smaller than unity. Therefore the theory of surface tension based on 'image force' seems incompatible with the experimental data.

Next let us consider the question of how Oka's theory will be applied in this case. Let us consider an ion of charge $+\epsilon$ situated at a distance x from the surface. We shall take a cylindrical coordinate origin at this point, choosing z axis normal to the surface. Then for $x<d$, the dielectric constant is D'_a, and for $x>d$, the dielectric constant is D'. For simplicity of notation let us write these as $D'_a=D$, and $D'=D_2$. The surface of the solution is taken as $x=0$. We set up Debye-Hückel equations

$$\begin{aligned} \Delta\psi_1 &= k_1^2\psi_1 \\ \Delta\psi_2 &= k_2^2\psi_2 \\ \Delta\psi' &= 0\,, \end{aligned} \tag{5}$$

where ψ_1 is a potential at (r, z) in the adsorption layer d, ψ_2 is a potential at (r, z) in the bulk of the solution, and ψ' is the potential at any point in the air. k_1 and k_2 are given by

$$k_1^2=\frac{8\pi n\epsilon^2}{D_1kT},\quad k_2^2=\frac{8\pi n\epsilon^2}{D_2kT},$$

where n is the average number of ions in c.c.

We want to determine ψ_1 and ψ_2 under the following boundary conditions

$$\psi_{1z=x}=\psi'_{z=x}$$

$$D_1\left(\frac{\partial\psi_1}{\partial z}\right)_{z=x} = \left(\frac{\partial\psi'}{\partial z}\right)_{z=x}$$

$$\psi_{1z=x_1'=x-d} = \psi_{2z=x_1} \tag{6}$$

$$D_2\left(\frac{\partial\psi_2}{\partial z}\right)_{z=x_1} = D_1\left(\frac{\partial\psi_1}{\partial z}\right)_{z=x_1}$$

Suppose we obtained solutions for ψ_1 and ψ_2 satisfying these conditions. Then the negative adsorption is given by

$$\Gamma = -n\int_0^d\left(1-e^{-\frac{\varphi_1(x)}{kT}}\right)dx - n\int_d^\infty\left(1-e^{-\frac{\varphi_2(x)}{kT}}\right)dx \tag{7}$$

where $\varphi_1(x) = \varphi_{1+}(x) = \varphi_{1-}(x) = \epsilon\psi_{1+} = -\epsilon\psi_{1-}$

and $\varphi_2(x) = \varphi_{2+}(x) = \varphi_{2-}(x) = +\epsilon\psi_{2+}(x) - \epsilon\psi_{5+}(\infty)$

$$= -\epsilon\psi_{2-}(x) + \epsilon\psi_{2-}(\infty)$$

So let $\varphi_2 = \psi(x) - \psi(\infty)$

If we write eq. (5) in full, we get

$$\frac{\partial^2\psi_1}{\partial r^2} + \frac{1}{r}\frac{\partial\psi_1}{\partial r} + \frac{\partial^2\psi_1}{\partial z^2} = k_1^2\psi_1, \text{ etc.}$$

We shall let the solutions take the following from

$$\psi_1 = \int_0^\infty\left[A(\alpha)e^{\sqrt{\alpha^2+k_1^2}z} + B(\alpha)e^{-\alpha z}\right]J_0(\alpha r)d\alpha$$

$$\psi_2 = \int_0^\infty\left[D(\alpha)e^{\sqrt{\alpha^2+k_2^2}z} + \frac{\alpha}{D_1\sqrt{\alpha^3+k_2^2}}e^{-\sqrt{\alpha^2+k_2^2}z}\right]\delta_0(\alpha r)dr$$

$$\psi' = \int_0^\infty C(\alpha)e^{-\alpha z}J_0(\alpha r)d\alpha,$$

where $A(\alpha)$, $B(\alpha)$, $C(\alpha)$, and $D(\alpha)$ are the coefficients that have to be determined by 4 boundary conditions. $J_0(\alpha r)$ is the Bessel functions of zero order.

It is easy to obtain these coefficients, and they are given by

$$A(\alpha) = \frac{-2\alpha(1-D_1\alpha)e^{-\alpha x-\sqrt{\alpha^2+k_2^2}x_1}}{P}$$

$$B(\alpha) = \frac{+2\alpha(\alpha+D_1\sqrt{\alpha^2+k_1^2})e^{\sqrt{\alpha^2+k_1^2}x-\sqrt{\alpha^2+k_2^2}x_1}}{P},$$

where $$P = (\alpha-D_1\sqrt{\alpha^2+k_1^2})(D_2\sqrt{\alpha^2+k_2^2}+D_1)e^{\sqrt{\alpha^2+k_2^2}x-\alpha_1}$$

$$-(D_1\sqrt{\alpha^2+k_1^2}-D_2\sqrt{\alpha^2+k_2^2})(1-D_1\alpha)e^{\sqrt{\alpha^2+k_1^2}x_1-\alpha x}$$

and $C(\alpha)$ and $D(\alpha)$ are obtained from the following boundary equations:

$$A(\alpha)e^{\sqrt{\alpha^2+k_1^2}x}+B(\alpha)e^{-\alpha x} = C(\alpha)e^{-\alpha x}$$

and $$A(\alpha)e^{\sqrt{\alpha^2+k_1^2}x_1}+B(\alpha)e^{-\alpha x_1} = D(\alpha)e^{\sqrt{\alpha^2+k_2^2}x_1}+\frac{\alpha}{D_2\sqrt{\alpha^2+k_2^2}}e^{\sqrt{\alpha^2+k_2^2}x_1}.$$

Thus[11] $$\varphi_1(x)/\epsilon^2 = \int_0^\infty A(\alpha)d\alpha+\int_0^\infty B(\alpha)d\alpha \qquad (8)$$

and $$\varphi_2(x)/\epsilon^2 = \int_0^\infty D(\alpha)d\alpha.$$

Therefore the formal solution of the problem is obtained. But since expressions for $\varphi_1(x)$ and $\varphi_2(x)$ are so complicated, that it is not possible to evaluate the negative adsorption Γ unless some method of simplification is discovered. However, it may be possible that this sort of theory might reproduce a result which is demanded by the experimental fact that $\Gamma_1/{}_0\Gamma_1$ is smaller than unity.

Now we shall discuss the application of the theory[6] that the present author has proposed recently. If we consider an adsorption layer of thickness d at the surface, the potential energy of inward force for ions is accordingly modified. Let the dielectric constant in d be D' and the dielectric constant of the bulk of the solution be D. The thickness of the ion atmosphere in d be represented by a', and in the solution by a. Then in the first approximation, the potential energy of inward force on an ion situated at a distance $r(a+d)$ from the surface is given by

$$E = \frac{\epsilon^2}{2Da}\left[1-\left(\frac{r-d}{a}\right)\right]-\frac{\epsilon^2}{2D'a'}\left[1-\frac{(r-d)}{a'}\right]+\frac{\epsilon^2}{2D'a'}\left(1-\frac{r}{a'}\right)$$

$$= \frac{\epsilon^2}{2Da}\left(1-\frac{r}{a}\right)+\frac{\epsilon^2}{2Da}\left(\frac{d}{a}\right)-\frac{\epsilon^2}{2D'a'}\left(\frac{d}{a'}\right).$$

(11) See Oka's paper in this connection.

According to the Maxwell-Boltzmann statistics, the probability that an ion lies at a distance r and $r+dr$ will be proportional to $e^{-\frac{E}{kT}}dr$. Therefore if C is the average number of ions in cm.^{3} the number of ions at a distance between r and $r+dr$ will be given by

$$C_r = Ce^{-\frac{E}{kT}}dr.$$

Therefore the negative adsorption is given by

$$\Gamma = -C\int_0^{a+d}\left(1-e^{-\frac{E}{kT}}\right)dr.$$

Substituting the value of E in the above equation, and carrying out the integration, we obtain after simplification

$$\Gamma = -\frac{c}{kT}\left[\frac{\epsilon^2}{4D}+\frac{\epsilon^2}{4D}\left(\frac{d^2+2da}{a}\right)-\frac{\epsilon^2}{2D'}-\left(\frac{da+d^2}{a'^2}\right)\right]. \qquad (9)$$

The first term represents the amount of adsorption which would result if the adsorption layer d of dielectric constant D' were not present. Since in general $D > D'$ and $a > a'$, the third term is much larger than the second term. In other words the negative adsorption decreases as the adsorption layer d increases.

Since for mixture of alcohol-water-salt solutions in Belton's experiment the dielectric constant of the system is not appreciably different from that of aqueous solutions, the decrease in negative adsorption must be attributed to the effect we have discussed above.

In conclusion, the author wishes to express his thanks to Professor H. Erikson for his kind encouragement.

Summary.

The theories of surface tension of Debye-Hückel electrolyte can be divided into two main groups; one which is based on the assumption of the existence of the 'image force' near the boundary between water and air, and the other based on the calculation of surface free energy caused by the electrostatic force of ions. On the basis of experimental evidence on the surface tension of ternary solution, the theories of former category are shown to be unacceptable. Theories of Oka and also of Ariyama which belong to the latter category are applied to explain the surface tension of ternary solutions. Agreement with experiment is satisfactory.

A Note on the Osmotic Coefficient and the Activity Coefficient at the Surface.

By Kyozo ARIYAMA.

(Received June 20th, 1936.)

The exact theoretical calculation of the negative adsorption of Debye-Hückel electrolyte requires the knowledge of activity coefficient of the solute at the surface of the solution. The surface tension of the solution is given by the Gibbs thermodynamic equation.

$$-\frac{1}{2RT}\left(\frac{\partial\sigma}{\partial c}\right)=\,{}_0\Gamma\left(\frac{1}{c}+\frac{\partial\log f}{\partial c}\right), \tag{1}$$

where σ is the surface tension of the solution, c the molar concentration of solute, Γ the negative adsorption, f the activity coefficient of the solute at the surface of the solution. If a non-electrolyte is added to the system, the above simple equation does not apply, but become if the concentration of non-electrolyte is kept constant.

$$-\frac{1}{2RT}\left(\frac{\partial\sigma}{\partial c_1}\right)_{c_2}=2RT\Gamma_1\left[\frac{1}{c_1}+\left(\frac{\partial\log f_1}{\partial c_1}\right)_{c_2}\right]+RT\Gamma_2\left(\frac{\partial\log f_2}{\partial c_1}\right)_{c_2}. \tag{2}$$

Now for dilute solution of Debye-Hückel electrolyte, the surface tension is experimentally found to be given by

$$\sigma-\sigma_0=KC_1, \tag{3}$$

where σ_0 is the surface tension of water, K a constant.

In order to calculate the change of negative adsorption due to the addition of non-electrolyte, Belton[1] assumed the relation $\frac{\partial\log f}{\partial c}=\left(\frac{\partial\log f_1}{\partial c_1}\right)_{c_2}$ at the surface and $\left(\frac{\partial\log f_2}{\partial c_1}\right)_{c_2}$ is the same at the surface of the solution as in the interior of the solution.

Then by equations (1), (2), and (3) we get

$$\left(\frac{\partial\sigma_{12}}{\partial c_1}\right)_{c_2}=K_1\frac{\Gamma_1}{{}_0\Gamma_1}-RT\Gamma_2\left(\frac{\partial\log f_2}{\partial c_1}\right)_{c_2}. \tag{4}$$

(1) Belton, *Trans. Faraday Soc.*, **31** (1935), 1420.

Therefore we can calculate the value of $\Gamma_1/{}_0\Gamma_1$ knowing all the other factors in the equation. The present author wishes to prove theoretically by taking a specific example that the above two assumptions that Belton made is justified.

Osmotic coefficient of ions at the surface.[2] We shall first consider the total mutual potential energy of the ions with respect to their ionic atmospheres, considering mono-mono-valent electrolyte first for the sake of simplicity. The potetial energy of one ion of charge $+\epsilon$ as well as $-\epsilon$ is equal to $-\frac{\epsilon^2 m}{D}$, where $m^2 = \frac{8\pi C_\infty \epsilon^2}{DkT}$, D is dielectric constant of the solution, C_∞, the average number of ions in cm.^{3} If we have altogether $2N$ ions, the total potential energy is therefore $-\frac{N\epsilon^2 m}{D}$ since if we have a number of charges e_i at points where the potentials are ψ_i, the total potential energy is given by

$$U = \frac{1}{2}\sum e_i \psi_i .$$

As is shown in the previous paper, the potential energy of an ion near the surface is greater than the potential energy of an ion sufficiently far away from the surface. The ion which is situated at a distance $r < \frac{1}{m}$ from the surface of the solution has potential energy $-\frac{\epsilon^2 m}{2Da}\left(1-\frac{r}{a}\right)$, where $a = 1/m$. Since N is the average concentration of the positive ions in the solution, the total lack of potential energy for the unit surface of depth a is given by

$$\Delta U = \frac{\epsilon^2 N}{4D}.$$

Therefore the average total potential energy per cm^3 at the surface is given by

$$U = -\left(\frac{N\epsilon^2}{aD} - \frac{N\epsilon^2}{4Da}\right) = -\frac{3}{4}\frac{N\epsilon^2}{aD}.$$

This result can easily be generalized for an electrolyte containing $N_1, \ldots, N_i, \ldots, N_s$ ions of valencies $z_1, \ldots, z_i, \ldots, z_s$. In this case the potential energy of the central ion with respect to its ionic atmosphere is given by $\frac{z_i^2 \epsilon^2 m}{D}$ and the potential energy of the solution is then given by

$$U_e = -\sum_i \frac{3}{8}\frac{N_i z_i^2 \epsilon^2 m}{D}, \quad \text{where} \quad m^2 = \frac{4\pi\epsilon^2}{DkT}\sum_i N_i z_i^2 .$$

(2) The argument presented in the following follows closely the Debye's theory presented by Falkenhagen in "Electrolyte."

The total electric work w necessary to discharge and recharge the ions at the surface becomes correspondingly

$$W = -\sum \frac{1}{3}\frac{3}{4}\frac{N_i\epsilon^2 z_i^2 m}{D}$$

$$= -\sum \frac{1}{4}\frac{N_i\epsilon^2 z_i^2 m}{D}.$$

In order to calculate the osmotic pressure, we must differentiate the electrical work with respect to the volume V. It must be noted that the expression for m contains V implicitly since $n_i = N_i/V$, $e_i = \epsilon z_i$ we have $\frac{\partial w}{\partial V} = \frac{\partial w}{\partial m}\cdot\frac{\partial m}{\partial V}$. $= -\Sigma\frac{N_i e_i^2}{4D}\cdot\frac{\partial m}{\partial V}$ since $\frac{\partial m}{\partial V} = -\frac{m}{2V}$, we get

$$\frac{\partial W}{\partial V} = \sum \frac{n_i e_i^2 m}{8D}.$$

The osmotic pressure of real solution is given by

$$P = \sum n_i kT - \sum \frac{n_i e_i^2 m}{8D}$$

$$= \sum\left(1-\frac{e_i^2}{8DkT}\right)n_i kT = \sum g_i n_i kT, \qquad (5)$$

where $g_i = 1-\frac{e_i^2}{8DkT}$ is called osmotic coefficient of the ions. The osmotic coefficient of the ions in the interior of the solution is given by

$$G_i = 1-\frac{e_i^2}{6DkT}.$$

We see that the osmotic coefficient of the ions is slightly greater at the surface than in the interior of the solution.

Activity coefficient of ions at the surface. With the parallel argument with that of Debye, the thermodynamic potential of the real solution Φ is given by

$$\Phi = \sum_0^s N_i\left(\Phi_i + kT\log y_i - \frac{e_i^2 m}{4D}\right),$$

where Φ_i's depend only on the pressure and temperature, and y_i is the mol fraction of the solute.

The change of thermodynamic potential with changing temperature and pressure being kept constant is given by

$$\delta\Phi = \sum_{i=0} \delta N_i \left[\Phi_i + k \log y_i - \frac{e_i^2 m}{4D} - \sum_{j=0}^{s} \frac{e_i^2}{4D} N_i \frac{\partial m}{\partial N_i} \right].$$

If the index i refers to the dissolved particles, i.e., one of the values $i = 1, 2, \ldots, s$ we have

$$\sum_{j=0}^{s} \frac{e_j^2}{4D} N_j \frac{\partial m}{\partial N_i} = \frac{e_i^2 m}{8D} \quad \text{for} \quad i = 1, \ldots, s.$$

If on the other hand, $i = 0$ i.e. we are dealing with variations in the solvent, we may proceed as follows. We can write the total volume of the solution V in the linear form

$$V = V_0 N_0 + \sum^{s} N_i v_i,$$

where v_0 and v_i represent the changes in the total volume caused by adding respectively a molecule of the solvent or a particle of the sort the solution. We then have

$$\frac{\partial m}{\partial N_i} = \frac{\partial m}{\partial V} \frac{\partial V}{\partial N_0} = V_0 \frac{\partial m}{\partial V} = -\frac{V_0}{2V} m$$

and hence

$$\sum_{j} \frac{e_j^2}{4D} N_j \frac{\partial m}{\partial N_0} = -V_0 \frac{n_j e_i^2}{8D}.$$

The total variation in thermodynamic potential is thus

$$\delta\Phi = \delta N_0 \left[\Phi_0 + kT \log y_0 + v_0 \sum \frac{n_j e_j^2 m}{8D} \right]$$

$$+ \sum_{1} \delta N_i \left[\Phi_i + kT \log y_i - \frac{3}{8} \frac{e_i^2 m}{D} \right].$$

The coefficient of δN_i is termed the chemical potential. In the case of ideal dilute solution, the chemical potential is given by

$$\xi_i = \Phi_i + kT \log y_i$$

The chemical potential of the real solution is obtained by replacing the concentration y_i by the activity $f_i y_i$ for dilute solutions, where f_i being the activity coefficient. We then have

$$\xi_i = \Phi_i + kT \log (f_i y_i).$$

Thus $$\log f_i = -\frac{3}{8} \frac{e_i^2 m}{DkT}. \tag{6}$$

The activity of the solvent is also affected by the dissolved ions, the activity coefficient being given by

$$\log f_0 = v_0 \sum_j \frac{n_j e_j^2 m}{8DkT}. \tag{7}$$

Thus the decrease in the activity coefficient of the ions at the surface is smaller than that of the interior. The increase in the activity coefficient of the solvent at the surface is also smaller than that of the interior.

The limiting law for the activity coefficients of binary salts in water at the surface is given by

$$0°\text{C.} \quad \log f = -0.839\sqrt{J},$$

$$15°\text{C.} \quad \log f = -0.860\sqrt{J},$$

$$20°\text{C.} \quad \log f = -0.872\sqrt{J},$$

where J is the ionic strength defined by

$$J = \frac{1}{2} \sum \gamma_i z_i^2$$

and γ_i is expressed in moles per litre.

Thus we get for

$$\frac{\partial \log f}{\partial J} = -0.419 \frac{1}{\sqrt{J}}.$$

Therefore for concentration $J = 0.01$, the absolute magnitude of $\frac{d \log f}{dJ}$ is about 4.2 % of the value of $\frac{1}{J}$. Therefore for very dilute solutions this term can be neglected in rough calculations.

Osmotic pressure and activities in dilute mixture of electrolyte and non-electrolyte. In order to find the additional free energy caused by the pressence of the ionic charges, we shall proceed in the same way as before. We imagine the ions discharged in an infinitely dilute solution, and recharged in a solution of finite concentration. If the solution contains $N_1, \ldots, N_i, \ldots,$

N_s ions of the species $1,\ldots,i,\ldots,s$ having charges $e_1,\ldots,e_i,\ldots,e_s$ the work necessary to carry out this process W is given by

$$W = -\sum \frac{N_i e_i^2}{2D_0 b_i} + \sum \frac{N_i e_i^2}{2D_m b_i} - \sum \frac{N_i e_i^2 m}{4D_m}. \tag{8}$$

For the sake of simplicity, an ion of the i th sort is considered as a sphere of radius b_i which is charged in pure water of dielectric constant D_0, and subsequently in the solution of given concentration D_m at the surface of the solution. m is the reciprocal thickness of the ionic atmosphere. Since we are dealing only with a first approximation, we can represent the dielectric constant of the mixture D_m by the linear interpolation formula.

$$D_m = D_0(1-\alpha n-\beta n'), \tag{9}$$

where n and n' represent the number of molecules of non-electrolyte and electrolyte respectively per c.c., and α and β are two constants which may be determined from experiment.

We introduce (9) in (8) and expand $1/D_m$ in the 2nd term in powers of n and n', retaining only the 1st term of the expansion, and write D_0 for D_m in the third term. We then have

$$W = \alpha n \sum \frac{N_i e_i^2}{2D_0 b_i} + \beta n' \sum \frac{N_i e_i^2}{2D_0 b_i} - \sum \frac{N_i e_i^2 m}{4D_0}.$$

Thus we get

$$-\frac{\partial W}{\partial V} = \alpha n \sum \frac{n_i e_i^2}{2D_0 b_i} + \beta n' \sum \frac{n_i e_i^2}{2b_i D_0} - \sum \frac{n_i e_i^2 m}{8D_0},$$

where $n = N/V$, $n' = N'/V$.

If one molecule of the electrolyte dissociate into ν_i of the species $1,\ldots,\nu_s$ of the species s, having valencies $z_1,\ldots,z_i\ldots,z_s$, we have $n_i = \nu_i n'$, $e_i = z_i\epsilon$. Introducing abreviations

$$\nu = \sum \nu_i$$

$$P_N = nkT$$

$$P_E = \nu n' kT\left(1 - \frac{n_0\epsilon^2}{8D_0 kT}\frac{\sum \nu_i z_i^2}{\nu}\right)$$

$$p = \alpha \frac{n\nu n'\epsilon^2}{2D_0\nu} \sum \frac{\nu_i z_i^2}{b_i}$$

we can write for the osmotic pressure

$$P = P_N + P_E + p. \tag{10}$$

Thus the effect of surface on the osmotic pressure appears only in osmotic pressure P_E which would be exerted by the $n'\nu$ ions of electrolyte if present alone in the surface phase.

The effect of surface is to increase the osmotic pressure P_E slightly.

We shall now calculate the effect of the electrolyte on the activity of the non-electrolyte at the surface of the solution. If we write the electrical energy contribution W in the form $W = \Sigma N_i \bar{\omega}_i$, where $\bar{\omega}_i = \omega_i / N$ the activity potential h_i is defined by

$$\log h_i = \frac{\bar{\omega}_i}{kT} = \frac{\alpha n e_i^2}{2D_0 b_i kT} + \beta \frac{n' e_i^2}{2D_0 b_i kT} - \frac{e_i^2 m}{4D_0 kT}.$$

The activity potential of the non-electrolyte is unity, and only the activity potential of the ions differs from unity. Activity coefficient f_i of any component i is

$$\log f_i = \log h_i + \sum_j N_j \frac{\partial \log h_i}{\partial N_i}.$$

Since $h = 1$, $\log h = 0$. Activity coefficient of non-electrolyte is given by

$$\log f = \alpha \sum \frac{n_j e_j^2}{2D_0 b_i kT}. \tag{11}$$

Thus the activity coefficient of non-electrolyte at the surface of the solution is the same as the activity coefficient in the bulk of the solution in the first approximation.

The activity coefficient of ions at the surface is calculated by means of

$$\sum_j N_j \frac{\partial \log h_i}{\partial N_i} = -\frac{1}{8} \frac{e_i^2 m}{D_0 kT}.$$

The second term of $\log h_i$ can be neglected for solution of dilute concentration. Then

$$\log f_i = \frac{\alpha n e_i^2}{2D_0 b_i kT} - \frac{3}{8} \frac{e_i^2 m}{D_0 kT}. \tag{12}$$

Since n is the concentration of non-electrolyte,

$$\left(\frac{\partial \log f_i}{\partial c_1}\right)_{c_2} = \frac{\partial \log f_i}{\partial c_1}.$$

This is what we wanted to prove. From the above discussion it may be apparent that the above relation will hold for the case in which a more general form of energy is assumed than the one discussed in the paper.

In conclusion, the author wishes to express his thanks to Professor H. Erikson for his kind encouragement.

Summary.

The osmotic pressures and the activity coefficients for strong electrolyte solution and for solutions of mixture of electrolyte and non-electrolyte at the surface are calculated on the basis of Debye-Hückel theory. Some relations between the activity coefficients for two cases are given.

Physics Department, University of Minnesota,
Minneapolis, Minn., U.S.A.

The Addition of Hydrogen Bromide to Allyl Bromide in the Presence of Various Substances. IV. The Effect of the Ferro-magnetic Metals Free from Oxides. Remarks on the Catalytic Action of the Ferro-magnetic Metals and Oxygen.

By Yoshiyuki URUSHIBARA and Matsuji TAKEBAYASHI.

(Received December 28th, 1936.)

The authors have found that the ferro-magnetic metals in such forms as reduced iron and reduced nickel influence the addition of hydrogen bromide to allyl bromide in the same way as oxygen and peroxides:[1] In the presence of reduced iron or reduced nickel, hydrogen bromide adds rapidly to allyl bromide (in the dark at room temperature in the absence of solvents, oxygen, and peroxides) and the greater part of the product is the abnormal addition product 1,3-dibromopropane, while in the absence of foreign substances the addition is slow and proceeds mainly to the formation of the normal product 1,2-dibromopropane. A difference, however, exists between these two groups of catalysts in that, while the influence of oxygen or peroxides is totally eliminated by

(1) The first paper of this series, this Bulletin, **11** (1936), 692.

the addition of an antioxidant such as diphenylamine, the effect of the ferro-magnetic metals undergoes no modification in the presence of the antioxidant.[2] Now, with a special precaution of removing traces of oxides from the reduced metals, the ferro-magnetic metals have been found more effective in the sense of the predomination of 1,3-dibromopropane in the product of addition of hydrogen bromide to allyl bromide than in the previous experiments carried out with no such precaution.

In the previous experiments with freshly reduced nickel the percentage of 1,3-dibromopropane in the addition product was found 68[1], 63[1], and 58[2]. Reduced nickel used in those additions was prepared under the conditions suitable for the preparation of the hydrogenating catalyst by passing pure hydrogen gas over nickel oxide (Kahlbaum, "cobalt free") heated at 300–400°. Reduction might possibly be incomplete at this temperature, and, moreover, the metal reduced in this way evolved heat when taken to the air. Thus it may be suspected that even freshly reduced nickel was not free from traces of oxides.[3] As it was really found that the power of accelerating the abnormal addition is far diminished by keeping reduced nickel long in the air,[2] it seemed very important to examine the effect of reduced nickel free from oxides. For this purpose nickel oxide was reduced at a higher temperature (dull red-heat). The metal was obtained in a loosely coalescent form crumbling readily on shaking and evolved heat when taken to the air. The metal (3.5 g.) contained in the reaction tube was again heated at 300-400° in the atmosphere of hydrogen, then, without entrance of air, treated in vacuum at 250°, and washed with hydrogen bromide gas. Hydrogen bromide (20 g.) and allyl bromide (24 g.) collected in the mixing tube were then distilled in vacuum into the reaction tube containing reduced nickel. The reaction tube was sealed off without entrance of air, slipped into an iron pipe, and shaken at room temperature for three days. The contents were treated as described previously.[4] The results are shown in the accompanying table (exp. 1 and exp. 2). Ninety-five per cent. of the product was 1,3-dibromopropane in both experiments. The reduced nickel appeared to have not suffered the slightest attack by hydrogen bromide and the liquid remained colourless after reaction.

In the additions in the presence of commercial reduced iron (Kahlbaum) about seventy per cent. of the product was 1,3-dibromopropane (see the tables of the first and the second papers).[1][2] It was already anticipated that the effect of freshly reduced iron would be more conspicuous.[5] A result as

(2) The second paper of this series, this Bulletin, **11** (1936), 754.

(3) Adsorbed or absorbed oxygen, if any, was removed by evacuating at 250° and washing with hydrogen bromide gas.

(4) For the details of the experimental procedure see the first paper.

(5) This Bulletin, **11** (1936), 756.

No. of exp.	Catalyst	Product: Dibromopropanes			
		Yield (%)	Boiling point (°C./mm.)	1,3-(%)	1,2-(%)
1	Reduced nickel free from oxides, 3.5 g.	40	44—53/11	95	5
2	Reduced nickel free from oxides, 3.5 g.	60(6)	43—54/10	95	5
3	Freshly reduced iron, 3.4 g.	40	40—53/10	92	8
4	Reduced cobalt free from oxides, 3.5 g.	30	32—46/10	38	62

shown in the table (exp. 3) has really been obtained with reduced iron prepared by freshly heating the commercial product at 300–400° in the stream of hydrogen. Reduced iron prepared in this way evolved no heat in the air. The addition was carried out in the same way as with reduced nickel, except that in this case the metal was used without treating with hydrogen in the reaction tube. The addition product was found to contain more than 90 per cent. 1,3-dibromopropane. The metal was not attacked by hydrogen bromide also in this case and the liquid remained colourless after the reaction.

On account of the fact that cobalt does not resist against the action of hydrogen bromide in allyl bromide in contrast with nickel and iron, with commercial reduced cobalt no effect, and even with freshly reduced cobalt only a small effect, on the direction of addition of hydrogen bromide to allyl bromide were observed (see the table of the second paper).[2] With reduced cobalt prepared by heating the commercial product at dull red-heat in the stream of hydrogen and freed from traces of oxides by reducing again in the reaction tube, a similar result has been obtained (exp. 4). The metal suffered seriously the attack by hydrogen bromide.

The alternating resistance of the three metals of the iron group to hydrogen bromide in allyl bromide finds its counterpart, for instance, in the alternating ease with which they form metal-carbonyls.

The results obtained with the special precaution of eliminating traces of oxides have thus established the well-defined influence of the ferro-magnetic metals on the addition of hydrogen bromide to allyl bromide. They not only inverse the proportion of the normal and the abnormal addition products, but also increase the total yield of the products. Thus the effect of the ferro-

(6) The cause of the exceptionally good yield of exp. 2 is unknown, except that reduced nickel used in this experiment was prepared with nickel oxide from a new bottle (Kahlbaum, "cobalt free").

magnetic metals resembles the so-called peroxide effect of oxygen so far as the results of addition of hydrogen bromide to allyl bromide are concerned. It has now been made very probable that the peroxide effect of oxygen, and also even of peroxides, may be attributed to the action of oxygen itself and not of any formed peroxide.[7] Then, oxygen, the gaseous substance with the greatest magnetic susceptibility, and the ferro-magnetic metals exert similar influences on the addition of hydrogen bromide to allyl bromide. It may be assumed that these substances with great magnetic susceptibilities activate allyl bromide by changing the state of its molecule from a type suitable for the normal addition into one suitable for the abnormal addition, say by means of electron displacement, while platinum black with no significant influence on the composition, but with an increasing effect on the yield, of the product[8] seems to activate hydrogen bromide.

It is thinkable that in organic chemistry there may be not a few cases of the catalytic action by aerial oxygen which have hitherto been unnoticed. For instance, M.S. Kharasch and M. Foy[9] state that the presence of peroxides is necessary for the Cannizzaro reaction to take place, air or oxygen being also effective because of the formation of peroxides, and the heavy metal ions, which were once considered to accelerate the Cannizzaro reaction by themselves, have only a catalytic effect on the peroxide formation but no direct influence on the Cannizzaro reaction itself. But it may be more reasonable to consider that the heavy metal ions would facilitate the decomposition of peroxides, and that peroxides could not stay long in alkali so strong as used in the Cannizzaro reaction, unless very minute traces of peroxides are concerned. Thus it is possible that the active catalyst is really molecular oxygen. The decision awaits for further experimental evidence.

The authors express their hearty thanks to the Imperial Academy of Japan for a grant.

Chemical Institute, Faculty of Science,
Imperial University of Tokyo.

(7) The third paper of this series, this Bulletin, **11** (1936), 798. P.L. Harris and J.C. Smith, *J. Chem. Soc.*, **1935**, 1572, "emphasize that in the absence of air the catalysts perbenzoic acid, benzoyl peroxide, 10,11-epoxyundecoic acid, and α-heptenylheptaldehyde have a very small influence on the composition of the product from hydrogen bromide and undecenoic acid," and point out that "at least with this olefin molecular oxygen is essential for the peroxide effect." But, that the peroxide effect is to be attributed to the catalytic action of molecular oxygen itself, neither is shown by their investigations, nor seems to be meant by their statement, because they summarize their results by saying "none of the catalysts is effective in absence of molecular oxygen," thus recognizing the necessity for the presence of molecular oxygen only in order that their "catalysts" may bring about the peroxide effect.

(8) See the table of the first paper, this Bulletin, **11** (1936), 693.

(9) *J. Am. Chem. Soc.*, **57** (1935), 1510.

Über die chemische Natur der Taka-Amylase. I. Enzymatische Verdauung von Taka-Amylase-Präparaten durch Proteinasen.

Von Shiro AKABORI und Kunio OKAHARA.

(Eingegangen am 7. Dezember 1936.)

Über die chemische Natur der Amylase bestand durch Jahre ein Argument zwischen den Schulen von Willstätter und Sherman. Die erstere behauptete[1] auf Grund Reinigungsversuche der Pankreas-amylase, dass dieses Enzym kein Protein, die letztere dagegen[2] dass Amylase ein Protein sei. Nishimura[3] hat Taka-amylase mit Hilfe der Adsorptionsmethode gereinigt und ein hochaktives Amylase-präparat gewonnen. Sein Präparat gibt fast alle Eiweissreaktionen und enthält 27% Kohlenhydrat. Dagegen fehlen Eiweisseigenschaften bei den gereinigten Amylasen aus *Ipomoea Batatas* nach Giri[4] und aus Reismalz nach Itoh.[5]

Wir haben die Wirkung von Trypsin und Papain auf teilweise gereinigtes, proteinhaltiges Taka-amylase-präparat geprüft und konnten feststellen, dass die Stärkeverzuckerungswirkung dieser Amylase durch die beiden proteolytischen Enzyme nicht zerstört wird, während der Proteinanteil deutlich verdaut wird. Taka-amylase geht bei der Dialyse mit Kollodiummembran gegen 50%iges Methanol teilweise in die Aussenflüssigkeit. Aus dieser Flüssigkeit gewinnt man durch Fällen mit Methanol, Auflösen in Wasser, Adsorbieren an Tonerde und Eluieren mit einer 0.1 N Lösung von sekundärem Natriumphosphat ein Amylasepräparat, das mit Trichloressigsäure keine Fällung, aber deutliche Molisch-Reaktion gibt. Bei der Erepsinwirkung auf dieses Amylase-präparat lässt sich auch keine Abnahme der Stärkeverzuckerungswirkung beobachten.

Aus den obigen Resultaten kann man den Schluss ziehen, dass Taka-amylase kein Protein oder Polypeptid ist.

---

(1) R. Willstätter, E. Waldschmidt-Leitz und A. R. F. Hesse, *Z. physiol. Chem.*, **126** (1923), 143; **142** (1925), 14; E. Waldschmidt-Leitz und M. Reichel, *Z. physiol. Chem.*, **204** (1932), 197.

(2) H. C. Sherman, M. L. Caldwell und M. Adams, *J. Am. Chem. Soc.*, **48** (1926), 2947; M. L. Caldwell, L. E. Booher und H. C. Sherman, *Science*, **74** (1931), 37; H. C. Sherman, M. L. Caldwell und S. E. Doebbeling, *J. Biol. Chem.*, **104** (1934), 501.

(3) S. Nishimura, *J. Agr. Chem. Soc. Japan*, **2** (1926), 129.

(4) K. V. Giri, *Biochem. Z.*, **275** (1935), 106.

(5) R. Itoh, *J. Biochem.*, **23** (1936), 125.

Beschreibung der Versuche.

Amylase-präparat-A. 50 g. Taka-diastase wurden in 200 c.c. Wasser gelöst, mit 233 c.c. Methanol versetzt und die von dem abgeschiedenen Niederschlag abfiltrierte Lösung wiederum mit 367 c.c. Methanol versetzt (die Methanolkonzentration der entstandenen Lösung soll 70% sein). Der zweite Niederschlag wurde abzentrifugiert und im Vakuum getrocknet. Das so erhaltene Präparat (Sf. 2.1–3.3) wurde in 75 c.c. Wasser gelöst und bei pH = 5 eine grosse Menge von gesättigter Ammoniumsulfatlösung zugegeben. Der abgeschiedene Niederschlag wurde wiederum in Wasser gelöst und mittels einer Kollodiumhülse dialysiert. Das durch Trocknen der Innenlösung gewonnene proteinhaltige Präparat hat Sf. 12–22.

Verdauungsversuche mit Trypsin. Ansätze: 〈5 % ige Lösung des Amylase-präparats-A〉 5 c.c.+〈1/5 Mol Na_2HPO_4〉 2 c.c.+〈Trypsin-Lösung〉 1 c.c. ($T_{(e)} = 0.6$). Nach dem Verlauf von 1 bzw. 5 Stunden wurde der Amino-N nach der van Slykeschen Methode gemessen.

	Stdn. d. Verd.	Amino-N (mg.)	Amino-N-Zuwachs (mg.)
I	0	2.86	—
II	1	4.51	1.65
III	5	6.43	3.57

Amylase-Trypsin-Gemische, wie oben hergestellt, wurden auf das 100-fache verdünnt und mit je 1 c.c. dieser verdünnten Enzymlösungen deren Stärkeverzuckerungswirkung nach der Methode von Willstätter, Waldschmidt-Leitz und Hesse[6] gemessen.

	Stdn. d. Verd. mit Trypsin	N/10 I_2 (c.c.)	Maltose (mg.)	A-E
I	0	4.95	84.9	0.0139
II	1	4.99	85.6	0.0140
III	5	4.97	85.2	0.0140

Verdauungsversuche mit Papain. Ansätze: 〈5 % ige Lösung des Amylase-präparats-A〉 1 c.c.+〈1 N Acetat (pH = 5.0)〉 0.4 c.c.+〈mit Cystein aktivierte Papain-Lösung〉 0.4 c.c. +〈Wasser〉 3.2 c.c. Nach ein bzw. fünf Stunden wurde der Amino-N bestimmt.

	Stdn. d. Verd.	Amino-N (mg.)	Amino-N-Zuwachs (mg.)
I	0	0.69	—
II	1	1.19	0.50
III	5	1.34	0.65

(6) R. Willstätter, E. Waldschmidt-Leitz und A. R. F. Hesse, *Z. physiol. Chem.*, **126** (1923), 143.

Wie oben bereitete Amylase-Papain-Lösungen wurde auf 20 c.c. verdünnt und mit je 1 c.c. davon deren Aktivitäten in üblicher Weise gemessen.

	Stdn. d. Verd. mit Papain	N/10 I_2 (c.c.)	Maltose (mg.)	A-E
I	0	4.11	70.3	0.0109
II	1	4.13	70.8	0.0110
III	5	4.08	70.0	0.0109

Man ersieht also aus den obigen Resultaten, dass das Amylase-präparat-A ein durch Trypsin und Papain spaltbares Protein enthält, bei dessen Spaltung aber keine Inaktivierung der Amylase selbst erfolgt.

Amylase-präparat-B. Das wie beim Amylase-präparat-A durch fraktionierende Fällung teilweise gereinigte Amylase-präparat wurde in 50%igem Methanol gelöst und in einer Kollodiumhülse gegen 50%iges Methanol dialysiert. Die Aussenflüssigkeit wurde mit einer grossen Menge von Methanol versetzt, der Niederschlag abgetrennt, in Wasser gelöst und bei pH = 5.0 an Tonerde C_T adsorbiert. Das Adsorbat wurde mit 0.1 N Na_2HPO_4 eluiert und wieder mit Methanol gefällt. Die Menge des getrockneten Niederschlags betrugt 0.5 g. aus 50 g. Taka-diastase. Sf. 17.6. Die wässrige Lösung dieses Präparats gab keine Fällung mit Trichloressigsäure, aber mit basischem Bleiacetat einen weissen Niederschlag und deutliche Molisch-Reaktion.

Verdauungsversuche mit Trypsin. Ansatz: 〈3 % ige Lösung des Amylase-präparats-B〉 5 c.c.+〈1/5 Mol Phosphat (pH = 7.7)〉 2 c.c.+〈Trypsin-Lösung〉 1 c.c. ($T_{(e)}$ = 0.45)+〈Wasser〉 2 c.c. Nach verschiedenen Zeiten wurde jeweils 1 c.c. der Ansatzlösung herausgenommen auf 50 c.c. verdünnt und mit 1 c.c. davon die Stärkeverzuckerungswirkung gemessen.

	Stdn. d. Verd. mit Trypsin	N/10 I_2 (c.c.)	Maltose (mg.)	A-E
I	0	1.34	23.0	0.0029
II	½	1.38	23.7	0.0030
III	1	1.34	23.0	0.0029
IV	5	1.35	23.2	0.0029

Verdauungsversuche mit Erepsin. Erepsin-Lösung wurde aus der Schleimhaut von Schweinsdünndarm hergestellt und ihre Aktivität mit Leucyl-diglycin und Leucyl-glycin nachgewiesen. Ansätze I: 〈1/5 Mol Tripeptid-Lösung (pH = 9)〉 5 c.c.+〈Erepsin-Lösung〉 2 c.c. Ansätze II: 〈1/5 Mol Dipeptid-Lösung (pH = 9)〉 5 c.c.+〈Erepsin-Lösung〉 2 c.c.

Verdauungsz. in Min.	COOH-Zuwachs (c.c. N/5 KOH)	
	Tripeptid	Dipeptid
20	0.93	0.17
60	1.29	0.45

Aktivität der Amylase-Erepsin-Lösung: 〈3 %ige Lösung des Amylase-präparats-B〉 5 c.c. + 〈1/5 Mol Phosphat (pH = 7.7)〉 + 〈Erepsin-Lösung〉 1 c.c. + 〈Wasser〉 2 c.c. Nach verschiedenen Zeiten wurde jeweils 1 c.c. der Verdauungslösung herauspipetiert, auf 50 c.c. verdünnt und mit 1 c.c. davon die Stärkeverzuckerungswirkung gemessen.

	Stdn. d. Verd. mit Erepsin	N/10 I_2 (c.c.)	Maltose (mg.)	A-E
I	0	1.35	23.0	0.0029
II	$\frac{1}{2}$	1.36	23.7	0.0030
III	1	1.33	23.0	0.0029
IV	5	1.34	23.2	0.0029

Zum Schluss möchten wir der Taniguchi Kogyo-shoreikai (der Taniguchi-Gesellschaft zur Förderung der technischen Industrie) für die finanzielle Unterstützung, die diese Versuche ermöglicht hat, unseren herzlichen Dank aussprechen.

Chemisches Institut der Kaiserlichen Universität zu Osaka.

Études spectrochimiques des matières colorantes dérivées de la quinone-imine[1].

Par Taku UÉMURA et Mochiyuki ABÉ.

(Reçu le 11 décembre 1936.)

Un des deux auteurs (Uémura) étudie[2] depuis longtemps des composés azoïques au moyen de leurs spectres d'absorption pour discuter leurs constitutions chimiques en solution aqueuse. Dans le présent mémoire nous exposons des recherches semblables faites sur des dérivés de la quinone-imine choisis comme composés renfermant l'azote.

La recherche actuelle est basée sur la méthode spectrochimique que nous avons déjà adoptée pour les composés azoïques, c'est-à-dire en nous servant du spectrographe en quartz de l'Anglais Adam Hilger; les courbes Hartley et Baly ont été obtenues de la photographie des spectres d'absorption. Nous avons discuté sur la structure chimique et l'influence des radicaux organiques introduits dans les colorants étudiés en comparant la position des bandes de l'absorption sélective de ces composés synthétisés avec celle de la quinone.

Procédé expérimental et préparation des corps étudiés. Les courbes des spectres d'absorption présentées dans le présent travail (courbes Hartley-Baly) ont été dessinées en portant les logarithmes des épaisseurs des solutions liquides correspondant à la concentration de 1/10000 mol sur l'axe des ordonnées, et la réciproque d'une longueur d'onde (la fréquence) sur celui des abscisses.

Les photographies ont été prises avec des plaques panchromatiques "Fuji" (marque japonaise) ou "Ilford" (marque anglaise). La source lumineuse pour le spectrographe a été fournie par un arc métallique en fer alimenté par un courant continu (4 à 5 ampères à 100 volts). Les solutions à étudier ont été préparées en dissolvant l'échantillon purifié dans l'alcool ou l'éther. Les auteurs ont quelquefois pris la photographie d'absorption en appliquant une méthode spéciale, celle de couvrir la solu-

(1) Une partie de ce mémoire a été publiée lors de la 57e Séance annuelle de la Société chimique du Japon, le 5 avril 1935, et l'autre partie, lors de la Séance mensuelle de la même Société, le 11 juillet 1936.

(2) Ce bulletin, **1** (1926), 260; **2** (1927), 10, 48, 229, 249; **3** (1928), 105; **10** (1935), 169.

tion à étudier avec de l'azote pour l'empêcher d'être oxydée. Parmi les produits formés dont il est question dans le présent mémoire, il y en a quelques-uns qui sont instables et difficiles à préparer. On a pu cependant synthétiser une quinzaine de corps pour les recherches actuelles.

(1) *Benzoquinone-monoïmine,* $O:C_6H_4:NH$. Nous avons essayé de préparer ce composé d'après la méthode proposée par Willstätter et Pfannenstiel[3] ou celle présentée par Kehrmann[4]. Mais comme ce composé est très instable et facilement influencé par l'air et l'humidité en appliquant la méthode de filtration ou condensation ordinairement utilisée, on n'a pas pu obtenir de cristaux clairs. Pour éviter les influences ci-dessus nommées, en faisant l'oxydation dans une atmosphère d'azote sec, nous avons obtenu une solution jaune et transparente que nous avons filtrée, condensée et refroidie moyennant un mélange réfrigérant. Dans l'azote nous avons ainsi obtenu un cristal blanc, que nous avons évité de retirer du vase clos. Comme nous étions bien convaincus qu'il est impossible de faire le dosage du corps dans l'air, l'appareil spécial ci-dessous décrit a été employé.

En dissolvant le *p*-aminophénol soigneusement purifié par l'éther suffisamment déshydraté, on obtient une solution de 1/100 ou 1/mol. L'ayant oxydée avec soin, une solution jaune a été formée. En admettant que le titre de la solution quinone-monoïmine était de 1/100 ou 1/50 mol, nous avons pris ses photographies d'absorption à l'aide du tube de Baly dans une atmosphère d'azote. Cette solution éthérique jaune prend rapidement une couleur brune par le contact de l'air et a un caractère de colorer fortement la peau.

Les auteurs ont essayé dans leur présent travail d'utiliser pour le courant d'azote un appareil d'oxydation spécial dont voici la description sommaire. On a installé la partie entourée par la ligne pointillée dans la figure 1, sur l'agitateur. En fermant les robinets 11 et 12 et ouvrant celui de 13, on fait passer l'azote sec de la bombe par les dessiccateurs 3 et 4, pendant quelques minutes. Ayant ainsi remplacé l'air dans l'appareil par l'azote, les substances à réagir toutes pesées d'avance sont rapidement introduites dans la bouteille 6 (fig. 1). Ayant fait lentement repasser l'azote pour chasser l'air qui pouvait s'y trouver, on ouvre le robinet 12 et on ajoute la quantité nécessaire d'éther moyennant une pipette par le robinet 11. Ensuite, en fermant les robinets 11 et 13, on agite cet appareil d'oxydation 6 avec ses accessoires qu'on met sur l'agitateur. L'oxydation étant terminée, en unissant l'appareil de filtration et le tube

(3) R. Willstätter et A. Pfannenstiel, *Ber.*, **37** (1904), 4607.
(4) F. Kehrmann, *Ber.*, **56** (1923), 2399.

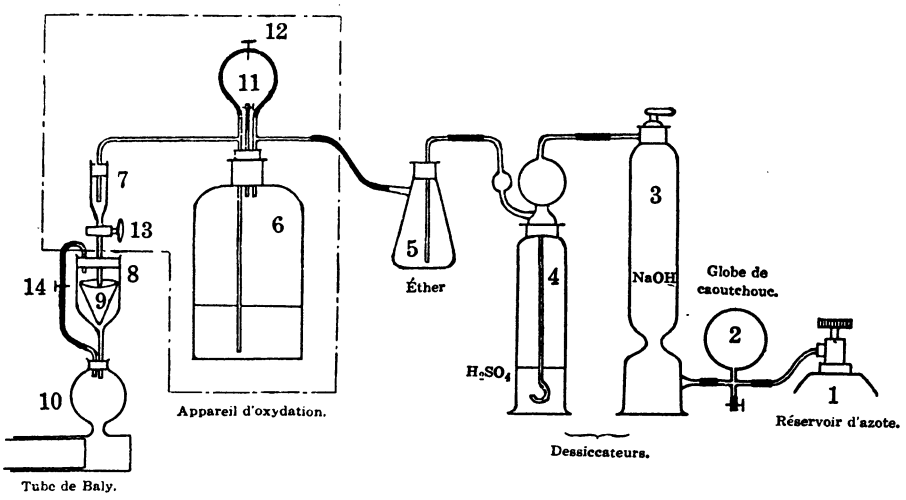


Fig. 1. Appareil d'oxydation dans un courant d'azote.

de Baly, l'air de ce vase est chassé par le courant d'azote et la solution éthérique passe directement dans le tube de Baly. En ouvrant le robinet 14 pour aider la descente de la solution et détachant la partie de jonction 7, on a photographié en laissant ce tube de Baly avec l'appareil de filtration. Une petite poire de caoutchouc installée auprès de la bombe d'azote peut constamment régler la pression et permet de juger de la quantité du gaz passant. Lorsqu'on peut procéder quantitativement, le vase 5 renfermant l'éther a été ajouté pour contrôler l'éther en excès s'échappant de l'équipement dans l'appareil d'oxydation 6. Les auteurs croient que cet appareil une fois bien installé met les solutions à l'abri de toute influence de l'air et de l'humidité.

Lorsque la réaction d'oxydation procède quantitativement, on obtiendra la solution éthérique de quinone-imine ayant une concentration déterminée par l'admixtion de aminophénol et d'éther etc. tous bien pesés d'avance. Une méthode pareille peut être appliquée aux corps difficiles à cristalliser, c'est-à-dire on peut obtenir directement cette solution éthérique au tube de Baly pour prendre la photographie d'absorption. Nous avons utilisé au cas actuel l'aminophénol extrêmement pur, l'oxyde d'argent fraîchement préparé, le sulfate de soude pur ou l'éther purifié.

(2) *Toluquinone-monoïmine,* $O:C_6H_3(CH_3):NH$. En appliquant la méthode de Staedel et Kolbe[5], on peut former le *p*-amino-*m*-crésol gris

(5) W. Staedel et A. Kolbe, *Ann.*, **259** (1890), 208.

en poudre en partant du *m*-crésol. Et encore, en nous basant sur la méthode de Cordone[6], nous l'avons pris matière première et l'avons oxydé par l'oxyde d'argent en solution éthérique. Nous avons ainsi préparé la toluquinone-monoïmine sous forme basique en solution difficile à obtenir cristallisée. Nous avons suivi le procédé appliqué au composé précédent (composé (1)), c'est-à-dire, nous avons utilisé le même appareil représenté dans la figure 1 pour la préparation du composé (2). En oxydant la 1/100 mol solution éthérique du *p*-amino-*m*-crésol, la toluquinone monoïmine de 1/100 mol solution a été supposée avoir été obtenue pour la photographie spectrale.

(3) *Méthylquinone-monoïmine,* $O:C_6H_4:N\cdot CH_3$. Ayant formé le *p*-aminophénol du métol (méthyl-*p*-aminophénol) et suivant les indications fournies par Willstätter et Pfannenstiel[7], nous obtenons le composé (3) en solution après l'avoir oxydé par l'oxyde d'argent et le peroxyde de plomb. Mais, comme ce composé est explosible, nous en avons un peu. L'oxydation s'est faite dans le courant d'azote comme pour les deux composés précédents. La solution obtenue par l'oxydation d'une 1/100 mol solution de méthylquinone-monoïmine a été supposée au même titre que celle de 1/100 mol du *p*-aminophénol.

(4) *Phénylquinone-monoïmine,* $O:C_6H_4:N\cdot C_6H_5$. Nous avons d'abord synthétisé la *p*-oxydiphénylamine d'après le procédé proposé par Calm[8] et l'avons suffisamment purifiée pour obtenir le solide ayant 66–68°C. pour point de fusion. Ensuite, l'ayant prise comme matière première, nous avons suivi les indications données par Bandrowski[9] en l'oxydant par l'oxyde de mercure jaune en solution benzénique et obtenu des cristaux aciculés brun-rouges. Nous les avons recristallisés par la ligroïne, et obtenu une substance bien purifiée rouge-foncée ayant 98°C. pour point de fusion. Pour le spectre d'absorption nous nous sommes servis d'une solution jaune en la dissolvant dans l'alcool.

(5) *Indoaniline,* $O:C_6H_4:N\cdot C_6H_4\cdot NH_2$. En se référant au livre de M. K. Goto[10], on a oxydé la solution aqueuse mélangée de la *p*-phénylènediamine et le phénol avec le peroxyde de plomb et le phosphate de soude. L'indoaniline a été extraite par l'alcool du précipité ainsi produit et on

(6) W. Cordone, *Helv. Chim. Acta,* **7** (1924), 962.
(7) R. Willstätter et A. Pfannenstiel, *Ber.,* **38** (1905), 2251.
(8) A. Calm, *Ber.,* **16** (1883), 2799.
(9) E. Bandrowski, *Monatsh.,* **9** (1888), 133.
(10) K. Goto, "Gôsei Yûki-Kagaku", (1928), 378.

obtint des cristaux fins aciculés ayant l'éclat métallique noir. Notre photographie d'absorption a été prise avec sa solution alcoolique violette.

(6) *Bleu de phénol,* $O:C_6H_4:N\cdot C_6H_4\cdot N(CH_3)_2$. En réduisant le chlorure de la nitrosodiméthylaniline par le chlorure d'étain et l'acide chlorhydrique, la *p*-aminodiméthylaniline long-aciculée non-colorée a été formée, et d'après la méthode présentée par Heller[11], on en a fait réagir l'hypochlorite de soude sur le mélange phénolique pour l'oxyder. En dissolvant le précipité amorphe ainsi obtenu dans l'alcool, on obtient la solution bleue qui donne la matière noire granuleuse par condensation et refroidissement. La substance ainsi obtenue en solution alcoolique se présente sous une couleur bleue sombre tournant au bleu lorsque la solution est basique.

(7) *Phénylindoaniline,* $O:C_6H_4:N\cdot C_6H_4\cdot NH\cdot C_6H_5$. En appliquant la méthode présentée par Heller[12], la *p*-oxydiphényl-*p*-phénylènediamine a été préparée de la *p*-aminodiphénylamine et la hydroquinone et nous l'avons oxydée en solution benzénique avec l'oxyde de mercure jaune; en condensant la solution, un cristal bleu-violet a été formé et par recristallisation il a tourné au violet-noir avec un joli brillant doré. Comme ce cristal ainsi obtenu renferme une molécule du dissolvant dans sa molécule, on l'a conservé dans le dessiccateur à vide pendant deux semaines pour en chasser le chloroforme avant de prendre la photographie d'absorption.

Le présent composé se présente sous une coloration différente suivant le dissolvant: bleu par l'alcool, violet par le chloroforme et rouge-violet par l'hexène. Toutes ces solutions différemment colorées ne donnent cependant qu'une seule substance indigo-bleue en volatilisant ces dissolvants. Lorsqu'on en fait sécher sur la flamme, le composé devient violet et lorsqu'on le retire de la flamme il vire de nouveau au bleu. Aucune influence n'est donnée par l'addition d'eau ou d'acide acétique glacial, mais il change de couleur par l'acide chlorhydrique ou la soude caustique. Nos photographies d'absorption du composé actuel ont été prises de solutions alcooliques et hexéniques.

(8) *Chloroquinone-monoïmine,* $O:C_6H_4:N\cdot Cl$. Ce composé a été préparé d'après la méthode donnée dans le livre écrit par Vanino[13]. C'est un cristal jaune aciculé donnant 88°C. pour point de fusion et

(11) G. Heller, *Ann.*, **392** (1912), 47.
(12) G. Heller, *Ann.*, **418** (1918), 273.
(13) L. Vanino, "Präparative Chemie", II (1923), 689.

soluble dans l'eau chaude, l'alcool et l'éther; sa couleur superficielle change dans l'air; il se décompose en le chauffant avec l'eau chaude.

(9) *Quinone-diimine,* $NH:C_6H_4:NH$. Ce composé a été préparé par une méthode semblable à celle employée pour la quinone-monoïmine, c'est-à-dire d'après les indications présentées par Willstätter et Pfannenstiel[14] ou par Kehrmann[15] en employant l'appareil spécial qu'on a déjà décrit. A l'état solide la substance est incolore tandis que sa solution est jaune à cause de la polymérisation. Comme ce composé à l'état solide est assez instable, on ne peut pas le conserver dans l'air. Il faut le traiter sans l'extraire de sa solution éthérique pour le photographier.

(10) *Méthylquinone-diimine,* $HN:C_6H_4:N\cdot CH_3$. Nous sommes parvenus à former ce composé d'après la méthode indiquée par Willstätter et Moore[16] en employant l'appareil spécial comme pour le composé précédent, mais la purification est difficile à cause de la décomposition du produit formé et le traitement dans la solution éthérique est le même que celui pour le composé précédent. Le solide est instable formant un cristal aciculé incolore facile à décomposer, dont le point de fusion est 64–67°C.

(11) *Diméthylquinone-diimine,* $CH_3\cdot N:C_6H_4:N\cdot CH_3$. En appliquant les indications données par Willstätter et Pfannenstiel[17] et l'appareil employé pour la formation des composés (9) et (10), le présent composé a été synthétisé mais il est instable comme la quinone-diimine. Le solide incolore en fondant à 92.5–93°C. est instable et sa solution se présente jaunâtre.

(12) *Phénylquinone-diimine,* $HN:C_6H_4:N\cdot C_6H_5$. Ce composé a été formé en oxydant la *p*-aminodiphénylamine d'après la méthode présentée par Willstätter et Moore[16]. Le solide et la solution sont tous deux jaunes. Ce composé est comparativement stable dans le gaz sec, mais il se décompose par l'eau, même à basse température. Son point de fusion se trouve à 88–89°C.

(13) *Diphénylquinone-diimine,* $C_6H_5\cdot N:C_6H_4:N\cdot C_6H_5$. Les auteurs ont obtenu cette substance en suivant les indications données par Calm[18] et après par Piccard[19]. C'est un cristal aciculé rouge qui a le point de

(14) R. Willstätter et A. Pfannenstiel, *Ber.*, **37** (1904), 4607.
(15) F. Kehrmann, *Ber.*, **56** (1923), 2399.
(16) R. Willstätter et C. W. Moore, *Ber.*, **40** (1907), 2672.
(17) R. Willstätter et A. Pfannenstiel, *Ber.*, **38** (1905), 2249.
(18) A. Calm, *Ber.*, **16** (1883), 2803.
(19) J. Piccard, *Ber.*, **46** (1913), 1845, 1853.

fusion à 176–180°C. et donne une solution orangée, elle se montre violette dans l'acide sulfurique concentré. Elle semble être peu influencée dans le gaz sec et se dissout dans l'alcool.

(14) *2-Méthyl-4-oxy-phénylquinone-diimine,* $NH:C_6H_4:N\cdot C_6H_3(CH_3)(OH)$. Ce composé a été préparé d'après la méthode proposée par Heller[20]. C'est un cristal aciculé ayant un lustre vert et le point de fusion à 143–144°C. Il est soluble dans l'alcool, mais difficilement soluble dans l'eau et stable dans l'air.

(15) *Dichloroquinone-diimine,* $Cl\cdot N:C_6H_4:N\cdot Cl$. On a formé ce composé comme celui de (8) en se référant au livre écrit par Vanino[21]. Le produit obtenu est un cristal aciculé jaunâtre à peu près blanc qui ne varie pas dans le dessiccateur. Il est assez soluble dans l'acide acétique et peu soluble dans l'alcool et se décompose explosivement à 124°C.

Spectre d'absorption. (1) *Benzoquinone-monoïmine,* (2) *Toluquinone-monoïmine,* (3) *Méthylquinone-monoïmine,* (8) *Chloroquinone-monoïmine,* (a) *p-Quinone et* (b) *Toluquinone.* Les trois premiers composés, comme nous l'avons déjà décrit, sont difficiles à préparer, c'est pourquoi en supposant que la réaction puisse s'effectuer complètement pour obtenir la concentration prévue, leurs photographies d'absorption ont été prises avec les solutions éthériques.

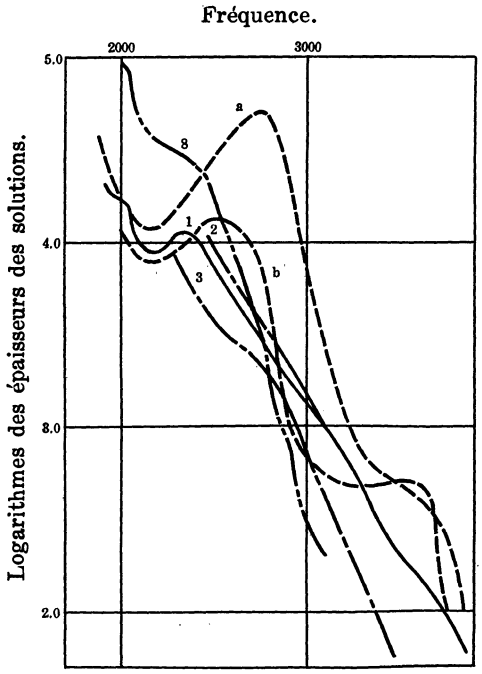
Les courbes 1, 2 et 3 dans la figure 2 ont été comparées avec celles données par la *p*-quinone (courbe a) et la toluquinone (courbe b). Le centre d'absorption sélective donnée par la benzoquinone-monoïmine (courbe 1) est situé à la fréquence 2150 qui est semblable à celle montrée par ces deux quinones (courbes a et b). L'influence du radical CH_3 dans la quinone-monoïmine est présentée dans la figure 2. Mais ces deux corps préparés n'ont pas donné de solutions concentrées et la position des centres de leurs courbes d'absorption n'a pas pu être bien fixée. Nous pouvons cependant admettre peu de différence avec celle de la quinone-monoïmine (courbe 1). La fin d'absorption de ces trois premiers composés se trouvent à peu près à la même position et la méthylquinone-monoïmine (courbe 3) montre peu de signes bathochromiques.

La solution alcoolique de chloroquinone-monoïmine (composé 8) ne montre pas d'absorption sélective distincte et n'est qu'une absorption

(20) G. Heller, *Ann.*, **392** (1912), 45.
(21) L. Vanino, "Präparative Chemie", II (1923), 689.

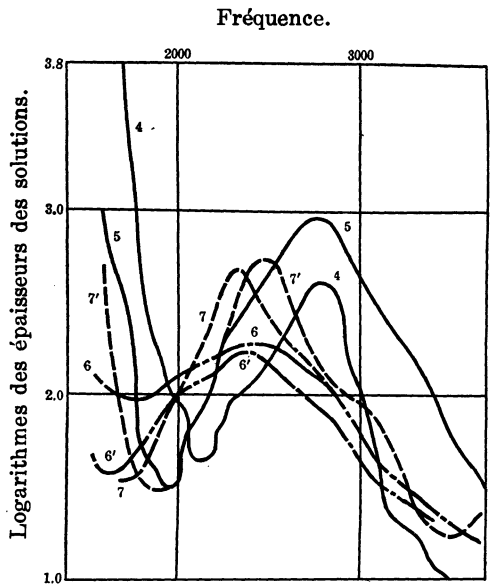
générale en partie de grande longueur d'onde. On peut cependant trouver une sinuosité nette à la position de centre d'absorption de la benzoquinone-monoïmine.

(4) *Phénylquinone-monoïmine,* (5) *Indoaniline,* (6) *Bleu de phénol et* (7) *Phénylindooniline.* La phénylquinone-monoïmine a une absorption sélective ayant le centre d'absorption à la fréquence 2100. Cette position du centre est presque la même que celle montrée par la méthyl-quinone-monoïmine (fig. 2), mais le pouvoir absorbant de la phénylquinone-monoïmine (fig. 3) est sensiblement hyperchromique. Il est naturel que l'indoaniline contenant l'auxochrome NH_2 montre une propriété plus



1. $O:C_6H_4:NH$ 2. $O:C_6H_3(CH_3):NH$
3. $O:C_6H_4:N\cdot CH_3$ 8. $O:C_6H_4:N\cdot Cl$
a. $O:C_6H_4:O$ b. $O:C_6H_3(CH_3):O$

Fig. 2.



4. $O:C_6H_4:N\cdot C_6H_5$
5. $O:C_6H_4:N\cdot C_6H_4\cdot NH_2$
6. $O:C_6H_4:N\cdot C_6H_4\cdot N(CH_3)_2$ (neutre)
7. $O:C_6H_4:N\cdot C_6H_4\cdot NH\cdot C_6H_5$ (alcoolique)
6′. $O:C_6H_4:N\cdot C_6H_4\cdot N(CH_3)_2$ (alcalin)
7′. $O:C_6H_4:N\cdot C_6H_4\cdot NH\cdot C_6H_5$ (hexénique)

Fig. 3.

bathochromique et plus ou moins hyperchromique, c'est-à-dire que le centre d'absorption de ce composé se trouve à peu près vers 2000 de fréquence.

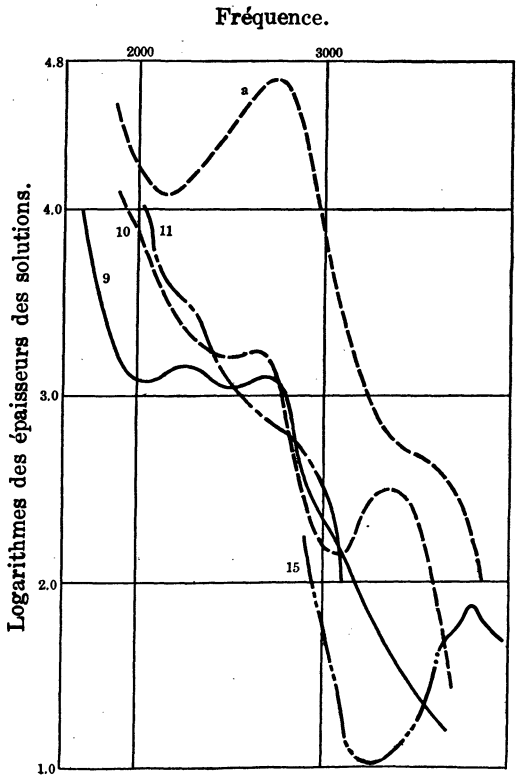
Le bleu de phénol et la phénylindoaniline sont deux composés où l'auxochrome NH_2 est remplacé par un radical différent, méthyl ou phényl. Le centre d'absorption donné par le bleu de phénol (courbe 6 – fig. 3) présente à peu près 1800 de fréquence en solution neutre tandis que celui en solution alcaline (courbe 6′ – fig. 3), 1640 de fréquence. Ces deux courbes données par le bleu de phénol sont plus bathochromiques et un peu plus hyperchromiques que celles de la phénylquinone-monoïmine et l'indoaniline (courbe 4 et 5 – fig. 3).

Nous avons pris la photographie d'absorption de la phénylindoaniline en la dissolvant dans l'alcool et l'hexène. Ces deux courbes obtenues coïncident approximativement, c'est-à-dire la solution alcoolique a son centre d'absorption à 1700 de fréquence et celle d'hexène à 1900 de fréquence. Toutes les deux sont un peu plus hyperchromiques que celle présentée par le bleu de phénol, mais on ne peut trouver que difficilement une grande différence au pouvoir absorbant des deux corps: le bleu de phénol et la phénylindoaniline.

(9) *Quinone-diimine,* (10) *Méthylquinone-diimine,* (11) *Diméthylquinone-diimine et* (15) *Dichloroquinone-diimine.* Ces trois premiers composés, comme nous l'avons déjà montré, sont relativement instables et ont été photographiés dans leurs solutions éthériques. La figure 4 présente leurs courbes d'absorption en les comparant avec celle de la *p*-quinone (courbe a – fig. 4). La quinone-diimine (courbe 9 – fig. 4), ne montrant pas considérablement l'absorption sélective, est plus hyperchromique que la *p*-quinone et présente deux petites absorptions, centre de l'une étant 2050 de fréquence et celui de l'autre 2500 de fréquence.

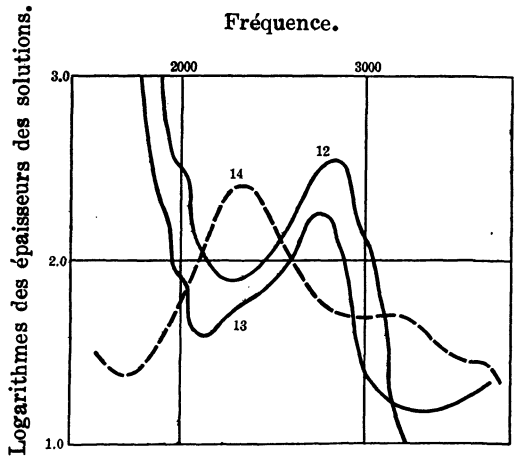
Lorsque un hydrogène du radical NH dans la quinone-diimine est remplacé par un radical alcoylé, son pouvoir absorbant devient faible et ne montrant qu'une absorption moins puissante. Les deux dérivés substitués par CH_3 de la quinone-diimine (composés 10 et 11) sont plutôt plus hypsochromiques que la substance non-substituée par CH_3. La méthylquinone-diimine a deux centres d'absorption, l'un à 2500 de fréquence l'autre à 3050 de fréquence (courbe 10 – fig. 4), tandis que la diméthylquinone-diimine ne donne qu'une absorption sélective presque indistincte (courbe 11 – fig. 4).

La solution de la dichloroquinone-diimine ne donne pas de couleur foncée et l'absorption distincte n'existe pas dans la région visible. Puisque la solubilité de ce composé pour les dissolvants ordinaires n'est pas grande, le spectre d'absorption d'une solution concentrée n'est pas encore obtenu mais une bande d'absorption se trouve clairement dans la région de la longueur d'onde courte (centre d'absorption: 3250 de fréquence).



9. $HN:C_6H_4:NH$
10. $HN:C_6H_4:N\cdot CH_3$
11. $CH_3\cdot N:C_6H_4:N\cdot CH_3$
15. $Cl\cdot N:C_6H_4:N\cdot Cl$
a. $O:C_6H_4:O$

Fig. 4.



12. $HN:C_6H_4:N\cdot C_6H_5$
13. $C_6H_5\cdot N:C_6N_4:N\cdot C_6H_5$
14. $HN:C_6H_4:N\cdot C_6H_3(CH_3)(OH)$

Fig. 5.

(12) *Phénylquinone-diimine,* (13) *Diphénylquinone-diimine et* (14) *2-Méthyl-4-oxy-phénylquinone-diimine.* D'après la figure 5, nous pouvons connaître les courbes d'absorption des composés dans lesquels le radical NH de la quinone-diimine est remplacé par le radical phényl. Nous avons trouvé une grande différence par la substitution de phényl à celui de méthyl, c'est-à-dire, le radical CH_3 n'a pas donnée d'influence sensible sur la courbe d'absorption de la quinone-diimine, tandis que le pouvoir absorbant est considérablement augmenté et l'absorption sélective devient remarquable par l'insertion du radical C_6H_5.

Le centre d'absorption de la phénylquinone-diimine se trouve à 2250 de fréquence et celui de la diphénylquinone-diimine à 2100 et à 3250 de fréquence (courbe 12 et 13 – fig. 5). D'après ces courbes obtenues, on

peut dire que la phénylquinone-diimine est dix fois plus hyperchromique que la quinone-diimine, et la diphénylquinone-diimine encore davantage.

La 2-méthyl-4-oxy-phénylquinone-diimine, après dissolution dans l'alcool neutre comme les deux premiers corps, a été photographiée pour obtenir la courbe d'absorption, et a été reconnue avoir une influence fortement bathochromique par l'insertion de l'auxochrome OH dans le radical phényl de la phénylquinone-diimine, Dans ce cas, comme on peut généralement négliger l'influence du radical méthyl substitué, nous pouvons en conclure que ce résultat bathochromique et hyperchromique est obtenu par le radical OH. Le centre d'absorption de ce composé existe à 1700 de fréquence (courbe 14 – fig. 5) et il est excessivement bathochromique.

Résumé.

(1) *Sur les quinone-monoïmines.* (a) Les courbes d'absorption données par les quinone-monoïmines sont fort semblables à celle de la *p*-quinone qui a une relation éroite avec les premiers composés.

(b) La substitution du radical CH_3 à celui NH dans les quinone-monoïmines donne peu d'influence sur l'absorption des composés étudiés, tandis que l'insertion du radical C_6H_5 peut donner un effet très hyperchromique.

(c) La substitution par l'auxochrome NH_2 dans le radical C_6H_5 de la phénylquinone-monoïmine donne une influence bathochromique et hyperchromique.

(d) Les photographies d'absorption du bleu de phénol et celles de la phénylindoaniline ont été prises en changeant l'état ou l'espèce de leurs dissolvants.

(e) La chloroquinone-monoïmine ne donne pas d'une absorption sélective nette mais sa courbe d'absorption a de l'analogie avec celle montrée par la *p*-quinone.

(2) *Sur les quinone-diimines.* (a) Les quinone-diimines étudiées ont leur centre d'absorption sélective à la fréquence 2050.

(b) La substitution par le radical C_6H_5 dans un radical NH des quinone-diimines a fortement montré le développement du pouvoir absorbant, tandis que l'insertion du radical CH_3 dans les corps a donné peu d'influence.

(c) Les dérivés substitués par CH_3 montrent l'effet hypsochromique sur la quinone-diimine non-substituée.

(d) Lorsque le radical C_6H_5 entre dans la quinone-diimine, le corps substitué par deux phényls est plus bathochromique et plus hyperchromique que celui remplacé par un seul phényl.

(e) Quand le radical NH de la quinone-diimine est remplacé par le radical C_6H_5, l'insertion du radical OH dans ce radical phényl substitué donne un effet fort bathochromique et hyperchromique.

(f) La dichloroquinone-diimine a une couleur peu foncée et elle ne montre pas une absorption distincte sélective dans la région visible.

(3) *Comparaison des monoïmines et des diimines.* (a) Les diimines ont généralement le pouvoir absorbant plus grand que celui donné par les monoïmines.

(b) On peut en conclure de même pour les dérivés alcoylés de ces deux espèces des imines.

(c) Les monoïmines substituées par un seul radical C_6H_5 se montrent plus bathochromiques et hyperchromiques que les diimines.

(d) L'effet absorbant du radical NH_2 ne donne pas une influence sensible aux quinone-monoïmines substituées par le radical C_6H_5, tandis que le radical OH montre une grande influence sur les diimines remplacées par le radical C_6H_5.

En terminant ce mémoire, nous tenons à exprimer nos sincères remerciements à "Nippon Gakujutsu-Shinkôkai" qui a bien voulu se charger d'une partie des frais de nos présentes études.

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

Recherches sur la concentration des ions d'hydrogène contenus dans les solutions aqueuses des ammines-cobaltiques complexes et sur leurs spectres d'absorption. III. Solutions aqueuses des complexes renfermant le radical nitro.

Par Hidéo SUÉDA.

(Reçu le 16 janvier 1937.)

Le présent mémoire est la suite de ceux[2] qui ont déjà été publiés dans ce bulletin avec la collaboration de M. Uémura. Le but est donc parfaitement d'accord avec celui déjà exposé dans les publications précédentes; c'est-à-dire la recherche spectrochimique de l'état des ammines-cobaltiques complexes en solution aqueuse en faisant varier leur concentration des ions d'hydrogène (la valeur du pH). Les complexes cobaltiques contenant le radical d'un acide fort comme Cl ont été étudiés dans les études précédentes tandis que dans le travail actuel ont été pris les complexes renfermant le radical d'un acide faible NO_2. Mon motif d'avoir étudié les complexes contenant ce radical nitro est de connaître les différences obtenues entre ces deux séries, l'une renfermant le radical d'un acide fort, l'autre celui d'un acide faible.

Corps étudiés et procédé expérimental. J'ai préparé plus d'une dizaine des ammines-cobaltiques renfermant le radical NO_2 dans leur noyau complexe par les méthodes indiquées.

(1) $[Co(NH_3)_5NO_2]Cl_2$[3]
(2) $[Co(NH_3)_5ONO]Cl_2$[4]
(3) $[Co(NH_3)_4(NO_2)_2]Cl$ (cis et trans)[5]
(4) $[Co(NH_3)_3(NO_2)_3]$[5]
(5) $[Co(NH_3)_2(NO_2)_4]K$[5]
(6) $[Co(NO_2)_6]Na_3$[5]
(7) $[Co(NH_3)_4NO_2Cl]Cl$[6]
(8) $[Co(NH_3)_4NO_2Cl]Cl\cdot H_2O$[7]
(9) $[Co(NH_3)_4(H_2O)NO_2]Cl_2$[7]
(10) $[Co(NH_3)_4NO_2OH]Cl$[7]
(11) $\{[Co(NH_3)_4NO_2OH]Cl\}_2HCl$[7]
(12) $[Co(NH_3)_4(H_2O)NO_2](NO_3)_2$[3][7]
(13) $[Co(NH_3)_4NO_2OH]NO_3$[7]

J'ai étudié une série des composés ci-dessus nommés en changeant la concentration des solutions. La concentration des ions d'hydrogène des solutions a été déterminée par l'électrode d'antimoine décrite dans un

(1) Publié lors de la 58e Séance annuelle de la Société chimique du Japon, le 2 avril 1936, à Sendaï (Japon).

(2) T. Uémura et H. Suéda, ce bulletin, **10** (1935), 50, 85, 267.

de nos mémoires précédents[8] et les coefficients d'extinction ont été mesurés au moyen du spectrographe en quartz des Français Jobin et Yvon en employant 20 mm. d'épaisseur de solution pour la détermination du spectre d'absorption. J'ai aussi pris, comme auparavant, une lampe à mercure en quartz comme source lumineuse et ai employé en certains cas des plaques spéciales photographiques "Fuji" (marque japonaise) et pour la plupart, celles "extra rapide" Lumière (marque française).

Relation entre la concentration des ions d'hydrogène (*p*H) et la courbe d'absorption des sels complexes. (1) $[Co(NH_3)_5NO_2]Cl_2$, *Chlorure de cobalti-nitro-pentammine;* (2) $[Co(NH_3)_5ONO]Cl_2$, *Chlorure de cobalti-nitrito-pentammine.* La figure 1 montre les courbes d'absorption du sel $[Co(NH_3)_5NO_2]Cl_2$ en solution aqueuse de 1/2500 mol à l'épaisseur liquide de 20 mm. La concentration des ions d'hydrogène de la solution jaune du composé 1 mésurée par l'électrode d'antimoine donne approximativement 8.5, c'est-à-dire faiblement basique. Les solutions portant 8.4 ou 8.6 du *p*H montrent des courbes semblables et j'ai obtenu 9.0 du *p*H par l'addition de 1/2500 liqueur titrée de NaOH pour déterminer les coefficient d'extinction. J'y ai cependant trouvé quelques précipitations par décomposition au cours des mesures spectrochimiques et reconnu en même temps une absorption sélective plus forte que celle trouvée en solution ayant de valeur du *p*H 8.6, mais la position de cette absorption est identique en deux cas. On ne peut donc supposer la variation de constitution jusqu'au moment de la production du précipité. On y peut observer l'analyse reconnue dans le cas de sel lutéo cobaltique $[Co(NH_3)_6]Cl_3$ qui a été expliqué dans notre mémoire déjà publié. Par contre, en prenant 3.2 du *p*H, le composé 1 dissout dans 1/2500 titre HCl montre une position et une intensité semblable au cas où la solution donne la valeur du *p*H 8.6, mais une absorption un peu plus faible dans la région de courtes longueurs d'onde. In globo, j'ai aussi reconnu l'application de la loi de Beer en mesurant l'absorption de 1/1000 mol solution.

Le composé 2 $[Co(NH_3)_5ONO]Cl_2$ est un isomère du composé précédent et un solide rose. Comme il tourne au corps précédent en le gardant plusieurs jours, j'en ai fait l'expérience tout de suite après la préparation.

---

(3) S. M. Jörgensen, *Z. anorg. Chem.*, **17** (1898), 463.

(4) L. Vanino, "Präparative Chemie" I (1923), 644.

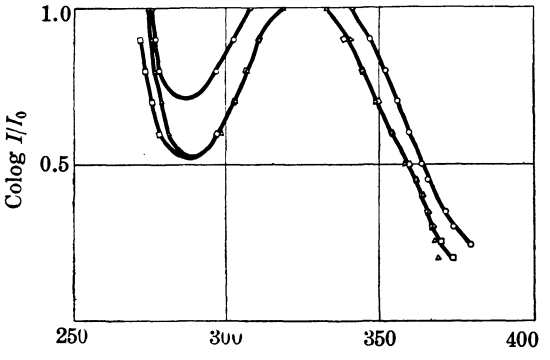
(5) H. Biltz et W. Biltz, "Übungsbeispiele aus der unorganischen Experimentalchemie", 3e et 4e édition (1920).

(6) S. M. Jörgensen, *Z. anorg. Chem.*, **7** (1894), 290.

(7) A. Werner, *Ber.*, **40** (1907), 4120.

(8) T. Uémura et H. Suéda, ce bulletin, **8** (1933), 1.

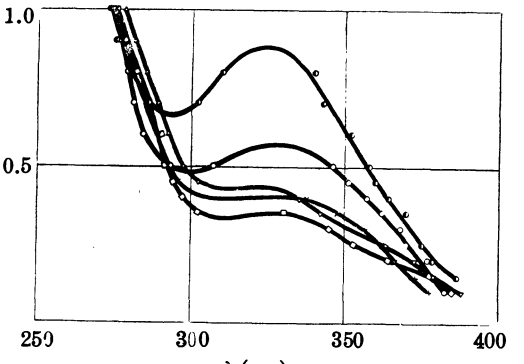
Une solution aqueuse de ce complexe à 1/2500 mol de concentration est légèrement basique et son pH est de 8.5. On obtient respectivement les pH 2.9 et 9.4 en le dissolvant dans 1/1000 N HCl ou 1/2500 N NaOH. L'absorption de ces trois solutés avec les différents pH se présentent dans



$[Co(NH_3)_5NO_2]Cl_2$ ($^1/_{2500}$ mol)

□ pH = 3.2 △ pH = 8.6 ○ pH = 9.0

Fig. 1.



$[Co(NH_3)_5ONO]Cl_2$ ($^1/_{2500}$ mol)

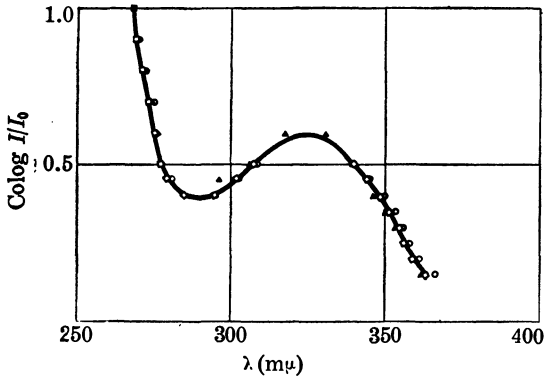
□ pH = 2.9
× pH = 8.5
□ ,, ,, (2.5 heures après)
○ ,, ,, (1 jour après)
△ pH = 9.4

Fig. 2.

la figure 2. Le degré d'agrandissement de l'absorption a été légèrement observé en augmentant les valeurs du pH. Ce corps n'est influencé ni par l'acide ni par la base. La précipitation a été observée en solution du pH 9.4 après la mesure, c'est-à-dire la transformation à l'isomère est difficilement reconnaissable. Toutes ces déterminations ont été rapidement faites après la préparation d'une solution, car la solution rose vire graduellement à jaune. La vitesse de ce virement est plus sensible en solution basique qu'en acide ou en neutre. Cette solution virée au jaune contient l'isomère $[Co(NH_3)_5NO_2]Cl_2$ (composé 1), ce qui a été déjà publié par Y. Shibata[9]. Pour le vérifier, j'ai photographié deux fois la solution du pH 8.5, une 2.5 heures et l'autre 1 jour après la préparation et n'ai pas trouvé de changement du pH après un jour, c'est-à-dire la valeur du pH reste encore à 8.5. En comparant les figures 1 et 2, on peut facilement observer la transformation du complexe $[Co(NH_3)_5ONO]Cl_2$ à son isomère $[Co(NH_3)_5NO_2]Cl_2$. La loi de Beer est aussi reconnue applicable au composé 2 en déterminant son absorption à 1/10000 mol et à 1/1000 mol.

(9) Y. Shibata, *J. Chem. Soc. Japan*, **36** (1915), 1234; *J. Coll. Sci., Imp. Univ. Tokyo*, **37** (1915), Sect. I.

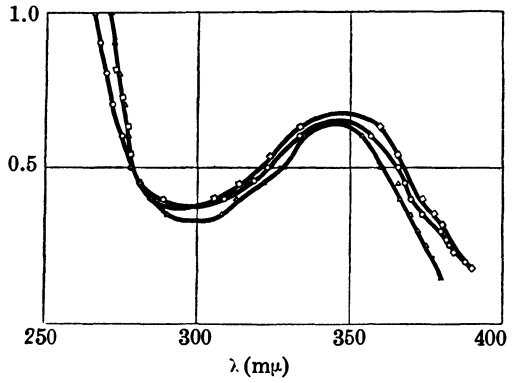
(3) $[Co(NH_3)_4(NO_2)_2]Cl$, *Chlorure de cobalti-dinitro-tétrammine (cis et trans)*. Le composé cis (sel flavo) est d'abord pris en solution aqueuse à 1/10000 mol qui est légèrement basique et montre le *p*H de 8.2. Comme on le voit dans la figure 3, la position d'absorption est à peu près invariable en changeant le *p*H de 8.2 à 9.1; et l'absorption de la solution du *p*H 3.7 n'est pas non plus différente de celle du *p*H 8.2. Cela montre que les radicaux NO_2 à cis n'ont pas affaibli l'absorption dans la région des longueurs d'onde plus petites, peu influencé en solution acide, contrairement au composé 1 et au sel crocéo (corps trans) comme on le voit dans la figure suivante. La loi de Beer est aussi reconnue être applicable à ce complexe par la détermination d'absorption en solution à 1/2500 mol.



$[Co(NH_3)_4(NO_2)_2]Cl$ (cis) ($^1/_{10000}$ mol)

□ *p*H = 3.7 ○ *p*H = 8.2 △ *p*H = 9.1

Fig. 3.



$[Co(NH_3)_4(NO_2)_2]Cl$ (trans) ($^1/_{10000}$ mol)

○ *p*H = 4.0 □ *p*H = 8.2 △ *p*H = 8.9

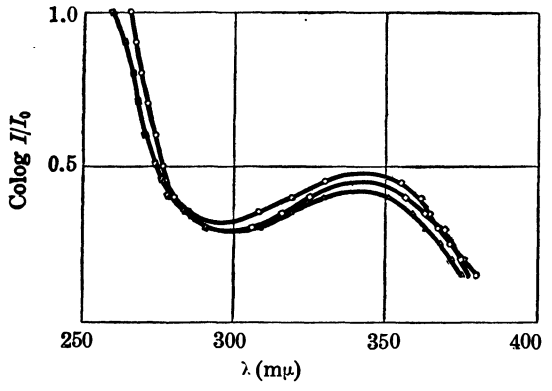
Fig. 4.

La solution à 1/10000 mol du composé trans (sel crocéo) est légèrement basique comme son isomère précédent montrant son *p*H de 8.2. En le dissolvant dans une solution normale à 1/10000 de NaOH, il présente le *p*H à 8.9 et, comme on l'observe dans la figure 4, a été reconnu de n'avoir qu'une tendance qui a affaibli son pouvoir absorbant. La précipitation ne s'y produit pas 15 minutes après la formation de cette solution, tandis qu'elle se produit nettement après une heure. On peut donc supposer que le changement de la structure du composé crocéo ne se montre pas en solution jusqu'à la production de la précipitation par la décomposition.

Lorsque ce corps trans se dissout dans HCl à 1/10000 N., il a la valeur du *p*H de 4.0 et la position et l'intensité de sa bande d'absorption est presque d'accord avec une solution basique et l'affaiblissement d'absorption dans la région de courtes longueurs d'onde au dessous de 270 mμ est reconnu comme dans le cas du composé 1 (voir la figure 1); cela n'a

pas été observé pour la solution de sel flavo (fig. 3). Le présent corps du type trans permet aussi d'appliquer la loi de Beer en examinant la mesure d'absorption d'une solution aqueuse à 1/2500 mol.

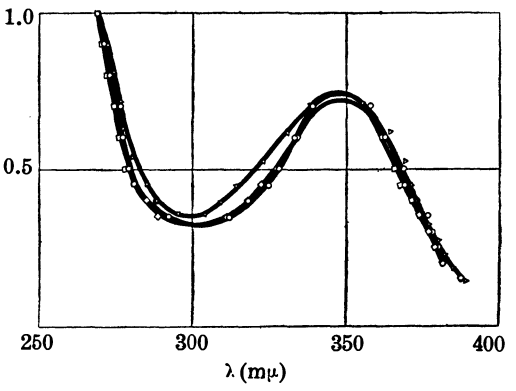
(4) $[Co(NH_3)_3(NO_2)_3]$, *Cobalti-trinitro-triammine.* La solution du présent complexe à 1/20000 mol est légèrement basique en donnant le *p*H de 7.8. La courbe d'absorption de cette solution est comparée, dans la figure 5, avec celle du *p*H à 4.1 pour une 1/10000 N de HCl et celle du *p*H à 9.0 pour une 1/20000 N de NaOH. On peut montrer que la position de la bande d'absorption de ces trois solutions différentes quant à leur *p*H est à peu près la même et que le pouvoir absorbant est plus ou moins grand en augmentant la valeur du *p*H. Les deux courbes données par les solutions de *p*H à 4.1 et à 7.8 coïncident dans la région des longueurs d'onde au dessous de 270 mμ, tandis que la solution du *p*H à 9.0 s'y présente plus fortement, ce qui est semblable aux complexes 1 et 3 (type trans), mais non aussi net que pour ces deux composés. Son peu d'influence sur l'alcali et l'application de la loi de Beer sont aussi reconnues.



$[Co(NH_3)_3(NO_2)_3]$ ($^1/_{20000}$ mol)

△ *p*H = 4.1 □ *p*H = 7.8 ○ *p*H = 9.0

Fig. 5.



$[Co(NH_3)_2(NO_2)_4]K$. ($^1/_{20000}$ mol)

□ *p*H = 4.1 △ *p*H = 6.3 ○ *p*H = 8.6

Fig. 6.

(5) $[Co(NH_3)_2(NO_2)_4]K$, *Cobalti-diammonio-tétranitrite de potassium.* La solution du composé à 1/20000 mol est faiblement acide en donnant pour *p*H la valeur de 6.3; c'est un résultat opposé du cas des complexes contenant un noyau positif. Le présent corps a montré le *p*H à 4.1 pour un 1/1000 N HCl et celui à 8.6 pour une 1/10000 N de NaOH.

Dans la figure 6, on observe que les trois courbes données par ces solutions différentes de leur *p*H sont à peu près analogues présentant un centre identique de la bande d'absorption. Comme la variation de fin

d'absorption en région de longueurs d'onde plus basses est difficilement observée, il me semble que ce complexe n'est influencé ni par l'acide ni par l'alcali en solution aqueuse. L'application de la loi de Beer a été examinée en solution à 1/2500 mol.

(6) $[Co(NO_2)_6]Na_3$. *Cobalti-hexanitrite de sodium.* Y. Shibata[9] a déjà exposé que la solution de ce complexe ne comporte pas l'application de la loi de Beer. On peut facilement observer la décoloration rapide par décomposition en diluant sa solution, c'est pourquoi j'ai fait l'expérience avec une concentration à 1/2000 mol avec l'épaisseur liquide de 20 mm.

La solution du composé à 1/2000 mol est acide en montrant son *p*H 3.8; cette valeur change à 3.5 en le dissolvant dans HCl à 1/5000 N et à 4.3 dans NaOH à 1/5000 N. Dans le cas où l'alcali est un dissolvant, une variation de couleur devient plus sensible avec le temps, c'est-à-dire l'instabilité sur l'alcali est nettement montrée. L'échantillon qu'on a préparé en ajoutant l'alcali est photographié tout de suite après la préparation. La courbe de cette solution du *p*H 4.3 est assez différente de celles données par les solutions des *p*H 3.5 et 3.8. Son pouvoir absorbant est aussi beaucoup plus faible que ceux présentés par les deux dernières solutions; cela vient peut-être du résultat de décomposition partielle du complexe. Le pouvoir absorbant de la solution du *p*H 3.5 est plus grand que celle du *p*H 3.8; cela explique que ce complexe est plus stable en solution du *p*H faible et que la vitesse de décomposition en solution aqueuse est sensiblement grande.

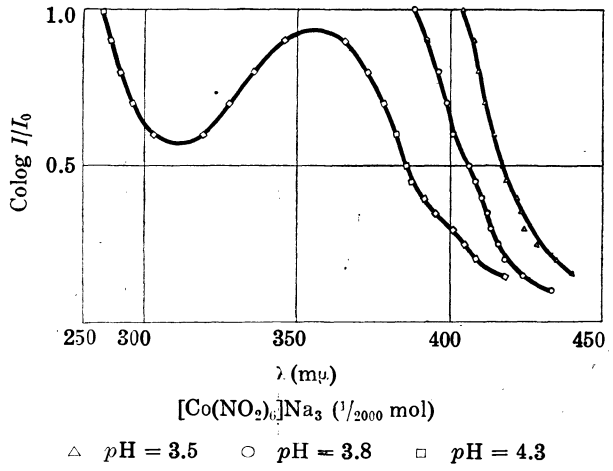


Fig. 7.

(7) $[Co(NH_3)_4NO_2Cl]Cl$, *Chlorure de cobalti-nitro-chloro-tétrammine (jaune)*; (8) $[Co(NH_3)_4NO_2Cl]Cl \cdot H_2O$, *Chlorure de cobalti-nitro-chloro-tétrammine (rouge) (Esohydrate)*. Pour le composé 7, on a préparé trois solutions différentes de leur concentration: 1/5000 mol, 1/2500 mol et 1/1000 mol. La solution à 1/2500 mol est légèrement basique en

montrant son pH à 8.3. Les solutions à 1/5000 mol préparées de 1/5000 N HCl et 1/5000 N NaOH donnent respectivement la valeur de pH à 4.1 et à 8.8. Les courbes d'absorption calculées à 1/5000 mol de toutes ces concentrations différentes sont comparées dans la figure 8. Comme les deux courbes des pH élevés coïncident les unes avec les autres, l'addition d'alcali ne donne pas d'influence sur la solution aqueuse des pH forts. Par contre, la solution ayant son pH de 4.1 montre la position des longueurs d'onde d'absorption semblable aux deux autres, tandis que son pouvoir absorbant est plus ou moins intensifié. Lorsqu'on ajoute une solution concentrée d'alcali en solution du complexe 7, on voit une couleur rouge foncée, mais en même temps une décomposition donnant un précipité de $Co(OH)_3$; c'est pourquoi on n'a pu déterminer l'absorption de cette solution alcaline.

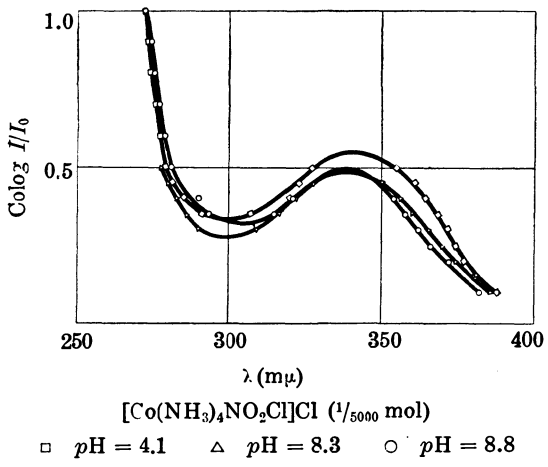
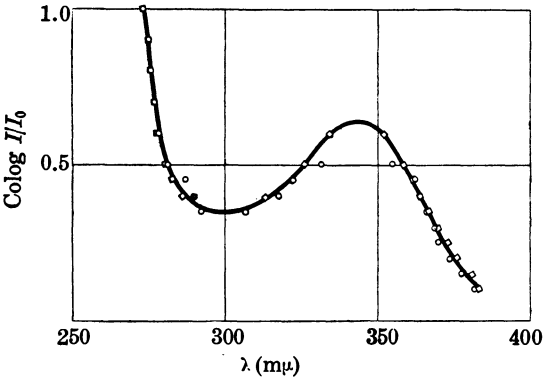


Fig. 8.

Le complexe 8 est un hydrate du composé 7 qui est un peu basique en solution à 1/2500 mol, et son pH est à 8.4. Sa 1/5000 mol solution dissoute en solution de NaOH à 1.5/5000 normale donne le pH à 11.1. Les courbes d'absorption de ces deux solutions calculées pour la même concentration coïncident sur la figure 9 et elles sont aussi analogiques à celle montrée par le composé précédent au pH 4.1. On peut donc conclure que les deux complexes 7 et 8 prennent en solution une même constitution par cette analogie des courbes d'absorption. La conclusion que ces deux complexes en dissolvant dans l'eau tournent à celui de $[Co(NH_3)_4(H_2O)NO_2]Cl_2$ en combinant une molécule d'eau à leur noyau complexe est définitivement admise dans certains mémoires chimiques déjà publiés[10]. Mes échantillons forment peut-être un complexe hydrine, mais il faut connaître à ne donner aucune variation sur l'absorption en ajoutant l'alcali au complexe hydrine.

(10) A. Werner, *Ber.*, **40** (1907), 4119; K. Matsuno, *J. Coll. Sci., Imp. Univ. Tokyo*, **41** (1921), Sec. I, Art. 11.

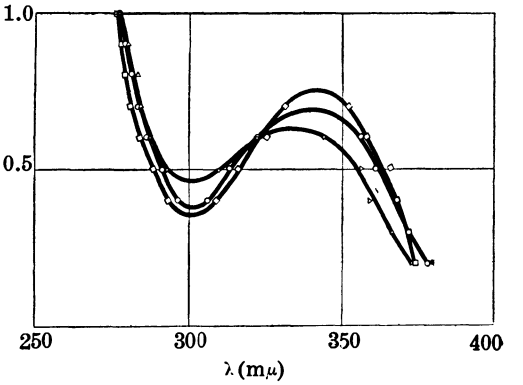
(9) $[Co(NH_3)_4(H_2O)NO_2]Cl_2$, *Chlorure de cobalti-nitro-tétrammino-hydrine*; (10) $[Co(NH_3)_4NO_2OH]Cl{\cdot}H_2O$, *Chlorure de cobalti-hydroxo-nitro-tétrammine*; (11) $\{[Co(NH_3)_4NO_2OH]Cl\}_2HCl{\cdot}4H_2O$, *Chlorure de cobalti-hydroxo-nitro-tétrammine* (*Oxonium anomal*). Le corps 9 est instable et en l'exposant à l'air, il tourne au rouge en donnant le composé $[Co(NH_3)_4NO_2Cl]Cl$. L'expérience a été donc faite rapidement, et une impureté inévitable y doit être permise. L'acidité de cette solution aqueuse est décrite dans le mémoire présenté par Werner[7], cependant ma solution aqueuse à 1/5000 mol a montré le *p*H à 8.4 et le *p*H devient 5.4 quand ce corps est dissout dans HCl à 1/5000 N; ces solutions sont dorées. Lorsqu'on dissout le corps dans une solution NaOH au titre



$[Co(NH_3)_4NO_2Cl]Cl{\cdot}H_2O$ ($^1/_{2500}$ mol)

□ *p*H = 8.4 ○ *p*H = 11.1

Fig. 9.



$[Co(NH_3)_4(H_2O)NO_2]Cl_2$ ($^1/_{2500}$ mol)

□ *p*H = 5.4 ○ *p*H = 8.4 △ *p*H = 8.7

Fig. 10.

1/5000, son *p*H change à 8.7 et la solution vire à un brun plus ou moins rougeâtre. Parmi les courbes d'absorption, sur la figure 10, données par ce complexe 9, les deux qui ont leur *p*H à 5.4 et à 8.4 montrent leur centre d'absorption à 340 mμ et en comparant leur pouvoir absorbant on reconnaît qu'il est plus fort dans le cas basique que dans le cas acide, mais la fin d'absorption dans la région des longueurs d'onde plus basses est par contre changée plus ou moins aux petites longueurs d'onde au cas acide. Une bande d'absorption de la solution ayant le *p*H à 8.7 se trouve aux environs de 330 mμ et on comprend que son pouvoir absorbant est plus faible que le cas des deux courbes précédentes. La solution du *p*H à 8.4 a un pouvoir absorbant plus faible que celle du *p*H à 5.4; peut-être que le corps $[Co(NH_3)_4(H_2O)NO_2]Cl_2$ est en équilibre avec un complexe renfermant un radical OH dans son noyau complexe, qui se forme en substituant une molécule H_2O dans le noyau complexe par un radical OH.

Dans ce cas, ce complexe contenant un radical OH se produit en une certaine quantité non négligeable et son équilibre tend vers le complexe hydrine en diminuant la valeur du *p*H. Pour vérifier la pureté du complexe $[Co(NH_3)_4(H_2O)NO_2]Cl_2$, une expérience a été répétée avec le sel nitré et un résultat semblable, décrit plus loin, a pu être obtenu.

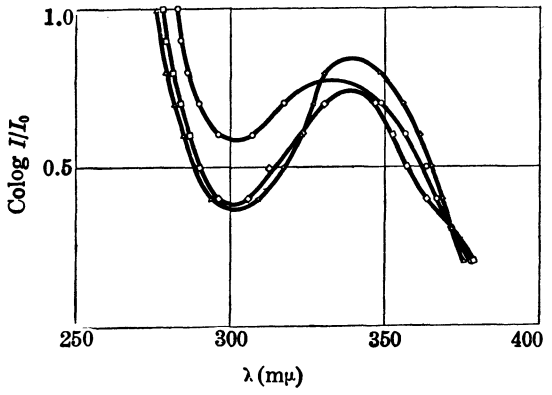
Le composé 10, c'est-à-dire $[Co(NH_3)_4NO_2OH]Cl$, est plus stable que celui hydrine, cependant l'expérience a été faite tout de suite après la formation du corps. Sa solution aqueuse à 1/5000 mol a le *p*H à 8.9, tandis que le *p*H change à 8.4 en le dissolvant dans un 1/5000 N HCl et le *p*H, à 3.1 dans un 1/1000 N HCl. Ces solutions des *p*H faibles sont jaune-brunes, mais la solution devient rouge-brune quand ce complexe donne le *p*H à 8.9 ou il se dissout dans une solution de NaOH à 1/5000 N en présentant le *p*H à 9.1. En se référant à la figure 10, on peut observer que les deux courbes des *p*H à 8.4 et à 3.1, sur la figure 11, sont fort semblables au complexe hydrine précédent, c'est-à-dire une bande d'absorption se trouve au voisinage de 340 mμ et son pouvoir absorbant augmente avec la diminution du *p*H. La précipitation a été observée dans la solution ayant le *p*H à 9.1, mais sa position d'absorption est à peu près la même que celle montrée par la solution du *p*H à 8.9 et on a donc éliminé sa courbe dans la figure 11. Tous ces résultats spectrochimiques m'ont prouvé que ce composé ne prend pas d'autre forme jusqu'à décomposition et les deux complexes 9 et 10 suivent en solution aqueuse une relation équilibrée suivante qui est dépendante de la valeur du *p*H.

$$[Co(NH_3)_4(H_2O)NO_2]^{++} \underset{\longleftarrow}{\overset{pH = 8.4 \sim 8.7}{\longrightarrow}} [Co(NH_3)_4NO_2OH]^{+}$$

L'ion complexe $[Co(NH_3)_4(H_2O)NO_2]^{++}$ est influencé par l'alcali, tandis que celui de $[Co(NH_3)_4NO_2Cl]^{+}$ n'a presque pas changé sa courbe par l'addition d'alcali (voir les figures 8 et 9). L'ion $[Co(NH_3)_4(H_2O)Cl]$ déjà expliqué dans le mémoire précédent qui contient le radical Cl avec une molécule H_2O est facilement influencé par l'addition de solution alcaline. Tous ces résultats reposent sur une différence de constitution et d'espèce du radical.

La formule du composé 11 a été donnée par Werner[7] comme une forme $\{[Co(NH_3)_4NO_2OH]Cl\}_2HCl\cdot 4H_2O$, tandis que Dubsky[11] a reconnu trois molécules d'eau de cristallisation. Je l'ai préparé par la méthode indiquée par Werner[7]. La solution aqueuse du corps à 1/5000 mol donne le *p*H à 8.5 tandis que les *p*H 8.2 ou 8.7 ont été respectivement

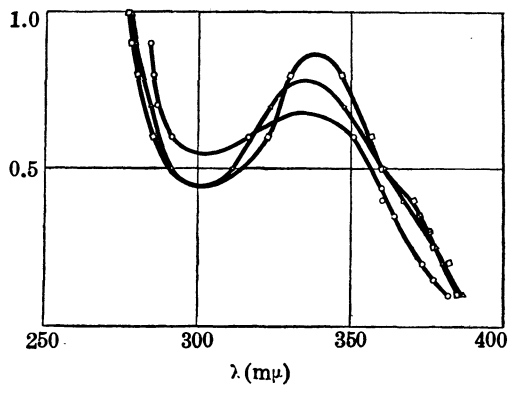
(11) J. Dubsky, *J. prakt. Chem.*, **90** (1914), 107.



$[Co(NH_3)_4NO_2OH]Cl$ ($^1/_{2500}$ mol)

△ pH = 3.1 □ pH = 8.4 ○ pH = 8.9

Fig. 11.



$\{[Co(NH_3)_4NO_2OH]Cl\}_2HCl$ ($^1/_{5000}$ mol)

□ pH = 8.2 △ pH = 8.5 ○ pH = 8.7

Fig. 12.

obtenus en le dissolvant dans HCl au titre 1/5000 et une solution de NaOH au titre 1/5000 pour qu'on puisse prendre une même concentration. La solution qui est une concentration à 1/10000 mol en employant HCl à 1/1000 de solution normale présente comme pH 3.1. Parmi ces solutions, celle qui donne un pH à 8.5 est brune-rougeâtre, celles des pH 8.2 ou 3.1 virent au jaune-foncé et celle du pH à 8.7 devient d'un rougeâtre un peu foncé. La figure 12 m'a montré que la bande d'absorption produite par la solution de pH à 8.5 se trouve au voisinage de 335 mμ qui se trouve entre les deux données par les complexes $[Co(NH_3)_4(H_2O)NO_2]Cl_2$ et $[Co(NH_3)_4NO_2OH]Cl$. La courbe du présent corps (composé 11) donné par sa solution du pH à 8.7 est semblable aux deux courbes de la solution du pH à 8.9 du hydroxo-complexe (composé 10) et par celle du pH à 8.7 du complexe hydrine (composé 9). Les courbes d'absorption observées pour ces trois complexes donnant respectivement les pH 5.4, 3.1 et 8.2 ont encore une forme analogue (voir les figures 10, 11 et 12). Par conséquent, il est tout naturel de constater la relation suivante:

$$[Co(NH_3)_4(H_2O)NO_2]^{++} \xleftarrow{p\text{H}=8.2\sim8.5} \underset{\text{(oxonium anomal)}}{\text{le complexe 11}} \xrightarrow{p\text{H}=8.5\sim8.7} [Co(NH_3)_4NO_2OH]^{+}$$

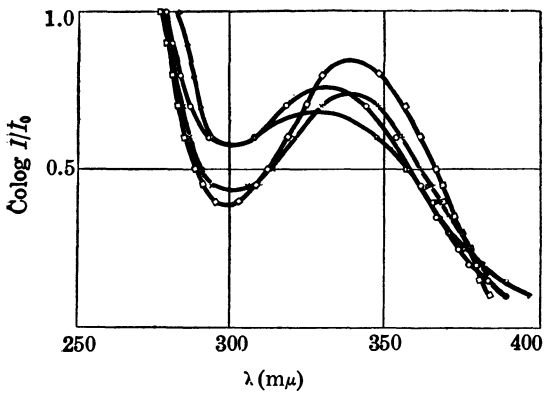
Dans ce cas, quand on admet la formule donnée au complexe 11 par Werner, j'ai à reconnaître une courbe d'absorption semblable à celle donnée par le hydroxo-complexe (composé 10). Mes résultats ont été cependant montrés que le corps 11 existe entre les composés 9 et 10 dans

sa courbe d'absorption. Voilà pourquoi, il me semble qu'il est plutôt commode de donner une formule du type d'un sel double, c'est-à-dire $[Co(NH_3)_4(H_2O)NO_2][Co(NH_3)_4NO_2OH]Cl_3 \cdot 4H_2O$, au corps 11.

(12) $[Co(NH_3)_4(H_2O)NO_2](NO_3)_2$, *Azotate de cobalti-nitro-tétrammino-hydrine*; (13) $[Co(NH_3)_4NO_2OH]NO_3$, *Azotate de cobalti-hydroxo-nitro-tétrammine.* Comme j'ai déjà écrit sur l'instabilité du complexe $[Co(NH_3)_4(H_2O)NO_2]Cl_2$ (composé 9) qui est difficile à obtenir pur, l'état du changement en solution a été étudié par les azotates.

Le complexe 12 donne son *p*H à 8.1 en solution aqueuse à 1/2500 mol, tandis que son *p*H devient 3.4 quand il se dissout dans HCl au titre 1/2000, et 8.7, dans une solution de NaOH au titre 1/5000; 9.4, dans une solution de NaOH au titre 1/1000. La solution de ce composé à 1/10000 mol était jaune et tournait au violet et montrait son *p*H à 8.1 après une heure, tandis que sa solution fraîchement préparée donnait le *p*H à 7.7. Jörgensen[6] avait déjà attiré l'attention sur l'acidité de solution de ce complexe et j'ai obtenu cependant le *p*H de 8.1 à sa solution aqueuse à 1/1000 mol et aussi reconnu l'application de la loi de Beer.

Une bande d'absorption d'une solution du composé 12 est montrée en figure 13 aux environs des longueurs d'onde à 340 mμ. Sa position est presque semblable à la courbe donnée par la solution ayant la valeur du *p*H à 3.4, mais le pouvoir absorbant d'une solution du *p*H fort est beaucoup moins puissant que celui d'une solution du *p*H faible. La solution aqueuse

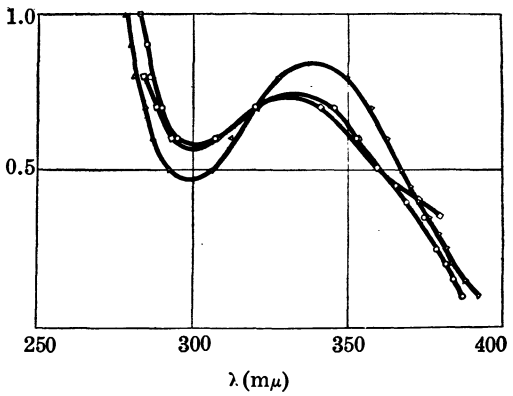


$[Co(NH_3)_4(H_2O)NO_2](NO_3)_2$ ($^1/_{2500}$ mol)

□ *p*H = 3.4 × *p*H = 8.1

○ *p*H = 8.7 △ *p*H = 9.4

Fig. 13.



$[Co(NH_3)_4NO_2OH]NO_3$ ($^1/_{2500}$ mol)

△ *p*H = 8.4 □ *p*H = 8.8 ○ *p*H = 9.0

Fig. 14.

portant son pH à 8.7 a donné une variation de couleur présentant sa bande d'absorption au voisinage de 330 mμ ce qui montre un pouvoir absorbant un peu plus fort que la solution du pH à 8.1. Une solution du pH 9.4 se troublait pendant la mesure et montrait sa bande d'absorption à une position semblable de la solution ayant le pH à 8.7.

Le complexe $[Co(NH_3)_4NO_2OH]NO_3$ (composé 13) donne son pH à 8.8 en solution aqueuse à 1/5000 mol en montrant une couleur rouge-brune. Quand on le dissout dans HCl au titre 1/2000 en donnant le pH à 8.4 en solution à 1/2500 mol, il est encore basique et vire au jaune-brun, et en le dissolvant dans la solution de NaOH à 1/5000 N., son pH devient 9.0 et sa couleur retourne au rouge-brun comme une solution aqueuse du pH à 8.8. En se référant aux deux figures 13 et 14, on peut observer une courbe de la solution du pH 8.4 du présent complexe qui ressemble à peu près aux courbes des pH à 3.4 ou 8.1 données par le composé 12, et les deux courbes des solutions des pH 8.8 et 9.0 du présent composé sont semblables à la courbe d'absorption montrée par une solution du pH 8.7 du complexe précédent. Ces résultats indiqués m'ont expliqué que les azotates, comme les chlorures déjà observés dans les corps 9 et 10, sont nettement reconnus avoir la relation suivante:

$$(Co(NH_3)_4(H_2O)NO_2]^{++} \underset{\longleftarrow}{\overset{p\mathrm{H}=8.4\sim8.7}{\longrightarrow}} [Co(NH_3)_4NO_2OH]^{+}$$

Résumé.

(1) Le spectre d'absorption dans la région ultra-violette des 14 ammines-cobaltiques complexes contenant le radical NO_2 a été étudié en leurs solutions aqueuses, celles de HCl et celles de NaOH en faisant varier la concentration des ions d'hydrogène.

(2) Parmi ces échantillons étudiés, lorsque le noyau complexe renferme une molécule de H_2O, on a reconnu une variation d'absorption au voisinage du pH 8.5 en la solution de NaOH. Cette variation du noyau fait supposer le remplacement de la molécule H_2O par un radical OH.

(3) Les complexes qui ne contiennent pas de molécule H_2O ne manifestent pas de changement provenant d'une variation du pH.

(4) Un radical NO_2 co-existant avec une molécule H_2O dans un noyau complexe n'est pas spectrochimiquement influencé, comme le radical Cl, par l'addition de l'alcali.

(5) La constitution du sel "oxonium anomal" a été aussi discutée.

En terminant ce compte-rendu de mes recherches actuelles, j'ai à exprimer mes sincères remerciements à M. Uémura, professeur adjoint à la Faculté, qui m'a bien encouragé pendant mes expériences, et à l'autorité de la Faculté qui a bien voulu m'aider à défrayer une partie des dépenses occasionnées par mes présentes études.

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

The Third Absorption Bands of Co-ordination Compounds. III. The Configuration of [Co dg'_2 NH_3 Cl]. A New Type of Optically Active Complex Radicals.

By Ryutaro TSUCHIDA and Masahisa KOBAYASHI.

(Received January 4th, 1937.)

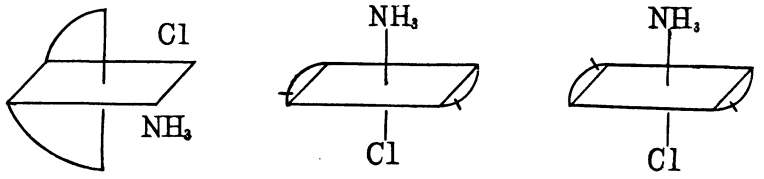
By the method of asymmetric adsorption[1] on quartz powder, the authors have proved that chloro-bisdimethylglyoximo-ammine-cobalt[2] has an asymmetric structure and conventionally assigned to this non-electrolyte a cis-configuration as (a) in Fig. 1, i.e., [Co dg'_2 NH_3 $Cl^{(1)}_{(2)}$], where dg' denotes a dimethylglyoxime radical, $CH_3–C:NOH$ / $CH_3–\dot{C}:NO'$.

On the other hand, however, it has been concluded by Nakatsuka[3] that, in hexa-coordinated cobaltic complex salts which have a general formula [Co dg'_2 a_2]X, the two dimethylglyoxime radicals are strongly combined to the central cobalt atom in a common plane; viz., two a's are co-ordinated in trans position to each other. Also in hexa-coordinated cobaltous complex compounds of general formulæ [Co dg_2 X_2] and [Co dg_2 X Y], the two dimethylglyoxime molecules have been shown to form a plane, co-ordinating simply by auxiliary valences.[4] Moreover, tetra-coordinated metallic complexes, which contain two glyoxime radicals, such as nickel-dimethylglyoxime, nickel-benzoyl-methyl-

(1) R. Tsuchida, M. Kobayashi, and A. Nakamura, *J. Chem. Soc. Japan*, **56** (1935), 1339.
(2) R. Tsuchida, M. Kobayashi, and A. Nakamura, this Bulletin, **11** (1936), 38.
(3) Y. Nakatsuka, this Bulletin, **11** (1936), 48.
(4) Thilo and Heilborn, *Ber.*, **64** (1931), 1441.

glyoxime[5] and palladium-benzoyl-methyl-glyoxime[6], have also been proved to have all alike planar configuration.

The authors, therefore, are now inclined to the planar disposition and should like to assign to the optically active complex in question a trans-configuration, [Co $dg_2^{\prime}$ NH_3 $Cl_{(6)}^{(1)}$]. The types of uni-nuclear complex radicals, which have hitherto been shown to be resoluble into optical antimers, are [M ch_3], [M ch_2 $a_{2(2)}^{(1)}$], [M ch_2 a $b_{(2)}^{(1)}$] and [M ch $a_{2(2)}^{(1)}$ $b_{2(6)}^{(5)}$][7], where ch represents a chelate group. None of these types has trans-configuration. This apparent discrepancy may easily be overcome by reflecting upon the nature of dimethyl-glyoxime radical, which is co-ordinated to a central metallic atom by one auxiliary valence on one hand and by one principal valence on the other. Though NH_3 and Cl are co-ordinated in trans-position and the two dimethyl-glyoxime radicals form a plane, the complex molecule remains asymmetric so long as the amphi-chelate radicals keep their two principal valences in trans-position to each other as (c) in Fig. 1.



(a) *cis*-Form active (b) *trans-cis*-Form inactive (c) *trans-trans*-Form active

Fig. 1.

If this be the case, the complex compound should have a third absorption band as will be predicted from the results given in the previous paper[8] of this series, in which it has been concluded that a pair of negative radicals co-ordinated in trans-position to each other gives rise to a third band. For the purpose of detecting the third band in order to verify the trans-configuration, the complex compound was prepared according to the method of Tschugaeff[9] and the molar extinction coefficients ε's were measured with aqueous solutions of concentrations between 0.010 and 0.002 mol/l. As had been expected, the third band was found at $\nu = 121 \times 10^{13}$ as in Fig. 2.

(5) Sugden, *J. Chem. Soc.*, **1932**, 246.

(6) Dweyer and Mellor, *J. Am. Chem. Soc.*, **57** (1935), 605.

(7) This type has first been illustrated by Y. Shibata and T. Maruki, *J. Coll. Sci., Imp. Univ. Tokyo*, Sect. I, **41** (1917), Art. 2.

(8) R. Tsuchida and S. Kashimoto, this Bulletin, **11** (1936), 785.

(9) Tschugaeff, *Ber.*, **39** (1906), 2695.

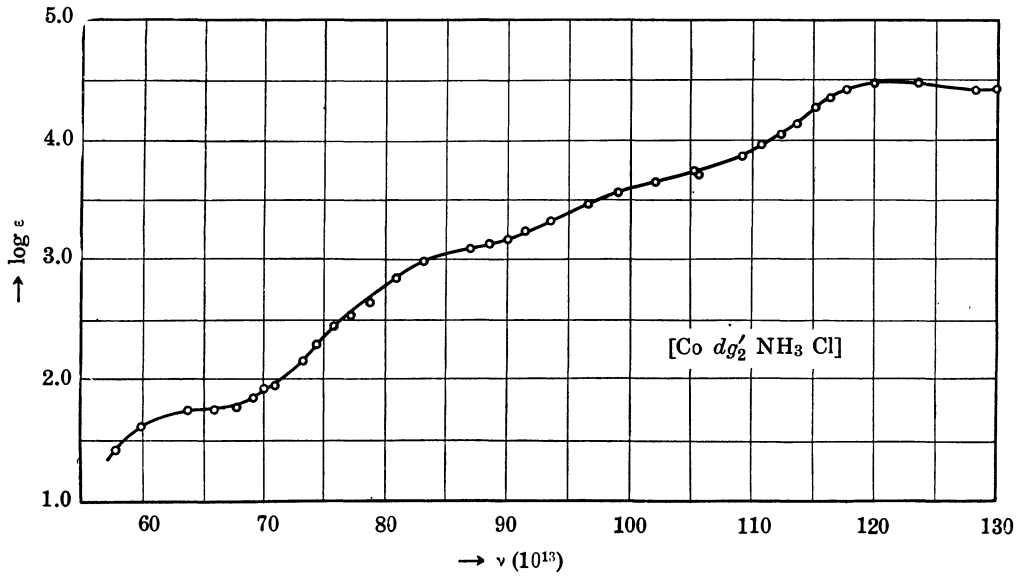


Fig. 2.

Thus the new types of active complex compound, [M ch_2 a $b_{(6)}^{(1)}$], has been introduced, and similar compounds of this type are now under investigation from the viewpoint of asymmetric resolution.

The authors wish to express sincere thanks to Prof. Y. Shibata for his kind interest in this work.

Chemical Laboratory, Faculty of Science,
Imperial University of Osaka.

Die kolloidchemische Untersuchung der Systeme von drei flüssigen Komponenten. II. System Benzol-Wasser-Methylalkohol und Tetrachlorkohlenstoff-Wasser-Methylalkohol.

Von Naoyasu SATA und Yosiaki NIWASE.

(Eingegangen am 18. Januar 1937.)

(1) **Einleitung.** Über das kolloidchemische Verhalten der kritischen Gemische von drei flüssigen Komponenten, haben wir in vorhergehender Mitteilung ein übersichtliches Bild von verschiedenen Kombinationen der Komponenten gegeben.[1] Die genaueren Untersuchungen wurden an einigen einzelnen Fällen ausgeführt, deren Ergebnisse im folgenden angegeben werden.

(2) **System: Benzol-Wasser-Methylalkohol.** In dem vorhergehenden Versuch hat man sich davon überzeugt, dass das System Benzol-Wasser-Äthylalkohol das grösste und auch beständigste Bereich bläulich opaleszierender, kolloid-charakteristischer, kritischer Gemische ergibt. Wir haben zunächst den Versuch an das System angestellt, welches statt Äthylalkohol das Methylalkohol enthält. Das verwendete Methylalkohol ist „Methanol, reinst, Acetonfrei" von E. Merck. Der Versuch ist genau in vorigem Fall ausgeführt. Die Ergebnisse sind in folgender Tabelle 1 zusammengestellt.

Tabelle 1.

% Benzol	% Methanol	% Wasser	Zustandsänderung °C.		
			Homogen	Bläulich opalesz.	Weisslich trübe
72.4	25.3	2.3	27.0	26.0—23.5	23.0
72.3	25.2	2.5	29.0	28.1—27.0	26.0
72.0	25.1	2.9	—	——	30.0
64.45	32.25	3.30	24.0	23.0—21.1	19.0
64.44	32.21	3.35	28.0	27.5—24.5	23.5
64.36	32.17	3.47	33.0	32.0—26.5	24.0
64.28	32.13	3.59	36.0	35.0—29.0	28.0
64.19	32.09	3.72	37.0	36.5—32.0	31.0
64.10	32.00	3.90	—	——	30.0
57.40	38.20	4.40	31.0	30.0—26.5	25.5
57.30	38.10	4.60	26.0	24.8—22.8	22.0
57.20	38.10	4.70	—	——	30.0
47.00	46.90	6.10	28.0	27.0—26.0	25.0
46.90	46.80	6.30	32.0	31.0—30.0	29.0
46.80	46.70	6.50	—	——	30.0

(1) N. Sata und O. Kimura, dieses Bulletin, **10** (1935), 409.

Wenn man die Werte der Grenz-Gemische bei 30°C. auf einem Dreieck-diagramm überträgt, erhält man die Abb. 1.

Von obenstehender Resultate sieht man, dass es prinzipiell keinen grossen Unterschied ergibt, wenn man Äthylalkohol durch Methylalkohol ersetzt. Nur bemerkt man bei letzteren eine viel schmalere Insel des Übergangsgebiets und auch ein viel kleineres Temperaturbereich von bläulich opaleszierenden Systemen, als im Fall mit Äthylalkohol.

Die Schichthöhe-Messung wird dann auch wie vorher ausgeführt. Die Versuchsergebnisse sind in folgender Tabelle 2–9 und Abb. 2–9 angegeben.

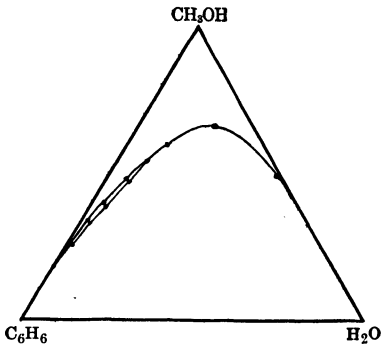


Abb. 1.

Tabelle 2.

Initiale Zusammensetzung =2.0 c.c. H_2O+8.0 c.c. C_6H_6 (20% Wasser)		
Zugefügter Alkohol (c.c.)	Höhe der Unterschicht (cm.)*	Totale Höhe (cm.)*
0.5	2.15	9.60
1.0	2.55	10.05
1.5	2.90	10.50
2.0	3.40	10.90
2.5	3 80	11.35
3.0	4.20	11.75
3.5	4.60	12.15
4.0	5.00	12.60
4.5	5.65	13.10
5.0	6.10	13.55
5.5	6.90	14.00
6.5	7.00	14.85
7.5	6.15	16.10
8.0	5.60	16.60
8.5	5.30	17.10
9.0	4.80	17.50
9.5	4.20	17.95
10.0	3.50	18.40
10.5	2.60	18.90
11.0	1.50	19.30
11.5	0.30	19.80
11.8		20.00

* 1.0 cm. = 1.097 c.c.

Tabelle 3.

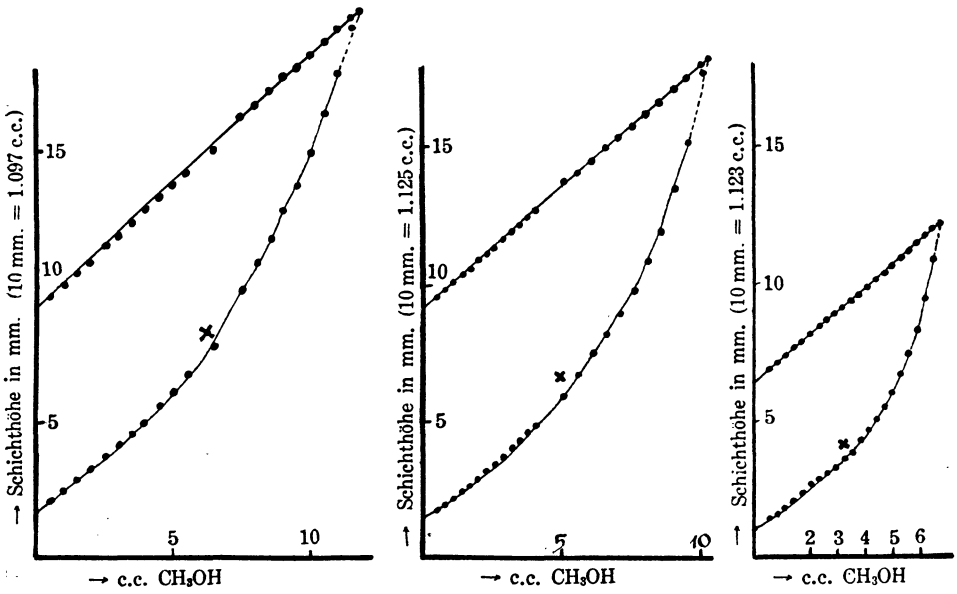
Initiale Zusammensetzung =1.5 c.c. H_2O+8.5 c.c. C_6H_6 (15% Wasser)		
Zugefügter Alkohol (c.c.)	Höhe der Unterschicht (cm.)*	Totale Höhe (cm.)*
0.5	1.80	9.60
0.8	2.00	9.85
1.1	2.25	10.15
1.4	2.50	10.40
1.7	2.70	10.65
2.0	3.00	10.90
2.3	3.25	11.15
2.6	3.50	11.40
2.9	3.85	11.70
3.2	4.10	11.95
3.5	4.30	12.20
3.8	4.65	12.50
4.1	4.90	12.80
5.1	7.70	13.70
5.6	7.45	14.10
6.1	7.10	14.55
6.6	6.80	15.00
7.1	6.40	15.40
7.6	5.95	15.75
8.1	5.35	16.20
8.6	4.65	16.60
9.1	3.65	17.10
9.6	2.35	17.50
10.1	0.20	18.00
10.4		18.10

* 1.0 cm. = 1.125 c.c.

Tabelle 4.

Initiale Zusammensetzung =1.0 c.c. H_2O+6.0 c.c. C_6H_6 (14.3% Wasser)		
Zugefügter Alkohol (c.c.)	Höhe der Unterschicht (cm.)*	Totale Höhe (cm.)*
0.5	1.40	6.90
0.8	1.60	7.15
1.1	1.85	7.40
1.4	2.10	7.65
1.7	2.35	7.90
2.0	2.60	8.15
2.3	2.85	8.35
2.6	3.10	8.60
2.9	3.40	8.85
3.2	5.45	9.05
3.5	5.55	9.30
3.8	5.35	9.60
4.1	5.20	9.85
4.4	5.00	10.05
4.7	4.80	10.30
5.0	4.50	10.60
5.3	4.10	10.90
5.6	3.65	11.25
5.9	3.05	11.50
6.2	2.30	11.75
6.5	1.20	12.05
6.8		12.20

* 1.0 cm. = 1.123 c.c.



× : Stelle, wo Platzwechsel beider Schichte geschieht.

Abb. 2. Abb. 3. Abb. 4.

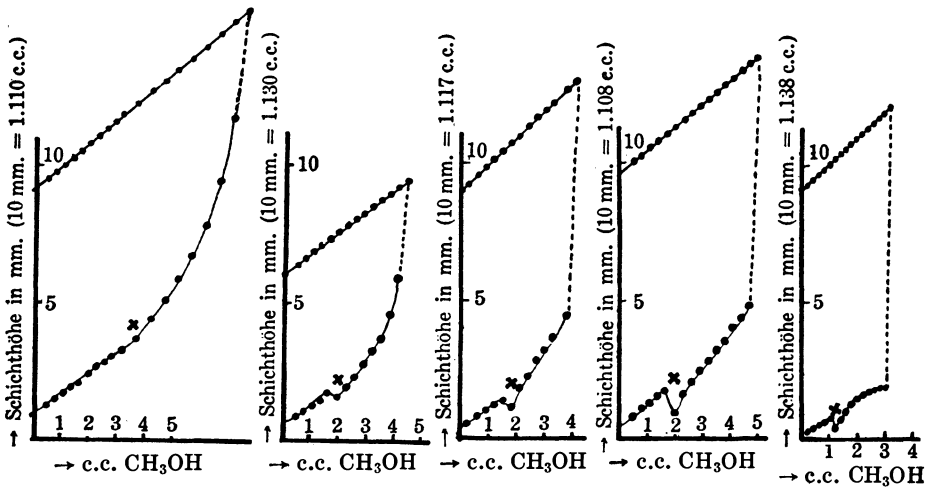


Abb. 5. Abb. 6. Abb. 7. Abb. 8. Abb. 9.

Tabelle 5.

Initiale Zusammensetzung = 1.0 c.c. H_2O + 9.0 c.c. C_6H_6 (10% Wasser)		
Zugefügter Alkohol (c.c.)	Höhe der Unterschicht (cm.)*	Totale Höhe (cm.)*
0.5	1.30	9.60
0.8	1.50	9.90
1.1	1.75	10.10
1.4	1.95	10.35
1.7	2.15	10.60
2.0	2.45	10.85
2.3	2.70	11.15
2.6	2.95	11.40
2.9	3.20	11.65
3.2	3.25	11.90
3.7	8.50	12.25
4.2	8.20	12 65
4.7	7.95	13.10
5.2	7.60	13.55
5.7	7.15	13.95
6.2	6.50	14.40
6.7	5.40	14.90
7.2	3.60	15.30
7.7		15.70

* 1.0 cm. = 1.110 c.c.

Tabelle 6.

Initiale Zusammensetzung = 0.5 c.c. H_2O + 6.0 c c. C_6H_6 (7.6% Wasser)		
Zugefügter Alkohol (c.c.)	Höhe der Unterschicht (cm.)*	Totale Höhe (cm.)*
0.5	0.90	6.40
0.8	1.15	6.70
1.1	1.35	6.90
1.4	1.60	7.15
1.7	1.80	7.35
2.0	5.90	7.60
2.3	5.70	7.80
2.6	5.50	8.05
2.9	5.40	8.30
3.2	5.15	8.55
3.5	4.90	8.80
3.8	4.35	9.05
4.1	3.40	9.35
4.4		9.60

* 1.0 cm. = 1.130 c.c.

Tabelle 7.

Initiale Zusammensetzung = 0.5 c.c. H_2O + 9.5 c.c. C_6H_6 (5% Wasser)		
Zugefügter Alkohol (c.c.)	Höhe der Unterschicht (cm.)*	Totale Höhe (cm.)*
0.30	0.55	9.25
0.60	0.85	9.60
0.90	1.05	9.90
1.20	1.20	10.15
1.50	1.40	10.45
1.80	9.50	10.70
2.10	9.10	11.00
2.40	8.95	11.30
2.70	8.80	11.70
3.00	8.70	11.95
3.30	8.60	11.25
3.80	8.25	12.70
4.20		13.00

* 1.0 cm. = 1.117 c.c.

Tabelle 8.

Initiale Zusammensetzung = 0.5 c.c. H_2O + 10.0 c.c. C_6H_6 (4.8% Wasser)		
Zugefügter Alkohol (c.c.)	Höhe der Unterschicht (cm.)*	Totale Höhe (cm.)*
0.5	0.85	10.20
0.8	1.05	10.40
1.1	1.25	10.70
1.4	1.50	10.95
1.7	1.65	11.15
2.0	10.50	11.40
2.3	9.80	11.60
2.6	9.70	11.90
2.9	9.60	12.10
3.2	9.50	12.35
3.5	9.40	12.65
3.8	9.30	12.90
4.1	9.10	13.20
4.4	9.00	13.40
4.7	8.90	13.70
5.0		13.90

* 1.0 cm. = 1.108 c.c.

Tabelle 9.

Initiale Zusammensetzung = 0.3 c.c. H_2O + 10.0 c.c. C_6H_6 (2.9% Wasser)		
Zugefügter Alkohol (c.c.)	Höhe der Unterschicht (cm.)*	Totale Höhe (cm.)*
0.2	0.25	9.35
0.4	0.45	9.55
0.6	0.55	9.70
0.8	0.70	9.95
1.0	0.80	10.20
1.2	9.90	10.30
1.4	9.70	10.50
1.6	9.65	10.70
1.8	9.65	10.90
2.0	9.65	11.10
2.2	9.65	11.30
2.4	9.70	11.45
2.6	9.80	11.60
2.8	9.90	11.80
3.0	10.00	12.00
3.2		12.15

* 1.0 cm. = 1.138 c.c.

Dass der Hauptteil des zugefügten Alkohols zur Wasserschicht absorbiert wird ist wie beim Fall mit Äthylalkohol. Nur möchten wir darauf aufmerksam machen dass bei dem Versuch mit Methylalkohol die Stelle des Platzwechsels beider Schichten und die des Zusammenmischens sich weiter entfernen, während im Fall mit Äthylalkohol, sie gleich hintereinander stattgefunden hatten. Diese Tatsache kann man aber leicht verstehen, wenn man daran denkt, dass Methylalkohol in seinem spezifischen Gewicht viel kleiner ist als Äthylalkohol. Was man aber hier besonders beachten muss, ist dass das bläulich opaleszierende System nicht gleich nach dem Platzwechsels beider Schichten ausgeschieden ist, sondern vor dem homogenen Zusammenmischen beider Schichte erst sich erkennen lässt. Da beim Platzwechsel[2] die spezifische Gewichte beider Schichten ein und dieselben sein müssen, vom mechanischen Standpunkt aus, ist bei dieser Stelle eine kolloide Dispergation von einer Phase zur andern sehr wohl möglich und da, wirklich im vorigen Fall mit Äthyalkohol das bläulich opaleszierende System gleich nach dem Platzwechsel beider Schichten ausgeschieden war, hätten wir auch geglaubt, dass diese beide Erscheinungen in etwaigem Zusammenhang stehen. Aber jetzt wurde es uns durch obenausgeführten Versuch mit Methylalkohol klar, dass der Platzwechsel der Schichten und das Ausscheiden des bläulich opaleszierenden Systemes eine voneinander ganz unabhängige Erscheinung sind.

(3) **System: Tetrachlorkohlenstoff-Wasser-Methylalkohol.** Wie schon darauf hingewiesen, liess sich bis jetzt nur in Benzol- oder Benzolderivate-enthaltenden Systemen das Ausscheiden bläulich opaleszierender Gemische erkennen. Diese Tatsache lässt uns vermuten, dass die Erscheinung von der chemischen Struktur der Komponenten abhängig wäre. Um Antwort auf dieser Frage zu finden, haben wir den nächsten Versuch mit dem System mit Tetrachlorkohlenstoff statt Benzol, angestellt. Dieser Versuch ist nicht nur wegen seiner Verschiedenheit an chemischer Struktur der Komponenten von Interesse, sondern auch dadurch, dass das Tetrachlorkohlenstoff ein ziemlich grosses spezifisches Gewicht für eine Flüssigkeit ($d = 1.40$) besitzt.

Die Ergebnisse sind in folgender Tabelle 10 und Abb. 10 zusammengestellt.

Das Versuchsresultat dieses Systems mit Tetrachlorkohlenstoff zeigt sich, dass die Insel von bläulich opaleszierendem Gebiet auch vorhanden ist, obwohl sie viel schmaler ist und ihre Temperaturbeständigkeit auch viel geringer als im Vergleich mit vorhergehendem Benzol-haltigen System

(2) N. Sata, dieses Bulletin, **2** (1927), 142.

Tabelle 10.

% Tetrachlor-kohlenstoff	% Methyl-alkohol	% Wasser	Zustandsänderung °C.		
			Homogen	Bläulich opalesz.	Weisslich trübe
65.2	32.7	2.1	28.0	27.5—22.5	20.5
65.1	32.7	2.2	28.0	27.5—20.5	18.5
65.0	32.6	2.4	34.0	33.0—31.0	28.0
64.9	32.6	2.5	—	—	30.0
82.78	16.56	0.66	—	—	30.0
47.6	47.7	4.7	—	—	30.0
30.5	61.1	8.4	—	—	30.0
13.6	68.6	17.8	—	—	30.0
0.99	49.51	49.5	—	—	30.0
0.66	33.14	66.86	—	—	30.0

ist. Aber darf man hierbei nicht übersehen, dass doch ein ganz deutlicher Unterschied zu erkennen ist, im Vergleich mit den Systemen, welche Pentan, Hexan usw. enthalten, in denen das bläulich opalesz ierende Gebiet ganz und gar ausfällt unter allen Bedingungen.[3] Wenn man daran erinnert, dass Pentan, Hexan usw. eine Ketten-Struktur besitzen, wohingegen Benzol und Tetrachlorkohlenstoff in ihrer Struktur wenigstens soweit ähnlich sind, dass sie von einer symmetrischen Struktur ausgehen, obwohl Benzol eine Ringstruktur hat und Tetrachlorkohlenstoff keine Ringstruktur hat. Es bringt uns die Vermutung nahe, dass diese Erscheinung doch von der chemischen Struktur der Komponente abhängig wäre.

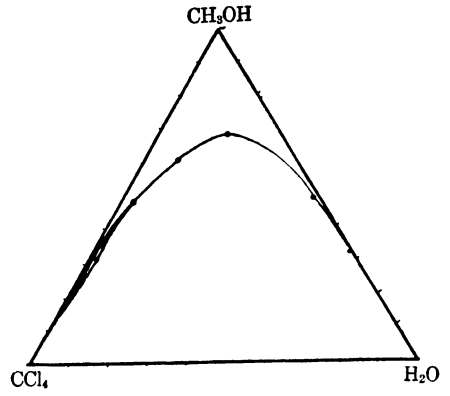


Abb. 10.

Die Resultate der demnächst ausgeführten Schichthöhe-Messung sind in folgenden Tabellen 11–18 und Abb. 11–18 zusammengestellt.

Wie man es erwartet hat, verlaufen die Kurve der Schichthöhe in diesem Fall ganz anders, wegen des grossen spezifischen Gewichtes von Tetrachlorkohlenstoff; und zwar nimmt hier die obere Schicht immer

(3) Siehe Tabelle 1, dieses Bulletin, **10** (1935), 411.

Tabelle 11.

Initiale Zusammensetzung = 0.5 c.c H_2O + 9.5 c.c. CCl_4 (5% Wasser)		
Zugefügter Alkohol (c.c.)	Höhe der Unterschicht (cm.)*	Totale Höhe (cm.)*
0.5	9.72	10.3
1.0	9.71	10.9
1.5	9.70	11.3
2.0	9.60	11.8
2.5	9.50	12.3
3.0	9.40	12.7
3.3	9.30	13.0
3.6	9.10	13.3
3.9	8.90	13.7
4.2	8.70	14.0
4.5	8.50	14.2
4.8	8.20	14.4
5.1	7.70	14.7
5.4	7.20	15.0
5.7	6.70	15.3
6.0	5.80	15.6
6.3	4.50	15.9
6.6	2.20	16.1
6.7		16.3

* 1.0 cm. = 1.117 c.c.

Tabelle 12.

Initiale Zusammensetzung = 0.45 c.c. H_2O + 9.55 c.c. CCl_4 (4.5% Wasser)		
Zugefügter Alkohol (c.c.)	Höhe der Unterschicht (cm.)*	Totale Höhe (cm.)*
0.5	9.80	10.5
1.0	9.70	11.0
1.5	9.65	11.5
2.0	9.60	12.0
2.5	9.50	12.5
2.8	9.40	12.8
3.1	9.30	13.0
3.4	9.00	13.3
3.7	8.70	13.5
4.0	8.50	13.8
4.3	8.10	14.1
4.6	7.50	14.4
4.9	6.90	14.7
5.2	5.80	15.0
5.5	3.80	15.2
5.6		15.3

* 1.0 cm. = 1.110 c.c.

Tabelle 13.

Initiale Zusammensetzung = 0.4 c.c. H_2O + 9.6 c.c. CCl_4 (4% Wasser)		
Zugefügter Alkohol (c.c.)	Höhe der Unterschicht (cm.)*	Totale Höhe (cm.)*
0.5	10.0	10.9
1.0	10.0	11.3
1.5	10.0	11.7
1.8	10.0	12.1
2.1	9.9	12.4
2.4	9.8	12.6
2.7	9.7	12.9
3.0	9.5	13.2
3.3	9.3	13.5
3.6	9.0	13.9
3.9	8.6	14.1
4.2	8.2	14.4
4.5	7.5	14.8
4.8	6.6	15.0
5.1	3.9	15.3
5.4		15.4

* 1.0 cm. = 1.125 c.c.

Tabelle 14.

Initiale Zusammensetzung = 0.35 c.c. H_2O + 9.65 c.c. CCl_4 (3.5% Wasser)		
Zugefügter Alkohol (c.c.)	Höhe der Unterschicht (cm.)*	Totale Höhe (cm.)*
0.5	10.03	10.7
1.0	10.03	11.2
1.5	9.98	11.6
2.0	9.90	12.1
2.5	9.70	12.6
2.8	9.50	12.9
3.1	9.30	13.1
3.4	9.00	13.4
3.7	8.50	13.7
4.0	8.10	14.0
4.3	7.30	14.3
4.5		14.5

* 1.0 cm. = 1.108 c.c.

Tabelle 15.

Initiale Zusammensetzung = 0.3 c.c. H_2O + 9.7 c.c. CCl_4 (3% Wasser)		
Zugefügter Alkohol (c.c.)	Höhe der Unterschicht (cm.)*	Totale Höhe (cm.)*
0.5	10.0	10.8
1.0	10.0	11.2
1.5	10.0	11.8
1.8	9.9	12.0
2.1	9.8	12.3
2.4	9.7	12.6
2.7	9.6	12.8
3.0	9.4	13.1
3.3	9.0	13.4
3.6	8.7	13.7
3.9	8.2	13.9
4.2		14.3

* 1.0 cm. = 1.138 c.c.

Tabelle 16.

Initiale Zusammensetzung = 0.25 c.c. H_2O + 9.75 c.c. CCl_4 (2.5% Wasser)		
Zugefügter Alkohol (c.c.)	Höhe der Unterschicht (cm.)*	Totale Höhe (cm.)*
0.5	9.95	10.7
1.0	9.95	11.2
1.5	9.90	11.7
2.0	9.80	12.1
2.5	9.60	12.6
2.8	9.40	13.0
3.1	9.30	13.2
3.4	9.00	13.5
3.5	8.70	13.6
3.6		13.7

* 1.0cm. = 1.120 c.c.

Tabelle 17.

Initiale Zusammensetzung =0.2 c.c. H_2O+9.8 c.c. CCl_4 (2% Wasser)		
Zugefügter Alkohol (c.c.)	Höhe der Unterschicht (cm.)*	Totale Höhe (cm.)*
0.5	10.3	11.0
1.0	10.4	11.5
1.5	10.5	12.0
1.8	10.6	12.3
2.1	10.8	12.5
2.4		12.9

* 1.0 cm. = 1.123 c.c.

Tabelle 18.

Initiale Zusammensetzung =0.1 c.c. H_2O+9.9 c.c. CCl_4 (1% Wasser)		
Zugefügter Alkohol (c.c.)	Höhe der Unterschicht (cm.)*	Totale Höhe (cm.)*
0.5	10.4	11.07
1.0	10.6	11.50
1.5	11.2	12.03
2.0		12.70

* 1.0 cm. = 1.130 c.c.

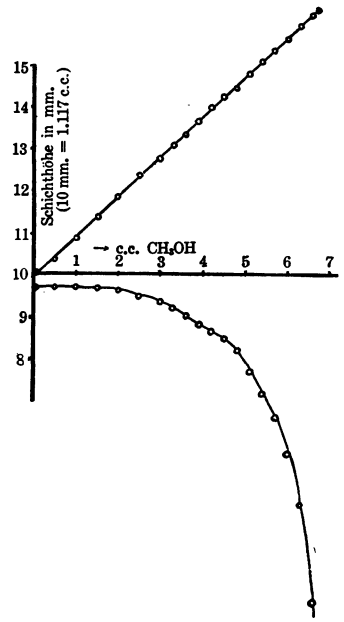


Abb. 11.

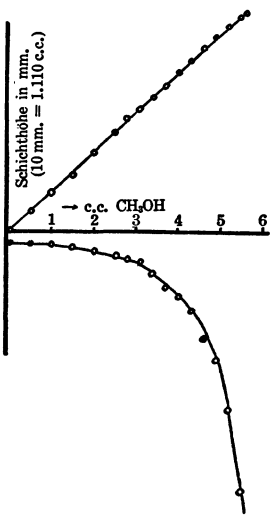


Abb. 12.

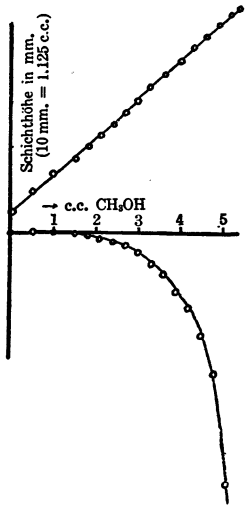


Abb. 13.

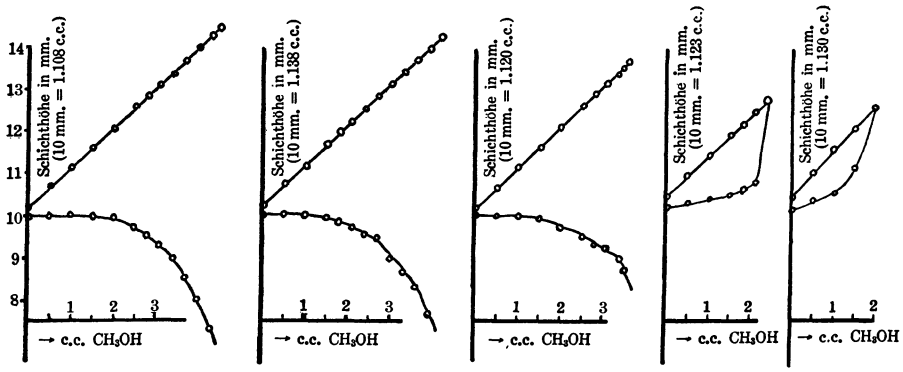


Abb. 14. Abb. 15. Abb. 16. Abb. 17. Abb. 18.

mehr zu und endlich mischen sich die beide Schichten zu einem homogenen System ohne Platzwechsels in dessen Gegend der bläulich opaleszierende Zustand sich erkennen lässt. Dieser Vorgang ist selbstverständlich, wenn man daran denkt, dass der zugefügte Alkohol auch hier fast vollkommen zur Wasserschicht absorbiert wird und die spezifische Gewichte der Wasser-Methylalkohol-Gemische niemals das von Tetrachlorkohlenstoff überschreiten können.

(4) **Schluss und Zusammenfassung.** Durch die obenausgeführte Versuche sind die folgenden Punkte klar geworden und zwar erstens; die bläulich opaleszierende Erscheinung bei den kritischen Gemische ist eine von der gegenseitigen Änderung des spezifischen Gewichtes beider Schichten ganz unabhängige Erscheinung. Zweitens; als Komponent A, d.h. mit Wasser nicht mischbare Flüssigkeit scheint eine Verbindung symmetrischer chemischen Struktur nötig zu sein, wie z.B. Benzol, Tetrachlorkohlenstoff usw. und mit Flüssigkeiten mit Ketten-Struktur wie Pentan, Hexan usw. keine bläuliche Opaleszenz bei den kritischen Gemische zu erkennen.

Daraus könnte man wenigstens soweit vermuten, dass diese Erscheinung durch die Änderung der Grenzflächenbedingungen verursacht würde, die zu beiden nicht mischbaren Komponenten A und C durch Zufügen von Komponent B, welche mit diese beide A und C mischbar ist, hervorgerufen ist.

Hier möchten wir noch darauf aufmerksam machen, dass die Meinungen über das grundliegende Problem, ob diese Opaleszenz-Erscheinung eine Erscheinung molekular-disperses oder kolloid-disperses Systems ist

noch nicht ganz übereinstimmend sind.[4] Die Entscheidung darüber ist durch weitere kolloidwissenschaftliche Untersuchungen an den einzelnen Fällen zu erwarten.

Zusammenfassung. (1) Die bläulich-opaleszierende Erscheinung kritischer Gemische der Systeme „Benzol-Wasser-Methylalkohol" und „Tetrachlorkohlenstoff-Wasser-Methylalkohol" ist untersucht worden.

(2) Es wurde bestätigt, dass diese Systeme auch obengenannte Erscheinung zeigten, obwohl viel weniger und unbeständiger als es bei dem System „Benzol-Wasser-Äthylalkohol" der Fall ist.

(3) Die Schichthöhe-Messung hat gezeigt, dass die spezifischen Gewichte und die gegenseitige Dispergation beider Schichten eine ganz unabhängige Erscheinung ist.

(4) Es wurde darauf aufmerksam gemacht, dass diese Erscheinung in den Systemen mit Benzol, Tetrachlorkohlenstoff usw., die die symmetrische chemische Struktur haben, stattfindet, wohingegen sie in den Systemen mit Pentan, Hexan usw., die Ketten-förmig in ihrer chemischen Struktur sind, ganz und gar ausfällt.

(5) Von den Untersuchungsergebnissen wurde vermutet, dass der grundliegende Faktor für diese Erscheinung eine Änderung der Grenzflächenbedingung zwischen zwei in einander nicht mischbaren Flüssigkeiten wäre, durch Zusatz einer dritten, mit dieser beiden mischbaren Flüssigkeit, hervorgerufen würde.

Chemisches Institut der Kaiserlichen Universität
zu Osaka
und
Schiomi-Institut für physikalische
und chemische Forschung.

---

(4) H. Schlegel, *J. chim. phys.*, **32** (1935), 227.

Studies on the Oiliness of Liquids. III. Measurements of the Kinetic Friction Coefficients.

By Jitsusaburo SAMESHIMA and Moriji MIYAKE.

(Received January 19th, 1937.)

We shall describe, in the present paper, the measurements of the kinetic friction coefficients of liquids. There are already many a types of machine which are used for the measurement of the kinetic friction in the industrial purpose. They measure, usually, the power of complete or film lubrication of oil. Recently, Beare and Bowden have published a paper on this subject and described an apparatus for the measurement of kinetic boundary lubrication which was constructed by Hardy.(1)

We have measured the kinetic friction coefficients by the apparatus described in the following lines.

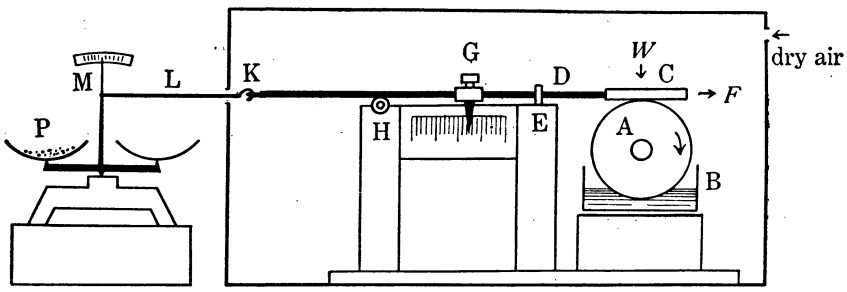


Fig. 1.

Fig. 1 is the schematic view of the whole apparatus. In this figure, A is a steel cylinder of 5 cm. diameter and 3 cm. length, the surface being highly polished. B is a vessel containing the liquid to be tested. The lower part of the cylinder A is dipped in the liquid. By rotating A in the direction shown in the figure, the surface of cylinder is covered with the film of the liquid. C is a small piece of steel plate of the dimension $4 \times 1 \times 0.3$ cm., the lower surface of which being polished. D is the elongation of C and has a pointer G at its middle part, and a loop of wire K at the end. The system CDGK is mounted on the rotating cylinder A

(1) Beare and Bowden, *Trans. Roy. Soc.* (London), A, **234** (1935), 329.

and a small wheel H. Fig. 2 is the plan of this part. H is a small pulley which can rotate with little friction, so as to move the rod D to right or left. E is the guide to keep from the movement in the direction of fore and aft. At the loop K one end of the wire L is hooked, the other end of which being attached to the pointer M of a balance as shown in Fig. 1. The pointer G is adjusted so as to come to zero reading on the scale when the balance pointer M is in the perpendicular position. The function of the balance is quite the same with that in the measurement of the static friction coefficient which has already been explained in the first paper.(2) The apparatus, excepting the balance, is put in a glass case in which the dry air is passed.

A few grams of liquid is put in B, and let the cylinder A start to rotate. Then the plate C will be pulled rightward and accordingly the pointer M will incline rightward. Now fine sand is poured on the balance pan P in a fine stream until the pointer M returns to the per-

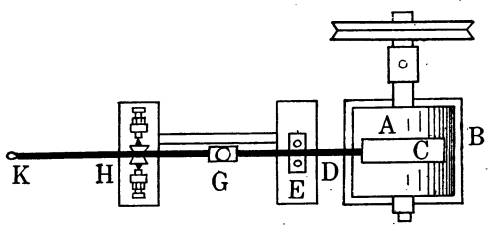


Fig. 2.

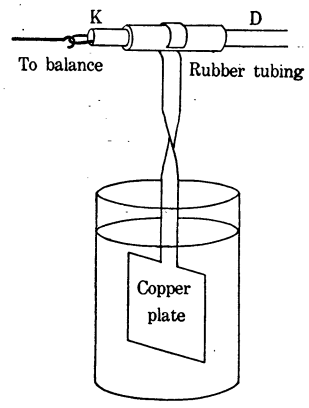


Fig. 3.

pendicular position. In such a state, the friction force F is in equilibrium with the weight in P. So the friction force can be obtained by a simple calculation as described in the former paper.

The contact line between A and C must be in the same height with the joint between L and M. The load W is measured by replacing the cylinder A with a balance.

(2) Sameshima, Kidokoro and Akamatu, this Bulletin, **11** (1936), 659.

When the sample is a nonpolar and low viscosity liquid, then the equilibrium point can hardly be determined owing to the movement of G to and fro. This is probably caused by the seizure between the solid surface A and C without the film of liquid. In this case a damper, shown in Fig. 3, is attached to D. This consists simply of dipping a copper plate in a viscous liquid made of the liquid paraffin and vaselin.

The surface of the steel cylinder A and the steel plate C have been cleaned, at first, by washing with benzene, with soap solution rubbing by finger tip, and finally with alcohol. The cleaning is satisfactory, by this treatment, in the measurements of the friction coefficients of alcohols. In the case of hydrocarbons and of water, however, the surfaces are not sufficiently cleaned by this method, for the values of friction coefficient fluctuate considerably in each observation. So, at last, the surfaces have been cleaned by the electrolytic method described in the followings.

The electrolytic solution is the mixture of the equal volume of 1% NaCl solution and alcohol. The electrolytic cell consists of the platinum anode and the steel cathode. The electrolysis is conducted at 4–6 volts and less than 0.1 ampere, being continued for 10–30 seconds. The surface of the cathode is cleaned by the discharge of hydrogen on it. After this treatment, the surface is rinsed with distilled water and dried in a desiccator passing a current of dry air. The steel surface cleaned by such a manner is readily wetted with water or alcohols, and gives fairly concordant value of friction coefficient in each liquid.

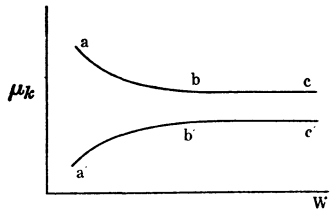


Fig. 4.

The friction coefficients are measured for the varying values of the load W. The relations are shown by the two curves of Fig. 4. In the region where W is large the friction coefficient becomes constant, while in the region where W is small the coefficient is not constant and changes with W. The former is represented by the portion of the curves bc or b′c′, and the latter ab or a′b′. The portion bc or b′c′ corresponds to the boundary lubrication while ab or a′b′ to the film one. In the present report the friction coefficient for the boundary lubrication will be given.

The rotation velocity of the cylinder A was, in the present experiment, 0.80 second for one rotation. The diameter of the cylinder is 5 cm., so the velocity of the sliding surface is calculated to be 19.6 cm. per

second. Diverse results were obtained by numerous authors on the relation between the friction coefficient and the moving velocity of the sliding surfaces.[3] It seems so far probable that the kinetic friction is smaller than the static friction unless the sliding velocity is extremely small. The quantitative relations on this subject will be studied in the further experiments.

Care must be taken on the moisture of the air, which considerably affects the friction of some liquids. The air in the glass case of sliding machine is kept dry by inserting a considerable quantity of anhydrous calcium chloride, and moreover, a current of dried air is passed during the measurement.

The experimental results are given in Table 1. In this table, W shows the load and F the tangential force, both in gram unit. The kinetic friction coefficient μ_k are calculated as the ratio of F and W. The values of μ_k in parenthesis are excluded in the calculation of mean value, for these correspond to the portion ab or a'b' in the μ_k-W curves shown in Fig. 4.

The value of μ_k of water fluctuate considerably in repeating the measurements. Hardy and Doubleday described as follows[4]: "Water, considered as a lubricant, is of a remarkable character. It is neutral to clean surfaces of glass or steel in that it neither lowers nor raises the friction." The value of μ_k for water obtained in our experiments may or may not be the friction coefficient between steel surfaces of no lubricant. Further experiments are necessary to decide this question. We take, however, $\mu_k = 0.255$ as a provisional value for the kinetic friction coefficient of steel surfaces lubricated with water.

Fig. 5 and Fig. 6 show the relation between the kinetic friction coefficient and the number of carbon atom in the chemical formula of the lubricant liquid.

Measurements have been done on the mixture of water and alcohol, the results of which are given in Table 2. The relations between the kinetic friction coefficient and the composition of the mixture are depicted in Fig. 7.

---

(3) Jacob, *Ann. Physik*, [4], **38** (1912), 126. More literatures are given in Bear and Bowden's paper, *loc. cit.*

(4) Hardy and Doubleday, *Proc. Roy. Soc.* (London), A, **104** (1923), 34.

Table 1.

Lubricant	W(g.)	F(g.)	μ_k
Methyl alcohol CH_3OH (b.p. 64.2–64.5°C.)	35.5	6.06	0.171
	65.5	11.64	0.178
	92.7	15.94	0.172
	115.5	19.84	0.172
		Mean	0.173
Ethyl alcohol C_2H_5OH (b.p. 78.3–78.4°C.)	26.7	4.64	0.174
	36.7	6.39	0.174
	66.7	12.28	0.184
		Mean	0.177
n-Propyl alcohol C_3H_7OH (b.p. 97.0–97.5°C.)	65.5	10.41	0.159
	65.5	10.26	0.157
	92.7	14.70	0.159
	92.7	15.06	0.163
	115.5	18.64	0.161
		Mean	0.160
n-Butyl alcohol $CH_3(CH_2)_3OH$ (b.p. 116.5–117.0°C.)	92.7	13.14	0.142
	115.5	16.90	0.146
	115.5	15.60	0.135
	160.5	22.73	0.142
	160.5	22.14	0.138
		Mean	0.141
n-Amyl alcohol $CH_3(CH_2)_4OH$	65.5	4.08	(0.062)
	115.5	11.10	(0.096)
	173.5	19.92	(0.115)
	223.5	28.02	0.125
	273.5	34.96	0.128
		Mean	0.127

Lubricant	W(g.)	F(g.)	μ_k
n-Hexyl alcohol $CH_3(CH_2)_5OH$ (b.p. 154–155.5°C.)	318.5	32.28	(0.101)
	418.5	46.60	(0.111)
	553.9	64.44	0.116
	653.9	75.24	0.115
	653.9	76.50	0.117
	753.9	88.14	0.117
	753.9	87.86	0.117
		Mean	0.116
n-Heptyl alcohol $CH_3(CH_2)_6OH$	173.5	11.88	(0.069)
	318.5	31.32	(0.098)
	368.5	38.50	0.105
	418.5	45.22	0.108
	462.0	49.56	0.107
		Mean	0.107
n-Octyl alcohol $CH_3(CH_2)_7OH$	173.5	6.78	(0.039)
	318.5	26.88	(0.084)
	418.5	38.34	(0.092)
	489.1	45.36	0.093
	539.1	50.86	0.094
	553.9	52.08	0.094
	589.1	55.44	0.094
	653.9	60.46	0.093
	753.9	71.70	0.095
		Mean	0.094
Primary isoamyl alcohol CH_3>$CH\cdot CH_2CH_2OH$ CH_3 (b.p. 130.0–130.2°C.)	115.5	9.48	(0.082)
	223.3	24.48	(0.109)
	418.5	47.88	(0.114)
	489.1	63.84	0.130
	553.9	72.24	0.130
	653.9	81.84	0.125
	653.9	86.80	0.133
	753.9	94.80	0.126
	753.9	100.30	0.133
		Mean	0.130

Table 1.—(*Continued*)

Lubricant	W(g.)	F(g.)	μ_k
n-Hexane $CH_3(CH_2)_4CH_3$ (b.p. 68-69°C.)	65.5	13.42	0.205
	92.7	19.86	0.214
	115.5	25.66	0.222
	173.5	41.22	0.238
		Mean	0.220
	35.5	10.80	0.304
	65.5	19.84	0.303
	115.5	36.72	0.318
		Mean	0.308[5]
n-Heptane $CH_3(CH_2)_5CH_3$ (b.p. 98.4-99.2°C.)	65.5	12.10	0.185
	92.7	16.72	0.180
	115.5	20.28	0.176
	173.5	30.18	0.174
	215.5	37.98	0.176
		Mean	0.178
n-Octane $CH_3(CH_2)_6CH_3$ (b.p. 124-125°C.)	65.5	13.26	0.203
	92.7	18.94	0.204
	115.5	22.80	0.206
	173.5	35.70	0.206
	215.5	44.10	0.205
		Mean	0.205
n-Nonane $CH_3(CH_2)_7CH_3$ (b.p. 147.0-147.8°C.)	65.5	15.34	0.234
	92.7	21.28	0.229
	115.5	27.46	0.238
	173.5	41.15	0.237
		Mean	0.235

Lubricant	W(g.)	F(g.)	μ_k
n-Valeric acid $CH_3(CH_2)_3COOH$	115.5	12.06	(0.104)
	215.5	27.48	(0.127)
	318.5	42.24	0.133
	418.5	54.72	0.131
	563.8	73.32	0.130
	663.8	86.82	0.131
		Mean	0.131
n-Caproic acid $CH_3(CH_2)_4COOH$ (b.p. 194-195°C.)	215.5	17.94	(0.083)
	563.8	67.52	0.120
	563.8	64.62	0.113
	663.8	80.40	0.121
	663.8	76.04	0.115
	763.8	91.55	0.120
	763.8	87.16	0.114
		Mean	0.117
n-Heptylic acid $CH_3(CH_2)_5COOH$	698.5	66.66	0.095
	848.1	82.94	0.098
	948.1	93.10	0.098
	948.1	85.14	0.090
	1093.8	102.90	0.094
	1193.8	108.42	0.091
		Mean	0.094
n-Caprylic acid $CH_3(CH_2)_6COOH$	598.5	36.30	(0.061)
	848.1	65.14	0.077
	948.1	75.18	0.079
	948.1	68.06	0.072
	1083.8	79.40	0.073
	1183.8	87.88	0.074
	1343.4	101.34	0.075
		Mean	0.075

(5) Hexane gives two different values of μ_k, 0.220 and 0.308, the reason of which is yet unknown.

Table 1.—(*Concluded*)

Lubricant	W(g.)	F(g.)	μ_k	Lubricant	W(g.)	F(g.)	μ_k
	598.5	25.20	(0.042)		35.5	9.40	0.265
	948.1	50.34	(0.053)		65.5	17.26	0.264
n-Nonylic acid	1083.8	62.40	0.058		92.7	25.20	0.272
$CH_3(CH_2)_7COOH$	1183.8	68.64	0.058		115.5	31.96	0.277
	1343.4	77.78	0.058		173.5	48.34	0.279
	1443.4	84.64	0.059				
		Mean	0.058		35.5	8.74	0.246
					65.5	16.30	0.249
					92.7	24.66	0.266
	25.5	6.24	0.245	Water	115.5	29.74	0.258
	35.5	8.76	0.247		173.5	45.42	0.262
	65.5	15.66	0.239				
	92.7	23.02	0.248		35.5	9.94	0.280
Water					65.5	17.68	0.270
	35.5	8.4	0.237		92.7	28.84	0.311
	65.5	14.16	0.216		115.5	33.82	0.293
	92.7	21.76	0.235		173.5	51.10	0.294
	115.5	26.28	0.228			Mean	0.255
	173.5	39.86	0.230				

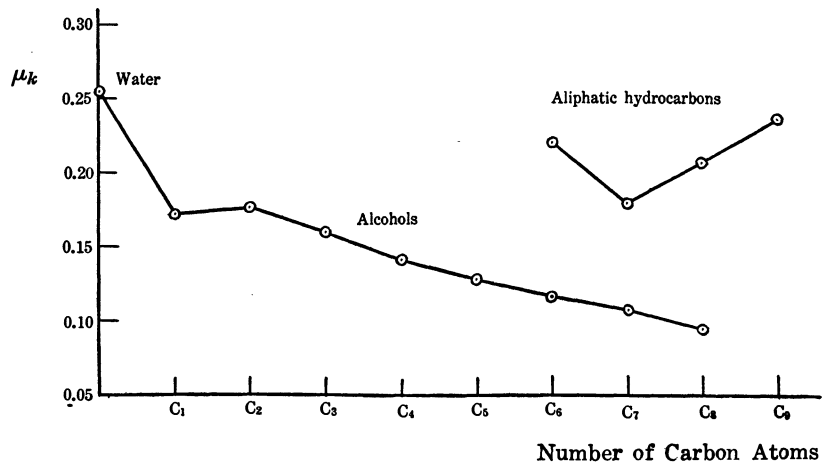


Fig. 5.

Table 2. Mixture of Water and Ethyl Alcohol.

Lubricant	W(g.)	F(g.)	μ_k
water 90% alcohol 10%	65.5	13.86	0.212
	65.5	13.44	0.205
	92.7	19.32	0.209
	115.5	21.88	0.189
		Mean	0.204
water 74.9% alcohol 25.1%	65.5	13.26	0.202
	65.5	11.70	0.179
	92.7	20.46	0.221
	92.7	16.14	0.174
	115.5	20.40	0.177
	173.5	31.18	0.180
		Mean	0.189

Lubricant	W(g)	F(g.)	μ_k
water 50.1% alcohol 49.9%	65.5	11.76	0.180
	92.7	16.92	0.183
	92.7	16.83	0.182
	115.5	20.40	0.177
	115.5	21.78	0.189
	173.5	33.82	0.195
		Mean	0.184
water 25% alcohol 75%	65.5	11.52	0.176
	92.7	16.50	0.178
	115.5	20.49	0.177
		Mean	0.177

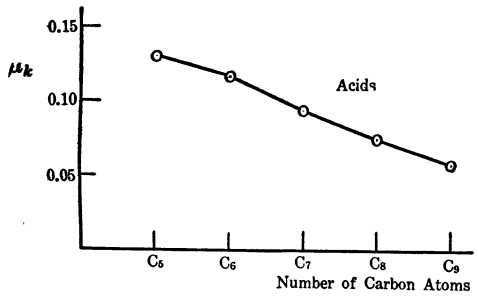


Fig. 6.

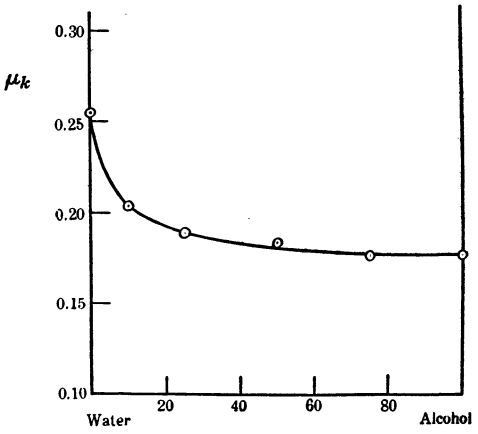


Fig. 7.

The expense of the present experiments has been defrayed from a grant given by Nippon Gakujutsu Shinkokwai (Japan Society for the Promotion of Scientific Research) for which the authors' sincere thanks are due.

Chemical Institute, Faculty of Science,
Imperial University of Tokyo,
Tokyo.

Der katalytische Isotopenaustausch zwischen Wasser und Sauerstoff.

Von Noriyoshi MORITA und Toshizo TITANI.

(Eingegangen am 1. Februar 1937.)

Wir untersuchten die katalytische Austauschreaktion der schweren Sauerstoffatome zwischen Sauerstoff und flüssigem sowie dampfförmigem Wasser. Obwohl der Versuch noch nicht beendet ist, wollen wir die bisher erhaltenen Resultate vorläufig mitteilen. Das zum Versuch benutzte Wasser war an schwerem Sauerstoff angereichertes „schweres Wasser", das durch die Destillation von gewöhnlichem Wasser hergestellt wurde und um etwa 20 γ schwerer als Osaka-Leitungswasser war. Der isotopischen Analyse[1] dieses „schweren Wassers" nach rührten von dem obenangegebenen gesamten Dichteüberschuss von 20 γ fast 80% von der Anreicherung an schwerem Sauerstoff her.

Bei der ersten Reihe der Versuche, wo wir flüssiges Wasser verwendeten, wurde das „schwere Wasser" zusammen mit Platinschwarz in einem mit Rückflusskühler versehenen Rundkolben gebracht, durch den wir den aus gewöhnlichem Wasser elektrolytisch entwickelten Sauerstoff langsam blasen liessen, wobei wir das „schwere Wasser" konstant auf der Temperatur von 0° bis 55°C. hielten. Obgleich der Sauerstoff von sechzig bis hundertfünfzig Stunden lang durchgeleitet wurde, war doch in keinem Fall nach dem Experiment eine nennenswerte Abnahme der Dichte des verwendeten „schweren Wassers" zu bemerken. Deshalb benutzten wir in der nächsten, zweiten Versuchsreihe das „schwere Wasser" in Dampfform und leiteten das Gemisch aus diesem und elektrolytischem Sauerstoff (ungefähres Volumenverhältnis $H_2O:O_2 = 4:1$) über verschiedene auf verschiedene Temperaturen erhitzte Katalysatoren. Das dazu benutzte Gasgemisch wurde dadurch hergestellt, dass wir den elektrolytisch entwickelten Sauerstoffstrom durch die in einem Kolben befindliche auf 61° bis 62°C. gehaltene Menge des „schweren Wassers" leiteten und sich mit dessen Dampf sättigen liessen. Das so bereitete Gasgemisch wurde langsam durch das Katalysatorrohr geleitet und der daraus ausströmende „schwere Wasserdampf" vollständig kondensiert aufgefangen. Nachdem die gegebene Menge des „schweren Wassers" auf diese Weise restlos verdampft und durch das Katalysatorrohr abdestilliert worden

(1) Vgl. N. Morita und T. Titani, dies Bulletin, **11** (1936), 695.

war, wurde es gereinigt und seine Dichte genau bestimmt. Wir führten insgesamt sechs Versuche mit verschiedenen Katalysatoren bei verschiedenen Temperaturen aus, nämlich: mit (1) auf 290°C. erhitztem Kupferoxyd, (2) auf 400°C. erhitztem Eisenoxyd, (3) auf 90° sowie (4) 400°C. erhitztem Silberoxyd und (5) schwach sowie (6) stark rot erhitztem metallischem Platin. Aber bei allen diesen Fällen mit Ausnahme von (6) stimmte der Dichteüberschuss des verwendeten „schweren Wassers" vor mit dem nach dem Experiment innerhalb des Messfehlersbereichs gut überein. Bei dem (6) Fall nahm aber der anfängliche Dichteüberschuss des benutzten „schweren Wassers" durch die obenangegebene Behandlung von $\Delta s_a = 22.2\,\gamma$ bis endlich auf $\Delta s_e = 5.1\,\gamma$ ab.

Von dem Resultate des Experimentes (6) angeregt, führten wir die dritte Reihe der Versuche ebenfalls mit dampfförmigem „schweren Wasser" aus. Der anfängliche Dichteüberschuss des in dieser Versuchsreihe verwendeten „schweren Wassers" betrug $\Delta s_a = 22.2\,\gamma$, wovon $18.0\,\gamma$ von der Anreicherung mit schwerem Sauerstoff herrührten. Aus diesem „schweren Wasser" und dem aus gewöhnlichem Wasser elektrolytisch entwickelten Sauerstoff wurde ein Gasgemisch von der ungefähren Zusammensetzung $H_2O:O_2 = 1:2$ auf ähnliche Weise, wie obenangegeben, hergestellt, indem wir den Sauerstoffstrom sich bei 72°C. mit dem „schweren Wasserdampf" sättigen liessen. Das so gewonnene Gasgemisch wurde dann durch das mit Platinschwamm beschickte und auf verschiedene Temperaturen erhitzte Katalysatorrohr geleitet. Der Platinschwamm wurde hergestellt, indem wir „Platinchlorid" zunächst durch langsame Erhitzung teilweise zersetzten und das so erhaltene Präparat in dem Katalysatorrohr mittels Wasserstoffs bei ca. 200°C. vollständig reduzierten. Das Volumen des benutzten Platinschwamms betrug 1.7 c.c. Darüber wurde das Gasgemisch mit der Geschwindigkeit von 1.0 c.c. pro Sekunde geleitet, bis die gegebene Menge des „schweren Wassers" durch das Katalysatorrohr restlos abdestilliert war. Die Versuchsergebnisse sind in der folgenden Tabelle wiedergegeben.

Die Nummern in der ersten Vertikalreihe der Tabelle zeigen die Ordnung, in der die einzelnen Experimente ausgeführt wurden. Berechnet man die Abnahme des Dichteüberschusses des „schweren Wassers", zu der es durch die Austauschreaktion der schweren Sauerstoffatome mit dem zugemischten elektrolytischen Sauerstoff kommt, unter der Annahme, dass der letztere um $1\,\gamma$ leichter als gewöhnlicher Wassersauerstoff und der Verteilungsquotient von O^{18} zwischen Wasserdampf und Sauerstoff ungefähr gleich eins ist,[2] dann ergibt sich beim vollständigen Austausch

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

Tabelle

Nr.	Temperatur °C.	Endlicher Dichteüberschuss des „schweren Wassers" Δs_e in γ	$\Delta s_a - \Delta s_e$ in γ
3	300	21.5	0.7
4	400	19.3	2.9
7	430	14.2	8.0
8	470	9.1	13.1
1	500	12.1	10.1
9	540	6.5	15.7
10	580	5.9	16.3
5	600	5.9	16.3
2	730	5.0	17.2
6	800	5.7	16.5

Der anfängliche Dichteüberschuss des „schweren Wassers" betrug $\Delta s_a = 22.2\gamma$.

im obenangegebenen Gasgemisch $\Delta s_a - \Delta s_e = 16 \pm 1\,\gamma$. Vergleicht man diesen Wert mit den in der letzten Vertikalreihe der Tabelle gegebenen Werten, so darf man wohl schliessen, dass die katalytische Austauschreaktion der Sauerstoffatome zwischen Sauerstoff und Wasserdampf unter den angegebenen Versuchsbedingungen erst oberhalb 450° bis 500°C. lebhaft stattfand. Reischauer[3] sah „bei etwa 400°C. ziemlich plötzlich erneute (zweite aktivierte) Adsorption" des Sauerstoffs auf metallischem Platin „einsetzen". Diesem Befunde nach dürften unsere Versuchsergebnisse mit der „zweiten" aktivierten Adsorption des Sauerstoffs auf Platin in engem Zusammenhang stehen.

Zum Schluss sagen wir der Nippon Gakujutsu-Shinkohkai (der Gesellschaft zur Förderung der japanischen Wissenschaft) sowie der Hattori-Hohkohkai (der Hattori-Stiftung) für ihre finanzielle Unterstützung bei Ausführung dieser Versuche unseren wärmesten Dank.

Physikalisch-chemisches Laboratorium
der Kaiserlichen Universität zu Osaka
und
Schiomi-Institut für physikalische
und chemische Forschung.

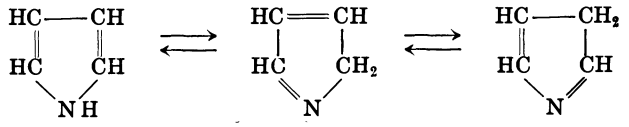
(3) H. Reischauer, *Z. physik. Chem.*, B, **26** (1934), 399.

Austausch der Wasserstoffatome zwischen Pyrrol und Wasser. (Vorläufige Mitteilung.)

Von Masao KOIZUMI* und Toshizo TITANI.

(Eingegangen am 3. Februar 1937.)

Auf Grund der chemischen Eigenschaften des Pyrrols besitzt diese Verbindung die Möglichkeit der desmotropischen Umwandlung, wie das folgende Schema zeigt:[1]



Sollte eine solche Umwandlung wirklich stattfinden, so liegt weiter die Möglichkeit nahe, dass nicht nur das an N gebundene H-Atom des Pyrrolmoleküls, sondern unter Umständen auch solche H-Atome, die an C gebunden sind, gegen die des Wassers ausgetauscht werden. In unserem früheren Versuch,[2] wo wir Pyrrol zusammen mit neutralem verdünntem schwerem Wasser schüttelten, fanden wir aber, dass nur ein einziges und höchstwahrscheinlich an N gebundenes H-Atom des Pyrrolmoleküls gegen die H-Atome des Wassers ausgetauscht wurde, es aber selbst nach fünfzig Stunden bei 50°C. zu keinem Austausch weiterer H-Atome des Pyrrolmoleküls gegen die des Wassers kam. Im Anschluss an diesen Versuch führten wir einen ähnlichen unter Verwendung von HCl-sauerem sowie KOH-alkalischem verdünntem schwerem Wasser aus, dessen Ergebnisse wir vorläufig mitteilen wollen. Die bei diesem Versuch gefundenen Tatsachen sind kurz zusammengefasst wie folgt:

(1) Solange die Wasserstoffionenkonzentration im verwendeten schweren Wasser von pH = 14 bis 2 blieb, wurde nur ein einziges H-Atom des Pyrrolmoleküls gegen die des Wassers sehr schnell ausgetauscht, aber selbst im Verlaufe von zehn Stunden bei 30°C. keine weiteren H-Atome gegen die des Wassers, auch wenn 0.01 normales saueres schweres Wasser verwendet wurde.

---

* Früher Masao HARADA.

(1) Vgl. H. Fischer und H. Orth, „Die Chemie des Pyrrols", Bd. I, Leipzig (1934).

(2) M. Harada und T. Titani, dies Bulletin, **11** (1936), 465.

(2) Als dagegen die Wasserstoffionenkonzentration im schweren Wasser bis zu pH = 2 bis 1 erhöht wurde, setzte ziemlich plötzlich eine neue Art der Austauschreaktion ein, bei der mehr als ein H-Atom des Pyrrolmoleküls gegen die H-Atome des Wassers ausgetauscht wurden. Diese neue Austauschreaktion verlief innerhalb der obenangegebenen pH-Grenzen mit gut messbarer Geschwindigkeit.

(3) Als wir aber die Wasserstoffionenkonzentration im schweren Wasser noch weiter erhöhten und dessen pH unterhalb 1 sank, wurde die Austauschgeschwindigkeit so gross, dass sie sich fast als unmessbar erwies.

(4) Bei Benutzung von fast reinem schwerem Wasser fanden wir, dass in dieser neuen Austauschreaktion die sämtlichen fünf H-Atome des Pyrrolmoleküls gegen die des Wassers austauschbar waren. Daraus folgte, dass der Verteilungsquotient[2] der D-Atome zwischen dem CH-Radikal des Pyrrolmoleküls und dem Wasser $k(\mathrm{CH}/\mathrm{H_2O}) = 0.70$ sein muss, wenn man den V.Q. zwischen dem NH-Radikal des Pyrrols und dem Wasser $k(\mathrm{NH}/\mathrm{H_2O}) = 0.88$ setzt.[2]

Alle obenangegebenen Experimente wurden bei 30°C. ausgeführt, und es handelt sich bei den sich dabei abspielenden Vorgängen höchstwahrscheinlich um die desmotropische Umwandlung des Pyrrolmoleküls, besonders da die neue Austauschreaktion ziemlich plötzlich bei einer bestimmten pH-Grenze einsetzte. Die ausführliche Mitteilung soll später in diesem Bulletin erscheinen.

Zum Schlusse sagen wir warmen Dank der Nippon Gakujutsu-Shinkohkai (der Gesellschaft zur Förderung der japanischen Wissenschaft) sowie der Hattori-Hohkohkai (der Hattori-Stiftung) für die finanzielle Unterstützung bei Ausführung dieser Untersuchung.

Schiomi-Institut für physikalische
und chemische Forschung
und
Physikalisch-chemisches Laboratorium
der Kaiserlichen Universität zu Osaka.

A Theory of Surface Tension of Aqueous Solutions of Inorganic Acids.

By Kyozo ARIYAMA.

(Received January 27th, 1937.)

1. Introduction. Since Heydweiller and his co-workers[1] discovered that the surface tension of the solution of inorganic salts in water increases as the solute is increased, various attempts[2] have been made to explain the phenomenon. The recent theories proposed[3],[4],[5],[6] to account for the phenomenon are all based on the Debye-Hückel[7] theory of strong electrolyte. All these theories treated with varied degrees of success the normal effect, that is, the increase of surface tension with increase in the concentration of the electrolyte. None of these theories, however, treat the anomalous behaviour of inorganic acids which exhibit a decrease of surface tension as the concentration is increased. The lack of any theoretical account for the anomalous effect for inorganic acids is due primarily to the fact that the effect is just opposite to what we might expect from the Debye-Hückel theory of strong electrolyte. This simple fact suggests at once that the structure of water at the surface is the most important factor to be considered in any theoretical discussion of this anomaly. The present paper shows that the anomaly can be explained quantitatively if we accept two hypotheses, that is, a special orientation of water molecules at the surface different from the interior and the semi-empirical structure of water as proposed by Bernard and Fowler.[8]

2. In order to understand the especially high value found for the decrease of surface tension due to ammonia solution of water, we shall discuss briefly the structure of water and similar compounds from a general point of view.[9]

The hydrogen atom occupies a very peculiar position in the structure of atoms, and exhibits in many ways peculiar characteristics different

(1) Heydweiller, *Ann. Physik*, [4], **33** (1910), 145.
(2) Wagner, *Physik. Z.*, **25** (1924), 474.
(3) Onsager and Samaras, *J. Chem. Phys.*, **2** (1934), 529.
(4) Oka, *Proc. Phys.-Math. Soc. Japan*, [3], **14** (1932), 649.
(5) Shiba, *Bull. Inst. Phys. Chem. Research* (Tokyo), **8** (1934), 110.
(6) Ariyama, this Bulletin, **11** (1936), 887.
(7) See for example Falkenhagen, "Electrolyte."
(8) Bernal and Fowler, *J. Chem. Phys.*, **1** (1933), 515.
(9) The author is indebted to Dr. J. Horiuchi for the following discussion.

from all other elements. Most of these peculiarities owe their origin to the fact that the positive ion of the hydrogen atom is simply a proton, which carries no extra-nuclear electrons. An example of such peculiarity is given in the case of an extraordinarily high absorption of hydrogen by palladium. This is explained if we consider that the hydrogen atom when going into palladium separates into electron and proton, and that these are separately absorbed.[10] The greatest peculiarities appear when hydrogen atoms combine with atoms of oxygen or nitrogen.

The peculiarities are indicated in the structure of the compounds as well as in various chemical and physical properties of the compounds. In the case of water, for example, the distance between the two hydrogen atoms is 0.97Å, while the diameter of hydrogen molecule is 2.76Å. Thus two protons of the water molecule lie within the distance of orbital radius of the outermost electrons of oxygen atoms. Bernal and Fowler[8] in their extensive treatment on water give the following model for the structure of water, basing their argument partially on quantum mechanics and partially on experimental data: If we suppose an oxygen atom at the center of a tetrahedron the two heads of the tetrahedron are occupied by the two protons, and at the other two heads of the tetrahedron are distributed the negative charges. The structure of alcohol is obtained if we replace a hydrogen with an alkyl radical in the tetrahedron. In the case of ammonia, three corners of the tetrahedron are occupied by protons and the remaining corner is occupied by negative charges. If we replace one hydrogen by alkyl radicals we obtain the structure for amines.

If, for example, molecules which have similar structure to water approach a water molecule, it is quite evident from the above discussion that the corners of the tetrahedron of water at which negative charges are distributed will attract the protons of other molecules. Such union of two molecules by means of a proton is called a "hydrogen bond," and this hydrogen bond is considered responsible for the association of water, alcohol, and ammonia molecules.

From these general discussions it may be expected that the hydrogen ions and ammonia molecules behave somewhat differently from all other inorganic ions in water. If the molecules of water are distributed at random both at the surface and in the interior of the liquid, the negative adsorption should result from solutions of inorganic acid. For the ions forming the hydrogen bond between molecules of water will be uniformly distributed everywhere so that the effect due to hydrogen bond can be neglected as far as the distribution of hydrogen ions in water is concerned.

(10) Frank, *Göttinger Nachrichten*, **1933**, 293.

Thus the hydrogen bond alone does not give rise to the positive adsorption of hydrogen ions at the surface of water.

In order that the positive adsorption of hydrogen ions at the surface of water should result the distribution of the hydrogen bond must be different at the surface than in the interior of the water. If at the surface the number of water molecules having their hydrogen heads facing upward sufficiently exceeds the number having their oxygen atoms facing upward so that as a consequence there is a resultant of hydrogen heads extending into the liquid, we might expect positive adsorption of hydrogen ions at the surface due to the hydrogen bond. Since this seems to be the only way for the positive adsorption of hydrogen ions to occur at the surface, we shall assume that the majority of water molecules are oriented at the surface in such a way that the proton heads of the molecular tetrahedrons lie on the surface causing the negatively charged corners to extend downward into the liquid.

3. For the quantitative discussion of the surface tension of inorganic acids, we shall take, for sake of simplicity and convenience, one-half molar concentration for all the compounds, and the temperature at which the surface tension is given is corrected to 20°C. unless otherwise stated. The Table 1 shows the experimental data mainly collected from the International Critical Tables.

In the fourth row of the Table the calculated values for the surface tension decrease due to one hydrogen-bond at the surface are given. The methods of the calculations are given in the following: We shall take the case of HCl as an example. The surface tension increase due to half normal solution of NaCl at 20° is 0.83 dynes/cm. Since the charge of Na^+ and Cl^- ions are the same, and their ionic volume approximately the same according to the theories proposed for the negative adsorption of Debye-Hückel electrolyte,[3],[4],[5],[6] the contribution of these two ions to the increase of the surface tension of the solution will be approximately the same. Thus we get the same contribution from Na^+ as from Cl^- namely 0.41 dynes/cm. If the Cl^- behaves in the same way in the half normal solution of HCl as in the half normal solution of NaCl, then the contribution of Cl^- to the increase in surface tension will be the same. Therefore, in order to obtain the decrease of the surface tension of the HCl solution by -0.2 dynes/cm., the contribution due to H^+ should be $-0.2 - 0.41 = -0.61$. dynes/cm. In the similar manner the contribution due to one hydrogen bond for the compounds HNO_3 and HBr is calculated. The values assigned for negative ions for respective compounds are listed

(11) Rice, *J. Phys. Chem.*, **32** (1928), 583.

Table 1.

$\Delta\gamma$ is the difference between the surface tension of the solution and that of the solvent at the same temperature.
$\Delta\gamma$ is expressed in dynes per centimeter.

Formula	Temperature °C.	$\Delta\gamma$ for 0.5 mol/kg.	$\Delta\gamma$ due to H
HCl	20	−0.16	−0.57±0.1
NH_3	18	−1.4	−0.46±0.3
HNO_3	20	−0.42	−0.61±0.2
HBr	18	−0.38±0.2	−0.56±0.2
H_2SO_4(12)	20	−0.18	−0.55±0.3
Na_2HPO_4	30	−0.81±0.2	−0.23±0.3
KH_2PO_4(12)	20	−0.53±0.05	−0.81±0.3
H_3PO_4(12)	20	0.00±0.3	−0.33±0.3
		The average for the last 3 cases	−0.46±0.3

Table 2.

Uni-valent case

Ions	$\Delta\gamma$
Na^+	0.41
Cl^-	0.41
NO_3^-	0.19
OH^-	0.50
Br^-	0.29
NH_4^+	0.5

Bi-valent case

Ions	$\Delta\gamma$
Na^+	0.23
SO_4^{--}	0.91

Tri-valent case

Na^+	0.11
K^+	0.11
PO_4^{---}	0.99

in the Table 2. These values can be used to check their reasonableness with many other compounds containing these negative ions in the solutions.

When the negative ions happen to be bi-valent or of the higher valency, the calculation is carried out in the following manner: Let us take as an example the half normal solution of Na_2SO_4. According to the theories of the negative adsorption,[3],[4],[5],[6] the contribution of ions

(12) Morgan and Bole, *J. Am. Chem. Soc.*, **35** (1913), 1750.

to the increase in the surface tension of the solution is proportional to the number of respective ions and to the squares of their ionic charges. Thus the increase of surface tension by 1.36 dynes/cm. for the Na_2SO_4 solution gives 0.91 dynes/cm. to SO_4 ions, that is 4/6 of the total effect. A similar argument applies to the case of H_3PO_4 and the related compounds. The values assigned for the negative ions are given in Table 2. Using these values for the negative ions, we obtain values for one hydrogen-bond for various compounds.

The calculation for ammonia differs from the above procedure. As we have already discussed, the ammonia molecule has a very similar structure to water, and any one of three protons of the ammonia molecule can form a hydrogen bond with a water molecule. Thus the probability of ammonia being adsorbed by water molecules at the surface is approximately three times as large as that of single hydrogen ion, so that it is to be expected that the half normal ammonia solution will show three times as large an effect as is to be expected from HCl solution. Therefore, we simply divide -1.4 dynes/cm. by 3 to obtain the effect due to a single hydrogen bond. We obtain a value for the single hydrogen-bond which agrees within experimental error with those found for other compounds.

The examination of NH_4NO_3, NH_4Cl, and NH_4Br indicates that the NH_4^+ ion behaves as if it were a metallic ion which gives rise to the negative adsorption. Therefore when the ammonia NH_3 is dissolved in water,[11] the NH_3 molecule is adsorbed at the surface of water forming a hydrogen bond with a water molecule, and the NH_3^+ ion is not formed by the capture of hydrogen ions in water. This is a very interesting conclusion which we can derive from the above experimental data.

As is clearly indicated in Table 1, the values found for $\Delta\gamma$ due to the hydrogen bond agree very well within the experimental error. This fact strongly supports the assumptions which we have stated at the beginning of the paper. Thus the anomaly of the surface tension exhibited by inorganic acids can be attributed to the hydrogen-bond formation at the surface of water.

In conclusion, the author wishes to express his thanks to Professor H. Erikson for his kind encouragement.

A Note on the Theory of Surface Tension of Ternary Solutions.

By Kyozo ARIYAMA.

(Received February 5th, 1937.)

The present author has recently proposed a theory of surface tension of dilute solution of strong electrolyte,[1] and in the succeeding papers[2],[3],[4] the theory is extended to include the case of ternary solutions. More recently he has developed a theory of surface tension of aqueous solutions of inorganic acids.[5] If we have experimental data on the surface tension of ternary solutions of inorganic salt and inorganic acid, we will have a very interesting test on those theories in addition to those experimental tests which have been dealt with previously. Belton recently in his series of papers has given the experimental data on such ternary solutions.[6]

Since the surface tension of 0.1 mol hydrochloric acid is only 0.02 dynes/cm. less than that of water, it might be expected that its presence in strong solutions of salts could therefore be neglected. This would be so if the surface tension change for the mixture were the sum of the changes each solute would produce if present separately. This simple additive relation does not result however, and the effect of hydrocholoric acid increases with increasing salt concentration. Belton[6] confirmed this result with many solutions using many salts. A few examples of his results are given in the Table 1. In this Table the ratio $\Gamma_1/_0\Gamma_1$ stands for the ratio of the negative adsorption of the salt when the hydrocholoric acid is added to the negative adsorption of the salt when present alone in water.[4] This ratio was found to be less than one always.

This experimental fact can be accounted for theoretically by the theories mentioned above if the dielectric constant of adsorption layer is shown to be smaller than that of pure water when the inorganic acid is added.[4] We have no way of measuring the dielectric constant of the adsorption layer at present, but we can estimate it quite reasonably in the following way. When the hydrogen ions from inorganic acid are

(1) K. Ariyama, this Bulletin, **11** (1936), 687.
(2) *Ibid.*, **12** (1937), 32. (3) *Ibid.*, **12** (1937), 38. (4) *Ibid.*, **12** (1937), 44.
(5) *Ibid.*, **12** (1937), 109.
(6) Belton, *Trans. Faraday Soc.*, **31** (1935), 1413; **32** (1936), 1717.

positively adsorbed at the surface forming the hydrogen bond with water molecules,[5] the molecules of water will be of the structure similar to ammonia molecules having three hydrogen attached to three corners of the tetrahedron. Some water molecules at the surface may carry even four hydrogen atoms on the four corners of their tetrahedrons due to the hydrogen bond. As the number of such ammonia-like water molecules increases the dielectric constant of water is expected to decrease at the surface due to the following reasons.

The H_2O molecule is of the neon type with ten electrons as are also CH_4, NH_3, and FH. The dielectric constants for these substances as well as some other similar compounds are listed in the Table 2. It is clear

Table 1.

NaCl	HCl	$\Gamma_1/_0\Gamma_1$	KCl	HCl	$\Gamma_1/_0\Gamma_2$
m_1	m_2		m_1	m_2	
1	0.1	0.91	1	0.1	0.95
2	0.1	0.91	2	0.1	0.95
3	0.1	0.91	3	0.1	0.95
4	0.1	0.91	4	0.1	0.95
5	0.1	0.91			

Table 2.

	Dielectric constant		Dielectric constant
CH_4	2.3	PH_3	—
NH_3	25.4	SH_2	5.92
OH_2	80.	ClH	8.85
FH	83.5	HOOH	92.8

from this Table that as the number of hydrogen increases in molecule, the dielectric constant decreases. Thus it may be reasonable to expect that the ammonia-like water molecules will have a dielectric constant approximately the same as that of ammonia. If the number of such ammonia-like water molecules increases at the surface, it is reasonable to suppose that the dielectric constant of the adsorption layer is decreased from that of water.

Thus we can explain at least qualitatively Belton's experiments very easily.

Since it is very difficult to consider that the dielectric constant of adsorption layer is increased by the addition of inorganic acid in salt solution, the theories of the negative adsorption proposed by various other workers[7] seem to be unacceptable since they give a reverse result of the theory of the peresnt author.

In conclusion, author wishes to express his thanks to Dr. H. Erikson for his interest in the work.

Physics Department, University of Minnesota,
Minneapolis, Minn., U.S.A.

(7) Wagner, *Physik, Z.*, **25** (1924), 474; Shiba, *Bull. Inst. Phys. Chem. Research* (Tokyo), **13** (1934), 109; Onsagar and Samaras, *J. Chem. Phys.*, **2** (1934), 529.

The Formation of *l*-Threose.

By Koichi IWADARE, Shozo FUKUNAGA, and Bennosuke KUBOTA.

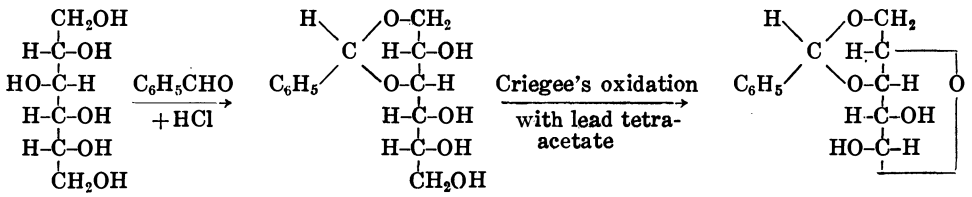
(Received January, 25th, 1937.)

Obtaining *l*-threose by Wohl's method of degradation of *l*-xylose which was prepared from *l*-gulonolactone, Deulofeu[1] reported its specific rotation as to the left. It was, however, reported by R. Hockett[2] that the specific rotation of *d*-threose prepared by the Wohl degradation of *d*-xylose was lævorotation of $-12.5°$ in equilibrium. Hockett was thus forced to the conclusion that Deulofeu did not have pure substance and that the *l*-isomer should obviously have dextrorotation of equal numerical value with his *d*-isomer. The formation of *l*-threose, therefore, has not yet been accepted.[3]

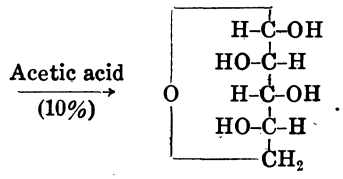
---

(1) Deulofeu, *J. Chem. Soc.*, **1929**, 2458; *J. Am. Chem. Soc.*, **58** (1936), 855.
(2) R. Hockett, *J. Am. Chem. Soc.*, **57** (1935), 2265.
(3) See H. Vogel and A. Georg, "Tabellen der Zucker," (1931).

In the course of our investigation of monoses[4], we prepared, for the purpose of formation of *l*-talonic acid, a considerable quantity of *l*-galactonic acid, which is easily degraded to *l*-lyxose. In the hope of ascertaining the properties of *l*-threose, we made attempts to degrade *l*-lyxose to *l*-threose and to isolate it. Meanwhile we found that *l*-xylose was obtained very conveniently from *d*-sorbitol by Vargha's method[5]. This can be used as well as *l*-lyxose in obtaining *l*-threose and it was thus used as a starting material of this investigation, and the process of the reaction is shown in the scheme below.



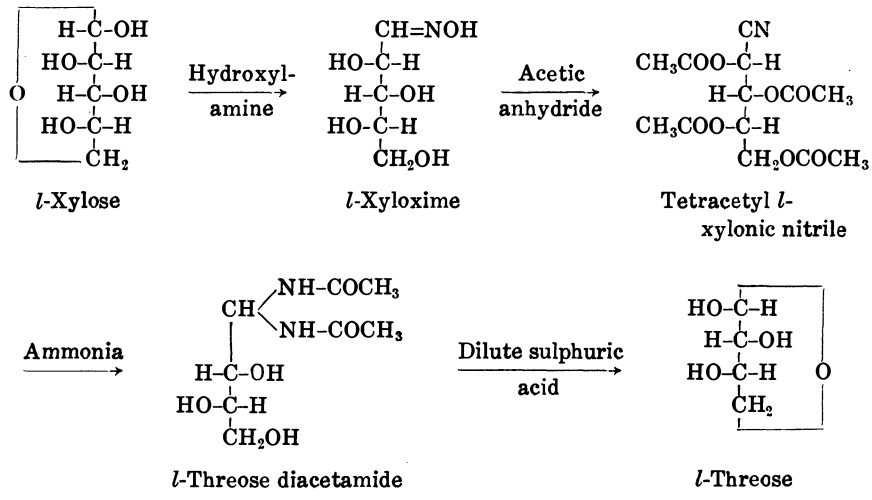
d-Sorbitol 1,3-Monobenzal-*d*-sorbitol 3,5-Benzal-*l*-xylofuranose



β-*l*-Xylose

l-Xylose thus obtained melts at 143° and rotates in equilibrium 18.2° to the left. Following the method of Deulofeu, it was submitted to degradation to *l*-threose by the method of Wohl. Being treated with hydroxylamine hydrochloride and sodium methylate, it changed into a thick syrup which consists mainly of *l*-xyloxime. When the *l*-xyloxime was warmed with acetic anhydride and sodium acetate in dioxane, a precipitate of tetracetyl-*l*-xylonic nitrile melting at 82° separated out. It was then decomposed with ammonia, and a colourless crystalline substance melting at 164–165°, the composition of which was $C_8H_{16}O_5N_2$, was obtained. It is nothing but *l*-threose diacetamide, and it rotates 10.8° to the right in water solution. Hockett's *d*-isomer rotates 10.9° to the left.

(4) S. Fukunaga, *J. Chem. Soc. Japan*, **57** (1936), 551.
(5) L. v. Vargha, *Ber.*, **68** (1935), 18.



l-Xylose — *l*-Xyloxime — Tetracetyl *l*-xylonic nitrile

l-Threose diacetamide — *l*-Threose

The equilibrium rotation of the sugar itself was determined with two solutions which were prepared by two different kinds of hydrolysis. The one solution which was prepared by hydrolysing *l*-threose diacetamide with 1/3 N sulphuric acid as in Deulofeu's experiment, rotated 13.2° to the right. The other which was prepared by hydrolysis with 1/10 N sulphuric acid and whose degree of hydrolysis was observed quantitatively as in Hockett's experiment, rotated also 13.1° to the right. The values obtained through these two observations show an almost satisfactory agreement. So we came to the conclusion that *l*-threose diacetamide could be completely hydrolysed with 1/3 N sulphuric acid.

Comparing, as shown below, the properties of *l*-threose and its derivative we obtained with those of Hockett's *d*-isomer, it seems to us that the two sugars are almost in good agreement as *d*- and *l*-isomer, and it seems to be clear that pure *l*-threose and its derivative are now formed, although Deulofeu could not have them from *l*-gulonolactone.

	Melting point of threose diacetamide	Specific rotation of threose diacetamide	Equilibrium specific rotation of threose
Deulofeu's *l*-threose	165–166°	−7.68°	−24.6°
Hockett's *d*-threose	165–167°	−10.9°	−12.5°
Authors' *l*-threose	164–165°	+10.8°	+13.1°

Experimental.

l-Xylose. This substance was obtained by a method which was recently published by Vargha. That is, 1 kg. of *d*-sorbitol, dissolved in one litre of water, was mechanically shaken with 100 c.c. of concentrated hydrochloric acid and 500 g. of benzaldehyde for 5–6 hours in a cool place. Monobenzal-*d*-sorbitol thus obtained was recrystallised from absolute alcohol and suspended in glacial acetic acid with equivalent tetracetyl lead. The mixture was shaken for an hour and the resulting almost clear solution was evaporated up in vacuo, and the syrup thus obtained was dissolved in ethyl acetate and water, and the ethyl acetate layer was distilled in vacuo to remove the solvent, and the resulting thick syrup of monobenzal-*l*-xylose was hydrolysed with 10% acetic acid. The syrup, obtained by distilling off the solvent under diminished pressure, was dissolved in a little water, charcoal added, and filtered. The solution was again evaporated under diminished pressure, and the remaining syrup or the impure crystal of *l*-xylose was recrystallised from alcohol. Melting point, 143°.

Its rotation in water was:

15 minutes after dissolution	$[\alpha]_D^{20} = -38.6°$;
63 minutes after dissolution	,, $= -18.4°$;
ca. 20 hours after dissolution (equilibrium)	,, $= -18.2°$.

Melting point of *l*-xylosazone, 163°.

The method devised by Wohl was selected for degrading *l*-xylose to *l*-threose, because both Hockett and Deulofeu used this method for degradation.

Tetracetyl-l-xylonic nitrile. *l*-Xylose (50 g.) was added to the neutral solution of hydroxylamine, which was made by neutralising 30 g. of hydroxylamine hydrochloride with sodium methylate. The mixture was warmed a little to dissolve the sugar after two days' standing and filtered. The filtrate was concentrated under diminished pressure to a thick syrup, keeping the outer bath under 50°, a little dioxane was added, and reconcentrated. Then 15 g. of recently fused sodium acetate and 30 c.c. of dioxane were added. The mixture was warmed a little, 10 c.c. of acetic anhydride added, and shaken vigorously. When spontaneous heating was ended, 10 c.c. more of acetic anhydride was added. This was repeated ten times. Then the mixture was warmed on a water bath for an hour and poured over cracked ice. A little sodium bicarbonate was added to partially neutralise the acetic acid, and the precipitate was filtered. It was recrystallised from absolute alcohol. Melting point, 82°.

l-Threose diacetamide. To 25 g. of tetracetyl-*l*-xylonic nitrile, 300 c.c. of ammonia was added. The mixture was warmed a little to dissolve the solid material, and, after three hours' standing, concentrated to syrup under diminished pressure. Then again ammonia was added and reconcentrated. The resulting syrup was dissolved in absolute alcohol, and a little ether was added. After two days' standing in refrigerator, the precipitated *l*-threose diacetamide was filtered. It was recrystallised several times from 85% alcohol, adding charcoal to remove gummy substance and colour. Then sharp needles separated very slowly. Melting point, 164–165° (corr.): $[\alpha]_D^{20} = +10.8°$. (Found: N, 12.69. Calculated for $C_6H_{10}O_5N_2$: N, 12.72%).

Equilibrium rotation of l-threose. To get the equilibrium rotation of *l*-threose, we performed two kinds of hydrolysis by using sulphuric acid of different concentra-

tions. Firstly, 0.3067 g. of *l*-threose diacetamide was made up to 10 c.c. with 1/3 N sulphuric acid. The solution was heated in a boiling water bath for three quarters of an hour. Thus we got the specific rotation of +13.2° (calculated from the weight of *l*-threose formed, the direct reading being +0.22° at 20°C.). This method is almost the same as Deulofeu's. Secondly, just as Hockett did, 0.2036 g. of *l*-threose diacetamide was made up to 10 c.c. with 0.100 N sulphuric acid. The solution was heated in a boiling water bath for 150 minutes, and 5 c.c. of it was titrated by Cajori's iodine oxidation method. This showed that, in 10 c.c. of the solution, 0.0913 g. of threose was formed by hydrolysis, and so 0.0362 g. of *l*-threose diacetamide remained unhydrolysed. The rotation of the hydrolysed solution was +0.16° in 10 cm. tube at 20°C. And the specific rotation calculated from these is +13.1°. The two values thus obtained showed an excellent agreement.

l-Threose. The sulphuric acid solution of *l*-threose was extracted with ether fifteen times to remove acetic acid, almost neutralised with barium hydroxide and then excess of barium carbonate and charcoal were added. The mixture was warmed on a water bath for a short while, and filtered. The filtrate was evaporated in vacuo to a thick syrup, and the latter was taken in absolute alcohol. The solution was filtered from inorganic impurities and evaporated. Thus the syrup of *l*-threose was obtained. But it did not crystallise on standing in a desiccator. To prepare the osazone, a portion of the syrup of *l*-threose was dissolved in a little water, and phenylhydrazine and acetic acid were added to it. The mixture was heated on a boiling water bath for about three hours. The precipitated *l*-threosazone (*l*-erythrosazone) was washed with a little benzene, and recrystallised from dilute alcohol. Yellow needles. Melting point, 162–163°.

Summary.

(1) *l*-Threose diacetamide has been obtained by the Wohl's method of degrading sugars from *l*-xylose which was prepared from *d*-sorbitol by Vargha's method.

(2) It has been found that this *l*-threose diacetamide melts at 164–165° (corr.) and has a specific dextrorotation of +10.8° in water. These properties are in good harmony with R. Hockett's value and sign, and do not agree with those of Deulofeu.

(3) This *l*-threose diacetamide has been submitted to hydrolysis with 1/3 N and 1/10 N sulphuric acid respectively. From these experiments the equilibrium specific rotation of *l*-threose in dilute sulphuric acid was determined to be +13.1°. It has a little higher value (about 0.6°) compared with Hockett's *d*-isomer, but it is now clear that the pure *l*-threose expected by Hockett has been obtained.

Chemical Institute, Faculty of Science,
Imperial University of Tokyo.

Catalytic Hydrogenation of Amides of α-Hydroxy-Acids.[1]

By Haruomi ÔEDA.

(Received February 13th, 1937.)

Several papers have been published on the reduction of acid amides. Reduction hitherto described are brought about by means of sodium, sodium amalgam or catalytic hydrogenation. The reaction goes along, according to the nature of amides in question and to the mode of reduction adopted, in two different directions as follows:

(I)[2] Amides are converted into alcohols, amino-groups being detached as ammonia:

$$R\cdot CO\cdot NH_2 \xrightarrow{4H} R\cdot CH_2\cdot OH + NH_3,$$

or (II)[3] converted into amines, with the formation of water:

$$R\cdot CO\cdot NH_2 \xrightarrow{4H} R\cdot CH_2\cdot NH_2 + H_2O.$$

Recently H. Adkins and B. Wojcik[4] have succeeded in preparing various amines by catalytic hydrogenation of amides with such a fair yield as had not been recorded in preceding reports. In unsubstituted amides, it is reported that the combined yields of primary and secondary amines amounted to 80–95%.

The present study was tried with the object of obtaining α-amino-alcohols from amides of α-hydroxy-acids in the same experimental conditions as in the works of Adkins. Hydrogenation was carried out in the presence of copper-chromium oxides at the temperature of 250°, initial pressure of hydrogen being 100–110 atmospheres at room temperature and dioxane was used as reaction medium. The present results carried out with two aliphatic amides (lactamide and leucic acid amide), however, are contrary to the expectation; and they never gave rise to α-amino-alcohols.

---

(1) Studies on Hydroxy-acids and their Derivatives. V.

(2) Guareschi, *Ber.*, **7** (1874), 1462; Bouveault and Blanc, *Compt. rend.*, **138** (1904), 148.

(3) Guerbet, *Chem. Zentr.*, **70** (1899), II, 623; Sabatier and Maihe, *Ann. chim.*, [8], **16** (1909), 70.

(4) *J. Am. Chem. Soc.*, **56** (1934), 2419. Adkins described one case of hydroxy-amide. γ-Hydroxy-valeramide, on hydrogenation, gave some 4-hydroxy-1-aminopentane, while for the most part, it was recovered as valerolactone.

From both amides, neutral as well as basic substances were isolated by distillation of hydrogenated products. The former were found to be propylene glycol and isohexylene glycol, which were identified as such by preparing their phenylurethanes.

From leucic acid amide, an amine was obtained, whose boiling point is almost the same as that of the corresponding amino-alcohol. But the base easily solidifies (m.p. 62–64°) and the properties of its derivatives are not concordant with those of the amino-alcohol as shown in Table 1.

Table 1.

	HCl salt decomp. p.	Pt double choride decomp. p.	Benzoyl comp. m.p.	Picrate decomp. p.
Amine from C_6-amide	over 330°	over 330°	223–224° (corr.)	about 245°
$(CH_3)_2CH\cdot CH_2\cdot \underset{\underset{OH}{|}}{CH}\cdot CH_2\cdot NH_2$[5]	175°	215°	128°	—

The analytical results of the free base and of every derivative tabulated closely resemble the value calculated for $C_6H_{13}\cdot NH_2$, but the base, viewed from its properties, can never be regarded as isohexylamine (e.g. discrepancy of boiling points: the difference attains to 100°). Molecular weight of the free base, determined by Rast's method, is equivalent nearly to the double that of hexylamine. From these facts, the base is concluded to be the following diprimary-diamine:

$$(CH_3)_2CH\cdot CH_2\cdot \underset{\underset{(CH_3)_2CH\cdot CH_2\cdot \underset{|}{C}H\cdot CH_2\cdot NH_2}{|}}{CH}\cdot CH_2\cdot NH_2$$

2,3-Di-isobutyl-tetramethylene diamine.

From lactamide a liquid base was obtained. As it could not be isolated as hydrochloride in crystalline state, the base was converted into picrate. But the picrate was found to be a mixture and an attempt was made to separate them by recrystallisation from hot glacial acetic acid. The base (A in Table 2) of the picrate less soluble in the hot solvent was identified as the following diprimary-diamine by converting it into benzoyl compound:

$$CH_3\cdot \underset{\underset{CH_3\cdot \underset{|}{C}H\cdot CH_2\cdot NH_2}{|}}{CH}\cdot CH_2\cdot NH_2$$

2,3-Dimethyl-tetramethylene diamine.

(5) Mousset, *J. Chem. Soc.*, **82** (1902), I, 254; Kanao, *J. Pharm. Soc. Japan*, **49** (1929), 173.

Table 2.

		Picrate decomp. p.	Benzoyl comp. m.p.	Pt double chloride decomp. p.
Amine for C_3-amide	A	over 260°	227–228° (corr.)	—
	B	about 238°	—	265–270°
$CH_3\cdot\underset{\underset{OH}{|}}{CH}\cdot CH_2\cdot NH_2$[6]		142°	87°	195°

The other base B, whose picrate is more soluble, could not be definitely determined, as it does not give solid benzoyl compound, but the analytical data of the picrate as well as of the platinum double chloride coincide with those of the following primary-secondary-diamine:

$$\begin{matrix} CH_3\cdot CH\cdot CH_2\cdot NH_2 \\ CH_3\cdot CH\cdot CH_2\cdot NH\cdot CH_2\cdot CH_2\cdot CH_3 \end{matrix}$$ *N*-Propyl-2,3-dimethyl-tetramethylene diamine.

No information of these diamines was found in literature. They are the first substances obtained, which belong to 2,3-dialkyl derivatives of tetramethylene diamine.

From both amides, besides glycol and diamine, the higher boiling fractions were obtained in considerable quantity. All attempts to prepare crystalline derivatives from these fractions were unsuccessful.

The above hydrogenation can be regarded as the two known types of reduction of amides occurring side by side:

$$R\cdot\underset{\underset{OH}{|}}{CH}\cdot CO\cdot NH_2 \begin{cases} \nearrow & R\cdot\underset{\underset{OH}{|}}{CH}\cdot CH_2\cdot OH + NH_3 \\ \searrow & R\cdot\underset{\underset{R\cdot CH\cdot CH_2\cdot NH_2}{|}}{CH}\cdot CH_2\cdot NH_2 + H_2O. \end{cases}$$

In reduction to amines, these amides do not give amino-alcohols, but they are transformed into diamines by the elimination of two hydroxyls by further reduction.[7]

(6) Peeters, *Rec. trav. chim.*, **20** (1901), 264; Gabriel and Ohle, *Ber.*, **50** (1917), 808.

(7) An example of the similar condensation, taking place in hydroxy-groups, is described in the formation of bis-camphorylethane by the reduction (with sodium) of camphoryl carbinol. Rupe and Ackermann, *Helv. Chim. Acta*, **2** (1919), 221.

$$C_8H_{14}\begin{matrix} CO \\ | \\ CH\cdot CH_2\cdot OH \end{matrix} \rightarrow C_8H_{14}\begin{matrix} CO \\ | \\ CH\cdot CH_2\cdot CH_2\cdot CH \end{matrix}\begin{matrix} CO \\ | \\ \end{matrix}C_8H_{14}$$

Experimental.

Copper-chromium oxide catalyser (containing a little barium) was prepared according to Adkins.[8] Acid amides[9] were mixed with 1/4–1/5 parts of the above catalyser and diluted with four times of its weight of distilled (over sodium) dioxane. The hydrogenation was carried out in the same conditions as described in the previous paper.[10]

Hydrogenated products were separated from catalyser with glass filter and dioxane was removed by distillation through Widmer column. The residue was fractionated in vacuum into several fractions again with the aid of Widmer column.

Hydrogenation of Amide of *l*-Leucic acid.

Amide (m.p. 82–83°) 24 g. (0.18 mol); dioxane 75 c.c.; catalyser 5.0 g.; time of hydrogenation 2.5 hrs. at 245–255°; fractionation:

I	110–120° under 14 mm.	4.4 g.
II	120–130° ,,	3.2 g.
III	over 140° ,,	7.5 g.

Fraction II has the tendency to solidify instantly in the delivery tube, and to prevent the blockade, hot water must be circulated through the jacket. Fraction III, on the contrary, does not solidify and remains as yellowish viscous fluid even after long standing.

(A) **Neutral Part (Isohexylene glycol).** Fraction I was separated into neutral and basic parts by extracting the acidified mixture with ether as usual. The neutral part distilled at 109–111° under 13 mm. after refractionation. (The same neutral part was also obtained from fraction III by the same treatment.) It was found to be isohexylene glycol and the combined yield amounted to 10 mol%.[11]

Bis-phenylurethane. Prepared from the glycol and phenyl isocyanate by heating at 120–130° for one hour, the urethane being precipitated by adding ligroin. After recrystallisation from ligroin-alcohol, it melted at 116.5–117.5° (corr.), no depression of melting point was observed when mixed with the specimen described in the previous paper, m.p. 117.5° (corr.).[10]

---

(8) *J. Am. Chem. Soc.*, **54** (1932), 1139.

(9) Leucic acid amide: prepared from liquid ammonia and acetone-leucic acid at −33°. Lactamide: from liquid ammonia and ethyl lactate at room temperature. Ôeda, this Bulletin, **11** (1936), 385.

(10) Ôeda, this Bulletin, **10** (1935), 531.

(11) The activity of this glycol was not examined owing to its minute quantity. The same glycol obtained in the previous experiment was found to be active. The two glycols show the same boiling range and give the phenylurethane of the same m.p. Rotation was determined in a 1-dm. tube (5 c.c.). $d_{18.5}^{13.5} = 0.9506$; $[\alpha]_D^{14} = -0.23°/0.95 = -0.24°$. The sample may be partially racemised during hydrogenation.

(B) **Basic Part.** Hydrochlorides obtained from fractions I and II were combined and evaporated to dryness on water bath and extracted with hot alcohol, when 2.3 g. of the sample remained unextracted.

(a) **Hydrochloride Insoluble in Alcohol (2,3-Di-isobutyl-tetramethylene diamine).** The insoluble hydrochloride was dissolved in a large bulk of hot water, filtered and was concentrated on water bath. During evaporation, a colourless hydrochloride began to crystallise out while still hot before the solution was completely dried up. After being purified by repeated crystallisation, it became, on heating, gradually coloured at 300° but did not decompose up to 330°. (Found: N, 10.46; Cl, 26.00. Calculated for $C_{12}H_{28}N_2 \cdot 2HCl$: N, 10.25; Cl, 25.98%.) Yield 9 mol%.

Platinum double chloride. Insoluble in alcohol. It turned black at 270° but did not decompose up to 330°. (Found: Pt, 32.07. Calculated for $C_{12}H_{28}N_2 \cdot H_2PtCl_6$: Pt, 32.00%.)

Free base. When the insoluble hydrochloride was warmed with an excess of dilute caustic potash, an oil separated out, which crystallised on cooling. The free base thus prepared was dissolved in alcohol, and decolourised with charcoal. By evaporation of the solvent colourless base (m.p. about 60°) was obtained as main product. It can also be recrystallised from ligroin, m.p. 62–64° after drying over caustic soda. (Found: C, 72.24; H, 13.66; N, 14.22. Calculated for $C_{12}H_{28}N_2$: C, 71.94; H, 14.09; N, 14.00%.) *Optical rotation.* Determined in a 1-dm. tube (5 c.c.) containing 0.250 g. of the free base and made up to 5.00 c.c. with alcohol. No rotation was observed. *Molecular weight* (camphor): 208. Calculated for $C_{12}H_{28}N_2$: 202.

Benzoyl compound. To a suspension of the powdered free base in 15% caustic potash, benzoyl chloride was gradually added with constant stirring. An oil formed first, then turned to a crystalline sticky mass, which was separated by suction and washed with hydrochloric acid, sodium bicarbonate solution and finally with water. It melted at 223–224° (corr.) after recrystallisation from alcohol. (Found: C, 76.58; H, 9.26; N, 7.12. Calculated for $C_{26}H_{36}O_2N_2$: C, 76.42; H, 8.88; N, 6.86%.)

Picrate. Obtained by mixing alcoholic solutions of the free base and of picric acid in excess. After recrystallisation from alcohol, it turned black at 240° and decomposed at about 248° with violent evolution of gas. (Found: C, 43.99; H, 5.05; N, 17.27. Calculated for $C_{12}H_{28}N_2 \cdot 2C_6H_3O_7N_3$: C, 43.74; H, 5.20; N, 17.03%.)

(b) **Hydrochloride Soluble in Alcohol (A base left undetermined).** After recrystallisation from a little alcohol, powder of silky luster was obtained, it melted with decomposition at 220–230°. (Found: Cl, 18.94%. It corresponds to a free mono-amine, mol. wt. 151.[12] Owing to the minute quantity of purified sample, further study was given up.

(C) **Higher Fraction.** Fraction III was fractionated through Widmer column. It distilled between 135–180° under 13 mm. and showed no distinct boiling fraction. It was dissolved in hydrochloric acid, and insoluble resinous matter was filtered off. The hydrochloride of the base could not be brought into crystallisation. A ferrocyanate, insoluble in water, was obtained from the above solution, but no further study on this line has been made.

---

(12) Supposing the existence of a prim.-sec.-diamine, similar as in the case of lactamide, its molecular weight (calculated as mono-amine) will be: $\frac{1}{2}C_{18}H_{40}N_2 = 142$.

Hydrogenation of *dl*-Lactamide.

Amide (m.p. 77–78°) 14.5 g. (0.16 mol); dioxane 60 c.c.; catalyser 4.0 g.; time of hydrogenation, 3 hrs. at 240–255°; initial pressure of hydrogen 112 atms.; fractionation:

I	60 – 90° under 20 mm.	0.9 g.
II	90 – 100° ,,	1.4 g.
III	over 100° ,,	2.2 g.

(A) **Picrates from Fractions I and II.** Obtained from the free base and a little excess of alcoholic picric acid. Yield, 1.9 g. from fraction I, 1.1 g. from II. The picrate is insoluble in water and alcohol, but partly soluble in hot glacial acetic acid. After washing completely with hot alcohol, it was extracted with hot glacial acetic acid, the residue being collected and again extracted with a new bulk of the solvent. The extraction was repeated until the amount of final residue decreased to one-tenth of the initial sample. The final residue so obtained is designated as picrate A. Each extract was cooled, the precipitated picrate being separately collected. The most soluble part (picrate B) was obtained by fractional crystallisation.

(a) **Picrate A.** Pale yellow amorphous powder. It showed no change in appearance up to 230–240°, and thereafter gradually coloured, but did not decompose up to 260°. The result of analysis is not actually identical with the value calculated for the diprimary-diamine. The discrepancy may be due to the incomplete separation of picrate B. (Found: C, 38.64, 38.78; H, 4.00, 3.42; N, 20.02. Calculated for $C_6H_{16}N_2 \cdot 2C_6H_3O_7N_3$: C, 37.61; H, 3.87; N, 19.50%.)

Benzoyl compound. The picrate was transformed into hydrochloride, from which benzoyl compound was prepared with benzoyl chloride in the presence of caustic potash. It separated as an oil, aqueous solution was removed by decantation, and the oil, on rubbing together with a little ether, yielded colourless crystals. Recrystallised from alcohol, it melted at 227–228° (corr.). (Found: C, 74.45; H, 7.46; N, 8.42. Calculated for $C_{20}H_{24}N_2$: C, 74.03; H, 7.47; N, 8.64%.)

(b) **Picrate B.** Yellow crystals. It decomposed at 237–240° with violent evolution of gas. (Found: C, 40.50, 40.34; H, 4.30, 3.70; N, 18.51. Calculated for prim.-sec.-diamine, $C_9H_{22}N_2 \cdot 2C_6H_3O_7N_3$: C, 40.88; H, 4.58; N, 18.17%.) The preparation of benzoyl compound was tried in similar way as above, but it could not be obtained in crystalline state.

Platinum double chloride. Obtained from the syrupy hydrochloride which was prepared from the above purified picrate. It decomposed at 265–270°. (Found: Pt, 34.50. Calculated for $C_9H_{22}N_2 \cdot H_2PtCl_6$: Pt, 34.33%.)

(B) **Glycol.** A little hydrochloric acid was added to another sample of fraction II and a neutral part was collected by extraction with a large bulk of ether. The extract distilled at 77–79° under 8 mm. It was found to be isohexylene glycol by converting it into bis-phenylurethane.

Bis-phenylurethane. Prepared from the glycol and phenyl isocyanate by heating at 120–130° for one hour. After recrystallisation from alcohol, it melted at 145–146° (corr.), alone or in admixture with the specimen (m.p. the same) described in the previous paper.[10]

The present study was carried out in the Chemical Institute, Faculty of Science, Imperial University of Tokyo. The author expresses his sincere thanks to Prof. K. Matsubara for kind inspection of this paper. His best thanks are also due to Dr. Y. Takayama for constant encouragement during this study.

Studies on the Oiliness of Liquids. IV. Measurements of the Static Friction Coefficients by the Method of Inclination.

By Jitsusaburo SAMESHIMA and Yasuji TSUBUKU.

(Received February 26th, 1937.)

The measurements of the static friction coefficients by the balance method have already been described in one of the former papers.(1) In the present paper, the method of inclination and the results obtained therefrom are described. The method is based on the measurement of the critical angle of inclination of the sliding surface at which the slider begins to slide.

Fig. 1 shows the apparatus. A and B are brass plates joined together with a hinge at one end C. The other end of the plate B can be lifted by rotating the handle D and pulling the string fastened to E. Thus the plate B is made to incline from the horizontal plane, the angle of inclination being measured by the protractor G.

H is a glass plate on which a microscopic slide glass K is placed. L is the slider made of an optical lens of the diameter 2.5 cm. M is the brass discs pasted on the slider, which is used to adjust the weight of the slider. N is the supporter to keep the slider from going too far.

At first the liquid is applied on K and then the slider is put on it, the plate B and the sliding surface K being in horizontal position. Now rotate the handle D gently and make the plate B inclines gradually, until finally the slider L begins to slide down the inclined plane. At this instant the angle of inclination is read by the protractor G.

(1) Sameshima, Kidokoro, and Akamatu, this Bulletin, **11** (1936), 659.

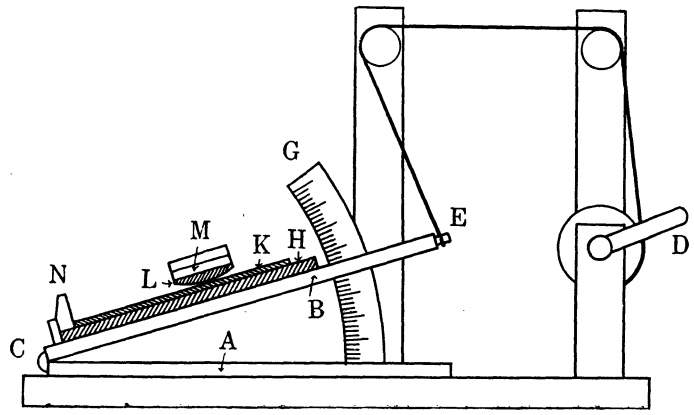


Fig. 1.

We shall denote the sliding angle with θ, the total weight of the slider and brass discs with w, and the force acting in the direction of parallel and normal to the sliding plane with F and W respectively. There are the relations:

$$F = w \sin\theta ,$$

$$W = w \cos\theta .$$

The friction coefficient μ is,

$$\mu = \frac{F}{W} = \tan\theta .$$

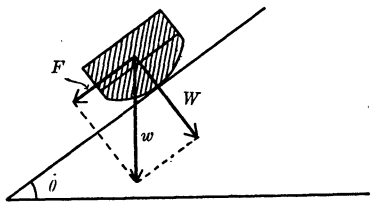


Fig. 2.

These relations are shown in Fig. 2.

The sliding angle θ decreases with increasing value of w when the weight of slider w is small. If w is sufficiently large, however, the angle θ is practically independent of w. The friction coefficient μ is to be calculated from such a constant sliding angle θ. The results of measurements are summarized in Table 1. The experiments have been done at the room temperature of 20–24°C.

The values of friction coefficient μ against the number of carbon atoms in the molecules are plotted in Fig. 3 and Fig. 4.

From Fig. 3 we see that the friction coefficients of aliphatic acids are nearly constant, while those of aliphatic alcohols diminish with the number of carbon atoms in their molecular formula. These facts have already been noticed in the results of the previous experiments.[2] We might

(2) Sameshima, Kidokoro, and Akamatu, this Bulletin, **11** (1936), 666.

Table 1.

Lubricant	w (g.)	$\tan\theta$	μ
Methyl alcohol CH_3OH	32	0.81	
	42	0.77	
	52	0.72	
	62	0.68	
	72	0.66	0.66
	82	0.66	
Ethyl alcohol C_2H_5OH	52	0.74	
	62	0.68	
	72	0.65	0.65
	82	0.65	
n-Propyl alcohol $CH_3(CH_2)_2OH$	52	0.67	
	62	0.66	
	72	0.64	0.635
	82	0.63	
n-Butyl alcohol $CH_3(CH_2)_3OH$	62	0 71	
	72	0.69	
	82	0.66	
	92	0.65	
	102	0.63	0.63
n-Amyl alcohol $CH_3(CH_2)_4OH$	62	0.66	
	72	0.64	
	82	0.60	
	92	0.60	0.60
	102	0.60	
n-Hexyl alcohol $CH_3(CH_2)_5OH$	92	0.65	
	101	0.61	0.61
	111	0.61	
n-Heptyl alcohol $CH_3(CH_2)_6OH$	82	0.68	
	92	0.66	
	102	0.65	
	112	0.62	
	122	0.60	0.60
	132	0.60	
n-Octyl alcohol $CH_3(CH_2)_7OH$	91	0.64	
	101	0.59	
	111	0.59	
	121	0.58	0.58
	131	0.58	
Acetic acid CH_3COOH	82	0.65	
	91.9	0.63	
	101.5	0.59	
	111.1	0.59	0.59
	121.1	0.59	
	131.2	0.59	

Lubricant	w (g.)	$\tan\theta$	μ
Propionic acid CH_3CH_2COOH	101 5	0.63	
	111.1	0.60	
	121.1	0.59	
	131.2	0.59	0.59
	140.6	0.59	
n-Butyric acid $CH_3(CH_2)_2COOH$	111.1	0.64	
	120.9	0.62	
	131.0	0.60	0.60
	140.6	0.60	
n-Valeric acid $CH_3(CH_2)_3COOH$	111.1	0.61	
	120.9	0.60	0.60
	131.0	0.60	
Caproic acid $CH_3(CH_2)_4COOH$	111.1	0.59	
	120.9	0.59	
	131.0	0.58	0.58
	140.6	0.58	
Heptylic acid $CH_3(CH_2)_5COOH$	111.1	0.60	
	120.9	0.60	
	131.0	0.58	0.58
	140.6	0.58	
Caprylic acid $CH_3(CH_2)_6COOH$	111.1	0.59	
	120.9	0.57	
	131.0	0.55	0.55
	140.6	0.55	
Nonylic acid $CH_3(CH_2)_7COOH$	111.1	0.61	
	120.9	0.61	
	131.0	0.60	
	140.6	0.58	
	152.2	0.58	0.58
	162.3	0.58	
Oleic acid $C_{17}H_{33}COOH$	120.9	0.37	
	131.0	0.36	0.36
	140.6	0.36	
Water H_2O	32	0.82	
	42	0.76	
	52	0.73	
	62	0.69	
	71.5	0.65	0.65
	81.5	0.65	
	72	0.74	
	82.2	0.69	0.69
	92	0.69	
		Mean	0.67

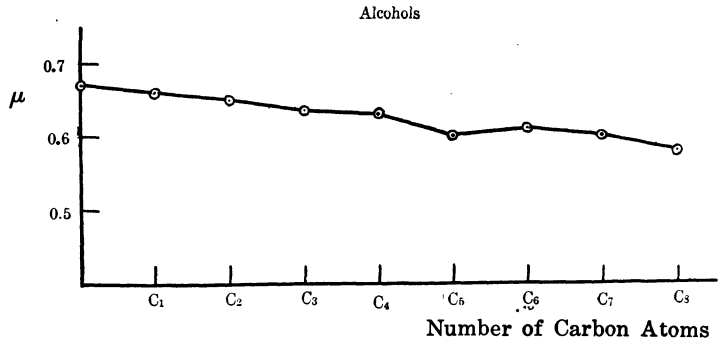


Fig. 3.

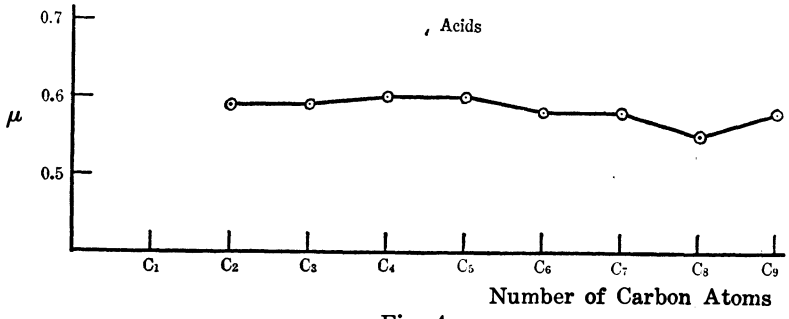


Fig. 4.

perhaps venture the following hypothesis to explain the observed results of the friction coefficient.

It has been proved that the coefficient of static boundary friction of the flooded liquid is practically the same with that of the monomolecular film of the substance.[3] So the friction coefficients obtained in the present experiments are considered to depend only on the properties of the monomolecular film attached to the glass surface.

The molecules of the aliphatic alcohols or the acids tested in the present experiments are composed from the hydrocarbon groups and the hydroxyl or carboxyl group, thus,

$$CH_3CH_2 \ldots\ldots\ldots\ldots CH_2(OH),$$

$$CH_3CH_2 \ldots\ldots\ldots\ldots CH_2(COOH).$$

The hydrocarbon group is nonpolar, while hydroxyl or carboxyl group polar. The molecules, therefore, will take orientation on the sliding surface, the polar group being attached to the glass surface. The attraction force between glass and COOH group will be stronger than that

(3) Akamatu and Sameshima, this Bulletin, **11** (1936), 791.

between glass and OH group, for the glass is an alkaline substance. The acid molecules, therefore, will stand more firmly on glass surface than alcohol molecules.

Fig. 5 shows the model of the molecules of acid and alcohol standing on the glass surface.

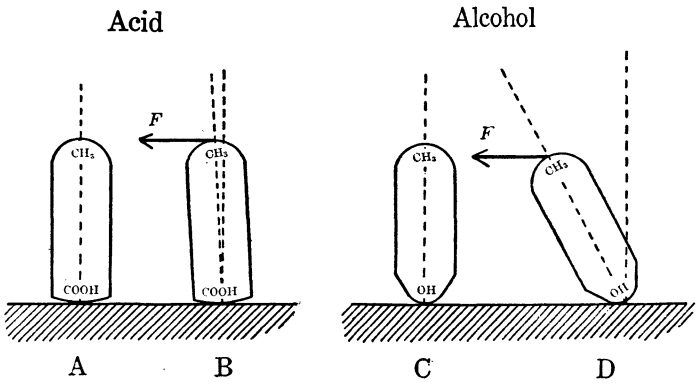


Fig. 5.

If the force F is applied at the heads, CH_3 group, of the molecules, then they will incline as shown in Fig. 5, B or D. The COOH or OH group will act as the hinge. The acid molecule has strong affinity with glass, or it may be considered that the hinge is stiff while alcohol molecule has weak affinity or the hinge is loose. So the acid molecule inclines in smaller angle by the force F than the alcohol molecule.

The force acting on the hinge point is the product of the pulling force and the length of the molecule. So the longer the molecule the greater is the angle of inclination of the molecule. Or the long molecule can be made incline at definite angle with the small pulling force. Thus the alcohols of long chain have small friction coefficients than those of short chain. The acid molecule, however, can hardly be made incline by the pulling force, as is shown in Fig. 5, B, so the friction coefficient is not practically change with the number of carbon atoms. If the length of molecule becomes very long, such as palmitic or stearic acid etc. then the force will act very strong on the COOH hinge and, moreover, the flexibility of the molecule may show some effect on the friction coefficient as is supposed by Adam[4] and others. In the present experiment, however, only comparatively short molecules are tested, so the flexibility of the molecule will not have serious effect on the friction coefficient.

(4) N. K. Adam, "The Physics and Chemistry of Surfaces," p. 227, Oxford (1930).

The lengths and the diameters of the molecule of octyl alcohol and nonylic acid are calculated as shown in Table 2.

Table 2.

Molecular formula	Density of liquid	Cross sectional area of molecule	Diameter of molecule	Length of molecule
$CH_3(CH_2)_7OH$	0.83	21.6 Å^2	4.6 Å	12.1 Å
$CH_3(CH_2)_7COOH$	0.91	20.5 Å^2	4.5 Å	14.1 Å

Thus the length of molecule is about three times of the diameter. So the molecule is comparatively short, and therefore, the molecule will not bend by the pulling force.

The expence of the present experiments has been defrayed from a grant given by Nippon Gakujutsu Shinkokwai (Japan Society for the Promotion of Scientific Research) for which the authors' sincere thanks are due.

Chemical Institute, Faculty of Science,
Tokyo Imperial University, Tokyo.

The OH-Vibration Spectrum in the Photographic Infrared.

By San-ichiro MIZUSHIMA, Yasuo UEHARA, and Yonezo MORINO.

(Received March 1st, 1937.)

The result of our dipole measurement on ortho-substituted phenols[1] is in accordance with Pauling's theory[2] of quantum mechanical resonance, which was originally put forward for the interpretation of the infrared absorption spectra observed by Wulf and Liddel.[3] To supply further experimental evidence to this conclusion as well as to complete our former research[4] on the vibration spectra of alcohols, we have

(1) Mizushima, *J. Chem. Soc. Japan*, **57** (1936), 936; see also Mizushima, Morino, and co-workers, *Physik. Z.*, **35** (1934), 905; *Sci. Papers Inst. Phys. Chem. Research* (Tokyo), **25** (1934), 159; **29** (1936), 63, 111, 188.

(2) Pauling, *J. Am. Chem. Soc.*, **58** (1936), 94.

(3) Wulf and Liddel, *J. Am. Chem. Soc.*, **57** (1935), 1464; Wulf, Liddel, and Hendricks, *ibid.*, **58** (1936), 2287.

(4) Mizushima, Morino, and Okamoto, this Bulletin, **11** (1936), 553, 698.

studied the overtones of the OH vibration as absorption spectra in the photographic infrared. The measurement was carried out with a glass spectrograph of our own construction which has a dispersion of 74 A per mm. at 9000 Å, iron and barium lines being used as reference. The samples were Kahlbaum's products, which were purified by redistillation or recrystallization. The accompanying table contains the experimental results obtained for carbon tetrachloride solutions of the concentration of 0.5 mol. We have also measured the absorption spectra in the pure liquid or fused state and found that some of the bands are changed in frequency as well as in intensity.[5] We shall, however, confine ourselves to the discussion of the experimental data obtained for the dilute nonpolar solutions, in which the normal vibration of a solute molecule is not greatly affected by the surrounding solvent molecules.[6]

Frequencies (cm.$^{-1}$) of Absorption Maxima of OH Vibration Bands.

(Solvent: CCl_4)

Substance	ν_2	ν_3	$x\omega$	ω	ν_1		D
					calc.	obs.	
CH_3OH	10424 (9593 Å)	13557 (7376 Å)	85	3816	7120	7120	116
C_2H_5OH	10394 (9621 Å)	13493 (7411 Å)	91	3830	7112	7090	109
n-C_3H_7OH	10388 (9626 Å)	13493 (7411 Å)	89	3820	7104		111
n-C_4H_9OH	10406 (9610 Å)	13459 (7430 Å)	104	3884	7144		98
C_6H_5OH	10332 (9679 Å)	13430 (7446 Å)	87	3790	7061	7050	113
p-C_6H_4ClOH	10322 (9688 Å)	13430 (7446 Å)	83	3773	7047		116
o-C_6H_4ClOH	10094 (9907 Å) st.*	13122 (7621 Å) st.	84	3701	6897	6910	110
	10323 (9687 Å) w.	13430 (7446 Å) w.	84	3775	7049	7050	116
o-C_6H_4BrOH	10005 (9995 Å) st.	12970 (7710 Å) st.	93	3705	6855	6860	100
	10328 (9682 Å) w.	13401 (7462 Å) w.	92	3812	7070	7050	106
o-$C_6H_4CH_3OH$	10328 (9682 Å)	13430 (7446 Å)	85	3783	7055	7060	114

* st. means strong intensity and w. weak intensity.

(5) Measurements with alcohols in the pure liquid state were already carried out by several investigators, among which Freymann (Thèse Paris, 1933) gave experimental values close to those of our second overtones.

(6) The absorption bands at 9500Å of alcohols in the vapour state recently observed by Badger and Bauer (*J. Chem. Phys.*, **4** (1936), 711) have larger frequencies owing to the difference in the state of aggregation.

Let the vibrational level of the quantum number v be approximately expressed as

$$G(v) = \omega\left(v+\frac{1}{2}\right)-x\omega\left(v+\frac{1}{2}\right)^2 \qquad (1)$$

Then the frequency of infinitesimal vibration ω and the anharmonicity factor x can be calculated, if we assign our observed bands to the second (ν_2) and third overtones (ν_3) of the OH vibration respectively. Using the values of ω and x *thus* evaluated, we have calculated the frequencies of the first overtone (ν_1) and compared them with the experimental values which Wulf and his co-workers[3] obtained in the same solution (sixth column of the table). The agreement is satisfactory within the limit of experimental error, so that the assignment of the absorption bands given above is proved to be correct.

By the extrapolation method the dissociation energy is calculated as

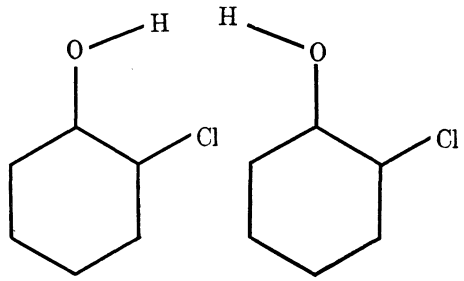
$$D = \frac{(\omega-x\omega)^2}{4x\omega} \qquad (2)$$

which we can now evaluate by the use of ω and x given in the table. The calculated values (in Kcal.) shown in the last column of the table are in good agreement with those obtained from the thermochemical data (106 Kcal. for alcohols). Of course the comparison between these two kinds of dissociation energy is of no significance, if there is any complication of the electronic levels such as the crossing of them, but for these substances such does not seem to be actually the case.

Thus the experimental results obtained here together with all the other evidence available at present are consistent with the interpretation of these spectra to be due to one normal mode of vibration of the molecule, which is essentially the vibration of the hydrogen atom of the OH radical relative to the rest of the molecule. The two frequencies observed in all of the overtones for the ortho-halogenated phenols can therefore be ascribed to the stereoisomers I and II respectively,[7] which owe their existence to the quantum mechanical resonance between single and double bonds

(7) The frequency which is approximately equal to that of phenol is assigned to the isomer II, in which the OH vibration is not affected by the halogen atom appreciably.

as suggested first by Pauling.[2] The absorption intensity for I is much larger than that for II, indicating that the number of molecules of the type I is much larger than that for II in conformity with the experimental result obtained in the dipole measurement.[1]



(I) (II)

We have also observed a very interesting fact that the absorption intensity due to the OH vibration becomes very strong as compared with that due to the CH vibration in the dilute CCl_4 solution, while both of them do not seem much different in the pure liquid state.[8] This can be explained by assuming the association caused by hydrogen bond, which has a large effect in decreasing the intensity of a vibration spectrum.[9] Owing to the large difference in the polar character the inherent absorption intensity of the OH vibration must be much larger than that of the CH vibration as was actually observed in the dilute non-polar solutions, but the considerable formation of hydrogen bond in the pure liquid state decreases the intensity of the former, so that it becomes comparable with (in some cases weaker than) that of the latter.

We thank Prof. M. Katayama for his kind advices. Our thanks are also due to Dr. K. Nagaoka (Rokuôsha), who supplied us with the infrared plates. We are indebted to Hattori-Hôkôkai for a grant in aid of this research.

Chemical Institute, Faculty of Science,
Imperial University of Tokyo.

---

(8) In some cases the absorption due to the CH vibration is much stronger than that due to the OH vibration in the pure liquid state.

(9) For *o*-nitrophenol we could not observe the second and third overtones of the OH vibration, just as Wulf and Liddel did not in the first overtone. This is ascribed to the formation of a hydrogen bond.[3]

A Note on the Polymerisation of Styrene as revealed by the Raman Effect.

By San-ichiro MIZUSHIMA, Yonezo MORINO, and Yoshiki INOUE.

(Received March 5th, 1937.)

The polymerisation of styrene is considered to proceed by the opening of the double bonds of monomeric molecules $C_6H_5CH = CH_2$ to form macromolecules.(1) Signer and Weiler applied the Raman effect to prove this polymerisation mechanism,(2) showing that the Raman line due to the presence of a double bond disappeared in the polymerisation product. If we assume, as Staudinger and Steinhofer(3) considered, that the terminal valency of the long thread molecule acquires a double bond, we cannot expect the complete disappearance of the said line for polystyrene. It would, however, be very difficult in the case of Signer's experiment to prove the existence of this line, the intensity of which must be very small owing to the high molecular weight (40000) of the sample used. For this reason we have carried out an intensity measurement on the Raman lines of polystyrene having a lower polymerisation degree according to the method described in our previous communication.(4) For a polymer,(5) for which the cryoscopic measurement (in benzene solution) gave a molecular weight of 1150, the intensity of the line 1602 was found to be five times as large as that of the line 1634, while for the monomer the latter was twice as strong as the former; so that the line 1634 decreased in intensity by 1/10 relatively to the line 1602, when about 11 molecules in the mean polymerised to form one long molecule. If we assume quite simply that the intensities of the lines of 1634 and 1602 are proportional to the number of ethylene bonds and benzene nuclei respectively, the observed intensity change can conform with the view that polystyrene does not consist of ring molecules but of thread molecules which have ethylene bonds as the terminal valency.(3)

---

(1) Staudinger, "Die hochmolekularen organischen Verbindungen", Berlin, (1932).

(2) Signer and Weiler, *Helv. Chim. Acta*, **15** (1932), 649.

(3) Staudinger and Steinhofer, *Ann.*, **517** (1935), 35.

(4) Mizushima, Morino and Higasi, *Sci. Papers Inst. Phys. Chem. Research* (Tokyo), **25** (1934), 159; see also *Physik. Z.*, **35** (1934), 905.

(5) The sample was prepared by heating the monomer at 130°C for ten hours.

We have also followed the polymerisation process at room temperature by means of such an intensity measurement and found that the viscosity of the sample changed considerably, before the intensity change was appreciable. Hence we must consider that the viscosity change is in some cases caused by the formation of micelle built up from small single molecules held together by the van der Waals force, but not by the formation of macromolecule in which all the atoms are linked together by electron pair bonds.

We thank Prof. M. Katayama for his kind advices. Our thanks are also due to Dr. S. Kimura who supplied us with the samples used in this experiment. We are indebted to Hattori-Hôkôkai for a grant in aid of this research.

Raman Lines of Styrene and Polystyrene.

Monomer	Polymer(6)	Monomer	Polymer
212 (1)	224 (2)	1204 (6)	
241 (3)		1240 (0)	
445 (1b)		1301 (1)	
510 (0)		1321 (3)	
558 (1)	558 (2)	1414 (6)	
621 (3)	622 (4)	1450 (0)	1450 (1)
	763 (1)	1496 (2)	
774 (4)		1555 (0)	
796 (0)	795 (1)	1575 (1)	1580 (1)
835 (0)	835 (0)	1601 (10)	1602 (10)
909 (2)	904 (0)	1632 (20)	1634 (2)
999 (9)	999 (12)	2909 (0)	
1035 (2)	1031 (3)		2930 (2)
1156 (2)	1156 (3b)	3009 (3)	
1183 (3)		3059 (7)	3050 (8)
	1197 (4b)		

Chemical Institute, Faculty of Science,
Imperial University of Tokyo.

(6) For the polymer some of the weak lines might escape our observation owing to the inevitable background.

The Addition of Hydrogen Bromide to Allyl Bromide in the Presence of Various Substances. V. A Comparison of the Effect of Oxygen with That of Peroxide. The Relation between the Amount of Oxygen Present and the Result of Addition.

By Yoshiyuki URUSHIBARA and Matsuji TAKEBAYASHI.

(Received February 12th, 1937.)

Two groups of substances, oxygen and peroxides as one group and the ferro-magnetic metals as the other, have been found capable of not only inversing the proportion of 1,3-dibromopropane and 1,2-dibromopropane in the product from allyl bromide and hydrogen bromide but also increasing the total yield of the addition. While the catalytic action of the ferro-magnetic metals has been established exactly by the authors,(1) there has been no experimental evidence to decide whether the so-called peroxide effect is caused by oxygen or by peroxides or by both. But, as mentioned in the third paper of this series,(2) at least the effect by oxygen seems to be due to the action of molecular oxygen. The reason for it is given above all by the fact that the addition of hydrogen bromide to peroxide-free allyl bromide in the presence of oxygen in the dark gives mainly the abnormal addition product, 1,3-dibromopropane, while no peroxide can be formed from allyl bromide and oxygen in the dark as judged from the test with ammonium thiocyanate and ferrous ammonium sulphate, and hydrogen bromide can not be considered to facilitate the formation of a peroxide. The only possible alternative is to attribute the effect to a peroxide which might be formed even in the dark in such a minute quantity as not detected by the above-mentioned test.

---

(1) Y. Urushibara and M. Takebayashi, this Bulletin, **11** (1936), 692, 754; **12** (1937), 51.

(2) Y. Urushibara and M. Takebayashi, this Bulletin, **11** (1936), 798.

Corrections to the third paper: All the numerical values of liberated bromine expressed in volumes of corresponding amounts of oxygen should be divided by 10. The mistakes were caused by errors in calculation. As the authors were then aware of some inevitable sources of errors involved in the estimation of bromine, they did not attach importance to the obtained figures, and discussions made in that paper and the conclusions drawn from them require no alteration nor modification. It has now become clear that only a small fraction of the oxygen in the air admitted into the reaction tube was consumed to oxidize hydrogen bromide in the presence of platinum black (exp. 1).

In Table 1 the results of additions to peroxide-containing allyl bromide in vacuum are compared with those of additions to peroxide-free allyl bromide in the presence of oxygen. Allyl bromide treated with oxygen was placed in diffused light for a few days for the formation of the peroxide. The peroxide content was determined by iodometry, assuming that all the oxygen atoms in the peroxide of allyl bromide are available for the oxidation of the iodide:

$$\underset{\overset{|}{O}\text{—}\overset{|}{O}}{CH_2\text{-}CH\text{-}CH_2Br} + 4KI + 2H_2O = CH_2{=}CH\text{-}CH_2Br + 4KOH + 2I_2.$$

The allyl bromide (24 g.) was taken in a reaction tube (135–140 c.c.). The contents were frozen by cooling in liquid air and the tube was evacuated, dissolved, uncombined oxygen being removed by this process. Then hydrogen bromide was condensed while the reaction tube was cooled in solid carbon dioxide and chloroform until a volume increase corresponding to 20 g. of hydrogen bromide was reached (total volume of the liquid 27 c.c.). The tube was evacuated again under cooling in liquid air and sealed off without entrance of air. On the other hand, in a quite similar manner, another reaction tube was charged with peroxide-free allyl bromide and hydrogen bromide, a volume of oxygen corresponding to the above peroxide content (the available peroxidic oxygen and the molecular oxygen equal in the number of atoms) being admitted at sealing. The tubes were shaken at room temperature in the dark for three days. In order that the reaction may occur under the same conditions, the additions to be compared were carried out simultaneously. Thus additions belonging to the same series occurred at the same time.

As allyl bromide (commercial product distilled once) used in exp. 2–4 was found not pure later, it was redistilled for exp. 5. In exp. 6–8 portions from the same specimen of especially purified allyl bromide were employed. The influence of impurities on the catalytic action of oxygen will be discussed later, but for the present more weight may be attached to the experiments of Series III.

Exp. 4 and 7 were carried out to see how quickly the peroxide is decomposed by the action of hydrogen bromide, allyl bromide being treated with hydrogen bromide in the reaction tube at room temperature for a short time before cooling in liquid air. The peroxide is decomposed rather rapidly, if not instantaneously. In the third paper[2] it was shown that the peroxide is not decomposed by hydrogen bromide at the temperature of solid carbon dioxide and chloroform, and that uncombined oxygen is removed by evacuation under cooling in liquid air.

Table 1. Comparison of Oxygen and Peroxide.

Series of exp.	No. of exp.	Remarks	Product: Dibromopropanes			
			Yield (%)	Boiling point (°C/mm.)	1,3- (%)	1,2- (%)
I	1	Allyl bromide containing peroxide corresponding to 4.8 c.c. O_2 per 24 g.	52	44-53.5/12	87	13
	2	Peroxide-free allyl bromide. 4.8 c.c. O_2 admitted.	53	44-54/12	95	5
II	3	Allyl bromide containing peroxide corresponding to 0.9 c.c. O_2 per 24 g.	28	41-52.5/11	62	38
	4	The same allyl bromide as above, treated with HBr for 2 min. at room temp. and left to stand for 10 min. before condensing HBr.	16	36-49/11	26	74
	5	Peroxide-free allyl bromide. 0.9 c.c. O_2 admitted.	57	43-52.5/11	81	19
III	6	Allyl bromide containing peroxide corresponding to 0.8 c.c. O_2 per 24 g.	43	42-53.5/10	70	30
	7	The same allyl bromide as above, treated with HBr for 1 min. at room temp. and HBr condensed immediately.	35	41-53/10	65	35
	8	Peroxide-free allyl bromide. 0.8 c.c. O_2 admitted.	46	42-53.5/10	78	22

Experiments of each series were carried out simultaneously. The peroxide content of allyl bromide is given in the volume of the corresponding amount of oxygen for the temperature and pressure at which oxygen was taken in the run for comparison.

Table 2. Relation between the Amount of Oxygen Present and the Result of Addition.

Series of exp.	No. of exp.	Volume of oxygen admitted (c.c.)	Product: Dibromopropanes			
			Yield (%)	Boiling point (°C./mm.)	1,3- (%)	1,2- (%)
IV Purified allyl bromide. Time of reaction: 3 days.	9	0	14	32-36/10	4	96
	10	0.5	21	34-46/10	38	62
	11	1.5	44	42-51.5/9	95	5
	12	2.5	53	42-51.5/9	96	4
V Purified allyl bromide. Time of reaction: 5 days.	13	0	24	35-42/10	12	88
	14	0.5	37	37-51/10	60	40
	15	1.5	56	42-51.5/9	96	4
	16	2.5	62	42-51.5/9	96	4
VI Once distilled allyl bromide. Time of reaction: 5 days.	17	0	28	38-47/13	44	56
	18	0.5	64	45-56.5/13	89	11
	19	1.5	68	45-56.5/13	96	4
	20	2.5	73	45-56.5/13	96	4

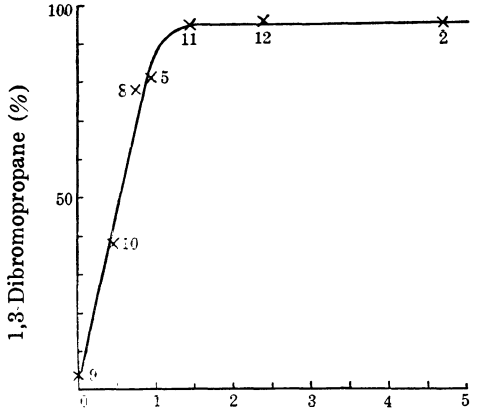


Fig. 1. Series IV (Exp. 9-12). Exp. 2, 5, and 8.

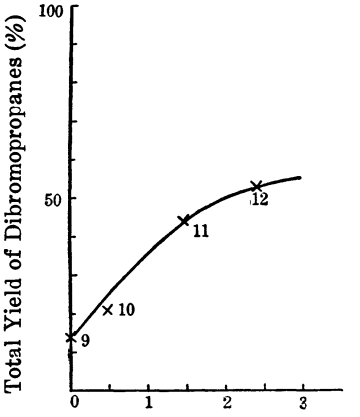


Fig. 2. Series IV (Exp. 9-12).

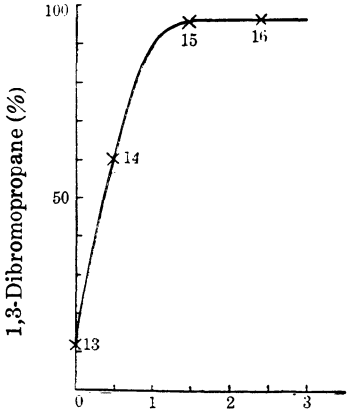


Fig. 3. Series V (Exp. 13-16).

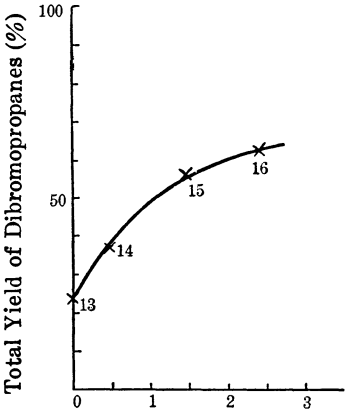


Fig. 4. Series V (Exp. 13-16).

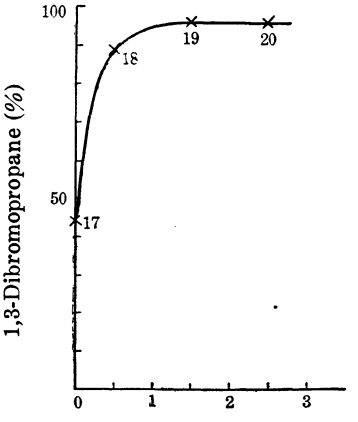


Fig. 5. Series VI (Exp. 17-20).

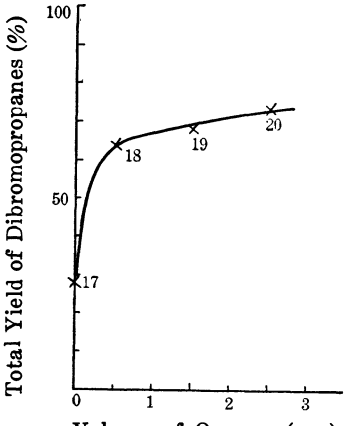


Fig. 6. Series VI (Exp. 17-20).

From Table 1 it can be seen that both the total yield of the product and the proportion of 1,3-dibromopropane in the product are greater in additions with peroxide-free allyl bromide in the presence of oxygen than in the additions with peroxide-containing allyl bromide in vacuum. On the one hand, part of oxygen introduced in gas into the reaction tube may be dissolved by the liquid and part of the dissolved oxygen may be transformed into a peroxide (one molecule from one). On the other hand, the peroxide may gradually decompose to liberate oxygen (one molecule from one) and part of the generated oxygen may leave the liquid. No matter how fast these changes may proceed, and no matter whether or not the changes from both sides go so far as to attain sooner or later the same equilibrium state, both the amount of peroxide alone and the total amount of the peroxide and molecular oxygen in the liquid where the addition takes place must be always greater in the experiments with peroxide-containing allyl bromide than in the experiments with peroxide-free allyl bromide. Such must be the case even if only one half of oxygen in the peroxide were liberated as molecular oxygen on decomposition, because then it could be much more naturally taken for granted that also one half of oxygen would be available in iodometry. In this connection it may be pointed out that neither oxygen nor peroxide oxidizes hydrogen bromide during the addition reaction with allyl bromide, but both do in the presence of platinum black.[2]

Under these circumstances the peroxide effect still appeared more marked in the additions with peroxide-free allyl bromide in the presence of oxygen. This observation permits to draw the following conclusions: (1) Molecular oxygen possesses catalytic activity in the sense of the so-called peroxide effect; and (2) the catalytic activity of the peroxide, if any, is smaller than that of molecular oxygen. It can not be decided, however, whether the peroxide is active at all or not. The fact that, while the action of oxygen is very regular as shown also by the experiments described below, the action of the peroxide is rather irregular as seen from Table 1, suggests the possibility that the peroxide exerts catalytic action not directly but through molecular oxygen generated by its decomposition. It must be taken into consideration that the peroxide is decomposed by hydrogen bromide rather quickly (exp. 4 and 7).

The above conclusions exclude the assignment of any catalytic effect to an undetectable amount of the peroxide and the effect observed with oxygen must be wholly due to the action of molecular oxygen.

Table 2 and the accompanying figures show the results of three series of additions with peroxide-free allyl bromide in the presence of various

volumes (0, 0.5, 1.5, and 2.5 c.c.) of oxygen. The capacities of the reaction tubes were 135–140 c.c. and the total volume of the reacting liquid (allyl bromide and hydrogen bromide) was 27 c.c. in condensed state. The experimental procedure was the same as described above, except that respective volumes of oxygen were admitted at sealing after evacuation. Purified allyl bromide was used in Series IV and V, and once distilled commercial product in Series VI. The time of reaction was 3 days in Series IV, and 5 days in Series V and VI. Additions to be related to one another were carried out as simultaneously as possible. For Series IV and V volumes of oxygen corrected to the normal temperature and pressure were used in the figures.

An experimental procedure as described above does not allow of taking an exact amount of hydrogen bromide nor of controlling the temperature at all. Moreover, the yield is calculated by weighing the dibromopropane mixture really obtained through routine processes for preparation involving the removal of unchanged allyl bromide with dimethylaniline. Hence, the numerical values of yields could not be expected to be exact nor even to be comparable with one another. Nevertheless, it can be seen that the yield increases with the amount of oxygen and with the time of reaction, and is greater in additions with impure allyl bromide than in additions with pure allyl bromide.

On the other hand, it is possible to make more exact mention of the relation between the amount of oxygen and the composition of the product. When the amount of oxygen is 1.5 c.c. and more, the proportion of 1,3-dibromopropane in the product is constant at about 95%, irrespective of the time of reaction and the purity of allyl bromide. In exp. 2 where once distilled allyl bromide was used as in exp. 17–20, and oxygen as much as 4.8 c.c. was admitted, the proportion of 1,3-dibromopropane was 95% (see Fig. 2). Also in the range of less than 1.5 c.c. of oxygen the three series are qualitatively similar: the proportion of 1,3-dibromopropane increases rapidly with the increase of oxygen. In this region, however, the formation of 1,3-dibromopropane is favoured slightly by the longer time of reaction and greatly by the presence of impurities. It is worthy of note that, although the yields of exp. 5 and 8 carried out with purified allyl bromide deviate from the curve of Fig. 2, the proportions of 1,3-dibromopropane come well into line with the results of Series IV (Fig. 1).

Exp. 2 falls in the region where impurities do not affect the composition of the product, which justifies the comparison of it with exp. 1. Allyl bromide was purer in exp. 5 than in exp. 3, and, therefore, a comparison as made above is reasonable. Exp. 6, 7, and 8 were carried out

with portions from the same purified specimen, and they are quite comparable.

As mentioned above, impurities in allyl bromide influence the catalytic action of oxygen, exaggerating both the inversing effect on the direction of addition and the increasing effect on the yield of the product. But there has been no indications to the possibility that impurities may play the leading part in the so-called peroxide effect.

In this way the action of oxygen has been established. The next problem is to decide whether the catalytic action of oxygen is homogeneous (dissolved oxygen acting) or heterogeneous (oxygen adsorbed on the glass wall coming into play). Experiments devised for the solution of this problem are now under way.

In conclusion the authors express their hearty thanks to the Imperial Academy of Japan for a grant.

Chemical Institute, Faculty of Science,
Imperial University of Tokyo.

"Zonal Effect" in the Slow Coagulation of Colloid Arsenious Sulphide.

By Shridhar Sarvottam JOSHI and Sadashiv S. KULKARNI.

(Received February 27th, 1937.)

The results of numerous viscosity measurements reported in previous publications[1] suggested that the progress of a slow coagulation, contrary to the mechanism contemplated in Smoluchowski's classical theory,[2] for the kinetics of coagulation is not time continuous but zonal. Subsequent work on the behaviour of colloid manganese dioxide studied by the familiar opacity method[3] and that dependent on the determination of μ_D the refractivity[4] during numerous coagulations has confirmed the above deduction. That this zonal effect in slow coagulations is not merely an instance of the somewhat abnormal behaviour of colloid MnO_2,[5] but obtains more widely, is shown by results on the electrolytic coagulations of aqueous sodium oleate[4e] and different oil suspensions[4g] on the coagulations of other systems. Similar results are obtained with colloidal solutions of gold, antimony trisulphide and ferric oxide, which will be published shortly. The present paper reports the occurrence of the zonal effect in colloid As_2S_3.

Experimental. The colloid was prepared and its strength estimated as described by Joshi and Kulkarni.[4a] The course of coagulation was followed by measuring the variation of μ_D the refractive index for the sodium line by means of a Pulfrich refractometer. The general experimental procedure, the precautions observed during these measurements

(1) Joshi and Viswanath, *J. Indian Chem. Soc.*, **10** (1933), 329; Joshi and Menon, *ibid.*, **10** (1933), 599; Joshi and Nanjappa, *ibid.*, **11** (1934), 133; Joshi and Iyengar, *ibid.*, **11** (1934), 55, 573; Joshi and Panikkar, *ibid*, **11** (1934), 797; *J. chim. phys.*, **32** (1935), 455; *Proc. Acad. Sci.* (United Provinces Agra Oudh, India), **5** (1935), 41.

(2) Smoluchowski, *Z. physik. Chem.*, **92** (1917), 129.

(3) Joshi and Purushottam, *Current Sci.*, **4** (1936), 870; Joshi and S. J. Rao, *J. Indian Chem. Soc.*, **13** (1936), 311.

(4a) Joshi and Kulkarni, *ibid.*, **13** (1936), 441.

(4b) Joshi and S. J. Rao, *ibid.*, **13** (1936), 141.

(4c) Joshi and Panikkar, *ibid.*, **13** (1936), 309.

(4d) Joshi and S. J. Rao, *Kolloid-Z.*, **76** (1936), 145.

(4e) Joshi and S. J. Rao, *Fettchem. Umshau*, **43** (1936), 36.

(4f) Joshi and Purushottam, *Current Sci.*, **4** (1936), 481.

(4g) Joshi and Sarkar, *J. Bombay Univ.*, **4** (1935), 140.

(5) Joshi and T. S. Narayan, *Kolloid-Z.*, **49** (1932), 335; *J. Indian Chem. Soc.*, **7** (1930), 883; Joshi and V. L. Narayan, *ibid.*, *Sir P. C. Ray Comm. Vol.*, 1933, p. 41.

have been described previously.[4b] The measurements were continued until the coagulating mixture in the refractometer cell remained sensibly homogeneous, that is, free from local and random turbidities due to the coagulam. Although a large number of coagulations were studied in regard to change of μ_D, only two μ_D-time curves are shown in Fig. 1 to indicate the generality of the results. The coagulant used was a suitably

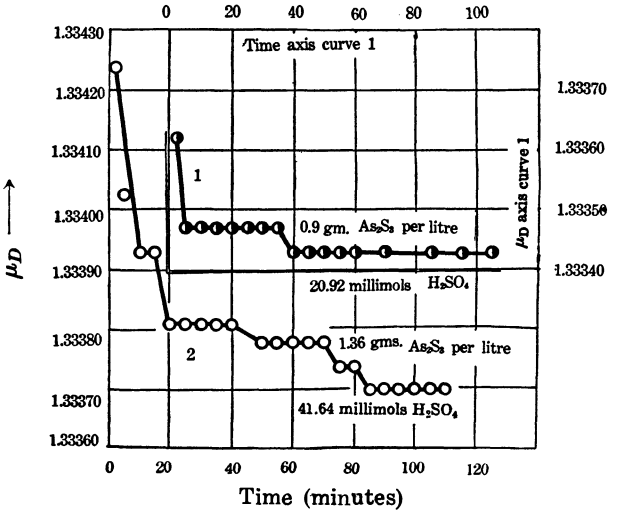


Fig. 1.

diluted solution of H_2SO_4, so as to produce a measurable change in μ_D during a moderate period. The concentration of the coagulant and of the colloid as indicated in Fig. 1 refer to their values in the coagulating mixture. The temperature was maintained constant at 25° ± 0.1°. The least changes in μ_D refer to 0.5 minute, which could be definitely measured with the instrument, and which corresponds to a change of about 0.00004 in μ_D.

Discussion. The two typical curves in Fig. 1 show definitely that the progress of coagulation as recorded by change of μ_D is not time-continuous, but discontinuous or zonal. It was observed that for a given concentration of the colloid, the net change in μ_D during the coagulation and the number of discontinuities or the zonal effect tends to diminish for very large and small values of the concentration of the coagulant. Similar, though not indentical is the influence of the change of colloid content at constant concentration of the coagulant. This is in complete accord with the results obtained previously.[1] It was observed, for

example, that a viscosity-time curve corresponding to a moderately high concentration of the coagulant showed a slight initial fall and then a continuous rise. With a lower concentration, the coagulation curve consisted of a definitely greater number of breaks or discontinuities. A satisfactory theory for the refractivity of a colloid is fundamental to the elucidation of the turbidity phenomena, which are the chief characteristic (for evidence indicating limitation of the validity of this familiar notion, compare Joshi and Kulkarni[4a]) of the coagulation phenomena; it must analyse the influence of such factors as the micellar charge, the nature of the surrounding Helmholtz layer, the refractivity of the continuous and the micellar material, the size and perhaps the shape of the particles; these determine the magnitude of the path in unit time of a light beam passing through the system, and therefore, its refractivity. These quantities are manifestly subject to change during coagulation. During the process, the coalescence of the particles increases the proportion of the medium viz. water in the light path. μ_D is expected to approach its value and therefore, diminish, since the refractivity of the dispersed material is ordinarily greater than that of water. That this change, concomitant with coagulation proceeds zonally is an interesting and hitherto practically an ignored feature of the phenomenon of coagulation in the slow region, and observed perhaps for the first time in colloid arsenious sulphide which has had about the longest and widest usage in studies of the coagulation phenomena.

Chemical Laboratories,
Benares Hindu University,
Benares, India.

Études de l'effet du champ électrique sur la viscosité des liquides. I.

Par Osamu KIMURA.

(Reçu le 15 mars 1937.)

La viscosité d'un liquide est en général remarquablement influencée par des facteurs qui se rapportent à sa structure intérieure tels que la forme et la grandeur des molécules qui composent ce liquide et l'association de ces molécules, aussi bien que par l'attraction mutuelle entre ces molécules. Comme il en est ainsi, si l'on peut en changer volontairement sa structure intérieure par un certain champ de force, on trouvera

certainement le changement de la viscosité dû à ce champ appliqué. Il sera très intéressant d'utiliser ce changement pour étudier sa structure intérieure.

Quand on place un liquide polaire dans le champ électrique, ces molécules qui sont de forme allongée, auront une tendence à se diriger vers la direction du champ susdit, et sa structure intérieure changera, et par conséquent la viscosité le sera aussi. De ce point de vue, R. Herzog et ses collaborateurs[1] ont récemment étudié quelques solvants organiques, et A. Passynski[2] la solution benzénique de caoutchouc. Mais, on pourrait dire que leurs expériences ne seraient pas suffisantes pour comprendre la relation entre le changement de viscosité et la structure intérieure du liquide. Pour comprendre mieux, on a besoin de choisir une substance plus simple et de mesurer la viscosité plus précisément. Pour cette raison, j'ai construit un viscosimètre spécial, au moyen duquel on peut mesurer exactement la viscosité du liquide sous le champ électrique. Et j'ai choisi ici comme solvant le benzène qui est non polaire, et comme corps dissous l'acide stéarique dont la molécule a assez de longueur, en possédant un groupe polaire. Dans cet appareil le liquide s'écoule entre deux plaques-électrodes séparées de 0.2 mm. La direction du champ électrique est perpendiculaire à celle du courant de liquide.

Les résultats obtenus sont représentés dans le tableau et dans la figure, où on porte en abscisses les tensions électriques et en ordonnées les durées d'écoulement qui sont proportionnelles à la viscosité. La concentration de la solution était de 5%, et la température était 27.0° durant nos expériences.

Tableau 1.

Durée d'écoulement en secondes.	Intensité du champ en volts
47.4	0
47.6	4500
47.8	8750
48.1	13750
48.2	20000
48.2	25000
48.2	30000

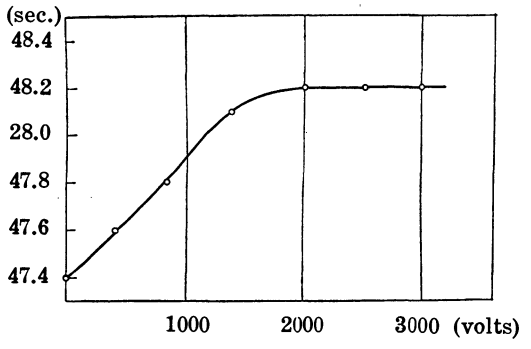


Fig. 1.

(1) R. Herzog, H. Kuder, et E. Paersch, *Physik. Z.*, **35** (1934), 446.
(2) A. Passynski, *Kolloid-Z.*, **70** (1935), 180.

Dans la figure on voit que, durant que la tension n'est pas encore grande, la viscosité s'augmente graduellement au fur et à mesure de l'accroissement de la tension, mais la viscosité arrive à un état de saturation, en n'y changeant plus sa valeur pour la variation de la tension. Pour comprendre mieux cet événement, j'ai essayé un calcul simple.

Si l'on indique par μ le moment électrique de l'acide stéarique et par F l'intensité du champ électrique, on peut calculer, selon la loi de Maxwell-Boltzmann, le nombre des molécules f qui font un angle α avec la direction du champ et un angle solide entre Ω et $\Omega+d\Omega$; donc on a:

$$f = Ae^{\frac{\mu F}{kT}\cos\alpha}\, d\Omega\,.$$

Comparons maintenant la valeur de μF à celle de kT, afin de trouver la relation qui existe entre l'agitation thermique moléculaire et le champ électrique appliqué. Si on pose le moment électrique de l'acide stéarique $= 1.8 \times 10^{-18}$ E.S.U., et la tension F la plus haute dans cette expérience $= 30{,}000$ volt/cm. $(= 100$ E.S.U.), on obtient

$$\frac{\mu F}{kT} = \frac{1.8\times10^{-18}\times100}{300\times1.37\times10^{-16}} = 4.4\times10^{-3}\,.$$

où $k = 1.37 \times 10^{-16}$, et $T = 300$.

On voit que la valeur de μF est beaucoup plus petite que celle de kT. Cela signifie que les molécules qui se dirigent parallèlement à la direction du champ ne sont pas encore nombreux. A la première vue, il semble que la viscosité doive s'augmenter proportionnellement à l'élévation de la tension, mais il n'en est pas ainsi. Elle atteint déjà à l'état de saturation pour une tension pas si grande. Il est très naturel de supposer que cette anomalie soit peut-être due à l'association de molécules de l'acide stéarique. Je ferai un rapport sur ce point dans le prochain mémoire.

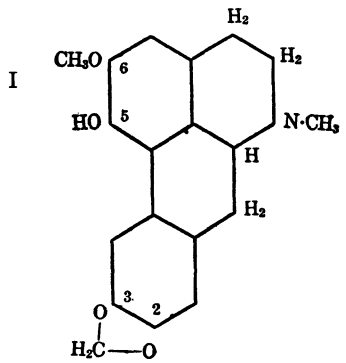
Ce travail a été effectué aux laboratoires de Chimie Colloïdale de l'Institut Shiomi et de l'Université Impériale d'Osaka. Tous mes remerciements sont dus à M. le Prof. N. Sata qui n'a pas cessé de s'intéresser très activement à mon travail et de donner tant de renseignements précieux.

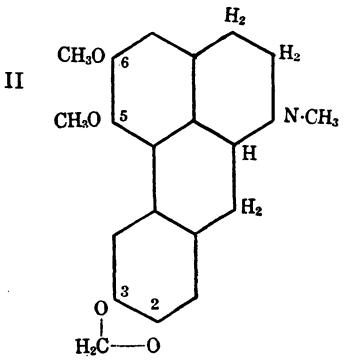
Synthese des Domesticin-äthyläthers.

Von Hideo SHISHIDO.

(Eingegangen am 23. März 1937.)

Die Konstitution von Domesticin[1] ist früher als eine Phenolbase (I) des *d*-Epidicentrins (II), welchem das Methoxyl in der 5-Stellung durch ein Hydroxyl ersetzt ist, angesprochen worden.[1] Zu dieser Vorstellung könnte man einen Beweis dadurch erbringen, dass man seinen

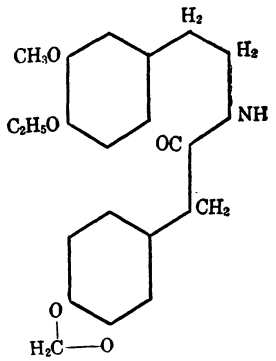


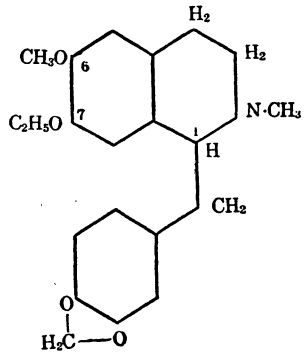


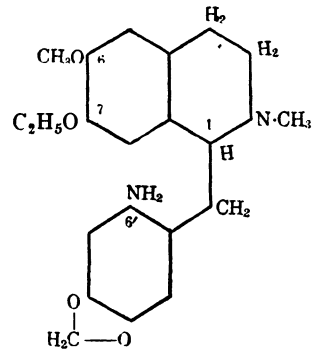
Äthyläther, i.e. Domesticin-äthyläther (VI), in der Weise synthetisiert,[2] dass in der Domesticin-methyläther-synthese[3] statt Veratrumaldehyds Äthylvanillin angewandt wird.

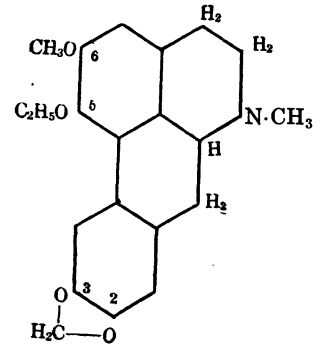
Zunächst wurde β-(3-Methoxy-4-äthoxy-phenyl)-äthyl-3′,4′-methylendioxy-phenacetamid (III) (Schmp. 115°) aus 3-Methoxy-4-äthoxy-β-phenyl-äthylamin und Homopiperonylsäure dargestellt. Dieses Amid wurde dann durch Phosphoroxychlorid in ein Dihydroisochinolinderivat übergeführt, mit Jodmethyl an seinem N methyliert, und durch Reduktion in eine Tetrahydro-verbindung (IV) (Schmp. 106°) umgewandelt. Diese letztere wurde schliesslich mit Salpetersäure an der 6′-Stellung nitriert, dann durch Reduktion mittels Stannochlorids und Salzsäure in eine 6′-Amino-verbindung (V) (Schmp. 90–92°) übergeführt, und diese unter Ringschluss zu inaktivem 2,3-Methylendioxy-5-äthoxy-6-methoxy-*N*-methyl-aporphin (VI) (Schmp. 132°) diazotiert. Dieses racemische

(1) Z. Kitasato, *Acta Phytochim.* (Japan), **3** (1927), 187.
(2) *Ibid.*, **9** (1937), 265.
(3) *Ann.*, **527** (1937), 176.

III 

IV 

V 

VI 

Produkt wurde nun mittels der *d*- und *l*-Weinsäure in beide aktive Komponenten gespaltet.

Die so synthetisch erhaltene *d*-Base schmolz bei 131°, zeigt $[\alpha]_D^{14} = +110.8°$ und ergibt keine Erniedrigung des Schmelzpunktes bei der Mischprobe mit dem natürlichen Domesticin-äthyläther.[4]

Beschreibung der Versuche.

β-(3-Methoxy-4-äthoxy-phenyl)-äthyl-3′, 4′-methylendioxy-phenacetamid (III). 36 g. Homopiperonylsäure werden mit 39 g. 3-Methoxy-4-äthoxy-β-phenyläthylamin[5] zwei Stunden am Rückflusskühler auf 180–190° erhitzt. Nach dem Erkalten wird das

(4) *Acta Phytochim.* (Japan), **9** (1937), 265.

(5) Zuerst wird 3-Methoxy-4-äthoxy-zimtsäure (Schmp. 199°) durch katalytische Reduktion (Palladium-Kohle) zu 3-Methoxy-4-äthoxy-phenylpropionsäure (Schmp. 132°) reduziert und dann wird diese in Chloroformlösung mit Thionylchlorid behandelt. Nach dem Stehen über Nacht wird die Lösung in ein Gemisch von Natronlauge und konz. Ammoniak eingegossen. Beim Verdunsten von Chloroform scheiden sich die Krystalle von 3-Methoxy-4-äthoxy-phenylpropionsäureamid ab (Schmp. 121°) (Gef.: C, 64.84; H, 7.90. Ber. für $C_{12}H_{17}O_3N$ (223): C, 64.57; H, 7.62%.). Dieses Säureamid wird dann durch Natriumhypochlorit in Äthylamin übergeführt.

krystallinische Reaktionsgemisch in 200 c.c. Chloroform gelöst und die Chloroformlösung je dreimal mit verdünnter Natronlauge und verdünnter Salzsäure und dann zweimal mit Wasser geschüttelt. Nach dem Trocknen mit festem Kaliumhydroxyd wird das Chloroform abgedampft und der Rückstand aus Benzol umkrystallisiert. Prismen vom Schmp. 114–115° (Ausbeute 42 g.). (Gef.: C, 67.08; H, 6.72. Ber. für $C_{20}H_{23}NO_5$ (357): C, 67.23; H, 6.44%.)

1-Piperonyl-6-methoxy-7-äthoxy-*N*-methyl-tetrahydroisochinolin (IV). 30 g. obiges Amid (III) werden mit 150 c.c. Toluol und 60 c.c. Phosphoroxychlorid anderthalb Stunden bei 130–140° gekocht. Nach dem Erkalten wird das Toluol mit Petroläther verdünnt und nach einigen Minuten wird die obenstehende Flüssigkeit abgegossen, und der krystallinische Rückstand mit Petroläther gut gewaschen und mit 150 c.c. Benzol, 300 c.c. Wasser und 10 c.c. konzentrierter Salzsäure unter Erwärmen auf dem Wasserbad vermischt. Nach Trennung der heissen Benzolschicht, wird die untere Schicht mit Natronlauge stark alkalisch gemacht und mit Benzol unter Zusatz von etwas Alkohol geschüttelt. Die Benzollösung wird mit Wasser gewaschen, mit Kaliumcarbonat getrocknet und nach dem Einengen mit 20 c.c. Jodmethyl gekocht. Das abgeschiedene rotbraune Öl erstarrt bald zu Krystallen. Nach 3–4-stündigem Kochen wird das Jodmethylat aus Alkohol umkrystallisiert. Prismen vom Schmp. 145° und Zersetzungsp. 155–157°. (Gef.: C, 52.23; H, 5.30. Ber. für $C_{21}H_{24}NO_4I$ (481): C, 52.39; H, 4.99%.)

Das obige Jodmethylat wird in Alkohol gelöst und mit einer genügenden Menge von dem neu gefällten Silberchlorid auf dem Wasserbad erhitzt. Dann wird das Reaktionsgemisch mit 800 c.c. Wasser auf dem Wasserbad bis zum vollständigen Verschwinden des Alkoholgruchs erwärmt. Das Filtrat vom Jodsilber wird bis auf 200 c.c. eingedampft, mit 50 c.c. 15%-iger Schwefelsäure versetzt und mit einem Überschuss von Zinkpulver auf dem Wasserbad reduziert. Das dabei gebildete schwer lösliche Sulfat wird unter Zusatz von Alkohol gelöst. Nach 5–6-stündigem Kochen wird die Lösung von Zinkpulver abfiltriert und der Alkohol abgedampft, wobei sich das Sulfat vollständig krystallinisch abscheidet. Das Sulfat wird in 50%-igem Alkohol gelöst und mit Ammoniak zersetzt. Das abgeschiedene Öl krystallisiert sofort in Prismen. Das so gewonnene 1-Piperonyl-6-methoxy-7-äthoxy-*N*-methyl-tetrahydroisochinolin wird dann aus Äthanol umkrystallisiert. Prismen vom Schmp. 105–106°. Ausbeute ca. 15 g. (Gef.: C, 71.22; H, 7.18. Ber. für $C_{21}H_{25}NO_4$ (355): C, 70.99; H, 7.04%.)

6′-Nitro-1-piperonyl-6-methoxy-7-äthoxy-*N*-methyl-tetrahydroisochinolin. Eine Lösung von 5 g. 1-Piperonyl-6-methoxy-7-äthoxy-*N*-methyl-tetrahydroisochinolin in 25 c.c. Eisessig wird mit 10 c.c. konzentrierter Salpetersäure unterhalb 5° nitriert. Nach 15 Minuten giesst man das Reaktionsgemisch in ein Gemisch von 300 c.c. gesättigter Ammoniumcarbonat-lösung und 200 g. Eis und sammelt nach 30 Minuten den abgeschiedenen Niederschlag und wäscht mit Eiswasser. Die so gewonnene Nitro-verbindung wird in 150 c.c. 3%-iger Salzsäure gelöst und mit Tierkohle 20 Minuten auf dem Wasserbad erhitzt. Nach dem Filtrieren macht man mit verdünntem Ammoniak unter Eiskühlung schwach alkalisch, saugt die Abscheidung ab, wäscht mit Wasser und trocknet auf der Tonplatte. Diese Substanz wird aus Alkohol und dann aus Benzol umkrystallisiert. Gelbe Prismen von Schmp. 178–179°. (Gef.: C, 63.33; H, 6.19. Ber. für $C_{21}H_{24}N_2O_6$ (400): C, 63.00; H, 6.00%.)

6′-Amino-1-piperonyl-6-methoxy-7-äthoxy-*N*-methyl-tetrahydroisochinolin (V). Die obige Nitro-verbindung (nicht umkrystallisiert) wird in 20 c.c. Eisessig gelöst und mit 10 g. Stannochlorid und 20 c.c. konzentrierter Salzsäure bei 35° reduziert.[6] Nach 12 Stunden wird das Reaktionsgemisch in 300 c.c. Wasser eingegossen und nach Zusatz von Kalilauge (70 g. KOH in 100 c.c. Wasser) dreimal mit Chloroform ausgezogen. Der Rückstand dieser Lösung wird in 10 c.c. Äthanol gelöst und mit einer Lösung von 1 g. Oxalsäure in 10 c.c. Äthanol versetzt. Das so erhaltene Oxalat schmilzt bei 193° unter Zersetzung. Ausbeute 3 g. Die Suspension dieses Oxalates in Kalilauge wird mit Äther ausgeschüttelt und der Abdampfungsrückstand der Ätherlösung wird aus Methanol umkrystallisiert. Lange Prismen vom Schmp. 96–98°. (Gef.: C, 68.38; H, 7.32. Ber. für $C_{21}H_{26}N_2O_4$ (370): C, 68.11; H, 7.03%.)

Das Mono-chlorhydrat wird auf übliche Weise dargestellt und aus methanolhaltigem Benzol umkrystallisiert. Prismen vom Schmp. 228° unter Zersetzung. (Gef.: C, 62.09; H, 6.94; N, 6.80. Ber. für $C_{21}H_{27}N_2O_4Cl$ (406.5): C, 61.99; H, 6.64; N, 6.89%.)

***d,l*-2,3-Methylendioxy-5-äthoxy-6-methoxy-*N*-methyl-aporphin** (VI). 6.5 g. 6′-Amino-1-piperonyl-6-methoxy-7-äthoxy-*N*-methyl-tetrahydroisochinolin-oxalat werden, wie bei der Synthese von Epidicentrin,[7] in 25 c.c. 10%-iger Schwefelsäure gelöst und mit 75 g. zerkleinerten Eisstücken versetzt, und zu diesem Gemisch 7.5 c.c. 2 N Natriumnitritlösung sehr langsam zugetropft. Nach etwa 30 Minuten wird die diazotierte Lösung mit Kupferpulver versetzt, wobei man Entwicklung von Stickstoff und die Farbveränderung der Flüssigkeit beobachtet. Nach 4 Stunden wird die vom Kupferpulver abfiltrierte Flüssigkeit unter Zusatz von Methanol mit 2.5 g. Zinkpulver und 7.5 c.c. konzentrierter Salzsäure auf dem kochenden Wasserbad 15 Minuten reduziert. Das Filtrat vom Zink wird mit Ammoniak alkalisch gemacht, mit Äther sechsmal ausgezogen und der Rückstand des Äthers in Methanol gelöst. Wird die Lösung mit wenig 20%-iger Salzsäure versetzt, so krystallisiert das Chlorhydrat der *d,l*-Base (VI) aus. Es färbt sich gegen 250° und schmilzt bei 275–277° unter Zersetzung. Ausbeute an Chlorhydrat ca. 15%. Es ist schwer löslich in heissem Wasser und Äthanol. (Gef.: C, 64.26; H, 6.63. Ber. für $C_{21}H_{24}NO_4Cl$ (389.5): C, 64.70; H, 6.16%.)

Die Suspension des so dargestellten Chlorhydrats in Natronlauge wird mit Äther ausgeschüttelt, und die Ätherlösung mit Wasser gewaschen. Der Abdampfungsrückstand des Äthers wird aus Äthanol umkrystallisiert. Prismen vom Schmp. 132°. Sie sind leicht löslich in heissem Äthanol, Methanol und Chloroform, aber etwas schwerer in Äther. (Gef.: C, 71.72; H, 6.97. Ber. für $C_{21}H_{23}NO_4$ (353): C, 71.39; H, 6.52%.)

Spaltung der racemischen Base in optische Antipode. In eine Lösung von 1.6 g. der wie oben erhaltenen *d,l*-Base (VI) in 70 c.c. Äthanol werden 3.3 c.c. einer 2 N alkoholischen Lösung von *d*-Weinsäure hinzugefügt. Das gebildete *l*-2,3-Methylendioxy-5-äthoxy-6-methoxy-*N*-methyl-aporphin-*d*-tartrat wird nach 10 Minuten Stehen abfiltriert und mit Alkohol gut gewaschen. Das Tartrat wird aus Äthanol umkrystallisiert in Prismen vom Schmp. 237° unter Zersetzung. Es wird in warmem Wasser gelöst, mit verdünnter Natronlauge alkalisch gemacht und mit Äther aus-

(6) Vgl. *J. Chem. Soc.*, **127** (1925), 2018.
(7) *Ann.*, **527** (1937), 180.

geschüttelt. Der Rückstand der Ätherlösung wird aus Methanol umkrystallisiert. Feine Prismen vom Schmp. 129–131°. (Gef.: C, 71.95; H, 6.82. Ber. für $C_{21}H_{23}NO_4$ (353): C, 71.39; H, 6.52%.) $[\alpha]_D^{14} = -110.9°$ (in Methanol).

Das Chlorhydrat wird auf übliche Weise dargestellt und aus einem Gemisch von Methanol, Äther und Petroläther umkrystallisiert. Prismen vom Schmp. 257° unter Zersetzung. (Gef.: C, 65.01; H, 6.23. Ber. für $C_{21}H_{24}NO_4Cl$ (389.5): C, 64.70; H, 6.16%.)

Die Mutterlauge sammt dem Wasch-Alkohol von *l*-Base-*d*-tartrat wird in Vakuum abgedampft, der Rückstand wird in Wasser gelöst, mit verdünnter Natronlauge alkalisch gemacht und mit Äther extrahiert. Der Rückstand des Äthers wird in 35 c.c. Äthanol gelöst und mit 4.6 c.c. einer N alkoholischen Lösung von *l*-Weinsäure versetzt. Man saugt die so abgeschiedenen Krystalle von *d*-Base-*l*-tartrat ab und wäscht mit Äthanol. Prismen vom Schmp. 237° unter Zersetzung. Man suspendiert sie in Natronlauge und nimmt die frei gesetzte Base mit Äther. Dann verdampft man den Äther und krystallisiert den Rückstand aus Methanol um, wobei man *d*-2,3-Methylendioxy-5-äthoxy-6-methoxy-*N*-methyl-aporphin (VI) in Prismen vom Schmp. 131° erhält. Es nimmt mit konzentrierter Schwefelsäure eine rotviolette Farbe an, die durch Salpetersäure-dampf ins Blaugrün umschlägt. Diese Farbenreaktion tritt auch bei Domesticin-äthyläther auf. Die Mischprobe dieser Base mit dem natürlichen Domesticin-äthyläther zeigt keine Erniedrigung des Schmelzpunktes.[8] (Gef.: C, 71.66; H, 6.81. Ber. für $C_{21}H_{23}NO_4$ (353): C, 71.39; H, 6.52%.) $[\alpha]_D^{14} = +110.8°$ (in Methanol).

Man erhält das Chlorhydrat auf übliche Weise und es krystallisiert aus einem Gemisch von Methanol, Äther und Petroläther in Prismen vom Schmp. 257° unter Zersetzung (es färbt sich gegen ca. 230°). Es ist identisch mit natürlichem Domesticin-äthyläther-chlorhydrat (Mischprobe). (Gef.: C, 64.88; H, 6.06; N, 3.53. Ber. für $C_{21}H_{24}NO_4Cl$ (389.5): C, 64.70; H, 6.16; N, 3.59%.)

Natürlicher Domesticin-äthyläther. Es wurde nach der Angabe Kitasatos[9] dargestellt und krystallisiert aus Petroläther, Äther und dann aus Methanol in Prismen vom Schmp. 130–131° aus. (Gef.: C, 71.52; H, 6.84. Ber. für $C_{21}H_{23}NO_4$ (353): C, 71.39; H, 6.52%.)

Das Chlorhydrat wird aus einem Gemisch von Methanol, Äther und Petroläther umkrystallisiert. Es bildet Prismen, färbt sich gegen ca. 230° und schmilzt bei 257° unter Zersetzung. Es ist leicht löslich in gewöhnlichen Lösungsmitteln. (Gef.: C, 65.05; H, 6.55; N, 3.61. Ber. für $C_{21}H_{24}NO_4Cl$ (389.5): C, 64.70; H, 6.16; N, 3.59%.)

Zum Schluss möchte ich Herrn Dr. Zenjiro Kitasato für seine freundliche Leitung und gütige Unterstützung meinen herzlichsten Dank aussprechen.

Chem. Laboratorium des Kitasato-Institut, Tokyo.

(8) *Acta Phytochim.* (Japan), **9** (1937), 265.
(9) *Ibid.*, **3** (1927), 202; **9** (1937), 265.

Studies on the Raman Effect of Organic Substances. VIII. Raman Effect of Furane Derivatives.

By Kichimatsu MATSUNO and Kwan HAN.

(Received April 5th, 1937.)

Introduction. In our two previous papers,[1][2] investigations on the Raman spectra of ethyl cinnamate and ethyl α-furfuracrylate were described. In the present investigation, the Raman spectra of methyl and ethyl esters of the so-called stable α-furfuracrylic acid, *trans*-cinnamic acid, and the reduced products, viz., α-furylpropionates and hydrocinnamates, have been taken, in order to study the relation between the Raman spectra and the isomerism.

Experimental. The substances used were synthesized by the following processes: Methyl α-furfuracrylate (I) (m.p. 26.5°, b.p. 96°/3 mm.) and ethyl α-furfuracrylate (II) (b.p. 114°/3 mm.) were prepared by treating the mixtures of the silver salt of stable α-furfuracrylic acid, F-CH:CH·COOH* (m.p. 140°) and the corresponding alkyl iodides.

trans-Methyl cinnamate (III) (m.p. 34°, b.p. 127°/10 mm.) and *trans*-ethyl cinnamate (IV) (b.p. 136°/10 mm.) were obtained by treating Kahlbaum's cinnamic acid (m.p. 133°) and the corresponding alcohols in the presence of concentrated sulphuric acid, according to the method of Fischer and Speier.[3]

Methyl α-furylpropionate (V) (b.p. 67°/3 mm.) and ethyl α-furylpropionate (VI) (b.p. 74°/8 mm.) were obtained by reducing the corresponding α-furfuracrylate, F-CH:CH·COOR, with 2.5% sodium amalgam in alcohol solution in the presence of acetic acid. The reduction was repeated until the intense Raman line at $\Delta\nu$ 1640 cm.$^{-1}$ in the Raman spectra, associated with the C:C bond, disappeared.

Methyl hydrocinnamate[4] (VII) (b.p. 105°/8 mm.) and ethyl hydrocinnamate[4] (VIII) (b.p. 127°/15 mm.) were prepared by warming the

(1) This Bulletin, **9** (1934), 88.

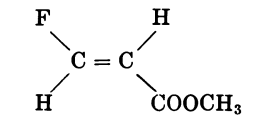
(2) *Ibid.*, **9** (1934), 327.

* F denotes α-furyl group  in this paper.

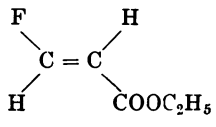
(3) Fischer and Speier, *Ber.*, **28** (1895), 3254.

(4) Erlenmeyer, *Ann.*, **137** (1866), 334.

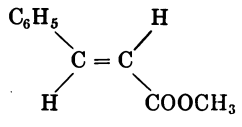
mixtures of hydrocinnamic acid (m.p. 48°) and the corresponding alcohols by the action of dry hydrogen chloride. All the substances were washed with the solution of sodium bicarbonate or sodium carbonate and finally with water. After dehydrating over calcium chloride and sucking off all the ether, the esters were distilled under reduced pressure. The middle fraction in the final distillation was employed in the investigation. The structural formulæ of the substances are as follows:



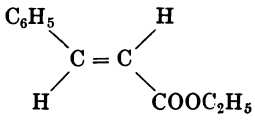
I



II



III



(IV)

F-CH_2·CH_2·$COOCH_3$

V

F-CH_2·CH_2·$COOC_2H_5$

VI

C_6H_5·CH_2·CH_2·$COOCH_3$

VII

C_6H_5·CH_2·CH_2·$COOC_2H_5$

VIII

trans-Methyl cinnamate (m.p. 34°) is colourless crystals at room temperature, while *cis*-methyl cinnamate being a liquid (m.p. −3.5°) which agrees with the results obtained by Kistiakowsky and his co-worker.[5] The so-called stable methyl *α*-furfuracrylate is also colourless crystals (m.p. 26.5°). The ether solution (ca. 1/5 mol) of methyl furfuracrylate and methyl cinnamate were used in the experiments of the Raman spectra. After long exposure the solvent was removed off and the crystals identical with the *trans*-methyl cinnamate and methyl *α*-furfuracrylate were recovered.

The Raman spectra were taken by means of a spectrograph with three prisms,[2] using a saturated solution of sodium nitrite as a filter, in order to prevent the samples from the isomerization due to the action of the light in ultra-violet region. The numbers of the Raman lines (n), the numbers of the plates, and the conditions under which the spectra were taken, are summarized in Table 1. The results of the Raman spectra are shown in Table 2. Methyl cinnamate in the fused state and ethyl cinnamate have been studied by Kohlrausch and his co-worker.[6] The results are compared in Table 3.

(5) G. B. Kistiakowsky and Walter R. Smith, *J. Am. Chem. Soc.*, **57** (1935), 269.
(6) K. W. F. Kohlrausch and A. Pongratz, *Monatsh.*, **64** (1934), 374.

Table 1.

Substance	n	No. of plates	Width of slit (10^{-2} mm.)	Temp. (°C.)	Time of exposure (hours)
Methyl α-furfuracrylate (I)	20	365	65	15	8
Ethyl α-furfuracrylate (II)	32	372	55	15	14
trans-Methyl cinnamate (III)	59	356	65	22	14
trans-Ethyl cinnamate (IV)	65	354	65	23	6
Methyl α-furylpropionate (V)	33	360	60	22	8
		361	65	21	14
Ethyl α-furylpropionate (VI)	23	366	65	15	8
Methyl hydrocinnamate (VII)	27	363	65	20	12
Ethyl hydrocinnamate (VIII)	25	359	65	23	8

Table 2. The $\overline{\Delta\nu}$ Values of the Raman Spectra of Furane Derivatives.

(1) Methyl α-Furfuracrylate (I).

135 (2d); 384 (1/2d); 776 (4); 887 (2); 930 (1); 1023 (6); 1081 (3); 1160 (5); 1217 (5); 1268 (4); 1287 (5); 1396 (6); 1441 (2); 1485 (8); 1574 (2); 1644 (10); 1715 (5d); 3130 (3).

(2) Ethyl α-furfuracrylate (II).

761 (2); 794 (2); 817 (1); 862 (1); 887 (3); 934 (4); 978 (1d); 1021 (8); 1082 (4); 1160 (6); 1190 (2); 1212 (6); 1265 (5); 1283 (8); 1311 (1/2); 1334 (1/2); 1361 (1); 1389 (9); 1478 (10); 1575 (3); 1642 (10); 1704 (8d); 2928 (1d); 2976 (2); 3121 (2); 3151 (1/2).

(3) *trans*-Methyl cinnamate (III).

216 (1b, d); 360 (1/2); 576 (2); 616 (4); 718 (4); 769 (1d); 834 (3b); 861 (3); 933 (2b); 998 (8); 1028 (2b); 1158 (6b); 1179 (6b); 1201 (5); 1267 (4b, d); 1307 (3b, d); 1335 (2); 1443 (5d); 1494 (4); 1574 (4); 1597 (9b); 1634 (10b); 1713 (6b); 2841 (2b, d); 2875 (3b, d); 2963 (3); 3058 (1b, d).

(4) *trans*-Ethyl cinnamate (IV).

177 (2b, d); 279 (1b, d); 403 (2d); 475 (0); 571 (4); 616 (6s); 717 (4b, d); 740 (2); 775 (3); 836 (5); 867 (5d); 977 (1d); 996 (10s); 1025 (3); 1116 (3b, d); 1156 (3); 1178 (8); 1200 (8); 1259 (6d); 1303 (5d); 1331 (3); 1363 (3); 1392 (3); 1447 (5); 1494 (5); 1572 (3); 1597 (10); 1634 (10); 1706 (8); 2922 (3d); 2981 (3); 3067 (5d).

Table 2.—(*Concluded*)

(5) Methyl *α*-furylpropionate (V).

384 (1/2 d); 700 (1/2); 837 (1); 886 (2); 922 (1/2 d); 1019 (2); 1054 (1); 1078 (5); 1145 (4b, d); 1215 (3); 1388 (5); 1450 (1b, d); 1508 (10); 1599 (5); 1735 (2d); 2924 (2d); 2954 (3); 3118 (5); 3155 (2).

(6) Ethyl *α*-furylpropionate (VI).

699 (1/2); 858 (2); 882 (2); 922 (1/2); 1017 (1); 1050 (1/2); 1079 (4); 1118 (1/2); 1143 (2b); 1213 (3); 1387 (3); 1451 (2d); 1505 (8); 1597 (5); 1734 (2d); 2929 (3d); 2983 (2); 3126 (2); (3154) (3).

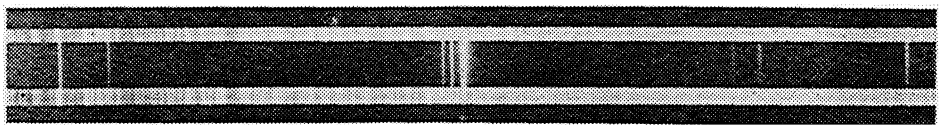
(7) Methyl hydrocinnamate (VII).

244 (2d); 424 (2d); 618 (5); 749 (1d); 759 (3); 837 (1d); 889 (3); 941 (2b); 997 (10); 1025 (5); 1178 (2); 1197 (5); 1443 (2d); 1578 (2); 1597 (6); 1630 (2); 1730 (3d); 2841 (1); 2917 (3b); 2945 (2d); 2997 (2); 3053 (3d).

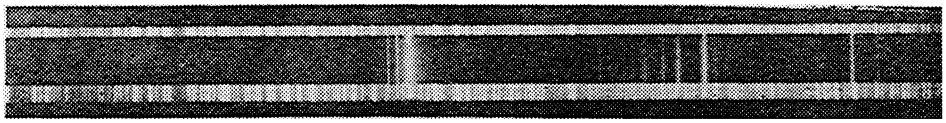
(8) Ethyl hydrocinnamate (VIII).

374 (1/2); 618 (3); 767 (2); 859 (1); 999 (8); 1028 (4); 1105 (2d); 1174 (3); 1196 (6); 1261 (5); 1446 (2); 1589 (1); 1602 (6); 1724 (3d); 2926 (2d); 2970 (1); 3056 (5d).

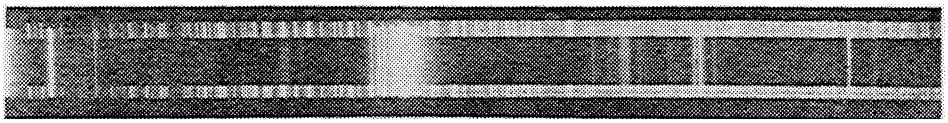
(1) Methyl α-furfuracrylate (I)



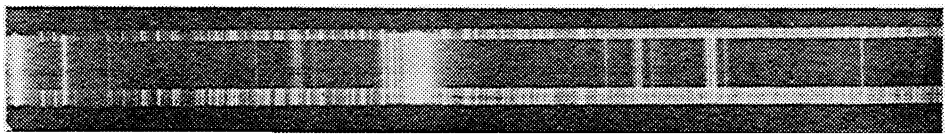
(2) Ethyl α-furfuracrylate (II)



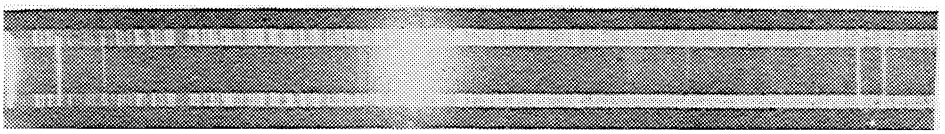
(3) *trans*-Methyl cinnamate (III)



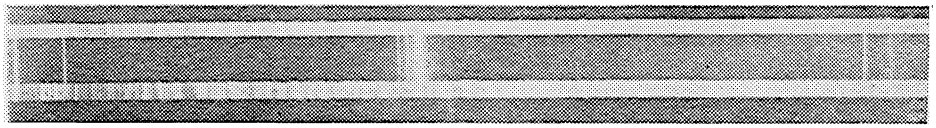
(4) *trans*-Ethyl cinnamate (IV)



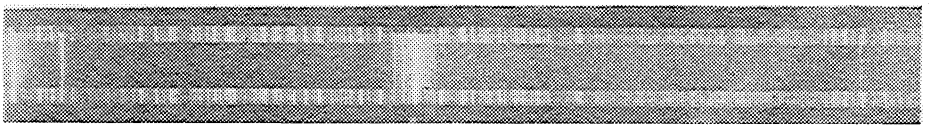
(5) Methyl α-furylpropionate (V)



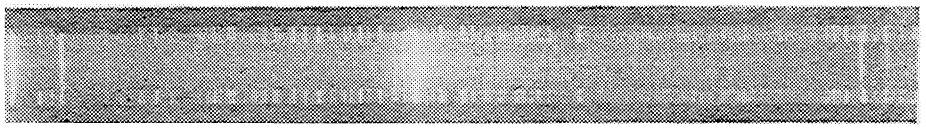
(6) Ethyl α-furylpropionate (VI)



(7) Methyl hydrocinnamate (VII)



(8) Ethyl hydrocinnamate (VIII)



Discussion. In the previous papers,[1][2] one of the authors has shown that the Raman frequencies, ω_1 626, ω_2 885, ω_3 923, ω_4 1018, ω_5 1083, ω_6 1150, ω_7 1223, ω_8 1384, ω_9 1505, ω_{10} 1602, ω_{11} 3117, and ω_{12} 3150 cm.$^{-1}$ are characteristic of the α-furfuryl-compounds, and the frequencies in the region between $\Delta\nu$ 1460 and 1600 cm.$^{-1}$ can be used as an indicator to distinguish α-furfuryl- from α-furfuridene or α-furoyl-compounds. In the present investigation, the frequencies of $\Delta\nu$ 1478, 1575, and 1642 cm.$^{-1}$ are found in α-furfuracrylates while 1505 and 1597 cm.$^{-1}$ are found in α-furylpropionates, as shown in Table 4. The appearance of $\Delta\nu$ 1642 cm.$^{-1}$ in the former but not in the latter cases is reasonable, for the appearance of a Raman shift, $\Delta\nu$ 1640 ± 20 is quite indicative of a double linkage in the side chain.

It has been observed that there is a considerable difference between the spectra of the *cis*- and *trans*-isomers.[7] Grédy[8] has investigated the Raman spectra of the *cis-trans*-isomers of cinnamic compounds and concluded that 1264, 1408, 1642, and 3021 cm.$^{-1}$ are found in the

(7) H. Hibben, *Chem. Rev.*, **18** (1936), 31.
(8) Blanche Grédy, *Compt. rend.*, **202** (1936), 664.

Table 3. Comparison of the Results on Cinnamates.

Methyl cinnamate		Ethyl cinnamate	
Kohlrausch	The authors	Kohlrausch	The authors
217	216	—	177
274	—	—	279
357	360	—	403
402	—	—	475
576	576	582	571
616	616	616	616
710	718	718	717
—	—	—	740
771	769	—	775
837	834	846	836
862	861	865	867
938	933	—	—
977	—	—	977
998	998	1004	996
1028	1028	1030	1025
—	—	—	1116
1165	1158	1163	1156
1181	1179	1185	1178
1201	1201	1201	1200
1268	1267	1264	1259
1311	1306	1303	1303
1336	1335	1324	1331
—	—	—	1363
—	—	—	1392
1447	1443	1446	1447
1495	1494	1496	1494
1578	1574	—	1572
1598	1597	1595	1597
1634	1634	1631	1634
1712	1713	1706	1706
2836	2841	—	—
2880	2875	2934	2922
2956	2963	2980	2981
3037	3058	3055	3067

Table 4.

C_6H_5·CH : CH·COOR		F-CH : CH·COOR		F-CH_2·CH_2·COOR	
R = CH_3	R = C_2H_5	R = CH_3	R = C_2H_5	R = CH_3	R = C_2H_5
718	717	—	—	700	699
—	740	—	—		
769	775	776	761	—	—
—	—	—	794	—	—
834	836	—	817	837	—
861	867	—	862	—	858
—	—	887	887	886	882
933	977	930	934	922	922
			978		
998	996	—	—	—	—
1028	1025	1023	1021	1019	1017
				1054	1050
—	—	1081	1082	1078	1079
—	1116	—	—	—	1118
1158	1156	1160	1160	1145	1143
1179	1178	—	1190	—	—
1201	1200	1217	1212	1215	1213
1267	1259	1268	1265	—	—
1306	1303	1287	1283	—	—
			1311		
1335	1331	—	1334	—	—
—	1363	—	1361	—	—
—	1392	1396	1389	1388	1387
1443	1447	1441	—	1450	1451
1494	1494	1485	1478	1508	1505
1572	1572	1574	1575	—	—
1597	1597	—	—	1599	1597
1634	1634	1644	1642	—	—
1713	1706	1715	1704	1735	1734

cis-forms, while 1209, 1274, and 1657 cm.$^{-1}$ in the *trans*-forms as shown in Table 5. The disappearance of $\Delta\nu$ 1408 and the appearance of 1201, 1306, and 1634 in the *trans*-cinnamates may give an evidence that a little transition from *cis*- to *trans*-forms takes place during the experiment of the Raman spectra under the filtered mercury light. It is likewise

possible to consider that the disappearance of 1408 and the appearance of 1190, 1212,[9] 1283, and 1642 cm.$^{-1}$ in furfuracrylates are attributable to the *trans*-forms of the esters.

Table 5. Some Raman shifts in the *cis*- and *trans*-isomers of cinnamic compounds observed by Grédy.[8]

C_6H_5·CH : CH·CH_3	*cis*		1264	1408	1642	3021
	trans	1210	1278		1665	
C_6H_5·CH : CH·CH_2OH	*cis*		1256	1408	1642	3022
	trans	1209	1274		1657	
C_6H_5·CH : CH·CH_2OCH_3	*cis*		1255	1410	1643	3025
	trans	1208	1278		1657	
C_6H_5·CH : CH·CH_2OCOCH_3	*cis*		1250	1412	1645	3032
	trans		1281		1659	
C_6H_5·CH : CH·CH_2Br	*trans*	1206	1282		1646	

It is doubtful, at a glance, that the important Raman shift associated with the C:C linkage has the values of $\Delta\nu$ 1634 in *trans*-cinnamates and 1642 cm.$^{-1}$ in α-furfuracrylates. But it is reasonable to consider that the shift questioned above is due to the effect of a conjugated double bond of carbonyl group, C:O. It is well-known that the C:C frequency is decreased by the effect of the conjugated double bonds. We may consider some other examples from the work of Hibben.[7]

Table 6. The Effect of Substitution on the C : C Shifts.

Radical R	CH_2 : CH-R	R-CH : CH-R	
		cis	*trans*
CH_3	1647		
CH_2OH	1646	1658	1677
C_nH_{2n+1} (n = 2–6)	1642	1658	1674
C_6H_5	1631	1642	1665
COOH	1638	1645	1652
COOR		1644	1655
CHO	1618	1625	1642
CN		1628	1645

(9) $\Delta\nu$ 1212 cm.$^{-1}$ is also attributable to the furane ring.

It is obvious that the carbonyl or the aromatic radical has an effect to decrease the C:C shift on account of the conjugated double bonds. Consequently, a remarkable decrease of the C:C shift will be expected in cinnamates and α-furfuracrylates which have the aromatic and the carbonyl radicals attached to the two sides of the ethylene linkage. The fact that $\Delta\nu$ 1634 cm.$^{-1}$ was found in stilbene[10] and $\Delta\nu$ 1640 cm.$^{-1}$ in diethyl fumarate[11] seems to make an other confirmation about it. If the *cis*- and *trans*-isomers were co-existent, other Raman lines, associated with the *cis*-compound, would be found at ca. $\Delta\nu$ 1620–1630 cm.$^{-1}$ besides the shift mentioned above. We may consider that the appearance of the intense lines at $\Delta\nu$ 1634 cm.$^{-1}$ in cinnamates and at $\Delta\nu$ 1642 cm.$^{-1}$ in the so-called stable α-furfuracrylates is attributable to the *trans*-form of the substances.

Summary.

(1) The Raman spectra of methyl and ethyl esters of α-furfuracrylic acid, cinnamic acid, α-furylpropionic acid, and hydrocinnamic acid have been measured.

(2) On comparing the Raman spectra of α-furfuracrylates with those of *trans*-cinnamates and other cinnamic compounds, the so-called stable furfuracrylates are considered as the *trans*-esters.

In conclusion, the authors are indebted to Ass. Prof. T. Nozoe for his valuable advice in the work of synthesis of the samples. The expense of this experiment was paid from a grant given by the Nippon Gakuzyutu Sinko Kwai, for which thanks are due.

Laboratory of Physical and Inorganic Chemistry,
Taihoku Imperial University, Taihoku.

---

(10) Dadieu, Pongratz, and Kohlrausch, *Sitzber. Akad. Wiss. Wien, Math.-naturw. Klasse*, Abt. II a, **140** (1931), 353.

(11) Dadieu, Pongratz, and Kohlrausch, *ibid.*, **140** (1931), 647.

On the Silver Oxide Positive of the Alkaline Accumulator. I.

By Kyôji KINOSHITA.

(Received April 5th, 1937.)

The alkaline accumulator composed of the silver oxide positive and copper negative was already described by E. W. Jungner. The fundamental chemical reactions involved in the discharge of this accumulator are said to be the followings:

$$Ag_2O_2+2\,KOH+2\,Cu = Ag_2O+2\,KOH+Cu_2O \qquad (1),$$
$$Ag_2O+2\,KOH+2\,Cu = 2\,Ag+2\,KOH+Cu_2O \qquad (2).$$

The terminal voltages of the cell corresponding to the reaction (1) and (2) were reported to be 0.93 volt and 0.65–0.7 volt respectively. In 1927 F. Jirsa[1] studied the cell of the form Ag/OH′/Fe. He prepared the silver oxide electrodes of the cell by pressing powdered silver oxide or iron on the suitable wire gauze.

The author prepared the silver oxide positive of the alkaline cell in powdered and in pasted forms, and made some experiments on this positive electrode. The present report is the abstract from the detailed description published in Japanese.[2]

Silver Oxide Positives Prepared in Powdered Form. At first the electrode was prepared by packing the powdered silver oxide (Ag_2O) into the pocket made of silver wire gauze. The size of the pocket was 9 cm.× 3.5 cm. × 2 cm. The cell was made by combining this positive with a negative electrode of a "Nife accumulator." The negative electrode, therefore, was composed principally of iron. The electrolyte used was 20% KOH solution.

The initial charge of the positive electrode was continued for about 20 hours by the current of 1 ampere. The open circuit voltage was found to be 1.260 volts. Eleven cycles of charge and discharge were undertaken and the results obtained are tabulated in Table 1. The characteristic curves of discharge are shown in Fig. 1, the number of cycle being indicated by the figure from 1 to 11.

---

(1) Jirsa, *Z. Elektrochem.*, **33** (1927), 129.
(2) Kinoshita, *Toyoda Kenkyu Iho*, **3** (1935), 88; *ibid.*, **4** (1936), 96.

Table 1.

Number of cycles	Discharge current (milliamp.)	End point voltage (volts)	Discharge capacity (a. h.)
1	200-600	0.92	3.10
2	1000	0.0	5.42
3	1000	0.0	4.13
4	1000	0.0	3.43
5	1000	0.57	2.83
6	500	0.49	4.09
7	700	0.0	5.32
8	600	0.0	4.67
9	600	0.0	5.05
10	600	0.36	5.30
11	700	0.0	5.23

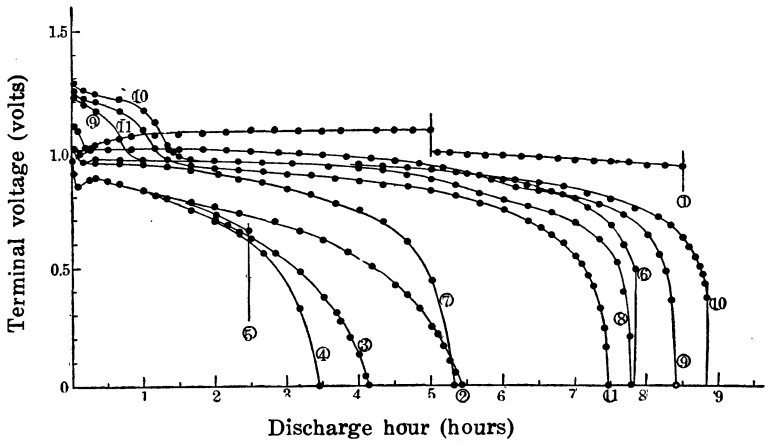


Fig. 1.

In the course of these experiments, as was already noticed by Jirsa, peptization of the active material of the positive electrode took place. As seen from Fig. 1 the forms of the curves for the last three cycles, i.e. 9, 10, and 11th cycle, differ remarkably from the other one. The terminal voltage of the cell falls in two steps, 1.2 volts and 1.0–0.9 volt, and then finally it drops to zero volt. This fact may be interpreted in the following manner.

The active material of the positive plate at the first discharge may be Ag_2O, but this will be then oxidized to Ag_2O_2 in the course of repetition of the cycles of charges and discharges. As the results of this electrolytic oxidation of the active material, the chemical reactions accompanied by the process of discharge may proceed in two stages as shown in the following equations.

$$Ag_2O_2 = Ag_2O + {}^1/_2\, O_2 \quad (3),$$

$$Ag_2O = 2\,Ag + {}^1/_2\, O_2 \quad (4).$$

The higher terminal voltage at the beginning is considered to be the result of reaction (3), and the lower terminal voltage reaction (4).

Silver Oxide Positives Prepared in Pasted Form. The experiments have been undertaken, then, on the silver oxide positives prepared in the pasted form. The powdered silver oxide was made into paste by mixing with NH_4OH or KOH solution and applied to the grid in the same manner as the ordinary pasted type electrodes of the lead acid cell. The grid was prepared by plating silver on the ordinary grid of lead-antimony alloy. The size of the grid was about 6.0 cm. × 1.5 cm. × 0.3 cm.

The paste was made by adding 1.7 c.c. of 20% KOH or 1.5 c.c. of 5N NH_4OH solution drop by drop to 10 g. of Ag_2O. After pasting the grids were left to dry in the room temperature for about 72 hours, and then were formed into the positives in 20% KOH solution by the current of 40–60 milliamperes.

The silver oxide positives thus prepared was combined with the Nife's negative in 20% KOH solution. The results of charges and discharges obtained on the positive electrode are tabulated in Table 2. The amount of Ag_2O pasted in this grid was 5.21 g.

Table 2. Results from an Electrode.

Discharge current 500 milliamp.

Number of cycles	Discharge capacity (a. h.)	Discharge capacity per 1 g. of Ag_2O. (m. a. h./g.)	Coefficient of utility (%)
1	2.285	439	94.8
2	1.642	315	68.1
3	1.666	320	69.1
4	1.576	303	65.4
5	1.642	315	68.1
6	1.616	310	67.0
7	1.576	303	65.4
8	1.542	296	64.0
9	1.550	298	64.3
10	1.550	298	64.3

The discharge current, in this case, was 500 milliamperes and the end point voltage of the cell was taken to be zero volt against Nife's negative. The 3rd column of Table 2 shows the capacities per one gram of Ag_2O, and the 4th column the percentage ratio of the actual capacity of the plate to the theoretical one. The theoretical capacity was calculated assuming the fundamental chemical reaction for discharge, for 4F of the electricity, to be

$$Ag_2O_2 \rightarrow Ag_2O \rightarrow 2\,Ag$$

The ratio thus obtained may be considered to represent the coefficient of utility of the active material in the plate. As seen from this table very large discharge capacity was obtained at the first cycle of discharge, the utility coefficient of which amounting to 94.8%. From the 2nd cycle of discharge onwards the utility coefficient falls to about 60–70%.

This particularity of the 1st discharge was noticed in all silver oxide positives other than exemplified in Table 2.

Characteristic curves of the electrodes in charge and discharge are shown in Fig. 2, Fig. 3, and Fig. 4.

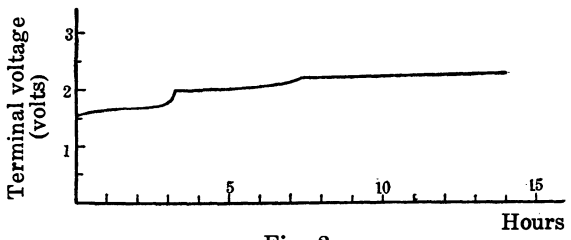


Fig. 2.

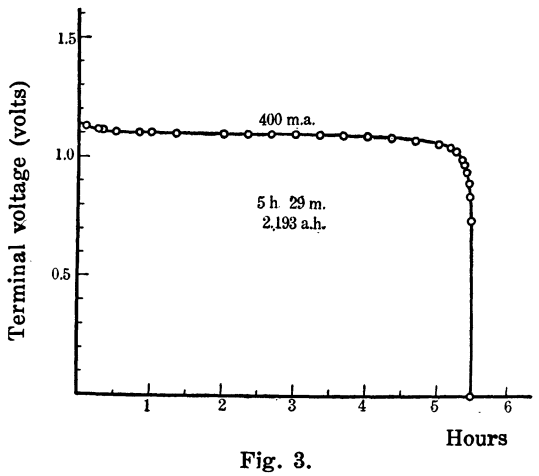


Fig. 3.

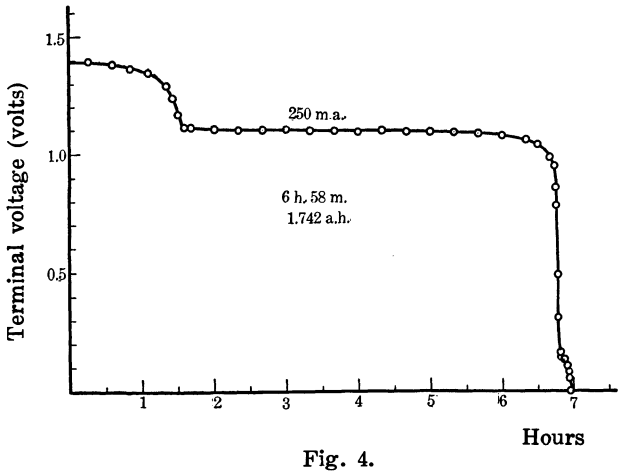


Fig. 4.

Fig. 2 is the charging curve of the positive electrode of a cell. The terminal voltage of this cell in charge rises abruptly at two points, namely at about 3.25 hours and 7.25 hours.

Fig. 3 and Fig. 4 show the discharge curves of another positive at the 1st discharge (discharge current 400 milliamperes) and the 8th discharge (discharge current 250 milliamperes) respectively.

At the first cycle of discharge, the silver oxide electrode always shows a curve of the form like Fig. 3. After repeating a few cycles of discharge the curve transforms to the form like Fig. 4. An overcharged Nife's negative was always used as the auxiliary electrode for the measurement of the terminal voltage of the electrode.

The above described change of form of the discharge curve, therefore, is considered to be due to the special feature of the silver oxide electrode.

The form of the discharge characteristic curve shown in Fig. 4 may be understood by considering that the fundamental chemical reactions (3) and (4) are involved in the electrode.

Comparison of the Silver Oxide Electrode with Lead Peroxide Positives. As already shown in Table 2 the utility coefficient of the silver oxide positive amounts to extraordinary high value in comparison with that of the positive of the lead acid cell. The coefficient of utility of the positive electrode of the lead acid cell is said to be about 25%–50% in 5 hour rate of discharge.

The capacities per 1 gram of the active materials of silver oxide and lead peroxide electrodes are plotted against the magnitude of discharge

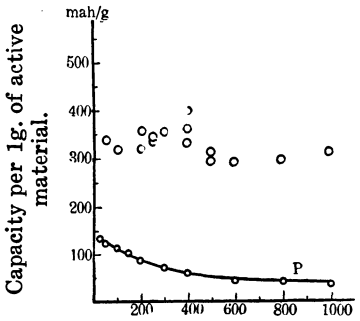


Fig. 5.

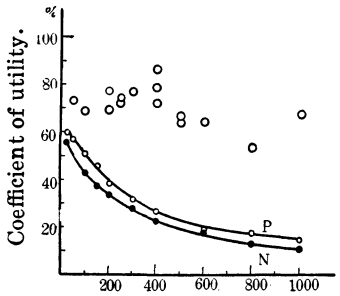


Fig. 6.

current in Fig. 5. The coefficient of utility of the active materials of these electrodes are plotted against the discharge current in Fig. 6. The points indicated by the circlets are the values for the silver oxide electrode.

The curves marked with P are the results of the positive electrodes, and the curve marked with N is the results of the negative electrode of the lead acid cell respectively.

These figures show that the capacities and the utility coefficients of the silver oxide positives are practically independent of the discharge current, and that this electrode has much higher utility coefficient than that of the electrode of lead accumulator.

The watt-hour output of the silver oxide cell and the lead acid cell are compared in Table 3. As seen in this table the watt-hour output of the silver oxide positive is greater than that of the lead peroxide positive so much as about 50%.

Table 3.

	PbO_2 electrode	Ag_2O electrode	
		Example 1	Example 2
Concentration of electrolyte	28% H_2SO_4	20% KOH	20% KOH
Discharge current	200 m. amp.	200 m. amp.	200 m. amp.
Discharge capacity	0.567 a. h.	1.580 a. h.	1.653 a. h.
Coefficient of utility	38.1%	75.2%	78.7%
Mean terminal voltage	1.908 volts	0.984 volts	0.991 volts
w. h. output	1.082 w. h.	1.555 w. h.	1.637 w. h.
Weight per unit w. h. output	6.24 g./w. h.	3.12 g./w. h.	2.96 g./w. h.

The Chemical Reaction Involved in Discharging the Silver Oxide Positive. The discharge characteristic curves of silver positive become in two stages as have already been shown in Fig. 1 and Fig. 4. This can be interpreted by the fact that the chemical reactions of the electrode proceed in two stages expressed by (3) and (4). In order to bring out this fact more clearly, the chemical analysis was made of the active material of electrode in charged state. The electrode which had been subjected to a few cycles of charge and discharge was now fully charged by the current of 200 milliamperes for 72 hours. It was, then, rinsed thoroughly with water in order to be freed from alkali, and the active material was taken out of the grid and made to powder. The sample thus obtained was dried in a deccicator for about 72 hours. The dried sample was dissolved in a small amount of dilute nitric acid and the solution was diluted to 500 c.c. and then was titrated with NH_4CNS solution according to Volhard's method.[3] The results were as follows. Dried sample taken: 5.9745 g. Content of Ag, found: 5.204 g. Ag calculated, assuming the sample to be Ag_2O_2: 5.204 g. Ag calculated, assuming the sample to be Ag_2O: 5.562 g. From this results, we see that the active material of the silver oxide positive in charged state is Ag_2O_2.

The weighed sample of the active material was heated to 120°C. until the weight becomes constant. In the process of this heating the sample changes its colour from bluish black to brown. This corresponds to the decomposition of Ag_2O_2 to Ag_2O and O_2. The brown powder was then heated to dull red heat. The colour now changes readily to silver white. These reactions are expressed by the followings.

$$Ag_2O_2 \xrightarrow{\text{above 100°C.}} Ag_2O + {}^1/_2\,O_2 \xrightarrow{\text{above 300°C.}} 2\,Ag + {}^1/_2\,O_2$$

The results of the chemical analysis are given in Table 4.

Table 4.

Heating bluish black sample to 120°C.	Sample taken		1.9174 g.
	Decrease of weight	Calculated	0.1238 g.
		Found	0.1126
	Content of Ag_2O_2 calculated from the decrease of weight		90.95%

(3) Treadwell, "Lehrbuch der analytische Chemie," II, (1927), 612.

Table 4.—(*Concluded*)

Heating brown sample to dull red.	Sample taken		1.3869 g.
	Decrease of weight	Calculated	0.0957 g.
		Found	0.1029 g.
	Content of Ag_2O calculated from the decrease of weight		107.5%
Heating bluish black sample to 120°C.	Sample taken		3.0008 g.
	Decrease of weight	Calculated	0.1937 g.
		Found	0.1925 g.
	Content of Ag_2O_2 calculated from the decrease of weight		99.33%
Heating brown sample to dull red.	Sample taken		1.3957 g.
	Decrease of weight	Calculated	0.0964 g.
		Found	0.0987 g.
	Content of Ag_2O calculated from the decrease of weight		102.4%

We will consider the relation between the chemical reactions and the utility coefficient of the electrode. Table 5 gives the utility coefficient of an electrode assuming the chemical reaction to be

$$Ag_2O_2 \rightarrow Ag_2O \rightarrow 2\,Ag$$

and

$$Ag_2O \rightarrow 2\,Ag.$$

The values always exceed 100% if they are calculated from the latter equation, while less than 100% from the former one. We know, therefore, that the active material of silver positive in charged state is composed of some higher oxide than Ag_2O.

In conclusion the author wishes to express his hearty thanks to Prof. Sameshima of the Tokyo Imperial University, and Dr. Tiku of the Toyoda Research Laboratory, for their valuable advice on this experiments.

Table 5.

Number of cycle	Discharge hour (h. m.)	Discharge capacity (a. h.)	Coeff. of utility considering chem. reaction to be $Ag_2O_2 \rightarrow 2\,Ag$	Coeff. of utility considering chem. reaction to be $Ag_2O \rightarrow Ag$
1	8.36	2.146	96.4%	192.8%
2	6.08	1.533	68.8	137.6
3	5.39	1.413	63.4	126.8
4	5.50	1.458	65 5	131.0
5	6.38	1.658	74.5	149.0
6	6.43	1.678	75.4	150.8
7	6.46	1.692	76.0	152.0
8	6.35	1.646	74.0	148.0
9	6.17	1.572	70.6	141.2
10	7.06	1.775	79.8	159.6
11	6.49	1.703	76.5	153.0
12	6.28	1.617	72.6	145.2
13	6.12	1.550	69.6	139.2
14	6.10	1.542	69.3	138.6

Summary.

(1) A cell was constructed from the silver positive and iron negative in KOH solution, and the charge and discharge curves of the positive were examined.

(2) It was known that the discharge curve runs in two steps in general, which can be interpreted by assuming that there occurs the following consecutive chemical reactions.

$$Ag_2O_2 \rightarrow Ag_2O \rightarrow 2\,Ag$$

(3) The chemical analysis of the active material of charged silver positive supports the above consideration.

(4) The coefficient of utility of the active material of the silver positive is much higher than that of the lead peroxide positive of the lead acid cell.

Toyoda Research Laboratory,
Imperial Invention Society, Shimomeguro, Tokyo.

The Addition of Hydrogen Bromide to Allyl Bromide in the Presence of Various Substances. VI. The Homogeneity of the Catalytic Action of Oxygen. A Theory of the Oxygen Effect.

By Yoshiyuki URUSHIBARA and Matsuji TAKEBAYASHI.

(Received March 31st, 1937.)

While in the absence of oxygen hydrogen bromide adds slowly to allyl bromide (free from peroxides) to give mainly 1,2-dibromopropane (the normal addition), in the presence of oxygen the addition is rapid and the product consists mainly of 1,3-dibromopropane (the abnormal addition). In last paper of this series[1] the authors established that the oxygen effect is caused by molecular oxygen, and pointed out that the next problem was to decide whether the catalytic action of oxygen is homogeneous or heterogeneous.

Kharasch and Mayo[2] observed that the addition of hydrogen bromide to allyl bromide is not influenced by the presence of broken glass pieces and glass wool, showing the reaction is homogeneous. The present authors have confirmed the homogeneity of this reaction by repeating similar experiments.

The ferro-magnetic metals influencing the addition of hydrogen bromide to allyl bromide similarly to oxygen are obviously heterogenous catalysts, because they remain undissolved and unchanged after reaction.

To see whether the active catalyst is dissolved oxygen or adsorbed oxygen the following experiments were carried out. Two Pyrex tubes (capacity about 140 c.c., inner surface area about 280 sq. cm.), one containing a few thin Pyrex tubes with a total surface measuring about 110 sq. cm., were charged each with 24 g. of allyl bromide and 20 g. of hydrogen bromide and 1.5 c.c. of oxygen was admitted at sealing after evacuation. The tubes were placed in the dark at room temperature for three days. They were not shaken but moved now and then. The two additions were effected simultaneously. The total yields of addition (41% for smaller surface area and 43% for greater surface area) and the compositions of the products (1,3-dibromopropane 95% for both) were the same. If oxygen adsorbed on the wall were the active catalyst, a greater

(1) This Bulletin, **12** (1937), 138.
(2) *J. Am. Chem. Soc.*, **55** (1933), 2490.

yield would be expected for the greater surface area in contact with the reacting liquid. But the two experiments resulted similar, thus demonstrating that dissolved oxygen is the active catalyst.

In this way the catalysis by oxygen has been shown to be homogeneous. As recorded in the fifth paper[1], when the amount of oxygen is 1.5 c.c. for 24 g. of allyl bromide and 20 g. of hydrogen bromide in the reaction tube with a capacity 135–140 c.c., the proportion of 1,3-dibromopropane in the product reaches 95%, and any further increase in the amount of oxygen causes no more change in the composition of the product. Even under the assumption that all the oxygen admitted were dissolved in the liquid, 1.5 c.c. correspond to only one molecule of oxygen against 3000 molecules of allyl bromide. How can such a comparatively small amount of oxygen influence so radically the addition of hydrogen bromide to allyl bromide?

The simplest explanation of the oxygen effect might be that oxygen would accelerate the abnormal addition only, say by means of chemical intervention, the normal addition being uninfluenced but conditioned only by the concentrations of the reacting substances. But then it is difficult to reconcile the following findings: The total yield obtained with 1.5 c.c. of oxygen admitted is not more than two to three times that in vacuum in three days' reaction, and in vacuum more than 90% of the product is 1,2-dibromopropane, while, in the presence of oxygen, as much as 95% is 1,3-dibromopropane, although the normal and the abnormal additions might be considered to proceed simultaneously with not very different velocities. Further the proportion of 1,3-dibromopropane should approach asymptotically a certain value as the amount of oxygen increases, whereas the curves obtained are of a quite different type (see the figures of the fifth paper). Moreover, such an explanation can not be compatible with the fact that the total yield of addition increases with the amount of oxygen admitted even after the proportion of 1,3-dibromopropane has reached the constant maximal value (95%): The absolute yield of 1,2-dibromopropane decreases rapidly as the amount of oxygen increases until the latter reaches 1.5 c.c. and thence increases in the same rate as that of 1,3-dibromopropane.

The assumption of a double action of inhibiting the normal addition and accelerating the abnormal addition is none the less inconsistent with the fact, inasmuch as the yield of 1,2-dibromopropane does not keep on decreasing as oxygen increases.

The relation between the amount of oxygen present and the result of addition can be understood if the addition catalysed by oxygen yields

95% 1,3-dibromopropane and 5% 1,2-dibromopropane and in the presence of a sufficient amount of oxygen (1.5 c.c. under the conditions of the experiments) the catalysed addition only takes place.

Thus the authors have been led to advance a theory on the oxygen effect. It is assumed that the oxygen molecule exerts some physical influence on a great number (at least 3000) of molecules of allyl bromide around it. The oxygen molecule may possess a considerably large sphere of influence capable of holding more than 3000 molecules of allyl bromide and a corresponding number of molecules of hydrogen bromide. Otherwise it may influence molecules of allyl bromide colliding with, or coming near to, it, the influenced molecules of allyl bromide keeping their influenced state for a considerably long period—there exist always more than 3000 influenced molecules of allyl bromide per one molecule of oxygen. If allyl bromide has been influenced at all by oxygen in either way, hydrogen bromide adds rapidly to it, 95% of the influenced allyl bromide being transformed into 1,3-dibromopropane and 5% into 1,2-dibromopropane, and thus both dibromopropanes being formed from the influenced molecules of allyl bromide in the presence of a sufficient amount of oxygen. The strength or the freshness of the oxygen influence affects only the rate of addition.

The theory explains satisfactorily the results recorded in the fifth paper: When about 1.5 c.c. of oxygen is admitted under the conditions of the experiments, the whole liquid is just filled with such spheres of influence or all the molecules of allyl bromide exist in the influenced state, and the proportion of 1,3-dibromopropane in the product is 95%. An increase in the amount of oxygen augments the strength or the freshness of the oxygen influence, and an increase in the total yield of the addition is obtained without any further appreciable change in the composition of the product.

It may be considered that the effect of the ferro-magnetic metals is caused by a similar influence. That the normal addition is far inhibited by the presence of these heterogeneous catalysts can not be explained except by the above-mentioned theory. But, the metals are very coarsely divided compared with the dissolved oxygen, and, therefore, their influence must be very strong compared with that of oxygen, corresponding to a very large sphere of influence or to a very long preservation of the influenced state on the part of allyl bromide.

The influence exerted by oxygen and the ferro-magnetic metals is considered to be related closely to the great magnetic susceptibilities with which these substances are endowed. What change occurs in the molecule

of allyl bromide under the influence of oxygen and the ferro-magnetic metals is unknown, but it can be said that the ordinary form preferring the normal addition is changed into an extraordinary form preferring the abnormal addition.

The theory advanced by the authors explains satisfactorily the effect of oxygen and the ferro-magnetic metals on the addition of hydrogen bromide to allyl bromide. Nevertheless, it may be open to question that the authors have taken it for granted that oxygen and the ferro-magnetic metals have nothing to do with hydrogen bromide, because hydrogen bromide could take the place of allyl bromide in the theory stated above. Further experiments are required before it can be decided whether the substance to be influenced by oxygen and the ferro-magnetic metals is allyl bromide or hydrogen bromide.

In conclusion the authors express their hearty thanks to the Imperial Academy of Japan for a grant. They are also indebted to Prof. M. Katayama and Prof. S. Mizushima for valuable suggestions.

Chemical Institute, Faculty of Science,
Imperial University of Tokyo.

Cryoscopic Studies on the Transition Points of the Compounds of Organic Solvents with Salts. III. The Congruent Melting Points of some Alcoholates of Alkali Halides.

By Hazime OOSAKA.

(Received April 12th, 1937.)

In previous papers[1][2] certain transition points at which the solid solvate melted to form the anhydrous salt and a solution saturated with this salt were cryoscopically studied and it was shown that this temperature was lowered by the addition of foreign substances according to the following relation,

$$\Delta T = K\frac{100w}{WM}, \qquad (1)$$

where ΔT is the depression of the transition point, K the molecular depression referred to 100 g. of the pure solvent, w the weight of a foreign substance dissolved in W g. of the pure solvent and M the molecular weight of the foreign substance. The constant K referred to 100 g. of the pure solvent was preferred to that referred to 100 g. of the solvate corresponding to the experimental procedure.

In a number of systems there exists a congruent melting point at which a solid solvate melts completely and yields a liquid of the same composition as the crystalline solvate. This temperature may be also considered as a transition point for the alcoholate and its melt. The lowering of the congruent m. p. by the addition of foreign substances has been similarly investigated on the systems formed by alcohols and alkali halides: LiCl–CH_3OH, LiCl–C_2H_5OH, LiBr–C_2H_5OH, and LiBr–*n*-C_3H_7OH, and the results are given in the present communication.

The Solubilities of the Systems and the Congruent Melting Points. In the present systems the forms of the solubility curves exhibit a close parallelism to each other and the general type is shown by the diagrammatic curve in Fig. 1. The solubility curve of the alcoholate ABC possesses a retroflex region, represented in the figure by BC. The point B is the congruent m.p. The solubility of the anhydrous salt changes

(1) H. Oosaka, this Bulletin, **3** (1928), 289.
(2) H. Oosaka, *Sci. Repts. Tokyo Bunrika Daigaku*, A, **1** (1933), 241.

only slowly with temperature and its curve CD cuts the curve ABC at the point C. This point is the transition or eutectic point for the alcoholate and the anhydrous salt.

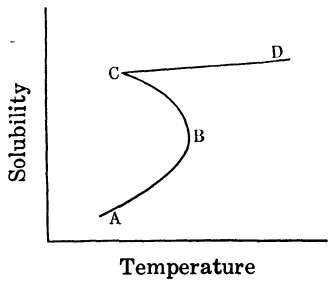


Fig. 1.

The system LiCl–CH_3OH. Simon[3] observed the existence of the solid alcoholate $LiCl \cdot 3CH_3OH$. The solubility curve of the anhydrous salt was determined by Lloyd, Brown, Bonnell and Jones,[4] and they described the transition point as 0.1°C. The solubility of the alcoholate had not been found so that the author made the preliminary determination and redetermined the solubility of the anhydrous salt.[5] The results showed that the congruent m.p. (B in Fig. 1.) coincided approximately with the transition point (C in Fig. 1.) and was 12.9°C.

The system LiCl–C_2H_5OH. The solubilities of the alcoholate $LiCl \cdot 4C_2H_5OH$ and the anhydrous salt were determined by Turner and Bissett,[6] the existence of the crystalline alcoholate being confirmed by them. Their solubility curve of the alcoholate possesses a retroflex portion, but they did not describe this behaviour. From their curve about 18°C. can be read as the congruent m.p. By the cryoscopic determination of the author this point was found to lie at 20.5°C.

The system LiBr–C_2H_5OH. Turner and Bissett[7] observed the existence of the alcoholate $LiBr \cdot 4C_2H_5OH$ and Bonnell and Jones[8] determined the solubility curves of the alcoholate and the anhydrous salt. The congruent m.p. was 23.8°C.

The system LiBr–*n*-C_3H_7OH. The solubilities of the system are not found in the literature, but the existence of the alcoholate $LiBr \cdot 4n\text{-}C_3H_7OH$ was confirmed by Turner and Bissett.[7] The author determined preliminarily the solubilities and obtained the transition point as about 7°C., and the congruent m.p. as 35.8°C.

---

(3) S. E. Simon, *J. prak. Chem.*, **20** (1879), 371.
(4) E. Lloyd, C. B. Brown, D. G. R. Bonnel and W. F. Jones, *J. Chem. Soc.*, **1928**, 658.
(5) The preliminary determination of solubility was carried out on the systems LiCl-CH_3OH and LiBr-*n*-C_3H_7OH, but the results are not given here.
(6) W. E. S. Turner and C. C. Bissett, *J. Chem. Soc.*, **103** (1913), 1904.
(7) W. E. S. Turner and C. C. Bissett, *ibid.*, **105** (1914), 1777.
(8) D. G. R. Bonnel and W. J. Jones, *ibid.*, **1926**, 318.

Apparatus and Method of Procedure.

The apparatus used was similar to that already described.[2] A solution having the composition of the alcoholate was prepared from the pure alcohol and the anhydrous salt in a freezing-point tube with proper precaution against moisture. The tube was placed in the air-jacket immersed in a cooling bath at a temperature about 5°C. below the m.p. When the solution supercooled and the solid alcoholate commenced to separate out without induced by infection, the tube was transferred to the other air-jacket immersed in a thermostat at a temperature of 0.3–0.5°C. below the m.p. and the constant highest temperature was observed by a Beckmann thermometer. In certain cases, however, some crystals of the alcoholate were allowed to remain on melting the solid phase after each measurement and then used as nuclei for crystallisation in the following freezing. After the m.p. of the pure alcoholate was determined, a foreign substance was added into the solution and the same procedure was carried out. Since the molten alcoholate prepared was slightly turbid because of minute amounts of the suspended particles, centrifuging was in some cases applied to it. The clear solution thus obtained showed, however, the same result for the cryoscopic determination.

Preparation of Materials.

Alcohols. With the exception of ethyl alcohol these were dehydrated by aluminium amalgam.[9] The dehydration of ethyl alcohol was carried out by the method of Adickes,[10] using metallic sodium and ethyl formate.

Lithium chloride. Merck's salt was recrystallised from water as hydrate and was dehydrated by heating at 120–130°C.

Lithium bromide. This salt was prepared by the neutralisation of hydrobromic acid with lithium carbonate and then dehydrated at 130°C.

Other substances were purified by ordinary methods.

Experimental Results.

The system LiCl–CH_3OH. The solution of the composition $LiCl \cdot 3CH_3OH$ was liable to supercooling and the freezing commenced almost always at temperatures below −10°C., much lower than the congruent m.p. 12.9°C. Owing to this fact care was taken not to lose completely the crystalline alcoholate during the cryoscopic experiment.

(9) R. F. Brunel, J. L. Crenshaw and E. Tobin, *J. Am. Chem. Soc.*, **43** (1921), 561.
(10) F. Adickes, *Ber.*, **63** (1930), 2753.

The molecular depressions for 100 g. of the pure alcohol were determined using water and acetone as solutes and the values 38 and 39 were obtained respectively.

The system LiCl–C_2H_5OH. The lowering of the congruent m.p. was measured for the following eight solutes and the constant K was calculated by the relation (1). The results are given in Tables 1 to 7.

Table 1. Solute: Water, mol. wt. = 18.

Weigt of alcohol W in g.	Weight of solute w in g.	Observed lowering of temperature ΔT in °C.	Molecular depression K
31.8	0.159	1.275	45.9
31.7	0.191	1.506	45.0
32.1	0.220	1.733	45.5
32.0	0.273	2.135	45.0
26.4	0.290	2.757	45.3

Mean: 45.3

Table 2. Solute: Acetone, mol. wt. = 58.

W	w	ΔT	K
31.8	0.346	0.851	45.4
25.7	0.347	1.059	45.5
31.9	0.452	1.102	45.1

Mean: 45.3

Table 3. Solute: Acetanilide, mol. wt. = 135.

W	w	ΔT	K
23.8	0.346	0.491	45.6

Table 4. Solute: Camphor, mol. wt. = 152.

W	w	ΔT	K
31.7	0.348	0.329	45.6
31.7	0.532	0.499	45.2
32.1	0.814	0.752	45.1

Mean: 45.3

Table 5. Solute: Carbon tetrachloride, mol. wt. = 154.

W	w	ΔT	K
31.7	0.765	0.690	44.0
31.3	0.886	0.803	43.7
31.8	0.971	0.864	43.6
33.1	1.459	1.271	44.4

Mean: 43.9

Table 6. Solute: Benzene, mol. wt. = 78.

W	w	ΔT	K
32.1	0.361	0.641	44.5
32.1	0.412	0.717	43.6
32.2	0.457	0.794	43.6
32.1	0.660	1.134	43.0

Mean: 43.7

Table 7. Solute: Toluene, mol. wt. = 92.

W	w	ΔT	K
31.9	0.320	0.481	44.1
32.6	0.470	0.674	43.0
32.5	0.694	0.989	42.6
31.6	0.675	1.004	43.2
31.6	0.715	1.046	42 5

Mean: 43.1

As shown in Tables 5 to 7 non-polar liquids give a little lower values for the constant K. This behaviour may be, as previously described,[2] qualitatively interpreted as follows. The polarity of solute affects the activity of the solvent alcohol and thus on the dissolution of non-polar substances the decrease of this activity is smaller than in the case of polar solutes.

The system LiBr–C_2H_5OH. The molecular depression was determined quite similarly to the foregoing system. The supercooling was less than 1°C. The results are given in Tables 8 to 12.

Table 8. Solute: Water, mol. wt. = 18.

W	w	ΔT	K
31.1	0.046	0.493	60.0
31.6	0.078	0.778	56.8
31.8	0.200	2.023	57.9

Mean: 58.2

Table 9. Solute: Acetone, mol. wt. = 58.

W	w	ΔT	K
31.4	0.284	0.900	57.7
24.9	0.309	1.217	56.9

Mean: 57.3

Table 10. Solute: Benzoic acid, mol. wt. = 122.

W	w	ΔT	K
31.5	0.117	0.181	59.4

Table 11. Solute: Carbon tetrachloride, mol. wt. = 154.

W	w	ΔT	K
31.5	0.647	0.647	55.3
31.9	1.279	1.428	54.8

Mean: 55.1

Table 12. Solute: Benzene, mol. wt. = 78.

W	w	ΔT	K
31.4	0.245	0.553	55.3
31.5	0.446	0.992	54.7

Mean: 55.0

As shown in Tables 11 and 12 non-polar solutes give a little lower constants as in the foregoing system.

The system LiCl–n-C_3H_7OH. The equilibrium at the congruent m.p. was less stable in comparison with the other systems and the influence of supercooling was greater. Thus the results were somewhat irregular.

Table 13. Solute: Acetone, mol. wt. = 58.

W	w	ΔT	K
33.1	0.251	0.79	60.4
32.8	0.321	1.02	60.5
27.7	0.564	1.96	55.8

Mean: 58.9

Table 14. Solute: Water, mol. wt. = 18.

W	w	ΔT	K
33.1	0.122	1.10	53.7
25.3	0.211	2.48	53.5
32.8	0.293	2.76	55.6

Mean: 54.3

Table 15. Solute: Nitrobenzene, mol. wt. = 123.

W	w	ΔT	K
32.9	0.623	0.91	58.5
32.7	0.654	0.94	57.8

Mean: 58.2

The lower value for water cannot be explained only by these data. This will be discussed after more data are obtained.

Calculation of the Heat of Fusion from the Cryoscopic Constant.

It was shown before[1] that the molecular depression of the transition point at which a crystalline solvate melted to form the anhydrous salt and a saturated solution with regard to this salt could be expressed by the following equation,

$$K = \frac{RT^2}{H}\frac{nM_0}{100}\frac{c}{c+i}, \qquad (2)$$

where R denotes the gas constant, T the absolute transition point, H the heat of fusion per mol of the solvate, n the number of mols of the solvent per mol of the salt in the solvate, M_0 the molecular weight of the pure solvent, c the number of mols of the solvent per mol of the salt in the solution, and i the van't Hoff factor. This factor may be assumed as unity because of the high concentration and the previous result[11] of the vapour pressure determination of the similar system.

In the present case the molten solvate has the same composition as that of the solvate and c is equal to n. Therefore (2) becomes,

(11) H. Oosaka, *Bull. Inst. Phys. Chem. Research* (Tokyo), **10** (1931), 466; Abstracts therefrom, **4** (1931), 48.

$$K = \frac{RT^2}{H}\frac{M_0}{100}\frac{n^2}{n+1}. \qquad (3)$$

Taking the probable value of the constant for polar solutes the heat of fusion was calculated and the results are given in Table 16.

Table 16.

Alcoholate	Congruent m.p. °C.	Molecular depression		Heat of fusion	
		K	$\overline{K}$	kcal. per mol	cal. per g.
$LiCl{\cdot}3CH_3OH$	12.9	38	55	3.08	22.2
$LiCl{\cdot}4C_2H_5OH$	20.5	45	55	5.60	24.7
$LiBr{\cdot}4C_2H_5OH$	23.8	58	85	4.44	16.4
$LiBr\ 4n\text{-}C_3H_7OH$	35.8	58	79	6.28	19.2

The values of the cryoscopic constant $\overline{K}$ referred to 100 g. of the solvate are also included in the table for referrence. These were obtained by multiplication of K with $\overline{M}/nM_0$, $\overline{M}$ being the molecular weight of the solvate.

The Abnormal Molecular Depressions when Homologous Alcohols are dissolved as Foreign Substances.

When homologous alcohols were used as solutes in the cryoscopy, abnormally low values of the molecular depression were obtained. The results are given in Tables 17 to 27.

The system $LiCl\text{-}CH_3OH$.

Table 17.

Solute	W	w	ΔT	K
C_2H_5OH	24.6	0.601	1.76	33.1
$n\text{-}C_3H_7OH$	23.9	0.490	1.22	35.7
$n\text{-}C_4H_9OH$	23.9	0.336	0.69	36.3
$iso\text{-}C_5H_{11}OH$	23.1	0.462	0.82	36.1

The system $LiCl\text{-}C_2H_5OH$.

Table 18. Solute: Methyl alcohol, mol. wt. = 32.

W	w	ΔT	K
32.0	0.138	0.473	35.1
31.4	0.421	1.494	35.7
32.1	0.685	2.378	35.7

Mean: 35.5

Table 19. Solute: *n*-Propyl alcohol, mol. wt. = 60.

W	*w*	*ΔT*	*K*
32.1	0.479	0.713	28.7
22.7	0.469	0.953	27.7
31.5	0.660	0.972	27.8
31.9	0.822	1.190	27.7
31.1	0.990	1.534	28.9
24.6	0.914	1.677	27.1
25.0	1.124	2.108	28.1

Mean: 28.0

Table 20. Solute: *n*-Butyl alcohol, mol. wt. = 74.

W	*w*	*ΔT*	*K*
32.7	0.205	0.371	43.8
32.3	0.450	0.835	44.4
33.9	0.494	1.230	44.0
32.3	0.648	1.240	45.7

Mean: 44.5

Table 21. Solute: iso-Amyl alcohol, mol. wt. = 88.

W	*w*	*ΔT*	*K*
31.2	0.197	0.317	44.2
31.6	0.462	0.755	45.4
25.3	0.607	1.268	46.5
31.4	0.803	1.364	46.9
24.0	0.982	2.139	46.0

Mean: 45.8

The system LiBr-C_2H_5OH.

Table 22. Solute: Methyl alcohol, mol. wt. = 32.

W	*w*	*ΔT*	*K*
31.5	0.150	0.620	41.7
31.4	0.278	1.142	41.3

Mean: 41.5

Table 23. Solute: *n*-Propyl alcohol, mol. wt. = 60.

W	*w*	*ΔT*	*K*
23.7	0.433	0.430	14.1
25.0	0.648	0.648	15.0
31.4	1.040	0.789	14.3
31.4	1.172	0.917	14.7
21.9	0.936	0.971	13.6

Mean: 14.3

Table 24. Solute: iso-Propyl alcohol, mol. wt. = 60.

W	*w*	*ΔT*	*K*
32.3	0.416	0.689	32.1
31.8	0.473	0.774	31.2

Mean: 31.7

Table 25. Solute: *n*-Butyl alcohol, mol. wt. = 74.

W	*w*	*ΔT*	*K*
32.3	0.411	0.890	51.8

Table 26. Solute: iso-Amyl alcohol, mol. wt. = 88.

W	*w*	*ΔT*	*K*
25.7	0.361	0.889	55.7
31.5	0.473	0.983	57.6
24.3	0.613	1.659	57.9

Mean: 57.1

The system LiBr-*n*-C_3H_7OH.

Table 27.

Solute	*W*	*w*	*ΔT*	*K*
CH_3OH	26.5	0.481	2.70	47.6
C_2H_5OH	21.9	0.286	0.50	17.6
C_2H_5OH	32.1	0.861	1.06	18.2
n-C_4H_9OH	27.3	0.487	0.93	38.7
iso-$C_5H_{11}OH$	27.5	0.579	1.23	51.4

Consideration on the Anomalous Depression.

The results for the abnormal depression are summarized in Table 28.

Table 28.

Solute	Solvent			
	$LiCl\text{-}CH_3OH$	$LiCl\text{-}C_2H_5OH$	$LiBr\text{-}C_2H_5OH$	$LiBr\text{-}C_3H_7OH$
CH_3OH	Solvent	36	42	48
C_2H_5OH	33	Solvent	Solvent	18
$n\text{-}C_3H_7OH$	36	28	14	Solvent
iso-C_3H_7OH	--	—	32	—
$n\text{-}C_4H_9OH$	36	45	52	39
iso-$C_5H_{11}OH$	36	46	57	51
The normal value	38	45	58	58

It is clearly seen from the table that the anomaly becomes greater as the molecular weight of the solute alcohol approaches to that of the solvent alcohol. This anomaly may be accounted for by assuming that the solute alcohol forms a solid solution with the solid solvate, and can be formulated by considering vapour pressures of the system. In Fig. 2 the curves AC and BC show the vapour pressures of the pure solid alcoholate and its melt respectively, both dissociating to the anhydrous salt and alcohol vapour. The curve DE represents the vapour pressure of the solid solution and AE that of the liquid solution when a solute forming a solid solution is added to the system. The point C is the congruent m.p. of the pure alcoholate, E the m.p. of the solid solution, hence EF the depression of the m.p. ΔT, AD the depression of vapour pressure for the solid solution Δp_1, and AB that for the liquid solution Δp_2. If one mol of the solid solution contains n_1 mols of the solute alcohol and one mol of the liquid solution n_2 mols, then according to the Raoult's law

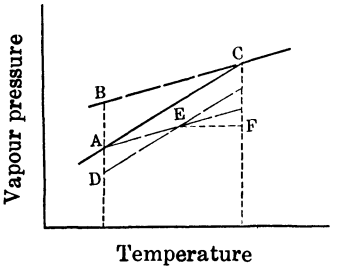


Fig. 2.

$$\Delta p_1 = n_1 p\,, \qquad \text{and} \qquad \Delta p_2 = n_2 p\,,$$

where p is the vapour pressure of the system at the m.p. Considering the geometrical relations of the figure over an infinitesimal range and applying the Clapeyron-Clausius equation the following relation is obtained,

$$n_2-n_1 = \Delta T \frac{q_1-q_2}{RT^2} , \tag{4}$$

where q_1 and q_2 are the molar heats of evaporation of alcohol from the alcoholate and the melt respectively. As the molar heat of fusion H can be represented by the following expression,[1]

$$H = n(q_1-q_2) ,$$

and hence (4) becomes

$$\Delta T = (n_2-n_1)\frac{nRT^2}{H} . \tag{5}$$

When the melt contains w g. of the solute alcohol per W g. of the solvent alcohol,

$$n_2 = \frac{M_0 w}{WM}\left(\frac{n}{1+n}\right) . \tag{6}$$

This relation is approximate but may hold within the experimental error because of the low concentration of the solute alcohol.

If r represents the partition coefficient of the solute alcohol between the liquid and solid solutions, and the solute has the same molecular weight in each phase,

$$r = n_1/n_2 . \tag{7}$$

The constancy of the values of r can be seen from that of the values of K indifferent to the concentration. By using (6) and (7), (5) becomes

$$\Delta T = (1-r)\left(\frac{RT^2}{H}\frac{M}{100}\frac{n^2}{1+n}\right)\frac{100w}{WM} ,$$

where the term in the second brackets is the normal constant K already referred to. If the cryoscopic constant in the abnormal case is K', then

$$K' = (1-r)K .$$

In order to test this relation experimentally, tetra-alcoholate of lithium chloride as solvent and n-propyl alcohol as solute were chosen

and the constant r was determined by measuring the concentrations of the solute alcohol in the liquid and solid phases in equilibrium, using a Zeiss water-interferometer. This experiment accompanied some difficulties on account of the similarity of the alcohols, the small concentration of the solute alcohol and the existence of salt in the solution, and besides the separation of both phases was not complete. The results were accordingly not very accurate but the value of r thus observed was in approximate accordance with the value calculated from the values K and K' which were in turn determined by the cryoscopic experiment.

Summary.

(1) The lowerings of the congruent melting points of the alcoholates: $LiCl \cdot 3CH_3OH$, $LiCl \cdot 4C_2H_5OH$, $LiBr \cdot 4C_2H_5OH$, and $LiBr \cdot 4n\text{-}C_3H_7OH$ by the addition of foreign substances have been measured and the molecular depressions referred to 100 g. of each alcohol have been determined.

(2) From these cryoscopic constants the heats of fusion of the alcoholates have been calculated.

(3) When homologues of the solvent alcohol have been used as solutes, abnormally low values have been obtained for the cryoscopic constant. This discrepancy may be considered as due to the formation of a solid solution between the alcoholate and the solute alcohol and this fact has been semi-quantitatively verified.

In conclusion the author expresses his hearty thanks to Professor M. Katayama for his continued interest and advice throughout this series of research. Thanks are also due to Professor I. Wada for giving to the author facilities for carrying out this work.

Chemical Laboratory, Tokyo Bunrika University,
Koishikawa, Tokyo.

On the Relation between the Configuration of Metallic Complex Salts and their Absorption Spectra.[1]

By Hideo SUEDA.

(Received April 24th, 1937.)

Introduction. Many valuable but qualitative conclusions on the absorption spectra of metallic complex salts have already been obtained by Y. Shibata[2]. By means of quantitative studies, R. Luther and A. Nikolopulos[3], R. I. Colmar and F. W. Schwartz[4] and A. Mead[5] have also found that whenever a certain substitution occurs in a complex radical, a constant change of the maximum absorption is consequently produced. But, as these authors did not take notice of the position of those substituents, their point of view cannot generally apply to all complex salts. I. Lifschitz[6], expressing his interest in his work about the relation between the absorption and the stereoisomer, could not obtain any conclusion on it. A. Uspenski and A. Bamdas[7] have recently measured the absorption of some isomers, and have only reported that the position of maximum absorption of cis-salts corresponds to that of the minimum absorption of trans-salts. In fact, no papers have as yet appeared in which the absorptions of complexes were quantitatively discussed with a stereochemical consideration.

Thereupon, it seemed very interesting to the author to study this question. In the present research, I have found a new relation between the configuration of nitro-ammine-cobaltic salts and their absorption spectra, and have applied it to the other series of complex salts.

Nitro-ammine-cobaltic complex salts. As these salts are comparatively stable and prepared in a pure state forming a most perfect series of compounds, they are the best materials for the author's purpose of study. Although their absorption spectra have been individually

(1) Summarized the author's two reports already published in Japanese: *J. Chem. Soc. Japan*, **57** (1936), 406, 542.
(2) Y. Shibata, *J. Coll. Sci., Tokyo Imp. Univ.*, **37** (1915), Art. 2.
(3) *Z. physik. Chem.*, **82** (1913), 361.
(4) *J. Am. Chem. Soc.*, **54** (1932), 3204.
(5) *Trans. Faraday Soc.*, **30** (1934), 1053.
(6) "Spektroskopie u. Kolorimetrie", 2. Aufl., 228 (1927).
(7) *Trans. Inst. Pure Chem. Reagents* (U.S.S.R.), No. 13 (1933), 48; *Chem. Abstracts*, **27** (1933), 4736.

measured by many authors[8], only Y. Shibata has studied all nitro-compounds of the series. H. Ley and Y. Shibata have discovered that *trans*-dinitro-tetrammine-cobaltic salts have an absorption band at 4000 mm.$^{-1}$ of the wave number, i.e. the third band, that is wanted in the cis-isomers. Y. Shibata has also indicated that two of the nitro-radicals in trinitro-triammine- and tetranitro-diammine-cobaltic salts must occupy the trans-position on account of the existence of this third band. Still, I have studied on the absorption band in the neighbourhood of 320–350 mμ of wave length, i.e. the second band, and have found that this band changes owing to the position and the number of nitro-radicals in the complex salts.

Comparison of the absorption curves[9]. (1) $[Co(NH_3)_5(NO_2)]Cl_2$ and *cis*-$[Co(NH_3)_4(NO_2)_2]Cl$. The absorption curves of both salts (curves A and B in Fig. 1) are similar except in their extinction coefficients: both have their maximum absorption at 325 mμ of wave length. The comparison of their extinction coefficient shows that the absorption power of *cis*-$[Co(NH_3)_4(NO_2)_2]Cl$ is about double that of $[Co(NH_3)_5(NO_2)]Cl_2$. This absorption curve of pentammine-salt is different from that given in the paper of R. Samuel[8], but similar to that of $[Co(NH_3)_5(NO_2)]SO_4$ obtained by R. Samuel and M. Uddin[10].

(2) *cis*-$[Co(NH_3)_4(NO_2)_2]Cl$ and *trans*-$[Co(NH_3)_4(NO_2)_2]Cl$. The maximum absorption of these salts is different from each other, i.e. that of cis-salt is found at 325 mμ showing $\log \varepsilon = 3.46$ (ε denotes an extinction coefficient) at this wave length, but the trans-salt (curve C in Fig. 1) gives its maximum absorption at 347 mμ and $\log \varepsilon = 3.55$ at that wave length. The trans-salt is more hyperchromic and more bathochromic than the cis-salt, and this is analogous to the Ley's curves measured qualitatively. In spite of the difference of position and intensity of the absorption bands, both absorptions are found to be almost coincident at 270–280 mμ of wave length[11].

(3) $[Co(NH_3)_3(NO_2)_3]$. This salt has the maximum absorption near 340 mμ of wave length where $\log \varepsilon$ is 3.65 (curve D in Fig. 1). For

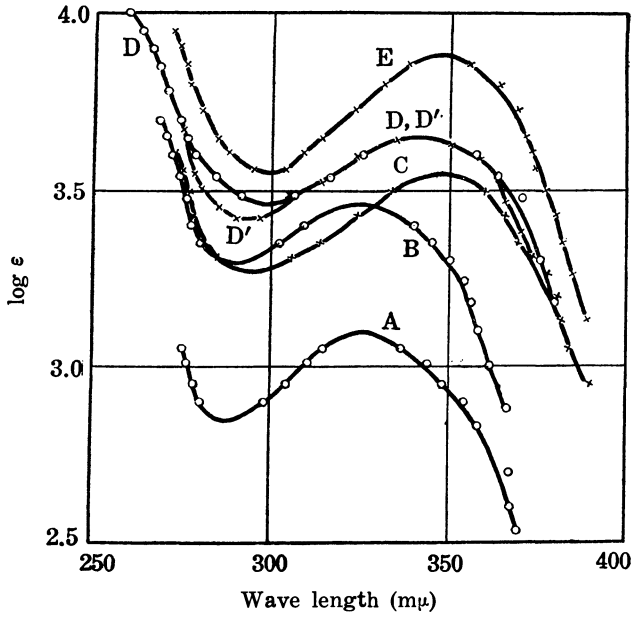
(8) A. Hantzsch, *Z. physik. Chem.*, **70** (1910), 372; H. Ley and H. Winkler, *Ber.*, **45** (1912), 372; A. Piutti, *Ber.*, **45** (1912), 1830; R. Luther and A. Nikolopulos, *Z. physik. Chem.*, **82** (1913), 361; Y. Shibata, *J. Chem. Soc. Japan*, **30** (1915), 1243; R. Samuel, *Z. Physik*, **70** (1931), 43.

(9) Measured by the author, this Bulletin, **12** (1937), 71.

(10) *Trans. Faraday Soc.*, **31** (1935), 423.

(11) The author thinks that the electric valencies of complex ions have a certain relation with their absorption which exists in their shorter wave length as in this case. Refer also to the paper: T. Uemura and H. Sueda, this Bulletin, **10** (1935), 267.

a reason which will be explained later, I have arbitrarily selected fifteen wave lengths between 275 mμ and 380 mμ by using the absorption coefficients of *trans*-$[Co(NH_3)_4(NO_2)_2]Cl$ and that of $[Co(NH_3)_5(NO_2)]Cl_2$, and the extinction coefficients corresponding to these selected wave lengths were added to form a curve D′ in Fig. 1. Curve D′ is therefore traced



A $[Co(NH_3)_5(NO_2)]Cl_2$
B *cis* $[Co(NH_3)_4(NO_2)_2]Cl$
C *trans* $[Co(NH_3)_4(NO_2)_2]Cl$
D $[Co(NH_3)_3(NO_2)_3]$
D′ A+C
E K $[Co(NH_3)_2(NO_2)_4]$

Fig. 1.

by mixing one mol of each salt, and it should be assumed as a curve expressing one mol. Curves D and D′ in Fig. 1 show a good coincidence in the position and the intensity of the absorption band, but a slight difference can be seen only in the shorter wave length below 300 mμ.

(4) *trans*-$[Co(NH_3)_4(NO_2)_2]Cl$ and $K[Co(NH_3)_2(NO_2)_4]$. The curves given by these two salts are similar except their absorption power: both have the maximum absorption at 347 mμ. The relation of the absorption powers shown by both salts is perfectly the same as in case (2), i.e. the absorption power of $K[Co(NH_3)_2(NO_2)_4]$ is double that of *trans*-$[Co(NH_3)_4(NO_2)_2]Cl$.

Discussion. It is generally accepted that an absorption of the co-ordinatedly saturated complex ion is due to a mutual action produced between a central ion and co-ordinated atomic groups. In the above comparison, cobalt is selected as the central atom and only ammonia molecules and nitro-radicals are co-ordinated in the complex ion, so the difference which occurs in the absorption can be considered in connection with the configuration of complex ions, whatever the mechanism of the light absorption may be. It is convenient to say that the absorption capacity due to the ammonia molecules which are co-ordinated with cobalt atom is very weak in comparison with that of nitro-radicals, i.e. the extinction coefficient of the maximum absorption given by $[Co(NH_3)_6]Cl_3$ is only about 40 (at 336 mμ) [12], while that given by $[Co(NH_3)_5(NO_2)]Cl_2$, the weakest absorbent of nitro-ammines, expresses 1260 (at 325 mμ). As an additivity can apply to the intensity of light absorption, an absorption given by nitro-ammine-cobaltic salts may be supposed only with the nitro-radicals, in neglecting the influences due to ammonia molecules.

According to Werner's co-ordination theory, we can safely conclude that any groups co-ordinated with the hexacovalent central ion can have no positions but cis and trans.

In comparison (1), the complex ion containing two nitro-radicals in cis-position shows that its absorption band is situated almost similarly to that given by the complex which has only one nitro-radical, but the absorption capacity of the former is nearly double that of the latter. In this case, no change on the position of the absorption band and the increase in extinction coefficients can tell me that the mutual actions between the cis-co-ordinated groups are themselves so weak that they are negligible. It is also true that the action upon the central atom of two co-ordinated groups which occupy cis-position is nearly identical when the groups is alone in a complex radical, and they show only the additivity. An analogous case can be found in organic dyes which contain several identical chromophores in the molecule, and these chromophores cannot be supposed to react one upon another from the constitution. J. D. Piper and W. R. Brode[13] have recently reported that, in such a case, the absorption band does not change its position, and its absorption capacity is increased in proportion to the number of chromophores.

From comparison (2), when two nitro-radicals take the trans-position in a complex radical, the position of the absorption band due to these

(12) T. Uemura and H. Sueda, this Bulletin, **10** (1935), 50; R. Samuel, *loc. cit.*; J. Kranig, *Arch. phys. biol.*, **7** (1929), 148.

(13) *J. Am. Chem. Soc.*, **57** (1935), 135.

radicals is different from that given by a cis-compound, and the absorption capacity is also slightly different in these cases. It can be proved that these spectrochemical differences based on stereoisomers are produced by the central ion and co-ordinated groups and also by the stereochemical configuration that must be taken into account. When these co-ordinated groups are supposed to take a position at every corner of a regular octahedron having some influences upon the central ion, the influence of a co-ordinated group upon the centre may be said to have the deepest relation to that which is situated on its opposite side. The consequence of this consideration is that the most important factor to control the position of an absorption band must be a pair of co-ordinated groups situated in trans-position. The existence of a characteristic absorption band due to such a pair of groups which occupy the trans-position may be assumed, and the author has provisionally given the name of "characteristic absorption" to such an absorption. On the other hand, as the influence against an absorption given by cis-group is not found on the position of bands but only an additivity can be observed, we can make the following assumption: an absorption due to a metallic complex ion is represented by the sum of characteristic absorption given by the pair of groups occupied in trans-position in a co-ordinated complex. It is very important to analyse an absorption spectrum of a solution to give it a theoretical meaning, and Y. Shibata and K. Harai[14] as well as others[15] have already studied this question. Although the idea proposed by the present author is somewhat hypothetical, yet, it may also be recognized as a kind of analysis for an absorption spectrum of complex salt solutions.

With this assumption, the absorption spectra of nitro-ammine salts can be explained as follows: the absorption of *cis*-$[Co(NH_3)_4(NO_2)_2]Cl$ is assumed as a sum of three characteristic absorptions, i.e. (NH_3-Co-NH_3)[16] and 2(NH_3-Co-NO_2) (see Fig. 2). The absorption of $[Co(NH_3)_5(NO_2)]Cl_2$ can also be resolved into 2(NH_3-Co-NH_3) and (NH_3-Co-NO_2). Since (NH_3-Co-NH_3) can be neglected in comparison with (NH_3-Co-NO_2), as described before, the absorption given by both salts shows therefore that, due to the number of (NH_3-Co-NO_2) contained,

(14) *J. Chem. Soc. Japan*, **56** (1935), 1.

(15) W. R. Brode, *Proc. Roy. Soc.* (London), A, **118** (1928), 286; *J. Am. Chem. Soc.*, **56** (1934), 1842.

J. P. Mathiue (*Bull. soc. chim.*, [5], **3** (1936), 463) has recently reported a very interesting relation between the constitution of co-ordinated complex salts and the separation of their absorption bands.

(16) This symbol represents the characteristic absorption assumed to be produced by two ammonia molecules in trans-position having cobalt as the central ion.

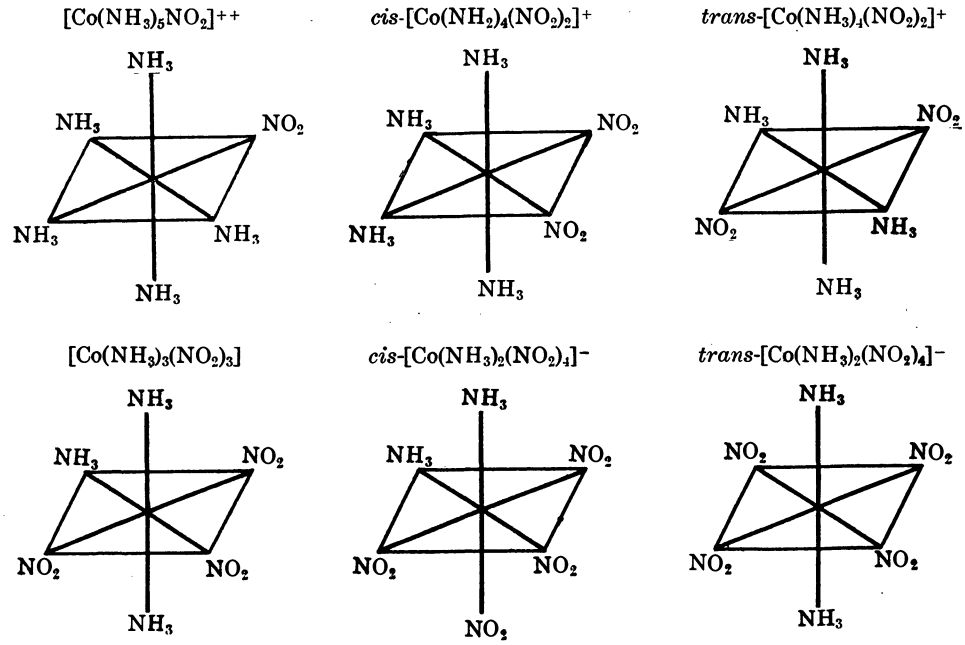


Fig. 2.

the former cis-compound has double the absorption intensity of the latter pentammine-complex showing similar curves. With regard to the *trans*-$[Co(NH_3)_4(NO_2)_2]Cl$, its absorption may be considered as the sum produced by $2(NH_3\text{-}Co\text{-}NH_3)$ and $(NO_2\text{-}Co\text{-}NO_2)$, and it is almost the same with $(NO_2\text{-}Co\text{-}NO_2)$.

This point of view is also held in comparison (3). Y. Shibata has already determined the configuration of $[Co(NH_3)_3(NO_2)_3]$ as described in Fig. 2, i.e. two of nitro-radicals are in trans-position. Its absorption can therefore be resolved into $(NH_3\text{-}Co\text{-}NH_3)$, $(NH_3\text{-}Co\text{-}NO_2)$ and $(NO_2\text{-}Co\text{-}NO_2)$. So, it is expected that the absorption might be represented as a sum of those given by $[Co(NH_3)_5(NO_2)]Cl_2$ and *trans*-$[Co(NH_3)_4(NO_2)_2]Cl$ by neglecting the effect of $(NH_3\text{-}Co\text{-}NH_3)$ as before. Curve D′ in Fig. 1, traced by taking this sum, shows a good coincidence especially in the band with the observed curve D obtained from the complex $[Co(NH_3)_3(NO_2)_3]$.

The configuration of $K[Co(NH_3)_2(NO_2)_4]$ has not yet been determined. Y. Shibata, T. Maruki[17] and W. Thomas[18] have already

(17) *J. Coll. Sci., Tokyo Imp. Univ.*, **41** (1917), Art. 2.
(18) *J. Chem. Soc.*, **123** (1923), 617.

given a cis-configuration to the compound, while E. H. Riesenfeld and R. Klement[19], a trans-configuration.

As shown in the comparison (4), the absorption intensity due to the complex $K[Co(NH_3)_2(NO_2)_4]$ is nearly twice that of the *trans*-$[Co(NH_3)_4(NO_2)_2]Cl$. According to the above-mentioned idea, this is easily understood by assuming that $K[Co(NH_3)_2(NO_2)_4]$ may contain two (NO_2-Co-NO_2) in its complex radical. The author wishes to give a trans-configuration (see Fig. 2) to this Erdemann's salt.

Application of the above-mentioned assumption to aquo-chloro-ammine salts of cobalt and chromium. In the case of the already described nitro-ammine complex salts, as their absorption capacity is so remarkably increased by the nitro-radical that the influence due to (NH_3-Co-NH_3) can be neglected, the discussion becomes comparatively simple. But to give more weight to the assumption, the author has tried to apply it to the cases where the absorptions are little influenced by the substitution which occurs in a complex radical.

According to the author's assumption, when two or three absorption curves are known for some compounds in a series, a characteristic absorption can be deduced, and an absorption of an other salt can be assumed by a suitable combination of those characteristic absorptions. To verify this assumption, observed curves were compared with those which are assumed from the characteristic curves.

(1) *Absorption curves given by cobalti-ammine complex salts in visible region.* Absorption curves of $[Co(NH_3)_6]Cl_3$[20], $[Co(NH_3)_5(H_2O)]Cl_3$[20], $[Co(NH_3)_4(H_2O)_2]Cl_3$[20], $[Co(NH_3)_5Cl]Cl_2$[20], $[Co(NH_3)_4Cl(H_2O)]Cl_2$[21] and *cis*-$[Co(NH_3)_4Cl_2]Cl$[21] were used for calculation.

According to my assumption, the absorption of $[Co(NH_3)_6]Cl_3$ should be three times the characteristic absorption (NH_3-Co-NH_3). The absorption of $[Co(NH_3)_4(H_2O)_2]Cl_3$ should be represented by the sum of (NH_3-Co-NH_3) and 2(NH_3-Co-H_2O), as this complex salt is supposed to take cis-configuration. Therefore, (NH_3-Co-H_2O) can be calculated by deducting (NH_3-Co-NH_3), which is given as 1/3 of the absorption $[Co(NH_3)_6]Cl_3$, from the absorption of $[Co(NH_3)_4(H_2O)_2]Cl_3$ and

(19) *Z. anorg. allgem. Chem.*, **124** (1922), 1.

(20) The absorption data of these salts were transferred from Colmar and Schwartz's work (*loc. cit.*).

(21) The absorption data of these salts were obtained from the curves published in the paper by Luther and Nikolopulos (*loc. cit.*).

dividing the difference in two. By combining (NH_3-Co-NH_3) and (NH_3-Co-H_2O), the value of "2(NH_3-Co-NH_3)+(NH_3-Co-H_2O)" can easily be deduced as the calculated value corresponding to the absorption shown by $[Co(NH_3)_5(H_2O)]Cl_3$. This calculation gives a good coincidence with the observation as seen in Table 1.

Table 1[22].

λ (mμ)	$[Co(NH_3)_6]Cl_3$	(NH_3-Co-NH_3)	$[Co(NH_3)_4(H_2O)_2]Cl_3$	(NH_3-Co-H_2O)	$[Co(NH_3)_5(H_2O)]Cl_3$	
					obs.	calc.
450	46.1	15.4	22.4	3.5	34.9	34.3
460	53.8	17.9	30.4	6.3	40.8	42.1
470	56.1	18.7	36.4	8.9	45.5	46.3
480	55.5	18.5	44.9	13.2	46.5	50.2
490	49.1	16.4	49.5	16.6	47.9	49.4
500	33.6	11.2	52.9	20.9	45.5	43.3
520	18.9	6.3	49.1	21.4	39.2	34.0
540	5.7	1.9	39.3	18.7	25.9	22.5
560	0.4	0.1	26.2	13.4	13.6	13.6

The value of (NH_3-Co-Cl) can be obtained from (NH_3-Co-NH_3) and the absorption data shown by $[Co(NH_3)_5Cl]Cl_2$ which should be represented as "2(NH_3-Co-NH_3)+(NH_3-Co-Cl)". As $[Co(NH_3)_4(H_2O)Cl]Cl_2$ takes a cis-configuration, its absorption should be given by "(NH_3-Co-NH_3)+(NH_3-Co-H_2O)+(NH_3-Co-Cl)". As Table 2 indicates, the sum of these characteristic absorptions obtained from calculation are somewhat greater than the observed values, but the position of the maximum absorption band is nearly matched.

The absorption of *cis*-$[Co(NH_3)_4Cl_2]Cl$ can be resolved into "(NH_3-Co-NH_3)+2(NH_3-Co-Cl)", and the calculated values are also much greater than the observed data, although a coincidence for the position of the absorption band can be recognized. A part of the discordance of calculated and observed values in extinction coefficients comes perhaps

(22) The numerical data in the tables used in this paper are shown in extinction coefficient (ε), defined from the formula: $\log I_0/I = \varepsilon cd$, where I_0 and I represent respectively the light intensity given before and after its transmission; c, concentration of solution in mol; d, layer length of solution in cm.

from the difficulty of accurate measurement which is due to the instability of the salt in aqueous solution.

Table 2.

λ (mμ)	$\left[\begin{matrix}Co(NH_3)_5\\Cl\\Cl_2\end{matrix}\right]$	(NH_3-Co-Cl)	$[Co(NH_3)_4(H_2O)Cl]Cl_2$		*cis*-$[Co(NH_3)_4Cl_2]Cl$	
			obs.	calc.	obs.	calc.
450	24.2	-6.6	16	12.3	15.5	2.2
460	30.4	-5.4	20	18.8	20	7.1
470	33.4	-4.0	25	23.6	25	10.7
480	37.5	0.5	29.5	32.2	29.5	19.5
490	40.9	8.1	35	41.1	35	32.6
500	43.1	20.7	40	52.8	41	52.6
520	47.5	34.9	46.5	62.6	48	76.1
540	44.0	40.2	48	60.8	48	82.3
560	34.6	34.4	33	47.8	41	68.9

(2) *Absorption curves given by chromi-ammine complex salts in visible and ultraviolet regions.* $[Cr(NH_3)_6]Cl_3$[23], $[Cr(NH_3)_5(H_2O)]Cl_3$[23], $[Cr(NH_3)_4(H_2O)_2]Cl_3$[23], $[Cr(NH_3)_3(H_2O)_3]Cl_3$[23], $[Cr(NH_3)_2(H_2O)_4]Cl_3$[20] and $[Cr(H_2O)_6]Cl_3$[20] were taken for calculation. Analysis and synthesis of the absorption curves can be performed in the same manner when applied to the cobalt-ammines. The value of (NH_3-Cr-H_2O) was obtained from the absorption of $[Cr(NH_3)_3(H_2O)_3]Cl_3$, and that of (NH_3-Cr-NH_3), from the absorption given by $[Cr(NH_3)_5(H_2O)]Cl_3$ and (NH_3-Cr-H_2O). By combining these characteristic absorptions, the calculated values of $[Cr(NH_3)_4(H_2O)_2]Cl_3$ and $[Cr(NH_3)_6]Cl_3$ were deduced. These are compared with the observed data in Table 3. Next, the absorption of $[Cr(NH_3)_2(H_2O)_4]Cl_3$ was calculated from the value of (H_2O-Cr-H_2O) which is given from $[Cr(H_2O)_6]Cl_3$, and that of (NH_3-Cr-H_2O) for comparing with the observed data. These observed and calculated values are considered as showing a passable coincidence in Table 3.

(23) The absorption data in the visible region of these salts were taken from Colmar and Schwartz's publication (*loc. cit.*), and those in ultraviolet from the curves measured by Uemura and Sueda (*loc. cit.*).

Table 3.

λ(mμ)	$[Cr(NH_3)_3(H_2O)_3]Cl_3$	$(NH_3\text{-}Cr\text{-}H_2O)$	$[Cr(NH_3)_5(H_2O)]Cl_3$	$(NH_3\text{-}Cr\text{-}NH_3)$	$[Cr(NH_3)_4(H_2O)_2]Cl_3$		$[Cr(NH_3)_6]Cl_3$	
					obs.	calc.	obs.	calc.
320	6	2	8	3	7	7	8	9
330	9	3	15	6	10	12	18	18
340	11	4	19	8	14	16	22	24
350	15	5	24	9	18	19	28	27
360	19	6	29	12	23	24	29	36
370	23	8	30	11	26	27	21	33
380	26	9	26	9	28	27	16	27
390	29	10	23	7	25	27	10	21
400	29	10	20	5	22	25	7	15
410	26	9	20	6	19	24	7	16
420	23	8	21	7	—	—	14	21
450	12.2	4.1	26.7	11.3	19.7	19.5	36.1	33.9
460	16.5	5.5	31.9	13.2	22.8	24.2	40.8	39.6
470	18.7	6.2	34.1	14.0	26.6	26.4	39.2	42.0
480	22.0	7.3	35.4	14.0	30.5	28.6	33.8	42.0
490	25.6	8.5	34.4	13.0	30.9	30.0	27.5	39.0
500	26.1	8.7	31.5	11.4	30.6	28.8	19.7	34.2
510	25.4	8.5	27.8	9.7	28.1	26.7	12.6	29.1
520	24.8	8.3	21.9	6.8	24.0	23.4	8.4	20.4
530	22.0	7.3	17 2	5.0	19.8	19.6		
540	19.7	6.6	12.1	2.8	14.4	16.0		
550	16.7	5.6	9.4	1.9	10.0	13.1		

λ (mμ)	$[Cr(H_2O)_6]Cl_3$	$(H_2O\text{-}Cr\text{-}H_2O)$	$[Cr(NH_3)_2(H_2O)_4]Cl_3$	
			obs.	calc.
500	3.6	1.2	19.1	18.6
510	4.3	1.4	20.1	18.4
520	5.0	1.7	20.6	18.3
530	5.8	1.9	20.2	16.5
540	6.7	2.2	19.3	15.4
550	7.4	2.5	16.7	13.7

Consideration on results. Some discordances between the calculated and observed values were found in the above comparison. I think that the causes of this difference come first from the weakness of the assumption itself and secondly from the experimental error produced by the quantitative measurement of absorption.

The weakness of the assumption is due to the complete neglect of the influence given by the groups situated in cis-position. If the oscillations of the co-ordinated groups for central ion may be supposed to have an effect upon an absorption, some influences, produced by the groups in cis-position, would be naturally taken into account, though they might be slight. So, it is sure that one of the causes has appeared in adopting the data which are neglected for the corrections due to the cis-groups.

The second cause can of course be considered as nearly inevitable. For the purpose of ascertaining the number of experimental errors produced by an absorption measurement, I have taken an example of results given by R. I. Colmar, F. W. Schwartz[4] and F. W. Beyer[24] for the absorption of $[Co(NH_3)_6]Cl_3$. The mean difference in the extinction coefficients measured by these authors was found to be about 8% between 450 mμ and 500 mμ of wave length.

Strictly speaking, the assumption that I have proposed, needs some corrections. But the author believes his assumption can afford a means to determine the configurations of complex salts within a limit of the present accuracy of absorption measurement. It may also suggest some physical meanings on light absorption of complex salts.

Summary.

(1) From the comparison of absorption curves given by nitro-ammine-cobaltic complex salts near 360 mμ of wave length, the following assumption was deduced: the absorption band presented by complex salt solutions can be resolved into the elements (characteristic absorption) which are due to the pairs of co-ordinated groups situated in trans-position in a complex radical, and these elements show an additive property in the same complex ion.

(2) By taking into account of the above-mentioned point of view, $K[Co(NH_3)_2(NO_2)_4]$ (Erdemann's salt) should have a trans-configuration.

(3) This assumption may also be applied to the absorptions given by aquo-chloro-ammine salts of cobalt and chromium, in visible and ultra-violet regions.

In conclusion, the author wishes to express his sincere thanks to Prof. Y. Shibata of the Imperial University of Tokyo, and also to Assist. Prof. T. Uemura of the Tokyo University of Engineering for their kind encouragements.

Laboratory of Inorganic Chemistry,
Tokyo University of Engineering (Tokyo Kôgyô-Daigaku).

---

(24) *Z. Physik*, **83** (1933), 806.

Studies on the Flow of Gaseous Mixtures through Capillaries. I. The Viscosity of Binary Gaseous Mixtures.

By Hiroshi ADZUMI.

(Received April 24th, 1937.)

Introduction.

When a gas flows through capillaries, the flowing formula is not unique over a wide range of pressure but depends on the proportions of the mean free path and the diameters of the capillaries, and three following cases can be distinguished: (1) If the mean free path is very small in comparison with the diameter the flowing quantity is inversely proportional to the viscosity coefficient of the gas. Such flow is called Poiseuille's or the viscous flow, and the rate of flow can be used as a means of determining the viscosity. (2) If the mean free path is large in comparison with the diameter the flowing quantity is independent of the viscosity but inversely proportional to the square root of the molecular weight of the gas, and such flow is called Knudsen's or the molecular flow. (3) When the mean free path is comparable with the diameter the mode of flow is a mixture of the above two types.

The object of the author's study is to know how gaseous mixtures flow through capillaries under various conditions and in this paper the case where the pure viscous flow takes place is treated.

Viscosities of gaseous mixtures have been measured by many authors. Viscosity—composition curves are in general not straight and some mixtures show maximum values. Several formulæ to express the viscosity of gaseous mixtures, have been given by Maxwell(1), Puluj(2), Sutherland(3), Thiessen(4), Enskog(5), and others, but these formulæ do not represent satisfactorily the results of observations. The conditions for the occurrence of a maximum point were also discussed by many authors in special cases but not considered generally.

The present author measured the viscosities of some gaseous mixtures of organic compounds, and considered the conditions for the occurrence of a maximum point for a general case. The results will be reported below.

(1) Maxwell, *Phil. Mag.*, (IV), **35** (1868), 212.
(2) Puluj, *Sitzber. Akad. Wiss. Wien, Math.-naturw. Klasse*, Abt. IIa, **79** (1879), 97, 745.
(3) W. Sutherland, *Phil. Mag.*, (V), **40** (1895), 421.
(4) M. Thiessen, *Verh. deut. phys. Ges.*, **4** (1902), 348.
(5) Enskog, *Inaug. Diss. Upsala*, (1917).

Experimental.

Viscosimeter. The method of measuring the viscosity is a transpiration type devised by T. Titani[6] and the capillary of the viscosimeter has the following dimensions: internal diameter, about 0.19 mm.; length, about 79 cm.

By measuring the time of flow of a definite volume of the gas (ca. 0.85 c.c. of about 1 atm. pressure) and taking air as a standard substance the viscosity for other gases can be determined relatively. As the separation of gaseous mixtures into components caused by flowing through capillaries is negligible under the experimental conditions, mixtures are treated by the same method as in the case of a simple gas. The temperatures of measurements are between 20° and 100°C.

Apparatus for Mixing Gases. The apparatus is shown schematically in Fig. 1. Cylindrical vessels A and B, each having a capacity of about 200 c.c., are connected with a capillary tube, about 2 mm. in diameter,

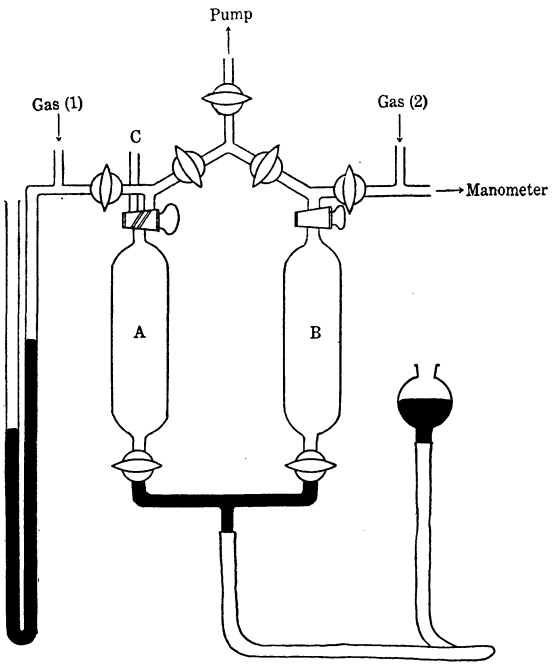


Fig. 1. Apparatus for Mixing Gases.

(6) T. Titani, this Bulletin, **4** (1929), 277.

provided with stopcocks. After evacuation, A and B are filled with the required quantity (read with pressure) of gases to be mixed and then by means of a mercury reservoir the gas in B is driven into A. By the equation of state of gas the molar composition of the mixture is calculated. After standing overnight, the homogeneous mixture is taken out from D.

Preparation of Gases. The preparation of gases used for experiments is as follows: *Hydrogen*: Obtained by the electrolysis of water from 30% sodium hydroxide solution, washed with conc. sulphuric acid, neutral potassium permanganate solution, basic sodium hydrosulphite sloution and then dried with calcium chloride and phosphorous pentoxide, the trace of oxygen being thoroughly removed by passing the gas over red-heated copper wire netting beforehand.

Methane and ethane: Prepared with great care by Dr. J. Horiuti. Methane was obtained from aluminium carbide and water, and ethane by the electrolysis of potassium acetate.

Acetylene: Prepared from calcium carbide and water, passed through sodium hydroxide, washed with solutions of ferric nitrate, copper sulphate, mercuric nitrate, and nitric acid, and finally acidic mercury chloride solution, then dried with calcium chloride. The sample thus purified was condensed with liquid air and carefully fractionated several times.

Propane: Obtained by the action of dilute alcoholic solution of iso-propyl alcohol on Zn-Cu couple[7], washed with fuming sulphuric acid, 2% of potassium permanganate solution, potassium hydroxide solution (1:1), then condensed and fractionated.

Propylene: Obtained by dehydration of iso-propyl alcohol with hot-concentrated phosphoric acid, washed with dilute sodium hydroxide solution and water, then condensed and fractionated.

Results of Measurements. (I) *Simple gases.* Viscosities of six following gases are shown in Table 1: H_2, CH_4, C_2H_2, C_2H_6, C_3H_6, C_3H_8. Sutherland's formula has been found to be applicable for all gases with satisfactory results. The viscosity values calculated by this formula are given in the table.

(7) Glastone and Tribe, *J. Chem. Soc.*, **45** (1884), 154.

Table 1. Viscosities of Simple Gases.

t°C.	Hydrogen $\eta = 68.4\frac{T_2^3}{T+79}\cdot10^{-7}$		Methane $\eta = 103.9\frac{T_2^3}{T+170}\cdot10^{-7}$		Acetylene $\eta = 104.5\frac{T_2^3}{T+220}\cdot10^{-7}$	
	$\eta\times10^7$		$\eta\times10^7$		$\eta\times10^7$	
	Obs.	Calc.	Obs.	Calc.	Obs.	Calc.
0	—	877	—	1059	—	957
20	924	923	1125	1126	1022	1022
30	942	945	1171	1159	1055	1054
40	965	967	1191	1192	1085	1086
50	989	988	1220	1224	1114	1117
60	1008	1009	1255	1256	1146	1149
70	1032	1030	1289	1287	1180	1179
80	1048	1050	1316	1318	1208	1210
90	1072	1070	1345	1348	1246	1240
100	1090	1090	1380	1379	1274	1270

t°C.	Ethane $\eta = 106.0\frac{T_2^3}{T+280}\cdot10^{-7}$		Propane $\eta = 99.8\frac{T_2^3}{T+318}\cdot10^{-7}$		Propylene $\eta = 100.5\frac{T_2^3}{T+302}\cdot10^{-7}$	
	$\eta\times10^7$		$\eta\times10^7$		$\eta\times10^7$	
	Obs.	Calc.	Obs.	Calc.	Obs.	Calc.
0	—	865	—	762	—	789
20	928	923	—	820	—	848
30	960	959	845	848	876	876
40	991	990	873	876	904	905
50	1016	1021	908	904	935	934
60	1051	1051	932	932	960	962
70	1080	1081	961	959	995	990
80	1109	1111	988	987	1016	1018
90	1143	1140	1013	1014	1048	1045
100	1171	1170	1040	1041	1070	1073

(II) *Gaseous mixtures.* Viscosities of seven following mixtures are given in Tables 2–8: $H_2\sim CH_4$, $H_2\sim C_2H_2$, $H_2\sim C_2H_6$, $H_2\sim C_3H_6$, $CH_4\sim C_2H_2$, $C_2H_2\sim C_3H_6$, $C_3H_6\sim C_3H_8$. The formula used for calculation of viscosities will be discussed later.

Table 2. Viscosities of $H_2 \sim CH_4$. (Fig. 2.)

General formula : $$\eta = \frac{\eta_{H_2}}{1+\frac{n_2}{n_1}1.309\frac{T+169}{T+79}} + \frac{\eta_{CH_4}}{1+\frac{n_1}{n_2}0.478\frac{T+169}{T+170}}$$

H_2 %	CH_4 %	100°		60°		20°	
		$\eta\times10^7$		$\eta\times10^7$		$\eta\times10^7$	
		Obs.	Calc.	Obs.	Calc.	Obs.	Calc.
100.00	0.00	1090	1090	1008	1008	924	924
79.17	20.83	1271	1263	1160	1159	1052	1048
69.91	30.09	1312	1305	1190	1194	1074	1078
50.96	49.04	1359	1360	1234	1237	1110	1112
31.05	68.95	1380	1379	1254	1256	1126	1128
0.00	100.00	1380	1380	1255	1255	1125	1125

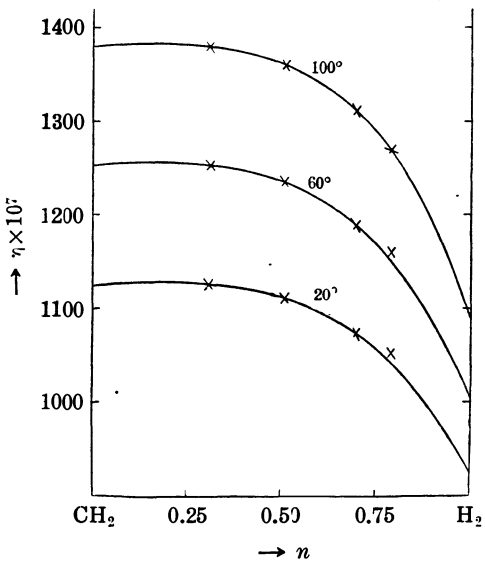


Fig. 2. $H_2 \sim CH_4$

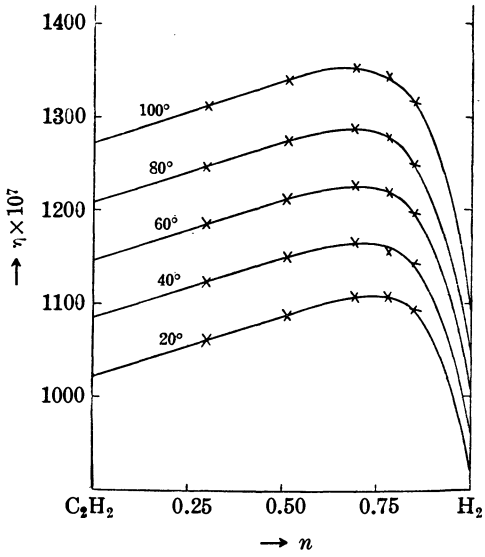


Fig. 3. $H_2 \sim C_2H_2$

Table 3. Viscosities of $H_2 \sim C_2H_2$. (Fig. 3.)

General formula: $$\eta = \frac{\eta_{H_2}}{1+\frac{n_2}{n_2}1.478\frac{T+157}{T+79}} + \frac{\eta_{C_2H_2}}{1+\frac{n_1}{n_2}0.354\frac{T+157}{T+220}}$$

H_2 %	C_2H_2 %	100°		80°		60°	
		$\eta\times10^7$		$\eta\times10^7$		$\eta\times10^7$	
		Obs.	Calc.	Obs.	Calc.	Obs.	Calc.
100.00	0.00	1090	1090	1048	1048	1008	1008
84.87	15.13	1318	1293	1250	1237	1197	1183
77.88	22.12	1346	1333	1278	1274	1219	1218
69.01	30.99	1354	1360	1288	1298	1227	1239
51.28	48.72	1339	1366	1274	1301	1211	1239
29.71	70.29	1312	1335	1245	1270	1184	1206
0.00	100.00	1274	1274	1208	1208	1146	1146

H_2 %	C_2H_2 %	40°		20°	
		$\eta\times10^7$		$\eta\times10^7$	
		Obs.	Calc.	Obs.	Calc.
100.00	0.00	965	965	924	924
84.87	15.13	1142	1128	1094	1073
77.88	22.12	1164	1160	1106	1100
69.01	30.99	1166	1179	1106	1116
51.28	48.72	1150	1176	1086	1112
29.71	70.29	1122	1145	1059	1079
0.00	100.00	1085	1085	1022	1022

Table 4. Viscosities of $H_2 \sim C_2H_6$. (Fig. 4.)

General formula: $$\eta = \frac{\eta_{H_2}}{1+\frac{n_2}{n_1}1.516\frac{T+243}{T+79}} + \frac{\eta_{C_2H_6}}{1+\frac{n_1}{n^2}0.328\frac{T+243}{T+280}}$$

H_2 %	C_2H_6 %	100°		80°		60°	
		$\eta\times10^7$		$\eta\times10^7$		$\eta\times10^7$	
		Obs.	Calc.	Obs.	Calc.	Obs.	Calc.
100.00	0.00	1090	1090	1048	1048	1008	1008
83.69	16.31	1240	1230	1183	1176	1126	1122
66.51	33.49	1255	1260	1196	1199	1138	1141
50.84	49.16	1240	1251	1181	1188	1124	1129
37.16	62.84	1224	1232	1163	1169	1104	1110
0.00	100.00	1171	1171	1109	1109	1051	1051

Table 4.—(*Concluded*)

H_2 %	C_2H_6 %	40°		20°	
		$\eta \times 10^7$		$\eta \times 10^7$	
		Obs.	Calc.	Obs.	Calc.
100.00	0.00	965	965	924	924
83.69	16.31	1071	1071	1013	1008
66.51	33.49	1077	1078	1013	1017
50.84	49.16	1062	1065	998	1001
37.16	62.84	1044	1046	98)	981
0.00	100.00	991	991	928	928

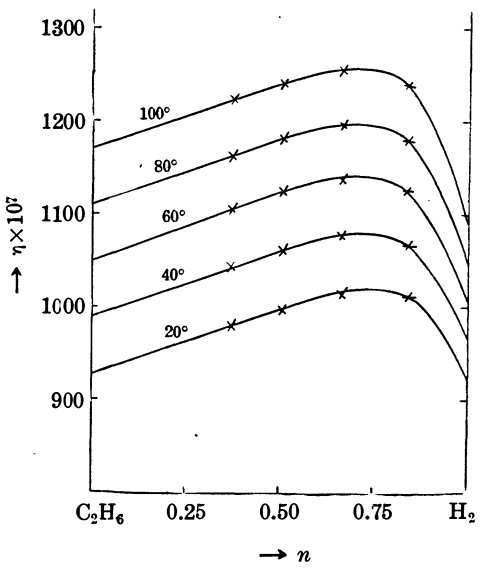


Fig. 4. H_2~C_2H_6

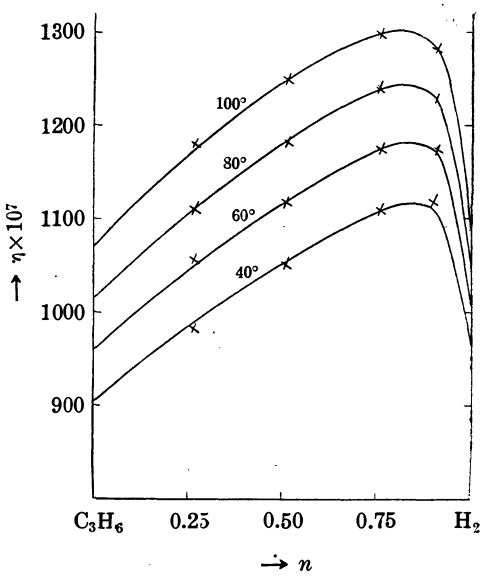


Fig. 5. H_2~C_3H_6

Table 5. Viscosities of $H_2 \sim C_3H_6$. (Fig. 5.)

General formula: $$\eta = \frac{\eta_{H_2}}{1+\frac{n_2}{n_1}1.746\frac{T+155}{T+79}} + \frac{\eta_{C_3H_6}}{1+\frac{n_1}{n_2}0.254\frac{T+155}{T+302}}$$

H_2 %	C_3H_6 %	100°		80°	
		$\eta\times10^7$		$\eta\times10^7$	
		Obs.	Calc.	Obs.	Calc.
100.00	0.00	1090	1090	1048	1048
91.10	8.90	1284	1263	1231	1221
75.88	24.12	1296	1320	1240	1263
51.02	48.98	1250	1255	1181	1197
26.76	73.24	1181	1166	1110	1107
0.00	100.00	1070	1070	1016	1016

H_2 %	C_3H_6 %	60°		40°	
		$\eta\times10^7$		$\eta\times10^7$	
		Obs.	Calc.	Obs.	Calc.
100.00	0.00	1008	1008	965	965
91.10	8.90	1174	1160	1118	1106
75.88	24.12	1175	1203	1110	1142
51.02	48.98	1118	1136	1050	1073
26.76	73.24	1057	1047	983	987
0.00	100.00	960	960	904	904

Table 6. Viscosities of $CH_4 \sim C_2H_2$. (Fig. 6.)

General formula: $$\eta = \frac{\eta_{CH_4}}{1+\frac{n_2}{n_1}1.135\frac{T+172}{T+170}} + \frac{\eta_{C_2H_2}}{1+\frac{n_1}{n_2}0.854\frac{T+172}{T+220}}$$

CH_4 %	C_2H_2 %	100°		80°	
		$\eta\times10^7$		$\eta\times10^7$	
		Obs.	Calc.	Obs.	Calc.
100.00	0.00	1330	1330	1316	1316
75.11	24.89	1378	1379	1310	1316
49.53	50.47	1360	1359	1300	1294
24.72	75.28	1330	1320	1264	1257
0.00	100.00	1274	1274	1208	1208

Table 6.—(*Concluded*)

CH_4 %	C_2H_2 %	60°		40°	
		$\eta\times10^7$		$\eta\times10^7$	
		Obs.	Calc.	Obs.	Calc.
100.00	0.00	1255	1255	1191	1191
75.11	24.89	1250	1254	1186	1190
49.53	50.47	1236	1231	1171	1168
24.72	75.28	1200	1193	1138	1132
0.00	100.05	1146	1146	1085	1085

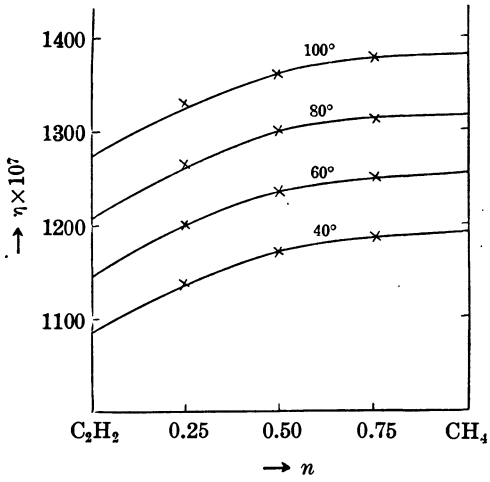


Fig. 6. CH_4~C_2H_2

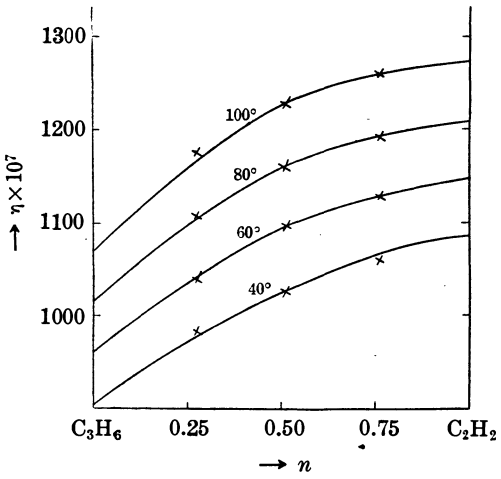


Fig. 7. C_2H_2~C_3H_6

Table 7. Viscosities of C_2H_2~C_3H_6. (Fig. 7.)

General formula: $\eta = \dfrac{\eta_{C_2H_2}}{1+\frac{n_2}{n_1}1.165\frac{T+222}{T+220}} + \dfrac{\eta_{C_3H_6}}{1+\frac{n_1}{n_2}0.817\frac{T+222}{T+302}}$

C_2H_2 %	C_3H_6 %	100°		80°	
		$\eta\times10^7$		$\eta\times10^7$	
		Obs.	Calc.	Obs.	Calc.
100.00	0.00	1274	1274	1208	1208
75.99	24.01	1261	1256	1192	1194
50.79	49.21	1228	1212	1160	1151
27.39	72.61	1176	1154	1108	1095
0.00	100.00	1070	1070	1016	1016

Table 7.—(*Concluded*)

C_2H_2 %	C_3H_6 %	60°		40°	
		$\eta\times10^7$		$\eta\times10^7$	
		Obs.	Calc.	Obs.	Calc.
100.00	0.00	1146	1146	1085	1085
75.99	24.01	1130	1132	1060	1071
50.79	49.21	1094	1080	1026	1031
27.39	72.61	1040	1036	982	977
0.00	100.00	960	960	904	904

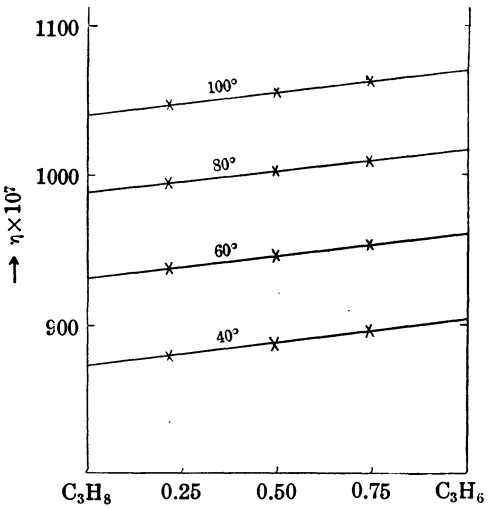


Fig. 8. C_3H_6~C_3H_8

Table 8. Viscosities of C_3H_6~C_3H_8. (Fig. 8.)

General formula: $\eta=\dfrac{\eta_{C_3H_6}}{1+\frac{n_2}{n_1}1.008\frac{T+310}{T+302}}+\dfrac{\eta_{C_3H_8}}{1+\frac{n_1}{n_2}0.985\frac{T+310}{T+318}}$

C_3H_6 %	C_3H_8 %	100°		80°	
		$\eta\times10^7$		$\eta\times10^7$	
		Obs.	Calc.	Obs.	Calc.
100.00	0.00	1070	1070	1016	1016
73.92	26.08	1062	1064	1009	1011
49.03	50.97	1056	1058	1001	1003
21.31	78.69	1046	1048	996	995
0.00	100.09	1040	1040	988	988

Table 8.—(*Concluded*)

C_3H_6 %	C_3H_8 %	60°		40°	
		$\eta \times 10^7$		$\eta \times 10^7$	
		Obs.	Calc.	Obs.	Calc.
100.00	0.00	960	960	904	904
73.92	26.08	952	954	896	897
49.03	50.97	946	947	886	890
21.31	78.69	940	939	878	881
0.00	100.00	932	932	873	873

As seen from the figure, the viscosities of the first four mixtures attain maximum values at definite compositions, which are about 20% of H_2 for the mixture $H_2 \sim CH_4$ and about 70–80% of H_2 for the other three. The viscosity-composition curve of the mixture $C_3H_6 \sim C_3H_8$ is quite linear.

Discussion.

Viscosity Formula for Binary Gaseous Mixture. The viscosity of gases depends on the diameter, the mass, and the attraction of the molecule, and further the mutual collision of the different gases must be considered in the case of a mixture and the theoretical treatment is difficult. As described above, many formulæ are proposed to express the viscosity of a gaseous mixture but they are derived almost empirically. Of those formulæ, that in which Kuenen's[8] consideration of the persistence of molecular velocity is introduced is somewhat more theoretical than the other. The experimental results will be examined first of all by this formula.

The viscosity η of a simple gas is given by

$$\eta = k m N \bar{u} \lambda f, \qquad (1)$$

where m is the mass, $\bar{u}$ the mean velocity, λ the mean free path of the molecule, N the number of molecules per unit volume, f the correction factor in consideration of the persistence of molecular velocity (1/0.797 in simple gas) and k a constant (0.499×0.797).

(8) J. P. Kuenen, "Die Eigenschaften der Gase," 111 (1919).

The viscosity of binary gaseous mixtures is given in a rather complicated formula. If the mean free path of the molecule in the mixture of the first type is λ_1' and the correction factor owing to the persistence in the mixture is f_1', there is obtained the following relations:

$$\eta = km_1n_1N\bar{u}_1\lambda_1'f_1' + km_2n_2N\bar{u}_2\lambda_2'f_2' , \qquad (2)$$

where n_1 and n_2 are mol fractions of two components. The mean free paths in a mixture are

$$\lambda_1' = \frac{1}{n_1N\pi S_1^2\sqrt{2}\left(1+\frac{C_1}{T}\right)+n_2N\pi S^2\sqrt{\frac{m_1+m_2}{m_2}}\left(1+\frac{C_{12}}{T}\right)} ,$$

$$\lambda_2' = \frac{1}{n_2N\pi S_2^2\sqrt{2}\left(1+\frac{C_2}{T}\right)+n_1N\pi S^2\sqrt{\frac{m_1+m_2}{m_1}}\left(1+\frac{C_{12}}{T}\right)} ,$$

where S_1 and S_2 are molecular diameters of two gases, S is a mean of these ($S = 1/2(S_1 + S_2)$), C_1 and C_2 are Sutherland's constants of two gases due to the attraction between the same molecules and C_{12} that between the different molecules.

According to Kuenen, the correction factors for a mixture, f', are as follows:

$$f_1' = \frac{1}{1-\frac{\sqrt{2}}{2}n_1N\pi S_1^2\left(1+\frac{C_1}{T}\right)\lambda_1'\times 0\cdot 406-\frac{m_1}{m_1+m_2}n_2N\pi S^2\sqrt{\frac{m_1+m_2}{m_2}}\left(1+\frac{C_{12}}{T}\right)\lambda_1'\vartheta_1} ,$$

where $$\vartheta_1 = \frac{m_1}{2(m_1+m_2)}+\frac{1}{4}\frac{m_1^2}{\sqrt{m_2}(m_1+m_2)^{\frac{3}{2}}}\ln\frac{\sqrt{m_1+m_2}+\sqrt{m_2}}{\sqrt{m_1+m_2}-\sqrt{m_2}} ,$$

and analogous formulæ for f_2' and ϑ_2.

The viscosities of the components are also expressed by

$$\eta_1 = \frac{km_1\bar{u}_1}{\pi S_1^2\sqrt{2}\left(1+\frac{C_1}{T}\right)}\frac{1}{0\cdot 797} , \qquad \eta_2 = \frac{km_2\bar{u}_2}{\pi S_2^2\sqrt{2}\left(1+\frac{C_2}{T}\right)}\frac{1}{0\cdot 797} .$$

By inserting these values to equation (2), the viscosity of a mixture becomes

$$\eta = \frac{\eta_1}{1+\frac{n_2}{n_1}\alpha_1} + \frac{\eta_2}{1+\frac{n_1}{n_2}\alpha_2}, \qquad (3)$$

where
$$\alpha_1 = \left(\frac{S}{S_1}\right)^2 \sqrt{\frac{m_1+m_2}{2m_2}} \frac{1-\frac{m_1}{m_1+m_2}\vartheta_1}{0.797} \frac{T+C_{12}}{T+C_1},$$

$$\alpha_2 = \left(\frac{S}{S_2}\right)^2 \sqrt{\frac{m_1+m_2}{2m_1}} \frac{1-\frac{m_2}{m_1+m_2}\vartheta_2}{0.797} \frac{T+C_{12}}{T+C_2}.$$

Sutherland's constant C_{12} is proportional to the potential energy of two different molecules, and the only coefficient in equation (3) that can not be determined directly, and is often considered to be a geometrical mean of C_1 and C_2. For almost all mixtures, whose viscosities have been measured by many authors, such calculations of this coefficient is inadequate to adapt the experiments. However, if we take a proper value for C_{12}, the results of observation can be expressed satisfactorily by equation (3). By using such values, viscosity formulæ for all mixtures can be obtained and these are given in Tables 3–8. The viscosity curve III in Fig. 9 is obtained by equation (3) by using C_{12} calculated as a geometrical mean and curve II by observed C_{12} computed empirically from the results of observation. The comparison of the calculated and the observed values of C_{12} are shown below in Table 9.

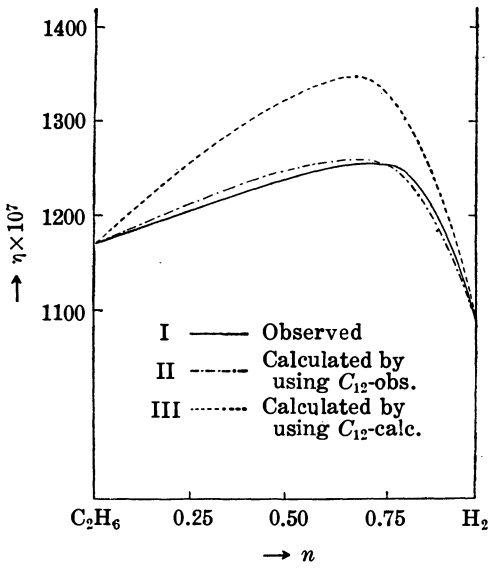


Fig. 9. H_2~C_2H_6 (100°C.)

Sutherland's Constant between Different Molecules. As described above, according to the classical theory, Sutherland's constant C_{12} has been considered to be a geometrical mean of C_1 and C_2. In 1928,

Schmick[9] reported that, when a dipole and a quadrupole molecules collide, the constant becomes smaller than the geometrical mean.

The potential energies between two dipole molecules, Ed_1d_2, between two quadrupole molecules, Eq_1q_2, and between a dipole and a quadrupole molecules, Edq, are expressed as follows:

$$Ed_1d_2 = -\frac{2}{3\sigma^6}\frac{\mu_1^2\mu_2^2}{kT}, \quad Eq_1q_2 = -\frac{14}{5\sigma^{10}}\frac{\nu_1^2\nu_2^2}{kT}, \quad Edq = -\frac{1}{\sigma^8}\frac{\mu^2\nu^2}{kT},$$

where μ and ν are the dipole and the quadrupole moments respectively, and σ the distance between two molecules.

Then for the same sort of molecules $Edd = -\frac{2}{3\sigma^6}\frac{\mu^4}{kT}$ and $Eqq = -\frac{14}{5\sigma^{10}}\frac{\nu^4}{kT}$, hence $Edq = 0.733\sqrt{Edd \times Eqq}$. As Sutherland's constant is proportional to the potential energy between two molecules, this becomes

$$C_{12} = 0.733\sqrt{C_1 \times C_2}.$$

According to London's consideration[10] from the standpoint of wave mechanics, C_{12} is always smaller than the geometrical mean, and if it be larger, we can say that some forces other than van der Waals's, for example, valency force etc. must have acted between the molecules.

There is no method to determine C_{12} directly, but as described above, we can compute it inversely from viscosities of a mixture by using equation (3).

The values of C_{12} calculated for several paires by using viscosities obtained by the present author and other authors are given in Table 9. For nine mixtures out of thirty-two the values of C_{12} are equal to, and for thirteen larger than, the geometrical means. As the examples of a dipole and a quadrupole mixtures, C_{12}'s of $NH_3 \sim O_2$ and $NH_3 \sim N_2$ agree very well with Schmick's theory, but those of $NH_3 \sim C_2H_4$ and $NH_3 \sim H_2$ do not.

It is doubtful whether the values of C_{12} obtained by such a method are exactly proportional to the potential energies or not, and therefore, such calculations serve only to the estimation of the approximate values of the constant and it is dangerous to interpret the values of C_{12} larger than the geometrical mean by the consideration of London.

(9) H. Schmick, *Physik. Z.*, **29** (1928), 638.
(10) F. London, *Z. physik, Chem.*, B, **11** (1931), 222.

Table 9. Calculated Values of C_{12} and the Comparison with the Geometrical Means of C_1 and C_2.

Mixture	C_1	C_2	C_{12}	$\frac{C_{12}}{\sqrt{C_1C_2}}$	Mixture	C_1	C_2	C_{12}	$\frac{C_{12}}{\sqrt{C_1C_2}}$
NH_3~N_2	370	114	151	0.733	CH_4~C_2H_6	170	280	230	1.05
NH_3~O_2	370	137	165	0.733	H_2~He	79	76	82	1.05
He~Ne	76	56	62	0.80	N_2~NO	114	195	156	1.05
C_2H_4~O_2	259	137	160	0.85	H_2~NH_3	79	370	195	1.14
C_2H_4~C_3H_6	259	302	222	0.86	C_2H_4~CO_2	259	257	290	1.14
NH_3~C_2H_4	370	259	270	0.88	H_2~O_2	79	137	120	1.15
CH_4~C_2H_2	170	220	172	0.89	Ne~A	56	163	110	1.15
CO_2~C_3H_8	257	318	257	0.90	H_2~C_2H_2	79	220	159	1.19
O_2~CO_2	137	257	170	0.90	H_2~Ne	79	56	81	1.23
N_2~C_2H_4	114	259	160	0.93	CH_4~C_3H_8	170	318	305	1.31
CO~N_2	102	114	105	0.97	H_2~C_2H_4	79	259	200	1.40
H_2~C_3H_6	79	302	155	1.00	H_2~A	79	163	163	1.44
C_3H_6~C_3H_8	302	318	310	1.00	H_2~CH_4	79	170	169	1.46
N_2O~C_3H_8	314	318	316	1.00	H_2~CO_2	79	257	210	1.47
N_2~O_2	114	137	128	1.03	He~A	76	163	163	1.47
C_2H_6~C_3H_8	280	318	312	1.04	H_2~C_2H_6	79	280	243	1.63

The Conditions for the Occurrence of a Maximum Point. The conditions for the occurrence of a maximum point have been discussed by many authors in special cases. For example, Thomsen[11] reported that in the case of mixtures of two gases of nearly equal viscosities, maximum point occurs when the ratio of molecular weights is great; and Schmick[12] stated that, of mixtures of two gases, whose viscosities and molecular weights are nearly equal, those of a polar and a nonpolar molecules show maximum points.

We can not find any papers dealing with the conditions for the occurrence of a maximum point for a general case.

The general formula expressing the viscosity of a gaseous mixture is given by

$$\eta = \frac{\eta_1}{1+\frac{n_2}{n_1}\alpha_1} + \frac{\eta_2}{1+\frac{n_1}{n_2}\alpha_2}, \qquad (4)$$

(11) E. Thomsen, *Ann. Physik*, **36** (1911), 815.

(12) G. Jung and H. Schmick, *Z. physik. Chem.*, B, **7** (1930), 130.

and by introducing Kuenen's consideration into α_1 and α_2, we can derive the special form of this equation as given in equation (3). If we write $n_1 = n$, $n_2 = 1 - n$, then

$$\eta = \frac{\eta_1}{1+\frac{1-n}{n}\alpha_1} + \frac{\eta_2}{1+\frac{n}{1-n}\alpha_2} = \frac{n\eta_1}{n+(1-n)\alpha_1} + \frac{(1-n)\eta_2}{1-n+n\alpha_2} .$$

By differentiation we have

$$\frac{d\eta}{dn} = \frac{\alpha_1\eta_1\{(\alpha_2-1)n+1\}^2 - \alpha_2\eta_2\{(\alpha_1-1)n-\alpha_1\}^2}{(n+\alpha_1-n\alpha_1)^2(1-n+n\alpha_2)^2}$$

$$= A\left[\sqrt{\alpha_1\eta_1}\{\alpha_2+(1-n)\} - \sqrt{\alpha_2\eta_2}\{\alpha_1(1-n)+n\}\right], \quad (5)$$

where $$A \equiv \frac{\sqrt{\alpha_1\eta_1}\{\alpha_2+(1-n)\} + \sqrt{\alpha_2\eta_2}\{\alpha_1(1-n)+n\}}{(n+\alpha_1-n\alpha_1)^2(1-n+n\alpha_2)^2} .$$

If we equate $d\eta/dn$ to zero, we have the following equation, A being positive and not equal to zero.

$$\sqrt{\alpha_1\eta_1}\{\alpha_2+(1-n)\} - \sqrt{\alpha_2\eta_2}\{\alpha_1(1-n)+n\} = 0 .$$

Then the composition of the maximum or the minimum point, n_0, becomes

$$n_0 = \frac{\sqrt{\alpha_1}(\sqrt{\alpha_1\alpha_2\beta}-1)}{\sqrt{\alpha_1}(\alpha_2-1) + \sqrt{\alpha_2\beta}(\alpha_1-1)} = \frac{\sqrt{\alpha_1\alpha_2\beta}-1}{\sqrt{\alpha_1\alpha_2\beta}-1+\sqrt{\frac{\alpha_2}{\alpha_1}}(\sqrt{\alpha_1\alpha_2}-\sqrt{\beta})} , \quad (6)$$

where $\beta \equiv \eta_2/\eta_1$.

For the existence of a maximum or a minimum point, n_0 must be greater than nought and smaller than unity or as seen from equation (6), following conditions must be fulfilled:

$$\alpha_1\alpha_2 > \beta > \frac{1}{\alpha_1\alpha_2} \quad \text{or} \quad \alpha_1\alpha_2 < \beta < \frac{1}{\alpha_1\alpha_2} .$$

By inserting the values of n_0 given by (6), equation (5) becomes

$$\frac{d\eta}{dn} = A\sqrt{\alpha_1}\,\frac{n-n_0}{\sqrt{\alpha_1\alpha_2\beta}-1+\sqrt{\frac{\alpha_2}{\alpha_1}}(\sqrt{\alpha_2\alpha_1}-\sqrt{\beta})} . \quad (7)$$

where $A\sqrt{\alpha_1}$ is positive if $0 < n_0 < 1$.

Then if $\alpha_1\alpha_2 > \beta > \frac{1}{\alpha_1\alpha_2}$, the demoninator of equation (7) becomes positive and

$$\frac{d\eta}{dn} < 0 \qquad \text{when} \quad n < n_0 ,$$

$$\frac{d\eta}{dn} > 0 \qquad \text{when} \quad n > n_0 ,$$

hence η becomes minimum when $n = n_0$.

Next, if $\alpha_1\alpha_2 < \beta < \frac{1}{\alpha_1\alpha_2}$, the denominator of equation (7) becomes negative and

$$\frac{d\eta}{dn} > 0 \qquad \text{when} \quad n < n_0 ,$$

$$\frac{d\eta}{dn} < 0 \qquad \text{when} \quad n > n_0 ,$$

hence η becomes maximum when $n = n_0$.

By summarising,

$$\left.\begin{array}{lll} \text{when} \quad \alpha_1\alpha_2 > \beta > \dfrac{1}{\alpha_1\alpha_2} & \text{viscosity shows} & \text{a minimum,} \\ \alpha_1\alpha_2 < \beta < \dfrac{1}{\alpha_1\alpha_2} & ,, \quad ,, & \text{a maximum,} \\ \left.\begin{array}{l} \dfrac{1}{\beta} < \alpha_1\alpha_2 < \beta \\ \text{or} \quad \beta < \alpha_1\alpha_2 < \dfrac{1}{\beta} \end{array}\right\} & ,, \quad ,, & \text{neither.} \end{array}\right\} \qquad (8)$$

This relations hold in the general formula of binary mixtures whatever the values of α_1 and α_2 may be, but in order to examine numerically by examples, let us insert the values given in (3) to α_1 and α_2. If we write $m_2/m_1 \equiv \mu$, $S_2/S_1 \equiv a$, $\dfrac{1+\frac{C_2}{T}}{1+\frac{C_1}{T}} \equiv \nu$ and assume $\dfrac{(T+C_{12})^2}{(T+C_1)(T+C_2)} = 1$, then

$$\left.\begin{array}{l} \alpha_1\alpha_2\beta = \left(\dfrac{1+a}{2a}\right)^4 \dfrac{B}{\nu} , \\ \dfrac{\alpha_1\alpha_2}{\beta} = \left(\dfrac{1+a}{2}\right)^4 \dfrac{B\nu}{\mu} , \end{array}\right\} \qquad (9)$$

where $B = \frac{1+\mu}{1.27}\left(1-\frac{\vartheta_1}{1+\mu}\right)\left(1-\frac{\vartheta_2}{1+\mu}\mu\right)$.

Above assumption is not rigorous, but, if C_{12} lies between C_1 and C_2, $(T + C_{12})^2/(T + C_1)(T + C_2)$ is not very far from unity.

The results of calculations of $\alpha_1\alpha_2\beta$ and $\alpha_1\alpha_2/\beta$ at 0°C. by formula (8) for fifty-five kinds of gaseous mixtures are tabulated in Table 10, the components of mixtures being selected as $m_2 > m_1$.

Table 10.

(1) Mixtures showing a maximum.

Mixture	$\alpha_1\alpha_2\beta$	$\frac{\alpha_1\alpha_2}{\beta}$	Observers
H_2~CH_4	0.740	0.526	Adzumi, Graham[13], Trautz and Sorg[28].
H_2~C_2H_2	0.574	0.485	Adzumi.
H_2~C_2H_4	0.537	0.498	Thomsen[11], Trautz and Stauf[22].
H_2~C_2H_6	0.499	0.517	Adzumi.
H_2~C_3H_6	0.416	0.514	Adzumi.
H_2~C_3H_8	0.385	0.510	
H_2~NH_3	0.622	0.574	Thomsen[11], Trautz and Heberling[29].
H_2~CO_2	0.675	0.242	Graham[13], Puluj[2] Thomsen[11], Breitenbach[14], Trautz and Kurz[27].
H_2~SO_2	0.433	0.265	Trautz and Weizel[18].
H_2~NO	0.890	0.245	Graham[13].
H_2~N_2O	0.646	0.249	Graham[13], Trautz and Kurz[27].
H_2~HCl	0.662	0.279	Trautz and Narath[19].
H_2~Cl_2	0.479	0.243	Thomsen[11].
He~A	0.718	0.460	Tänzler[16], Trautz and Kipphan[23], Trautz and Binkele[25].
He~Kr	0.552	0.374	Nasini and Rossi[20].
*CH_4~NH_3	0.852	1.120	Jung and Schmick[12].
*NH_3~C_2H_4	0.990	1.004	Thomsen[11], Trautz and Heberling[29].

(13) Graham, *Trans. Roy. Soc.* (London), A, **136** (1846), 662.
(14) Breitenbach, *Wied. Ann.*, **67** (1899), 803.
(15) K. Kleint, *Verh. deut. phys. Ges.*, **7** (1905), 146.
(16) P. Tänzler, *Verh. deut. phys. Ges.*, **8** (1906), 221.
(17) A. Gille, *Ann. Physik*, **48** (1915), 799.
(18) M. Trautz and W. Weizel, *Ann. Physik*, **78** (1925), 305.
(19) M. Trautz and A. Narath, *ibid.*, **79** (1926), 637.
(20) Nasini and Rossi, *Gazz. chim. ital.*, **58** (1928), 433.
(21) M. Trautz and P. B. Baumann, *Ann. Physik*, (V), **2** (1929), 733.

Table 10.—(*Continued*)

(2) Mixtures showing no maximum.

Mixture	$\alpha_1\alpha_2\beta$	$\frac{\alpha_1\alpha_2}{\beta}$	Observers
* H_2~CO	0.928	0.260	Graham[13], Tratz and Baumann[21].
H_2~O_2	1.018	0.205	Kleint[15], Graham[13], Trautz and Melster[26].
* H_2~N_2	0.960	0.254	Graham[13], Kleint[15], Trautz and Baumann[21].
* H_2~Air	0.954	0.247	Graham[13].
H_2~He	2.110	0.308	Gille[17], Trauz and Kipphan[23], Trauz and Baumann[21].
H_2~A	1.110	0.152	Trautz and Ludewigs[24], Trauz and Binkele[25].
H_2~Ne	1.901	0.157	Trautz and Binkele[25].
He~Ne	1.20	0.455	Trautz and Kipphan[23].
Ne~A	0.744	1.260	Trautz and Kipphan[23], Trauz and Binkele[15].
NH_3~N_2	1.694	0.521	Thomsen[11], Trautz and Heberling[29].
NH_3~O_2	1.435	0.566	Thomsen[11], Trautz and Heberling[29].
NH_3~Air	1.82	0.520	Jung and Schmick[12].
NH_3~CO_2	1.435	0.566	Thomsen[11].
NH_3~Cl_2	1.08	0.459	Thomsen[11].
Air~CO_2	0.837	1.160	Jung and Schmick[12].
Air~HCl	0.770	1.212	
Air~H_2S	0.657	1.456	
CO~N_2	1.032	0.97	Trautz and Melster[26].
CO_2~N_2O	0.963	1.039	Trautz and Kurz[27].
CO_2~SO_2	0.773	1.266	Jung and Schmick[12].
O_2~CO_2	0.745	1.333	Graham[13].
CO~O_2	1.20	0.837	Graham[13], Trautz and Melster[26].
N_2~O_2	1.16	0.817	Graham[13], Kleint[15], Trautz and Melster[26].
N_2~NO	0.978	1.055	Trautz and Gabriel[30].

(22) M. Trautz and F. W. Stauf, *Ann. Physik*, (V), **2** (1929), 737.
(23) M. Trautz and K. F. Kipphan, *ibid.*, (V), **2** (1929), 743.
(24) M. Trautz and W. Ludewigs, *ibid.*, (V), **3** (1929), 409.
(25) M. Trautz and H. E. Binkele, *ibid.*, (V), **5** (1930), 561.
(26) M. Trautz and A. Melster, *ibid.*, (V), **7** (1930), 409.
(27) M. Trautz and F. Kurz, *ibid.*, (V), **9** (1931), 981.
(28) M. Trautz and K. G. Sorg, *ibid.*, (V), **10** (1931), 81.
(29) M. Trautz and R. Heberling, *ibid.*, (V), **10** (1931), 155.
(30) M. Trautz and E. Gabriel, *ibid.*, (V), **11** (1931), 606.

Table 10.—(*Concluded*)

Mixture	$\alpha_1\alpha_2\beta$	$\frac{\alpha_1\alpha_2}{\beta}$	Observers
CH_4~O_2	1.84	0.463	Graham[15].
CH_4~C_2H_2	0.900	1.074	Adzumi.
CH_4~C_2H_6	0.793	1.180	Trautz and Sorg[28].
CH_4~C_3H_8	0.656	1.258	Trautz and Sorg[28].
C_2H_2~C_3H_6	0.808	1.20	Adzumi.
N_2~C_2H_4	0.539	1.895	Trautz and Melster[26].
CO~C_2H_4	0.556	1.833	Trautz and Melster[26].
C_2H_4~O_2	2.27	0.496	Trautz and Melster[26].
C_2H_4~Air	1.92	0.524	Breitenbach[14].
C_2H_4~CO_2	1.565	0.603	
C_2H_6~C_3H_8	0.920	1.10	Trautz and Sorg[28].
C_3H_6~C_3H_8	0.945	1.02	Adzumi.
C_3H_8~N_2O	1.945	0.564	Trautz and Kurz[27].
C_3H_8~CO_2	2.01	0.538	Trauz and Kurz[27].

As seen from Table 10, all mixtures showing a maximum have the values of $\alpha_1\alpha_2\beta$ and $\alpha_1\alpha_2/\beta$ always smaller than unity and in the case of mixtures showing no maximum the values are either $\left.\begin{matrix}\alpha_1\alpha_2\beta<1\\ \alpha_1\alpha_2>\beta\end{matrix}\right\}$ or $\left.\begin{matrix}\alpha_1\alpha_2\beta<1\\ \alpha_1\alpha_2<\beta\end{matrix}\right\}$, thus the conditions (8) are satisfied excepting a few mixtures prefixed by an asterisk which have values only a little different from unity, but by inserting the correct values to C_{12}, all of these will perhaps satisfy the conditions (8).

Fig. 10 is a graphical interpretation of the conditions (8). The boundary curves between the region in which a maximum point occurs and that in which a maximum point does not occur are

$$\left.\begin{aligned} &\alpha_1\alpha_2\beta = 1 \quad \text{or} \quad \alpha = \frac{1}{2\sqrt[4]{\frac{\nu}{B}-1}},\\ &\text{and} \quad \alpha_1\alpha_2 = \beta \quad \text{or} \quad \alpha = 2\sqrt[4]{\frac{\mu}{B\nu}-1}. \end{aligned}\right\} \tag{10}$$

In Fig. 10 μ is taken as ordinate and α as abscissa when ν equals to 0.5, 1.0, and 2.0, and the shaded part between two curves of $\alpha_1\alpha_2\beta = 1$ and $\alpha_1\alpha_2 = \beta$ is the region of a maximum or a minimum point.

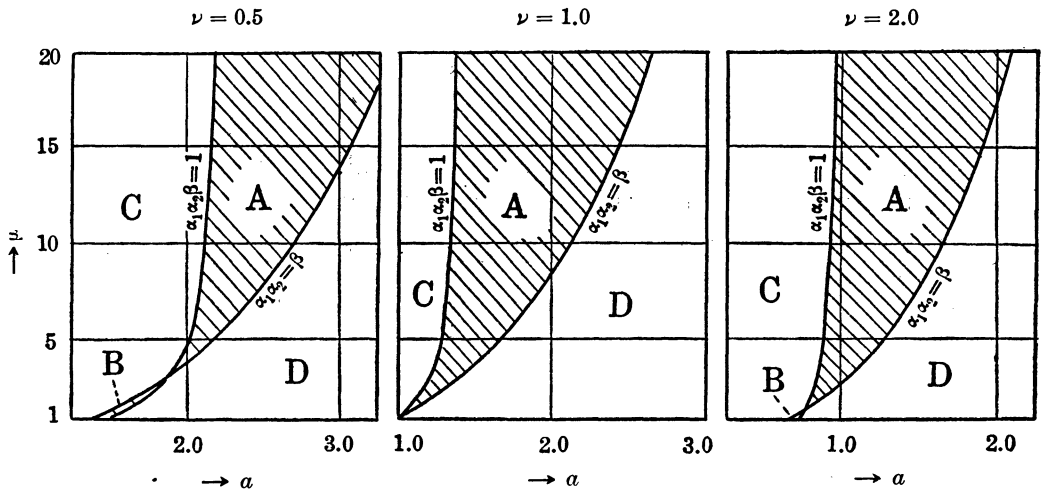


Fig. 10. Graphical Interpretation of the Conditions for the Occurrence of a Max. or a Min. Point. $\left(\mu = \frac{m_2}{m_1},\ a = \frac{S_2}{S_1},\ \nu = \frac{T+C_2}{T+C_1}\right)$.

(A) is a region of $\left.\begin{matrix} \alpha_1\alpha_2\beta < 1 \\ \alpha_1\alpha_2 < \beta \end{matrix}\right\}$ and in which a maximum point occurs,

(B) ,, $\left.\begin{matrix} \alpha_1\alpha_2\beta > 1 \\ \alpha_1\alpha_2 > \beta \end{matrix}\right\}$,, a minimum ,, ,

(C) ,, $\left.\begin{matrix} \alpha_1\alpha_2\beta > 1 \\ \alpha_1\alpha_2 < \beta \end{matrix}\right\}$,, neither max. nor min. occurs,

(D) ,, $\left.\begin{matrix} \alpha_1\alpha_2\beta < 1 \\ \alpha_1\alpha_2 > \beta \end{matrix}\right\}$,, ,, ,, ,

The mean free path of a molecule in a mixture is different from that of a simple molecule on account of the mutual collision between the different molecules, sometimes greater and sometimes smaller depending on the other molecule, and consequently the viscosity of the mixture is much complicated. It is a special case that the viscosity of a mixture follows the additive law, that is a case when $\alpha_1 = \alpha_2 = 1$. As seen from Fig. 8, for example, the viscosity of $C_3H_6 \sim C_3H_8$ is almost additive, because the molecular weights, the molecular diameters and Sutherland's constants of C_3H_6 and C_3H_8 are nearly equal respectively and then $\alpha_1 \fallingdotseq \alpha_2 \fallingdotseq 1$. In general, the viscosity curve deviates from a straight line, and by the mutual combination between a, μ, and ν, sometimes a maximum point occurs as easily seen from Fig. 10.

The existence of a minimum point is not improbable though any example has not been found. The area of (B) in Fig. 10 is very small, so that the probability of the occurrence of such a case by the combination of a few constants is very small, and when $C_1 = C_2$ a minimum point does not exist.

In order to know the relation between the conditions for the occurrence of a maximum point and the ratios of viscosities of two gases, β, we insert $a = \frac{\sqrt[4]{\mu}}{\sqrt{\beta\nu}}$ to equation (10), then we have as the formulæ of the boundary curves:

$$\left.\begin{aligned} &\beta = \frac{\sqrt{\mu}}{\nu}\left(2\sqrt[4]{\frac{\nu}{B}}-1\right)^2, \\ \text{and}\quad &\beta = \frac{\sqrt{\mu}}{\left(2\sqrt[4]{\frac{\mu}{B\nu}}-1\right)^2\nu}. \end{aligned}\right\} \tag{11}$$

As similarly as equation (10), this is represented graphically in Fig. 11, β being taken as abscissa. The shaded part indicates also the region of a maximum point and the greater the ratio μ is the wider this region becomes, and therefore the maximum point is very apt to occur if the ratio of two molecular weights is great. But if the ratio of two viscosities is great, the maximum point occurs only when the ratio of molecular weights is very great.

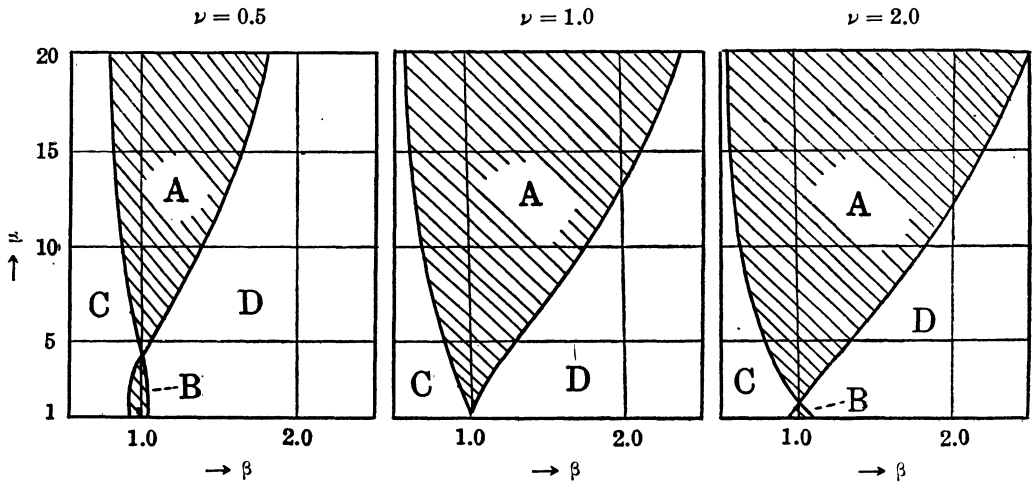


Fig. 11. $\left(\beta = \frac{\eta_0}{\eta_1}\right)$.

The above discussions are based on equation (3), in which the factor of the persistence of molecular velocity is introduced. Next, let us consider the case when the persistence of velocity is neglected, then α_1 and α_2 become:

$$\alpha_1 = \left(\frac{S}{S_1}\right)^2 \sqrt{\frac{m_1+m_2}{2m_2}} \frac{T+C_{12}}{T+C_1},$$

$$\alpha_2 = \left(\frac{S}{S_2}\right)^2 \sqrt{\frac{m_1+m_2}{2m_1}} \frac{T+C_{12}}{T+C_2}.$$

By inserting these values, $\alpha_1\alpha_2\beta$ and $\alpha_1\alpha_2/\beta$ become the same formulæ as (9), excepting that B has the following value:

$$B = \frac{1+\mu}{2}.$$

As similarly as equation (10), this relation is represented graphically in Fig. 12. As seen from the figure, not only the shape of the shaped part is different from Fig. 10, but also the relative position of two curves

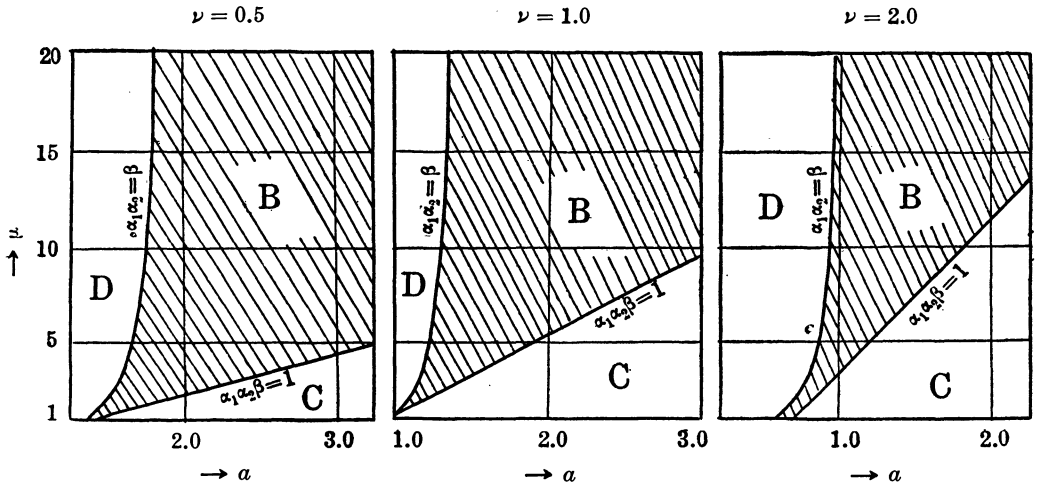


Fig. 12.

of $\alpha_1\alpha_2\beta = 1$ and $\alpha_1\alpha_2 = \beta$ is inverted, and consequently the shaded part in Fig. 12 corresponds to the region of a minimum point and that of a maximum point does not exist. This is of course contrary to the fact. Namely, the consideration of the persistence of velocity is absolutely necessary to explain the occurrence of a maximum point.

On the Displacement of the Composition of the Maximum Point. The composition of the maximum point displaces with the change of temperature. The displacements of four mixtures are given in Table 11. As seen from the table, the maximum point displaces to the lower concentration of hydrogen with the rise of temperature.

Table 11. The Compositions (H_2 %) of Maximum Points.

t°C	n_0			
	H_2~CH_4	H_2~C_2H_2	H_2~C_2H_6	H_2~C_3H_6
100	0.146	0.692	0.691	0.810
80	—	0.703	0.703	0.822
60	0.180	0.720	0.718	0.840
40	—	0.731	0.730	0.853
20	0.214	0.746	0.741	—

The composition of the maximum point is by (6)

$$n_0 = \frac{\sqrt{\alpha_1\alpha_2\beta}-1}{\sqrt{\alpha_1\alpha_2\beta}-1+\sqrt{\frac{\alpha_2}{\alpha_1}}(\sqrt{\alpha_1\alpha_2}-\sqrt{\beta})}.$$

This formula contains α, μ, ν, and $\frac{(T+C_{12})^2}{(T+C_1)(T+C_2)}$ and as the first three is independent of temperature, the displacement of n_0 is due to the change of the term of Sutherland's constant. If $C_1 = C_2$, perhaps C_{12} being also the same, this term vanishes and n_0 becomes independent of temperature. Therefore, the displacement of n_0 is due to the difference of Sutherland's constants of two gases.

The Mean Free Paths of Gas Molecules in a Mixture. The mean free paths of a molecule in a simple gas and in a mixture are expressed by the following formulæ, the persistence of molecular velocity being taken into consideration.

In a simple gas: $$\lambda_{01}^{(31)} = \frac{1}{N\pi S_1^2\sqrt{2}\left(1+\frac{C_1}{T}\right)\times 0.797}$$

(31) The suffix o is used to indicate that the persistence of velocity is considered and to distinguish from the mean free path without consideration of it used in equation (3).

$$\text{or} \qquad \lambda_{02} = \frac{1}{N\pi S_2^2 \sqrt{2}\left(1+\frac{C_2}{T}\right)\times 0.797}$$

$$\text{and in a mixture:} \qquad \left.\begin{aligned} \lambda'_{01} &= \frac{\lambda_{01}}{n_1+n_2a_1}, \\ \lambda'_{02} &= \frac{\lambda_{02}}{n_2+n_1a_2}, \end{aligned}\right\} \qquad (12)$$

where a_1 and a_2 have the same values as given in (3).

λ'_0's at 0°C. and 1 atm. pressure calculated by (12) for seven mixtures, whose viscosities have been measured by the present author, are given in Table 12, in which the value in brackets is the path when extremely small quantities of a gas are in another.

Table 12.

$H_2 \sim CH_4$

H_2 (n_1)	$\lambda'_{01}\times10^8$	CH_4 (n_2)	$\lambda'_{02}\times10^8$
1.00	1445	1.00	615
0.75	1244	0.75	708
0.50	1093	0.50	834
0.25	977	0.25	1010
0.00	(880)	0.00	(1288)

$H_2 \sim C_2H_2$

H_2 (n_1)	$\lambda'_{01}\times10^8$	C_2H_2 (n_2)	$\lambda'_{02}\times10^8$
1.00	1445	1.00	439
0.75	1272	0.75	530
0.50	1030	0.50	670
0.25	902	0.25	910
0.00	(801)	0.00	(1420)

$H_2 \sim C_2H_6$

H_2 (n_1)	$\lambda'_{01}\times10^8$	C_2H_6 (n_2)	$\lambda'_{02}\times10^8$
1.00	1445	1.00	370
0.75	1106	0.75	447
0.50	898	0.50	567
0.25	755	0.25	772
0.00	(651)	0.00	(1209)

$H_2 \sim C_3H_6$

H_2 (n_1)	$\lambda'_{01}\times10^8$	C_3H_6 (n_2)	$\lambda'_{02}\times10^8$
1.00	1445	1.00	285
0.75	1123	0.75	358
0.50	927	0.50	479
0.25	786	0.25	728
0.00	(682)	0.00	(1506)

$CH_4 \sim C_2H_2$

CH_4 (n_1)	$\lambda'_{01}\times10^8$	C_2H_2 (n_2)	$\lambda'_{02}\times10^8$
1.00	615	1.00	439
0.75	594	0.75	466
0.50	574	0.50	496
0.25	556	0.25	530
0.00	(540)	0.00	(570)

$C_2H_2 \sim C_3H_6$

C_2H_2 (n_1)	$\lambda'_{01}\times10^8$	C_3H_6 (n_2)	$\lambda'_{02}\times10^8$
1.00	439	1.00	285
0.75	422	0.75	308
0.50	405	0.50	335
0.25	389	0.25	367
0.00	(375)	0.00	(406)

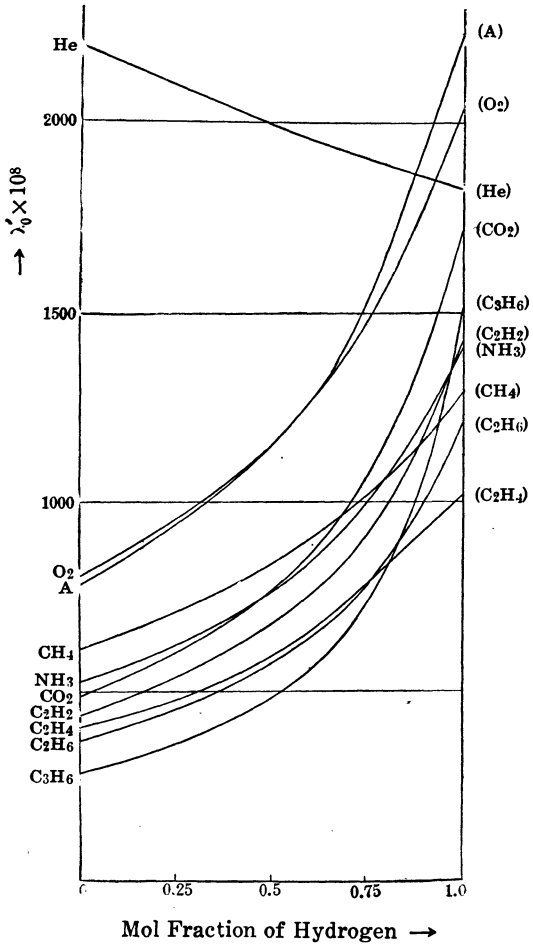


Fig. 13. The Change of the Mean Free Paths of Molecules in Hydrogen.

Table 12.—(*Concluded*)

$C_3H_6 \sim C_3H_8$

C_3H_6 (n_1)	$\lambda'_{01}\times10^8$	C_3H_8 (n_2)	$\lambda'_{02}\times10^8$
1.00	285	1.00	270
0.75	283.5	0.75	272
0.50	282	0.50	274
0.25	280	0.25	276
0.00	(279)	0.00	(278)

$NH_3 \sim N_2$

NH_3 (n_1)	$\lambda'_{01}\times10^8$	N_2 (n_2)	$\lambda'_{02}\times10^8$
1.00	522	1.00	751
0.75	558	0.75	754
0.50	600	0.50	756
0.25	648	0.25	759
0.00	(704)	0.00	(762)

$C_2H_6 \sim C_3H_8$

C_2H_6 (n_1)	$\lambda'_{01}\times10^8$	C_3H_8 (n_2)	$\lambda'_{01}\times10^8$
1.00	370	1.00	270
0.75	380	0.75	260
0.50	389	0.50	250
0.25	400	0.25	241
0.00	(412)	0.00	(233)

The change of the mean free paths of many gases due to the mixing of hydrogen are represented graphically in Fig. 13.

Generally the smaller mean free paths increases in the presence of molecules with the greater mean free paths and vice versa, excepting the case of $N_2 \sim NH_3$ and $C_2H_6 \sim C_3H_8$ whose change of paths are also given in Fig. 12.

Summary.

(1) Viscosities of six following simple gases and seven binary gaseous mixtures have been measured by the transpiration method over the temperature range between 20° and 100°C.

H_2, CH_4, C_2H_2, C_3H_6, C_3H_8, $H_2 \sim CH_4$, $H_2 \sim C_2H_2$, $H_2 \sim C_2H_6$, $H_2 \sim C_3H_6$, $CH_4 \sim C_2H_2$, $C_2H_2 \sim C_3H_6$, $C_3H_6 \sim C_3H_8$.

(2) The viscosities of the first four mixtures attain maximum values at definite compositions, which are about 20% of H_2 for the mixture $H_2 \sim CH_4$ and about 70–80% of H_2 for the other three.

(3) Of several formulæ proposed to express the viscosity of gaseous mixtures, that in which Kuenen's consideration of the persistence of molecular velocity is introduced seems to be the most appropriate. The results of observation can be expressed satisfactorily by that formula, if we take a proper value for one of Sutherland's constants which is due to the attraction between the different molecules and can not be determined directly.

(4) The theoretical consideration of this Sutherland's constant by Schmick and London have been examined by thirty-two examples.

(5) The conditions for the occurrence of a maximum and a minimum points have been obtained from the discussion of the viscosity formula and these have been examined numerically for fifty-five mixtures, and found to be always correct except for only five cases.

The viscosity-composition curve deviates in general from a straight line. The deviation depends on the ratios of molecular weights, molecular diameters, and Sutherland's constants of two component gases. Especially the maximum point is very liable to occur if the ratio of two molecular weights is great.

(6) It has been shown that, if the persistence of molecular velocity be neglected, the condition for the occurrence of a maximum point cannot be fulfilled and the consideration of the persistence is absolutely necessary to explain this point.

(7) The composition of the maximum point displaces with the change of temperature. This is found to be due to the difference of Sutherland's constants of two component gases.

(8) The mean free path of each component gas has been calculated. Generally the smaller mean free paths increases in the presence of

molecules with the greater mean free paths and vice versa, excepting a few cases.

In conclusion, the author wishes to express his sincere thanks to Prof. M. Katayama for his kind guidance throughout the present study.

Chemical Institute, Faculty of Science,
Imperial University of Tokyo.

On a New Unsaturated Fatty Acid, $C_{10}H_{18}O_2$, Present in the Oil of *Rindera obtusiloda*.

By Saburo KOMORI and Sei-ichi UENO.

(Received April 30th, 1937.)

The oil (5 kg.), extracted with ether from the nuts of *Rindera obtusiloda* grown in Korea, was saponified, decomposed, and the mixed fatty acids thus obtained were subjected to fractional distillation under a reduced pressure of 13 mm. A fraction up to 160° was taken, and, after the removal of the unsaponifiable matter, was again fractionally distilled. The low boiling portion was separated into unsaturated and saturated acids by the Ba-salt-ether method. The unsaturated acid portion was fractionally distilled once more, and finally 2.94 g. of the unsaturated acid possessing the following values were obtained: neutralisation value 327.5, iodine value 128.5.

The unsaturated acid thus obtained was hydrogenated, and the product recrystallized from 70% alcohol had m.p. 30.5–30.9° and no depression was observed in admixture with pure capric acid. Hence it was recognized that the original acid was a straight chain compound with 10 carbon atoms. Further this unsaturated acid was converted into methyl ester and the methyl ester, subjected to oxidation and splitting with powdered potassium permanganate in acetone solution, yielded succinic and caproic acids, thus establishing that the original unsaturated fatty acid has the constitution $CH_3(CH_2)_4CH:CH(CH_2)_2COOH$. No compound with this structure is found in literature and the authors propose the name "obtusilic acid" for it.

Department of Chemical Technology,
Faculty of Engineering, Imperial University of Osaka.

Adsorption of Solvent Vapour by the Solute Crystal.

By Ituro UHARA and Morizumi NAKAMURA.

(Received April 13th, 1937.)

Lumping of Powder of the Soluble Substance. Lumping of the powder of cane sugar or common salt in the wet air is usually attributed to deliquescence, but this explanation is not necessarily correct. When the dry powder of pure substances (the humidity of the vapour from the saturated aqueous solution being h_s) containing no deliquescent impurities is exposed to the air of the humidity h, lumping is observed even when h is less than h_s in a few minutes and sometimes even in under one minute, if h is larger than about two-third of h_s in the cases of fairly soluble salts.

Table.

Powder (magnitude)	h_s %	h % of air bubbled through H_2SO_4 or the saturated solution of		Lumping of powder
NaCl (0.1—0.3 mm.)	76.0 (25°)	0 (25°)	conc. H_2SO_4	not observed (—)
		36.9 ,,	50 % ,,	— ?
		46.2 ,,	45 % ,,	+
KBr (0.1—0.3 mm.)	84 (20°)	55.5 (20°)	$Ca(NO_3)_2 \cdot 4H_2O$	a little
		63.4 ,,	NH_4NO_3	+
		77.9 ,,	NaCl	strongly +
		79.4 ,,	NH_4Cl	strongly +
		81.0 ,,	$(NH_4)_2SO_4$	strongly +
Tartaric acid (0.1—1 mm.)	86 (26.18°)	0 (25°)	conc. H_2SO_4	—
		62.1 ,,	NH_4NO_3	?
		76.0 ,,	NaCl	+
		79.5 ,,	NH_4Cl	strongly +
Cane sugar (0.2—0.8 mm.)	81.2—79.5[2] (25°)	76.0 ,,	NaCl	+

As the lump maintains its form on quiet heating, this phenomenon is not due to the cohesion of condensed water. The regional formation of

(1) NaCl was heated for several hours at 400°.

(2) This value is between that of ammonium sulphate and ammonium chloride and determined by observing deliquescence putting in one vessel.

the saturated solution and recrystallization of particles through this liquid layer is probable, as h_s is depressed due to the incomplete surface structure of the powder, but this not considered the most important cause, for lumping is also observed when h is less than h_s in the case of the following samples of which surface structure is fairly normal:

(1) powder of sodium chloride is put in the saturated solution for hours, filtered, washed with alcohol, and dried without touching each other. After putting in the air of $h = 60\%$ for several hours water adsorbed is driven away by heating quietly.

(2) powder of sodium chloride or potassium bromide, which had undergone the repeated adsorption and desorption of water vapour and is supposed to have lost the abnormally active part at the crystal surface by recrystallization if the liquid layer is formed.

(3) powder of these salts heated for hours at 200–400° where the motion of ions is violent enough to rearrange the irregular surface.[3]

Adsorption of the Solvent Vapour on the Solute Crystal. After repeated adsorption and desorption of water vapour, powder of potassium bromide (0.1–0.3 mm., 47.7816 g.) is put in an evacuated small desiccator with the saturated solution of a salt of which h_s is known and weighed after two hours (20.8°).

The dimension of each particle of a part of the well mixed sample is measured under the microscope and the surface area (0.563 cm.^{2}

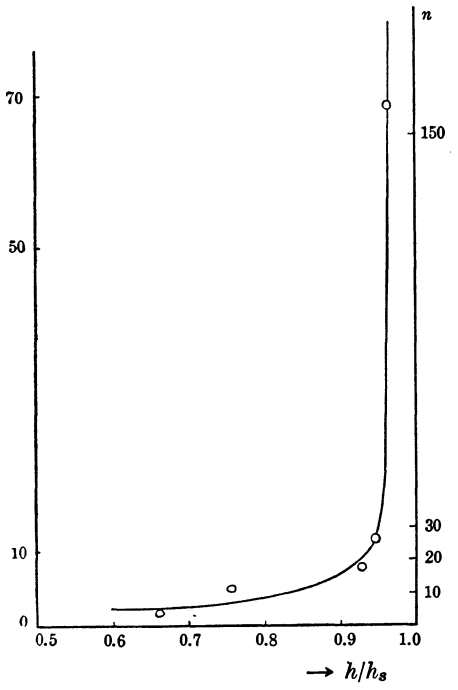


Fig. 1. Water Adsorbed by 47.7816 g. n-Molecular Layer of KBr Powder at 20.8°.

(3) According to Tammann, *Z. anorg. Chem.*, **126** (1923), 119, powders of various substances lump even at temperatures considerably lower than the melting point (NaCl 260°, cane sugar 69° ..), and this is attributed to the recrystalization due to the increased vibration of ions or molecules in the crystal. As our results were obtained at common temperature, they can not be explained in this way.

for 340 particles) and weight (density = 2.756, volume = 1.40×10^{-3}c.c., $\therefore 3.85 \times 10^{-3}$g.) are computed as the rectangular parallelopiped and the total area is 7.0×10^{3}cm.^{2}[4] The thickness of the adsorption layer is calculated assuming the real surface area is twice the geometrically determined value and is shown in Fig. 1. (monomolecular layer corresponds 3.1×10^{-8}g. H_2O/cm.^{2}) Only little is known about the adsorption of the solvent vapour on the solute crystal. Durau[5] studied the adsorption of water vapour by sodium chloride powder by measuring the pressure and obtained the analogous curve with that in Fig. 1, but he described that this method does not give exact results for soluble solids.

Electric Conductance and Electrolysis in the Adsorbed Layer. A crystal of potassium bromide is heated to 400–500° and is cooled in the apparatus shown in Fig. 2 in the current of dry air, then the surface con-

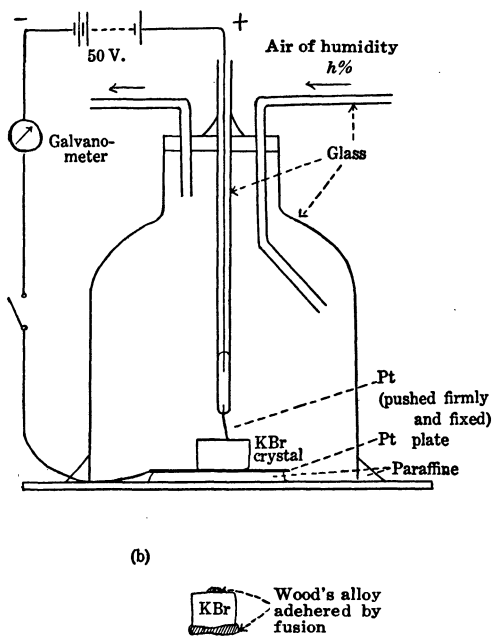


Fig. 2.

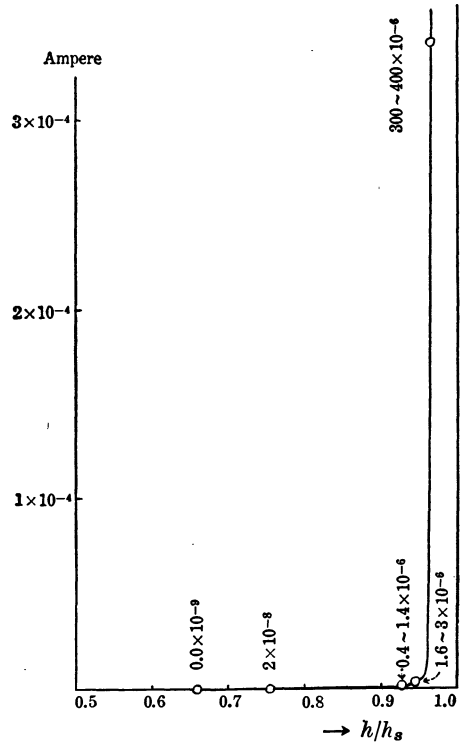


Fig. 3. The Current which flows through the Surface of KBr Crystal.

(4) This value may be more exact than that calculated from the real weight and calculated area of a small part of the sample.

(5) Durau, *Ann. Physik*, (4), **87** (1928), 307.

ductivity is measured passing the air of known humidity, when the circuit is closed only for a short time to avoid the polarization as far as possible.[6] (Fig. 3). In the dry air the conductance and consequently electrolysis are not observed at common temperature, while in the air of $h/h_s = 79.4/84$ alkali is detected at the cathode after a few hours.

Discussion of the Results. That potassium bromide or sugar is soluble in water means that it is more stable for ions or molecules at the crystal surface to exist hydrated by water molecules or in the dissolved state apart from the crystal. When water vapour is adsorbed at the surface of these crystals, it is easily supposed that this layer shows the affinity as the solvent to the ions (or molecules) at the surface though the properties of the adsorbed water under the influence of the surface field are somewhat different from those of the ordinary water.

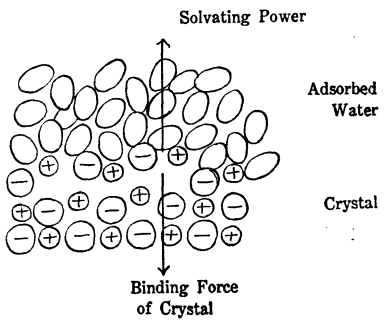


Fig. 4.

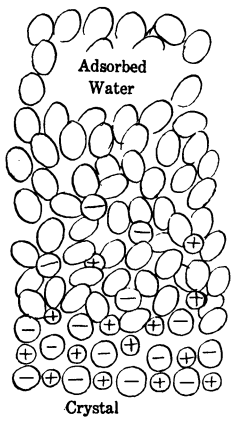


Fig. 5.

When the adsorbed quantity is little, complete hydration of ions (or molecules) is impossible as shown in Fig. 4 and so ions can not be separated from the crystal (accordingly no conductance in the case of electrolytes) though the binding force of the crystal may be weakened. When the adsorbed layer is thicker, comparatively perfect hydration being possible, some of ions (or molecules) can be dissolved in this (Fig. 5), and consequently conductance or electrolysis is observed in the case of electrolytes. As the ions are negatively adsorbed at the surface of the aqueous solution, it may be also true in the adsorbed layer

(6) Values of the same order were obtained when the sample shown in (b) was used

and so surface conductance is not observed until the layer has a certain thickness. This "solution" has the vapour tension lower than that of the usual saturated solution by the influence of the surface field of the crystal. This field may be more far-reaching than in the case of insoluble adsorbent as the surface of the solute is disturbed and becomes mobile when the solvent is adsorbed.

When the humidity of the atmosphere h becomes h_s, the adsorbed layer is thick enough and so the surface of which is not influenced by the crystal field and has the same vapour tension with that of the usual saturated solution. This vapour tension being independent of the thickness, the layer can become infinitely thick and deliquescence takes place. Accordingly adsorption of the solvent vapour and dissolution are continuous processes in the case of the soluble adsorbent.

The range of mobility of the surface ions (or molecules) is broadened by such an adsorption and rearrangement of the crystal surface takes place through this adsorbed layer so that the surface energy or area of the crystals may be decreased, and this results in the lumping of the powder. (Fig. 6. a→b).

Therefore lumping by humidity is not remarkable when the solubility is not large (sodium bicarbonate, potassium chlorate etc.) and is not observed in the case of insoluble substances (calcium phosphate, calcium carbonate etc.). The analogous phenomena can be observed for other solvent. For instance, sulphur particles which are large enough not to lump by sublimation lump in carbon disulphide vapour of which tension is lower than that of the saturated solution. A sample of sodium chloride sealed in a glass tube with water vapour lumped at 29° but not at 36°. This is easily explained as the result of the decrease of adsorption with rising temperature.

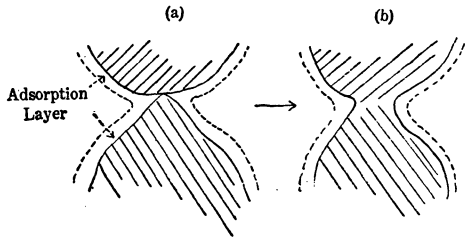


Fig. 6.

Humidity and Reaction between Solids. As the reaction between solid substances takes place at the contact point at the temperature where sublimation is negligible, the reaction velocity is increased when the surface ions (or molecules) become mobile and so the contact area is increased by the adsorption of the solvent vapour as shown above. Reactions which occur only in the solution may be also accelerated in this layer. (Fig. 7 and 6 a.) For examples, at common temperature tartaric

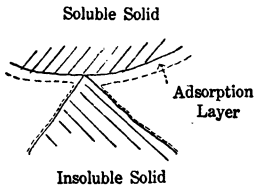


Fig. 7.

acid ($h_s = 86\%$) does not react with calcium carbonate in the desiccator but evolves carbon dioxide in the air of $h = 76\%$. The fact that this mixture lumps when the chemical change occurs shows that these phenomena have a common cause, mobility of tartaric acid molecule at the surface. On mixing calcium hydroxide and ammonium sulphate ($h_s = 81.2\%$) no change is observed in the air of $h = 63.0\%$, but when $h = 76.0\%$ ammonia smells strongly after a few hours, while the mixture of calcium hydroxide and magnesium ammonium phosphate, the latter being insoluble in water and so the surface mobility not increased by adsorption, does not evolve ammonia even when $h = 100\%$. The reaction between sodium chloride and sodium bisulphate is also greatly accelerated by the trace of water.[7] Balarev[8] studied many solid reactions at high temperature and found that a small quantity of water depresses the reaction temperature greatly and he attributed this to the relaxing of the binding of the surface molecules due to the adsorption, but he did not noticed the relation between this and the solubility. Though at high temperature adsorbed quantity is very little, the accelerating power is reported to be strong and may perhaps be catalytic, while at common temperature water seems to act as solvent.

Soluble and Insoluble Adsorbent. In the case of insoluble adsorbent which has been studied exclusively, the range of the surface force is very limited, and so monomolecular layer is formed when the adsorption takes place at low pressure. Though the multimolecular layer is formed when the pressure is higher, adsorbed molecules except in the first layer is held by the cohesion force among them. In the case of soluble adsorbent the range of force is broadened by the mobility of the surface ions (or molecules) due to the adsorption of solvent vapour, and this force, with the cohesion force among the adsorbed molecules, takes part in the formation of the multimolecular layer.

The authors express their thanks to Mr. S. Arakawa, Mr. H. Wakesima, and Mr. K. Yamazi for the kind helps.

Summary.

1) When some quantity of the solvent vapour is adsorbed by the solute crystal, a sort of solution is formed in the adsorbed layer.

(7) Isikawa, Masuda and Takai, *Bull. Inst. Phys. Chem. Research* (Tokyo), **14** (1935), 833.
(8) Balarev, many papers in *Z. anorg. Chem.*, (1924–1925).

2) Lumping of the powder, surface conductivity of the crystal, and the increase of the velocity of reactions between solids are explained as the result of the mobility of ions (or molecules) in this layer at the crystal surface.

Taihoku Higher School.

Studies on the Constitution of Shonanic Acid, One of the Two Characteristic Volatile Acids from the Wood of *Libocedrus formosana*, Florin. II. On the Reduction and Bromination of Shonanic Acid.

By Nobutoshi ICHIKAWA.

(Received September 16th, 1936.)

In a previous communication[1] the author has reported the presence of a new acid (shonanic acid) among the volatile acidic ingredients of the wood of *Libocedrus formosana*, Florin, or "Shônan-Boku" and the general properties of the acid. The present communication deals with its reduction, the addition of bromine and some derivatives derived from the bromination product.

The behaviour of shonanic acid toward reducing agents is rather delicate and complicated. If shonanic acid be reduced with sodium and ethyl alcohol the product consists of about 92% of dihydroshonanic acid $C_{10}H_{16}O_2$ $\digamma_1$ and 8% of tetrahydroshonanic acid $C_{10}H_{18}O_2$ (saturated acid), while if amyl alcohol be used instead of ethyl alcohol, about 75% dihydroshonanic and 25% tetrahydroshonanic acids resulted. In the latter case by using 20 times the theoretical amount of sodium necessary for the production of dihydro-acid, nearly all of the acid was converted into the tetrahydro-acid. With sodium amalgam dihydroshonanic acid can not be reduced any further, and with sodium and ethyl alcohol a very small portion of the acid is reduced to the tetrahydroshonanic acid, while in case of using excess of metallic sodium and amyl alcohol the reduction proceeds steadily until nearly all of the acid (dihydro-acid) is converted into the tetrahydro-acid.

(1) This Bulletin, **11** (1936), 759.

The reason why shonanic acid, which contains two conjugated double bonds, produces the saturated acid when reduced with amyl alcohol and large amount of sodium, may be explained as follows:—

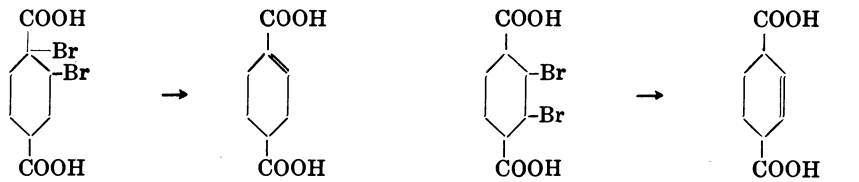
The reduction product of the first step, namely dihydroshonanic acid, may be isomerized to readily reducible α,β-unsaturated acid as in the case of $\Delta^{2,5}$-dihydroterephthalic[2] or of $\Delta^{1,3}$-dihydroterephthalic[3] acids by the action of amyl alcoholate at tolerable high temperature and the isomerized acids thus formed will be transformed into the saturated acid by further action of sodium and amyl alcohol.

On adding bromine to a solution of shonanic acid in ether, glacial acetic acid or carbon tetrachloride, two atoms of bromine will be taken up by the acid. The product, namely shonanic acid dibromide $C_{10}H_{14}O_2Br_2$, is a viscous liquid with a pale yellowish tint. It is unstable against permanganate solution even in cold but does not admit any further addition of bromine. Shonanic acid dibromide is soluble in alkaline solution and when treated with zinc dust in hot glacial acetic acid shonanic acid is regenerated with expulsion of bromine. From this fact it should be anticipated that the addition of two bromine atoms takes place at 1,2 or 3,4-position of the conjugated system. There are three modes of addition of bromine atom to the conjugated system as shown in the following:—

$$\text{R-CH=CH-CH=CH-R}' \xrightarrow{+2\text{Br}} \begin{cases} \text{R-CHBr-CHBr-CH=CH-R}' & \text{(A)} \\ \text{R-CH=CH-CHBr-CHBr-R}' & \text{(B)} \\ \text{R-CHBr-CH=CH-CHBr-R}' & \text{(C)} \end{cases}$$

In the case of (A) or (B) bromine atoms are taken away by zinc as to produce double bond, while in the case of (C) bromine atoms are substituted by hydrogen atoms. The examples of these reactions are shown in the following scheme:—

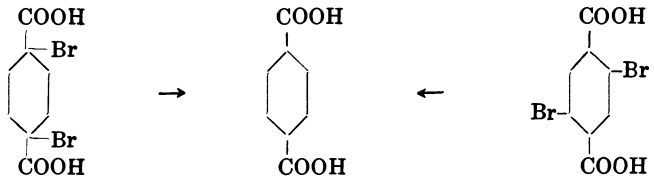
Example of the case of (A) or (B).[4]



Δ^1-Tetrahydroterephthalic acid dibromide — Δ^1-Tetrahydroterephthalic acid — Δ^2-Tetrahydroterephthalic acid dibromide — Δ^2-Tetrahydroterephthalic acid

(2) Baeyer, *Ann.*, **251** (1889), 281, 290, 306.
(3) Baeyer, *Ann.*, **269** (1892), 189.
(4) Baeyer, *Ann.*, **245** (1889), 169; Baeyer and Herb, *Ann.*, **258** (1890), 38.

Example of the case of (C).[5]



1,4-Dibromo-hexahydro-terephthalic acid — Hexahydro-terephthalic acid — 2,5-Dibromo-hexahydro-terephthalic acid

Following these examples, the addition of bromine to shonanic acid should represent the case of (A) or (B), and in the literature we find examples of this mode of addition in cases of sorbic acid[6] and cynnamylidene acetic acid.[7]

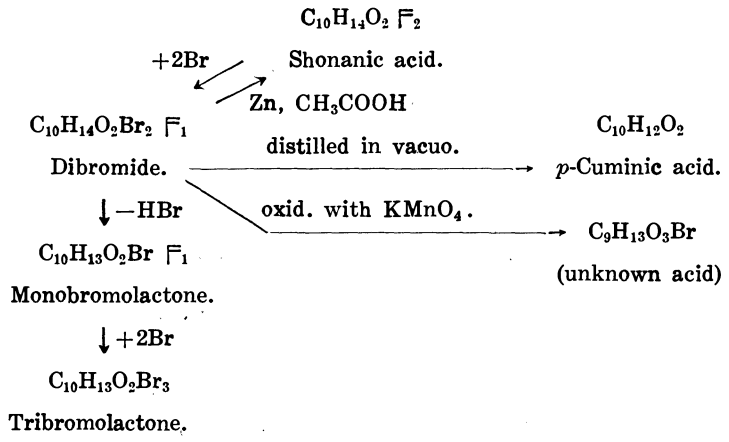
When shonanic acid dibromide is distilled in vacuo it decomposes to give *p*-cuminic acid. This formation of *p*-cuminic acid, however, must not be taken as the proof of the presence of isopropyl group in the molecule of shonanic acid, as shonanic acid as well as dihydroshonanyl alcohol on oxidation with permanganate give dimethylmalonic or dimethylglutaric acids, and no derivatives containing isopropyl group were obtained, the detailed description of which will be reported in the next communication.

Shonanic acid dibromide, on the other hand, on standing at ordinary temperature gradually turns into monobromolactone $C_{10}H_{13}O_2Br$ by giving off one mol of HBr. The substance is no more soluble in alkali but absorbs two more bromine atoms to give rise to a crystalline tribromolactone $C_{10}H_{13}O_2Br_3$, melting at 212° (with decomp.). The monobromolactone seems to be a γ-lactone from its mode of formation as analogous in cases of diallylmalonic,[8] phenylallylacetic,[9] or aticonic acids:[10] these substances add bromine to give dibromides and then giving off HBr gas form γ-lactones. A large number of experiments about the formation of lactones from Δ^{β}-, Δ^{γ}- and Δ^{α}-acids in which addition of bromine accompanied by fission of one mol of HBr are reported by J. Bougault,[11] by whom it was ascertained that Δ^{β}- and Δ^{γ}-acids give γ-lactones in these cases.

(5) Baeyer, *Ann.*, **245** (1889), 176, 151.
(6) Auwers and Heyna, *Ann.*, **434** (1923), 140.
(7) Auwers and Müller, *Ann.*, **434** (1923), 165.
(8) Hjelt, *Ann.*, **216** (1882), 61.
(9) Wislicenus and Goldstein, *Ber.*, **29** (1896), 2601.
(10) Fittig, *Ann.*, **304** (1899), 133.
(11) Bougault, *Compt. rend.*, **139** (1904), 864; **143** (1906), 398; **146** (1906), 140.

On oxidation with alkaline permanganate shonanic acid dibromide gives a crystalline bromo-acid $C_9H_{13}O_3Br$ (m.p. 239° with decomp.), the nature of which is not yet clear.

The following scheme shows the various changes mentioned above:



Experimental.

I. Action of reducing agents on shonanic acid. (1) *Action of sodium amalgam.* 10 g. of shonanic acid was dissolved in sodium bicarbonate solution and 300 g. of sodium amalgam (2.5%) was added with constant stirring and cooling while CO_2 gas was introduced into the reaction mixture in order to neutralize NaOH set free during the course of the reaction. After all the sodium amalgam has been consumed, the alkaline solution was acidified with dilute sulphuric acid when an organic acid made appearance which was collected with ether. After removal of the solvent the residue was fractionally distilled under diminished pressure and it was found that almost whole of the substance distilled at 134–135° under 6 mm. The distillate solidified to a compact mass on standing in cold, which melted at 40° after one recrystallization from light petroleum ether. The amide prepared therefrom melted at 116–117° and showed no depression of the melting point when mixed with shonanic amide. (Analysis of the silver salt: Ag, 39.55. Calculated for $C_{10}H_{13}O_2Ag$: Ag, 39.53%.)

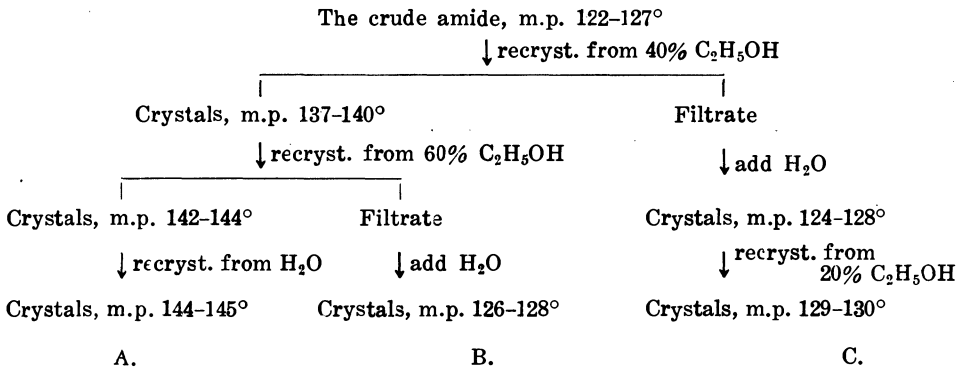
Thus it was shown that the reduction of shonanic acid can not be achieved by sodium amalgam as in the case of dihydro-*p*-xylic acid. The author, therefore, made a trial to obtain dihydro-acid $C_{10}H_{10}O_2$ F1 from shonanic acid by means of sodium and amyl alcohol, as by this treatment the above-mentioned dihydro-*p*-xylic acid gives tetrahydro-*p*-xylic acid.

(2) *Reduction with sodium and amyl alcohol.* 5 g. of shonanic acid was dissolved in 100 c.c. of amyl alcohol and 3.5 g. of metallic sodium (2.5 times of the theoretical amount necessary to produce $C_{10}H_{10}O_2$ F1 from $C_{10}H_{14}O_2$ F2) was added in small portions, heating the mixture, and adding water (about 2–3 c.c. at a time)

from time to time in order to ensure the complete dissolution of the metallic sodium. After all the sodium has been taken up, the reaction product was poured into water and the aqueous layer separated and shaken thoroughly with ether to remove traces of amyl alcohol. The alkaline solution was then acidified with dilute sulphuric acid and the organic acid set free was extracted with ether. The extract, after evaporating the excess of the solvent, was rectified under reduced pressure. B.p. 146–147°/9 mm.; d_4^{20} 1.0217; n_D^{20} 1.4892; M.R. obs. 47.48, calculated for $C_{10}H_{16}O_2$ F_1 47.35; bromine value 711 (0.1365 g. absorbed 0.097 g. of bromine), calculated for $C_{10}H_{16}O_2$ F_1 952.

The difference between the theoretical and the experimental bromine values may be attributed to the presence of the saturated acid (tetrahydroshonanic acid, $C_{10}H_{18}O_2$) and this conjecture was proved correct by the fact that tetrahydroshonanic amide was actually obtained from the reduction product. The ratio of saturated and unsaturated acid can roughly be calculated from the theoretical and experimental bromine values as follows: saturated acid 74.6, unsaturated acid 25.4%. (Found: C, 71.04, 70.96; H, 10.13, 10.06. Calculated for $C_{10}H_{16}O_2$: C, 71.4; H, 9.5; $C_{10}H_{18}O_2$: C, 70.6; H, 10.6%. Analysis of the silver salt: Ag, 39.27. Calculated for $C_{10}H_{15}O_2Ag$: Ag, 39.24; $C_{10}H_{17}O_2Ag$: Ag, 38.96%.)

Amide. The acid chloride was prepared from the acid (1 g.) and phosphorus trichloride as usual and it was added to cold aqueous ammonia to obtain the amide. The amide melted at 122–127°, which was subjected to fractional recrystallization as shown below:



Crystals A were proved to be identical with tetrahydroshonanic amide prepared from saturated acid (tetrahydro-acid) obtained by catalytic reduction of shonanic acid; crystals B might have been crude mixture of A and C, but on account of the scarcity of the substance further purification was not carried out; crystals C represented dihydroshonanic amide whose melting point remained constant on further purifications. (Found: N, 8.56. Calculated for $C_{10}H_{17}ON$: N, 8.4%.) Other evidences for the presence of the saturated acid therein may also be recognized among the experimental data observed in the analysis of the silver salt, elementary analysis and bromine value.

(3) *Reduction with a large amount of sodium and amyl alcohol.* 10 g. of the acid dissolved in 300 c.c. of amyl alcohol was kept hot on a boiling water-bath and 30 g. of sodium was added in small portions with vigorous stirring. 2–5 c.c. of water was added several times during the course of the reaction in order to promote the reaction. The reaction product was poured into water, stirred vigorously for 10 minutes and the alkaline layer was separated. The alkaline solution was acidified and the organic acid set free was extracted with ether. The extract after removal of the solvent was subjected to fractional distillation under reduced pressure. At the beginning of the distillation isovaleric acid, produced as by-product,[12] distilled and then the main fraction boiling at 143–144°/9 mm. came over. The distillate was rectified once more and thus an acid with the following properties was obtained: b.p. 140–141°/8 mm.; d^{30} 0.9863; n_D^{30} 1.4665; M.R. obs. 47.78, calculated for $C_{10}H_{18}O_2$ 47.72; acid value 336.4 (0.5238 g. required 32.11 c.c. of 0.098 N NaOH), calculated for $C_{10}H_{18}O_2$ 329.4; bromine value nil. (Found: C, 70.44, 70.42; H, 10.61, 10.60. Calculated for $C_{10}H_{18}O_2$: C, 70.58; H, 10.58%. Analysis of the silver salt: Ag, 38.90. Calculated for $C_{10}H_{17}O_2Ag$: Ag, 38.96%.)

Contrary to the previous case the product was an entirely saturated acid (tetrahydroshonanic acid) the amide showing the same melting point as tetrahydroshonanic amide.

Acid chloride. The acid chloride was prepared in the usual manner from 3 g. each of the acid and phosphorus trichloride. Its properties were as follows: b.p. 115–116°/20 mm.; d_4^{30} 1.016; n_D^{30} 1.4713.

Amide. The amide was obtained by the interaction of the acid chloride and aqueous ammonia in plate crystals with pearly lustre, which melted at 143–144° after a crystallization from 50% ethyl alcohol. (Found: N, 8.23. Calculated for $C_{10}H_{19}ON$: N, 8.28%.)

II. Action of reducing agents on dihydroshonanic acid. (1) *Catalytic hydrogenation of dihydroshonanic acid.* As already stated in the previous communication, it was found that dihydroshonanic acid absorbs two atoms of hydrogen to give tetrahydroshonanic acid $C_{10}H_{18}O_2$.

(2) *Action of sodium amalgam.* 5 g. of dihydroshonanic acid (containing ca. 92% of dihydroshonanic acid obtained by the experiment IV-(6) in the previous communication) was dissolved in an excess of 10% sodium hydroxide solution and was treated with 400 g. of sodium amalgam (2.5%) (6 times the calculated amount to give $C_{10}H_{18}O_2$) at ordinary temperature with vigorous stirring. The product showed the following properties: b.p. 143–144°/7 mm.; d_4^{30} 1.0328; n_D^{30} 1.4987; M.R. obs. 47.74, calculated for $C_{10}H_{16}O_2$ $\digamma_1$ 47.35; bromine value 885 (0.1922 g. absorbed 0.1698 g. of bromine), calculated for $C_{10}H_{16}O_2$ $\digamma_1$ 952.

That the unsaturated acid remains practically unchanged is clear from the bromine value, which tells that dihydroshonanic acid is not at all affected by sodium amalgam.

Amide. The amide was prepared from the acid chloride and aqueous ammonia which melted at 129–130° and was proved to be identical with dihydroshonanic amide

(12) Dumas and Stas, *Ann.*, **35** (1840), 143.

by melting in admixture with that obtained in the experiment IV-(6) (previous communication[1]).

(3) *Reduction with sodium and ethyl alcohol.* 3 g. of dihydroshonanic acid was dissolved in 100 c.c. of ethyl alcohol and 3.5 g. of sodium (3 times of the theoretical amount of sodium necessary to produce $C_{10}H_{18}O_2$ from $C_{10}H_{16}O_2F_1$) was added in small portions. The product showed the following properties: b.p. 141–143°/7 mm.; d_4^{30} 1.0298; n_D^{30} 1.4966; M.R. obs. 47.71, calculated for $C_{10}H_{16}O_2F_1$ 47.35; bromine value 875 (0.1108 g. absorbed 0.0906 g. of bromine), calculated for $C_{10}H_{16}O_2F_1$ 952.

The amount of the saturated acid calculated from the bromine value is ca. 15% showing an increase of the saturated acid by 7% as compared with the starting substance.

Amide. The amide prepared as usual from the acid chloride and aqueous ammonia melted at 107–120° without any purification, which was then subjected to fractional recrystallization as follows:—

The crude amide, m.p. 107–120°
↓ recryst. from 40% C_2H_5OH

Crystals, m.p. 123–133°
↓ recryst. from 60% C_2H_5OH

Crystals, m.p. 140–144°
↓ recryst. from 60% C_2H_5OH
Crystals, m.p. 142–145°
A.

Crystals from the filtrate, m.p. 124–127°
↓ recryst. from 20% C_2H_5OH
Crystals, m.p. 127–129°
↓ recryst. from H_2O
Crystals, m.p. 129°
B.

Crystals from the filtrate, m.p. 118–124°
↓ recryst. from 20% C_2H_5OH
Crystals, m.p. 126–129°
↓ recryst. from H_2O
Crystals, m.p. 128–129°
C.

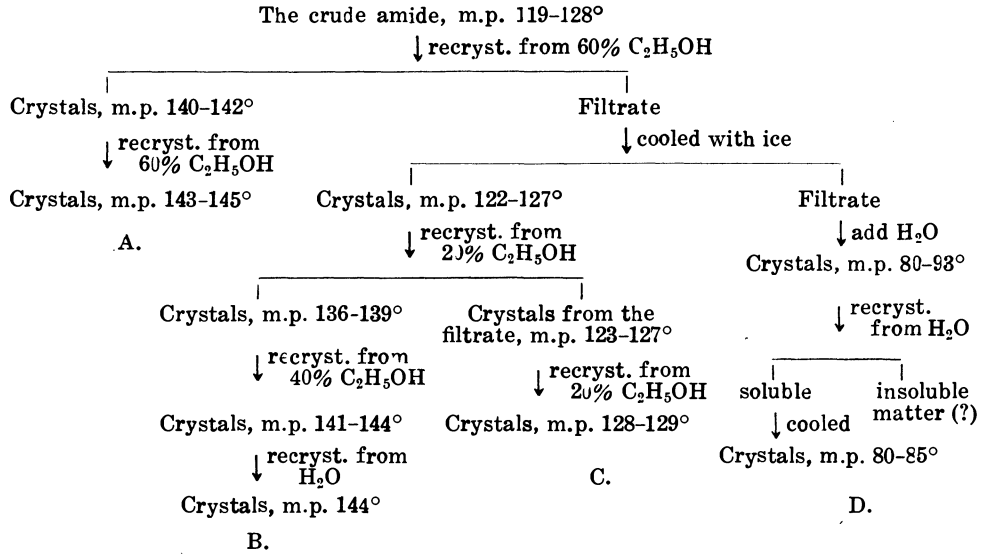
Owing to the scarcity of the material crystals A were without further purification mixed with tetrahydroshonanic amide and the melting point examined. They melted at 142–144°, from which it is obvious that this substance is tetrahydroshonanic amide. Crystals B and C were identified as dihydroshonanic amide in like manner.

(4) *Reduction with sodium and amyl alcohol.* 3 g. of dihydroshonanic acid (preparation of the experiment IV-(6) of the previous report, containing 92% dihydro-acid) was dissolved in 100 c.c. of amyl alcohol and was reduced with 3.5 g. of sodium. The product had the following properties: b.p. 142–144°/7 mm.; d_4^{30} 1.0160; n_D^{30} 1.4870; bromine value 378 (0.1635 g. absorbed 0.0616 g. of bromine), calculated for $C_{10}H_{16}O_2F_1$ 952.

The approximate amount of the saturated acid in the reaction product is about 60% as calculated from the bromine value. (Analysis of the silver salt: Ag, 39.03. Calculated for $C_{10}H_{15}O_2Ag$: Ag, 39.24; $C_{10}H_{17}O_2Ag$: Ag, 38.96%.)

Amide. The acid chloride obtained from 1.3 g. of the acid and 1.5 g. of phosphorus trichloride was treated with aqueous ammonia, and the crude amide

thus obtained melted at 119–128° without any purification, which was fractionally recrystallized as follows.



The crystals A and B were found to be identical with tetrahydroshonanic amide by observing the melting point of mixtures, while the crystals C were found to be identical with dihydroshonanic amide. The crystals D were not further purified as the quantity available became scarce but it can not be considered as crude crystals of C as the former is readily soluble in water while the latter is not.

(5) *Reduction with a large amount of sodium and amyl alcohol.* 3 g. of dihydroshonanic acid was dissolved in 100 c.c. of amyl alcohol and was treated with 10 g. of sodium as usual. The product showed the following properties: b.p. 141–143°/7 mm.; d_4^{30} 0.9930; n_D^{30} 1.4703; M.R. obs. 47.74, calculated for $C_{10}H_{18}O_2$ 47.72; bromine value 26 (0.1472 g. absorbed 0.0038 g. of bromine).

The percentage of the saturated acid therein was found to be about 97%.

Amide. The amide was prepared from the acid chloride (prepared from 2 g. of the acid and 3 g. of phosphorus trichloride) and aqueous ammonia. It melted at 144° after one recrystallization from 60% ethyl alcohol and was found to be identical with tetrahydroshonanic amide obtained by catalytic hydrogenation of shonanic acid.

III. Some derivatives of shonanic acid containing bromine. (1) *Shonanic acid dibromide.* To a well-cooled solution of shonanic acid (acid 10 g. in ether 100 c.c.) 10 g. of bromine was added drop by drop with constant shaking. The colour of the ethereal solution acquired yellowish tint and on removal of the solvent under diminished pressure there remained a colourless viscous oily substance, which showed no tendency of solidification even kept at −5° for several days. The dibromide thus obtained does not admit further addition of bromine whereas it is easily acted on by dilute permanganate solution at 0°. On standing at the ordinary temperature

a portion of the dibromide was gradually converted into grayish monobromolactone (see below).

The dibromide could not be distilled without decomposition and the physical properties of the crude preparation were as follows: d_4^{30} 1.603; n_D^{30} 1.5330; M.R. obs. 63.10, calculated for $C_{10}H_{14}O_2Br_2$ 1 62.78. (Found: C, 37.27; H, 4.35; Br, 48.78. Calculated for $C_{10}H_{14}O_2Br_2$: C, 36.81; H, 4.29; Br, 49.06%.)

(2) *Regeneration of shonanic acid from its dibromide.* 10 g. of shonanic acid dibromide freshly prepared as above was dissolved in 60 c.c. of glacial acetic acid, kept cool with the freezing mixture and 50 g. of zinc dust was added in small portions. After all zink dust has been added the reaction mixture was then warmed on a boiling water-bath for an hour. It was then poured into water and the oily acidic substance separated was extracted with ether. The ethereal solution was washed with water to remove acetic acid present, dried over anhydrous sodium sulphate and the ether was distilled off. The reddish brown substance remaining behind was fractionally distilled under reduced pressure, when 3.8 g. of acidic substance came over at 140°/7 mm. It contained no bromine at all, as it gave no Beilstein's flame reaction. The amide prepared from the acid chloride (b.p. 98°/12 mm.) of the substance and aqueous ammonia melted at 116–117° after recrystallization from 50% ethyl alcohol, it was identical with shonanic amide. Thus, by the action of zinc and glacial acetic acid, shonanic acid was regenerated from its dibromide.

(3) *The formation of monobromolactone from the dibromide.* 6.5 g. of shonanic acid dibromide was placed in a round flask and warmed on the water-bath at 40–50° for 4 hours under 40–50 mm. It was then dissolved in ether and by shaking with dilute sodium carbonate solution the unchanged acid was removed. From the ethereal solution a substance with the following properties was obtained (Yield 2.4 g.): d_4^{30} 1.4540; n_D^{20} 1.544; M.R. obs. 53.21, calculated for $C_{10}H_{13}O_2Br$ 1 52.81.

The substance is insoluble in alkaline solution, unstable against permanganate and absorbs bromine in cold, showing the substance to be unsaturated. The substance could not be distilled without decomposition. Bromine value 644.6 (0.7983 g. absorbed 0.5146 g. of bromine), calculated for $C_{10}H_{13}O_2Br$ 1 653.1. (Found: Br, 32.68. Calculated for $C_{10}H_{13}O_2Br$: Br, 32.65%.)

(4) *Preparation of tribromolactone from monobromolactone.* To a solution of 5 g. of monobromolactone in 50 c.c. of glacial acetic acid 5 g. of bromine was added in the cold, which was readily absorbed and a crystalline substance deposited on standing. The solution was kept cool over night and the crystalline substance was filtered, washed with cold glacial acetic acid then with ether. Yield 8.3 g. (91% of the theoretical). The tribromolactone, thus prepared, melted at 209° (with decomposition), insoluble in alkali, ether, ethyl alcohol, chloroform and glacial acetic acid and sparingly soluble in boiling alcohol, benzene and petroleum ether. When recrystallized from boiling alcohol the melting point was elevated to 212° (with decomposition). (Found: C, 29.34; H, 3.25; Br, 58.74. Calculated for $C_{10}H_{13}O_2Br_3$: C, 29.65; H, 3.21; Br, 59.23%.)

(5) *The formation of* p-*cuminic acid from shonanic acid dibromide.* When shonanic acid dibromide (10 g.) was subjected to distillation under reduced pressure

the evolution of hydrogen bromide set in at first and there happened no remarkable change until the temperature of the oil bath attained 200°, when suddenly a vigorous evolution of gas took place and on further heating a fraction boiling at 146°/7 mm. distilled over. This fraction on standing deposited a crystalline substance which was spread over a porous plate to remove liquid substance and then it was recrystallized from 40% ethyl alcohol. It melted at 119–120°. Another crop of crystals was obtained from the filtrate by the addition of water, which also melted at 119° after one recrystallization from 40% ethyl alcohol. The substance bears an acidic characteristic and is inert against permanganate and does not give flame colour reaction of Beilstein, showing the absence of bromine. Acid value 341.2 (0.1716 g. required 10.52 c.c. of 0.102N NaOH), calculated for $C_{10}H_{12}O_2$ 341.5. (Found: C, 73.35; H, 7.57. Calculated for $C_{10}H_{12}O_2$: C, 73.17; H, 7.31%. Analysis of the silver salt: Ag, 39.78. Calculated for $C_{10}H_{11}O_2Ag$: Ag, 39.82%.)

Acid chloride. A mixture of 1.4 g. of the acid and 1.5 g. of phosphorus pentachloride was heated on the water-bath for 20 minutes. The product distilled at 107–109°/15 mm. Yield 0.8 c.c.

Amide. The amide was prepared as usual by the interaction of the acid chloride and aqueous ammonia. It melted at 152–153° when recrystallized from 60% ethyl alcohol.

Among the acids of the formula $C_{10}H_{12}O_2$, *p*-cuminic acid melts at 119–120° and its amide at 152–153°. In order to ascertain that the acid under investigation is identical with *p*-cuminic acid the latter was prepared from *p*-cuminol by kali-fusion.

To molten potassium hydroxide (7 g.) in a nickel crucible, 5 g. of *p*-cuminol was added drop by drop with constant agitation. The reaction product was then treated with water and *p*-cuminic acid produced was liberated in the usual way and recrystallized from alcohol. It melted at 119° and on mixing it with the acid under investigation showed no depression of the melting point. Thus it is evident that the acid obtained by the decomposition of shonanic acid dibromide is *p*-cuminic acid.

IV. Oxidation of shonanic acid dibromide with potassium permanganate. To a well-cooled solution of shonanic acid dibromide (10 g.) in 5% sodium carbonate solution (300 c.c.) dilute permanganate solution ($KMnO_4$ 26 g. in 600 c.c. H_2O) was added drop by drop with constant stirring. The reaction mixture was left over night in an atmosphere of carbon dioxide, filtered from manganese dioxide and the alkaline solution thus obtained was evaporated nearly to dryness on the water-bath. The organic acid liberated by acidification with dilute sulphuric acid was extracted with ether. The ethereal solution was dried over anhydrous sodium sulphate and then the solvent was distilled away. The remainder crystallized on cooling in prismatic needles which was purified by washing with chloroform and twofold recrystallizations from absolute alcohol. It melted at 239° (with decomposition). The substance is insoluble in cold alcohol, chloroform, benzene and petroleum ether and soluble in alkali from which the original acid can be regenerated by the addition of mineral acid. The presence of bromine atom in the molecule of the acid was recognized by Beilstein's flame colour reaction. (Found: C, 43.37; H, 5.10; Br, 32.12. Calculated

for $C_9H_{13}O_3Br_3$: C, 43.37; H, 5.22; Br, 31.92%. Analysis of the silver salt: Ag, 30.41. Calculated for $C_9H_{12}O_3BrAg$: Ag, 30.33%.)

The acid being monobasic the third atom of oxygen therein may exist either as a carbonyl or as a hydroxyl oxygen, but as the material was scanty, it was not studied any further.

In conclusion, the author wishes to express his sincere thanks to Prof. Kinzô Kafuku for his kind guidance.

Department of Industry,
Government Research Institute of Taiwan.

Studies on the Constitution of Shonanic Acid, One of the Two Characteristic Volatile Acids from the Wood of *Libocedrus formosana*, Florin. III. Studies on the Oxidation of Shonanic Acid.

By Nobutoshi ICHIKAWA.

(Received September 16th, 1936.)

Shonanic acid, when oxidized in cold with dilute potassium permanganate solution, gives a crystalline dibasic acid of the formula $C_5H_8O_4$. The acid purified by sublimation in vacuo melts at 184–186° (with decomp.), its amide melting at 259–260°. There are four possible constitutional formulæ for this acid, viz.,

(1) $HOOC\text{-}(CH_2)_3\text{-}COOH$ Pyrotartaric acid, m.p. 97°.

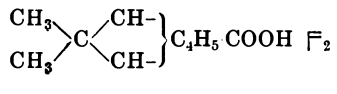
(2) $CH_3\text{-}CH(CH_3)\text{-}CH_2\text{-}COOH$ Methylsuccinic acid, m.p. 115°, 102°, 112.5°.

(3) $CH_3\text{-}CH_2\text{-}CH(COOH)_2$ Ethylmalonic acid, m.p. 111.5°.

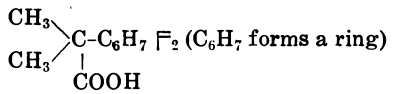
(4) $(CH_3)_2C(COOH)_2$ Dimethylmalonic acid, m.p. 186° (with decomp.).

As the present acid $C_5H_8O_4$, on heating somewhat above its melting point, loses exactly one mol of carbon dioxide and transforms into isobutyric acid, it is obvious that the acid has two carboxyl groups in union with one carbon atom, i.e. it must be dimethylmalonic acid. The formation of dimethylmalonic acid indicates that shonanic acid should be repre-

sented by I or II. In case of I the two carboxyl groups (in dimethylmalonic acid) were newly formed as the result of oxidation, while in the latter case one of the carboxyl groups is the originally contained one.



I.



II.

In order to determine the structural feature of the ring-forming nucleus of shonanic acid, the following methods were adopted.

(1) Preparation of hydrocarbon with the same number of carbon atoms as shonanic acid by reducing carboxyl group to methyl group. The resulting hydrocarbon was compared with the known hydrocarbons of the same formula in regard to their physical properties.

(2) Preparation of hydrocarbon with nine carbon atoms by eliminating the carboxyl group on heating the acid with soda-lime.

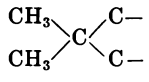
(3) Conversion of shonanic acid into known substances by oxidizing the side chain or substituents in the nucleus of shonanic acid.

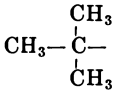
The results of the experiments were as follows.

(1) The hydrocarbon prepared by heating shonanic acid and tetrahydroshonanic acid respectively with hydroiodic acid in a sealed tube showed the following properties:

Hydrocarbon from shonanic acid.	Hydrocarbon from tetrahydroshonanic acid.
b.p. 157–158.3°/754 mm.	b.p. 158.5°/765 mm.
d_4^{20} 0.7866	d_4^{20} 0.7872
n_D^{20} 1.4344	n_D^{20} 1.4338

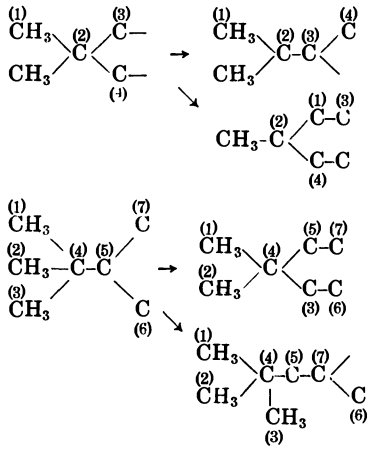
Whether the starting substance be the unsaturated shonanic acid or the saturated tetrahydroshonanic acid, that the product formed by the action of hydroiodic acid should represent the same hydrocarbon is experimentally assured as far as the physical properties are concerned. This hydrocarbon, as should be expected from the known partial structure of the original acid, contains an arrangement I or II, provided that no inversion takes place throughout the reduction by hydroiodic acid.

I. 

II. 

Thus in comparing it with known hydrocarbon, such ones containing a dimethyl or trimethyl group should be adopted, and further more, taking

into consideration the ring transformation often effected by hydroiodic acid, the cases of III to VI, viz.:



III. (Transformation into a smaller ring.)

IV. (Transformation into a larger ring.)

V. (Transformation into a larger ring.)

VI. (Transformation into a smaller ring.)

The properties of hydrocarbons $C_{10}H_{20}$ with atom groups mentioned above were tabulated in Table 1. As seen from the table the hydrocarbons $C_{10}H_{20}$ have the general value 0.78–0.81 for the density, 1.43–1.45 for the refractive index. Those with six-membered ring have the boiling points 166–171°, while those with five-membered ring have values lower than 160°. On comparing the physical properties of the hydrocarbon from shonanic acid with those of the known hydrocarbons it is likely that the former possesses a five-membered ring, but this should not at once extended to shonanic acid itself, as the ring transformation might have ensued by the action of hydroiodic acid as in the transformations of benzene to methylcyclopentane and cyclohexyl iodide or cyclohexanol to methylcyclopentane. But judging from its physical properties, it is evident that the hydrocarbon obtained from shonanic acid is either a compound with a five- or six-membered ring system.

(2) With a view to obtain a hydrocarbon C_9H_{18} tetrahydroshonanic acid was heated with soda-lime, when, contrary to the expectation, an unsaturated hydrocarbon C_9H_{16}, which showed the following properties, was obtained. B.p. 145–148°; d_4^{26} 0.8128; n_D^{20} 1.4593.

The attempt to obtain its nitrosochloride or nitrosite in the crystalline state was futile. Next, in order to study the ring system of the hydrocarbon obtained, its physical properties were compared with those of known hydrocarbons of the same formula C_9H_{16} ⌐1. For this purpose the following hydrocarbons were chosen (Table 2), taking into consideration the ring transformation or migration of atom groups which might have been accomplished by heating with soda-lime.

Table 1.

Substance	d	n_D	B.p.
o-Menthane[1]	0.8135 ($^{21}_{0}$)	1.447 (21)	171°
d-*m*-Menthane[2]	0.8116 ($^{23}_{0}$)	1.446 (23)	167–168°
l-*m*-Menthane[3]	0.7938–0.7956 ($^{20}_{0}$)	1.4358–1.4355 (20)	167–168°
i-*m*-Menthane[1]	0.7965 ($^{24}_{0}$)	1.440 (24)	166–167°
p-Menthane[4]	0.7974 ($^{20}_{4}$)	1.4380 (20)	172°
Hexahydrodurol[5]	0.811 ($^{20}_{4}$)	1.4451 (20)	169–170.5°
1,3-Diethyl-cyclohexane[6]	0.7957 ($^{22}_{4}$)	1.4388 (20)	169–171°
Butyl-cyclohexane[7]	0.8178 ($^{20}_{4}$)	—	178–180°
tert-Butyl-cyclohexane[8]	0.8305 ($^{16}_{4}$)	1.4556 (16)	166–167°
1-Methyl-3-propyl-cyclohexane[9]	0.7895 ($^{21}_{4}$)	1.4352 (21)	169–170°
1,2-Dimethyl-3-isopropyl-cyclopentane[10]	0.786 (^{16})	1.4337 (16)	146–148°
Hydrocarbon from thujane[11]	0.7923 ($^{20}_{0}$)	1.4377	157°
Hydrocarbon from shonanic acid	0.7872 ($^{19}_{4}$)	1.4338 (19)	158.5°

Table 2.

Substance	d	n_D	B.p.
1-Propyl-cyclohene[12]	0.838 (^{19})	1.4579 (19)	154–156°
Propyliden-cyclohexane[13]	0.8210 (^{19})	1.4631 (19)	157–158°
Δ^1-Tetrahydrocumol[14]	0.8290 (^{20})	1.4606 (20)	155–157°
Isopropyliden-cyclohexane[15]	0.836 (^{20})	1.4723 (20)	160–161°

(1) Sabatier and Murat, *Compt. rend.*, **156** (1913), 186.
(2) Sabatier and Murat, *ibid.*, **156** (1913), 187.
(3) Kishner, *Chem. Zentr.*, **83** (1912), I, 1456.
(4) Smirnow, *Chem. Zentr.*, **81** (1910), I, 740.
(5) Willstätter and Hatt, *Ber.*, **45** (1912), 1473.
(6) Zelinsky and Rudewith, *Ber.*, **28** (1895), 1343.
(7) Douris, *Compt. rend.*, **157** (1913), 57.
(8) Halse, *J. prakt. Chem.*, [2], **92** (1915), 41.
(9) Beilstein, "Handbuch der organischen Chemie," 4. Aufl., Bd. 5, Erstes Ergänzungswerk, 20 (1931).
(10) Godchot and Taboury, *Compt. rend.*, **156** (1913), 472.
(11) Kishner, *Chem. Zentr.*, **83** (1912), I, 1457.
(12) Wallach, Churchill, and Rentschler, *Ann.*, **360** (1908), 58.
(13) Wallach, Churchill, and Rentschler, *Ann.*, **360** (1908), 56.
(14) Wallach and Mallison, *Ann.*, **360** (1908), 69.
(15) Wallach and Mallison, *Ann.*, **360** (1908), 68.

Table 2.—(*Concluded*)

Substance	d	n_D	B.p.
1-Methyl-2-ethyliden-cyclohexane[16]	0.823 (^{0})	1.47	158°
1-Methyl-3-ethyliden-cyclohexane[17]	0.813 (^{0})	1.4584	153°
1-Methyl-3-ethyl-cyclohexene-(2 or 3)[18]	0.8154 ($^{19}_0$)	1.4538 (19)	148-149°
1-Methyl-4-ethyl-cyclohexene-(3)[19]	0.8169 ($^{16}_4$)	1.453 (16)	149°
1-Methyl-4-ethyliden-cyclohexane[20]	0.810 (^{20})	1.4571 (20)	152-153°
1,1,2-Trimethyl-cyclohexene-(2)[21]	0.8217 (^{20})	1.456 (20)	146.2-147.2°
1,1,3-Trimethyl-cyclohexene-(2)[22]	0.803 (^{20})	1.446 (21.5)	139-142°
1,1,4-Trimethyl-cyclohexene-(3)[23]	0.8032 ($^{18.8}_4$)	1.4415 (23)	139-140°
1,2,3-Trimethyl-cyclohexene-(1)[24]	0.8347 ($^{11.7}_4$)	1.463 (11.7)	149-150°
1,2,4-Trimethyl-cyclohexene-(4)[25]	0.8078 ($^{16}_4$)	1.450 (16)	144-146°
1,3,5-Trimethyl-cyclohexene-(1)[26]	0.7965 (^{21})	1.4447 (21)	142.5-143.5°
3,5-Dimethyl-1-methylen-cyclohexane[27]	0.7922 ($^{14}_4$)	1.446 (14)	135-136°
1-Methyl-3-isopropyl-cyclopentene-(1)[28]	0.801 (^{20})	1.4478 (20)	144-146°
1-Methyl-3-isopropyl-cyclopentene-(2)[29]	0.791 (^{22})	1.4380 (22)	138-139°
Apofenchene[30]	0.794 (^{21})	1.4403 (22)	142-143°
1-Methyl-2-isopropyliden-cyclopentane[31]	0.8104 ($^{20}_0$)	1.4518	149-151°
1-Methyl-2-isopropenyl-cyclopentane[31]	0.8006 (^{20})	1.4455	141-143°
Pulegene[32]	0.791 (^{22})	1.4380	138-139°
1,1,2-Trimethyl-3-methylen-cyclopentane[33]	—	—	138-140°
1,1,2,5-Tetramethyl-cyclopentene-(3)[34]	0.8034 (^{20})	1.44406 (20)	133-135°
Hydrocarbon from tetrahydroshonanic acid	0.8129 ($^{19}_4$)	1.4595 (19)	145-148°

(16) Murat, *Ann. chim.*, [8], **16** (1909), 125.
(17) Wallach and Evans, *Ann.*, **360** (1908), 51.
(18) Zelinsky and Gutt, *Ber.*, **35** (1902), 2140; Zelinsky and Zelikow, *Ber.*, **34** (1901), 3255
(19) Sabatier and Mailhe, *Compt. rend.*, **142** (1906), 439.
(20) Wallach and Rentschler, *Ann.*, **365** (1909), 271.
(21) v. Auwers and Lange, *Ann.*, **409** (1915), 174.
(22) Tiemann, *Ber.*, **33** (1900), 3711.
(23) v. Auwers and Lange, *Ann.*, **409** (1915), 167.
(24) v. Auwers and Krollpfeiffer, *Ber.*, **48** (1915), 1231.
(25) v. Auwers, *Ann.*, **420** (1919), 105.
(26) v. Auwers, Hinterseber, and Treppmann, *Ann.*, **410** (1915), 270.
(27) v. Auwers, Hinterseber, and Treppmann, *Ann.*, **410** (1915), 272.
(28) Semmler, *Ber.*, **37** (1904), 237.
(29) Wallach, Collmann, and Thede, *Ann.*, **327** (1903), 131.
(30) Wallach, *Ann.*, **369** (1909), 83.
(31) Kishner, *Chem. Zentr.*, **83** (1912), II, 1925.
(32) Wallach, Collmann, and Thede, *Chem. Zentr.*, **73** (1902), I, 1925.
(33) Bouveault and Blanc, *Compt. rend.*, **136** (1903), 1461.
(34) Tiemann, *Ber.*, **30** (1897), 595.

As seen from Table 2, the hydrocarbons with six-membered ring system have values 0.80–0.83 for density while those with five-membered ring 0.79–0.81. Thus it can not be decided by comparing the densities whether the hydrocarbon under investigation is of five- or six-membered ring. Viewed from refractive indices, hydrocarbon of six-membered ring system have values 1.44–1.47 while those of five-membered ring system values 1.43–1.45. The actual hydrocarbon has $n_D^{20} = 1.4595$ and consequently is likely to be one with six-membered ring system, but it should not be strongly taken into account, as its boiling point is found to be 145–148° which is close to those of hydrocarbons with five-membered ring as well as with six-membered ring.

(3) The attempt to obtain some known derivatives from shonanic acid by oxidation at last succeeded by the use of dilute nitric acid as oxidant. When shonanic acid was heated with dilute nitric acid for some hours *o*-dinitrobenzene was obtained with a fairly good yield. Though it can not easily be elucidated under what mechanism the acid was converted into *o*-dinitrobenzene, the formation of it may be taken as an evidence for the presence of six-membered ring in shonanic acid molecule, unless other data appear which are rigorously against the above reasoning.

Experimental.

I. Oxidation of shonanic acid with potassium permanganate. 600 c.c. of 4% potassium permanganate solution was added drop by drop to a well-cooled solution of the acid (5 g. of the acid in 500 c.c. of 7% Na_2CO_3 solution) with vigorous stirring. After all the permanganate solution has been added the reaction mixture was warmed on the water-bath at 40–50° for 30 minutes and filtered while hot in order to remove manganese dioxide precipitated. The filtrate was then evaporated nearly to dryness, acidified with dilute sulphuric acid and extracted with ether. On distilling off the solvent there remained about 3.5 g. of reddish yellow sticky substance, which on standing at the ordinary temperature for 7–10 days nearly half of the contents solidified to a crystalline mass. The crystalline substance thus obtained was filtered and spread over a porous plate to remove liquid matter.

(1) *The crystalline portion.* The crystalline substance thus separated was soluble in ether, alcohol and ethyl acetate but difficultly soluble in benzene, chloroform and petroleum ether. The substance was acidic and readily soluble in alkali, from which the original acid could be recovered by acidification. The test for aldehydic substance with Schiff's reagent and Tollens' solution proved negative. The substance melted at 178–180° when precipitated in prismatic needles from ethereal solution by addition of light petroleum. The melting point after purifications by sublimation at 115–120° under 5 mm. could be raised up to 184–186° (with decomp.).

The substance did not decolourise bromine or permanganate in cold showing the saturated nature of the substance. The acid was found to be dibasic by the electrolytic

conductivity method. The difference of the equivalent conductivities of N/32 and N/1024 sodium salt solutions was found 10×2.21. From the value 2.21 the substance under investigation must be dibasic. Acid value 844.3 (0.0810 g. of the sample required 39.08 c.c. of N/32 NaOH), calculated for $C_5H_8O_4$ 848.4. (Found: C, 45.53; H, 6.09. Calculated for $C_5H_8O_4$: C, 45.45; H, 6.06%. Analysis of the silver salt: Ag, 62.37. Calculated for $C_5H_6O_4Ag_2$ 62.42%.)

From the composition of the silver salt the molecular weight and the molecular formula of the acid were determined: molecular weight, 132.9; molecular formula, $C_5H_8O_4$.

We find among dibasic acids of the formula $C_5H_8O_4$, dimethylmalonic acid melting at 186° (with decomp.) whose identity with the actual substance was proved as follows.

(*a*) *Preparation of the amide.* The acid chloride prepared from 1.2 g. of the acid and 4 g. of phosphorus pentachloride was added to cold aqueous ammonia. Yellowish crystalline diamide was obtained, which after recrystallization from water furnished colourless scales melting at 262°, in good accordance with the melting point of dimethylmalonic diamide. (Found: N, 21.64. Calculated for $C_5H_{10}O_2N_2$: N, 21.54%.)

(*b*) *Conversion into isobutyric acid by elimination of carbon dioxide.* That the acid $C_5H_8O_4$ is dimethylmalonic acid was also proved by conversion into isobutyric acid by elimination of one mol of carbon dioxide from the original molecule. The acid, when heated somewhat above its melting point, loses readily one mol of carbon dioxide, the amount of which was quantitatively estimated by absorbing it in soda-lime. (Sample 2.2563 g. evolved 0.7518 g. of CO_2, calculated for $C_5H_8O_4$ 0.7521 g.) The resulted substance had the following properties: b.p. 153–153.5°/761 mm.; d_4^{20} 0.9505; n_D^{20} 1.3933; M.R. obs. 22.11, calculated for $C_4H_8O_2$ 22.21.

The substance has acidic properties and does not decolourize bromine and permanganate in cold. Acid value 636.4 (0.2033 g. of the sample required 24.32 c.c. of 0.095N NaOH), calculated for $C_4H_8O_2$ 636.3. (Found: C, 54.38; H, 9.15. Calculated for $C_4H_8O_2$: C, 54.55; H, 9.09. Analysis of the silver salt: Ag, 55.58. Calculated for $C_4H_7O_2Ag$: Ag, 55.31%.) The substance was proved to be identical with isobutyric acid by preparing its acid chloride and amide.

Isobutyryl chloride. A mixture of 1 g. of the acid and 1 g. of phosphorus trichloride was heated to gentle boiling for a few minutes. The acid chloride obtained showed the following properties: b.p. 90–93°; d_4^{20} 1.1079; n_D^{20} 1.4081. These constants are in good accordance with those of isobutyryl chloride (b.p. 92°; d_4^{20} 1.0174; n_D^{20} 1.40789) reported by Brühl[35].

Isobutyryl amide. The acid chloride was added drop by drop to well-cooled aqueous ammonia, when colourless glistening leaflets were obtained. It melted at 116–123° without purification, which was separated into two portions, namely, prismatic needles melting at 170–173° (separated at first) and glistening scaly crystals melting at 124–128°, by recrystallization from water. The substance melting at 170–173° might have been crude diisobutyryl amide, a by-product obtained by Hoffmann[36] in this reaction, but owing to the scarcity of the substance its confirmation could not be attained. The substance melting at 124–128° was once more recrystallized

(35) Brühl, *Ann.*, **203** (1880), 20.
(36) Hoffmann, *Ber.*, **15** (1882), 981.

from benzene, when it melted at 127–128° alone and in admixture with a specimen of isobutyryl amide.

(2) *Liquid portion.* The amount of liquid portion obtained after removal of dimethylmalonic acid was nearly the same with that of the latter. It showed acidic characteristics as well as those of aldehyde. The substance decolourized bromine in cold showing the unsaturated nature, and on oxidation with 4% potassium permanganate another crop of dimethylmalonic acid was obtained.

10 g. of the liquid substance was dissolved in 500 c.c. of 4% sodium bicarbonate solution and dilute permanganate solution (4%) was added drop by drop with stirring till the solution acquired permanent reddish colour, left over night at the ordinary temperature and manganese dioxide precipitated was filtered off. The filtrate after being saturated with carbon dioxide was evaporated to dryness, acidified by dilute hydrochloric acid and the oily substance thus set free was extracted with ether. The residue after removal of the solvent crystallized to a soft mass, from which a crystalline substance was separated by filtration. It proved to be dimethylmalonic acid. The liquid portion was then treated with a mixture of ether and light petroleum ether (1:1) in which dimethylmalonic acid was insoluble, and thus could be separated from the liquid portion. The filtered crystals were purified by reprecipitation from ethereal solution by adding light petroleum ether when it exhibited every characteristic property of dimethylmalonic acid.

Identification of formic acid. The ether–petroleum ether solution obtained above was then shaken vigorously with water for an hour in order to separate water-soluble acids. The aqueous layer was separated, neutralized with dilute ammonia and evaporated to smaller volume. The neutral solution produced an irritating odour on acidification with 5N sulphuric acid, while a quantity of the silver salt was precipitated on adding silver nitrate solution which immediately turned into bright grayish colour. It precipitates calomel from mercuric chloride solution. From these results it follows that the liquid portion contained formic acid.

II. Preparation of hydrocarbon from shonanic acid. (1) *By Rosenmund and Zetzche's method*[37] ($R\cdot COOH \rightarrow R\cdot CO\cdot Cl \rightarrow R\cdot CHO \rightarrow R\cdot CH_3$). By applying this method to the reduction of shonanic acid, the yield of aldehyde was very poor and almost all of the reaction product was a resinous matter, so that only the properties and the derivatives of the aldehyde were studied.

When shonanic acid chloride (freshly prepared) in benzene solution was treated with hydrogen in presence of palladium on barium sulphate as catalyser, the vigorous evolution of hydrochloric acid gas was observed. After the evolution of HCl gas was over, the reaction mixture was filtered from the catalyser and the yellowish matter which remained after removal of the solvent was distilled under reduced pressure. Most of the substance remained undistilled even on heating to 280° under 3 mm., and only a few drops of colourless mobile liquid (0.3 g.) of the following properties was obtained. B.p. 73°/5 mm.; d_4^{20} 0.935; n_D^{20} 1.4630; M.R. obs. 46.78, calculated for $C_{10}H_{18}O$ 46.50.

The substance showed aldehydic nature on testing with Schiff's reagent and Tollens' solution and gave a crystalline semicarbazone.

(37) *Ber.*, **51** (1918), 585, 594.

Semicarbazone. The semicarbazone was prepared from 0.22 g. of the sample, 0.14 g. of sodium bicarbonate and 0.15 g. of semicarbazide hydrochloride. Recrystallization from ethyl alcohol furnished a colourless scales melting at 165°. (Found: N, 20.03. Calculated for $C_{11}H_{21}ON_3$: N, 19.9%.) Thus it is clear that the substance obtained was the aldehyde corresponding to tetrahydroshonanic acid ($C_{10}H_{18}O_2$).

(2) *Preparation of hydrocarbon from shonanic acid by reduction with hydroiodic acid.* 5 g. of shonanic acid was heated with 10 g. of hydroiodic acid (d = 1.7) together with 1.6 g. of red phosphorus in a sealed tube as in the case of reduction of succinic,[38] palmitic[39] and hexahydro-*m*-xylic acid[40] for 5 hours at 220–225°, then another 4 hours at 240° with the further addition of 0.5 g. of red phosphorus, then 4 hours more at 250–270° with a third addition of 0.5 g. of red phosphorus and 0.7 c.c. of water. The contents of the sealed tube were then poured into 200 c.c. of water, shaken with 5% sodium hydroxide solution to remove acidic substance, dried over anhydrous sodium sulphate and then ether was distilled off. The light mobile oil remaining behind was rectified twice under the ordinary pressure over metallic sodium and in this manner a hydrocarbon of the following properties was obtained. (Yield 1.3 g.) B.p. 157–158.5°/754 mm.; d_4^{20} 0.7866; n_D^{20} 1.4344; M.R. obs. 46.37, calculated for $C_{10}H_{20}$ 46.18. The substance does not decolourize either bromine or permanganate showing that the substance is saturated. (Found: C, 85.62; H, 14.37; molecular weight in phenol, 144.7. Calculated for $C_{10}H_{20}$: C, 85.7; H, 14.3%; molecular weight, 140.2.)

(3) *Preparation of hydrocarbon from tetrahydroshonanic acid by reduction with hydroiodic acid.* Next, exactly the same method as in the case of (2) was applied to tetrahydroshonanic acid taking 16 g. of the acid and the product showed the following properties: b.p. 158.5°/765 mm.; d_4^{20} 0.7872; n_D^{20} 1.4338; M.R. obs. 46.34, calculated for $C_{10}H_{20}$ 46.18. Inert against bromine and permanganate. (Found: C, 85.49; H, 14.36. Calculated for $C_{10}H_{20}$: C, 85.7; H, 14.3%.)

(4) *Preparation of hydrocarbon* C_9H_{16} *by the dry distillation of tetrahydroshonanic acid with soda-lime.* Tetrahydroshonanic acid (10 g.) was heated with soda-lime (30 g.) under ordinary pressure. A little oily matter began to distil over at 134° which ceased at 150°. Yield 6.0 c.c. It was fractionally distilled over metallic sodium and was separated into three portions as shown in Table 3. The fraction (3) was again subjected to another fractional distillation under ordinary pressure and the following fractions were obtained (Table 4).

Table 3.

Fr. No.	B.p./753 mm.	Vol. (c.c.)
1	75–138°	0.8
2	138–141°	1.0
3	141–149°	3.8

Table 4.

Fr. No.	B.p./755 mm.	Vol. (c.c.)
a	142–145°	0.4
b	145–148°	3.1
c	148–149°	0.2

(38) Berthelot, *Ann.*, **147** (1868), 376.
(39) Kraft, *Ber.*, **15** (1882), 1689, 1711.
(40) Aschan, *Ber.*, **24** (1891), 2718.

The main fraction b was once more rectified and 2.7 g. of hydrocarbon with the following properties was obtained. B.p. 144.5–145°/757 mm.; d_4^{19} 0.8129; n_D^{19} 1.4595; M.R. obs. 41.12, calculated for C_9H_{16} ⌐1 41.07. The hydrocarbon obtained absorbs bromine readily and decolourizes permanganate in cold. Bromine value 1236 (0.2403 g. absorbed 0.297 g. bromine), calculated for C_9H_{16} ⌐1 1290. (Found: C, 86.95; H, 12.60. Calculated for C_9H_{16}: C, 87.1; H, 12.90%.) The attempt to obtain its nitrosochloride or nitrosite in the crystalline state was not successful.

III. Preparation of o-dinitrobenzene from shonanic acid. 5 g. of shonanic acid was heated on the water-bath with 50 c.c. of nitric acid (d = 1.12) with constant stirring. A brisk reaction took place at first, which soon subsided but the heating was continued for 5 hours. On standing over night long needle crystals appeared, which were filtered off and recrystallized from water. It melted at 117–118°. The filtrate bore an odour reminding of nitrobenzene and on evaporating another crop of crystals was obtained, which proved to be the same substance as the main product. The substance was neutral and the presence of nitrogen was recognized by the evolution of ammonia on heating with soda-lime. (Found: C, 42.75; H, 2.38; N, 16.67. Calculated for $C_6H_4O_4N_2$: C, 42.86; H, 2.38; N, 16.67%.)

The empirical formula of the substance calculated from the experimental data is $C_3H_2O_2N$ while among the substances corresponding to this empirical formula *o*-dinitrobenzene melts at 117.5°. The substance showed no depression of the melting point in admixture with *o*-dinitrobenzene, thus the identity of these two substances being proved.

Summary.

(1) Dimethylmalonic acid and formic acid were obtained by the oxidation of shonanic acid.

(2) A hydrocarbon $C_{10}H_{20}$ was obtained by the reduction of shonanic and tetrahydroshonanic acid with hydroiodic acid.

(3) A hydrocarbon C_9H_{16} ⌐1 was obtained by the dry distillation of shonanic acid with soda-lime.

(4) The attempt to determine the ring structure of shonanic acid by comparing the properties of these hydrocarbons with those of known hydrocarbons gave no reliable results.

(5) The formation of *o*-dinitrobenzene from shonanic acid by treating it with dilute nitric acid may be taken as an evidence for the presence of six-membered ring system in its molecule.

In conclusion, the author wishes to thank Prof. K. Kafuku for his kind advices and suggestions rendered during the course of this work.

Department of Industry,
Government Research Institute of Taiwan.

Studies on the Constitution of Shonanic Acid, One of the Two Characteristic Volatile Acids from the Wood of *Libocedrus formosana*, Florin. IV. On Dihydroshonanyl Alcohol and the Optical Activity of Shonanic Acid and its Derivatives.

By Nobutoshi ICHIKAWA.

(Received November 24th, 1936.)

In a previous communication,[1] the author has reported the presence of a dimethylmethylene group in the molecule of shonanic acid as a result of the investigations on the oxidation products of shonanic acid with permanganate. Next, with a view to examine the oxidation products of dihydroshonanic acid, the author attempted to prepare a sufficient quantity of the acid. But, as has been reported, the preparation of dihydroshonanic acid from shonanic acid by reduction with sodium and ethyl alcohol is always accompanied by the formation of by-products such as tetrahydroshonanic acid or isoshonanic acid, and furthermore, the separation of dihydroshonanic acid from these impurities can hardly be accomplished by the fractional distillation as there is but little difference between their boiling points. Attempt to separate it in the pure state by fractional crystallization of its metallic salts was also unsuccessful.

The author tried, hereupon, to prepare dihydroshonanyl alcohol, the unsaturated primary alcohol corresponding to dihydroshonanic acid, and to oxidise it, as such oxidation should lead to the same conclusion as might be expected from the oxidation of the dihydro-acid.

Thus, dihydroshonanyl alcohol was prepared from ethyl shonanate by reduction with sodium and ethyl alcohol. According to H. Rupe and P. Läuger[2] the yield of camphorcarbinol increased with the molecular weight of the ester-forming radicals e.g. 10–15% by ethyl ester, 22% by isobutyl ester, 25% by isoamyl ester, 64% by β-naphthyl ester, and 94–96% by phenol ester. The present author, in order to increase the yield of the desired alcohol, prepared phenyl shonanate and reduced it with sodium and ethyl alcohol, but contrary to the expectation the yield of carbinol-compound did not improved at all.

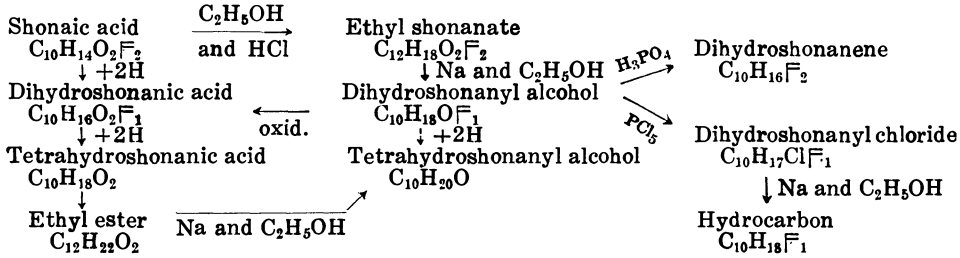
When oxidised with chromic acid, dihydroshonanyl alcohol gave the corresponding aldehyde ($C_{10}H_{16}O$ 冖$_1$, semicarbazone m.p. 149–150°) and

(1) This Bulletin, **12** (1937), 243.
(2) *Helv. Chim. Acta*, **3** (1920), 272.

acid, and when reduced catalytically with palladium and hydrogen it afforded tetrahydroshonanyl alcohol ($C_{10}H_{20}O$), the same as obtained from ethyl tetrahydroshonanate by reduction with sodium and ethyl alcohol, which gave tetrahydroshonanic acid on oxidation. On digesting dihydroshonanyl alcohol with phosphorus pentachloride, the corresponding chloride ($C_{10}H_{17}Cl$) was obtained, which could be transformed into a hydrocarbon of the formula $C_{10}H_{18}$ by reduction with sodium and ethyl alcohol. The dehydration of shonanyl alcohol with phosphoric acid afforded a hydrocarbon $C_{10}H_{16}$ (dihydroshonanene), but the attempt to obtain its hydrochloride, nitrosochloride and nitrosite in crystalline state was not successful.

These hydrocarbons, judging from their physical properties, viz., boiling points, specific gravities and refractive indices, seem likely to be compounds of six-membered ring type, hence shonanic acid is most likely a cyclohexene derivative.

The various relations mentioned above are tabulated in the following.



About the oxidation products of dihydroshonanyl alcohol, it will be reported in the next communication.

The values of optical rotatory power exhibited by shonanic acid and its derivatives are as follows, from which it is obvious that the acid is a compound with an asymmetric carbon atom.

Shonanic acid	$[\alpha]_D^{18} = -0.74°$ (in ethyl alcohol)
Shonanic acid dibromide	$[\alpha]_D^{27} = -5.02°$ (in glacial acetic acid)
Ethyl shonate	$\alpha_D^{18} = -4.24°$
Phenyl shonanate	$\alpha_D^{28} = -2.40°$
Shonanic amide	$[\alpha]_D^{27} = -9.84°$ (in ethyl alcohol)
Dihydroshonanic acid	$\alpha_D^{30} = -1.36°$
Tetrahydroshonanic acid	$\alpha_D^{26} = -0.84°$
Ethyl tetrahydroshonanate	$\alpha_D^{26} = -0.81°$
Dihydroshonanyl alcohol	$\alpha_D^{18} = -2.24°$
Dihydroshonanyl chloride	$\alpha_D^{20} = -2.00°$
Tetrahydroshonanyl alcohol	$\alpha_D^{28} = -1.64°$
Dihydroshonanene	$\alpha_D^{26} = \pm 0°$

Experimental.

(1) **Preparation of ethyl shonanate.** 10 g. of shonanic acid together with 50 c.c. of ethyl alcohol containing 2.5% of hydrochloric acid was heated on the water-bath for an hour, the product was poured into water, extracted with ether and ethereal solution washed with water and then with dilute sodium bicarbonate solution in order to remove hydrochloric acid and unchanged shonanic acid, dried over anhydrous sodium sulphate and the solvent distilled off. The remainder was then distilled under reduced pressure when a liquid ester with the following properties was obtained. (Yield 9.3 g.) B.p. 106–108°/7 mm., 228–229°/759 mm.; d_4^{30} 0.9568; n_D^{30} 1.4674; α_D^{20} −4.24°.

(2) **Preparation of dihydroshonanyl alcohol.** 10 g. of ethyl shonanate was dissolved in 200 c.c. of absolute alcohol and 15 g. of metallic sodium was added in small portions. When all the sodium has been taken up the excess of alcohol was distilled away in vacuo and the remainder was poured into 200 c.c. of 10% sodium chloride solution. The oily matter which made appearance was taken up with ether, dried over anhydrous sodium sulphate and then the solvent was distilled off. The product amounted to 3.3 g. corresponding to 41% of the theoretical yield. Several experiments were repeated, in all of which the yield of the alcoholic substance was found to lie between 35–40% of the theoretical. Dihydroshonanyl alcohol showed the following properties: b.p. 104°/7 mm., 228–230°/765 mm.; d_4^{30} 0.9328; n_D^{30} 1.4832; α_D^{20} −2.24°; M.R. obs. 47.16, calculated for $C_{10}H_{18}O$ F_1 47.23. Sample (0.1379 g.) absorbed 0.1476 g. of bromine, while $C_{10}H_{18}O$ F_1 requires 0.1433 g. The substance is readily attacked by permanganate solution in cold showing the substance is unsaturated.

(3) **Preparation of dihydroshonanyl alcohol from phenyl shonanate.** Phenyl shonanate was prepared by adding the acid chloride (9.2 g.) dissolved in 100 c.c. of petroleum ether to a solution of 4.7 g. of phenol in 10 c.c. of petroleum ether and heating the mixture on the water-bath until the evolution of hydrochloric acid gas ceased. Ether was then added to the reaction mixture and shaken with 5% sodium hydroxide solution to remove unchanged phenol. The ethereal solution was dried, the solvent distilled off, and then crude phenyl shonanate was distilled under reduced pressure. Yield 11.8 g. (97.5% of the theoretical). B.p. 153–155°/6 mm.; d_4^{30} 1.0415; n_D^{20} 1.5245; α_D^{26} −2.40°; M.R. obs. 71.16, calculated for $C_{16}H_{18}O_2$ F_5 71.36.

The phenol ester obtained above (11.8 g.) was dissolved in 120 c.c. of absolute alcohol and was reduced with 9 g. of sodium in the usual manner when 2.2 g. of the corresponding alcohol was obtained, the yield amounting to 29.5% of the theoretical. The yield of the carbinol was 27% and 29% of the theoretical respectively when the reduction was carried out by using smaller (6.5 g.) and larger (11 g.) proportions of metallic sodium. The physical properties of the dihydroshonanyl alcohol are as follows: b.p. 103–103.5°/6 mm.; d_4^{30} 0.9319; n_D^{30} 1.4826; α_D^{24} −2.09°.

(4) **Hydrogen dihydroshonanyl phthalate.** When heated with equivalent weight of phthalic anhydride in benzene solution dihydroshonanyl alcohol gave its acid phthalic ester. From 1 g. of the sample, 1 g. of phthalic anhydride and 2 c.c. of benzene, the acid phthalic ester was obtained in prismatic needles, which melted at 124° after a recrystallization from ethyl alcohol.

(5) **Oxidation of dihydroshonanyl alcohol with chromic acid.** 10 g. of the alcohol dissolved in 150 c.c. of glacial acetic acid was kept at 10–15° and a solution of chromic acid (10 g.) in a little water and glacial acetic acid (50 c.c.) was added drop by drop with constant stirring. After all the chromic acid solution has been consumed the reaction mixture was warmed on the water-bath at 50–60° for 30 minutes. The reaction mixture was then poured into water and aldehydic and acidic substances were extracted and separated as usual.

(a) *The aldehyde* showed the following properties: b.p. 107–110°/18 mm.; d_4^{30} 0.9630; n_D^{30} 1.4833; M.R. obs. 45.10, calculated for $C_{10}H_{16}O$F 45.78. The substance was a colourless mobile oil with pleasant odour and on testing with Schiff's reagent and Tollens' solution it showed the characteristic reactions of aldehyde.

Semicarbazone. A mixture of 1 g. of the sample, 0.8 g. of semicarbazide hydrochloride and 0.6 g. of sodium bicarbonate afforded a semicarbazone as glistening leaflets melting at 149–150° after recrystallizations from ethyl alcohol. (Found: N, 20.88. Calculated for $C_{11}H_{19}ON_3$: N, 20.10%.)

(b) *The acidic substance* showed the following properties: b.p. 132°/5 mm., d_4^{30} 1.022; n_D^{30} 1.4804; M.R. obs. 46.74, calculated for $C_{10}H_{16}O_2$F 47.30. It decolourized permanganate and bromine in cold showing its unsaturated nature. Sample (0.204 g.) absorbed 0.187 g. of bromine, while $C_{10}H_{16}O_2$F requires 0.194 g.

Amide. The amide was prepared by the interaction of the acid chloride and aqueous ammonia. It was glistening scales melting at 130° when recrystallized from 60% ethyl alcohol and was found to be identical by melting in admixture with dihydroshonanic amide.

(6) **Preparation of dihydroshonanyl chloride.** When dihydroshonanyl alcohol (3 g. in 10 c.c. of petroleum ether) was treated with phosphorus pentachloride (6.8 g.), the chloride with the following properties was obtained: b.p. 87°/13 mm.; d_4^{20} 0.9984; n_D^{30} 1.4900; α_D^{20} −2.00°; M.R. obs. 49.95, calculated for $C_{10}H_{17}Cl$F 50.54. At the end of the distillation the hydrocarbon of the following properties came over but its detailed examination was impossible owing to the scarcity of the material. B.p. 172–174°/757 mm.; d_4^{30} 0.8678; n_D^{30} 1.4730. (Found: C, 87.49; H, 12.04. Calculated for $C_{10}H_{16}$: C, 88.22; H, 11.78%.)

(7) **Preparation of hydrocarbon $C_{10}H_{18}$ from dihydroshonanyl chloride.** The chloride (3 g.) mentioned above was dissolved in 50 c.c. of absolute alcohol and 4 g. of metallic sodium was added in small portions. The reaction mixture was then heated on the water-bath and poured into a bulk of water and the hydrocarbon deposited was taken up with ether. The ethereal solution was dried over anhydrous sodium sulphate and the remainder after removal of the solvent was fractionally distilled under the ordinary pressure.

(1) B.p. 163–165° 0.2 c.c.; (2) B.p. 165–166° 1.3 c.c.; (3) B.p. 166–168° 0.3 c.c. The main fraction (2) showed the following properties: d_4^{30} 0.8401; n_D^{30} 1.4658; α_D^{26} +0.40°; M.R. obs. 45.48, calculated for $C_{10}H_{18}$F 45.60. (Found: C, 87.18; H, 13.14. Calculated for $C_{10}H_{18}$: C, 86.96; H, 13.04%.)

(8) **Dehydration of dihydroshonanyl alcohol.** 5 g. of dihydroshonanyl alcohol was heated with 20 g. of phosphoric acid at 200–210° for an hour. The reaction mixture was then poured into water and the oily substance was extracted with ether.

The ethereal solution was next heated with 1 g. of metallic sodium on the water-bath in order to recover the unchanged alcohol and the solvent was distilled off. The extract was then subjected to fractional distillation under the ordinary pressure over metallic sodium. The main fraction showed the following properties: b.p. 168–169°/759 mm.; d_4^{30} 0.8630; n_D^{30} 1.4870; α_D nil; M.R. obs. 45.32, calculated for $C_{10}H_{16}F_2$ 45.20. (Found: C, 88.28; H, 11.42. Calculated for $C_{10}H_{16}$: C, 88.23; H, 11.77%.)

(9) **Preparation of tetrahydroshonanyl alcohol.** Tetrahydroshonanyl alcohol was obtained by catalytic reduction of dihydroshonanyl alcohol on the one hand and by reducing tetrahydroshonanate with sodium and ethyl alcohol on the other.

(a) *Catalytic reduction of dihydroshonanyl alcohol.* 4.438 g. of dihydroshonanyl alcohol, dissolved in 40 c.c. of ethyl alcohol, was catalytically reduced by hydrogen and palladium. Hydrogen absorbed: 644 c.c. (0°, 760 mm.); calculated for $C_{10}H_{18}OF_1$: 645 c.c. (0°, 760 mm.). The product showed the following properties: b.p. 100–101°/7 mm.; d_4^{30} 0.9253; n_D^{30} 1.4764; α_D^{28} −1.64°; M.R. obs. 47.57, calculated for $C_{10}H_{20}O$ 47.52.

(b) *The reduction of ethyl tetrahydroshonanate with sodium and ethyl alcohol.* 5 g. of ethyl tetrahydroshonanate was dissolved in 150 c.c. of absolute alcohol and was reduced by 8 g. of sodium. The alcoholic substance produced showed the following properties, in good accord with those of the product of (a). B.p. 102°/8 mm.; d_4^{30} 0.9250; n_D^{30} 1.4761; α_D^{24} −1.68°; M.R. obs. 47.57, calculated for $C_{10}H_{20}O$ 47.52.

(10) **Oxidation of tetrahydroshonanyl alcohol with chromic acid.** To a solution of 3 g. of tetrahydroshonanyl alcohol in 70 c.c. of glacial acetic acid, 3 g. of chromic acid was added in small portions with vigorous stirring. The acid produced had the following properties (Yield 1.2 g.): b.p. 120°/2 mm.; d_4^{30} 0.9876; n_D^{30} 1.4650; α_D^{26} −0.84°; M.R. obs. 47.60, calculated for $C_{10}H_{16}O_2$ 47.70.

Amide. The amide prepared from 1 g. of the acid chloride and aqueous ammonia melted at 144° after recrystallization from 60% ethyl alcohol, which showed no depression of the melting point when mixed with an authentic specimen of tetrahydroshonanic amide.

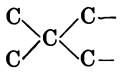
In conclusion, the author wishes to express his sincere thanks to Prof. Kinzô Kafuku for his kind guidance.

Department of Industry,
Government Research Institute of Taiwan.

Studies on the Constitution of Shonanic Acid, One of the Two Characteristic Volatile Acids from the Wood of *Libocedrus formosana*, Florin. V. Studies on the Oxidation of Dihydroshonanyl Alcohol and the Ozonolysis of Shonanic Acid.

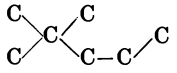
By Nobutoshi ICHIKAWA.

(Received November 24th, 1936.)

It was reported in the previous communications that the molecule of shonanic acid contains a linkage  as shown by the products of oxidation with potassium permanganate,[1] and that the elevation of boiling point accompanying its isomerisation to isoshonanic acid may be attributed to the migration of the semicyclic double bond into the ring system.[2]

Now, with a view to ascertain the presence of a semicyclic double bond and hence to establish the constitutional formula of shonanic acid, the author examined its ozonolysis as well as the oxidation of dihydroshonanyl alcohol with potassium permanganate, and was able to formulate further arrangement of atoms in the molecule of shonanic acid.

The ozonisation of shonanic acid gave a crystalline mono-ozonide, which on treatment with water gave an unsaturated acid of the formula $C_9H_{14}O_3$. This acid was found to be an unsaturated aldehydic acid and hence on further oxidation with hydrogen peroxide it gave an unsaturated dibasic acid of the formula $C_9H_{14}O_4$. The methyl ester of this dibasic acid was prepared, which on ozonolysis gave formaldehyde, formic acid and an acidic substance, which on treatment with dilute nitric acid gave dimethylmalonic acid and *asym*-dimethylsuccinic acid. When dihydroshonanyl alcohol was oxidised with dilute permanganate and then with dilute nitric acid, oxalic, *asym*-dimethylsuccinic and α,α-dimethylglutaric acids were produced.

The formation of α,α-dimethylglutaric acid reveals the presence of arrangement  in the molecule of dihydroshonanyl alcohol. As dihydroshonanyl alcohol is the alcohol derived from dihydro-

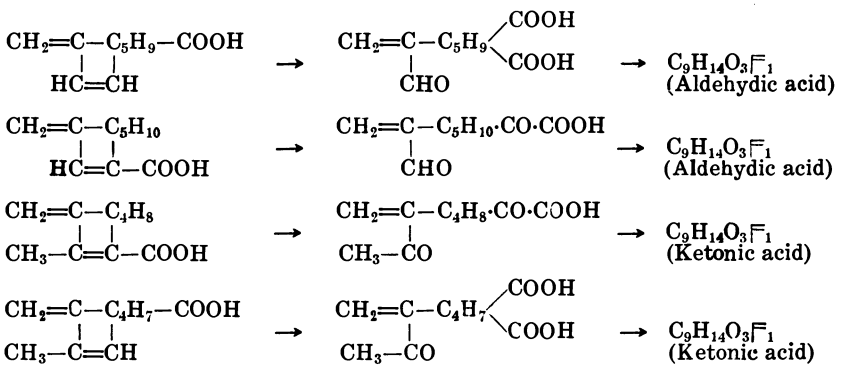
(1) This Bulletin, **12** (1937), 243.
(2) *Ibid.*, **11** (1936), 759.

shonanic acid, the conclusions about its constitution may directly be adopted to dihydroshonanic, as well as to shonanic acid.

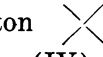
From considerations of the oxidation products mentioned above, the author has come to the following conclusions.

(1) The formation of mono-ozonide shows that the double bonds in shonanic acid are conjugated.[3]

(2) The formation of the unsaturated aldehydic acid $C_9H_{14}O_3$ cannot be explained unless the formation of the mono-ozonide takes place at the ring-forming double bond, and by presuming the ring fission to occur at this spot, this double bond must have existed either in the form $-\overset{|}{\underset{H}{C}}=\overset{|}{\underset{H}{C}}-$ or $-\overset{|}{\underset{H}{C}}=\overset{|}{\underset{COOH}{C}}-$, otherwise the formation of the aldehydic acid becomes impossible.

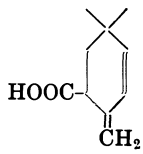


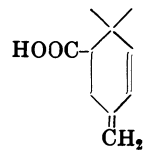
(3) The formation of formaldehyde and formic acid by ozonolysis of the methyl ester of the unsaturated dibasic acid $C_9H_{14}O_4$ shows the presence of a semicyclic double bond attached to the nucleus.

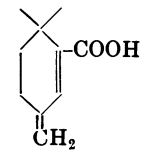
Now the data for the establishment of the structural formula of shonanic acid are almost complete. (I) Shonanic acid contains a six-membered carbon ring,—proved by the formation of dinitrobenzene.[1] (II) It has within itself a skeleton  . (III) It has an exocyclic double bond attached to the ring. (IV) It has the second ethylenic linkage which is conjugated to the exocyclic one. (V) It has a carboxylic group.

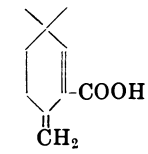
By putting these facts together, it remains now to determine the position of $=CH_2$ and $-COOH$ and the second ethylenic linkage in the dimethylcyclohexene nucleus. Thus there are 12 cases which fulfil the above requirements, viz.:

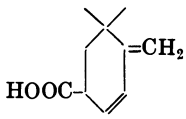
(3) Houben-Weyl, "Die Methoden der organischen Chemie," 3. Aufl., Bd. III, 409, 454.

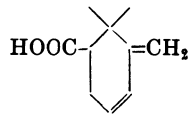

I.

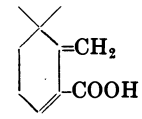

II.

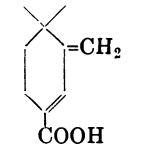

VII.

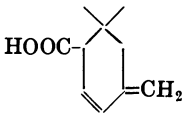

VIII.

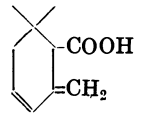

III.

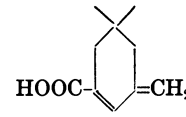

IV.

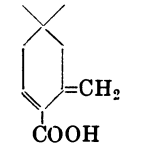

IX.


X.

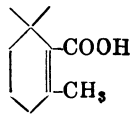

V.

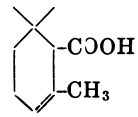

VI.

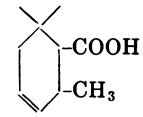

XI.

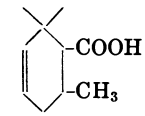

XII.

Among these formulæ those without an asymmetric carbon atom must be excluded as shonanic acid is optically active. Thus the formulæ I–VI remain to be inspected. And furthermore VI should be excluded for the following reason. If VI denotes shonanic acid, dihydroshonanic acid should be identical with one of the following substances, whereas dihydroshonanic acid proves to be a distinctly different substance.


β-Cyclogeranic acid[4] m.p. 93–94°


α-Cyclogeranic acid[5] m.p. 106°


Δ^3-Cyclogeranic acid[6] m.p. 75–76° or 83–84°


Δ^4-Cyclogeranic acid[7] m.p. 102–102.5°

Thus it follows that one of the first five formulæ (I–V) should represent the constitution of shonanic acid.

Experimental.

I. Oxidation of dihydroshonanyl alcohol.

The substance was prepared from ethyl shonanate by reduction with sodium and ethyl alcohol as previously reported.[8] It showed the following properties: b.p. 103–

(4) Tiemann, *Ber.*, **33** (1900), 3723.
(5) Tiemann, *Ber.*, **31** (1898), 827.
(6) Merling, *Ber.*, **41** (1908), 2066.
(7) Merling, *Chem. Zentr.*, **77** (1906), II, 1694.
(8) This Bulletin, **12** (1937), 253.

104°/7 mm., 229°/760 mm.; d_4^{30} 0.9328; n_D^{30} 1.4832; α_D^{18} −2.24°; M.R. obs. 47.17, calculated for $C_{10}H_{18}O$ 47.12.

20 g. of the substance was mixed with 1000 c.c. of 2% sodium hydroxide solution and then 3000 c.c. of 3.2% potassium permanganate solution was added drop by drop with vigorous stirring, the temperature of the reaction mixture being maintained at 20–25°. After all the permanganate had been consumed, the reaction mixture was saturated with carbon dioxide, and then warmed on the water-bath at 40–50° for an hour. Manganese dioxide precipitated was filtered off while hot and the filtrate was evaporated on the water-bath nearly to dryness and was acidified with dilute sulphuric acid. The organic acid set free was extracted with ether and dried over anhydrous sodium sulphate. After distilling off the solvent, there remained a sticky, slightly yellowish liquid, which amounted to 15 g. The substance was acidic, sparingly soluble in water and gradually acquired reddish yellow tint on exposure to the air. It was then warmed with 400 c.c. of dilute nitric acid (d = 1.12), evaporated on the water-bath, and ultimately under reduced pressure to remove traces of nitric acid present. The product thus obtained was a pale yellow viscous substance which was difficultly soluble in ether, chloroform and petroleum ether, but soluble in water, alcohol and warm benzene. On testing it with Schiff's reagent and Tollens' solution it proved to be perfectly free from aldehyde. On standing in cold some crystalline substance made appearance, which was spread over a porous plate previously cooled in an ice-box and stood over night in cold in order to remove the adhering fluid matter. The crystalline substance, which amounted to 7 g., was a colourless powder melting at 73–118° without any purification. The liquid portion absorbed by the porous plate was recovered by extracting it with ether, the details of which are described later.

(1) **Investigation of crystalline substances.** (a) *Oxalic acid.* The crystalline substance (7 g.) obtained above was boiled with 30 c.c. of chloroform, filtered while hot, washed with chloroform and dried in vacuo. It showed a m.p. 96–99°. On recrystallization from hot water it was obtained in colourless needles melting at 101°. It was identified as oxalic acid by mixed melting point.

(b) asym-*Dimethylsuccinic acid.* The above filtrate, on evaporating chloroform deposited a white crystalline powder melting at 133°. This was boiled with a little water and after quenching, needle crystals of oxalic acid were filtered off. The filtrate was evaporated and then cooled with freezing mixture, when prismatic needles with m.p. 134–136° were obtained. Another recrystallization from benzene furnished colourless needles melting at 139°. The substance was soluble in water, alcohol, benzene and chloroform. Acid value 767.4, calculated for $C_6H_{10}O_4$ 767.1. (Found: C, 48.87; H, 6.82. Calculated for $C_6H_{10}O_4$: C, 49.32; H, 6.85%. Analysis of the silver salt: Ag, 60.02. Calculated for $C_6H_8O_4Ag_2$: Ag, 59.97%.)

Among the acids represented by $C_6H_{10}O_4$, *asym*-dimethylsuccinic acid melts at the same temperature (139–140°) as the substance under investigation, whose identity with the former was confirmed by observing the melting point of the mixture.[9]

(9) *asym*-Dimethylsuccinic acid used for the trial was prepared by oxidation of dimethyl-dihydroresorcin according to the description of Vorländer and Gärtner [*Ann.*, **304** (1899), 5, 15].

(2) **Investigation of the liquid portion.** The liquid portion was recovered by extracting the porous plate broken into small bits with ether. The substance thus recovered was a viscous fluid with yellowish tint and amounted to 7.3 g. As the purification by vacuum distillation was ineffective, it was esterified by boiling it with 40 c.c. of ethyl alcohol containing 6% hydrochloric acid and the ester thus prepared was fractionated in vacuo.

(a) *Acetic acid.* As the ethyl alcohol recovered from the esterification mixture smelled of ethyl acetate, it was boiled with 5 c.c. of 50% potassium hydroxide solution under reflux condenser, and the remainder after removal of alcohol was evaporated nearly to dryness and acidified with 5N sulphuric acid and extracted with ether. From the ethereal solution about 0.8 g. of liquid acidic substance bearing the characteristic odour of acetic acid was obtained. The silver salt prepared from its neutralized solution contained 64.65% of the silver agreeing well with the theoretical silver content of the silver acetate.

(b) *α,α-Dimethylglutaric acid.* The ester portion thus obtained was dissolved in ether, washed with water and 5% sodium hydroxide solution successively in order to remove any traces of ethyl alcohol and unchanged acidic substances, dried over anhydrous sodium sulphate and the solvent was distilled off. The reddish brown matter remaining behind amounted to ca. 8 g., which was fractionally distilled under 10 mm.

Fr. No.	B.p.	Wt.(g.)
1	80–86°/10 mm.	1.2
2	86–95°/10 mm.	0.7
3	95–105°/10 mm.	—
4	105–107°/10 mm.	4.0
5	107°/10 mm.—105°/3 mm.	1.0
6	105–135°/3 mm.	0.6

Fraction 1 had the following properties: b.p. 185–187°/770 mm.; d_4^{20} 1.088; n_D^{20} 1.4160; M.R. obs. 33.67, calculated for $C_6H_{10}O_4$ 33.10. (Found: C, 49.08; H, 6.89. Calculated for $C_6H_{10}O_4$: C, 49.32; H, 6.85%.) The physical constants of the fraction agree well with those of diethyl oxalate (b.p. 186°/755 mm.; d_4^{20} 1.0793; n_D^{20} 1.4104)[10] and the free acid obtained by saponification melted at 101°, which was found to be identical with oxalic acid melting in admixture with authentic specimen.

Fraction 4 had the following properties: b.p. 233–235°/770 mm.; d_4^{20} 0.9956; n_D^{20} 1.4293; M.R. obs. 55.97, calculated for $C_{11}H_{20}O_4$ 56.42. (Found: C, 61.07; H, 9.21. Calculated for $C_{10}H_{20}O_4$: C, 61.11; H, 9.26%.) The analytical data showed that the substance represents a compound corresponding to the diethyl ester of a dibasic acid of the formula $C_7H_{12}O_4$. The substance was saponified by warming 3 g. of the sample with 2 g. of potassium hydroxide, 8 c.c. of water and 100 c.c. of ethyl alcohol for an

(10) Delfes, *Jahresbericht über die Fortschritte der Chemie*, **1854**, 26; Brühl, *Ann.*, **203** (1880), 27.

hour. The excess of alcohol was distilled off and the remainder was evaporated to a smaller bulk and was acidified with dilute hydrochloric acid and the organic acid thus set free was extracted 4 times with chloroform using 10 c.c. each time. The chloroform solution was collected, dried over anhydrous sodium sulphate and the solvent distilled off. The sticky liquid acid remaining behind was then warmed with 5 c.c. of conc. hydrochloric acid and then cooled with freezing mixture, when the substance became crystalline and melted at 67°. It was purified twice by precipitation from benzene solution with the addition of light petroleum ether. Thus its melting point attained 83°. (Found: C, 52.29; H, 7.56. Calculated for $C_7H_{12}O_4$: C, 52.50; H, 7.50%.) It is clear that the acid under investigation is a dibasic acid of the formula $C_7H_{12}O_4$ and the melting point of the sample is proximate to those of α,α-dimethylglutaric acid[11] (m.p. 83–84°, diethyl ester b.p. 235–236°), α,β-dimethylglutaric acid[12] (m.p. 84–84.5°) or *d*-β-methyladipic acid[13] (m.p. 84.5°). Among these three acids *d*-β-methyladipic acid can be excluded for the reason that it is insoluble in cold benzene, and furthermore its diethyl ester has a quite different boiling point[14] (b.p. 257°) from that of the diethyl ester in question. Reminding that dimethylmalonic acid and *asym*-dimethylsuccinic acid were found among the oxidation products of shonanic acid and dihydroshonanyl alcohol respectively, it should be expected that the present dibasic acid is α,α-dimethylglutaric acid. Now, it was found to be identical with α,α-dimethylglutaric acid by examining the melting point in admixture with the authentic sample prepared from ionone by oxidation as described by Tiemann.[15]

II. Ozonolysis of shonanic acid.

(1) **Preparation of mono-ozonide of shonanic acid.** To a well-cooled solution of the acid (10 g.) dissolved in carbon tetrachloride (100 c.c.), a current of ozonized oxygen containing ca. 3% ozone was passed through at a rate of 15–20 liters per hour until the absorption of ozone has ceased. The ozonide obtained was crystalline and floated on the surface of the solvent, which was filtered off, washed several times with carbon tetrachloride, spread over porous plate to remove the adhering solvent and finally dried in vacuo. The yield of the ozonide amounted to about 12 g., which is approximately the theoretical value calculated as mono-ozonide ($C_{10}H_{14}O_2 \cdot O_3$). The mono-ozonide showed the decomposition point 82° and when perfectly dry it decomposed vigorously with evolution of heat. It was quite insoluble in chloroform, benzene, carbon tetrachloride and ether, and was attacked very slowly by water at ordinary temperature but more rapidly at elevated temperature (above 60°).

(2) **Decomposition of the ozonide.** The ozonide was gently heated on the water-bath at about 75° with 5 times of its volume of water in a current of hydrogen and the decomposition products thus obtained were examined. The hydrogen gas escaping from the decomposition flask was introduced into ice-cold distilled water

(11) Kishner, *Chem. Zentr.*, **79** (1908), II, 1859; Blaise, *Bull. soc. chim.*, [3], **21** (1899), 626.

(12) Blaise, *Bull. soc. chim.*, [3], **29** (1903), 333.

(13) Semmler, *Ber.*, **25** (1892), 3516.

(14) Markownikow, *Chem. Zentr.*, **74** (1903), II, 288.

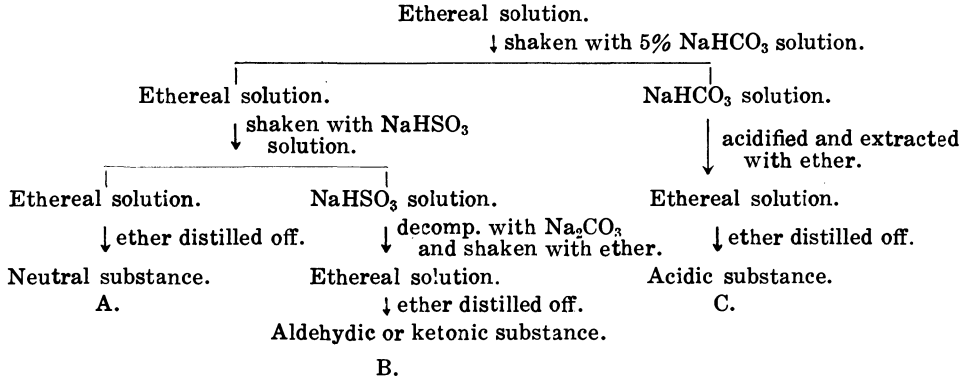
(15) Tiemann, *Ber.*, **31** (1898), 862.

in order to catch any soluble matter produced, and then into a saturated solution of barium hydroxide. Carbon dioxide was evolved and precipitated barium carbonate, which amounted to ca. 3.8 g. per 10 g. of the ozonide.

When the decomposition was over the presence of aldehydic substance in the water trap was tested with Schiff's reagent as well as with Tollens' solution which gave negative results. The iodoform reaction was also negative.

The oily product remaining in the decomposition flask was distilled in steam, and the distillate gave positive reaction with Schiff's reagent as well as with Tollens' solution whilst it gave no iodoform reaction showing the absence of acetone or acetaldehyde therein. The dimedon test was also thoroughly negative, showing the absence of formaldehyde in the distillate. The strong positive aldehydic reaction shown even by the first running may be attributed to the very nature of the product in question.

The product which came over with steam was then extracted with ether and was treated according to the following scheme.



Finally the substance was found to accumulate in C, and the portions going to A or B very minute.

(3) **The investigation of the acidic substance (C).** The yield of the acidic substance amounted to 24 g. from 50 g. of the ozonide. It showed all the characteristic properties of an aldehyde but the attempt to obtain its semicarbazone in crystalline state was not successful. As the purification of the substance by distillation in vacuo was not attained, the aldehyde group present was first oxidised to acid group, the resulting acid esterified and the ester fractionated in vacuo. The substance thus purified was subjected to more minute examinations.

Oxidation of the aldehydic acid. 20 g. of the aldehydic acid was dissolved in 200 c.c. of 10% sodium hydroxide solution and was oxidised with 22 c.c. of perhydrol (30%) at 40–45°, when the reddish colour of the solution changed gradually to a yellowish tint, and the solution gave no more positive result with Tollens' solution. The solution was then evaporated to a smaller bulk in an atmosphere of carbon dioxide, acidified with dilute sulphuric acid and the organic acid thus liberated was extracted with ether. Yield 16 g.

Preparation of the methyl ester. The acid obtained above was esterified by heating with 100 g. of methyl alcohol containing 3% hydrochloric acid on the water-bath for 2 hours and the product was extracted as usual and fractionally distilled under reduced pressure.

Fr. 1	b.p. 86–109°/19 mm.	3 c.c.
2	b.p. 109°/19 mm.—142°/7 mm.	9 c.c.
3	b.p. 142–147°/7 mm.	4 c.c.

The main fraction (2) was once more rectified when it showed the following properties. (Yield 7 c.c.) B.p. 138–140°/7 mm.; d_4^{30} 1.073; n_D^{30} 1.4733. (Found: C, 61.57; H, 8.52. Calculated for $C_{11}H_{18}O_4$: C, 61.68; H, 8.41%.)

The substance was undoubtedly unsaturated since it absorbed bromine and decolourlized permanganate solution in cold. Its empirical formula corresponded with $C_{2.7}H_{4.6}O$, but since it is a dimethyl ester of a dibasic acid, it must contain two $COOCH_3$ groups. It naturally follows that the formula of this acid should be $(C_{2.7}H_{4.6}O)_4$ or $C_{11}H_{18}O_4$ approximately. The experimental data concerning the molecular weight agreed fairly well with this formula, viz.: 0.2577 g. subst. absorbed 0.1856 g. of bromine, while $C_{11}H_{18}O_4$ requires 0.1927 g. 0.3858 g. subst. absorbed 45.1 c.c. of hydrogen (0°, 760 mm.), while $C_{11}H_{18}O_4$ requires 40.4 c.c. Saponification value 517.8, calculated for $C_{11}H_{18}O_4$ 523.4. Thus the free acid should be represented by $C_9H_{14}O_4$ ⌐1 or $C_7H_{12}(COOH)_2$, and the foregoing aldehydic acid by $C_9H_{14}O_3$ or $C_7H_{12}\begin{matrix}CHO\\COOH,\end{matrix}$ presumably aliphatic with one ethylenic linkage. The position of the double bond was determined by ozonolysis of the dimethyl ester of the former.

(4) **Ozonolysis of dimethyl ester of the acid $C_9H_{14}O_4$.** The methyl ester (10 g.) was dissolved in carbon tetrachloride (100 c.c.) and 3% ozonized oxygen made to bubble through until the solution became inactive against bromine. At the end of the reaction the solution was heated in a flask with 50 c.c. of water on the water-bath in a current of CO_2-free air and made to distil slowly. The decomposition of the ozonide set in with the distillation of carbon tetrachloride. In order to catch any water soluble substance such as formaldehyde, acetaldehyde or acetone, which may have been produced during the decomposition of the ozonide, a gas-washer containing a little water was put in place of the receiver and the air escaping out of this receiver was once more introduced into another gas-washer with a little water and then into barium hydroxide solution to detect carbon dioxide.

Carbon dioxide. The formation of carbon dioxide was recognized by the formation of barium carbonate in the gas-washer.

Formaldehyde. The water and carbon tetrachloride in the gas-washer was separated and the aqueous layer tested with Schiff's reagent as well as with Tollens' solution. When 8 c.c. of the aqueous distillate was mixed with 5 c.c. of alcoholic dimedon solution (10%) needle crystals of formaldimedon made appearance, which was filtered off, washed with water, and dried. It melted at 185°, and another recrystallization from alcohol furnished colourless needles melting at 191° alone and

(16) Fenton and Sisson, *J. Chem. Soc.*, **91** (1907), 690.

in admixture with pure specimen of formaldimedon. Thus the presence of formaldehyde was recognized.

Identification of formic acid. The residual liquid product in the decomposition flask was then extracted with ether and was saponified with alcoholic potash. The resulting acidic substance gave positive reaction with Schiff's reagent as well as Tollens' solution and it deposited mercurous chloride when heated with concentrated mercuric chloride solution.

The liquid acid obtained (8 g.) was stirred 3 times with 10 c.c. of water each time for about an hour and the water layer separated was neutralized with aqueous ammonia and evaporated to ca. 10 c.c. A portion of this solution when heated with mercuric chloride solution deposited mercurous chloride, while it showed a reducing action on Tollens' solution. The neutral solution was acidified with dilute hydrochloric acid and was extracted with ether several times.

The ethereal solution thus obtained was then mixed with about 10 c.c. of water and warmed on the water-bath and the ether was expelled. The residual aqueous solution was digested with magnesium powder at ordinary temperature and filtered.[16] From the filtrate on mixing with alcoholic dimedon solution, formaldimedon melting at 191° was obtained, which shows that the original solution contained formic acid.

Oxidation of the liquid acid obtained from the ozonide. The liquid acidic substance, after removal of formic acid, amounted to 6.5 g. It was warmed with 320 c.c. of dilute nitric acid (d = 1.12) on the boiling water-bath for 5 hours and then evaporated to syrup and extracted with ether. From the ethereal solution an oily substance was precipitated by the addition of light petroleum ether, which gradually turned into a crystalline mass on cooling. The mass softened at 111° and melted at 131° without any purification. By fractional recrystallization from a mixture of light petroleum ether and benzene (2:3) two kinds of crystalline acids were obtained, the one crystallizing at first melted at 123–129° and the other at 173–178° (with decomposition). By three successive purifications from the same solvent two acids with m.p. 139° and m.p. 186–187° (with decomp.) were obtained. The former had the formula $C_6H_{10}O_4$ and was identified as *asym*-dimethylsuccinic acid by melting in admixture with an authentic specimen. (Found: C, 49.12; H, 6.89. Calculated for $C_6H_{10}O_4$: C, 49.32; H, 6.85%.) The latter melting at 186–187° (with decomp.) had the composition $C_5H_8O_4$ and was found to be identical with dimethylmalonic acid by examining the melting point of the mixture of the sample with an authentic specimen.

In conclusion, the author wishes to thank Prof. K. Kafuku for his kind advices and suggestions rendered during the course of this work.

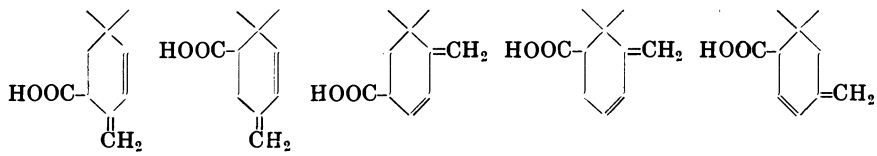
Department of Industry,
Government Research Institute of Taiwan.

Studies on the Constitution of Shonanic Acid, One of the Two Characteristic Volatile Acids from the Wood of *Libocedrus formosana*, Florin. VI. Studies on the Oxidation of Dihydroshonanic Acid with Ozone and Potassium Permanganate.

By Nobutoshi ICHIKAWA.

(Received November 24th, 1936.)

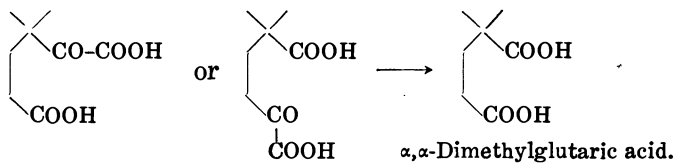
In the previous communication the author has reported that the constitution of shonanic acid should be represented by one of the following formulæ:



I. II. III. IV. V.

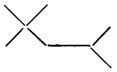
The present communication deals with the studies on the oxidation products of dihydroshonanic acid with ozone and potassium permanganate and as a result of these investigations the author has come to the conclusion that the acid must be represented by the formula III.

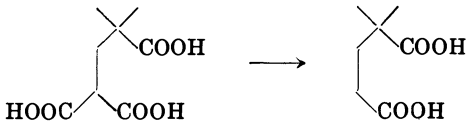
The ozonisation of dihydroshonanic acid and the subsequent decomposition of the ozonide, followed by the treatment with dilute nitric acid, furnished a dibasic ketonic acid of the formula $C_8H_{12}O_5$, which on further oxidation with perhydrol gave α,α-dimethylglutaric acid. These facts show that this dibasic ketonic acid may be represented by either VI or VII.



VI. VII. α,α-Dimethylglutaric acid.

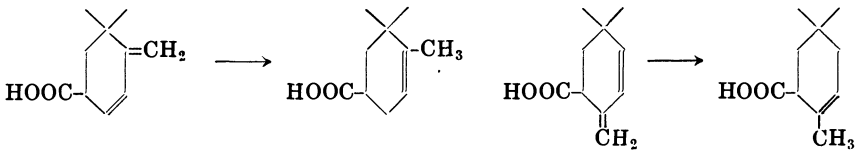
The oxidation of dihydroshonanic acid with potassium permanganate gave a crystalline dihydroxy-dihydroshonanic acid $C_{10}H_{18}O_4$ (m.p. 161–161.5°) together with a liquid dibasic ketonic acid with the formula $C_{10}H_{16}O_5$. On examination, the latter proved to be a chain compound and its optical activity revealed the presence of at least one asymmetric

carbon atom. It could be prepared from the former by oxidizing it with lead tetracetate as described by R. Criegee, L. Kraft and B. Rank[1] and subjecting the resulting aldehydic acid to the action of alkaline perhydrol. The ketonic acid was evidently a methyl ketonic acid as it could be converted into tribasic acid $C_9H_{14}O_6$ by digestion with sodium hypochlorite. This tribasic acid, on oxidation with dilute nitric acid, gave α,α-dimethylglutaric acid and another tribasic acid of the formula $C_8H_{12}O_6$, which was easily transformed into α,α-dimethylglutaric acid on treatment with hot concentrated hydrochloric acid. It naturally follows that the tribasic acid $C_8H_{12}O_6$ should be represented by VIII and as consequence an arrangement  in the molecule of dihydroshonanic acid is to be expected.



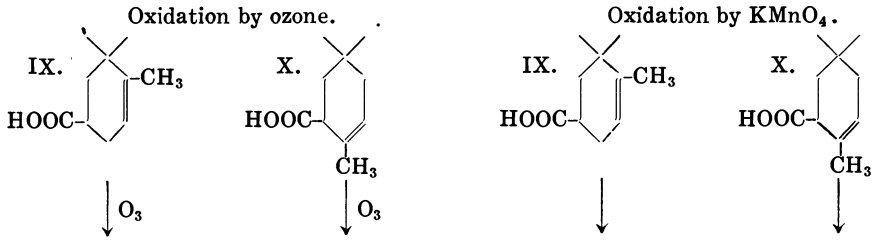
VIII. α,α-Dimethylglutaric acid.

There are two possible constitutional formulæ for dihydroshonanic acid which are capable of explaining the facts mentioned above, the one is IX which should be derived from III while the other is X transformed from I.

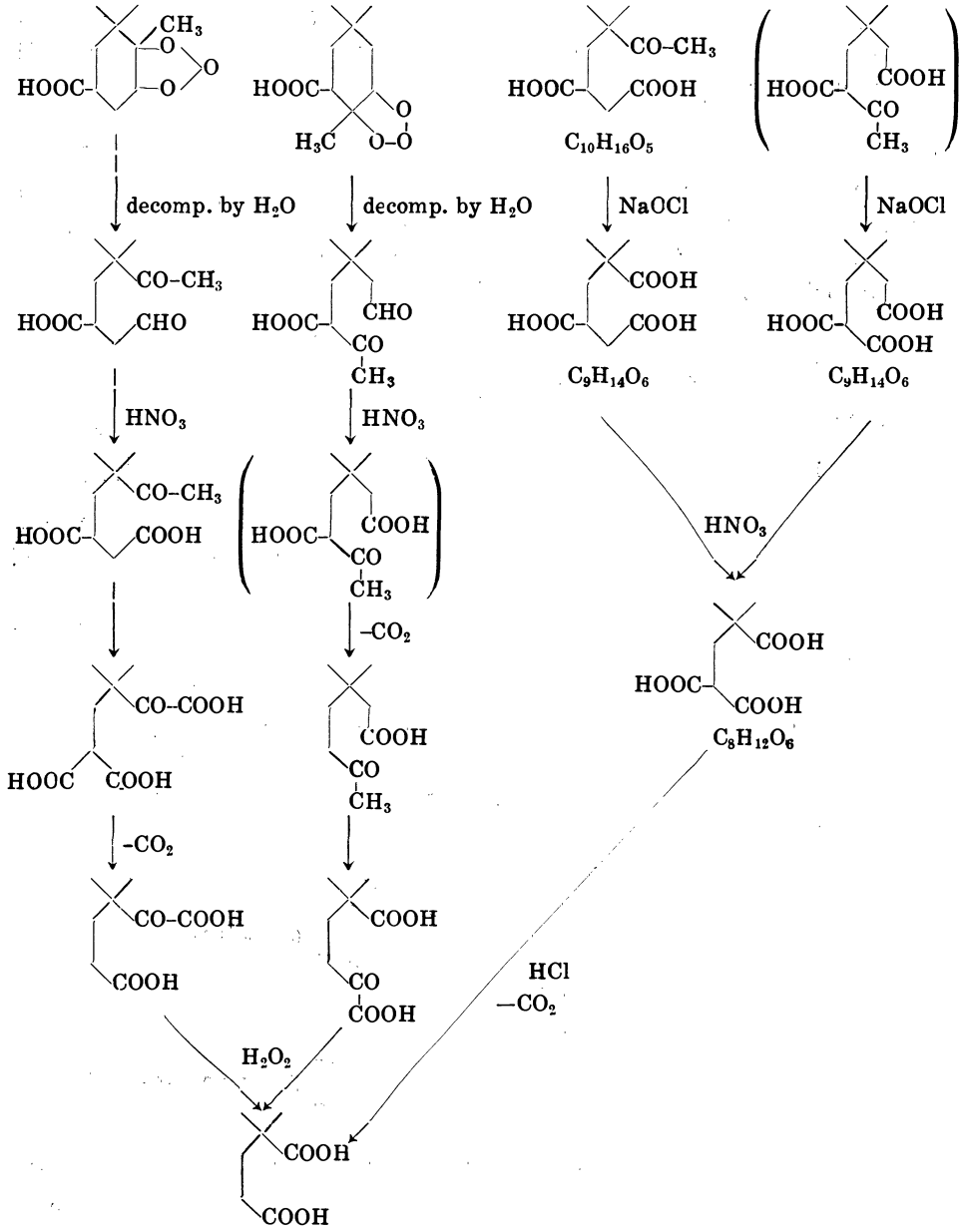


III. IX. I. X.

Oxidation by ozone. Oxidation by $KMnO_4$.



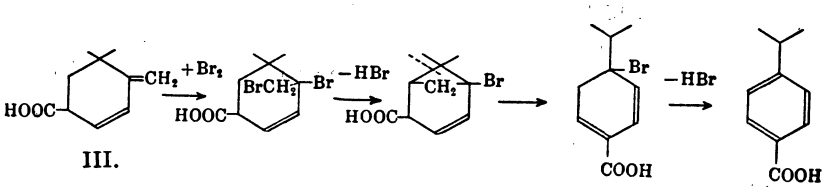
(1) *Ann.*, **507** (1933), 159.



The compound put in parentheses may not exist as free acid as it is a β-ketonic acid and consequently may transform into monoketo-monocarboxylic acid of the formula $C_9H_{16}O_3$ with liberation of carbon dioxide. For this reason the formula X seems not suitable for the constitution

of dihydroshonanic acid, whilst the constitution IX fulfils all the requirements of this compound. Now, the author will choose the formula III for shonanic acid by the two following reasons.

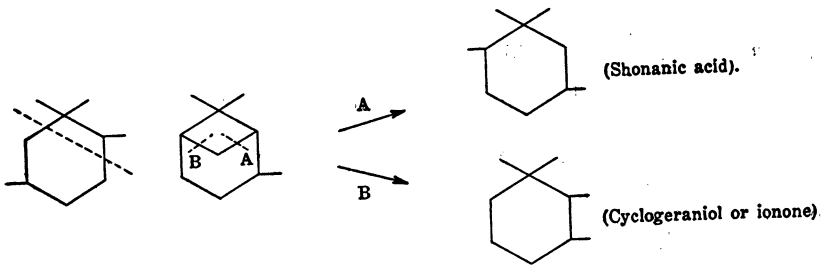
(1) The fact that by distillation under reduced pressure shonanic acid dibromide gives rise to *p*-cuminic acid, can very easily be explained by assuming the formula III as shown by the following scheme (as for the mode of addition of bromine see the second paper[2]), while the formula I necessitates to assume an extravagant migration of the carboxyl group in order to explain this conversion.



III. *p*-Cuminic acid

(2) The fact that shonanic acid can be esterified with fairly good yield (from 10 g. of the acid 9.3 g. of the ester), indicates that in shonanic acid the carbon atom in the ortho-position to its carboxyl group is unsubstituted.

The skeleton of III may be regarded as consisting of two isoprene nuclei as shown below whilst this structure may be considered as derived from pinane by cleavage of four-membered ring system at A. It is noteworthy that if the splitting of the four-membered ring occurs at B, the resulting skeleton represents that of cyclogeraniol or ionone.



Attention must also be drawn to the interesting fact that an acid of the structure closely related to pinene, the most widely distributed constituent of various essential oils, especially in those of coniferous trees, was found as the prevailing constituent of the conifer *"Libocedrus formosana,* Florin" or "Shônan-Boku".

(2) This Bulletin, **12** (1937), 233.

Experimental.

I. Separation of dihydroshonanic acid. Dihydroshonanic acid was separated by fractionation of the acidic portion obtained as by-product during the preparation of dihydroshonanyl alcohol by the reduction of ethyl shonanate with sodium and ethyl alcohol (see the fourth paper[3]).

140 g. of the material was subjected to fractional distillation under reduced pressure using Widmer's fractionating column. After three successive rectifications, the following fractions were obtained.

Fr. No.	B.p./6 mm.	d_4^{20}	n_D^{30}	α_D^{20}	Wt.(g.)	Wt.(%)
1	-137°	—	1.4796	—	3	2.17
2	137-138°	1.007	1.4798	—5.28°	43	31.16
3	138-139°	1.012	1.4800	—5.20°	32	23.19
4	139-140°	1.012	1.4810	—5.20°	18	13.04
5	140-141°	1.015	1.4824	—4.68°	7	5.07
6	141-144°	1.017	1.4834	—3.68°	4	2.90
7	144-147°	Crystallized	—	—	12	8.69
8	147-150°	,,	—	—	14	10.14
9	Residue				5	3.64

The main fractions 2 and 3 mainly consisted of dihydroshonanic acid. Further rectifications gave a distillate with the following properties: b.p. 138.7°/6 mm.; d_4^{30} 1.009; n_D^{30} 1.4795; α_D^{24} —5.26°; M.R. obs. 47.26, calculated for $C_{10}H_{16}O_2$ 47.30; Acid value 333.97, calculated for $C_{10}H_{16}O_2$ 333.3. (Found: C, 71.60; H, 9.49. Calculated for $C_{10}H_{16}O_2$: C, 71.43; H, 9.52%. Analysis of the silver salt: Ag, 39.32. Calculated for $C_{10}H_{15}O_2Ag$: Ag, 39.27%.)

Amide. The amide was prepared in white leaflets by the interaction of the acid chloride and aqueous ammonia. It was recrystallized once from 60% ethyl alcohol when it melted at 130°.

II. Oxidation of dihydroshonanic acid with potassium permanganate. 20 g. of the acid was dissolved in 600 c.c. of 1% caustic soda solution and 800 c.c. of 1.5% potassium permanganate solution was added drop by drop with vigorous stirring. After all the permanganate solution had been added, the reaction mixture was saturated in cold with carbon dioxide and then warmed on the water-bath for an hour until the permanganate has been completely consumed. The precipitate of manganese dioxide was filtered off and the filtrate was evaporated to a smaller bulk on the water-bath in an atmosphere of carbon dioxide. The solution was then slightly acidified with 5N hydrochloric acid, and the soft crystalline mass appeared was filtered and dried on a porous plate. Yield 8 g.

The crystalline substance thus separated represented dihydroxy-dihydroshonanic acid (A). A liquid acidic substance made appearance on further addition of 5N

(3) This Bulletin, **12** (1937), 253.

hydrochloric acid to the filtrate which was extracted with ether, and the ethereal solution was precipitated by the addition of light petroleum ether. The portion precipitated was separated and left to cool in an ice-box. A little dihydroxy-dihydroshonanic acid crystallized out, which was filtered off, washed with petroleum ether and dried. The viscous liquid acid obtained after the separation of the crystalline acid and evaporation of the solvent was found to consist mainly of ketonic acid of the formula $C_{10}H_{16}O_5$ (B).

Dihydroxy-dihydroshonanic acid. The crystalline acid (A) was insoluble in petroleum ether, ether and chloroform, difficultly soluble in water, but soluble in hot alcohol. The purified acid (recrystallized from hot water or alcohol) melted at 161–161.5°. The silver salt was found to dissolve readily in water. Acid value 276.22, calculated for $C_{10}H_{18}O_4$ 277.23. (Found: C, 59.09; H, 8.95. Calculated for $C_{10}H_{18}O_4$: C, 59.41; H, 8.91%.)

The liquid acid ($C_{10}H_{16}O_5$). The yield of the liquid acid (B) amounted to about 10 g. Its reactions were decidedly aldehydic. Thus it was dissolved in an excess of caustic soda solution, 5 c.c. of 30% perhydrol was added and left over night at ordinary temperature. The acid recovered from this alkaline solution was a viscous fluid with a faint reddish brown colour, which was then esterified by warming it with 30 c.c. of alcohol containing 4% hydrochloric acid.

The ethereal solution of the ester was washed with water then with 5% sodium carbonate solution successively, dried over anhydrous sodium sulphate and the ether was distilled off. The residual ester was fractionated twice under reduced pressure.

Fr. No.	B.p.	d_4^{30}	n_D^{20}	α_D^{28}	Vol. (c.c.)
1	113–116°/13 mm.	0.9738	1.4497	−6.3°	2.0
2	116–118°/13 mm.	0.9844	1.4499	−5.8°	1.0
3	118°/13 mm.–130°/3 mm.	—	—	—	1.1
4	130–140°/3 mm.	1.057	1.4583	−1.18°	3.5
5	140–150°/3 mm.	1.060	1.4563	−1.03°	2.0
6	over 150°/3 mm.	—	—	—	0.3

Judging from its physical properties as well as from its odour, fraction 1 appeared to be the ethyl ester of the unchanged dihydroshonanic acid, while the main fractions 4 and 5 were once more rectified under reduced pressure and a fraction with the following properties was obtained: b.p. 276°/758 mm.; d_4^{30} 1.059; n_D^{30} 1.4584; α_D^{28} −1.08°; M.R. obs. 70.14, calculated for $C_{14}H_{24}O_5$ 70.08; saponification value 429.3, calculated for $C_{14}H_{24}O_5$ (diethyl ester) 411.8. (Found: C, 61.85; H, 8.88. Calculated for $C_{14}H_{24}O_5$: C, 61.7; H, 8.8%.)

Application of Criegee's method on dihydroxy-dihydroshonanic acid. 10 g. of the acid was dissolved in warm benzene and 22 g. of lead tetracetate was added in small portions with vigorous stirring, filtered while hot from the precipitate and the precipitate was washed several times with ether. Then the benzene-ethereal solution was shaken with water in order to remove acetic acid liberated from lead tetracetate,

and evaporated. The viscous acid thus obtained was readily soluble in ether and alcohol but sparingly in petroleum ether. As the substance showed reactions of aldehyde its alkaline solution was treated with 5 c.c. of 30% perhydrol at 40–50°, when the reddish brown colour of the solution turned into yellow. The acid recovered as usual from this alkaline solution showed no tendency of solidification so that it was esterified by warming with 30 c.c. of alcohol containing 4% hydrochloric acid and the ester thus prepared showed the following properties: b.p. 274°/757 mm., 132–134°/2 mm.; d_4^{30} 1.054; n_D^{30} 1.4579; α_D^{30} −1.34°; saponification value 431.3, calculated for $C_{14}H_{24}O_5$ (diethyl ester) 411.8. (Found: C, 62.42; H, 8.98. Calculated for $C_{14}H_{24}O_5$: C, 61.7; H, 8.8%.)

The physical properties of the ethyl ester of the acid agreed well with those of the ester of the liquid acid $C_{10}H_{16}O_5$ (B) obtained by the oxidation of dihydroshonanic acid and was proved to be the same ketonic dicarboxylic acid by its behaviours toward oxidizing agents.

Oxidation of liquid acid $C_{10}H_{16}O_5$. The acid resulting from the saponification of the ethyl ester mentioned above was a viscous sticky substance but showed no tendency to crystallize. In order to ascertain whether the ketonic group in the molecule of the acid is an acetyl group or not, the substance was next subjected to oxidation with sodium hypochlorite, when a tricarboxylic acid should be obtained if the substance under investigation be a compound containing acetyl group.

To a solution of 4 g. of the substance dissolved in 20 c.c. of 10% sodium hydroxide solution, 8 c.c. of sodium hypochlorite solution (ca. 5.6%) was added in small portions with stirring. The reaction proceeded with evolution of heat and the smell of chloroform was perceived during the course of the reaction. After all the hypochlorite solution had been consumed the reaction mixture was refluxed for about half an hour on the water-bath, then it was evaporated to a smaller bulk and the acidic substance was recovered as usual. The ethereal solution (100 c.c.) of the acid was then stirred with 50 c.c. of water under reflux condenser at 40–50° for half an hour and the water layer separated. On evaporating the aqueous solution on the water-bath, a syrupy acid was obtained (yield 2.6 g.) which remained fluid even when kept cool for a week. The purification of the crude substance thus obtained could not be accomplished further by distillation but from the result of analysis of the silver salt and from its acid value, the substance seemed likely to represent a tribasic acid of the formula $C_9H_{14}O_6$. Acid value 744.8, calculated for $C_9H_{14}O_6$ 770.6. Analysis of the silver salt: Ag, 59.43. Calculated for $C_9H_{11}O_6Ag_3$: Ag, 60.11%. The difference between the theoretical and the experimental values may be attributed to the presence of a little unchanged acid.

Oxidation of the tricarboxylic acid $C_9H_{14}O_6$. With a view to obtain a C_8-acid, the tribasic acid obtained above was oxidized with dilute nitric acid. A mixture of 4 g. of the substance and 40 c.c. of nitric acid (d = 1.12) was warmed under reflux for 2 hours and then evaporated on the water-bath to a smaller bulk. On cooling, it deposited a little crystalline acid, which was filtered, dried on a porous plate and was purified by reprecipitation from benzene solution by the addition of light petroleum ether. Yield 0.4 g. It melted at 83° and was found to be identical with α,α-dimethylglutaric acid by melting in admixture with authentic specimen. The liquid acidic portion after removal of α,α-dimethylglutaric acid was esterified with 20 c.c. of 7% alcoholic hydrochloric acid and the ester formed was fractionally distilled under reduced pressure.

Fr. No.	B.p./5mm.	d_4^{30}	n_D^{30}	Vol. (c.c.)
1	95–103°	—	1.4228	0.2
2	103–107°	0.9946	1.4286	0.6
3	107–135°	—	—	0.3
4	135–149°	1.043	1.4328	1.3

Fraction 2 was saponified as usual and after evaporating the alkaline solution on the water-bath nearly to dryness it was acidified with 2N hydrochloric acid, and the organic acid set free was extracted with ether. After removal of ether remained syrupy mass, which, on boiling with conc. hydrochloric acid for a while in a test tube and subsequent cooling, turned into a crystalline mass. The crude crystals, dried on a porous plate, melted at 74–78°, and after recrystallization from benzene melted at 82.5° and was confirmed to be identical with α,α-dimethylglutaric acid by examining the mixed melting point.

Fraction 4 was analysed without further rectification owing to the scarcity of the material. Saponification value 567.0, calculated for $C_{14}H_{24}O_6$ (triethyl ester) 583.3. (Found: C, 58.77; H, 8.49. Calculated for $C_{14}H_{24}O_6$: C, 58.33; H, 8.33%.)

The analytical data showed that the fraction consisted mainly of the triethyl ester of a tricarboxylic acid $C_8H_{12}O_6$. The free acid was regenerated from the neutral solution resulting from the determination of the saponification value. The solution was evaporated nearly to dryness on the water-bath and was acidified with hydrochloric acid and the free organic acid liberated was extracted with chloroform, dried over anhydrous sodium sulphate, and evaporated. The residue showed no tendency to crystallize even when kept ice-cold for several days. Then it was gently heated with conc. hydrochloric acid for about half an hour under reflux as in the previous case. On cooling, a minute quantity of crystals made appearance, so that the heating was continued for further 3 hours and kept cool over night in an ice-box. The crystalline acid thus deposited was filtered, and dried on a porous plate. It melted at 87° when purified by reprecipitation from chloroform solution by the addition of light petroleum ether and proved to be identical with α,α-dimethylglutaric acid. Thus it should be concluded that the free tricarboxylic acid has transformed into α,α-dimethylglutaric acid by elimination of one mol of carbon dioxide therefrom.(4)

III. Ozonolysis of dihydroshonanic acid. A well-cooled solution of 10 g. of the acid in 100 c.c. of carbon tetrachloride was treated with ozonized oxygen (containing ca. 5% ozone) at a rate of 20–25 l. per hour. The ozonide formed was crystalline and remained suspended in the solution. It was filtered, washed with carbon tetrachloride, heated to gentle boiling with 100 c.c. of 3.5% solution of sodium carbonate, and then a calculated quantity of 3% perhydrol was added drop by drop with constant stirring in order to oxidize the aldehyde group into the carboxyl, meanwhile sodium carbonate solution being added little by little to maintain the reaction mixture

(4) Analogous with the case of preparation of α,α-dimethylsuccinic acid [Leukart, *Ber.*, **18** (1885), 2550] or α,α-dimethyladipic acid [Blanc, *Bull. soc. chim.*, [4], **3** (1890), 288] from isobutane-α,α,β-tricarboxylic acid or α,α-dimethyl-α′-carboxy-adipic acid respectively.

slightly alkaline. The acidic substance recovered (amounted to ca. 9 g.) from the reaction mixture was a viscous substance with a light reddish brown colour and showed positive reaction toward Schiff's reagent and Tollens' solution. As the substance remained liquid even when kept cold for several days, it was directly oxidized by heating it with dilute nitric acid (d = 1.12) on the water-bath for 2 hours, evaporated, and esterified by warming with 50 c.c. of ethyl alcohol containing 4% hydrochloric acid. The ester formed was fractionally distilled under reduced pressure.

Fr. No.	B.p./2mm.	d_4^{21}	n_D^{21}	α_D^{21}	Wt.(g.)
1	78–135°	0.9722	1.4614	−0.8°	1.8
2	135–140°	1.082	1.4570	−0.3°	5.2

Fraction 2 was once more rectified and the portion 138–140°/6 mm. was collected, which showed the following properties: d_4^{29} 1.083; n_D^{29} 1.4535; α_D nil; M.R. obs. 60.96, calculated for $C_{12}H_{20}O_5$ 60.88; saponification value 474.5, calculated for $C_{12}H_{20}O_5$ (diethyl ester) 459.0. (Found: C, 59.13; H, 8.41. Calculated for $C_{12}H_{20}O_5$: C, 59.0; H, 8.2%.)

Preparation of the semicarbazone. The ester gave a crystalline semicarbazone melting at ca. 149° without any purification, which when purified by one recrystallization from 60% alcohol melted at 154–156°. The further purification from the same solvent was impossible. (Found: N, 14.26. Calculated for $C_{13}H_{23}O_5N_3$: N, 13.95%.)

Preparation of α,α-dimethylglutaric acid from ketonic diethyl ester $C_{12}H_{20}O_5$. 3 g. of the viscous liquid acid obtained by saponification of the diethyl ester mentioned above was dissolved in 60 c.c. of caustic soda solution, to which 40 c.c. of 30% perhydrol was added with constant stirring at 40–50°. When the peculiar reddish brown colour of the solution disappeared, the reaction mixture was evaporated on the water-bath, acidified with dilute hydrochloric acid and organic acid set free was extracted with chloroform. On removal of chloroform there remained a yellowish sticky substance, which turned into a crystalline mass on warming with conc. hydrochloric acid as in the previous cases. The crystalline acid was also identical with α,α-dimethylglutarc acid.

In conclusion, the author wishes to thank Prof. Kinzô Kafuku for his kind advices and suggestions rendered during the course of this work.

Department of Industry,
Gevernment Research Institute of Taiwan.

Measurement of Circular Dichroism in the Ultra-Violet Regions. I.

By Ryutaro TSUCHIDA.

(Received May 7th, 1937.)

Introduction. A method of measuring circular dichroism in the ultra-violet as well as the visible regions was devised by Kuhn and Braun.[1] The general principle of the method is as follows. By means of a half-shadow polarizer of a split prism and a Fresnel rhomb set parallel to the polarizer, two elliptically polarized rays of opposite sign and of equal ellipticity are produced. On traversing d cm. of a c mol/l. solution of an optically active compound whose molar extinction coefficients for left and right circular vibrations are ε_l and ε_r, the two rays will have their ellipticities changed. By rotating the polarizer, the ellipticities of the rays incident on the solution can be made unequal until those of the emergent rays are again equal. This is tested by an analyser placed so as to transmit only those vibrations corresponding to the minor axes of the two ellipses. Let τ be the angle through which the polarizer has been rotated to obtain an equal brightness after passing through the optical system, then the difference between the molar extinction coefficients is given by the following relation

$$\varepsilon_l - \varepsilon_r = \frac{4\tau}{cd} . \qquad (1)$$

In deriving the relation, however, the following limitations have been introduced. Let θ be half the angle between the two vibration directions of the polarizer. The values of θ and τ should be so small as to satisfy the relations, $\tan\theta \simeq \theta$, $\tan(\theta+\tau) \simeq \theta+\tau$ and $\tan(\theta-\tau) \simeq \theta-\tau$, and α, the rotation caused by the active compound, should also be very small. Besides these limitations, some more approximate calculations have been introduced in course of derivation of the relation (1), and consequently it seems insufficient for further discussions. The present author has derived a general equation for circular dichroism measurements in which both the polarizer and the analyser are rotated and all

(1) Kuhn and Braun, *Z. physik. Chem.*, B, **8** (1930), 445.

the above-mentioned limitations have been abolished. By means of the equation, experimental conditions have been discussed.

Derivation of the Equation. Let 2θ be the angle between the vibration directions of prisms P_1 and P_2 of the half-shadow polarizer and τ, the angle between the bisectrix of the two planes of vibration of P and the Fresnel rhomb F, whose vibration directions are taken as co-ordinate axes throughout the calculation. Then the plane polarized rays produced by the prisms P_1 and P_2 contain $\tau+\theta$ and $\tau-\theta$ respectively with the x-axis. The intensity of the two rays after passing through the polarizer being equal, the amplitude is denoted by a_0. Then the two rays may be expressed by

$$a = a_0 \cos 2\pi\nu t .$$

On entering the Fresnel rhomb each of these rays is split into two components, one propagating in a plane parallel to the rhomb and the other perpendicular. The amplitudes of these components, a_x and a_y, are

$$\left.\begin{aligned}(a_x)_1 &= a_0 \,|\cos(\tau+\theta)|\\ (a_y)_1 &= a_0 \,|\sin(\tau+\theta)|\end{aligned}\right\} \text{for } P_1,$$

and

$$\left.\begin{aligned}(a_x)_2 &= a_0 \,|\cos(\tau-\theta)|\\ (a_y)_2 &= a_0 \,|\sin(\tau-\theta)|\end{aligned}\right\} \text{for } P_2.$$

The light waves before the first total reflexion in the rhomb are

$$\left.\begin{aligned}x_1 &= a_0 \cos(\tau+\theta)\cos 2\pi\nu t\\ y_1 &= a_0 \sin(\tau+\theta)\cos 2\pi\nu t\end{aligned}\right\} \text{for } P_1,$$

and

$$\left.\begin{aligned}x_2 &= a_0 \cos(\tau-\theta)\cos 2\pi\nu t\\ y_2 &= a_0 \sin(\tau-\theta)\cos 2\pi\nu t\end{aligned}\right\} \text{for } P_2.$$

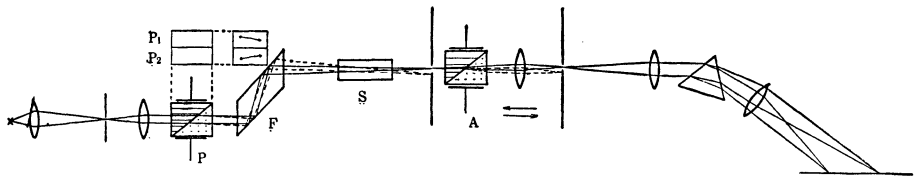


Fig. 1.

After the second total reflexion in the rhomb, each of these two pairs of plane polarized rays receives a phase difference of $\frac{\pi}{2}$, and the waves become

$$\left.\begin{aligned} x_1 &= a_0 \cos(\tau+\theta)\cos 2\pi\nu t \\ y_1 &= a_0 \sin(\tau+\theta)\sin 2\pi\nu t \end{aligned}\right\} \text{ for } P_1,$$

and

$$\left.\begin{aligned} x_2 &= a_0 \cos(\tau-\theta)\cos 2\pi\nu t \\ y_2 &= a_0 \sin(\tau-\theta)\sin 2\pi\nu t \end{aligned}\right\} \text{ for } P_2.$$

The resultant vibration for P_1 and P_2 after passing through the rhomb may, therefore, be expressed as

$$\left.\begin{aligned} \mathbf{R}_1 &= \mathbf{i}a_0 \cos(\tau+\theta)\cos 2\pi\nu t + \mathbf{j}a_0 \sin(\tau+\theta)\sin 2\pi\nu t \\ \text{and} \quad \mathbf{R}_2 &= \mathbf{i}a_0 \cos(\tau-\theta)\cos 2\pi\nu t + \mathbf{j}a_0 \sin(\tau-\theta)\sin 2\pi\nu t. \end{aligned}\right\} \qquad (2)$$

These expressions represent elliptically polarized lights whose sense of rotation depends on τ and θ. The elliptically polarized ray is lævorotatory when P_1 is in the first and the third quadrant, and dextrorotatory otherwise. The same holds for P_2.

First the intensity of the elliptically polarized lights is compared directly with the analyser A. Let the angle between the analyser and the Fresnel rhomb be δ_0, at which the two fields of the half-shadow are of equal brightness, then

$$a_0^2 \cos^2(\tau+\theta)\cos^2\delta_0 + a_0^2 \sin^2(\tau+\theta)\sin^2\delta_0 = a_0^2 \cos^2(\tau-\theta)\cos^2\delta_0 + a_0 \sin^2(\tau-\theta)\sin^2\delta_0.$$

Solving this equation we obtain

$$\tan\delta_0 = \pm 1. \qquad \therefore\ \delta_0 = \frac{\pi}{4}(1\pm 2n).$$

Then δ_0 is independent of τ and θ ; in other words the two fields of the half-shadow are of equal brightness when the analyser is placed at $\frac{\pi}{4}$ or $\frac{3}{4}\pi$ referring to the Fresnel rhomb, whatever the angle between the polarizer and the rhomb and that between the two vibration directions of the half-shadow polarizer may be. This relation gives us the means

of determining the relative angular position of the analyser referred to the Fresnel rhomb and consequently the zero point of the measurement.

Next let us consider the case when a solution of active substance is introduced between the Fresnel rhomb and the analyser. As the active substance has different extinction coefficients for left and right circularly polarized vibrations, each of the elliptically polarized rays represented by the equations (2) should first be transformed as a resultant of circularly polarized waves of opposite rotatory sense.

Thus
$$\mathbf{R}_1 = \frac{a_0}{2}\{\cos(\tau+\theta)+\sin(\tau+\theta)\}(\mathbf{i}\cos 2\pi\nu t+\mathbf{j}\sin 2\pi\nu t)$$
$$+\frac{a_0}{2}\{\cos(\tau+\theta)-\sin(\tau+\theta)\}(\mathbf{i}\cos 2\pi\nu t-\mathbf{j}\sin 2\pi\nu t)\ ,$$

or

$$\left.\begin{aligned}\mathbf{R}_1 &= \frac{a_0}{\sqrt{2}}\sin\left(\frac{\pi}{4}+\tau+\theta\right)\cdot(\mathbf{i}\cos 2\pi\nu t+\mathbf{j}\sin 2\pi\nu t)\\ &+\frac{a_0}{\sqrt{2}}\sin\left(\frac{\pi}{4}-\tau-\theta\right)\cdot(\mathbf{i}\cos 2\pi\nu t-\mathbf{j}\sin 2\pi\nu t)\ .\end{aligned}\right\}$$

And similarly

$$\left.\begin{aligned}\mathbf{R}_2 &= \frac{a_0}{\sqrt{2}}\sin\left(\frac{\pi}{4}+\tau-\theta\right)\cdot(\mathbf{i}\cos 2\pi\nu t+\mathbf{j}\sin 2\pi\nu t)\\ &+\frac{a_0}{\sqrt{2}}\sin\left(\frac{\pi}{4}-\tau+\theta\right)\cdot(\mathbf{i}\cos 2\pi\nu t-\mathbf{j}\sin 2\pi\nu t)\ .\end{aligned}\right\} \qquad (2)'$$

In each of these equations the first and the second term represents a circularly polarized ray whose sense of rotation is anticlockwise and clockwise respectively.

After traversing the solution S, the vibrations are changed as follows. follows.

$$\mathbf{R}_1' = \frac{a_0}{\sqrt{2}}e^{-\frac{1}{2}\varepsilon_l cd}\sin\left(\frac{\pi}{4}+\tau+\theta\right)\cdot(\mathbf{i}\cos 2\pi\nu t+\mathbf{j}\sin 2\pi\nu t)$$
$$+\frac{a_0}{\sqrt{2}}e^{-\frac{1}{2}\varepsilon_r cd}\sin\left(\frac{\pi}{4}-\tau-\theta\right)\cdot(\mathbf{i}\cos 2\pi\nu t-\mathbf{j}\sin 2\pi\nu t)\ ,$$

or

$$\mathbf{R}_1' = \mathbf{i}\frac{a_0}{\sqrt{2}}\left\{e^{-\frac{1}{2}\varepsilon_l cd}\sin\left(\frac{\pi}{4}+\tau+\theta\right)+e^{-\frac{1}{2}\varepsilon_r cd}\sin\left(\frac{\pi}{4}-\tau-\theta\right)\right\}\cos 2\pi\nu t$$

$$+\mathrm{j}\frac{a_0}{\sqrt{2}}\left\{e^{-\frac{1}{2}\varepsilon_l cd}\sin\left(\frac{\pi}{4}+\tau+\theta\right)-e^{-\frac{1}{2}\varepsilon_r cd}\sin\left(\frac{\pi}{4}-\tau-\theta\right)\right\}\sin 2\pi\nu t\,. \tag{3}$$

$$\mathbf{R}_2'=\mathrm{i}\frac{a_0}{\sqrt{2}}\left\{e^{-\frac{1}{2}\varepsilon_l cd}\sin\left(\frac{\pi}{4}+\tau-\theta\right)+e^{-\frac{1}{2}\varepsilon_r cd}\sin\left(\frac{\pi}{4}-\tau+\theta\right)\right\}\cos 2\pi\nu t$$

$$+\mathrm{j}\frac{a_0}{\sqrt{2}}\left\{e^{-\frac{1}{2}\varepsilon_l cd}\sin\left(\frac{\pi}{4}+\tau-\theta\right)-e^{-\frac{1}{2}\varepsilon_r cd}\sin\left(\frac{\pi}{4}-\tau+\theta\right)\right\}\sin 2\pi\nu t\,. \tag{4}$$

Both the expressions (3) and (4) represent elliptically polarized rays.

The intensity of the two half-shadow fields observed through the analyser A, which is placed at an angle ω to the common axis of the elliptically polarized rays, (3) and (4), corresponding to the x-axis of the co-ordinates, is given by the following expressions.

$$I_1=\frac{a_0^2}{2}\left\{e^{-\frac{1}{2}\varepsilon_l cd}\sin\left(\frac{\pi}{4}+\tau+\theta\right)+e^{-\frac{1}{2}\varepsilon_r cd}\sin\left(\frac{\pi}{4}-\tau-\theta\right)\right\}^2\cos^2\omega$$

$$+\frac{a_0^2}{2}\left\{e^{-\frac{1}{2}\varepsilon_l cd}\sin\left(\frac{\pi}{4}+\tau+\theta\right)-e^{-\frac{1}{2}\varepsilon_r cd}\sin\left(\frac{\pi}{4}-\tau-\theta\right)\right\}^2\sin^2\omega$$

$$=\frac{a_0^2}{2}\left\{e^{-\varepsilon_l cd}\sin^2\left(\frac{\pi}{4}+\tau+\theta\right)+e^{-\varepsilon_r cd}\sin^2\left(\frac{\pi}{4}-\tau-\theta\right)\right.$$

$$\left.+e^{-\frac{1}{2}(\varepsilon_l+\varepsilon_r)cd}\cos 2(\tau+\theta)\cos 2\omega\right\}. \tag{5}$$

$$I_2=\frac{a_0^2}{2}\left\{e^{-\frac{1}{2}\varepsilon_l cd}\sin\left(\frac{\pi}{4}+\tau-\theta\right)+e^{-\frac{1}{2}\varepsilon_r cd}\sin\left(\frac{\pi}{4}-\tau+\theta\right)\right\}^2\cos^2\omega$$

$$+\frac{a_0^2}{2}\left\{e^{-\frac{1}{2}\varepsilon_l cd}\sin\left(\frac{\pi}{4}+\tau-\theta\right)-e^{-\frac{1}{2}\varepsilon_r cd}\sin\left(\frac{\pi}{4}-\tau+\theta\right)\right\}^2\sin^2\omega$$

$$=\frac{a_0^2}{2}\left\{e^{-\varepsilon_l cd}\sin^2\left(\frac{\pi}{4}+\tau-\theta\right)+e^{-\varepsilon_r cd}\sin^2\left(\frac{\pi}{4}-\tau+\theta\right)\right.$$

$$\left.+e^{-\frac{1}{2}(\varepsilon_l+\varepsilon_r)cd}\cos 2(\tau-\theta)\cos 2\omega\right\}. \tag{6}$$

$$\therefore\quad I_1-I_2=\frac{a_0^2}{2}\sin 2\theta\left\{\left(e^{-\varepsilon_l cd}-e^{-\varepsilon_r cd}\right)\cos 2\tau-2e^{-(\varepsilon_l+\varepsilon_r)cd}\sin 2\tau\cos 2\omega\right) \tag{7}$$

and $$I_1+I_2=\frac{a_0^2}{2}\left\{e^{-\varepsilon_l cd}+e^{-\varepsilon_r cd}+\left(e^{-\varepsilon_l cd}-e^{-\varepsilon_r cd}\right)\cos 2\theta \sin 2\tau \right.$$
$$\left. +2e^{-\frac{1}{2}(\varepsilon_l+\varepsilon_r)cd}\cos 2\theta \cos 2\tau \cos 2\omega \right\} . \qquad (8)$$

When the two half-shadow fields are of equal brightness, the expression (7) must be zero. As $\sin 2\theta$ can not be zero, we obtain

$$e^{-\varepsilon_l cd}-e^{-\varepsilon_r cd}=2e^{-\frac{1}{2}(\varepsilon_l+\varepsilon_r)cd}\tan 2\tau \cos 2\omega . \qquad (9)$$

$$\therefore \quad e^{\frac{1}{2}(\varepsilon_r-\varepsilon_l)cd}-e^{-\frac{1}{2}(\varepsilon_r-\varepsilon_l)cd}=2\tan 2\tau \cos 2\omega ,$$

or $$\sinh\frac{1}{2}(\varepsilon_r-\varepsilon_l)cd=\tan 2\tau \cos 2\omega . \qquad (9)'$$

$$\therefore \quad \varepsilon_r-\varepsilon_l=\frac{2}{cd}\operatorname{arcsinh}(\tan 2\tau \cos 2\omega) . \qquad (10)$$

Now τ is the angle between the polarizer and the Fresnel rhomb, and ω is given by $\omega=\delta-\alpha$, where δ is the angle between the Fresnel rhomb and the analyser and α is the angle of rotation. By measuring these angles, the circular dichroism can be calculated by the relation (10).

Approximate Equations. As we have introduced neither limitation nor approximation of any kind in course of calculation, the relation (10) holds for any values of θ, ω, and τ, as well as for any values of c and d, provided that the two fields observed through the analyser are of equal brightness.

In special cases when $\frac{1}{2}(\varepsilon_r-\varepsilon_l)cd$ is small,

$$\varepsilon_e-\varepsilon_l\simeq\frac{2}{cd}\tan 2\tau \cos 2\omega . \qquad (11)$$

Moreover, when ω is $\frac{\pi}{2}$ and τ is very small, we obtain an approximate equation,

$$\varepsilon_l-\varepsilon_r\simeq\frac{4\tau}{cd} \qquad (1)$$

which is identical with that of Kuhn and Braun referred to in the introduction. In other words the Kuhn's equation is one of the most special cases of our equation (10).

Calculation of the error caused by applying the approximate equation (1) is complicated and very difficult, as there are too many approximations and neglections as to τ and $(\varepsilon_r - \varepsilon_l)cd$ as well as α which is again a function of c and d. Consequently it is impossible to find the range of applicability of the approximate equation (1).

On the other hand, however, it may be easily determined for the approximate equation (11) how far it could be applied without causing serious error in the results of the measurement. The calculation is as follows. From the relation (10)

$$\frac{\mathrm{d}(\varepsilon_r-\varepsilon_l)}{\varepsilon_r-\varepsilon_l} = -\frac{\mathrm{d}c}{c}-\frac{\mathrm{d}d}{d}+\frac{\mathrm{d}(\tan 2\tau\cos 2\omega)}{\sqrt{1+\tan^2 2\tau\cos^2 2\omega}\,\operatorname{arcsinh}(\tan 2\tau\cos 2\omega)}. \quad (12)$$

$$\operatorname{arcsinh}(\tan 2\tau\cos 2\omega) = \frac{1}{2}(\varepsilon_r-\varepsilon_l)cd \equiv x \quad \text{(put)}. \quad (10)'$$

Then

$$\tan 2\tau\cos 2\omega = \sinh x = x+\frac{x^3}{3!}+\frac{x^5}{5!}+\frac{x^7}{7!}+\cdots\cdots. \quad (9)''$$

Now the approximate equation (11) may be rewritten as

$$\tan 2\tau\cos 2\omega \simeq x. \quad (11)'$$

Thus the error caused by using the approximate equation (11) is given by comparing (9)″ and (11)′

$$\mathrm{d}(\tan 2\tau\cos 2\omega) = -\left\{\frac{x^3}{3!}+\frac{x^5}{5!}+\cdots\cdots\right\}. \quad (13)$$

Substituing (9)″ and (13) in (12), we obtain

$$\frac{\mathrm{d}(\varepsilon_r-\varepsilon_l)}{\varepsilon_r-\varepsilon_l} = -\frac{\mathrm{d}c}{c}-\frac{\mathrm{d}d}{d}-\frac{\dfrac{x^2}{3!}+\dfrac{x^4}{5!}+\cdots\cdots}{\sqrt{1+\tan^2 2\tau\cos^2 2\omega}}.$$

As the first and the second term has nothing to do with the approximate equation,

$$\frac{\mathrm{d}(\varepsilon_r-\varepsilon_l)}{\varepsilon_r-\varepsilon_l} = -\frac{\dfrac{x^2}{3!}+\dfrac{x^4}{5!}+\cdots\cdots}{\sqrt{1+\tan^2 2\tau\cos^2 2\omega}}. \quad (12)'$$

Therefore the value of x which would provoke an error of 1% in $(\varepsilon_r - \varepsilon_l)$ may be computed as follows.

$$-\frac{1}{100} = -\frac{\frac{x^2}{3!}+\frac{x^4}{5!}+\cdots}{\sqrt{1+\tan^2 2\tau \cos^2 2\omega}} .$$

When x is a small fraction

$$\frac{x^4}{5!}+\frac{x^2}{3!} = \frac{1}{100}\sqrt{1+x^2} .$$

Solving the equation, we obtain

$$x = \pm 0.253.$$

In order to make use of the approximate equation (11) with a permissible error less than 1%, the following condition should be complied with.

$$|(\varepsilon_r-\varepsilon_l)|\, cd < 0.50.$$

Similarly for a permissible error less than 0.1

$$|(\varepsilon_r-\varepsilon_l)|\, cd < 0.15.$$

and for 0.01

$$|(\varepsilon_r-\varepsilon_l)|\, cd < 0.04.$$

Circular Dichroism of Ammonium α-Bromocamphor-π-Sulphonate. The molar extinction coefficient κ (as in $I = I_0 \times 10^{-\kappa cd}$) and the specific rotation $[\alpha]$ of the salt were measured with 0.01 mol/l. aqueous solutions with thicknesses between 0.3 and 4 cm. The circular dichroism $\kappa_r - \kappa_l$, i.e., $0.434 \times (\varepsilon_r - \varepsilon_l)$ was determined according to the method described above. The strength of the solution was 0.01 mol/l. and the thickness of the layer was 1 cm. throughout the measurements. The results are shown in Fig. 2.

The author wishes to express his sincere thanks to Professor Y. Shibata for his kind advice and encouragement and also to the Hattori Hôkôkai for a grant. In addition the author should like to record his gratitude to Mr. M. Kobayashi and Mr. H. Watanabe for their helpful assistance.

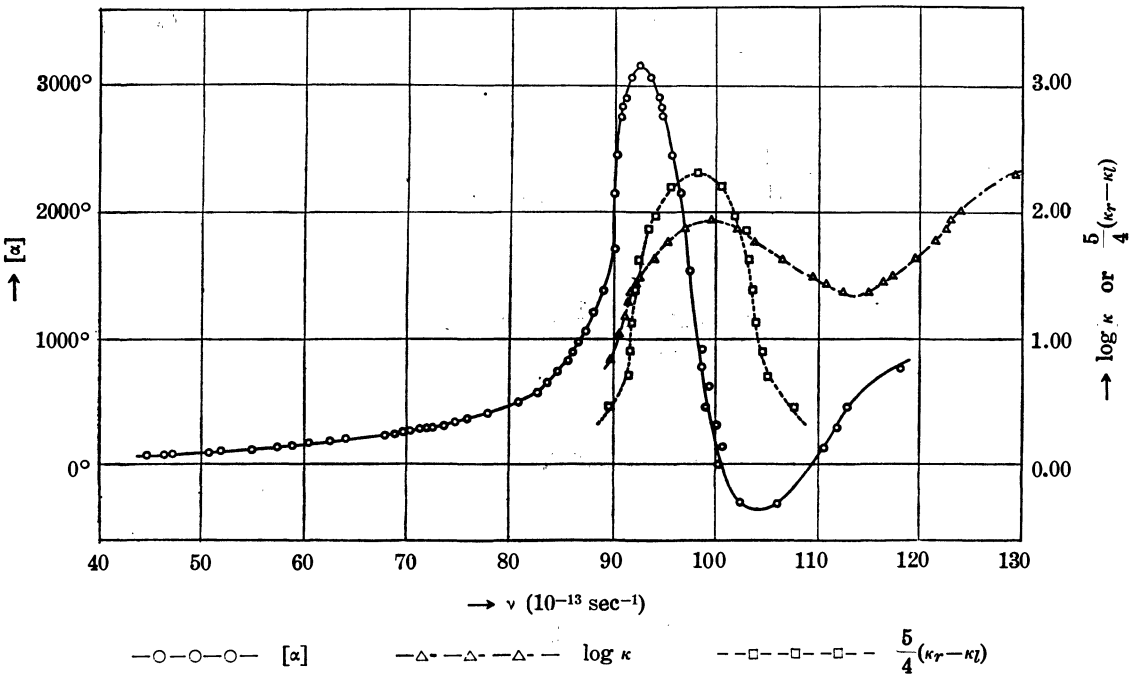


Fig. 2.

Summary.

1. An accurate method of measuring circular dichroism has been proposed.

2. The general equation for the measurement has been worked out.

$$\varepsilon_r - \varepsilon_l = \frac{2}{cd} \operatorname{arcsinh} (\tan 2\tau \cos 2\omega) .$$

3. The range of applicability was discussed for the approximate equation,

$$\varepsilon_r - \varepsilon_l = \frac{2}{cd} \tan 2\tau \cos 2\omega .$$

In order to make use of this equation with permissible errors less than 0.01, 0.1, and 1%, the following conditions should be complied with:

$$| (\varepsilon_r - \varepsilon_l) cd | < 0.04 \quad \text{for} \quad 0.01\% ,$$

$$|(\varepsilon_r-\varepsilon_l)cd| < 0.15 \quad \text{for} \quad 0.1\ \%\ ,$$

and $$|(\varepsilon_r-\varepsilon_l)cd| < 0.50 \quad \text{for} \quad 1\ \%\ .$$

4. The light absorption, the rotatory dispersion, and the circular dichroism in the visible and the ultra-violet regions were measured for ammonium α-bromocamphor-π-sulphonate.

Chemical Department, Faculty of Science,
Imperial University of Osaka.

Studies on the Flow of Gaseous Mixtures through Capillaries. II. The Molecular Flow of Gaseous Mixtures.

By Hiroshi ADZUMI.

(Received May 26th, 1937.)

In the preceding paper[1] on the flow of gaseous mixtures, the author dealt with the case where the mean free path of the gas molecule of each component is small in comparison with the diameter of the capillary. When the mean free path is large in comparison with the diameter, the number of mutual collisions between gas molecules is negligible as compared with that of collisions with the wall. In such a case, Knudsen[2] has assumed "the diffuse emission" from the wall of the capillary, namely, the molecules in the capillary leave a surface uniformly in all directions regardless of the directional distribution with which they hit the surface and are governed by the cosine law. As a result of this behaviour some of the molecules entering the mouth of the capillary are reversed and sent back to the vessel from which they came. Hence the number of molecules flowing through the capillary is a certain fraction of the total number of entering molecules and this fraction is determined only by the number of collisions with the wall of the capillary and not by the collisions between molecules.

(1) H. Adzumi, this Bulletin, **12** (1932), 199.
(2) M. Knudsen, *Ann. Physik*, (IV), **28** (1909), 75.

When the mean free path is large against the diameter of the capillary, the quantity of a simple gas flowing through the capillary in unit time is given by Knudsen as follows:

$$G_m = b(p_1 - p_2) , \tag{1}$$

where

$$b = \frac{4}{3}\sqrt{2\pi}\frac{1}{\sqrt{\rho_1}}\frac{r^3}{l} ,$$

ρ_1 is the density of the gas at the temperature of the capillary and at unit pressure (1 dyne/cm.^{2}), l and r are the length and the radius of the capillary respectively, p_1 and p_2 the pressures at the ends of the capillary, and G_m is measured by the product of its volume and pressure. Thus the amount of gas flowing per unit time is independent of the viscosity but inversely proportional to the square root of the molecular weight and therefore such a flow is called the molecular flow.

In their theoretical considerations of the flow of gases Maxwell[3], Smoluchowski[4], Gaede[5], and Baule[6] made the assumption that only a fraction f of the impinging molecules leave the wall according to the cosine law and that the reflection for remaining 1-f are specular. However, from the experiments, Knudsen gave the value of f as unity.

In an ideal gaseous mixture, each component is completely independent of the other, since the molecules do not affect each other within the capillary. Therefore the amount of flow of a mixture will be strictly additive or

$$b = n_1 b_1 + n_2 b_2 , \tag{2}$$

where n_1 and n_2 are mol fractions of two components.

In order to examine this point the following experiments have been done.

Experimental.

Apparatus for Measuring the Quantity of Flow. Fig. 1 is a schematic view of the apparatus. Glass bulbs A and B, both about 1 liter in capacity, are connected with the capillary C, whose radius is ca. 0.0121 cm. and length 8.7 cm. The pressure of each bulb is read by the McLeod gauge which is constructed to be able to measure from 10^{-5} to 10 mm. D and E are mercury cut-offs. When the mercury is raised to

(3) J. Maxwell, *Trans. Roy. Soc.* (London), A, **170** (1879), 251.
(4) M. v. Smoluchowski, *Ann. Physik*, (IV), **33** (1910), 1559.
(5) W. Gaede, *ibid.*, (IV), **41** (1913), 289.
(6) B. Baule, *ibid.*, (IV), **44** (1914), 145.

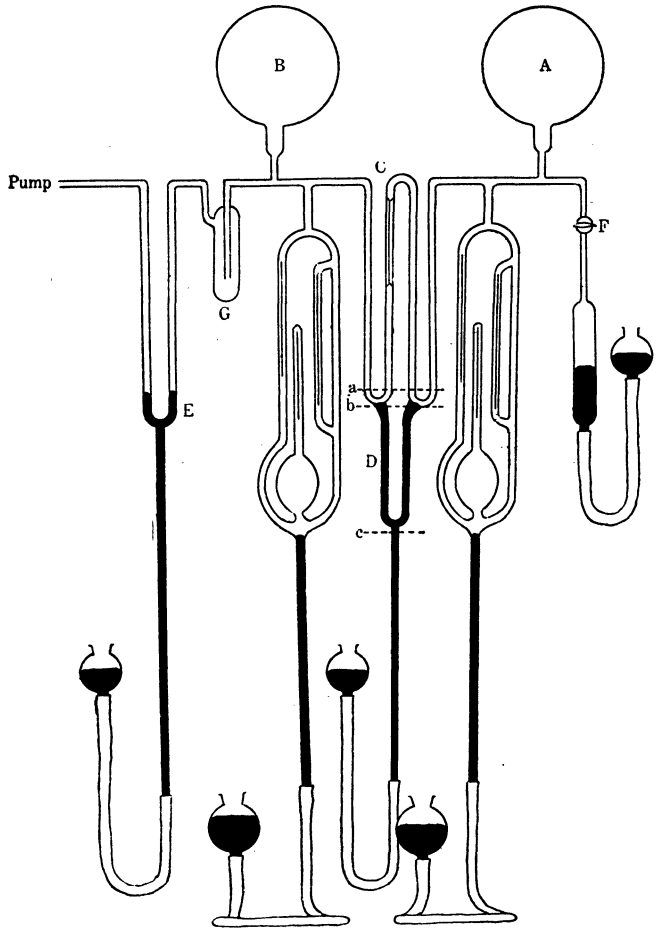


Fig. 1.

c, two bulbs are connected without the capillary, when raised to b, the gas flows through the capillary, and when raised to a, the flow is cut off.

After evacuation of the whole apparatus and raising the mercury to a, the required quantity of the gas is introduced into A from F. Then, by lowering the mercury to b, the gas in A begins to flow through the capillary, the volume on each side being kept constant.

If V_1 and p_1 represent the volume and the pressure of the right side of the capillary and V_2 and p_2 those of the left side, the quantity of gas flowing in time $d\tau$ through the capillary is expressed as

$$Q \cdot d\tau = K(p_1 - p_2)\ d\tau = -d(p_1 V_1) = d(p_2 V_2)\ ,$$

where K is a proportionality constant or the quantity of flow under unit pressure difference, $-d(p_1V_1)$ a quantity decreased in the right side of the capillary, and $d(p_2V_2)$ a quantity increased in the left side.
Then,

$$\frac{K\cdot d\tau}{V_1} = -\frac{dp_1}{p_1-p_2} \quad \text{and} \quad \frac{K\cdot d\tau}{V_2} = \frac{dp_2}{p_1-p_2},$$

From these formulæ,

$$\frac{d(p_1-p_2)}{p_1-p_2} = -K\left(\frac{1}{V_1}+\frac{1}{V_2}\right)d\tau .$$

By integration

$$K = -\frac{\ln\dfrac{p_1'-p_2'}{p_1-p_2}}{\tau}\,\frac{V_1\,V_2}{V_1+V_2},$$

where p_1' and p_2' are the pressures of bulbs after time $d\tau$. The values of V_1 and V_2 are 1371 c.c. and 1406 c.c. respectively, so that K is calculated by the following formula:

$$K = -\frac{\log\dfrac{p_1'-p_2'}{p_1-p_2}}{\tau}\times 1.856\times 10^3 \text{ (in mm.} \times \text{c.c.)}.$$

The mean pressure of both ends of the capillary is calculated by

$$p = \frac{p_1V_1+p_2V_2}{V_1+V_2}.$$

Results of Observation. The gaseous mixtures used for observation are $H_2\sim C_2H_2$ and $H_2\sim C_3H_6$. The preparation of these gases was described in the preceding paper.[1] The measuring temperature was $20 + 0.5°C$. The pressure range was between 4 and 10^{-3}mm. The time of flow was 2–4 hours.

Generally the values of K are a function of the mean pressure p, but become a constant when p is so small that the mean free path of the gas is large against the diameter of the capillary. This constant value corresponds to the rate of the molecular flow, b. When the pressures of hydrogen, acetylene, and propylene are lower than 0.06 mm., 0.03 mm., and 0.03 mm. respectively, the values of K become constants, which are 0.0750 for H_2, 0.0220 for C_2H_2, and 0.0164 for C_3H_6:

The values of K at the pressures higher than those will be reported in the following paper.

Table 1. The Rates of the Molecular Flow of Simple Gases.

Gas	b (mm.×c.c.)	
	obs.	calc.
H_2	0.0750	0.0750
C_2H_2	0.0220	0.0208
C_3H_6	0.0164	0.0164

The rates of the molecular flow, b, of three simple gases can be calculated by equation (1), by inserting the following values: $l = 8.7$ cm., $r = 0.0121$ cm.; ρ_1 at 20°C. of $H_2 = 8.266 \times 10^{-11}$, $C_2H_2 = 107.88 \times 10^{-11}$, $C_3H_6 = 172.21 \times 10^{-11}$. These calculated values of b agree very well with the observed values of K at very low pressures. (Table 1.) This agreement shows that the fraction f of the molecules which leave the wall according to the cosine law is unity.

The values of K of a mixture, similarly as a simple gas, become a constant at very low pressures. In the cases of the flow of mixtures at low pressures, the compositions change every moment, since the quantities were measured at every thirty minutes and the quantities of flow of the initial compositions were obtained by extrapolating to time zero.

The values of b of mixtures are given in Table 2.

Table 2. The Rates of the Molecular Flow of Mixtures.

H_2~C_2H_2

H_2%	C_2H_2%	b (mm.×c.c.)	
		obs.	calc.
100.00	0.00	0.0750	0.0750
75.69	24.31	0.0622	0.0621
51.18	48.82	0.0490	0.0491
25.97	74.03	0.0354	0.0358
0.00	100.00	0.0220	0.0220

H_2~C_3H_6

H_2%	C_3H_6%	b (mm.×c.c.)	
		obs.	calc.
100.00	0.00	0.0750	0.0750
75.18	24.82	0.0610	0.0604
50.82	49.18	0.0458	0.0462
0.00	100.00	0.0164	0.0164

In Table 2, the values of b given in the fourth column are calculated by formula (2).

As seen from Table 2, the rates of molecular flow of gaseous mixtures strictly follows the additivity law.

The Separation of Mixtures caused by Flowing through Capillaries at Low Pressures. At very low pressures, each component of a mixture flows independently of the other, namely the separation of a mixture into components takes place. Consequently, by measuring the separation of the mixtures after flow, the additivity of the flowing quantity of mixtures may be confirmed.

In order to know the separation of the mixture $H_2 \sim C_2H_2$, the quantities of acetylene after flow were analysed by the following method: The trap G in Fig. 1 was cooled with liquid air and hydrogen was removed by vacuum pump, acetylene being condensed to solid state in G. Then acetylene in the trap was vaporised by removing the liquid air and its pressure was read. If the total pressure before the application of liquid air is known, the composition of the mixture after flow can be calculated. This analytical method has been examined beforehand by analysing the mixtures of known compositions and has been found that it can be used to know the composition within the experimental error of a few per cent.

The changes of the compositions of the mixtures after flowing through the capillary for two hours are given in Table 3.

Table 3. The Change of the Compositions after Flowing through the Capillary. (Fig. 2.)

Mixture I.

(H_2: 51.18%, C_2H_2: 48.82%)

$p_{mm.}$	H_2%	C_2H_2%
3.161	51.0	49.0
2.064	51.2	48.8
0.828	54.0	46.0
0.518	59.6	40.4
0.200	69.0	31.0
0.1471	72.0	28.0
0.0659	76.0	24.0
0.0493	75.8	24.2

Mixture II.

(H_2: 75.69%, C_2H_2: 24.31%)

$p_{mm.}$	H_2%	C_2H_2%
2.780	75.7	24.3
1.914	75.6	24.4
1.204	75.7	24.3
0.725	79.0	21.0
0.475	81.9	18.1
0.273	85.8	14.2
0.1453	88.0	12.0
0.0581	89.5	10.5

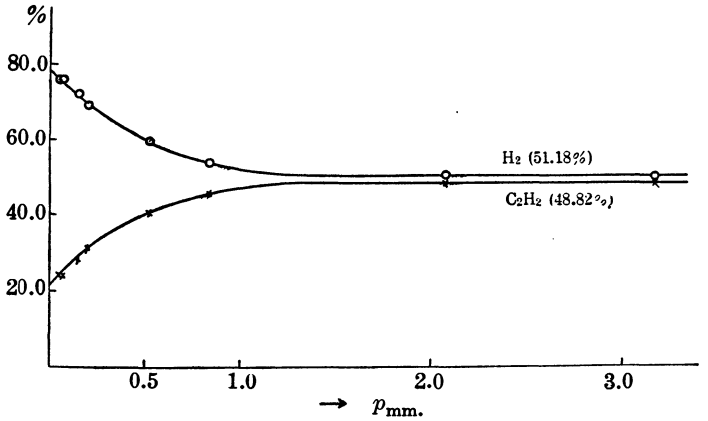


Fig. 2. The Change of the Compositions of Mix. I.

As seen from Fig. 2, the mixtures flow without separation at the pressures higher than about 1 mm. but at the pressures lower than this the separation takes place. By extrapolation of the curves to $p = 0$, the hydrogen percentages of the mixtures after flow at very low pressures can be obtained. These values are 78.5% for mixture I and 91.0% for mixture II and agree very well with the values which are calculated by considering that the component flows independently of the other. (Table 4.)

Table 4. The Hydrogen Percentages of the Mixtures after Flow at Very Low Pressures.

	H_2%	
	obs.	calc.
Mixture I	78.5	78.1
,, II	91.0	91.5

The same analytical method was applied to the mixture of hydrogen and propylene, but as the latter does not condense to solid state, there is an appreciable loss during the evacuation. Hence the reading of the pressure of propylene after evaporation was not accurate enough to compute the exact concentration.

Summary.

(1) The quantities of the following simple gases and gaseous mixtures flowing through the capillary at very low pressures have been measured.

$$H_2,\ C_2H_2,\ C_3H_6,\ H_2{\sim}C_2H_2,\ H_2{\sim}C_3H_6.$$

(2) The rates of the molecular flow of simple gases are expressed satisfactorily by Knudsen's formula.

(3) The rates of the molecular flow of mixtures are considered to be additive of the components. This consideration has been confirmed by the measurements of the quantities of flow of mixtures.

(4) The changes of the compositions of the mixtures after flowing through the capillary at low pressures have been measured and the results show also the validity of the additivity law.

In conclusion, the author wishes to express his cordial thanks to Prof. M. Katayama for his encouragement throughout this experiment.

Chemical Institute, Faculty of Science,
Imperial University of Tokyo.

Studies on the Flow of Gaseous Mixtures through Capillaries. III. The Flow of Gaseous Mixtures at Medium Pressures.

By Hiroshi ADZUMI.

(Received May 26th, 1937.)

In the previous papers[1][2], the author reported the studies on the flow of gaseous mixtures when the mean free paths of molecules are small or large in comparison with the diameter of the capillary. When the mean free path is small against the diameter, the quantity of a gas flowing in unit time is expressed by the following formula:

$$G_v = ap(p_1-p_2), \tag{1}$$

where

$$a = \frac{\pi}{8}\frac{1}{\eta}\frac{r^4}{l},$$

η is the viscosity of the gas, p_1 and p_2 the pressures at the ends of the capillary, p the mean of these, and l and r are the length and the radius of the capillary. When the mean free path is large against the diameter, the quantity is expressed by

$$G_m = b(p_1-p_2), \tag{2}$$

where

$$b = \frac{4}{3}\sqrt{2\pi}\frac{1}{\sqrt{\rho_1}}\frac{r^3}{l},$$

ρ_1 is the density of the gas at unit pressure.

At medium pressures when the mean free path is comparable with the diameter, two above formulæ overlap each other and we may set as follows:

$$Q = G_v+\gamma G_m = K(p_1-p_2),$$

or

$$K = ap+\gamma b, \tag{3}$$

where γ is a coefficient which is equal to or smaller than unity.

In order to examine formula (3) for simple gases and binary gaseous mixtures, the following experiments have been done.

The Quantities of Flow of Simple Gases. The procedure for measuring the quantity of flow is the same as already described.[2] The quanti-

(1) This Bulletin, **12** (1937), 199.
(2) *Ibid.*, **12** (1937), 285.

ties of hydrogen, acetylene, and propylene flowing in unit time and under unit pressure difference are given in Table 1. The mean pressures are measured in mm. In such a case, the formula of the quantity of flow becomes

$$K = \frac{\pi}{8}\frac{1}{\eta}\frac{r^4}{l}\frac{1013250}{760}p + \gamma \times 3.05 \times 10^4 \sqrt{\frac{T}{M}}\frac{r^3}{l}$$

$$= 5.236 \times 10^2 \frac{1}{\eta}\frac{r^4}{l}p + \gamma \times 3.05 \times 10^4 \sqrt{\frac{T}{M}}\frac{r^3}{l}, \qquad (4)$$

where M is the molecular weight of the gas and T the absolute temperature.

In Fig. 1, K is shown as function of the mean pressure. As seen from the figure, the observed values of K decrease with the decrease of the pressure, lying on a straight line at higher pressures, then after passing through a minimum, become a constant at very low pressures. As described in the preceding paper, this constant corresponds to the rate of the molecular flow. The shape of the curves in Fig. 1 shows that the flow can be expressed by formula (3).

The gradient a can be obtained from the straight part and by using it we can calculate the values of γ, which is shown in the fourth column

Table 1. The Quantities of Flow of Simple Gases. (Fig. 1.)

Hydrogen. (20°C.)

$p_{mm.}$	K	$K-ap$	γ	
2.811	0.1075	0.0680	0.91	
1.869	0.0939	0.0677	0.90	
1.269	0.0858	0.0680	0.91	
0.893	0.0814	0.0689	0.92	0.91
0.634	0.0769	0.0680	0.91	
0.526	0.0744	0.0670	0.89	
0.443	0.0742	0.0680	0.91	
0.1841	0.0730	0.0704	0.94	
0.0606	0.0745	0.0737	0.98	
0.0438	0.0746	0.0740	0.99	
0.0382	0.0748	0.0743	0.99	
0.0211	0.0750	0.0747	1.00	
0.0137	0.0750	0.0748	1.00	

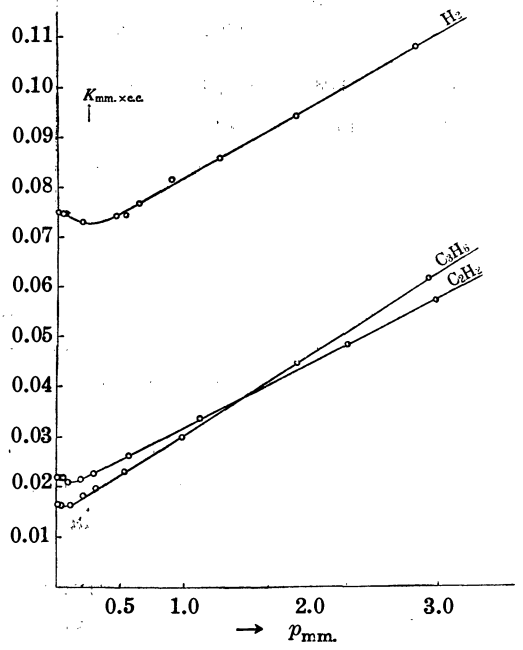


Fig. 1.

Acetylene. (20°C.)

$p_{mm.}$	K	$K-ap$	γ	
2.993	0.0575	0.0195	0.89	
2.284	0.0485	0.0195	0.89	
1.125	0.0336	0.0193	0.88	0.88
0.564	0.0264	0.0192	0.87	
0.287	0.0226	0.0190	0.86	
0.1824	0.0215	0.0192	0.87	
0.0913	0.0210	0.0198	0.90	
0·0453	0.0218	0.0212	0.96	
0.0239	0.0222	0.0219	1.00	
0.0119	0.0220	0.0218	0.99	
0.0066	0.0220	0.0219	1.00	

Propylene. (20°C.)

$p_{mm.}$	K	$K-ap$	γ	
2.940	0.0616	0.0149	0.91	
1.894	0.0448	0.0148	0.90	
0.984	0.0302	0.0147	0.90	
0.531	0.0232	0.0148	0.90	0.90
0.303	0.0197	0·0149	0.91	
0.213	0.0183	0.0149	0.91	
0.1050	0.0165	0.0148	0.90	
0.0585	0.0162	0.0153	0.93	
0.0353	0·0164	0.0158	0.96	
0.0243	0.0164	0.0160	0.98	
0.0102	0.0164	0.0162	0.99	

of Table 1. The observed values of a agree very well with the values calculated from the viscosities and this comparison is shown in Table 2.

Table 2.

	$\eta_{20°} \times 10^7$	a	
		obs.	calc.
H_2	924	0.0141	0.0141
C_2H_2	1022	0.0127	0.0127
C_3H_6	848	0.0159	0.0153

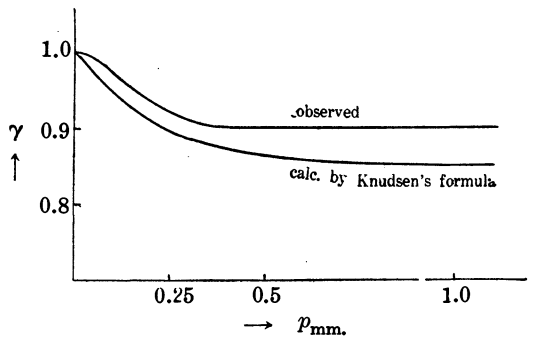


Fig. 2. γ of Hydrogen

The coefficient γ of simple gas is a function of the mean pressure and is constant at very low pressures, where it is equal to 1.0, and also constant at the pressures higher than about 0.4 mm., where it is equal to 0.9.

Hence equation (3) is the general formula over a wide range of pressures. If the pressure is so low that the mean free path of the molecule is large against the diameter of the capillary, the first term of equation (3) can be neglected and γ becomes unity, so that the formula of pure molecular flow is obtained. If the pressure is so high that the mean free path is negligible against the diameter, the second term of equation (3) is negligible and we have the formula of pure viscous flow.

Knudsen[3] introduced empirically the following formula for γ and as the value at higher pressures gave 0.81 which is smaller than the value obtained by the present author.

$$\gamma = \frac{1+c_1 p}{1+c_2 p} \tag{5}$$

where $$c_1 = 2.00\frac{\sqrt{\rho_1}}{\eta}r, \qquad c_2 = 2.47\frac{\sqrt{\rho_1}}{\eta}r.$$

The comparison between the values of γ calculated by (5) and those observed for hydrogen is graphically shown in Fig. 2.

As seen from Fig. 2, the observed values of γ can not be appropriately expressed by Knudsen's formula.

If only a fraction f of the impinging molecules leave the wall according to the cosine law and the remainder, $1-f$, are regularly reflected, some factor must be introduced into the formula of the molecular flow. This factor was given as $(2-f)/f$ by Smoluchowski[4] and $f/(2-f)$ by Gaede.[5] As described in foregoing paper, this factor is unity at the pure molecular flow. However, if we assume that f is not unity at medium pressures, it will be able to interpret, by using Gaede's factor, that γ becomes smaller than unity. This assumption of f smaller than unity at medium pressures deserves further theoretical investigation.

The existence of a minimum point of the K–p curve seems to be peculiar and has been experimentally examined by many authors. However, as seen from the results of the present author, Knudsen, and Klose,[6] the existence is probably correct, notwithstanding that the theoretical interpretation has not yet been done.

There is a close connection between the decrease of the values of γ and the existence of a minimum point, and if the former can be interpreted, the latter point will be clear.

The Quantities of Flow of Gaseous Mixtures. The quantities of flow of the mixtures (K') of $H_2 \sim C_2H_2$ and $H_2 \sim C_3H_6$ were measured and the results are tabulated in Tables 3 and 4.

The shape of $K'-p$ curves of mixtures is similar to that of simple gases. As seen from the fourth columns of Tables 4 and 5, γ's of mixtures, similarly as in the case of simple gases, become constant at higher pressures. Hence the quantity of flow of a mixture can be expressed by a formula analogous to (3), namely,

(3) M. Knudsen, *Ann. Physik*, (IV), **28** (1909), 75.
(4) M. v. Smoluchowski, *ibid.*, (IV), **33** (1910), 1559.
(5) W. Gaede, *ibid.*. (IV). **41** (1913), 289.
(6) W. Klose, *ibid.*, (V), **11** (1931), 73.

Table 3. The Quantities of Flow of $H_2 \sim C_2H_2$. (Fig. 3.)

Mixture I.
(H_2: 75.6%, C_2H_2: 24.31%)

$p_{mm.}$	K'	$K'-\alpha' p$	γ'	
2.780	0.0768	0.0445	0.72	
1.914	0.0665	0.0443	0.71	0.72
1.343	0.0601	0.0445	0.72	
0.725	0.0530	0.0446	0.72	
0.4756	0.0535	0.0480	0.77	
0.2730	0.0558	0.0526	0.85	
0.1458	0.0576	0.0559	0.90	
0.0581	0.0620	0.0613	0.99	
0.0503	0.0621	0.0615	0.99	
0.0221	0.0621	0.0619	1.00	

Mixture II.
(H_2: 51.18%, C_2H_2: 48.82%)

$p_{mm.}$	K'	$K'-\alpha' p$	γ'	
3.161	0.0730	0.0356	0.73	
2.064	0.0601	0.0357	0.73	0.73
1.422	0.0525	0.0357	0.73	
0.858	0.0458	0.0357	0.73	
0.518	0.0430	0.0369	0.75	
0.3281	0.0435	0.0396	0.81	
0.2002	0.0459	0.0435	0.89	
0.1471	0.0470	0.0453	0.92	
0.0659	0.0485	0.0477	0.97	
0.0374	0.0490	0.0485	0.99	

Mixture III.
(H_2: 25.97%, C_2H_2: 74.03%)

$p_{mm.}$	K'	$K'-\alpha' p$	γ'	
2.886	0.0624	0.0260	0.73	
1.944	0.0503	0.0258	0.73	0.73
0.925	0.0374	0.0257	0.73	
0.694	0.0345	0.0258	0.73	
0.4154	0.0322	0.0270	0.76	
0.2260	0.0317	0.0284	0.80	
0.1374	0.0320	0.0303	0.85	
0.0276	0.0341	0.0337	0.95	
0.0187	0.0352	0.0350	0.99	
0.0113	0.0354	0.0353	0.99	

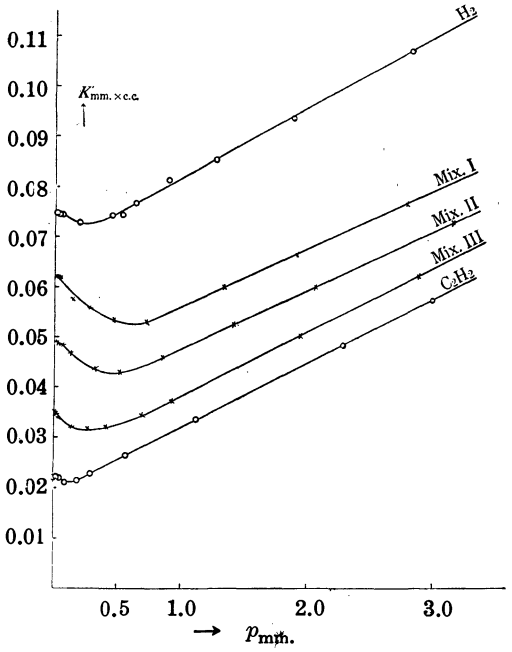


Fig. 3. $H_2 \sim C_2H_2$ (20°C.)

Table 4. The Quantities of Flow of $H_2 \sim C_3H_6$. (Fig. 4.)

Mixture I.

(H_2: 50.82%, C_3H_6: 49.18%)

$p_{mm.}$	K'	$K'-a'p$	γ'	
3.000	0.0699	0.0302	0.66	
2.034	0.0570	0.0300	0.66	0.66
0.995	0.0431	0.0299	0.65	
0.591	0.0381	0.0303	0.66	
0.3013	0.0385	0.0345	0.75	
0.2093	0.0402	0.0374	0.82	
0.0980	0.0450	0.0437	0.95	
0.0619	0.0455	0.0447	0.98	
0.0390	0.0459	0.0454	0.99	
0.0128	0.0458	0.0456	1.00	

Mixture II.

(H_2: 75.18%, C_3H_6: 24.82%)

$p_{mm.}$	K'	$K'-a'p$	γ'	
3.008	0.0780	0.0401	0.66	
1.982	0.0648	0.0398	0.65	0.66
0.942	0.0510	0.0401	0.66	
0.710	0.0496	0.0406	0.67	
0.450	0.0518	0.0461	0.76	
0.2621	0.0550	0.0517	0.85	
0.1899	0.0588	0.0564	0.92	
0.0848	0.0603	0.0592	0.97	
0.0403	0.0609	0.0604	0.99	
0.0117	0.0610	0.0609	1.00	

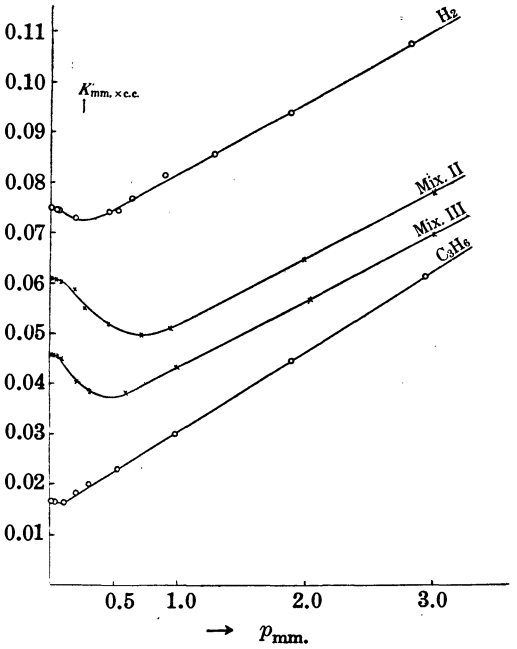


Fig. 4. $H_2 \sim C_3H_6$ (20°C.)

$$K' = a'p + \gamma' b', \qquad (6)$$

where $$a' = \frac{\pi}{8}\frac{1}{\eta'}\frac{r^4}{l}, \qquad b' = \frac{4}{3}\sqrt{2\pi}\frac{r^3}{l}\left(\frac{n_1}{\sqrt{\rho_1}} + \frac{n_2}{\sqrt{\rho_2}}\right),$$

n_1 and n_2 are mol fractions of components and the prime means the values of a mixture.

The comparison between the observed and calculated values of a' is given in Table 5.

Table 5.

		$\eta'_{20°}\times10^7$	a'		γ' at higher press.
			obs.	calc.	
$H_2\sim C_2H_2$	Mixture I	1107	0.0116	0.0117	0.72 } 0.73
	Mixture II	1088	0.0118	0.0119	0.73 }
	Mixture III	1055	0.0126	0.0123	0.73 }
$H_2\sim C_3H_6$	Mixture I	1082	0.0126	0.0120	0.66 } 0.66
	Mixture II	1011	0.0133	0.0128	0.66 }

The calculated values of a' are obtained by using the viscosities which are computed, in the case of $H_2\sim C_2H_2$, by interpolation from the observed values at 20°C. and, in the case of $H_2 \sim C_3H_6$, by the viscosity formula for the mixture, the viscosities at 20° being not observed.

The values of γ' at higher pressures of the mixtures are summarized in the last column of Table 5. These are constant for varying compositions of the same combination of components, but different from those for different combinations and simple gases.

As seen from the K'–p curves in Fig. 3 and 4, the occurrence of minimum point of mixtures is very much remarkable. It was already shown in a preceding paper that when a mixture flows through the capillary, the separation takes place at low pressures, for example at the pressures lower than about 1 mm. for the mixture $H_2\sim C_2H_2$. Owing to this separation the flow of hydrogen is comparatively larger at pressures lower than 1 mm., consequently the minimum point occurs at the pressure higher than in the case of simple gases.

The Quantities of Flow of Mixtures of Organic Vapours. The quantities of flow of the following mixtures of organic vapours were measured at the pressures lower than about 3 mm.

$$C_6H_6\sim CCl_4,\quad CCl_4\sim CHCl_3,\quad (C_2H_5)_2O\sim CHCl_3.$$

In order to increase the accuracy of measurement and to be able to compute the viscosities from K–p curves, the essential parts of the apparatus were kept in the thermostat and the McLeod gauge of short type was read by using a cathetometer. The experimental procedure is the same as described in the preceding paper.

The results of observation are shown graphically in Fig. 5–7. The flowing quantities of these mixtures can be expressed, similarly as the mixtures described above, by equation (6).

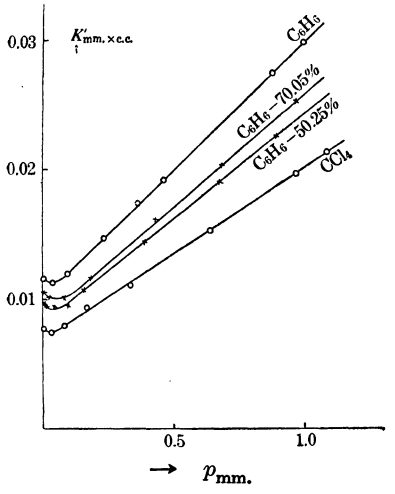


Fig. 5. $C_6H_6 \sim CCl_4$ (20°C.)

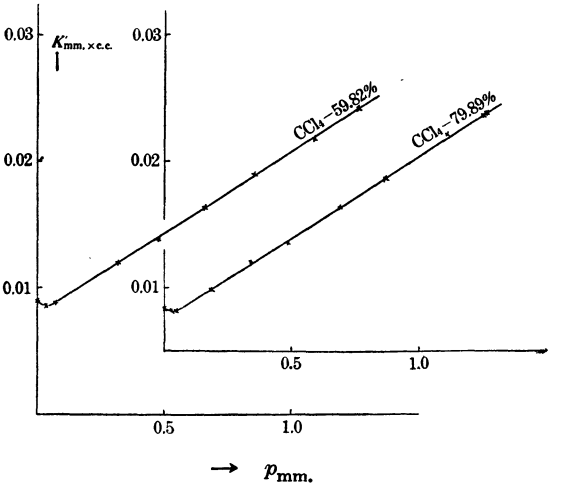


Fig. 6. $CCl_4 \sim CHCl_3$ (20°C.)

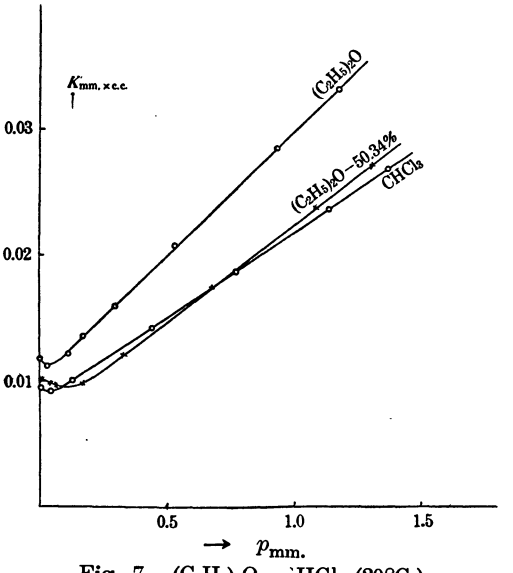
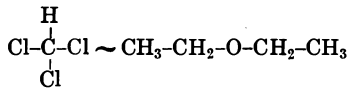
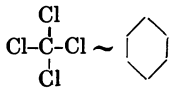
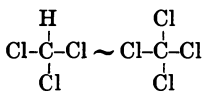


Fig. 7. $(C_2H_5)_2O \sim CHCl_3$ (20°C.)

The values of γ' at higher pressures are 0.69 for $CHCl_3 \sim (C_2H_5)_2O$, 0.80 for $CCl_4 \sim C_6H_6$, and 0.89 for $CHCl_3 \sim CCl_4$. Those together with other two are summarized in Table 6. γ' are about 0.9 for simple gases but smaller for mixtures. It can be noticed that the value of γ' depends upon the configurations of two components. Namely as the configurations of $CHCl_3$ and CCl_4 are alike, the mixture of these vapours has the value

of γ' nearly equal to that of a simple gas. But the values of the mixtures of $H_2 \sim C_3H_6$ and $CHCl_3 \sim (C_2H_5)_2O$, whose components are considered to have not similar configurations, are far smaller than 0.9.

Table 6. The Values of γ' at Higher Pressures.

	γ' at higher press.
$H_2 \sim CH_3\text{-}CH{=}CH_2$	0.66
	0.69
$H_2 \sim CH{\equiv}CH$	0.73
	0.80
	0.89
H_2	0.91
C_2H_2	0.88
C_3H_6	0.90
C_6H_6	0.87
$CHCl_3$	0.90
CCl_4	0.88
$(C_2H_5)_2O$	0.86

The Viscosities of Benzene, Carbon tetrachloride, Chloroform, Ethyl ether, and Their Mixtures. From the quantities of flow the viscosities of the vapours can be calculated by equation (4). The values at 20°C. for C_6H_6, CCl_4, $CHCl_3$, and $(C_2H_5)_2O$ are given in Table 7.

Table 7.

Vapour	$\eta \times 10^7$ at 20°C.	
	obs.	calc.
C_6H_6	662	705
CCl_4	983	939
$CHCl_3$	976	971
$(C_2H_5)_2O$	666	695

The values given in the third column of Table 7 are calculated using Sutherland's constants obtained by T. Titani.[7] The agreement of the calculated and observed values is not good. This is perhaps due to the fact that Sutherland's constants were obtained from the observations above the boiling point and this constant is not satisfactorily accurate for low temperature.

The viscosities of mixtures of $C_6H_6 \sim CCl_4$, $CCl_4 \sim CHCl_3$, and $(C_2H_5)_2O \sim CHCl_3$ are given in Tables 8–10 and Fig. 6–8.

Table 8. Viscosities of $C_6H_6 \sim CCl_4$ at 20°C. (Fig. 8.)

$$\eta' = \frac{662\times10^{-7}}{1+\frac{n_2}{n_1}1.0} + \frac{983\times10^{-7}}{1+\frac{n_1}{n_2}1.0}$$

C_6H_6 %	CCl_4 %	$\eta'\times10^7$	
		obs.	calc.
100.00	0.00	662	662
75.05	24.95	746	740
50.25	49.75	816	822
0.00	100.00	983	983
$\alpha_1\alpha_2\beta = 1.39$, $\alpha_1\alpha_2/\beta = 0.63$			

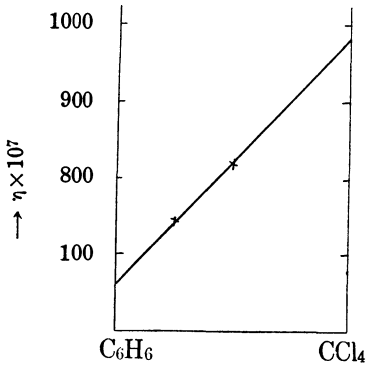


Fig. 8. $C_6H_6 \sim CCl_4$ (20°C.)

Table 9. Viscosities of $CCl_4 \sim CHCl_3$ at 20°C. (Fig. 9.)

$$\eta' = \frac{983\times10^{-7}}{1+\frac{n_2}{n_1}0.82} + \frac{976\times10^{-7}}{1+\frac{n_1}{n_2}0.96}$$

CCl_4 %	$CHCl_3$ %	$\eta'\times10^7$	
		obs.	calc.
100.00	0.00	983	983
79.89	20.11	1020	1017
59.82	50.18	1038	1038
0.00	100.00	976	976
$\alpha_1\alpha_2\beta = 0.99$, $\alpha_1\alpha_2/\beta = 0.985$			

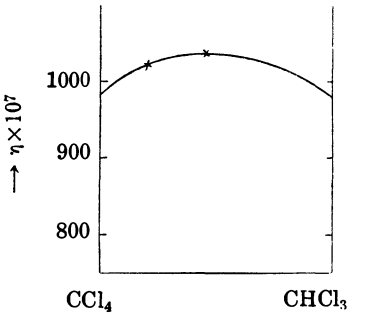


Fig. 9. $CCl_4 \sim CHCl_3$ (20°C.)

(7) T. Titani, this Bulletin, **8** (1933), 255.

Table 10. Viscosities of $(C_2H_5)_2O \sim CHCl_3$ at 20°C. (Fig. 10.)

$$\eta' = \frac{666\times10^{-7}}{1+\frac{n_2}{n_1}0.877} + \frac{976\times10^{-7}}{1+\frac{n_1}{n_2}0.982}$$

$(C_2H_5)_2O$%	$CHCl_3$ %	$\eta'\times10^7$	
		obs.	calc.
100.00	0.00	666	666
50.34	49.66	848	847
0.00	100.00	976	976
$\alpha_1\alpha_2\beta = 1.425$, $\alpha_1\alpha_2/\beta = 0.66$			

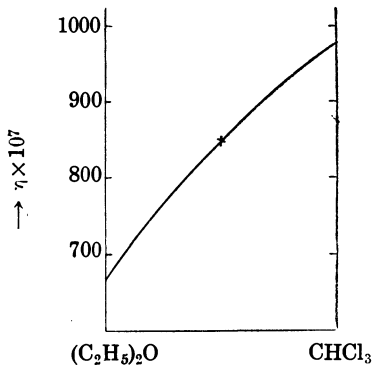


Fig. 10. $(C_2H_5)_2O \sim CHCl_3$ (20°C.)

The mixture $CCl_4 \sim CHCl_3$ shows a maximum at about 50% of $CHCl_3$ and the viscosity curves of the other two are nearly straight. The occurrence of the maximum point in the case of $CCl_4 \sim CHCl_3$ is very well explained by the conditions theoretically discussed in the first paper of this series.

The values of Sutherland's constants between different molecules obtained from the viscosity data of mixtures are given in Table 11.

Table 11. Sutherland's Constants of Mixtures.

Mixture		C_1	C_2	C_{12}
1	2			
C_6H_6	CCl_4	448	365	720
CCl_4	$CHCl_3$	365	373	301
$CHCl_3$	$(C_2H_5)_2O$	373	404	352

Summary.

(1) The quantities of seven following simple gases and six gaseous mixtures flowing through the capillary have been measured at the pressures between 4 and 0.01 mm.

H_2, C_2H_2, C_3H_6, $H_2 \sim C_2H_2$, $H_2 \sim C_3H_6$;

C_6H_6, CCl_4, $CHCl_3$, $(C_2H_5)_2O$, $C_6H_6 \sim CCl_4$, $CCl_4 \sim CHCl_3$, $(C_2H_5)_2O \sim CHCl_3$.

(2) The quantities of flow, K, is a function of the mean pressure, p, and the K–p curve passes through a minimum point. The occurrence of a minimum point of mixtures is more remarkable than in the case of simple gases.

(3) The quantities of flow of simple gases are satisfactorily expressed by

$$K = ap + \gamma b,$$

where γ is a coefficient which becomes a constant at higher pressures ($= 0.9$) or at very low pressures ($= 1.0$), and varies from 0.9 to 1.0 at the intermediate conditions.

(4) The quantities of flow of mixtures are also expressed by a formula analogous to that of simple gases. The values of γ' at higher pressures of the mixtures are constant for varying compositions of the same combination of components, but different from those for different combinations and simple gases. These values are also considered to depend on the chemical configurations of two components.

(5) The viscosities of the following mixtures have been calculated from the quantities of flow.

$$C_6H_6 \sim CCl_4, \qquad CCl_4 \sim CHCl_3, \qquad (C_2H_5)_2O \sim CHCl_3.$$

The mixture $CCl_4 \sim CHCl_3$ shows a maximum at about 50% of $CHCl_3$ and the viscosity curves of the other two are nearly straight.

In conclusion, the author wishes to express his cordial thanks to Prof. M. Katayama for his encouragement throughout this experiment.

Chemical Institute, Faculty of Science,
Imperial University of Tokyo.

On the Flow of Gases through a Porous Wall.

By Hiroshi ADZUMI.

(Received May 31st, 1937.)

The rate of flow of gases through a porous plate was studied by Sameshima[1] and the following formula was introduced empirically by him.

$$t = k\eta^n M^{\frac{1-n}{2}},$$

where t is the time of flow of a definite volume of the gas, η the viscosity, M the molecular weight of the gas, k and n are constants independent of the kind of the gas but dependent on the nature of the porous plate and the pressure of the gas.

It was reported by the present author[2] that, when a gas flows through a capillary, the quantity flowing in unit time is expressed by the following formula:

$$Q = K(p_1 - p_2)$$

$$\text{or} \qquad K = A\frac{r^4}{l}p + \gamma B\frac{r^3}{l} \quad (\text{in mm.} \times \text{c.c.}), \tag{1}$$

where $$A = 5.236 \times 10^2 \frac{1}{\eta}, \qquad B = 3.05 \times 10^4 \sqrt{\frac{T}{M}},$$

K is the quantity of flow for unit pressure difference, measured by the product of the pressure and the volume, l and r the length and the radius of the capillary, p_1 and p_2 the pressures (measured in mm.) at the ends of the capillary, p the mean of these, T the temperature and γ a coefficient depending on pressure. This formula holds generally over a wide range of pressure, namely for various values of the ratios of the mean free path of the gas and the diameter of the capillary.

A porous plate may be considered to be composed of numerous pores of various diameters. If the diameters of all pores are large against the mean free path, the part of the molecular flow becomes negligible, and if the diameters are small against the mean free path, pure molecular flow will take place. However, in the case of an actual porous plate, the

(1) J. Sameshima, this Bulletin, **1** (1926), 5.
(2) This Bulletin, **12** (1937), 292.

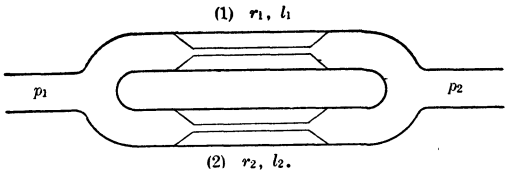
diameters of some pores may be large while those of others small against the mean free path.

Therefore, by using equation (1) we will be able to derive the formula of flow through a porous plate of any kind.

Flowing Formula of a Gas through a Porous Plate. We assume, before everything, that all pores of a porous plate are parallel and each pore may not have an uniform diameter but be composed of short pores of various diameters.

In order to know the flowing formula of a gas through a porous plate, we will treat, in the first place, the simple cases of the flow through many capillaries, whose radii and state of connection are known.

(i) **Flowing formula of a gas through numerous capillaries, which are connected in parallel.** When two capillaries, whose radii and lengths



are r_1, r_2 and l_1, l_2, are connected in parallel, the quantity flowing through capillary (1) in unit time and under unit pressure difference is given by

$$K_1 = A\frac{r_1^4}{l_1}p + \gamma B\frac{r_1^3}{l_1},$$

and the quantity through capillary (2) by

$$K_2 = A\frac{r_2^4}{l_2}p + \gamma B\frac{r_2^3}{l_2},$$

then the total quantity, K', becomes

$$K' = K_1 + K_2 = A\left(\frac{r_1^4}{l_1} + \frac{r_2^4}{l_2}\right)p + \gamma B\left(\frac{r_1^3}{l_1} + \frac{r_2^3}{l_2}\right).$$

The validity of this equation was examined numerically by measuring the quantities of hydrogen through the following capillaries:

Capillary (1): $r_1 = 0.0121$ cm., $l_1 \fallingdotseq 8.7$ cm.,

,, (2): $r_2 = 0.0073$ cm., $l_2 \fallingdotseq 8.8$ cm.

The values of K_1, K_2, and K' are given in Table 1. In this table, for the convenience of comparison, the values of three kinds of K are obtained respectively by the interpolation for the same pressures.

Table 1.

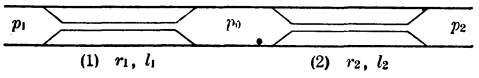
$p_{mm.}$	K_1	K_2	K_1+K_2	$K'_{obs.}$
3.0	0.1103	0.0181	0.1286	0.1285
2.0	0.0960	0.0170	0.1130	0.1132
1.0	0.0822	0.0160	0.0982	0.0980
0.8	0.0795	0.0154	0.0949	0.0950
0.6	0.0766	0.0150	0.0916	0.0917
0.4	0.0742	0.0147	0.0889	0.0889
0.2	0.0730	0.0144	0.0874	0.0865
0.1	0.0737	0.0155	0.0892	0.0890
0.05	0.0745	0.0164	0.0909	0.0905

As seen from Table 1, the observed values of K' agree very well with those calculated by the equation. Hence, when numerous capillaries, whose radii and lengths are r_1, r_2, r_3, ... r_n, and l_1, l_2, l_3, ... l_n, are connected in parallel, the quantity of flow is expressed by

$$K' = A\left(\frac{r_1^4}{l_1}+\frac{r_2^4}{l_2}+\frac{r_3^4}{l_3}+\cdots\right)p+\gamma B\left(\frac{r_1^3}{l_1}+\frac{r_2^3}{l_2}+\frac{r_3^3}{l_3}+\cdots\right)$$

$$= Ap\sum^{n}\frac{r_i^4}{l_i}+\gamma B\sum^{n}\frac{r_i^3}{l_i} . \qquad (2)$$

(ii) **Flowing formula through numerous capillaries, which are connected in series.** When two capillaries are connected in series, we



denote the pressure between the capillaries as p_0. The quantity flowing through capillary (1) in unit time is given by

$$Q_1 = A\frac{r_1^4}{l_1}\frac{p_1+p_0}{2}(p_1-p_0)+\gamma B\frac{r_1^3}{l_1}(p_1-p_0) ,$$

and that through capillary (2) by

$$Q_2 = A\frac{r_2^4}{l_2}\frac{p_0+p_2}{2}(p_0-p_2)+\gamma B\frac{r_2^3}{l_2}(p_0-p_2) .$$

As these two quantities are equal, then

$$Q'' = K''(p_1-p_2) = Q_1 = Q_2 ,$$

where K'' is the quantity flowing in unit time and under unit pressure difference through two capillaries connected in series,

From these three formulæ

$$\frac{1}{K''} = \frac{1}{K_1 + A\frac{r_1^4}{l_1}\frac{p_0 - p_2}{2}} + \frac{1}{K_2 - A\frac{r_2^4}{l_2}\frac{p_1 - p_0}{2}},$$

where K_1 and K_2 are the quantities flowing through capillaries (1) and (2) respectively, when each of them is alone.

Thus when two capillaries are connected in series, $1/K''$ is not equal to $(1/K_1 + 1/K_2)$.

By eliminating p_0, $1/K''$ is also written in the form

$$\frac{1}{K''} = \frac{1}{K_1} + \frac{1}{K_2} + \Delta_1,$$

where $$\Delta_1 = \frac{(c_2 d_1 - c_1 d_2)/c_1}{K_1 K_2} \cdot \frac{1}{1 + \dfrac{2K_1(c_1 + c_2)/c_1}{(c_1 + c_2) - (K_1 + K_2) + \sqrt{\{(K_1 - K_2) + (c_1 + c_2)\}^2 + 4K_1 K_2}}}$$

$$c_1 = \frac{1}{2} A\frac{r_1^4}{l_1}, \quad c_2 = \frac{1}{2} A\frac{r_2^4}{l_2}, \quad d_1 = \gamma B\frac{r_1^3}{l_1}, \quad d_2 = \gamma B\frac{r_2^3}{l_2}.$$

The value of Δ_1 is estimated, by inserting numerical values, to be so small that it affects the value of K'' only less than 1%. Then, by neglecting Δ_1

$$K'' = \frac{1}{\frac{1}{K_1} + \frac{1}{K_2}} = Ap\frac{1}{\frac{l_1}{r_1^4} + \frac{l_2}{r_2^4}} + \gamma B\frac{1}{\frac{l_1}{r_1^3} + \frac{l_2}{r_2^3}} + \Delta_2,$$

where $$\Delta_2 = \frac{Ap \cdot \gamma B \dfrac{\left(\frac{r_1^3}{l_1}\frac{r_2^3}{l_2}\right)^2 (r_1 - r_2)^2}{\left(\frac{r_1^4}{l_1} + \frac{r_2^4}{l_2}\right)\left(\frac{r_1^3}{l_1} + \frac{r_2^3}{l_2}\right)}}{Ap\left(\frac{r_1^4}{l_1} + \frac{r_2^4}{l_2}\right) + \gamma B\left(\frac{r_1^3}{l_1} + \frac{r_2^3}{l_2}\right)}.$$

Δ_2 is also found under ordinary experimental conditions to have a value smaller than 1% of the other terms. Then we have

$$K'' = Ap\frac{1}{\frac{l_1}{r_1^4} + \frac{l_2}{r_2^4}} + \gamma B\frac{1}{\frac{l_1}{r_1^3} + \frac{l_2}{r_2^3}}.$$

Table 2.

$p_{mm.}$	K''	
	obs.	calc.
3.0	0.0159	0.0165
2.0	0.0144	0.0148
1.0	0.0130	0.0133
0.5	0.0199	0.0123
0.1	0.0128	0.0128
0.05	0.0129	0.0129

This equation was examined numerically by using the two capillaries described above. (Table 2.)

It will be seen from the table, that the results are satisfactorily expressed by the above equation justifies the neglections made in obtaining it.

When numerous capillaries are connected in series, the quantity of flow is expressed by

$$K'' = A\frac{1}{\sum_m \frac{l_i}{r_i^4}}p + \gamma B\frac{1}{\sum_m \frac{l_i}{r_i^3}} . \qquad (3)$$

As it was assumed, if all pores of a porous plate are parallel and each pore is composed of series of short pores having various diameters, the quantity of a gas flowing through a porous plate can be expressed by the combination of equations (2) and (3) as follows:

$$K = Ap\sum^n \frac{1}{\sum_m \frac{l_i}{r_i^4}} + \gamma B\sum^n \frac{1}{\sum_m \frac{l_i}{r_i^3}} ,$$

or $$K = ApE + \gamma BF$$

$$= 5.236\times 10^2 \frac{1}{\eta}Ep + 2.743\times 10^4\sqrt{\frac{T}{M}}F \text{ (in mm.} \times \text{c.c.)}, \quad (4_1)$$

where $E = \sum \frac{1}{\sum_m \frac{l_i}{r_i^4}}$, $F = \sum \frac{1}{\sum_m \frac{l_i}{r_i^3}}$, and γ is taken as 0.9. E and F are functions of the radii and lengths of pores. The actual construction of pores is so complicated that the functional forms of these coefficients can not be obtained directly. If pressures are measured in atmospheric unit, the above equation becomes

$$K = 3.979\times 10^5 \frac{1}{\eta}Ep + 2.743\times 10^4\sqrt{\frac{T}{M}}F \text{ (in atm.} \times \text{c.c.)}. \quad (4_2)$$

Equation (4) was examined numerically by measuring the quantities of flow through a few kinds of porous plates. As an example, the results of comparison between the values observed by Sameshima[1] and those

of calculated by (4) are given in Table 3. Sameshima measured the time of flow of a definite volume (ca. 70 c.c.) of seven gases at the following pressures: $p_1 = 1.0, 1.5, 2.0, 2.5$ atm.; $p_2 = 0$; so that $p = 0.5, 0.75, 1.0, 1.25$ atm. By the method of least square, the values of two constants E and F were obtained as follows: $E = 1.83 \times 10^{-11}$, $F = 3.45 \times 10^{-7}$. Hence the flowing formula of a gas at 25°C. through the porous plate (an unglazed earthen-ware) used by Sameshima becomes

$$K = 7.282 \times 10^{-6} \frac{1}{\eta} p + 1.636 \times 10^{-1} \frac{1}{\sqrt{M}} \quad \text{(in atm.} \times \text{c.c.)}.$$

This formula was used for the calculation of the values of K given in Table 3.

Table 3. The Quantities of Flow of Gases through the Porous Plate observed by Sameshima.

$p_{atm.}$	0.5		0.75	
	K		K	
	obs.	calc.	obs.	calc.
CH_4	0.0728	0.0735	0.0892	0.0898
NH_3	0.0742	0.0747	0.0919	0.0922
C_2H_2	0.0668	0.0672	0.0844	0.0847
C_2H_4	0.0648	0.0669	0.0825	0.0849
Air	0.0495	0.0504	0.0600	0.0603
O_2	0.0460	0.0465	0 0552	0.0552
CO_2	0.0480	0.0482	0.0602	0.0600
$p_{atm.}$	1.0		1.25	
	K		K	
	obs.	calc.	obs.	calc.
CH_4	0.1054	0.1061	0.1220	0.1224
NH_3	0.1098	0.1096	0.1276	0.1282
C_2H_2	0.1021	0.1023	0.1200	0.1198
C_2H_4	0.1000	0.1029	0.1167	0.1209
Air	0.0698	0.0702	0.0798	0.0802
O_2	0.0642	0.0640	0.0732	0.0727
CO_2	0.0724	0.0717	0.0844	0.0834

As seen from Table 3, the quantity of a gas flowing through the porous plate is expressed satisfactorily by equation (4).

The present author with M. Tachimori measured also the quantities of flow through a few kinds of porous plates and found that the quantities

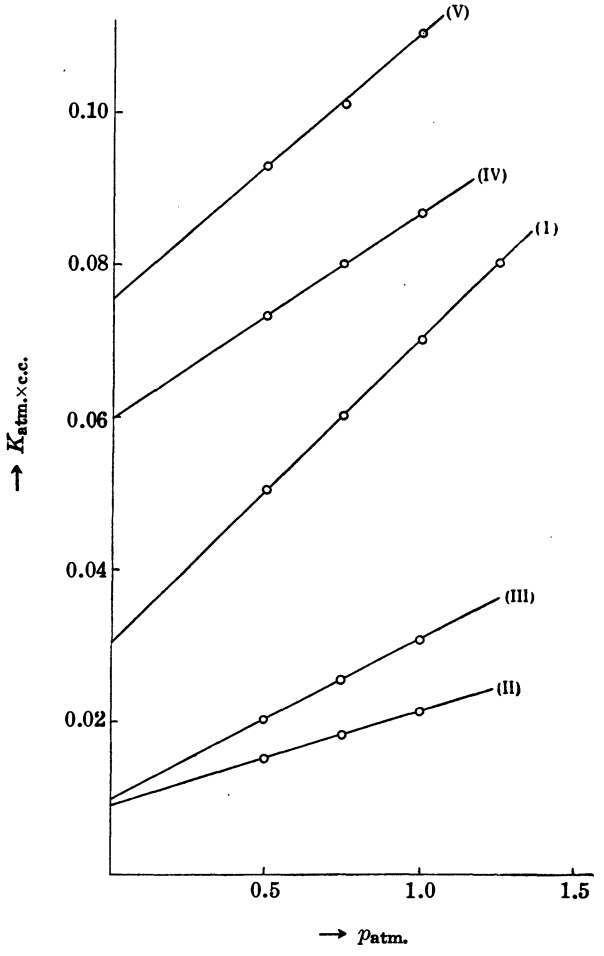


Fig. 1. Quantities of Air Flowing through Porous Plates.

are also expressed by equation (4). The results are represented graphically in Fig. 1.

The values of E and F for the several porous plates and gases used for experiments are tabulated in Table 4.

Table 4.

Porous plate	Gas	Temp.	$E\times10^{11}$	$F\times10^{7}$
(I) Unglazed earthen-ware used by Sameshima	CH_4, etc.	25°C.	1.83	3.45
(II) Porous plate used in organic preparation (compact)	Air	20	0.45	1.64
(III) ,, (rough)	Air	20	0.83	1.72
(IV) Mantle of a Daniell cell (white)	Air	25	1.1	6.82
(V) ,, (red)	Air	25	1.5	8.58

Mean Radius and Number of Pores per unit Area of a Porous Matter. For many purpose it is sufficient to know the mean value of the pore radii of porous matters, for example unglazed earthen-wares, glass-filters, filterpapers, membranes of colloidon, etc. As already pointed out, the construction of pores of a porous matter is so complicated that we can not find any method to obtain the actual radius and number of pores. Therefore, in order to estimate the radius, we must take some simplifications about the construction of pores. The simplest assumption is that each pore has an uniform radius. Several methods of obtaining the radius, under this assumption, have been introduced. Bartell and Osterhof[3], and Uehara[4] obtained the radii of porous matters by measuring the pressure necessary to prevent ascension of a liquid in the capillaries and Anderson[5] by measuring the change of the vapour pressure in the capillaries. Kawakami[6] estimated them from the measurements of the quantity of effusion, the electric conductivity, and the maximum linear velocity of a liquid in a porous matter.

If all pores of the porous plate have the uniform radius, R, and are normal to the surface, E and F can be written in a very simple form as follows:

$$E = nR^4/d\,, \qquad F = nR^3/d\,,$$

where n is the number of pores and d the thickness of the porous plate. Hence, E and F are proportional to the area of the surface and inversely proportional to the thickness of the plate, so that the values for unit area

(3) F. E. Bartell and H. J. Osterhof, *J. Phys. Chem.*, **32** (1928), 1553.
(4) K. Uehara, *J. Chem. Soc. Japan*, **55** (1934), 75.
(5) J. S. Anderson, *Z. physik. Chem.*, **88** (1914), 191.
(6) M. Kawakami, *J. Chem. Soc. Japan*, **53** (1932), 1085; **54** (1933), 133.

and unit thickness, E_0, F_0, can be easily obtained by $E_0 = Ed/\text{area}$, $F_0 = Fd/\text{area}$.
Then we have

$$E_0 = NR^4 \quad \text{and} \quad F_0 = NR^3 ,$$

where N is the number of pores per unit area of the surface.
From these formulæ,

$$R = E_0/F_0 , \qquad N = F_0^4/E_0^3 . \tag{5}$$

The values of R and N for several porous plates calculated by equation (5) are given in Table 5.

Table 5. Mean Diameters of Pores and Number of Pores per Unit Area.

Porous plate	Thickness	Area	$E_0\times10^{11}$	$F_0\times10^7$	$R\times10^5$ cm.	N
(I)	0.15 cm.	0.28 cm.^{2}	0.97	1.83	5.3	1.2×10^6
(II)	0.27	2.22	0.054	0.195	2.77	2.4×10^5
(III)	0.41	2.22	0.154	0.318	4.84	2.8 ,,
(IV)	0.2	0.27	0.80	4.98	1.61	0.96×10^8
(V)	0.2	0.27	1.09	6.26	1.74	1.19 ,,

Summary.

(1) A formula for the flow of a gas through a porous plate has been derived and found that the observed quantity of flow is satisfactorily expressed by this formula.

(2) The method of estimating the values of the mean radius and the number of pores of a porous plate has been proposed.

In conclusion, the author wishes to express his cordial thanks to Prof. M. Katayama for his encouragement throughout this experiment.

Chemical Institute, Faculty of Science,
Imperial University of Tokyo.

Chemical Reactions in the Silent Electric Discharge. XVI. Reactions between Hydrogen and Solid Inorganic Compounds.

By Susumu MIYAMOTO.

(Received April 16th, 1937.)

Studies on the reduction of a number of solid inorganic substances by hydrogen under the silent electric discharge were carried out; there follows an account of the results obtained since the publication of the previous papers.[1]

(1) Potassium chromate. It was proved that chromic oxide is a principal reaction product. Potassium chromate employed = 5 g. Time of silent electric discharge = 12 hours. The quantity of chromic oxide produced = 0.1083 g.

The principal reaction in the discharge tube is expressed by

$$2K_2CrO_4 + 3H_2 = 4KOH + Cr_2O_3 + H_2O\,.$$

(2) Potassium bichromate. Potassium bichromate is reduced to chromic oxide also. Potassium bichromate employed = 5 g. Time of silent electric discharge = 12 hours. The quantity of chromic oxide produced = 0.0463 g.

The principal reaction in the discharge tube is expressed by

$$K_2Cr_2O_7 + 3H_2 = 2KOH + Cr_2O_3 + 2H_2O\,.$$

(3) Ammonium chromate. A gas absorption bottle, containing dilute sulphuric acid solution, was connected to the discharge tube, and the quantity of ammonia absorbed was determined in the normal manner. Ammonium chromate employed = 5 g. Time of silent electric discharge = 8 hours. Volume of the sulphuric acid solution of 0.1000 normal, equivalent to the quantity of ammonia absorbed = 6.68 c.c. The quantity of chromic oxide produced = 0.0357 g.

The principal reaction in the reaction tube is expressed by

$$2(NH_4)_2CrO_4 + 3H_2 = 4NH_3 + Cr_2O_3 + 5H_2O\,.$$

(4) Ammonium bichromate. Ammonium bichromate employed = 5 g. Time of silent electric discharge = 12 hours. Volume of the sulphuric acid solution of 0.1000 normal, equivalent to the quantity of ammonia absorbed = 3.21 c.c. The quantity of chromic oxide produced = 0.0210 g.

(1) S. Miyamoto, *J. Chem. Soc. Japan*, **53** (1932), 724, 788, 914, 933; **54** (1933), 85, 202, 705, 1223; **55** (1934), 320, 1143; **56** (1935), 521; this Bulletin, **9** (1934), 139, 165, 175, 505; **10** (1935), 199.

The principal reaction is expressed by

$$(NH_4)_2Cr_2O_7 + 3H_2 = 2NH_3 + Cr_2O_3 + 4H_2O\,.$$

(5) Calcium chlorate. Calcium chlorate is reduced to chloride in the discharge tube. The quantity of chloride produced was determined in the normal manner. Calcium chlorate employed = 7.0 g. Time of silent electric discharge = 6 hours. Volume of the silver nitrate solution of 0.01000 normal, equivalent to the quantity of calcium chloride produced = 37.40 c.c.

The reaction in the discharge tube is expressed by

$$Ca(ClO_3)_2 + 6H_2 = CaCl_2 + 6H_2O\,.$$

(6) Sodium chlorate. Sodium chlorate employed = 7 g. Time of silent electric discharge = 6 hours. Volume of the silver nitrate solution of 0.01000 normal, equivalent to the quantity of sodium chloride produced = 28.50 c.c.

The reaction in the discharge tube is expressed by

$$NaClO_3 + 3H_2 = NaCl + 3H_2O\,.$$

(7) Barium sulphite. It was proved that barium sulphide and hydrogen sulphide are the principal reaction products. The reactions in the discharge tube will be expressed by

$$BaSO_3 + 3H_2 = BaS + 3H_2O\,,$$
$$BaS + 2H_2O = Ba(OH)_2 + H_2S\,,$$
$$BaS + H_2 = Ba + H_2S\,.$$

(8) Thorium nitrate. Exp. 1. The formation of thorium hydroxide, ammonium salt and nitrite was proved.

Exp. 2. The quantity of ammonium salt produced was determined in the normal manner. Thorium nitrate, $Th(NO_3)_4 \cdot 12H_2O$, employed = 5 g. Time of silent electric discharge = 6 hours. Volume of the sulphuric acid solution of 0.1000 normal, equivalent to the quantity of ammonium salt produced = 8.12 c.c.

Exp. 3. The quantity of nitrite produced was determined. Thorium nitrate employed = 5 g. Time of silent electric discharge = 6 hours. Volume of the potassium permanganate solution of 0.0100 normal, equivalent to the quantity of nitrite produced = 7.78 c.c.

The reactions in the discharge tube will be expressed by

$$Th(NO_3)_4 + 16H_2 = Th(OH)_4 + 4NH_3 + 8H_2O\,,$$
$$Th(NO_3)_4 + 4NH_3 + 4H_2O = 4NH_4NO_3 + Th(OH)_4\,,$$
$$NH_4NO_3 + H_2 = NH_4NO_2 + H_2O\,.$$

(9) Ammonium persulphate. It was proved that sulphate and hydrogen sulphide are the principal reaction products. The reactions in the reaction tube will be expressed by

$$(NH_4)_2S_2O_8 + 5H_2 = (NH_4)_2SO_4 + H_2S + 4H_2O,$$
$$(NH_4)_2S_2O_8 + H_2 = (NH_4)_2SO_4 + H_2SO_4.$$

(10) Potassium persulphate. The formation of sulphate and hydrogen sulphide was proved. The velocity of the reaction was very small. The reactions in the discharge tube will be expressed by

$$K_2S_2O_8 + 5H_2 = K_2SO_4 + H_2S + 4H_2O,$$
$$K_2S_2O_8 + H_2 = K_2SO_4 + H_2SO_4.$$

Summary.

The chemical reactions under the silent electric discharge were studied when hydrogen reacts with the following inorganic solid substances.

Reacting substance	Reaction products
(1) Potassium chromate	Chromic oxide and potassium hydroxide
(2) Potassium bichromate	Chromic oxide and potassium hydroxide
(3) Ammonium chromate	Chromic oxide and ammonia gas
(4) Ammonium bichromate	Chromic oxide and ammonia gas
(5) Calcium chlorate	Calcium chloride
(6) Sodium chlorate	Sodium chloride
(7) Barium sulphite	Barium sulphide and hydrogen sulphide
(8) Thorium nitrate	Thorium hydroxide, nitrite and ammonium salt.
(9) Ammonium persulphate	Sulphate and hydrogen sulphide,
(10) Potassium persulphate	Sulphate and hydrogen sulphide.

The author acknowledges with thanks the receipt of a grant from the Imperial Academy of Japan.

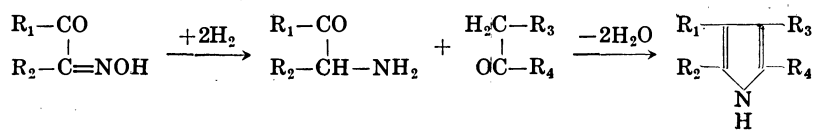
Laboratory of Physical Chemistry,
Hirosima University.

Ein neues Verfahren zur Synthese von Pyrrol-Derivaten.

Von Bun-ichi TOI und Shiro AKABORI.

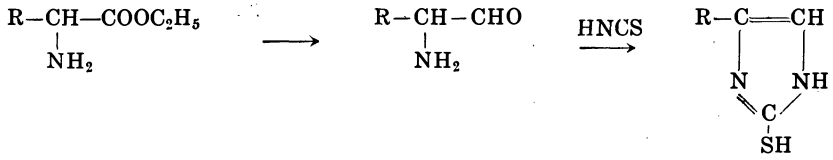
(Eingegangen am 28. Mai 1937.)

Für die Synthese der Pyrrol-derivate wendet man fast ausschliesslich die Knorrsche Methode[1] an, die auf der Kondensation von Aminoketonen mit Ketonen beruht. Bei der praktischen Ausführung der Synthese geht man aber zumeist von einem äquimolekularen Gemenge von Isonitrosoketonen und Ketonen aus. Wenn man das Gemenge in essigsaurer Lösung mittels Zinkstaub reduziert, so verläuft die Reaktion nach dem folgenden, allgemein gültigen Schema:



Es ist aber sehr wahrscheinlich, dass man an Stelle von Aminoketonen Aminoaldehyd anwenden kann, wenn diese Verbindungen auch im allgemeinen schwer zugänglich sind.

Einer der Verfasser (S. Akabori)[2] hat vor einigen Jahren ein allgemeines Verfahren für die Imidazolsynthese aus α-Aminosäuren eingeführt, indem er α-Aminosäureester mit Natriumamalgam zu α-Aminoaldehyd reduzierte und diesen mit Rhodanwasserstoffsäure zu Thiolimidazol kondensierte:

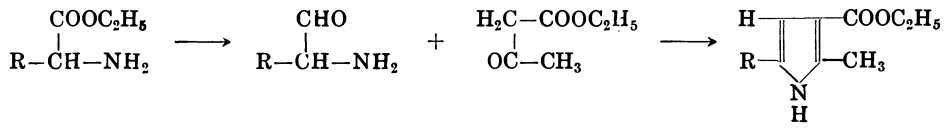


Wir konnten nun bei der Kondensation von Aminoaldehyden, die wir durch Reduktion von Aminosäureestern erhalten hatten, mit Acetessigester einige Pyrrol-derivate erhalten.

Die Reaktion geht im allgemeinen nach dem folgenden Schema vor sich:

(1) L. Knorr, *Ann.*, **236** (1886), 326.

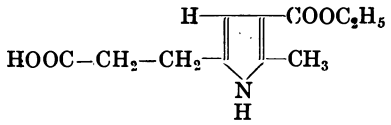
(2) S. Akabori, *Ber.*, **66** (1933), 152; S. Akabori und S. Numano, *Ber.*, **66** (1933), 159.



(I) R = H; (II) R = $-CH_3$; (III) R = $-CH_2-CH(CH_3)_2$

So gewinnt man aus Glykokoll 2-Methyl-3-carbäthoxy-pyrrol (I), aus Alanin 2,5-Dimethyl-3-carbäthxoy-pyrrol (II), aus Leucin 2-Methyl-3-carbäthoxy-5-isobutyl-pyrrol (III).

Interessanterweise erhält man aus Glutaminsäure 2-Methyl-3-carbäthoxy-pyrrol-5-propionsäure (IV),



IV,

die ein Carbäthoxyderivat eines Isomers der Opsopyrrolcarbonsäure ist.

III und IV sind zwei bisher noch nicht in der Literatur beschriebene Pyrrol-derivate.

Beschreibung der Versuche.

2-Methyl-3-carbäthoxy-pyrrol (I). 14 g. Glykokollester-chlorhydrat wurden in 150 c.c. Alkohol und 100 c.c. Wasser gelöst, mittels Kältemischung auf $-10°$ abgekühlt und dann unter stetigem Rühren 400 g. 2.3%iges Natriumamalgam in kleinen Portionen eingeworfen. Während der Reduktion wurden, um die Lösung stets sauer zu halten, 80 c.c. 5 N Salzsäure zugetropft.

Die Reaktionsflüssigkeit wurde vom Quecksilber getrennt, filtriert, unter vermindertem Druck unterhalb 50° auf ca. 100 c.c. eingeengt und von ausgeschiedenem Kochsalz durch Filtrieren abgetrennt. Die so erhaltene Aminoaldehyd-lösung wurde mit 13 g. Acetessigester versetzt und 5 N Natriumhydroxyd zugefügt, bis die Lösung alkalisch reagierte.

Das Reaktionsprodukt wurde mit Äther ausgezogen und nach dem Trocknen mit wasserfreiem Natriumsulfat der Äther bis auf 15 c.c. abdestilliert. Beim Stehen der konzentrierten ätherischen Lösung im Eisschrank schieden sich Kristalle aus, die nach wiederholtem Umkrystallisieren aus verdünntem Alkohol bei 78–78.5° schmolzen. Ausbeute 1.5 g. Sie sind leicht löslich in Alkohol und Äther, schwerlöslich in kaltem Wasser. Die Analysenwerte stimmten mit den für 2-Methyl-3-carbäthoxy-pyrrol berechneten überein (Gefunden: C, 62.80, 62.76; H, 7.43, 7.20; N, 9.27. Ber. für $C_8H_{11}O_2N$: C, 62.71; H, 7.24; N, 9.15%). Nach E. Benary[3] schmilzt 2-Methyl-3-carbäthoxy-pyrrol bei 78–79°.

2,5-Dimethyl-3-carbäthoxy-pyrrol (II). 15.5 g. *dl*-Alaninäthylester-chlorhydrat wurden in gleicher Weise wie Glykokolläthylester-chlorhydrat mit 400 g. 2.3%igem

(3) *Ber.*, **44** (1911), 495.

Natriumamalgam reduziert und mit 13 g. Acetessigester versetzt, wobei 3 g. krystallinisches Kondensationsprodukt erhalten werden konnten. Nach mehrmaligem Umkrystallisieren aus 70%igem Alkohol schmolz es bei 117–117.5°. Der Schmelzpunkt steht mit dem in der Literatur gegebenen[4] im guter Übereinstimmung (Gefunden: C, 64.39, 64.23; H, 7.71, 7.45; N, 8.48. Ber. für $C_9H_{13}O_2N$: C, 64.63; H, 7.84; N, 8.38%).

2-Methyl-3-carbäthoxy-5-isobutyl-pyrrol (III). 20 g. *dl*-Leucinäthylester-chlorhydrat wurden in gleicher Weise wie Alaninäthylester-chlorhydrat mit 400 g. 2.3%igem Natriumamalgam reduziert und mit 13 g. Acetessigester versetzt, wobei sich 2 g. krystallinisches Kondensationsprodukt erhalten liessen.

Nach mehrmaligem Umkrystallisieren aus 70%igem Alkohol schmolz es bei 66.5–67.5° (Gefunden: C, 68.83, 69.07; H, 9.31, 9.04; N, 6.83. Ber. für $C_{12}H_{19}O_2N$: C, 68.85; H, 9.16; N, 6.70%).

2-Methyl-3-carbäthoxy-pyrrol-5-propionsäure (IV). 15 g. Glutaminsäure wurden unter vermindertem Druck 3 Stunden bei 160–180° gehalten und so in Pyrrolidoncarbonsäure übergeführt. Dann gab man 200 c.c. absoluten Alkohol hinzu, sättigte bei Zimmertemperatur mit trocknem Chlorwasserstoff und kochte 4 Stunden auf dem Wasserbade. Nachdem man den Alkohol unter vermindertem Druck abdestilliert hat, wurde das zurückgebliebene sirupöse Glutaminsäurediäthylester-hydrochlorid wieder in absolutem Alkohol aufgelöst.

150 c.c. der alkoholischen Lösung, die 15 g. Glutaminsäure entsprechen, wurden mit 100 c.c. Wasser verdünnt und mittels Kältemischung unterhalb −10° abgekühlt; dann wurf man unter heftigem Rühren 400 g. 2.3%iges Natriumamalgam innerhalb ungefähr 1 Stunde in kleinen Portionen ein; gleichzeitig fügte man 5 N Salzsäure tropfenweise hinzu, um die Lösung sauer zu halten. Man fuhr mit dem Rühren noch ½ Stunde fort und filtrierte dann die vom Quecksilber abgetrennte Lösung.

Das Filtrat wurde unter vermindertem Druck unterhalb 50° auf ca. 100 c.c. eingeengt und von dem ausgeschiedenen Kochsalz durch Filtrieren getrennt. Die so erhaltene Aminoaldehyd-lösung wurde mit 13 g. Acetessigester versetzt, 5 N Natriumhydroxyd hinzugefügt, bis die Lösung alkalisch reagierte, und dann mittels Salzsäure auf etwa $pH = 3$ eingestellt. Das Reaktionsprodukt wurde mit Äther ausgezogen und nach dem Trocknen mit wasserfreiem Natriumsulfat der Äther bis auf 15 c.c. abdestilliert. Beim Stehen der konzentrierten ätherischen Lösung im Eisschrank schieden sich die Kristalle aus, die nach wiederholtem Umkrystallisieren aus 70%igem Alkohol bei 176–177° schmolzen; Ausbeute 2.5 g. Sie sind leicht löslich in Alkohol und Äther, schwer löslich in Wasser. Die Analysenwerte stimmten mit den für 2-Methyl-3-carbäthoxy-pyrrol-5-propionsäure berechneten überein (Gefunden: C, 58.64, 58.60; H, 6.12, 6.41; N, 5.97. Ber. für $C_{11}H_{15}O_4N$: C, 58.63; H, 6.72; N, 6.22%).

Chemisches Institut der Kaiserlichen
Universität zu Osaka.

(4) A. Hantzsch, *Ber.*, **23** (1890), 1474; H. Fischer und Heyse, *Ann.*, **439** (1924), 254.

Über die chemische Natur des Papains.

Von Shigeo MAEDA.

(Eingegangen am 28. Mai 1937.)

Willstätter und Grassmann haben die ersten sorgfältigen Untersuchungen über das Papain angestellt. Sie fanden[1], dass die Aktivierung des Papains mit HCN mit der Beziehung zwischen Enterokinase und Tryptase[2] grosse Ähnlichkeit hat. Der wichtigste Befund der genannten Autoren ist der, dass die Spezifität des nativen Papains von der des aktivierten Enzyms deutlich verschieden ist. Z.B. spaltet das native Papain Gelatine und nicht Pepton; Papaincyanhydrin dagegen spaltet die beiden Substrate.

Vor einigen Jahren hat W. Grassmann angegeben, dass in Papainpräparaten eine schwefelhaltige Verbindung vorkommt, die unter dem Einfluss von Cyanwasserstoff in eine SH-Verbindung von phytokinaseartiger Wirkung übergeht[3].

Diese Vorstellung wurde durch E. Maschmann[4] eingehend experimentell bestätigt. Die Weiterentwicklung dieser Anschauung, besonders auf Grund von Befunden über teilweise reversible Inaktivierung mit Oxydationsmitteln, führte ihn zur Postulierung der Thiolnatur für das Papain[5]. Th. Bersin hat angenommen, dass die die Aktivität hervorrufenden SS- und SH-Gruppen wie beim Insulin in die Peptidkette des Papainmoleküls eingebaut sind[6].

$$\underset{\text{(aktiv)}}{\text{Papain (Pa-SH)}} \underset{\text{HCN, } H_2S\text{, GSH}}{\overset{H_2O_2\text{, Jod, } SeO_3}{\rightleftharpoons}} \underset{\text{(inaktiv)}}{\text{Oxydiertes Papain (Pa-S-S-Pa)}}$$

Im Rahmen dieser Forschung ist von E. Maschmann[7] in einer gründlichen Untersuchung die Frage erörtert worden, welche Rolle ein "Begleitstoff-X" für die Proteolyse spielt, der Papainpräparaten durch wässrigen Alkohol entzogen werden kann. Er kommt zu dem Ergebnis,

(1) R. Willstätter und W. Grassmann, *Z. physiol. Chem.*, **138** (1924), 184.

(2) E. Waldschmidt-Leitz, *Z. physiol. Chem.*, **132** (1923-1924), 181.

(3) W. Grassman, *Z. angew. Chem.*, **44** (1931). 105.

(4) *Z. physiol. Chem.*, **219** (1933), 99; **228** (1934), 141; *Biochem. Z.*, **277** (1935), 97.

(5) *Z. physiol. Chem.*, **220** (1933), 209; **222** (1933), 177; *Ergeb. Enzymforsch.*, **4** (1935), 68.

(6) *Z. physiol. Chem.*, **233** (1935), 59.

(7) *Z. physiol. Chem.*, **228** (1934). 141.

dass der "Begleitstoff-X" mit S-S-Glutathion nicht identisch ist, aber ein noch unbekanntes disulfidhaltiges Polypeptid sein kann[8]. W. Grassmann[9] hat den schwefelhaltigen Begleitstoff des Papains nach vorausgegangener Reduktion mit Schwefelwasserstoff auf Grund seiner Löslichkeit in 70%igem Alkohol vom Enzym abgetrennt und gefunden, dass die so gewonnenen Akitivatorfraktionen zum wesentlichen Teil aus einem oder mehreren Cystein-Glutaminsäurepeptiden bestehen. Auf Grund dieser Tatsache könnte man zu dem Schluss geführt werden, dass die Postulierung der Thiolnatur für das Papain nach Bersin zum mindesten unwahrscheinlich ist, und dass vielmehr ein spezifischerer, SH-Gruppen tragender Begleitstoff, dessen Existenz für die Aktivierung des Enzyms notwendig ist, im Papainpräparat vorkommt[10].

M. Bergmann und Mitarbeiter[11] wollen durch teilweise Inaktivierung des Papains mit verschiedenen Reagenzien und darauffolgende Reaktivierung das Vorkommen von zwei Peptidasen und einer Proteinase im gewöhnlichen Papainpräparat festgestellt haben, und zwar soll nur eine von beiden Peptidasen durch Phenylhydrazin oder Hydroxylamin inaktiviert werden und dieselbe daher ein Carbonylgruppen enthaltendes Enzym sein. Nach den genannten Autoren soll aber im Proteinase-anteil kein Carbonylgruppen enthaltendes Enzym sein, weil es durch Phenylhydrazin nicht inaktiviert wird.

Der Verfasser hat auch die vorliegende Arbeit zu dem Zwecke unternommen, die stoffliche Natur des Papains auf chemische und enzymatische Weise zu untersuchen.

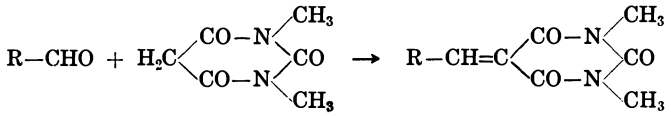
Wurde Handelspapain in Wasser gelöst und durch eine Kolloidiumhülse dialysiert, so verminderte sich dabei die Aktivität des Papains stark, konnte aber durch Zugabe von Cyanwasserstoff in hohem Masse reaktiviert werden. Die Aussenflüssigkeit der Dialyse wies keine enzymatische Wirkung auf. Aus der Innenlösung wurde durch Fällung mit Methanol ein Enzym-präparat gewonnen, das 15.02%N enthielt. Es war eine gelatineartige amorphe Masse, die sich durch relativ hohen Gehalt an Tryptophan (3.43%) auszeichnete und deren relative Aktivität vor und nach der Aktivierung mit Cyanwasserstoff 0.44 und 1.66 betrug.

Der Verfasser hat die Wirkungen verschiedener Reagenzien, nämlich Hydrazin, Phenylhydrazin, Hydroxylamin, Natriumbisulfit und Dimethylbarbitursäure, auf das Papain geprüft. Die Hemmungswirkung der

(8) *Biochem. Z.*, **277** (1935), 111.
(9) *Biochem. Z.*, **279** (1935). 131.
(10) A. Purr, *Biochem. J.*, **29** (1934), 5.
(11) M. Bergmann und W. F. Ross, *J. Biol. Chem.*, **111** (1935), 659.

Carbonylreagenzien auf Papain ist eine Zeitreaktion und wird erst beim tagelangem Stehen vollständig. Beim 2–3 tägiger Einwirkung der Reagenzien wurde nicht nur die Peptidasewirkung, sondern auch die Wirkung der Gelatinespaltung (Proteinase) fast völlig gehemmt, und durch Cyanwasserstoff oder Benzaldehyd konnte keine Reaktivierung erzielt werden. Nach den obigen Resultaten müsste man zu einem von der Bergmannschen Ansicht verschiedenen Schluss kommen, dass nämlich nicht nur der Papainpeptidase-, sondern auch der Proteinase-anteil des Papains ein Carbonylgruppen enthaltender Komplex ist.

Und die Hemmung durch Dimethylbarbitursäure lehrt uns, dass die Carbonylgruppe, die mit der Aktivität des Papains in engem Zusammenhang steht, zu einer Aldehydgruppe gehört, weil Dimethylbarbitursäure nur mit Aldehyden, aber nicht mit Ketonen reagiert.[12]



Die entstandenen Aldeh d-dimethylbarbitursäuren sind gelb gefärbt, wenn die Aldehyd aromatisch oder Furanderivate sind. Die Papain-dimethylbarbitursäurelösung färbt sich allmählich beim Stehen und die Hemmung schreitet parallel mit der Vertiefung der Farbe fort.

Mein Papainpräparat ist durch proteolytische Enzyme schwer verdaubar. Bei der Trypsin- und Pepsin-wirkung war eine kleine Zunahme des COOH zu beobachten, während sich die Aktivität des Enzyms nicht verminderte.

Ob Papain ein Protein ist oder nicht, kann man jetzt noch nicht mit Sicherheit sagen. Jedenfalls ist aber Papain eine hochmolekulare Substanz und vielleicht ein spezielles Protein, das eine Aldehyd-gruppe trägt.

Beschreibung der Versuche.

1. Reinigung des Papains. 50 g. Handelspapain wurden mit 500 c.c. destilliertem Wasser durchgeschüttelt, 4–5 Stunden bei Zimmertemperatur stehen gelassen, abzentrifugiert und die klare Lösung mittels einer Kollodiumhülse 70 Stunden lang gegen destilliertes Wasser dialysiert. Aus der Innenflüssigkeit wurden durch Zusatz von Methanol 10.7 g. eines Niederschlags gewonnen, der relativ geringe Aktivität aufwies, aber durch HCN stark aktiviert wurde.

(12) S. Akabori, *Ber.*, **66** (1933), 139.

Tabelle 1.

Ansatz: N/5 Acetatpuffer (pH = 5) 1 c.c.+5%ige Gelatinelösung 5 c.c. (oder 1/5 Mol Hippuramidlösung 5 c.c.)+5%ige Papainlösung 1 c.c.

COOH Zuwachs (c.c. N/5 KOH) bei 36°						
	Gelatine			Hippuramid		
Stunde	1	4	24	1	4	24
Gereinigtes Papain	0.44	0.98	1.68	0.02	0.04	0.84
HCN (16 mg.)	1.66	2.46	3.42	0.10	0.48	1.26

2. Analysen des Papains. (a) *Gesamt-Stickstoff nach Kjeldahl.* Gef.: N, 15.10, 15.05, 14.92; mittlerer Wert, 15.02%.

(b) *Amino-Stickstoff nach Van Slyke.* Gef.: NH_2–N, 2.14, 2.45, 2.23; mittlerer Wert, 2.27%.

$$\frac{NH_2\text{-}N}{N} = 0.144....$$ etwas höher als gewöhnliche Proteine.

(c) *Bestimmung von Tryptophan.* Es ist heute eine ganze Anzahl von Methoden zur Bestimmung von Tryptophan unter verschiedenen Bedingungen bekannt. Es sei an die kolorimetrische von J. Tillmans und A. Alt[13] erinnert, die auf Verwendung von Formalin in Gegenwart von Schwefelsäure beruht, an die jodometrische von A. Homer[14], die auf der Bildung des Octabromtryptophans basiert. C. Itagaki und R. Masayama[15] verbesserten die Methode von Tillmans und Alt mit Hilfe eines Stufenphotometers. Diese von Itagaki und Masayama angegebene Methode wird als sehr zweckmässig empfohlen.

Ausführung: Zu 1 c.c. der zu bestimmenden Enzymlösung (geeigneter Konzentration), die sich in einem 20 c.c.-Messkolben befindet, fügt man 2 Tropfen einer 2%igen Formalinlösung hinzu und füllt mit 66%iger Schwefelsäure genau bis zur Marke auf. Nachdem man die Mischung 5 Minuten stehen gelassen hat, (dabei zeigt die Lösung eine Gelbfärbung), pipettiert man eine Probe in eine Küvette von geeignetem Inhalt und bestimmt den Extinktionskoeffizienten K mittels eine Stufenphotometers (als Filter Zeiss S 47 verwendet). Als Kontrolllösung wurde ein Probelösung ohne Zusatz von Formalinlösung verwendet. Die Berechnung des Tryptophangehaltes erfolg mit Hilfe einer Kurve, durch die vorher der Zusammenhang zwischen Tryptophangehalt und Extinktionskoeffizient festgestellt worden ist. (Gef.: Tryptophan, 3.34, 3.57, 3.40; mittlerer Wert, 3.43%.)

Herrn Dr. R. Masayama im medizinischen Institut der hiesigen Universität, unter dessen freundlicher Leitung diese Bestimmungen durchgeführt worden sind, bin ich sehr verbunden.

3. Einfluss von verschiedenen Reagenzien auf Papain. Es wurden jeweils 0.2 g. Reagens in 5 c.c. 5%iger Papainlösung aufgelöst (4%ige Probelösung). Dann wurde nach einer bestimmten Zeitspanne 1 c.c. abpipettiert und die Aktivität geprüft.

(13) *Biochem. Z.*, **164** (1925), 135.
(14) *J. Biol. Chem.*, **22** (1915), 369.
(15) *Mitt. Med. Ges. Osaka*, **35** (1936), 1743.

Tabelle 2. Einfluss von verschiedenen Reagenzien auf Papain.

Nr.	Reagenzien (%)		Wirkungsdauer von Reagens auf Papain bei Zimmertemperatur (Stunden)	COOH Zuwachs (c c. N/5 KOH) bei 36°					
				Gelatine			Hippuramid		
				1 St.	5 St.	24 St.	1 St.	5 St.	24 St.
1	NH_2OH	4	15 auf HCN-Papain	—	1.12	1.51	00	00	0.03
			ohne Reagens	—	1.96	2.76	—	0.37	0.78
2	NH_2OH	4	24 auf Papain	0.34	0.36	0.57	00	00	00
3	NH_2OH	10	52 auf Papain	00	0.08	0.13	00	00	00
			ohne Reagens	1.54	2.38	3.23	0.22	0.84	1.36
4	NH_2OH $+C_6H_5CHO$	8	120 auf Papain	00	00	00	—	—	—
			24 auf Papain	00	00	00	—	—	—
			ohne Reagens	—	1.19	2.27	—	—	—
	NH_2OH $+HCN$	4	120 auf Papain	00	00	00	—	—	—
			48 auf Papain	00	00	00	—	—	—
5	CH_3COCH_3	4	12 auf Papain	1.52	2.18	2.91	0.39	0.90	1.13
			ohne Reagens	1.54	2.38	3.23	0.22	0.84	1.36
6	$C_6H_5NH_2$	4	0.5 auf Papain	1.30	1.78	2.02	0.12	0.40	0.92
			ohne Reagens	1.70	2.20	3.09	0.24	0.60	1.22
7	$NaHSO_3$	4	24 auf HCN-Papain	0.41	0.59	2.26	—	—	—
			ohne Reagens	1.56	2.09	2.82	—	—	—
8	$NaHSO_3$	4	24 auf Papain	0.31	0.63	1.19	—	—	—
			ohne Reagens	1.21	1.54	1.90	—	—	—
9	$NaHSO_3$	4	120 auf Papain	00	0.02	0.04	—	—	—
			ohne Reagens	—	1.10	2.26	—	—	—
10	$NaHSO_3$ $+CH_3COCH_3$	4	24 auf Papain	0.29	0.52	1.23	—	—	—
			24 auf Papain	0.38	1.42	1.93	—	—	—
			ohne Reagens	0.96	1.68	2.48	—	—	—
11	$C_6H_5NHNH_2$	4	24 auf Papain	0.05	0.31	—	—	—	—
			ohne Reagens	1.08	1.52	—	—	—	—
12	$C_6H_5NHNH_2$ $+C_6H_5CHO$	4	68 auf Papain	00	0.10	—	—	—	—
			22 auf Papain	00	00	—	—	—	—
			ohne Reagens	0.76	1.34	—	—	—	—
13	$C_6H_5NHNH_2$	4	92 auf Papain	00	00	—	—	—	—
			ohne Reagens	0.56	1.36	—	—	—	—
14	D. B. S.*	4	40 auf Papain	0.27	0.67	1.11	00	00	00
			ohne Reagens	0.61	1.44	2.05	0.02	0.08	0.44
15	D. B. S.	4	sofort nach Zusatz	1.41	1.96	2.23	—	—	—
			ohne Reagens	1.49	1.88	2.23	—	—	—
16	D. B. S.	4	40 auf HCN-Papain	1.49	1.88	2.11	—	—	—
			ohne Reagens	1.59	2.19	2.87	—	—	—
17	D. B. S.	4	120 auf Papain	0.24	0.48	0.56	—	—	—
			ohne Reagens	0.89	1.57	2.31			

* D. B. S. = Dimethylbarbitursäure.

Bergmann[16] sagt, dass bei der Inaktivierung durch Phenylhydrazin bei einer Konzentration von 0.03 millimol Reagens pro c.c. einer 0.45%igen Papainlösung die maximale Schädigung erreicht wird und eine weitere Zunahme der Phenylhydrazinkonzentration keine stärkere Hemmung mehr erzeugt. Und er hat daher angenommen, dass die Verdauung von Gelatine durch HCN-Papain über zwei verschiedene enzymatische Prozesse geht. In diesem Zusammenhang habe ich festgestellt, dass diese Aktivitätshemmung durch Vergiftung des Papains eine Zeitreaktion ist, dass also durch 68-stündige Einwirkungsdauer von Phenylhydrazin die Aktivität des Papains fast völlig beseitigt werden kann.

Dimethylbarbitursäure ist etwas schwerer zu kondensieren mit Papaincarbonyl als allgemeine Carbonylreagenzien, und deshalb ist zur vollkommenen Hemmung durch Dimethylbarbitursäure etwas längere Zeit erforderlich als im Fall des Hydroxylamins, Hydrazins und Phenylhydrazins.

Tabelle 3. Zeitlicher Verlauf der Inaktivierung durch Hydroxylamin, Hydrazin und Phenylhydrazin.

	COOH Zuwachs (c.c. N/5 KOH)		
Stunde	NH_2OH	NH_2NH_2	$C_6H_5NHNH_2$
0	1.51	1.51	1.51
0.5	1.04	1.25	0.36
1	—	1.06	—
3	0.62	0.70	0.20
6	0.38	0.46	0.10
23	0.18	0.12	0.02

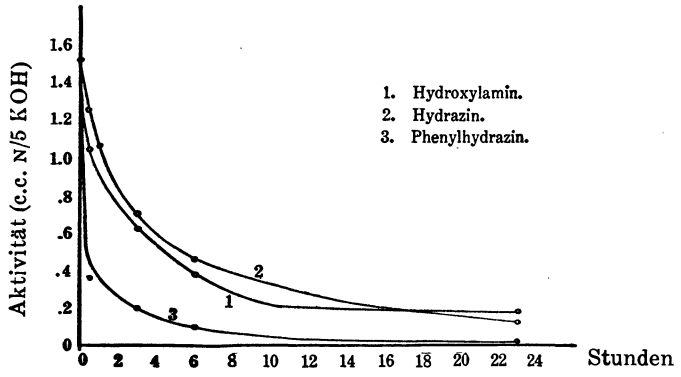


Abb. 1. Hemmungskurven.

Zu einer Lösung von 0.6 g. Inaktivator in 15 c.c. destilliertem Wasser, das nötigenfalls vorher auf etwa pH = 5.0 eingestellt worden ist, setzt man 15 c.c. 5%ige Papainlösung zu. Nachdem die Mischung eine bestimmte Zeitspanne bei 36° verblieben ist,

(16) M. Bergmann und W. F. Ross, *J. Biol. Chem.*, **114** (1936), 717.

pipettiert man 2 c.c. ab, fügt 5 c.c. 5%ige Gelatine und 3 c.c. N/5 Acetatpuffer hinzu und titriert sie. Die Resultate sind in den Tabelle 3 und Abb. 1 angegeben.

4. Einwirkung proteolytischer Enzyme. Ich prüfte die Beständigkeit von gereinigtem Papain-präparat gegenüber der Wirkung von Pepsin und Trypsin-kinase, wobei sich in keinem Falle irgendwelche messbare Aktivitäts-einbusse bemerken liess.

Verdauung durch Trypsin-kinase und Pepsin. (Tabelle 4.)

Tabelle 4.

Ansatz: A. 5%ige Papain-lösung (pH = 8) 5 c.c.+N Phosphatpuffer (Na_2HPO_4) 1 c.c. +Trypsin-kinase 2 c.c. bei 30°; B. 5%ige Papain-lösung 2 c.c.+N Glykokollmischung (pH = 1.93) 1 c.c.+Pepsin (1%) 1 c.c. bei 36°.

COOH Zuwachs (c.c. N/5 KOH)				
Stunde	1/3	1	4	24
Trypsin-kinase	0.08	0.06	0.19	0.21
Pepsin	—	0.06	0.10	0.28

Aktivität des durch Trypsin-kinase und Pepsin verdauten Papains gegenüber Gelatine. Kontrollversuch: Nachdem die Mischung von 5 c.c. einer 5%igen Papain-lösung und 1 c.c. N Phosphatpuffer jeweils eine entsprechende Anzahl Stunden bei 30° stehen gelassen worden war, wurden 2 c.c. Trypsin-kinase zugesetzt, sofort auf pH = 5.0 eingestellt und die Aktivität gegenüber Gelatine (5%ige Gelatine 5 c.c.) während einer Stunde bei 36° geprüft. Beim Pepsin: 5%iges Papain 2 c.c., N Glykokollmischung (pH = 1.93) 1 c.c. und 1%iges Pepsin 1 c.c. In gleicher Weise ausgeführt. Die Versuchsergebnisse sind in Tabelle 5 zusammengestellt.

Tabelle 5.

	COOH Zuwachs (c.c. N/5 KOH)			
	Stunde	1	4	24
Kontroll-versuch	Trypsin-kinase	1.66	1.64	—
	Pepsin	1.20	1.26	1.18
Haupt-versuch	Trypsin-kinase	1.57	1.58	—
	Pepsin	1.22	1.30	1.18

Es sei mir an dieser Stelle erlaubt, Herrn Prof. S. Akabori für die Überlassung dieser Arbeit, sowie für Anregungen und Ratschläge meinen verbindlichsten Dank auszusprechen.

Chemisches Institut der Kaiserlichen
Universität zu Osaka.

The Dielectric Constant of Cetyl Alcohol Near its Melting Point.

By Ken-iti HIGASI and Masaji KUBO.

(Received May 31st, 1937.)

Using a heterodyne beat apparatus[1] of 3000 kilocycles, we studied the temperature dependence of the dielectric constant of cetyl alcohol.

The dielectric constant of this substance increases on solidification, passes through a maximum at a temperature a little below the melting point and then drops to a nearly constant value at lower temperatures, which is the same order of the magnitude as non-polar substances (Cf. Table 1 and the figure).

Table 1.
The Dielectric Constant of Cetyl Alcohol ($\lambda = 100$ m.)

t (°C.)	ε	t (°C.)	ε	t (°C.)	ε (liquid)
−13.5	2.55	25.0	4.19	50.0	3.86
−12.6	2.56	29.7	5.65	50.0	3.86
3.5	2.77	29.8	5.65	57.0	3.74
4.2	2.75	34.9	5.70	57.1	3.74
13.8	2.85	35.0	5.70	63.7	3.65
14.1	2.85	42.0	5.27	64.0	3.64
20.8	3.25	42.0	5.27		
20.9	3.28	45.4	4.81		
25.0	4.10	45.7	4.78		

Methyl alcohol[2] and normal long chain ketones[3] are reported to show a considerable increase in the dielectric constant in a wide range below their melting points. But any of them differs from cetyl alcohol in that it gives lower dielectric constant in solid state than in liquid state. Piekara's observation[4] on oleic acid reveals a feature similar to that by our experiment, but in the case of cetyl alcohol it is exhibited much more distinctly.

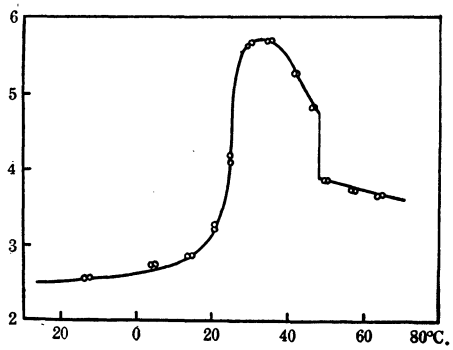
(1) The same apparatus used in the determination of the dielectric constant of gases, was employed in the present work with a slight modification. See M. Kubo, *Sci. Papers Inst. Phys. Chem. Research* (Tokyo), **26** (1935), 242 ; **27** (1935), 65.

(2) C. P. Smyth and S. A. McNeight, *J. Am. Chem. Soc.*, **58** (1936), 1597.

(3) A. Müller, *Proc. Roy. Soc.* (London), A, **158** (1937), 403.

(4) B. Piekara, *Physik. Z.*, **37** (1936), 624.

In Table 2, the dipole moment[5] of this substance in solution are recorded. Excepting the values in hexane solution, which are not free from the errors of association, the observed moments are remarkably constant. It is clear from this that no abnormality occurs in the dipole moment in the range of the temperature observed.



Temperature dependence of the dielectric constant of cetyl alcohol

Table 2. The Dipole Moment of Cetyl Alcohol

t (°C.)	benzene		hexane	
	P	μ	P	μ
20	140.0	1.70	114.3	1.30
30	137.3	1.70		
40	135.8	1.70	122.0	1.48
50	132.7	1.68		
60	131.8	1.69	125.0	1.58

$P_E + P_A = P_{solid}$[6] $= 78.5$ c.c.

According to the X-ray studies by Malkins,[7] two lattice constants are given to this alcohol and a transition between them is supposed to occur when it is near room temperature. If this observation be correct, has this transition any relation with the observed anormaly in the dielectric constant?

No satisfactory explanation can be given at the present stage of the investigation. And in the following paper a fuller discussion on this problem will be given.

In conclusion, the writers wish to express their cordial thanks to Prof. M. Katayama and Prof. S. Mizushima for their kind guidance and encouragement throughout this experiment.

The Institute of Physical and Chemical Research,
Tokyo.

(5) From the result of our previous work, which was published in Japanese: K. Higasi, *Bull. Inst. Phys. Chem. Research* (Tokyo), **12** (1933), 780.

(6) P_{solid} used here is the polarisation obtained by using an apparatus of shorter wavelength at very low temperature.

(7) T. Malkins, *J. Am. Chem. Soc.*, **52** (1930), 3739.

A Note on the Cannizzaro Reaction.

By Yoshiyuki URUSHIBARA and Matsuji TAKEBAYASHI.

(Received May 27th, 1937.)

In the course of the investigation on the effect of oxygen and ferromagnetic metals on the addition of hydrogen bromide to allyl bromide, the authors[1] came to suspect that the effect of peroxides on the Cannizzaro reaction observed by M. S. Kharasch and M. Foy[2] was really caused by molecular oxygen, because molecular oxygen was found the active catalyst influencing the direction of addition and the yield of the products in the reaction of hydrogen bromide with allyl bromide although the experimental evidence so far obtained could not totally exclude the possibility that peroxides were active also as such.[3] But the authors'

Series of experiment	No. of exp.	Added	Extent of Cannizzaro reaction (%)
I Peroxide-free benzaldehyde	1	None	10
	2	None	9
	3	Hydroquinone, 0.1 g.	8
II Purified benzaldehyde, exposed to air for 5 minutes	4	None	53
III Commercial benzaldehyde	5*	None	76
	6	None	83
IV Peroxide-free benzaldehyde	7	Reduced iron, 1.5 g.	10
	8	Reduced nickel, 1.5 g.	11
	9	Reduced nickel, 1.5 g. Hydroquinone, 0.1 g.	9
	10	Reduced nickel, 1.5 g. Hydroquinone, 0.1 g.	10

* Reaction time: 2 hours.

(1) This Bulletin, **12** (1937), 54.
(2) *J. Am. Chem. Soc.*, **57** (1935), 1510.
(3) This Bulletin, **11** (1936), 798; **12** (1937), 133, 173.

expectation has not been proved, and the Cannizzaro reaction may be more reasonably regarded as a chain reaction in which the peroxide of the aldehyde concerned, even though present in very minute traces, plays an important part. A support to such an interpretation is given by the fact that benzaldehyde has been found extremely sensitive to peroxide formation even in the dark,[4] and that the Cannizzaro reaction does not undergo even the slightest influence of ferro-magnetic metals, which cause an effect quite similar to that of oxygen, in the addition of hydrogen bromide to allyl bromide. The experimental results are summarised in the accompanying table. Benzaldehyde (10 c.c.) was shaken with an excess of aqueous potassium hydroxide (13.8 N, 10 c.c.) in vacuum in the dark at room temperature for three hours, and the extent of Cannizzaro reaction was determined from the alkali consumed.

The authors express their hearty thanks to Nippon Gakujutsu Shinkokwai (the Japan Society for the Promotion of Scientific Research) for a grant.

Chemical Institute, Faculty of Science,
Imperial University of Tokyo.

(4) Allyl bromide does not form peroxide in the dark, this Bulletin, **11** (1936), 798.

The Electrolytic Formation of Persulphate. Part III. Study of the Electrodes.

By Ryoichi MATSUDA and Teruichi NISHIMORI.

(Received June 2nd, 1937.)

The anode plays a very important part in electrolytic oxidation. Selection of the anode material, its treatment and other conditions are limited especially in the case of electrolysis which involves strong acid solutions as in the present one. Platinum is the anode material which can be used exclusively in such a case, and an alternative to it has been long sought in vain.

The influence of igniting a Pt-anode previously to electrolysis was studied in Part II[1] of this investigation, and several other treatments of the anode are subsequently dealt with in this paper. The length of the Pt-wire cathode is also changed to see the influence of the cathodic current density, but nothing remarkable is found to take place.

Experiment 1. Influence of the Cathodic Current Density. The anode consists of a spiral of Pt-wire which is 0.05 cm. in diameter and 20.7 cm. in length, and the cathode also of Pt-wire as thick as the anode, which is wound spirally against the wall of the electrolytic vessel. Three different lengths of the cathode are employed, i.e., 20, 45, and 107 cm. 130 c.c. of 15 N sulphuric acid are electrolysed with these electrodes at 15°C. without diaphragm. Current efficiency (to be abbreviated as C.E. hereafter) for different current densities is shown in Table 1 and Fig. 1 and 2, the same amount of electricity being supplied in each case.

Table 1. Current Efficiency with the Length of the Cathode varied, the Electrolyte being 15 N Sulphuric Acid.

The length of the cathode \ The current (amp.)		0.163	0.325	0.650	0.975	1.30	1.95	2.60
The Caro's acid C.E.	20 cm.	22.8%	34.2	38.0	34.3	30.4	28.4	27.0
	45	20.0	24.1	24.1	23.5	24.8	25.5	24.1
	107	4.8	33.4	31.5	28.4	25.8	19.2	15.7
The total C.E.	20	31.0	49.1	65.6	74.8	77.7	76.0	75.6
	45	25.5	40.0	58.7	67.3	71.7	74.0	65.5
	107	14.1	38.5	57.1	70.0	70.9	70.9	70.1

(1) This Bulletin, **11** (1936), 650.

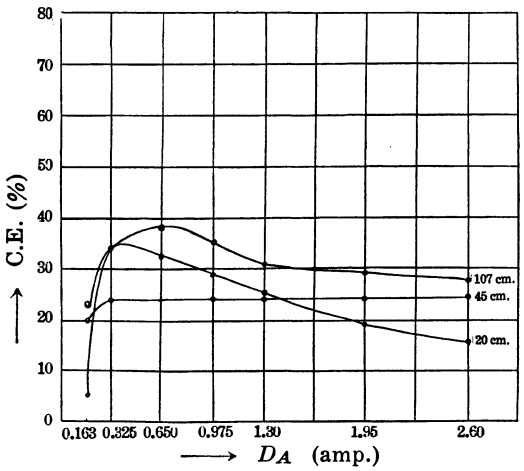


Fig. 1. Caro's Acid C.E. with Various Lengths of the Cathode.

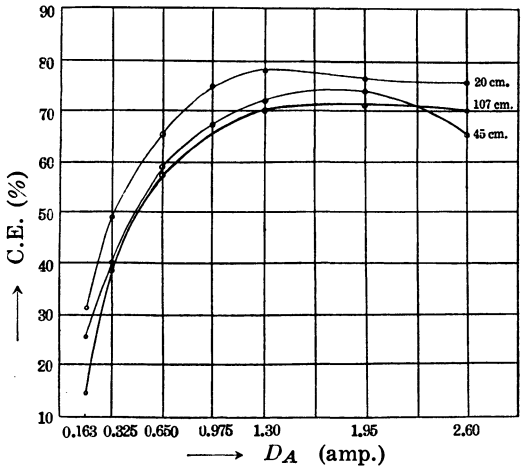


Fig. 2. The Total C.E. with Various Lengths of the Cathode.

The total C.E. is greater, the shorter the cathode: therefore a longer cathode is evidently more effective in reducing the peroxidic anodic products in spite of its smaller cathodic current density, because the influence of the cathode on C.E. probably consists merely in reducing the anodic products.

The greater the total C.E., in this experiment, the smaller the C.E. as to Caro's acid, which was the case also in Experiment 3 of Part II in which 15 N sulphate solutions containing various amounts of ammonium sulphate and sulphuric acid were electrolysed. In the latter case the fact was explained by means of the difference of sulphuric acid concentration. In the present case, however, the reason must be attributed to the condition of the cathode or something connected with it, because both the electrolyte and the anode are similar. Although it is not clearly known why, it seems likely that firstly Caro's acid is formed in greater amount when the cathode is longer, and secondly Caro's acid is reduced more easily than persulphuric acid when it comes near, or in contact with, the cathode irrespective of the magnitude of the cathodic current density.

Experiment 2. PbO_2-anode. PbO_2-anode was studied by several investigators, e.g., its preparation from lead nitrate solution by Y. Kato and K. Koizumi[2] and that from lead tartrate solution by G. Angel and H. Mellquist[3]. Both of these methods are examined in their adoptability

(2) *J. Electrochem. Assoc. Japan*, **2** (1934), 309.
(3) *Z. Elektrochem.*, **40** (1934), 702.

for the present purpose. Lead dioxide is deposited electrolytically on a Pt-anode from lead nitrate solution, whose compositions are varied as follows: 5 to 39 g. $Pb(NO_3)_2$, 1 to 10 c.c. conc. HNO_3, 0 to 1 g. gelatine, 90 to 95 c.c. water.

The Pt-anode is the same as used in Experiment 1 and the cathode is one of 45 cm. in length described above. The current is varied 0.04 to 3.0 amp., the temperature 50° to 80°C., and the time of electrolysis 1 to 30 minutes. It is found that the deposition of lead dioxide is the hardest, the most uniform and adherent when the solution contains 39.0 g. $Pb(NO_3)_2$, 1.0 c.c. conc. HNO_3, 90 c.c. water and 1 g. gelatine, and the temperature 77°C., the current 0.5 amp., and the time of electrolysis 30 minutes. A solution which is 3 and 4 N respectively as regards ammonium sulphate and sulphuric acid is electrolysed without diaphragm at 15°C. with the PbO_2-anode prepared under the best conditions as mentioned above. Three different intensities of current, 1.30, 1.95 and 2.60 amp., are applied for the electrolysis, the amount of electricity being the same, i.e., 1170 coulombs in each case. The total C.E. remains 3.0 to 3.1% for all the three intensities of current. When 15 N sulphuric acid is electrolysed under the same conditions as above, the total C.E. is even less than 3.0%. The PbO_2-anode prepared from lead nitrate solution under the other conditions is proved unavailable for the electrolysis, since the PbO_2-layer comes off partly or entirely during electrolysis.

Angel and Mellquist[3] say that they succeeded in preparing a PbO_2-anode by depositing lead dioxide on iron, steel or copper from lead tartrate solution, and the deposition of the same on platinum is here examined. A 13% KOH solution containing 17.7 g. lead tartrate in 100 c.c. is electrolysed at 14° to 17°C. by a current of 1.30 amp. for 15 minutes with the same anode and cathode as used in the previous case, and lead dioxide is deposited on the anode. While a solution which is 3 and 4 N respectively as regards ammonium sulphate and sulphuric acid is being electrolysed with the PbO_2-anode thus prepared and a Pt-cathode by a current of 1.30 amp. at 15°C., it is found that lead dioxide comes off entirely from the Pt-base.

Experiment 3. Carbon-anode. An anode is made of gas carbon which is of rectangular section 4 $mm.^2$ and 3 cm. in length. The cathode is the Pt-one as used in previous cases. Three electrolyses are tested with these electrodes at 15°C. without diaphragm: 10 N sulphuric acid with a current of 2.6 amp., 6 N ammonium sulphate solution with 0.163 amp., and 6 N ammonium sulphate solution containing ammonia with 0.163 amp. The

carbon-anode is found, in each of these cases, partly to disintegrate, therefore its use is not promising.

Experiment 4. Various Treatments of the Pt-anode. 130 c.c. of 15 N sulphuric acid are electrolysed without diaphragm for 30 minutes at 15°C. with an anodic current density of 20 amp./dm.^{2} Both the anode and cathode which is 45 cm. long are as described in Experiment 1, and the former, however, is subjected, immediately before use, to various heat treatments as follows.

When hydrogen and acetylene are used as the fuel for the treatments, each of these is led to a blast lamp and burned with air whose amount is so controlled as to keep the temperature of the Pt-anode which is put in the blast just to white heat. The temperatures to which the anode is heated are kept as near as possible throughout the treatments.

Table 2. Various Treatments of the Pt-Anode.

	Caro's acid C.E.	The Total C.E.
Coal gas flame[1]	24.1%	58.7%
Hydrogen flame	17.0 18.9 mean 18.0	50.0 46.1 mean 48.1
Acetylene flame	16.1 16.2 mean 16.2	63.0 60.5 mean 61.8
D.C. (downwards)	18.3 19.5 mean 18.9	50.2 58.7 mean 54.5
D.C. (upwards)	17.4 17.7 mean 17.6	53.5 54.4 mean 54.0
A.C.	20.9 21.1 mean 21.0	63.8 64.4 mean 64.1

Though it is not clear what takes place in the Pt-anode as the result of its heat treatments, more or less differences of C.E. are seen to occur according to the kind of treatment. Among the three kinds of flame

acetylene gives the best total C.E., hydrogen the poorest, and coal gas comes between them. Therefore the presence of hydrocarbon in the combustible gas or its combustion seems favourable to improve the anode activity.

The electrical treatment in which D.C. is flowed from the top of the anode to its lower end is denoted in the table as D.C. (downwards) and the reversed case as D.C. (upwards). There is no considerable difference between the influences of these two on C.E. The A.C. treatment, however, is superior to the D.C. treatment in increasing C.E. and gives the greatest total C.E. of all.

Tokushima Technical College, Tokushima.

Note on a Theory of the Expanded Film.

By Kyozo ARIYAMA.

(Received June 5th, 1937.)

Although numerous theories have been proposed, the nature of the expanded film appears still undecided. In a recent paper Langmuir[1] tried to explain the phenomena and proposed the equation of state of the following form

$$(F-F_0)(a-a_0) = kT, \qquad (1)$$

where F is the two dimensional gas pressure, a the surface area for a molecule, T the absolute temperature, k the Boltzmann's constant. F_0 and a_0 appear as constants to be determined by experiments. With suitable choice of F_0 and a_0, he shows that equation (1) represents the equation of state fairly well. However he does not discuss the nature of these constants, and considers that the presence of a kink in the observed F–a curve is due to the sudden appearance of micelles. Why the micelles, if any, should appear suddenly is still a subject of theoretical speculation.

I would like to propose the following explanation for the sudden appearance of the expanded state. According to the theory of Langevin-Weiss, an ensemble of molecules with permanent magnetic moment or

(1) *J. Chem. Phys.*, **1** (1933), 756.

electric moment can exhibit the 'Ferromagnetic state', and there is a sharp critical temperature at which the transition from paramagnetic to ferromagnetic state takes place. Born[2] applied this theory to the explanation of the existence of the sharp critical temperature at which the anisotropy of a liquid crystal disappears. According to Born, there is the following relation between the electric moment μ of the molecule and the critical temperature T_c

$$\mu^2 = \frac{9kT_c}{4\pi N}, \qquad (2)$$

where N is the number of the molecules in a cubic centimeter.

Now in the case of solids for which the 'ferromagnetic state' is possible, the number of molecules N is an almost fixed quantity, so that there is only one critical temperature. If on the other hand, we have a substance whose density can be varied so that N takes on continuously changing values, then there will be corresponding continuous changes in the critical temperature T_c. In other words for any given temperature, there is one and only one density at which the 'ferromagnetic state' can set in for any molecules having dipole moments.

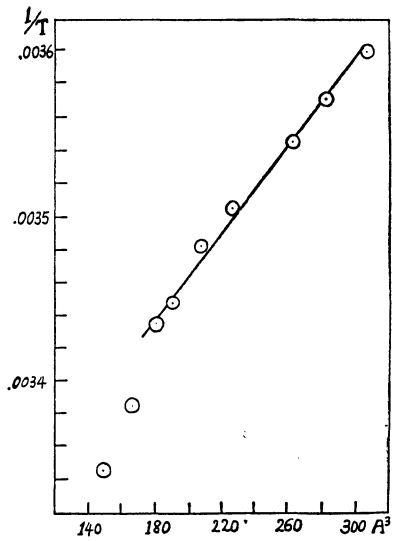


Fig. 1. The Relation between the Reciprocal of Temperature and the Critical Molecular Volume for Films of Myristic Acid.

Let us consider for a moment that the 'ferromagnetic state' is also possible for two dimensional states, and assume that Born's argument applies here in unmodified form. Then the critical volume V_c of the molecule for any given temperature T will be given by

$$V_c = \frac{1}{N} = \frac{4\pi}{9}\frac{\mu^2}{kT}. \qquad (3)$$

Thus it is expected that V_c should vary inversely as the temperature. This can be tested by the experimental data on myristic acid films.[3] Figure 1

(2) *Ann. Physik*, **55** (1918), 222.

(3) Adam and Jessop, *Proc. Roy. Soc.* (London), A, **112** (1926), 362.

shows the experimental relation. We see that the theoretical conclusion holds fairly well except for the two lowest points at which the discrepancy becomes quite marked.

Assuming equation (3) to be correct, we can calculate the electric moment μ of the myristic acid. The value found from Figure 1 is 2.5×10^{-18} e.s.u. No direct measurement of the electric moment of myristic acid seems to have been reported; but Meyer[4] has calculated that rotation within the carboxyl group should cause a variation of moment with temperature, the lower limit and the upper limit being 1.1×10^{-18} and 3.5×10^{-18} respectively. Thus the value 2.5×10^{-18} seems quite reasonable. The point of view described here does not seem to conflict with various experimental facts of the expanded films.

Physics Department, University of Minnesota,
Minneapolis, Minn., U.S.A.

Corrections to the papers published in Vol. 12, No. 1.

Page	Line	Read
35	21	in the case of $SrCl_2$, however, for K_2SO_4, $MgCl_2$, $BaCl_2$, and Na_2SO_4
42	2	$e^{\sqrt{\alpha^2+k_2^2}x-\alpha x_1}$
43	equation (9)	$\Gamma=-\frac{c}{kT}\left[\frac{\epsilon^2}{4D}+\frac{\epsilon^2}{4D}\left(\frac{d^2+2da}{a^2}\right)-\frac{\epsilon^2}{2D'}\left(\frac{da+d^2}{a'^2}\right)\right]$
44	left hand side of equation (2)	$-\left(\frac{\partial\tau}{\partial c_1}\right)_{c_2}$

---

(4) *Z. physik. Chem.*, B, **8** (1930), 27.

Studies on Amino-Acids and Related Compounds. Part X. Electrolytic Oxidation of Aspartic Acid and Malonic Acid.*

By Yoshitaro TAKAYAMA and Saburo MIDUNO.

(Received June 19th, 1937.)

In a previous paper,(1) it was briefly described that the electrolytic oxidation of aspartic acid is rather more complicated in mechanism than that of glutamic acid, although the two compounds are analogous in their structure. In the present paper, the course of oxidation of aspartic acid will be further discussed in its details.

By oxidizing aspartic acid with hydrogen peroxide, Dakin(2) obtained formic acid, acetic acid and acetaldehyde together with a little malonic acid. Langheld(3) obtained acetaldehyde on heating aspartic acid with sodium hypochlorite, and considered malonic acid semialdehyde to be an intermediate product.

In the present experiments, aspartic acid was oxidized with lead peroxide anode in sulphuric acid solution under two different conditions in temperature, one at 35° and the other at about 100°. Malonic acid, which can be presumed to be one of the reaction products in the above oxidation, was also oxidized just in the same way.

In the experiment carried out at 35°, formic acid (10.8 mol%), malonic acid (1.4%), succinic acid (small quantity), ammonia and carbon dioxide were isolated as the oxidation products of aspartic acid. In the same condition, formic acid and carbon dioxide were isolated from malonic acid.

In the case of 100°, the aspect of reaction is somewhat different. Volatile products formed during the electrolysis were slowly distilled off at this temperature and further oxidation of these products was thus prevented. Acetaldehyde (4.1 mol%), formic acid (28.14%), succinic acid (0.36%), ammonia and carbon dioxide were isolated from the oxidation products of aspartic acid. Formic acid (35.2%) together with a little formaldehyde was isolated from those of malonic acid.(4)

---

* Translated by the authors from *J. Chem. Soc. Japan*, **56** (1935), 1460.

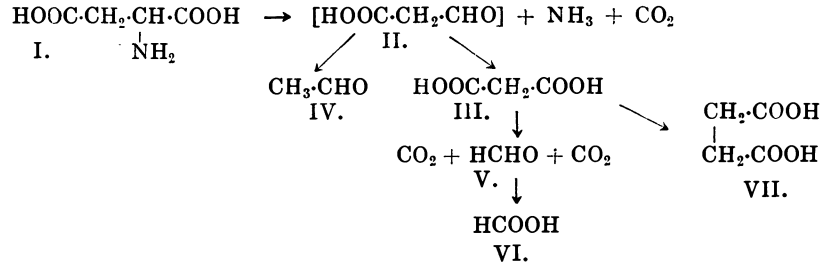
(1) Part VII, this Bulletin, **8** (1933), 215.

(2) H. D. Dakin, *J. Biol. Chem.*, **5** (1909), 409.

(3) K. L. Langheld, *Ber.*, **42** (1909), 2370.

(4) E. Durand, *Chem. Zentr.*, **1903**, II, 968.

From these results, the mechanism of the electrolytic oxidation of aspartic acid and malonic acid may be represented as follows.



The first stage of the oxidation of aspartic acid (I) is doubtless the formation of malonic acid semialdehyde (II). This unstable aldehyde immediately produces malonic acid (III) by further oxidation. Another change occurs without oxidation, and the aldehyde, at the temperature of 100°, losing carbon dioxide,[5] turns into acetaldehyde (IV). Further oxidation of malonic acid leads to the formation of formic acid (VI) through formaldehyde (V). While the formation of succinic acid (VII), as Fichter[6] pointed out, is due to the electrolytic oxidation of malonic acid.

Experimental.

I. Electrolytic oxidation of aspartic acid.

Aspartic acid (Kahlbaum) (Found: N, 10.52. Calculated for $C_4H_7O_4N$: N, 10.53%). Apparatus. In the case of 35°, an undivided cell, electrodes (4 cm. × 5 cm.): lead peroxide—lead. In the case of 98–99°, a cylindrical glass vessel (diameter 3 cm., height 12 cm.) provided with a rubber stopper carrying two electrodes, a thermometer and a dropping funnel. A delivery tube connecting to a receiver through a condenser was fused to the cell. During the electrolysis, the volatile oxidation products were distilled into the receiver which was cooled in ice. Electrodes: lead peroxide anode (6 cm. × 7.5 cm.), lead cathode (6 cm. × 4 cm.).

Experiment at 35°. Two cells (each of which contained 6.653 g. or 1/10 mol of aspartic acid in 120 c.c. of N H_2SO_4) were connected in series and immersed in a thermostat of 35°. C.D.: 2 amp./dm.^{2} Current quantities 8.146 F./mol. After the electrolysis the nitrogen distribution (NH_3-N/total N) in the electrolyzate was determined (73.9%) and the main bulk was subjected to steam distillation. In the distillate, no substance giving aldehydic reaction was found.

Volatile acid (formic acid). The distillate was titrated with N/10NaOH (106.5 c.c., 10.8 mol%). The resulting salt was converted into lead salt and analysed. Lead formate (Found: Pb, 69.32. Calculated for $(HCO_2)_2Pb$: Pb, 69.71%).

(5) A. Wohl, *Ber.*, **33** (1900), 2763.

(6) Fr. Fichter and J. Heer, *Helv. Chim. Acta*, **18** (1935), 704.

Non-volatile acids (*malonic and succinic acids*). The residue of the steam distillation was concentrated and extracted with ether. The first part of the ethereal extract yielded a little quantity of crystals on evaporation of the solvent. The crystalline acid, recrystallized from water, melted at 183°. It was identified as succinic acid by the determination of acid equivalent, mixed melting point test and colour reaction of resorcine—sulphuric acid test. The last part of the ethereal extract was evaporated, leaving an oil which slowly crystallized (0.07 g., 1.4 mol% as malonic acid). The crystals, when recrystallized from dilute alcohol, melted at 132–133° and no depression of melting point was observed when mixed with a pure sample of malonic acid. 0.0414 g. of the acid required 7.89 c.c. of N/10NaOH. Calculated for malonic acid ($C_3H_4O_4$): 7.96 c.c. The malonic acid was also identified as barium salt. The salt was dissolved in hot water and reprecipitated with alcohol. Barium malonate[7] (Found: Ba, 52.93. Calculated for $C_3H_2O_4Ba \cdot H_2O$: Ba, 53.38%).

Volatile base (*ammonia*). The residual solution of above extraction was distilled under reduced pressure with an excess of barium hydroxide. The volatile base was collected in dilute hydrochloric acid. Hydrochloride 1.4 g. Ammonium chloroplatinate (Found: Pt, 43.69. Calculated for $(NH_4)_2PtCl_6$: Pt, 43.96%).

After above treatments, the solution was freed from SO_4'' and $Ba^{\cdot\cdot}$ as usual. Crystalline acid (0.55 g.) was isolated which was identified to be unchanged aspartic acid by the ninhydrin reaction and determination of nitrogen (N, 10.48%).

Experiment at 98–99°. Aspartic acid (3.326 g. × 2, 1/20 mol) was dissolved in N H_2SO_4 (40 c.c. × 2) and electrolyzed in two undivided cells connected in series. The cells were placed in an air thermostat of 98–99°. C.D.: 2 amp./dm.^{2} Current quantities: 8.148 F./mol. The distribution of nitrogen of the electrolyzate: NH_3-N/total N = 73.93%. During the electrolysis, loss of water in the cell caused by distillation was compensated continuously through the dropping funnel.

Volatile substances (*acetaldehyde, formic acid*). Volatile acid, distilled during electrolysis, required 125.1 c.c. of N/10 NaOH; ditto, obtained by steam distillation after electrolysis, 13.9 c.c. of N/10 NaOH; total: 139.0 c.c. of N/10 NaOH, or 28.1 mol% to aspartic acid. The volatile acid was identified to be formic acid by the reaction with mercuric chloride and silver nitrate as well as by the analysis of its lead salt. Lead formate (Found: Pb, 69.47. Calculated for $(CHO_2)_2Pb$: Pb, 69.71%).

Amount of the aldehyde in the distillate was estimated by the titration of the neutralized distillate with bisulphite solution: 2.021 millimol (4.10 mol%) or 0.0890 g. of acetaldehyde. Acetaldehyde-*p*-nitrophenylhydrazone, m.p. 125–126° (Found: N, 23.56. Calculated for $C_8H_9N_3O_2$: N, 23.46%). It showed no depression of melting point when mixed with a specimen of *p*-nitrophenylhydrazone prepared from pure acetaldehyde (Kahlbaum).

Non-volatile acid (*succinic acid*). The residual solution was extracted thoroughly with ether. The ethereal solution was evaporated, leaving crystalline acid which was recrystallized from water. It melted at 183° and was identified as succinic acid by the mixed melting point test. 21 mg. (0.36 mol%) of succinic acid from 1/20 mol aspartic acid (current quantities: 6.17 F./mol; NH_3-N/total N = 41%). The presence of malonic acid could not be confirmed.

(7) C. Coutelle, *J. prakt. Chem.*, **73** (1906), 73.

Volatile base (*ammonia*). Hydrochloride 0.9 g. Chloroplatinate (Found: Pt, 43.79. Calculated for $(NH_4)_2PtCl_6$: Pt, 43.96%).

After the removal of the substances described above, unchanged aspartic acid (0.144 g.) was recovered from the residue (Found: N, 10.38. Calculated for $C_4H_7O_4N$: N, 10.53%).

II. **Electrolytic oxidation of Malonic Acid.**

Experiment at 35°. Malonic acid (Kahlbaum, 1.3005 g. × 2, 1/40 mol) was dissolved in N H_2SO_4 (120 c.c. × 2) and electrolyzed in two cells connected in series. C.D.: 2 amp./dm.^{2} Current quantities 3.07 F./mol. The electrolyzate was treated in the same manner as in the case of aspartic acid.

Volatile acid (*formic acid*). It required 16.70 c.c. of N/10 NaOH, corresponding to 13.4 mol%, and the acid was identified as formic acid by the reaction with silver nitrate and mercuric chloride and also by the crystalline form of the lead salt.

Experiment at 97°. Malonic acid (2.601 g. × 2, 1/20 mol) was dissolved in N H_2SO_4 (40 c.c. × 2) and electrolyzed under the same condition as in the case of aspartic acid. Current quantities: 8.25 F./mol.

Volatile substances (*formic acid, formaldehyde*). The acid, distilled during the electrolysis (A) required 103.16 c.c. of N/10 NaOH; ditto, obtained by steam distillation after electrolysis (B), 73.00 c.c. of N/10 NaOH; total: 176.16 c.c. of N/10 NaOH, 35.2 mol%. Lead formate (Found: Pb, 70.03% (A), 69.89% (B). Calculated for $(CHO_2)_2Pb$: Pb, 69.71%).

The volatile neutral part of the distillate gave fuchsin reaction and Rimini's reaction, and produced silver mirror. The formaldehyde was determined by the method of G. Romijn: 4.835 mg. (0.32 mol%).

Non-volatile acid (*succinic acid*). The residue of steam distillation was extracted with ether. The crystals (m.p. 183°, 7.1 mg.) obtained from the ethereal solution were identified as succinic acid by mixed melting point test, as well as by the colour reaction of resorcine-sulphuric acid test.

In conclusion, the authors wish to express their sincere thanks to Prof. K. Matsubara for kind inspection of this paper.

Chemical Laboratory, S. Suzuki (Ajinomoto) & Co., Ltd.,
Kawasaki, near Tokyo.

Studies on Amino-Acids and Related Compounds. Part XI. The Formation of Aldehydes by the Electrolytic Oxidation of α-Amino-Acids.*

By Yoshitaro TAKAYAMA, Takeshi HARADA, and Saburo MIDUNO.

(Received June 19th, 1937.)

In connection with biological oxidation, numerous attempts have been made to elucidate the mechanism of oxidation of α-amino-acids, and several compounds[1] (ketonic acid, imino-acid etc.) have been suggested as the intermediate products of their oxidation.

It was experimentally confirmed that by chemical oxidation amino-acids always produce the next lower aldehydes at the first stage of their oxidation. By electrolytic oxidation of amino-acids in sulphuric acid with platinum anodes, Fichter[2] obtained a little of aldehyde together with other oxidation products, and concluded that the aldehyde is the first oxidation product.

As described in Part VII,[3] when amino-acids were oxidized electrolytically with lead peroxide anode, the aldehyde was found in only a few case, and the author mentioned that aldehyde may be formed but soon further oxidized, and also that the course of reaction may proceed as follows:

$$\begin{array}{l} \mathrm{R{\cdot}CH{\cdot}COOH} \longrightarrow \mathrm{R{\cdot}CHO} + \mathrm{NH_3} + \mathrm{CO_2} \\ \quad\mathrm{NH_2}\ \downarrow \qquad\qquad\ \downarrow \\ \quad\text{Melanin} \qquad \mathrm{R{\cdot}COOH} \end{array}$$

where R denotes the radicals of aliphatic, aromatic and heterocyclic compounds.

In Part X,[4] it was proved that malonic acid semialdehyde was the first oxidation product of aspartic acid, and the present experiments were undertaken in the same manner to confirm the aldehyde formation from other amino-acids. By removing the oxidation products as quickly as possible from the electrolyzates to prevent further oxidation, aldehydes were successfully obtained in comparatively abundant quantity from four amino-acids.

---

* Translated by the authors from *J. Chem. Soc. Japan*, **57** (1936), 449.

(1) Bergel and Bolz, *Z. physiol. Chem.*, **215** (1933), 25; Bergel, *ibid.*, **233** (1934), 66.

(2) Fichter and Schmid, *Helv. Chim. Acta*, **3** (1920), 704.

(3) Takayama, this Bulletin, **8** (1933), 213.

(4) Takayama, this Bulletin, **12** (1937), 338.

On oxidizing glycine, alanine and leucine, Fichter[5] obtained formaldehyde, formic acid, ammonia, amines and carbon dioxide from glycine; acetaldehyde, acetic acid, formaldehyde, formic acid and ammonia, as well as carbon dioxide from alanine; isovaleraldehyde, isovaleric acid, isobutyric acid, acetone and acetic acid from leucine.

In the present experiments, alanine was oxidized in dilute sulphuric acid with lead peroxide anode at 35°, and acetic acid, ammonia and carbon dioxide were isolated, but no aldehyde was found. On the contrary, when alanine was oxidized in the same manner as aspartic acid at about 100°, the volatile oxidation products being distilled off during electrolysis, acetaldehyde (36.5%[6] as *p*-nitrophenylhydrazone) together with acetic acid (17.8%), ammonia and carbon dioxide was obtained.

Even in the experiment at 35°, when the volatile oxidation products were driven into absorption bottles by bubbling air through the cell, other conditions being the same, acetaldehyde could be abundantly separated in the form of *p*-nitrophenylhydrazone and dimedon-derivative. From this fact it was concluded that the absence of the aldehyde in the former experiments was due to further oxidation.

Glycine was oxidized in the same manner and formaldehyde (16.6%) together with formic acid (4.85%) was obtained. Ammonia, methyl-, dimethyl- and trimethyl-amines were isolated as volatile bases. These amines probably resulted from the action of formaldehyde with ammonia.[7] Likewise, valine gave isobutyraldehyde (32.1%) and isobutyric acid (27.5%) on its oxidation.

Fichter[5] mentioned that the electrolytic oxidation of leucine is vigorous and proceeds on even to acetone. This fact was observed also in Part VII.[3] Leucine was oxidized in the same way as alanine at about 100°, and the distillate thus obtained consisted of oily and aqueous layers. The former almost exclusively consisted of isovaleraldehyde (yield 53–56%). The latter contained isovaleric acid (yield 20–22%), but not the lower fatty acids.

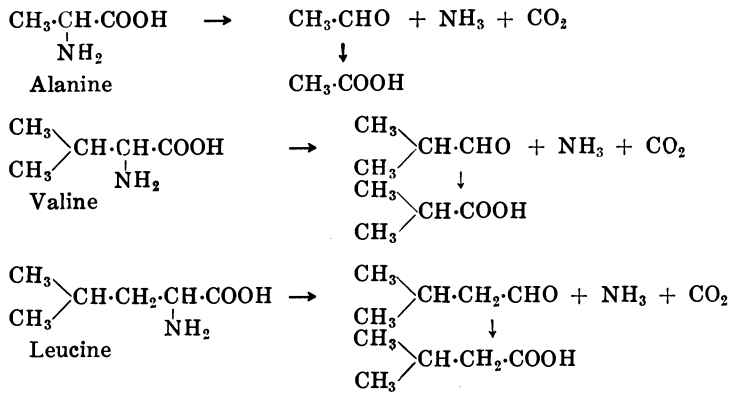
From these results, the mechanism of the electrolytic oxidation described above may be represented as follows:

$$\begin{array}{lcl} \mathrm{CH_2\cdot COOH} & \longrightarrow & \mathrm{H\cdot CHO + NH_3 + CO_2} \\ \mathrm{NH_2} & & \downarrow \\ \text{Glycine} & & \mathrm{H\cdot COOH} \end{array}$$

(5) Fichter and Kuhn, *Helv. Chim. Acta*, **7** (1924), 164.

(6) The percentages in this paper were expressed in molar per cent.

(7) Plöchl, *Ber.*, **21** (1888), 2117.



Thus, from the experiments on glycine, alanine, valine, leucine and aspartic acid,[4] it may be concluded that the first stage of the electrolytic oxidation of α-amino-acid is the aldehyde formation, and that the general expression described before will represent the course of the electrolytic oxidation of α-amino-acid. Some of these reactions may be applied to industrial purposes.[8]

Experimental.

I. Electrolytic oxidation of alanine.

Experiment at 35°. Alanine (Kahlbaum) (Found: N, 15.83. Calculated for $C_3H_7O_2N$: N, 15.73%). Alanine (8.911 g., 1/10 mol) was dissolved in N H_2SO_4 (120 c.c. × 2) and electrolyzed in two undivided cells connected in series, under following conditions. Cell: similar as described in Part IV.[9] Electrodes (4 cm. × 5 cm.): lead peroxide anode and lead cathode. C.D.: 2 amp./dm.^{2} Current quantities: 7.923 F./mol. The distribution of nitrogen in the electrolyzate after electrolysis: NH_3-N/total N = 96.6%.

During the electrolysis, evolved gas was led to ice-cooled washing bottles containing water to catch both acidic and neutral substances. The aqueous solution in the above bottle gave no aldehydic reaction. The electrolyzate was subjected to steam distillation. The distillate was separated into neutral and acidic parts. The former gave no aldehydic reaction, and the latter was converted into sodium salt.

Volatile acid (*acetic acid*). The sodium salt (4.34 g.) of volatile acid was identified as acetate by acetic ester test and by iodine-lanthanum reaction. Silver acetate (Found: Ag, 64.72. Calculated for $C_2H_3O_2Ag$: Ag, 64.64%).

Volatile base (*ammonia*). After the removal of the volatile acid from the electrolyzate, the residue was distilled with an excess of barium hydroxide under reduced pressure. The volatile base was converted into hydrochloride. It was identified as ammonia. Ammonium chloroplatinate (Found: Pt, 43.68. Calculated for $(NH_4)_2PtCl_6$: Pt, 43.96%).

(8) Japanese patent 110,640.
(9) This Bulletin, **8** (1933), 175.

Only unchanged alanine was recovered from the residue of the above base.

Experiment at 96°. Alanine (2.227 g., 1/40 mol) was dissolved in N H_2SO_4 (40 c.c.) and electrolyzed under the following conditions. Apparatus: the same apparatus as described in Part X.[4] During the electrolysis, the volatile oxidation product was distilled into a receiver which was cooled in ice. Temperature: 96°. Electrodes: lead peroxide anode (6 cm. × 7.5 cm.), lead cathode (6 cm. × 4 cm.). C.D.: 2 amp./dm.^{2} Current quantities: 8.09 F./mol. 3 volts. The distribution of nitrogen in the electrolyzate: NH_3-N/total N = 98.11%. The electrolyzate was treated in the same way as in the case of 35°.

Volatile neutral solution (acetaldehyde). Both the distillate caught in the ice-cooled water and the distillate obtained from the electrolyzate by steam distillation were combined, neutralized and separated into neutral and acidic parts by distillation. Neutral part gave fuchsin-sulphurous acid reaction and silver mirror. *p*-Nitrophenylhydrazone (1.6 g., 36.5%), recrystallized from carbon tetrachloride, gave m.p. 126°. It was identified as acetaldehyde-*p*-nitrophenylhydrazone (m.p. 126°) by mixed melting point test and by nitrogen determination (Found: N, 23.77. Calculated for $C_8H_9N_3O_2$: N, 23.46%).

Volatile acid (acetic acid). The acidic part described above required 43.70 c.c. of N/10 NaOH. That is 17.8% to decomposed alanine. Silver acetate (Found: Ag, 64.72. Calculated for $C_2H_3O_2Ag$: Ag, 64.64%).

Volatile base (ammonia). It was treated in the same manner as in the case of 35°. Hydrochloride 1.1 g. Chloroplatinate (Found: Pt, 43.67. Calculated for $(NH_4)_2PtCl_6$: Pt, 43.96%).

Unchanged alanine (0.05 g.) was recovered from the final residue.

Detection of acetaldehyde. Alanine (1.1375 g., 1/80 mol) was electrolyzed in N H_2SO_4 (120 c.c.) at 35°, bubbling air current between the electrodes in order to expel the volatile substances as quickly as possible. The volatile substances were caught in three washing bottles containing water. C.D.: 2 amp./dm.^{2} Current quantities: 7.203 F./mol. NH_3-N/total N = 47.52%. The solution of volatile substances caught in the washing bottles gave aldehydic reactions and yielded 0.318 g. of acetaldehyde (57.7%, estimated by the bisulphite method). *p*-Nitrophenylhydrazone was precipitated from the solution and recrystallized from dilute alcohol. M.p. 126°. It was identified as acetaldehyde-*p*-nitrophenyhydrazone.

In the same manner, alanine (1/80 mol) was electrolyzed with the current quantities of 6.02 F./mol. The distribution of nitrogen in the electrolyzate: NH_3-N/total N = 47.0%. In this case, the three washing bottles consisted of the one containing water (I) and the others containing dilute alcoholic solution (5%) of dimedon[10] (II, III). Acetaldehyde-*p*-nitrophenylhydrazone (0.04 g.) was obtained from the bottle I, m.p. 120° before and 126° after recrystallization. Acetaldehyde-dimedon was obtained from the bottle II (0.04 g., m.p. 139°) and the bottle III (0.09 g., m.p. 132–134°). The latter was recrystallized from dilute alcohol and it melted at 139°.

II. Electrolytic oxidation of glycine.

Glycine (Kahlbaum) (0.9381 g., 1/80 mol) was dissolved in N H_2SO_4 (30 c.c.) and

(10) Vorländer, *Z. anal. Chem.*, **77** (1929), 241.

electrolyzed under the following conditions. The apparatus is the same as in the case of alanine. Temperature: 99°. Electrodes: lead peroxide anode (2 cm. × 5 cm.), lead cathode (2 cm. × 5 cm.). C.D.: 2 amp./dm.^{2} Current quantities: 6.292 F./mol. The distribution of nitrogen in the electrolyzed solution: NH_3-N/total N = 69.36% (total nitrogen calculated from the glycine).

Volatile acid (*formic acid*). The acid in the distillate driven out during the electrolysis required 4.28 c.c. of 0.1011 N NaOH. The acid in the distillate obtained by the steam distillation required 1.72 c.c. of 0.1011 N NaOH. The total acid amounted to 0.6066 millimol (4.85% to glycine). The acid gave intensely the characteristic reactions of formic acid (the reduction of silver nitrate and mercuric chloride, and the reaction of Hottenroth).

Volatile neutral substance (*formaldehyde*). The above neutralized solution gave the characteristic formaldehyde reaction of fuchsin-sulphurous acid solution containing a little sulphuric acid (Grosse-Bohle). Formaldehyde was estimated by the Romijn's iodine method.[11] Yield 6.2 mg. (16.6% to glycine).

Volatile bases (*ammonia, methylamine, dimethylamine, trimethylamine*).[12] The residue, after the removal of volatile substances by steam distillation, was distilled with an excess of barium hydroxide under reduced pressure. The volatile bases were caught in hydrochloric acid. The very hygroscopic chlorides (1.4 g.) were obtained and treated with absolute alcohol to separate into the soluble and insoluble (0.85 g.) parts. The crystals obtained from the part insoluble in absolute alcohol were identified as ammonium chloride by the behaviour under poralisation microscope and by the analysis of its chloroplatinate (Found: Pt, 43.71. Calculated for $(NH_4)_2PtCl_6$: Pt, 43.96%).

After distilling off alcohol from the part soluble in absolute alcohol, the residual chloride was mixed with sea sand, dried and extracted with hot chloroform. The part insoluble in chloroform was treated with yellow mercuric oxide to make it free from ammonia by the method of François, and then converted into chloroplatinate (0.48 g.), which decomposed at 220°. It was identified as monomethylamine (Found: Pt, 41.56. Calculated for $(CH_3 \cdot NH_2)_2H_2PtCl_6$: Pt, 41.35%). Monomethylamine-picrolonate was obtained, which decomposed at 244°.

The part soluble in chloroform (dimethyl- and trimethyl-amines) was freed from chloroform, dissolved in water and cooled to 0°, from which a small quantity of crystals of trimethylamine periodide was precipitated by adding iodine–potassium iodide solution. The crystals were dissolved in sodium bisulphite solution, and distilled with steam after an addition of sodium hydroxide solution. The distillate containing trimethylamine required 0.30 c.c. of 0.1065 N H_2SO_4. The mother liquor of precipitate of trimethylamine periodide was distilled with steam after an addition of sodium bisulphite and sodium hydroxide. The distillate containing dimethylamine required 2.80 c.c. of 0.1065 N H_2SO_4. The chloroplatinate decomposed at 206° (Found: Pt, 39.57. Calculated for $[(CH_3)_2NH]_2H_2PtCl_6$: Pt, 39.04%).

Only unchanged glycine was recovered from the final residue.

III. **Electrolytic oxidation of valine.**

dl-Valine (Fränkel, 0.5855 g., 5 millimols) was electrolyzed in N H_2SO_4 (30 c.c.)

(11) G. Romijn, *Z. anal. Chem.*, **36** (1897), 19.
(12) Abderhalden, "Handbuch der Biologischen Arbeitsmethoden," Abt. I, **7**, 349, Berlin (1925); J. Bertheaume, *Compt. rend.*, **150** (1910), 1063, 1251.

at 99°. Electrodes: lead peroxide anode (4 cm. × 7.5 cm.), lead cathode (4 cm. × 4 cm.). C.D.: 2 amp./dm.^{2} Current quantities: 6.209 F./mol. NH_3-N/total N = 89.3%.

Volatile acid (*isobutyric acid*). The acid required 12.24 c.c. of N/10 NaOH. Yield 27.5% to valine.

Volatile neutral substance (*isobutyraldehyde*). Isobutyraldehyde-*p*-nitrophenylhydrazone (0.3328 g., 32.1% to total valine, 36% to decomposed valine), recrystallized from dilute alcohol gave m.p. 132° (Found: N, 20.33. Calculated for $C_{10}H_{13}N_3O_2$: N, 20.29%).

Volatile base (*ammonia*). Hydrochloride (0.2 g.). Ammonium chloroplatinate (Found: Pt, 43.81. Calculated for $(NH_4)_2PtCl_6$: Pt, 43.96%).

IV. Electrolytic oxidation of leucine.

Leucine (Found: N, 10.50. Calculated for $C_6H_{13}O_2N$: N, 10.69%). Cell: glass cylinder (diameter 7 cm., height 23 cm.) with a rubber stopper which carried two electrodes, a gas delivery tube, a thermometer and a dropping funnel. Electrodes: lead peroxide anode (10 cm. × 16 cm.), nickel cathode (10 cm. × 7 cm.).

Leucine (40 g.) was dissolved in N H_2SO_4 (400 c.c.) and electrolyzed at about 100° in the same manner as in the case of aspartic acid. During the electrolysis a solution of leucine (160 g.) in 4N H_2SO_4 (400 c.c.) was dropped into the cell from a dropping funnel. C.D.: 2 amp./dm.^{2} Current quantities: 6.98 F./mol. 3 volts. The distillate obtained during the electrolysis consisted of oily (83 g.) and aqueous layers. The former consisted almost solely of isovaleraldehyde. The latter was an aqueous solution of isovaleric acid (0.0331 equivalent) together with a little isovaleraldehyde. In the same manner, a comparatively large amount of leucine was electrolyzed, and the product was separated into the following four fractions (A, B, C, D):

(A) Acidic part of oily layer. Oil (3 kg.) was shaken with 2% sodium carbonate solution and separated into acidic and neutral parts. The acidic part was extracted with ether and dried over anhydrous sodium sulphate. After expelling off the ether, the residue was fractionated under reduced pressure as described in Table 1.

Table 1.

Fraction	Boiling point at 26 mm.	Distillate (g.)	Isovaleric acid (%) (determined by titration)	Ag % of the silver salt
1	up to 80°	0.9	—	—
2	80–88°	44.7	100.5	51.80
3	88–89°	25.2	100.2	51.78
4	89–91°	4.4	99.4	51.56
5	91°	0.7	99.4	51.51
		Total 75.9		

Calc. for $C_5H_9O_2Ag$: Ag, 51.63%

Anilides were prepared from the fractions 2 and 3, and recrystallized from dilute alcohol. Both melted at 110–111° (isovaleranilide m.p. 110–111°).

(B) Neutral part of oily layer. The neutral part obtained above was dried over anhydrous sodium sulphate, and fractionated as described in Table 2.

Table 2.

Fraction	Boiling point	Distillate (g.)	Specific gravity (23°)
1	75–90°	318	0.7945
2	90–100°	1592	0.7948
3	100–110°	239	0.8076
4	residue	(297)	0.8157

The greater part of this neutral part was aldehyde. Isovaleraldehyde-*p*-nitrophenylhydrazone (0.3 g.) was prepared from the fraction 1 and recrystallized from chloroform. It melted at 110–111°. The same nitrophenylhydrazone was obtained from the fractions 2 and 3; both melted at 110–111°. Isovaleraldehyde-*p*-nitrophenylhydrazone (Found: N, 19.12 (2), 19.14 (3). Calculated for $C_{11}H_{15}N_3O_2$: N, 19.00%).

As the residue (297 g.) in Table 2 contained 3.91% of acid, it was treated with dilute sodium carbonate solution to remove the acid, then dried and fractionated.

Table 3.

Fraction	Boiling point	Distillate (g.)	Fraction	Boiling point	Distillate (g.)
1	84–89°	0.6	6	129–130°	20.0
2	89–92°	2.7	7	130–132°	2.0
3	92–125°	1.6	8	132–135°	2.1
4	125–128°	28.3		residue	7.6
5	128–129°	38.0			Total 102.9

Fractions 1, 2 and 3 contained isovaleraldehyde. Fractions 4, 5 and 6 are now under investigation.

(C) Acidic part of aqueous layer. Aqueous solution (105 litres) was neutralized with sodium carbonate solution and distilled to remove the neutral part. The sodium salt thus obtained was decomposed with dilute sulphuric acid. The acid was dried and fractionated under reduced pressure.

Table 4.

Fraction	Boiling point at 29.4 mm.	Distillate (g.)	Isovaleric acid (%) (determined by titration)	Ag % of the silver salt
1	37–51°	27.7	—	—
2	51–89°	14.3	86.4	51.86
3	89–92°	202.1	101.1	51.94
4	92–95°	34.2	99.6	51.45

Calc. for $C_5H_9O_2Ag$: Ag, 51.63%

Isovaleranilide was prepared. M.p. 110–111°. The acids lower than isovaleric acid were not found.

(D) Neutral part of aqueous layer. The aqueous layer of the distillate (obtained during electrolysis) was neutralized with sodium carbonate solution and extracted with ether. The ethereal extract was dried as usual, and fractionated after removing the ether.

Table 5.

Fraction	Boiling point	Distillate (g.)	Fraction	Boiling point	Distillate (g.)
1	50–75°	2.1	5	105–115°	0.9
2	75–85°	1.7	6	115–125°	1.7
3	85–95°	35.7	7	125–127°	8.1
4	95–105°	1.3		residue	11.3
					Total 62.8

Fraction 3 gave isovaleraldehyde-*p*-nitrophenylhydrazone, m.p. 110–111° (Found: N, 18.98. Calculated for $C_{11}H_{15}N_3O_2$: N, 19.00%). The main portion of this neutral part consisted of isovaleraldehyde.

Volatile base (ammonia). Ammonium chloroplatinate (Found: Pt, 43.95. Calculated for $(NH_4)_2PtCl_6$: Pt, 43.96%).

In conclusion, the authors express their sincere thanks to Prof. K. Matsubara for kind inspection of this paper.

Chemical Laboratory, S. Suzuki (Ajinomoto) & Co., Ltd.,
Kawasaki, near Tokyo.

The Third Absorption Bands of Co-ordination Compounds. IV. [Co $dg_2' py$ Cl], [Co$(NH_3)_2(NO_2)_2 ox$]$NH_4 \cdot H_2O$ and [Co ox_3]$K_3 \cdot 3.5H_2O$.

By Shin KASHIMOTO and Masahisa KOBAYASHI.

(Received June 23rd, 1937.)

According to Y. Shibata[1] and R. Tsuchida,[2] the third absorption bands of co-ordination compounds in aqueous solutions are due to a pair or pairs of negative radicals co-ordinated in trans positions, and a number of cobaltic complex compounds which have such third absorption bands have been illustrated by those[1][2][3] and the present[2][3][4] authors. The couples of negative radicals hitherto proved to give rise to the third bands may be classified according to their nature: (a) two univalent

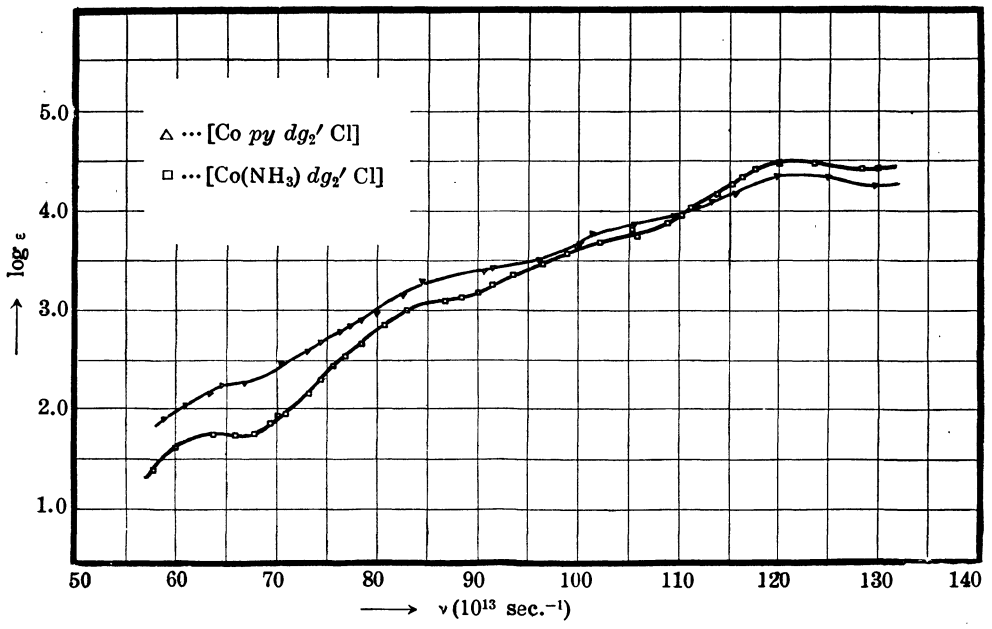


Fig. 1.

(1) Y. Shibata, *J. Chem. Soc. Japan*, **36** (1915), 1243.
(2) R. Tsuchida and S. Kashimoto, this Bulletin, **11** (1936), 785.
(3) R. Tsuchida and M. Kobayashi, this Bulletin, **12** (1937), 83.
(4) M. Kobayashi, A. Hagitani, and I. Mita, *J. Chem. Soc. Japan*, **58** (1937), 391.

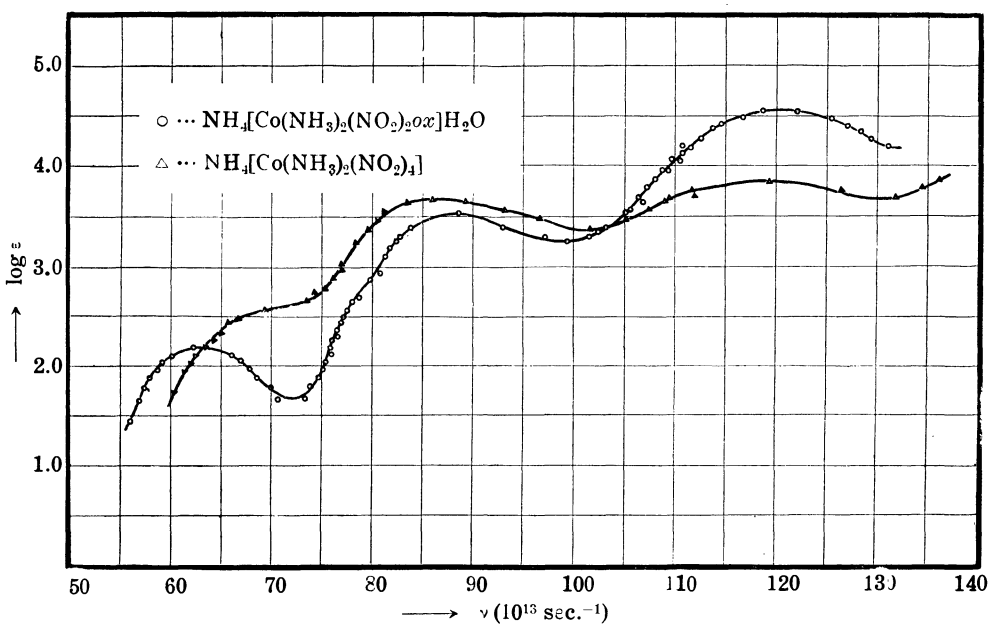

5.0
4.0
3.0
2.0
1.0
log ε
○ ··· $NH_4[Co(NH_3)_2(NO_2)_2ox]H_2O$
△ ··· $NH_4[Co(NH_3)_2(NO_2)_4]$
50
60
70
80
90
100
110
120
130
140
ν (10^{13} sec.$^{-1}$)

Fig. 2.

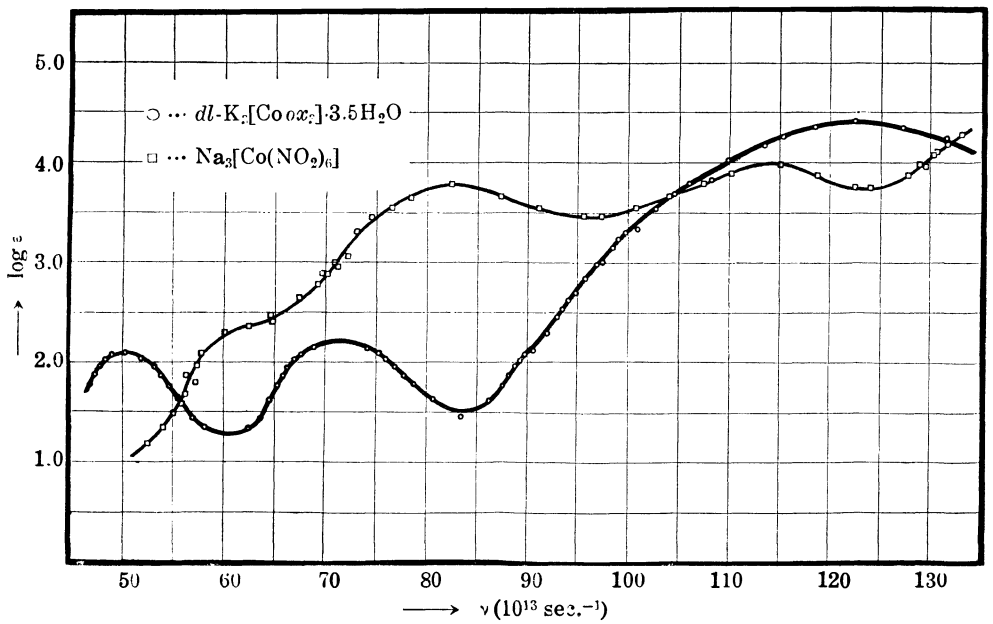

5.0
4.0
3.0
2.0
1.0
log ε
○ ··· *dl*-$K_3[Co\,ox_3]\cdot 3.5H_2O$
□ ··· $Na_3[Co(NO_2)_6]$
50
60
70
80
90
100
110
120
130
ν (10^{13} sec.$^{-1}$)

Fig. 3.

radicals, e.g., NO_2–NO_2, NO_2–Cl and Cl–Cl; and (b) two chelate univalent groups, e.g., dimethylglyoxime–dimethylglyoxime.

In the present paper another example of the class (b) is reported and moreover two other classes have been introduced: (c) one univalent and one bivalent radicals, i.e., NO_2–C_2O_4; and (d) two chelate bivalent radicals coupled with one valence each, i.e., C_2O_4–C_2O_4. In other words, it has been shown that a chelate bivalent radical such as oxalate can also give rise to the third band when it is coupled with a negative radical co-ordinated in trans position.

$[Co(NH_3)_2(NO_2)_2ox]NH_4 \cdot H_2O$[5] and $[Co\, ox_3]K_3 \cdot 3.5H_2O$[6] were prepared by the methods of Jörgensen and $[Co\, dg'_2\, py\, Cl]$[7], by that of Tschugaeff. The extinction coefficients of these compounds in aqueous solutions were determined for concentrations between 0.01 and 0.002 mol/l. and with varying thicknesses from 0.2 to 50 mm. The absorption curves are given in Fig. 1, 2, and 3.

The authors are indebted to Prof. R. Tsuchida for suggestion and advice on this work.

Chemical Department, Faculty of Science,
Imperial University of Osaka.

(5) S. M. Jörgensen, *Z. anorg. Chem.*, **11** (1896), 416. The symbol *ox* denotes an oxalate radical.

(6) *Ibid.*, **11** (1896), 440.

(7) L. Tschugaeff, *Ber.*, **40** (1907), 3503, 3505. The symbols *dg'* and *py* represent a dimethylglyoxime radical and a pyridine molecule respectively.

Some Cholesterol Derivatives.

By Yoshiyuki URUSHIBARA, Toshio ANDO, Hisakazu ARAKI, and Asaitirô OZAWA.

(Received July 5th, 1937.)

3-Phenyl-cholestadiene and 3-α-Naphthyl-cholestadiene. The reaction mixture of cholestenone (I) (1 mol) and phenyl magnesium bromide (3 mols) as Grignard's reagent was treated with dilute sulphuric acid. The product was freed from diphenyl and unchanged bromobenzene by steam distillation, and recrystallized from a mixture of acetone and methyl alcohol, colourless plates, m.p. 174–5° (corr.), $[\alpha]_D^{29°} = -133°$ (12.0 mg. in 1 c.c. $CHCl_3$ solution, $l = 1$ dm., $\alpha_D^{29°} = -1.60°$), absorption maxima in hexane, 235, 285 mμ. The substance was found to be a 3-phenyl-cholestadiene (III, R = C_6H_5) (Found: C, 89.60, 89.32; H, 11.76, 12.12; molecular weight by Rast's method, 449. Calculated for $C_{33}H_{48}$: C, 89.12; H, 10.88%; molecular weight, 445).(1)

Similarly, from cholestenone and α-naphthyl magnesium bromide a 3-α-naphthyl-cholestadiene (III, R = α-$C_{10}H_7$) was obtained in colourless prisms, m.p. 131–3° (corr.), $[\alpha]_D^{29°} = -49.7°$ (14.3 mg. in 1 c.c. $CHCl_3$ solution, l=1 dm., $\alpha_D^{29°} = -0.71°$), absorption maximum in hexane, 283 mμ (Found: C, 90.57, 90.95; H, 10.51, 10.51; molecular weight by Rast's method, 501. Calculated for $C_{37}H_{50}$: C, 89.80; H, 10.20%; molecular weight, 495).(1)

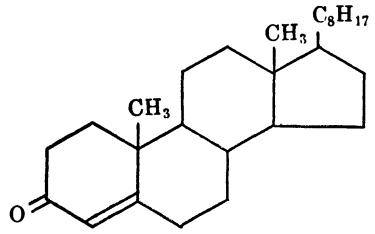
These cholestadiene derivatives distil unchanged in high vacuum. In Rosenheim test the phenyl compound gives a violetish blue colouration, while the α-naphthyl compound a greenish blue colouration. No exact evidence is yet available for the positions (as accepted in formula III) of the two double bonds in the cholestadiene part of these compounds, and the alternative formula III′ can not totally be excluded.

On evaporating a benzene solution (orange red) containing equi-molecular amounts of the α-naphthyl-cholestadiene and picric acid a picrate melting at 161–3° (corr.) was obtained in orange red crystals. The fusion curve of the two compounds also shows the existence of a molecular compound (1:1), giving a maximum (161°) at the molecular ratio 1:1(2).

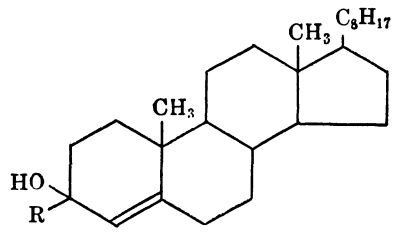
Tertiary alcohols as represented by formula II are considered to be the primary products of the Grignard reactions described above. But they

(1) Owing to the sultry weather of the rainy season when the experiments were carried out, the data of micro-analyses are not quite satisfactory.

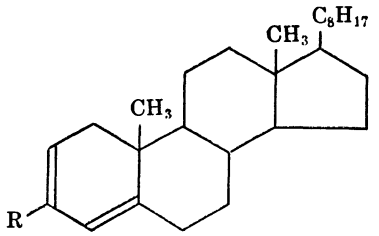
(2) The fusion curve was obtained by Dr. C. Shinomiya, to whom the authors' thanks are due.



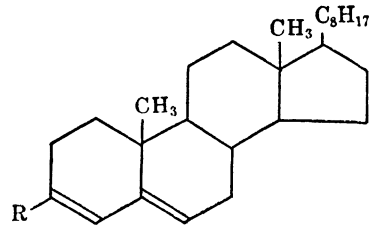
I



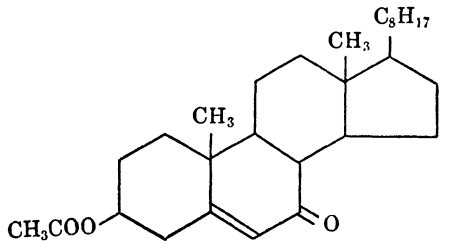
II



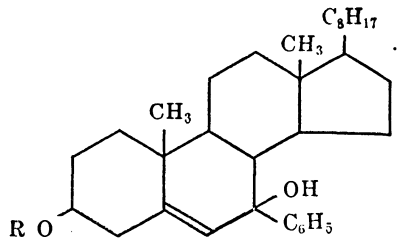
III



III′



IV



V

could not be isolated and dehydration took place readily under the conditions of the experiments, giving rise to the cholestadiene derivatives (III). Such easy dehydration of tertiary alcohols is sometimes the case in Grignard reactions. To give an example in the sterol series, 7-methylene-cholesterol is formed in the reaction of methyl magnesium iodide with 7-keto-cholesteryl acetate[3][4]. The ready formation of the cholestadiene derivatives (III) may be quite natural in view of the fact that the tertiary alcohols (II) are 3-aryl derivatives of either allocholesterol or *epi*-allocholesterol, because both

(3) B. Bann, I. M. Heilbron, and F. S. Spring, *J. Chem. Soc.*, **1936**, 1274.
(4) S. Weinhouse and M. S. Kharasch, *J. Org. Chem.*, **1** (1936-7), 490.

allocholesterol and *epi*-allocholesterol lose easily water[5], and the tertiary nature of the hydroxyl group would facilitate dehydration.

7-Hydroxy-7-phenyl-cholesterol and Its Benzoate. Action of phenyl magnesium bromide (4 mols) on 7-keto-cholesteryl acetate (IV) (1 mol), followed by decomposition by aqueous ammonium chloride and recrystallization from benzene, yielded 7-hydroxy-7-phenyl-cholesterol (V, R = H) in colourless needles, m.p. 150.5–151.5° (corr.), $[\alpha]_D^{29°} = -137°$ (18.1 mg. in 1 c.c. $CHCl_3$ solution, $l = 1$ dm., $\alpha_D^{29°} = -2.48°$). Its monobenzoate (V, R = C_6H_5CO), prepared by the action of benzoyl chloride and pyridine, was recrystallized from acetone in colourless needles, m.p. 205.5–206° (corr.), $[\alpha]_D^{29°} = -79.1°$ (21.5 mg. in 1 c.c. $CHCl_3$ solution, $l = 1$ dm., $\alpha_D^{29°} = -1.70°$) (Found : C, 82.31 ; H, 10.12. Calculated for $C_{40}H_{54}O_3$: C, 82.41 ; H, 9.35%).

When the benzoate was heated in high vacuum (0.0005 mm.), a small amount of benzoic acid sublimed (about 200°), but the most part (90%) of the material distilled unchanged (up to 280°). On heating the benzoate under a higher pressure (200–250°, 0.18 mm.), a greater amount of benzoic acid sublimed, but from the residue the unchanged material only was isolated. Thus it seems that 7-hydroxy-7-phenyl-cholesteryl benzoate loses practically neither water nor benzoic acid on heating in vacuum. S. Weinhouse and M.S. Kharasch[4] also have described 7-hydroxy-7-phenyl-cholesterol, which they could not dehydrate. Informations so far obtained show that elimination of water from the tertiary hydroxyl group at carbon atom 7 in cholesterol derivatives is either effected with the formation of an exocyclic double linkage or not effected at all[3][4][6]. 7-Hydroxy-7-phenyl-cholesterol can not afford the formation of an exocyclic double linkage, and must necessarily resist dehydration.

The authors express their hearty thanks to Mr. Yasohachi Yamaguchi of Teikokusha Co. for his kind support of this work.

Chemical Institute, Faculty of Science,
Imperial University of Tokyo.

---

(5) R. Schoenheimer and E. A. Evans, Jr., *J. Biol. Chem.*, **114** (1936), 567.
(6) E. R. H. Jones and F. S. Spring, *J. Chem. Soc.*, **1937**, 302.

The Effect of Oxygen on the Addition of Bromine to Cinnamic Acid in Carbon Tetrachloride.

By Yoshiyuki URUSHIBARA and Matsuji TAKEBAYASHI.

(Received July 5th, 1937.)

The inhibiting effect of oxygen on the addition of bromine to cinnamic acid in carbon tetrachloride was first observed by W. H. Bauer and F. Daniels.[1] They found that bromine and cinnamic acid combine rapidly in the dark at room temperature when dissolved oxygen has been removed from the solution, and when the oxygen has not been removed, the reaction is very slow in the dark, but it proceeds rapidly in the light.

The present paper records the results of somewhat quantitative experiments on the effect of oxygen on the addition of bromine to cinnamic acid in carbon tetrachloride. Special care was taken in purifying the materials, viz. cinnamic acid, bromine, and carbon tetrachloride, and in excluding moisture. A solution of 1 millimol (0.1480 g.) of cinnamic acid in 30 c.c. of carbon tetrachloride was placed in a reaction tube of Pyrex glass with a capacity of 140 c.c. A sealed small glass bulb containing a slight excess of bromine was slipped into the tube. The tube was cooled in liquid air, evacuated, and sealed off with or without admission of oxygen. The contents were melted and mixed well by shaking. The breaking of the bromine bulb usually took place on freezing the contents of the reaction tube in liquid air, otherwise effected by shaking. The tube was then placed in the dark at room temperature for 22 hours. An excess of aqueous potassium iodide was added to the reaction mixture, and the liberated iodine was titrated with N/10 sodium thiosulphate. The extent of addition (in percentage to the cinnamic acid used) was determined from the amount of bromine consumed. The results are summarized in Table 1.

Each one group of experiments were carried out simultaneously, and thus under the same conditions. According to the measurements of the solubility of oxygen in carbon tetrachloride by J. Horiuti[2] the ratio of the concentration of oxygen dissolved in carbon tetrachloride to that in the gaseous phase is 0.3 at ordinary temperature. The partial pressure of oxygen in the tube at respective temperature, and the amount of oxygen

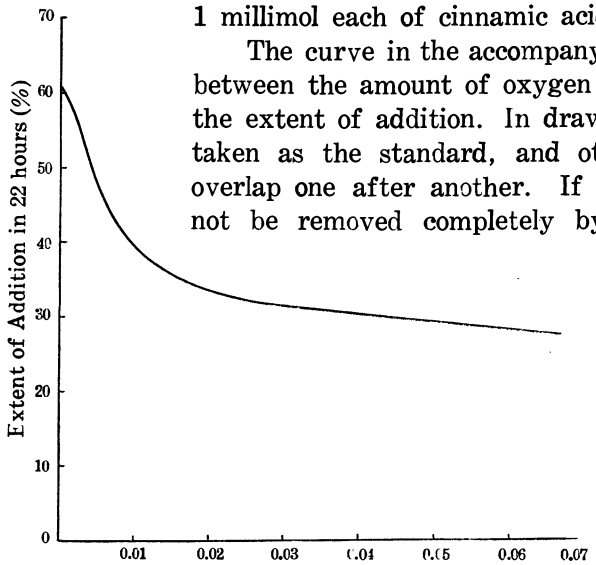
(1) *J. Am. Chem. Soc.*, **56** (1934). 2014.

(2) *Sci. Papers Inst. Phys. Chem. Research* (Tokyo), **17** (1931), 213.

Table 1.

Group of exp.	No. of exp.	Bromine (g.)	Oxygen						Extent of addition (%)
			Vol. (c.c.)	Temp. (°C.)	Pres. (mm.)	Vol. n.p.t. (c.c.)	Partial pressure in the tube (mm.)	Amount dissolved in CCl_4 solution (millimol)	
I	1	0.1758	0			0	0	0	60.6
	2	0.1778	0.5	22	757.8	0.46	3.2	0.0016	57.8
	3	0.1800	1.0	22	757.8	0.92	6.4	0.0031	53.4
	4	0.1849	2.0	22	757.8	1.85	13	0.0062	44.9
II	5	0.1854	0			0	0	0	56.6
	6	0.2011	2.0	21	757.0	1.85	13	0.0062	40.7
	7	0.2004	5.0	21	757.0	4.63	32	0.016	31.2
III	8	0.2170	5.0	21	756.7	4.62	32	0.016	32.4
	9	0.2151	10.0	21	756.7	9.25	64	0.031	28.5
IV	10	0.2035	10.0	20	757.3	9.28	64	0.031	33.1
	11	0.2033	20.0	20	757.3	18.57	127	0.063	29.4

dissolved in the carbon tetrachloride solution were calculated on the assumption that this ratio holds in the carbon tetrachloride solution containing 1 millimol each of cinnamic acid and bromine in 30 c.c.



Milli-mols of Oxygen in 30 c.c. CCl_4 Solution containing 1 millimol of Cinnamic acid.

The curve in the accompanying figure shows the relation between the amount of oxygen present in the solution and the extent of addition. In drawing this curve Group I was taken as the standard, and others were shifted so as to overlap one after another. If the dissolved oxygen could not be removed completely by the process of evacuation under cooling in liquid air, as it seems possible from the observation of Bauer and Daniels that the addition was so rapid in absence of oxygen that the rate of reaction could not be measured conveniently, the ordinate must be displaced as much to the left.

In Table 2 addition in vacuum with 1 millimol of

cinnamic acid in 30 c.c. of carbon tetrachloride (exp. 12 and 14) is compared with that on a half scale but in a tube of the same dimensions (exp. 13 and 15). There is no significant difference in the extent of addition. The last group of experiments recorded in Table 3 shows that the shaking of the tube during the reaction had practically no influence on the extent of addition. (The greater values of the extent of addition for the last group of experiments were probably caused by the higher room temperature.) These results seem to indicate that the addition of bromine to cinnamic acid in carbon tetrachloride under the conditions as described above is a homogeneous reaction.

Table 2. (Reaction time, 22 hours.)

Group of exp.	No. of exp.	Cinnamic acid (millimol)	CCl_4 (c.c.)	Bromine (g.)	Extent of addition (%)
V	12	1	30	0.1924	61.8
	13	0.5	15	0.0807	56.7
VI	14	1	30	0.1912	62.1
	15	0.5	15	0.0790	65.5

Table 3. (Cinnamic acid, 1 millimol; CCl_4, 30 c.c.; Reaction time, 22 hours.)

Group of exp.	No. of exp.	Bromine	Extent of addition (%)	Remarks
VII	16	0.1779	75.72	The tube was shaken during the reaction.
	17	0.1768	75.28	The tube was not shaken

No detectable peroxide was formed from cinnamic acid and oxygen in carbon tetrachloride even in bright diffused light. This fact makes it very probable that the effect of oxygen on the addition of bromine to cinnamic acid in carbon tetrachloride is caused by the action of molecular oxygen.

The authors wish to express their hearty thanks to Nippon Gakujutsu Shinkokwai (the Japan Society for the Promotion of Scientific Research) for a grant.

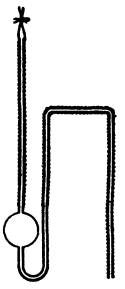
Chemical Institute, Faculty of Science,
Imperial University of Tokyo.

Effect of Water on the Potential of the Glass Electrode.[1]

By Hisato YOSHIMURA.

(Received July 5th, 1937.)

Since Haber and Kremensiewicz[2] set forth the hypothesis that the water absorbed by the glass membrane of a glass electrode transforms it into a hydrogen electrode, its importance has been in general implicitly recognized. No experimental studies on this point have been reported, however, except that of Laug[3], who found that, on drying the surface of one side of the electrode membrane, the hydrogen electrode function of that surface decreased and its potential level against that of the other side rose. He attributed the phenomenon to the decreased permeability of the hydrogen ion through the glass phase. The interrelation between the two facts was proved, however, neither theoretically nor experimentally. The aim of the present study is directed to these points.



The dotted line indicates the paraffin layer. The bulb part of the electrode is made either of MacInnes glass or of commercial glass, while the capillary support is always of commercial soft glass. On the details of the use of this electrode, see the previous report[4].

Fig. 1.

Experimental.

Glass electrodes made of MacInnes glass and also of commercial glass were used, the form of which is sketched in Fig. 1. The potential was measured at 25°C. with a Lindemann electrometer. The sign of the value given in this paper refers to the inside of the bulb of the electrode which serves as the electrode membrane.

(a) Experiments on the effect of submerging the glass electrode in water. After a glass electrode was prepared, it was preserved in water. Measurements of its asymmetry potential (usually in a buffer solution of *p*H 7.3), the hydrogen electrode function, the error of glass electrode

---

(1) Studies on the Nature of the Glass Electrode Potential. II. I: *J. Biochem.* (Japan), **23** (1936), 91.

(2) Haber and Kremensiewicz, *Z. physik. Chem.*, **67** (1909), 385.

(3) Laug, *J. Am. Chem. Soc.*, **56** (1934), 1034.

(4) Yoshimura, *J. Biochem.* (Japan), **21** (1935), 335.

(defined by Dole[5]) in an alkaline solution of pH 10.9 (its sodium ion concentration being 0.1 mol), and the degree of corrosion of the glass membrane due to water were repeated daily. The hydrogen electrode function, here stated, is the change in the potential of a glass electrode corresponding to the unit change of pH of the solution, and is expressed by $\Delta E/\Delta p$H. Estimations were made over a range of pH 2–7, where a rectilinear relationship exists between the potential and the pH. The degree of corrosion of the glass membrane due to water was examined by the following way: a 0.0001 N hydrochloric acid solution containing 0.001% methyl red was placed in the bulb of the glass electrode including a small air bubble. The electrode being rotated in a bath of 50°C., the time required for the fading of the red colour in the solution was measured. Measurements, being repeated on different days, indicate the relative degrees of corrosion by water on those days.

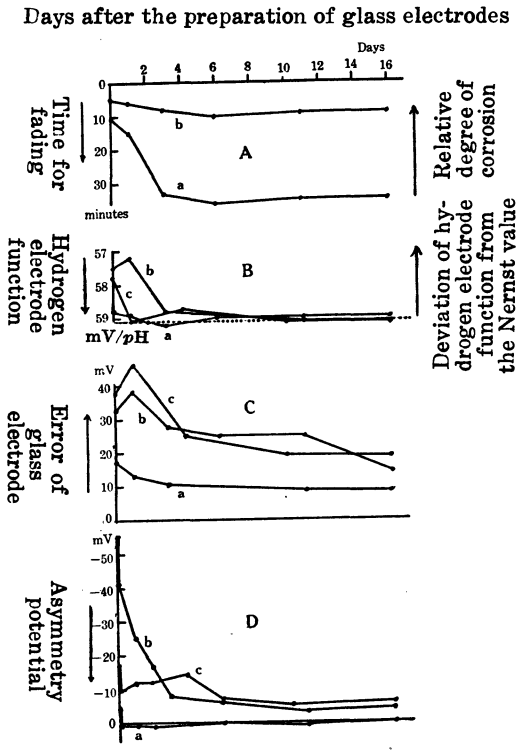


Fig. 2.

The above-mentioned examinations were carried out on a number of electrodes, examples of which are given in Fig. 2. The results of two electrodes made of MacInnes glass are given by curves a and b and those of an electrode of commercial glass by curves c. As is seen in A, the corrosion of the glass membrane decreased day by day and finally it attained a constant value after being submerged for about a week, when an equilibrium between the glass surface and the water was presumably attained. Similarly, the deviation of $\Delta E/\Delta p$H from the Nernst value (indicated by the dotted line) (B) and the error of glass electrode in the alkaline solution (C)

(5) Dole, *J. Am. Chem. Soc.*, **53** (1931), 4260.

decreased day by day and the asymmetry potential (D) approached zero from a negative value, each finally attaining a constant value.

The time required for the potential equilibration after the electrode was mounted in the solution was shortened by first submerging the electrode in water after its preparation.

(b) Experiments on the effect of drying the surface of electrode membrane. Further to clarify the relationship of water to the potential of a glass electrode, the effect of drying one surface of the electrode membrane was examined. The surface was dried either by passing through hot air (1) or by means of a desiccator (2).

(1) A commercial glass electrode which had attained the equilibrium with water was dried on one side, either inner or outer, by passing hot air of ca. 180°C. through or over it for about 6 hours, while the other side was prevented from drying by passing vapour or hot water through or over it. The asymmetry potential and $\Delta E/\Delta p$H were examined before and shortly after drying. After the examinations were completed, the electrode was preserved in water and the electromotive reactions of the electrode were observed to determine the effect of the immersion on the potential. An example of the results is given in Fig. 3, where A gives the asymmetry potential and B gives $\Delta E/\Delta p$H of the dried surface. The shadowed range represents the time of drying. The effect of drying the inner surface of an electrode is represented by continuous lines (electrode 1), while that of drying the outer surface of another electrode is shown in broken lines (electrodes 2 and 3). As is seen in the figure, drying changes the asymmetry potential by raising the potential level of the side of the dried surface, while it decreases $\Delta E/\Delta p$H on the same side. When the electrode was submerged in water after this drying experiment, this effect on the potential was reversed. Though it is doubtful whether the effect of the passage of hot air on the potential is completely due to the evaporation of water from the glass

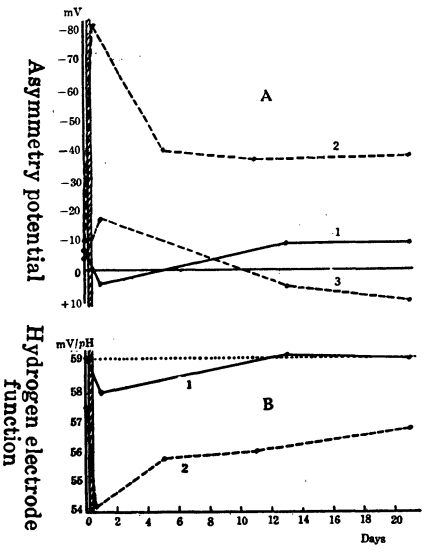


Fig. 3.

surface, drying seems to play an important rôle, as the reverse effect was produced by submerging it in water.

(2) The electrode which was equilibrated in water being connected with a sulphuric acid desiccator, its inner surface was dried for 8 days, while the outer surface was kept submerged in water. The asymmetry potential (in a buffer solution of *p*H 2.8) and $\Delta E/\Delta p$H before and after drying are given in Table 1, where m refers an electrode of MacInnes glass, and c that of a commercial glass electrode. The effect of drying on the asymmetry potential was similar to that found in the experiment (1), while the change in $\Delta E/\Delta p$H by drying was minute in this case.

Table 1.

			Before desiccation	After desiccation
Asymmetry potential		m	−11.5 mV	− 1.2 mV
		c	−27.4	− 5.8
$\frac{\Delta E}{\Delta p\text{H}}$	Inner surface	m	58.7 $\frac{\text{mV}}{p\text{H}}$	58.3 $\frac{\text{mV}}{p\text{H}}$
		c	58.7	57.3
	Outer surface	m	57.6	58.0
		c	57.5	58.2

The attainment of the equilibrated potential after the electrode was mounted in the solution was retarded if measured shortly after the electrode was dried. But when the electrode was submerged in water for a few days, this effect disappeared.

Discussion.

From the above experimental results, it is clear that, water being removed from one surface of the electrode membrane, the $\Delta E/\Delta p$H on that surface is decreased and the potential level is raised on that side against the other, thus causing a change of the asymmetry potential. These changes in the electromotive effect of the glass membrane can be reversed by submerging the electrode in water, probably because water is absorbed in the glass surface. The asymmetry potential is created by the differences in electromotive effect between the surfaces of the electrode

membrane. Thus the change in the asymmetry potential from a negative value to zero when a freshly prepared electrode is submerged in water (refer to D of Fig. 2) is due to the fact that the effect of water on the outer surface is more severe than that on the inner surface. Thereby the electromotive effect of both surfaces is equalized by water.

While the reason for this difference between the inner and the outer surfaces is a matter for further study, the correlation between the asymmetry potential and $\Delta E/\Delta p\mathrm{H}$ can be explained qualitatively by three current important theories of the glass electrode: Dole's statistical mechanical theory[6], the partition potential theory by Gross and Halpern[7], and the ion exchange theory of Horovitz[8], all belonging to the phase boundary theory. No experimental results have yet been produced to support one against the other two, so that these three theories are taken into consideration.

In all of these theories, the phase boundary potential E is given by

$$E = -\frac{RT}{F}\ln C_{\mathrm{H}}\left\{1+\frac{C_{\mathrm{Na}}}{C_{\mathrm{H}}}\frac{Y}{X}\right\}^{n} - \frac{RT}{F}\ln X \qquad (1),$$

E being positive when the potential level of the solution is high against that of the glass phase. C_{H} is the hydrogen ion concentration (strictly the hydrogen ion activity) of the solution and C_{Na} the sodium ion concentration (the cation of the salt in the solution being assumed to be Na^{+}). n is 1 in both Dole's and Horovitz's theories, and is ½ in Gross and Halpern's theory. X and Y are the constants which depend upon the nature of glass or, strictly speaking, upon that of the membrane surface, and are given as follows:

$$X = \beta_{\mathrm{H}} e^{\frac{Q_{\mathrm{H}}}{RT}}, \quad Y = \beta_{\mathrm{Na}} e^{\frac{Q_{\mathrm{Na}}}{RT}} \quad \text{(Dole)},$$

$$X = \frac{K_4 M_4}{K_1 L_4}\sqrt{\frac{L_1}{M_1}} \times \text{const.}, \quad Y = \sqrt{\frac{M_1}{L_1}} \times \text{const.}$$

(Gross and Halpern),

$$X = \frac{u_{\mathrm{H}}}{aK_{\mathrm{H}}u_{\mathrm{Na}}}, \quad Y = \frac{1}{aK_{\mathrm{Na}}} \quad \text{(Horovitz)}.$$

---

(6) Dole, *J. Chem. Phys.*, **2** (1934), 862.

(7) Gross and Halpern, *Z. physik. Chem.*, **115** (1925), 54; *J. Chem. Phys.*, **2** (1934), 136.

(8) Horovitz, *Nature*, **127** (1931), 440.

Various symbols in these equations are the constants which are independent of one another. On their physical meanings, refer to the original papers.

From the equation (1), the asymmetry potential e_g and the hydrogen electrode function $\Delta E/\Delta p\mathrm{H}$ are given as follows:

$$e_g = \frac{RT}{F} \ln \left\{ \frac{1+\frac{C_{Na}}{C_H}\frac{Y_o}{X_o}}{1+\frac{C_{Na}}{C_H}\frac{Y_i}{X_i}} \right\}^n + \frac{RT}{F} \ln \frac{X_o}{X_i} \qquad (2),$$

where the suffixes i and o refer to the inner and the outer surfaces of the electrode membrane respectively, and

$$\frac{\Delta E}{\Delta p\mathrm{H}} = \frac{R'T}{F}\left\{1-\frac{\log\left(1+\frac{C_{Na}}{C_H}\frac{Y}{X}\right)^n}{\Delta p\mathrm{H}}\right\} \qquad (3),$$

where R' represents $2.303R$.

Before using these equations to explain the experimental results, the two following points should be discussed: (i) It is noticeable that, according to these theories, the only way to explain the deviation of $\Delta E/\Delta p\mathrm{H}$ from the theoretical value ($R'T/F$) is by the cation effect, i.e. by the term $\frac{C_{Na}}{C_H}\frac{Y}{X}$ in the equation (3). This term is generally thought to be negligible in solutions of pH lower than 8. Moreover, it is a function of C_H and C_{Na}. The deviation of the experimental values of $\Delta E/\Delta p\mathrm{H}$ from the theoretical is, however, approximately a constant at least in the range of pH 2–8. Therefore, it is a matter of question whether or not the deviation of $\Delta E/\Delta p\mathrm{H}$ from the theoretical value can be explained by the cation effect. From these points, Kahler and DeEds[9] offered the deviation film theory apart from the cation effect to explain the deviation of $\Delta E/\Delta p\mathrm{H}$. This theory has, however, already been denied by the present author[1] who maintains that the magnitude of the hydrogen electrode function is closely connected with the property of the glass surface. Then the question being left to further study, the equation (3) will be adopted provisionally in the present discussion to explain the deviation of $\Delta E/\Delta p\mathrm{H}$ from the theoretical value. (ii) All these theoretically derived equations refer to the equilibrated potential, while

(9) Kahler and DeEds, *J. Am. Chem. Soc.*, **53** (1931), 2998.

the potential observed experimentally showed the diurnal change. Regarding the observed potential be in a state of the quasi-equilibrium, these equations can be said to apply, and the diurnal change of the potential can be explained by the change in the constants in the equations.

Now, from the equations (2) and (3), it is clear that when the constant X of one surface of the electrode membrane is decreased $\Delta E/\Delta p\mathrm{H}$ on that surface decreases and the potential level on that side rises, causing the change of the asymmetry potential, and vice versa. The fact is corroborated by the experiments.

From the equation (1), the error of the glass electrode in an alkaline solution (designated by Δ) is given by the equation

$$\Delta = \frac{RT}{F} \ln \left\{1+\frac{C_{\mathrm{Na}}}{C_{\mathrm{H}}} \frac{Y}{X}\right\}^{n} \qquad (4).$$

Thus the decrease in Δ is accompanied by the increase in $\Delta E/\Delta p\mathrm{H}$. This is the fact which was found in most cases of the experiment (a).

As the level of the potential on one side of the membrane falls and $\Delta E/\Delta p\mathrm{H}$ increases when the surface of the membrane on that side is corroded with water, it must be that the constant X is increased by water corrosion, and decreased by drying. The physical meaning of this change in X can be explained separately by each of the above-mentioned three theories. For example, according to Gross and Halpern's theory, the increase of X by water corrosion can be explained by the increase in the partition coefficient of water in the glass phase; and according to Dole's theory, it is explained by the decrease in energy of the hydrogen ion on the lowest quantum level in the glass phase or by the increase in that of sodium ion.

Thus we can explain qualitatively our experimental findings by current theories of the glass electrode. It is impossible, however, to say which of the three theories is correct.

Summary.

(1) When one surface of the membrane of a glass electrode is dried, the asymmetry potential is raised on that side against the other side, and the hydrogen electrode function is decreased. This membrane being kept submerged in water, the reverse effect is observed. These facts can be explained qualitatively by any of the latest theories concerning the glass electrode.

(2) The significance of preserving the glass electrode in water after its preparation, which is a generally accepted procedure in the use of the glass electrode, can be stated as follows: (i) It makes the hydrogen electrode function approach Nernst's theoretical value, probably decreasing the cation effect on the potential of the glass electrode, (ii) it decreases the asymmetry potential, equalizing the electromotive nature of both the inner and outer surfaces of the electrode membrane, and (iii) it facilitates the equilibration of the potential after the electrode is mounted in a solution for test.

The author expresses his cordial thanks to Prof. Dr. I. Sawai of the Institute of Industrial Chemistry for his kind advices, and also to the Hattori-Hokokwai for a grant.

Institute of Physiology, Faculty of Medicine,
Imperial University of Kyoto.

On the Silver Oxide Positive of the Alkaline Accumulator. II.

By Kyôji KINOSHITA.

(Received July 15th, 1937.)

The author reported some experimental investigations on the general features of the silver oxide positives of alkaline accumulator.[1] The present report describes the further experiments, the detailed description[2] being published in Japanese.

In the previous paper, the author pointed out that the chemical reactions corresponding to the discharge of the positives are

$$Ag_2O_2 \rightarrow Ag_2O + \frac{1}{2}O_2 \rightarrow 2Ag + \frac{1}{2}O_2 \qquad (1).$$

It has also been found that the coefficient of utility of the active material and the capacity of the positive electrode are higher than those of the

(1) Kinoshita, this Bulletin, **12** (1937), 164.
(2) Kinoshita, *Toyoda Kenkyu Iho*, **4** (1936), 116-141.

lead peroxide positive of the lead acid cell. In order to bring out the cause of these special features of the silver positive, further experiments have been done, especially on the charging characteristic of the positive.

Experimental. (a) Amount of Oxygen Fixed in the Active Material, and the Discharge Capacity of the Positive. Silver oxide positives were prepared by applying silver oxide paste to the grid as stated in the previous paper. The grid was made of iron plated with silver, the size being about $5.8 \times 1.6 \times 0.25$ cm. "Formation" of the positives was continued for about 17–21 hours by a current of 60 milliamperes.

Fig. 1 shows the construction of the cell. A is a glass vessel of H-shape, P a silver oxide electrode, and N a negative electrode of the "Nife" accumulator. The amount of gas evolved at the positive P was measured by collecting in a glass cylinder G through the tube B. The total amount of electricity, K', passed for charging the cell was measured by means of a copper coulombmeter connected in series to the cell. Nine cycles of discharges were made on the cell. The results are summarized in Table 1.

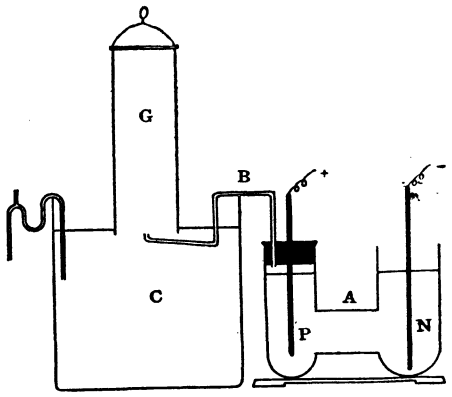


Fig. 1.

Table 1. Comparison of K and C.

Number of cycle	Total amount of elect. used for charging (K') (A.H.)	Volume of gas evolved (0°C., 1 atm.) (c.c.)	Amount of elect. as a loss (K'') (A.H.)	$K = K' - K''$ (A.H.)	Discharge capacity (C) (A.H.)
1					2.080
2	9.30	1506	7.21	2.09	2.030
3	7.80				2.115
4	3.17	394	1.89	1.28	1.260
5	1.89	170	0.81	1.08	1.065
6	1.60	93.7	0.45	1.15	1.149
7	1.72	105	0.50	1.22	1.200
8	1.80	140	0.67	1.13	1.125
9	1.69	122	0.58	1.11	0.949

In the 3rd and 4th columns of the table, the total volume of the gas evolved at P and the amount of electricity (K'') corresponding to the volume of gas are tabulated respectively. The values $K = K' - K''$ in the table are considered to represent the amount of electricity consumed in oxidizing the active material in the positive. The values of K are in good coincidence with the discharge capacity C in the succeeding discharge. This may lead to the consideration that the entire amount of oxygen fixed in the active material of the positive in the charge, may be consumed in the succeeding discharge.

In the case of the 1st discharge in Table 1, for example, K' amounted to 9.30 ampere-hours, and if K' be used only for the electrolysis of water, the amount of oxygen which will be evolved at P is calculated to be 1946 c.c. at 0°C. and 1 atm. So that the volume of oxygen which was fixed in the active material in the charge will be

$$1946 \text{ c.c.} - 1506 \text{ c.c.} = 440 \text{ c.c.} \quad (0°\text{C.}, 1 \text{ atm.}).$$

On the other hand, the electrode used contains 5.08 g. of Ag_2O as an active material, accordingly, the amount of oxygen in the electrode may be as follow:

$$22400 \times (5.08 \times O_2/2\,Ag_2O) \times (1/O_2) = 245 \text{ c.c.} \quad (0°\text{C.}, 1 \text{ atm.}).$$

The amount of oxygen which is expected to exist in the positive considering the charged active material to be Ag_2O_2 will be $245 \times 2 = 490$ c.c. (0°C., 1 atm.). From these calculations, it can be concluded that the active material of the plate, in charged state, is composed of a silver oxide of a higher degree of oxidation than Ag_2O. The same result was already described in the preceding paper.

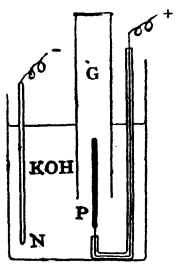


Fig. 2.

In the above experiments the grids made of iron were used for the preparation of the positive. By the use of such a grid, however, the discharge capacity of the positive diminishes gradually as the cycles of discharge are repeated. So in the following experiments the grids of lead-antimony instead of iron was used. In this case the positive P was fixed in a large vessel A, as shown in Fig. 2. N is a negative electrode, and G a glass cylinder for collecting the gas evolved at P. The results are tabulated in Table 2. The same conclusion can be obtained from this table as from Table 1.

Table 2. Comparison of K and C.

Number of cycle	Total amount of elect. used for charging (K') (A.H.)	Volume of gas evolved (0°C., 1 atm.) (c.c.)	Amount of elect. as a loss (K'') (A.H.)	$K = K'-K''$ (A.H.)	Discharge capacity (C) (A.H.)
1					2.242
2	3.363	330.2	1.58	1.78	1.780
3	2.376	142.2	0.68	1.70	1.634
4	2.450	144.0	0.69	1.76	1.750
5	2.750	204.0	0.98	1.77	1.759
6	2.708	178.9			

(b) **Changes of the Rates of Gas Evolution in the Course of Charge.** Rates of gas evolution at a silver oxide electrode in the course of charges were measured. Fig. 3 shows an example of the results obtained. In the figure the ordinate indicates the velocity of gas evolution (c.c./min.) or the terminal voltage of the cell (volts), and the abscissa the time of charge and discharge (min.). The curve represented by circlets shows the evolved gas, and the curves represented by black dots are the characteristic curves of the cell in charge and discharge, the current being taken as 500 milliamperes. The terminal voltage of the cell in charge rises abruptly at about 75 min., accompanied by a slow evolution of gas. The rate of gas evolution rose slowly, and at last it reached nearly 1.74 c.c./min. The value 1.74 c.c./min. coincides with theoretical rate of gas evolution at the positive electrode in the electrolysis of water by the current of 500 milliamperes. So that the curve is considered to indicate the change of rate of propagation of oxidizing reaction at the electrode, and the reaction proceeds no more when the rate of gas evolution reached 1.74 c.c./min.

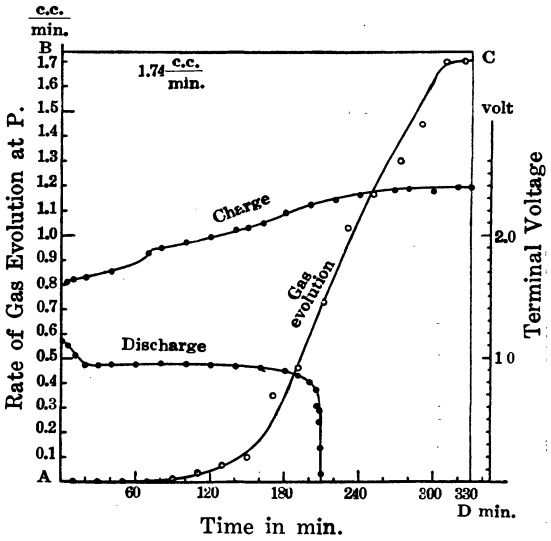


Fig. 3.

The area ABCD in Fig. 3 corresponds to the total amount of gas which will be evolved at the positive in the case of electrolysis of water by the current of 500 milliamperes in 330 min. The area surrounded by the straight lines AB and BC, and the gas evolution curve, corresponds to the amount of oxygen, which was fixed in the active material of the plates, and the rest, which lies on the right side of the curve indicates the amount of gas evolved at the positive as a loss.

(c) Proceeding of Oxidizing Reaction at the Electrode and the Amount of Electricity Used for Charging the Cell. Now, a very interesting special feature of the silver oxide positive was observed. The silver oxide positive in the pasted form could be discharged before applying any electrolytic treatment, i.e., "formation". The discharge capacity of the positive, in this case, almost coincides with those expected from the amount of silver oxide pasted in the positive and from the following chemical reaction:

$$Ag_2O \rightarrow 2Ag + \frac{1}{2}O_2 \qquad (2).$$

The calculated and the observed capacities are compared in Table 3. As seen in the table the coefficient of utility reaches from 90 to 97%. In this case the capacity S of the electrode may be considered to be the in-

Table 3. Comparison of Discharge Capacity at First Discharge with the Calculated Value.

Electrode	Amount of Ag_2O pasted (g.)	Discharge capacity (calc.) S (A.H.)	Discharge capacity (obs.) S' (A.H.)	Coefficient of utility (%)	Capacity per 1 g. of Ag_2O (mA.H./g.)
6 a	4.61	1.066	1.038	97.3	225
6 b	4.66	1.078	1.050	97.4	225
6 c	4.91	1.146	1.100	95.9	224
6 d	4.72	1.092	1.058	96.8	224
6 e	4.84	1.119	1.038	92.8	215
6 f	4.89	1.130	1.050	93.0	215
6 g	4.82	1.115	1.038	93.1	215
6 h	4.90	1.134	1.050	92.6	214
7 a	4.97	1.150	1.075	93.4	216
7 b	4.84	1.121	1.033	92.1	214
7 c	5.13	1.188	1.104	92.8	215
7 d	5.33	1.235	1.150	94.1	216

herent capacity of the electrode, which is to be determined by the amount of Ag_2O pasted in the grids.

In the following experiments the relation between the progress of the oxidizing chemical reaction at the electrode, and the amount of electricity used for charging the cell was examined. The degree of the oxidizing reacton at the electrode in charge can be measured from the discharge capacity of the cell in the succeeding discharge.

Four silver oxide electrodes were subjected to charge and discharge by the current of 250 milliamperes, and the values of K (which was measured from C in the succeeding discharge) was estimated, the values of K' being varied at the same time.

In Fig. 4 the values of C of the electrodes are taken in ordinate, and the K' in abscissa. As seen in the figure, if K' be smaller than 1.5 S_m[3], it is nearly equal to C in the succeeding discharge. In this case, there-

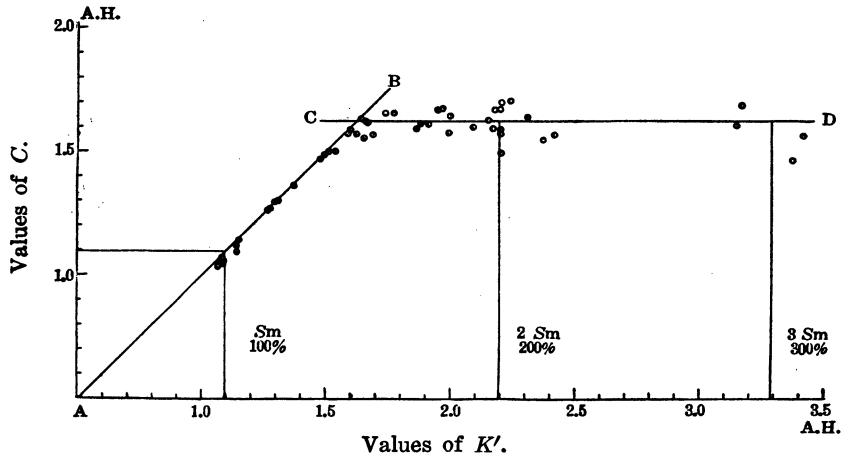


Fig. 4.

fore, we can forecast the end of the discharge by dividing K' by the magnitude of discharge current in the ranges of a few minutes. If K' be greater than 1.5 S_m, C becomes constant and nearly equal to 1.5 S_m.

The inherent capacity of the electrode S is the theoretical one, the fundamental chemical reaction of the electrode being assumed to be (2). Accordingly, it may be expected that the total capacity of the electrode will increase to as much as $2S$, if the active material of the electrode

(3) S_m means the mean inherent capacity of the four electrodes used in the experiments.

be oxidized into Ag_2O_2, as the result of repeating the cycles of charge and discharge.

Relations between K' and K (or C) were examined by varying the magnitude of the charging current. The results obtained are diagramatically represented in Fig. 5 and Fig. 6, which correspond to the data obtained by the charging current of 500 milliamperes and 1000 milliamperes respectively.

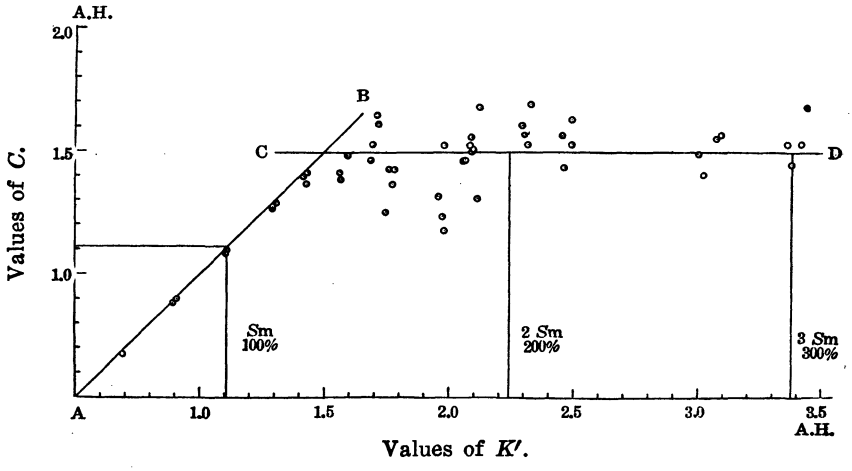


Fig. 5.

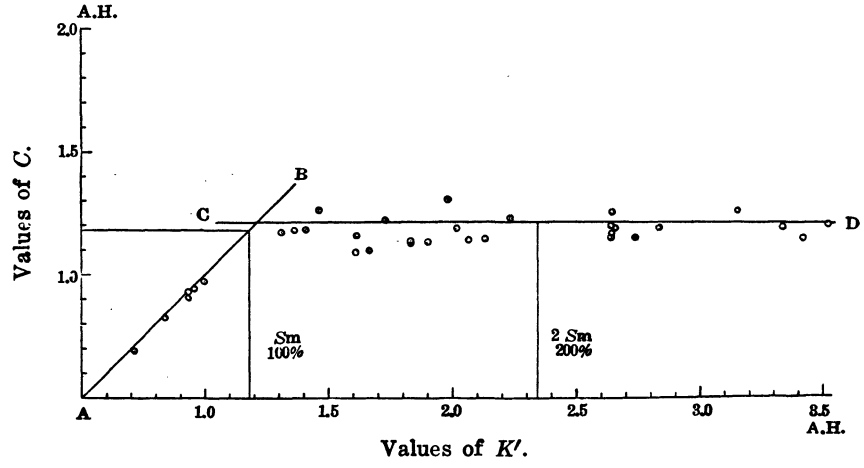


Fig. 6.

(d) Relation between Magnitude of Charging Current and Charged Amount of Electricity. As the result of experiments (c) it may be expected that the amount of electricity actually accumulated in the active material i.e., the amount of electricity consumed for oxidizing the active material of the electrode, changes with the magnitude of the charging current.

The silver oxide positives were charged fourteen times as much as their inherent capacities, the magnitude of the charging current in this case being from 100 milliamperes to 1300 milliamperes. And then they were discharged by a current of 250 milliamperes. The results thus obtained are summarized in Table 4.

Table 4.

Charging current (I) (ampere)	Time of discharge (t) (hours)	Discharge capacity (C) (A.H.)	log I	log t	log t (calc.)
0.100	6.471	1.604	−1.000	0.808	
0.200	5.566	1.392	−0.699	0.746	
0.300	5.750	1.438	−0.523	0.760	0.761
0.400	5.558	1.389	−0.398	0.745	0.744
0.500	5.383	1.346	−0.301	0.731	0.731
0.700	5.142	1.286	−0.155	0.711	0.711
1.000	4.892	1.223	0.000	0.688	0.690
1.300	4.725	1.181	0.114	0.675	0.675

The following tendency can be noticed from the table: the discharge capacities (C) of the electrodes become smaller with the increase of the charging current, but an especially small discharge capacity was observed when the charging current was 200 milliamperes. In the 4th and the 5th columns of the table, the values of $\log I$ and $\log t$ are tabulated. Plotting these values on a $\log I - \log t$ diagram, we obtain a straight line, as seen in Fig. 7. So that the relation can be represented by the following equations;

$$\log t = -n \log I + \log k \qquad (3),$$

$$I^n t = k \qquad (4),$$

where n and k represent constants. The equation (4) is analogous in form to Peukert's formula[4] which gives the relation between discharge

(4) Peukert, *Elektrotech. Z.*, (1897), 287.

hour rate and the magnitude of the discharge current in the lead acid storage cell. Two constants in the equations (3) and (4) were found to be $n = 0.136$, and $\log k = 0.690$. In the 6th column of the table, the values of $\log t$ calculated from the equation (4) are tabulated.

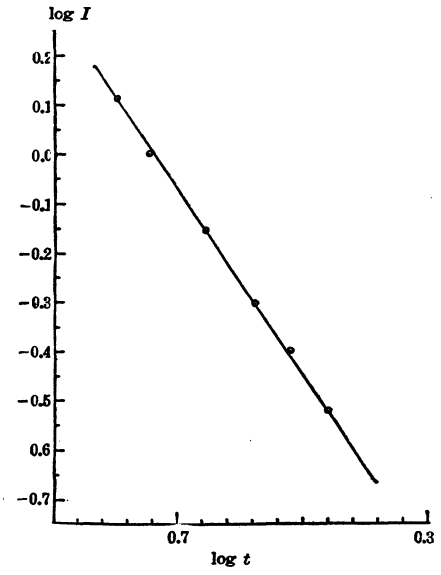


Fig. 7.

(e) On the Peptization of the Active Material at the Electrode. The silver oxide positives, in many cases, dispersed their active material into the solution of electrolyte when they were subjected to charge and discharge, forming a colloidal solution of silver oxide. This phenomenon was already noticed by Jirsa,[5] the author,[2] and Tanaka.[6] The colour of the colloidal silver observed in these experiments[7] was sometimes pink, yellow, brown, bluish brown or black. In order to see the effect of the concentration of the electrolyte upon the formation of the colloid, two electrodes (4H and 4I) were charged and discharged by a current of 100 milliamperes. The result observed at their first charge is summarized in Table 5. As seen in the table the formation of the colloid seems to have some relation to the concentration of the electrolyte. From

Table 5.

Electrode	Conc. of electrolyte	Colour of colloid	Remark
4 H	40% KOH	Pink	Upper part of the electrolyte: pink; lower part: transparent.
4 G	2.5% KOH	Dark yellow	Upper part of the electrolyte: transparent; lower part: dark yellow.

(5) Jirsa, *Z. Elektrochem.*, **33** (1927), 129.

(6) Tanaka, *J. Electrochem. Assoc. Japan*, **3** (1935), 9.

(7) The photographs showing the formation of the colloids can be seen in the original paper (2).

the second charge onward the formation of the colloid in pink colour cannot be observed even in the case of electrode 4 H.

Positive and negative electrodes of the cell were put into two separate glass vessels, each containing 20% KOH solution, and the vessels were connected with a U-tube, which was also filled with 20% KOH solution. The charging current of this cell was taken to be 100 milliamperes, the peptization of the active material could be noticed only in the electrolyte into which the silver oxide positives were dipped. In discharging the positives, formation of the colloids could also be observed.

Consideration of the Results. The fundamental chemical reactions involved in the charge and discharge of the silver oxide positives will be considered to be as follows:

$$Ag_2O_2 \rightarrow Ag_2O + \frac{1}{2}O_2 \rightarrow 2Ag + \frac{1}{2}O_2 .$$

Of these the decomposing reactions of silver oxide into metallic silver corresponds to the discharge of the cell.

On the other hand, it was noticed, that the reduction of the active material occurred at first at the ribs of the grid, and then propagated into the inner part of the active material. This fact can easily be known from the colour difference between Ag_2O and Ag.[8] The material in discharged part is metallic silver, which is good electrical conductor, so that the discharge reaction will proceed smoothly and completely even in the innermost part of the active material.

In case of a charge, on the other hand, the active material in uncharged state (metallic silver) will be separated from the rib by a layer of charged material (silver oxide) which has small electrical conductivity. Accordingly the charging chemical reaction will not proceed so smoothly into the active material.

The following characteristic properties of the silver oxide positives may be explained from the above considerations: (1) Silver oxide positive gives very high values of coefficient of utility of the active material; (2) discharge capacities and the utility coefficient are not so seriously affected by the magnitude of the discharge current; (3) the oxygen fixed in the active material of the positives in a charged state is

(8) The photographs showing the propagation of chemical change at the electrode in discharge can be seen in the paper published in Japanese: Kinoshita, *J. Electrochem Assoc. Japan*, **4** (1936), 27; *Toyoda Kenkyu Iho*, **4** (1936), 108.

consumed completely in the succeeding discharge; (4) the amount of electricity charged in the active material is affected seriously by the magnitude of the charging current.

In conclusion, the author wishes to express his hearty thanks to Prof. J. Sameshima of the Tokyo Imperial University for his valuable advice.

Summary.

(1) Further experimental investigations were made on the charge and discharge characteristics of the silver electrode of the cell which was constructed from the silver positive and the iron negative in KOH solution.

(2) Silver oxide positive gives very high value of the coefficient of utility of the active material.

(3) Discharge capacity and the utility coefficient are not seriously affected by the strength of the discharge current.

(4) The oxygen fixed in the active material in the charged state is consumed completely in the succeeding discharge.

(5) The amount of electricity charged is affected seriously by the strength of the charging current.

(6) These phenomena can well be explained by the following chemical reactions.

$$Ag_2O_2 \underset{\text{charge}}{\overset{\text{discharge}}{\rightleftarrows}} Ag_2O + \frac{1}{2}O_2 \underset{\text{charge}}{\overset{\text{discharge}}{\rightleftarrows}} 2\,Ag + \frac{1}{2}O_2 .$$

Toyoda Research Laboratory, Imperial Invention Society, Shimomeguro, Tokyo.

Catalytic Hydrogenation of Amides of *a*-Hydroxy-Acids (Continued).[1]

By Haruomi ÔEDA.

(Received July 24th, 1937.)

Experiments on the formation of 1,4-diamine and of 1,2-glycol from *a*-hydroxy-amide by catalytic hydrogenation in the presence of copper-chromium oxides, were extended to phenyl-lactamide.

From this amide benzyl-ethylene glycol and a solid base were obtained. The solid base, when fractionally recrystallized from alcohol, can be separated into two fractions, one of which melts at 142–144° (A) and the other at 166–167° (B). Results of analysis of both bases show that they correspond to the same diprimary diamine shown below, i.e. they are isomeric with each other.

On benzoylation, the latter base (B) gives a derivative melting at 280–282° (*Bz*.B) in pure state, whereas the former (A) gives the same derivative (*Bz*.B) admixed with an isomeride which melts at 199–201° (*Bz*.A), and this mixture is easily separated into the components by the difference of their solubilities in alcohol. These results seem to indicate that base A[2] contains some component besides one which is common in both bases (A and B).

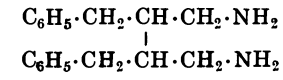
By hydrolysis of the benzoyl derivative melting at 199–201° (*Bz*.A) with concentrated hydrochloric acid at 150–160°, a base was regenerated which melted at 153–155°. A component of base A is thus isolated. On the other hand, the benzoyl derivative (*Bz*.B) which is common in both bases and the corresponding benzenesulphonyl derivative (m.p. 226–227°) are very resistent to hydrochloric acid and can not be hydrolyzed by the same treatment. Thus the second component which is common in both bases (A and B) can not be isolated in the form of free base, but the fact that base B gives only one benzoyl (*Bz*.B) or benzenesulphonyl derivative, leads to the conclusion that base B represents the second component in its pure state.

---

(1) Studies on Hydroxy-Acids and Their Derivatives. VI. Continued from this Bulletin, **12** (1937), 121.

(2) Attempts to separate the base-mixture in the form of hydrochloride, picrate or oxalate were tried but they were found to be unfavourable on account of their small solubilities in ordinary solvents.

To summarize, the existence of two bases having the same composition (m.p. 153–155° and 166–167°) is ascertained which correspond to some two optical isomerides[3] among three possible forms (active, meso and racemic) of this base.



2,3-Dibenzyl-tetramethylene-diamine

Free base	Benzoyl derivative	Benzenesulphonyl derivative
M.p. 153–155°	M.p. 199–201°	—
M.p. 166–167°	M.p. 280–282°	M.p. 226–227°

Uniting the present results with previous ones[1] it is established that the scheme giving 1,4-diamine and 1,2-glycol from α-hydroxy-amides is similar for the three amides, namely, amides of lactic, leucic[4] and phenyl-lactic acids.

Experimental.

The experimental procedures of the hydrogenation and the separation of reaction products are the same as described in the previous paper.[1]

Phenyl-lactamide (m.p. 113–114°), 23 g. (0.14 mol); dioxane, 60 c.c.; catalyzer, 5.0 g.; time of hydrogenation, 2 hours at 245–255°; fractionation through Widmer column after expelling off the dioxane:

I	130 - 140°	under 5 mm.	3.9 g.
II	160 - 190°	,,	4.9 g.
III	over 190°	,,	

Fraction II tends to solidify in the receiver, while fraction III remains as viscous fluid even after long standing. Considerable amount of residue was found undistilled in the flask.

---

(3) Meso and racemic forms may be assigned to the above bases from the follwing reason: Measurement of optical rotation can not be carried out with both forms separately due to scarcity of the sample, but the measurement with their mixture (base A) showed no activity.

(4) As to dimethyl- and di-isobutyl-tetramethylene-diamines[1], derived from amides of lactic acid and leucic acid respectively, three isomerides are also possible and in fact, in the latter diamine, the author obtained two isomeric forms by the recrystallization of the crude base from alcohol, one melting at 60–62°, and the other at about 80°, but the latter was not reported in the previous paper because the higher melting fraction was not isolated in its pure state even in the form of its derivatives.

(A) **Fraction I.** (a) **Neutral Part.** Fraction I was separated into neutral and basic parts by extracting the acidified mixture with ether. The neutral part, after boiling with sodium hydroxide solution, was twice refractionated through Widmer column, when the main part distilled at 147–149° (uncorr.) under 6 mm. Yield, 7.2 g. from 0.42 mol of amide. It was identified as benzyl-ethylene glycol by preparing its bis-phenylurethane.

Bis-phenylurethane. Prepared from the glycol (1.0 g.) and phenyl isocyanate (2.0 g.) by heating at 120–130° for half an hour, crude urethane (3.2 g.) being crystallized by adding ligroin. It melted at 133–134° (uncorr.) or 135–136° (corr.) after recrystallization from benzene (Found: C, 70.19; H, 6.11; N, 7.22. Calculated for $C_9H_{10}O_2(OC\cdot NH\cdot C_6H_5)_2$: C, 70.73; H, 5.68; N, 7.18%). $[\alpha]_D^{28} = -13°$ (1 dm. tube; 26.5 mg. in 1.00 c.c. of alcoholic solution). When the crude sample was recrystallized from alcohol, it showed the same m.p. as above and lower melting fraction was never isolated even when seeded with a crystal of sample A (see below). $[\alpha]_D^{28} = -11°$ (25.7 mg. in 1.00 c.c.)

Supplement to Previous Paper[5]: It was already described that this glycol is also obtainable from phenyl-lactic acid when hydrogenated in the form of its acetone-compound. The sample of hydroxy-acid was the same one as was used in the present experiment and is lævo-rotatory. In that paper two forms of urethane of this glycol were mentioned and their interconvertibility by crystallization and their monotropic change by heating were described. Preparation of those urethanes were tried again and it was proved that the previous descriptions are correct. Their analyses were repeated and their optical rotations were measured. Urethane recrystallized from alcohol (sample A), m.p. 109–110° (uncorr.) (Found: C, 70.06; H, 6.15; N, 7.15%). No rotation was observed (1 dm. tube; 26.9 mg. in 1.00 c.c. of alcoholic solution). Urethane recrystallized from benzene (sample B), m.p. 132–133° (uncorr.) (Found: C, 69.96; H, 6.16; N, 7.15. Calculated for $C_9H_{10}O_2(OC\cdot NH\cdot C_6H_5)_2$: C, 70.73; H, 5.68; N, 7.18%). No rotation was observed (26.4 mg. in 1.00 c.c.).

Now, it is shown that the present urethane is active, while both forms of the former are inactive. As to the nature of the two forms of inactive urethane, following facts were observed. Sample B shows nearly the same m.p. as the active urethane and moreover mixing of them caused no appreciable depression. Mixtures (once melted and left at 110° to solidify), on heating, slightly soften below 130° and melt clearly at 131–133° (uncorr.), in every case when ratio of mixing were varied as 3:1, 2:2 and 1:3. From these behaviours of sample B it is probable that B belongs to the type of mixed crystals. If the molten mixtures are kept at room temperature, they become hard glassy masses and never tend to crystallize. Thus the formation of sample A from the molten mixture can not be realized. Sample A must be racemic compound or *dl*-mixture, and as to the last point, because of the lack of data, no decision can be given. There exists a transition point[6] between the two forms of inactive urethane. Sample A, on rapid heating, clearly melted at 110°, but when

(5) this Bulletin, **10** (1935), 531.

(6) Existence of a transition point between two inactive forms was observed in several substances, such as camphoroxime, π-chlorocamphor and methyl-mannoside. But the formation of two forms by crystallization from different solvents was not mentioned on these substances (Freudenberg, "Stereochemie," 560, Leipzig (1932).).

maintained at this temperature, it gradually resolidified and the m.p. of the resolidified mass was just the same as that of sample B.

(b) **Basic Part.** A hydrochloride, easily soluble in hot water, was obtained in small quantity. It can be recrystallized from alcohol, m.p. 271–272° (corr.). No further study on this base was made.

(B) **Fractions II and III.** Combined fractions were diluted with five times its volume of alcohol and concentrated hydrochloric acid was added to it. A hydrochloride gradually precipitated, the yield was not good: 4.3 g. of crude hydrochloride was obtained from 0.42 mol of the amide. After extraction with hot alcohol, the residue was dissolved in a large bulk of hot water, filtered, and was concentrated on water bath. During evaporation, a hydrochloride began to crystallize out while still hot before the solution was completely dried up. Hydrochloride (2.5 g.) thus purified was colourless and on heating showed no change of appearance up to 300°.

When the above hydrochloride was warmed with a little excess of dilute caustic soda, it changed to a crystalline free base (1.8 g. from 2.5 g. of the hydrochloride). The free base was dissolved in hot alcohol and filtered. On cooling without evaporation of the solvent, a base melting between 145° and 160° was obtained. The base which was obtained from the above filtrate by evaporation of the solvent, melted below 150°. The former fraction, after repeated recrystallization from alcohol, melted sharply at 163–164° (uncorr.) or 166–167° (corr.) (base B) and weighed 249 mg., melting point remaining unchanged on further recrystallization. The melting range of latter fraction, after repeated recrystallization, became narrower and 584 mg. of the base which melted at 140–142° (uncorr.) or 142–144° (corr.) (base A) was obtained.

(a) **Free Base Melting at 142–144° (base A).** (Found: C, 80.74; H, 9.31; N, 10.24. Calculated for $C_{18}H_{24}N_2$: C, 80.72; H, 9.02; N, 10.44%.) No rotation was observed (1 dm. tube; 25.8 mg. in 1.00 c.c. of alcoholic solution).

Benzoyl derivative melting at 199–201° (*Bz.*A). To a suspension of the base in dilute caustic soda, benzoyl chloride was added drop by drop with constant stirring. A sticky mass first formed, turned to crystallize. Benzoyl compound thus separated (660 mg. from 465 mg. of the free base) was extracted with alcohol. Benzoyl compound which was obtained from the alcoholic extract after expelling off the alcohol, melted at 195–197° (uncorr.) or 199–201° (corr.) after recrystallizations from alcohol (Found: C, 80.48; H, 6.47; N, 6.06. Calculated for $C_{18}H_{20}(NH\cdot CO\cdot C_6H_5)_2$: C, 80.60; H, 6.80; N, 5.88%).

The residue of the above extraction (149 mg.), on purification, was found to be identical in m.p. with a benzoyl compound (*Bz.*B) obtainable from the other base (base B) and it was combined with that fraction described below.

Hydrolysis. Mixture of the benzoyl compound (*Bz.* A: 85 mg.) and concentrated hydrochloric acid (10 c.c.) was heated at 150–160° in a closed vessel for four hours. After cooling, a gelatinous precipitate of hydrochloride of the regenerated base (55 mg.) was separated and it was recrystallized from water after being washed with alcohol (Found: N, 7.97. Calculated for $C_{18}H_{24}N_2\cdot 2HCl$: N, 8.21%).

Free Base Regenerated. The base (26 mg.) which was obtained from the above hydrochloride (36 mg.) was recrystallized from alcohol and dried on porous plate over

solid caustic soda, m.p. 150–152° (uncorr.) or 153–155° (corr.) (Found: C, 80.76; H, 8.54; N, 10.58. Calculated for $C_{18}H_{24}N_2$: C, 80.72; H, 9.02; N, 10.44%).

(b) Free Base Melting at 166-167° (Base B). (Found: C, 80.53; H, 8.55; N, 10.47. Calculated for $C_{18}H_{24}N_2$: C, 80.72; H, 9.02; N, 10.44%).

Benzoyl compound melting at 280–282° (*Bz.*B). The base was benzoylated in the same way as above, 233 mg. being obtained from 150 mg. of the free base. After extraction with hot alcohol, the residue was recrystallized from glacial acetic acid, m.p. 273–275° (uncorr.) or 280–282° (corr.) (Found: C, 80.23; H, 6.94; N, 5.78. Calculated for $C_{18}H_{20}(NH\cdot CO\cdot C_6H_5)_2$: C, 80.60; H, 6.80; N, 5.88%).

Attempted Hydrolysis. The benzoyl compound is insoluble in hot concentrated hydrochloric acid and was not hydrolyzed by this reagent at 150–160°, 85% of the sample (77 mg. out of 91 mg.) being recovered unchanged after heating for four hours.

Sulphamide melting at 226–227°. The free base was added to dilute caustic soda and benzenesulphonyl chloride was added to it drop by drop. A sticky mass separated, which gradually turned to crystals on heating over water bath. After separation of the sulphamide by suction, hydrochloric acid was added to the filtrate but no precipitate was formed. The insoluble sulphamide[7] (133 mg. from 83 mg. of the free base), after acidifying with hydrochloric acid, was recrystallized from glacial acetic acid, m.p. 220–221° (uncorr.) or 226–227° (corr.) (Found: C, 65.47; H, 6.19; N, 5.12. Calculated for $C_{18}H_{20}(NH\cdot SO_2\cdot C_6H_5)_2$: C, 65.61; H, 5.91; N, 5.10%).

Attempted Hydrolysis. The sulphamide was added to a mixture of glacial acetic acid and hydrochloric acid (1:3) and was heated in sealed tube at 150–160° for four hours. The sample was not hydrolyzed: 21 mg. of sulphamide out of 25 mg. was recovered unchanged.

The present study was carried out in the Chemical Institute, Faculty of Science, Imperial University of Tokyo. The author expresses his sincere thanks to Prof. K. Matsubara for kind inspection of this paper. His best thanks are also due to Dr. Y. Takayama for constant encouragement during this study.

(7) Yielding of sulphamide, insoluble in alkaline media, is a usual reaction of secondary amines, but the base in question, on analysis, was proved to be primary amine. It was known that some sulphamide of primary amine remained undissolved even in alkaline solution, i.e. the sodium compounds are insoluble in water, differing from the usual ones.

The Paramagnetic Isomerisation of Maleic Acid into Fumaric Acid in Aqueous Solution.

By Bunichi TAMAMUSHI and Hajime AKIYAMA.

(Received July 30th, 1937.)

R. Kuhn,[1] who demonstrated the cis-trans-isomerisation of some ethylene compounds (dimethyl ester of maleic acid and *cis*-stilbene) catalysed by paramagnetic metals, suggested as regards the mechanism of the reaction, that the absence of rotation imposed by the double bond would be overcome by the interaction between magnetically uncompensated electrons of the reacting molecule and the catalyst. Later it was shown by the present authors,[2] that the isomerisation of dimethyl ester of maleic acid can be catalysed by molecular oxygen, whose molecule is paramagnetic in spite of its even number of electrons, so that this result can be accounted for by the same mechanism. The similar view seems to be possible also in the catalysed conversion of maleic acid into fumaric acid by hydrogen ions in aqueous solution.[3]

Now in the following experiments, we attempted to ascertain the possible catalytic influence of the molecular oxygen, some paramagnetic metals and ions, on the isomerisation of maleic acid into fumaric acid in aqueous solution. It is already known that the para-ortho-hydrogen conversion in solution can be accerelated by the presence of paramagnetic molecules and ions.[4]

I.

In the first part of the following experiments, we have simply compared the amounts of the fumaric acid produced after a relapse of certain time in the reaction mixture, in the presence of paramagnetic substances with various magnetic moments. The experiments with oxygen have been always coupled with the similar experiments with nitrogen, whose molecule is diamagnetic. Thus we may be justified to conclude that the relative catalytic effects of the substances are determinable, taking into con-

(1) K. Freudenberg, "Stereochemie," 913, Leipzig (1933).
(2) B. Tamamushi and H. Akiyama, *Z. Elektrochem.*, **43** (1937), 156.
(3) C. Horrex, *Trans. Faraday Soc.*, **33** (1937), 570.
(4) L. Farkas and H. Sachsse, *Z. physik. Chem.*, B, **23** (1933), 1, 19.

sideration the role of the thermal or solvent effect, which may take place in every case under those conditions, which controlled our measurements.

The method of analysis of the reaction product which was adopted in the present work is due to Freundlich and Schikorr,[5] who studied the nature of the isomerisation of maleic acid to fumaric acid in aqueous solution in the presence of colloidal sulphur. The analysis, which is based upon the difference of solubilities of maleic acid and fumaric acid, proceeds in the following way.

Twenty c.c. of the solution to be analysed is pipetted into a 100 c.c. beaker and gently dried up on the water bath. To the residue is added 2–3 c.c. of water, which is just enough to dissolve the maleic acid in the mixture. As soon as we are sure that this process is completed, we filter the liquid with a small funnel into a small dry beaker, and then we take 1 c.c. of the filtrate for the titration with standard baryta solution, using phenolphthalein as an indicator. Thus we find out the amount of the maleic acid in the solution. The rest of the filtrate and the acids which remain in the pipette, funnel and filter paper are then transferred to the first beaker. The liquid is then boiled and titrated in the similar way as above, without newly charging the burette, so that the last reading of the baryta solution gives the total amount of the acids in the given solution. We have thus only to take the difference of the total amount of acids and the amount of the maleic acid, in order to find out the amount of the fumaric acid produced.

Since the error in the reading of burette greatly affects the result, we have constructed a special precision burette for the present purpose, which enabled us to read 0.005 c.c. accurately.

Now the amount of maleic acid which will be dissolved in the above procedure is so large, that its own volume will change the volume of the water taken, and this must be taken in account in the calculation.

If x equivalents of maleic acid are dissolved in q c.c. of water and one equivalent occupies the volume v c.c., then the volume of the solution after dissolving maleic acid will be $(q + vx)$ c.c. Assuming that 1 c.c. of the solution uses a c.c. of the normal solution, i.e. $a\frac{f}{1000}$ acid-equivalents, we have for $(q + vx)$ c.c. solution $(q + vx)\frac{af}{1000}$ acid-equivalents, where f denotes the factor of the normal solution. So that we get the equation:

(5) H. Freundlich and G. Schikorr, *Kolloid-Beihefte*, **22** (1926), 1.

$$(q+vx)\frac{af}{1000} = x\ ,$$

from which we obtain x.

The equivalent volume v was in our case determined by special experiments with the following results: $v = 39.1$ c.c. at 10°C. and $v = 40.0$ c.c. at 14°C.

The control experiments were made with a known mixture of the two acids, which contained namely 0.058 g. of fumaric acid and 1.102 g. of maleic acid and consequently just 5.00% of fumaric acid. The results obtained are given in Table 1.

Table 1.

No. of Exp.	Fumaric Acid (%)		Error (%)
	theor.	exp.	
1	5.00	4.62	7.6
2	5.00	4.85	3.0
3	5.00	5.07	1.4
4	5.00	4.67	6.2
			Mean 4.6

The accuracy of the analysis can therefore be estimated to about 5 percent in the mean.

A small quartz or Pyrex flask with reflex condenser, into which 30–50 c.c. half molar solution of maleic acid had been introduced, was put in a boiling water bath thermostat, temperature of which was regulated electrically within ± 0.2°, during the reaction time. The upper part of the flask was covered with an aluminium foil to protect the solution from light, which is well known to have an influence on the rate of the isomerisation.

In the case of measurements with oxygen or nitrogen, the gas was bubbled through the solution under a constant pressure during the reaction to ensure the solution to be saturated with the gas. By the method of Kautzky and Thiele[6] we prepared the nitrogen used in the experiment, which was completely free from oxygen.

In the following series of experiments with paramagnetic ions, a small amount of sulphates of divalent metals or nitrates of trivalent metals was added to the solution, the concentration of the salt being 5 millimolar per litre in each case, so that any secondary chemical change in the solution could be excluded.

The platinum black and the palladium black were prepared by the method of Mond, Ramsay, and Shields,[7] which exhibited high catalytic

(6) H. Kautzky and H. Thiele, *Z. anorg. allgem. Chem.*, **152** (1926), 342.
(7) L. Mond, W. Ramsay, and J. Shields, *Phil. Trans.*, **186** A (1895), 661.

activity in burning hydrogen. The chemicals used were the purest ones of either Merck or Kahlbaum.

The results obtained are summarized in the following tables, in which the values of magnetic moments or of magnetic susceptibilities of the catalysts are too noted. The adopted values of the fumaric acid produced in Table 3 and 4 are the mean of two or three measurements, since they fluctuate considerably within the error of the analysis.

Table 2. Conc. of Maleic Acid = 0.5 mol/l. Temp. = 99.5°C. Reaction Time = 10 hours.

No. of Exp.	Fumaric Acid produced (%) in presence of	
	O_2	N_2
1	8.7	5.1
2	9.1	5.7
3	9.0	6.1

Table 3. Conc. of Maleic Acid = 0.5 mol/l. Temp. = 99.5°C. Reaction Time = 10 hours.

Ion (5 millimol/l.)	Fumaric Acid produced (%)	Magnetic Moment[8] in Bohr Magneton Number
Zn^{2+}	6.5	0
Cu^{2+}	7.7	3.53
Mn^{2+}	8.6	5.92
Fe^{2+}	8.9	6.54
Co^{2+}	11.1	6.56
Ni^{2+}	11.3	5.56
Pr^{3+}	9.5	3.62
Nd^{3+}	10.1	3.68
Er^{3+}	11.1	9.70

Table 4. Conc. of Maleic Acid = 0.5 mol/l. Temp. = 99.5°C. Reaction Time = 10 hours.

Catalyst (0.03 g. in 30 c.c. solution)	Fumaric Acid produced (%)	Specific Mass Susceptibility $\chi \cdot 10^6$
Pt-black	8.8	1.1
Pd-black	10.7	5.8

As we see in Table 2, the amount of the fumaric acid produced in the presence of oxygen evidently exceeds that produced in the presence of nitrogen. The isomerisation must have been accerelated by the non-homogeneous magnetic field of the O_2-molecules in the process of collision. A more or less considerable isomerisation is also observed in the presence of the paramagnetic ions or metals, where a certain parallelism being displayed between the fumaric acid produced and the magnetic moment of the catalyst. We dare not, however, formulate quantitatively the relation between them, in order to make use of it in further discus-

(8) J. H. van Vleck, "The Theory of Electric and Magnetic Susceptibilities," Oxford (1932).

sions, for our experiments have not yet so far advanced as to determine the velocity constant of the reaction in each case, whereas an interesting quantitative treatment has been performed in the case of the para-ortho-hydrogen conversion in solution catalysed by paramagnetic ions.[9]

The concentration of the paramagnetic ions seems to have in general no remarkable effect on the rate of the isomerisation, as is shown in Table 5, although a slight increase of the reaction product with the ion-concentration is noticed in the case of Nd^{3+}. The effect of the anion has been examined with the salts of the same cation in the same molar concentration and it was found to be negative, as is given in Table 6.

Table 5. Conc. of Maleic Acid = 0.5 mol/l. Temp. = 99.5°C. Reaction Time = 10 hours.

Salt	Concentration of Salt (millimol/l.)	Fumaric Acid produced (%)
$NiSO_4$	5	11.3
	10	11.4
	20	11.4
$Nd(NO_3)_3$	5	9.7
	10	10.7
	20	12.7

Table 6. Conc. of Maleic Acid = 0.5 mol/l. Temp. = 99.5°C. Reaction Time = 10 hours.

Salt (5 millimol/l.)	Fumaric Acid produced (%)
$NiCl_2$	11.9
$NiSO_4$	11.9
$Ni(NO_3)_2$	12.5

It is of interest to compare these results with those, which have been obtained by Farkas and Sachsse in the para-ortho-hydrogen conversion.

The effect of water itself as a solvent on the isomerisation of maleic acid in solution, which will be brought about by the nuclear moment of the protons of water molecules and which may probably take place as in the case of the para-ortho-hydrogen conversion,[10] can not, however, be brought out so long as the reaction is not studied in other solvents.

II.

The next step in our studies was to get some informations about the nature of the reaction under consideration, and for this purpose we have made kinetic measurements, which however concern only the reaction in the presence of paramagnetic oxygen molecules on the one hand, and on the other the reaction in the presence of diamagnetic nitrogen molecules.

(9) Farkas and Sachsse, *Z. physik. Chem.*, B, **23** (1933), 19; H. Sachsse, *Z. Elektrochem.*, **40** (1934), 531.

(10) Farkas and Sachsse, *Z. physik. Chem.*, B, **23** (1933), 14.

The rate of the reaction was determined in both cases at different temperatures, namely at 80°, 90° and 100°C., while the reaction vessel was put in an electrically regulated oil thermostat with the temperature variation within ± 0.1°.

The reaction mixture was taken from time to time to be analysed in the manner as described above. The results are tabulated in Table 7 and 8, where k denotes the unimolecular velocity constant. Although this constant shows some irregular variations, the correctness of the assumption of unimolecularity can be accepted on the ground of the experiment with varied initial concentrations of the reacting substance, the results of which being shown in Table 9.

Table 7. Conc. of Maleic Acid = 0.5 mol/l. Saturated with O_2.

Temp. (°C.)	Time (hours)	Fumaric Acid produced (%)	$k \cdot 10^6$ (sec.$^{-1}$)
80	15	3.2	0.60
	25	5.4	0.62
	40	9.9	0.72
			Mean 0.65
90	10	5.3	1.52
	23	7.8	0.98
	35	11.9	1.00
			Mean 1.17
100	10	9.0	2.62
	17	11.0	1.90
	20	11.8	1.73
			Mean 2.04

Table 8. Conc. of Maleic Acid = 0.5 mol/l. Saturated with N_2.

Temp. (°C.)	Time (hours)	Fumaric Acid produced (%)	$k \cdot 10^6$ (sec.$^{-1}$)
80	15	2.1	0.39
	25	3.7	0.42
	40	6.1	0.44
			Mean 0.42
90	10	3.4	0.97
	23	5.4	0.68
	35	7.0	0.58
			Mean 0.74
100	10	6.1	1.75
	14	7.1	1.47
	23	8.1	1.01
			Mean 1.41

Table 9. Maleic Acid Solution, saturated with O_2. Reaction Time = 15 hours.

Initial Conc. of Solution (mol/l.)	Fumaric Acid produced in millimol/l. after			$k \cdot 10^6$ (sec.$^{-1}$)
	5 hours	10 hours	15 hours	
0.25	0.0013	0.0023	0.0030	2.53
0.5	0.0031	0.0045	0.0070	2.75
1.0	0.0069	0.0092	0.0113	2.87
2.0	0.0126	0.0176	0.0206	2.73

Of the values of the fumaric acid which was produced in the above experiments at lower temperatures than 100°, due corrections were made

according to the circumstance, that in the reaction mixture, which was used for the analysis, the reaction would proceed, during the process of evaporation, further than the proper stage of the reaction. These corrections are not more than one percent, which was proved by special experiments and also by calculations from the data obtained at 100°.

From the data in Table 7 and 8, it is again obvious that the isomerisation proceeds remarkably quicker in the presence of oxygen than in the presence of nitrogen. The variation of the velocity constant with temperature follows the equation of Arrhenius:

$$\ln k = \ln Z - \frac{E}{RT},$$

as is illustrated in Fig. 1. We obtain thus for the reaction with oxygen the equation:

$$\ln k = 6.75 - \frac{14600}{RT},$$

and for the reaction with nitrogen:

$$\ln k = 7.96 - \frac{15800}{RT},$$

where k being measured in sec.$^{-1}$

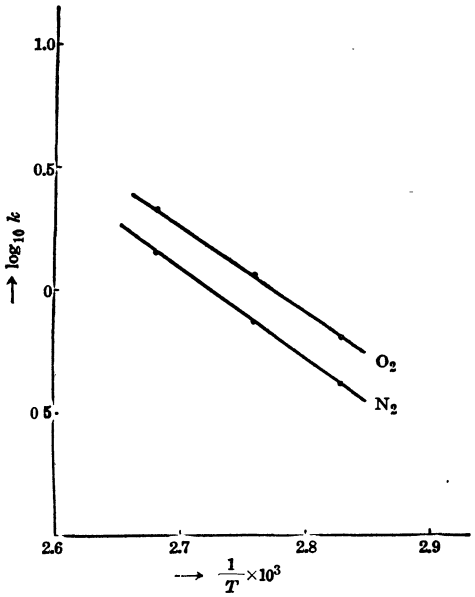


Fig. 1.

The energy of activation is thus lowered in the presence of oxygen, and this accounts for the catalytic action of molecular oxygen. The comparatively low values of ln Z are due to the slowness of the reaction in question.

It would be rather accidental that the energy of activation obtained above in the reaction with nitrogen i.e. 15.8 Cal. per mol is coincident with that, which was found by Höjendahl[11] for the isomerisation of maleic acid into fumaric acid in fused state, while Kistiakowsky and Nelles[12] found 26.5 Cal. per mol for the isomerisation of dimethyl maleic acid to dimethyl fumaric acid in gaseous state.

(11) K. Höjendahl, *J. Phys. Chem.*, **28** (1924), 758.

(12) G. B. Kistiakowsky and Nelles, *Z. physik. Chem.*, Bodenstein-Festband (1931), 369.

We hope that we can enter into further discussions on this subject, when we shall make reports of the studies of kinetics, which are now under way in our laboratory, concerning the isomerisation of dimethyl ester of maleic acid in gaseous phase in presence and in absence of molecular oxygen.

Summary.

It has been demonstrated that the isomerisation of maleic acid into fumaric acid in aqueous solution is accerelated by the presence of molecular oxygen, platinum black, palladium black, and various paramagnetic ions, where the isomerisation being probably effectuated by the non-homogeneous magnetic fields of the catalysts in the collision.

The isomerisation of maleic acid to fumaric acid in aqueous solution has been kinetically studied both in the presence of paramagnetic oxygen molecules and in the presence of diamagnetic nitrogen molecules, and the energy of activation of the reaction has been calculated. The lower energy of activation in the reaction with oxygen accounts for the catalytic action of the oxygen molecules.

We are much indebted to the Nippon Gakujutsu Shinkokai for a grant.

Chemical Laboratory,
The Musashi Higher School, Tokyo, Itabashiku.

Absorptionsspektren von Metallkomplexsalzen des 2,2'-Dipyridyls. I.

Von Kazuo YAMASAKI.

(Eingegangen am 2. August 1937.)

Seit der Auffindung des 2,2'-Dipyridyls durch F. Blau, haben zahlreiche Arbeiten[1] über die Komplexsalze des Dipyridyls mit verschiedenen Metallen schon erschienen, aber keine spektrochemische Untersuchung derselben ist anbei geschehen. In vorliegender Arbeit teile ich die Messergebnisse der Absorptionsspektren der Komplexsalze $[M(Dip)_3]Cl_{2(3)}$ mit, hierbei bedeuten *Dip* Dipyridyl und M zweiwertige Kupfer, Zink, Eisen, Nickel und Kobalt, sowie dreiwertiges Kobalt.

Experimentelles. Das 2,2'-Dipyridyl wurde aus Pyridin und wasserfreiem Eisenchlorid im Autoklave dargestellt.[2] Die Komplexsalze wurden meist durch Mischung der Lösungen des betreffenden Metallchlorids (1 Mol) und des Dipyridyls (3 Mol) hergestellt.[3] Sie sind beständig und löslich in Wasser und Alkohol. Im Falle der alkoholischen Lösung wurden die Absorptionsmessungen auch bis tiefen Temperaturen ($-60° \sim -70°$C.) ausgedehnt.

Die Absorptionsspektren wurde mit Hilfe von Quarzspektrograph (Hilger E2) nach der Hartley-Balyschen Methode aufgenommen. Der beobachtete Spektralbereich reichte von 220 mμ bis 850 mμ und als Lichtquelle dienten, je nach der Messbedingungen, Eisenbogen, Glühlampe und Wasserstofflampe mit Quarzfenster. Für die Versuche bei Zimmertemperatur ($+15°$) wurde ein gewöhnliches Balyrohr benutzt, aber die Messungen bei tiefen Temperaturen wurden mit einem speziellen Balyrohr von verschmolzener Quarz[4] ausgeführt (Abb. 1). Die Temperatur

(1) F. Blau, *Ber.*, **21** (1888), 1077; *Monatsh.*, **10** (1889), 372; **19** (1898), 647; G. T. Morgan und F. H. Burstall, *J. Chem. Soc.*, **1930**, 2594; **1931**, 2213; **1934**, 965; P. Pfeiffer, K. Quehl und F. Tappermann, *Ber.*, **64** (1931), 2667; *Z. anorg. Chem.*, **215** (1933), 273; G. A. Barbieri und A. Tettamanzi, *Atti accad. Lincei*, **15** (1932), 877; **16** (1933), 44; **20** (1934), 273; F. Rosenblatt und A. Schleede, *Ann.*, **505** (1933), 51; F. M. Jaeger und J. A. van Dijk, *Z. anorg. Chem.*, **227** (1936), 273; A. Simon, *Z. anorg. Chem.*, **230** (1937), 160.

(2) F. Hein und H. Schwedler, *Ber.*, **68** (1935), 681.

(3) F. M. Jaeger und J. A. van Dijk, *Z. anorg. Chem.*, **227** (1936), 273.

(4) Y. Shibata und K. Harai, *J. Chem. Soc. Japan*, **56** (1935), 1.

der Lösung wurde mit einem Thermoelement von Kupfer-Konstantan gemessen und die Temperaturänderung während eines Versuches im Sichtbaren (20 Min.) war ca. ± 5° bei − 65°. Im Ultraviolett wurde die photographische Aufnahme bei Zimmertemperatur mit der Wasserstofflampe ausgeführt, wobei die mehrstündige Belichtung immer nötig war, infolge ihrer schwachen Lichtstärke; also, bei tiefen Temperaturen, konnte man diese Lichtquelle nicht benutzen, weil die Lösungstemperatur so lange Zeit keineswegs konstant erhalten werden kann. Infolgedessen wurden die Absorptionsmessungen bei tiefen Temperaturen nur in sichtbarem Gebiet beschränkt, indem die Glühlampe als die Lichtquelle in Verwendung gebracht wurde.

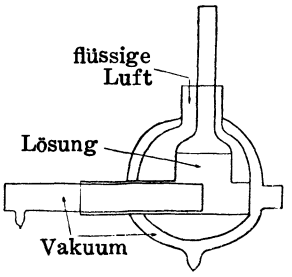


Abb. 1.

Messergebnisse. Dipyridyl: Farblose Kristalle. Es wurden die Lösung in Wasser und Hexan von Konzentration 1/5000 Mol untersucht. Das benutzte Hexan wurde nach Henri[5] gereinigt (Abb. 2,[6] Kurve 5, 6).

in Wasser (15°), λ_{max} in mμ: 280, 230.
in Hexan (15°), ,, : 280, 244+235.

In Hexan ist die zweite Bande nach längeren Wellen um 10 mμ verschoben und teilte sich in zwei schmalen Banden.

$[Cu(Dip)_3]Cl_2$: Blauviolette Tafeln. Wie andere Kupferkomplexsalze, zeigte dieses Salz auch keine Absorptionsbande im Sichtbaren, aber nur eine breite Bande im Ultraviolett ist beobachtet (Abb. 2, Kurve 1, 2, 3).

in Wasser (15°), λ_{max} in mμ: 298.
in Alkohol (15°), ,, : 293.
Konzentration: 1/50—1/10000 Mol.

$[Zn(Dip)_3]Cl_2$: Farblose Blättchen. In wässriger Lösung hat es einige Absorptionsbanden bei 307, 295 und 240 mμ (Abb. 2, Kurve 4).

$[Ni(Dip)_3]Cl_2$: Dunkelrote Tafeln. Konzentration: 1/20—1/10000 Mol[7] (Abb. 3).

---

(5) V. Henri, *Bull. soc. chim. biol.*, **6** (1924), 299.

(6) Auf der Ordinate wurde die Logarithmen der Schichtdicke (mm.) der Lösung entsprechend 1/10000 Mol aufgetragen.

(7) Bei −65° war die untersuchte grösste Konzentration der Lösung 1/40 Mol.

in Wasser (15°), λ_{max} in mμ: 750, 508, 308+296, 245.
in Alkohol (15°), ,, : 750, 520, 309+296, —[8].
,, (−65°), ,, : 520, 430.

In Alkohol trat die Verschiebung der Banden nach Rot auf und bei −65° trat eine neue Bande in Erscheinung. Vergleicht man die Lage der Absorptionsmaxima im Sichtbaren mit den der anderen Nickelhexamminsalze,[9] so zeigt sich die folgende Werte:

$[Ni(NH_3)_6]Cl_2$, $1/\lambda$: 170, 275.
$[Ni(en)_3]Cl_2$, ,, : 180, 290.
$[Ni(Dip)_3]Cl_2$, ,, : 197 (508 mμ).

Die Verschiebung der erste Bande nach kürzeren Wellen tritt mit zunehmender Molekulargrösse der Liganden. Die zweite Bande bei 275 in $1/\lambda$ fehlt beim Dipyridylkomplexsalz, aber es besitzt die Knicke der Absorptionskurve bei 410–330 mμ ($1/\lambda$ = 244–303).

$[Fe(Dip)_3]Cl_2$: Weinrotes Blättchen. Es wurden die Lösungen von Konzentration 1/2000–1/10000 Mol untersucht (Abb. 4).

in Wasser (15°), λ_{max} in mμ: 500, 352, 299+290, 247.
in Alkohol (15°), ,, : 510, 350, 300+290.
,, (−60°), ,, : 530, 420, 400.

In Alkohol trat die Verschiebung der erste Bande nach Rot auf und bei −60° zeigte das Spektrum zwei neue schmale Absorptionsbande.

$[Co(Dip)_3]Cl_2$: Komplexsalz des zweiwertigen Kobalts. Gelbe Schuppen. Konzentration: 1/50–1/10000 Mol (Abb. 5, Kurve 1, 2, 3).

in Wasser (15°), λ_{max} in mμ: 305+295, 243.
in Alkohol (15°), ,, : 307+295.

$[Co(Dip)_3]Cl_3$: Komplexsalz des dreiwertigen Kobalts. Gelbbraune Kristalle. Durch anodische Oxydation hergestellte Kobaltisulfat wurde mit Dipyridyl versetzt und das so erhaltene Tridipyridylkobaltisulfat wurde mittels Bariumchlorids in das Chlorid umgesetzt. Es ist ziemlich schwer löslich in Alkohol, aber leicht in Wasser. Konzentration: 1/50–1/10000 Mol (Abb. 5, Kurve 4, 5).

in Wasser (15°), λ_{max} in mμ: 450, 319+307.
in Alkohol (15°), ,, : 320+310.

---

(8) Die bei 250 mμ beginnende Absorption von Alkohol überdeckt diese Bande und macht die Messung unmöglich.
(9) Y. Shibata, *J. Chem. Soc. Japan.*, **39** (1918), 661; *J. Coll. Sci., Imp. Univ. Tokyo*, **41** (1918), Art. 6, S. 23.

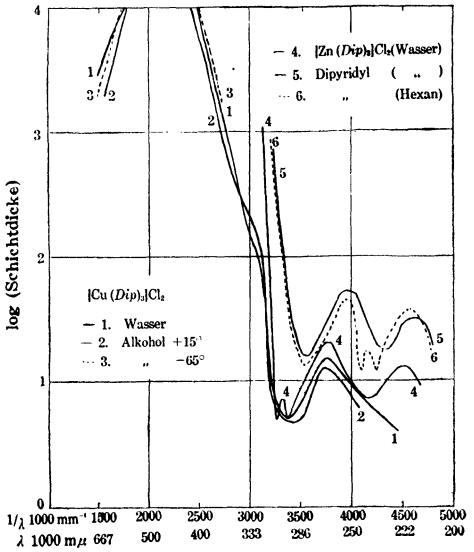


Abb. 2.

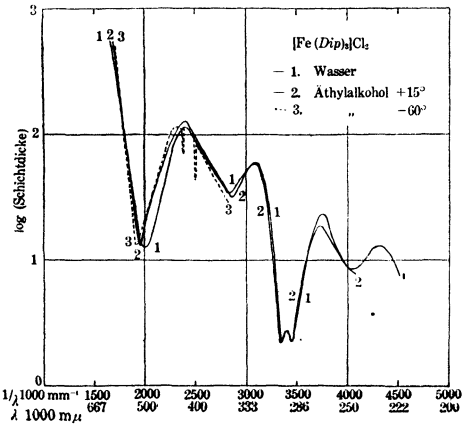


Abb. 4.

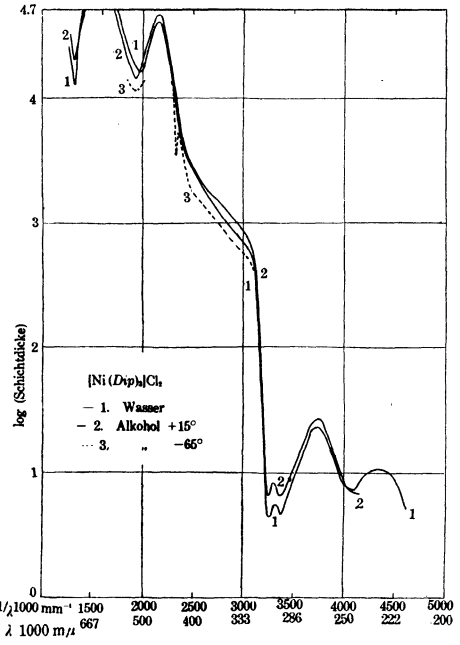


Abb. 3.

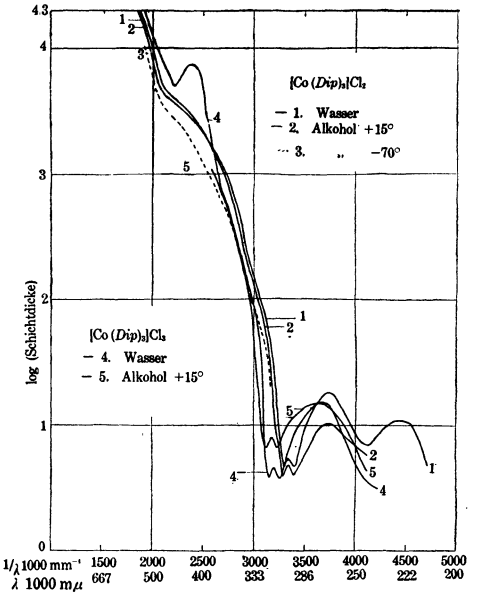


Abb. 5.

Die erste Absorptionsbande im Sichtbaren der Kobaltihexamminsalze verschiebt sich nach kürzeren Wellen mit dem zunehmenden Molekulargrösse der Liganden.

$[Co(NH_3)_6]Cl_3$: 475 mμ.[10]
$[Co(en)_3]Cl_3$: 467 mμ.
$[Co(Dip)_3]Cl_3$: 450 mμ.

Die Differenz zwischen Kobalto- und Kobalti-salz liegt darin, dass die Absorptionsbande im Sichtbaren fehlt beim Kobaltosalz, während die ultraviolette Bande von Kobaltisalz um 15 mμ nach längeren Wellen als die des Kobaltosalzes liegt.

Alle Komplexsalze, die Dipyridyl in koordinativer Bindung enthalten, sind durch zwei Banden im Ultraviolett charakterisiert, deren Formen sich der des Dipyridyls stark ähneln. Die eine von diesen zwei Banden liegt bei ca. 300 mμ, die andere bei 245 mμ, von denen die erste, in allen Fällen mit Ausnahme von Kupfersalz, die Spaltung in zwei schmalen Banden beobachtet wurden. Die zweite Bande bei 245 mμ ist nicht vorhanden bei Kupfer- und Kobaltisalz. Zwar diese zwei Bande treten sich erst bei grosser Verdünnung (1/8000–1/10000 Mol) auf, aber es scheint mir, dass sie durch die Zersetzung (oder Hydrolyse) des Komplexsalzes und durch die Befreiung des Dipyridyls nicht verursacht werden, denn ihrer Lagen stark von den des freien Dipyridyls abweichen. Sie müssen den Dipyridylmoleküle in koordinativer Bindung zugeordnet werden.

Zusammenfassung.

Die Absorptionsspektren der wässrigen und alkoholischen Lösungen von Tridipyridylkomplexsalze des zweiwertigen Kupfers, Zinkes, Nickels, Eisens, und Kobalts, sowie des dreiwertigen Kobalts wurden untersucht. In der alkoholischen Lösungen wurde die Messung auch bei tiefen Temperaturen wie $-60° \sim -70°$ ausgeführt. In Alkohol sind einige Absorptionsbanden im Sichtbaren nach längeren Wellen verschoben, aber die ultraviolette Banden sind durch Lösungsmittel wenig beeinflusst. Ausserdem, bei tiefen Temperaturen, wurden einige schmale Banden beobachtet.

Es sei mir gestattet, Herrn Prof. Yuji Shibata für seine freundliche Anleitung und Ratschläge bei der Ausführung dieser Arbeit meinen herzlichen Dank auszusprechen.

Chemisches Institut, Naturwissenschaftliche Fakultät,
Kaiserliche Universität zu Tokyo.

(10) J. P. Mathieu, *Bull. soc. chim.*, [5], **3** (1936), 647.

Studies on the Partial Hydrogenation of Fish Oil. VIII. The Constituents of Docosatrienic Acid Produced on Hydrogenating Methyl Clupanodonate.

By Masakichi TAKANO.

(Received June 21st, 1937.)

In the 6th report[1] of this series, it was pointed out that two isomers, which vary in the degree of absorbing thiocyanogen, existed in docosatrienic acid produced on hydrogenating methyl clupanodonate. The one giving tetrarhodanate was subjected to ozonolysis, and among the resulting decomposition products, the following were identified, as was stated in the 7th report[2]: propylaldehyde, propionic acid, succinic acid, succinic acid monomethyl ester, capric acid, adipic acid, nonanedicarboxylic acid, pimelic acid though not assuredly, heptoic or caprylic acid or both, carbon dioxide though in extremely small amount.

Monobasic acids such as propionic acid, capric acid, and heptoic or caprylic acid are to be formed from the terminal group opposite to the carboxyl group of the original acid, so that the formation of such monobasic acids shows that the original acid is not composed of a single compound, but of three or more isomeric acids of different chemical constitutions. The present paper deals with the constitutions of these isomers based on the decomposition products of ozonolysis which were described in the previous paper. Before this experiment, Inoue and Sahashi[3] had made an examination of the partially hydrogenated products of methyl clupanodonate; the products were separated into several fractions as bromides, and by subsequent oxidation with potassium permanganate in acetone, a fraction yielding a hexabromide was designated to be of the combination of the following acids: undecanoic acid (C_{11}), succinic acid (C_4), malonic acid (C_3), and succinic acid (C_4). It shows the existence of $\Delta^{4:5,\ 7:8,\ 11:12}$-docosatrienic acid in the hydrogenation product of methyl clupanodonate, but no other isomers were mentioned in their description. Thus, they gave to clupanodonic acid a formula having one triple and three double linkings. After that, Toyama and Tsuchiya[4],

(1) Takano, *J. Soc. Chem. Ind., Japan*, **40** (1937), 165 B.
(2) Takano, *ibid.*, **40** (1937), 166 B.
(3) Inoue and Sahashi, *Proc. Imp. Acad.* (Tokyo), **8** (1932), 371.
(4) Toyama and Tsuchiya, this Bulletin, **10** (1935), 441.

applying ozonolysis to the amyl ester, proposed a formula having five double linkings, and recently[5], oxidizing the methyl ester with permanganate in acetone and the potassium soap in aqueous solution, they confirmed their conclusion drawn before.

As was stated in the preceding paper, nearly all of the hexabromide of docosatrienic acid produced on bromination of partially hydrogenated clupanodonic acid, associating with tetrabromide, forms a petroleum-ether-insoluble oily substance, and, in general, these bromides can be difficultly separated from one another. Moreover, the docosatrienic acid yielding hexabromide was already found to consist of various isomers, and the oxidation products which were identified by the author markedly differ from those obtained by Inoue and Sahashi; they obtained undecanoic acid and malonic acid among the oxidation products, while in the present experiment, these acids were not formed to a perceptible extent.

Granting that malonic acid occur intermediately, it will, at the very moment of its occurrence, be converted into carbon dioxide and acetaldehyde or acetic acid by a further degradation. However, neither of them was detected in an appreciable amount. The fundamental differences between the author's results and Inoue and Sahashi's gave in conclusion different suggestions for the constituent and the constitution of docosatrienic acid giving hexabromide.

Now concerning the constitutions of isomers which may exist in docosatrienic acid, the author will discuss below.

(I) Ozonide Decomposition Products and Original Constructive Groups. For ozonolysis, 17 grams of methyl ester of docosatrienic acid $C_{22}H_{38}O_2$ giving tetrarhodanate was used, and its decomposition products obtained in usual manner gave some volatile matters (A) which were carried into water and baryta solution. The remaining not volatilized substances were then separated by filtration into two parts: the water-soluble portion (B) and the water-insoluble oily portion (C). From each portion, subsequently treated with petroleum ether, soluble and insoluble substances were obtained. The following oxidation products were identified.

Carbon dioxide. Carbon dioxide is believed to be formed by a secondary decomposition of the intermediate product derived from the group $=CH\text{-}CH_2\text{-}CH=$. However, its amount was extremely small scarcely amounting to 0.1% of the original sample, so that the isomer having this group may be an exceedingly minor constituent.

(5) Toyama and Tsuchiya, this Bulletin, **11** (1936), 745, 751.

Propylaldehyde and propionic acid. Propylaldehyde, contaminated with propionic acid, was detected in aqueous solution of volatile matters (A). To determine its content, the solution was analysed by using $NaHSO_3$ and iodine solution. A greater part of propionic acid was obtained as barium-salt from the petroleum-ether-soluble substance of the not volatilized water-soluble portion (B). Both of these products seem to be derived from the same group CH_3-CH_2-CH= . Assuming that one such group exists in the original ester, the theoretical yield as propionic acid is 21.4%, while the experiment yielded only 3%, all being calculated as the acid. Hence, the presence of isomer I containing this group may be less than 10% of the total.

Succinic acid and its monomethyl ester. Succinic acid was obtained from the petroleum-ether-insoluble part of the not volatilized portion (B). Formation of this acid evidently shows the existence of the group =CH-$(CH_2)_2$-CH= , and if one such group exists in the original ester, the isomer having this group should be 33.5% of the original ester. In view of the fact that the experimental content of succinic acid is by far greater than is calculated theoretically on the assumption, that there exists only one such group in each isomer, there seems to exist some isomer which has two such groups. On saponifying the not volatilized water-insoluble portion (C), petroleum-ether-insoluble succinic acid was liberated, whereby succinic acid monomethyl ester was suggested to exist in the portion mainly. Taking a little operative loss into consideration, the amount of this ester altogether seems to be 30–35% of the original sample. This is derived from the group =CH-$(CH_2)_2$-$COOCH_3$, and if one such group in average exists in the original sample, it should be 37.9%. Therefore, the existence of one group may be supposed in every isomer.

Monobasic acids of higher molecular weights excepting propionic acid. In the petroleum-ether-soluble part of the not volatilized water-soluble oily portion (C), there was suggested the existence of either heptoic acid or caprylic acid, otherwise, both of these acids. On distilling the collected substances, two fractions were obtained; the one having lower boiling point gave neutralisation value 395.5 and the other having higher boiling point 340.7, respectively. Accordingly, these monobasic acids proved to be contained in the former fraction, and a small portion of the acids mixed with propionic acid will possibly remain in the petroleum-ether-soluble part of the water-soluble portion (B). Heptoic and caprylic acids are derived from CH_3-$(CH_2)_5$-CH= and CH_3-$(CH_2)_6$-CH= , respectively. If either of these groups is to be contained in a proportion of one group to the original ester, it will be found in a range of 37–40%. Eventually,

isomer II giving either heptoic or caprylic acid seemed to be the most plentiful, amounting to a half of the original sample. The component of the latter fraction having higher boiling point mainly consisted of capric acid. Its amount was by far smaller than that of the acids which were contained in the former fraction. The presence of capric acid indicates the existence of isomer III having the group CH_3-$(CH_2)_8$-CH= . The quantity of this isomer (III) seemed to be somewhat greater than that of isomer I.

Dibasic acids of higher molecular weights. Adipic acid together with nonanedicarboxylic acid was found in the petroleum-ether-insoluble substances of not volatilized water-soluble portion (C). This acid is evidently derived from the group =CH-$(CH_2)_4$-CH= , and from one such group contained in the original ester, 40% is to be obtained. The existence of pimelic acid was recognized, though not assuredly, in the same portion as adipic acid. Therefore, it shows the presence of the group =CH-$(CH_2)_5$-CH= . Nonanedicarboxylic acid, being inferred to exist in a smaller extent than adipic acid, was found also in the same fraction as before. This acid is produced obviously from the group =CH-$(CH_2)_9$-CH= , and taking into consideration the theoretical yield from one such group existed in the original sample, an isomer having this group seems to exist in a range of 5–10%.

(II) Kinds of Isomers and Their Chemical Constitutions. Clupanodonic acid is already known to be a normal chain compound by the fact that it is converted into behenic acid having a series connection of 22 carbon atoms on complete hydrogenation. Hence every isomer of docosatrienic acid which is produced from clupanodonic acid by partial hydrogenation will be also normal chain compound. The terminal group opposite to the carboxyl group always gives monobasic acid for every isomer. Of the isomers, which are suggested by the production of the monobasic acids, the existence of the following isomers will be most probable: isomer I giving propionic acid; isomer II which gives either heptoic or caprylic acid or both; isomer III giving capric acid.

The group on the side of the carboxyl group is identical giving the same succinic acid for every isomer. These isomers are also proved to have three double linkings in different positions. It may be considered, therefore, that each of the three isomers described above contains, besides two terminal groups already mentioned, two more groups which give respective dibasic acids in the middle position of the carbon chain. One of the two dibasic acids which come from the middle of the respective

chain is succinic acid, the other being adipic acid, nonanedicarboxylic acid, and probably succinic acid, respectively. Consequently, the following distribution is proposed regarding the variety of combinations of the derived acids, counting their yields and arranging the numbers of their carbon atoms so as to make 22 in total:

Isomer	Monobasic	Dibasic	Dibasic	Dibasic
I (C_{22})	propionic (C_3)	nonanedicarboxylic (C_{11})	succinic (C_4)	succinic (C_4)
II (C_{22})	heptoic (C_7)	pimelic (C_7)	succinic (C_4)	succinic (C_4)
	caprylic (C_8)	adipic (C_6)	succinic (C_4)	succinic (C_4)
III (C_{22})	capric (C_{10})	succinic (C_4)	succinic (C_4)	succinic (C_4)

For isomer II, two combinations are made, viz. $C_8C_6C_4C_4$ and $C_7C_7C_4C_4$. Furthermore in respect to isomers I and II, the following combinations may be possible:

I: $C_3C_4C_{11}C_4$; II: $C_8C_4C_6C_4$ and $C_7C_4C_7C_4$.

The double linkings suggested from these forms show multifarious positions, so that they are inconvenient to judge of the constitution of the clupanodonic acid. The distribution given first is more convenient to explain the positions of double linkings in clupanodonic acid; the distribution shows that the two double linkings near the carboxyl group in each isomer are identically situated at the positions 4:5 and 8:9, accordingly it will be concluded that these isomers are derived from the clupanodonic acid having double linkings at the position 4:5 and 8:9. Eventually, among the isomers of docosatrienic acid produced by hydrogenation of methyl clupanodonate, four following isomers should be suggested:

I: $CH_3\cdot CH_2\cdot CH{=}CH\cdot(CH_2)_9\cdot CH{=}CH\cdot(CH_2)_2\cdot CH{=}CH\cdot(CH_2)_2\cdot COOH$

II: (a) $CH_3\cdot(CH_2)_6\cdot CH{=}CH\cdot(CH_2)_4\cdot CH{=}CH\cdot(CH_2)_2\cdot CH{=}CH\cdot(CH_2)_2\cdot COOH$

(b) $CH_3\cdot(CH_2)_5\cdot CH{=}CH\cdot(CH_2)_5\cdot CH{=}CH\cdot(CH_2)_2\cdot CH{=}CH\cdot(CH_2)_2\cdot COOH$

III: $CH_3\cdot(CH_2)_8\cdot CH{=}CH\cdot(CH_2)_2\cdot CH{=}CH\cdot(CH_2)_2\cdot CH{=}CH\cdot(CH_2)_2\cdot COOH$

Of these acids, isomer II seemed to be of the largest quantity and isomer I the smallest, the yields of their decomposition products being taken into account. Supposing that these isomers are the main components of docosatrienic acid, the existence of two double linkings at the positions 4:5 and 8:9 throughout every isomer will show that these linkings, originally contained in clupanodonic acid, must have remained unattacked, though they are easily attacked by thiocyanogen. Moreover,

from the above formulæ, assuming that no displacement of unsaturated linkings occurred during hydrogenation, it may be suggested that there is possibility of the existence of such double linkings as 12:13, 14:15, 15:16 and 19:20 in the clupanodonic acid. Judging from the result of the investigation of the oxidation products, a form, which keeps both of the double linkings 14:15 and 15:16, is impossible to exist in clupanodonic acid. Therefore, the suggestion is that, an existence of either combination 12:13, 14:15, 19:20 or 12:13, 15:16, 19:20 is possible, and that, one of the double linkings 14:15 and 15:16 is formed by the displacement of the other. Two following formulæ are made for clupanodonic acid from the above combinations.

(a) $\Delta^{4:5,\ 8:9,\ 12:13,\ 14:15,\ 19:20}$-docosapentenic acid;

(b) $\Delta^{4:5,\ 8:9,\ 12:13,\ 15:16,\ 19:20}$-docosapentenic acid.

Concerning its constitution, the formulæ described below were hitherto proposed:

$\Delta^{4:5,\ 7:8,\ 11:12,\ 15:16,\ 19:20}$-docosapentenic acid or $\Delta^{4:5,\ 8:9,\ 11:12,\ 15:16,\ 19:20}$-docosapentenic acid by Tsujimoto[6];

$$CH_3\cdot(CH_2)_2\cdot C\equiv C\cdot(CH_2)_5\cdot CH=CH\cdot(CH_2)_2\cdot CH=CH\cdot CH_2\cdot CH=CH\cdot(CH_2)_2\cdot COOH$$

by Inoue and Sahashi, also maintained by Inoue and Kato[7];

$$CH_3\cdot CH_2\cdot CH=CH\cdot(CH_2)_2\cdot CH=CH\cdot CH_2\cdot CH=CH\cdot(CH_2)_2\cdot CH=CH\cdot(CH_2)_2\cdot CH=CH\cdot(CH_2)_2\cdot COOH$$

by Toyama and Tsuchiya, who established this formula by further investigations[5].

Of the formulæ described by the present author, (b) is quite identical with that proposed by Toyama and Tsuchiya. In compliance with this formula, it will be understood that the double linking 14:15 was formed by a displacement of 15:16 in the course of hydrogenation. It was already pointed out in the previous report that the hydrogenation always tends to take place selectively in the unsaturated linking which hardly absorbs thiocyanogen. Toyama and Tsuchiya[8] had subjected the clupanodonic acid to selective absorption of thiocyanogen in various graduations for the purpose of investigation of its constitution, whereby its tetrarhodanate indicated an absorption of thiocyanogen in unsaturated linkings near the carboxyl group; i.e. 4:5 and 8:9. It is evident through this experiment that the unsaturated linkings 4:5 and 8:9 which absorb

(6) Tsujimoto, this Bulletin, **3** (1928), 299.

(7) Inoue and Kato, *Proc. Imp. Acad.* (Tokyo), **10** (1934), 463.

(8) Toyama and Tsuchiya, *Repts. Tokyo Imp. Ind. Research Inst. Lab.*, **30** (1935), No. 6.

thiocyanogen show more difficulties than the other in hydrogenation, while, on the contrary, the unsaturated linkings 12:13, 15:16 and 19:20 which are unattacked by thiocyanogen are comparatively easily hydrogenated.

The docosatrienic acid together with docosadienic acid is an important component which occurs in the course of hydrogenation of clupanodonic acid; this amounts to half quantities of the total products, when all the original clupanodonic acid just disappeared by hydrogenation, and it is noticeable that this acid has somewhat great drying property, though in a little less degree than linolenic acid which belongs to the same series and is found in vegetable drying oils.

The Hakodate College of Fisheries, Japan.

Spektroskopische Studien über Reaktionsflammen. I. Die Reaktionsflamme von Acetylen und Halogen.

Von Hitoshi TOMINAGA und Go OKAMOTO.

(Eingegangen am 6. August 1937.)

Über die Reaktion von Acetylen gibt es viele und mannigfache Studien, die bis zur Zeit von Berthelot heraufreichen.[1] Besonders waren katalytische Herstellungen des Dichloräthylens sowie des Tetrachloräthans wegen ihrer technischen Bedeutung von verschiedenen Seiten berücksichtigt worden. Studien über die Explosion bei Mischung von Acetylen und Halogen sind aber noch verhältnismässig selten. Trautz[2] beobachtete die Chemilumineszenz bei der Reaktion von Acetylen mit Chlor, doch ohne spektroskopische Messungen vorzunehmen. Hier wird über eine spektrale Beobachtung der Reaktionsflamme berichtet und ferner ihr Reaktionsmechanismus erörtert.

Experimentelles. Die Flamme der Reaktion von Acetylen mit Chlor bzw. Brom unter atmosphärem Druck wurde mittels der einfachen Apparatur hergestellt, die in Abb. 1 schematisch skizziert ist. Alle bei

(1) Berthelot und Gaudechon, *Compt. rend.*, **156** (1913), 1243.
(2) Trautz, *Z. physik. Chem.*, **53** (1905). 1.

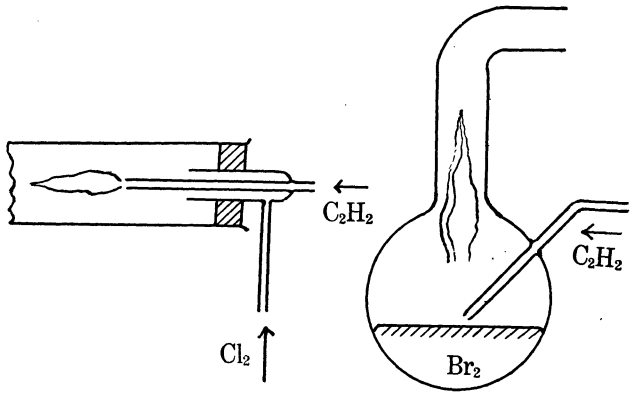


Abb. 1.

den Versuchen gebrauchten Reaktionsgase sind zuerst auf die gewöhnliche Weise gereinigt und dann durch einmaliges Frieren mittels flüssiger Luft möglichst von dem Einfluss der Luftbeimengung befreit. Wenn Brom in Gebrauch ist, wird die Reaktionsflasche bis zur Nähe des Siedepunkts (60°C.) erwärmt und Acetylen gleich oberhalb der Flüssigkeitsoberfläche zugeführt.

Im Dunkelraum sowie in diffusem Licht, wenn Acetylen im Überschuss vorhanden ist, tritt die Reaktion schon deutlich auf, und zwar ohne dass die Erscheinung der Reaktionsflamme auftritt. Wenn man aber die Konzentration des Halogens nach und nach zunehmen lässt, wird nach einer Induktionsperiode, zuerst eine Verpuffung und dann eine stetige Flamme beobachtet, sofort begleitet von einer bedeutenden Russabscheidung an der Wand.

Wenn Wasserdampf im Reaktionsraum vorhanden ist, wird die Explosion nie stattfinden, solange es dunkel bleibt. Wenn man aber einmal einen Augenblick lang beleuchtet, so erfolgt die Explosion sofort.

Die Lichtstärke der Flamme hängt von dem Verhältnis von Acetylen: Halogen ab, und zwar je grösser die Halogenkonzentration ist, desto heller die Flamme.

Die Temperatur der Flamme bei starker Halogenzuführung ist, mit Hilfe der Pt-PtRh-Thermosäule gemessen, 350–400°C.; sie scheint sich bei weiterem Fortbrennen wahrscheinlich noch höher zu steigern. Wenn die Reaktionsgase mit Kohlensäure so verdünnt sind, dass die Flamme kaum bemerkbar wird, bleibt die Temperatur höchstens ca. 100°C.

Die spektrographische Aufnahme ist wegen der Russabscheidung an der Wand ziemlich schwer, und jede Aufnahme brauchte mit unserem „Lichtstark" Spektrograph von Füss eine 30 Minuten lange Belichtung.

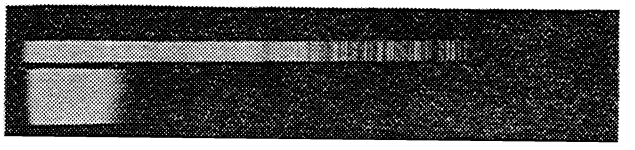


Abb. 2. $C_2H_2 + Cl_2$

Wie das Spektrogramm Abb. 2 zeigt, liegt das Intensitätsmaximum des Spektrums im roten Gebiet; es schwächt sich monoton nach dem Gebiet der kürzeren Wellen hin. Im Ganzen ist das Spektrum kontinuierlich; man kann kein diskretes Band darin finden.

Erörterung des Reaktionsmechanismus. Hier scheint es sich wieder um eine Kettenreaktion von folgendem Typus handeln.

$$C_2H_2 + Cl_2 \longrightarrow C_2H_2Cl_2$$

$$C_2H_2Cl_2 + Cl_2 \longrightarrow C_2H_2Cl_4$$

$$C_2H_2Cl_4 + Cl_2 \longrightarrow C_2\begin{matrix}H\\Cl\end{matrix} \cdot Cl_4 + HCl^*$$

$$HCl^* + Cl_2 \longrightarrow \underset{\text{Kettenkopf}}{2\,Cl} + HCl$$

Kette

$$Cl + C_2H_2 \longrightarrow C_2\begin{matrix}H\\Cl\end{matrix} + H$$

$$H + Cl_2 \longrightarrow HCl + Cl$$

$$C_2\begin{matrix}H\\Cl\end{matrix} \longrightarrow C_2^* + HCl + H$$

$$C_2^* \longrightarrow C_{Gas} + C_{fest}$$

Wenn Wasserdampf im Reaktionsraum vorhanden ist, wird HCl*, die Quelle der Startreaktion, deaktiviert, so dass keine weitere Kettenreaktion fortschreiten kann. Setzt man aber das Gefäss sichtbarem Strahlen aus, so ist es schon möglich, das Chloratom, das den Kopf der Kette bildet, nicht durch hier erörterte chemische Reaktion, sondern photochemisch zu erzeugen.[3] $C_2\begin{matrix}H\\Cl\end{matrix}$, welches wir in der Kette annahmen, ist eine schon von den Organikern synthetierte isolierbare Verbindung,[4] die sich aus Mangel an Wasserstoff leicht zersetzt in den Russ

(3) Elliot, *Proc. Roy. Soc.* (London), A, **127** (1930), 638; Brown, *Phys. Rev.*, **38** (1931), 1179.

(4) Beilstein, "Handbuch der organischen Chemie," 4. Aufl., Bd. I., S. 244.

und Chlorwasserstoff. Der bei diesem Zerfall entstandene Kohlenstoff sollte, durch Kondensation, thermisch das Kontinuum unseres Spektrogrammes ausstrahlen.[5]

In Bezug auf die Konstitution des Chloracetylens, möchten wir nach Cohen[6] Acetylidenform $=C=C\begin{matrix}H\\Cl\end{matrix}$ annehmen, in dem die beide C-Atome im ^5S-Zustand angeregt sind. Bei der Abspaltung des Chlorwasserstoffes, trennen sich diese beiden C-Atome, da wir kein C_2-Band in unserem Spektrogramm finden können.

Zum Schluss möchten wir dem Gakuzyutu-Sinkokwai für seine finanzielle Hilfe herzlichsten Dank aussprechen.

Chemisches Institut, Hokkaido Universität,
Sapporo, Japan.

---

(5) Dunkel, *Z. physk. Chem.*, B, **10** (1930), 434; Freudenberg, "Stereochemie," S. 659, Leipzig (1933).

(6) Cohen, "Organic Chemistry," Bd. I, S. 75.

Spektroskopische Studien über Reaktionsflammen. II. Die Reaktionsflamme von Quecksilber und Halogen.

Von Hitoshi TOMINAGA und Go OKAMOTO.

(Eingegangen am 6. August 1937.)

Einer der Autoren (O.)[1] teilte vor kurzem über das Flammenspektrum mit, das bei Einwirkung von Chlor auf Quecksilber emittieren wird. Er hat ein neues Band gefunden, das Haber,[2] Kallmann[3] und Kondratjew[4] bei ihren Versuchen über Verbrennung von Quecksilber in Halogen nicht bemerkt hatten. Wir haben nochmals die Versuche von Haber und Kallmann wiederholt und neue Aufnahme von der Quecksilber-Brom-Flamme gemacht, dadurch es uns erklärbar wurde, welcher Art der Reaktionsmechanismus war, und wodurch die Bandenemission verursacht wird.

---

(1) Okamoto, *J. Chem. Soc. Japan*, **54** (1933), 702.
(2) Haber und Zisch, *Z. Physik*, **9** (1922), 302.
(3) Frank und Kallmann, *ibid.*, **34** (1925), 924.
(4) Kondratjew, *ibid.*, **45** (1927), 67.

Experimentelles. Um eine für die Versuche bequeme, stabile und lichtstarke Flamme hervorzubringen, war es nötig, immer einen Überschuss von Halogen zu gebrauchen. Bei Anwendung der Apparatur A in Abb. 1 hat das neue Band eine besonders deutliche Struktur. Spektrograph: Hilgersches „Constant deviation type"; Füsssches „Lichtstark". Platte: „Wratten hypersensitive panchromatic". Beleuchtungsdauer: 2 bis 5 Stunden mit „Constant deviation type"; 30 Minuten mit „Lichtstark". Spektrogramm: Abb. 2.

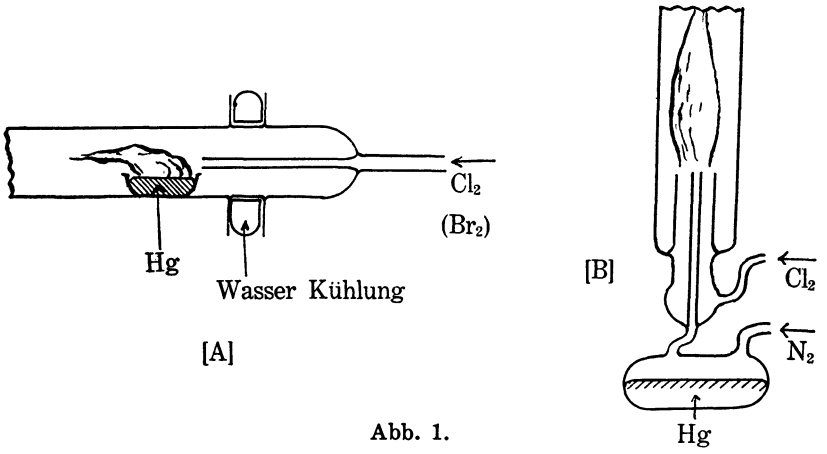


Abb. 1.

[A] sowie [B] von aussen bis ca. 300°C. elektrisch geheizt.

A. Flamme mit $Cl_2 + Hg$. Band(1), das seine Intensitätsmaximum bei 5600 Å hat und nach dem Gebiet der kürzeren Wellen zu diffus ist. Band(2), ein Band zwischen 6700 und 5700Å.

B. Flamme mit $Br_2 + Hg$. Band(3), ein Band zwischen 6700 und 4300Å.

Tabelle 1. Messungsresultate der Bandenkante.

A. Flamme mit $Cl_2 + Hg$.		B. Flamme mit $Br_2 + Hg$.			
6519Å	6151	6602Å	6297	6065	5880
6436	6086	6569	6238	6029	5835
6358	6015	6476	6181	5994	5798
6214	5897	6413	6136	5953	5769
		6365	6108	5914	5736

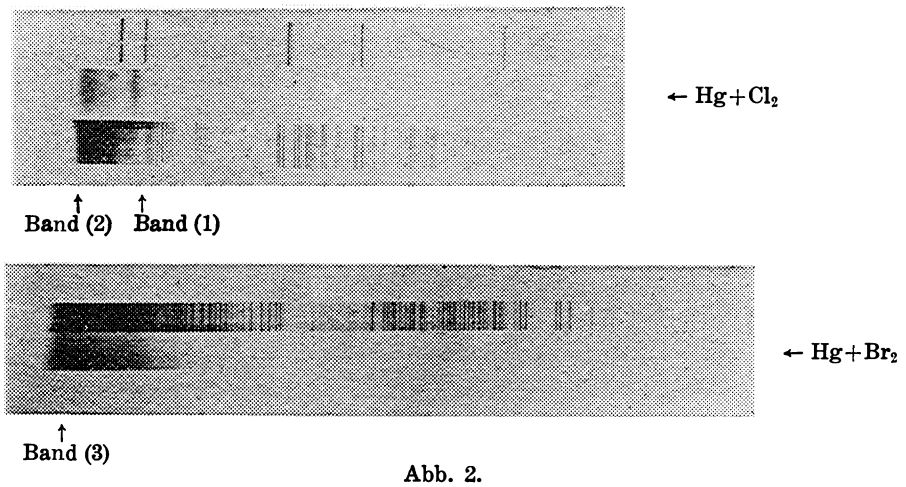


Abb. 2.

Erörterung der Resultate. Von der Analyse der oben angegebenen Spektrogramme ist es leicht zu vermuten, dass die Bande von zweiatomigen Halogenmoleküle verursacht werden. Unsere Bande zeigen hinreichend gute Übereinstimmung mit denjenigen, die Kitagawa[5] bei der H_2-Cl_2-Reaktion, und Brown[6] bei molekularem Br_2 fand. Im ganzen sind diese Bande von der Übergang von $O_u^+ \rightarrow {}^1\Sigma_g^+$.

Tabelle 2. Vergleich von der Bande der Reaktionsflamme mit der Absorption des molekularen Halogens.

Cl_2

v' \ v''	4	5	6
2			
3			
4			15352 (15339)
5	16638		15550 (15537)
6	16816	16300 (16257)	15757 (15728)
7	17008 (16957)	16484 (16431)	15957 (15903)
8	17180	16638 (16627)	16113 (16092)
9	17350	16816 (16802)	16300

$$\nu = 17657.7 + (255.7\, v' - 5.42\, v'^2) - (560.9\, v'' - 4.0\, v''^2)$$

(5) Kitagawa, *Rev. Phys. Chem.* (Japan), **8** (1934), 1; **11** (1937), 25.
(6) Brown, *Phys. Rev.*, **39** (1932), 777.

Br_2

v' \ v''	1	2	3	4	5
6					15169 (15146)
7					15311 (15223)
8					15450 (15441)
9				15898 (15880)	15585 (15593)
10			16343 (16371)	16029 (16031)	15714 (15711)
11		16789 (16798)	16472 (16488)	16156 (16178)	
12		16912 (16909)	16594 (16586)	16278 (16297)	
13	17353 (17334)	17033 (17006)	16718 (16683)		
14	17467 (17434)	17150 (17138)	16831		
15	17579	17259 (17247)			

$$\nu = 15831.2 + (163.81\, v' - 1.59\, v'^2 - 0.0087\, v'^3) - (322.71\, v'' - 1.15\, v''^2)$$

Eingeklammerte Zahlen sind die von unseren Beobachtungen ausgerechneten Werte.

Nun möchten wir den Mechanismus der Entstehung des aktiven Chlor- bzw. Brom-Moleküls darlegen. Die Bildungswärme des $HgCl_2$ und des $HgBr_2$ aus den normalen Molekülen der Bestandteilen ist wie folgt:

$$Hg + Cl_2 \rightarrow HgCl_2 + 53 \text{ Kcal. } (2.3 \text{ e.v.})$$

$$Hg + Br_2 \rightarrow HgBr_2 + 48 \text{ Kcal. } (2.1 \text{ e.v.})$$

Die Aktivierungsenergien, die Cl_2^* bzw. Br_2^* erzeugen, müssen nach dem Anfangs-v''-Zustand der Moleküle verschieden sein, wie man aus der folgenden, mittels unserer spektroskopischen Daten ausgerechneten Tabellen ersieht.

Tabelle 3. Abhängigkeit der Aktivierungsenergie von der Anfangszuständen

$Cl_2 \rightarrow Cl_2^*$		$Br_2 \rightarrow Br_2^*$	
$v'' = 0$	58 Kcal.	$v'' = 0$	50.6 Kcal.
1	56		
2	53	1	49
3	52		
4	49	2	46

Aus den oben angegebenen Zahlen, könnte man folgern, dass die aus der Reaktion von Quecksilber mit Halogen entstandenen Quecksilberhalogenide, die ihre Bildungsenergie als eigne innere Energie in sich behalten, durch den Stoss zweiter Art andere Halogenmoleküle aktivieren, wenn nur bei Cl_2 $v''>2$ und bei Brom $v''>1$ ist. Diese innere Energie ist von solcher Grösse anzunehmen, dass sie als Schwingungsenergie im Moleküle vorhanden ist; für Elektronenenergie reicht sie nicht aus.

$$HgCl_2 \xrightarrow{6.6\ e.v.} HgCl_2^* \text{ (elektronisch angeregt)}^{(7)}$$

$$HgBr_2 \xrightarrow{5.5\ e.v.} HgBr_2^* \text{ (elektronisch angeregt)}$$

In Bezug auf die Ursache des diffusen Bandes(1) möchten wir annehmen, dass das HgCl-Molekül, das aus einer der folgenden beiden Reaktionen entstanden ist, durch den Stoss mit $HgCl_2^*$, aktives HgCl* bildet, das der Bandenaussender sein kann.

$$HgCl_2 + Hg \rightarrow 2HgCl$$

oder

$$Hg + Cl_2 \rightarrow HgCl + Cl$$

Bei dem Brom ist die Entstehung eines Band(1)-ähnlichen Bandes ausgeschlossen, weil die elektronische Anregungsenergie des HgBr 2.5 e.v., also grösser als die Energie des $HgBr_2^*$ (2.1 e.v.) ist.

Der Grund, aus dem kein Cl_2^* in $v''>2$-Zustand bei der Reaktion $Hg + Cl_2$ zu finden ist, könnte darin liegen, dass es dem diffusen Band(1) superponiert und von ihm verdeckt ist.

Weitere Einzelheiten des Reaktionsmechanismus möchten wir später durch Anwendung reaktionskinetischer Methoden untersuchen.

Dem Gakuzyutu-Sinkokwai möchten wir an dieser Stelle auch für seine finanzielle Hilfe vielen Dank aussprechen.

Chemisches Institut, Hokkaido Universität,
Sapporo, Japan.

(7) Wieland, *Z. Physik*, **77** (1932), 157.

Studies on Fluorine at Low Temperatures. I. Preparation, Analysis and Handling of Fluorine.

By Shin-ichi AOYAMA and Eizo KANDA.

(Received August 12th, 1937.)

General Introduction. Although fluorine is as abundant in nature as many other ordinary elements, no great progress has yet been made in the study of its physical or chemical properties. This is probably due to the fact that its chemical property is so violent that it can be handled with great difficulty and accordingly its use has not yet been well known.

Studies on fluorine have so far been made chiefly by (i) Moissan and Dewar. Moissan discovered fluorine in the form of element in 1886. Since then he carried out various qualitative investigations, and in collaboration with Dewar, went so far as liquefying and solidifying it, thus accomplishing preliminary studies on fluorine at low temperatures by the beginning of this century.

His studies went far ahead of his age, but no further study has since been made on the properties of fluorine at low temperatures. This is the reason why the somewhat inaccurate results of his studies are still in use. For instance, the melting point of fluorine has been given as −223°C. or −233°C. in several papers[1] since Moissan and Dewar[2] reported that "the melting point of fluorine was a little higher than that of oxygen—it was 40°K. or about −223°C." (The melting point of oxygen is now regarded as −219°C.)[3]

(ii) Ruff and his followers. Ruff carried out investigations for obtaining chemical compounds of fluorine and other halogens or oxygen, nitrogen, carbon, etc. As a result of his painstaking investigations extending over more than a quarter of a century, he took initiative in producing almost all new gaseous compounds of fluorine, the number of his papers published on such compounds coming to about 30. Ruff's investigations, however, were intended for producing new compounds, the chemical kinetics of the reactions concerned or various properties of the products of the reactions generally being left out of consideration.

(1) "International Critical Table"; Landolt and Börnstein, "Physikalisch-chemische Tabellen"; Mellor, "Comprehensive Treatise on Inorganic and Theoretical Chemistry," Vol. II; Henglein, *Z. anorg. allgem. Chem.*, **118** (1921), 165.

(2) Moissan and Dewar, *Compt. rend.*, **136** (1903), 641.

(3) Clusius, *Z. physik. Chem.*, B, **3** (1929), 41.

(iii) Simmon, Cady, Schumacher, and others. They are making studies on oxides of fluorine and organic compounds of fluorine. A few others are making researches on the compounds of fluorine.

In short, investigations of fluorine are lagging far behind those of other elements and compounds, and enumeration of all the books and papers on the studies of fluorine would not be very difficult.

The boiling point and melting point of this element are as low as −188°C. and about −220°C. respectively. It resembles oxygen in this respect. The characteristics of permanent gases, such as oxygen, nitrogen, hydrogen, etc. in their liquid and solid states have been examined from every point, while those of fluorine alone have been left almost untouched. Further, fluorine shows chemical reaction even at a very low temperature, which is not the case with other elements, and for this reason, the study of this element at low temperatures was the more interesting and valuable. The experiments on fluorine at low temperatures were technically easier than at ordinary temperature, as it becomes somewhat less corrosive to the apparatus and material used. But it was found that the results of investigations so far made on the characteristics of fluorine itself were so unreliable that no experiment or theoretical studies could be carried out with confidence on the basis of these results. The authors first intended to make clear the various characteristics of fluorine at low temperatures. In the following papers are given the results of the studies on fluorine gas at low temperatures and on liquid and solid fluorine.

On account of the chemical activity, the preparation, analysis, and experiment of this element are attended with many technical difficulties. But owing to the improvements in the apparatus and in the materials as well as to the valuable experiences of former investigators in this field, the present authors are now in a position to make experiments for not only qualitative but also quantitative determination of some properties of fluorine. Our first paper deals with the preparation of fluorine and a few experiences in handling fluorine.

I. Preparation of Fluorine. Fluorine was prepared by electrolysis of molten potassium bi-fluoride (KF·HF). There are several papers referring to such a method of preparing fluorine.[4] The authors use improved Dennis's V-shaped electrolyser.

(4) Argo, Mathers, and Humiston, *J. Phys. Chem.*, **23** (1919), 348; Simon, *J. Am. Chem. Soc.*, **46** (1924), 2175; Lebeau, *Compt. rend.*, **181** (1925), 915; Ishikawa, *Bull. nst. Phys. Chem. Research* (Tokyo), **10** (1931), 176; Dennis, *J. Am. Chem. Soc.*, **53** (1931), 3236; Miller and Bigelow, *ibid.*, **58** (1936), 1585.

(1) *Electrolyser.* As shown in Fig. 1, copper pipes 60 mm. in outside diameter, 50 mm. in inside diameter, and 35 cm. in length are brazed into a V-shaped pipe, and a tube to hold the thermometer is also brazed at the joint.

The caps are of flange type, and lead rings are used as the gasket for making the contact between the caps and the pipes gas-tight. In the centre of the flanges there are hollow spots for keeping cement with which the electrodes are fixed to the caps. The electrodes are of ordinary Acheson graphite, 12 mm. in diameter. But, as the rods are slender and too fragile, about one third of their total length is replaced by copper rods, into which the graphite is inserted. The joints are fastened with belts as represented by b in the figure. In this way the fixing of the electrodes with cement at a becomes easy. For preventing the electrodes from loosening at a and for fixing them firmly, the copper rods are fitted with iron nails. Further, molten potassium hydrogen fluoride was spread over the cement when the gas-tightness with cement alone became imperfect in the course of use of the apparatus. A nichrome wire is wound around the vessel pipe for heating. The exit c for the gas produced is made as wide as possible. If it is narrow, the vaporized fluoride will condense here while the vessel is being used, and will choke the exit. The cell was charged with one kg. of Merck's potassium bi-fluoride, which was melted at 230–240°C.

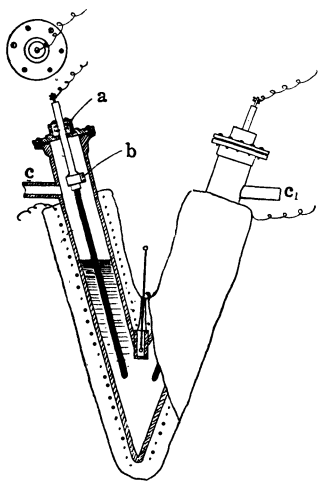


Fig. 1.

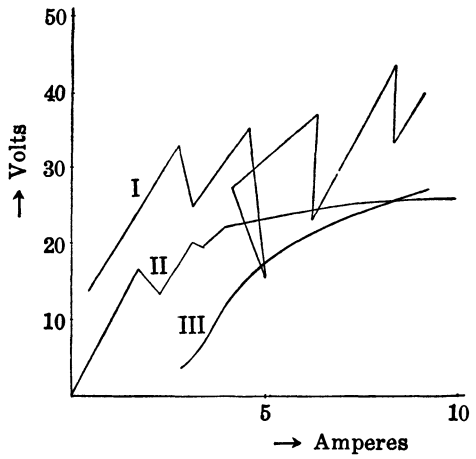


Fig. 2. I: Nondehydrated salt.
II: Dehydrated salt.
III: Salt dehydrated and subjected to a few hours' electrolysis.

(2) *Electrolysis and drying of salt.* The salt began to melt at about 240°C. according to the thermometer in the middle of the arms of the cell. As the fresh salt contained much water, oxygen alone was produced on electrolysis. After this process was continued for a certain time, fluorine was produced. Until this time, the voltage and the current between the two poles varied much (Fig. 2), discharge occurred between the anode and the molten salt, the graphite pole was broken, and the salt became very dirty. There was also a fear of explosive production of the gas. It was therefore necessary to dehydrate perfectly the salt before electrolysis.

To dry the salt, the flange-shaped caps holding the electrodes were replaced by caps having an opening for the gas, by which the tube was connected with a gas-circulating device with a desiccator of phosphorus pentoxide. Air was circulated for 24 hours through the salt kept at 230–240°C. After this treatment, fluorine was produced smoothly as soon as the current ran. The electrolysis was effected at about 5 amp., 15 volts, 240–250°C. in the early stage and at 270–280°C. when hydrogen fluoride in the salt became scanty after several hours. The salt was renewed in about 200 ampere-hours.

The gas produced during a given time with a current kept constant at 5 amp. was led into an aqueous solution of potassium iodide, and the amount of fluorine was determined by iodometry. The efficiency of current was 75–90%, varying with aging of the salt.

(3) *Purity of fluorine.* For the quantitative determination of fluorine, iodometry using an aqueous solution of potassium iodide was carried out, while for examination of the purity of the gas produced, the following method was adopted in view of the fact that mercury acts on fluorine quantitatively to form mercury fluoride.

A Pyrex glass bulb was filled with the sample of fluorine with the addition of a small quantity of mercury, and was shaken. Then the bulb was connected with a mercury pressure gauge and the pressure of the remaining gas was examined.

Naturally, the purity of fluorine varied also according to the time lapse in the electrolysis. The following figures were obtained from a salt dried for 24 hours: F_2 97%, O_2 2.5% after 5 hours' electrolysis; F_2 99.8% after 20 hours' electrolysis. There were other impurities such as CF_4, O_3, Cl_2, HF, etc.

(4) *Purification and storing of fluorine.* The above-mentioned impurities in fluorine decrease with aging of the salt, only hydrogen fluoride remains in the same quantity. Hydrogen fluoride can be eliminated by

passing the gas over powdered sodium fluoride. Other impurities and a trace of hydrogen fluoride are solidified in a trap cooled by liquid oxygen (the boiling point of fluorine is about −188°C. and that of oxygen −183°C.).

Fluorine perfectly dried and freed from hydrogen fluoride is not very corrosive to glass. If it is to be kept in a glass bulb, however, an extremely large volume is needed. Moreover, it will attack glass to some extent at ordinary temperature. On this account, it is desirable to keep it in the liquid state in a trap cooled by liquid nitrogen.

II. Some Techniques of Experiments on Fluorine. (1) *Materials for the apparatus.* The progress of chemical and physical researches on fluorine has been greatly hindered by the highly corrosive nature of fluorine and the difficulties in manufacture of the apparatus. The following is the summary of the authors' experiences gained from the studies in this field.

(i) Fluorine is far less corrosive when it does not contain any trace of hydrogen fluoride nor any moisture than when it does.

(ii) Hard glass is of course preferable to ordinary glass, while Pyrex glass is better than hard glass.

(iii) Quartz is a little more anti-corrosive than glass. But the life of a quartz film pressure gauge and the like which are used for other corrosive gases (such as chlorine) becomes very short when used for fluorine at ordinary temperature.

(iv) Apparatus made of anti-corrosive metals are more durable than those made of glass. According to the results of tests on the exposure of various metal pieces to fluorine, platinum, gold, magnesium, nickel, monel-metal, and copper are anti-corrosive. Of these metals, magnesium and the others that follow form a very tight anti-corrosive film. Especially, the fluoride film on magnesium is generally expected to serve for an anti-corrosive agent when this metal is used for industrial purposes, because the film is very tight and insoluble in water. In workability, copper and monel-metal are the best for the apparatus. Platinum filament (about 0.1 mm. in diameter), when used in fluorine for heating it, formed platinum fluoride at about 400°C., emitting yellow smoke. Ordinary solder may be used at ordinary temperature. Lead plates were used as the gasket of the electrolyser. This gasket, which was heated to about 150°C., could be kept gas-tight, but it had to be renewed at times.

(v) Gas-tight materials. Of course D'kotinsky cement and pitches cannot be used in the experiment on fluorine. For keeping the apparatus proof against fluorine gas, the following substances may be used for the packing or coating for the joint in the apparatus: (a) molten potassium fluoride; (b) molten potassium hydrogen fluoride; (c) plaster, lead oxide, and the like as kneaded with glycerine; (d) further, as both gas-tight and insulating material may be used bakelite which has been properly heat-treated.

(vi) Lubricating materials. Grease naturally burns when it is used as lubricating material on the ground glass surface of a glass cock. Even very hard grease, though it did not burn when the cock was turned off and fluorine remained still in a glass vessel, burst into blue flame every time when the cock was turned and fluorine was streaming. Accordingly a paste of glycerine or of phosphoric acid was used. Even such a material, however, can not be used for a long time. In the experiment in which gas-tightness was required, an anti-corrosive metal valve as shown in Fig. 3 was used.

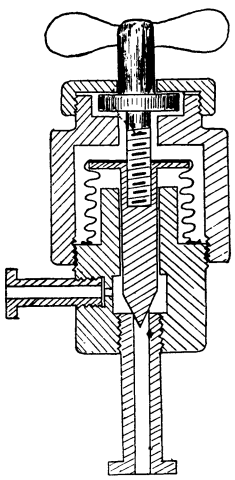


Fig. 3.

(2) *Vacuum cocks.* Since Bodenstein devised a metal valve, a number of similar kinds have been worked out. The present authors used a valve as shown in Fig. 3. In this valve, the ground metal surface can be renewed and a corrugated copper tube is used. Its construction and function will be understood by the section diagram in Fig. 3.

(3) *Mercury.* As stationary mercury makes a tight fluorine film, it may be used for hermetically sealing a joint between ground glass surfaces. If used in a mercury pressure gauge, it must not be in direct contact with fluorine. A quartz film pressure gauge or a platinum film pressure gauge may be used for fluorine. (See the paper on the determination of vapour pressure.)

In rough determination of the pressure, mercury with glycerine placed on it may be used.

III. Reaction between Fluorine and Inflammable Solids at Ordinary Temperature. According to Moissan, fluorine burns various elements such as carbon, sulphur, phosphorus, silicon, tellurium and selenium when it comes in contact with them, and scrupurous care should be taken in

handling these elements. The reports of Moissan and others, however, are too brief to make the matter clear. The present authors know cases in which the reaction made no remarkable progress during their experiments with fluorine, though they felt at first uneasy about the danger of burning. The authors examined the conditions for the combustion of these inflammable solids so that they might thence be able to handle fluorine with confidence. The results of qualitative experiments on the reactions between fluorine and charcoal, phosphorus, sulphur, or selenium are given below:

(1) *Reaction between stationary gaseous fluorine and solids.* A spring balance similar to one used in the study of adsorption of fluorine gas was adopted in this experiment. About 1 g. of each sample was placed on a scale attached to the lower end of the balance and fluorine was slowly introduced. Then the change in the sample and spring was observed. The results of the experiment at 0°, 15° and 30°C. were as follows: (i) Red phosphorus showed reaction at these temperatures, and its quantity decreased. At 15°C., it emitted white smoke at the moment when the fluorine gas was introduced, while at 30°C. it burst into blue flame. (ii) Sulphur emitted white smoke at 15°C. and 30°C., but without flame. (iii) Selenium gave the same phenomenon as seen with sulphur. (iv) Charcoal emitted neither smoke nor flame at any of these temperatures, and was the most inactive.

(2) *Experiment in flowing gas.* As stated above, some substances do not burn in stationary fluorine at ordinary temperature. But even these substances burnt at the moment when, or a little after, they were exposed to fluorine jetting out of a small bore of a tube. It seems that the combustion takes place in a certain range of velocity of the gas flow. Of course this depends upon the bore of the pipe and, therefore, cannot be said to be an established fact. The experiment was carried out by means of an apparatus illustrated in Fig. 4.

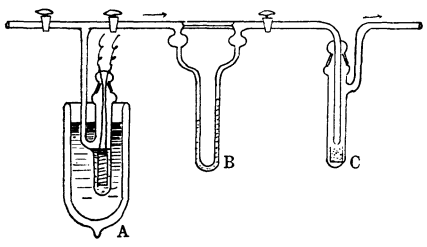


Fig. 4.

Although charcoal did not burn in stationary fluorine gas at ordinary temperature, it did at 15°C. on coming in contact with a flow of fluorine running at a velocity of about 60 c.c./min. The combustion of the samples

as related to the velocity of the fluorine gas flow was as follows:

Sample	Phosphorus	Selenium	Sulphur	Charcoal
Velocity of flow (c.c./min.)	15	20	22	60

The authors express their hearty thanks to the Japan Society for the Promotion of Scientific Research for the contribution of the expense of this experiment.

Cryogenic Section, Research Institute for Iron, Steel and Other Metals, Tohoku Imperial University.

Studies on Fluorine at Low Temperatures. II. Vapour Pressure of Fluorine.

By Shin-ichi AOYAMA and Eizo KANDA.

(Received August 12th, 1937.)

In the study of liquid and solid fluorine, the vapour pressure of fluorine must first of all be determined. The present authors determined the boiling point and the vapour pressure of fluorine, and calculated heat of vaporization.

I. Apparatus for the Experiment. The method was nearly the same as employed in the measurements of the vapour pressure of oxygen and nitrogen,[1] both the quartz film pressure gauge and the platinum film pressure gauge being used in the present experiment. The platinum film pressure gauge is shown in Fig. 1. The hatched part is made of copper. Concentric waves are impressed, by means of a stamp separately devised, on the platinum film (containing 10% rhodium), 0.04 mm. thick. The film is inserted between c and d and is made gas-tight by fastening it to the copper body with a number of screws. A needle is set in the centre of the film and the mirror m at the end of the needle turns on its stem s with the vertical movement of the film. The movement of the mirror is

(1) Aoyama and Kanda, this Bulletin, **10** (1935), 482.

observed by means of a telescope and a scale at a distance of 1 metre. The lower surface of the platinum film p is exposed to, and under the pressure of, the fluorine, and the upper surface is under the air pressure. This air pressure acts on the mercury pressure gauge through the pipe l. The gauge is used as a zero instrument, always having an accuracy of 0.05 mm. Hg.

The device in which the quartz film pressure gauge is used as the zero instrument is illustrated in Fig. 2. The life of the quartz film will be rather short if it is under ordinary pressure of fluorine vapour.

The cryostat is shown in Fig. 2,[2] in which a liquid hydrogen vessel is used for adjusting the temperature when measurement is to be made at −195°C. and below.

Fluorine was produced in an electrolyser more than 20 hours after the start of electrolysis. The fluorine was introduced at A after a number of fractional distillations, and was condensed in the bulb B.

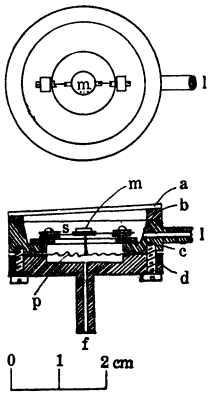


Fig. 1.

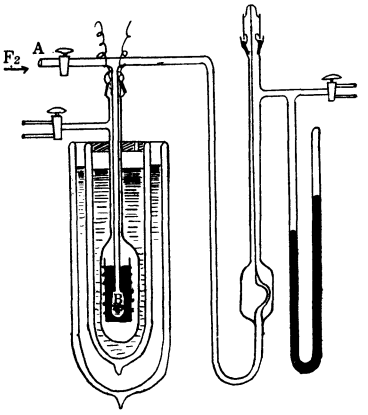


Fig. 2.

II. Results of Measurements. (1) Measurements were made at about 14 points between −187°C. and −213°C. It has been found that the vapour pressure can be expressed by the following equation:

$$\log p_{\text{mm.}} = -\frac{442.72}{T} + 9.1975 - 0.013150\,T\,.$$

The observed and the calculated values are given in Table 1.

(2) For particulars, see (1).

Table 1.

T	$p_{obs.}$	$p_{cal.}$	$p_{cal.}-p_{obs.}$
59.90	10.10	10.445	+ 0.35
63.61	26.30	25.20	− 0.90
65.00	35.50	34.02	− 1.50
68.70	65.20	70.78	+ 5.6
69.99	92.05	89.56	− 2.4
72.85	143.35	145.34	+ 2.0
75.01	209.10	203.70	− 5.4
77.51	289.50	292.81	+ 3.3
79.35	381.50	375.66	− 5.8
79.98	402.35	407.85	− 4.5
83.43	608.10	622.30	+14.2
84.52	712.75	704.85	+ 7.9
85.00	740.10	743.70	+ 3.6
86.21	845.20	848.20	+ 3.0

From the same equation the boiling point at $p = 760$ mm. was calculated as follows:

$$T_o = 85.19°\text{K}\ (-188°\text{C.}),$$

while Clausen[3] gives 85.21°K, Cady[4] 84.93°K, and Moissan[5] 86°K.

From the above equation for the vapour pressure we have for the heat of vaporization:

$$Q_o = 1581 \text{ cal, according to } Q_o = RT^2 \frac{d \ln p}{dT}.$$

(2) Vapour pressure of solid fluorine is given in Table 2.

Table 2.

T	55.15	54.50	53.90	52.55	51.85
p	2.70	2.10	1.75	1.55	0.10

(3) *J. Am. Chem. Soc.*, **56** (1934), 614.
(4) *Ibid.*, **52** (1930), 3839.
(5) *Compt. rend.*, **125** (1897), 505.

It gives $\log p_{\text{mm.}} = -\frac{430.06}{T} + 8.233$. This equation gives $Q \fallingdotseq 1970$ cal. for the heat of vaporization of solid fluorine. From this value and the heat of vaporization of the liquid, $Q_S \fallingdotseq 390$ cal. was obtained for the heat of fusion.

The authors express their hearty thanks to the Japan Society for the Promotion of Scientific Research for a grant.

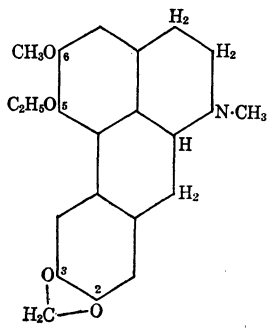
Cryogenic Section, Research Institute for Iron, Steel and other Metals, Tohoku Imperial University.

Synthese von einem Isomeren des Domesticin-äthyläthers.

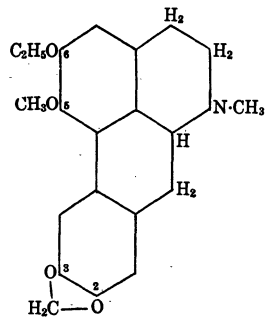
Von Hideo SHISHIDO.

(Eingegangen am 21. August 1937.)

In der letzten Mitteilung habe ich über die Synthese des Domesticin-äthyläthers, d.h. *d*-2,3-Methylendioxy-5-äthoxy-6-methoxy-*N*-methyl-aporphins (I), berichtet[1], und es ist mir nun gelungen, eines seiner Isomeren, d.h. *d*-2,3-Methylendioxy-5-methoxy-6-äthoxy-*N*-methyl-aporphin (II), in analoger Weise zu synthetisieren, indem als ein Ausgangsmaterial anstatt Äthylvanillins Isoäthylvanillin angewendet wurde, womit Vergleich beider Substanzen erst ermöglicht wird.



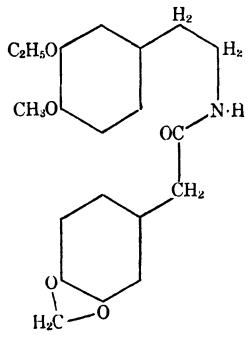
I



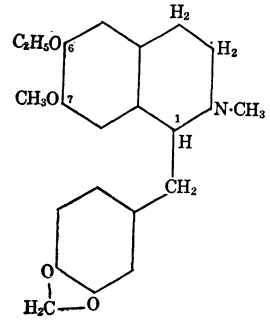
II

(1) This Bulletin, **12** (1937), 150.

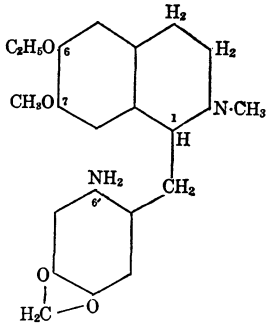
Zunächst wurde β-(3-Äthoxy-4-methoxy-phenyl)-äthyl-3′,4′-methylendioxy-phenacetamid (III) (Schmp. 131°) aus 3-Äthoxy-4-methoxy-β-phenyläthylamin (Schmp. des Oxalats 226–227°) und Homopiperonylsäure dargestellt. Dieses Amid wurde dann durch Phosphoroxychlorid in ein Dihydroisochinolinderivat übergeführt, mit Jodmethyl an seinem N methyliert, und dann durch Reduktion in eine Tetrahydroverbindung (IV) (Schmp. 154–155.5°) umgewandelt. Diese letztere Substanz wurde schliesslich mit Salpetersäure an der 6′-Stellung nitriert, dann durch Reduktion mittels Stannochlorids und Salzsäure in eine 6′-Amino-Verbindung (V) (Schmp. 105–107°) übergeführt, und diese unter Ringschluss zu inaktivem 2,3-Methylendioxy-5-methoxy-6-äthoxy-*N*-methyl-aporphin (VI) (Schmp. 136°) diazotiert. Dieses racemische Produkt wurde nun mittels der *d*- und *l*-Weinsäure in beide aktive Komponenten gespaltet.



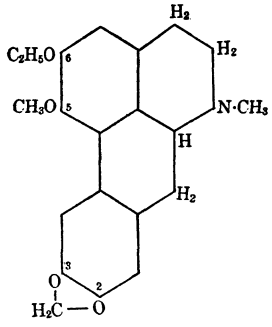
III



IV



V



VI

Die so synthetisch erhaltene *d*-Base (II) schmolz bei 144°, zeigt $[\alpha]_D^{28} = +90°$ und nimmt mit konz. Schwefelsäure eine rotviolette Farbe

an, die sich durch Salpetersäure-Dampf blaugrün verändert. Diese Farbenreaktion teilt es mit dem Domesticin-äthyläther[2], aber bei der Mischprobe ergab eine Erniedrigung des Schmelzpunktes um 16°, wodurch man die Konstitution des Domesticins (I), welche in den früheren Mitteilungen festgestellt wurde[3], stark unterstützt wird.

Beschreibung der Versuche.

3-Äthoxy-4-methoxy-β-phenyläthylamin. 100 g. 3-Äthoxy-4-methoxybenzaldehyd (Isoäthylvanillin) werden nach Perkin[4] mit Malonsäure in Pyridin unter Zugabe von Piperidin umgesetzt. Die so erhaltene 3-Äthoxy-4-methoxyzimtsäure wird aus Methanol zu Prismen vom Schmp. 176–177.5° umkrystallisiert. (Gef.: C, 64.60; H, 6.66. Ber. für $C_{12}H_{14}O_4$ (222): C, 64.86; H, 6.31%.)

Diese Zimtsäure wird in Eisessig der katalytischen Hydrierung mit Palladiumkohle unterworfen. Nach beendigter Reaktion wird vom Palladiumkohle abfiltriert und das Filtrat im Vakuum abgedampft. Die 3-Äthoxy-4-methoxy-phenylpropionsäure wird aus Benzol in Blättchen vom Schmp. 104–106° umkrystallisiert. (Gef.: C, 64.58; H, 7.40. Ber. für $C_{12}H_{16}O_4$(224): C, 64.29; H, 7.14%.)

Diese Phenylpropionsäure wird in Chloroformlösung mit Thionylchlorid[5] in 3-Äthoxy-4-methoxy-phenylpropionsäurechlorid und dann durch Ammoniak in dessen Amid übergeführt. Aus Benzol umkrystallisiert bildet es Nadeln vom Schmp. 123–124°. (Gef.: C, 64.35; H, 7.74. Ber. für $C_{12}H_{17}O_3N$ (223): C, 64.57; H, 7.62%.)

Dieses Amid wird durch Einwirkung von Natriumhypochlorit[6] in 3-Äthoxy-4-methoxy-β-phenyläthylamin umgewandelt und in Äthanol mit Oxalsäure neutralisiert. Das gebildete Oxalat wird nun aus Wasser umkrystallisiert. Prismen vom Schmp. 226–227° unter Zersetzung (Gef.: C, 59.89; H, 7.68. Ber. für $C_{24}H_{36}N_2O_8$ (480): C, 60.00; H, 7.50%.). Das Chlorhydrat wird durch Einleiten von Salzsäuregas in die ätherische Lösung dieses Amins erhalten und aus Benzol zu Prismen vom Schmp. 166–168° umgelöst. (Gef.: C, 57.37; H, 8.07. Ber. für $C_{11}H_{18}NO_2Cl$ (231.5): C, 57.02; H, 7.78%.)

β-(3-Äthoxy-4-methoxy-phenyl)-äthyl-3′,4′-methylendioxy-phenacetamid (III). 36 g. Homopiperonylsäure werden mit 39 g. 3-Äthoxy-4-methoxy-β-phenyl-äthylamin zwei Stunden am Rückflusskühler auf 180–190° erhitzt[7]. Nach dem Erkalten wird das krystallisierende Reaktionsgemisch in 400 c.c. Chloroform gelöst und die Chloroformlösung mit verdünnter Natronlauge und verdünnter Salzsäure je dreimal und dann mit Wasser zweimal geschüttelt. Nach dem Trocknen mit festem Kaliumhydroxyd wird das Chloroform abgedampft und der Rückstand aus Benzol umkrystallisiert. Prismen vom Schmp. 129–131°. Ausbeute ca. 53 g. (Gef.: C, 67.50; H, 6.69. Ber. für $C_{20}H_{23}NO_5$ (357): C, 67.23; H, 6.44%.)

(2) Domesticin-äthyläther schmolz bei 131° und zeigt $[\alpha]_D^{14} = +110.8°$ (This Bulletin, **12** (1937), 151.)

(3) Z. Kitasato und H. Shishido, *Acta Phytochim.* (Japan), **9** (1937), 265; H. Shishido, this Bulletin, **12** (1937), 150.

(4) W. H. Perkin, *J. Chem. Soc.*, **127** (1925), 1714.

(5) W. H. Perkin, *ibid.*, **125** (1924), 1694.

(6) Decker, *Ann.*, **395** (1915), 291.

(7) This Bulletin, **12** (1937), 151.

1-Piperonyl-6-äthoxy-7-methoxy-dihydroisochinolin-oxalat. 30 g. obiges Acetamid (III) werden mit 150 c.c. Toluol und 60 c.c. Phosphoroxychlorid anderthalb Stunden bei 130–140° gekocht. Nach dem Erkalten wird das Toluol mit Petroläther verdünnt und nach einigen Minuten wird die obenstehende Flüssigkeit abgegossen, und der krystallinische Rückstand mit Petroläther gut gewaschen und mit 200 c.c. Benzol und 10 c.c. konzentrierter Salzsäure unter Erwärmen auf dem Wasserbad vermischt. Nach Trennung der heissen Benzolschicht wird die untere Schicht mit viel Wasser umgeschüttelt, und das braune Öl erstarrt bald zu krystallisieren. Die Suspension dieser Krystalle in Natronlauge wird dann mit Benzol unter Zusatz von etwas Äthanol geschüttelt, die Benzolschicht mit Wasser geschüttelt, mit Kaliumcarbonat getrocknet und abgedampft. Der Rückstand wird durch Oxalsäure in ein Oxalat übergeführt. Das so erhaltene Dihydroisochinolin-oxalat wird aus Wasser umkrystallisiert. Prismen vom Schmp. 227–228° unter Zersetzung. (Gef.: C, 61.68; H, 5.74. Ber. für $C_{22}H_{23}O_8N$ (429): C, 61.54; H, 5.36%.)

1-Piperonyl-6-äthoxy-7-methoxy-*N*-methyl-tetrahydroisochinolin (IV). Die obige Dihydroisochinolin (aus Oxalat) wird in 20 c.c. Benzol gelöst und mit 20 c.c. Jodmethyl gekocht. Nach 4–5-stündigem Kochen wird das abgeschiedene rotbraune Öl erstarrt langsam zu Krystallmasse. Das Jodmethylat wird aus Äthanol umkrystallisiert und in Prismen vom Schmp. 142–144° unter Zersetzung erhalten. (Gef.: C, 52.43; H, 5.30. Ber. für $C_{21}H_{24}NO_4I$ (481): C, 52.39; H, 4.99%.)

Nun wird das Jodmethylat mit Silberchlorid umgesetzt und das Produkt durch Zinkpulver-Schwefelsäure reduziert, wie bei 1-Piperonyl-6-methoxy-7-äthoxy-*N*-methyl-tetrahydroisochinolin[7]. Nach 5–6-stündigem Kochen wird die Lösung von Zink abfiltriert, mit Ammoniak unter Eiskühlung stark alkalisch gemacht und mit Äther dreimal ausgezogen. Die Ätherlösung wird zweimal mit Wasser geschüttelt und mit Kaliumcarbonat getrocknet. Der Abdampfungsrückstand des Äthers wird in 40 c.c. Äthanol gelöst und mit einer Lösung von 8 g. Oxalsäure in 40 c.c. Äthanol versetzt. Das so gebildete Oxalat schmilzt bei 186–187° unter Zersetzung. Ausbeute 23 g. (Gef.: C, 61.76; H, 6.16. Ber. für $C_{23}H_{27}NO_8$ (445): C, 62.02; H, 6.07%.)

Die Suspension dieses Oxalats in Kalilauge wird mit Äther ausgeschüttelt und der Abdampfungsrückstand des Lösungsmittels wird aus Äthanol umkrystallisiert. Prismen vom Schmp. 154–155.5°. (Gef.: C, 71.15; H, 6.99. Ber. für $C_{21}H_{25}NO_4$ (355): C, 70.99; H, 7.04%.)

Das Chlorhydrat wird auf übliche Weise dargestellt und aus Methanol umkrystallisiert. Prismen vom Schmp. 237–239° unter Zersetzung. (Gef.: C, 64.20; H, 6.98. Ber. für $C_{21}H_{26}NO_4Cl$ (391.5): C, 64.36; H, 6.64%.)

Das Sulfat wird durch gewöhnliche Methode dargestellt und aus Äthanol umkrystallisiert. Prismen vom Schmp. 114–115° unter Zersetzung. (Gef.: C, 62.66; H, 6.42. Ber. für $C_{42}H_{52}N_2O_{12}S$ (808): C, 62.38; H, 6.44%.)

6′-Nitro-1-piperonyl-6-äthoxy-7-methoxy-*N*-methyl-tetrahydroisochinolin. Eine Lösung von 5 g. 1-Piperonyl-6-äthoxy-7-methoxy-*N*-methyl-tetrahydroisochinolin in 25 c.c. Eisessig wird mit 10 c.c. konz. Salpetersäure unterhalb 5° nitriert. Man behandelt das Reaktionsgemisch wie bei 6′-Nitro-1-piperonyl-6-methoxy-7-äthoxy-Verbindung[8] und nimmt mit Äther auf. Die ätherische Lösung wird mit Wasser gewaschen und der Abdampfungsrückstand wird aus Methanol umkrystallisiert. Gelbe Prismen vom

(8) This Bulletin, **12** (1937), 152.

Schmp. 128° (sintern bei 123°). (Gef.: C, 63.20; H, 6.31. Ber. für $C_{21}H_{24}N_2O_6$ (400): C, 63.00; H, 6.00%.)

6'-Amino-1-piperonyl-6-äthoxy-7-methoxy-*N*-methyl-tetrahydroisochinolin (V). Die Reduktion der obigen Nitro-Verbindung wird mit Stannochlorid auf dieselbe Weise wie bei 6'-Amino-1-piperonyl-6-methoxy-7-äthoxy-Verbindung[9] ausgeführt. Das so erhaltene Produkt wird mit Äther ausgezogen und der Rückstand des Lösungsmittels aus Methanol umkrystallisiert. Prismen vom Schmp. 105–107°. (Gef.: C, 67.98; H, 7.19; N, 7.70. Ber. für $C_{21}H_{26}N_2O_4$ (370): C, 68.11; H, 7.03; N, 7.57%.)

Das Oxalat wird auf übliche Weise dargestellt und aus wasserhaltigem Äthanol umkrystallisiert. Hellbraune Prismen vom Schmp. 186–188° unter Zersetzung. (Gef.: C, 59.80; H, 6.23. Ber. für $C_{23}H_{28}N_2O_8$ (460): C, 60.00; H, 6.09%.)

Das Monochlorhydrat wird durch Versetzung von wenig 20-proz. Salzsäure in alkoholische Lösung der freien Base dargestellt. Es krystallisiert aus Äthanol in Prismen vom Schmp. 220–222° unter Zersetzung. (Gef.: C, 61.80; H, 6.87. Ber. für $C_{21}H_{27}N_2O_4Cl$ (406.5): C, 61.99; H, 6.64%.)

Das Sulfat wird durch Mischung der alkoholischen Lösung der Base mit wenig 5-proz. Schwefelsäure gewonnen und aus Äthanol umkrystallisiert. Prismen vom Schmp. 179–181° unter Zersetzung. (Gef.: C, 53.44; H, 6.35. Ber. für $C_{21}H_{28}N_2O_8S$ (468): C, 53.85; H, 5.98%.)

***d,l*-2,3-Methylendioxy-5-methoxy-6-äthoxy-*N*-methyl-aporphin (VI).** Die oben angegebene Amino-Verbindung (V) wird, wie beim Fall von Domesticin-äthyläther[9], mit Natriumnitrit diazotiert und mit Kupferpulver behandelt und dann mit Zinkpulver-Salzsäure reduziert. Das Filtrat vom Zink wird mit Ammoniak alkalisch gemacht, mit Äther sechsmal ausgezogen, und die ätherische Lösung dreimal mit verdünnter Natronlauge und dann mit Wasser gut gewaschen. Man löst den Abdampfungsrückstand des Äthers in Methanol und versetzt mit wenig 20-proz. Bromwasserstoffwasserlösung, wobei sich das Bromhydrat der *d,l*-Base (VI) abscheidet. Das Bromhydrat wird aus Äthanol umkrystallisiert und in Prismen vom Schmp. 250–252° unter Zersetzung (färbt sich bei ca. 230°) erhalten. Ausbeute ca. 20%. (Gef.: C, 57.85; H, 5.87. Ber. für $C_{21}H_{24}NO_4Br$ (434): C, 58.06; H, 5.53%.)

Das Bromhydrat wird in warmem sehr verdünntem Äthanol gelöst, mit verdünnter Natronlauge alkalisch gemacht und mit Äther geschüttelt und die Ätherlösung wird mit Wasser gewaschen und der Abdampfungsrückstand des Äthers wird aus Petroläther umkrystallisiert. Derbe Blättchen vom Schmp. 136°. Sie sind leicht löslich in Äther, Methanol, Äthanol und Chloroform und etwas schwerer löslich in Petroläther. (Gef.: C, 71.57; H, 6.65. Ber. für $C_{21}H_{23}NO_4$ (353): C, 71.39; H, 6.52%.)

Spaltung der racemischen Base in optische Antipode. In eine Lösung von 1.5 g. der wie oben erhaltenen *d,l*-Base (VI) in 35 c.c. Äthanol werden 5 c.c. einer 2 N alkoholischen Lösung von *d*-Weinsäure hinzugefügt. Nach eintägigem Stehen wird das abgeschiedene krystallinische *l*-2,3-Methylendioxy-5-methoxy-6-äthoxy-*N*-methyl-aporphin-*d*-tartrat abfiltriert und mit Äthanol gut gewaschen. Das Tartrat wird in warmem Wasser gelöst, mit verdünnter Natronlauge alkalisch gemacht und mit Äther ausgeschüttelt. Der Rückstand der Ätherlösung wird aus Petroläther umkrystallisiert.

(9) This Bulletin, **12** (1937), 153.

Derbe Prismen vom Schmp. ca. 126°. Das Drehungsvermögen der Base wird $[\alpha]_D^{28} = -47.4°$ (in Äthanol) erhalten. Dass aber damit der Endwert des Drehungsvermögens noch nicht erreicht ist, ergibt die weitere Verarbeitung dieses Produktes.

0.3723 g. der obigen Base werden in 10 c.c. Äthanol gelöst und mit 5 c.c. einer alkoholischen Lösung von 0.1867 g. *d*-Weinsäure versetzt. Nach einem Tag wird die ausgeschiedenen Krystalle von *l*-Base-*d*-tartrat gesammelt und mit Äthanol gut gewaschen. Das Tartrat wird aus Äthanol umkrystallisiert und bildet Prismen vom Schmp. 186–188° unter Zersetzung. Man suspendiert sie in Natronlauge und nimmt die freie Base mit Äther auf. Der Abdampfungsrückstand des Äthers wird aus Petroläther umkrystallisiert. Derbe Prismen vom Schmp. 142–144°. (Gef.: C, 71.69; H, 6.78. Ber. für $C_{21}H_{23}NO_4$ (353): C, 71.39; H, 6.52%). $[\alpha]_D^{28} = -90.9°$ in Äthanol.

Das Bromhydrat wird auf übliche Weise dargestellt und aus Äthanol umkrystallisiert. Prismen vom Schmp. 260–261° unter Zersetzung (es färbt sich gegen ca. 230°). (Gef.: C, 57.78; H, 5.72. Ber. für $C_{21}H_{24}NO_4Br$ (434): C, 58.06; H, 5.53%.)

Die Mutterlauge samt dem Wasch-Alkohol von *l*-Base-*d*-tartrat wird bis 20 c.c. eingedampft und einen Tag stehen gelassen. Man filtriert den abgeschiedenen Krystalle und verdampft das Filtrat, löst den Rückstand in Wasser, macht mit verdünnter Natronlauge alkalisch und extrahiert mit Äther. Der Abdampfungsrückstand des Äthers (0.7 g.) wird in 20 c.c. Äthanol gelöst und mit einer 4.6 c.c. N alkoholischen Lösung von *l*-Weinsäure versetzt. Nach eintägigem Stehen wird der abgeschiedene krystallinische *d*-2,3-Methylendioxy-5-methoxy-6-äthoxy-*N*-methyl-aporphin-*l*-tartrat gesammelt und aus Äthanol umkrystallisiert in Prismen vom Schmp. 186–188° unter Zersetzung erhalten. Man suspendiert sie in Natronlauge, nimmt die frei gesetzte Base mit Äther auf und krystallisiert den Abdampfungsrückstand des Äthers aus Petroläther um, wobei man *d*-2,3-Methylendioxy-5-methoxy-6-äthoxy-*N*-methyl-aporphin (II) in derben Prismen vom Schmp. 142–144° erhält. (Gef.: C, 71.46; H, 6.69. Ber. für $C_{21}H_{23}NO_4$ (353): C, 71.39; H, 6.52%.). $[\alpha]_D^{28} = +90.0°$ in Äthanol.

Es nimmt mit konzentrierter Schwefelsäure eine rotviolette Farbe an, die durch Salpetersäure-Dampf ins Blaugrün umschlägt. Diese Farbenreaktion tritt auch bei Domesticin-äthyläther auf[10], aber der Mischschmelzpunkt dieser Base mit dem Domesticin-äthyläther liegt bei ca. 128° (Sinterung schon gegen 110°).

Man erhält das Bromhydrat auf übliche Weise und krystallisiert aus Äthanol in Prismen vom Schmp. 260–261° unter Zersetzung (es färbt sich gegen ca. 230°). (Gef.: C, 57.76; H, 5.85. Ber. für $C_{21}H_{24}NO_4Br$ (434): C, 58.06; H, 5.53%.)

Zum Schluss möchte ich Herrn Dr. Zenjiro Kitasato für seine freundliche Leitung und gütige Unterstützung meinen herzlichsten Dank aussprechen.

Chemisches Laboratorium des Kitasato-Institutes, Tokyo.

(10) This Bulletin, **12** (1937), 154.

The Electrolytic Formation of Persulphate. Part IV. Influence of Temperature.*

By Ryoichi MATSUDA, Hideo KONYA, and Teruichi NISHIMORI.

(Received August 25th, 1937.)

It was stated in Part I[1] of this investigation as the result of observing the important rôle played by OH′-ions concentration of the electrolyte that oxidation of sulphuric acid with the anodic oxygen is responsible for the persulphate formation by electrolysis and then Part II[2] gave the confirmation of this view. Discharge of HSO_4'-ions or oxidation of SO_4''-ions can hardly account for the mechanism of this anodic reaction satisfactorily.

There are a number of conditions which seem to control the anodic formation of persulphate: among them are the concentration of the electrolyte, the treatment and nature of the electrodes, the use of diaphragm, etc. which were studied to some extent in the previous papers. Temperature is one of the most important conditions of electrolysis, and it is generally known that a lower temperature is favourable to this sort of anodic reaction, but not to what extent the temperature is best lowered, nor to what kind of change the lower temperature gives rise in the nature of reaction. Temperature must have connexions with various aspects of the anodic reaction, but here the temperature of the electrolyte is mainly studied in this paper.

Experimental. In each case of the electrolyses recorded in the present paper 130 c.c. of electrolyte are employed without diaphragm. The anode consists of a spiral of Pt-wire which is 0.05 cm. in diameter and 20.7 cm. in length. It is thoroughly ignited immediately before use and is kept rotating at the center of the electrolytic vessel. The cathode is also of Pt-wire as thick as the anode and 45 cm. long, which is wound spirally against the wall of the vessel. The same quantity of electricity, 1170 coulombs, is supplied in each electrolysis. The electrolyte is kept at the temperature under study by surrounding the vessel from outside with

* The contribution to this work by one of the authors (H. K.) was made as his graduation research in this college.

(1) This Bulletin, **11** (1936), 1.

(2) *Ibid.*, **11** (1936), 650.

water of adequate temperature. The analysis of the electrolysed solution is made by the same methods as those described in Part I.

Experiment 1. Electrolyses of 7 N ammonium sulphate solution. 7 N ammonium sulphate solution is electrolysed at 5°, 15°, and 25° C. to examine the change in the C. E. (the abbreviation of current efficiency) for the different temperatures. The increase of the anodic current density is favourable to the C. E., and so is the lowering of the temperature also as shown in Table 1. These C. E.'es are all greater than those of 10 N sulphuric acid electrolysis at the corresponding temperatures and current densities described in Experiment 2. The latter solution is obviously more concentrated with respect to sulphate radical than the former and is known to contain HSO_4'-ions which were considered by certain investigators[3] as responsible, on being discharged at the anode, to persulphate formation.

A question will be raised, then, if the fact that the latter solution gives smaller C. E. may be due to its peroxidic products being reduced by the cathodic hydrogen to a considerable extent. Two further electrolyses, accordingly, are undertaken to solve the question as follows: 10 N sulphuric acid is electrolysed at 15°C. with two current densities, 40 and 80 amp./dm.^{2}, as will be seen in Experiment 2, with diaphragm to keep the anodic products from the cathodic influences. The C. E.'es of these two electrolyses are even smaller than those of 7 N ammonium sulphate solution under the similar conditions. The HSO_4'-ion discharge theory is not applicable to explain these facts, but the sulphuric acid oxidation theory well enables us to account for them.

The C. E. as regard to Caro's acid is generally insignificantly small in this case, and those figures mentioned above are all referred to the total peroxidic oxygen.

Experiment 2. Electrolyses of 10 N sulphuric acid. 10 N sulphuric acid is electrolysed at 5°, 15°, and 25°C., and its C. E. is shown in Table 2 and Fig. 1. The lower the temperature, the greater the total C. E., and the C. E. at 5°C. is far greater than those at the other temperatures. The increase of the current density is favourable to the C. E. especially at 5°C. It seems likely, then, that the accumulation of ions or their discharge products plays its favourable influences on the persulphate formation at 5°C. with little influences which are unfavourable to the anodic reaction like, e.g., the cathodic reduction, or decomposition at, or in the vicinity of, the cathode.

Since no diaphragm is used in all these electrolyses, the anodic products are open to the cathodic reduction. In the case of 7 N sulphuric

(3) R. Elbs and O. Schönherr, *Z. Elektrochem.*, **1** (1894), 417.

acid electrolysed at 18°C. it was shown in Parts I and II that the C. E. is far better when diaphragm is used than otherwise, and this is obviously because the cathodic reduction is prevented by the use of diaphragm. It is highly probable, then, in the present experiment that the C. E. would be improved as the result of preventing the cathodic influences, if diaphragm were used in the electrolysis of 10 N sulphuric acid at 15° and 25°C. It is known, moreover, that the conductivity of sulphuric acid decreases, but its degree of electrolytic dissociation increases, with the lowering of temperature and also that persulphuric acid is endothermic with regard to its decomposition products, oxygen and sulphuric acid. Then the highest C. E. obtained in this case at 5°C. must be attributed to the fact that the cathodic reduction is the least effective at this temperature and the poorer C. E.'es at 15° and 25°C., partly at least, to the fact that the cathodic reduction increases its effectiveness upon the anodic products at these temperatures.

The C. E. as to Caro's acid is small in each case, because the electrolyte is comparatively dilute.

10 N sulphuric acid is electrolysed with diaphragm, unlike the other electrolyses in this paper, at 15°C., whose total C. E.'es are 36.9 and 40.9% for the current densities of 40 and 80 amp./dm.^{2} respectively, which fact is referred to already in the previous experiment.

Experiment 3. Electrolyses of 15 N sulphuric acid. 15 N sulphuric acid is electrolysed at 5°, 15°, and 25°C., whose C. E. is shown in Table 3 and Fig. 2. Lower temperature and greater current density both seem to be favourable to the C. E. just as in Experiment 2. The degree of electrolytic dissociation is smaller with rising temperature as described in the previous case, hence the concentration of HSO_4'-ions becomes greater with rising temperature in contrast with that of SO_4''-ions getting smaller. So the change of the degree of dissociation caused by that of temperature will evidently affect the C. E. The result of the present experiment, however, cannot be dealt with merely from the viewpoint of the degree of dissociation.

The difference between the C. E.'es at different temperatures is smaller than that of the corresponding cases of 10 N sulphuric acid in the previous experiment. This is probably because the temperature coefficient of the degree of dissociation of sulphuric acid is smaller in this case, the concentration of the acid being greater than the previous case.

Each C. E. in this case is greater than the corresponding one in the previous case, because not only the concentration of the electrolyte is greater in this case, but also the concentration of OH'-ions is greater in

consequence of that of the electrolyte itself increasing. It was already stated in Parts I and II that the increase of the concentration of OH′-ions is favourable to the anodic formation of persulphate. The C. E. with respect to Caro's acid on the contrary is generally the greater, the higher the temperature.

Comparison of the present case with Experiment 3 in Part II of this investigation which dealt with the electrolyses of 15 N sulphate solutions containing various amounts of sulphuric acid and ammonium sulphate is of particular interest to the study of the mechanism of persulphate formation: one deals with the influence of temperature on the electrolysis of 15 N sulphuric acid and the other that of OH′-ions on the electrolysis of 15 N sulphate solution. In the former case the lowering of temperature results in retardation of the cathodic reduction as described above and also in increase of the degree of dissociation of sulphuric acid which necessarily involves decrease of the concentration of molecular sulphuric acid. A high concentration of molecular sulphuric acid is indispensable for persulphuric acid to become Caro's acid. Under these circumstances, therefore, persulphuric acid which is formed at the anode can mostly remain as it is, when the temperature is lower, without being transformed into Caro's acid or reduced at the cathode.

When the temperature is higher, however, as can be easily understood from what has been mentioned above, not only the cathodic reduction becomes more active, but also persulphuric acid which is formed at the anode becomes more liable to be changed into Caro's acid, which latter substance is much more reducible than persulphuric acid itself. From these reasons the total C. E. is comparatively great and the Caro's acid C. E. is comparatively small when the temperature is lower, and vice versa when the temperature is higher.

In the latter case which deals with the influence of OH′-ions concentration on 15 N sulphate solutions the concentration of ammonium sulphate stands for the temperature in the former. The high concentration of the sulphate corresponds to the low temperature and vice versa. So these two cases under consideration are alike each other in having the greatest total C. E. when the Caro's acid C. E. is smallest and the smallest total C. E. when the Caro's acid C. E. is greatest because of the radically similar reasons.

Experiment 4. Electrolyses of 20 N sulphuric acid. Influence of the temperature on the electrolyses of 20 N sulphuric acid is studied. The C. E.'es are shown in Table 4 and Fig. 3, of which those at 15°C. were already given in Part II. As to each pair of curves in the figure the higher one represents the total C. E. and the lower the Caro's acid C. E.

The Caro's acid C. E. is generally greater, compared with that in Experiment 3, because the concentration of the electrolyte is greater in this case; the total C. E. is consequently smaller in general for the reason stated above. The influence of the temperature on the C. E. is the same as before when the current density is smaller, but it is reversed when the current density is greater.

Experiment 5. Results of electrolyses of 25, 30, and 36 N sulphuric acid are shown in Table 5 and Fig. 4, Table 6 and Fig. 5, and Table 7 and Fig. 6, respectively.

Table 1. The Current Efficiency of 7 N Ammonium Sulphate.

C. D. (amp./dm.^{2})		5	10	20	40	80
The Caro's Acid C. E.	5°C.	—	—	—	—	—
	15	—	—	trace	—	—
	25	0.5%	0.5	0.5	0.5	0.5
The Total C. E.	5°C.	34.8	49.5	62.4	75.9	78.7
	15	27.9	38.4	56.8	65.1	67.1
	25	7.8	14.8	22.6	37.5	48.5

Table 2. The Current Efficiency of 10 N Sulphuric Acid.

C. D. (amp./dm.^{2})		5	10	20	40	80
The Caro's Acid C. E.	5°C.	0.4%	0.4	0.4	0.4	0.4
	15	0.4	0.5	0.5	0.8	0.8
	25	0.2	—	1.0	0.5	0.7
The Total C. E.	5°C.	1.9	11.2	43.8	64.0	66.0
	15	6.9	8.1	10.4	17.8	30.0
	25	1.6	2.3	3.1	6.6	13.2

Table 3. The Current Efficiency of 15 N Sulphuric Acid.

C. D. (amp./dm.^{2})		5	10	20	40	80
The Caro's Acid C. E.	5°C.	9.9%	8.4	8.2	6.0	4.2
	15	20.0	24.1	24.1	24.8	24.1
	25	1.2	12.1	22.2	27.4	24.2
The Total C. E.	5°C.	36.0	54.3	72.2	83.1	81.3
	15	25.5	40.0	58.7	71.7	66.0
	25	2.0	18.4	38.1	59.3	64.5

Table 4. The Current Efficiency of 20 N Sulphuric Acid.

C. D. (amp./dm.²)		5	10	20	40	80
The Caro's Acid C. E.	5°C.	39.6%	48.5	43.3	20.7	1.2
	15	38.5	46.5	51.2	51.2	43.8
	25	10.3	16.8	44.8	47.7	41.0
The Total C. E.	5°C.	58.4	61.2	63.0	52.7	1.2
	15	39.3	55.2	62.1	59.9	54.4
	25	33.2	50.8	54.4	62.5	63.4

Table 5. The Current Efficiency of 25 N Sulphuric Acid.

C. D. (amp./dm.²)		5	10	20	30	40	50	80
The Caro's Acid C. E.	5°C.	57.4%	56.9	26.8	24.3	24.3	—	—
	15	42.0	48.7	50.7	23.1	20.1	—	22.5
	25	43.3	49.0	58.2	59.6	51.9	47.8	31.9
The Total C. E.	5°C.	71.8	66.3	30.0	26.2	26.2	—	—
	15	60.8	67.1	63.7	26.8	21.1	—	23.6
	25	51.2	55.5	61.4	61.0	54.0	48.5	31.9

Table 6. The Current Efficiency of 30 N Sulphuric Acid.

C. D. (amp./dm.²)		5	10	20	40	60	80
The Caro's Acid C. E.	5°C.	26.3%	28.9	10.0	10.3	—	8.9
	15	46.0	42.6	35.1	11.2	—	12.1
	25	27.4	34.6	37.4	31.8	16.6	11.5
The Total C. E.	5°C.	40.0	35.8	16.7	18.1	—	17.3
	15	51.2	50.1	42.9	14.7	—	13.5
	25	41.2	42.3	44.6	42.3	24.2	17.0

Table 7. The Current Efficiency of 36 N Sulphuric Acid.

C. D. (amp./dm.²)		5	10	20	40	80
The Caro's Acid C. E.	5°C.	18.1%	23.2	9.2	9.7	8.3
	15	35.3	36.0	33.4	13.6	12.8
	25	22.3	20.9	16.3	17.5	6.8
The Total C. E.	5°C.	38.0	42.2	15.7	18.9	16.6
	15	40.4	44.2	39.8	14.3	14.3
	25	23.6	35.4	37.6	27.2	15.7

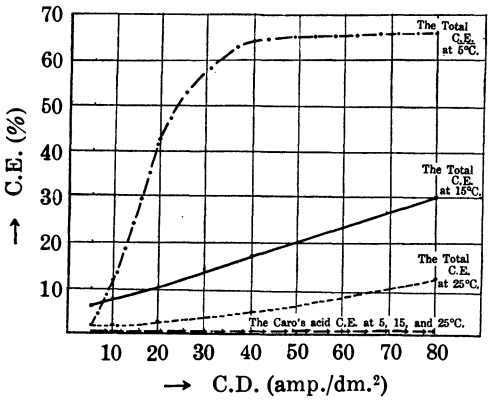


Fig. 1.

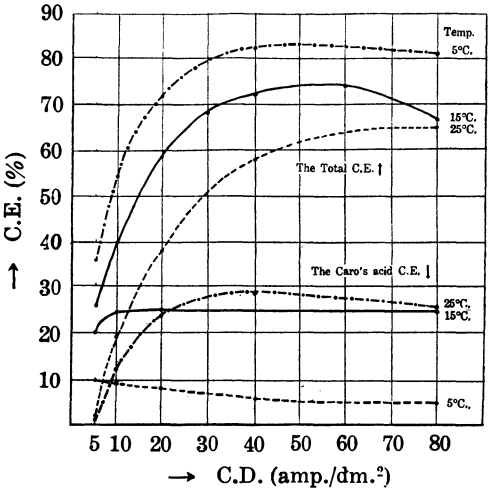


Fig. 2.

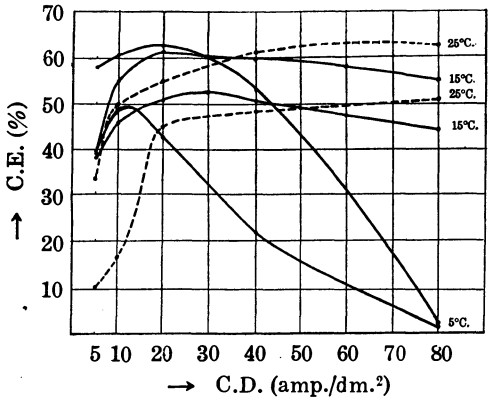


Fig. 3.

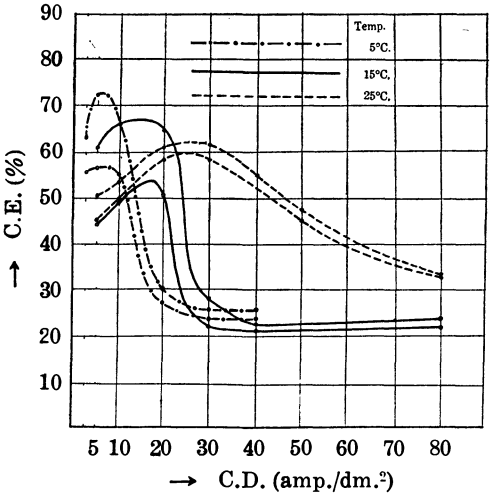


Fig. 4.

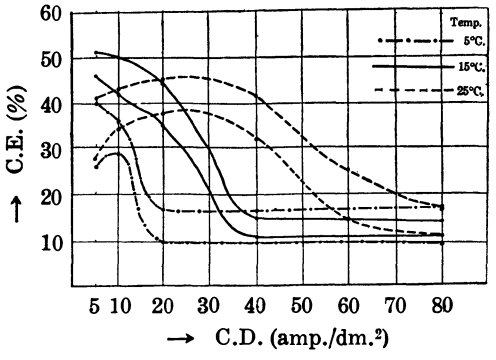


Fig. 5.

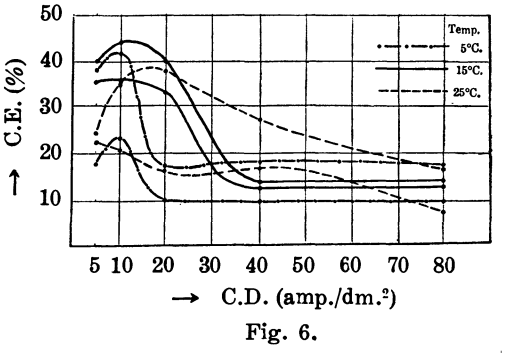


Fig. 6.

Summary.

(1) 7 N ammonium sulphate solution and 10, 15, 20, 25, 30, and 36 N sulphuric acid are electrolysed without diaphragm. 10 N sulphuric acid is also electrolysed with diaphragm. Current efficiency is observed for various current densities and temperatures, the latter being 5°, 15°, and 25°C.

(2) The mechanism of the anodic formation of persulphuric acid is discussed from the relation between the temperature and current efficiency, and the fresh results of electrolyses described in this paper can be accounted for by the view that persulphuric acid is formed by the oxidation of sulphuric acid with the anodic oxygen which was proposed in Part I, and confirmed in Part II of this investigation.

(3) An interesting similarity is noticed which exists between the electrolysis of 15 N sulphuric acid made at various temperatures and that of the same made with various OH'-ion concentrations.

The Department of Applied Chemistry,
Tokushima Technical College, Tokushima.

Studies on the Unsaturated Lower Fatty Acids. On the Crystalline Derivatives of the Unsaturated Lower Fatty Acids.

By Saburo KOMORI and Sei-ichi UENO.

(Received August 27th, 1937.)

It is a problem all important to determine the melting points of crystalline derivatives of unsaturated fatty acids, but the work on this line is very imperfect. We have only the data of tiglic,[1] oleic,[2][3][4] erucic,[4] and cetoleic[4] acids. The authors have prepared pure obtusilic,[5] linderic, and tetradecenoic acids from the oil of the nuts of *Lindera obtusiloba*, and determined their physical properties and the melting points of their crystalline derivatives. The tetradecenoic acid of this oil was formerly concluded to be physeteric acid by M. Tsujimoto.[6] The tetradecenoic acid the authors have prepared this time, however, was a solid melting at 18.0–18.5°. From the result of ozonolysis, it has been recognized to be tsuzuic acid.

Experimental.

The basis of this work was the oil of nuts of "Tohaku" (*Lindera obtusiloba*) as in previous report.[5] It had the following characteristics: d_4^{20} 0.9494, n_D^{20} 1.4701, acid value 28.2, iodine value (Wijs) 77.7, saponification value 236.1.

(1) *Obtusilic Acid.* The oil (3 kg.) was saponified, decomposed, and the mixed fatty acids thus obtained were subjected to fractional distillation under a diminished pressure of 13 mm. A fraction (32.5 g.) up to 153° was taken, and after the removal of the unsaponifiable matter, the fatty acids were converted into methyl esters, and the latter were brominated in ethereal solution cooled with ice. The product of bromination was fractionally distilled under a diminished pressure of 2 mm. The fraction boiling at 149–154°/2 mm. (12 g.) was taken, and after debromination, the obtained methyl ester was saponified. The liberated fatty acid was subjected to a further fractionation, and a fraction (3.2 g.) boiling at 148–150°/13 mm. was collected as decenoic acid. It had the following constants: d_4^{15} 0.9222, d_4^{20} 0.9197, n_D^{15} 1.4519, n_D^{20} 1.4497, mol. ref. 49.76, neutralization value 328.3, iodine value 146.0 (calc. for $C_{10}H_{18}O_2$: mol. ref. 49.47, neutralization value 329.7, iodine value 149.2). This fatty

(1) Lund and Langvad, *J. Am. Chem. Soc.*, **54** (1932), 4107.
(2) Escher, *Helv. Chim. Acta*, **12** (1929), 45.
(3) Drake and Bronitsky, *J. Am. Chem. Soc.*, **52** (1930), 3715.
(4) Kimura, *J. Soc. Chem. Ind., Japan*, **35** (1932), 2213.
(5) Komori and Ueno, this Bulletin, **12** (1937), 226.
(6) *J. Soc. Chem. Ind., Japan*, **27** (1924), 329.

acid was methylated and oxidized with potassium permanganate in acetone solution. In the decomposition product, succinic and caproic acids were detected. This result showed that no isomeric change involving the shifting of an ethylenic linkage had taken place during the process of purification. The obtusilic acid obtained (0.4 g.) was oxidized by Hazura's method (cooled to 0–2° and oxidized with 0.5% $KMnO_4$), but we could not obtain any solid oxidation product. The *p*-bromophenacyl ester of obtusilic acid was prepared according to the method of Y. Kimura.[4] The ester formed lustrous scaly crystals, and had the melting point 43.3°.

(2) **Linderic Acid.** The "Tohaku" oil (5 kg.) was saponified, decomposed, and the mixed fatty acids thus obtained were subjected to fractional distillation under a diminished pressure of 13 mm. The results of the fractional distillation are given in Table 1.

Table 1.

Fraction	B.p. (°C./13 mm.)	Yield (g.)	n_D^{20}	Saponif. value	Neutr. value	Iodine value
1	—160	666	1.4409	268.9	238.5	77.4
2	160—170	1591	1.4410	272.6	259.1	90.9
3	Residue	2158				

150 g. of fraction 2, after separation of unsaponifiable matter, was subjected to the bromo-ester method of Grün and Janko, and the obtained fraction 178–182°/2 mm. (118 g.), (dibromolinderic acid methyl ester), was debrominated with zink powder and hydrochloric acid in methanol solution. The produced methyl ester was saponified and the liberated fatty acid was subjected to a further fractionation, by which a fraction (29 g.) boiling at 170–172°/13 mm. was collected as linderic acid. The linderic acid had a following properties: d_4^{15} 0.9106, d_4^{20} 0.9081, n_D^1 1.4545, n_D^{20} 1.4529, mol. ref. 58.98, neutralization value 282.1, iodine value 128.4, melting point 1.0–1.3° (calc. for $C_{12}H_{22}O_2$: mol. ref. 58.69, neutralization value 282.0, iodine value 128.1). On oxidizing the linderic acid by Hazura's method, it yielded dihydroxy-lauric acid having the melting point 102°. The cooling curve of this acid is shown in Fig. 1. The melting points of crystalline derivatives were as follows: *p*-phenylphenacyl ester 42.5°, *p*-bromophenacyl ester 47.5°, *S*-benzylthiuronium salt[7] 139.0°.

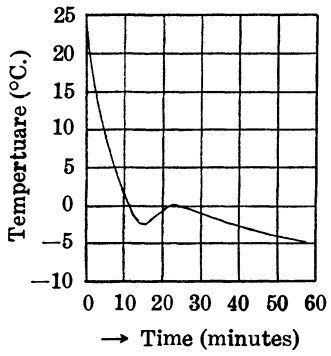


Fig. 1.

(3) **Tetradecenoic Acid.** The residue (1.5 kg.) of the fractional distillation (Table 1), after the removal of the unsaponifiable matter, was converted into methyl ester, and fractionally distilled. The fraction boiling between 145–170°/13 mm. (102 g.) was again fractionated as shown in Table 2.

(7) J. J. Donleavy, *J. Am. Chem. Soc.*, **58** (1936), 1004.

Table 2.

Fraction	B.p. (°C./13 mm.)	Yield (g.)	n_D^{20}	Saponif. value	Iodine value
1	—145	39	1.4383	255.3	63.5
2	145—150	12	1.4400	255.2	63.7
3	150—155	5	1.4414	246.6	62.9
4	155—160	4.5	1.4420	242.9	63.9
5	160—165	11.5	1.4440	234.9	64.2
6	165—170	5	1.4441	233.7	63.5
7	170—175	11		222.6	
	Residue	13			

The fatty acids liberated from fraction 5, were separated into unsaturated and saturated acids by the lead salt petroleum ether method. The unsaturated acid portion was fractionally distilled once more, and finally 2.2 g. of the unsaturated acid possessing the following values was obtained: melting point 18.0–18.5°, boiling point 185–188°/13 mm., d_4^{15} 0.9055, d_4^{20} 0.9024, n_D^{15} 1.4575, n_D^{20} 1.4557, mol. ref. 67.83, neutralization value 248.3, iodine value 111.5 (calc. for $C_{14}H_{26}O_2$: mol. ref. 67.93, neutralization value 248.0, iodine value 112.0). The cooling curve of this acid is shown in Fig. 2. 1.3 g. of this fatty acid was subjected to ozonolysis, and from the decomposition product, succinic acid was detected. It is certain, therefore, that the fatty acid is tsuzuic acid. The melting point of *p*-phenylphenacyl ester and *p*-bromophenacyl ester of this acid were respectively 54.5° and 61.3°.

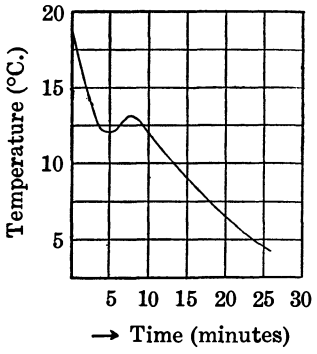


Fig. 2.

Summary.

(1) It is recognized that the tetradecenoic acid of "Tohaku" oil is tsuzuic acid.

(2) The authors have prepared pure obtusilic, linderic, and tetradecenoic acids from the "Tohaku" oil, and have determined their physical properties and the melting points of their crystalline derivatives.

Department of Chemical Technology, Faculty of Engineering,
Imperial University of Osaka.

Über die Konstitution des Cerberins.

Von **Tamaki MATSUBARA.**

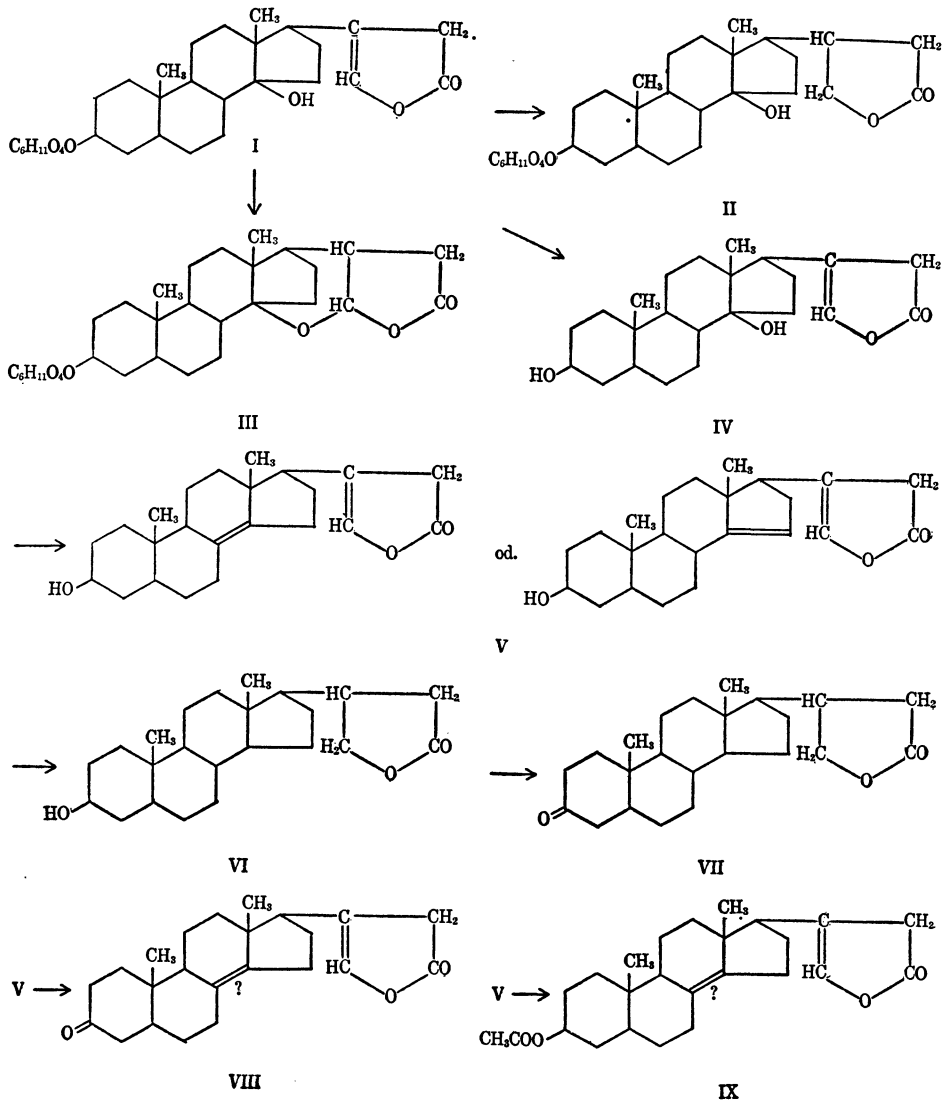
(Eingegangen am 30. August 1937.)

Aus dem Samen der in Indien als giftig bekannten *Apocynaceae Cerbera Odollam* (Gaertner) stellte zuerst de Vrij im Jahre 1864, später dann Plugge,[1] kristallisiertes Glykosid mit dem Schmelzpunkt 190–192° dar und gab diesem die Formel $C_{27}H_{40}O_8$. Plugge, nachdem er Cerberin in einer alkoholischen Lösung mit einem Zusatz von Schwefelsäure längere Zeit kochte, gewann ein zitronengelbes amorphes Pulver, das bei 85.5° schmolz und für welches er die Formel $C_{19}H_{26}O_4$ aufstellte.

Seitdem hat man keine weiteren Forschungsberichte über Cerberin gefunden. Ich habe daher vor einigen Jahren ein paar Kilogramm Samenkerne von *Cerbera Odollam* (Gaertner) aus Okinawa (den Luchu Inseln im Süden Japans) bezogen und mich mit der Bearbeitung des Cerberins beschäftigt. Dieses Glykosid schiesst aus seiner 95-proz. alkoholischer Lösung in Prismen an, enthält weder Kristallwasser noch Asche und schmilzt bei 191–193°. Das Glykosid bildet aus verdünnter alkoholischer Lösung Nadeln von ½ Mol Kristallwasser (0.4227 g. Substanz, unter 110° und 30 mm. 6 Stunden getrocknet, ergab eine Gewichtsabnahme von 0.0075 g. Gefunden: Kristallwasser 1.77. Berechnet für $C_{29}H_{44}O_8 \cdot \frac{1}{2}H_2O$: Kristallwasser 1.70%). Auf Grund seiner Elementaranalyse und Molekulargewichtsbestimmung darf man dem Cerberin mit Recht die Formel $C_{29}H_{44}O_8$ geben, $[\alpha]_D^{19.5°} = -77.9°$ (0.1315 g. Substanz in 13 c.c. Chloroform, $l = 1.894$ dm., $\alpha_D^{19.5°} = -1.48°$) (Gefunden: C, 66.71, 66.41, 66.88, 66.71; H, 8.37, 8.23, 8.91, 8.47; Molekulargewicht nach Rastscher Methode, 527, 520. Berechnet für $C_{29}H_{44}O_8$: C, 66.87; H, 8.52%; Molekulargewicht, 520).

Cerberin nimmt, nicht in Kälte, sondern in Wärme Alkali auf, zeigt die Legalsche[2] und Baljetsche[3] Reaktion; durch die katalytische Hydrierung ergibt es Dihydro-cerberin (II) (Gefunden: C, 65.52, 65.41; H, 8.32, 8.26. Berechnet für $C_{29}H_{46}O_8 \cdot \frac{1}{2}H_2O$: C, 65.30; H, 8.92%); das (II) aus Äther Nadeln vom Schmelzpunkt 185–186° bildet und dessen Legalsche und Baljetsche Reaktion sich als negativ erweist. Cerberin ist infolgedessen β,γ-ungesättigtes Oxylacton. Wie andere Herzgifte liefert

(1) *Arch. Pharm.*, **231** (1896), 10.
(2) *J. Biol. Chem.*, **67** (1926), 333.
(3) *Schweiz. Apoth.-Ztg.*, **56** (1918), 84.



das Cerberin auch Iso-cerberin (III), aus Alkohol, in kleinen Prismen vom Schmelzpunkt 252–253°, $[\alpha]_D^{20°} = -73.8°$ (0.1349 g. Substanz in 13 c.c. Chloroform, $l = 1.894$ dm., $\alpha_D^{20°} = -1.45°$) (Gefunden: C, 66.98, 66.86; H, 8.34, 8.33; Molekulargewicht nach Rastscher Methode, 515, 529. Berechnet für $C_{29}H_{44}O_8$: C, 66.87; H, 8.52%; Molekulargewicht, 520). Daraus erklärt sich das Vorhandensein einer Hydroxylgruppe an C_{14} in Cerberin,

welches bei der Säure-Einwirkung als Wasser herausgenommen wird.[4] Bei längerem Kochen in 5-proz. alkoholischer Schwefelsäure spaltet sich das Cerberin ab unter Bildung von Cerberose (eines neuen Zuckers) und einer zitronengelben amorphen Substanz. Wenn man diese Substanz in Äther löst und dann einige Tage liegen lässt, verwandelt sich ein Teil derselben in Nadeln und wenn diese Nadeln aus Alkohol umkristallisiert werden, gewinnt man farblose, längere Nadeln vom Schmelzpunkt 220–222°, die nach ihrer Elementaranalyse und Molekulargewichtsbestimmung als Anhydro-cerberigenin festgestellt werden, $[\alpha]_D^{21°} = +46.8°$ (0.1319 g. Substanz in 13 c.c. Chloroform, $l = 1.894$ dm., $\alpha_D^{21°} = +0.9°$) (Gefunden: C, 77.43, 77.43, 77.49, 77.50; H, 9.11, 8.93, 9.09, 9.25; Molekulargewicht nach Rastscher Methode, 348, 354. Berechnet für $C_{23}H_{32}O_3$: C, 77.47; H, 9.05%; Molekulargewicht, 356). Dieses Anhydro-Genin wird mit Digitonin gefällt (0.0396 g. dieses Anhydro-Genins ergaben 0.1764 g. Digitonid). Die Verseifungszahl des Anhydro-cerberigenins lässt einen Lactonring erkennen (0.1703 g. bzw. 0.1506 g. dieser Substanz verbrauchten 4.7 c.c. bzw. 4.1 c.c. N/10 Kalilauge. Gefunden: Verseifungszahl: 154, 153. Berechnet für $C_{23}H_{32}O_3$ (per 1 Mol Kalilauge): Verseifungszahl, 158); dasselbe liefert bei katalytischer Hydrierung Tetrahydro-anhydro-cerberigenin (VI), aus Alkohol, in Nadeln vom Schmelzpunkt 155–156° (Gefunden: C, 76.61, 76.34, 76.56; H, 9.71, 9.81, 9.94. Berechnet für $C_{23}H_{36}O_3$: C, 76.61; H, 10.07%). Durch die Oxydation dieser Verbindung mit Chromsäureanhydrid gewinnt man Tetrahydro-anhydro-cerberigenon (VII), welches aus Alkohol Nadeln vom Schmelzpunkt 181–182° bildet (Gefunden: C, 77.19, 77.39; H, 8.96, 9.23; Molekulargewicht nach Rastscher Methode, 349. Berechnet für $C_{23}H_{34}O_3$: C, 77.04; H, 9.56%; Molekulargewicht, 358). Wenn man auf das Tetrahydro-anhydro-cerberigenon Hydroxylamin einwirken lässt, ergibt es Tetrahydro-anhydro-cerberigenon-oxim, welches aus Alkohol feine Nadeln vom Schmelzpunkt 210–212° bildet (Gefunden: C, 74.63, 74.83; H, 8.76, 8.68. Berechnet für $C_{23}H_{35}O_3N$: C, 74.94; H, 9.45%).

Wird Anhydro-cerberigenin mit Chromsäureanhydrid oxydiert, erhält man Anhydro-cerberigenon (VIII), welches aus Alkohol Nadeln vom Schmelzpunkt 195–196° bildet, $[\alpha]_D^{20°} = +74.4°$ (0.1295 g. Substanz in 13 c.c. Chloroform, $l = 1.894$ dm., $\alpha_D^{20°} = +1.4°$) (Gefunden: C, 77.64; H, 8.95. Berechnet für $C_{23}H_{30}O_3$: C, 77.92; H, 8.54%). Bei Behandlung dieses Ketons mit Hydroxylamin erhält man Anhydro-cerberigenon-oxim, aus Alkohol, in Nadeln vom Schmelzpunkt 221–223° (Gefunden: C, 74.79, 74.81; H, 8.32, 8.48. Berechnet für $C_{23}H_{31}O_3N$: C, 74.75; H, 8.46%).

(4) *J. Biol. Chem.*, **102** (1933), 237.

Das aus Anhydro-cerberigenin, Essigsäureanhydrid und trockenem Natriumacetat hergestellte Anhydro-cerberigenin-acetat (IX) lieferte aus Alkohol farblose hexagonale Platten vom Schmelzpunkt 175–176°, $[\alpha]_D^{20°} = +58°$ (0.1124 g. Substanz in 13 c.c. Chloroform, $l = 1.894$ dm., $\alpha_D^{20°} = +0.95°$) (Gefunden: C, 75.26, 75.54; H, 8.83, 8.59; Molekulargewicht nach Rastscher Methode, 393, 399. Berechnet für $C_{25}H_{34}O_4$: C,75.33; H, 8.59%. Molekulargewicht, 398). Die oben angeführten Tatsachen bestätigen, dass Anhydro-cerberigenin ein β,γ-ungesättigtes Oxylacton ist und zwei Doppelbindungen hat und da es Digitonid bildet, erkennt man, dass eine sekundäre Hydroxylgruppe an C_3 steht.[5] Das Anhydro-cerberigenin hat die Konstitutionsformel V. Aus der Elementaranalyse und Molekulargewichtsbestimmung desjenigen Anteils (Schmelzpunkt 92–94°) von zitronengelben Genin, der aus seiner Ätherlösung keinen Kristall bildet, ergibt sich im Durchschnitt C, 75.67; H, 9.21% und das Molekulargewicht beträgt 367 (Gefunden: C, 75.64, 75.72; H, 9.02, 9.39; Molekulargewicht nach Rastscher Methode, 367. Berechnet für $C_{23}H_{32}O_3$: C, 77.47; H, 9.05%; Molekulargewicht, 356; $C_{23}H_{34}O_4$: C, 73.74; H, 9.16%; Molekulargewicht, 374), was also dem Durchschnittswert von C und H bei $C_{23}H_{32}O_3$ und $C_{23}H_{34}O_4$ nahekommt. Aus den Tatsachen, dass dieses zitronengelbe Genin Digitonid liefert und dass ein Teil des ersteren durch nochmalige Hydrolyse in Anhydro-cerberigenin $C_{23}H_{32}O_3$ in nadelkristalliner Form verwandelt werden kann, konnte man zum Schluss kommen, dass derjenige Teil, der sich aus der Ätherlösung von Aglykon nicht kristallisiert, ein Gemisch von $C_{23}H_{32}O_3$ und $C_{23}H_{34}O_4$ war, und da Cerberin Iso-cerberin (III) ergibt, muss auch im Genin selbstverständlich eine tertiäre Hydroxylgruppe an C_{14} stehen.[4] Das primäre Genin $C_{23}H_{34}O_4$ konnte unter den angewandten Spaltungsbedingungen nicht isoliert werden, sondern es war ganz unverkennbar, dass es sich unter der Einwirkung der alkoholischen Schwefelsäure allmählich in Anhydro-cerberigenin $C_{23}H_{32}O_3$ verwandelte. Dieser Vorgang verhält sich ganz ähnlich wie bei der Hydrolyse von Oleandrin,[6] Digitalinum verum[7] und Thevetin.[8] Es ist mir nicht gelungen, Cerberigenin als primäres Genin zu isolieren, welches durch die Hydrolyse von Cerberin hervorkommen sollte. Ich konnte aber, die obenerwähnten Tatsachen zusammengenommen, auf das Vorhandensein von Cerberigenin folgern, das wahr-

(5) Fernholz, *Z. physiol. Chem.*, **232** (1935), 97; R. Tschesche, *Ber.*, **68** (1935), 2247.
(6) K. Westphal, *Chem. Zentr.*, **97** (1926), I, 1814.
(7) Kiliani, *Arch. Pharm.*, **230** (1892), 250.
(8) R. Tschesche, *Ber.*, **69** (1936), 2368.

scheinlich die Konstitutionsformel IV haben müsste. Das Cerberigenin ist ein Isomeres von Uzarigenin,[9] Thevetigenin[8] und Digitoxigenin.[10]

Da Anhydro-cerberigenin Digitonid ergibt, ist es unverkennbar, dass auch Cerberigenin Digitonid liefert; und Cerberigenin, Uzarigenin und Thevetigenin enthalten folglich nach der Ansicht von R. Tschesche[11] eine Hydroxylgruppe an C_3 in cis-Stellung zur Methylgruppe an C_{10} und Digitoxigenin bildet eine trans-Stellung.

Da Cerberin bei physiologischen Versuchen sich als ein ziemlich starkes Herzgift bewährt, wäre es möglich, diese Herzwirksamkeit des Cerberins der cis-Verknüpfung von Ring A und B zuzuschreiben. Wenn das der Fall ist, kann sich die Konstitution des Cerberigenins mit der des Thevetigenins identifizieren; nämlich: Cerberigenin: OH an C_3 cis, Ring A und B cis; Thevetigenin: OH an C_3 cis, Ring A und B cis. Die Schmelzpunkte der Derivate von Genin, die ich aus Cerberin gewann und die Schmelzpunkte der Derivate von Genin, welche R. Tschesche aus Thevetin gewann, zeigen beträchtliche Abweichungen; es wäre also verfrüht, darauf zu folgern, dass sich Thevetigenin mit Cerberigenin identifiziert, was ich in Zukunft durch die Mischprobe der Derivate, welche R. Tschesche und ich hergestellt haben, festzustellen beabsichtige. Nachstehende Aufstellung gibt eine klare Übersicht hinsichtlich der Stoffe, deren Schmelzpunkte (A) annähernd gleich sind und (B) (C) beträchtliche Abweichungen zeigen: (A) Anhydro-cerberigenin $C_{23}H_{32}O_3$, Nadeln aus Äthanol, Schmp. 220–222°, $[\alpha]_D^{21°} = +46.8°$. Anhydro-thevetigenin $C_{23}H_{32}O_3$, Polyeder aus Methanol, Schmp. 218–220°, $[\alpha]_D^{18°} = +40°$. (B) Anhydro-cerberigenon $C_{23}H_{30}O_3$, Nadeln aus Alkohol, Schmp. 195–196°, $[\alpha]_D^{20°} = +74.4°$. Anhydro-thevetigenon (Anhydro-digitoxigenon[12]) $C_{23}H_{30}O_3$, Schmp. 265–270°. (C) Tetrahydro-anhydro-cerberigenon $C_{23}H_{34}O_3$, Nadeln aus Alkohol, Schmp. 181–182°. Tetrahydro-anhydro-thevetigenon (Tetrahydro-anhydro-digitoxigenon[10]) $C_{23}H_{34}O_3$, glänzende Blätter aus Essigester, Schmp. 245–248°.

Über Zucker. Der Zucker, der durch Hydrolyse des Cerberins mit 5-proz. Schwefelsäure gewonnen wird, reduziert die Fehlingsche Lösung. Seine Rosenthalersche Reaktion stellt sich als eine positive heraus und zeigt dauernde Rotfärbung. Die Flüssigkeit, die man gewinnt, nachdem man die sirupartige Substanz, welche Zucker enthält, unter Hinzufügung von 12-proz. Salzsäure erhitzt und dann abdestilliert hat, zeigt bei der

(9) *Ber.*, **68** (1935), 2252.
(10) *Ber.*, **61** (1928), 2436.
(11) *Ber.*, **69** (1936), 2443.
(12) *Ber.*, **53** (1920), 247.

Reaktion auf Anilinacetatpapier Gelbfärbung und aus diesen oben angegebenen Proben erkennt man das Vorhandensein von Methylpentose. Indem man diese Zuckerlösung mit Phenylhydrazin behandelt, gewinnt man Osazon, das in kaltem Aceton löslich ist und wenn man dasselbe aus 50-proz. Alkohol umkristallisiert, werden gelbe, dünne, viereckige Blättchen vom Schmelzpunkt 121–122° gewonnen. Werden diese Blättchen bei 100° und 30 mm. getrocknet, dann haben dieselben den Schmelzpunkt 141–142°. $[\alpha]_D^{21°} = +62.5°$ (0.1349 g. Osazon in 13 c.c. Chloroform, $l = 1.894$ dm., $\alpha_D^{21°} = +1.23°$) (Gefunden: C, 63.26, 63.15; H, 6.74, 6.91; N, 15.72, 15.70; Molekulargewicht nach Rastscher Methode, 341, 343. Berechnet für $C_{18}H_{22}O_3N_4$: C, 63.13; H, 6.41; N, 16.34%; Molekulargewicht, 342). Folglich wäre dieser Zucker $C_6H_{12}O_5$, nach dem Schmelzpunkt von Osazon und dessen Kristallform zu urteilen, eine neue Art Methylpentose, welche ein Isomeres von Rhamnose bildet. Ich habe diesem Zucker den Namen Cerberose gegeben.

Die Konstitution des Cerberins. Aus den Tatsachen, dass Cerberin Dihydro-cerberin ergibt und dass seine Legalsche und Baljetsche Reaktion sich als eine positive herausstellt, erkennt man, dass Cerberin β,γ-ungesättigtes Oxylacton ist; und dass Cerberin Iso-cerberin liefert, gibt das Vorhandensein einer tertiären Hydroxylgruppe an C_{14} bei Sterinskelett zu erkennen.[4] Aus den Tatsachen, dass Anhydro-cerberigenin Digitonid, Keton und Acetat liefert, erkennt man das Vorhandensein einer sekundären Hydroxylgruppe an C_3. Daraus kann man schliessen, dass das Zuckermolekül in Cerberin an C_3 steht. Nach der Tatsache, dass sich Cerberose $C_6H_{12}O_5$ durch Hydrolyse von Cerberin abspaltet, zu urteilen, hat Cerberin die Konstitutionsformel I.

Unter Zusammenfassung der bisher erwähnten Experimentsergebnisse führte mich die hydrolytische Spaltung des Cerberins zu den nachstehenden Gleichungen:

$$\underset{\text{Cerberin}}{C_{29}H_{44}O_8} + H_2O = \underset{\text{Cerberigenin}}{C_{23}H_{34}O_4} + \underset{\text{Cerberose}}{C_6H_{12}O_5}$$

$$\underset{\text{Cerberigenin}}{C_{23}H_{34}O_4} = \underset{\text{Anhydro-cerberigenin}}{C_{23}H_{32}O_3} + H_2O$$

Siebente Staatshochschule, Kagoshima.

Studies on the Nature of the Glass Electrode Potential. III. On the Cause of the Asymmetry Potential of the Glass Electrode.

By Hisato YOSHIMURA.

(Received September 2nd, 1937.)

According to the so-called Haber theory of the glass electrode, there should exist no potential, when both surfaces of a glass electrode membrane are brought into contact with one and the same solution. Actually, however, a certain potential appears, which is called the asymmetry potential. As to the cause of this potential, some experimental studies were performed by Elder[1], Buchböck[2], and Kahler and DeEds[3], though none of them can be regarded as fundamental. (The Chemical Abstracts recorded a paper by Haugaard[4]. Not having read his paper, however, we must necessarily refrain from commenting upon his conclusions.) In the present investigation, this problem is examined from the point of view of current theories concerning the glass electrode. The experimental methods and the sign of the potential are the same as described in the previous report[5]. Experiments were carried out at 25°C. in most cases.

(1) The Asymmetry Potential and the Difference of Hydrogen Electrode Function on Outer and Inner Surfaces of the Electrode Membrane. The hydrogen electrode functions $\Delta E/\Delta p$H of both the inner and the outer surfaces of the electrode bulb (which serves as the electrode membrane), and its asymmetry potentials in two buffer solutions of pH 3 and 7 were determined after the electrode had been fully equilibrated with water, using many glass electrodes made of commercial soft glass, MacInnes glass, and Morton glass purchased in England. As to the meaning of $\Delta E/\Delta p$H, refer to the previous report[5]. The measurement of $\Delta E/\Delta p$H on both surfaces of the electrode membrane was performed with the two buffer solutions in a way similar to that of Kahler and DeEds[3].

(1) Elder, *J. Am. Chem. Soc.*, **51** (1929), 3266.
(2) Buchböck, *Z. physik. Chem.*, A, **156** (1931), 232.
(3) Kahler and DeEds, *J. Am. Chem. Soc.*, **53** (1931), 2998.
(4) Haugaard, *Chem. Abstracts*, **31** (1937), 930; *Kem. Maanedsblad*, **17** (1936), 33.
(5) Yoshimura, this Bulletin, **12** (1937), 359.

On examining the data obtained, no correlation was found to exist between the asymmetry potential and the hydrogen electrode function of either side of the membrane, but there was a correlation between the asymmetry potential and the difference of $\Delta E/\Delta p\mathrm{H}$ of both surfaces, as shown in Fig. 1, where dots represent data referring to the MacInnes glass electrode, crosses those of the Morton glass electrode, and circles those of the commercial glass electrode. While these are data at 25°C., triangles represent those of commercial glass electrode determined at 18°C. The abscissa of Fig. 1 is the asymmetry potential in the solution of pH 3, e_3. The ordinate is the difference of the asymmetry potentials in the two solutions cf pH 3 and pH 7, e_3-e_7, which is given by

$$e_3-e_7=\left\{\left(\frac{\Delta E}{\Delta p\mathrm{H}}\right)_o-\left(\frac{\Delta E}{\Delta p\mathrm{H}}\right)_i\right\}\Delta p\mathrm{H} \qquad (1),$$

where ΔpH is the pH difference of the two solutions and is numerically 4. Suffixes i and o refer to the inner surface and the outer surface of the electrode membrane respectively. Thus the ordinate of the figure corresponds to the difference of $\Delta E/\Delta p\mathrm{H}$ between the two surfaces of the membrane as ΔpH is constant. The plots of all the electrodes made of the three mentioned sorts of glass tend to lie on the respective straight lines which pass near the origin with a slope of about 2. This indicates that the asymmetry potential approaches zero when the hydrogen electrode functions of both surfaces of the electrode membrane approach each other. This fact suggests in turn that the electromotive nature of the membrane surface which determines the hydrogen electrode function is correlated closely with that determining the potential level of the surface, because the asymmetry potential corresponds to the difference of the potential levels of the inner and the outer surfaces. Moreover, it is suggested that this relation differs according to the chemical composition of the glass, as correlation lines of the three sorts of glass differ from one another.

(2) **The Relation between the Electromotive Effect and the Curvature of the Glass Membrane.** It is seen in Fig. 1 that the hydrogen electrode function of the outer surface of an electrode membrane is in most cases lower than that of the inner surface and the asymmetry potential is negative, that is, the potential level on the inner side of the membrane is lower than that on the outer side. This difference of the electromotive effect of the outer and the inner surfaces of the electrode bulb is supposed to be due to the difference in the curvature of these

surfaces, and therefore to the strain or atomic arrangement of the surface layer. Elder[1] and also Buchböck[2] attempted to prove this supposition experimentally. The former failed in the experiment, while the latter succeeded. The present author also attempted to examine the problem. For the purpose, a bulb membrane of MacInnes glass electrode being fused into one end of a commercial glass tube, a MacInnes and Dole electrode of the diaphragm type was constructed. The convex surface of this electrode membrane is directed inside the electrode and the concave surface outside, while the relation is reverse in the electrode of bulb type. The asymmetry potential and the hydrogen electrode function of both the surfaces being estimated, data are plotted in Fig. 1 (designated with asterisks). The points tend to lie on the positive side of the correlation line of MacInnes glass electrode. It shows that the difference of the electromotive effect between the inner and the outer surfaces of the electrode membrane is caused by the difference of the curvature. This suggests that the electromotive effect of the glass membrane is closely related to the atomic arrangement of the surface layer[6]. Thus the asymmetry potential is supposed to be due to the difference of the atomic arrangement between the two surfaces of the electrode membrane.

(3) **The Relation between the Electromotive Effect of the Glass Membrane and its Thickness.** Kahler and DeEds[3] pointed out that the asymmetry potential of a glass electrode approaches zero as the thickness of the electrode membrane diminishes. This can be ascertained by the data given in Fig. 2, where the asymmetry potential (e_3 at 18°C. in most cases) of various electrodes of MacInnes glass (dots) and of commercial glass (circles) are plotted against the electrical resistance of the electrodes. The plots of the electrodes made of one and the same sort of glass tend to lie vaguely on a correlation line. Though the electrical resistance depends on the size of the electrode bulb besides the thickness of its membrane, it is principally determined by the latter, the size of the bulb depending also upon the thickness of the membrane, as the bulbs are blown on capillaries of about the same bore and the same thickness. Thus it can be maintained that a correlation exists between the thickness of the membrane and the asymmetry potential.

(6) To prove this experimentally, the effect of annealing on the glass electrode potential was examined. Unfortunately, however, the effect of heat treatment of the electrode on its potential such as the effect or drying previously reported[5] covered the effect of annealing and the experiments ended in a failure. But the above suggestion as to the relation between the electromotive effect and the atomic arrangement cannot be denied on account of this failure.

This fact was ascertained further by the two following experiments: (i) A short MacInnes glass tubing of thick wall (which is about 0.4 mm. thick and serves as the electrode membrane) being connected with supports of commercial capillary tubing, an electrode of the type given in Fig. 1 in the previous report[5] was constructed. After its asymmetry potential and the hydrogen electrode function had been estimated on both the inner and the outer surfaces, the thick MacInnes glass tubing was blown to make a bulb of which the thickness of the thinnest part was 10 μ or so. The effect of this blowing on its potential was examined. See an example of the results given in Table 1. On making the membrane thinner, the asymmetry potential (in the absolute value) and the difference of the hydrogen electrode function between the inner and the outer surfaces decreased.

Table 1. Effect of Blowing the Bulb.

Experiment	$\Delta E / \Delta p$H (mV./pH)			e_3 (mV.)	Thickness of the membrane (mm.)
	Inner surface	Outer surface	Difference		
Before blowing	58.3	47.8	10.5	−110.7	ca. 0.4
After blowing	58.2	58.1	0.1	−10.5	0.01

(ii) Either the inner or the outer surface of the thick membrane of the above-mentioned electrode being soaked in a concentrated HF for 1–2 hours, and thereafter in streaming water for several days, a thin lamella of the surface was stript off. The thickness of the membrane thus being reduced, the change in its electromotive effect was examined. Examples of data are given in Table 2. It was found in most cases that the hydrogen electrode function of the corroded surface approached that of the other surface of the membrane and the asymmetry potential decreased (in absolute value), while the reverse result was found in a few cases. As HF corrodes the glass surface ununiformly, the corroded surface may not be regarded as the same as that shaven mechanically. Deducing from the results of all experiments mentioned above, however, it is concluded that the asymmetry potential (in absolute value) and the difference of the hydrogen electrode function between the inner and the outer surfaces of the electrode membrane decrease simultaneously as the thickness of the membrane decreases.

Table 2. Effect of Hydrochloric Acid Treatment.

Experiment		$\Delta E/\Delta p$H (mV./pH)			e_3 (mV.)	Resistance (Ω)
		Inner surface	Outer surface	Difference		
I	Before treatment	58.0	47.6	10.4	−108 5	1.2×10^9
	After treatment	55.9	47.6	8.3	−89.5	1.0×10^9
II	Before treatment	57.9	52.8	5.1	−71.5	1.4×10^9
	After treatment	58.5	56.7	1.8	−23.5	1.2×10^9

I. The inner surface etched with HF.
II. The outer surface etched with HF.

The above-mentioned results cannot be explained by the deviation film theory of Kahler and DeEds[3] who maintained that the decrease of the thickness of the membrane is accompanied by increase of the hydrogen electrode function, for it is clear in Table 2 that the hydrogen electrode function on one surface has no direct correlation with the thickness of the electrode membrane. A plausible explanation is that the atomic arrangement of the inner and the outer surfaces of the membrane which are closely related with the factor determining both the hydrogen electrode function and the potential level of the surface tend to equalize with each other, as the thickness of the membrane decreases.

From data given in Table 2, it is also maintained that the glass membrane being regarded as an ensemble of many unit lamellæ, the electromotive effect of each lamella is different from the others. In the previous report[7], the same fact was maintained concerning assumed unit parts of the surface of the electrode membrane. This fact suggests that the atomic arrangement of the electrode membrane is different both lengthwise and breadthwise.

(4) **Dependence of the Asymmetry Potential on the *p*H of the Solution and Discussion of the Above-Mentioned Results.** From the above-mentioned experimental results, it is certain that the asymmetry potential is closely correlated with the difference of $\Delta E/\Delta p$H between the inner and the outer surfaces of the electrode membrane. This fact can be explained in either of the two following ways: (i) Experiments show that a linear relationship exists between the potential of the glass electrode and the *p*H of the solution at least in the range of *p*H 2–8, even when the hydrogen electrode function of the glass electrode is lower than

(7) Yoshimura, *J. Biochem.* (Japan), **21** (1935), 335.

the theoretical value. If this is correct not only roughly in the scope of experimental error, but also theoretically in the whole range of pH, the asymmetry potential e' in a solution of which the pH is higher by $\Delta p\mathrm{H}'$ than 3, is given by

$$e' = e_3 - \left\{\left(\frac{\Delta E}{\Delta p\mathrm{H}}\right)_o - \left(\frac{\Delta E}{\Delta p\mathrm{H}}\right)_i\right\}\Delta p\mathrm{H}' \qquad (2).$$

Thus the asymmetry potential of one and the same glass electrode is a linear function of pH. This equation has already been suggested by Kahler and DeEds[3]. If it is assumed in this equation that the asymmetry potential e' in a solution of a certain pH is kept constant among the electrodes made of one and the same sort of glass, a rectilinear relationship should exist between e_3 of the electrodes and the differences of $\Delta E/\Delta p\mathrm{H}$ between the inner and the outer surfaces of the electrode membranes. This certain pH should be ca. 11, as the slope of the correlation line experimentally found, i.e. $\Delta p\mathrm{H}'$, is ca. 2.

(ii) According to the current theories of the glass electrode, mentioned in the previous report[5], $\Delta E/\Delta p\mathrm{H}$ is given by

$$\frac{\Delta E}{\Delta p\mathrm{H}} = \frac{R'T}{F}\left[1 - \frac{1}{\Delta p\mathrm{H}}\log\left\{\frac{\left(1+\frac{C'_{\mathrm{Na}}}{C'_{\mathrm{H}}}\frac{Y}{X}\right)^n}{\left(1+\frac{C_{\mathrm{Na}}}{C_{\mathrm{H}}}\frac{Y}{X}\right)^n}\right\}\right] \qquad (3).$$

R' represents 2.303 R. C_{H} and C'_{H} are the hydrogen ion concentrations of the two buffer solutions used for the determination of $\Delta E/\Delta p\mathrm{H}$, and C_{Na} and C'_{Na} their sodium ion concentrations, the cation of the salt being assumed to be sodium ion. $\Delta p\mathrm{H}$ is equal to $\log C_{\mathrm{H}}/C'_{\mathrm{H}}$. As to the constants n, X and Y, see the previous report. When the hydrogen ion concentration C_{H} is sufficiently high, the term $\frac{C_{\mathrm{Na}}}{C_{\mathrm{H}}}\frac{Y}{X}$ can be neglected, and we have

$$\frac{\Delta E}{\Delta p\mathrm{H}} = \frac{R'T}{F}\left[1 - \log\left(1+\frac{C'_{\mathrm{Na}}}{C'_{\mathrm{H}}}\frac{Y}{X}\right)^n \Big/ \Delta p\mathrm{H}\right] \qquad (4).$$

This is the equation of $\Delta E/\Delta p\mathrm{H}$ given in the previous report[8]. From this equation, it is clear that $\Delta E/\Delta p\mathrm{H}$ is not a constant but a function of pH and the salt concentration when $\Delta E/\Delta p\mathrm{H}$ is smaller than the

(8) The derivation of this equation is given here as an addendum to the previous report[5].

theoretical value $R'T/F$. Thus equation (2) is not valid theoretically, and the asymmetry potential e_g is given by

$$e_g = \frac{R'T}{F} \log \left\{ \frac{1+\frac{C_{Na}}{C_H}\frac{Y_o}{X_o}}{1+\frac{C_{Na}}{C_H}\frac{Y_i}{X_i}} \right\}^n + \frac{R'T}{F} \log \frac{X_o}{X_i} \qquad (5),$$

which is equal to equation (2) given in the previous report. Suffixes i and o refer to the inner and the outer surfaces of the electrode membrane respectively. When C_H is sufficiently large, we have

$$e_g = \frac{R'T}{F} \log \frac{X_o}{X_i} \qquad (6).$$

From equations (4) and (6), it is clear that, when the constant X decreases on one surface of the membrane as compared with that on the other surface, the potential level of that surface rises against that of the other surface, causing the change in the asymmetry potential, and the hydrogen electrode function on that surface decreases. Thus the fact found in the present experiments can be explained by the current theories of the glass electrode.

Now it should be decided which of explanations (i) and (ii) is correct. For this purpose, equations (2) and (5) were examined experimentally, of which the former indicates that the asymmetry potential is a linear function of the pH of the solution, while the latter indicates that the function is a curve which tends to transit into a plateau in the range of low pH, as C_{Na}/C_H decreases.

Measuring the asymmetry potential of one and the same electrode in various buffer solutions of different pH but of 0.1 molar sodium ion concentration, data were plotted against the pH, of which examples obtained on a MacInnes glass electrode (dots) as well as a commercial glass electrode (circles) is given in Fig. 3. Plots did not lie on a straight line, but on a curve which showed that the asymmetry potential (not in absolute value) decreases with the decrease in pH but tends to attain a constant value in the range of low pH. Thus explanation (ii), but not (i), is to be adopted.

The above-mentioned theoretical correlation between the asymmetry potential and the difference of hydrogen electrode functions of both surfaces of the electrode membrane can be verified quantitatively to a certain extent as follows:

Putting $$\delta \equiv \frac{R'T}{F} \log \left(1+\frac{C_{Na}}{C_H}\frac{Y}{X}\right)^n,$$

we have

$$\log \left\{ \frac{\text{Antilog} \dfrac{\delta_i}{\dfrac{nR'T}{F}} - 1}{\text{Antilog} \dfrac{\delta_o}{\dfrac{nR'T}{F}} - 1} \right\} = \text{const.} + \log \frac{X_o}{X_i} \qquad (7),$$

the suffixes o and i referring to the outer and the inner surfaces of the membrane respectively. From equation (4),

$$\delta = \frac{R'T}{F} \Delta p\mathrm{H} - \Delta E \qquad (8),$$

and from equation (6),

$$\log \frac{X_o}{X_i} \fallingdotseq -\frac{e_3}{\dfrac{R'T}{F}} \qquad (9),$$

assuming that the cation effect on the asymmetry potential is negligible in the range near pH 3. Thus equation (7) was quantitatively examined, calculating δ and log (X_o/X_i) by equations (8) and (9) from the experimental data obtained in section (1). The result is given in Fig. 4, where n in the equation (7) is taken as 1/2 according to Gross and Halpern[9]. The plots lie vaguely between two parallel boundary lines of which the slope is 1. The reason why the plots do not lie on a straight line, but scattered in a zone is probably that the "const." in equation (7) is not the same among different electrodes, and moreover the assumptions made in this examination may not be completely correct. Thus it can be stated that equation (7) was verified somewhat quantitatively. Even when n is taken as 1 according to Dole[9] and Horovitz[9], the same result is obtainable. Therefore the decisive criticism of the three current theories cited in the previous report can not be deduced from the present experimental results. Moreover, it would be premature to accept any one of the current theories as completely correct only from the present experimental results.

It is interesting, however, to try to explain the experimental facts by the current theories. It was found in the above-mentioned experiments

(9) See the discussion in the previous report[5].

that the hydrogen electrode function of the outer surface is lower than that of the inner surface and the potential level of the former which determines the asymmetry potential is higher than that of the latter. The explanation given for the fact is that the constant X in equations (4) and (6) on the outer surface is smaller than that on the inner surface. The physical meaning of this explanations is that the energy

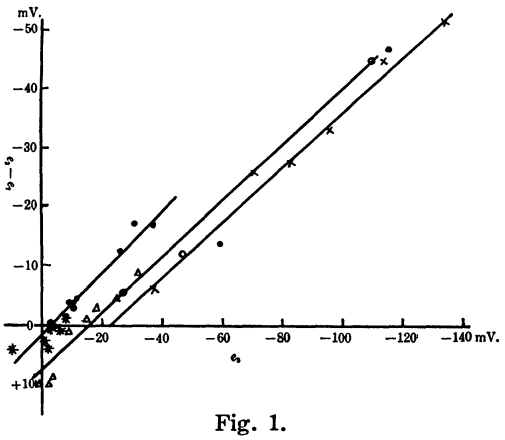


Fig. 1.

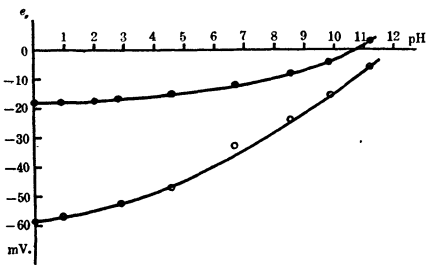


Fig. 3.

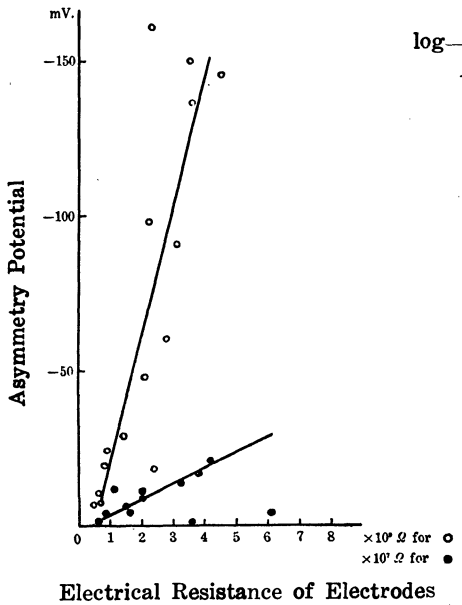


Fig. 2.

$$\log \frac{\text{Antilog}\,\dfrac{\delta_i}{\frac{R'T}{2F}} - 1}{\text{Antilog}\,\dfrac{\delta_o}{\frac{R'T}{2F}} - 1}$$

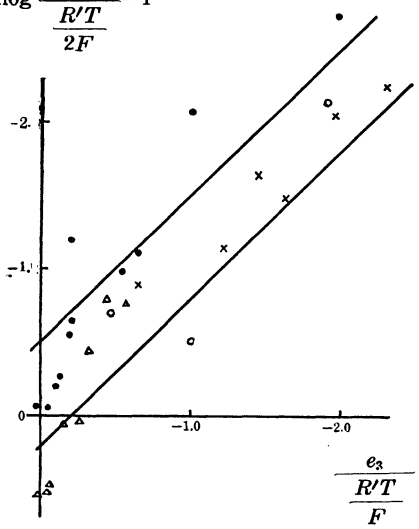


Fig. 4.

of hydrogen ion on the lowest quantum level of the glass phase according to Dole[9] is greater on the convex surface than that on the concave surface, probably owing to the difference of the atomic arrangements of these surfaces. To elucidate further the interrelation between the constants in the above-mentioned theoretical equation and the atomic arrangement of the surface is a problem left for future study.

Conclusions. (1) When the difference between the hydrogen electrode functions of the inner and the outer surfaces of a glass membrane is large, a high asymmetry potential appears, and the hydrogen electrode function on the positive side of the asymmetry potential is in most cases smaller than that on the other side. Thus a correlation exists between the difference of the hydrogen electrode functions of the two surfaces and the asymmetry potential. This indicates that an intimate relationship exists between the factor which determines the potential level of the surface referring to the asymmetry potential, and that of the hydrogen electrode function. This fact can be explained qualitatively by the current theories of glass electrode.

(2) The hydrogen electrode function is, in most cases, less on the convex surface than on the concave surface of an electrode membrane, and the positive pole of the asymmetry potential is, in most cases, on the convex side. This difference between the hydrogen electrode functions of both surfaces and also the magnitude of the asymmetry potential tend to decrease as the thickness of the electrode membrane diminishes. These facts suggest that the electromotive effect of the surface of a glass membrane is closely connected with the atomic arrangement between the inner and the outer surfaces of the electrode membrane.

A glass membrane being regarded as an ensemble of many lamellæ and unit surfaces, the electromotive effects of these parts are different from one another. Therefore, the atomic arrangement of the glass membrane is probably different in each part both lengthwise and breadthwise.

The author expresses his cordial thanks to Prof. Dr. I. Sawai of the Institute of Engineering Chemistry for his kind advices and also to the Hattori-Hoko-Kwai for a grant.

Institute of Physiology, Faculty of Medicine,
Kyoto Imperial University.

Über eine hochungesättigte Fettsäure $C_{24}H_{38}O_2$ aus dem Öle des Thunfisches, *Tynnus tynnus* L.

Von Sei-ichi UENO und Shin-ichiro TAKASE.

(Eingegangen am 22. September 1937.)

Über hochungesättigte Fettsäuren der C_{24}-Reihe aus Fischölen sind von mehreren Autoren Untersuchungen angestellt worden. H. Bull[1] fand eine Säure $C_{24}H_{40}O_2$ im Heringsöle. S. Ueno und M. Iwai[2] erhielten Scoliodonsäure $C_{24}H_{38}O_2$ aus dem Lebertran von „Hiragashira", *Scoliodon laticaudus* Müller und Henle. Y. Toyama und T. Tsuchiya[3] beschrieben das Vorkommen von $C_{24}H_{36}O_2$, $C_{24}H_{38}O_2$ und $C_{24}H_{40}O_2$ in Sardinenöle und die Konstitution der Nisinsäure $C_{24}H_{36}O_2$. S. Ueno und C. Yonese[4] konnten aus dem Öle des Thunfisches eine Säure $C_{24}H_{38}O_2$ isolieren, der vermutlich eine Säure $C_{24}H_{36}O_2$ beigemischt sein dürfte.

In der vorliegenden Arbeit haben wir den Ozonabbau der aus dem Thunfischöle gewonnenen Säure $C_{24}H_{38}O_2$ studiert, um die Konstitution dieser Säure aufzuklären. Im Abbauprodukt des Ozonides konnten wir Acetaldehyd, Propionaldehyd, Kohlendioxyd und Bernsteinsäure feststellen. Daraus lässt sich ableiten, dass sich folgende Atomgruppen in der Säure $C_{24}H_{38}O_2$ befinden: CH_3-CH_2-CH=, =CH-CH_2-CH= bzw. =CH-CH_2-COOH, =CH-CH_2-CH_2-CH= bzw. =CH-CH_2-CH_2-COOH. Kohlendioxyd und Acetaldehyd sind möglicherweise sekundäre Abbauprodukte von Malonaldehydsäure, die aus dem Gruppenteile =CH-CH_2-CH= od. =CH-CH_2-COOH entstehen mag. Eine eingehendere Untersuchung konnten wir wegen Mangels an Material noch nicht ausführen.

Beschreibung der Versuche.

Die hochungesättigte Säure, welche der Formel $C_{24}H_{38}O_2$ entspricht, war ein Nebenprodukt bei der Untersuchung der gesättigten Fettsäuren im Thunfischöle; darüber haben S. Ueno und C. Yonese in Nippon Kwagaku Kwaishi (japanisch) berichtet. Die Eigenschaften des Thunfischöles waren: d_4^{20} 0.9264; n_D^{20} 1.4820; J.Z. (Wijs) 190.1; S.Z. 4.2; V.Z. 183.4. Die aus dem obigen Öle (3 kg.) gewonnenen

(1) H. Bull, *Chem.-Ztg.*, **23** (1899), 996.

(2) S. Ueno und M. Iwai, *J. Soc. Chem. Ind., Japan*, **37** (1934), 251.

(3) Y. Toyama und T. Tsuchiya, *J. Soc. Chem. Ind., Japan*, **37** (1934), 530; dieses Bulletin, **10** (1935), 543, 547.

(4) S. Ueno und C. Yonese, dieses Bulletin, **11** (1936), 440.

Methylester der Fettsäuren wurden fraktioniert und die über 200°/3 mm. siedende Fraktion wurde noch zweimal der fraktionierten Destillation unterworfen. Die Resultate der letzten Destillation waren wie folgt.

Nr.	Siedept. (°C./3 mm.)	Ausbeute (g.)	n_D^{20}
1	-200	3.0	1.4815
2	200-205	6.0	
3	205-209	29.0	1.4840
4	209-210	64.5	1.4850
5	210-220	41.0	1.4870
6	220-224	51.0	1.4880
7	224-226	46.0	1.4875
8	226-	15.0	1.4885
9	Rückstand		

Die Trennung und der Ozonabbau der hochungesättigten Säure $C_{24}H_{38}O_2$. Die aus der Fr.Nr.7 gewonnene Fettsäure wurde mit Hilfe der Bleisalz-Alkohol-Methode und Natriumsalz-Aceton-Methode weiter gereinigt. So ergaben sich zum Schluss 6 g. hochungesättigte Fettsäure mit folgenden Eigenschaften: N.Z. 154.0; J.Z. (Wijs) 342.9; n_D^{20} 1.5075. Der Bromgehalt des ätherunlöslichen Polybromides war 67.7%. (Ber. für $C_{24}H_{38}O_2$: N.Z. 156.6; J.Z. 354.2. Ber. für $C_{24}H_{38}O_2Br_{10}$: Br, 69.05%). Die hochungesättigte Fettsäure (3.85 g.) wurde in 50 c.c. Chloroform gelöst und unter Kühlung mit einer Kältemischung ca. 7%iges Ozon 4 Stunden lang eingeleitet. Bei der Abdestillation des Lösungsmittels unter vermindertem Druck blieben 5.2 g. eines gelben harzigen Ozonides zurück. Das Ozonid wurde mit 50 c.c. Wasser unter Rückfluss auf dem siedenden Wasserbad im Wasserstoffstrom erhitzt. Die entwickelten Gase wurden in 50 c.c. kaltem Wasser, dann in 300 c.c. und schliesslich noch in 200 c.c. Barytwasser (ca. N/3) absorbiert.

Nachweis des Acetaldehyds und des Propionaldehyds. Die wässrige Lösung des flüchtigen Zersetzungsprodukts hatte einen angenehmen Geruch und gab die Schiffsche Reaktion; mit Natriumnitroprussid und Kalilauge färbte sie sich rot; mit Piperidin und Natriumnitroprussid blau; mit *m*-Phenylendiamin-Salzsäure Lösung zeigte sie grüne Fluorescenz. Beim Versetzen mit einer Lösung von *p*-Nitrophenylhydrazin schieden sich gelbe nadelförmige Kristalle aus, welche nachdem sie aus Toluol und verdünntem Alkohol umkristallisiert wurden, bei 117.5–119° schmolzen. Dieser Schmelzpunkt ist sowohl niedriger als der des Acetaldehyd-*p*-nitrophenylhydrazons (Schmp. 128°), als auch des Propionaldehyd-*p*-nitrophenylhydrazons (Schmp. 124°), aber eine Mischung von den gelben nadelförmigen Kristallen mit Propionaldehyd-*p*-nitrophenylhydrazon (Schmp. 123–124°), das aus Kahlbaumschem Propionaldehyd hergestellt wurde, schmolz bei 119.5–121° (Gef.: N, 22.48. Ber. für $C_9H_{11}O_2H_3$: N, 21.76; Ber. für $C_3H_9O_2N_3$: N, 23.46%). Aus den Analysenwerten könnte man unter Berücksichtigung der oben beschriebenen Farbenreaktionen schliessen, dass die gelben Kristalle eine Mischung von Acetaldehyd- und Propionaldehyd-*p*-nitrophenylhydrazon sind.

Kohlendioxyd. In der Baryt-Lösung entstand ein weisser Niederschlag von Bariumcarbonat (1.6 g.), woraus das entstandene Kohlendioxyd berechnet wurde (Gef.: CO_2, 9.4%). Kohlendioxyd ist ein sekundäres Zersetzungsprodukt der Malonsäure od. ihres Halbaldehyds; die vollkommene Abspaltung von Kohlendioxyd aus einer Atomgruppe $=CH\text{-}CH_2\text{-}CH=$ od. $=CH\text{-}CH_2\text{-}COOH$ in $C_{24}H_{38}O_2$ müsste 12.3% betragen.

Bernsteinsäure. Die wässrige Lösung der nichtflüchtigen Zersetzungsprodukte wurde von der harzigen Substanzen getrennt. Ein Teil der Lösung wurde mit Ammoniak versetzt, konzentriert und der Zinkstaubdestillation unterworfen. Der entstehende Dampf färbte einen mit Salzsäure befeuchten Holzspan rot. Auf Grund dieser charakteristischen Farbenreaktion des Pyrrols kann man auf das Vorhandensein von Bernsteinsäure in der wässrigen Lösung schliessen. Den Ätherextrakt der wässrigen Lösung haben wir mit Kaliumpermanganat oxydiert und konnten aus dem Oxydationsprodukt weisse Kristalle erhalten, die, nachdem sie aus Essigäther umkristallisiert wurden, bei 182° schmolzen. Die Mischprobe mit einem reinen Präparat der Bernsteinsäure (Schmp. 183–184°) zeigte keine Depression des Schmelzpunktes.

Über die harzigen Substanzen haben wir keine genauere Untersuchung gemacht, sondern lediglich festgestellt, dass es nicht gelingt eine höhere Dicarbonsäure als Bernsteinsäure daraus zu isolieren. Wir wollen mit einer grösseren Menge Material weitere Untersuchungen ausführen.

Chemische Institut, Technische Fakultät,
Kaiserliche Universität zu Osaka.

Studies on Fluorine at Low Temperatures. III. Dissolution of Chlorine in Liquid Fluorine.

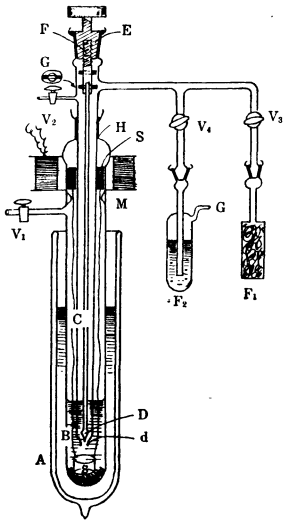
By Shin-ichi AOYAMA and Eizo KANDA.

(Received August 12th, 1937.)

Merck's potassium bifluoride contains 0.17% chlorine. When it is electrolysed, chlorine of the chloride in the molten salt is expelled by fluorine and the produced fluorine gas is contaminated with chlorine gas, and sometimes traces of chlorine can be found in liquid fluorine. Of course, such occurs only while the salt is fresh, and no chlorine exists in the salt which has been subjected to electrolysis for a long time.

It is unusual that a solution of crystals exists at such a low temperature as that of liquid fluorine. The present authors carried out measurements as to this interesting case.

I. **Apparatus.** A special apparatus as shown in the accompanying figure was devised for the purpose of taking a sample for analysis, and used in the analysis of liquid air and a solution of chlorine in liquid fluorine. A is a Dewar vessel to keep liquid nitrogen, B a glass pipe 30 mm. in diameter, where fluorine entering at V_2 is condensed, C a Pyrex glass sampler for the solution, 10 mm. in diameter, D a valve spindle made of Pyrex glass, the top of which is connected with the lower end of the copper rod. F has a screw-thread cut on it and the spindle goes up and down as cap E in the upper part with ground glass surface is turned, and thus the ground glass surface joint between D and d at the lower end is opened or closed. Two copper pieces are attached to the lower part of F as shown in the figure. The cross-section of the pipe at this point is made elliptical (G), so that F does not rotate but only goes up and down when E rotates. S is a stirrer, M an electric magnet for working the stirrer S, F_1 a silver-plated copper vessel filled with many small coils of silver filament and acts as an absorber of fluorine, and F_2 a glass vessel in which an aqueous solution of silver nitrate is placed to absorb fluorine and chlorine.



II. **Operation.** Fluorine or chlorine is introduced at V_2. V_1 is an opening for evacuating the apparatus in advance. The interior of F_1 is also previously evacuated. When a proper amount of solution is condensed on the bottom of B, the stirrer S is moved up and down by operating M and the liquid is made homogeneous. The valve D is closed by turning E and the sample of liquid is accumulated in C.

By turning H, B and C are disconnected at the ground glass surface junction. C is drawn up slightly from the liquid fluorine and the solution is gradually vaporized. When V_3 is opened and F_1 is heated to 200°C., the sample in C is vaporized and the fluorine, acting on the silver, is absorbed. Care must be taken so that sudden boiling may not take place at the time of vaporization and the crystals of the segregated solute and a small quantity of the solution may finally remain. Then V_3 is closed and V_4 is opened. In this way the remainder of fluorine and the crystals of the segregated chlorine are vaporized and the vapour produced is passed through the solution of silver nitrate in F_2.

The solution of silver nitrate is first made ammoniacal, and is acidified with nitric acid after the halogens have been passed through it. To make ammoniacal is intended for preventing a part of chlorine from becoming soluble $AgClO_3$.

The gas in C is drawn by working a pump at G and by introducing air at V_2. All the gas in C is passed through F_2.

III. **Quantitative determination of fluorine and chlorine.** (1) The greater part of fluorine, apart from chlorine, is acted on by the silver filament in F_1, and makes silver fluoride. The quantity of fluorine is determined by weighing F_1.

(2) The solution of silver nitrate, the deposits of silver fluoride and silver chloride are carefully poured from F_2 into a bakelite beaker and are acidified with nitric acid, whereby the silver fluoride is dissolved. Then the solution is filtered and the residue of silver chloride is weighed. Thus, the quantity of chlorine can separately be determined.

(3) The filtrate contains silver fluoride and silver nitrate. With an addition of aqueous solution of NaCl, it is precipitated as silver chloride. Then by removing the deposit a filtrate of NaF can be obtained. This filtrate is made alkaline by adding an aqueous solution of Na_2CO_3 to it. Then deposits of $CaCO_3$ and CaF_2 are formed by adding a solution of $CaCl_2$ to this alkaline filtrate. When $CaCO_3$ alone is dissolved by acetic acid, CaF_2 remains as deposit. This deposit is filtered and weighed, and the quantity of fluorine is determined from CaF_2.

IV. **Results of measurements.** (1) Fluorine obtained from a new electrolyte of potassium bifluoride. Fluorine as AgF in F_1 1.0524 g., as CaF_2 in F_2 0.1155 g., total 1.1679 g. Chlorine as AgCl in F_2 0.0075 g. Thus, the percentage of chlorine in the mixture was found 0.64.

(2) The percentage of chlorine in fluorine produced from an old electrolytic salt was 0.09%.

(3) Quantity of chlorine in liquid fluorine saturated at −195°C. Chlorine was separately introduced, condensed, and precipitated. After stirring, the solution was analysed with the result as follows: Fluorine as AgF in F_1 0.7145 g., as CaF_2 in F_2 0.1227 g. Chlorine as AgCl in F_2 0.0088 g. The quantity of chlorine in the solution saturated at −195°C. was 1.04%.

The authors express their hearty thanks to the Japan Society for the Promotion of Scientific Research for a grant.

Cryogenic Section, Research Institute for Iron, Steel and Other Metals, Tohoku Imperial University.

Studies on Fluorine at Low Temperatures. IV. Separation of Fluorine from Oxygen by Adsorption and Rectification.

By Eizo KANDA.

(Received August 12th, 1937.)

As was stated in the first paper, fluorine is often contaminated with oxygen, the boiling points, −188°C. and −183°C. respectively, being rather close. Removal of oxygen from fluorine with chemical reagents would be practically impossible, because fluorine acts upon almost all substances at ordinary temperature. Besides, it is desired to handle fluorine at low temperatures to avoid its chemical activity. Therefore, the author examined the possibility of separation of fluorine from oxygen by adsorption upon charcoal at low temperatures.

Experiments on separation were also made by means of a rectification still, because the difference between the boiling points is as small as 5°, and accordingly the separation by fractional distillation of the liquid might be very difficult.

I. **Experiment on Adsorption.** (1) *Apparatus.* The ordinary method of determining the adsorption of gases, in which the sample of the adsorbent (for instance, charcoal) is placed in a glass or quartz vessel and the variation of the volume or pressure of the gas due to adsorption is determined by reading the mercury column, was not applicable in this case, because glass, quartz and mercury are attacked by fluorine. The author, therefore, used the method with a spring balance for reducing the error.

In Fig. 1, A is a trap in which pure liquid fluorine is kept and which is cooled by liquid nitrogen. In the trap is a heating coil H. The fluorine is vaporized in a desired quantity and the vapour is carried into B. B has a spring balance in it, and at the end of the balance a platinum-plated quartz scale is hung by a platinum filament. T is a thermocouple made of copper and constantan wires, which is placed near the test piece for determining the temperature. An outline of the apparatus for obtaining desired low temperatures is represented by two Dewar vessels, which are similar to one used by the author for calibrating thermocouples by means of a hydrogen thermometer[1].

(1) Aoyama and Kanda, this Bulletin, **10** (1935), 472.

Spring balance. A quartz thread 0.4 mm. in diameter was wound in the form of a spring having a diameter of about 15 mm., the number of turns being 60 and the sensitivity 25 mm./0.1 g. The platinum-filament was fitted with the scale at its lower end in advance, and platinum weights of 0.1 g., 0.2 g.,....2 g. were placed on the scale. The elongation of the spring was determined by a cathetometer and was calibrated against the weights. As illustrated, the upper end of the spring was connected to a platinum thread, which was wound round a cock placed on the top of B, and the scale was brought into a proper position by turning the cock. Otherwise, the temperature of the test piece would have varied with the movement of the scale, which must take place as the result of expansion

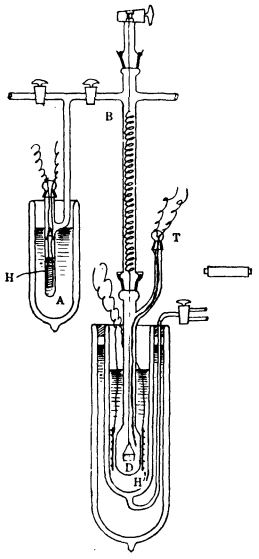


Fig. 1.

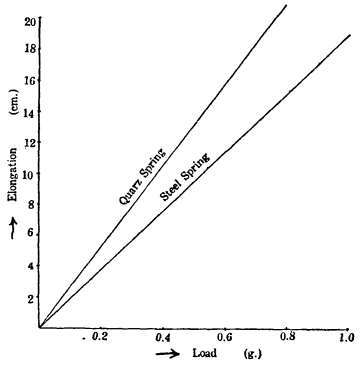


Fig. 2.

and contraction of the spring due to variation of the weight of the test piece during the experiment. The quartz thread was covered with platinum film for fear of its being destroyed by fluorine. A steel spring (0.2 mm.) was also used. The weights were examined before and after each experiment. An example of the results of experiments is given in Fig. 2.

(2) *Adsorption of oxygen gas.* The adsorption of oxygen gas was determined at −160°, −100°, −40°C. and at the pressures of 600, 400, 350, and 200 mm. As for the adsorbent, cocoanut-charcoal was baked at 700°C., activated with oxygen, and made vacuous while it was being baked.

The adsorption for 1 g. of charcoal as expressed in c.c. at N.T.P. was shown in Table 1. This result, together with the adsorption of fluorine, is illustrated in Fig. 4.

(3) *Adsorption of fluorine gas.* Similar experiments were made with fluorine. The progress of adsorption with the lapse of time is given in Fig. 3. The time required for saturation was about 3 hours.

Table 1.

Temp. (°C.) / Press. (mm.)	−160	−100	−40	0
760	136	50	32	10
600	123	44	26	—
400	104	30	20	—
200	80	18	—	—

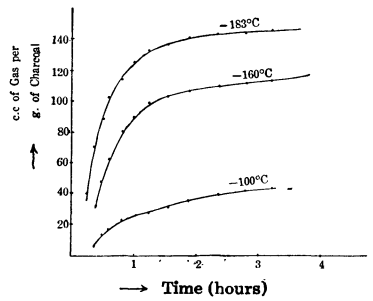


Fig. 3.

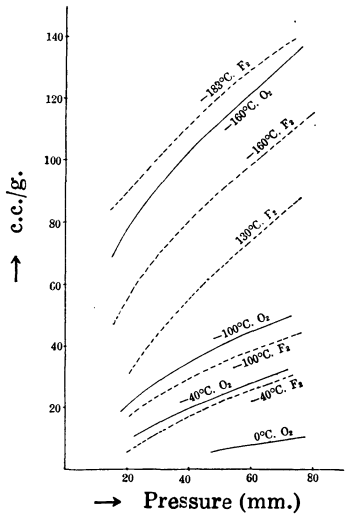


Fig. 4.

The amounts of adsorption in the saturated state are given in Table 2. Fluorine gas was introduced slowly after the charcoal had attained the temperature of the cooling vessel lest it should act upon charcoal. Further, the spring balance was examined several times.

The author expected that fluorine would be adsorbed in a greater quantity than oxygen because of its chemical reactivity against charcoal at ordinary temperature, but the reverse was the case. Oxygen was adsorbed in a greater quantity than fluorine at every temperature. The difference of the amounts of adsorption between them became greater with the fall of temperature. After a mixture of 96% fluorine and 3.7%

Table 2.

Temp. (°C.) / Press. (mm.)	−183	−160	−100	−40	0
760	142	111	44	30	13
600	128	98	40	24	—
400	109	80	30	16	—
200	86	60	17	—	—

oxygen was adsorbed upon the charcoal at −180°C., the remaining gas contained 97% fluorine and 2.8% oxygen. After the same operation was repeated 5 times, the gas was refined up to 99.4% fluorine and 0.4% oxygen. Adsorption, therefore, may be used for refining fluorine.

II. Experiment on Rectification. A rectifier made of Pyrex glass and filled with glass beads was used for the experiment (Fig. 5). V_1 and V_2 are Dewar vessels, and the inside of V_1 forms the rectifying tower. A heating coil H is placed on the bottom, and a mixed liquid of fluorine and oxygen is vaporized in it. The still is 80 cm. long, and is filled with glass beads 5 mm. in diameter. The top of the still has a glass tube C inserted, and is made air-tight with plaster. Liquid air is poured into C from another Dewar vessel, V_3. The temperature of the liquid air in C is controlled by varying its composition and serves as a condenser. A part of the vapour rising in the still is condensed by this condenser, and

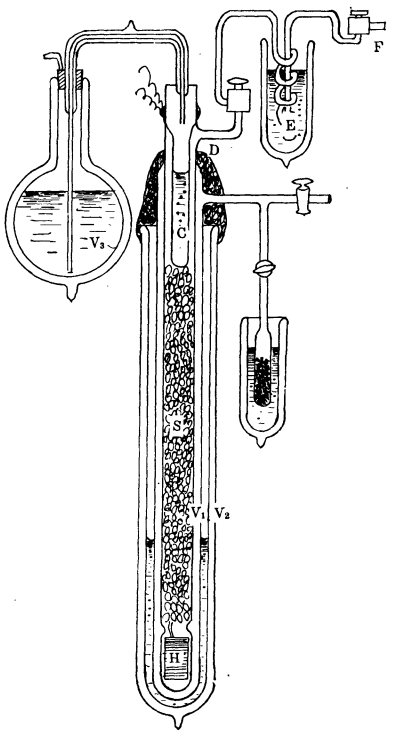


Fig. 5.

the vapour which has become fluorine-rich goes through D and is condensed in the trap E which has been cooled by liquid nitrogen. The substance which has been collected in E is taken out through F, and then subjected to the analysis of fluorine using mercury.

The vaporizer, still, and condenser are fitted with thermocouples for observing the temperature. Dewar vessel V_2, the gas-introducing tube attached on the outside of the Dewar vessel V_1, and the charcoal trap serve for cooling the rectifying tower and keeping it at a proper temperature. By using this refining apparatus, 99% pure fluorine could be obtained in E from an original liquid containing 95% fluorine.

In short, purification of fluorine must always be done at a low temperature, but the purest fluorine that can be obtained by the rectifying process is 99%, and therefore a percentage higher than this can be reached only by means of adsorption.

In conclusion, the author expresses his cordial thanks to Prof. Aoyama who advised him through this work. The author also expresses his hearty thanks to the Japan Society for the Promotion of Scientific Research for a grant.

Cryogenic Section,
Research Institute for Iron, Steel and other Metals,
Tohoku Imperial University.

Studies on Fluorine at Low Temperatures. V. Viscosity of Fluorine Gas at Low Temperatures.

By Eizo KANDA.

(Received August 12th, 1937.)

Determination of the size, mean free path, and mean velocity of fluorine molecule, though important in the study of the reaction of fluorine gas, has not yet been made. The present author is now making a study of the reaction velocity of fluorine gas. But prior to this, he determined the viscosity of fluorine, and deduced the above-mentioned constants from it.

I. **Method and Apparatus.** For the determination of viscosity, two methods are available: observation of flow in a capillary tube and that of oscillation-rotation of a disc. In the author's measurements with fluorine, (i) the apparatus had to be as compact as possible for ensuring a constant low temperature, and (ii) mercury could not be used because of the corrosive nature of the gas. For this reason, the author adopted the second method in which decrement of the oscillation-rotation of the disc was measured.

H. Vogel's apparatus[1] was remodelled in some measure. The author's apparatus is illustrated in Fig. 1, where A, B, and C are made of hard glass and they are connected by ground junctions S_1 and S_2. C has a glass cock S_3, around which a platinum filament is wound. The filament is moved upward and downward by turning the cock. B has a window W, and A is fitted with a branch tube D for introducing fluorine and with a device of the oscillating disc E. E, as separately illustrated in details, consists of a, b, and c, where b is the oscillatory rotating disc and is hung from S_3 with a nickel wire N and a platinum wire P, thus lying at equal distances from a and c. Further, a, b, and c are made of nickel-plated brass, and E is set in contact with c on the ground glass

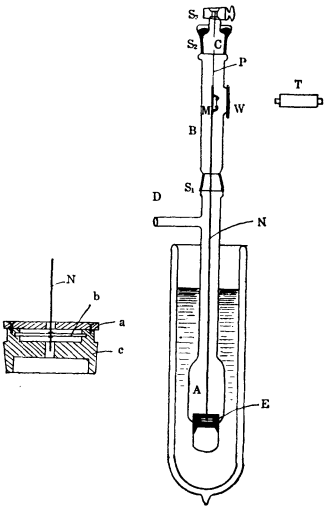


Fig. 1.

(1) Vogel, *Ann. Physik*, **43** (1914), 1235.

surfaces. In B, as illustrated, is a mirror M, whose oscillation-rotation is observed by means of a telescope through W at a distance of 2 metres. The dimensions of the important parts of E are as follows: diameter of the oscillating disc 30 mm., thickness 1.8 mm., weight 10.8 g., weight of the suspended parts 13.1 g., distance of surfaces between a and b or b and c 1.2 mm., and period of oscillation about 10 sec.

The device for winding up the platinum wire lowers the disc when the experiment has been finished or puts the disc in a proper position between a and c when the experiment is about to be made. On being slightly revolved, S_2 gives a moment of revolution to the disc.

Apparatus for maintaining a low temperature and for measuring the temperature are represented in a simple way by Dewar vessels. In practice, however, a thermostat was used, which had been often used in the author's experiments at low temperatures. The temperature was determined by means of a thermocouple made of copper and constantan.

II. **Determination of the Viscosity.** From the ratio of damping of the oscillation of the revolving disc, the viscosity can be determined by the following equation:

$$\eta = \frac{\lambda - K}{\tau c} \qquad (1),$$

where η is viscosity, τ period of oscillation, λ logarithmic decrement of oscillation, K a part of λ, that is, logarithmic decrement due to friction of the parts other than the disc, and c a constant peculiar to the apparatus.

λ and τ in the foregoing equation are obtained by observation using the mirror, scale, and stop-watch. It will be seen that c can be eliminated by the method described below. K is determined by the following somewhat complicated process.

K consists of (i) decrement due to the torsion of the platinum wire, K_1, and (ii) decrement due to friction between the gas and the mirror and other parts, K_2. Namely, $K=K_1+K_2$. K_1 depends upon the tension of the platinum wire and K_2 upon the kind and pressure of gas. In the case of vacuum, $K_2=0$.

When the material and weight of the disc are varied, with its geometrical dimensions being kept unvaried, $K'=K_1'+K_2$.

Since the period of the oscillation, τ, is independent of the temperature nor the kind of gas, but depends upon the apparatus alone, we may put $c\tau=C$.

As, in the case of vacuum, the total decrement λ which is obtained by observation is K_1, K_1 is a magnitude which can be determined by

observation. In the case of the author's experiment, $K_1=0.00031$, and $K_1'=0.00034$.

In the case of air, if the viscosity at 0°C. and T are represented by η_0 and η_T respectively, we shall have, from equation (1),

$$C\eta_0 = \lambda-(K_1+K_2) \quad (2), \qquad C'\eta_0 = \lambda'-(K_1'+K_2) \quad (3),$$
$$\eta_0(C-C') = (\lambda-K_1)-(\lambda'-K_1') \quad (4).$$

Similarly,

$$C\eta_T = \lambda_T-(K_1+K_2) \quad (5), \qquad C'\eta_T = \lambda_T'-(K_1'+K_2) \quad (6),$$
$$\eta_T(C-C') = (\lambda_T-K_1)-(\lambda_T'-K_1') \quad (7).$$

From (4) and (7)

$$\frac{\eta_0}{\eta_T} = \frac{(\lambda-K_1)-(\lambda'-K_1')}{(\lambda_T-K_1)-(\lambda_T'-K_1')} \qquad (8).$$

In equation (7), K_2 is eliminated, and the terms on the right side are magnitudes each of which can be determined by observation.

If η_0 is given, η_T will be obtained from the foregoing equation.

From (2) and (5), we have

$$\frac{\eta_0}{\eta_T} = \frac{\lambda-(K_1+K_2)}{\lambda_T-(K_1+K_2)} \qquad (9).$$

From this equation, we get

$$K_2 = \frac{\eta_0(\lambda_T-K_1)-\eta_T(\lambda-K_1)}{\eta_0-\eta_T} \qquad (10).$$

Thus K_2 is finally determined. K_2 is proportional to the square root of the viscosity of gas, that is,

$$K_2 \propto \sqrt{\frac{\eta}{\eta_0}} \qquad (11).$$

With the author's apparatus, the decrement obtained in vacuum was $K_1=0.00031$. As to air, K_2 obtained from equation (10) was $K_2=0.00010$. Hence,

$$K = K_1+K_2 = \left(31+10\sqrt{\frac{\eta}{\eta_0}}\right)\times 10^{-5}.$$

If we use λ_0 and K_0 for the logarithmic decrement of air at 0°C., and λ and K for any other gas, with a given apparatus at a given temperature, we shall have

$$\eta = \eta_0 \frac{\lambda - K}{\lambda_0 - K_0} \tag{12}$$

Thus, if the viscosity of air at 0°C. is given, η of any other gas can be deduced from it.

Further, in equation (11), the ratio of λ can stand for the ratio of viscosity. Thus, $K_2 \propto \sqrt{\frac{\lambda}{\lambda_0}}$.

III. **Determination of the Logarithmic Decrement.** Let the reading of a certain leftward movement of the mirror in the course of oscillatory rotation be represented by a and the succeeding rightward movement by b, then $a/b=n$, $\lambda=\log n$.

In practice, the mirror is vibrated several times, and its deflection is observed. The following relation exists:

$$\frac{a_\nu + b_{\nu+1}}{a_{\nu+15} + b_{\nu+16}} = n^{30}, \quad \lambda = \log n = \frac{1}{30} \log \frac{a_\nu + b_{\nu+1}}{a_{\nu+15} + b_{\nu+16}}.$$

IV. **Results of Measurement.** (1) *Air.* The observed values of decrement of oscillation are given in Table 1.

Table 1.

$a_\nu + b_{\nu+1}$	$\log (a_\nu + b_{\nu+1})$	30λ
53.79	1.73070	
43.54	1.63889	
35.49	1.55011	
28.83	1.45984	
23.40	1.36920	
19.03	1.27944	0.45126
15.44	1.18893	0.44998
12.55	1.09864	0.45147
		Average 0.45090

$\lambda_0=1/30$ (0.45090) $=0.015030$.

Further, $\tau=11.20$ sec., $\lambda_0-K_0=0.015030-0.00041=0.014620$.

(2) *Hydrogen.* To check the above-mentioned method and apparatus, determination was made with hydrogen gas at various low tem-

peratures. The hydrogen was obtained by electrolysis of water and refined by means of palladium catalyser. The results are given in Table 2.

Table 2.

t	T	p	λ	K	$\eta\times10^7$
0	273.2	764	0.007639	0.00038	856
−102.8	170.5	766	0.005595	,,	615
−181.9	91.3	758	0.003789	,,	402
−194.7	78.5	759	0.003527	,,	371

$$K = K_1 + K_0\sqrt{\frac{\lambda_0'}{\lambda_0}} = 0.00031 + 10\sqrt{\frac{0.007639}{0.01503}} = 0.00038$$

The value of η at 0°C. obtained by the present author is compared with those obtained by other authors in Table 3. The present author's value, though a little too large, may be considered good. (The author adopted $\eta_0=1724\times10^{-7}$ for air.)

Table 3.

$\eta\times10^7$	Authors
840	Graham and Meyer
870	Paluj
841	Markowski
850	Volker
849	Vogel
856	Kanda

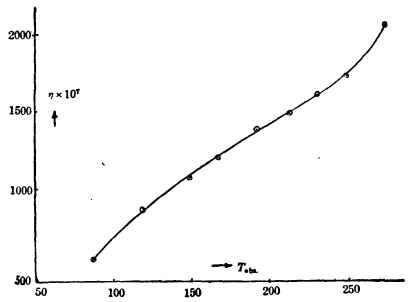


Fig. 2.

(3) *Fluorine.* The results are given in Table 4 and illustrated in Fig. 2.

$$\tau = 11.20\ \text{sec.},\quad \eta_0\,(\text{air}) = 1724\times10^{-7}.$$

$$K = 0.00031 + 10\sqrt{\frac{0.01816}{0.01503}} = .0.00042$$

Table 4.

T	p	λ	K	$\eta\times10^{-7}$
273.2	763	0.01816	0.00042	2093
248.9	,,	0.01505	,,	1727
229.6	,,	0.01407	,,	1611
213.1	765	0.01221	,,	1492
192.3	,,	0.01210	,,	1379
167.9	,,	0.01059	,,	1201
148.8	758	0.00957	,,	1080
118.9	,,	0.00783	,,	875
86.8	,,	0.00512	,,	555

V. Determination of the Diameter of Fluorine Molecule, etc. From the foregoing value of the viscosity, we get Sutherland's constant of fluorine, $C=129$.

As for the diameter of the molecule, we have $d=3.02$Å from

$$d^2 = 4.56\times10^{-20}\sqrt{M}\,/\,\eta_0\left(1+\frac{C}{273.2}\right).$$

Magat[2] obtained $b=3.4$Å.

The author got the mean free path

$$L = 9.12\times10^{-6}\text{cm.} \quad \text{from } L=\frac{1}{N\pi\sqrt{2}}\frac{1}{d^2}.$$

In conclusion, the author wishes to express his cordial thanks to Prof. Aoyama who gave him direction and kind guidance throughout this work. The author expresses his heartful thanks to the Japan Society for the Promotion of Scientific Research for a grant.

Cryogenic Section,
Research Institute for Iron, Steel and Other Metals,
Tohoku Imperial University.

(2) Magat, *Z. physik. Chem.*, B, **16** (1932), 1.

Studies on Fluorine at Low Temperatures. VI. Surface Tension of Liquid Fluorine.

By Eizo KANDA.

(Received August 12th, 1937.)

Surface tension, as well as dielectric constant, is a characteristic of a liquid and its value is necessary in the determination of the state of molecule of the liquid. As to the surface tension of liquid fluorine, Moissan[1] reported that "the rise in a capillary tube of fluorine, oxygen, alcohol, and water was 3.5, 5.0, 14, and 22 respectively". As a matter of fact, however, the surface tension of oxygen is about 13 dyne/cm. at its boiling point and neighbourhood and that of water is about 71 dyne/cm. at the ordinary temperature. Thus, Moissan's report, like his note on the melting point of fluorine, is very ambiguous. He gave no numerical value except those mentioned above.

The value of vapour pressure of oxygen shows that oxygen is quite a normal liquid. Further, the molecular weight, molecular volume, boiling point, and critical point of fluorine are very close to those of oxygen, and accordingly it may, like oxygen, be conceived to be a normal liquid. In fact, the vapour pressure of liquid fluorine shows that this element is a normal liquid governed by Hildebrand's rule. In view of this fact, the author thought it necessary to obtain an exact value of its surface tension.

I. Method and Apparatus of the Experiment. The author adopted the method in which the rise in a capillary tube is observed, and consulted the method of Onnes and Kuypers[2] for the determination of the surface tension of liquid hydrogen. The apparatus used is illustrated in Fig. 1, where B_3 is a trap containing the test liquid and a capillary tube K for measuring the capillarity. In B_3 are projections b supporting the capillary tube. The capillary rise was observed by means of a comparator having an accuracy up to 1/100 mm. At the same time the vapour pressure of the liquid was measured by a quartz pressure gauge.

The temperature at which the surface tension was determined ranged from the boiling point to the melting point of fluorine. In the experiment liquid hydrogen was not used, because the phenomenon inside the Dewar

(1) Moissan, *Compt. rend.*, **125** (1897), 502.
(2) Onnes and Kuypers, *Commun. Phys. Lab. Univ. Leiden*, **No. 142** (1914).

vessel had to be distinctly observed. The Dewar vessel A_3 contained liquid oxygen and was made air-tight with a cap C fixed to the upper. D is fitted with a pump and the liquid oxygen was vigorously vaporized. In this way, the temperature up to the triple point of oxygen (85°K) was obtained.

B_1 and B_2 are traps for refining the fluorine by fractional distillation. Liquid nitrogen was used in A_1 and A_2.

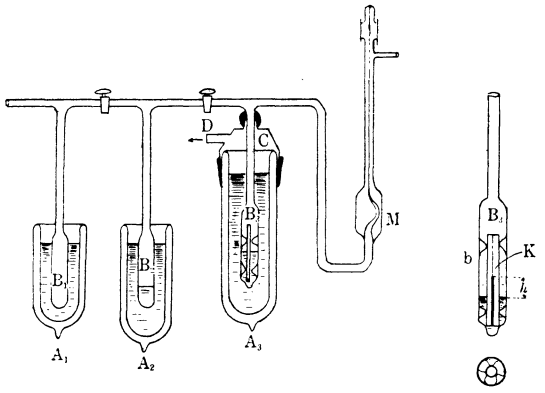


Fig. 1.

Capillary tube. As liquid fluorine is of smaller surface tension than ordinary liquids, capillary tubes having a very small inside diameter had to be used for obtaining a satisfactory rise of the liquid. Because of a small amount of rise of the liquid, however, the inside diameter of the tubes had to be uniform only for a small length. Tubes with cross-sections the most approximate to a perfect circle and with diameters about 0.16 mm. were selected from among more than 50 glass tubes by microscopic examination.

As the capillary tube would have been attacked by fluorine at ordinary temperature, fluorine was to be introduced into the trap and condensed therein after it had been cooled down to the temperature of the liquid nitrogen. The capillary tube was renewed for each series of observations.

Determination of the surface tension. The surface tension γ (dyne/cm.) is expressed by the following formula, on the assumption that the cross-section of the tube is a perfect circle and that the angle of contact is zero:

$$\gamma = \frac{1}{2} rg(\rho_l - \rho_g)h \ ,$$

where r is inside radius of the tube, g acceleration due to gravity (980), ρ_l density of the liquid (g/c.c.), ρ_g density of the coexisting vapour, and h the capillary rise (cm.). ρ_l was separately determined at various temperatures. ρ_g was calculated by using the values of vapour pressure and the temperature for each experiment.

II. Results of the Measurements with Liquid Oxygen. (Table 1).

Table 1. $r = 0.00805$ cm.

T	p(mm.)	ρ_l	ρ_g	h(cm.)	γ(dyne/cm.)
58.10	3.3	1.291	—	4.166	21.25
62.49	10.0	1.275	—	4.032	20.32
71.10	57.4	1.235	0.41×10^{-3}	3.732	18.21
76.69	142.2	1.218	0.95 ,,	3.468	16.68
81.40	274.6	1.182	1.73 ,,	3.237	15.54
89.50	711.7	1.150	4.14 ,,	2.996	13.55

These values, as compared with Baly and Donnan's[3] three values, are given in Fig. 2.

Eötvös's constant calculated from the above data was $K = 1.92$ ($T_k = 155°$), and this fact shows that oxygen is a normal liquid.

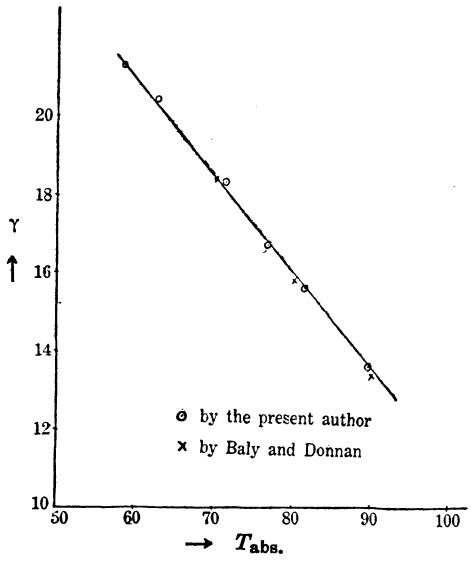


Fig. 2.

III. Surface Tension of Fluorine.

Examples of measurements are given in Table 2 and values obtained with another capillary tube in Table 3.

The values of γ are graphically shown in Fig. 3. $K = 1.78$ was obtained for $\gamma v^{2/3} = K(T_k - T)$, a fact which practically conforms with Eötvös's law. Thus, liquid fluorine may also be regarded as a normal

(3) Baly and Donnan, *J. Chem. Soc.*, **81** (1902), 907.

Table 2. $r = 0.00805$ cm.

T	p	ρ_l	ρ_g	h(cm.)	γ
57.10	—	1.205	—	3.068	14.61
59.95	—	1.195	—	3.002	14.16
64.20	28.22	1.181	0.27×10^{-3}	2.884	31.46
72.11	129.90	1.155	1.10 ,,	2.654	12.10
76.30	247.50	1.140	2.02 ,,	2.536	11.40
84.91	733.50	1.112	5.76 ,,	2.254	9.85

Table 3.

T	γ
61.41	13.85
65.30	13.17
71.00	12.20
81.50	10.41

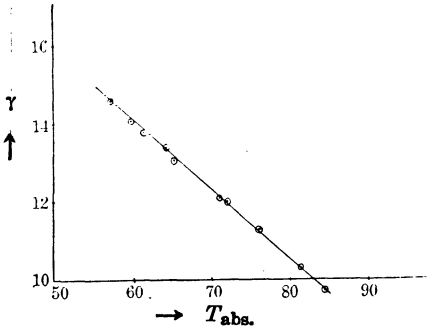


Fig. 3.

liquid. Further, the surface tension of fluorine is lower than that of liquid oxygen, but not so much as Moissan reported.

In conclusion, the author wishes to express his cordial thanks to Prof. Aoyama who gave him the kind guidance through this work. He also expresses his hearty thanks to the Japan Society for the Promotion of Scientific Research for a grant.

Cryogenic Section,
Research Institute for Iron, Steel and Other Metals,
Tohoku Imperial University.

Studies on Fluorine at Low Temperatures. VII. Determination of Dielectric Constants of Condensed Gases.

By Eizo KANDA.

(Received August 12th, 1937.)

The author set about determining the dielectric constants of condensed gases as a means of studying the state of their molecules. This paper deals with the determination of the dielectric constants of liquid oxygen, fluorine, chlorine, and hydrogen chloride.

I. Method and Apparatus. (1) *Electric circuit for determining the dielectric constant.* The electric capacity was determined by the "beat method". As this method is now extensively used and is well known, its essential points alone are given in the circuit diagram of Fig. 1. In Fig. 1, I is a variable frequency oscillator circuit comprising a cell C_x to be subjected to measurement and a variable condenser of high precision C_v (capacity, 1500 $\mu\mu$F) which is arranged parallel with C_x. III is a fixed frequency (10^6C.) oscillator circuit comprising a quartz-oscillator. The beat between I and III (1000 cycles) is amplified and detected by means of II which is loosely coupled with I and III. The sound is received by a loud speaker. The whole apparatus is kept in a copper case that it may be protected from external disturbances.

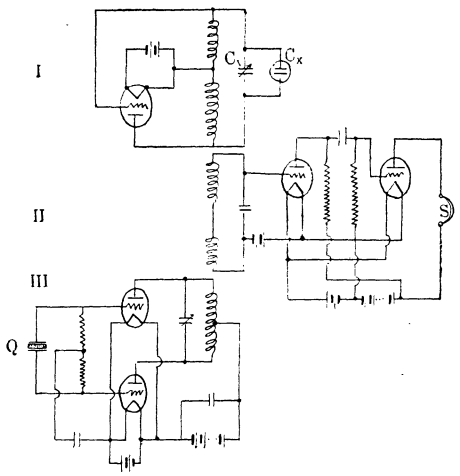


Fig. 1.

(2) *Cell.* (See Fig. 2, C) The cell consists of brass cylinders 90 mm. long and 1 mm. thick which are concentrically put one in another between the walls of a double-walled glass cylinder 39 mm. in outside diameter and 23 mm. in inside diameter. Some difficulties were encountered in working the glass so as to make it stand the low temperature. With such a device the temperature of the sample therein could be made uniform and a small amount of the sample was enough for the purpose.

Further, the cell-electrodes were gold-plated for fear of any great error being caused by a dielectric film which might have been formed on their surfaces by the action of fluorine or chlorine. Care was taken not to use them continuously for a long time. The cell had four long glass tubes for introducing lead wires and for taking in and out the sample. A quartz film pressure gauge was attached to one of the tubes. A platinum resistance thermometer R occupies the space in the centre of the cell. The capacity of the cell in the vacuous state was about 70 $\mu\mu$F.

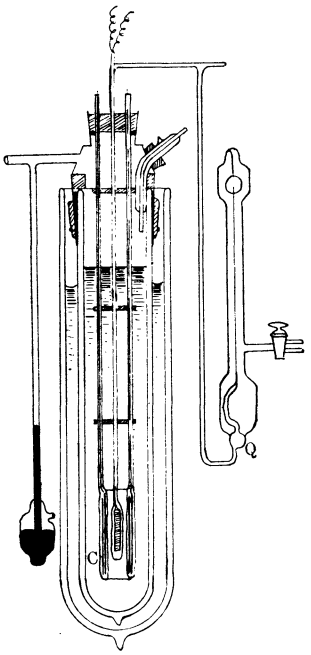


Fig. 2.

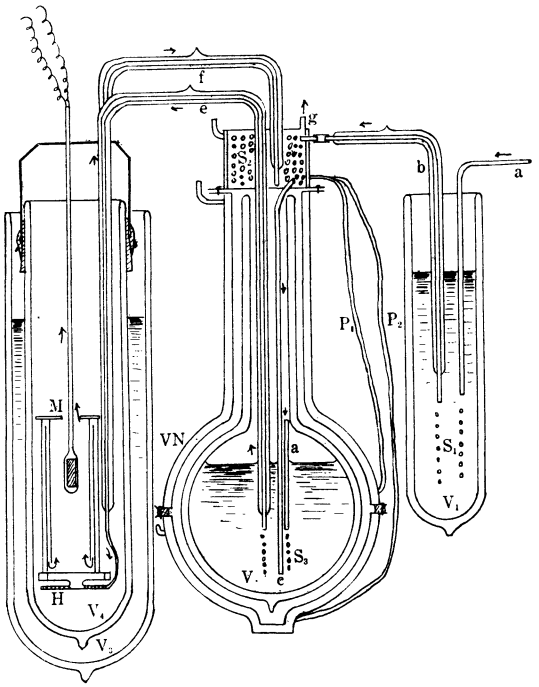


Fig. 3.

(3) *Cooling device.* Liquid nitrogen or liquid hydrogen was used for condensing the sample and for keeping the cell at a constant temperature. For keeping a constant low temperature, different devices were used according to the range of temperature of the measurement. Thus five kinds were used, which were (a) for 0° to −130°C., a device for automatically keeping a constant temperature, with pentane as the vessel liquid and indirectly cooled by liquid nitrogen, (b) for −130° to −183°C., a cryostat with vapour of liquid nitrogen as the cooling medium, (c) for −183° to −195°C., a cryostat using liquid oxygen and liquid nitrogen,

(d) for −195° to −250°C., a cryostat with vapour of liquid hydrogen as the cooling medium, (e) for −252° to −258°C., a cryostat using liquid hydrogen and solid hydrogen.

Of these, (a) and (c) have often been used in the author's experiments, and (e) is one which was used in the measurement of the specific heat of solid fluorine[1] and is outlined in Fig. 2. (b) and (d) were used for the first time.

Cryostat using hydrogen vapour. The apparatus illustrated in Fig. 3 was devised by consulting Leiden's[2]. V_1 is a Dewar vessel for liquid nitrogen, V_2 a Dewar vessel for storing and vaporizing liquid hydrogen, V_4 a cryostat containing hydrogen vapour, and V_3 a Dewar vessel containing liquid nitrogen and intended for reducing thermal conduction to V_4. Outside V_2 there is a double-walled jar V_N made of copper plate. Through the pipes P_1 and P_2 liquid nitrogen and its vapour are introduced between the walls of the jar for keeping the wall of V_2 at a low temperature. It is difficult to store liquid hydrogen for a long time on account of its very low temperature and its heat of vaporization per unit volume being very small as compared with that of liquid air (about 1/7). When V_2 was not protected by V_N, 4 litres of liquid hydrogen was vaporized in about 12 hours. When it was surrounded by V_N and kept at a low temperature with liquid nitrogen, it remained for about 18 hours.

The hydrogen gas enters at a and is cooled by the liquid nitrogen and liquid hydrogen vapour as it goes through S_1, b and S_2, and gets out in bubbles by C at the bottom of V_2. At the same time the liquid hydrogen in V_2 is vaporized. The vapour, starting from d, passes through S_3 and e and enters the spiral H near the bottom of V_4. There is a heating coil outside H, by which the temperature of the hydrogen vapour in H is adjusted. Thus the vapour goes up and down through the spacings in the triple wall of the copper cylinder over H, and finally enters the cylinder. This cylinder, intended for ensuring a uniform temperature, has a resistance thermometer. By controlling the flow of hydrogen gas and the heating of H, the temperature is adjusted. The hydrogen gas goes out by an opening in the upper part of M, and passes through the double-walled pipe f, and cooling the group of spirals S_2, gets out by g.

With this apparatus, any temperature between −195°C. and −250°C. could be kept constant with a variation of not more than 0.05°.

(4) *Determination of the density of condensed liquids.* For obtaining the molecular polarization of a liquid by measuring its dielectric con-

(1) See the eighth paper of this series.

(2) Onnes and Crommelin, *Commun. Phys. Lab. Univ. Leiden*, No. **154C** (1921).

stant the density of the liquid must be determined. For this purpose an apparatus as shown in Fig. 4 was used. The whole apparatus was made of thin Pyrex glass. The volume of the capillary tube was accurately determined in advance. The test liquid was condensed in the capillary tube. The neck in the upper part of the apparatus was sealed by fusion. The temperature of the capillary tube was varied and the height of the liquid was measured by means of a comparator or cathetometer. Then the whole apparatus was brought to an ordinary temperature and the liquid was vaporized in the spherical part. Thus the weight of the sample was determined.

Table 1.

$T_{abs.}$	ρ (specific weight)	ε	P_M
87.62	1.158	1.487	3.856
78.20	1.202	1.511	3.872
68.00	1.250	1.538	3.891
59.51	1.290	1.556	3.882

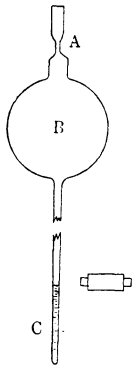


Fig. 4.

II. **Results of the Measurements.** (1) *Liquid oxygen.* See Table 1. The error of the dielectric constant was in a range of ±0.1%.

The molecular polarization of oxygen could be regarded as almost independent of the temperature. Thus, m (molecular moment of liquid oxygen) = 0 could naturally be expected.

(2) *Liquid fluorine.* See Table 2. Table 2 also shows that there was no regular variation in P_M. The irregular variation was considered due to the error of measurement. Therefore the molecular moment is zero.

(3) *Liquid chlorine.* Commercial liquid chlorine, after subjected to five fractional distillations, was used (Table 3).

According to Lewis,[3] liquid chlorine also has a very small moment, which, however, could not be ascertained from the above P_M. The author

(3) Lewis, "Valence and the Structure of Atoms and Molecules"; C. Smyth, *J. Am. Chem. Soc.*, **46** (1924), 2151.

Table 2.

$T_{abs.}$	ρ	ε	P_M
57.40	1.204	1.567	5.012
60.51	1.195	1.561	5.008
64.41	1.185	1.553	4.989
68.38	1.154	1.546	5.069
73.00	1.141	1.536	5.046
75.01	1.136	1.533	5.100
79.40	1.124	1.524	5.024
83.21	1.113	1.517	5.016

Table 3.

$T_{abs.}$	ρ	ε	P_M
208.00	1.643	2.147	11.94
210.51	1.636	2.139	11.93
215.60	1.621	2.123	11.92
220.61	1.605	2.104	11.90
227.90	1.580	2.088	11.95
235.50	1.555	2.059	11.90
239.96	1.530	2.048	12.00

intends to make further determination of the dielectric constant with a dilute solution.

(4) *Hydrogen chloride.* Hydrogen chloride was prepared by dropping concentrated sulphuric acid on sodium chloride and warming of the mixture. The gas thus produced was washed with sulphuric acid. After dried with phosphorus pentoxide, the gas was liquefied and refined by repeated fractional distillation. The liquid boiled at 168°K. and freezed at 159°K.

Table 4.

$T_{abs.}$	ρ	ε	P_M
160.01	1.267	11.80	22.55
163.25	1.258	11.42	22 52
165.60	1.251	11.16	22.52
168.11	1.244	10.85	22.49
170.25	1.239	10.60	22.44
173.50	1.230	10.21	22.38
176.75	1.221	9.84	22.32
178.00	1.218	9.70	22.28
181 15	1.211	9.31	21.99
182.76	1.206	9.12	22.15

Table 5.

$T_{abs.}$	ε
101.50	11.01
106.82	11.21
112.50	11.42
121.75	11.76
130.05	12.23
136.90	12.68
140.35	13.06
149.21	13.12
153.50	13.06
99	Transition point
98.5	3.10

P_M (Table 4) clearly showed a tendency to decrease with the rise of temperature. It may be said to have a great moment. Measurements with liquid hydrogen chloride at three points between 158°K. and 165°K.

were made by Cone[4] and by Smyth,[5] but, as the ranges of temperature of their measurements were very small and the number of points of measurements also very small, no such tendency was seen in their experiments.

Measurement was also carried out with solid hydrogen chloride, Table 5. ε had at first a tendency to increase with the fall of temperature as was the case with liquid hydrogen chloride. However, this was the reverse of the tendency of normal solids. The fact shows that hydrogen chloride does not immediately form perfect crystals even when it is brought to a temperature below the freezing point, but that it ceases innermolecular rotation and makes perfect crystals only when it reaches the next transition point (99°K.).

P_M was not calculated because the density of the solid was not clear.

It will be interesting to make a study of the change in the molecular heat, especially in the electric field with reference to the result of the study on the dielectric constant, of hydrogen chloride making "Rotationsumwandlung" and of other hydrogen halides, ammonium halides, and others making similar transition.[6]

The results of measurements with O_2, F_2, Cl_2, and HCl are illustrated in Figs. 5 to 8.

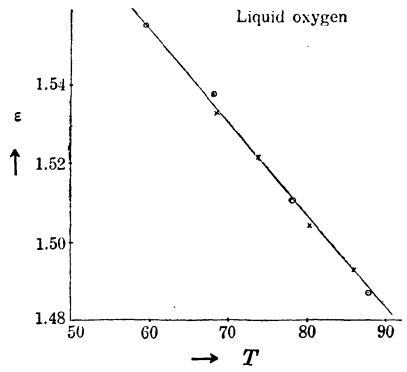


Fig. 5.

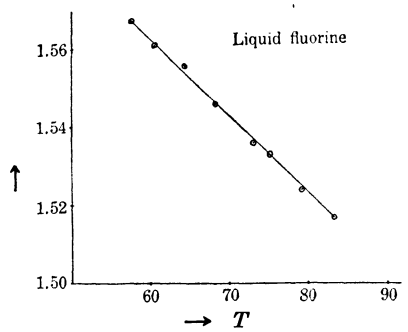


Fig. 6.

⊙ Kanda × Werner and Onnes[7]

(4) Cone, *J. Am. Chem. Soc.*, **53** (1931), 1278.

(5) Smyth, *J. Am. Chem. Soc.*, **55** (1933), 1830.

(6) Pauling, *Phys. Rev.*, **36** (1930), 480; Fowler, *Proc. Roy. Soc.* (London), A, **149** (1935), 1.

(7) Werner and Onnes, *Commun. Phys. Lab. Univ. Leiden*, **No. 178C** (1926).

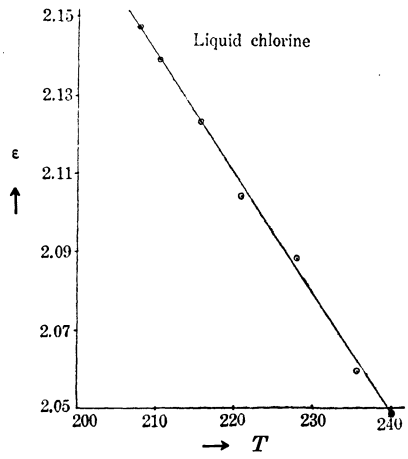


Fig. 7.

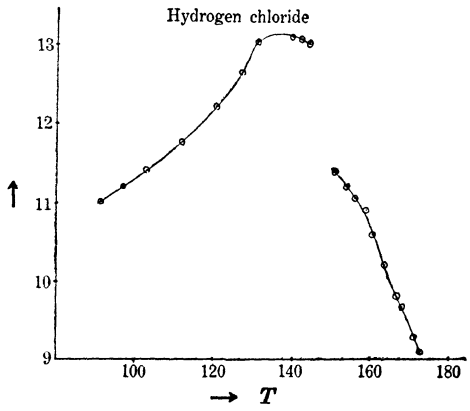


Fig. 8.

The author expresses his cordial thanks to Prof. Aoyama under whose guidance the present work was carried out and thanks are due to Prof. Mizushima of the Tokyo Imperial University, who kindly advised him through the investigation. He is also very much indebted to the Japan Society for the Promotion of Scientific Research for a grant.

Cryogenic Section,
Research Institute for Iron, Steel and Other Metals,
Tohoku Imperial University.

Studies on the Aqueous Solutions of Some Chromic Salts. I. Spectrochemical Studies of the Chloro-aquo Compounds.

By Hideo SUEDA.

(Received October 12th, 1937.)

Studies on the chromic salts were active until about 1910, but were not continued after the perfect explanation of the three isomers of chromic chloride hydrate, then discovered by A. Recoura[1] and N. Bjerrum[2], was given by Werner's co-ordination theory. For the purpose of investigating the constitution of these salts in various hydrogen ion concentrations, the author has quantitatively measured their absorption spectra in the ultra-violet region by changing the *p*H values. Such researches have not yet been systematically performed[3].

The measurements of the absorption spectra and hydrogen ion concentration are similar to those which were applied to the author's previous studies on the cobalt[4] and chromium[5] ammine-complex salts.

The absorption spectra were determined as soon as the chromic salts were dissolved, because the structural changes of these complex salts occurred after their solutions had been left standing for a long time. The thickness of the layer and the concentration of solutions were suitably chosen in the ranges of 10–50 mm. and 1/50–1/100 N (for the chromium atom), respectively. As the Lambert-Beer law holds under these conditions, log ε[6] was adopted for the unit of the absorption intensity, and the details of the descriptions about the conditions of measurement were neglected. The following chromic compounds have been studied in the present work: violet chloride $[Cr(H_2O)_6]Cl_3$[7], violet sulphate $Cr_2(SO_4)_3 \cdot 17H_2O$[8], chrome alum $KCr(SO_4)_2 \cdot 12H_2O$[9], Bjerrum's salt

(1) *Compt. rend.*, **102** (1886), 548; *Ann. chim. phys.*, **10** (1887), 34.

(2) *Z. physik. Chem.*, **59** (1907), 581.

(3) A. Byk and H. Jaffe did not obtain the absorption curves, *Z. physik. Chem.*, **68** (1909), 323.

(4) This Bulletin, **10** (1935), 50, 85; **12** (1937), 71.

(5) This Bulletin, **10** (1935), 267.

(6) ε is defined from the formula: $\log I_0/I = \varepsilon cd$, where I_0 and I represent respectively the light intensity given before and after its transmission; c, concentration of solution in normal; d, layer thickness of solution in cm.

(7) N. Bjerrum, *Z. physik. Chem.*, **59** (1907), 339.

(8) R. F. Weinland and R. Krebs, *Z. anorg. allgem. Chem.*, **49** (1906), 165.

(9) Recrystallised two times below 35°C. Merck's extra pure chrome alum.

$[Cr(H_2O)_5Cl]Cl_2 \cdot H_2O$[2], $[Cr(H_2O)_5Cl]SO_4$[10], green chromic chloride $[Cr(H_2O)_4Cl_2]Cl \cdot 2H_2O$[7]. They were prepared by referring the papers indicated in the foot notes.

I. The absorption curves and the hydrogen ion concentration of the solutions. (A) $[Cr(H_2O)_6]Cl_3$; $Cr_2(SO_4)_3 \cdot 17H_2O$; $KCr(SO_4)_2 \cdot 12H_2O$. The experiments made for the three above-mentioned salts are summarised in Table 1. Curve numbers given in the table correspond to those noted in Fig. 1.

Table 1.

	Compound	Conc.	Solvent	*p*H	Curve no.
1	$[Cr(H_2O)_6]Cl_3$	1/50 N	1/100 N HCl	1.8	I
2	$Cr_2(SO_4)_3 \cdot 17H_2O$	,,	,,	1.9	,,
3	$KCr(SO_4)_2 \cdot 12H_2O$	,,	,,	1.8	,,
4	$[Cr(H_2O)_6]Cl_3$	,,	H_2O	2.7	,,
5	$Cr_2(SO_4)_3 \cdot 17H_2O$	,,	,,	2.9	,,
6	$KCr(SO_4)_2 \cdot 12H_2O$	,,	,,	,,	,,
7	$[Cr(H_2O)_6]Cl_3$	,,	1/1000 N NaOH	3.1	,,
8	,,	,,	5/1000 N NaOH	3.6	II
9	$Cr_2(SO_4)_3 \cdot 17H_2O$	,,	8/1000 N NaOH	4.1	III
10	$KCr(SO_4)_2 \cdot 12H_2O$	,,	,,	4.0	,,
11	$Cr_2(SO_4)_3 \cdot 17H_2O$	,,	1/100 N NaOH	4.3	,,
12	$KCr(SO_4)_2 \cdot 12H_2O$	,,	,,	,,	,,
13	$[Cr(H_2O)_6]Cl_3$	1/100 N	,,	4.7	—
14	$KCr(SO_4)_2 \cdot 12H_2O$	,,	,,	,,	—

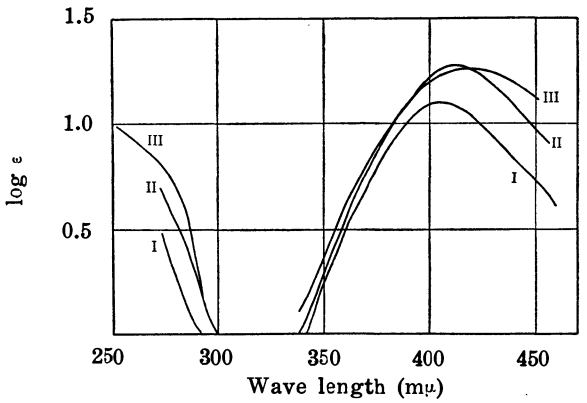


Fig. 1. The absorption spectra of $[Cr(H_2O)_6]^{+++}$

(10) R. F. Weinland and T. Schumann, *Ber.*, **40** (1907), 3091.

As the absorption spectra of the solutions 1–7 in Table 1 are almost coincident, they are shown by a curve (curve I, Fig. 1). All these solutions are bluish-violet, but they become greener with the addition of sodium hydroxide to the solution, and their absorption curves then approach curve III in Fig. 1, that is, their absorption curves shift to the longer wave length, increasing their absorption capacities.

In the solutions containing sodium hydroxide equivalent to the chromium atom (13 and 14 in Table 1), the precipitation of chromic hydroxide was recognized when ultra-violet light was projected. The precipitation began in the part where light was projected. But, it did not occur when the solution was protected from light, even under the same conditions. It can therefore be safely concluded that this reaction is accelerated by light.

As the absorption curves of these three salt solutions were almost identical[11] in the range of *p*H 1.8 and 3.1, these salts must have the same chromofore. A. Werner and A. Gubster[12] gave already formula $[Cr(H_2O)_6]Cl_3$ to the violet chromic chloride hydrate, and other researchers also confirmed their opinion[13]. This suggests that the violet chromic sulphate as well as the chrome alum should have the same complex ion with the above-mentioned violet chloride. A. Sénéchal[14] and W. R. Whitney[15] gave already formula $[Cr_2(H_2O)_{12}](SO_4)_3$ to the violet sulphate, but their confirmation for giving the formula to this salt seems to be weak. From the present results of the absorption spectra, the author wishes to give formulæ $[Cr(H_2O)_6]_2(SO_4)_3 \cdot 5H_2O$ and $K[Cr(H_2O)_6](SO_4)_2 \cdot 6H_2O$ to the violet chromic sulphate and the chrome alum respectively.

(B) $[Cr(H_2O)_5Cl]Cl_2 \cdot H_2O$; $[Cr(H_2O)_5Cl]SO_4$. For $[Cr(H_2O)_5Cl]Cl_2$ absorptions in three different *p*H were observed as indicated in Table 2. In this case, the absorption of the aqueous solution (curve II, Fig. 2) was not similar to that of the solution in hydrochloric acid (curve I, Fig. 2). The latter curve was, on the whole, shifted to a longer wave length than the former. On the contrary, the absorption curve of the solution with sodium hydroxide (curve III, Fig. 2) moved to the shorter

(11) The violet chloride and sulphate indicated identical curves also in the visible region, N. Bjerrum, *Z. anorg. allgem. Chem.*, **63** (1909), 140.

(12) *Ber.*, **34** (1901), 1579.

(13) P. Pascal, "Traité de Chimie Minérale," Vol. X, 1021 (1933).

(14) *Compt. rend.*, **156** (1913), 552.

(15) *Z. physik. Chem.*, **20** (1896), 40.

Table 2.

Compound	Conc.	Solvent	*p*H	Curve no.
$[Cr(H_2O)_5Cl]Cl_2$	1/70 N	1/100 N HCl	1.9	I
,,	1/58 N	H_2O	3.2	II
,,	1/72 N	1/100 N NaOH	4.3	III
,,	1/110 N	9/1000 N NaOH	4.7	—
$[Cr(H_2O)_5Cl]SO_4$	1/50 N	1/100 N HCl	2.0	IV
,,	,,	H_2O	2.9	,,
,,	,,	8/1000 N NaOH	4.1	V
,,	,,	1/100 N NaOH	4.2	,,

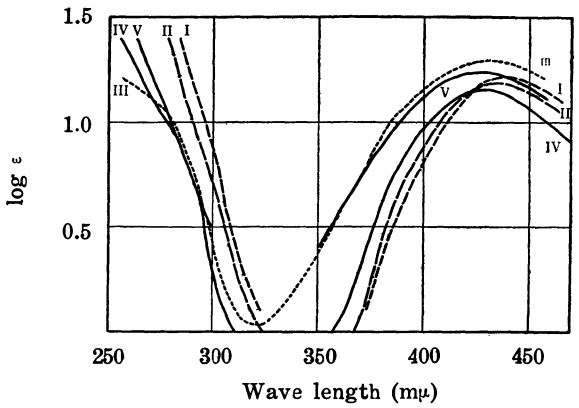


Fig. 2. The absorption spectra of $[Cr(H_2O)_5Cl]^{++}$

wave length[16]. A precipitate of chromic hydroxide was observed in the solution of *p*H 4.7, when it was exposed to light.

As $[Cr(H_2O)_5Cl]Cl_2$ is very hygroscopic and unstable, the complex ion $[Cr(H_2O)_5Cl]^{++}$ cannot be easily studied by its absorption spectra. Similar experiments were therefore repeated with the sulphate which is more stable than the chloride. The absorption curve given by the aqueous solution of the sulphate (curve IV, Fig. 2) was identical with that observed with the solution in hydrochloric acid. The solution of this salt with sodium hydroxide showed similar absorption curves (curve V, Fig. 2) when *p*H was 4.1 and 4.2.

(16) Except hydroxo-compounds, among the salts already studied by the author, this salt is the only one that shows different absorption spectra in neutral and in acidic solutions.

The wave length representing the absorption band of curve V, Fig. 2 almost coincides with curve IV, and the intensity observed in the former curve is a little stronger than that shown by the latter. But, the absorptions in the range of shorter wave length (near 300 mμ) were observed to be quite similar in these two curves. A few minutes after the end of the measurement, a precipitation of chromic hydroxide occurred in the solution of *p*H 4.2.

From the fact that the chloride and the sulphate show different absorptions in spite of the same complex ion, it can be safely assumed that either of these two salts is impure. As the chloride is unstable in solution as well as in the solid state, it can be naturally supposed to be impure. If the impurity is based on $[Cr(H_2O)_4Cl_2]Cl$ which is prepared by the transformation of $[Cr(H_2O)_5Cl]Cl_2$, the anormality in the absorption can be easily explained by assuming that the transformation of Bjerrum's salt into the green chloride is more rapid in hydrochloric acid than in the neutral aqueous solution.

(C) $[Cr(H_2O)_4Cl_2]Cl$. The results obtained with this compound are summarised in Table 3 and Fig. 3.

When the *p*H-value increased in the solution, the absorption was generally shifted to the shorter wave length, accompanying the increase of the absorption capacity in the absorption band.

As seen in (A), (B) and (C), the absorption curves shown by solutions of higher *p*H-values are similar with one another.

Table 3.

Conc.	Solvent	*p*H	Curve no.
1/50 N	1/100 N HCl	1.9	I
,,	H_2O	3.3	I
1/100 N	8/1000 N NaOH	4.3	II
,,	1/100 N NaOH	4.6	III

Table 4.

Compound	$\lambda_{max.}$ (mμ)	log ε
$[Cr(H_2O)_6]^{+++}$	405	1.10
$[Cr(H_2O)_5Cl]^{++}$	430	1.15
$[Cr(H_2O)_4Cl_2]^{+}$	443	1.24

Table 5.

The Absorption of $[Cr(H_2O)_4Cl_2]Cl$.

λ (mμ)	ε	
	(obs.)	(calc.)
400	6.8	6.3
410	10.0	11.1
420	13.2	15.9
430	15.8	19.2
440	17.4	20.1
450	16.6	17.9
460	15.1	15.3

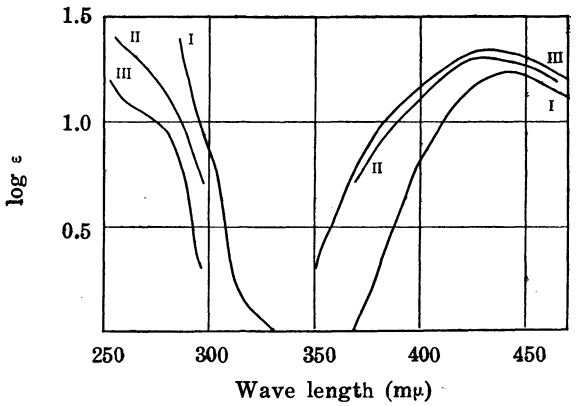


Fig. 3. The absorption spectra of $[Cr(H_2O)_4Cl_2]Cl$

II. Action of alkali on the aqueous solutions of aquo-chloro chromic salts. By the thorough investigations of the aqueous solution of violet chloride, N. Bjerrum[7] confirmed the existence of the following equilibrium, and the equilibrium constant has been already determined by many authors[17]:

$$[Cr(H_2O)_6]^{+++} \rightleftarrows [Cr(H_2O)_5OH]^{++} + H^+.$$

When sodium hydroxide is added to the aqueous solution of this salt, $[Cr(H_2O)_5OH]^{++}$ must be formed, and it is quite natural that the absorption given by its solution of high *p*H is more similar with that given by $[Cr(H_2O)_5OH]^{++}$.

As to the aqueous solution of $[Cr(H_2O)_4Cl_2]Cl$, the following hydrolysis was suggested by A. B. Lamb[18], who already measured its equilibrium constant[19].

$$[Cr(H_2O)_4Cl_2]^+ + 2H_2O \rightleftarrows [Cr(H_2O)_5OH]^{++} + H^+ + 2Cl^-.$$

For the aqueous solution of $[Cr(H_2O)_5Cl]^{++}$, the hydrolysis has not yet been reported. As the absorption given by a solution of higher *p*H-value of this salt becomes almost the same as that represented by the solutions of $[Cr(H_2O)_6]^{+++}$ and $[Cr(H_2O)_4Cl_2]^+$ with sodium hydroxide, the addition of alkali to the solution of $[Cr(H_2O)_5Cl]^{++}$ tends to form

(17) N. Bjerrum, *Z. physik. Chem.*, **59** (1907), 339; A. B. Lamb and G. R. Fonda, *J. Am. Chem. Soc.*, **43** (1921), 1154; H. G. Denham, *J. Chem. Soc.*, **93** (1908), 53; J. N. Brönsted and K. Volgvartz, *Z. physik. Chem.*, **134** (1928), 97.

(18) *J. Am. Chem. Soc.*, **28** (1906), 1710.

(19) A. B. Lamb and G. R. Fonda, *J. Am. Chem. Soc.*, **43** (1921), 1154.

$[Cr(H_2O)_5OH]^{++}$. Hereupon, the author has assumed the following equilibrium in the aqueous solution of $[Cr(H_2O)_5Cl]^{++}$ like $[Cr(H_2O)_6]^{+++}$ and $[Cr(H_2O)_4Cl_2]^{+}$.

$$[Cr(H_2O)_5Cl]^{++} + H_2O \rightleftarrows [Cr(H_2O)_5OH]^{++} + HCl.$$

III. Absorption of aquo-chloro compounds and configuration of $[Cr(H_2O)_4Cl_2]Cl$. It has already been reported[5] that the absorption curve near 250 mμ, given by the chloro-ammine chromic complex salts, is regularly shifted to a longer wave length, as often as a chlorine atom enters into a complex radical. The same fact was also observed with this chloro-aquo salt, that is, the wave lengths, where $[Cr(H_2O)_6]^{+++}$, $[Cr(H_2O)_5Cl]^{++}$, and $[Cr(H_2O)_4Cl_2]^{+}$ absorbed the light by the intensity of $\log\varepsilon = 0.5$, were 273 mμ, 296 mμ, and 307 mμ.

The wave lengths and extinction coefficients of the maximum absorptions of these three salts have a certain relation with the number of chlorine atoms in a complex radical, and as indicated in Table 4, they are shifted in a definite direction in proportion to the number of chlorine atoms.

From the point of view of Werner's co-ordination theory, there should be two isomers of $[Cr(H_2O)_4Cl_2]Cl$, i.e. cis and trans. But, it has not yet been determined whether the ordinary salt has cis- or trans-configuration. Applying to this salt the hypothesis[20], which the present author already proposed, and assuming this salt to have cis-form, he has calculated the absorption of $[Cr(H_2O)_4Cl_2]^{+}$ from absorption curves given by $[Cr(H_2O)_6]Cl_3$ and $[Cr(H_2O)_5Cl]SO_4$. The calculated values show a coincidence with the observed values to the extent indicated in Table 5. But, from this comparison of values only, the author cannot give a cis-configuration to this salt, because when this salt is assumed to be trans, a better coincidence might be obtained by calculation, which, however, has as yet been impossible.

Summary.

(1) The absorption spectra of six solutions of chromic chloride and sulphate hydrates were quantitatively measured in the ultra-violet region.

(2) Violet chromic sulphate and chrome alum should respectively have the formula $[Cr(H_2O)_6]_2(SO_4)_3$ and $K[Cr(H_2O)_6](SO_4)_2$.

(20) The hypothesis is related to the configuration of complex salts and their absorption spectra; this Bulletin, **12** (1937), 188.

(3) Chloro-aquo chromic salts were transformed into the hydroxo-pentaquo chromic salts in the solutions where the *p*H-values were higher than 4.0.

(4) The substitution of a chlorine atom for a molecule of water in these salts caused the absorption band to shift in the direction of the increasing wave length and absorption capacity.

(5) Following his method, the author has made a comparison of calculated and observed values of the absorption of green chromic chloride.

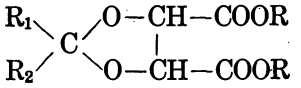
In conclusion, the author wishes to express his sincere thanks to Assist. Prof. T. Uemura of the Tokyo University of Engineering for his kind encouragement.

Laboratory of Inorganic Chemistry,
Tokyo University of Engineering (Tokyo Kôgyô-Daigaku).

Condensation of Diethyl Tartrate with Cyclic Ketones and the Molecular Rotation of the Resulting Compounds.*

By Yojiro TSUZUKI.

(Received October 23rd, 1937.)

It was reported in the previous papers[1] that alkyl tartrates can be condensed with some simple carbonyl compounds giving bridged derivatives of tartaric acid of the type  , and was shown that these compounds would afford suitable materials for the study of the optical activity of tartaric acid. Thus it was pointed out that the molecular rotation of these compounds shows a certain regularity, i.e. the power of the strong lævo-rotation of these compounds falls off as the bulk of the radicals R_1 and R_2 increases, and on the other hand it increases with the increasing bulk of the radical R. And further the rotatory dispersion of these bridged derivatives of tartaric acid was in-

* Synthesis of bridged derivatives of tartaric acid and their optical activity. IV.

(1) Y. Tsuzuki, this Bulletin, **10** (1935), 255; **11** (1936), 362.

vestigated, with a view to interpret the complex nature of the optical activity of tartaric acid and of its derivatives, the results of which brought out a suggesting relation between the radicals R_1 and R_2 and the optically active absorption bands of the compounds.[2] The number of these compounds are, however, very small, so that materials must be substantiated, in order to consolidate the above statement. The present paper aimes to supply some materials for this purpose and to give some simple suggestion of the tendency of the molecular rotation of the newly synthesized bridged compounds. The author has, in the first place, prepared condensation products with one cyclic radical instead of the separate two radicals R_1 and R_2 which were contained in the already synthesized compounds.

Condensation. Diethyl tartrate has been condensed with the following cyclic ketones: cyclopentanone, cyclohexanone, *o*-methylcyclohexanone, *m*-methylcyclohexanone, and *p*-methylcyclohexanone. Cyclopentanone was prepared by distilling adipic acid with barium hydroxide at 315–320°. The three methylcyclohexanones were prepared by oxidising the corresponding alcohols with Beckmann's mixture. *o*-Methyl- and *m*-methylcyclohexanols were Takeda samples and *p*-compound[3] was prepared from *p*-cresol by catalytic hydrogenation. Cyclopentanone, b.p. 128.5–129.5° (760 mm.), $n_D^{20} = 1.4358$. Cyclohexanone, b.p. 153–154° (760 mm.), $n_D^{20} = 1.4506$. *o*-Methylcyclohexanone, b.p. 164° (760 mm.), $n_D^{20} = 1.4482$. *m*-Methylcyclohexanone, b.p. 165° (755 mm.), $n_D^{20} = 1.4482$. *p*-Methylcyclohexanone, b.p. 163–164° (751 mm.), $n_D^{20} = 1.4448$.

The condensation reaction proceeds very smoothly in every case. The yield is fairly good, from 50 to 70% of the theoretical amount. The purification of the condensation product is easy. As the condensation reagent phosphorus pentoxide was employed exclusively, which proved to be very useful, but in the reactions[1] previously performed, various condensation reagents had to be applied according to the nature of the carbonyl compound.[2]

The condensation and the purification of the product has been carried out in the following way: to the mixture of diethyl tartrate (1/20 mol) and cyclic ketone (1/20 mol) is added in portions 10 g. phosphorus pentoxide at 80–90°, in the course of 30–60 minutes. The solid phase of the phosphorus pentoxide is coloured quite strongly, but the liquid mixture remains almost colourless, only in some cases faintly yellowish coloured. In the case of higher members of the ketone homologue the

(2) Y. Tsuzuki, this Bulletin, **11** (1936), 586.

(3) The author is grateful to Dr. K. Ishimura who kindly afforded this material.

temperature must be raised comparatively higher and the duration of reaction must be prolonged. After the whole of phosphorus pentoxide has been added, the heating of the reaction mixture is further continued at that temperature for 30–60 minutes, with occasional stirring. Then the liquid mixture is decanted from the phosphorus pentoxide portion and evaporated at 130° under the pressure 20–30 mm., by which process the unchanged ketone distils over. The product is dissolved in 70 c.c. ether. The ethereal solution is shaken 4 times with each 30 c.c. saturated aqueous solution of borax, whereby the unchanged ethyl tartrate can be almost completely removed into the borax layer, and further shaken with water and dried with anhydrous sodium sulphate. After the ether was evaporated off, the remaining liquid is distilled under reduced pressure.

Reaction products. The condensation products thus obtained and purified are all transparent colourless liquid, but they show some pale yellowish colouration when freshly distilled, which fades away on standing for a few days. This is probably due to some similar cause of the phenomenon, which was observed by Patterson long ago in the case of diethyl tartrate—green colouration produced by its vacuum distillation and disappearance of the colour on its standing—and quite recently given a plausible explanation by the same author.[4]

The physical constants of the new condensation products thus obtained will not be individually described, but are put into Table 1, together with the analytical data.

Molecular rotation. As seen in Table 2 the molecular rotation of the condensation product decreases in magnitude with the increasing bulk of the ketone-residue in the compound, thus the molecular rotation of diethyl cyclopentylidene-tartrate is smaller than that of diethyl isopropylidene-tartrate, but larger than that of diethyl cyclohexylidene-tartrate.

These facts will be understood by the molecular theory of de Malleman[5] as well as of Boys[6], who regards the volumes of the radicals as a dominating factor of the optical activity. In fact the molecular rotation goes almost inversely proportional with the parachor, a quantity equivalent to the molecular volume of the radical.

(4) T. S. Patterson, *J. Chem. Soc.*, **121** (1922), 1042; T. S. Patterson and A. H. Lamberton, *J. Chem. Soc.*, **1937**, 963.

(5) *Trans. Faraday Soc.*, **26** (1930), 281.

(6) *Proc. Roy. Soc.* (London), A, **144** (1934), 655.

Table 1. The Physical Constants and the Analytical Data of the Bridged Derivatives of Tartaric Acid Obtained by Condensing Diethyl Tartrate with Cyclic Ketones.

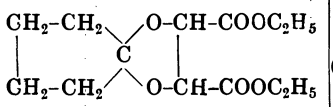
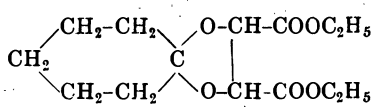
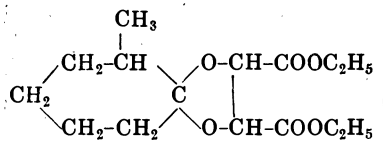
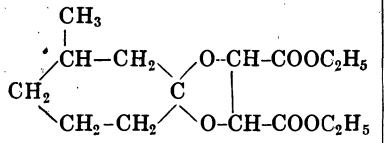
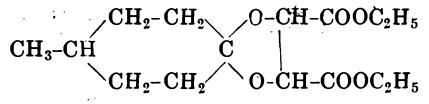
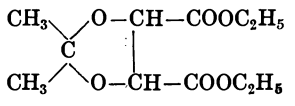
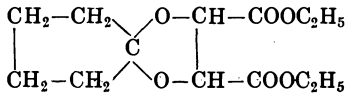
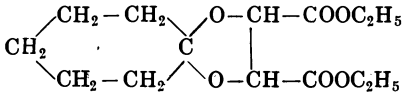
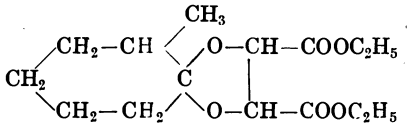
Substance	Structural Formula	Boiling Point (corr.)	d_4^{20}	n_D^{20}	Molecular Refraction	$[\alpha]_D^{20}$	$[M]_D^{20}$	Elementary Analysis		Yield (%)
								Found	Calc.	
Diethyl cyclopentylidenetartrate		170–171° (12 mm.)	1.1468	1.4560	obs. 64.50 calc. 64.44	−40.55°	−110.4°	C 57.07 H 7.35	C 57.31 H 7.41	49
Diethyl cyclohexylidenetartrate		178° (12 mm.)	1.1329	1.4605	obs. 69.25 calc. 69.05	−35.57°	−101.8°	C 58.63 H 7.77	C 58.70 H 7.75	51
Diethyl *o*-methylcyclohexylidenetartrate		184° (14 mm.)	1.1140	1.4590	obs. 73.66 calc. 73.66	−21.81°	−65.48°	C 59.63 H 8.11	C 59.96 H 8.06	52
Diethyl *m*-methylcyclohexylidenetartrate		186° (14 mm.)	1.1085	1.4572	obs. 73.78 calc. 73.66	−35.42°	−106.3°	C 59.73 H 7.96	C 59.96 H 8.06	61
Diethyl *p*-methylcyclohexylidenetartrate		188° (14 mm.)	1.1109	1.4580	obs. 73.73 calc. 73.66	−30.49°	−91.53°	C 59.66 H 8.06	C 59.96 H 8.06	69

Table 2. Molecular Rotation and Parachor of the Condensation Products.

	Molecular Rotation at 20°	Parachor of Ketone-residue
	−120.9°	117.0
	−110.4°	160.8
	−101.8°	199.8
	−65.48°	238.8

The introduction of one methyl group in the cyclohexylidene residue tends to decrease the molecular rotation of the resulting compound. But it is seen that the position of a substituent exerts a great influence on the molecular rotation. The ortho-position has the most diminishing effect, while the meta-position has the least effect, rather an increasing effect. Although these methylcyclohexylidene residues may have the same magnitude of parachor, but their volumes effective to the asymmetric carbon atoms of the compounds must be different. The nearest ortho-position exerts a most intense influence and the meta-position at the least. In the flexible cyclohexane-ring structure of Sachse and Mohr the group attached to the meta-position is situated a little farther than that of the para-position. The differences of these influences by position are, however, quite remarkable, so that the electronic effect due to the position of a group must also be considered in these cases, in order to comprehend more satisfactorily the molecular rotation. Similar phenomena of the effects of position have been already known in the absorption of light in

aromatic compounds, where the ortho effect is largest and the meta effect is least or none.[7] These facts would be understood by the electronic theory of aromatic substitution.

Summary.

(1) It has been shown that the condensation of diethyl tartrate with cyclic ketones can be effected with great ease by the use of phosphorus pentoxide as condensation reagent.

(2) New products obtained by condensing diethyl tartrate with cyclic ketones, namely cyclopentanone, cyclohexanone, and three isomeric methylcyclohexanones, have been described, and their physical constants have been compared in a table.

(3) The molecular rotation of these homologous compounds decreases as the parachor of the ketone-residue in the condensation product increases, but the influence by the position of the substituent is noticed: the substitution of a methyl group at ortho-position is the most effective, and that of meta-position is nearly ineffective.

Musashi Higher School,
Naka-arai, Tokyo.

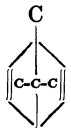
(7) Y. Shibata, *Acta Phytochim.* (Japan), **1** (1923), 91; S. Hattori, *ibid.*, **6** (1932), 131.

An Isomer of Cymene from Camphor.

By Irwin A. PEARL and William M. DEHN.

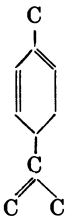
(Received October 26th, 1937.)

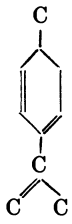
Cymene in 50–60% yields has been obtained from camphor by treatment with phosphorus pentoxide.[1] We have found that prolonged heating with 85% phosphoric acid,[2] gives as the large fraction, an isomer of cymene, but little or no cymene.

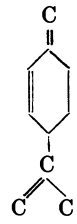
The theoretical isomers of cymene are  and those with double bonds indicated by the following numbers:

I. 1, 3, 8(9)	V. 2, 5, 1(7)	IX. 3, 5, 1(7)
II. 1, 4, 8(9)	VI. 2, 5, 4(8)	X. 3, 5, 8(9)
III. 1, 5, 8(9)	VII. 2, 5, 8(9)	XI. 5, 1(7), 4(8)
IV. 1, 5, 4(8)	VIII. 3, 1(7), 8(9)	XII. 5, 1(7), 8(9)

and of these only III, X, and XII contain asymmetrical carbon atoms. Since our large fraction boiled at 180–182°, possessed the formula $C_{10}H_{14}$ and a specific rotation of 6.82°, it must be one of these three:

III. 

X. 

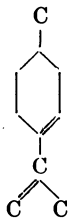
XII. 

Since it agrees more closely in boiling point with *p*-menthadiene (b.p. 184°) than with limonene (b.p. 176.5°), formula X or 1-methyl-4-isopropenyl-cyclohexadiene-(2,4) is indicated.

---

(1) Fittica, *Ann.*, **172** (1874), 307.

(2) Dehn and Jackson, *J. Am. Chem. Soc.*, **55** (1933), 4284. These authors showed that phosphoric acid (85%) yields hydrocarbons from certain oxygenated terpenes etc.

p-Menthadiene. 

Limonene. 

Formula XII is surely excluded for the reason that methylene groups attached directly to the ring are unstable in the presence of acids. Formula III is probably excluded on the basis of Horiuchi's[3] isomer (b.p. 183–186°) formed by the dehydration of citral. Though he reports no optical activity, he assigns to his isomer formula II or III. Wallach[4] also reports an isomer of cymene (b.p. 183°) derived from limonene tribromide, but assigns to it no structural formula.

Experimental.

A mixture of 340 g. of camphor and 290 g. of 85% phosphoric acid in a flask was heated under a reflux air condenser in an oil bath heated at 200° for about 7 hours after all the camphor had liquefied. The mixture was then distilled with steam. The distillate was extracted with ether and the ether was evaporated. Some of the unchanged camphor that came over with the steam was separated from the oil by freezing out in a salt-ice mixture and filtering. A trace of camphor that remained was transformed into cymene by repeated distilling over phosphorus pentoxide. The yield of oil was 75 g. or about 25% of the theoretical. The oil was then fractionated eleven times giving the following fractions: below 176°, 3 c.c.; 176–178°, 2; 178–180°, 13; 180–182°, 20; 182–184°, 2; 184–186°, 6; 186–188°, 2; 188–190°, 3; 190–192°, 8; 192–194°, 2; 194–196°, 2; 196–198°, 2; 198–200°, 3; above 200°, 10.

Evidently longer refluxing would have yielded more oil because both camphor and phosphoric acid were contained in the mixture.

Fraction boiling at 180–182° was analysed (Found: C, 89.27; H, 10.77. Calc. for $C_{10}H_{14}$: C, 89.48; H, 10.52%). Its odour was different from that of cymene. At 22° its refractive index was $n_a = 1.4874$; its specific rotation was $[\alpha]_D = 6.94°$; its specific gravity was 0.875.

That cymene was not first formed by the dehydration of camphor was proved by an experiment in which cymene itself was refluxed for 5 hours with 85% phosphoric acid; it was recovered unchanged at its lower boiling point.

Department of Chemistry and Chemical Engineering,
University of Washington,
Seattle, Washington.

---

(3) Horiuchi, *Mem. Coll. Sci., Kyoto Imp. Univ.*, A, **11** (1928), 171.
(4) Wallach, *Ann.*, **264** (1891), 27. This isomer at 20° has a refractive index of $n_D = 1.49693$ and a specific gravity of 0.863. No optical activity was reported.

The Photochemical Dehydrogenation of 7-Dehydrocholesterol and the Pyrolysis of the Product.

By Yoshiyuki URUSHIBARA and Toshio ANDO.

(Received October 29th, 1937.)

In a preliminary note[1] the authors reported that the photochemical dehydrogenation of 7-dehydrocholesterol (I) yielded a dimolecular derivative ("pinacone") analogous to ergopinacone from ergosterol. Nearly at the same time F. Schenck, K. Buchholz, and O. Wiese[2] published a paper on the studies of 7-dehydrocholesterol, in which they described "7-dehydrocholesterol-pinacone" obtained from 7-dehydrocholesterol by a method similar to, but not identical with, that by which the present authors dehydrogenated 7-dehydrocholesterol (see the experimental part). However, the "pinacone" of the German investigators melted at 196–197°, higher by about 10° than the present authors' "pinacone". The German investigators gave to their "pinacone" a formula with one and a half molecules of water: $C_{54}H_{86}O_2 + 1\frac{1}{2}H_2O$.

The present authors repeated the dehydrogenation of 7-dehydrocholesterol by the same method as before and obtained the same results. The "pinacone", recrystallized from benzene-alcohol, had formula $C_{54}H_{86}O_2 + H_2O$ and melted at 184–185° (corr.) with decomposition. The substance dried in vacuum at 110° had formula $C_{54}H_{86}O_2$ and melted at 185.5–186° (corr.) with decomposition.

The "pinacone" was subjected to pyrolytic decomposition followed by distillation in high vacuum. The distillate obtained in a yield of 70–78% was a viscous greenish yellow oil which crystallized with difficulty. Recrystallized from methanol, the substance formed small long plates melting at 110–111° (corr.). Its 3,5-dinitrobenzoate formed light-yellow small plates melting at 210.5–211° (corr.). Analyses showed the substance was 10-desmethyl-cholestatrienol-(3) (II), analogous to neoergosterol from ergopinacone.

Schenck and co-workers, by boiling their "pinacone" with acetic anhydride and saponifying the uncrystallizable product with potash in

(1) Y. Urushibara and T. Ando, this Bulletin, **11** (1936), 802.
(2) *Ber.*, **69** (1936), 2696.

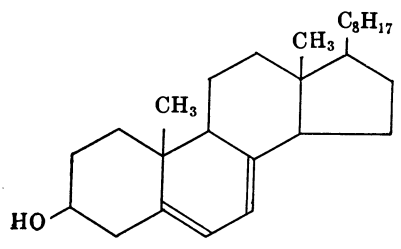
methanol, obtained "norsterol" melting at 111°. Its 3,5-dinitrobenzoate melted at 207° with decomposition.

As indicated in the accompanying table, the substances obtained by the present authors and the corresponding substances described by the German investigators show similar properties except the melting points of the "pinacone". However, it cannot be decided whether or not they are identical each with each.

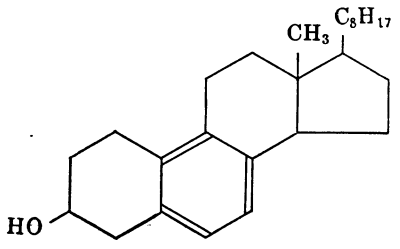
Schenck, Buchholz, and Wiese			Urushibara and Ando		
Substance	Melting point	$[\alpha]_D$	Substance	Melting point	$[\alpha]_D$
"Pinacone" $C_{54}H_{86}O_2+1\frac{1}{2}H_2O$	196–197°	−181.6°(22°) in C_5H_5N	"Pinacone" $C_{54}H_{86}O_2+H_2O$ $C_{54}H_{86}O_2$	184–185° (corr.) 185.5–186° (corr.)	−171°(18°) in C_5H_5N
Norsterol	111°	+1.6°(22°) in $CHCl_3$	10-Desmethyl-cholesta-trienol-(3)	110–111° (corr.)	Nearly null in $CHCl_3$
3,5-Dinitro-benzoate of the above	207°	−2.5°(22°) in $CHCl_3$	3,5-Dinitro-benzoate of the above	210.5–211° (corr.)	−3.8°(17°) in $CHCl_3$

Dehydrogenation of 7-dehydrocholesteryl benzoate by the same method yielded the dibenzoate of the "pinacone", $C_{68}H_{94}O_4$, which, recrystallized from benzene-alcohol, formed colourless needles melting at 183–183.5° (corr.) with gas evolution. On mixing it with the free "pinacone" a depression of the melting point was observed.

While the free "pinacone" does not keep long, its dibenzoate is so stable that no change was observed in six months.



I



II

Experimental.

7-Dehydrocholesterol. Prepared according to the directions of A. Windaus, H. Lettré and F. Schenck.[3] Recrystallized from ether-methanol, colourless needles, m.p. 143–146.5° (corr.). The 3,5-dinitrobenzoate, recrystallized from chloroform-acetone, formed yellow needles, m.p. 212–212.5° (corr.) with decomposition[4] (Found for the dinitrobenzoate dried over phosphorus pentoxide in vacuum at 110°: C, 70.68; H, 8.28; N, 4.76. Calculated for $C_{34}H_{46}O_6N_2$: C, 70.55; H, 8.02; N, 4.84%).

"Pinacone" from 7-dehydrocholesterol. 7-Dehydrocholesterol was dehydrogenated according to the directions of H. H. Inhoffen[5] for the preparation of ergopinacone from ergosterol: 7-Dehydrocholesterol and an equal amount of eosin (Eosin, spirit-löslich, Dr. G. Grübler and Co., Leipzig) were dissolved in a mixture of 95% alcohol and a small amount of benzene. The solution was boiled thoroughly to remove air,[6] and exposed to the sun for two weeks in exclusion of air. The crystalline precipitate was collected, boiled with alcohol, and recrystallized from benzene-alcohol. Colourless thin needles, m.p. 180.5–181.5° (uncorr.) or 184–185° (corr.) with decomposition (Found: C, 82.19; H, 11.04. Calculated for $C_{54}H_{86}O_2 + H_2O$: C, 82.58; H, 11.31%). On being dried over phosphorus pentoxide in vacuum at 110°, the substance gave up the combined water (Found: H_2O, 2.06. Calculated for $C_{54}H_{86}O_2 + H_2O$: H_2O, 2.29%). The dried substance melted at 185.5–186° (corr.) with decomposition (Found: C, 84.37; H, 11.29. Calculated for $C_{54}H_{86}O_2$: C, 84.53; H, 11.31%). $[\alpha]_D^{18°} = -171°$ (9.2 mg. of the dried substance in 1 c.c. pyridine solution, $l = 1$ dm., $\alpha_D^{18°} = -1.57°$).

The "pinacone" was decomposed by keeping.

10-Desmethyl-cholestatrienol-(3) and its 3,5-dinitrobenzoate. The "pinacone" was heated at 175° under the pressure of 0.28 mm. for 15 minutes, and immediately distilled at 210–250° under 0.004–0.0015 mm. The distillate (yield 70%), forming a viscous greenish yellow oil, was heated for 30 minutes with 3,5-dinitrobenzoyl chloride and pyridine. The crystals separating out on adding water to the reaction mixture were washed with dilute acetic acid and with water, boiled with dilute acetone, and recrystallized repeatedly from benzene-methanol. Glittering light-yellow small plates, m.p. 206.5–207° (uncorr.) or 210.5–211° (corr.) (Found: C, 70.66; H, 7.42; N, 4.94. Calculated for $C_{33}H_{42}O_6N_2$: C, 70.44; H, 7.53; N, 4.98%). $[\alpha]_D^{17°} = -3.8°$ (13.3 mg. in 1 c.c. chloroform solution, $l = 1$ dm., $\alpha_D^{17°} = -0.05°$).

In another experiment of pyrolysis, the "pinacone" was heated at 185°, 0.25 mm., for 20 minutes, and distilled at 210–260°, 0.0035–0.0008 mm., in the course of 10

(3) *Ann.*, **520** (1935), 98.

(4) Windaus and co-workers give m.p. 207°.

(5) *Ann.*, **497** (1932), 130.

(6) Schenck and co-workers removed air from the alcoholic solution (with no benzene) of 7-dehydrocholesterol and eosin by passing carbon dioxide.

minutes. The distillate (78%) forming a viscous light greenish yellow oil solidified to an opaque yellowish mass. It was collected with ether, the ether was evaporated, and the residue was brought to crystallization by rubbing with methanol. The substance was recrystallized repeatedly from methanol. Colourless glittering small long plates, m.p. 109–110° (uncorr.) or 110–111° (corr.). $[\alpha]_D^{15°}$ = nearly null (6.7 mg. in 1 c.c. chloroform solution, $l = 1$ dm., $\alpha_D^{15°} = \pm 0.01°$). For analysis the substance was dried over phosphorus pentoxide in vacuum at 76° (Found: C, 84.60; H, 10.86. Calculated for $C_{26}H_{40}O$: C, 84.72; H, 10.95%).

The 3,5-dinitrobenzoate prepared from the purified 10-desmethyl compound was identical with the above specimen obtained from the crude oily distillate.

The dibenzoate of the "pinacone" from 7-dehydrocholesteryl benzoate. 7-Dehydrocholesteryl benzoate (m.p. 141–142.5°, clear at 187°, corr.) was dehydrogenated in the same manner as described above. The product depositing in needles was collected, boiled with alcohol, and recrystallized from benzene-alcohol. Colourless needles, m.p. 183–183.5° (corr.) with gas evolution (Found: C, 84.03; H, 10.01. Calculated for $C_{68}H_{94}O_4$: C, 83.70; H, 9.72%). $[\alpha]_D^{17°} = -114°$ (11.9 mg. in 1 c.c. chloroform solution, $l = 1$ dm., $\alpha_D^{17°} = -1.36°$). In admixture with the free "pinacone" the dibenzoate showed a depression of the melting point. The substance is stable in air, no change being observed in six months.

The authors express their hearty thanks to Mr. Yasohachi Yamaguchi for his generous support of this work.

Chemical Institute, Faculty of Science,
Imperial University of Tokyo.

The Effects of Oxygen and Peroxides on the Rate of Addition of Bromine to Cinnamic Acid in Carbon Tetrachloride.

By Yoshiyuki URUSHIBARA and Matsuji TAKEBAYASHI.

(Received October 30th, 1937.)

I. **The Effect of Oxygen.** In the previous paper on the same subject[1] the authors showed the relation between the extent of addition of bromine to cinnamic acid in carbon tetrachloride and the amount of oxygen present. The extent of addition in vacuum, however, was rather too small (about 60%) in view of the observation of W. H. Bauer and F. Daniels[2] that the addition was so rapid in absence of oxygen that the rate of reaction could not be measured conveniently. Then it was suspected that dissolved oxygen might not have been removed completely by the process of evacuation under cooling in liquid air. Hence, experiments were repeated by a procedure which differed from the previous method only in that a part of the solvent was evaporated in vacuum in order to remove dissolved oxygen.

Materials used in the experiments were prepared by treating commercial products as follows: Cinnamic acid was recrystallized from alcohol, melting point 133°. Bromine was refluxed with the addition of potassium bromide, distilled, shaken with concentrated sulphuric acid, and redistilled. Carbon tetrachloride was refluxed with an alkaline aqueous solution of potassium permanganate for two days, washed with water, dried over calcium chloride, distilled, and redistilled with the addition of phosphorus pentoxide on the day of use. Oxygen from the bomb was dried with calcium chloride and then with phosphorus pentoxide.

The experimental procedure was as follows: One millimol (0.1481 g.) of cinnamic acid was taken in a reaction tube of Pyrex glass with a capacity of 140 c.c., and dissolved in 40 c.c. of carbon tetrachloride. A sealed small glass bulb containing a slight excess of bromine was slipped into the tube. The tube was evacuated by a vacuum-pump at room temperature until 10 c.c. of carbon tetrachloride distilled over, 30 c.c. being left in the tube, then cooled in liquid air, evacuation being continued, and sealed off with or without admission of oxygen. The contents were melted and mixed well by shaking. The bromine bulb was broken usually

(1) This Bulletin, **12** (1937), 356.
(2) *J. Am. Chem. Soc.*, **56** (1934), 2014.

on freezing the contents of the reaction tube in liquid air, otherwise on shaking. The tube was placed in the dark at room temperature for 22 hours. An excess of aqueous potassium iodide was added to the reaction mixture, and the liberated iodine was titrated with N/10 sodium thiosulphate. The extent of addition in percentage to the cinnamic acid used was determined from the amount of bromine consumed. When the extent of addition was greater than 60%, the crystals of cinnamic acid dibromide (melting point 198°, corr.) appeared in the reaction mixture.

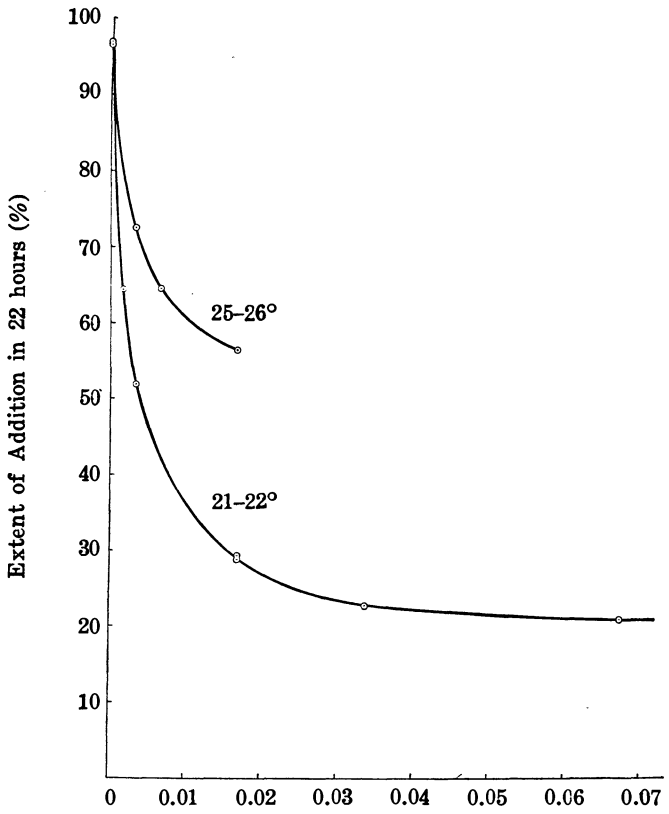
The temperatures recorded in all the tables given below are those at the beginning of the experiments. Additions of the same groups were carried out simultaneously, and thus under the same conditions. Only the experiments that belong to the same groups are strictly comparable.

Table 1.

Group of exp.	No. of exp.	Temp. (°C.)	Bromine (g.)	Amount of oxygen		Extent of addition (%)
				Admitted (c.c., n.p.t.)	Dissolved in CCl_4 solution (millimol)	
I	1	26	0.1820	0	0	96.9
	2	26	0.1798	1.0	0.0034	72.5
II	4	25	0.1851	2.0	0.0067	64.3
	5	25	0.1885	5.0	0.017	56.3
III	6	22	0.2089	0	0	96.6
	7	22	0.2002	0.5	0.0017	64.3
	8	22	0.1949	1.0	0.0034	51.8
	9	22	0.2081	5.0	0.017	28.6
IV	10	21	0.2080	5.0	0.017	29 0
	11	21	0.2075	10.0	0 034	22.0
	12	21	0.2010	20.0	0.067	18.7

The results of experiments are shown in Table 1. The amount of oxygen dissolved in the carbon tetrachloride solution was calculated on the same basis as described in the previous paper.[1] The relation between the amount of oxygen and the extent of addition is illustrated in the accompanying figure, the upper curve representing the experiments at 25–26° (Exp. 1, 2, 4, and 5) and the lower those at 21–22° (Exp. 6–12). The addition in vacuum proceeded so rapidly that the extent in 22 hours was nigh upon 100% both at 21–22° and at 25–26°, while in the presence

of oxygen a difference of about 4° in the temperature caused a remarkable separation of the two curves.



Millimol of Oxygen in 30 c.c. CCl_4 Solution containing 1 millimol of Cinnamic Acid.

II. **The Effect of Peroxides.** Benzoyl peroxide was used. The commercial product was dried in vacuum over sulphuric acid. The purity was found 99.63% by iodometry in acetone solution.[3] Weighed amounts of benzoyl peroxide were dissolved together with cinnamic acid in carbon tetrachloride in the reaction tubes, the experimental procedure in all other respects being the same as described above.

In the iodometric determination of the extent of addition the added peroxide might liberate iodine, thus causing too small values of the extent. However, it was found that benzoyl peroxide liberates only a trace of

(3) H. Gelissen and P. H. Hermans, *Ber.*, **59** (1926), 68.

iodine under the conditions as described above: 0.05 g. of benzoyl peroxide was dissolved in 30 c.c. of carbon tetrachloride, and the solution was mixed with 30 c.c. of concentrated aqueous potassium iodide. The mixture, after placed in the dark during such a time (6–7 minutes) as required usually in the iodometric determination of the extent of reaction, was titrated with N/10 sodium thiosulphate. Only 0.05 c.c. was consumed, while 0.05 g. of the peroxide corresponds theoretically to about 4 c.c. of N/10 sodium thiosulphate. The amounts of the peroxide used in the additions ranged from about 0.1 to 0.01 g., and the volumes of N/10 sodium thiosulphate required to titrate the iodine liberated by bromine remaining after the reactions in the presence of the peroxide from 3.7 to 16 c.c. The correction value −0.05 c.c. for 0.05 g. of the peroxide was taken into account in all titrations in the presence of the peroxide under the assumption that the peroxide had not been decomposed during the reaction. Although the peroxide seems to be subject to a chemical change with bromine as indicated by the experiments described below, this assumption is valid so long as the peroxidic oxygen remains unchanged.

Benzoyl peroxide is not decomposed by cinnamic acid in carbon tetrachloride, or strictly speaking, the amount of peroxidic oxygen is not changed. Benzoyl peroxide (0.1084 and 0.0108 g. corresponding to 0.1132 and 0.0113 g. of iodine respectively) and cinnamic acid (0.1481 g. each) were dissolved in carbon tetrachloride (30 c.c. each), and the solution was sealed in vacuum in a tube in the same manner as in the experiments of addition. After 22 hours (in the dark at room temperature) the amount of the peroxide was determined by iodometry in acetone solution and found to be unchanged (0.1166 and 0.0117 g. of iodine respectively).

On the other hand, benzoyl peroxide seems to react with bromine in carbon tetrachloride. Just in the same manner as in the experiments of addition, benzoyl peroxide and bromine was dissolved in carbon tetrachloride in absence of air. After 22 hours' standing in the dark at room temperature, the solution was mixed with aqueous potassium iodide, bromine being replaced by iodine, and then, by adding acetone, the peroxide was converted into iodine. The total iodine thus liberated was determined and compared with the value calculated from the initial amounts of benzoyl peroxide (the purity 99.63% being taken into account) and bromine. In Table 2 the change is shown in terms of the corresponding amounts of bromine (designated as g.Br).

The values of decrease shown in Table 2 are less than, and roughly half, the amounts (expressed in g.Br) of benzoyl peroxide used. If this decrease had been caused by the decomposition of the peroxide, matters

Table 2.

Benzoyl peroxide (g.)	Benzoyl peroxide (g.Br)	Bromine (g.)	Total (g.Br)	Found after reaction (g.Br)	Decrease (g.Br)
0.1084	0.0714	0.2106	0.2820	0.2517	0.0303
0.1084	0.0714	0.1852	0.2566	0.2079	0.0487
0.2168	0.1427	0.1813	0.3240	0.2367	0.0873

would have been simpler, because the decrease in the amounts of the peroxide would have been no obstacle to qualitative consideration of the results of additions in the presence of the peroxide, and, even if oxygen should have been liberated by the decomposition, its retarding effect on the addition having been well explored, little difficulty would have been encountered in learning the effect of the peroxide from the results of experiments. However, it had to be assumed that a part of bromine was consumed by the peroxide, and that a substitution took place.[4] If so, while the amount of the peroxidic oxygen remains unchanged, bromine will be consumed both by cinnamic acid and by benzoyl peroxide in the reaction of bromine with cinnamic acid in the presence of the peroxide. What might complicate matters more seriously is the formation of hydrogen bromide by the substitution. On this account, it had to be determined what influence is exerted by hydrogen bromide on the addition of bromine to cinnamic acid.

Fortunately enough, it has been found that hydrogen bromide is indifferent to the addition reaction either in presence or in absence of oxygen: As shown in Table 3, in the presence of hydrogen bromide the addition proceeded as rapidly as in vacuum and cinnamic acid dibromide melting at 198° separated in quantity (Exp. 13), while hydrogen bromide exerted no accelerating effect on the reactions retarded by the addition of oxygen (Exp. 15–17).

Now the authors are ready for discussing the results of additions in the presence of benzoyl peroxide, which are summarized in Table 4. The apparent extent of addition corresponds to the total amount of bromine consumed. If the apparent extent is corrected under the assumption that the peroxide consumed half its number of molecules of bromine, the values given in the last column of Table 4 are obtained. However,

(4) Compare L. Vanino and E. Uhlfelder, *Ber.*, **33** (1900), 1046.

Table 3.

Group of exp.	No. of exp.	Temp. (°C.)	Bromine (g.)	Oxygen admitted (c c., n.p.t.)	Hydrogen bromide admitted (c.c., n.p.t.)	Extent of addition (%)
V	13	17	0.2043	0	2.4	96.9
VI	14	17	0.1910	5.0	0	14.7
	15	17	0.1943	5.0	2.0	19.3
VII	16	17	0.2144	5.0	2.0	11.6
	17	17	0.2167	5.0	1.0	15.2

Table 4.

Group of exp.	No. of exp.	Temp. (°C.)	Bromine (g.)	Benzoyl peroxide		Extent of addition	
				(g.)	(millimol)	Apparent (%)	Corrected (%)
I	1	26	0.1820	0	0	96.9	96.9
	3	26	0.1850	0.0108	0.045	96.7	94
VIII	19	25	0.1976	0.0217	0.090	95.2	91
	20	25	0.1923	0.0434	0.179	97.2	88
	21	25	0.1919	0.1084	0.448	99.2	77

they do not indicate any retarding effect of the peroxide, because the amount of bromine used was only slightly excessive to cinnamic acid alone, and nearly all of it was consumed. On the contrary, the fact that the more benzoyl peroxide was present the sooner the crystals of cinnamic acid dibromide (melting point 198°) appeared indicates qualitatively the accelerating effect of benzoyl peroxide, provided that the presence of the peroxide or the products from the reaction of the peroxide with bromine did not diminish the solubility of the dibromide.

The accelerating effect of benzoyl peroxide is definitely demonstrated by the additions in the presence of both oxygen and the peroxide. The results collected in Table 5 show the effect of the peroxide on the reactions retarded by admitting 5 c.c. of oxygen.

The apparent extent of addition was corrected on the basis of the same assumption as stated above (the last column of Table 5). It can

Table 5.

Group of exp.	No. of exp.	Temp. (°C.)	Bromine (g.)	Benzoyl peroxide		Oxygen		Extent of addition	
				(g.)	(m.mol)	Admitted (c.c., n.p.t.)	Dissolved in CCl_4 sol. (m.mol)	Apparent (%)	Corrected (%)
VII	18	17	0.2164	0.0217	0.090	5.0	0.017	56.9	52
IX	22	19	0.1990	0.0217	0.090	0	0	97.2	93
	23	19	0.1966	0	0	5.0	0.017	20.8	20.8
	24	19	0.1952	0.0217	0.090	5.0	0.017	77.5	73
X	25	20	0.2107	0	0	5.0	0.017	20.1	20.1
	26	20	0.2106	0.0108	0.045	5.0	0.017	49.9	48

be seen from the table that the presence of the peroxide compensated partly the retardation by oxygen. As it can be assumed that there should be no direct interference between the peroxide and oxygen, the effect of the former on the reactions retarded by the latter must be attributed to the inherent accelerating effect of the benzoyl peroxide on the addition of bromine to cinnamic acid.

Although it has been proved that hydrogen bromide is quite indifferent to the reaction, it does not necessarily exclude the possibility that it might be active in cooperation with a peroxide. But this seems improbable from the fact that hydrogen bromide is inactive in the addition of bromine to cinnamic acid even in the presence of oxygen while it is active in the isomerization of isostilbene into stilbene in the presence of either benzoyl peroxide or oxygen.[5]

Some contradictions may be found between the results recorded in the present paper and those published by P. W. Robertson and coworkers.[6] But, no mention being made of air and light there, no comparison can be justified. In this connection, however, it may be emphasized that the addition of bromine to cinnamic acid in carbon tetrachloride under the conditions of the experiments carried out by the present authors is homogeneous[1] and the addition product was always cinnamic acid dibromide melting at 198°.

(5) See the following paper, this volume, p. 507.

(6) P. W. Robertson, N. T. Clare, K. J. McNaught, and G. W. Paul, *J. Chem. Soc.*, **1937**, 335.

Addendum: The Addition in the Presence of Reduced Iron. The perfect resistance of iron and nickel against hydrogen bromide was essential to the success in the experiments on the addition of hydrogen bromide to allyl bromide in the presence of these metals. If they were resistant also to bromine in carbon tetrachloride, interesting results might be expected from the experiments on the addition of bromine to cinnamic acid in the presence of these metals. However, it has been found that these metals are subject to serious attack by bromine in carbon tetrachloride, and in an addition in the presence of reduced iron the consumption of bromine was more than 100% in reference to cinnamic acid.

Summary.

(1) The relation between the extent of addition of bromine to cinnamic acid in carbon tetrachloride and the amount of oxygen present has been shown.

(2) It has been indicated that hydrogen bromide is indifferent to the reaction of bromine with cinnamic acid in carbon tetrachloride either in presence or in absence of oxygen.

(3) The accelerating effect of benzoyl peroxide on the addition of bromine to cinnamic acid in carbon tetrachloride has been demonstrated.

(4) In all cases, namely in vacuum and in the presence of any of oxygen, benzoyl peroxide, and hydrogen bromide, the products separating out in crystals were cinnamic acid dibromide melting at 198°.

(5) All the results mentioned above were obtained from the additions in the dark at room temperature.

The authors express their sincere thanks to the Nippon Gakujutsu Shinko-kwai (the Japan Society for the Promotion of Scientific Research) for a grant.

Chemical Institute, Faculty of Science,
Imperial University of Tokyo.

The Effect of Oxygen and Reduced Nickel on the Catalytic Action of Hydrogen Bromide in the Isomerization of Isostilbene into Stilbene.

By Yoshiyuki URUSHIBARA and Osamu SIMAMURA.

(Received November 2nd, 1937.)

The influence of oxygen and ferromagnetic metals on the addition of hydrogen bromide or bromine to ethylenic compounds has been investigated in this laboratory.[1] The scope of investigation has been extended to other types of reactions and it has been examined whether or not the cis-trans-isomerization is influenced by the presence of oxygen and ferromagnetic metals. Nevertheless neither oxygen nor reduced nickel showed a defined accelerating effect on the isomerization of dimethyl maleate into dimethyl fumarate and of isostilbene into stilbene even in the heat (in absence of solvents).[2]

Then the authors became aware of a short communication by M. S. Kharasch, J. V. Mansfield, and F. R. Mayo.[3] They found that in the dark carefully purified isostilbene, dissolved in benzene, was not isomerized into stilbene by hydrogen bromide when the reactants were mixed either in air or in vaccum, or in the presence of antioxidants, and that the addition of a peroxide to the reaction mixture caused complete isomerization in a few minutes.

The present authors' experiments in absence of solvents resulted in part similarly to the experiments in benzene solution by the American investigators: The presence of hydrogen bromide alone did not accelerate the isomerization of isostilbene into stilbene in the dark at room temperature, but the addition of a sufficient amount of benzoyl peroxide caused complete solidification of isostilbene into stilbene in a few minutes.

Oxygen showed a similar effect on the same reaction: When dry oxygen and dry hydrogen bromide were introduced into the tube con-

(1) Y. Urushibara and M. Takebayashi, this Bulletin, **11** (1936), 692, 754, 798; **12** (1937), 51, 138, 173, 356, 499.

(2) B. Tamamushi and H. Akiyama observe that the isomerizations of dimethyl maleate into dimethyl fumarate and of maleic acid into fumaric acid in aqueous solution are accelerated by the presence of molecular oxygen. *Z. Elektrochem.*, **43** (1937), 156; this Bulletin, **12** (1937), 382.

(3) *J. Am. Chem. Soc.*, **59** (1937), 1155.

taining isostilbene, the latter solidified completely in a few minutes in the dark at room temperature. The American investigators state that isostilbene in benzene solution was not isomerized to stilbene by hydrogen bromide even when the reactants were mixed in air. It may be suspected that no sufficient amount of oxygen was absorbed under the conditions of their experiments or the solvent prevented oxygen from exerting its influence.

As it was found that isostilbene does not form any peroxide with oxygen in the dark and even in diffuse light, the effect of oxygen must be attributed to the action of molecular oxygen. On the other hand, from the experimental evidence so far obtained, it cannot be decided whether benzoyl peroxide is active as such or oxygen liberated by its decomposition is the real agent.

Reduced nickel, which exhibits a catalytic action similar to that of oxygen in the addition of hydrogen bromide to allyl bromide,[4] was found also to cooperate with hydrogen bromide to accelerate the isomerization of isostilbene into stilbene. However, the effect displayed by reduced nickel and hydrogen bromide was much smaller than that by oxygen and hydrogen bromide so far as the preliminary experiments indicated. Reduced nickel contained in a reaction tube was heated at 310–320° in the atmosphere of hydrogen and then in vacuum, and cooled in vacuum. The tube, after introducing hydrogen bromide, was sealed, and isostilbene contained in a side tube attached to the reaction tube was decanted on the reduced nickel. The crystals of stilbene began to appear in the course of ½–3 hours in the dark at room temperature, and finally the whole mass solidified. The change was naturally much more rapid at the temperature of the hot water bath.

Thus it has been shown that oxygen and reduced nickel exert no direct influence on the isomerization of isostilbene into stilbene, but cooperate with hydrogen bromide, which is also inactive by itself, in accelerating the isomerization. It seems very probable that in the presence of oxygen or reduced nickel hydrogen bromide is excited to an active catalyst to promote the isomerization.

In a theory advanced for explaining the influence of oxygen and ferromagnetic metals on the addition of hydrogen bromide to allyl bromide, one of the authors (Y. U.) with M. Takebayashi assumed that these active catalysts exert some physical influence on allyl bromide,[5] but they reserved the possibility that the substance which is influenced by

(4) This Bulletin, **11** (1936), 692, 754; **12** (1937), 51.
(5) This Bulletin, **12** (1937), 54, 175.

oxygen and ferromagnetic metals might be hydrogen bromide.[6] The results recorded in the present paper suggest the possibility that hydrogen bromide is excited by oxygen or ferromagnetic metals and the excited hydrogen bromide adds rapidly to allyl bromide to give the abnormal addition product.

M. S. Kharasch and co-workers in the cited communication bring forward a hypothesis that bromine atoms are the active catalysts in the isomerization of isostilbene into stilbene, and seem to be of the opinion that bromine atoms are responsible also for the so-called peroxide effect in the addition of hydrogen bromide to unsaturated compounds.[7] However, the effect of ferromagnetic metals on the addition of hydrogen bromide to allyl bromide cannot be explained by assuming bromine atoms, because the action of ferromagnetic metals, in contrast with oxygen and peroxides, does not undergo even the slightest modification in the presence of an antioxidant.[8] Moreover, it may be difficult to introduce a similar idea into the case of the addition of bromine to cinnamic acid in carbon tetrachloride, where oxygen retards the rate of addition while peroxides accelerate the reaction and hydrogen bromide is indifferent either in presence or in absence of oxygen.[9]

The authors express their hearty thanks to the Nippon Gakujutsu Shinko-kwai (the Japan Society for the Promotion of Scientific Research) for a grant.

Chemical Institute, Faculty of Science,
Imperial University of Tokyo.

---

(6) This Bulletin, **12** (1937), 176.

(7) They state the hypothesis is proposed in an article in press, but the article is not yet available here.

(8) This Bulletin, **11** (1936), 754.

(9) This Bulletin, **12** (1937), 356, 499.

the vapour pressure of the liquid hydrogen is 40 mm., the hydrogen gradually solidifies, and reaches the triple point, that is, −258°C.

(2) *Apparatus for determining the temperature.* Inside the device for measuring the specific heat, there is a platinum resistance thermometer which is made by winding a platinum thread around a copper cylinder insulated with bakelite. The precision of this thermometer is determined in advance by comparing its resistance with the temperature of the gas thermometer.[2] The resistance is shown in Table 1.

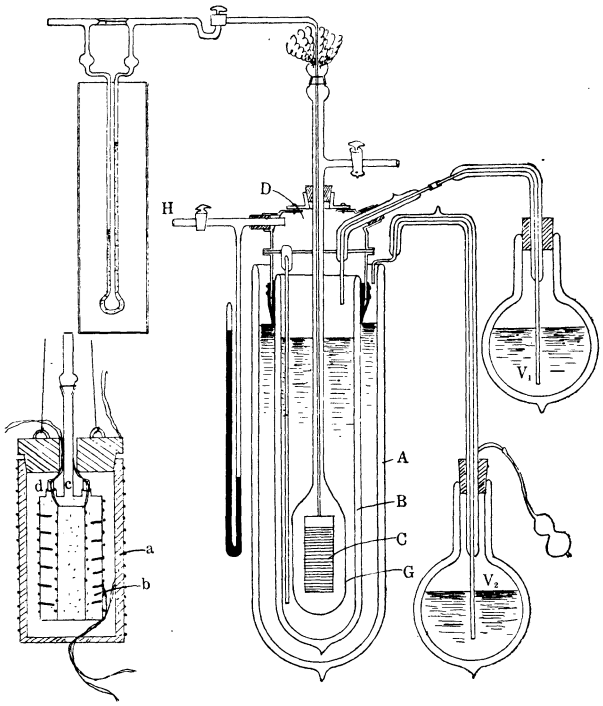


Fig. 1.

Fig. 2.

Table 1.

Temperature (°C.)	Resistance (ohm)
0°	20.1550
−25.50	18.2597
−39.10	17.1710
−68.38	14.8130
−125.55	10.1146
−158.75	7.3203
−183.40	5.2059
−195.85	4.2633
−252.66	0.9652
−254.53	0.8154
−256.50	0.6637
−258.17	0.5324

At temperatures lower than −252.66°C., the calibration was made by means of a hydrogen vapour thermometer.[3]

According to the formula

(2) Aoyama and Kanda, this Bulletin, **10** (1935), 472.

(3) Wrede-Rankine-Keesom's formula (Onnes and Keesom, *Commun. Phys. Lab. Univ. Leiden*, Suppl. No. 23) is used, which is

$$\log p_{\text{cm.}} = 4.6063 - \frac{58.40}{T} + \frac{61}{T^2}.$$

$$R_t = \alpha R_0\left[\frac{1}{\alpha}+t+\delta\left(1-\frac{t}{100}\right)\frac{t}{100}+\beta\left(1-\frac{t}{100}\right)\left(\frac{t}{100}\right)^3\right],$$

the relation between the resistance and the temperature at −252.66°C. and upward can be expressed in

$$R_t = 0.0038745 \times 20.1550 \times \left[258.097+t+1.4950 \times \left(1-\frac{t}{100}\right)\frac{t}{100}+ 0.11251 \times \left(1-\frac{t}{100}\right)\left(\frac{t}{100}\right)^3\right].$$

(3) *Apparatus for measuring the specific heat.* The apparatus for measuring the specific heat was nearly the same as one formerly used in the measurement on organic substances, but was made suitable for condensed gases.

In Fig. 2, a is a case made of a thick copper plate. The temperature is adjusted by means of a heating coil around the outside of the case. b is a cylinder made of a thin copper plate and has a resistance thermometer and a few ledges in it with a heating coil of a constantan wire on the outside. There are junction points of a thermocouple on the inside and outside of a and b respectively for determining the difference in temperature between the two sides. The exit d for the platinum resistance wire is sealed with fused glass as shown in the figure. The sample is introduced through C and condensed in b. This device is put in a glass bulb G, which is set up in the cooling vessel.

(4) *Determination of the amount of the sample.* The determination of the amount is very difficult in the case of condensed gases. This is especially the case with fluorine, for which a gas reservoir cannot be used. The author used a 200 c.c. gas-burette, in which glycerine was placed on the mercury as shown in Fig. 3.

(5) *Apparatus for determining the heating energy.* The electrical connections for measuring the temperature of the sample and heating energy electrically applied to the calorimeter are illustrated in Fig. 4. To make the construction of the device well understood and to give an exact idea of the apparatus, the platinum thermometer, the sample, the heating coil, and the case are separately illustrated.

The measuring apparatus consists of a system in which the current in the heating coil and the potential difference between the ends of the coil are measured and of a system in which the resistance of the platinum thermometer is measured. In both systems there are standard resistances connected with the potentiometers. The heating energy was

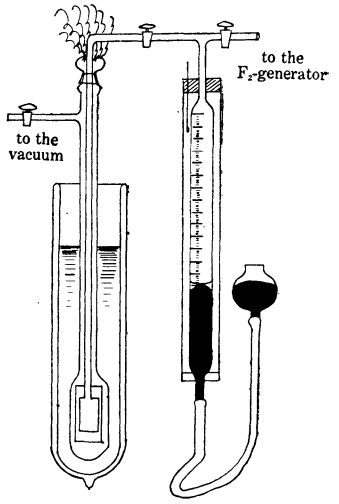


Fig. 3.

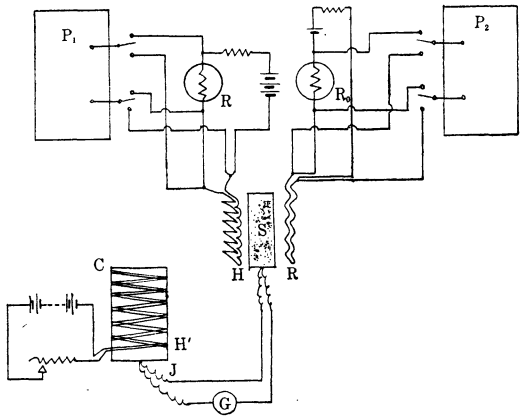


Fig. 4.

determined by means of the Leeds and Northrup type potentiometer, and the potentiometer for low potential free from thermoelectromotive force was used for the resistance thermometer.

(6) *Construction of the calorimeter and heat loss.* For obtaining a desired low temperature, dry air or dry hydrogen gas was introduced into the glass bulb G in Fig. 2, and the low temperature of the liquid nitrogen or liquid hydrogen on the outside was transmitted to the case and the calorimeter by conduction of this gas. The temperature of the sample was observed by means of the platinum thermometer, and when a proper temperature was reached, G was cleared of the hydrogen gas, and was made highly vacuous (about 10^{-5} mm. Hg). In this way the inward transmission of cold through the wall of G was prevented. Further, for preventing cooling of the calorimeter by conduction of any remaining gas, the case was heated slowly through the coil on its surface. The difference in temperature between the outer surface of the colorimeter and the inner surface of the case was observed even while the specific heat was being measured by means of a galvanometer, and the heating current on the case was adjusted during the rise of temperature so that the difference might not exceed 0.5°. Although this process is far more complicated than one in which the calorimeter is simply hung in G, it greatly decreases the heat loss due to radiation and conduction, and minimizes the error.

Supposing that the vacuum in G is about 10^{-5} mm. Hg, that the temperature at which the specific heat is to be measured is −200°C., and that

the difference in temperature between the walls of G and b is 50°, the heat loss of the calorimeter due to radiation q_r and due to conduction q_g will be approximately expressed by

$$q_r \fallingdotseq \frac{F_i}{\frac{1}{C}+\frac{F_i}{F_e}\left(\frac{1}{C}-\frac{1}{C_b}\right)}(T_e^4-T_i^4) \fallingdotseq F_iC(T_e^4-T_i^4)\ , \quad \text{and}$$

$$q_g = \frac{a}{2-a}\eta p\sqrt{\frac{273}{T_i}}(T_e-T_i)F_i \fallingdotseq \eta p\sqrt{\frac{273}{T_i}}(T_e-T_i)F_i\ ,$$

where F_i is the surface area of the calorimeter, F_e that of glass bulb G, T_i temperature of the calorimeter, T_e the surface temperature of G, C radiation constant of the material of the calorimeter, etc., C_b that of the black body, a the accommodation coefficient of the gas (air or hydrogen), η a constant dependent upon the viscosity, and p the pressure of the remaining gas (mm. Hg).

For example, in case F_i=50 cm.^{2}, T_i=73°K(−200°C.), and T_e=23°K (−250°C.), we have $q_r=5.86\times10^{-5}$ cal./sec., and $q_g=27.8\times10^{-5}$ cal./sec.

In the actual measurement, the temperature of the sample is raised usually by 0.2° for every 5 minutes. For 5 minutes $q_r'=0.0176$ cal., $q_g'=0.0834$ cal., and $\Sigma q'=0.101$ cal.

The test fluorine (about 20 g.) actually requires about 1 cal. at this temperature or neighbourhood for a rise of 0.2°, and so the above-mentioned heat loss amounts to more than 10%. If, however, the temperature of the wall of the case is kept at −199.5°C. by adjusting against −200°C. of the device, we shall have $\Sigma q'=0.0088$ (for 5 minutes).

This shows that the heat loss is about 0.9% of the heat required. In this way the heat loss must be kept small for making the experiment with a very small temperature rise of the sample and for obtaining a specific heat as near the true one as possible.

II. **Measurment of Specific Heat.** (1) Quantity of heat which is electrically given is (a) consumed in the temperature rise of the sample and (b) consumed in the temperature rise of the calorimeter itself, and (c) escapes outward, resulting in heat loss.

$$Q = I^2RZ = (CM+w)\times\Delta t+q = (CM+w)\times\Delta t'\ ,$$

where I is electric current flowing through the heating coil of the calorimeter, R resistance of the heating coil of the calorimeter, Z duration of heating, C specific heat of the sample, M mass of the sample, w water

equivalent of the device, and Δt rise of the temperature. Of these, w was determined in advance at various temperatures.

The heat escaping outward was, as stated before, about 1 to 2%, and was determined experimentally by a temperature-time curve. Thus the specific heat of the sample could be determined by the foregoing formula.

(2) *Correction for the heat loss and determination of the temperature rise.* As for the correction for the heat loss and the determination of the true temperature rise, the resistance of the platinum thermometer and the time were observed before and after the heating of the sample and the temperature-time curve was constructed (Fig. 5). From this curve the true rise of temperature was obtained. For instance, let us suppose that the temperature of the sample is not kept perfectly constant but has a tendency slightly to rise before the heating (A–B) and that the heating is begun at B (the time Z_1) and ends at C (the time Z_2), the sample then gradually being cooled along the C–D line. The lines AB and CD are extended as in the figure, and F is taken on the extension of the DC line so that ΔZ may be equal to BCE/Δt. If G is the point of intersection of the ordinate through F and the extension of the AB line, FG=$\Delta t'$ will be the true rise of temperature. The area BCE is determined on section paper.

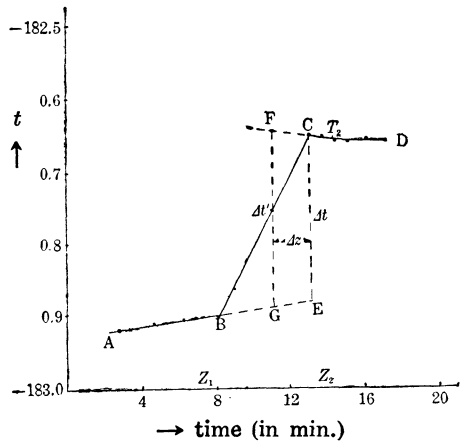


Fig. 5.

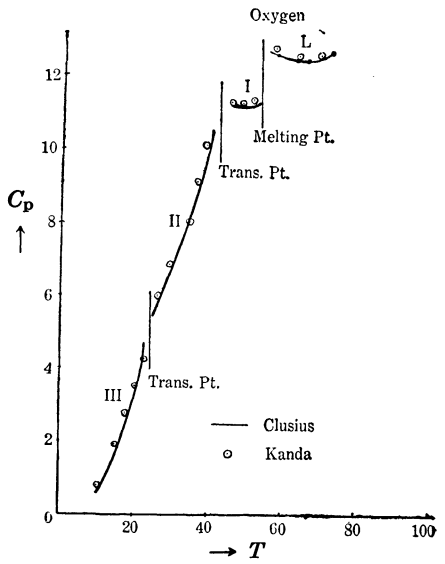


Fig. 6.

(3) *Water equivalent of the calorimeter.* See Table 2.

Table 2.

Temperature	Water equivalent	Temperature	Water equivalent
0°	2.141	−159.17	1.608
−15.50	2.120	−172.15	1.521
−37.85	2.074	−185.55	1.480
−50.17	2.041	−192.50	1.293
−58.56	2.024	−199.13	1.209
−67.21	2.005	−207.21	1.121
−86.17	1.950	−211.50	1.063
−94.54	1.921	−219.10	0.941
−103.13	1.889	−225.86	0.841
−118.55	1.821	−232.10	0.705
−127.34	1.782	−238.11	0.558
−134.85	1.744	−250.18	0.221
−145.76	1.690	−258.22	0.0045

III. Results of the Measurements. (1) *Oxygen.* In the preliminary experiment, measurement was carried out on liquid oxygen and solid oxygen. It was intended only for comparing its result with those already obtained by Eucken[4] and Clusius[5] (see Fig. 6). The values are shown in Table 3. The values obtained in the author's experiment were somewhat greater than those obtained by Clusius for liquid and solid I, but were close to the values reached by Eucken, which, however, are not given here.

Table 3.

Author	Eucken	Clusius	Kanda
Transition point I	23.5°K	23.8°K	24.1°K
,, ,, II	42.5	43.5	42.9
Melting point	54.1	54.1	54.3

(2) *Fluorine.* The quantity of the sample used in each experiment was about 0.5 mol. The result as reduced to the molecular heat according to the value of specific heat is tabulated below.

(4) Eucken, *Verhandl. Phys. Ges.*, **18** (1915), 4.
(5) Clusius, *Z. physik. Chem.*, B, **3** (1929), 41.

(a) Molecular heat. See Table 4.

Table 4.

T	C_p	C_v	θ	T	C_p
14.91	1.167	11.59	99.8	47.95	7.741
17.75	1.807	1.786	100.2	52.98	8.210
20.01	2.240	2.203	101.0	53.98	8.761
23.10	2.841			55.20	Melting point
25.42	3.440			57.50	10.84
29.50	4.310			62.51	10.92
32.00	4.795			67.49	10.98
35.40	5.561			77.10	11.12
39.11	6.280			83.41	11.20
43.10	7.120			85.19	Boiling point

(b) Melting point and heat of fusion. According to thermal analysis, the melting point is 55.20°K. The heat of fusion was determined by measuring the total heat quantity used for heating from a point a little below the melting point up to a point a little higher than this point, and by subtracting from this total heat quantity the sensitive heat used for the respective rises of temperature from the values of the specific heat of the solid and liquid. The heat of fusion is Q_s=372 cal./mol. The value of C_p is given in Fig. 7.

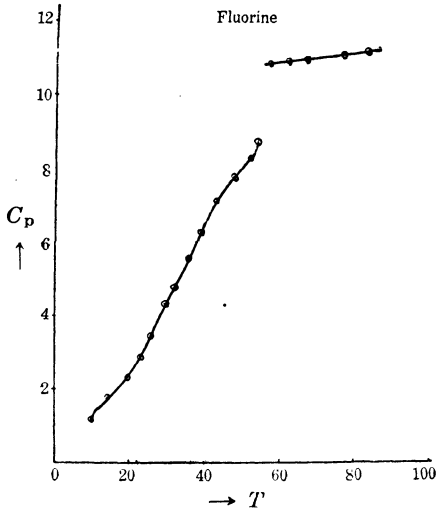


Fig. 7.

IV. **Characteristic Temperature and Entropy as Determined from the Result of Measurements.** (1) *Characteristic temperature.* Debye's law of T^3 for the atomic heat at constant volume is, strictly speaking, applicable only in the case of a monatomic and cubic system. But if the molecule of crystal of solid fluorine also can be regarded as making Debye's vibration at a temperature below 20°K as if it were a single atom, its molecular heat may be said to be proportional to the cube of

the absolute temperature. On this assumption, the characteristic temperature Θ was obtained from the molecular heat at three points below 20°K.

For determining the molecular heat at constant pressure, the following formula was used:

$$C_v = C_p - 0.0214\frac{T}{T_s}C_p^2,$$

where T_s is the melting point, 55.20°K.

The characteristic temperature Θ was determined from the value of C_v by using

$$C_v = \frac{12\pi^4}{5}R\left(\frac{T}{\Theta}\right)^3.$$

The results obtained at three points below 20°K well coincide with one another and show the above-mentioned assumption is right. Thus we have $\Theta=100.3$.

(2) *Entropy of fluorine vapour.* The entropy of fluorine vapour is obtained from

$$S = \int_0^T \frac{C_p}{T}dT.$$

There being no measured value of the molecular heat at temperatures below 15°K, the author made integration, using Debye's function and putting $\Theta=100.3$.

For determining $\int_0^T \frac{C_p}{T}dT$ as to the solid and liquid between 15°K and 55.2°K, and 56.2°K and 85.19°K, by using $T_s=55.2$, $Q_s=372$ cal. at the melting point and $T_\sigma=85.19$, $Q_\sigma=1581$ cal. (from the vapour pressure data) at the boiling point, a curve is drawn for the measured values of C_p at various temperatures against $\ln T$, and mensuration was graphically made of $\int C_p d\ln T$.

Further, to the value of entropy of such an ideal gas must be added correction for the entropy of a real gas.

From Berthelot's equation of state

$$PV = RT\left[1+\frac{9}{128}\frac{PT_c}{P_cT}\left(1-6\frac{T_c^2}{T^2}\right)\right],$$

where T_c is the critical temperature (144 for fluorine) and P_c is the critical pressure (55 atm.), and from the thermodynamical relation $\left(\frac{\partial S}{\partial P}\right)_T = -\left(\frac{\partial V}{\partial T}\right)_P$, we have

$$\Delta S = S_{\text{real}} - S_{\text{ideal}} = \frac{27}{32} R \frac{T_c^3}{T^3} \frac{P}{P_c} .$$

Putting $T=85.19°K$ (boiling point), $T_c=144°K$, $P_c=55$ atm., and $P=1$ atm. in this equation, we have $\Delta S=0.15$ cal./degree mol.

In fine, the entropy of fluorine vapour at the boiling point of 85.19°K is as follows:

$\int_0^{15} \frac{C_p}{T} dT = 0.49$ according to Debye's law, $\int_{15}^{55.2} C_p d \ln T = 5.86$ from the molecular heat of solid, $Q_s/T_s = 6.73$ at melting point, $\int_{55.2}^{85.19} C_p d \ln T = 5.46$ from the molecular heat of liquid, $Q_o/T_o = 18.60$ at boiling point, $\Delta S = 0.15$ correction for real gas, entropy of fluorine vapour at boiling point = 37.29 entropy unit.

Conclusion. As the results of the investigations recorded in the papers I–VIII the various properties of fluorine, knowledge of which is necessary for the study of fluorine at low temperatures, have been made clear. The experiments, however, were of such a nature that one or two instruments or apparatus were not enough for dealing with several kinds of materials or problems, but one material had to be studied from various points of view, and therefore various apparatus had to be devised for the purposes. Of these apparatus, some will not stand further use, because their lives have been exhausted by the highly corrosive nature of fluorine, while others will be usable in future studies of condensed gases.

In conclusion the author expresses his deepest gratitude to Prof. Aoyama, who advised him to get about the present investigation and who kindly directed him throughout his work. And he also wishes to express his heartful thanks to Prof. Katayama of the Tokyo Imperial University, who encouraged him throughout these studies. Sincere thanks are also due to Mr. Katsumi Oeda, who earnestly and incessantly assisted the author in the experiments dealing with very unmanageable and dangerous test substances. Further, the author embraces this opportunity of thanking the Japan Society for the Promotion of Scientific Research, who gave him great assistance for many years and placed at his disposal various kinds of apparatus required in the investigation and of thanking the Saitô Gratitude Foundation, who provided the Research Institute for Iron, Steel and Other Metals with the useful apparatus for obtaining low temperatures.

Cryogenic Section, Research Institute for Iron, Steel and Other Metals, Tôhoku Imperial University.

Studies on Fluorine at Low Temperatures. IX. Experiment on the Reaction between Solid Fluorine and Liquid Hydrogen.

By Shin-ichi AOYAMA and Eizo KANDA.

(Received August 12th, 1937.)

The reaction between fluorine and hydrogen is much complicated. Although close investigations have been made and numerous papers are still being published on the reactions between other halogens and hydrogen in the gaseous state, any systematic study has scarcely been made on the reaction between fluorine and hydrogen. Moreover, strange to say, the results obtained by the few who have studied this problem have been contradictory to one another. For illustrating this fact, the present authors will give the results of their tentative study on the reaction between solid fluorine and liquid hydrogen, and state their own opinion about it.

Moissan and Dewar[1] reported that explosion took place when a kind of test-tube with solid fluorine placed on its bottom was dipped into liquid hydrogen and the two elements were brought in contact with each other by breaking the bottom of the tube with a metallic bar thrust in at the upper end of the tube. But Wartenberg[2] and Eyring[3] reported that they saw no remarkable reaction between fluorine and hydrogen at ordinary or low temperatures, though they made no such experiment as Dewar's.

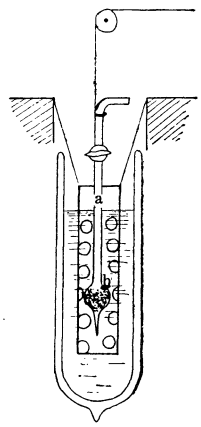
The present authors carried out the following experiments for ascertaining validity of these conflicting reports and the conditions for an explosion of this kind, if any.

I. Experiments and Results. Experiments such as Dewar's, in which, as stated above, a metallic bar is thrust in at the upper end of the tube, have the following drawback: (i) Air may be mixed in the samples, and (ii) it is doubtful whether the hydrogen and fluorine will come in contact with each other respectively in the true liquid and solid states, because the temperature of the metal is probably higher than that of the liquid hydrogen.

---

(1) Moissan and Dewar, *Compt. rend.*, **136** (1903), 641.
(2) Wartenberg, *Nachr. Ges. Wiss. Göttingen*, **1** (1930), 119.
(3) Eyring, *J. Am. Chem. Soc.*, **55** (1933), 2796.

In the authors' experiment, an apparatus as shown in the figure was used. A brass cylinder was hung in the liquid hydrogen. In this cylinder was also hung a glass bulb containing condensed fluorine. A thread by which the bulb was suspended through a roller was drawn out, and the bulb was dropped. A thin-walled capillary tube of the bulb was broken at the bottom of the cylinder, whereby the solid fluorine and liquid hydrogen touched each other. The following is the summary of the results of experiments:



(1) With an inside diameter of about 10 mm. at a and about 1 c.c. of fluorine in b; the weather cloudy. Immediately after the thread was drawn out and the bulb dropped, a slight explosion was heard and flames were seen on the surface of the liquid hydrogen (surface burning). In about one minute, the Dewar vessel burst, perhaps on account of explosion of the liquid hydrogen (or hydrogen gas) or of thermal strain in the vessel.

(2) With an inside diameter of 1 mm. at a and about 1 c.c. of fluorine in b; exposed directly to the sun. Even after the capillary tube was broken, no explosion took place. When the bulb, with the broken capillary tube but still containing the solid fluorine, was taken out, a slight explosion was heard.

(3) With an inside diameter of 6 mm. at a and about 1 c.c. of fluorine in b; exposed directly to the sun. Explosion took place after the breakage of the capillary tube and the Dewar vessel burst shortly after the explosion.

(4) With a diameter of 13 mm. at a and about 1 c.c. in b; exposed directly to the sun. Violent explosion was experienced and even the brass cylinder was crushed.

All these experiments being carried out outdoors and examined at a distance of about 1 metre from the apparatus, the observation might not be very accurate. Nevertheless, a little smoke of light brown colour was seen rising at the opening of the vessel in each case of (1), (3), and (4) after the breakage of the end of the tube.

II. **Discussion of the Results.** (1) Eyring's denial of the explosion of solid fluorine at the temperature of liquid hydrogen has no ground in experiments. The present authors' experiment was the first to be made after Dewar's investigation. The authors cannot fall in with Eyring's views that there is no explosion between solid fluorine and liquid hydrogen, and that the explosion, if any, is caused by contaminating

organic matters (Eyring admitted explosion of a mixture of hydrogen gas and fluorine gas at an ordinary temperature, but attributed it to organic matters such as rubber). In the authors' experiment, grease or other organic matters were not used.

(2) Explosion did not always occur. With a capillary tube as used in experiment (2), no explosion took place.

(3) The explosion was more frequent and violent with a tube having a larger diameter. In the authors' opinion, the reaction in question may be one not between the solid and liquid but in the gas phase existing over the solid and liquid, thus resulting in the above-mentioned explosion.

(4) No explosion, however, was experienced when the gases of the two elements were mixed in a large glass vessel at ordinary temperature —even when the vessel was exposed to the sun or to the light of a mercury lamp. (Explosion sometimes occurred when the wall of the vessel was fresh.) If so, how is the explosion at such a low temperature explained? The following questions arose in the authors' mind:

(a) Does a condensed gas become chemically more active when it is liquefied or vaporized?

(b) Is there any transition into an active form in solid fluorine at this temperature?

(c) Does any negative catalyser exist in this reaction in the gas phase? Can the explosion not be explained by degeneration at low temperature of the negative catalyser?

As for (a), fluorine fresh from the electrolyser was found, in the authors' experiment, more apt to chemical reaction than one which was first liquefied and condensed and then vaporized, but there was no ground for answering (a) in the negative.

As for existence of the transition referred to in (b), although there was a slight change in the colour of the solid fluorine at the temperature of the liquid hydrogen, such is also the case with other halogens. Determination of the molecular heat showed no transition.

As for degeneration of a negative catalyser, the results of the authors' investigation on the reaction of gases $H_2 + F_2 \rightarrow 2HF$ have shown that this reaction is greatly affected by the wall of the vessel used, and have pointed to the probability of negative catalysis of SiF_4 coming from the glass wall. It may also be conceived that a negative catalyser of this kind will completely freeze and will degenerate at such a low temperature as that of liquid hydrogen.

The foregoing, however, is a mere supposition, and the authors cannot give any definite opinion about the reaction in these seemingly heterogeneous phases until the reaction between hydrogen and fluorine in the gas phase is thoroughly investigated.

The authors wish to express their heartful thanks to the Japan Society for the Promotion of Scientific Research for a grant.

Cryogenic Section, Research Institute for Iron, Steel and Other Metals, Tohoku Imperial University.

Studies on the Aqueous Solutions of Some Chromic Salts. II. Modified Green Chromic Sulphate, Ol Green Chromic Chloride and Green Chromic Sulphate.

By Hideo SUEDA.

(Received October 12th, 1937.)

I. **Modified Green Chromic Sulphate.** When the aqueous solution of the violet chromic sulphate is boiled for two or three minutes, the colour of the solution changes to green and retains the colour even after it is cooled. The compound which is prepared from the violet sulphate in such a manner is generally called "modified green chromic sulphate". Many researches have already been reported on this compound. From the thermochemical point of view, A. Recoura[1] discovered the formation of sulphuric acid at the rate of one molecule per four chromium atoms in the solution, when the violet sulphate was transformed into this compound. Before Recoura, P. A. Favre and C. A. Valson[2] observed that one-third of the sulphate radical was precipitated by addition of barium chloride in the freshly prepared modified green sulphate solution. A. Recoura, having combined his results with this experiment, recognized that the following equation explains the reaction when the violet sulphate solution is heated. He gave therefore formula $[Cr_4(SO_4)_4O]SO_4$ to the modi-

(1) *Bull. soc. chim.*, [3], **9** (1893), 586; [3], **15** (1896), 315; *Ann. chim. phys.*, [7], **4** (1895), 494.

(2) *Compt. rend.*, **74** (1872), 1023.

fied green chromic sulphate. W. R. Whitney[3] also supported this idea after his measurement of the electric conductivity of this salt.

$$2Cr_2(SO_4)_3 + H_2O = [Cr_4(SO_4)_4O]SO_4 + H_2SO_4$$

After that, H. G. Denham[4] measured the *p*H-value of the solution in various dilutions, and the molecular weight of the salt was shown to be double or more that of the violet sulphate. Taking the experimental results proposed by T. W. Richards and F. Bonnet[5] as his idea, he assumed the formula $[Cr_4(SO_4)_4](SO_4)_2$ for this salt, and the hydrolysis of this salt in the solution was expressed according to its concentration as follows:

$$[Cr_4(SO_4)_4](SO_4)_2 + 2H_2O \rightleftarrows [Cr_4(SO_4)_4]SO_4(OH)_2 + H_2SO_4 \quad (1),$$

$$[Cr_4(SO_4)_4](SO_4)_2 + 4H_2O \rightleftarrows [Cr_4(SO_4)_4](OH)_4 + 2H_2SO_4 \quad (2),$$

where the reaction of equation (1) takes place in such a concentration as that experimented on by Recoura, while equation (2) is suitable for a very dilute solution. This consideration enabled him to explain his experiment, and his idea seems nowadays to have been generally adopted.

But, the complex ion $[Cr_4(SO_4)_4]^{4+}$ is not easily deduced from Werner's co-ordination theory, and there are some questions on the number of chromium atoms in the complex radical. The salt $[Cr_4(SO_4)_4](SO_4)_2$ which Denham assumed, should be obtained, according to his idea, when the infinitely concentrated violet sulphate solution is heated. But the compound, which is actually produced when the crystals of violet sulphate hydrate are heated, is difficultly soluble in water, contrary to the expectation from Denham's idea. Such circumstances tempted the author to study this compound.

(1) *Relation between the concentration of the modified green sulphate and the quantity of the sulphate ion precipitable by barium chloride.* According to Denham, the complex ion of the modified sulphate $[Cr_4(SO_4)_4]^{4+}$ is not changed, whatever the concentration of the solution may be. If so, the total quantity of the sulphate radical should be three times the quantity of the sulphate ion to be precipitated by barium chloride in any concentration. As the experimental proof of it was wanting, the author has determined the quantity of barium sulphate produced on adding concentrated barium chloride to the solutions in three different

(3) *Z. physik. Chem.*, **20** (1896), 40.
(4) *Z. anorg. allgem. Chem.*, **57** (1908), 361.
(5) *Z. physik. Chem.*, **47** (1904), 29.

concentrations prepared by immediate cooling after boiling violet sulphate for three minutes, i.e. 0.06, 0.005 and 0.0006 mol/l. (molecular formula of violet sulphate being $Cr_2(SO_4)_3 \cdot 17H_2O$). The ratio of the precipitated sulphate ion to the total sulphate radical are shown in Table 1.

Table 1.

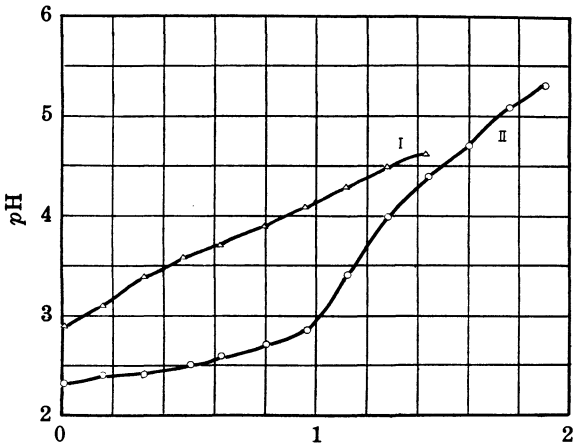
Conc. of the solution (mol/l.)	0.06	0.005	0.0006
Precipitated sulphate (%)	34.6	50.5	64.6

These results show that the percentage of sulphate ion depends on the concentration of the solution, and cannot be deduced from Denham's idea. In other words, the concentration of the solution controls the quantity of the sulphate radical in the complex ion of the modified green sulphate, and the quantity was between one-third and two-thirds of the total sulphate in the range of these concentrations.

(2) *The relation between the concentration of the solution and the quantity of sulphuric acid formed in the solution.* As described above, Recoura and Whitney showed that one molecule of sulphuric acid was liberated for four chromium atoms, when the violet sulphate was transformed into the modified sulphate. The concentrations of the solutions employed by them were moderately great, i.e. 1/12 and 1/30 mol/l., and the case of a smaller concentration has not yet been studied. The present author has examined such a case. Electrometric titration has been applied for this purpose, by using the antimony electrode[6]. A sodium hydroxide solution was added to 1/200 mol/l. violet and modified green sulphate solutions. The latter green sulphate solution was prepared from the former violet sulphate solution by the usual method. The titration curves are shown in Fig. 1. The curve of violet sulphate (I) smoothly rises, while that of modified green sulphate (II) begins at a lower *pH*-value than curve I, the increase of *p*H is not considerable till the molecular ratio of sodium hydroxide and chromic sulphate becomes equal, and it becomes noticeable after the point of equilibrium is passed. This result shows that one sulphuric acid molecule is liberated for four chromium atoms, even when a modified sulphate is formed in such a dilute solution. As described in (1), the relative quantity of sulphate ion increases when the

(6) T. Uemura and H. Sueda, this Bulletin, **8** (1933), 1.

concentration of the solution changes from 6/100 to 1/200 mol/l., but the relative quantity of the liberated sulphuric acid is independent of the concentration of the solution.



Molecular ratio [NaOH] : $[Cr_2(SO_4)_3]$

I: Violet chromic sulphate.

II: Modified green chromic sulphate.

Fig. 1.

(3) *Absorption spectra.* The absorption spectra, given by the following six solutions, were measured with the concentration of 1/100 N: (a) solution immediately cooled after heating, (b) solution prepared to *p*H 1.0 by adding sulphuric acid, (c) solution standing for 24 hours, (d) solution standing for several days, (e) solution in which the liberated sulphuric acid was neutralised with sodium hydroxide, and (f) solution in which the sulphate ion was removed by filtering off barium sulphate after the addition of the equivalent amount of barium chloride. These solutions show similar curves which can be represented by one curve (I in Fig. 2). Curve I compares with that given by $[Cr(H_2O)_5OH]Cl_2$, but the absorption capacity of the former is higher than that of the latter in shorter wave length. The absorption of the modified sulphate solution does not show any change by the addition of acid, while the colour of the hydroxo-pentaquo chromic chloride solution becomes bluish violet. The properties of these two salts were

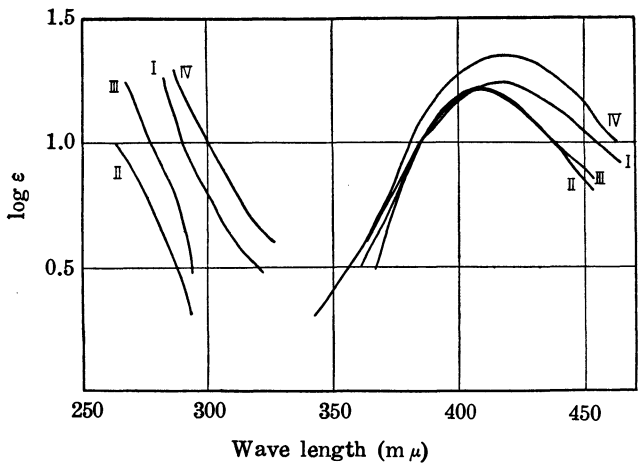


Fig. 2.

essentially different at this point, and the author cannot accept the idea of H. T. S. Britton[7].

As an addition of acid to the modified green chromic sulphate solution does not influence the absorption, the compound must be ol-salt. The removal of sulphate ion or the neutralisation of the liberated acid does not show any effect nor does it change the curves, so they are independent of the complex ion.

(4) *Constitution of the modified green chromic sulphate.* Denham considered that the modified sulphate should contain four chromium atoms in its complex radical. This consideration came from his confirmation that the molecular weight of its cation could be double that of violet sulphate which was assumed as $[Cr_2--]^{6+}$. As the author, however, indicated in the previous paper that the cation of violet sulphate should be $[Cr(H_2O)_6]^{3+}$, the cation of modified sulphate must be considered to contain two chromium atoms, since it has about double the molecular weight of $[Cr(H_2O)_6]^{3+}$.

It has been shown that in (1) one-third of the sulphate radical of modified sulphate can be found as ion in the solution of 6/100 mol/l., but when the concentration decreases to 6/10000 mol/l., the quantity of the sulphate ion becomes two-thirds of whole sulphate radical, while in (2) ratio of the liberated sulphuric acid to the chromium atom does not show any relation with its concentration, that is, one sulphuric acid molecule is produced for four chromium atoms, and in (3) the modified green sulphate must be ol-compound. After all, the author considers the following schema for the formation of the modified green sulphate:

$$2[Cr(H_2O)_6]_2(SO_4)_3 \longrightarrow [(H_2O)_3Cr(OH)(SO_4)_2Cr(H_2O)_3]_2SO_4 + H_2SO_4$$

(concentrated solution, about 6/100 mol/l.),

$$2[Cr(H_2O)_6]_2(SO_4)_3 \longrightarrow [(H_2O)_4Cr(OH)(SO_4)Cr(H_2O)_4]_2(SO_4)_3 + H_2SO_4$$

(dilute solution, about 6/10000 mol/l.),

and when the concentration of the solution is intermediate between the above-mentioned, a mixture of both salts can be obtained. The reason for giving the μ-sulphato form to the modified green sulphate will be explained later. The number of water molecules in the complex radical has been selected in order to comply with the demand of Werner's co-ordination theory.

(5) *Relation between the time of standing of the modified green chromic sulphate and the quantity of the sulphate radical precipitated by*

(7) *J. Chem. Soc.*, **127** (1925), 2120.

barium chloride. As mentioned above, 50.5% of the sulphate radical was precipitated by barium chloride in the fresh modified sulphate solution, but after standing for 24 and 130 hours, 53.6 and 59.1% of sulphate could be respectively precipitated. This shows that the sulphate radical in the complex radical decreases proportionally to the time of standing of the solution. This can be expressed as follows:

$$[(H_2O)_3Cr(OH)(SO_4)_2Cr(H_2O)_3]^+ \ (1) \longrightarrow [(H_2O)_4Cr(OH)(SO_4)Cr(H_2O)_4]^{3+} \ (2).$$

From the quantity of the sulphate ion in the fresh solution, the ratio of the quantity of compound (1) to that of (2) should be 1:1.07, while it becomes 1:3.44 after standing for 130 hours. In spite of such a change, the absorption spectra do not differ. This result cannot be explained unless the absorption spectra of these two compounds are quite similar.

II. **Ol Green Chromic Chloride.** As described in the previous section, when the colour of the violet chromic sulphate solution is once changed to green by heating, the latter colour does not easily change even at a low temperature. But, the violet chromic chloride solution returns to bluish violet, in proportion to the depression of the temperature, though it is green in the hot state producing $[Cr(H_2O)_5OH]Cl_2$ according to Bjerrum[8]. It is very interesting to note that sulphate and chloride behave differently in spite of the same cation[9]. The author already published a paper[10] of an analogous example, i.e. diaquo-tetrammine-cobaltic sulphate changes to ol-compound by the addition of an alkali, while the corresponding chloride has not a similar reaction.

Although the violet chromic chloride solution changes reversibly by heating and cooling, the hydroxo-pentaquo-chromic chloride solution given by adding equivalent sodium hydroxide to violet chloride solution does not return to the original hydroxo-compound when it is cooled after heating, but is transformed into another salt which is called, in this paper "ol green chromic chloride".

(1) *Absorption spectra.* Absorption spectra of the four following solutions were observed: (a) solution prepared by cooling immediately

(8) *Z. physik. Chem.*, **59** (1907), 339.

(9) Violet nitrate solution behaves similarly to chloride: it returns to bluish violet after cooling. According to H. Brinzinger and F. Jahn, *Z. anorg. allgem. Chem.*, **229** (1936), 410, $[Cr(NH_3)_6]^{3+}$ and $[Cr(en)_3]^{3+}$ are transformed into "zweischalige" complex salts $[[Cr(NH_3)_6](SO_4)_4]^{5-}$ and $[[Cr(en)_3](SO_4)_4]^{5-}$ by ammonium sulphate, but ammonium nitrate cannot transform them into the salts of this kind.

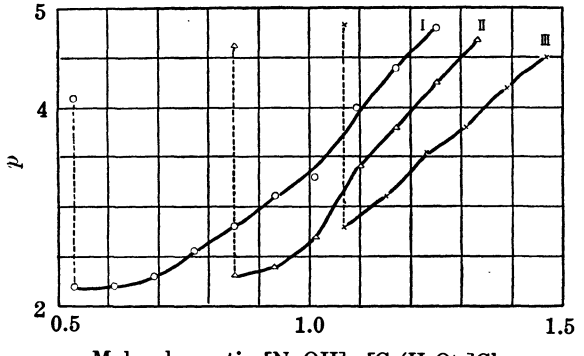
(10) This Bulletin, **10** (1935), 50.

after boiling 1/100 mol/l. violet chloride $[Cr(H_2O)_6]Cl_3$ solution for two or three minutes (curve II in Fig. 2), and (b) solution obtained by treating 1/100 mol/l. green chloride $[Cr(H_2O)_4Cl_2]Cl$ similarly as above (curve III). As these two curves are similar to that of violet chloride, it can be said that this violet chloride at least predominated in the solutions then obtained. Their *p*H-values do not change before and after heating . (c) 1/100 mol/l. violet chloride solution was prepared by using 1/100 N sodium hydroxide as solvent (precipitation then occurred but was dissolved by heating the solution), and it was heated to boiling and then cooled immediately. (d) Solution obtained by adding concentrated hydrochloric acid to solution (c) to *p*H 1.1.

As solutions (c) and (d) show similar absorption spectra, they can be represented by one curve (curve IV in Fig. 2) which is different from that given by hydroxo-pentaquo salt. As solution (c) showed no different absorption on the addition of acid, an ol-compound must be assumed to be produced when the solution of $[Cr(H_2O)_5OH]Cl_2$ was heated.

(2) *Potentiometric titration.* To confirm that the "ol green chromic chloride" is actually an ol-compound, and to determine the number of OH in the complex radical in case of ol-compound, potentiometric titration was applied after heating and immediately cooling the solutions, where violet chloride and sodium hydroxide was mixed in various proportions.

When the violet chloride was dissolved to 1/100 mol/l. in 0.0053 N sodium hydroxide, the resulting solution showed *p*H 4.1, but *p*H 2.2 after heat treatment[11]. The solution was then titrated with sodium hydroxide, the titration curve being indicated in Fig. 3 (curve I). The solutions, where the molar ratios of violet chloride to sodium hydroxide were respectively 1.00 to 0.85 and 1.00 to 1.07, showed *p*H 4.6 and 4.8 before heating. The *p*H-values, however,



Molecular ratio [NaOH] : $[Cr(H_2O)_6]Cl_3$

Fig. 3.

(11) This was done as in the case of preparing the modified sulphate from the violet sulphate.

changed to 2.3 and 2.8 respectively after heat treatment. The titration curves are shown in Fig. 3 (curve II and III respectively). This decrease of *p*H-value of the solution of violet chloride with sodium hydroxide after heat treatment must be due to the formation of ol-compound. The change in inclination of the titration curve suggested that the number of OH contained in the complex radical is equal to that of the chromium atoms in the radical.

(3) *Constitution of the ol green chromic chloride.* Bjerrum's "latent basic salt"[12] perhaps corresponds to ol green chromic chloride discussed in this paper. But as the preparation method is somewhat different from Bjerrum's, it is probably vain to compare these two compounds[13].

In (1) and (2), it has been proved that "ol green chromic chloride" is an ol-compound, and the number of OH and that of the chromium atoms in the complex radical are equal. In order to examine the existence of the chlorine atom in the radical, an excess of silver nitrate was added to cold solution of this salt, and the quantity of immediately precipitated silver chloride was measured. As all chlorine atoms was then precipitated, they cannot be contained in the complex radical. Summarising the facts observed, the author considers the following equation for the formation of this salt and gives it the formula shown below:

$$Cl_2[(H_2O)_5CrOH] + [OHCr(H_2O)_5]Cl_2 \rightarrow [(H_2O)_4Cr(OH)_2Cr(H_2O)_4]Cl_4 .$$

The author has not yet obtained any confirmation that this salt contains two chromium atoms in its complex radical. But such has been deduced from the two following points: (i) Pfeiffer[14] already proved the formation of $[(en)_2Cr(OH)_2Cr(en)_2]X_4$ on heating $[Cr(en)_2H_2OOH]X_2$, and (ii) the salt produced by heating the violet sulphate is di-chromium salt and the absorption spectra of the di-chromium salt is somewhat similar to that of this salt. According to Werner's co-ordination theory, eight molecules of water must exist in the complex radical in this case. Instead of ol-compound, the salt in question can be assumed to be oxo-compound which is closely related with ol-compound. But in general ol-compound is difficultly transformed into oxo-compound, except by heating or by standing for a long time. It may therefore be reasonable to take the ol-combination in this case.

(12) *Z. physik. Chem.*, **59** (1907), 336, 581; **73** (1910), 724; N. Bjerrum and C. Faurholt, *ibid.*, **130** (1927), 585.

(13) Properties of the salt depend on the method of preparation, as Bjerrum has pointed out in his papers.

(14) *Z. anorg. allgem. Chem.*, **56** (1908), 261.

III. **Green Chromic Sulphate $[Cr_2(SO_4)_3(H_2O)_3]$ and $[Cr_2(SO_4)_3(H_2O)_6]$.** When violet sulphate is heated in aqueous solution, a modified green chromic sulphate, i.e. μ-ol-mono- or di-sulphato-dichromic sulphate is produced, but when it is heated in a crystalline state at 90°C., it changes into the green chromic sulphate $[Cr_2(SO_4)_3(H_2O)_3]$[15]. This green sulphate cannot be rapidly dissolved in water. It took about 100 minutes to dissolve 2 g. of this salt in 500 c.c. of water at 25°C. with constant stirring. The fresh solution so obtained shows an absorption analogous to that given by the solution of $[Cr_2(SO_4)_3(H_2O)_6]$[15], and neither solution gives immediately a precipitate of barium sulphate on the addition of barium chloride. These two salts, therefore, become the same substance in solution.

The quantity of the sulphate radical, that is precipitable by barium chloride, increases proportionally to the time of standing. In order to explain this fact, A. Colson[16] assumed three types of green chromic sulphate from his thermochemical studies: (a) all sulphate radicals, (b) two-thirds and (c) one-third, are masked in the complex radical:

$$[(H_2O)_3Cr(SO_4)_3Cr(H_2O)_3] \longrightarrow [(H_2O)_4Cr(SO_4)_2Cr(H_2O)_4]SO_4$$
$$\longrightarrow [(H_2O)_5Cr(SO_4)Cr(H_2O)_5](SO_4)_2 \quad (1).$$

On the other hand, he considered that $[Cr_2(SO_4)_3(H_2O)_6]$ is in equilibrium with the modified green chromic sulphate in aqueous solution:

$$[(H_2O)_3Cr(SO_4)_3Cr(H_2O)_3] \rightleftarrows [(H_2O)_3Cr(OH)(SO_4)_2Cr(H_2O)_3]SO_4H$$
$$\rightleftarrows [(H_2O)_3Cr(OH)_2(SO_4)Cr(H_2O)_3](SO_4H)_2 \quad (2).$$

The relation between these two schemata is not clear to the present author. After taking the absorption spectra, the author studied to know which of these schemata should be taken in this case, and, besides, examined some reactions of the solution with alkali and in heat treatment.

(1) *Relations found on leaving the aqueous solution of the green chromic sulphate to stand.* 1/112 mol/l. green chromic sulphate solutions was kept for 10 min., 245 min., 25.5 hours and 90 hours after the salt was completely dissolved, and their absorption spectra were observed. The absorption spectra of the first two solutions (10 min. and 245 min.) are similar to each other and are represented by one curve in Fig. 4 (curve I), and the other two solutions gave also analogous absorption curves, which

(15) A. Sénéchal, *Compt. rend.*, **159** (1914), 243.

(16) *Bull. soc. chim.*, [4], **1** (1907), 438, 889; **3** (1908), 90; *Ann. chim. phys.*, [8], **12** (1907), 433.

are represented by another curve (curve II in Fig. 4). The absorption spectra of the modified green chromic sulphate is given as curve III. If the schema (2) can express the reaction which occurs on leaving the aqueous solution of green chromic sulphate to stand, the production of the modified sulphate being recognised, curve II should come between curve I and III. However, curve II is found to be outside the other two in the ranges of wave lengths below 300 mμ and above 410 mμ. The *p*H-value does not change on standing, and remains at 2.5. For these reasons, the author believes this reaction must be explained by schema (1) but not by (2).

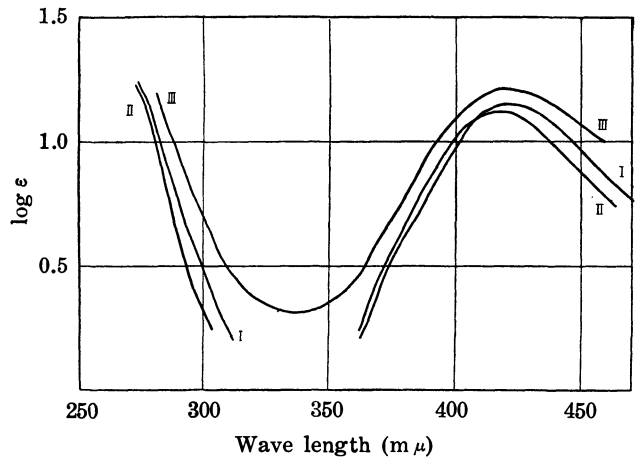


Fig. 4. The absorption spectra of green chromic sulphate.

After standing for 60 minutes and 75 hours, 1/200 mol/l. solutions of the salt precipitated respectively 14.9 and 54.6% of the sulphate radical on the addition of barium chloride. The precipitation of barium sulphate cannot be observed in the fresh solution, so the reaction $[Cr_2(SO_4)_3(H_2O)_6] \rightarrow [Cr_2(SO_4)_2(H_2O)_8]SO_4$ is assumed to take place rapidly as compared with the reaction $[Cr_2(SO_4)_2(H_2O)_8]SO_4 \rightarrow [Cr_2(SO_4)(H_2O)_{10}](SO_4)_2$. $[Cr_2(SO_4)_3(H_2O)_6]$ and $[Cr_2(SO_4)_2(H_2O)_8]SO_4$ can be assumed to exist in different ratios in the solutions after standing for 10 min. and 245 min., but their absorptions are alike. This must be caused by the originally similar absorption of the two salts. In this case, as well as in the case of modified green chromic sulphate, it seems that the absorptions were not much influenced, whether the chromium combination in the radical be with two bridges or three.

(2) *Reaction with alkali.* Sodium hydroxide was added to the solutions of green chromic sulphate, which were left for 110 minutes and 90 hours respectively, in order to make the molecular ratio $[Cr_2(SO_4)_3(H_2O)_6] : [NaOH] = 1.00 : 1.26$. The *p*H-values were the same and 4.2. Both solutions gave similar absorption curves represented by curve III in Fig. 4, and the curve is similar to that given by the modified

green chromic sulphate. From this result, it is evident that when the green sulphate solution is left for a time, the modified sulphate is obtained by the addition of sodium hydroxide. However, potentiometric titration is necessary to confirm it.

1/200 mol/l. green sulphate solutions were titrated with 8/100 N sodium hydroxide after standing for 3 hours and 75 hours respectively. The titration curves are shown in Fig. 5 (curve I and II). Next, sodium hydroxide was added to the solution, which was left for 75 hours, to make the molecular ratio $[Cr_2(SO_4)_3(H_2O)_6]$: [NaOH]=1.0: 1.6. The solution then obtained was titrated with hydrochloric acid, and the result is shown by curve III.

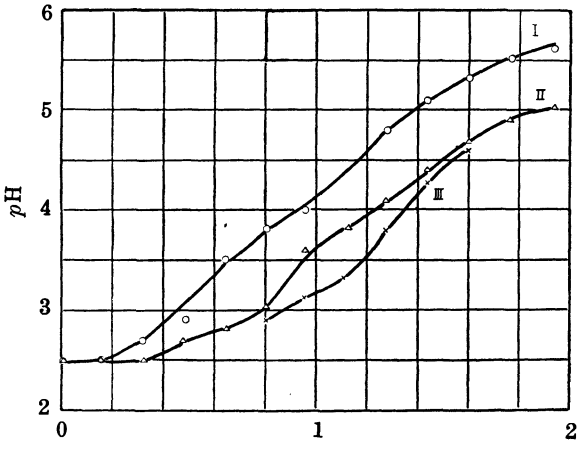


Fig. 5.

The time of standing has no relation with *p*H-value of the solution, when sodium hydroxide is not added (*p*H=2.5). This shows that ol-compound or free acid is not produced by standing. Titration curves (I and II) do not so rapidly rise at the beginning of the process, and this is explained by assuming that a part of the green sulphate is converted into ol-compound when sodium hydroxide is added to the solution. This assumption is also confirmed by the disagreement of curves II and III. In conclusion, the green sulphate is transformed into the modified sulphate in aqueous solution by the addition of sodium hydroxide. This is the reason why the author assumed the sulphato-bridge in the formula of the modified sulphate. As shown in Fig. 5, the elevation of curve I begins earlier than that of curve II, and this means that $[Cr_2SO_4(H_2O)_{10}](SO_4)_2$ can more easily be converted into ol-compound than $[Cr_2(SO_4)_2(H_2O)_8]SO_4$ or $[Cr_2(SO_4)_3(H_2O)_6]$.

(3) *Reaction in heat treatment.* The heat treatment[11] was performed with 1/200 mol/l. solutions, which had been left for 10 minutes and 75 hours respectively. The absorption curves given by these solutions thoroughly coincide with curve III in Fig. 4.

Titration curves of the solutions are shown in Fig. 6, where curves I and II respectively belong to the solutions left for 3 hours and 75 hours. These curves are analogous to that of modified green sulphate (Fig. 1).

The author next measured the quantity of sulphate radical which can be precipitated by barium chloride, and obtained the results summarised in Table 2. As for the solution left for one hour, the precipitated sulphate radical is smaller before the heat treatment, but it becomes larger after treatment, and for the solution left for 75 hours, this relation is quite contrary. The disagreement between the quantities of the precipitable sulphate radical obtained from these two solutions after heat treatment, comes perhaps from the difference of the heating intervals, and the values are approximately that obtained from the modified sulphate (50.5%). Hence, modified green chromic sulphate can always be obtained by heating the green chromic sulphate in aqueous solution.

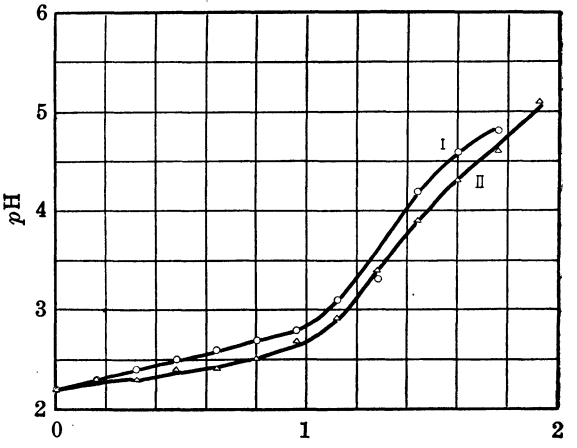


Fig. 6.

Table 2. Quantity of the precipitated sulphate radical (%).

Time after dissolution	1 hour	75 hours
Before heat treatment	14.9	54.6
After heat treatment	53.9	47.4

Summary.

(1) For the modified green chromic sulphate, the formula μ-ol-mono- or di-sulphato-di-chromic sulphate has been deduced (i) from its absorption spectra, (ii) from the quantities of sulphuric acid produced

when this salt is formed from violet chromic sulphate, and (iii) from the sulphate ions which is precipitated by barium chloride in various dilutions.

(2) When hydroxo-pentaquo chromic chloride solution was heated, the author recognized the production of ol-compound, to which the formula di-ol-octaquo-di-chromic chloride has been given.

(3) The modification of the green chromic sulphate in aqueous solution, produced on standing, or on heating, or on adding sodium hydroxide, has been discussed.

In conclusion, the author wishes to express his sincere thanks to Assist. Prof. T. Uemura of the Tokyo University of Engineering for his kind encouragement.

Laboratory of Inorganic Chemistry,
Tokyo University of Engineering (Tokyo Kogyo-Daigaku).

Über das durch Zersetzen von Schwefelwasserstoffwasser hergestellte disperse System von Schwefel und dessen Reaktion mit dispersem Quecksilber.

Von Naoyasu SATA.

(Eingegangen am 26. November 1937.)

I. **Einleitung.** Dass das H_2S-Wasser oder der H_2S unter Vorhandensein von Wasserdampf, thermisch zersetzt wird und bläuliche Flüssigkeit mit weisser Trübung ergibt, ist schon seit C. Geitner,[1] A. Gautier[2] usw. beobachtet worden. Obwohl diese Forscher diese Flüssigkeit als ein kolloid-disperses System von Schwefel aufmerksam gemacht hatten, fehlt noch weitere Untersuchung von kolloidchemischem Standpunkt aus. Ich habe zufälligerweise gefunden, dass beim Zuschmelzen eines H_2S-Wasser haltendes Probierglases ein ähnlicher Vorgang vor sich läuft; nämlich nach dem Zuschmelzen das H_2S-Wasser zu einer weiss trübe, bläulich opaleszierenden Flüssigkeit umgewandelt wird. Eingehende Untersuchung hat gezeigt, dass sie eine Art hydrophobes

(1) C. Geitner, *Ann.*, **129** (1864), 364.
(2) A. Gautier, *Compt. rend.*, **142** (1906), 1469.

Schwefel-Sol ist, wie Weimarnsches Sol[3] oder durch Explosionsmethode hergestelltes Sol.[4] Da die Herstellungsweise so einfach und praktisch ist wurde einige Eigenschaften dieses Sols, sowie die Reaktion von demselben mit dispersem Quecksilber im folgenden behandelt.

II. **Die Methodik.** Zum Zweck der Vorlesungsdemonstration ist es sehr einfach und zwar erfüllt man etwa 1/3 von einem Probierglas mit H_2S-Wasser und schmilzt es zu, unter Berücksichtigung das Erhitzen der Flüssigkeit möglichst zu vermeiden. Der H_2S in der Nähe der Schmelzstelle wurde unter Vorhandensein genügender Wasserdämpfe thermisch zersetzt und scheidet das Schwefel in dispersem Zustand aus. Während sowie nach dem Zuschmelzen, ersieht man milchweisse Flüssigkeit an der Innenwand des Probierglases herunterströmt, welche beim Zusammenmischen mit H_2S-Wasser ein weiss trübes, bläulich opaleszierendes System ergibt. Dieses Sol, wie die andere von hydrophober Natur, ist nicht sehr beständig und fängt nach dem Entstehen gleich an zu koagulieren und absetzen. Während dieses Stadiums, zeigt das System genau denselben polychromische Verlauf, wie die andere Sole nach Weimarn bzw. Auerbach[5]. Neue Methode ist dadurch bevorzugt, dass es dabei keine besondere Vorbereitung an Reagentien verlangt wird, wie z.B. Lösungen bestimmter Konzentrationen vorzubereiten, Mengenverhältnis der Reaktionsflüssigkeiten zu berücksichtigen usw. wie bei den anderen Methoden.

Zum Herstellen grösserer Menge empfehlt es sich, als Reaktionsgefäss, ein enghalsiges Kolben, wie z.B. ein Messkolben, benutzen. Am besten habe ich ein Quarz-Messkolben genommen, welches etwa bis zur Hälfte H_2S-Wasser enthält, wie in Abb. 1 skizziert ist. Wenn man an den Hals des Kolbens stark erhitzt, wird die Flüssigkeit bläulich, bläulich weiss opaleszierend und endlich milchweiss mit rötlicher Durchsichtsfarbe. In der Literatur wurde hingewiesen, dass die Schwefelsäure bei diesem Zersetzen entstehen würde[1][2][6]. Aber nach meinem Versuch lässt die Schwefelsäure, weder mit $BaCl_2$-Lösung noch an Lackmuspapier, sich nachweisen.

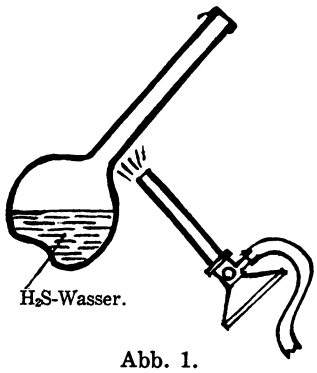
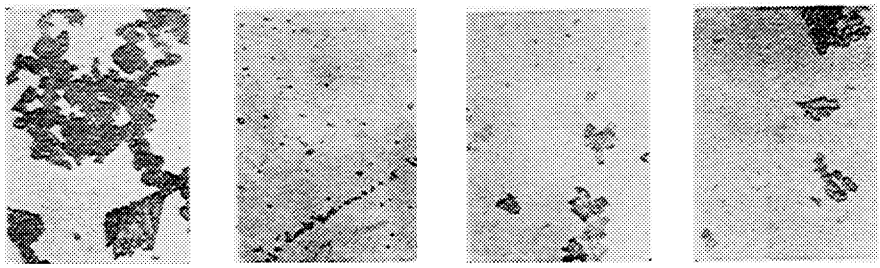


Abb. 1.

(3) P. P. von Weimarn und B. W. Malyschew, *Kolloid-Beihefte*, **8** (1911), 216.
(4) P. P. von Weimarn und N. Sata, *Kolloid-Z.*, **66** (1934), 1; N. Sata, dieses Bulletin **11** (1936), 501.
(5) R. Auerbach, *Kolloid-Z.*, **27** (1920), 223.
(6) J. W. Mellor, "A Comprehensive Treatise on Inorganic and Theoretical Chemistry," Bd. X, 130, London (1923).

III. **Der Absetzungsvorgang des dispersen Systems und die mikro- und ultramikroskopische Untersuchung des Sedimentes.** Von dem dispersen System, wie erwähnt hergestellt ist, wurde der übrig gebliebene H_2S durch Kochen bzw. durch Bestrahlen von USW.[7] ausgetrieben. Die Absetzungsvorgänge der dispersen Systeme und die Resultate der mikro- und ultramikroskopischen Untersuchungen der Sedimente sind in folgender Tabelle 1, Abb. 2-a, 2-b, 2-c und 2-d zusammengestellt.



(a) (b) (c) (d)

Abb. 2. (Vergrösserung = 305×)

Von den Versuchsergebnissen, möchte ich auf folgenden Punkte aufmerksam machen.

(1) *Einfluss von Kochen.* Beim Vergleich der Probe (a) und (c) in der Tabelle 1, ersieht man, dass zum Absetzungsvorgang das Kochen kaum einen Einfluss auszuüben ist. Aber die mikro- und ultramikroskopische Untersuchung lässt sich bedeutenden Unterschied zwischen ihnen erkennen; nämlich scheidet die Probe (a) (H_2S-haltiges Präparat) viel grössere Kristalle als (c) (durch Kochen H_2S ausgetriebenes Präparat) aus. Daraus könnte man konstatieren, dass im vorigen Fall sich der H_2S allmählich zersetzte und dadurch ausgeschiedener Schwefel zu grösseren Kristallen angehäuft hatte.

(2) *Wirkung von USW.* Die Wirkung von USW. auf dem dispersen System ist besonders bemerkenswert. Die Mikro-Aufnahme des Sedimentes von USW.-bestrahltem Präparat (b) gibt ein eigenartiges Bild, wie aus der Abb. 2-b ersichtlich ist. Darauf ist es deutlich zu erkennen, dass die grössere Kristalle darin ganz und gar ausfallen und nur verhältnismässig kleine Kriställchen in ausserordentlich gleichmässiger Dimension ausgeschieden sind. Das könnte man vielleicht so erklären,

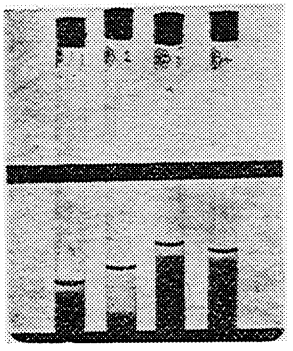
(7) Abkürzung von Ultraschallwellen; über Entgasung durch USW., siehe L. Bergmann, "Der Ultraschall", 178, Berlin (1937); G. Schmid, *Angew. Chem.*, **49** (1936), 117.

Tabelle 1.

<table>
<tr><th></th><th>a</th><th>b</th><th>c</th><th>d</th></tr>
<tr><td>Behandlung.</td><td>H_2S-haltig. (Kontrolle)</td><td>USW. bestrahlt für 1 Min.</td><td>2 Min. gekocht.</td><td>2 Min. gekocht u. dann 1 Min. USW.</td></tr>
<tr><td>Anfangs.</td><td>Milchweiss trübe und fast undurchsichtig; Durchsichtsfarbe ist organe-rot.</td><td>Trübung und Farbton ist genau wie (a); riecht noch schwach nach H_2S.</td><td colspan="2">Milchweiss trübe, ganz undurchsichtig; riecht vollkommen nicht nach H_2S.</td></tr>
<tr><td></td><td></td><td></td><td colspan="2">Nach 1 Tag: 1 mm. von oben ist ganz klar u. unten undurchsichtig wie (a).</td></tr>
<tr><td>Nach 1 Tag.</td><td>1 mm. von oben ist ganz klar; unten undurchsichtig.</td><td>Setzt schon halbdurchsichtig ab.</td><td colspan="2">Nach 3 Tagen.</td></tr>
<tr><td rowspan="2">Nach 3 Tagen.</td><td rowspan="2">1/2 von oben ist fast klar; unten noch weiss trübe mit violetter Durchsichtsfarbe.</td><td rowspan="2">Setzt fast ganz klar ab.</td><td>1/2 von oben ist fast klar und unten weiss trübe wie (a).</td><td>1/2 von oben ist bläulich klar mit Opaleszenz; unten wie (a) bzw. (c).</td></tr>
<tr><td colspan="2">Nach 6 Tagen.</td></tr>
<tr><td>Nach 6 Tagen.</td><td>Fast ganz klar.</td><td>Ganz klar.</td><td rowspan="2">Fast ganz klar. Durch Hand-Schütteln nicht peptisierbar.</td><td rowspan="2">Flüssigkeit ist bläulich opaleszierend. Das System ist durch Hand-Schütteln wieder milchweisses, in Durchsicht rotes Sol peptisierbar.</td></tr>
<tr><td>Nach dem Absetzen.</td><td colspan="2">Durch Hand-Schütteln nicht wieder peptisierbar u. setzen sofort ganz klar ab.</td></tr>
<tr><td>Mikro- und ultramikroskopischer Befund der Sedimente.</td><td>Sediment besteht grobe Kristallen in verschiedenen Formen (Platten, Prismen, Nadeln, Oktaedern, Kügeln usw.) aus. Ultramikroskopische Teilchen sind sehr wenig u. fast keine in Brownscher Bewegung. (Siehe Abb. 2-a)</td><td>Fehlt hier die grössere Kristalle vollkommen aus und nur kleine Kristalle in ähnlicher Grösse sind vorhanden. Ultramikroskopische Teilchen sind mehr als in (a), die aber kaum in Brownscher Bewegung sind. (Siehe Abb. 2-b)</td><td>Kristalle in verschiedener Formen u. Grössen, wie in (a) sichtbar. Sie sind aber durchschnittlich kleiner als in (a) u. bedeckt mit ultram kroskopischen Teilchen. Ausserdem ziemlich viele Teilchen sind in Brownscher Bewegung. (Siehe Abb. 2-c)</td><td>Mikroskopischer Befund ist fast genau wie (c), aber die ultramikroskopische Teilchen sind alle in lebhafter Brownschen Bewegung. (Siehe Abb. 2-d)</td></tr>
</table>

dass die innere Schwankung der Konzentration des Systems durch Anregung der USW. ausgeglichen wurde und ein gleichmässiges Erwachsen der Kristallkeime hervorgerufen hat. Da die USW. bekanntlich an der Grenzfläche "flüssig/fest" besonders kräftig wirken,[8] ist es auch sehr möglich, dass sie auf der Oberfläche der Kristallkeime etwaigen Einfluss gegeben hatten, welcher das gleichmässige Kristallwachstum verursachen würde. Dass die einzelne Kristalle klein sind, könnte davon kommen, weil der grösste Teil von H_2S durch USW.-Bestrahlen ausgetrieben worden war.

(3) *Über die Beständigkeit des dispersen Systems.* Zuletzt möchte ich noch über die Beständigkeit etwas hinzufügen. Hierbei ist es auch zu beachten, dass das USW.-bestrahlte System (b) besonders unbeständig ist, wie aus der Tabelle 1 und Abb. 3 zu ersehen ist. Andere drei Präparate haben ungefähr ähnliche Beständigkeit. Nur das gekochte und dann USW.-bestrahlte System (d) zeigt wieder eine spezielle Eigenschaft und zwar dieses Präparat lässt nach dem Absetzen gröberer Teilchen die bläulich opaleszierende, typisch kolloidale Flüssigkeit hinter. Noch dazu ist dieses abgesetzte Präparat durch einfaches Handschütteln wieder zu milchweisses in Durchsicht orange-rotes System peptisierbar. Bei den anderen Proben findet solche Erscheinung auf keinem Fall statt, so dass das Sediment setzt nach wiederholten Schütteln sofort ab und die Flüssigkeit bleibt immer vollkommen klar. Die Tatsache, dass das USW.-bestrahlte Präparat (b) sehr unbeständig ist und wohingegen das gekochte und dann USW.-bestrahlte Präparat (d) ein typisches Kolloid-Verhalten vor sich zeigt, lässt uns erinnern, dass die USW. die entgegengesetzte, koagulierende und stabilisierende Wirkung ausgeübt hätten. Nach K. Söllner und C. Bondy[9] wirken die USW. auf System "flüssig/flüssig" emulgierend und auch koagulierend in gleicher Zeit. Da unser Fall von Schwefel-dispersem System nicht mit System "flüssig/flüssig" sondern mit "flüssig/fest" zu tun hat, kann man nicht gleicherweise behandeln. Obwohl das Experiment dafür noch ungenügend ist, möchte ich vorläufig folgendes hinweisen. Erstens, scheint die USW. im allgemeinen das Kristallwachstum zu beschleunigen. Die Unbeständigkeit des



(a) (b) (c) (d)

Abb. 3.

(8) *Angew. Chem.*, **49** (1936), 117.

(9) K. Söllner und C. Bondy, *Trans. Faraday Soc.*, **31** (1935), 835; **32** (1936), 616.

USW.-bestrahlten Präparats (b), würde dadurch hervorgerufen sein. Bei anderem Versuch habe ich auch gleiches Resultat erhalten.[10] Was dem letzten Fall betrifft, ist die Sache etwas anders. Es wurde hier das System erst erhitzt zum Sieden und dann mit USW. bestrahlt. Daraus möchte ich vermuten, dass es beim Kochen einige Schwefel-Verbindungen und ultramikroskopische Teilchen entstanden wäre. Diese Teilchen wurden durch nachfolgendes Bestrahlen von USW. im einzelnen zerteilt und die genannte Schwefel-Verbindungen wurden gleichzeitig an denen adsorbiert, die jetzt als Stabilisator die Beständigkeit des Systems verursacht hatten. Das ist also dieselbe Erscheinung, wie wir schon als USW.-Peptisation hingewiesen haben.[11] Die mikro- und ultramikroskopische Untersuchung erklärt das Verhalten sehr deutlich. Nämlich, in nur gekochtem Präparat (c) lassen auch viele ultramikroskopische Teilchen sich erkennen, die aber an der Oberfläche grösserer Kristallen kleben und kaum in Brownscher Bewegung sind; dahingegen in gekocht und dann USW.-bestrahltem Präparat (d) sind alle Teilchen in lebhafter Brownschen Bewegung sich befinden.

IV. **Über die Reaktion zwischen Schwefel und Quecksilber in dispersem Zustand.** E. Sauer[12] hat schon nachgewiesen, dass durch Reaktion von Schwefel und Quecksilber in kolloid-dispersem Zustand, das Quecksilbersulfid in schwarzer Modifikation sich entsteht. Zu diesem Zweck hat er die chemisch hergestellte sehr beständige Sole verwendet, in denen man annehmen muss, dass die Teilchen mit stabilisierendwirkenden Hüllen von Ionen bzw. Oberflächen-Verbindungen überzogen sind.[13] Wie erwähnt, konnte ich gerade das reine Schwefel-disperse System in hydrophobem Zustand erhalten. Da sich das Quecksilber durch einfaches Schütteln,[14] USW.-Bestrahlen[15] oder Dampf-Explosion[16] leicht dispergieren lässt, war es mir von Interesse die Reaktion beider Substanzen in hydrophob-dispersem Zustand nachzuprüfen.

Es wurde 5.0–7.5 c.c., wie oben erwähnt, hergestelltes Schwefel-disperses System und 0.5–1.0 c.c. reines Quecksilber in einem Probiergläschen zugeschmolzen. Diese Probe wurden mechanisch geschüttelt

(10) Nach noch unveröffentlichem Versuch von uns, wurde auch festgestellt, dass die Beständigkeit von Weimarnschem Schwefel-Sol auch durch Bestrahlen von USW. stark herabgesetzt wird.

(11) N. Sata und S. Watanabe, *Kolloid-Z.*, **73** (1935), 50; **78** (1937), 277; H. A. Wannow, *ibid.*, **81** (1937), 105.

(12) E. Sauer, *Kolloid-Z.*, **73** (1935), 45.

(13) N. Sata, dieses Bulletin, **11** (1936), 624; H. Freundlich, "Kapillarchemie", Bd. II, 191, Leipzig (1932).

(14) I. Nordlund, "Experimentelle Studien über Hg-Hydrosole", Dissertation, Upsala (1918); *Kolloid-Z.*, **26** (1920), 128; N. Sata, *ibid.*, **71** (1935), 48.

(15) *Kolloid-Z.*, **71** (1935), 48.

(16) Dieses Bulletin, **11** (1936), 443.

oder USW. bestrahlt, so dass dadurch dispergiertes Quecksilber sofort mit zusammenvorhandenem dispersen Schwefel reagieren würde. Weil der H_2S in diesem Fall die einzige Verunreinigung ist, wurden die Kontroll-Versuche mit H_2S-haltigen Systeme auch ausgeführt. Die Ergebnisse sind in folgender Tabelle 2 zusammengestellt.

Tabelle 2.

<table>
<tr><td rowspan="2">Zusammensetzung der Proben.</td><td colspan="2">H_2S-freie Systeme.</td><td colspan="4">H_2S-haltige Systeme.</td></tr>
<tr><td colspan="2">S-Sol (aus H_2S-Wasser hergestellt und H_2S ausgetrieben durch Kochen).
Hg-Metall.</td><td>H_2S-Wasser.
Hg-Metall.</td><td>H_2S-Wasser.
S-Sol.
Hg-Metall.</td><td>H_2S-Wasser.
Hg-Metall.</td><td>H_2S-Wasser.
S-Sol.
Hg-Metall.</td></tr>
<tr><td>Anfängiger Befund.</td><td colspan="2">Milchweiss trübe mit orange-roter Durchsichtsfarbe.</td><td>Ganz klar.</td><td>Bläulichweiss getrübt mit Opaleszenz.</td><td>Ganz klar.</td><td>Bläulichweiss getrübt mit Opaleszenz.</td></tr>
<tr><td>Behandlung.</td><td>Maschine-Schütteln. (10 Min.)</td><td>USW. bestrahlt für 1 Min.</td><td colspan="2">Maschine-Schütteln. (10 Min.)</td><td colspan="2">USW. bestrahlt für 1 Min.</td></tr>
<tr><td>Gleich nach der Behandlung.</td><td colspan="2">Flüssigkeit ist grau undurchsichtig. Hg-Oberfläche ist schön goldgelb.</td><td colspan="2">Flüssigkeit ist bräunlich grau undurchsichtig. Hg-Oberfläche ist mit grauem Anflug bedeckt.</td><td colspan="2">Flüssigkeit ist grau undurchsichtig. Hg-Oberfläche ist schön goldgelb.</td></tr>
<tr><td rowspan="4"></td><td rowspan="2">Setzt nach 6-7 Tagen fast ganz klar ab.</td><td rowspan="2">Nach 6-7 Tagen ist es fast ganz klar und nur ein Spur bläulicher Opaleszenz ist erkennbar.</td><td colspan="4">Nach 1 Tag.</td></tr>
<tr><td>Braun undurchsichtig.</td><td>Gräulich braun undurchsichtig.</td><td>Gelblich braun undurchsichtig.</td><td>Gräulich braun undurchsichtig.</td></tr>
<tr><td>Nach 1 Monat ist die Flüssigkeit ganz klar. Der Bodensatz ist schwarz u. durch Schütteln nicht wieder peptisierbar. Nach langem Stehen (5-6 Mon.) erleidet der Bodensatz gar keine Änderung.</td><td>Nach 7-8 Tagen setzt der undurchsichtige Teil ab. Die Flüssigkeit ist bläulich opaleszierend.</td><td>Nach 12 Tagen setzt wie nebenstehende ab.</td><td colspan="2">Nach 10 Tagen setzt der undurchsichtige Teil ab. Die Flüssigkeit zeigt Spuren von bräunlich weisser Trübung.</td></tr>
<tr><td colspan="4">Der Bodensatz ist anfangs gräulich braun. Seine Farbe ändert sich mit der Zeit zu rötlichem Ton u. nach 6-8 Mon. ist er schön zinnober-rot. Er ist durch Schütteln wieder peptisierbar u. bleibt etwa 1 Woche beständig.</td></tr>
</table>

Von der Ergebnissen der Tabelle 2, sollte folgendes hingewiesen werden.

(1) Wenn das System den H_2S in irgendwelcher Menge enthält, so entsteht gelb-oranges Sulfid und zwar in kolloid-dispersem Zustand. Nach C. Doelter[17] ergibt das Quecksilber und H_2S-Wasser bei der Wasserbad-Temperatur ein Gemisch von rotem und schwarzem Sulfid. Nach meinem Versuch wurde festgestellt, dass die ähnliche Reaktion bei Zimmertemperatur vor sich läuft, wenn das Quecksilber in dispersem Zustand vorhanden ist. Dass sich das entstandene gelbliche Sulfid seine Farbe mit der Zeit rötlicher ändert und nach 6–8 monatigem Stehen vollkommen zinnoberroten Farbton ergibt, stimmt einigermassen mit der Meinung von J. L. Proust.[17] Ausserdem ist es zu beachten, dass dieses Sulfid immer in fein-zerteiltem Zustand bleibt; d.h. ist das System nach dem Absetzen durch einfaches Schütteln wieder zu ziemlich beständigem System peptisierbar, welches 7–8 Tage beständig bleibt. Es bringt uns die Vermutung nahe, dass es ausser Sulfiden noch stabilisierend-wirkende Substanzen dabei entstanden wäre.

(2) Durch die Reaktion von reinem Quecksilber und Schwefel in hydrophob-dispersem Zustand, scheint nur das Sulfid in schwarzer Modifikation entstehen. Das Resultat ist also dasselbe wie bei der Reaktion in hydrophil-dispersem Zustand nach E. Sauer.[12] Dass die Hg-Oberfläche nach dem Schütteln goldene Farbe erhält, sollte der Beweis sein, dass der H_2S noch in Spuren geblieben war. Dann könnte er an der Hg-Oberfläche das goldgelbe Sulfid ausscheiden, wie bei obenerwähntem H_2S-haltigen System der der Fall war. Dieses schwarze Sulfid ist, nach dem Absetzen, im Gegenteil zu vorhergehendem Fall H_2S-haltiger Systeme, durch Schütteln nicht wieder beständig peptisierbar und der Niederschlag setzt sofort ab und die Flüssigkeit bleibt ganz klar. Da das System anfangs nach erstem Schütteln, etwa für eine Woche doch beständig bleibt, könnte man schliessen, dass die Teilchen in diesem Fall mit der Zeit von amorph-kolloidal zu grob-kristallin sich verändert hätten. Die kristallographische Zustandsänderung der Niederschlägen durch Altern ist schon eine wohlbekannte Tatsache.[18]

(3) Das gemeinsame Vorhandensein von H_2S und disperses Schwefel scheint nur den additive Einfluss ausüben und zwar erhält das System gräulich braune Trübung, von denen der gräuliche Ton ziemlich schnell verschwindet.

---

(17) J. W. Mellor, "A Comprehensive Treatise on Inorganic and Theoretical Chemistry," Bd. IV, 946, London (1923).

(18) *Kolloid-Z.*, **73** (1935), 55.

(4) Von der Menge des entstandenen Niederschlags erkennt man sich darauf, dass die Wirkung von USW. hier viel schwächer ist, als die des mechanischen Schüttelns. Ausserdem ist es besonders zu bemerken, dass das Reaktionsprodukt durch USW.-Bestrahlen und mechanisches Schütteln qualitativ ganz gleichartig ist. Daraus könnte man konstatieren, dass die USW. in diesem Fall keine eigenartige Wirkung vor sich gezeigt hatten, wie bei einige anderen Fällen.[19]

Zusammenfassung.

(1) Eine neue einfache Methode der Herstellung hydrophob-disperses Systems von Schwefel ist beschrieben.

(2) Die Methode besteht darin, dass man das H_2S-Wasser unter bestimmten Bedingung durch Hitze zersetzt und das Schwefel in kolloiddispersem Zustand ausscheiden lässt.

(3) Wenn man übrich bleibenden H_2S durch verschiedenen Behandlungen (Kochen, Bestrahlen von USW. oder die beide) austreibt, so zeigen die Systeme auch verschiedenen Absetzungsvorgänge, je nach der Behandlungsart.

(4) Die mikro- und ultramikroskopische Untersuchung an den Bodensatz hat gezeigt, dass die USW. eine interessante Wirkung auf der Keimbildung und dem Kristallwachstum ausüben.

(5) Die chemische Reaktion von hydrophob-dispersem Schwefel und Quecksilber unter Wirkung von Maschine-Schütteln bzw. USW.-Bestrahlen wurde untersucht.

(6) Es wurde dadurch festgestellt, dass wenn das System den H_2S als Verunreinigung enthält, das gelbe bis orange Sulfid entstehen wird und nur das schwarze Sulfid, wenn kein H_2S vorhanden ist.

(7) Vor der Natur und der Menge der Reaktionsprodukte wurde konstatiert, dass hier die Wirksamkeit von USW. und Maschine-Schütteln qualitativ ganz gleich, nur aber quantitativ verschieden ist.

Chemisches Institut der Kaiserlichen Universität zu Osaka und Siomi-Institut für physikalische und chemische Forschungen.

(19) *Kolloid-Z.*, **73** (1935), 50; **78** (1937), 277.

Optical Rotatory Power of *l*-Menthol in Heavy Methyl Alcohol.

By Eijiro OGAWA.

(Received November 15th, 1937.)

The author[1] measured specific rotatory power of *d*-tartaric acid in ordinary water and 2.15% heavy water and obtained the results given in Table 1.

Table 1.

Solvent	$[\alpha]_D^{29.0}$	$[\alpha]_D^{26.9}$
2.15% Heavy water	8.84°	8.56°
Ordinary water	8.89°	8.60°

This difference was explained quantitatively by the decrease of hydrogen ion concentration under the assumption that the degree of dissociation of *d*-tartaric acid in heavy water is the same as acetic acid.

Biilmann, Jensen, and Knuth[2] observed the specific rotatory power $[\alpha]_D^{20} = +0.40°$ in 2-deutero-camphane.

The present author[3] carried out the following experiments: 2.5 g. of *l*-menthol was dissolved in 7 c.c. of ordinary methyl alcohol or 27.5% heavy methyl alcohol. No difference in specific rotatory power was observed (Table 2).

Table 2.

Solvent	α	$[\alpha]_D^{14.4}$
Ordinary methyl alcohol	17.49°	48.63°±0.03°
27.5% Heavy methyl alcohol	17.49°	48.63°±0.03°

(1) *Tech. Repts. Kyushu Imp. Univ.*, **11** (1936), 21.
(2) *Ber.*, **69** (1936), 1031.
(3) *Tech. Repts. Kyushu Imp. Univ.*, **12** (1937), 169.

From these results it is concluded that the difference of specific rotatory power in pure heavy methyl alcohol is at most 0.10° and the isotopic effect in hydroxyl bond has little influence upon the field of asymmetric carbon atom.

Recently H. Erlenmeyer and H. Schenkel[4] observed remarkable differences in specific rotatory power in *l*-mandelic acid and *d*-atrolactic acid namely 5.83° ± 0.26° and 1.19° ± 0.2° respectively. In these cases the isotopic effect upon the field around asymmetric carbon atom are remarkable as compared with camphane or menthol. This is probably due to cyclic nature of latter molecules.

Chemical Institute, Faculty of Engineering,
Kyushu Imperial University,
Fukuoka, Japan.

(4) *Helv. Chim. Acta*, **19** (1936), 1199, 1381.