

BULLETIN OF THE CHEMICAL SOCIETY OF JAPAN

Analyse des Mineralwassers von Aoki in der Provinz Yamanasi.

Von Kazuo KURODA und Nobuyuki TANAKA.

(Eingegangen am 3. Oktober, 1941.)

Die Mineralquellen von Aoki, in der Provinz Yamanasi, wurden im letzten Jahre durch Prof. T. Misawa vom therapeutischen Standpunkt aus untersucht. Wir wurden nun kürzlich von Prof. Misawa mit der genauen Analyse dieses Mineralwassers betraut. Dieser Aufforderung folgten wir um so lieber, als es sehr interessant schien, das schon therapeutisch genau untersuchte Mineralwasser zu analysieren.

Thermometrische Beobachtungen und andere Messungen, welche am 28. September 1941 vorgenommen wurden, ergaben folgendes Resultat.

Tabelle 1.

	Temp. der Quelle in °C.	pH	Fe ⁺⁺ (g/L)	Ergiebigkeit der Quelle (in L/Min.)
Nr. 1	11.2	4.0	0.3306	3.7
Nr. 2	14.0	2.9	0.7452	0.70
Nr. 3	14.2	2.9	0.5923	0.25

Tabelle 2. Radioaktivität der Quelle Nr. 3.

Datum	Radongehalt	
	Mache/L	Curie L
28. Sept. 1941	0.25	0.91×10^{-10}

Die Bestimmung des Abdampfrückstandes ergab die in nachfolgender Tabelle verzeichneten Resultate (Tabelle 3.).

Tabelle 3.

Datum	Abdampfrückstand (g/L)	
	110°C.	>1000°C.
(1) 17. Nov. 1940	15.24	4.29
(2) Juli 1941	22.450	6.337

Die Existenz folgender Elemente in Mineralwasser wurde durch die spektroskopische Methode gefunden (s. Tabelle 4).

Tabelle 4.

Na	Cu	Mg	Ca	Zn	B(?)	Al
Si	Ti	V	Mn	Fe	Ni	

Die Spektrallinie von Zink war besonders stark und zeigte den hohen Zinkgehalt dieses Wassers. Deshalb haben wir zuerst das Zink nach der polarographischen Methode bestimmt.

Für die Bestimmung von Zink, wurde das im November 1940 von uns gewonnene Wasser benutzt.

Das Mineralwasser wurde nach der Methode von Heller und anderen analysiert.⁽¹⁾ Das Mineralwasser wurde mit Kohlenstofftetrachloridlösung von Dithizon behandelt. Die Kohlenstofftetrachloridlösung wurde mit konz. Salzsäure rückgeschüttelt. Der nach dem Eindampfen erhaltene Rückstand wurde in folgender Grundlösung, die im Jahre 1938 von Stout, Levy und Williams untersucht worden war,⁽²⁾ gelöst.

$$\text{Grundlösung: } \begin{cases} 0,1 \text{ N Ammoniumacetat.} \\ 0,025 \text{ N Kaliumrhodanid.} \end{cases}$$

Die Lösung wurde in ein kleines, verschliessbares Elektrolysiergefäß gebracht, reiner Wasserstoff durchgeleitet und mit 1/10 Empfindlichkeit polarographiert. Beim 11. Teilstrich erschien eine schöne Zinkstufe von etwa 16 mm Höhe (s. Abb. 1). Die Höhe der Zinkstufe entspricht einer Menge von etwa 90 mg. Zink per Liter Mineralwasser. Die Bestimmung von Zink wurde im Jahre 1941 nach der gravimetrischen Methode wiederholt. Das Resultat ist in Tabelle 5 dargestellt.

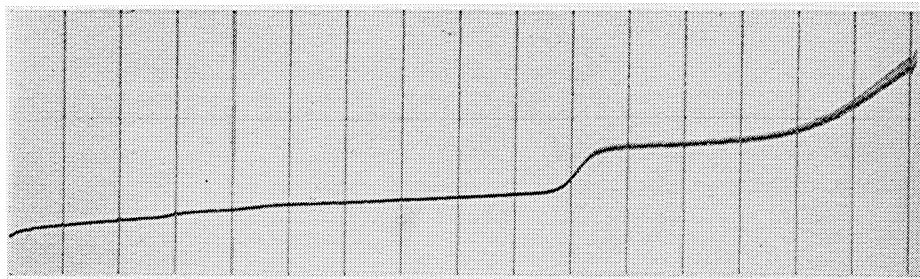


Abb. 1. Mineralwasser von Aoki Empfindlichkeit 1/10.
Messspannung von 0–1.6 Volt.

(1) Heller, Kuhla und Machek, *Mikrochemie*, **23** (1937), 78.

(2) Stout, Levy und Williams, *Collection Czechoslov. Chem. Commun.*, **10** (1938), 129.

Tabelle 5. (a)

	Empfindlichkeit	Höhe der Stufe (mm)
(1) 100 γ Zn Grundlösung: 10 ml	1/10	18
(2) Das Mineralwasser (1 ml) wurde mit CCl_4 -Lösung von Dithizon behandelt. Grundlösung: 10 ml	1/10	16

Tabelle 5. (b) Zinkgehalt des Mineralwassers.

Datum	mg/L	% (Abdampfrückstand)	Methode der Analyse
(1) 17. Nov. 1940	88.9	0.58	Polarographisch
(2) Juli 1941	133.1	0.59	Gravimetrisch

Das Mineralwasser von Aoki enthält eine bemerkenswerte Menge von Arsen. Arsen wurde zuerst nach der im Snellschen Buch beschriebenen Sanger-Black-Gutzeitschen Methode bestimmt,⁽³⁾ dieser Versuch endigte jedoch mit einem Misserfolg. Deshalb haben wir die gravimetrische Methode benutzt.⁽⁴⁾ Das Resultat ist in Tabelle 6 angegeben.

Tabelle 6. Arsengehalt des Mineralwassers.

Datum	g HAsO_4^{--} /L	g As_2O_3 /L	% As_2O_3 (Abdampfrückstand)
17. Nov. 1940	0.0173	0.0122	0.080

Zur Analyse der Hauptbestandteile wurde im Juli 1941 von Prof. Misawa uns übergebenes Wasser benutzt. Mangan ist colorimetrisch nach der Kaliumperiodat-Methode, Kupfer colorimetrisch mit Ammoniak, und Zink gravimetrisch bestimmt worden. Bei Ausführung der Analyse der übrigen Bestandteile hielten wir uns an den gewöhnlichen Gang der Mineralwasseranalyse. Die vorgenommenen Bestimmungen ergaben die in nachfolgender Tabelle verzeichneten Resultate.

Wie man aus Tabelle 7 ersieht, ist der Hauptbestandteil dieses Mineralwassers Schwefelsäure, Magnesiumsulfat, Eisensulfat und Aluminiumsulfat. Dieses Mineralwasser ist also eine saure Alaun-Vitriolquelle, welche grosse Mengen von Magnesium enthält. Sehr interessant ist der hohe Magnesiumgehalt dieses Mineralwassers: 1,0027 g. Mg per Liter

(3) Snell, "Colorimetric Methods of Analysis", 1936 (New York) 236.

(4) Steiner, *Z. anal. Chem.*, **81** (1930), 389.

Tabelle 7.

(a) Mineralwasser von Aoki (Nr. 3)

H ⁺	0.00130 g/L
Ca ⁺⁺	0.0857
Mg ⁺⁺	1.0027
Mn ⁺⁺	0.0046
Cu ⁺⁺	0.0146
Zn ⁺⁺	0.1331
Fe ⁺⁺	1.4422
Fe ⁺⁺⁺	0.2547
Al ⁺⁺⁺	0.9706
SO ₄ ⁻	12.7131
HSO ₄ ⁻	0.1257
H ₂ SiO ₃	0.2511
	16.99940

Tabelle 7.

(b) 17. November 1940. pH 2.9.

Ca ⁺⁺	0.1219 g/L
Mg ⁺⁺	0.7910
Fe ⁺⁺ + Fe ⁺⁺⁺	0.6330
Cu ⁺⁺	0.0043

oder 7,40% (Abdampfrückstand bei 110°C). Dieses Mineralwasser ist vielleicht eines der magnesiumreichsten Mineralwasser Japans.

Wir möchten hiermit Herrn Prof. Kenjiro Kimura für seine freundlich Anleitung und steten Ratschläge, die uns bei der Ausführung dieser Arbeit zuteil geworden sind, unseren herzlichsten Dank aussprechen. Herrn Prof. Yuji Shibata möchten wir für sein warmes Interesse an dieser Arbeit ergebenst danken. Herrn Prof. T. Misawa danken wir auch herzlichst für seine freundliche Anleitung. Der Kaiserlichen Akademie der Wissenschaft sind wir für ihre finanzielle Unterstützung zu grossem Dank verpflichtet. Dem Unterrichtsministerium sei gedankt für die Gewährung einer Unterstützung zur Anregung wissenschaftlicher Forschung.

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Über die unregelmässige Reihe der Kolloiden Lösungen durch Elektrolyten: IV. Über die Rolle des H_2S auf die unregelmässige Reihe von HgS -Sol.⁽¹⁾

Von Naoyasu SATA und Sigeru ITÔ.

(Eingegangen am 3. Oktober 1941.)

(1) **Einleitung.** Im vorhergehenden Versuch⁽²⁾ haben wir gezeigt, dass alle HgS -Sole, trotzdem sie aus verschiedenen Hg -Salzen hergestellt sind, immer die unregelmässigen Reihen aufweisen; d.h. die Ausgangsmaterialien keine entscheidende Rolle spielen. Mit anderen Worten, die

(1) N. Sata u. Y. Niwase, *Kolloid-Z.*, **84** (1938), 314; N. Sata u. S. Ito, dieses Bulletin, **15** (1940), 271; N. Sata u. K. Môri, dieses Bulletin, **16** (1941), 139.

(2) N. Sata u. K. Môri, dieses Bulletin, **16** (1941), 139.

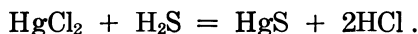
beigemischten Fremdionen zur unregelmässigen Reihe sind von keiner grossen Bedeutung.

Die dabei angewandte Herstellungsmethode des Sulfid-Sols nach Winssinger⁽³⁾ ist dadurch gekennzeichnet, dass ein Sulfid zuerst mit H_2S niedergeschlagen und dann mit abermaligem H_2S -Durchleiten kolloidal peptisiert wird. Kolloidwissenschaftlich versteht man H_2S als ein Stabilisator, welcher bekanntlich im bestimmten Bereich mittlerer Konzentrationen wirksam ist.⁽⁴⁾

Nachstehend wurde ein Versuch angestellt hinsichtlich der Wirkung von H_2S auf die unregelmässige Reihe des HgS -Sols.

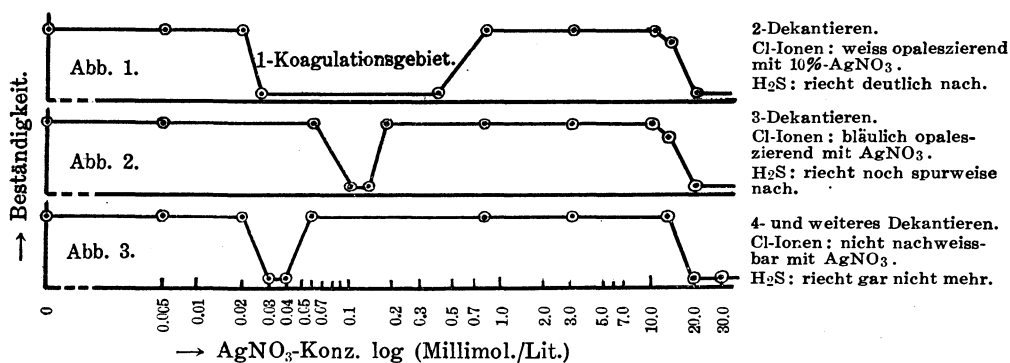
(2) **Gegenseitige Wirkung von H_2S und Cl -Ionen auf der Koagulationskurve.** Wie erwähnt, wird H_2S bei der Herstellungsmethode nach Winssinger zweimal gebraucht, namentlich zum Niederschlagen des Sulfides und zu dessen Peptisieren.

Da die erste Reaktion nach der Formel



verläuft, ausser dem HgS -Niederschlag, musste man gemeinsam vorhandenen Cl -Ionen in Betracht ziehen. Um die gegenseitige Wirkung von H_2S und Cl -Ionen zu Sol-Eigenschaften zu ermitteln, wurde folgendermassen untersucht. Aus 100 c.c. 2.5% HgCl_2 -Lösung wird das HgS mit H_2S niedergeschlagen. Der Niederschlag wurde mit einem Filtrierpapier abfiltriert, welcher in 100 c.c. destilliertem Wasser suspendiert wird. Diese Behandlung nennen wir 1-Dekantieren. Die Suspension des 2-, 3-Dekantieren u.s.w. wird durch Wiederholung gleicher Behandlung hergestellt. Aus dieser Niederschlagsuspension erhält man HgS -Sol durch abermaliges H_2S -Durchleiten, mit welchem die unregelmässige Koagulationsreihe mit AgNO_3 als Elektrolyt, geprüft wurde. Ähnlichen Versuch haben wir schon einmal durchgeführt.⁽¹⁾ Aber weil damals nicht die ganze Koagulationskurve sondern nur bei einigen ausgewählten AgNO_3 -Konzentrationen die Koagulation gemessen wurde, kam der Versuch hier von neuem zur Wiederholung.

Die Resultate sind in Abb. 1–3 übertragen. Die Menge der Cl -Ionen und H_2S in der Mutterlauge wurde nebenbei kontrolliert.



(3) C. Winssinger, *Bull. Acad. roy. Belgique*, (3), **15** (1888), 390.

(4) P. P. von Weimarn, *Kolloid-Z.*, **4** (1909), 127; *Kolloid-Beihfte*, **1** (1910), 105; *Kolloid-Z.*, **37** (1925), 151.

Das Sol aus 1-dekantierter Suspension ist so unbeständig, dass es sich schon koaguliert, wenn man überschüssigen H_2S austreibt. Es ist leicht verständlich, erinnert man daran, dass die Suspension noch zu viel Cl-Ionen enthält, um ein beständiges Sol zu ergeben.

Bei allen Kurven ersieht man eine ausgesprochene unregelmässige Reihe. Es ist dabei besonders zu beachten, dass 2- und 3-dekantierter Sole, trotz des deutlichen Vorhandenseins von H_2S und Cl-Ionen doch die unregelmässige Reihe aufweisen. Wir haben die Reinigung des Niederschlags durch Kochen und Dekantieren fortgesetzt. Über 300 Tage gereinigte Suspension ergibt noch das Sol mit unregelmässiger Reihe.⁽⁵⁾

Der Unterschied der Koagulationskurve Cl-haltigen und Cl-freien Sols lässt sich im 1-Koagulationsgebiet erkennen. Nicht nur Cl-Ionen, sondern alle beigemischten Ionen, wenn auch nicht viel, haben zur unregelmässigen Reihe keinen Einfluss, wie wir schon bestätigten.⁽²⁾ Deshalb haben wir zum weiteren Versuche immer die Suspension von 6-Dekantieren benutzt, wenn es nicht besonders erwähnt ist.

(3) **Über die Wirkung von H_2S als Peptisator bzw. Stabilisator.** Der mit H_2S gefällte HgS -Niederschlag wird nach der Reinigung durch Dekantieren, mit abermaligem H_2S -Durchleiten kolloidal peptisiert. Der überschüssige H_2S wird mit H_2 -Durchleiten oder Erhitzen ausgetrieben und das Sol ist bereit zum weiteren Experiment.

Der H_2S spielt hier die wichtige Rolle als Stabilisator, von welchem die Sol-Eigenschaften stark abhängig sein werden, was selbstverständlich beim Studium der unregelmässigen Reihe unbedingt zu berücksichtigen ist. Wir haben zuerst untersucht, wie die Sol-Beständigkeit beeinflusst wird nach verschiedenen Behandlungen beim H_2S -Austreiben.

Um den überschüssigen H_2S nach der Peptisation auszutreiben, gibt es gewöhnlich zwei Methoden, nämlich durch Erhitzen oder Durchleiten indifferenten, fremder Gase, wie z.B. Wasserstoff, Stickstoff u.s.w.. Beim Vergleichen dieser Methode unter verschiedenen Bedingungen, wurde folgendes zusammengefasst.

I. Durch das Erhitzen mit direktem Feuer eines Bunsenbrenners.

(a) Wird es so stark erhitzt, dass das Sol kocht, verliert es gleich die Beständigkeit und koaguliert schon nach 3 minutigem Kochen.

(b) Man hält das Sol gerade vor dem Kochen ($98^\circ\text{--}99^\circ\text{C.}$) über das Feuer. War es vorher H_2S -haltig, 8–10 Minuten erhitztes Sol bleibt 5–7 Stunden beständig.

Wenn der H_2S vorher mit H_2 -Durchleiten ausgetrieben ist, wird das Sol viel unbeständiger und zwar 8–10 Minuten erhitztes Sol hält nicht über 4 Stunden beständig.

II. Das Erhitzen im kochenden Wasserbad ($94^\circ\text{--}95^\circ\text{C.}$).

(a) H_2S -haltiges Sol, nach 30–40 minutigem Erhitzen, bleibt noch einige Tage beständig. Das Sol ist aber noch nicht vollständig H_2S frei, und man riecht Spuren von H_2S nach.

(5) Noch unveröffentlicher Versuch von uns. Siehe auch N. Sata u. Y. Niwase, *Kolloid-Z.*, **81** (1937), 298.

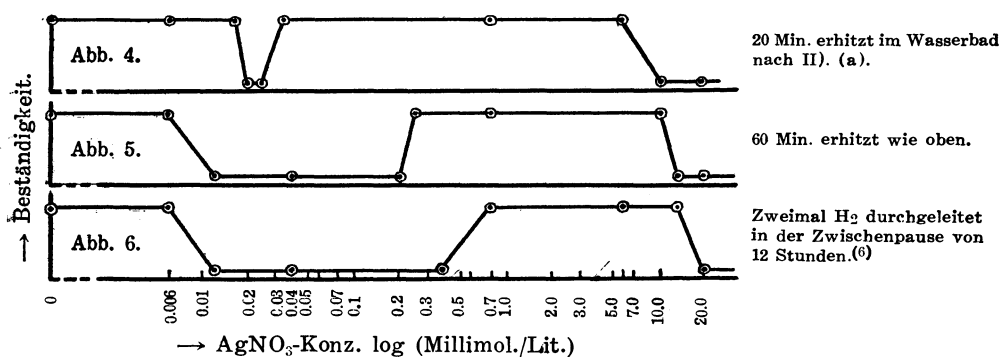
- (b) Ist der H_2S vorher mit H_2 -Durchleiten ausgetrieben, so koaguliert das 5–7 Minuten erhitzte Sol erst nach 12 Stunden.

III. Nach 20 Minuten H_2 -Durchleiten wird das Sol vollkommen H_2S frei und ist über 10 Tage beständig.

Daraus lässt sich wohl ohne weiteres ersehen, das Durchleiten indifferenten Gase um H_2S auszutreiben, am besten zu empfehlen ist.

Die Anwendung von Wärme muss möglichst vermieden werden, da sie zum H_2S -Austreiben nicht nur nicht ausreichend ist, sondern auf die Sol-Beständigkeit sogar schädlich wirkt.

Die Koagulationskurven der Sole nach obenerwähnten verschiedenen Behandlungen sind in Abb. 4–6 zusammengestellt.



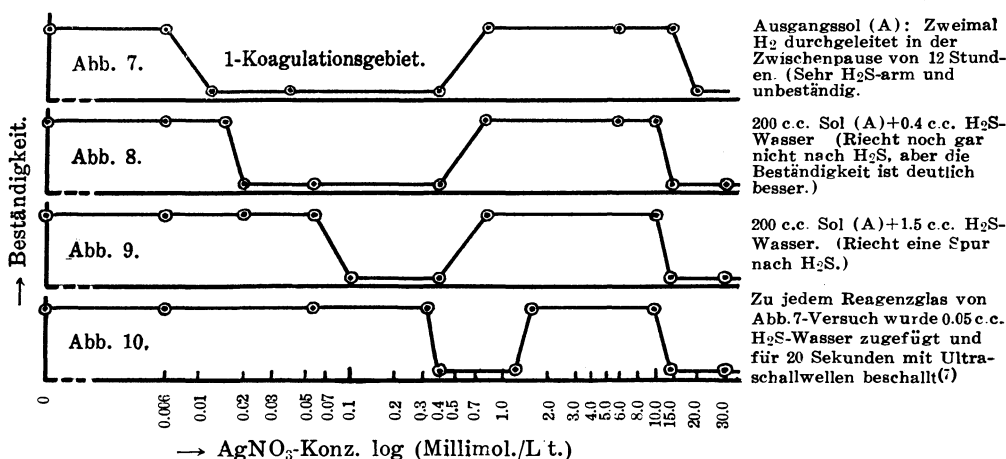
Aus den Versuchsergebnissen ersieht man deutlich die Abhängigkeit zwischen der Behandlungsweise des Sols beim H_2S -Austreiben und dessen unregelmässiger Reihe, die unmittelbar mit der im Sol als Stabilisator enthaltenden kleinen Menge des H_2S verbunden ist.

(4) **Der Einfluss verschiedener Menge H_2S auf die unregelmässige Reihe.** Um den H_2S -Einfluss auf die unregelmässige Reihe zu untersuchen, haben wir die Koagulationskurve unter Zusatz einer zunehmenden Menge von H_2S verfolgt.

Die Ergebnisse sind in Abb. 7–10 ersichtlich.

Beim Vergleich der Koagulationskurven wird ohne weiteres ersichtlich, dass das 1-Koagulationsgebiet desto schmäler ist, je mehr H_2S -haltig das Sol ist. Dem letzten Versuch (Abb. 10) ist darum besondere Bedeutung beizumessen, weil das H_2S -Wasser hier im Vorhandensein des Elektrolyts (AgNO_3) zugefügt ist, während in anderen Fällen (Abb. 8 und 9) das H_2S -Wasser zuerst im Sol zugesetzt ist; der Elektrolyt wird danach zugegeben. Wie erwartet, war das Ergebnis recht bemerkenswert; nämlich nach H_2S -Wasser-Zusatz, nur durch Handschütteln lässt sich keine Änderung in jeder Probe erkennen. Der H_2S -Effekt macht sich erst durch

(6) Obwohl ein Sol nach 30 minutigem H_2 -Durchleiten ganz H_2S frei ist, riecht es nach intägigem Stehenlassen wieder deutlich nach H_2S , was auf den Adsorptionsrückgang zurückzuführen ist. (H. Freundlich u. K. Schucht, *Z. physik. Chem.*, **87** (1913), 660; H. Freundlich u. E. Hase, ebendort **89** (1915), 417.



Ultraschallbeschallung⁽⁷⁾ merkbar und zwar wird das 1-Koagulationsgebiet deutlich schmäler wie Abb. 8 bzw. 9 zeigen.

(5) **Schlussbemerkung.** In obenstehenden Versuchen wurde die Wirkung von stabilisierendem H_2S unter Berücksichtigung koagulierend-wirkenden Cl-Ionen (Fremdionen im allgemeinen) untersucht.

Der erste bemerkenswerte Punkt ist, dass die beiden sonst gegenseitig wirkenden Substanzen der unregelmässigen Reihe keinen radikalen Einfluss zu geben vermögen. Denn, obwohl die Sol-Beständigkeit nach den Konzentrationen beider Substanzen stark beeinflusst wird, ergibt die Koagulationskurve immer die unregelmässige Reihe. Wie aus den Abb. 2–3 bzw. 7–10 zu ersehen ist, haben die Koagulationskurven jedenfalls zwei Koagulationspunkte. Der einzige Unterschied zwischen den Koagulationskurven lässt sich im 1-Koagulationsgebiet erkennen, welches von den verschiedenen Sol-Beständigkeiten abhängig ist. Das 1-Koagulationsgebiet wird nämlich desto schmäler mit den zunehmenden Beständigkeiten. Zweitens möchten wir darauf aufmerksam machen, dass soweit es das Unbeständigwerden eines Sols betrifft, wenigstens zwei Möglichkeiten aufzuzählen sind. Der Mangel an Stabilisatoren ist selbstverständlich eine wichtige Ursache. Dazu musste man nicht vergessen, dass das Vorhandensein zu vieler Fremdsbstanz (Verunreinigungen einschliesslich) in den meisten Fällen ein Sol unbeständig macht. Die unbeständigkeit des H_2S -armen Sols in Abb. 7 und des zu viel Cl-enthaltenden Sols in Abb. 1 ergibt gerade ein entsprechendes Beispiel. Vermutlich ist die Oberflächenstruktur der Teilchen (oder Stabilisierungsmechanismus) in beiden Fällen mässig verschieden; trotzdem stellen sie ganz ähnliche Koagulationskurven dar. Daraus könnte man sagen, dass die Struktur der stabilisierenden Hülle mit der unregelmässigen Reihe dieses Sols nicht viel zu tun habe. Im vorhergehenden Versuch wurde schon gezeigt, dass die beigemischten Fremdionen zur unregelmässigen Reihe auch unabhängig sind. Andererseits sind nach der Winssinger-Methode, die Sole ver-

(7) Über die Wirkung von Ultraschallwellen auf die unregelmässige Reihe von HgS -Sol wird in der folgenden Mitteilung weiter eingegangen werden. Siehe auch, N. Sata u. Y. Niwase, *Kolloid-Z.*, **81** (1937), 294.

schiedener Sulfide leicht erhältlich, in denen die Teilchen mit ähnlicher Oberflächenstruktur stabilisiert sein müssen.⁽⁸⁾

In diesem Fall haben wir uns als nächste Aufgabe, die schon einigermaßen im Gang ist, die Frage gestellt: Wie verhält sich die Erscheinung der unregelmässigen Reihe?

Zusammenfassung.

(1) Die Wirkung von H_2S auf die unregelmässige Reihe von HgS -Sol wurde systematisch untersucht.

(2) Zuerst wurde die gegenseitige Wirkung von H_2S und Cl -Ionen zur Sol-Beständigkeit und unregelmässigen Reihe vergleichend untersucht.

(3) Die Beständigkeit ist stark vermindert durch Vorhandensein einer messbaren Menge von Cl -Ionen. Die unregelmässige Reihe ist, der Beständigkeit nach, unabhängig erkennbar.

(4) Zweitens wurden verschiedene Methoden des H_2S -Austreibens verglichen und dessen Beziehung zur Sol-Beständigkeit und unregelmässigen Reihe verfolgt.

(5) Dadurch wurde bestätigt, dass zum H_2S -Austreiben das Durchleiten indifferenten Gase am besten ist und die Anwendung der Wärme möglichst zu vermeiden ist.

(6) Die Beständigkeit wird desto schlechter, je vollständiger H_2S ausgetrieben ist. Die unregelmässige Reihe bekommt in diesem Fall durch Beständigkeitsänderung auch keinen radikalen Einfluss.

(7) Es ist darauf aufmerksam gemacht, dass beide unbeständigen Sole, bei denen die eine wegen zu wenigem stabilisierenden H_2S , und die andere wegen zu vielen koagulierenden Cl -Ionen ihre Unbeständigkeit verursacht hat, ganz ähnliche Koagulationskurven ergeben, trotzdem die Oberflächenstruktur der Teilchen nicht als ähnlich angenommen werden kann.

(8) Das Resultat ergab, dass die unregelmässige Reihe von HgS -Sol mit der Oberflächenstruktur der Teilchen vielleicht nicht viel zu tun haben mag.

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zu Osaka und Siomi-Institut für physikalische
und chemische Forschung.*

(8) E. A. Hauser, "Colloidal Phenomena", S. 98, New York and London (1939).

Studies on the Derivatives of Biphenylene Oxide. VII. The Influence of Substitution on the Opening and Closing of the Furan-ring of Biphenylene Oxide.

By Seishi YAMASHIRO.

(Received October 4, 1941)

It was communicated by the present author in Part IV⁽¹⁾ that when the nitro derivatives of 2,2'-diacetoxydiphenyl were melted in the presence of dry carbonate of barium or sodium, they converted mainly into the corresponding derivatives of biphenylene oxide, while 2,2'-diacetoxydiphenyl itself was converted by the same treatment exclusively into *o,o'*-biphenol, and, therefore, the formation of the furan-ring of this type may require the presence of some negative groups in the derivatives of 2,2'-diacetoxydiphenyl. Now, if this be the case, changes in the number and negativities of the substituents of the substitution products of 2,2'-diacetoxydiphenyl must show parallel changes in the yields of the derivatives of biphenylene oxide. With this in view, the nitro groups of the nitro derivatives of 2,2'-diacetoxydiphenyl were replaced step by step by the less negative bromine atoms, and then the bromonitro and bromo derivatives thus obtained were submitted to the tests of the formation of the furan-ring in comparison with the case of the corresponding nitro compounds. And in that case, it might be expected, of course, that the positions, at which the substitutions were to take place, would give certain effects to the formation of the furan-ring. For the purpose of making a complete test of this effect exerted by the nitro group, 4,4'-dinitro- and 4,4',6,6'-tetranitro-2,2'-diacetoxydiphenyls were also prepared.

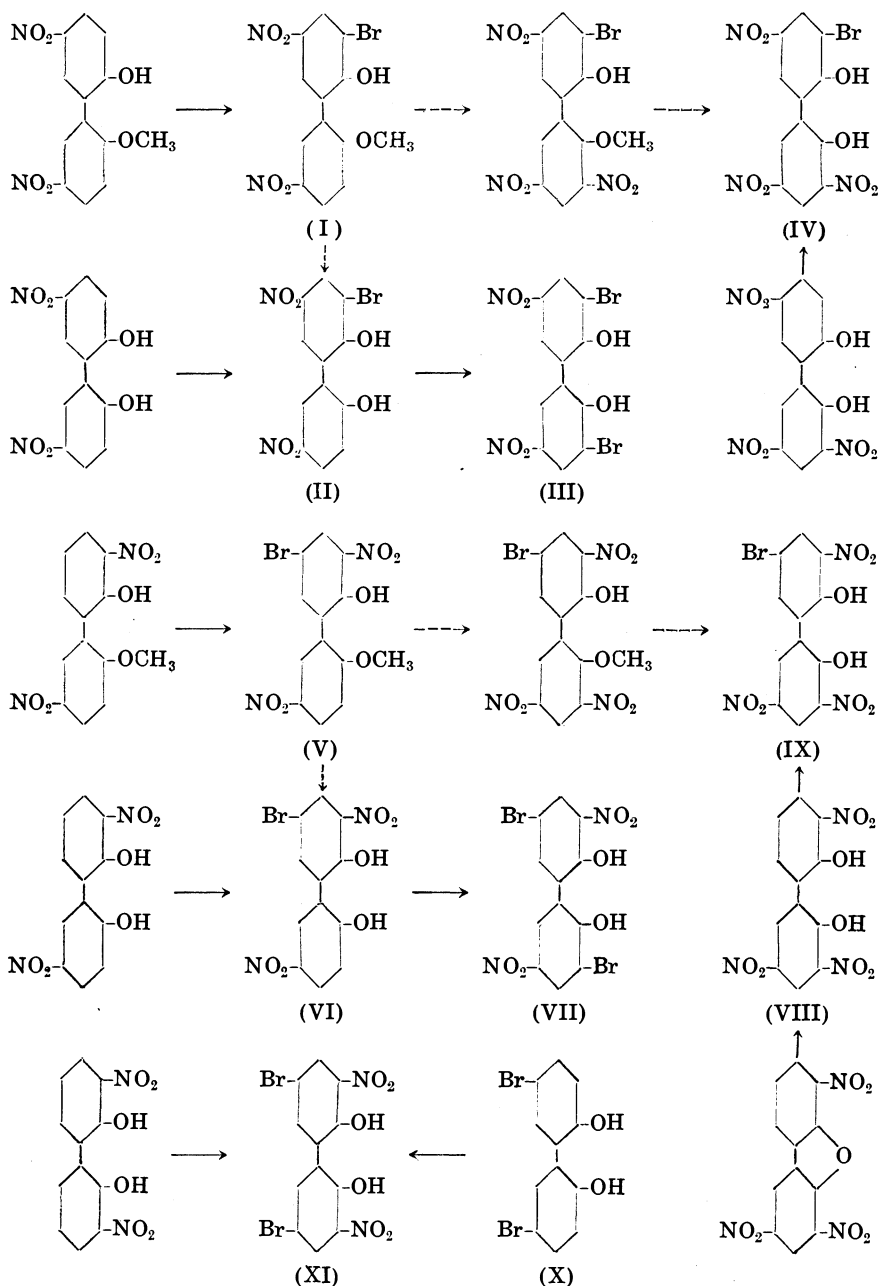
Among the derivatives of *o,o'*-biphenol which were submitted to the tests, 3-bromo-5,5'-dinitro-(II), 3,3'-dibromo-5,5'-dinitro-(III), 3-bromo-3',5,5'-trinitro-(IV), 5-bromo-3,5'-dinitro-(VI), 3,5'-dibromo-3',5'-dinitro-(VII), 5-bromo-3,3',5'-trinitro-(IX), 5,5'-dibromo-3,3'-dinitro-(XI), 4,4'-dinitro-(XIV), and 4,4',6,6'-tetranitro-(XVII)-2,2'-dihydroxydiphenyls were newly obtained by the present author in the scheme shown below, in which the reactions that proceeded smoothly are represented by the arrows in full line, and those which were brought about unsuccessfully, by the arrows in dotted line.

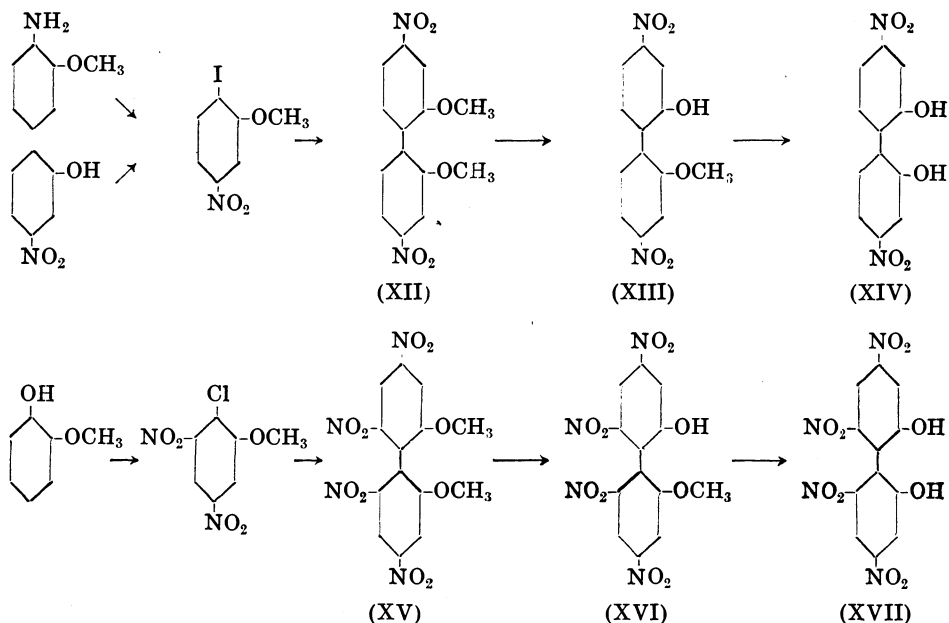
On the preparation of 3,3'-dibromo-5,5'-dinitro-2,2'-dihydroxydiphenyl R. W. Robertson and H. V. A. Briscoe⁽²⁾ reported that it was obtained either by nitration of 5,5'-dibromo-2,2'-dihydroxydiphenyl or by bromination of 5,5'-dinitro-2,2'-dihydroxydiphenyl, and that both products melting at 201° would be identical. The present author, however, considered that their report was unreasonable to be accepted as it is, and prepared 3,3'-dibromo-5,5'-dinitro-2,2'-dihydroxydiphenyl melting at 314–315° (corr.) by bromination of 5,5'-dinitro-2,2'-dihydroxydiphenyl. 3,3'-Dinitro-2,2'-

(1) S. Yamashiro, *J. Chem. Soc. Japan*, **59** (1938), 945.

(2) P. W. Robertson and H. V. A. Briscoe, *J. Chem. Soc.*, **101** (1912), 1974.

dihydroxydiphenyl, which was hardly brominated by the preceding investigators, was converted by the present author into 5,5'-dibromo-3,3'-dinitro-2,2'-dihydroxydiphenyl melting at 207–208° (corr.), which was also obtained by nitration of 5,5'-dibromo-2,2'-dihydroxydiphenyl to the confirmation of its constitution. In consequence the dibromodinitrobiphenol obtained by Robertson and his coworker should be 5,5'-dibromo-3,3'-dinitro-2,2'-dihydroxydiphenyl.





In the courses of these reactions it was found that the brominations of the derivatives of *o,o'*-biphenol and its monomethyl ether took place in the lower boiling solvents, such as chloroform, carbon bisulphide and carbon tetrachloride, principally at the *p*-position to the hydroxyl group, while in the higher boiling solvent such as acetic acid, at both of the *o*- and *p*-positions to the same hydroxyl group; but the same reaction took place neither at the *o*-position nor at the *p*-position relative to the methoxyl group, even when the methoxyl compounds were heated for a long time with a large excess of bromine in glacial acetic acid.

5,5'-Dibromo-(X) and 3,3',5,5'-tetrabromo-2,2'-dihydroxydiphenyls, which have been submitted to the test of the closing of furan-ring, were obtained from *o,o'*-biphenol after the method communicated by O. Diels and his coworker.⁽³⁾ And, as to these bromo compounds, the former converted into 3,6-dibromobiphenylene oxide when heated in a sealed tube with hydrobromic acid in the presence of red phosphorus, and the latter gave none other than an oily matter in the same treatment.

4,4',6,6'-Tetranitro-2,2'-dimethoxydiphenyl (XV) was prepared after the method described by J. van Alphen,⁽⁴⁾ viz., by taking guaiacol as a starting material, changing it into 3,5-dinitroguaiacol and 2-chloro-3,5-dinitroanisole in succession, and then condensing the last compound into the tetranitrodianisole.

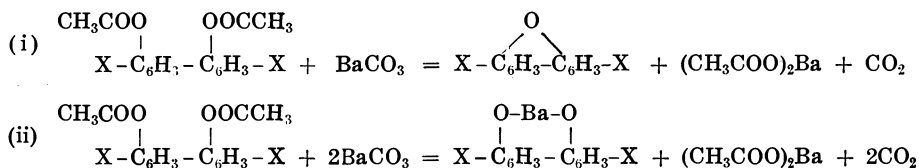
Now, *o,o'*-biphenol and its sixteen derivatives were converted into the corresponding diacetoxy compounds by heating them with acetic anhydride in presence of a little sulphuric acid, and then the diacetoxy compounds thus obtained were submitted to the tests of the formation of furan-ring.

(3) O. Diels and A. Bibergeil, *Ber.*, **35** (1902), 306.

(4) J. van Alphen, *Rec. trav. chim.*, **51** (1932), 453-459.

(5) W. Borsche, *Ber.*, **50** (1917), 1347.

As shown in Part IV by the present author, the reactions between the *o,o'*-diacetoxydiphenyl compounds and the dry carbonate of barium or sodium will proceed in two ways, producing biphenylene oxides and *o,o'*-biphenolates.



From the comparison of the yields of the reaction products given in Tables 3 and 4, it is realized that the predominance of one of these two reactions depends upon the nature and the position of the substituents introduced into the phenylene residues; namely.

(1) The introduction of the nitro group facilitates generally the removal of the acetyl groups from the derivatives of *o,o'*-diacetoxydiphenyl. This facilitating tendency can be represented in the order of the positions of the nitro groups introduced, i.e., ortho>para>meta relative to the acetoxyl groups, because it was found from the comparison of the experimental results (Tables 2, 3 and 4 in Part IV, and Table 3 in this report) that the velocities of the removal of the acetyl groups of dinitrodiacetoxydiphenyls can be represented in the order of these compounds, i. e., 3,3'->3,5'->5,5'->4,4'-dinitro-2,2'-diacetoxydiphenyl.

The *m*-nitrosubstitution relative to the acetoxyl groups does not induce the reaction (i), while the *o*- and *p*-nitrosubstitutions, especially the former, promote the reaction (i). The increase in the number of the nitro groups introduced in the latter two substitutions increases appreciably the yields of the resulting biphenylene oxides, although the yield of 1,3,6-trinitrobiphenylene oxide has come out exceptionally smaller than those of 1,6- and 3,6-dinitrobiphenylene oxides.

(2) The introduction of bromine into the nitro derivatives of *o,o'*-diacetoxydiphenyl hinders somewhat the removal of the acetyl groups, and reduces the reaction (i), increasing the yields of the biphenols. The last effect of bromine comes out remarkably when the bromination takes place at the *o*-position relative to the acetoxyl groups.

(3) The bromo derivatives of *o,o'*-diacetoxydiphenyl resist strongly against the action of barium carbonate, although they react readily with sodium carbonate. The reactions between the bromo compounds and these carbonates take place always in accordance with the reaction formula (ii), giving none of the bromo derivatives of biphenylene oxide.

In summarizing, so far as is concerned with the removal of the acetyl groups and the formation of the biphenylene oxides from the *o,o'*-diacetoxydiphenyls, the effects of bromine and the nitro group are unexpectedly opposite to each other. The velocity of the removal of the acetyl groups will be proportional to the thermal dissociation degrees of the acetoxyl groups of the diacetoxydiphenyls.

In order to compare the influence of substitution exerted on the opening of the furan-ring with that exerted on the formation of the same ring, eleven nitro derivatives of biphenylene oxide were submitted to the tests

of the ring-opening. The tests were carried out by heating the finely powdered biphenylene oxides for two hours with 5% solution of caustic soda at constant temperatures (20°, 40°, 60°, 80°, and 100°C.), and it was found from the experimental results (Table 6) that (1) the increase in the number of the nitro groups introduced into the phenylene residues of biphenylene oxide facilitates the ring-opening, (2) the favourable influence exerted by the nitro group on the ring-opening of this type depends upon the position of this group relative to the oxygen atom of the furan-ring, the order of the favourable positions being ortho>para>meta.

The tendency of the ring-opening of the nitrobiphenylene oxides in caustic soda solution will be proportional to the electrolytic dissociation degrees of the corresponding nitrobiphenols and again to those of the nitrophenols, of which the nitrobiphenols are composed. And it is because the yields of the nitrobiphenols obtainable from the nitrobiphenylene oxides (Table 6) and the electrolytic dissociation constants $K^{(6)}$ of the nitrophenols can be represented in the orders of the nitrobiphenylene oxides and the nitrophenols respectively as follows:

1,3,6,8-Tetranitro->1,3,6,7-tetranitro->1,3,8-trinitro->2,3,6,7-tetranitro->1,3,6-trinitro->2,3,6-trinitro->1,8-dinitro->1,6-dinitro->3,6-dinitro->2,6-dinitro->2,7-dinitro-biphenylene oxide ;

Components, 2,4-dinitro->3,4-dinitro->2-nitro->4-nitro->3-nitro-phenol.
 $K_{25^\circ} \times 10^{-6}$ 10000 430 6.8 6.5 1.0

Among the nitrobiphenols obtainable from the above-mentioned nitrobiphenylene oxides, 4,4',5,5'-tetranitro-2,2'-dihydroxydiphenyl has not been isolated in the pure crystalline form, because the reaction product obtained from 2,3,6,7-tetranitrobiphenylene oxide was liable to separate as a brown amorphous substance.

Experimental.

3-Bromo-5,5'-dinitro-2-hydroxy-2'-methoxydiphenyl (I). 5,5'-Dinitro-2-hydroxy-2'-methoxydiphenyl (2.9 g.) was heated for four hours with bromine (3 g.) in boiling acetic acid (30 c.c.), when the colour of bromine disappeared. The reaction product separated out on diluting; the reaction mixture was recrystallized from acetone-ethanol into colourless needles or prisms, m.p. 242–243° (corr.) with decomposition (Yield 3.6 g., 95%. Found: N, 7.72; Br, 21.81. Calc. for $C_{12}H_5OH(OCH_3)(NO_2)_2Br$: N, 7.59; Br, 21.66%). It is readily soluble in acetone and ethyl acetate, moderately in ethanol, and sparingly in benzene, chloroform, carbon tetrachloride, ether, ligroin, methanol and acetic acid.

3-Bromo-5,5'-dinitro-2-hydroxy-2'-methoxydiphenyl (2 g.) was dissolved in cold fuming nitric acid ($d=1.52$; 20 c.c.) in the hope of obtaining 3-bromo-3',5,5'-trinitro-2-hydroxy-2'-methoxydiphenyl, and the reaction mixture was poured into ice, separating yellow precipitates. The reaction product, however, readily decomposed into a brown mass, even when it was dried below 100°C., and gave no crystalline substance in the ordinary method of recrystallization.

3-Bromo-5,5'-dinitro-2,2'-dihydroxydiphenyl (II). (i) 5,5'-Dinitro-2,2'-dihydroxydiphenyl (8.28 g.) was dissolved in boiling glacial acetic acid (250 c.c.) and

(6) A. F. Holleman and R. Herwig, *Rec. trav. chim.*, **21** (1902), 444.

brominated at this temperature by the gradual addition of bromine (4.8 g.) diluted with ten times its weight of acetic acid. When the colour of bromine disappeared, acetic acid was distilled off, the residue was diluted with water, and the reaction product separated out was extracted with ether after drying to remove the sparingly soluble dibromo derivative. The extract was evaporated to dryness and the residue was recrystallized from acetic acid into colourless needles, m.p. 302–303°C. (corr.) with decomposition (Yield 11 g., 85.5%. Found: N, 7.85; Br, 28.83. Calc. for $C_{12}H_5(OH)_2(NO_2)_2Br$: N, 7.89; Br, 22.51%). It is readily soluble in alcohols, acetone, ether and ethyl acetate, fairly in acetic acid, and sparingly in benzene, chloroform, carbon tetrachloride and ligroin.

(ii) 3-Bromo-5,5'-dinitro-2-hydroxy-2'-methoxydiphenyl (3 g.) was heated for sixteen hours with hydrobromic acid ($d=1.49$; 40 c.c.) in boiling acetic acid (200 c.c.), and, after concentrating the reaction mixture, the residue was diluted with water, when dark brown precipitates separated out. The reaction product was extracted with dilute caustic soda solution, the extract was acidified separating out yellow precipitates, and the last product was then recrystallized from acetone-ethanol, when none other than 3-bromo-5,5'-dinitro-2-hydroxy-2'-methoxydiphenyl (1 g.) was isolated. The other part of the starting material decomposed into dark brown tarry matter.

3,3'-Dibromo-5,5'-dinitro-2,2'-dihydroxydiphenyl (III). 5,5'-Dinitro-2,2'-dihydroxydiphenyl (5.52 g.) was heated for four hours with bromine (6.4 g.) in acetic acid (100 c.c.), when the colour of bromine disappeared. The reaction mixture was concentrated and the reaction product separated out on cooling the mixture was recrystallized from dilute ethanol into small colourless needles, d.p. 314–315°C. (corr.) (Yield 7.93 g., 91.4%. Found: N, 6.53; Br, 36.99. Calc. for $C_{12}H_4(OH)_2(NO_2)_2Br_2$: N, 6.46; Br, 36.83%). It is readily soluble in acetone, alcohols and ethyl acetate, and sparingly in acetic acid, benzene, chloroform, carbon tetrachloride, ether and ligroin.

3-Bromo-3',5',5'-trinitro-2,2'-dihydroxydiphenyl (IV). 3,5,5'-Trinitro-2,2'-dihydroxydiphenyl (3.31 g.) was heated for four hours with bromine (1.7 g.) in boiling acetic acid (50 c.c.), and, after the same treatment as in the case of the compound (III), the reaction product was recrystallized from dilute ethanol into small yellow rectangular plates melting at 224–226°C. (corr.) with decomposition (Yield 3.9 g., 97.5%. Found: N, 10.49; Br, 20.04. Calc. for $C_{12}H_4(OH)_2(NO_2)_3Br$: N, 10.51; Br, 19.98%). It is readily soluble in acetone, alcohols, acetic acid and ethyl acetate, fairly in benzene, chloroform and ether, and sparingly in carbon tetrachloride and ligroin.

5-Bromo-3,5'-dinitro-2-hydroxy-2'-methoxydiphenyl (V). 3,5'-Dinitro-2-hydroxy-2'-methoxydiphenyl (5.8 g.) was brominated just as in the case of the preparation of 3-bromo-5,5'-dinitro-2-hydroxy-2'-methoxydiphenyl (I) and the reaction product was recrystallized from acetone-ethanol into small yellow needles, m.p. 219–220°C. (corr.) (Yield 7.27 g., 98.5%. Found: N, 7.63; Br, 21.79. Calc. for $C_{12}H_5OH(OCH_3)(NO_2)_2Br$: N, 7.59; Br, 21.66%). It is readily soluble in acetone, benzene, chloroform, carbon tetrachloride and ethyl acetate, moderately in acetic acid, and sparingly in alcohols, ether and ligroin.

5-Bromo-3,5'-dinitro-2,2'-dihydroxydiphenyl (VI). (i) 3,5'-Dinitro-2,2'-dihydroxydiphenyl (1.38 g.) was treated with bromine (0.8 g.) just as in the preparation of 3-bromo-5,5'-dinitro-2,2'-dihydroxydiphenyl. The reaction product was extracted with carbon tetrachloride to remove the more soluble dibromo derivative, and the residue was recrystallized from methanol into small yellow prisms, m.p. 216–217°C. (corr.) (Yield 0.75 g., 42%. Found: N, 6.58; Br, 36.76. Calc. for $C_{12}H_5(OH)_2(NO_2)_2Br$: N, 6.46; Br, 36.83%). It is readily soluble in acetone, acetic acid, benzene, chloroform, ethanol, ether and ethyl acetate, moderately in methanol, and sparingly in carbon tetrachloride and ligroin. This product must be the 5-bromo-derivative, because the bromination of *o,o'*-biphenol takes place more readily at the *p*-position than at the *o*-one relative to the hydroxyl groups.

The carbon tetrachloride extract was evaporated to dryness and then recrystallized from methanol, isolating 3',5'-dibromo-3,5'-dinitro-2,2'-dihydroxydiphenyl melting at 203–204°C. (corr.) (Yield 0.5 g., 23%).

(ii) 5-Bromo-3,5'-dinitro-2-hydroxy-2'-methoxydiphenyl (2.5 g.) was treated with hydrobromic acid just as in the case of 3-bromo-5,5'-dinitro-2-hydroxy-2'-methoxydiphenyl. From the reaction product, however, none of 5-bromo-3,5'-dinitro-2,2'-dihydroxydiphenyl was obtained.

3,5'-Dibromo-3'5-dinitro-2,2'-dihydroxydiphenyl (VII). 3,5'-Dinitro-2,2'-dihydroxydiphenyl (2.76 g.) was brominated just as in the preparation of 3,3'-dibromo-5,5'-dinitro-2,2'-dihydroxydiphenyl. The reaction product was recrystallized from methanol into yellow needles melting at 203–204°C. (corr.) with decomposition (Yield 4.21 g., 97%. Found: N, 6.55; Br, 36.78. Calc. for $C_{12}H_4(OH)_2(NO_2)_2Br_2$: N, 6.46; Br, 36.83%). It is readily soluble in acetone, benzene, chloroform, carbon tetrachloride, ethanol, ether and ethyl acetate, moderately in acetic acid and methanol, and sparingly in ligroin.

3,3',5-Trinitro-2,2'-dihydroxydiphenyl (VIII). 1,3,8-Trinitrobiphenylene oxide (3.03 g.) was dissolved in a hot dilute solution of caustic soda, and the reaction product separated out on acidifying the solution was recrystallized from ethanol into yellow rhombic plates, m.p. 156–157°C. (corr.) (Yield 3.0 g., 93.5%. Found: N, 13.14. Calc. for $C_{12}H_5(OH)_2(NO_2)_3$: N, 13.09%). It is readily soluble in acetone, acetic acid, benzene, chloroform and ethyl acetate, moderately in ethanol, and sparingly in carbon tetrachloride, ether, ligroin and methanol.

5-Bromo-3,3',5-trinitro-2,2'-dihydroxydiphenyl (IX). *3,3',5-Trinitro-2,2'-dihydroxydiphenyl* (1.605 g.) was brominated just as in the preparation of 3,3'-dibromo-5,5'-dinitro-2,2'-dihydroxydiphenyl, and the reaction product was recrystallized from methanol into yellow prisms, m.p. 191–192°C. (corr.) (Yield 1.94 g., 97%. Found: N, 10.64; Br, 19.86. Calc. for $C_{12}H_4(OH)_2(NO_2)_3Br$: N, 10.51; Br, 19.98%). It is readily soluble in acetone, acetic acid, benzene, chloroform, ethanol and ethyl acetate, fairly in carbon tetrachloride and methanol, and sparingly in ether and ligroin.

5,5'-Dibromo-3,3'-dinitro-2,2'-dihydroxydiphenyl (XI). (i) 3,3'-Dinitro-2,2'-dihydroxydiphenyl (2.76 g.) was brominated as in the preparation of 3,3'-dibromo-5,5'-dinitro-2,2'-dihydroxydiphenyl and the reaction product was recrystallized from acetone-ethanol into yellow needles, m.p. 207–208°C. (corr.) (Yield 3.95 g., 91%. Found: N, 6.55; Br, 36.69. Calc. for $C_{12}H_4(OH)_2(NO_2)_2Br_2$: N, 6.46; Br, 36.83%). It is readily soluble in acetone, benzene, chloroform, carbon tetrachloride, ether and ethyl acetate, moderately in alcohols and acetic acid, and sparingly in ligroin.

(ii) *5,5'-Dibromo-2,2'-dihydroxydiphenyl* (3.44 g.) was dissolved in glacial acetic acid (35 c.c.), fuming nitric acid ($d=1.52$; 2.1 g.) was added and the mixture was heated on the water bath. The reaction product separated out on diluting the reaction mixture was recrystallized from ethanol into yellow needles, m.p. 207–208°C. (corr.) (Yield 4.15 g., 95.6%). It is identical in all respects with the corresponding compound obtained from 3,3'-dinitro-2,2'-dihydroxydiphenyl.

3,6-Dibromobiphenylene oxide from 5,5'-dibromo-2,2'-dihydroxydiphenyl. A dibromo-2,2'-dihydroxydiphenyl (0.5 g.) melting at 191–192° (corr.), which was obtained by bromination of *o,o'*-biphenol in chloroform⁽³⁾ and for the confirmation of its constitution, it was heated for 6 hours, at about 190–200° in a sealed tube with hydrobromic acid ($d=1.49$; 5 c.c.) and a small proportion of red phosphorus, when a pale brown oily mass was obtained. This reaction product was extracted with caustic soda solution, and the residue was repeatedly recrystallized from ethanol and then from acetic acid into colourless rectangular plates, m.p. 199–200° (corr.). It is identical in all respects with 3,6-dibromobiphenylene oxide obtained by bromination of biphenylene oxide.

4,4'-Dinitro-2,2'-dimethoxydiphenyl (XII). 6-Iodo-3-nitroanisole was first obtained from *o*-anisidine in the usual way (by means of acetylation, nitration, hydrolysis and

diazo-reaction in succession), and also from *m*-nitrophenol by means of iodination⁽⁷⁾ (Yield of 6-iodo-3-nitrophenol, 40%, and that of 2-iodo-3-nitrophenol, 10%) and subsequent methylation.⁽⁸⁾ The iodonitroanisole (55.8 g.) thus obtained was heated for 2 hours at about 210–220° with copper bronze (20 g.) and nitrobenzene (30 c.c.) with constant stirring, in the atmosphere of carbon dioxide. The reaction mixture was submitted to a steam distillation, and the residue was pulverized after drying and then extracted with ether and benzene in succession. The benzene extract was concentrated and the condensation product separated out was recrystallized from the same solvent into pale yellow needles, m.p. 257–258° (corr.) (Yield 25.3 g., 83%. Found: N, 9.28. Calc. for $C_{12}H_6(OCH_3)_2(NO_2)_2$: N, 9.21%). It is sparingly soluble in acetone, alcohols, carbon tetrachloride, ether and ligroin, and fairly in acetic acid, benzene, chloroform and ethyl acetate.

4,4'-Dinitro-2-hydroxy-2'-methoxydiphenyl (XIII) and 4,4'-dinitro-2,2'-dihydroxydiphenyl (XIV) from 4,4'-dinitro-2,2'-dimethoxydiphenyl. 4,4'-Dinitro-2,2'-dimethoxydiphenyl (30.4 g.) was heated for 20 hours with hydrobromic acid ($d=1.49$, 300 c.c.) in a boiling mixture of acetic acid (200 c.c.) and acetic anhydride (200 c.c.), the reaction mixture was after concentration diluted with water, and the reaction product which separated out was after filtration extracted with caustic soda solution for the purpose of removing the unchanged dinitrodianisole (6 g.) and the carbonized product. The extract was neutralized, the precipitates separated out were after drying extracted with benzene, and the residue was recrystallized from ethanol into yellow needles melting at 253–254° (corr.) with decomposition (Yield 13 g. Found: N, 10.22. Calc. for $C_{12}H_6(OH)_2(NO_2)_2$: N, 10.14%). The benzene extract was evaporated to dryness, and the residue was recrystallized from methanol into yellow needles, m.p. 206–207° (corr.) (Yield 7 g. Found: N, 9.72. Calc. for $C_{12}H_6(OH)(OCH_3)(NO_2)_2$: N, 9.66%). The higher melting product is readily soluble in acetone, alcohols, acetic acid, ether and ethyl acetate, and sparingly in benzene, chloroform, carbon tetrachloride and ligroin. The lower melting one dissolves similarly in those solvents except benzene and chloroform, in which it dissolves readily. The lower melting product was converted into the higher melting one by a further treatment with hydrobromic acid.

4,4',6,6'-Tetranitro-2-hydroxy-2'-methoxydiphenyl (XVI) and 4,4',6,6'-tetranitro-2,2'-dihydroxydiphenyl (XVII) from 4,4',6,6'-tetranitro-2,2'-dimethoxydiphenyl (XV). 4,4',6,6'-Tetranitro-2,2'-dimethoxydiphenyl (7.88 g.), which was prepared after the method described by J. van Alphen⁽⁴⁾ from 2-chloro-3,5-dinitroanisole obtained from guaiacol, was heated for 20 hours with hydrobromic acid ($d=1.49$, 150 c.c.) in boiling glacial acetic acid (150 c.c.), and the reaction mixture was after concentration diluted with water, when a dark brown crystalline mass separated out along with yellow hexagonal-prismatic crystals which have double-melting points, i.e. 95–98° and 228–229° (uncorr.). The reaction product was dissolved in caustic soda solution, and, after the removal of the insoluble part, it was reprecipitated by acidifying the solution. The precipitates were extracted with hot water, and the residue was then recrystallized from benzene into reddish yellow rectangular plates, m.p. 208–209° (corr.) (Yield 1.4 g. Found: N, 14.88. Calc. for $C_{12}H_4(OH)(OCH_3)(NO_2)_4$: N, 14.75%). The aqueous extract was evaporated to dryness and then the residue was recrystallized from benzene into yellow prisms, m.p. 235–236° (corr.) (Yield 4.6 g., 63%. Found: N, 15.33. Calc. for $C_{12}H_4(OH)_2(NO_2)_4$: N, 15.31%). The lower melting product was converted into the higher melting one by a further treatment with hydrobromic acid as described above. Both products are readily soluble in acetone, alcohols, acetic acid, chloroform, ether and ethyl acetate, fairly in benzene, and sparingly in carbon tetrachloride; but the higher melting product is much more readily soluble in hot water than the lower melting one.

Formation of the bromo-, bromonitro- and nitro-derivatives of 2,2'-diacetoxy-

(7) F. W. Schlieper, *Ber.*, **26** (1893), 2467.

(8) R. Meldola and J. V. Eyre, *Proc. Chem. Soc.*, **238**.

diphenyl and 2-acetoxy-2'-methoxydiphenyl, from the corresponding derivatives of 2,2'-dihydroxydiphenyl and its monomethyl ether. The bromo-, bromonitro- and nitro-biphenols and their monomethyl ethers were boiled for a few minutes with ten times their weights of acetic anhydride in the presence of a little sulphuric acid, the reaction mixtures were treated with hot water to the decomposition of the excess of

Table

Derivatives of biphenol	Derivatives of 2,2'-diacetoxydiphenyl				Crystals and (their crystallizing solvents)
	M.p., (corr.)	Yield, %	Found, %	Calc., %	
II →	II' 3-Bromo-5,5'-dinitro-derivative 186-187°	95.7	N, 6.35	6.38	Colourless small needles (acetic-acid)
III →	III' 3,3'-Dibromo-5,5'-dinitro- 194-195°	99.8	N, 5.48	5.41	Pale yellow small needles (ethanol)
IV →	IV' 3-Bromo-3',5,5'-trinitro- 142-143°	99.7	N, 8.73	8.68	Colourless small needles (methanol)
VI →	VI' 5-Bromo-3,5'-dinitro- 113-114°	100	N, 6.41	6.38	Colourless granules (ether-ligroin)
VII →	VII' 3,5'-Dibromo-3',5'-dinitro- 147-148°	99.9	N, 5.44	5.41	Pale yellow rectangular plates (methanol)
IX →	IX' 5-Bromo-3,3',5',-trinitro- 154-155°	98.2	N, 8.71	8.68	Pale yellow rectangular plates (methanol)
X →	X' 5,5'-Dibromo- 102-103°	100	Br, 37.21	37.34	Colourless needles (ethanol)
XI →	XI' 5,5'-Dibromo-3,3'-dinitro- 120-121°	100	N, 5.45	5.41	Colourless rectangular plates (ligroin)
XIV →	XIV' 4,4'-Dinitro- 155-156°	86.6	N, 7.83	7.78	Pale yellow rhombic plates (methanol)
XVII →	XVII' 4,4',6,6'-Tetranitro- 165-166°	96.0	N, 12.50	12.45	Pale yellow rhombic plates (acetone-ethanol)

Table

Mono-methyl ethers	Derivatives of 2,2'-acetoxy-methoxydiphenyl				Crystals and (their crystallizing solvents)
	M.p., (corr.)	Yield, %	Found, %	Calc., %	
I →	I' 3-Bromo-5,5'-dinitro-derivative 160-161°	100	N, 6.94	6.82	Colourless needles (methanol)
V →	V' 5-Bromo-3,5'-dinitro- 170-171°	100	N, 6.99	6.82	Colourless rectangular plates (ethanol)
XIII →	XIII' 4,4'-Dinitro- 183-184°	98	N, 8.47	8.44	Pale yellow rhombic plates (methanol)
XVI →	XVI' 4,4',6,6'-Tetranitro- 157-158°	95	N, 13.25	13.28	Colourless small prisms (dilute ethanol)

acetic anhydride, and the reaction products separated out were washed with a cold dilute solution of caustic soda and then recrystallized from the suitable solvents. Among the experimental results thus obtained, those concerning the newly obtained compounds from the above-mentioned derivatives of biphenol and its monomethyl ether are as shown here in Tables 1 and 2.

1.

Solubility (e: easily soluble, m: moderately soluble, d: difficultly soluble: e > m > d.)									
Ligroin	Ether	Carbon tetra-chloride	Chloro-form	Benzene	Methanol	Ethanol	Acetone	Acetic acid	Ethyl acetate
d	d	e	e	e	m	m	e	m	e
d	d	e	e	e	m	m	e	e	e
d	d	m	e	e	m	m	e	e	e
d	e	e	e	e	e	e	e	e	e
d	e	e	e	e	m	m	e	e	e
d	d	e	e	e	m	e	e	e	e
d	e	e	e	e	m	m	e	e	e
d	e	e	e	e	e	e	e	e	e
d	m	e	e	e	e	m	m	e	e
d	d	d	e	e	d	d	e	e	e

2.

Solubility (e: easily soluble, m: moderately soluble, d: difficultly soluble: e > m > d.)									
Ligroin	Ether	Carbon tetra-chloride	Chloro-form	Benzene	Methanol	Ethanol	Acetone	Acetic acid	Ethyl acetate
d	m	e	e	e	m	m	e	e	e
d	d	e	e	e	m	m	e	e	e
d	d	m	e	e	m	m	e	m	e
d	m	e	e	e	m	m	e	e	e

Formation of the biphenylene oxides from the diacetoxydiphenyls. With the exception of 4,4',6,6'-tetranitro-2,2'-dihydroxydiphenyl, which was kept at about 170–180° on account of its unstability at higher temperature, the nitro and bromonitro derivatives of diacetoxydiphenyls were heated for 4 hours at about 200–210°, in mixing with dry barium carbonate; while diacetoxydiphenyl itself and its bromo derivatives were treated under the same condition with dry sodium carbonate because of their stability towards barium carbonate. The reaction products were treated with cold dilute hydrochloric acid, washed well with water and extracted with cold dilute solution of caustic soda, the biphenols formed being recovered. The residues were hydrolysed with hydrochloric acid in boiling acetone and again extracted with dilute caustic soda solution in order to remove the unacted diacetoxy compounds from the biphenylene oxides formed. The last compounds were recrystallized from suitable solvents. The experimental results thus obtained are as shown below in Tables 3, 4 and 5.

Tests of the opening of the furan-ring of the nitrobiphenylene oxides. The nitro derivatives of biphenylene oxide (0.3 g.) were finely pulverized, made into a paste with water and then suspended in a 5% solution of caustic soda (20 c.c.). These suspensions were treated for two hours under constant stirring at constant temperatures (20°, 40°, 60°, 80° and 100°), and the undissolved parts were filtered through

Table 3 (Acid-fixer : BaCO₃).

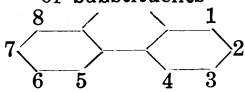
Nature and positions of substituents 	Diacetoxydiphenyls (unchanged)		Biphenols (formed)		Biphenylene oxides (formed)	
	Yield (%)		Yield (%)		Yield (%)	
2,4,5,6-Tetranitro-	XVII'	0	XVII	100		0
1,3,6,8-Tetranitro-		0		0		99.1
1,3,6-Trinitro-		0		20.0		79.5
1,8-Dinitro-		0		1.0		98.5
1,6-Dinitro-		0		1.0		98.1
3,6-Dinitro-		0		3.6		95.1
2,7-Dinitro-	XIV'	56.4	XIV	43.0		0
6-Bromo-1,3,8-trinitro-	IX'	0	IX	0.6	IX''	98.5
8-Bromo-1,3,6-trinitro-	IV'	0	IV	9.8	IV''	89.6
3-Bromo-1,6-dinitro-	VI'	0	VI	2.6	VI''	96.9
1-Bromo-3,6-dinitro-	II'	0	II	20.4	II''	79.0
3,6-Dibromo-1,8-dinitro-	XI'	0	XI	5.9	XI''	93.4
3,8-Dibromo-1,6-dinitro-	VII'	0	VII	31.5	VII''	67.7
1,8-Dibromo-3,6-dinitro-	III'	0	III	79.4	III''	19.8
1,3,6,8-Tetrabromo-		99.9		trace		0
3,6-Dibromo-		98.5		1.3		0
Unsubstituted		57.0		43.0		0

Table 4 (Acid-fixer: Na_2CO_3).

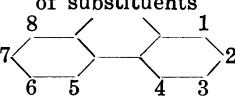
Nature and positions of substituents 	Diacetoxydiphenyls (unchanged) Yield (%)	Biphenols (formed) Yield (%)	Biphenylene oxides (formed) Yield (%)
1,3,6,8-Tetrabromo-	0	100	0
3,6-D.bromo-	0	100	0
Unsubstituted	0	100	0

Table 5. The properties of the bromonitrobiphenylene oxides.

Com- pounds	Crystals and (their crystallizing solvents)				M. p. (corr.)	N, %.		Br, %.			
						Found,	Calc.	Found,	Calc.		
IX''	Almost colourless rectangular plates (acetone-methanol)				264-265°	11.18	11.00	20.89	20.92		
IV''	Almost colourless hexagonal plates (acetone-methanol)				295-296°	11.13	11.00	21.00	20.92		
VI''	Almost colourless needles (acetone-methanol)				229-230°	8.42	8.31	23.99	23.71		
II''	Colourless small hexagonal plates (acetone-ethanol)				297-298°	8.29	8.31	24.02	23.71		
XI''	Colourless small rectangular plates (acetone)				317-318°	6.81	6.75	38.23	38.42		
VII''	Almost colourless rectangular plates (acetone-methanol)				226-227°	6.88	6.75	38.57	38.42		
III''	Colourless rectangular plates (acetone)				302-303°	6.66	6.75	38.72	38.42		
Com- pounds	Solubility (e: easily soluble, m: moderately soluble, d: difficultly soluble: e > m > d.)										
	Ligroin	Ether	Carbon tetra- chloride	Chloro- form	Ben- zene	Meth- anol	Ethanol	Acetone	Acetic acid	Ethyl acetate	
	IX''	d	d	d	e	e	d	d	e	m	e
	IV''	d	d	d	d	m	d	d	e	m	e
	VI''	d	d	m	e	e	d	d	e	m	e
	II''	d	d	m	e	e	d	d	e	m	e
	XI''	d	d	d	d	d	d	d	d	d	d
	VII''	d	d	d	e	e	d	d	e	e	e
	III''	d	d	d	m	m	d	d	m	d	m

a glass filter, washed well with hot water, dried and weighed. The filtrates were acidified with hydrochloric acid, precipitating the corresponding nitro derivatives of *o,o'*-biphenol or their decomposition products. This alkaline treatment of the nitro-biphenylene oxides at lower temperature brought about no colour change of their undissolved parts, but the same treatment at higher temperature changed the undissolved parts of some compounds into pale orange substances. In consequence, the precipitates recovered from the dissolved parts of the nitrobiphenylene oxides are not always the corresponding nitrobiphenols. The quantitative estimation of such compounds, therefore, must be carried out at a comparatively lower temperature. The experimental results obtained are as shown here in Table 6.

Table 6.

Nitro-derivatives of biphenylene oxide	Percentages of the dissolved parts yielding the biphenols				
	at 20°C.	40°C.	60°C.	80°C.	100°C.
1,3,6,8-Tetranitro-	1.2	11.2	49.6	100	—
1,3,6,7-Tetranitro-	0.9	3.3	11.3	99.7	—
2,3,6,7-Tetranitro-	0.5	2.6	6.5	23.3	—
1,3,8-Trinitro-	0.7	3.0	10.0	43.4	—
1,3,6-Trinitro-	0.3	1.0	4.8	20.9	—
2,3,6-Trinitro-	0.1	0.4	1.0	4.0	35.7
1,8-Dinitro-	—	—	—	1.0	3.8
1,6-Dinitro-	—	—	—	0	2.1
3,6-Dinitro-	—	—	—	0	1.3
2,6-Dinitro-	—	—	—	0	0.9
2,7-Dinitro-	—	—	—	0	0.5

Summary.

(1) The influence of substitution on the formation of a furan-ring has been compared among *o',o'*-biphenol and its nitro, bromonitro and bromo derivatives, the following results being obtained in the case of reactions between dry carbonate of barium or sodium and the diacetoxydiphenyls derived from those biphenols.

(i) The introduction of nitro groups into the diacetoxydiphenyls facilitates the removal of acetyl groups of those compounds and also the formation of the furan-ring. This facilitating effect varies with the relative position of the nitro group and the acetoxyl group, the order of the effect being *ortho*>*para*>*meta*; but the *m*-nitrosubstitution induces no ring-formation, giving exclusively nitrobiphenols.

(ii) The introduction of bromine into the diacetoxydiphenyls hinders the removal of the acetyl groups and also the formation of the furan-ring, no bromobiphenylene oxide being obtained. This effect is more

remarkable in the case of *o*-substitution than in that of *p*-one relative to the acetoxyl groups.

(2) The effect of nitrosubstitution on the opening of the furan-ring of biphenylene oxide in caustic soda solution was also studied, and it was found that the introduction of the nitro groups facilitates the ring-opening, and this facilitating effect varies with the relative position of the nitro group and the oxygen atom of biphenylene oxide, the order of the effect being *ortho*>*para*>*meta*. This effect appears to be proportional to the electrolytic dissociation degree of nitrobiphenols obtainable from the nitrobiphenylene oxides.

(3) In the course of these experiments, two nitrobiphenols and seven bromonitrobiphenols were newly prepared.

In conclusion, the author wishes to express his hearty thanks to Prof. R. Majima of Osaka Imperial University and Shigemi Ôba, the principal of Yonezawa Higher Technical School, for their kind advices and encouragements. A considerable part of the cost of the materials used for this work was defrayed from a grant of Nippon Gakuzyutu Shinko-kwai (the Japan Society for the Promotion of Scientific Research), for which also the author acknowledges gratefully.

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Über den Einfluss von einem polaren Stoff auf das Verhalten grob disperser Teilchen in apolaren organischen Flüssigkeiten.

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(Eingegangen am 11. October, 1941.)

Die Sedimentation und Agglomeration in grob dispersen Systemen sind im allgemeinen recht verwickelte Vorgänge, die von einer grossen Zahl von Einflüssen abhängen.⁽¹⁾ Indessen ist die Erforschung dieser Vorgänge von besonderer Bedeutung in der Hinsicht, dass sie mit der technisch und wissenschaftlich wichtigen Fliesseigenschaft (Thixotropie, Plastizität, Dilatanz, usw.) grob disperser Systeme in einem engen Zusammenhang stehen.

An den grob dispersen Systemen beobachtet man manchmal das sogenannte Sedimentationsvolumen (abgekürzt S.V.), d.h. das Volumen, das die sedimentierenden Teilchen in Flüssigkeit nach einiger Zeit schliesslich annehmen. Man hat bisweilen festgestellt, dass das Entstehen der thixotropen Eigenschaft eines grob dispersen Systems durch das grosse

(1) Vgl. z. B. A. v. Buzagh, *Kolloidik*, Dresden und Leipzig, (1936), 168.

Sedimentvolumen der Teilchen bedingt ist.⁽²⁾ In vielen hydrophoben Suspensionen, wie Bentonit in Elektrolytlösung, tritt aber hervor, dass es dabei auf dieselben Eigenschaften der Elektrolyte ankommt, die für die Koagulation, also für das Haften der Teilchen aneinander, massgebend sind.⁽³⁾ Sehr eigentümlich ist auch das Verhalten grob disperser Teilchen in organischen Flüssigkeiten, wo das S. V. eine allerdings sehr verwickelte Eigenschaft aufweist. Wenn man es aber einmal aufklärt, wird man wahrscheinlich die zur Zeit noch wenig durchsichtigen Beständigkeitsbedingungen in organischen Solen besser verstehen können.

Die Untersuchungen von Wo. Ostwald und Haller⁽⁴⁾ befassen sich mit dem S.V. einiger festen Stoffe (Alumina, Quarz, Graphit, Talkum) in verschiedenen organischen Flüssigkeiten, wobei gefunden wurde, dass die Sedimentvolumen in den organischen Flüssigkeiten grösser als im Wasser sind, weitgehend unabhängig von der Natur des festen Stoffes. Nach Buzagh⁽⁵⁾ ordnen sich die Flüssigkeiten in einer Reihenfolge, nämlich in der Reihe—Wasser, Äthyläther, Chloroform, Toluol, Benzol, Kohlenstofftetrachlorid—in der das S. V. der Quarzteilchen ansteigt. Nach den neuerdings von Akamatu⁽⁶⁾ angestellten Beobachtungen, weisen die polaren Teilchen wie Glas, ZnO, CaCO₃ grössere S.V. in apolaren Flüssigkeiten als in polaren Flüssigkeiten auf, während die unpolaren Teilchen wie Graphit, Kohle fast gleiche S.V. sowohl in apolaren als auch in polaren Flüssigkeiten zeigen. Es scheint jedenfalls, dass das S.V. und die damit zusammenhängenden Eigenschaften von der Polarität von festen Stoffen sowie von Flüssigkeiten stark beeinflusst werden.

Nun haben Harkins und Mitarbeiter⁽⁷⁾ festgestellt, dass die Flockung bzw. Sedimentvolumen der Pigmente (TiO₂ usw.) in organischen Flüssigkeiten durch die Adsorptionsschicht von einem fremden Stoffe wie Wasser und Ölsäure weitgehend verändert werden, und zwar wirkt Ölsäure die Teilchen dispergierend und das S.V. verkleinernd, dagegen Wasser die Teilchen agglomerierend und das S.V. vergrössernd. Inzwischen wurden neulich von Bloomquist und Schutt⁽⁸⁾ sehr bedeutende Beobachtungen durchgeführt, wonach die S.V. der Glasperlen (kugelförmige Glasperlen hergestellt nach Buzagh) in organischen Flüssigkeiten durch die Trockenheit des Systems stark beeinflusst werden. Die Ergebnisse der Arbeit werden folgendermassen zusammengefasst: 1) Die S. V. der Glasperlen in Wasser sowie in mit Wasser mischbaren organischen Flüssigkeiten zeigen Minimalwerte, die der engstmöglichen Teilchenpackung entsprechen. 2) In mit Wasser sich kaum vertragenden Flüssigkeiten sind die S.V. gering, wenn das System rein und trocken ist und kommen dem Minimalwert nahe, wenn die Trockenheit des Systems gesteigert wird. 3) In mit Wasser gestättigten Flüssigkeiten ergeben sich grössere S.V.,

(2) H. Freundlich, *Thixotropy*, Paris, (1935), 17.

(3) H. Freundlich, O. Schmidt und G. Lindau, *Kolloid-Beihefte*, **36** (1932), 43; B. Tamamushi, dieses Bulletin, **13** (1938), 234.

(4) Wo. Ostwald und W. Haller, *Kolloid-Beihefte*, **29** (1929), 354.

(5) A. v. Buzagh, *Kolloid-Beihefte*, **32** (1930), 114.

(6) H. Akamatu, dieses Bulletin, **13** (1938), 456.

(7) W. D. Harkins and D. M. Gans, *J. Phys. Chem.*, **36** (1932), 86; L. W. Ryan, W. D. Harkins and D. M. Gans, *Ind. Eng. Chem.*, **24** (1932), 1288.

(8) C. R. Bloomquist und R. S. Schutt, *Ind. Eng. Chem.*, **32** (1940), 827.

und bei niedrigerer Wasserkonzentration hängen die Einflüsse von der Natur der Flüssigkeit ab.

Alle diese Beobachtungen weisen darauf hin, dass das Vorhandensein der Adsorptionsschicht des Wassers in den Vorgängen der Sedimentation und Agglomeration grob disperser Teilchen in organischen Flüssigkeiten eine entscheidende Rolle spielt.

Die Suspensionen von Quarzteilchen oder Stärke in einer dipollosen Flüssigkeit, Tetrachlorkohlenstoff oder Benzol, verhalten sich nun, wie zuerst von Freundlich und Mitarbeitern⁽⁹⁾ gefunden ist, thixotrop. Da die Thixotropie einer Suspension allgemein durch das grosse S.V. der Teilchen bedingt ist, so ist es nicht unwahrscheinlich, dass die Thixotropie selbst durch das Vorhandensein von geringer Menge Wasser merklich beeinflusst wird, was in der Tat neulich von Kruyt und van Selms⁽¹⁰⁾, und unabhängig von uns bestätigt wurde, wie in der vorliegenden Arbeit beschrieben wird.

I. Zur Gewinnung der näheren Kenntnisse über solche eigentümliche Vorgänge in grob dispersen Systemen mit organischen Dispersionsmitteln, wurden im folgenden Beobachtungen angestellt einmal an dem System: Quarz-Tetrachlorkohlenstoff unter dem Zusatz von Wasser bzw. Fettsäuren, und dann an dem System: Stärke-Benzol oder Stärke-Dioxan unter dem Zusatz von Wasser, wobei wir das S.V. und die Sedimentierungszeit (abgekürzt S.Z.) beobachteten.

Das S.V. wurde durch die gewöhnliche Methode bestimmt, indem man die Suspensionen—1 g. Festkörper in 10 ccm Flüssigkeit—in kleine Messzylinder tat und das S.V. jeden Tag über Nacht nach Schüttelung ablas, bis der endgültige Wert erreicht war, während man die S.Z. durch die Messung der Zeit, in der die meisten Teilchen in der Suspension sedimentieren bis die obere Flüssigkeit klar wird, bestimmte.

Die hierzu verwendeten Quarzpulver wurden zuerst mit abs. Alkohol und Benzol gewaschen und dann auf 110°C getrocknet: die Pulver der Kartoffelstärke (*amylum solani*) wurden auch gleicherweise behandelt: sie wurden auf konz. H₂SO₄ aufbewahrt. Die organischen Flüssigkeiten: Tetrachlorkohlenstoff, Benzol und Dioxan wurden durch geeignete Methoden rein dargestellt. Der Einfluss von Luftfeuchtigkeit wurde achtsam ausgeschlossen.

Die Ergebnisse der Beobachtungen an dem System: Quarz-CCl₄ werden in Tabellen 1–3 zusammengefasst.

Tabelle 1. Quarz-Tetrachlorkohlenstoff-System:
Einfluss von Palmitinsäure.

Konzentration d. Palmitinsäure (10 ⁻⁴ Mol/l.L.)	Sediment- Volumen (ccm/g.)	Sedimentierungs- zeit		50%-Suspension
		(Min.)	(Sek.)	
0	1.07	2	30	unbeständig
0.25	1.05	4	5	„
0.50	1.05	4	10	„
1.00	0.95	7	0	unbeständiger
2.00	0.95	7	30	„

(9) H. Freundlich und H. L. Röder, *Trans. Faraday Soc.*, **34** (1938), 308.

(10) H. R. Kruyt und F. G. van Selms, *Proc. Acad. Amsterdam*, **43** (1940), 1171.

Tabelle 2. Quarz- CCl_4 -System: Einfluss von homologen Fettsäure.

Fettsäure (2.10^{-3} Mol/i.L.)	Sedimentvolumen (ccm/g.)	relative Sedi- mentierungszeit
rein (ohne Fett- säure)	1.07	1.0
Essigsäure	1.05	1.3
Buttersäure	1.04	1.8
Capronsäure	1.03	3.0
Nonylsäure	—	3.5
Laurinsäure	—	4.3
Palmitinsäure	1.00	6.0

Tabelle 3. Quarz- CCl_4 -System: Einfluss von Wasser.

	Sedimentvolumen (ccm/g.)	relative Sedi- mentierungszeit	55%-Suspension
Trocken	1.07	1.0	unbesändig (dilatant)
Nass	1.20	0.3	mehr oder wenig- er beständig (thixotrop)

Wie man aus Tabelle 1 sieht, tritt der Einfluss der Palmitinsäure auf das S.V. bzw. die S.Z. schon bei einer Konzentration von 1.10^{-3} Mol. i.L. merklich hervor, und zwar in der Weise, das S.V. zu verkleinern und die S.Z. zu vergrössern. Palmitinsäure wirkt also die Teilchen dispergierend. Die 50%-Suspension von Quarz in reinem CCl_4 gibt eine feste Masse, die aber nicht stabil ist; es tritt dabei leicht Dilatanz auf. Die Suspension wird unter Zusatz von Palmitinsäure noch instabiler.

Tabelle 2 zeigt wie die homologen Fettsäuren in gleicher Konzentration das S.V. bzw. die S.Z. der Quarzteilchen beeinflussen, wobei man sieht, dass der die Teilchen dispergierende Effekt mit der Molekulargrösse ansteigt.

Nun ist der Einfluss des Wassers sehr bedeutend. Die nassen Quarzteilchen, die man im voraus bei Zimmertemperatur auf Wasserdampf aufbewahrt hat, zeigen grössere S.V. und dementsprechend kleinere S.Z. Die 55%-Suspension von den nassen Stärkepulvern gibt ein mehr oder weniger stabiles thixotropes System, dagegen ist die 55%-Suspension von den getrockneten Pulvern instabil.

II. Die Beobachtungen wurden nächstens mit dem System: Stärke-Benzol unter Zusatz von Wasser durchgeführt. Man setzt im voraus eine gewogene Menge (1 g.) von den getrockneten Stärkepulvern in Gefässe mit H_2SO_4 -Wasser Gemisch in verschiedenen Mischungsverhältnissen und nach 3 Tagen bestimmte man durch Wägung den Wassergehalt, der von

Stärke aufgesaugt wurde. Die auf diese Weise vorbehandelten Stärkepolver liess man dann mit 10 ccm Benzol in Messzylindern suspendieren, darauf wurden das S.V. und die S.Z. gemessen. Die Ergebnisse sind in Tabelle 4 angegeben.

Tabelle 4. Stärke-Benzol-System: Einfluss von Wasser.

Wassergehalt (g./g. Stärke)	Sedimentvolumen (ccm/g. Stärke)	Sedimentierungs- zeit (Min.) (Sek.)		Thixotrope Suspension (% Stärke)
0.00	1.2	2		59
0.09	1.4			
0.14	1.9	1	30	
0.18	3.0			
0.22	4.5		40	40
0.25	5.0			
0.26	5.4		30	
0.28	5.8			
0.35	—			33

Man sieht hieraus, dass sich das S.V. mit dem Wassergehalt merklich vergrössert, dementsprechend die S.Z. sinkt. Im System mit grösserem Wassergehalt quellen die Teilchen sehr stark auf, sodass sie eine weiche elastische Masse bilden. Interessant ist der Vorgang, dass dabei sogenannte chromatische Zerstreuung in Erscheinung tritt, was von Herrn Sato in unserem Laboratorium näher untersucht wurde, worüber in folgender Mitteilung berichtet wird.

Dass das S.V. hierbei mit dem sich vergrössernden Wassergehalt stark ansteigt, deutet darauf hin, dass die nassen Stärkepolver in Benzol durch Aufnahme von Benzol aufquellen. In welcher Weise die Aufnahme des Benzols durch Stärke nach ihrem Wassergehalt veränderlich ist, wird von den in Tabelle 5 gezeigten Angaben illustriert.

Tabelle 5. Benzol-Aufnahme der Stärke.

Wassergehalt (g./g. Stärke)	Benzol-Aufnahme (ccm/g. Stärke)
0.00	0.34
0.09	0.35
0.14	—
0.18	0.5
0.22	0.58
0.25	0.68
0.26	0.68
0.28	0.70
0.35	0.71

Die Benzolaufnahme durch die Stärkepolver wurde mittels dem von Freundlich, Lindau und Schmidt⁽³⁾ angegebenen Apparat gemessen. Die Aufnahme des Benzols durch Stärke vergrössert sich tatsächlich bedeutend mit dem Wassergehalt.

Mit den getrockneten Stärkepolvern erhält man ein mehr oder weniger stabiles thixotropes Sol erst bei der Konzentration von 59%-Stärke in Benzol, während die Suspensionen mit genügend nassen Stärkepolvern bei noch geringeren Konzentrationen thixotrop sind.

III. Die nächsten Versuche befassen sich mit dem System: Stärke-Dioxan unter Zusatz von Wasser. Dieses System ist deshalb interessant zu untersuchen, weil Dioxan trotz seinen unpolaren Charakters, mit Wasser in willkürlichen Verhältnissen vertragbar ist. Tabelle 6 gibt die Ergebnisse an.

Tabelle 6. Stärke-Dioxan-System: Einfluss von Wasser.

Zusammensetzung (Dioxan : Wasser)	Sedimentvolumen (ccm/g. Stärke)	Sedimentierungszeit (Min.)	Dichte	Thixotrope Suspension (% Stärke)
100 : 0	1.25	25	1.0333	62
98 : 2	1.45	10	1.0361	60
94 : 6	1.72	8	1.0376	58
90 : 10	2.00	7	1.0406	59
80 : 20	1.95	25	1.0414	—
60 : 40	1.60	90	1.0410	—
40 : 60	1.60	75	1.0371	—
20 : 80	1.70	75	1.0212	—
0 : 100	1.75	60	1.0111	dilatant

Bemerkenswert ist hier, dass das S.V. einmal mit dem ansteigenden Wassergehalt anwächst, dann sinkt und schliesslich wieder ansteigt, dementsprechend die S.Z. einmal sinkt, dann steigt, und schliesslich wieder sinkt. Dieses Sachverhältnis wird ausserdem in Fig. 1 deutlich gemacht.

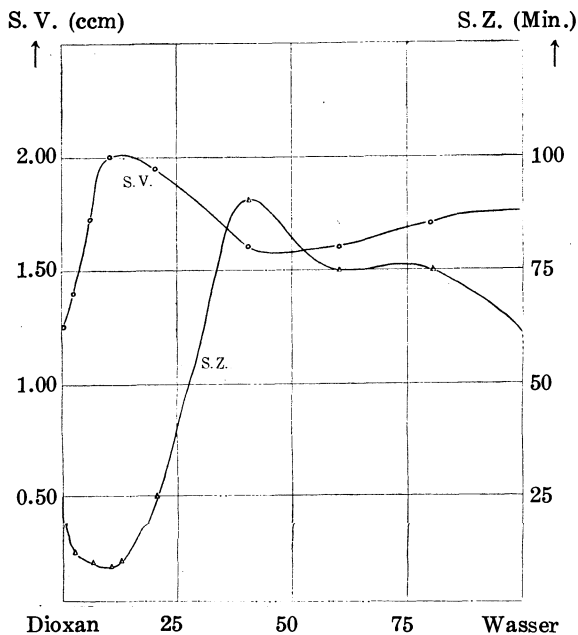


Fig. 1.

Das anfängliche Ansteigen von dem S.V. bzw. das Absinken von der S.Z. ist analog dem Stärke-Benzol System und der Teilchen agglomerierenden Wirkung des Wassers zuzuschreiben. Wie aber das Maximum vom S.V. bzw. Minimum von der S.Z. zustande kommt, lässt sich nicht ohne weiteres verstehen. Damit hängt wahrscheinlich die Änderung der Dichte der Dioxan-Wassergemische zusammen, die, wie Tabelle 6 zeigt, bei der Zusammensetzung von etwa 80%-Dioxan auch ein Maximum darstellt.

Die 62%-Stärke-Suspension in reinem Dioxan verhält sich thixotrop; das thixotrope Verhalten tritt

bei dem Zusatz von geringer Menge Wasser noch günstiger auf, was dem Ansteigen des S.V. der Teilchen entspricht. Es tritt aber hierbei in allen Fällen die Synärese auf. Bei Zusatz von grösserer Menge Wasser verlieren die Suspensionen wieder die Stabilität und zwar verhält sich die Suspensionen in reinem Wasser nicht mehr thixotrop sondern dilatant.

IV. Im System: Quarz- CCl_4 , scheint der Effekt der Fettsäuren, wie bereits Harkins und Gans⁽⁷⁾ darauf aufmerksam gemacht haben, durch die monomolekulare Adsorptionsschicht zur Wirkung zu kommen. Auch in den vorliegenden Versuchen wurden in der Tat die Grenzkonzentrationen der Fettsäuren, bei denen ein merklicher Effekt auf das S.V. bzw. die S.Z. hervortritt, so gering gefunden, dass sie nicht grösser sind als der Konzentrationen, die der monomolekularen Adsorptionsschicht entsprechen.

Die Kenntnisse über die von Teilchen aufgenommene Menge des Wassers wären auch nutzbar für die Aufklärung des Mechanismus der Erscheinung; die Bestimmung des adsorbierten Wassers ist aber gewöhnlich nicht leicht durchzuführen. Die Bestimmung von Wassergehalten durch die Messung der Dielektrizitätskonstanten (abgekürzt DK)⁽¹¹⁾ wird jedoch gerade hierzu anwendbar, wenn man insbesondere das System Dioxan-Wasser betrachtet. Mit Hilfe dieser Methode haben wir versucht die adsorbierte Wassermenge durch Quarz bzw. Stärke in Dioxan-Wasser-Gemischen zu bestimmen in der Weise, wie im folgenden beschrieben wird. Man bestimmte im voraus die DK der Dioxan-Wasser-Gemische von bekannten Zusammensetzungen, woraus man eine geradlinige Beziehung zwischen der DK und der Zusammensetzung erhielt, wie in Tabelle 7 und in Fig. 2 gezeigt ist. Man bereitete dann die Dioxan-Wasser-Gemische

Tabelle 7. Dielektrizitätskonstante der Dioxan-Wasser-Gemische.

Wassergehalt (%)	DK
0	2.281
2.30	2.866
4.14	3.454
6.12	4.132
6.65	4.269
8.09	4.848
8.73	5.004
11.15	5.783

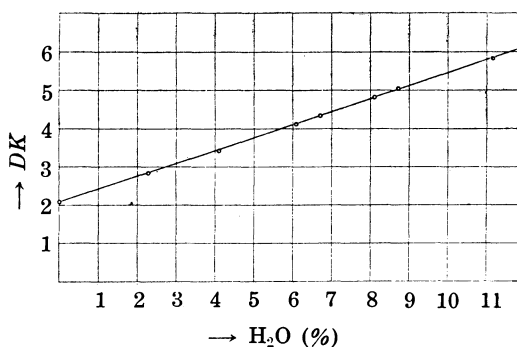


Fig. 2.

von willkürlichen Zusammensetzungen, in denen man Quarz bzw. Stärke suspendierte, stark schüttelte, und die DK der Lösung vor und nach der Adsorption bestimmte. Durch Interpolierung in der oben erhaltenen Linie bestimmte man die Differenz in Zusammensetzungen vor und nach der Adsorption, woraus sich die aufgenommene Wassermenge, wie in Tabelle 8 gezeigt ist, ergab.

(11) Vgl. L. Ebert, *Z. Angew. Chem.*, **47** (1934), 305; R. Büll, *Z. V. D. I.*, **79** (1935), 133.

Tabelle 8. Dielektrische Bestimmung adsorbierter Wassermenge.

	Zusammensetzung der Lösung (% Wasser)	D K der Lösung im Adsorptions- Gleichgewicht	Adsorbierte Wasser (Millimol/g.)	Zahl der Wasser- moleküle pro Teilchen
Quarz	2.55	2.766	0.3	$\approx 10^{12}$
	6.03	3.984	0.2	
Stärke	2.48	2.732	4.1	$\approx 2.10^{13}$
	4.29	3.302	4.3	
	6.22	3.761	5.1	
	8.16	4.427	5.1	

Verteilt man diese Wassermenge auf je ein Teilchen des festen Körpers, dessen Radius als eine Kugel betrachtet, im Mittel als $10\ \mu$ gesetzt ist, so erhält man die Zahl der zu einem Teilchen gebundenen Wassermoleküle, die auch in der Tabelle angegeben ist. 10^{10} Wassermoleküle bilden schon eine monomolekulare Adsorptionsschicht um die Teilchen, sodass die oben erhaltenen Zahlen eher einer multimolekularen Adsorptionsschicht entsprechen. Hier spielen also dickere Lyosphären eine Rolle. Die Methode der Messung der Dielektrizitätskonstante ist für die Bestimmung der Wasseradsorption von Quarz oder von Stärke in Benzol- bzw. Tetrachlorkohlenstoff-Lösungen nicht mit Sicherheit anzuwenden, da die Löslichkeit des Wassers in diesen Lösungsmitteln sehr beschränkt ist.

Zusammenfassung.

Die Sedimentation und Agglomeration grob disperser Teilchen in apolaren organischen Flüssigkeiten — Quarz in Tetrachlorkohlenstoff, Stärke in Benzol bzw. Dioxan — wurden bei Zusatz von einem polaren Stoff wie Fettsäure oder Wasser untersucht, unter besonderer Berücksichtigung des möglichen Zusammenhanges zwischen diesen Vorgängen und den Flieseigenschaften, insbesondere Thixotropie und Dilatanz der Suspensionen.

Im System: Quarz in CCl_4 wirkt eine geringe Menge von Palmitinsäure oder anderen Fettsäuren die Teilchen dispergierend, indem sie das Sedimentvolumen verkleinert und die Sedimentierungszeit vergrößert; dagegen wirkt Wasser die Teilchen agglomerierend, indem es das Sedimentvolumen vergrößert und die Sedimentierungszeit verkleinert. Eine instabile Suspension mit getrockneten Quarzpulvern wird bei Zusatz von geringer Menge Wasser mehr oder weniger stabiler und thixotrop.

Im System: Stärke in Benzol ist Einwirkung vom zugesetzten Wasser sehr bedeutend, wobei das Sedimentvolumen mit dem Wassergehalt allmählich ansteigt, während dabei die Sedimentierungszeit sinkt. Die Stärkepolver mit genügend grossem Wassergehalt quellen in Benzol stark auf, wobei die Benzol-Aufnahme von Stärke mit ihrem Wassergehalt anwächst. Die thixotrope Eigenschaft der Suspension wird allerdings durch Zusatz von Wasser begünstigt.

Das Sedimentvolumen und die Sedimentierungszeit der Stärke wurden in Gemischen von Dioxan und Wasser in verschiedenen Zusam-

mensetzungen beobachtet, wobei das Sedimentvolumen bei gewisser Zusammensetzung der Gemische (Dioxan 90: Wasser 10) ein Maximum aufweist, dementsprechend die Sedimentierungszeit dabei ein Minimum aufweist.

Die konzentrierten Suspensionen der Stärke in Dioxan-Wassergemischen mit kleinerem Wassergehalt verhalten sich thixotrop, dagegen verhalten sich die Suspensionen mit grösserem Wassergehalt nicht mehr thixotrop, sondern dilatant.

Zur Bestimmung der adsorbierten Menge des Wassers an den festen Teilchen wurde die Messung der Dielektrizitätskonstante angewandt, die aber vorläufig nur an den Systemen mit Dioxan als Dispersionsmittel durchgeführt wurde. Die Ergebnisse deuten darauf hin, dass die adsorbierten Wassermoleküle an Quarz- oder Stärke-Teilchen in Dioxanlösungen eine mehr oder weniger dickere Lyosphäre um die Teilchen bilden.

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Chromatische Suspensionen von löslicher Stärke in Benzol.

Von Koichi SATO.

(Eingegangen am 11. October, 1941.)

Vor einem halben Jahrhundert wurde von C. Christiansen ein sehr interessanter Versuch angestellt, in welchem disperse Systeme reine schöne und mannigfaltige Farben zeigten, ohne dass die disperse Phase oder das Dispersionsmittel selbst eine ausgesprochene selektive Absorption im sichtbaren Spektrum zeigte. Bringt man das farblose Glaspulver (oder Pulver von NaCl)⁽¹⁾ in eine Flüssigkeit, die annähernd denselben Brechungsexponenten wie Glas hat, so erscheint das System gefärbt. Diese hübschen Erscheinungen werden nicht nur in den Suspensionen von Pulver, sondern auch in Emulsionen, die "Chromatische Emulsionen" genannt werden,—z.B. in der Emulsion von Glycerin in einem Gemisch von Aceton und Benzol mit Nitrozellulose als Emulgator (Bodroux, Holmes und Cameron)⁽²⁾—beobachtet.

In den vorliegenden Versuchen wurde gefunden, dass die Suspensionen von löslicher Stärke in Mischungen von Benzol und Schwefelkohlenstoff auch eine chromatische Suspension darbieten, wobei die Beziehung zwischen den Breungskoeffizienten von Stärke und der Wasser-

(1) Wo. Ostwald, Licht und Farbe in Kolloiden. 1924; E. Knudsen, *Kolloid-Z.*, **66** (1934), 257; W. Geffcken, *Kolloid-Z.*, **86** (1939), 55.

(2) W. Clayton, The theory of emulsions and their technical treatment. third. ed. 1937.

dampfsorption aufgesucht wurde. Zur Feststellung einer allgemeinen Regel in den chromatischen Suspensionen wurde die Erscheinung auch an den Suspension von Glaspulver in Benzol mit geringer Menge von Äthylalkohol in Betracht gezogen.

Chromatische Suspensionen mit Glaspulver. Als Versuchsmaterial wurde Terexglas (Mazda) verwendet, indem man es zuerst im Mörser so fein wie möglich pulversierte, und dann die Glaspulver in den Exikator mit konz. H_2SO_4 legte bis sie ganz getrocknet waren. Wie man es in der Mineralogie tut, wurde der Brechungskoeffizient des Glaspulvers sowohl mittels der Immersionsmethode als auch mittels der Dispersionsmethode bestimmt, wobei man einen Monochromator (Leitz) als Lichtquelle verwendete. Der Brechungskoeffizient des Glaspulvers war $n_D=1.484$, mit der Dispersion von $n_F-n_C=0.007$ (20°C). Man bereitete nun eine Reihe Mischungen von Benzol und Äthylalkohol in Glasröhrchen aus folgenden Zusammensetzungen: 100, 90, 87.5, 85, 82.5, 80, 70, 60% in Volumkonzentration an Benzol. Tat man je 1 g. vom Glaspulver in diese Mischungen hinein, so traten die verschiedenen Farben in Erscheinung, wie in Tab. 1. gezeigt ist.

Tabelle 1.

Nr.	Benzol (ccm.)	Alkohol (ccm.)	Zerstreuungsfarbe	Durchgelassene Farbe
1	10	0	Blau, wie Tabaksrauch	—
2	9	1	Violettblau	Orange
3	8.75	1.25	Violett	Gelb
4	8.5	1.5	Rotviolett	Grün
5	8.25	1.75	Rot	Hellblau
6	8	2	Orange	Tiefblau
7	7	3	Gelb	
8	6	4	Weiss	

Die Messung des Brechungsvermögens der verwendeten Flüssigkeiten erfolgte im Refraktometer von Abbe bei 20°C . Dieses Instrument gestattet bekanntlich neben dem Brechungsindex n_D der untersuchten Flüssigkeiten zugleich auch dessen Dispersion n_F-n_C zu bestimmen.

In Tabelle 2 sind die auf diese Weise bestimmten Brechungskoeffizienten und die Dispersion angegeben.

Tabelle 2.

Nr.	Benzol (ccm.)	Alkohol (ccm.)	Brechungskoeffizient (n_D)	Dispersion (n_F-n_C)
1	10	0	1.501	0.017
2	9	1	1.489	0.016
3	8.75	1.25	1.485	0.016
4	8.5	1.5	1.481	0.016
5	8.25	1.75	1.478	0.015
6	8	2	1.474	0.015
7	7	3	1.461	0.014
8	6	4	1.447	0.013

Wenn man das violett erscheinende System erwärmt, so variiert die Farbe von violett zu rot bzw. orange.

Ganz ähnliche Erscheinungen wurden auch in folgenden Systemen beobachtet; nämlich in den Suspensionen von Terexglas (1) in Benzol-Chloroform, (2) in Benzol-Tetrachlorkohlenstoff, (3) in Pyridin-Äthylalkohol, (4) in Toluol, (5) in Xylol, und (6) in CS_2 -Äthylalkohol; auch in den Suspensionen von Fluoritpulver in Methylalkohol-Benzol traten diese Erscheinungen auf.

Die Brechungskoeffizienten von Glycerin oder Paraffinöl sind denen von Xylol oder Toluol sehr ähnlich, die Terexglaspulver zeigen indessen darin keine Farbenerscheinungen.

Chromatische Zerstreuung in den Suspensionen von Stärke und ihre Beziehung zu Wasserdampfsorption. Man mischte Schwefelkohlenstoff mit Benzol in folgenden Volumprozenten: 50, 40, 30, 20, 10, 0, an CS_2 . Mittels eines Refraktometers von Abbe wurden die Brechungskoeffizienten dieser Flüssigkeiten bei 20°C . bestimmt, wobei auch die Dispersion festgestellt wurde. Tab. 3 zeigt die Ergebnisse.

Tabelle 3.

Nr.	Benzol (ccm.)	CS_2 (ccm.)	Brechungskoeffizient (n_D)	Dispersion ($n_F - n_C$)
1	10	0	1.501	0.017
2	9	1	1.514	0.018
3	8	2	1.527	0.020
4	7	3	1.540	0.022
5	6	4	1.553	0.024
6	5	5	1.567	0.026

Setzt man je 1 g. von gut getrockneter löslicher Stärke (Merck) in Glasröhrchen mit Glasstöpsel, worin sich Benzol oder verschiedene Mischungen von Benzol und Schwefelkohlenstoff befinden, so entsteht da eine Reihe von Farben wie in Tab. 4 angezeigt ist.

Tabelle 4.

Nr.	Benzol (ccm.)	CS_2 (ccm.)	Färbung (20°C .)
1	10	0	Weiss
2	9	1	Orange
3	8	2	Rosefarbig
4	7	3	Lilafarben
5	6	4	Blau
6	5	5	Milchweiss

Die verwendete lösliche Stärke war nicht isotrop, sondern anisotrop, und zwar waren die anisotropen Mizellen schraubenförmig in den Stärke-

körnchen orientiert, auf denen bei Betrachtung mit einem Polarisationsmikroskop ein schwarzes Kreuz erschien. Deswegen war es schwer die genauen Brechungskoeffizienten dieses Materials zu bestimmen.

Die Farben in chromatischer Zerstreuung mit isotropen Substanzen sind rein und einfach. Wenn die Farben aber von doppelbrechenden Kristallen oder Micellen stammen, so treten auch Farben auf, die meist unrein sind und zwar stark mit weissem Licht gemischte Nuancen zeigen. Man könnte jedoch den Brechungskoeffizienten n_D von löslicher Stärke annähernd gleich 1.540 und dessen Dispersion gleich 0.008 setzen.

Zweitens wurde die Veränderung in der chromatischen Zerstreuung der löslichen Stärke durch Wasserdampfsorption beobachtet. Man brachte die Stärke, die in einer Uhrschale lag, in den Exikator, worin man anstatt Schwefelsäure, Wasser hinein getan hatte. Die Temperatur im Gefässe war 23°C.

Der kleine Wägebecher mit 3 g. der getrockneten löslichen Stärke wurde gleichzeitig ins Gefäss gesetzt. Nach 6 Stunden nahm man eine kleine Menge von der Stärke heraus, tat sie in ein Glasröhrchen mit reinem Benzol, und beobachtete die Färbung des Systems. Gleichzeitig bestimmte man durch Wägung des Bechers die von der Stärke aufgenommene Wassermenge, und je nach 24, 48 Stunden usw. wurde dieses Verfahren wiederholt. Die Ergebnisse sind in Tab. 5 gezeigt. Während die Wasserdampfsorption der löslichen Stärke mit der Zeit allmählich abwächst, variiert das System seine Färbung, wie in Tabelle 5 zusammengefasst ist.

Solange die Wassersorption der Stärke weniger als 10% bleibt, verhält sich das System dilatant in Benzol, aber bei einer grösseren Wasserdampfsorption verhält sich das System deutlich thixotrop.⁽³⁾

Tabelle 5.

Nr.	Zeit in Stunden	Wasserdampfsorption in Gewichtsprozent	Färbung in Benzol (23°C.)
1	6	1.24	Gelb
2	24	4.47	Orange
3	48	7.71	Rosefarbig
4	72	10.02	Lilafarben
5	96	11.80	Blau
6	120	13.20	Blau
7	168	15.45	Blau
8	336	20.96	Milchweiss

Diskussion über die Versuchsergebnisse. Trägt man die Dispersionskurven auf hyperbolische lineare Netze ein, so bekommen wir für alle Dispersionen gerade Linien. Fig. 1 zeigt also die Dispersionskurven des Terexglaspulvers und der verwendeten Flüssigkeitsgemische an.

(3) Vergl. B. Tamamushi und S. Tomatsu; dieses Bulletin, 17 (1942), 23.

Die Farben der durchgelassenen Strahlen sind schwer zu beobachten. Bei der chromatischen Suspension von Terexglaspulver in Mischung von Benzol 8.75 ccm. und Äthylalkohol 1.25 ccm. ist das Bündel von durchgelassenen Strahlen sehr schmal und alle anderen Strahlen werden zerstreut, wie in Fig. 2 gezeigt ist.

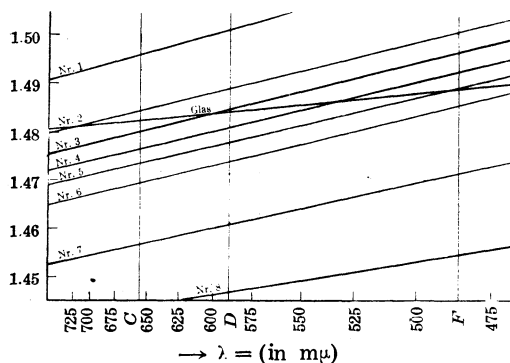


Fig. 1.

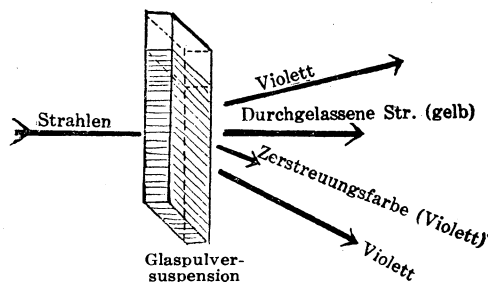


Fig. 2.

Um die Farben der durchgelassenen Strahlen zu beobachten, muss man eine Blende zur Verhinderung von Zerstreuungslight einsetzen. Wenn man die Farbe von den durchgelassenen Strahlen in Fig. 1 sieht, so findet man, dass die Wellenlänge von den durchgelassenen Strahlen zum Schnittpunkt der Dispersionskurven der zwei Phasen entspricht. Die Farbe des Zerstreuungslights ist komplementär zu den durchgelassenen Strahlen.

Die Färbung kommt dadurch zustande, dass sich die Dispersionskurven für zwei Phasen innerhalb des sichtbaren Gebietes der Strahlen schneiden, wobei die beiden Phasen ein gleiches Brechungsvermögen besitzen. Das Licht mit der Wellenlänge des Schnittpunktes der Dispersionskurven geht ungestört durch die beiden Phasen, während das Licht anderer Wellenlänge zerstreut wird, und zwar umso mehr je größer der Unterschied im Lichtbrechungsvermögen der zwei Phasen ist.

Die Terexglaspulver geben in Glycerin oder Paraffinöl keine deutliche Färbung, da die beiden Flüssigkeiten ähnlichen Brechungskoeffizienten und ähnliche Dispersionskurven wie Terexglas haben.

Wenn zwei Phasen die gleichen Brechungskoeffizienten bei D-Linie und die gleichen Dispersionen haben, so dass sich die Dispersionskurven für die zwei Phasen bei D-Linie schneiden, so erscheint die violette Färbung, komplementär zur gelben. Unter Verwendung der bekannten Flüssigkeiten kann man also den Brechungskoeffizienten und die Dispersion eines Pulvers bestimmen, indem man die Färbung der chromatischen Zerstreuung beobachtet.

Wenn man die Brechungskoeffizienten und die Dispersionen der löslichen Stärke und der abgestuften Flüssigkeiten auf das hyperbolische lineare Netz einträgt (Fig. 3), bemerkt man keine ähnliche Beziehung wie bei dem System von Glaspulver in Benzol-Alkohol-Gemisch. Die beobachteten Schnittpunkte der Dispersionslinien von Stärke und Flüssigkeiten sind von den erwarteten Punkten stark abweichend.

Da die Stärke in manchen Flüssigkeiten mehr oder weniger quellbar ist, so müssen die beobachteten Brechungskoeffizienten von den wirklichen Brechungskoeffizienten von Stärke abweichen und sich eher den Brechungskoeffizienten von den betreffenden Flüssigkeiten nähern. Dies ist schematisch in Fig. 4 gezeigt.

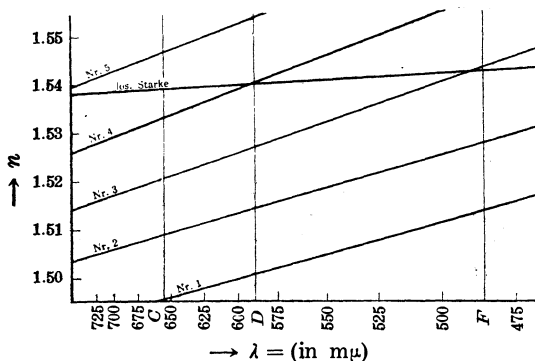


Fig. 3.

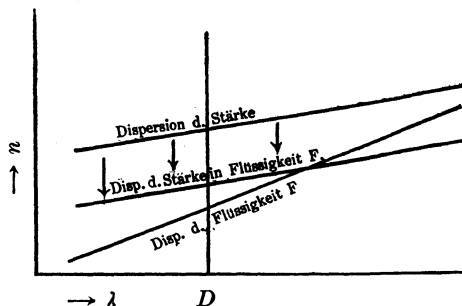


Fig. 4.

Wir stellen nun den Brechungskoeffizienten der Stärke mit Hilfe der Newtonschen Mischformel folgenderweise dar:

$$n^2 = \delta_1 n_1^2 + \delta_2 n_2^2,$$

wobei $n_1 = 1.540$ den Brechungskoeffizienten der Stärke und n_2 den Brechungskoeffizienten der Flüssigkeit bedeutet; δ_1 und δ_2 sind die relativen Volumanteile der beiden Phasen. Setzt man hierbei $\delta_1 = \delta_2 = 0.50$, so haben wir folgende Werte für n (Tabelle 6).

Tabelle 6.

n_1	Brechungskoeffizient der durchgetränkten Stärke (n)
1.514	1.527
1.527	1.533
1.540	1.540
1.553	1.547

Die Neigung der Dispersionskurve der Stärke variiert möglicherweise allmählich mit der Veränderung des Brechungsvermögens, es ist deshalb unmöglich in solchen Fällen die Schnittpunkte der beiden Dispersionslinien genau zu bestimmen.

Wenn man annehmen könnte, dass die Dispersionen dabei unverändert bleiben, so würden die Schnittpunkte der beiden Dispersionslinien mit den erwarteten übereinstimmen.

Diese Annahme kann allerdings nicht immer bestätigt werden. Auf Grund der oben erhaltenen Ergebnisse an der chromatischen Zerstreuung der löslichen Stärke, ist es jedenfalls schwierig eine eindeutige Erklärung über die Beziehung zwischen den Farben und Dispersionen zu geben.

Die lösliche Stärke, die 1.24-gewichtsprozent Wasser aufgesaugt hat, zeigt in Benzol eine gelbe chromatische Zerstreuung, während die Stärke mit Wasser in 4.47-gewichtsprozent die Orangefarbe zeigt. Diese Farbenverschiebung rührt vom Absteigen des Brechungskoeffizienten der Stärke.

her. Man berechnete die Brechungskoeffizienten der Stärke, die Wasser in verschiedenen Mengen enthält, mit Hilfe der Newtonschen Mischformel, wobei sich Werte, wie in Tabelle 7 angegeben sind, ergaben.

Tabelle 7.

Nr.	Zeit in Stunden	Wassersorption in Gewichtsprozent	Volumenanteil		n
			(Stärke)	(Wasser)	
1	0	0	1.00	0	1.540
2	6	1.24	0.98	0.02	1.536
3	24	4.47	0.94	0.06	1.528
4	48	7.72	0.90	0.10	1.521
5	72	10.02	0.87	0.13	1.515
6	96	11.80	0.85	0.15	1.511
7	120	13.20	0.83	0.17	1.507
8	168	15.45	0.81	0.19	1.503
9	336	20.96	0.76	0.24	1.493

(Dichte der Stärke: 1.5, Dispersion: $n_F - n_C$ 0.008)

Man kann die Färbung von diesen Systemen aus diesen Ergebnissen (Vergl. Fig. 5) nicht ohne weiteres erklären, auch wenn man den Einfluss der Durchtränkung der Stärke mit Benzol in Betracht zieht. In Systemen von Nr. 6, 7, 8, 9, erscheint in allen Fällen eine blaue Färbung, wonach der Brechungskoeffizienten von Stärke immer kleiner als 1.501 sein müsste, was aber in Wirklichkeit nicht der Fall ist.

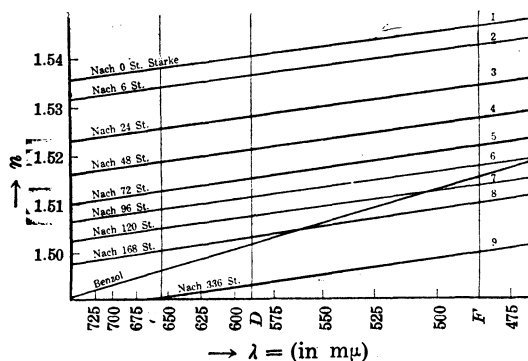


Fig. 5.

Dieser Widerspruch ist wahrscheinlich der Quellung der Stärke in Wasser zuzuschreiben, die in Stärkekörnchen sowohl intramizellar als auch intermizellar stattfinden

kann. Es ist noch zu bemerken, dass die Stärkekörnchen, die im voraus Wasserdampf aufgenommen hatten, auch in Benzol stark quellbar sind.⁽³⁾

Zum Schluss möchte ich Herrn Prof. B. Tamamushi für die Anregung zu vorliegender Arbeit herzlich danken. Auch Herrn Dr. Kotaro Tomiyama bin ich für seine wertvollen Ratschläge bei dieser Arbeit zu grossem Dank verpflichtet.

Zusammenfassung.

(1) Die chromatische Zerstreuung wurde an den Suspensionen von Glaspulver (Terexglas $n_D^{20} = 1.484$, $n_F - n_C = 0.007$) in Mischungen von Benzol und Äthylalkohol beobachtet.

(2) Eine ganz ähnliche Erscheinung wurde auch an den Suspensionen von getrockneter Stärke in Mischungen von Benzol und Schwefelkohlenstoff gefunden.

(3) Wenn die lösliche Stärke Wasserdampf aufnimmt, kommt die Färbung auch in Suspensionen in reinem Benzol zum Erscheinen.

(4) Durch Aufnahme des Wassers weicht sich der Brechungskoeffizient von Stärke von dem wirklichen stark ab, wodurch eine eindeutige Erklärung der Erscheinung in den chromatischen Suspensionen schwer zu geben ist.

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Über die Thixotropie und Rheopexie von Paraffin-Suspensionen.

Von Koichi SATO und Bunichi TAMAMUSHI.

(Eingegangen am 11. October, 1941.)

Die Suspensionen von polaren Teilchen wie Quarzpulver in einem apolaren Medium wie Tetrachlorkohlenstoff verhalten sich bei Vorhandensein von einem polaren Stoff wie Wasser thixotrop, wobei sich die Teilchen in dem Medium, indem sie eine Solvathülle um sich bilden, miteinander agglomerieren. Über diese Vorgänge haben bereits frühere Untersuchungen⁽¹⁾ berichtet.

Es könnte nun möglich sein, dass die Suspensionen von apolaren Teilchen in einem polaren Medium bei Vorhandensein von einem apolaren Stoff ebenfalls die thixotrope Eigenschaft erwerben. Die thixotropen Suspensionen von Myrizylpalmitat (aus Bienenwachs) in Äthylalkohol unter Zusatz von Benzol, die von einem von uns (B.T.) früher untersucht worden sind, bieten in der Tat ein Beispiel eines solchen Falles.⁽²⁾

Bringt man also je 1 g. Myrizylpalmitat (spezifisches Gewicht 0.802, und Schmelzpunkt 58°C) in Reagenzgläser von Durchmesser 15 mm. mit je 10 ccm. des Gemisches von Alkohol und Benzol in verschiedenen Mengenverhältnissen, indem man das ganze Gemisch einmal auf etwa 60°C erwärmt und dann unter kräftiger Schüttelung rasch abkühlt, so erhält man die Suspensionen, die sich folgenderweise verhalten (Tabelle 1).

Die Suspensionen sind also in gewissen Mengenverhältnissen von Alkohol und Benzol thixotrop, während die Suspensionen mit einer überschüssigen Menge von Alkohol oder Benzol nicht beständig sind.

(1) B. Tamamushi und S. Tomatsu, dieses Bulletin, S. 23.

(2) B. Tamamushi, *Kolloid-Z.*, **76** (1936), 171.

Tabelle 1. Myrizylpalmitat (aus Bienenwachs) in Alkohol-Benzol-Gemischen (1 g. in 10 ccm, 19°C).

Nr.	Alkohol : Benzol (im Volumprozent)		Mengenverhältnis (Alkohol/Benzol)	Verhalten gleich nach Herstellung
1	0	10	0	Lösung
2	1	9	0.11	unbeständige Suspension
3	2	8	0.25	unbeständige Suspension
4	3	7	0.44	schäumige unbeständige Suspension
5	4	6	0.66	schäumige unbeständige Suspension
6	5	5	1	thixotrop, Erstarrungszeit: 8 Minut.
7	6	4	1.5	thixotrop, Erstarrungszeit: 8 Minut.
8	7	3	2.3	thixotrop, Erstarrungszeit: 12 Minut.
9	8	2	4	thixotrop, Erstarrungszeit: 45 Minut.
10	9	1	9	unbeständig
11	10	0	∞	unbeständig

Wir haben nun gefunden, dass sich auch Paraffin, ein typisch apolarer Stoff, in Alkohol unter Zusatz von Benzol ganz ähnlich wie Myrizylpalmitat verhält. Man tut Paraffin (das reine Präparat Merck, Schmelzpunkt 50°C, sp. Gew. 0.86) je 1 g. in Reagenzgläser von Durchmesser 15 mm mit je 10 ccm. von Alkohol-Benzol-Gemisch in verschiedenen Mengenverhältnissen ein. Man erwärmt das Gemisch einmal auf etwa 50°C, wobei sich das Paraffin völlig löst, und kühlt es dann unter kräftigem Schütteln rasch ab. Die auf diese Weise erhaltenen Suspensionen zeigen folgende charakteristische Eigenschaften (Tabelle 2).

Wie man hieraus sieht, sind die Suspensionen bei gewissen Mengenverhältnissen von Alkohol und Benzol deutlich thixotrop; die Erstarrungszeit ist dabei angegeben. Bemerkenswert ist, dass sich diese Suspensionen nicht nur thixotrop, sondern auch rheopektisch verhalten. Die Suspensionen erstarren nämlich viel schneller, wenn sie nicht stillstehen lässt sondern sie leicht bewegt, indem man den Reagenzglasboden auf den Tisch rhythmisch klopft.⁽³⁾ Die rheopektische Erstarrungszeit ist auch in der Tabelle angegeben.

Die thixotropen Suspensionen von Myrizylpalmitat in Alkohol-Benzol-Gemischen weisen ebenfalls Rheopexie auf.

Es ist hier noch zu bemerken, dass die thixotrope bzw. rheopektische Eigenschaft dieser Suspensionen zeitabhängig ist, wobei sich die Erstarrungszeit mit der Zeit ändert, einmal sich verkürzt, aber dann verlängert, bis die Suspensionen endlich unbeständig werden.

In den Suspensionen mit überschüssigen Menge von Benzol (Nr. 2, 3, 4, 5) kommt beim Schütteln eine Schäumung zutage, und der dadurch auftretende Schaum verhält sich zuweilen ziemlich fest, indem er viele kleine Kriställchen von Paraffin enthält.

(3) H. Freundlich u. F. Juliusburger, *Trans. Faraday Soc.*, **31** (1935), 920.

(4) Vgl. E. A. Hauser u. C. E. Reed, *J. Amer. Chem. Soc.*, **58** (1936), 1822.

Tabelle 2. Paraffin in Alkohol-Benzol-Gemischen
(1 g. in 10 ccm, bei 19°C).

Nr.	Alkohol : Benzol (i. Volumprozent)	Mengenverhältnis (Alkohol/Benzol)	Verhalten		
			gleich nach Herstellung	nach 7 St.	nach 48 St.
1	0 10	0	Lösung		
2	1 9	0.11	schäumige Lösung		
3	2 8	0.25	schäumige unbeständige Suspension		
4	3 7	0.44			
5	4 6	0.66			
6	5 5	1	120 Sek. (TEZ) * 5 Sek. (REZ) **	10 Sek. (TEZ) 5 Sek. (REZ)	2 Min (TEZ)
7	6 4	1.5	90 Sek. (TEZ) 5 Sek. (REZ)	10 Sek. (TEZ) 5 Sek. (REZ)	18 Min (TEZ)
8	7 3	2.3	0 Sek. (TEZ) —	120 Sek. (TEZ) 30 Sek. (REZ)	
9	8 2	4	70 Sek. (TEZ) 55 Sek. (REZ)	unbeständig	
10	9 1	9	unbeständige Suspension		
11	10 0	∞			

* TEZ: Thixotrope Erstarrungszeit

** REZ: Rheopektische Erstarrungszeit

Die Suspensionen von Paraffin in Gemischen mit überschüssigen Mengen von Alkohol sind auch nicht beständig, indem die Teilchen darin zu dichten Packen sedimentieren. Bei grösseren Konzentrationen von Paraffin sind jedoch die Suspensionen mit überschüssigem Alkohol wieder mehr oder weniger beständig, und zwar werden bei gewissen

Tabelle 3. Paraffin in Alkohol
(1 g. Einwage, bei 19°C).

Nr.	Alkohol in ccm	Verhalten
1	1.20	schwer verflüssigt
2	1.25	schwer verflüssigt
3	1.30	schwer verflüssigt
4	1.35	Erstarrungszeit: 5 Sek.
5	1.40	Erstarrungszeit: 5 Sek.
6	1.50	Erstarrungszeit: 5 Sek.
7	1.70	Erstarrungszeit: 5 Sek.
8	1.80	unbeständig
9	2.0	unbeständig

Mengenverhältnissen von Paraffin und Flüssigkeit die Suspensionen selbst in reinem Alkohol genügend beständig um die Ganze Masse thixotrop zu festigen, wie folgender Versuch zeigt.

Man giesst eine konzentrierte Benzollösung Paraffins in absoluten Alkohol, filtriert die dabei entstandenen Paraffin-Niederschläge von der Flüssigkeit ab und dann trocknet und pulversiert man sie fein. Suspendiert man die auf diese Weise hergestellten Paraffinpulver in absolutem Alkohol in verschiedenen Konzentrationen,

so erhält man die Suspensionen die in den Reagenzgläsern (von 15 mm Durchmesser) folgende Eigenschaften aufweisen (Tabelle 3).

Die Suspensionen von Paraffin in absolutem Alkohol erweisen sich also in gewissen Konzentrationen (von 40 bis 50%) thixotrop. Ein ganz ähnliches Verhalten ist auch bei Myrizylpalmitat beobachtet worden. Wir haben auch gefunden, dass die Suspensionen von Paraffin in Xylol auch thixotrop sind.

In den oben untersuchten Fällen, handelt es sich allerdings um die anisometrischen—wahrscheinlich plattenförmigen—Teilchen, die sich aneinander anzuhaften streben. Wenn man nun diese Teilchen durch eine rythmische Bewegung zu einer Orientierung—parallel miteinander—veranlasst, so wird die augenblickliche Erstarrung (Rheopexie) auftreten.

Das Anhaften der Teilchen kommt in diesen Fällen wahrscheinlich dadurch zustande, dass zwischen den unpolaren Kohlenstoffketten bei gewisser Orientierung starke van der Waalssche Anziehungskräfte zur Wirkung kommen.

Die Anziehungskräfte zwischen den Teilchen können genügend gross sein, um die Teilchen auch in reinem polarem Medium (Alkohol) zur thixotropen Masse zu agglomerieren. Die Anziehungskräfte werden jedoch noch stärker, wenn die Teilchen mit einem apolaren Stoff (Benzol) aufgequellt sind und demnach mit dicken Solvathüllen umgeben sind.

Das Alterungsphänomen in den thixotropen Suspensionen könnte der allmählichen Zustandsänderung der Solvathülle zugeschrieben werden.

Mit diesen Ansichten stehen die oben beobachteten Vorgänge im Einklang. Es handelt sich hier also um solche Fälle, wo Quellung und Solvatation der Teilchen im Mechanismus der Thixotropie und der verwandten Erscheinungen eine wichtige Rolle spielen.

Zusammenfassung.

Es wurde demonstriert, dass die Suspensionen von Paraffin in Gemischen von Äthylalkohol und Benzol in gewissen Mengenverhältnissen, ebenso wie die Suspensionen von Myrizylpalmitat aus Bienenwachs, thixotrop und rheopektisch verhalten. Die Suspensionen von Paraffin in reinem Alkohol sind auch thixotrop, jedoch erst bei grösseren Konzentrationen von festem Stoff.

Die eigenartigen Vorgänge in diesen Suspensionen wurden von einem allgemeinen Gesichtspunkte aus betrachtet und diskutiert.

Dem Unterrichtsministerium sei gedankt für die Gewährung einer Unterstützung zur Anregung wissenschaftlicher Forschung.

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Enrichment of the Heavy Water by Thermal Diffusion.

By Kozo HIROTA and Osamu KIMURA.

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Introduction. It has been shown⁽¹⁾⁽²⁾ that heavy water which contains deuterium can be concentrated at the colder part in the thermal diffusion apparatus devised by Clusius and Dickel⁽³⁾. On the other hand, it has been also shown definitely by one of the present authors⁽⁴⁾ that the degree of the separation of salt solutions is changed by the addition of another salt, and that the separation of the added salt is also affected inversely at the same time. These results suggest that the isotopic composition of ordinary water may be shifted if it is treated in a thermal diffusion apparatus, especially in the case of salt solutions. The object of the present research is to study the effect of isotopic separation of water caused by the addition of some inorganic substances (1 N H₂SO₄, 0.1 N KCl and 1 N Na₂SO₄).

Experiments. *Apparatus:*—The thermal diffusion apparatus used is of the same type as that described in the paper published by one of the present authors⁽⁵⁾. The length (h) of the column which has an equidistant annular space is 30 cm., the width (a) of the annular space is 0.78 ± 10 mm., and the temperatures of the colder and the hotter walls are $20^\circ \pm 2^\circ\text{C}$. and $76^\circ \pm 1^\circ\text{C}$. respectively. The volumes of the upper and the lower reservoirs are 12 and 4 c.c. respectively.

Procedures:—As the experimental procedures are almost the same as those described in ref. (5), the details are omitted here. Using a part of the sample, which was treated in the apparatus for the desired length of time, the concentrations of H₂SO₄ and KCl were determined volumetrically, while that of Na₂SO₄ gravimetrically. Another part of the sample was distilled twice under the reduced pressure at room temperature. In the case of H₂SO₄, however, the distillation was carried out after neutralisation by metallic zinc. The density change of the purified water thus obtained was measured by means of the usual float method⁽⁶⁾. The accuracy of the density measurement was estimated to be $\pm 1 \gamma$.

Experimental Results. The experimental results are summarised in Table 1, where separation ratio (n'/n) denotes the ratio of the concentration of the solute at the bottom reservoir to that at the top.

(1) K. Clusius and G. Dickel, *Naturwiss.*, **27** (1939), 148.

(2) H. Korsching and K. Wirtz, *ibid.*, **27** (1939), 367.

(3) K. Clusius and G. Dickel, *ibid.*, **26** (1938), 546.

(4) K. Hirota, *Bull. Chem. Soc., Japan*, **16** (1941), 232; *J. Chem. Soc., Japan*, **62** (1941), 568; L. T. Gillespie and S. Breck, *J. Chem. Phys.*, **9** (1941), 370.

(5) K. Hirota, *J. Chem. Soc., Japan*, **62** (1941), 480; *Bull. Chem. Soc., Japan*, **16** (1941), 475.

(6) M. Harada, *J. Chem. Soc., Japan*, **56** (1935), 811.

Table 1. Summarised Experimental Results.

Sample Used (Conc.)	No. of Exp.	Time in Hours	Separation Ratio of the Solute	Density Increase at the Bottom Reservoir in γ
Pure Water (Twice Distilled Water)	15	4	—	2
	3	7	—	0.5
	1	16	—	3
	2	24	—	-0.5
	4	43	—	1
H ₂ SO ₄ (1 N)	8	5	1.5	1.5
	7	12	2.2	4
	6	24	2.7	8
	5	48	3.0	8
KCl (0.1 N)	11	8	1.0 ₇	8
	10	17	1.1 ₁	4
	9	24	1.1 ₁	6
	12	47	1.1 ₂	7
Na ₂ SO ₄ (1 N)	13	7	1.3 ₇	2
	14	24	1.6 ₆	16

As seen in the table, the density differences of pure water, H₂SO₄ and KCl solutions seem to become constant in 48 hours, i.e., 0 γ for pure water, 8 γ for H₂SO₄ and 7 γ for KCl. In the case of Na₂SO₄, however, the data are not sufficient to arrive at a definite conclusion.

It is possible that the density increase is caused by the isotopic shift during the distillation of pure water as well as of the solutions. This effect is, however, negligibly small at least in the case of KCl solution in which the degree of the separation of the solute is small, while in the case of H₂SO₄ there remains some ambiguity, because the separation of the solute is large, and an isotopic shift may also occur in the process of the neutralisation.

Discussion. To check the above results, the separation ratios of the solutes in this research were compared with those in ref. (5), in which an apparatus with such dimensions as $h = 94$ cm. and $a = 0.15$ cm. was used. As shown there, in these apparatus the separation ratios at the stationary state can be expressed as:

$$\ln \frac{n'}{n} = C \cdot D' \frac{h}{a^4},$$

where D' is the thermal diffusion constant and C is the constant which depends only on the kind of the solution. The ratios of the logarithm of the separation ratios of this experiment ($\ln(n'/n)_{II}$) to those in ref. (5) ($\ln(n'/n)_I$) were calculated in each solution, and it was found that these values agree fairly well with the theoretical value (4 ± 1). This is shown in Table 2.

Table 2. Comparison of the Separation Ratios.

(*)			n'/n	$\ln(n'/n)$	$\frac{\ln(n'/n)_{II}}{\ln(n'/n)_I}$
H_2SO_4	(1 N)	II	3	1.1	5.2
	(1 N)	I	1.23	0.21	
KCl	(0.1 N)	II	1.1 ₃	0.1 ₂	3 $\pm$ 1
	(1 N)	I	1.04	0.4	
Na_2SO_4	(1 N)	II	1.6 ₆	0.5 ₃	4.1
	(1 N)	I	1.14	0.13	

(*) I and II denote the values in the previous research (ref. 5) and those of the present one, respectively.

Next, the density increase of pure water will be discussed. The separation ratio of pure water containing about 30% of deuterium was 1.09₃, according to Korsching and Wirtz⁽²⁾, who used an apparatus with $h = 10$ cm. and $a = 0.25$ mm. From these dimensions, D' values of D_2O was calculated to be $5 \times 10^{-10} \frac{\text{cm}^2}{\text{sec. deg}}$ by the formula (1) as described in ref. (5), taking the ordinary diffusion constant of D_2O at 35°C. as $3.9 \times 10^{-5} \text{ cm}^2/\text{sec.}$ ⁽⁷⁾ Assuming that D' value of the water, containing heavy oxygen, is same as the above, the density increase due to both heavy hydrogen and heavy oxygen in our experiment was calculated to be 0.6 γ .⁽⁸⁾ This estimated value conforms to our experiment in the case of pure water where no separation was found within our experimental errors. The separations in the solutions, however, are large as compared with the above calculation.

As the mechanism of the separation of the solute is not clear at present, we cannot account definitely for the reason why the enrichment of the heavy water occurs in the case of the solutions. Here, a plausible explanation was tried as follows: In solutions, the zero-point energies in the vibration between ions and solvated water are different in various water molecules which are different in molecular weight. Owing to this, isotopic shift might occur between solvated water molecules and the non-solvated in the sense that the solvated become richer in heavier isotopes. Therefore, in the thermal diffusion column, the enrichment of heavy water and that of the solute occur at the same time, as is observed in our experiments.

This argument holds in the same way whether the density increase is due to deuterium or to heavy oxygen, and the present authors consider that it will be mainly caused by the latter. If the density increase is assumed to be the result of the deuterium, the separation ratio of the

(7) W. J. C. Orr and J. A. V. Butler, *J. Chem. Soc.*, **1935**, 1273.

(8) The natural contents of heavy hydrogen and heavy oxygen in water are 1/5800 and 1/500, which correspond to 18~19 γ and 200 γ as density. [H. L. Johnston: *J. Am. Chem. Soc.*, **57** (1935), 484; S. H. Manian, H. C. Urey, W. Bleakney: *ibid.*, **56** (1934), 2601.]

deuterium will take an improbably large value (1.4), which is much larger than the separation ratio of the solute itself in KCl solution.

In conclusion, the authors express their sincere thanks to Dr. S. Sato, the Director of the Laboratory, for the permission of the publication of this paper, and the senior author also to Dr. R. Yoshimura, the Chief of the Department of Inorganic Chemistry, for their encouragement throughout this research.

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Studies on Amino-Acids and Related Compounds. XII.* Electrolysis of Phenylalanine and its Derivatives in Nitric Acid.

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(Received October 20, 1941.)

In part V⁽¹⁾ it was stated that phenylalanine and tyrosine were readily oxidised at the anode in dilute sulphuric acid and resulted the rupture of benzene nucleus as well as the formation of humin-like substance. In the present paper the results of the electrolysis of phenylalanine and its derivatives in nitric acid are described.

Few reports on the electrolysis of organic compounds in nitric acid were found. Dunbrook and Lowy (1924)⁽²⁾ have obtained *p*-nitrobenzoic acid and *p*-chlorobenzoic acid from *p*-nitrotoluene and *p*-chlorotoluene respectively by the electrolysis in 20% nitric acid. Fichter and Plüss (1932)⁽³⁾ have reported on the formation of nitronaphthalene by the electrolysis of naphthalene in nitric acid.

Although phenylalanine and tyrosine, possessing NH₂-, HO-, and -COOH groups, have a more complicate constitution than nitrotoluene, the present experiments were carried out to find the conditions for preventing the rupture of benzene nucleus even in electrolysis.

Phenylalanine was dissolved in 4–13.7 N nitric acid and electrolysed in an undivided cell with platinum electrodes at 0°–100°C. under the following conditions: 4–10 amp./dm², 2–7 F./mol.

The results of the electrolysis of phenylalanine in nitric acid depend upon the concentration of nitric acid and the temperature of the cell. In the case of 4–13.7 N nitric acid, a great difference was observed between

* Translated by the authors from *J. Chem. Soc. Japan*, **59** (1938), 1375.

(1) Y. Takayama, this Bulletin, **8** (1933), 178.

(2) R. F. Dunbrook, and A. Lowy, *Trans. Amer. Electrochem. Soc.*, **45** (1924), 81.

(3) Fr. Fichter and E. Plüss, *Helv. chim. Acta*, **15** (1932), 236.

the experiments at 0°–35°, and those at 50°–100°C. The electrolysis at 0°–35°C. proceeded similarly as the electrolysis in dilute sulphuric acid, and the electrolyte gradually assumed a brown colour which was probably due to the formation of melanin-like substance. From the electrolysate no crystalline substance was isolated. On the contrary, at 50°–100°C. the behavior differed markedly from the fact described above. As an example, the result of the experiment under the following conditions: 100°C., 4 amp./dm², 8 N-NO₃H, will be given. After the application of the electric quantity of about 1 farady per mol, nitrogen dioxide gas began to evolve from the electrolysate. At about 2 faradies per mol, the gas evolution decreased, and yellow crystals of *p*-nitrobenzoic acid gradually deposited. Also in the case of 50° and 60° the same phenomena were observed, but the yields of *p*-nitrobenzoic acid were inferior to the case of 100°C.

Among the concentrations of 4 N, 8 N, and 13.7 N of nitric acid, the one of 8 N gave the best yield in obtaining *p*-nitrobenzoic acid, but it was somewhat less pure than that of 13.7 N. The 4 N one was inferior to 8 N and 13.7 N both in yield and in purity. Accordingly, for the preparation of *p*-nitrobenzoic acid, the use of 8 N nitric acid is recommended. As it will be easily seen from Table 3 and Table 4, the favourable conditions of obtaining *p*-nitrobenzoic acid may be the electric quantity: 3–5 F/mol., and the current density: 4–6 amps./dm.²

From the solution electrolysed at 50°–100°C, *p*-nitrobenzoic acid was separated as the main crystalline compound which was contaminated with a little of benzoic acid and oxalic acid, precipitated as calcium salt from the mother liquor of *p*-nitrobenzoic acid. From the solution electrolysed at 50°C., benzaldehyde was separated along with *p*-nitrobenzoic acid and identified as *p*-nitrophenylhydrazone.

For ascertaining whether the formation of *p*-nitrobenzoic acid from phenylalanine was caused by electrolysis or by merely heating with nitric acid, a solution of phenylalanine in 8 N-NO₃H was kept at 100°C. for the time corresponding to the application of 5 F/mol, but without passing electric current, and it was found that a little of *p*-nitrophenylalanine was obtained, but none of *p*-nitrobenzoic acid. Thus it was confirmed that the formation of *p*-nitrobenzoic acid was caused by the electrolysis.

p-Nitrophenylalanine was electrolysed in the same way as in the case of phenylalanine. *p*-Nitrobenzoic acid was obtained in a good yield and oxalic acid also separated. The electrolysis of benzoic acid as well as *p*-nitrobenzoic acid in nitric acid was performed, but only a small amount of oxalic acid was separated in both cases.

From these facts, the formation of *p*-nitrobenzoic- and benzoic acids from phenylalanine may have taken place as follows:

Phenylalanine changed into *p*-nitrophenylalanine by nitration, and the latter was electrolytically oxidised to *p*-nitrobenzoic acid. Benzoic acid was not an intermediate product in the course of formation of *p*-nitrobenzoic acid, but arose from the part of phenylalanine, unaffected by nitration.

As to the formation of nitronaphthalene by the electrolysis of naphthalene in nitric acid, Fichter and Plüss⁽³⁾ pointed out that it was ascribed to the increase of the total concentration of nitric acid in the anode compartment by electrolysis and to the temperature increase at the anode surface, but not to the increased concentration of nitric acid on

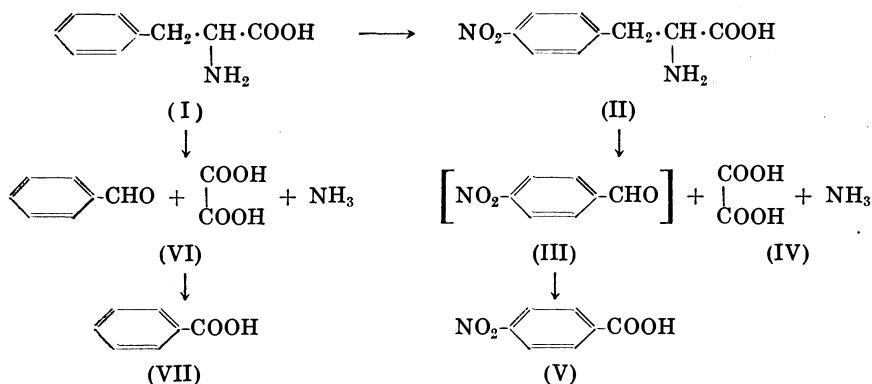
the anode surface. On the contrary, Calhause and Wilson⁽⁴⁾ have concluded from their experiments that the formation of nitronaphthalene by electrolysis was brought about by the highly concentrated film on the anode surface (within diffusion layer).

Though in the present experiments, the mechanism of electrolytical nitration of phenylalanine can not be elucidated, it may be inferred from our experimental results that the nitration of phenylalanine at 100°C. was of partly chemical, and partly electrolytical nature. By the electrolysis of phenylalanine and *p*-nitrophenylalanine in nitric acid, oxalic acid was obtained in yields of 21.8* and 15.5% respectively, while in case of benzoic acid and *p*-nitrobenzoic acid, the yields in oxalic acid was 5.1 and 2.5%, respectively. Thus it may be deduced from these facts that oxalic acid was produced principally by electrolytical oxidation of the side chain.

From the oxidised solution, ammonia was separated only in a small quantity which was probably due to its further decomposition⁽⁵⁾ into nitrogen by the nitrous acid formed during electrolysis.

Phenyllactic acid was electrolysed under the same conditions as phenylalanine, obtaining *p*-nitrobenzoic- and benzoic acids as well as oxalic acid.

Summarizing the facts described above, it may be concluded that the electrolysis of phenylalanine in the nitric acid solution proceeds as follows:



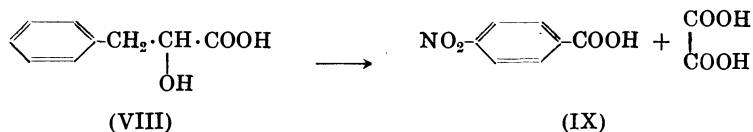
Phenylalanine (I) gave rise to *p*-nitrophenylalanine (II) by nitration, the latter was oxidised to *p*-nitrobenzaldehyde (III), oxalic acid (IV), and ammonia. The aldehyde was easily oxidised to *p*-nitrobenzoic acid (V). This course of reaction seems to be the principal one, considering the amount of the final products. As a side reaction, phenylalanine was oxidised to benzaldehyde (VI), oxalic acid, and ammonia, then the benzaldehyde was oxidised to benzoic acid (VII).

In the same way, phenylacetic acid (VIII) also produced *p*-nitrobenzoic acid (IX) instead of *p*-nitrophenylacetic acid which was expected.

* The percentages in this paper were expressed in molar per cent.

(4) Calhane and Wilson, *Trans. Amer. Electrochem. Soc.*, **63** (1933), 247.

(5) Abbe's Handbuch d. anorg. Chemie, III, (1907), 303.



Experimental.

Natural phenylalanine (N, 8.35. Calc. N, 8.49%) was dissolved in nitric acid and electrolysed in the following apparatus (Fig. 1). Cell: a glass cylinder (A), 14 cm. in height, dia. 3 cm., provided with a glass stopper (B) which carries two electrodes (E). A condenser was fused to the cell.

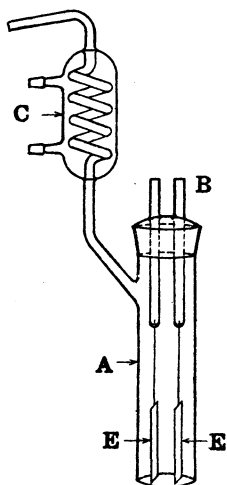


Fig. 1.

Electrode (E): both anode and cathode, platinum plates (2×4 cm.), distance between electrodes: 1 cm.

Electrolytic solution: phenylalanine (20 m. mols) was dissolved in 4–13.7 N NO_3H (30 c.c.).

Current density: 4–10 amps./dm.². Temperature: 0°, 35°, 50°, 60°, 100°C. Electric quantity: 2–7 F/mol. Volt: ca. 1.1 volts (4 amps./dm.²).

Preliminary experiment. (1) *Effect of temperature.* When the electrolysis was undertaken at 0° or 35°C., *p*-nitrobenzoic acid was not obtained, but the colour of the electrolytic solution gradually changed from reddish brown into brown, as the electrolysis proceeded. When the electrolysis was undertaken at above 50°C., *p*-nitrobenzoic acid separated out in yellow crystalline form, and the solution assumed yellow colour. The yields of *p*-nitrobenzoic acid obtained under the different conditions are shown in Tables 1–4.

Table 1.

(C. D.: 4 amps./dm.²).

Expt. No.	Phenylalanine (g.)	Temperature °C.	Conc. of NO_3H (N)	Electric quantities (F/mol.)	<i>p</i> -Nitrobenzoic acid		Melt. point °C.
					(g.)	(%)	
1	3.284	0	6	9	—	—	—
2	3.304	35	4	11	—	—	—
3	5.500	50	8	7 $\left\{ \begin{array}{l} 5\text{F} \\ 2\text{F} \end{array} \right.$	1.4 (oil) 0.45		190
4	3.298	60	8	5	0.91	17.2	190
5	3.297	100	4	7	0.48	14.2	170–183
6	3.332	100	6	7	1.14	33.8	190
7	3.319	100	8	7	1.74	51.4	185

In the above table $\text{NH}_3/\text{total-N.}$ of expt. (1) was 20.3%. whereas that of expt. (6) was 1.0%.

(2) *Effect of the concentration of nitric acid.*

Table 2.

(100°, 4 amps./dm²).

Phenyl- alanine (g.)	Conc. of NO_3H (N)	Temp. °C.	Electric quant. (F/mol.)	<i>p</i> -Nitrobenzoic acid		Melt. point. °C.
				(g.)	(%)	
3.297	4	100	7	0.48	14.2	178-183
3.332	6	100	7	1.14	33.8	190
3.319	8	100	7	1.74	51.4	185
3.307	8	100	5	1.32	39.2	190
3.395	13.7	100	7	1.15	33.2	227-229
3.266	13.7	100	5	1.12	33.7	232-234

(3) *Effect of electric quantity.*

Table 3.

(100°, 4 amps./dm², 13.7 N- NO_3H).

Phenyl- alanine (g.)	Electric quantity (F/mol.)	<i>p</i> -Nitrobenzoic acid		Melt. point. °C.
		(g.)	(%)	
5.50	2	1.80	32.4	231-234
6.60	3	2.25	33.7	231-233
3.27	5	1.12	33.9	232-234
3.31	7	1.15	34.4	227-229

(4) *Effect of current density.*

Table 4.

(100°, 8 N- NO_3H , 5 F/mol.).

Phenyl- alanine (g.)	C. D. (amps./dm ²)	<i>p</i> -Nitrobenzoic acid		Melt. point. °C.
		(g.)	(%)	
3.31	4	1.32	39.4	190
3.30	6	1.93	57.8	200
5.50	8	1.98	35.6	190-195
3.30	10	0.85	25.5	190

Separation of oxidation products. *p*-Nitrobenzoic acid. Phenyl-alanine (3.207 g., 19.43 m. mol) was dissolved in 8 N- NO_3H (30 c.c.) and

electrolysed under the conditions: 100°C., 4 amps./dm.² In a short time nitrogen dioxide gas began to evolve from the electrolysed solution. After applying the electric quantity of 2 F/mol, crystals began to deposit and increased gradually in quantity. When the electric quantity reached to 5 F/mol, the electrolysate was cooled. The crystals deposited in a large quantity, were filtered. The crystals had an odour of benzaldehyde and melted at 180–188°C. Yield: 1.53 g. The crystals were refluxed with benzene. The part insoluble in benzene gave 0.8 g. and melted at 205–210°C. The yield was 24.6% as *p*-nitrobenzoic acid. It melted at 236–237°C., after it was recrystallised from water (Found: N, 8.47, 8.57. Calc. for C₇H₅O₄N:N, 8.38%; Found: molecular weight, 167.7, 170.6 (Rast). Calc. for C₇H₅O₄N, 167.04).

Ethyl p-nitrobenzoate. A solution of *p*-nitrobenzoic acid (1 g.) in absolute ethyl alcohol (10 c.c.) was saturated with hydrogen chloride and refluxed for four hours. The crystals of the ester obtained amounted to 1.08 g. Yield: 93%. It melted at 57–57.5°C., after it was recrystallised from alcohol (Found: N, 7.08, 7.28. Calc. for C₉H₉NO₄: N, 7.18%).

The part soluble in benzene was evaporated and the residue was sublimed under reduced pressure obtaining 0.2 g., m.p. 120–121°C. It was found to be benzoic acid by the mixed melting point test and by the analysis of its silver salt (Found: Ag, 46.77. Calc. for C₇H₅O₂Ag: Ag, 47.12%).

Oxalic acid. The filtrate of *p*-nitrobenzoic acid was neutralized with sodium hydroxide and calcium oxalate was precipitated by the addition of calcium chloride solution. The precipitate amounted to 0.76 g. (air dried) and its purity was 81.4% determined by the titration with N/10-KMnO₄. It was dissolved in 50 c.c. of dilute hydrochloric acid (1:1) and thoroughly extracted with ether. After evaporating the ethereal solution, the crystalline residue was obtained, 0.4 g. (3.2 m. mols), m.p. 95–98°C. One part of the crystals was recrystallised from water in prisms, m.p. 101–102°C. (5.65 mg. of the acid required 8.93 c.c. of N/10-NaOH. Calc. for C₂H₄O₂·2H₂O: N/10-NaOH, 8.96 c.c.). The other part of the acid was sublimed, and it melted at 185.5°C.

Ammonia. The filtrate of the calcium oxalate was acidified with hydrochloric acid and distilled. From the distillate benzoic acid was obtained, 0.08 g. (0.7 m. mol). To the residue of distillation an excess of magnesium oxide was added and distilled under reduced pressure. The distillate was received in dilute sulphuric acid, 4.03 mg. (NH₃). The sulphate thus obtained was changed into its chloride as usual. By the observation under polarized microscope, it was identified as ammonium chloride: isotropic form, index of refraction $n = 1.641$ (chloronaphthalene-bromonaphthalene), its chloroplatinate: isotropic form.

Electrolyses. (1) Phenylalanine in 13.7 N-NO₃H. Electrolysis was undertaken under the following conditions and the electrolysate was treated in the same manner as in the case of 8 N-NO₃H.

Phenylalanine 3.261 g. (19.75 m. mols), 100°C., 4 amps./dm.², 5 F/mol.

Oxidation products:

p-Nitrobenzoic acid 1.11 g. (6.65 m. mols), m.p. 232–233°C. After

being recrystallised from water it melted at 235°C. Benzoic acid (0.02 g.), m.p. 121–122°C. Oxalic acid, pure calcium oxalate $C_2O_4Ca \cdot H_2O$, 3.92 m. mols, free acid m.p. 101–102°C. Ammonia, 0.54 mg.

(2) *Phenylalanine in 4N-NO₃H*. Electrolysis was undertaken as described above: phenylalanine 20 m. mols, 100°C., 5 amps./dm², 5 F/mol.

Oxidation products: *p*-nitrobenzoic acid, 0.40 g. (2.5 m. mols), m.p. 226–228°C. benzoic acid, 0.12 g. (1 m. mol), m.p. 121–122°C. oxalic acid, 2.3 m. mols, ammonia, 4.6 mg. (0.27 m. mol).

Formation of benzaldehyde and its identification. Phenylalanine (3.3 g., ca. 20 m. mols) was dissolved in 8N-NO₃H (30 c.c.) and submitted to electrolysis under the following conditions: 50°C., 6 amps./dm², 2 F/mol.

During the electrolysis, a reddish brown oily substance separated out from the electrolysate. After cooling the electrolysate, *p*-nitrobenzoic acid contaminated with the oil was separated. The mixture was neutralised with sodium hydroxide and submitted to steam distillation. The upper part of the distillate consisted of an oily layer (0.8 c.c.) with aromatic odour. The oil was dissolved in glacial acetic acid and converted into *p*-nitrophenylhydrazone as usual. After being recrystallised from dilute ethyl alcohol, it melted at 191.5°C., coinciding with benzaldehyde-*p*-nitrophenylhydrazone (m.p. 191–192°). 0.45 g. of *p*-nitrobenzoic acid was obtained from the above-mentioned mixture.

(3) *p*-Nitrophenylalanine in nitric acid. *p*-Nitrophenylalanine $NO_2C_6H_4CH_2CH(NH_2)COOH$, 1.5H₂O *p*-Nitrophenylalanine (4.7 g., 20 m. mols) was dissolved in 8N-NO₃H (30 c.c.) and electrolysed: 100°C., 6 amps./dm², 5 F/mol. *p*-Nitrobenzoic acid was also obtained from *p*-nitrophenylalanine as phenylalanine. Yield: 1.14 g. (6.8 m. mols, 34%). It melted at 235–238°C. After being crystallised from water it melted at 236–237°C. From the filtrate oxalic acid was separated as calcium salt, free acid (3.1 m. mols), m.p. 101–102°C. (Found: N/10-KMnO₄, 5.09 c.c. Calc. for $C_2O_4H_2 \cdot 2H_2O$, N/10-KMnO₄, 5.12 c.c.). Ammonia: 1.52 mg. (0.09 m. mol).

(4) *p*-Nitrobenzoic acid in nitric acid. *p*-Nitrobenzoic acid (m.p. 238°C., 0.542 g., 3.25 m. mols) was dissolved in 8N-NO₃H (30 c.c.) and electrolysed: 100°C., 4 amps./dm², 5 F/mol. On cooling 0.51 g. of *p*-nitrobenzoic acid (236–237°C.) was recovered from the electrolysate. Thus *p*-nitrobenzoic acid was attacked only to the extent of 5.9%. Calcium oxalate ($C_2O_4Ca \cdot H_2O$) which separated amounted to 0.0121 g. (0.08 m. mol) and was identified as described above.

(5) *Benzoic acid in nitric acid*. Benzoic acid (m.p. 121–122°C., 2.628 g., 21.5 m. mols,) was dissolved in 8N-NO₃H (30 c.c.) at 100°C. and electrolysed: 4 amps./dm², 5 F/mol. *p*-Nitrobenzoic acid was not obtained, but 1.965 g. (16.1 m. mols) of benzoic acid was recovered on cooling. From the filtrate oxalic acid was separated as calcium salt, 0.175 g. (purity, 92.96%, 1.1 m. mols). It was identified as oxalic acid by the titration with N/10-KMnO₄ and by the mixed melting point test. (Found: N/10-KMnO₄, 17.31 c.c. Calc. for $C_2O_4H_2 \cdot 2H_2O$: N/10-KMnO₄, 17.46 c.c.).

(6) *Oxalic acid in nitric acid.* Oxalic acid (2.51 g., 19.91 m. mols) was dissolved in 8 N- NO_3H (30 c.c.) at 100°C . and electrolysed: 4 amps./ dm^2 , 3 F/mol. Oxalic acid was recovered as described above in the form of calcium salt. The purity of calcium salt was determined by the titration with N/10- KMnO_4 and it was found that the oxalic acid was attacked by the electrolysis to the extent of 95%.

(7) *Phenyllactic acid in nitric acid.* Phenyllactic acid (1.696 g., 10.21 m. mols) was dissolved in 8 N- NO_3H (30 c.c.) and electrolysed: 100°C ., 4 amps./ dm^2 , 5 F/mol. The crystals separated from the electrolysate on cooling, were filtered. Yield: 0.44 g. (2.6 m. mols), 25% as *p*-nitrobenzoic acid. These crystals were boiled with benzene and the part insoluble in benzene melted at $235\text{--}236^\circ$, after being recrystallised from water. It was identified as *p*-nitrobenzoic acid by the mixed melting point test. From the part soluble in benzene, benzoic acid (0.16 g.) was obtained which melted at $122\text{--}123^\circ\text{C}$. after sublimation. Oxalic acid was separated from the filtrate of *p*-nitrobenzoic acid as calcium salt (3.18 m. mols.). The free acid melted at $101\text{--}102^\circ\text{C}$. (Found: N/10- KMnO_4 , 9.62 c.c. Calc. for $\text{C}_2\text{O}_4\text{H}_2 \cdot 2\text{H}_2\text{O}$: N/10- KMnO_4 , 9.58 c.c.). From these experiments it was found that *p*-nitrobenzoic acid could be obtained from both phenylalanine and phenyllactic acid, but the latter was inferior to the former in yield.

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Studies on Amino-Acids and Related Compounds. XIII. Electrolyses of some Amino-Acids in Nitric Acid.

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(Received October 20, 1941.)

In part XII⁽¹⁾ the mechanism of the electrolysis of phenylalanine in nitric acid has been discussed. In the present paper, the electrolyses of tyrosine, glycine, alanine, and glutamic acid in nitric acid are also reported.

It was found that tyrosine, in comparison to phenylalanine, was profoundly attacked by the electrolysis in nitric acid, and, except oxalic acid as the only crystalline substance, a small quantity of resinous matter with a little of phenolic substance was obtained.

The electrolyses of glycine, alanine, and glutamic acid were performed in 4 N- or 8 N-NO₃H at 100°C., and from the electrolysates there were isolated:

from *glycine*, oxalic acid (34%)**; from *alanine*, formaldehyde and oxalic acid (27%); and from *glutamic acid*, succinic acid and oxalic acid.

These data do not indicate whether the oxidation was due to electrolysis or merely to the reaction of nitric acid. However, Mörner⁽²⁾ has pointed out that the formation of oxalic acid from tyrosine occurred by heating with 25% or 60% nitric acid, but that oxalic acid was not obtained from glycine, alanine, phenylalanine, and glutamic acid by heating them even with 60% or 90% nitric acid, and that only when they were heated with fuming nitric acid (sp. gr. 1.50), oxalic acid was obtained from these amino-acids.

These facts ascertain that the formation of oxalic acid from these amino-acids is due to the electrolysis in nitric acid. In the previous paper,⁽¹⁾ it was confirmed that the formation of oxalic acid from phenylalanine by electrolysis originates principally from the side chain of phenylalanine. In the same way, it may be considered that the formation of oxalic acid is chiefly from the group -CH(NH₂)COOH in case of the above-mentioned amino-acids.

In the case of glutamic acid, the yields of oxalic- and succinic-acids by the electrolysis carried out under the same conditions, were as follows:

F/mol	Oxalic acid (%)	Succinic acid (%)
10	8.4	8.7
20	2.7	8.3

The table shows that, within the range of 10 to 20 F/mol, the yield of succinic acid did not change but that of oxalic acid greatly

* Translated by the author from *J. Chem. Soc. Japan*, **62** (1941), 31.

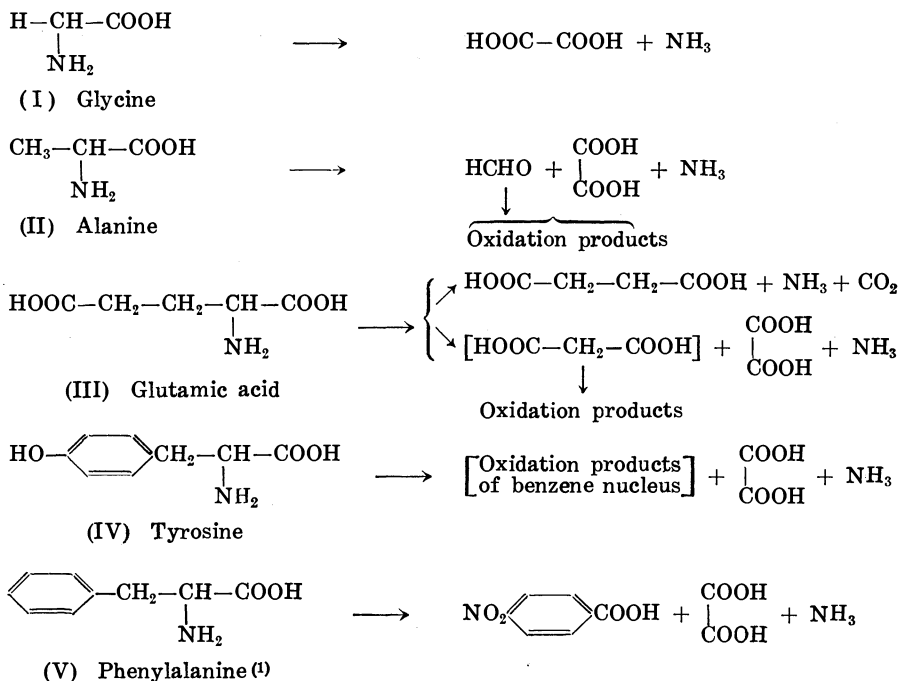
(1) Part XII, this Bulletin, **17** (1942), 45.

(2) C. Th. Mörner, *Z. physiol. Chem.*, **95** (1915), 263.

** The percentages in this paper were expressed in molar per cent.

decreased. It is known that in the electrolysis of succinic acid or oxalic acid in nitric acid, the former is stable, whereas the latter is unstable.⁽¹⁾ The fact described above, therefore, may be interpreted as follows: although the formation of oxalic acid from the group $-\text{CH}(\text{NH}_2)\text{COOH}$ was the principal reaction, yet oxalic acid thus formed was destroyed successively during the electrolysis, consequently it gave small yields.

From these facts it may be quite reasonable to consider that the electrolytic oxidation of glycine, alanine, glutamic acid, tyrosine, and phenylalanine in nitric acid proceeds as follows:



Experimental. (1) *Electrolysis of glycine.* 0.7545 g. (10 m. mols) of glycine (Kahlbaum) was dissolved in 30 c.c. of 8 N- NO_3H and electrolysed under the conditions: 100°C., 4 amps./dm², 5 F/mol. The electrolysate was neutralised with sodium carbonate solution and acidified with acetic acid. Calcium oxalate was precipitated with the addition of 20% calcium chloride solution; yield 0.5 g. (34%), purity 77.50% (determined by the titration with N/10- KMnO_4). The precipitate was decomposed with hydrochloric acid, and extracted with ether. From the ethereal extract crystals were obtained and recrystallised from water; m.p. 101.5–102°C., anhydride m.p. 186–187°C. (decomposed). It was identified as oxalic acid (Found: 0.009345 N- NaOH , 5.62 c.c. Calc. for $\text{C}_2\text{O}_4\text{H}_2\cdot 2\text{H}_2\text{O}$: 0.009345 N- NaOH , 5.62 c.c.; Found: N/10- KMnO_4 , 2.64 c.c. Calc. for $\text{C}_2\text{O}_4\text{H}_2\cdot 2\text{H}_2\text{O}$: N/10- KMnO_4 , 2.63 c.c.).

(2) *Electrolysis of alanine.* 0.9025 g. (101 m. mols) of alanine (Kahlbaum) was dissolved in 30 c.c. of 8 N- NO_3H and electrolysed: 100°C., 4 amps./dm², 5 F/mol. During the electrolysis, the volatile oxidation

product was led to two washing bottles containing water, by means of the delivery tube which was connected to the condenser of the cell. The volatile substance caught in water was identified as formaldehyde by the test with fuchsin-sulphurous acid solution and by the mercurous chloride reaction as well as the precipitation of *p*-nitrophenylhydrazone.

The electrolysate was neutralised with sodium carbonate solution and acidified with acetic acid. Oxalic acid was precipitated as in the case of glycine. Calcium oxalate 0.4 g. (27%), purity 94.2%. Oxalic acid was confirmed by the melting point test and by the titrations (Found: 0.009345 N-NaOH, 5.50 c.c. Calc. for $C_2O_4H_2 \cdot 2H_2O$: 0.009345 N-NaOH, 5.52 c.c. Found: N/10-KMnO₄, 2.64 c.c. Calc. for $C_2O_4H_2 \cdot 2H_2O$: N/10-KMnO₄, 2.56 c.c.).

(3) *Electrolysis of glutamic acid.* 3.011 g. (20.5 m. mols) of glutamic acid (N, 9.46%) was dissolved in 30 c.c. of 4N-NO₃H and submitted to electrolysis: 100°C., 4 amps./dm², 10 F/mol. The electrolysate was neutralised with sodium hydroxide solution and calcium oxalate was precipitated as usual. Calcium oxalate 0.155 g. (air dried), purity 78.8%. Pure calcium oxalate 0.84 m. mol. Free oxalic acid 0.07 g., m.p. 101–102°C. Volatile base NH₃ 0.1 m. mol. After distilling off the volatile base with barium hydroxide, the residue was acidified with sulphuric acid and extracted with ether. 0.3 g. of crystals was obtained from the ethereal extract. It was recrystallised from water and melted at 184°C. It was identified as succinic acid by the mixed melting point test and by the determination of acid equivalent (Found: N/20-NaOH, 6.62 c.c. Calc. for C₄H₆O₄: N/20-NaOH, 6.57 c.c.).

Glutamic acid (3.012 g., 20.5 m. mols) was electrolysed in 8N-NO₃H (30 c.c.) under the same conditions as in the case of 4N-NO₃H. From the electrolysate the following substances were obtained. Calcium oxalate 0.3 g. (2.67 m. mols), purity 67.2%. Free acid melted at 101–102°C. (Found: N/10-KMnO₄, 9.20 c.c. Calc. for $C_2O_4H_2 \cdot 2H_2O$: N/10-KMnO₄, 9.24 c.c.). Succinic acid 0.21 g. (1.76 m. mols). After recrystallising from water it melted at 183°C. (Found: N/10-NaOH, 13.09 c.c. Calc. for C₄H₆O₄: N/10-NaOH, 13.06 c.c.). NH₃ 0.08 m. mol.

Glutamic acid (3.003 g. 20.4 m. mols) was electrolysed in 8N-NO₃H (30 c.c.) under the conditions: 100°C., 4 amps./dm², 20 F./mol. Calcium oxalate 0.10 g. (0.68 m. mol), purity 79.4%. Succinic acid 0.20 g. (1.6 m. mols), m.p. 181–182°C. It was recrystallised from water and melted at 183°C. (Found: N/10-NaOH 7.24 c.c. Calc. for C₄H₆O₄: N/10-NaOH 7.19 c.c.). NH₃ 0.05 m. mol.

(4) *Electrolysis of succinic acid in nitric acid.* 2.284 g. (19.3 m. mols) of succinic acid was dissolved in 30 c.c. of 8N-NO₃H and submitted to electrolysis: 100°C., 4 amp./dm², 5 F./mol. When the electrolysate was cooled the colourless crystals were separated. 1.15 g. of crystals were obtained and identified as the unchanged succinic acid (m.p. 184°C.) by the mixed melting point test and by the determination of acid equivalent. From the mother liquor 1.16 g. of succinic acid were recovered by the extraction with ether. Thus the succinic acid was not at all attacked and was recovered quantitatively.

(5) *Electrolysis of tyrosine.* Natural tyrosine (3.612 g., 19.95 m.

mols) was electrolysed in 8N- NO_3H (30 c.c.) at 100°C ., 4 amps./ dm^2 ., 5 F./mol. The electrolysis was undertaken twice (expt. 1 and 2) in the same way. The electrolysate was colourless, but it became greenish yellow when neutralised with sodium hydroxide.

Calcium oxalate 0.33 g., purity 77.2% (1); 0.35 g., purity 82.1% (2). Free oxalic acid m.p. $101\text{--}102^\circ\text{C}$. (Found: N/10- KMnO_4 8.00 c.c. (1); 7.44 c.c. (2). Calc. for $\text{C}_2\text{H}_2\text{O}_4 \cdot 2\text{H}_2\text{O}$: N/10- KMnO_4 8.07 c.c. (1); 7.38 c.c. (2)). The filtrate of the calcium oxalate was extracted with ether. From the ethereal solution a small quantity of resinous and phenolic substances were obtained. NH_3 0.2 m. mol.

Tyrosine (20 m. mols) was electrolysed in 8N- NO_3H under the conditions: 100°C ., 2 amp./ dm^2 ., 0.65–3 F./mol. From the electrolysate, picric acid (0.2–0.4 m. mol) and oxalic acid (8.9–4.1 m. mols) were obtained. The formation of the picric acid and the oxalic acid thus obtained were not due to the electrolysis, but to the action of nitric acid upon the tyrosine. The mechanism of the formation of picric acid will be reported in the next paper.

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Über die unregelmässige Reihe der kolloiden Lösungen durch Elektrolyten. V.⁽¹⁾ Über die Bedingung bei der Ausführung der Koagulationsversuche mit besonderer Berücksichtigung der Wirkung von Ultraschall.

Von Naoyasu SATA und Sigeru ITÔ.

(Eingegangen am 1. November 1941.)

(1) **Einleitung.** Der Koagulationsversuch ist, wie bekannt, ein sehr heikles Experiment, dessen Versuchsbedingungen und Ausführungsweisen von tausend Kleinigkeiten abhängig sind. Es verlangt ganz besondere Vorsichtsmassregeln, wenn man eine reproduzierbare Regelmässigkeit erwartet, wie in unserem Fall der Untersuchung der unregelmässigen Koagulationsreihe. Schon allein wie die Kolloid- und Elektrolyt-Lösung gemischt und umgerührt wird, kann die Koagulationserscheinung bedeutend beeinflussen. Ein zu kräftiges Umrühren oder Schütteln erniedrigt die Koagulationswerte immer sehr stark. Viele Kolloid-Lösungen haben die Tendenz sich automatisch zu koagulieren durch

(1) N. Sata u. Y. Niwase, *Kolloid-Z.*, **84** (1938) 314; N. Sata u. S. Ito, dieses Bulletin, **15** (1940), 271.

mechanisches Umrühren, ohne Elektrolytzusatz.⁽²⁾ Ausserdem, wenn es mit Umrühren oder Schütteln zu tun hat, muss man sich der Wirkung des Ultraschalls erinnern, welcher auch als eine Art der Erschütterung einer enorm grossen Schwingungszahl zu betrachten ist.⁽³⁾

Mit dem Fortschreiten der Untersuchung der unregelmässigen Koagulationsreihe von HgS-Sol, macht sich der Wunsch geltend, die Abhängigkeit der Versuchsbedingungen eingehend zu untersuchen. Nachstehend wurde diesbezüglich ein Versuch angestellt unter besonderer Berücksichtigung der Wirkung des Ultraschalls.

(2) Über die Bedingung beim Ausführen einzelner Koagulationsversuche.

Bei Ausführung eines Koagulationsversuches ist vorerst das möglichst rasche und gleichmässige Mischen der Kolloid- und Elektrolyt-Lösung unumgänglich nötig. Das langsame Einströmenlassen der Elektrolyt-Lösung in Kolloid-Lösung aus Pipetten oder Büretten usw. sollte darum unbedingt vermieden werden. Deshalb empfehlen wir folgende Ausführungsweise. Die geeignete Menge der Kolloid- und Elektrolyt-Lösung misst man in separaten Probiergläschen. Dann wird die Flüssigkeitsmenge in einem Probiergläschen zum anderen auf einmal hineingegossen und durch sofortiges Umdrehen oder Schütteln eine innige Vermischung erreicht. Wie die Koagulationskurve des HgS-Sols mit AgNO_3 (unregelmässige Reihe) nach der Verschiedenheit der Ausführungsweise beeinflusst wird kann man aus Abb. 1 und 2 sehen.

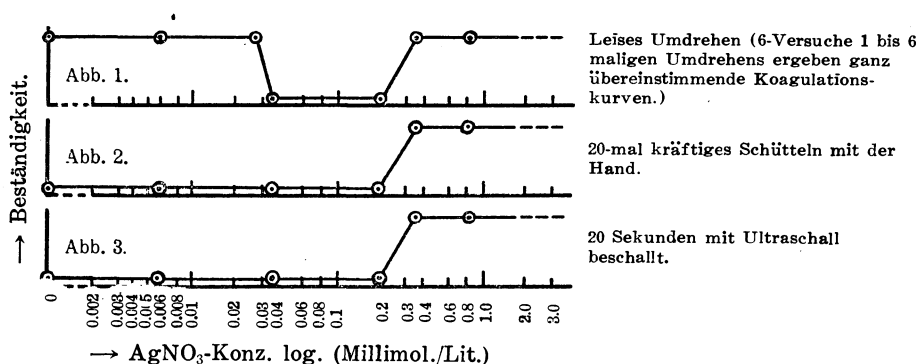


Abb. 1 zeigt, dass das Mischen durch vorsichtiges Umdrehen das beste reproduzierbare Resultat ergibt, wofür ein einmaliges oder höchstens mehrmaliges Umdrehen vollständig genügt. Dahingegen könnte das Mischen durch zu starkes Schütteln die Koagulationskurve ganz ändern, wie aus Abb. 2 ersichtlich ist. Hier möchten wir darauf hinweisen, dass durch das kräftige Schütteln in einem geschlossenem Gefäss nicht nur die einfache Vermischung der Flüssigkeiten verursacht, sondern durch Hin- und Herspritzen der Flüssigkeitsmasse gegen die Gefässwand, eine Art

(2) H. Freundlich, *Kapillarchemie*, Bd. II, S. 218 (Leipzig, 1932); H. Freundlich u. S. B. Basu, *Z. physik. Chem.*, **115** (1925), 203; H. Freundlich u. H. Kroch, ebendort, **124** (1926), 155; H. Freundlich u. S. Loebman, ebendort, **139** (1928), 368; *Kolloid-Beih.*, **28** (1929), 391.

(3) N. Sata, *Kagaku-Zikkengaku* (Handbuch der Experimentalchemie) Series I, Bd. IV, S. 287 (Tokyo, 1940).

spontaner Schaumbildung hervorgerufen wird. Dabei könnte eine sehr grosse Grenzfläche zwischen Flüssigkeit und Luft entstehen, welche sicher den Koagulationsvorgang der Solteilchen stark beeinflussen würde.⁽⁴⁾

(3) Die Wirkung des Ultraschalls auf die Koagulationsvorgänge von HgS-Sol.

Es ist auch eine bekannte Tatsache, dass die Schwingung des Ultraschalls die dispergierende und koagulierende Wirkung zu gleicher Zeit hervorrufen kann.⁽⁵⁾ In flüssigen Medien wird die Ultraschall-Dispergierung in manchen Fällen, wie z.B. an festen Substanzen, flockigen Niederschlägen, Gallerten, Flüssigkeiten usw. beobachtet. Dagegen wurde die Ultraschall-Koagulation in flüssigen Medien nur in begrenzten Fällen und zwar an Emulsionen und groben Suspensionen nachgewiesen. Mit anderen Worten ist sie an verhältnismässig grobdispersen Systemen, aber nicht in echt kolloid-dispersen beobachtet worden. Theoretisch gibt es keinen Grund dafür, dass die Ultraschall-Koagulation in echten kolloid-dispersen Systemen nicht stattfinden soll. Gelegentlich der Untersuchung der Versuchsbedingung bei der unregelmässigen Koagulation von HgS-Sol haben wir den Ultraschall-Einfluss auf diese Erscheinung geprüft.

Als Vorversuch wurde die Wirkung des Ultraschalls an einigen anderen Solen untersucht, welche durch Zusatz geeigneten Elektrolyts einigermassen im Zustand langsamer Koagulation künstlich gebracht worden sind.

Der Versuch wurde folgendermassen durchgeführt: Man begann mit einer gewöhnlichen Koagulationsmessung. Danach wurde der Inhalt jedes Probiergläschens halbiert. An eine Serie dieser Proben haben wir den Ultraschall für eine Minute lang beschallt, während die andere Serie, als Kontrolle, ohne Beschallung stehen gelassen wurde.

Der Ultraschall-Effekt musste durch Vergleich beider Serien erkennbar sein. Da die ganze Koagulationskurve kaum beeinflusst wurde, haben wir, als Resultat, nur die Koagulationswerte angegeben, wie in Tabelle 1 ersichtlich ist.

Tabelle 1.

Sol und seine Ladung	HgS (—)	As ₂ S ₃ (—)	CdS (—)	Mastix (—)	V ₂ O ₅ (—)	Fe ₂ O ₃ (+)
Ausgangsmaterial	HgCl ₂	As ₂ O ₃	CdSO ₄	Alkohol-lösung	NH ₄ VO ₃	FeCl ₃ ·6H ₂ O
Herstellungsmethode	Nach Winssinger			Wechsel des Lösungsmittels	Auswaschen	Hydrolyse
Ko. W. (*) ohne Beschallung	25	40	2.0	35	35	220
Ko. W. nach Beschallung	20	40	2.0	35	35	220

(*) Abkürzung des Koagulationswertes, der in Millimol./Lit. des Elektrolyts, (in diesem Fall, NaCl) angegeben wird.

(4) D. Deutsch, *Z. physik. Chem.*, **136** (1928), 374; auch (2).

(5) C. Bondy u. K. Söllner, *Trans. Farad. Soc.*, **31** (1935), 835; **32** (1936), 556; L. Bergmann "Der Ultraschall" S. 166, Berlin, (1938); auch (3).

Die erwartete Herabsetzung der Koagulationswerte durch Ultraschall-Beschallung konnten wir mit diesen Versuchsgegenständen nicht nachweisen.

Andererseits, bei der in Kapitel (2) geschilderten Untersuchung des Einflusses der Versuchsbedingungen über die unregelmässige Reihe des HgS-Sols, haben wir zufälligerweise eine eigenartige Ultraschall-Koagulation gefunden.

Nämlich, parallel dem Versuche des mechanischen Schüttelns, haben wir auch die Wirkung des Ultraschalls geprüft, und zwar nach Beendigung einer Serie des Versuches der unregelmässigen Reihe, die die Koagulationskurve wie Abb. 1 ergab, haben wir jede Probe mit Ultraschall beschallt, nach denen die Koagulationskurve wie Abb. 3 verändert wurde. Hier muss darauf aufmerksam gemacht werden, dass die Koagulationskurve nach Ultraschall-Beschallung mit der nach Handschütteln ganz übereinstimmend ist. Das ist unsere erste Erfahrung, dass der Ultraschall bei typischem kolloid-dispersen System die Koagulation verursacht hat. Diese Koagulation findet allerdings in der Umgebung sehr kleiner Elektrolyt-Konzentrationen (vor dem 1-Koagulationsgebiet der unregelmässigen Reihe) statt; während der letzte, endgültige Koagulationspunkt dagegen durch Ultraschall-Beschallung ganz unbeeinflusst bleibt, wie die Untersuchungen der Tabelle 1 auch der Fall waren.

(4) Die peptisierende Wirkung des Ultraschalls bei der unregelmässigen Reihe von HgS-Sol.

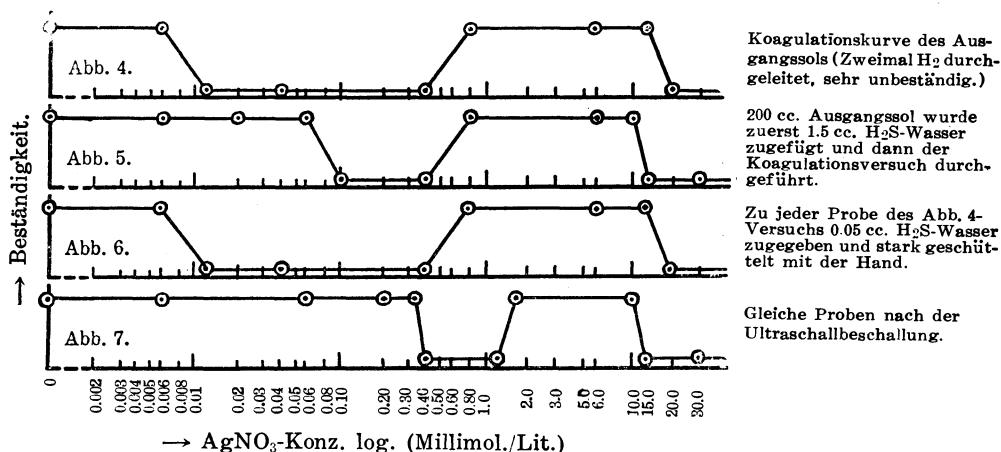
Wir dürfen hier nicht versäumen, die peptisierende Wirkung des Ultraschalls an HgS-Sol hinzuzufügen, die wir auch bei der Untersuchung der unregelmässigen Reihe dieses Sols gesehen haben.⁽⁶⁾ Dabei wurde gezeigt, dass mit zunehmendem H₂S-Gehalt des Sols, die Beständigkeitszunahme und das Schmalwerden des 1-Koagulationsgebietes der Koagulationskurve nachzuweisen ist. In diesem Versuch wurde das H₂S-Wasser zuerst zum Sol zugefügt, die Koagulationsmessung erfolgte dann. Um die Umkehrbarkeit dieses Experiments zu prüfen, haben wir noch folgenden Versuch angestellt.

Man beginnt mit dem gewöhnlichen Koagulationsversuch an H₂S-armem, unbeständigem HgS-Sol, welcher wie sonst die unregelmässige Reihe aufweist. Nach diesem Versuch haben wir in jedem Reagenzgläschen 0.05 ccm. H₂S-Wasser (1.5 c.c./200 ccm. Sol entspricht.) zugegeben und den H₂S-Effekt beobachtet. Der prinzipielle Unterschied dieses Versuches mit dem vorhergehendem liegt darin, dass der koagulierende Elektrolyt zuerst und der stabilisierende H₂S nachher hinzugefügt ist. Also in diesem Fall war, nach H₂S-Zusatz, weder durch Umdrehen noch kräftiges Schütteln, gar keine Änderung bei jeder Probe zu erkennen, d.h. die Koagulationskurve bleibt unbeeinflusst. Wir haben zuletzt versucht, jede Probe mit Ultraschall zu beschallen. Erst dann konnte man den erwarteten H₂S-Effekt wahrnehmen.

Der Verlauf ist in Abb. 4, 5, 6 und 7 deutlich veranschaulicht.

Was in obigem Versuch zu beachten ist, ist dass der Ultraschall hier peptisierend wirkt, wohingegen das Handschütteln gar keine Wirkung

(6) N. Sata u. S. Ito, dieses Bulletin, **16** (1942), 4.



aufweist. Die Stelle, wo der Ultraschall seine Wirkung zeigt, ist wie immer das 1-Koagulationsgebiet.

(5) **Erörterung.** Dass der Ultraschall die gegenseitige koagulierende und peptisierende Wirkung theoretisch zu gleicher Zeit verursachen könnte, haben wir schon oft erwähnt.

In diesem Versuch konnten wir zum erstenmal mit gleichem kolloid-dispersen System von HgS die Ultraschall-Koagulation und Peptisation separat nachweisen. Weil aber die Annahme ganz auszuschliessen ist, dass der Ultraschall dort nur einseitig seine Wirkung gezeigt hat, sollen die Resultate folgenderweise verstanden werden, und zwar der Fall von Tabelle 1, dass der Ultraschall nicht ohne Wirkung war, sondern koagulierende und peptisierende Wirkung eben sich auskompensierten, und der Fall von Abb. 3 bzw. 7, dass der Ultraschall nicht einfach koagulierend oder peptisierend wirkt, sondern die koagulierende oder peptisierende Wirkung überwiegend war. Es lässt die Vermutung aufkommen, dass die Wirkung des Ultraschalls nicht nur einfach von der Ladung oder Dicke diffuser Schicht der Teilchen abhängig ist, sondern alle möglichen Einzelheiten der Oberflächenstruktur der Teilchen damit zu tun haben. Denn in oben ausgeführten Versuchen sind den Solen vorher die Elektrolyten zugesetzt worden und die Teilchen befinden sich jedenfalls im Zustande langsamer Koagulation. Wenn nun das Adsorptionsverhalten der Elektrolyten bei der Koagulation an den Solen ähnlich wäre, müssten auch durch die Ultraschall-Beschallung ähnliche Erfolge zu erwarten sein.

In Wirklichkeit ergibt der Ultraschall alle Möglichkeiten der Effekte, (d.h. koagulierende, peptisierende und neutrale) für deren Erklärung man die Eigentümlichkeit der Ultraschall-Wirkung an einzelnen Fällen anzunehmen braucht. Jedenfalls ist es sehr interessant, dass man nach Wahl der Versuchsbedingungen den Ultraschall zum koagulierenden oder peptisierenden Zweck willkürlich benutzen kann, was die Anwendungsmöglichkeit des Ultraschalls als ein neues Forschungsmittel für die Kolloidwissenschaft verspricht.

Durch die Untersuchung in dieser Richtung könnte man nicht nur den Mechanismus der Ultraschall-Wirkung aufklären, sondern umgekehrt auch erhoffen, die Oberflächenstruktur der Kolloidteilchen aus dem Ultraschall-Effekt zu verstehen.

Zusammenfassung.

(1) Es wurde der Einfluss verschiedener Versuchsbedingungen untersucht bei der Koagulationsmessung, unter besonderer Berücksichtigung der Ultraschall-Wirkung.

(2) Zur Koagulationsmessung ist das Mischen des Sols mit der Elektrolyt-Lösung durch leises Umdrehen des Probierröschchens am besten und ausreichend. Zu kräftiges Schütteln ruft manchmal unerwartete mechanische Koagulation hervor.

(3) An einigen gewöhnlichen Solen zeigt der Ultraschall gar keine Wirkung, trotzdem sie vorher durch Elektrolyt-Zusatz einigermassen in den Zustand der langsamen Koagulation gebracht worden sind.

(4) Bei der Untersuchung der unregelmässigen Koagulationsreihe von HgS-Sol haben wir gefunden, dass der Ultraschall ganz unmittelbar eine koagulierende bzw. peptisierende Wirkung ergeben können unter geeigneter Versuchsbedingung.

(5) Die Resultate sind von der gegenseitigen Wirkung koagulierender und peptisierender Elektrolyten stark abhängig.

(6) Es wurde darauf aufmerksam gemacht, dass die Untersuchung koagulierender und peptisierender Wirkung des Ultraschalls nicht nur sehr wichtig ist, um seinen Wirkungsmechanismus aufzuklären, sondern man könnte über die Oberflächenstruktur der Kolloid-Teilchen dadurch näheren Aufschluss erhalten.

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A Method for Measuring the Surface Energy of Solid.

By Osamu KIMURA.

(Received November 5, 1941.)

It is well-known that the solubility of solid in liquid depends on the particle size of the solid. From this fact, we can calculate the surface energy of the solid which was studied by Hulett⁽¹⁾, Dundon⁽²⁾, and other investigators. Dundon's method of measuring the dependence of solu-

(1) Hulett, *Z. physik. Chem.*, **37** (1901), 385.

(2) Dundon, *J. Am. Chem. Soc.*, **45**(1923), 2479, 2658.

bility on the particle size consists of observing the difference of electrical conductivities of the solutions which are in equilibrium with large crystals and with finely pulverized crystals, and of calculating the solubility from electrical conductivity, with some assumptions. The present author has measured the solubility, using a float-pycnometer, which is devised by Gilfillan and Polanyi⁽³⁾ and modified by Toraisi and Outi⁽⁴⁾. By this float-pycnometer, we can measure the density of solution at constant temperature by controlling the pressure with an accuracy of *ca.* 10 γ .

The measurement was carried out on $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$. Pure crystals were obtained from CaCl_2 and H_2SO_4 . The size of crystals obtained in this way was larger than 50 μ . Some of these crystals were ground by hand in an agate mortar. It is pointed out by several authors that crystals of $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ lose water by being ground in dry room. In this experiment, the agate mortar was always moistened with water vapour. The microscopic examination of the powder showed that the particles were fairly uniform, and the average size was 0.4 μ . The experimental procedure is as follows:—A measuring vessel is dipped in a thermostat, the temperature fluctuation of which is less than $\pm 0.01^\circ$. The temperature of the thermostat is maintained at 33.30° throughout the experiment. About 5 g. of the large crystals are poured into the measuring vessel, filled with 50 c.c. of redistilled water. After violent agitation, the float is dipped, and then the pressure at which it is in equilibrium is read. Then 1 g. of the finely pulverized powder is added, and after violent agitation, the float is again dipped and the pressure is read. The results are shown in Table 1.

Table 1.

Exp.	Equilibrium Pressure in mm Hg		
	With large Crystals	With small Crystals	After 24 hours
I	596	686	600
II	593	699	598

From the table we see that, the pressure increases after the small crystals are added, and then it decreases gradually, and returns to the original value after 24 hours.

To calculate the increase of solubility from these data, we must know the relation between the density and the concentration of the solution. A general formula for electrolyte is given by Debye as follows:

$$D = D_0 + kc + k'c^{3/2},$$

where D and D_0 are the densities of the solution and water, respectively, c is the concentration of the solution in gram percent, and k , k' are constants. For a solution so dilute as that which is studied in our experiment,

(3) Gilfillan and Polanyi, *Z. physik. Chem.*, A. **166**(1933), 254.

(4) Toraisi and Outi, *J. Chem. Soc. Japan*, **55**(1935), 1325.

the third term in this equation can be neglected. The constant k is determined by experiment as follows:

The density of 0.200% solution at 33.30°	0.99624
The density of water at 33.30°	0.99463
The value of k calculated	0.805

From the compressibility of the float, the normal solubility of $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ at 33.30°, and from the above mentioned data, we obtain the solubility of finely pulverized $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$.

Normal solubility at 33.30°	0.210%
Solubility of fine powders at 33.30°	0.235% (mean value)

To calculate the surface energy, we use the following equation:

$$RT/M \ln S_2/S_1 = 2\gamma/\sigma (1/r_2 - 1/r_1),$$

where σ and γ are the density and the surface energy of the solid, and S_1 , S_2 are the solubilities of the spherical particles having radii r_1 and r_2 , respectively. Putting the above values, we obtain 3.9×10^2 dyne/cm for the surface energy of $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$. Although the applicability of this equation in this case is somewhat doubtful, the above value shows a satisfactory agreement with those of the prevalent experiments. (The value of Hulett is 1048 dyne/cm and that of Dundon is 370 dyne/cm.) The characteristic of this method is that it can be applied for measuring the surface energy of non-electrolyte, which is impossible with the conductivity method. Thus we can also measure the surface energies of organic substances with this method.

Summary.

(1) To measure the surface energy of solids, a float-pycnometer method has been applied.

(2) By this method, the surface energy of $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ has been measured, and found to be 3.9×10^2 dyne/cm.

In conclusion, the author wishes to express his sincere thanks to Dr. S. Sato, Director of the Laboratory, for his encouragement and permission of the publication of this research.

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Studies on the Reactions between Oxides in Solid State at Higher Temperatures. III.⁽¹⁾ The Reaction between Magnesium Oxide and Stannic Oxide.⁽²⁾

By Yasuo TANAKA.

(Received November 5, 1941.)

Introduction. In the system magnesium oxide and stannic oxide the existence of magnesium orthostannate ($2\text{MgO}\cdot\text{SnO}_2$), which has a cubic spinel structure with a unit cell size of $a=8.580\text{\AA}$ and a density of 4.738,⁽³⁾ has been known. The composition of the precipitate, obtained from a water solution of the two salts, has been considered as $\text{MgSnO}_3\cdot n\text{H}_2\text{O}$.⁽⁴⁾ But there has been no report on the solid reaction between magnesium oxide and stannic oxide. The phase equilibrium of this system at high temperatures is also unknown.

The present paper deals with the solid reaction with pressed cylinders of the powder mixtures of magnesium oxide and stannic oxide. The experiments were carried out in a current of dry oxygen. Since the solid reaction involving stannic oxide is, as it has been studied by Tamaru and Andô,⁽⁵⁾ accelerated remarkably by the existence of a minute quantity of a reducing agent, this effect should carefully be excluded.

I. Reaction Products at 1400°. As done in the previous experiments,⁽¹⁾ mixtures of various proportions of MgO and SnO_2 were heated at 1400° for 10 hours. The densities of the reaction products were measured, and the amounts of free MgO and those of MgO and SnO_2 soluble in 4N hydrochloric acid were determined. The methods of determinations were the same as described in the first report. The results are given in Table 1. The products were studied further by the X-ray method. As there was no indication of melting in all the reaction products, the reaction was considered to have proceeded in solid state.

The density of each of the reaction products was always smaller than the theoretical value calculated as a mechanical mixture of the components, but no singular point could be observed in the relationship between the mixing ratios and the densities.

From the results of the solubility measurements, it was found that MgO in the reaction products dissolved always in 4N HCl completely, and that, while SnO_2 preparation heated at 1200° was practically insoluble

(1) (a) I, *This Bulletin*, **16** (1941), 428.

(b) II, *This Bulletin*, **16** (1941), 455.

(2) The main part of this paper has been published in Japanese in *J. Chem. Soc. Japan*, **61** (1940), 1023.

(3) G. Natta, L. Passerini, *Atti. accad. Lincei, Rend.* [6], **9** (1929), 557; *Chem. Zentr.*, **1929**, II, 828.

(4) Cf. J. W. Mellor, "A Comprehensive Treatise on Inorganic and Theoretical Chemistry," Vol. VII, 419, London (1927).

(5) S. Tamaru and N. Andô, *Z. anorg. allgem. Chem.*, **184** (1929), 385; **195** (1931), 309; *J. Chem. Soc. Japan*, **52** (1931), 36, 107.

Table 1. Reaction products at 1400°.

Mixing ratio		Density	Free MgO (%)	Soluble in 4N HCl		
MgO (%)	MgO:SnO ₂ *			MgO (%)	SnO ₂ (%)	MgO/SnO ₂
100	—	3.493				
61.05	6:1	4.201	41.49	19.56	38.95	1.88
46.40	3:1	4.456	18.94	27.46	53.60	1.91
35.41	2:1	4.725	1.98	33.43	64.59	1.93
29.50	3:2	5.046	2.22	27.28	51.67	1.97
21.40	1:1	5.466	1.22	20.18	38.78	1.95
15.13	2:3	5.834	1.23	13.90	27.89	1.86
7.85	1:3	6.376	1.09	6.76	14.07	1.81
0	—	6.953				

* Approximately.

even in concentrated hydrochloric acid, SnO₂ in the reaction products became soluble in 4N HCl. As the molecular ratio of the amount of MgO to that of SnO₂, which was soluble in 4N HCl, respectively,⁽⁶⁾ was always nearly equal to 2, it was concluded that 2MgO·SnO₂ was the only addition compound formed in this condition. With a mixture of MgO:SnO₂=2:1, almost pure 2MgO·SnO₂ was obtained.

The results of the röntgenographic studies, too, agreed with these results. The lattice constant of 2MgO·SnO₂ was found to be $a=8.61\text{\AA}$, and it seemed that no distinct solid solutions were formed in this system.

II. Course of the reaction between 900° and 1100°. Mixtures of MgO:SnO₂=2:1 and 1:1 were heated at a certain temperature in the range between 900° and 1100°, and the course of reaction was followed analytically. The preparations were ignited at about 1200° before use. The results are given in Tables 2 and 3. No reaction was practically observed at 900°, and the reaction temperature,⁽⁷⁾ or the temperature at which the reaction begins to take place, was found to be about 950°. This temperature was far higher than those of the reactions between MgO or CaO and TiO₂;⁽¹⁾ however, it was easily recognized that the reaction velocity increased more rapidly than in the latter reactions with the increasing reaction temperature.

As the combination ratio of MgO to SnO₂ was found to be smaller than the normal molecular ratio of 2MgO·SnO₂ in the temperature range studied here and especially at the beginning of the reaction, it was suspected that a compound such as MgO·SnO₂ was formed at first. However, even in a mixture of MgO:SnO₂=1:1, the above ratio increased continuously toward 2 as the reaction proceeded, and, moreover, in the X-ray patterns of the reaction products in this period, only the inter-

(6) Hereafter, this ratio will be mentioned as the combination ratio of MgO to SnO₂.

(7) G. Tammann, *Z. anorg. allgem. Chem.*, **149**(1925), 21.

Table 2. Course of the reaction with a mixture of
 $\text{MgO}:\text{SnO}_2 = 2:1$ ($\text{MgO} = 34.70\%$).

Reaction temperature	Time (hrs.)	Free MgO (%)	Soluble in 4N HCl		
			MgO (%)	SnO ₂ (%)	MgO/SnO ₂
900°	10	34.75	—	—	—
950°	10	34.19	0.64	2.51	0.95
1000°	0.5	33.86	0.71	2.29	1.16
	1	33.27	1.42	3.91	1.36
	3	30.05	4.83	10.68	1.69
	6	26.40	8.27	18.12	1.71
	10	22.71	12.14	25.37	1.79
1050°	0.5	28.09	6.56	15.15	1.61
	1	23.65	11.27	25.09	1.68
	3	18.30	16.79	35.92	1.75
	6	13.42	21.35	46.90	1.70
	10	12.20	22.97	48.48	1.77
1100°	0.5	20.72	14.24	33.19	1.60
	1	15.17	19.88	42.36	1.75
	3	11.78	23.07	50.04	1.72
	6	8.04	27.17	54.38	1.87
	10	8.09	26.30	54.26*	1.81

Table 3. Course of the reaction with a mixture of
 $\text{MgO}:\text{SnO}_2 = 1:1$ ($\text{MgO} = 21.11\%$).

Reaction temperature	Time (hrs.)	Free MgO (%)	Soluble in 4N HCl		
			MgO (%)	SnO ₂ (%)	MgO/SnO ₂
900°	10	20.83	—	—	—
950°	10	20.55	0.56	2.17	0.97
1000°	0.5	20.90	0.20	2.27	0.33
	1	20.09	1.00	4.29	0.88
	3	17.49	3.72	11.91	1.17
	6	15.73	5.54	14.11	1.47
	10	12.73	8.82	22.73	1.45
1050°	0.5	18.10	2.99	10.18	1.10
	1	15.10	6.18	16.10	1.43
	3	7.73	13.83	31.78	1.63
	6	5.94	15.47	34.49	1.68
	10	6.40	15.06	34.89	1.61
1100°	0.5	10.81	10.62	26.57	1.49
	1	8.47	13.05	32.65	1.49
	3	6.53	14.91	36.49	1.53
	6	5.18	16.31	37.08	1.64
	10	4.67	16.83	38.07	1.65

ference lines of the addition compound, $2\text{MgO}\cdot\text{SnO}_2$, were observed besides those of the uncombined MgO and SnO₂. Therefore, the formation of a new compound other than $2\text{MgO}\cdot\text{SnO}_2$ was not probable. As no deviations of the positions of $2\text{MgO}\cdot\text{SnO}_2$ -lines were observed, the existence

of a solid solution between $2\text{MgO}\cdot\text{SnO}_2$ and SnO_2 , too, was hardly considered. The excess of SnO_2 existed perhaps in an amorphous state and was soluble in 4N HCl.⁽⁸⁾

III. Experiment in open air. As already mentioned, the above described experiments were carried out entirely in a current of dry oxygen. For comparison, the experiment in open air was made at 950° without passing dry oxygen. The change of free MgO is given in Table

Table 4. Experiment in open air at 950° .

Reaction time (hrs.)	Free MgO (%)	
	MgO : SnO ₂ = 2 : 1	MgO : SnO ₂ = 1 : 1
0.5	31.97	19.17
1	29.09	16.57
3	24.66	12.65
6	20.67	11.10
10	20.59	8.50

4 which shows that the reaction takes place more rapidly than in the previous experiments. But the composition of the reaction products changed with the reaction as before; for instance, with a mixture of $\text{MgO}:\text{SnO}_2=1:1$, the combination ratio of MgO to SnO_2 was found to be 1.64 after 10 hours.

The rapid reaction rate in this experiment is probably due to the effect of the traces of reducing gases, which are inevitably contained in air, because the effect of reducing atmosphere on the reactivity of stannic oxide is, as it is previously stated,⁽⁵⁾

very remarkable. The effect of water vapour may also be considered.⁽⁹⁾

IV. Discussion of the results. In the present reaction, it must be noticed that, although $2\text{MgO}\cdot\text{SnO}_2$ is the only stable addition compound, the product formed at first seems to contain a large excess of stannic oxide, and as the reaction proceeds the product tends gradually to have the normal composition of $2\text{MgO}\cdot\text{SnO}_2$. This phenomenon may be explained as follows:

By a solid reaction, as it has been discussed in the first report,^(1a) an amorphous layer of the mixture of the components is formed at first at their contact surface, and from which a new reaction product crystallizes out. The amorphous product may be regarded as a solid solution of the components. In the reaction between MgO and SnO_2 , it is considered that the crystallization of the addition compound, $2\text{MgO}\cdot\text{SnO}_2$, is somewhat difficult, and at lower temperatures the amorphous solid solution reaches to a considerable amount. The crystal lattices of SnO_2 in this state are disturbed, and the oxide becomes soluble in dilute hydrochloric acid, and while MgO in this state exists probably as free MgO, namely, it is soluble in 20% ammonium chloride solution; therefore the combination ratio of MgO to SnO_2 becomes apparently smaller than 2. When the amount of the amorphous product reaches to a definite value, the

(8) Formerly, the present author⁽²⁾ has considered that, while the excess of SnO_2 exists forming a solid solution with $2\text{MgO}\cdot\text{SnO}_2$, the crystal structure of which is the same as that of pure $2\text{MgO}\cdot\text{SnO}_2$. But it seems more probable to consider the existence of an amorphous state.

(9) Cf. J. A. Hedvall, "Reaktionsfähigkeit fester Stoffe," 157, 204, 221, etc., Leipzig (1938).

stable addition compound, $2\text{MgO}\cdot\text{SnO}_2$, begins to crystallize out smoothly. The later reaction proceeds by the diffusion of the two components through this crystalline layer, and, as the amount of $2\text{MgO}\cdot\text{SnO}_2$ increases, the above ratio tends gradually toward 2.

In the previous experiments,⁽¹⁾ it was considered that the stable addition compound crystallized out readily, and no particular attention was paid in the amorphous reaction product, although in the reaction between MgO and TiO_2 ,^(1a) as it was discussed on that occasion, the tendency of its existence was observed at lower temperatures. (In the reaction between CaO and TiO_2 ,^(1b) as only the amounts of free CaO were determined, the formation of the amorphous product was not certain.) As the temperature ranges in which the two reactions were studied were comparatively higher than their reaction temperatures, it was admitted that considerable amounts of the amorphous product did not exist in these experiments.

As it is already stated, the magnesium stannate obtained from a solution has been reported to have a composition of $\text{MgSnO}_3\cdot n\text{H}_2\text{O}$.⁽⁴⁾ On the other hand, it has been known that, in the system CoO and SnO_2 , though the composition of the stannate obtained from a water solution is $\text{CoC}\cdot\text{SnO}_2$, no interference lines of the compound are found in the X-ray patterns, and that at higher temperatures it is easily decomposed into $2\text{CoO}\cdot\text{SnO}_2$ and SnO_2 .⁽¹⁰⁾⁽¹¹⁾ In these systems, it seems that, while a metastannate hydrate ($\text{MO}\cdot\text{SnO}_2\cdot n\text{H}_2\text{O}$) is obtained from a solution, it is decomposed into an amorphous mixtures on heating, and from which an anhydrous orthostannate ($2\text{MO}\cdot\text{SnO}_2$) is formed.

In the solid reaction between ZnO and TiO_2 , Cole and Nelson⁽¹²⁾ have reported that, while the reaction product obtained at first at lower temperatures had an apparent composition of ZnTiO_3 , it was proved to be a solid solution between ZnTiO_4 and TiO_2 ; that the unit cell size of the solid solution, which had a cubic spinel structure, decreased with the content of TiO_2 ; and that the composition of the solid solution was altered as the reaction proceeded. Further, they stated that the formation of the solid solution, which dissociated into ZnTiO_4 and TiO_2 completely above 1050° , was reversible with temperature. This reaction resembles to the present reaction. However, while the excess of TiO_2 exists thereby as a solid solution with a definite crystal structure, the excess of SnO_3 exists as an amorphous state, or as an amorphous solid solution of the two components, in the present reaction. Besides, in the present case, the composition of the reaction product, obtained as low as 950° by the experiment in open air, too, tended gradually to $2\text{MgO}\cdot\text{SnO}_2$, and, moreover, it was proved that no decomposition of pure $2\text{MgO}\cdot\text{SnO}_2$ took place after 10 hour's tempering at 1100° . Therefore, the formation of the amorphous solid solution could hardly be regarded as reversible in these temperatures, and, as it is already mentioned, the formation of a solid solution with a definite crystal structure is also unlikely.

The existence of a solid solution has been observed in the system,

(10) J. A. Hedvall, *Z. anorg. allgem. Chem.*, **92**(1915), 369.

(11) G. Natta and L. Passerini, *Gazz. chim. ital.*, **59**(1929), 620; *Chem. Zentr.*, **1930**, I, 128.

(12) S. S. Cole and W. K. Nelson, *J. Phys. Chem.*, **42**(1938), 245.

CaO and TiO_2 , too.^(1b) In this reaction, however, no distinct deviation of the composition of the reaction product was observed during the main part of the reaction, and it might be considered that, only with mixtures containing an excess of CaO, after the major part of TiO_2 reacted forming $\text{CaO} \cdot \text{TiO}_2$, a solid solution rich in CaO was obtained.

In the present reaction, although a considerable amount of the amorphous reaction product exists, as the later reaction is possible by the diffusion of the two components through the layer of the crystalline reaction product, it is expected that the rate determining step of the whole reaction lies also in this process; and indeed the relation,⁽¹³⁾

$$\{1 - \sqrt[3]{1-x}\}^2 = 2kt,$$

holds approximately between 1000° and 1100° , and from which the apparent energy of activation is calculated roughly as $Q=100$ Kilocalories per mole.⁽¹⁴⁾

However, it must be mentioned that, while a rapid initial reaction has been found in the solid reactions between MgO or CaO and TiO_2 ,⁽¹⁾ the present reaction proceeds at the beginning of the reaction, especially at lower temperatures, more slowly than the rate expressed by the above equation, namely, there exists rather an induction period. Further, as it is already stated that the velocity of the present reaction increases rapidly with increasing reaction temperature, so the energy of activation, 100 Kilocalories per mole, is far greater than those of the reactions between MgO or CaO and TiO_2 and other reactions so far studied.^(1a) The reaction temperature of this reaction is also very high. From these facts it is anticipated that the mechanism of the present reaction is somewhat different from those of the reactions previously studied.

Summary.

(1) It has been found that $2\text{MgO} \cdot \text{SnO}_2$ is the only stable addition compound which is formed by the solid reaction between MgO and SnO_2 , and that the compound is soluble in 4N HCl.

(2) While the reaction in dry oxygen begins at about 950° , it takes place more readily in open air, probably, due to the effect of the traces of reducing gases contained in air.

(3) The reaction product seems to exist at first in an amorphous state, and, when the amount of which reaches to a certain value, $2\text{MgO} \cdot \text{SnO}_2$ becomes to crystallize out smoothly; the later reaction proceeds by the diffusion of the components through this crystalline layer.

(4) It has been considered that the main part of the reaction is controlled by the diffusion process, and the energy of activation of which has been estimated as about 100 Kilocalories per mole.

(5) An induction period has been observed at the beginning of the

(13) These notations have been given in the first report.

(14) Calculated from the amounts of combined MgO with a mixture, $\text{MgO}:\text{SnO}_2 = 1:1$. Nearly equal value was obtained from the amounts of combined SnO_2 , too.

reaction, and the energy of activation is very great when compared with those of the reactions hitherto studied.

The author wishes to express his hearty thanks to Dr. R. Yoshimura, Director of the Department, for his interest in this work. The author's thanks are also due to Mr. T. Takagi for his assistance with the experiments and to the Physics Section of the Laboratory for taking the X-ray photographs.

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Studies on the Reactions between Oxides in Solid State at Higher Temperatures. IV.⁽¹⁾ The Reaction between Calcium Oxide and Stannic Oxide.⁽²⁾

By Yasuo TANAKA.

(Received November 5, 1941.)

Introduction. In the system calcium oxide and stannic oxide, there exists calcium metastannate ($\text{CaO} \cdot \text{SnO}_2$), and it has been reported that the compound has a cubic perovskite structure with a lattice constant of $a=3.92\text{\AA}$.⁽³⁾ Zulkowski⁽⁴⁾ reported that he obtained $2\text{CaO} \cdot \text{SnO}_2$. Tamaru and Andô⁽⁵⁾ found that the solid reaction of this system was remarkably accelerated by the traces of reducing agents and they studied the mechanism of which in detail. They reported that, while in vacuum only a slight reaction was observed at 900° , in a reducing condition it proceeded smoothly even at still lower temperatures; that the end product of the reaction with a mixture of excess calcium oxide was $2\text{CaO} \cdot \text{SnO}_2$; and that the compound was soluble in dilute hydrochloric acid (1:1). Besides, Tamaru and Sakurai⁽⁶⁾ obtained $\text{CaO} \cdot \text{SnO}_2$ by the oxidation of $\text{CaO} \cdot \text{SnO}$ when an excess of stannous oxide was present.

The present paper deals with the solid reaction of this system in a current of dry oxygen. The experimental procedure was almost the same as in the previous reports.^{(1) (7) (8)}

(1) III, *This Bulletin*, **17** (1942), 64.

(2) Published in Japanese in *J. Chem. Soc. Japan*, **62** (1941), 199.

(3) V. M. Goldschmidt, *Skrifter Norske Videnskaps-Akad. i Oslo*, I, **1926**, No. 2; *Chem. Zentr.*, **1926**, II, 1390.

(4) K. Zulkowski, *Chem. Ind.*, **24** (1901), 422; *Chem. Zentr.*, **1901**, II, 564.

(5) S. Tamaru and N. Andô, *Z. anorg. allgem. Chem.*, **184** (1929), 385; **195** (1931), 309; *J. Chem. Soc. Japan*, **52** (1931), 36, 107.

(6) S. Tamaru and H. Sakurai, *Z. anorg. allgem. Chem.*, **195** (1931), 24; *J. Chem. Soc. Japan*, **52** (1931), 120.

(7) *This Bulletin*, **16** (1941), 428.

(8) *This Bulletin*, **16** (1941), 455.

I. Reaction Products at 1300°. Mixtures of various proportions of CaCO_3 and SnO_2 were heated at 1300° for 10 hours, and the amounts of free CaO and those of CaO and SnO_2 soluble in 4N HCl were determined. Some of the reaction products began to melt already at 1400°. The results of the experiment with the densities of the products are given in Table 1.

Table 1. Reaction products at 1300°.

Mixing ratio		Density	Free CaO (%)	Soluble in 4N HCl		
CaO (%)	$\text{CaO} : \text{SnO}_2$			CaO (%)	SnO_2 (%)	CaO/SnO_2
100	—	3.205				
69.07	6 : 1	3.816	45.99	—	—	—
52.75	3 : 1	4.359	17.77	35.02	47.30	1.99
42.67	2 : 1	4.727	0.00	42.05	57.51	1.96
35.82	3 : 2	5.058	0.00	—	—	—
27.13	1 : 1	5.608	0.00	26.31	67.50	1.05
15.69	1 : 2	6.192	0.00	15.04	40.81	0.99
0	—	6.981				

Table 2. X-ray data of $\text{CaO} \cdot \text{SnO}_2$.

Intensity	$\sin \theta^*$ (obs.)	hkl	$\sin \theta^*$ (calc.)
vw	0.225	β 100	0.223
m	246	100	246
w	314	β 011	315 ₅
vst	347 ₅	011	348
w	446	β 200	446
st	492 ₅	200	492
w	543 ₅	120	543 ₅
w	551	β 112	550 ₅
m	598 ₅	121	598
st	608	112	607 ₅
w	689	220	691
m	696 ₅	022	696
vw	706	β 301	706
w	735	221	734 ₅
vw	745	212	742
st	778 ₅	{ 310	777
vw	839	{ 301	779 ₅
vw	843	β 312	838
w	885 ₅	β 213	842
vw	906 ₅	320	883
		β 004	905 ₅
m	914	{ 231	913
st	922	{ 132	915
w	923	312	923
		213	928

$a = 3.93 \text{ \AA}$, $b = 3.99 \text{ \AA}$, $c = 3.87 \text{ \AA}$.

* For K_α and K_β lines of iron.Table 3. Interference lines of $2\text{CaO} \cdot \text{SnO}_2$.

Intensity	$\sin \theta^*$
vw	0.179 ₅
m	197
m	343
vst	356 ₅
w	447 ₅
vw	461
st	492
w	548 ₅
m	595 ₅
st	606 ₅
w	624
w	660
st	688
vw	737
m	836
vw	853
vw	862 ₅
w	911
w	919
w	932 ₅
vw	941
w	947 ₅
m	971
w	977
w	982

* Anticathode: Fe.

As more CaO than necessary to form $2\text{CaO}\cdot\text{SnO}_2$ remains in free state, and excess SnO_2 over $\text{CaO}\cdot\text{SnO}_2$ is insoluble in 4N HCl, it is admitted that the two stannates, calcium orthostannate ($2\text{CaO}\cdot\text{SnO}_2$), and metastannate ($\text{CaO}\cdot\text{SnO}_2$) are formed in this reaction, and both of them are soluble in 4N HCl.

From the corresponding mixtures, the two stannates were obtained almost in pure state. As the products were dissolved equally well in 1N HCl, it was difficult to determine the amounts of $2\text{CaO}\cdot\text{SnO}_2$ and $\text{CaO}\cdot\text{SnO}_2$ separately.

In the X-ray patterns of the reaction products, too, no indication of the existence of other addition compounds could be obtained, and it seemed that no appreciable amounts of solid solutions were formed in this system. As shown in Table 2, although the principal lines of $\text{CaO}\cdot\text{SnO}_2$ can be interpreted from the lattice constant, $a=3.92\text{\AA}$, which has hitherto been given,⁽³⁾ the values, $a=3.93\text{\AA}$, $b=3.99\text{\AA}$ and $c=3.87\text{\AA}$, must be given as correct. It has already been known that some crystals of the perovskite type is transformed from the cubic into the rhombic structure.⁽⁹⁾⁽¹⁰⁾ While the crystal structure of $2\text{CaO}\cdot\text{SnO}_2$ is not certain, as seen from the interference lines given in Table 3, so far is obvious that the compound has a different structure from that of $\text{CaO}\cdot\text{SnO}_2$.

II. Course of the reaction between 900° and 1200° . The course of the reaction was followed analytically with mixtures of CaO and SnO_2 , corresponding to $\text{CaO}:\text{SnO}_2=2:1$ and $1:1$, in the range between 900° and 1200° . The preparations were ignited at 1200° before use. The results are given in Tables 4 and 5. The reaction begins to take place at about 900° , which agrees with the result of Tamaru and Andô,⁽⁵⁾ and it proceeds smoothly with increasing reaction temperature.

With a mixture of $\text{CaO}:\text{SnO}_2=1:1$, when the reaction proceeded moderately, the ratio of CaO to SnO_2 , which was soluble in 4N HCl, respectively, was nearly equal to 1; so it was obvious that the final product

Table 4. Course of the reaction with a mixture of
 $\text{CaO}:\text{SnO}_2 = 1:1$ (CaO = 27.13%).

Reaction temperature	Time (hrs.)	Free CaO (%)	Soluble in 4N HCl		
			CaO (%)*	SnO_2 (%)	CaO/ SnO_2
900°	10	26.76	0.37	—	—
950°	1	26.56	0.57	4.36	0.36
	3	25.96	1.17	6.60	0.48
	6	24.40	2.73	8.86	0.83
	10	23.90	3.23	10.58	0.82
1000°	0.5	25.50	1.63	4.66	0.94
	1	—	—	6.16	—
	3	22.76	4.37	12.18	0.96
	6	21.06	6.07	16.58	0.98
	10	19.90	7.23	19.36	1.00

* Calculated.

(9) Cf. J. W. Mellor, "A Comprehensive Treatise on Inorganic and Theoretical Chemistry," Vol. VII, 52, London (1927).

(10) S. S. Cole and H. Espenschied, *J. Phys. Chem.*, **41** (1937), 445.

Table 4.—(Concluded)

Reaction temperature	Time (hrs.)	Free CaO (%)	Soluble in 4N HCl		
			CaO (%)*	SnO ₂ (%)	CaO/SnO ₂
1100°	0.5	20.26	6.87	17.80	1.04
	1	16.76	10.37	24.80	1.12
	3	12.30	14.83	33.70	1.18
	6	10.56	16.57	37.70	1.18
	10	10.30	16.83	38.06	1.19
1200°	0.5	10.90	16.23	38.06	1.15
	1	8.86	18.27	43.10	1.14
	3	6.60	20.53	48.20	1.14
	6	5.56	21.57	50.84	1.14
	10	5.10	22.03	51.82	1.14

* Calculated.

Table 5. Course of the reaction with a mixture of
CaO:SnO₂ = 2:1 (CaO = 41.75%).

Reaction temperature	Time (hrs.)	Free CaO (%)	Soluble in 4N HCl		
			CaO (%)*	SnO ₂ (%)	CaO/SnO ₂
900°	10	41.66	0.09	—	—
1000°	0.5	40.50	1.25	4.20	0.79
	1	40.16	1.59	5.70	0.82
	3	38.30	3.45	9.16	1.01
	6	36.38	5.37	14.18	1.02
	10	35.30	6.45	16.72	1.04
1100°	0.5	35.20	6.55	17.01	1.03
	1	31.70	10.05	23.40	1.15
	3	25.10	16.65	30.14	1.48
	6	21.56	20.19	33.72	1.61
	10	20.50	21.25	34.08	1.68
1200°	0.5	23.50	18.25	32.54	1.57
	1	21.36	20.39	35.62	1.60
	3	17.40	24.35	41.26	1.65
	6	16.00	25.75	42.98	1.68
	10	15.10	26.65	43.60	1.71

* Calculated.

in this case was CaO·SnO₂. However, at the early stage of the reaction, the ratio was smaller than 1, and, as neither interference lines of a new compound nor deviations of the positions of CaO·SnO₂-lines were observed in the X-ray photographs, it could be regarded, just as in the case of the reaction between MgO and SnO₂,⁽¹⁾ that the excess of SnO₂ existed in an amorphous state. With a mixture of CaO:SnO₂=2:1, as the reaction proceeded, the composition of the product tended gradually toward 2CaO·SnO₂. An example of this tendency is shown graphically in Figure 1.⁽¹¹⁾

(11) Calculated by assuming CaO·SnO₂ and 2CaO·SnO₂ are formed in their normal compositions.

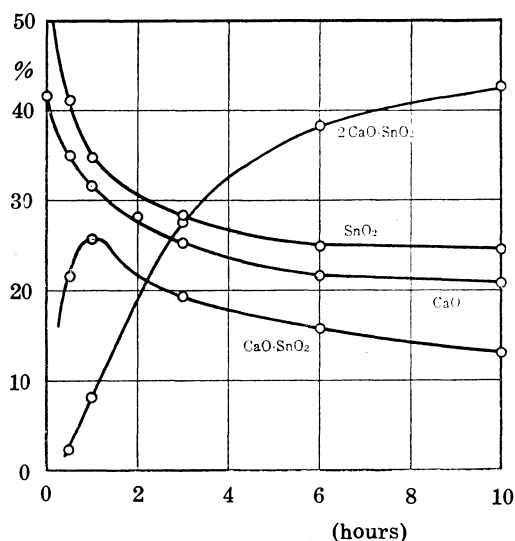


Fig. 1. $\text{CaO}:\text{SnO}_2 = 2:1$, 1100° .

previously formed, and the excess of CaO. The formation of a small amount of $2\text{CaO}\cdot\text{SnO}_2$ is also recognized with a mixture of $\text{CaO}:\text{SnO}_2=1:1$; however, it is probable that the compound is formed locally where CaO exists in excess. The course of the reaction is similar to that of the reaction between MgO and TiO_2 ,⁽⁷⁾ in which the first reaction product, $\text{MgO}\cdot 2\text{TiO}_2$, is the richest in the acid component, and $\text{MgO}\cdot\text{TiO}_2$ and $2\text{MgO}\cdot\text{TiO}_2$ are formed by the further reactions.

It is considered that, at lower temperatures, the amorphous solid solution, which is formed at the contact surface of the two components, reaches to a measureable amount, and SnO_2 in this state is soluble in 4N HCl; so that, at the beginning of the reaction, the ratio of soluble CaO to soluble SnO_2 becomes apparently smaller than 1. When the amorphous product reaches to a certain amount, $\text{CaO}\cdot\text{SnO}_2$ crystallizes out easily. Although the amount of the amorphous product is not so large, the tendency is the same as in the reaction between MgO and SnO_2 .⁽¹⁾

In their experiment on the reaction between CaO and SnO_2 , Tamaru and Andô⁽⁵⁾ have considered that soluble SnO_2 ⁽¹²⁾ exists as $2\text{CaO}\cdot\text{SnO}_2$. It is true that $2\text{CaO}\cdot\text{SnO}_2$ is the final reaction product in this reaction with a mixture of an excess of CaO; however, as it is obvious from the present experiment, $\text{CaO}\cdot\text{SnO}_2$ is formed at first and it is also soluble in dilute hydrochloric acid. Therefore, it must be considered also in their experiment that soluble SnO_2 exists as the two stannates, $\text{CaO}\cdot\text{SnO}_2$ and $2\text{CaO}\cdot\text{SnO}_2$. Further, although they have considered only the formation of $2\text{CaO}\cdot\text{SnO}_2$ in their discussion of the mechanism of the reaction, it must be admitted naturally that $\text{CaO}\cdot\text{SnO}_2$ is formed at first.

Finally, the relation,⁽⁷⁾

(12) In their experiment, soluble SnO_2 means that which is soluble in a dilute hydrochloric acid of 1:1.

Without passing dry oxygen, the reaction proceeded at 900° already with a moderate rate, but the course of the reaction was the same as before.

III. Discussion of the results.

As it is clear from the above experiments, two stable addition compounds, $2\text{CaO}\cdot\text{SnO}_2$ and $\text{CaO}\cdot\text{SnO}_2$, are formed by the solid reaction between CaO and SnO_2 , and there exist no appreciable solid solutions in this system. In this reaction $\text{CaO}\cdot\text{SnO}_2$ is formed at first, whatever the mixing ratio of the components may be, and, when an excess of CaO is present, $2\text{CaO}\cdot\text{SnO}_2$ is formed gradually by the further reaction between $\text{CaO}\cdot\text{SnO}_2$, thus

$$\{1 - \sqrt[3]{1-x}\}^2 = 2kt,$$

for the amount of combined CaO holds fairly well from the beginning of the reaction, and, in the present reaction, neither a rapid initial reaction nor an induction period exists. It is considered that the reaction is also controlled by the diffusion of the two components through the reaction product, and, with a mixture of $\text{CaO} \cdot \text{SnO}_2 = 1:1$, the energy of activation between 950° and 1200° is calculated as $Q=85$ Kilocalories per mole.⁽¹³⁾

While the value is far greater than those of the other reactions previously studied,^{(7) (8)} it is a little smaller than that of the reaction between MgO and SnO_2 ⁽¹⁾. On the other hand, the energy of activation of the reaction between CaO and TiO_2 ⁽⁸⁾ is also slightly smaller than that of the reaction between MgO and TiO_2 .⁽⁷⁾ Thus, whether the acidic component is TiO_2 or SnO_2 , the energy of activation of the reaction with CaO as the basic component is a little smaller than that of the reaction with MgO . While it has been studied in detail by Hedvall and others⁽¹⁴⁾ that CaO is more reactive than MgO in the exchange reactions between certain salts and oxides in solid state, the same tendency is obtained in the addition reactions between the oxides.

Summary.

(1) It has been confirmed that two stannates, $2\text{CaO} \cdot \text{SnO}_2$ and $\text{CaO} \cdot \text{SnO}_2$, are formed by the solid reaction between the components, and both of them are soluble in 4N HCl. The crystal structure of $\text{CaO} \cdot \text{SnO}_2$, which has been considered as cubic, should correctly be assigned as rhombic with a unit cell size of $a=3.93\text{\AA}$, $b=3.99\text{\AA}$ and $c=3.87\text{\AA}$.

(2) The reaction begins to take place at about 900° . The reaction product exists at first in an amorphous state; when the amount of which has reached a certain value, the reaction proceeds smoothly, forming $\text{CaO} \cdot \text{SnO}_2$. $2\text{CaO} \cdot \text{SnO}_2$ is formed gradually when an excess of CaO is present.

(3) It has been considered that the reaction is controlled by the diffusion of the components through the reaction product, and the energy of activation of $\text{CaO} \cdot \text{SnO}_2$ formation has been calculated as 85 Kilocalories per mole.

(4) Whether the acidic component is TiO_2 or SnO_2 , the energy of activation of the reaction with CaO has been found to be a little smaller than that of the reaction with MgO .

In conclusion, the author wishes to express his hearty thanks to Dr. R. Yoshimura, Director of the Department, for his sincere interest. He is also indebted to Mr. K. Oguro for his experimental assistance and to the Physics Section of this Laboratory for taking the X-ray photographs.

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(13) From the amounts of combined SnO_2 , the value of $Q=82$ Kilocalories was obtained approximately.

(14) Cf. J. A. Hedvall, "Reaktionsfähigkeit fester Stoffe," 67, Leipzig (1938).

Studies on the Derivatives of Biphenylene Oxide. VIII. Bromonitro-derivatives of Biphenylene Oxide.

By Seishi YAMASHIRO.

(Received November 10, 1941.)

As to the bromonitro-derivatives of biphenylene oxide, four of them, i.e. 2-bromo-3-nitro-,⁽¹⁾ 3-bromo-2-nitro-, 6-bromo-2-nitro- and 7-bromo-2-nitro-biphenylene oxides,⁽²⁾ were already obtained several years ago, and the present author also had recently the pleasure of adding ten more derivatives to them as described in Parts VI and VII,⁽³⁾ namely the three of them i.e. 6-bromo-1-nitro-, 6-bromo-3-nitro- and 6-bromo-4-nitro-biphenylene oxides, were obtained by the direct bromination of the corresponding nitro compounds, and the rest, i.e. 1-bromo-3,6-dinitro-, 3-bromo-1,8-dinitro-, 1,8-dibromo-3,6-dinitro-, 3,6-dibromo-1,8-dinitro-, 3,8-dibromo-1,6-dinitro-, 6-bromo-1,3,8-trinitro- and 8-bromo-1,3,6-trinitro-biphenylene oxides, by the intramolecular furan-ring-formation in the corresponding bromonitrobiphenols.

Now, with a view to extend the research on the tendency of the nitro-substitution and, at the same time, to supplement the bromonitro-derivatives which could hardly be obtained either by the direct bromination of nitrobiphenylene oxides or by the intramolecular furan-ring-formation in the corresponding bromonitrobiphenols, the present author nitrated bromobiphenylene oxides and their lower nitro derivatives in the following schemes. Of the newly obtained derivatives, twenty-seven compounds (I~XXVII) are reported in this paper. They are:

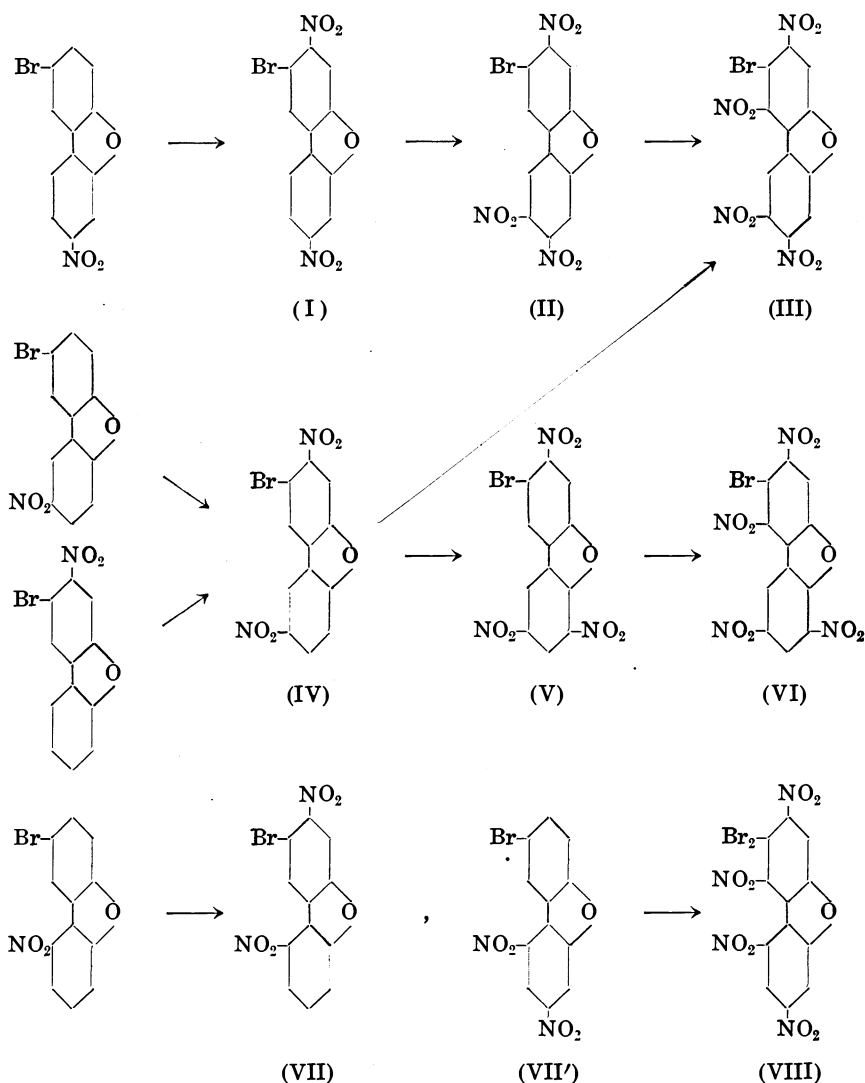
6-Bromo-2,7-dinitro-biphenylene oxide	(I)	M.p. (corr.)	254-255°
6-Bromo-2,3,7-trinitro-	" "	"	254-255°
6-Bromo-2,3,5,7-tetranitro-	" "	"	278-279°
6-Bromo-3,7-dinitro-	" "	"	216-217°
6-Bromo-1,3,7-trinitro-	" "	"	251-252°
6-Bromo-1,3,5,7-tetranitro-	" "	"	285-286°
6-Bromo-4,7-dinitro-	" "	"	198-199°
6-Bromo-2,4,5,7-tetranitro-	" "	D.p. (corr.)	329°
7-Bromo-2,6-dinitro-	" "	M.p. (corr.)	223-224°
7-Bromo-3,6-dinitro-	" "	"	254-255°
7-Bromo-2,3,6-trinitro-	" "	"	248-249°
3,6-Dibromo-2-nitro-	" "	"	190-191°
3,6-Dibromo-2,7-dinitro-	" "	"	297-298°
3,6-Dibromo-4-nitro-	" "	"	245-247°
3,6-Dibromo-4,7-dinitro-	" "	"	273-274°

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

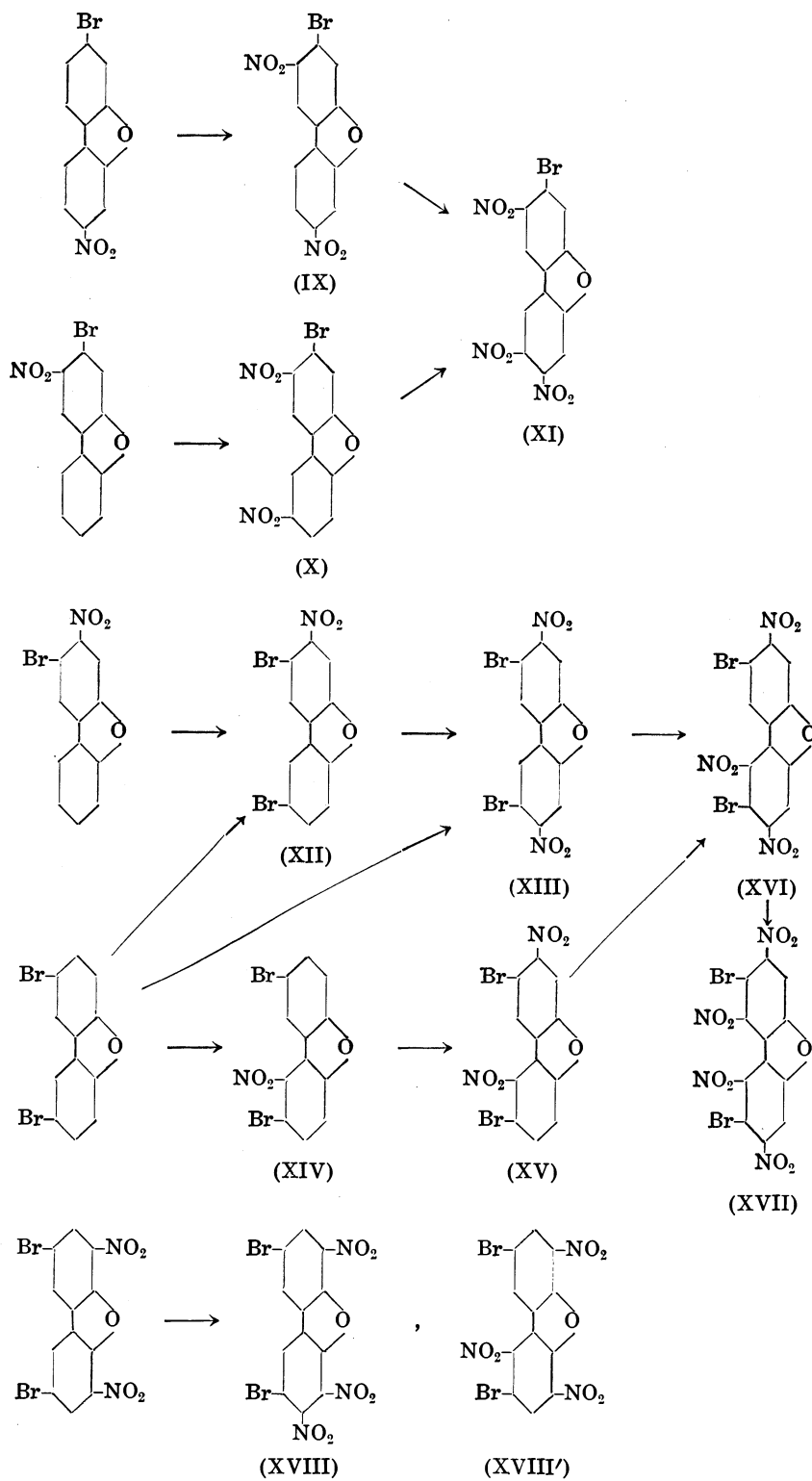
(2) H. Gilman, G. E. Brown, W. G. Bywater and W. H. Kirkpatrick, *J. Am. Chem. Soc.*, **56** (1934), 3473-7.

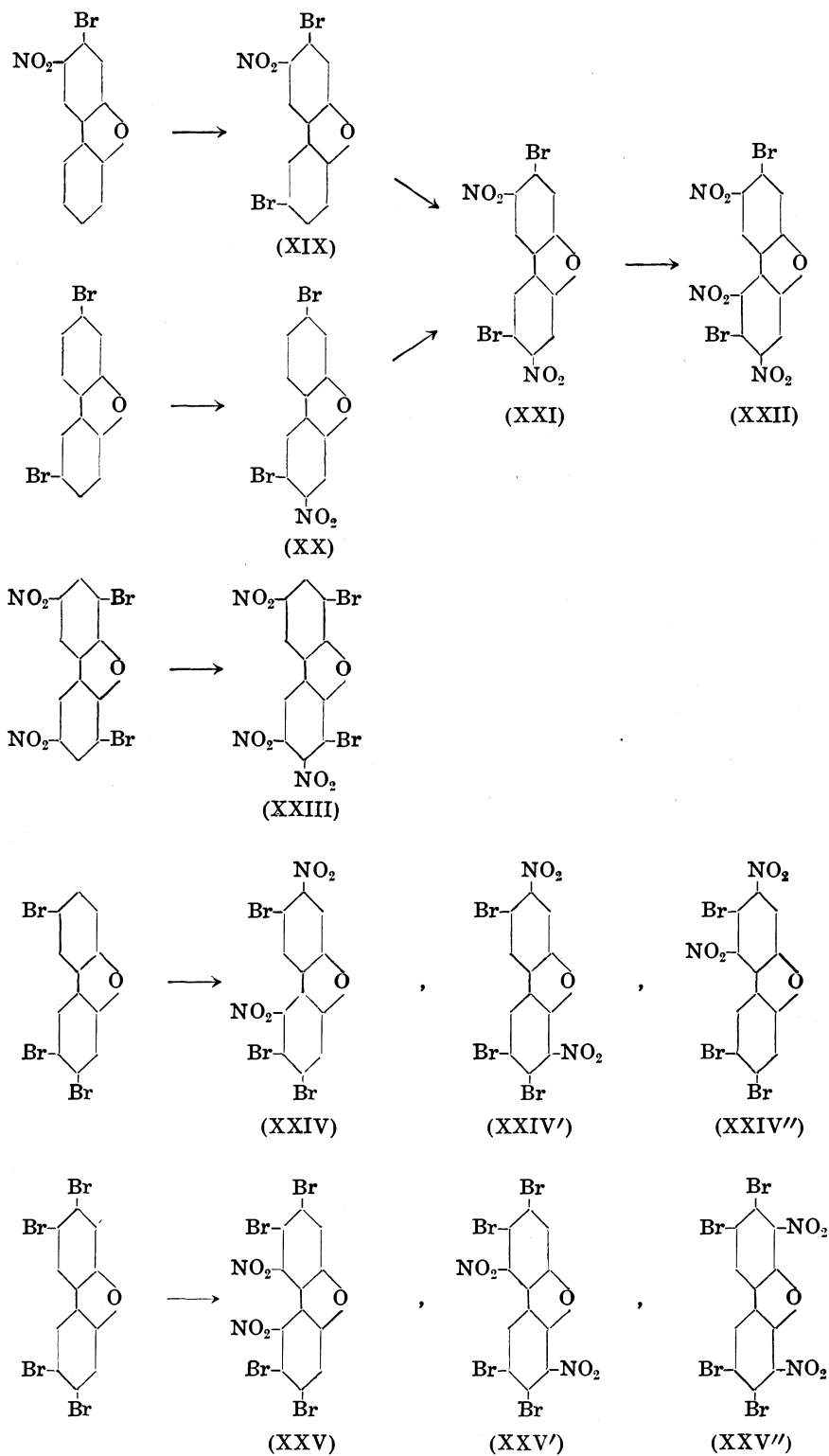
(3) S. Yamashiro, *This Bulletin*, **16** (1941), 68; **17** (1942), 10.

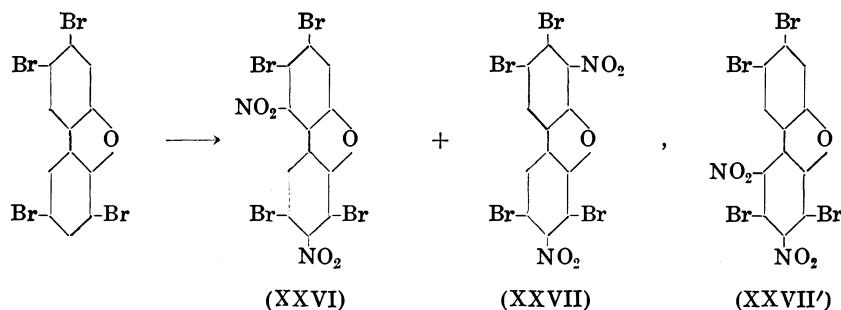
3,6-Dibromo-2,4,7-trinitro-	"	"	(XVI)	"	275-276°
3,6-Dibromo-2,4,5,7-tetranitro-	"	"	(XVII)	"	*352-354°
3,6-Dibromo-1,2,8-trinitro-	"	"	(XVIII)	"	334-334.5°
2,6-Dibromo-3-nitro-	"	"	(XIX)	"	205-206°
2,6-Dibromo-7-nitro-	"	"	(XX)	"	209-210°
2,6-Dibromo-3,7-dinitro-	"	"	(XXI)	"	262-263°
2,6-Dibromo-3,5,7-trinitro-	"	"	(XXII)	"	257-258°
1,8-Dibromo-2,3,6-trinitro-	"	"	(XXIII)	"	297-298°
2,3,6-Tribromo-4,7-dinitro-	"	"	(XXIV)	"	256-257°
2,3,6,7-Tetrabromo-4,5-dinitro-	"	"	(XXV)	"	*364-365°
1,3,6,7-Tetrabromo-2,5-dinitro-	"	"	(XXVI)	"	329-330°
1,3,6,7-Tetrabromo-2,8-dinitro-	"	"	(XXVII)	"	297-298°



* With decomp.







The constitutions of these compounds were mainly established by the following facts:

(1) Of the positions of biphenylene oxide, 2(7) and 3(6) are more active than 1(8) and 4(5) for the introduction of nitro groups. This fact excludes the formula XVIII'.

(2) The nitro groups and the nitro- or bromonitro-phenylene residues of the nitro- or bromonitro-biphenylene oxides exert generally the *m*-directing influence on the further introduction of nitro groups, while bromine and the bromophenylene residues of the bromo- or bromonitro-biphenylene oxides, the *o,p*-directing influence on the introduction of the same groups. And it must be noticed that this fact occurs only when it is compatible with the fact (1).

(3) The nitro groups introduced are found, in many cases, to be distributed evenly between both phenylene residues of biphenylene oxide. This fact excludes the formulas VII', XXIV'' and XXVII'.

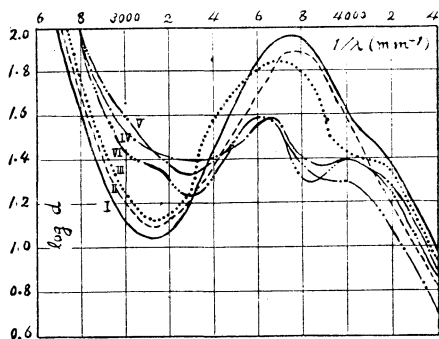
(4) When the nitro group already occupies the position 2 or 3, the further nitro-substitution does not take place at the position 1 or 4 respectively in correspondence with that 2 or 3. And when the nitro groups already occupy the positions 1 and 3, the further introduction of the same group does not occur at the position 2, though it takes place at the same position when the position 3 alone is already occupied by the nitro group.

(5) The nitro-substitution hardly takes place at the position 1 of the 2-bromo-3-nitrophenylene residue, whereas the same reaction occurs without too much difficulty at the position 4 of the 3-bromo-2-nitrophenylene residue, even though they contradict to the general rule (2), it is because of the compound XI which did not give any higher nitro derivative, while the compounds II, V and XIII gave the compounds III, VI and XVIII respectively as the higher nitro derivatives. This fact admits no dispute about the formula XXII, and also enables us to infer that the nitro-substitution will occur more readily at the position 4 than at the position 1 of the 2,3-dibromophenylene residue. From this reason the formulas XXIV' and XXV'' are excluded.

Of the dinitro derivatives of 1,3,6,7-tetrabromobiphenylene oxide, the higher melting one should be the 2,5-dinitro compound XXVI, and the lower melting one, the 2,8-dinitro compound XXVII, because the former is the main product and the latter, a by-product.

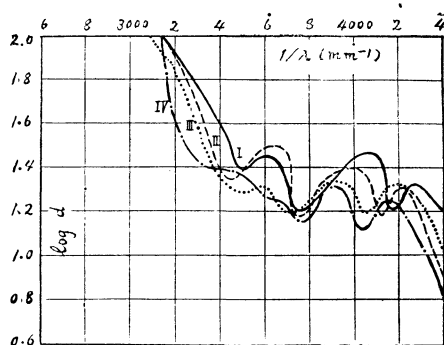
For the benefit of the confirmation of the constitutions of those bromo-nitrobiphenylene oxides, the absorption curves of those compounds were compared with those of the corresponding nitro compounds and the related bromo-nitrobiphenylene oxides as in Figs. 1~15.

Absorption curves of the derivatives of biphenylene oxide.
M/10000 alcoholic solutions.



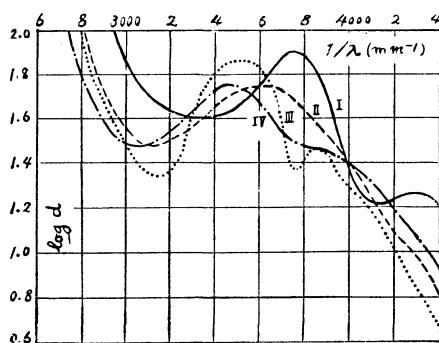
- I 2-Nitro derivative.
- II 6-Bromo-2-nitro derivative.
- III 7-Bromo-2-nitro derivative.
- IV 3-Bromo-2-nitro derivative.
- V 3,6-Dibromo-2-nitro derivative.
- VI 3,7-Dibromo-2-nitro derivative.

Fig. 1.



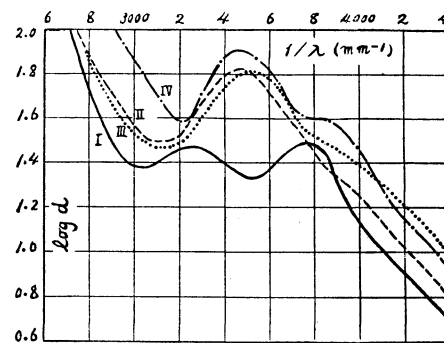
- I 3-Nitro derivative.
- II 6-Bromo-3-nitro derivative.
- III 2-Bromo-3-nitro derivative.
- IV 2,6-Dibromo-3-nitro derivative.

Fig. 2.



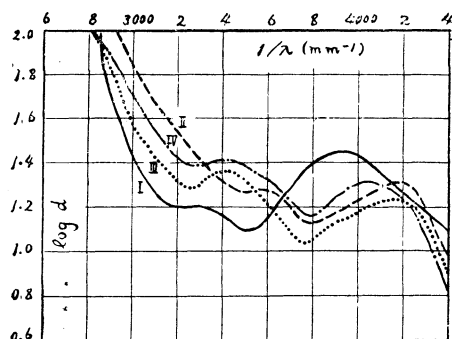
- I 1,8-Dinitro derivative.
- II 3,6-Dibromo-1,8-dinitro derivative.
- III 2,3,6,7-Tetrabromo-4,5-dinitro " .
- IV 3,6-Dibromo-1,2,8-trinitro " .

Fig. 3.



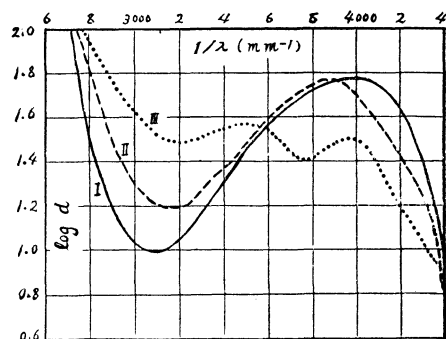
- I 6-Bromo-4,7-dinitro derivative.
- II 3,6-Dibromo-4,7-dinitro derivative.
- III 2,3,6-Tribromo-4,7-dinitro derivative.
- IV 2,3,6,8-Tetrabromo-4,7-dinitro " .

Fig. 4.



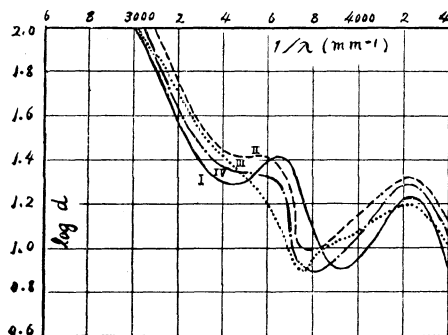
- I 2,6-Dinitro derivative.
 II 3-Bromo-2,6-dinitro derivative.
 III 7-Bromo-2,6-dinitro derivative.
 IV 3,7-Dibromo-2,6-dinitro derivative.

Fig. 5.



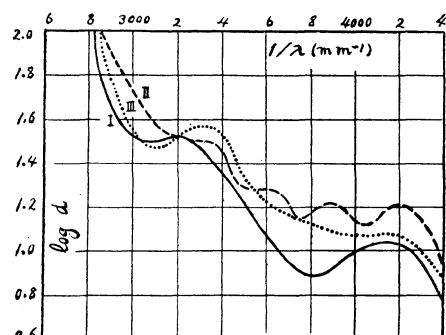
- I 2,7-Dinitro derivative.
 II 6-Bromo-2,7-dinitro derivative.
 III 3,6-Dibromo-2,7-dinitro derivative.

Fig. 6.



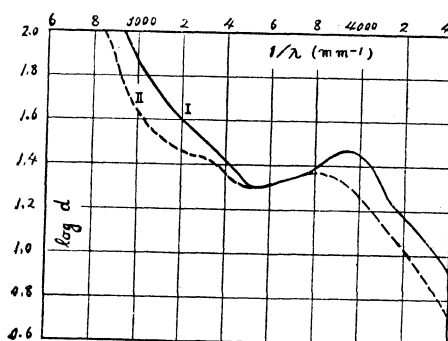
- I 3,6-Dinitro derivative.
 II 1-Bromo-3,6-dinitro derivative.
 III 7-Bromo-3,6-dinitro derivative.
 IV 1,8-Dibromo-3,6-dinitro derivative.

Fig. 7.



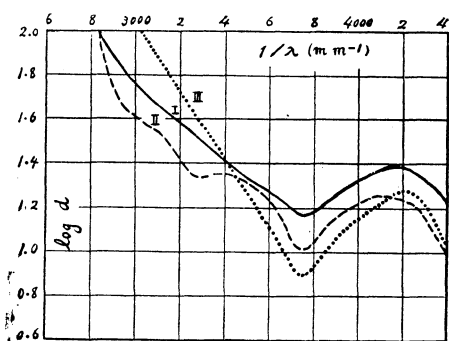
- I 1,3,6,7-Tetranitro derivative.
 II 6-Bromo-1,3,7-trinitro derivative.
 III 6-Bromo-1,3,5,7-tetranitro derivative.

Fig. 8.



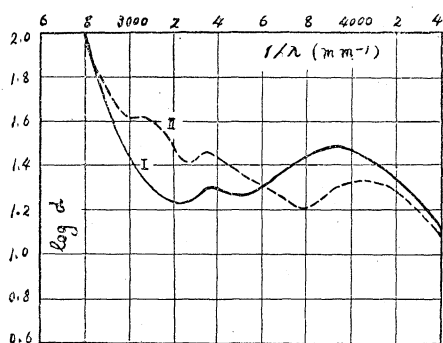
- I 1,3,8-Trinitro derivative.
 II 6-Bromo-1,3,8-trinitro derivative.

Fig. 9.



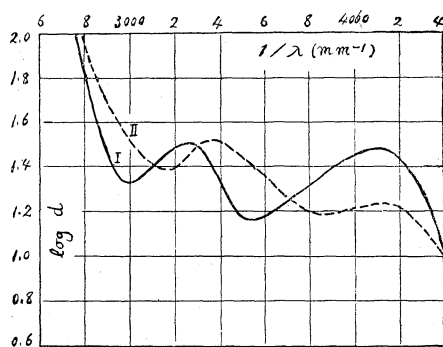
- I 2,3,6-Trinitro derivative.
 II 7-Bromo-2,3,6-trinitro derivative.
 III 1,8-Dibromo-2,3,6-trinitro derivative.

Fig. 10.



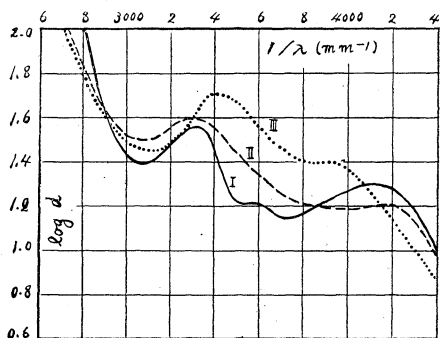
I 2,3,7-Trinitro derivative.
II 6-Bromo-2,3,7-trinitro derivative.

Fig. 11.



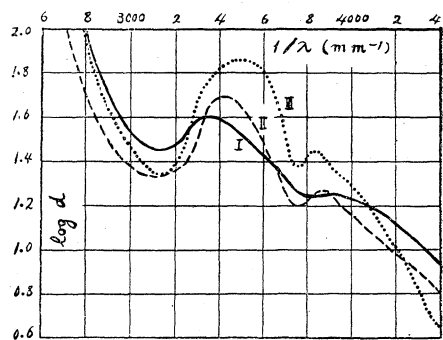
I 3,5,7-Trinitro derivative.
II - 2,6-Dibromo-3,5,7-trinitro derivative.

Fig. 12.



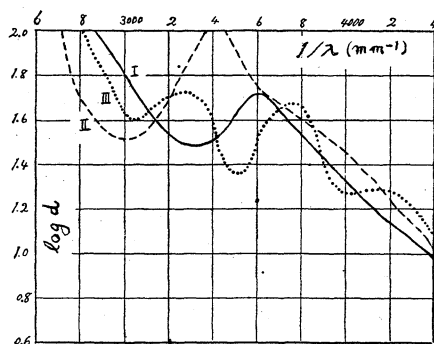
I 2,4,6,7-Tetranitro derivative.
II 3-Bromo-2,4,6,7-tetranitro derivative.
III 3,6-Dibromo-2,4,7-trinitro derivative.

Fig. 13.



I 6-Bromo-2,4,5,7-tetranitro derivative.
II 3,6-Dibromo-2,4,5,7-tetranitro " "
III 2,3,6,7-Tetrabromo-4,5-dinitro " "

Fig. 14.



I 3,6-Dibromo-4-nitro derivative.
II 6-Bromo-4-nitro derivative.
III 6-Bromo-1-nitro derivative.

Fig. 15.

The absorption curves of 1,6-dinitro- and 1,3,6-trinitro-biphenylene oxides have already been compared in Part V with those of their bromo-derivatives.

From the comparison among the curves in Figs. 1 and 2, especially in the former, it may be found that the bromo-substitution in the nitro-biphenylene oxides shifts and deforms the curves of the parent compounds, and that those effects of bromine are greater when the substitution takes place in the nitro-phenylene residues, than when it does in the phenylene residues which have no nitro group. These effects, however, are not so remarkable as to change completely the curves of the parent compounds, therefore, the curves in each of the above figures are liable to resemble to each other in some degree. In fact, the curve of the compound XIV, which was regarded as 3,6-dibromo-4-nitrobiphenylene oxide, resembles more closely to that of 6-bromo-4-nitrobiphenylene oxide, than to that of 6-bromo-1-nitrophenylene oxide in Fig. 15. And the curve of the compound XXV, which was regarded as 2,3,6,7-tetrabromo-4,5-dinitrobiphenylene oxide, resembles indeed more closely to those of the derivatives of 4,5-dinitrobiphenylene oxide in Fig. 14, rather than to those of the derivatives of 1,8-dinitrobiphenylene oxide in Fig. 3.

As seen from the comparison of the curves in Figs. 4 and 6, 6-bromo-4,7-dinitro and 3,6-dibromo-2,7-dinitro-biphenylene oxides have exceptionally special curves. But a certain resemblance can be found when both of these curves are compared with that of 3-bromo-2-nitrobiphenylene oxide, a parent compound, in Fig. 1.

Experimental.

(1) **Nitro-derivatives of 3-bromobiphenylene oxide.** *6-Bromo-2,7-dinitrobiphenylene oxide* (I). 6-Bromo-2-nitrobiphenylene oxide (5.28 g.) was dissolved in hot fuming nitric acid ($d=1.45$; 200 c.c.), and after being kept on standing 20 minutes the reaction mixture was poured into ice, when pale yellow precipitates separated out. The reaction product (6.67 g.) was recrystallized from acetic acid, into pale yellow needles, m.p. $254-255^\circ$ (corr.) (Yield 4.45 g. Found: N, 8.25; Br, 23.58. Calc. for $C_{12}H_5OBr(NO_2)_2$: N, 8.31; Br, 23.71%). It is readily soluble in acetone and chloroform, and fairly in benzene, acetic acid and ethyl acetate, and sparingly in alcohols, carbon tetrachloride, ether and ligroin.

6-Bromo-2,3,7-trinitrobiphenylene oxide (II). 6-Bromo-2,7-dinitrobiphenylene oxide (2 g.) was dissolved in warm fuming nitric acid ($d=1.52$; 10 c.c.), and when the reaction mixture was diluted with ice, pale yellow precipitates separated out. The reaction product (2.42 g.) was extracted with ethanol, and the residue was recrystallized from acetic acid into pale yellow short needles, m.p. $254-255^\circ$ (corr.) (Yield 1.2 g. Found: N, 11.14; Br, 20.97. Calc. for $C_{12}H_4OBr(NO_2)_3$: N, 11.00; Br, 20.92%). It is readily soluble in acetone, fairly in benzene, acetic acid and ethyl acetate, and sparingly in alcohols, chloroform, carbon tetrachloride, benzene, ether and ligroin.

6-Bromo-2,3,5,7-tetranitrobiphenylene oxide (III). 6-Bromo-2,3,7-trinitrobiphenylene oxide (1 g.) was heated for one hour with fuming nitric acid ($d=1.52$; 10 c.c.) on the water-bath, and when the reaction mixture was poured into ice, white precipitates separated out. The reaction product (0.9 g.) was recrystallized from acetone into almost colourless hexagonal plates, m.p. $278-279^\circ$ (corr.) (Yield 0.7 g. Found: N, 13.21; Br, 16.84. Calc. for $C_{12}H_3OBr(NO_2)_4$: N, 13.12; Br, 16.93%). The same compound was also isolated from the nitration products of 6-bromo-3,7-dinitro-

phenylene oxide. It is readily soluble in acetone and ethyl acetate, fairly in benzene and acetic acid, and sparingly in alcohols, chloroform, carbon tetrachloride, ether and ligroin.

6-Bromo-3,7-dinitro- (or 3-bromo-2,6-dinitro-) biphenylene oxide (IV). (i) 6-Bromo-3-nitrobiphenylene oxide (4 g.) was dissolved in warm nitric acid ($d=1.45$; 100 c.c.), and the reaction product separated out on dilution was recrystallized from acetic acid into pale yellow needles, m.p. $216-217^{\circ}$ (corr.) (Yield 4.2 g. Found: N, 8.33; Br, 23.76. Calc. for $C_{12}H_5OBr(NO_2)_2$: N, 8.31; Br, 23.71%). It is readily soluble in acetone, acetic acid, benzene, chloroform and ethyl acetate, and fairly in alcohols, carbon tetrachloride, ether and ligroin.

(ii) 3-Bromo-2-nitrobiphenylene oxide (2 g.), which was obtained from 3-amido-2-nitrobiphenylene oxide by the Sandmeyer's diazo-reaction, was dissolved in warm nitric acid ($d=1.45$; 30 c.c.), and the reaction product, separated out on dilution, was recrystallized from acetic acid into pale yellow needles melting at $216-217^{\circ}$ (corr.) (Yield 2.1 g.). No depression of its melting point was observed when it was mixed with the bromodinitrobiphenylene oxide obtained from 6-bromo-3-nitrobiphenylene oxide.

6-Bromo-1,3,7-trinitro- (V) and 6-bromo-2,3,5,7-tetranitro (or 3-bromo-2,4,6,7-tetranitro)- (III)-biphenylene oxides. 6-Bromo-3,7-dinitrobiphenylene oxide (3 g.) was heated for one hour on the water-bath with nitric acid ($d=1.52$; 30 c.c.), and the reaction product (2.9 g.) separated out on dilution was recrystallized from acetic acid into colourless small prismatic needles, m.p. $251-252^{\circ}$ (corr.) (Yield 0.2 g. Found: N, 10.91; Br, 20.78. Calc. for $C_{12}H_4OBr(NO_2)_3$: N, 11.00; Br, 20.92%). It is readily soluble in acetone, benzene and ethyl acetate, fairly in alcohols and acetic acid, and sparingly in chloroform, carbon tetrachloride, ether and ligroin. The dissolved part was recovered from the acetic mother-liquor and extracted with ethanol and chloroform. And the residue was recrystallized from a mixture of acetone and ethanol, colourless plates melting at $278-279^{\circ}$ (corr.) (Yield 0.6 g.). The latter compound is identical in all respects with the bromotetranitrobiphenylene oxide obtained from 6-bromo-2,3,7-trinitrobiphenylene oxide as above described.

6-Bromo-1,3,5,7-tetranitrobiphenylene oxide (VI). 6-Bromo-1,3,7-trinitrobiphenylene oxide (0.2 g.) was heated for 2 hours with a large excess of nitric acid ($d=1.52$). The reaction product (0.21 g.) separated out on dilution was recrystallized from benzene into colourless micro rectangular plates, m.p. $285-286^{\circ}$ (corr.) (Yield 0.18 g. Found: N, 13.22; Br, 16.89. Calc. for $C_{12}H_3OBr(NO_2)_4$: N, 13.12; Br, 16.93%). It is readily soluble in acetone and ethyl acetate, fairly in benzene and acetic acid, and sparingly in alcohols, chloroform, carbon tetrachloride, ether and ligroin.

6-Bromo-4,7-dinitrobiphenylene oxide (VII). When 6-Bromo-4-nitrobiphenylene oxide (2 g.) was treated for 1 hour with a large excess of warm nitric acid ($d=1.45$), the large crystals of this oxide perfectly changed into micro needles. These needle crystals were separated from the reaction mixture on cooling, and extracted with carbon tetrachloride to the removal of higher nitro-derivatives. The extract was evaporated to dryness and the residue was recrystallized from acetone-ethanol into pale yellow needles, m.p. $198-199^{\circ}$ (corr.) (Yield 1.6 g. Found: N, 8.58; Br, 23.53. Calc. for $C_{12}H_5OBr(NO_2)_2$: N, 8.31; Br, 23.71%). It is readily soluble in acetone, benzene, chloroform and ethyl acetate, fairly in acetic acid, carbon tetrachloride and ethanol, and sparingly in ether, ligroin and methanol.

6-Bromo-2,4,5,7-tetranitrobiphenylene oxide (VIII). 6-Bromo-4,7-dinitrobiphenylene oxide (1.5 g.) was strongly nitrated by being heated for 1 hour with fuming nitric acid ($d=1.52$; 15 c.c.), and the reaction product (1.3 g.) separated out on dilution was recrystallized from acetone into colourless rectangular plates, d.p. 329° (corr.) (Yield 0.9 g. Found: N, 13.29; Br, 16.88. Calc. for $C_{12}H_3OBr(NO_2)_4$: N, 13.12; Br, 16.93%). It is sparingly soluble in the ordinary organic solvents except acetone and ethyl acetate which dissolve it fairly.

(2) Nitro-derivatives of 2-bromobiphenylene oxide. 7-Bromo-2,6-dinitrobiphenylene oxide (IX). 7-Bromo-2-nitrobiphenylene oxide (2 g.) was dissolved in warm

nitric acid ($d=1.45$; 20 c.c.), and the crystals of the reaction product separated on cooling and recrystallized from acetic acid into pale yellow needles melting at $223-224^{\circ}$ (corr.) (Yield 1.9 g. Found: N, 8.27; Br, 23.62. Calc. for $C_{12}H_7OBr(NO_2)_2$: N, 8.31; Br, 23.71%). It is readily soluble in acetone, benzene, chloroform and ethyl acetate, fairly in alcohols, acetic acid and carbon tetrachloride, and difficultly in ether and ligroin.

7-Bromo-3,6-dinitrobiphenylene oxide (X). 2-Bromo-3-nitrobiphenylene oxide (2 g.), which was obtained from 2-amido-3-nitrobiphenylene oxide by the Sandmeyer's reaction according to B. Kubota and his co-worker⁽¹⁾, was treated for half an hour with warm nitric acid ($d=1.45$; 20 c.c.), and the reaction product (2.15 g.) separated out on dilution was recrystallized from acetone-ethanol into yellow needles melting at $254-255^{\circ}$ (corr.) (Yield 1.2 g. Found: N, 8.36; Br, 23.59. Calc. for $C_{12}H_5OBr(NO_2)_2$: N, 8.31; Br, 23.71%). It is readily soluble in acetone, benzene, chloroform and ethyl acetate, and sparingly in alcohols, acetic acid, carbon tetrachloride, ether and ligroin.

7-Bromo-2,3,6-trinitrobiphenylene oxide (XI). (i) 7-Bromo-2,6-dinitrobiphenylene oxide (2.5 g.) was dissolved in warm nitric acid ($d=1.52$; 25 c.c.), and, after being kept on standing for 1 hour, the reaction mixture was poured into water. The reaction product (2.4 g.) was separated and recrystallized from acetic acid into pale yellow prismatic needles melting at $248-249^{\circ}$ (corr.) (Yield 1.1 g. Found: N, 11.24; Br, 20.74. Calc. for $C_{12}H_4OBr(NO_2)_3$: N, 11.00; Br, 20.92%). It is readily soluble in acetone, benzene, chloroform and ethyl acetate, fairly in alcohols and acetic acid, and sparingly in ether, ligroin and carbon tetrachloride. This bromotrinitro compound gives no higher nitro derivative even when it is boiled with a large excess of fuming nitric acid ($d=1.52$).

(ii) 7-Bromo-3,6-dinitrobiphenylene oxide (1 g.) was strongly nitrated with fuming nitric acid ($d=1.52$), and the reaction product (1.1 g.) separated out on dilution was recrystallized from acetic acid into pale yellow prismatic needles melting at $248-249^{\circ}$ (corr.) (Yield 0.9 g.). When it was mixed with the corresponding compound obtained from 7-bromo-2,6-dinitrobiphenylene oxide no depression of its melting point was observed.

(3) **Nitro-derivatives of 3,6-dibromobiphenylene oxide.** *3,6-Dibromo-2-nitrobiphenylene oxide* (XII). When 3-Bromo-2-nitrobiphenylene oxide (1 g.) was heated for 12 hours with a large excess of bromine (2 g.) in boiling acetic acid (20 c.c.) the colour of bromine disappeared. The reaction product (1.25 g.) separated out on dilution was recrystallized from acetic acid into pale yellow needles, m.p. $190-191^{\circ}$ (corr.) (Yield 1.1 g. Found: N, 3.84; Br, 42.87. Calc. for $C_{12}H_5OBr_2NO_2$: N, 3.78; Br, 43.08%). It is readily soluble in acetone, benzene, chloroform and ethyl acetate, fairly in acetic acid and carbon tetrachloride, and sparingly in alcohols, ether and ligroin. It can also be obtained as below from 3,6-dibromobiphenylene oxide.

3,6-Dibromo-2,7-dinitrobiphenylene oxide (XIII). (i) 3,6-Dibromo-biphenylene oxide (3 g.) was treated for 1 hour with a large excess of warm nitric acid ($d=1.45$). The undissolved part of the reaction product was separated on cooling from the reaction mixture and extracted with acetone-alcohol to the removal of the unacted dibromo-compound. The residue was then recrystallized from acetic acid into pale yellow prisms, m.p. $297-298^{\circ}$ (corr.) (Yield 2.5 g. Found: N, 6.53; Br, 38.59. Calc. for $C_{12}H_4OBr_2(NO_2)_2$: N, 6.74; Br, 38.42%). It is fairly soluble in acetone, benzene, chloroform and ethyl acetate, and sparingly in alcohols, acetic acid, carbon tetrachloride, ether and ligroin.

(ii) 3,6-Dibromo-2-nitrobiphenylene oxide (0.5 g.) was treated for half an hour with a large excess of warm nitric acid ($d=1.45$). The undissolved part (0.35 g.) of the reaction product was separated on cooling and extracted with carbon tetrachloride to the removal of the unacted dibromonitro-compound, and the residue was successively recrystallized from acetone and acetic acid into pale yellow prisms, m.p. $297-298^{\circ}$ (corr.). It is identical in all respects with the corresponding compound obtained from 3,6-dibromobiphenylene oxide.

3,6-Dibromo-2-nitro (XII)- and 3,6-dibromo-4-nitro (XIV)-biphenylene oxides. Finely pulverized 3,6-dibromobiphenylene oxide (22 g.) was treated for 1 hour at about 50° with warm nitric acid ($d=1.45$; 50 c.c.), and the undissolved part (25.7 g.) of the reaction product was fractionated by the successive extractions with acetone. The readily soluble part was again extracted with acetic acid, and the dissolved part was recrystallized from the same solvent into pale yellow needles melting at 190–191° (corr.) (Yield 12 g.). It is identical with the corresponding compound obtained by the bromination of 3-bromo-2-nitrobiphenylene oxide, and, therefore, it must be 3,6-dibromo-2-nitrobiphenylene oxide. The sparingly soluble part (1.5 g.) of the reaction product was recrystallized from benzene into pale yellow needles, m.p. 245–247° (corr.) (Yield 1.03 g. Found: N, 3.55; Br, 44.05. Calc. for $C_{12}H_5OBr_2NO_2$: N, 3.78; Br, 43.08%). It is sparingly soluble in the ordinary organic solvents except benzene and chloroform which dissolve it fairly. The latter product should be 3,6-dibromo-4-nitrobiphenylene oxide, but not 3,6-dibromo-1-nitrobiphenylene oxide, because the product gives 3,6-dibromo-2,4,7-trinitrobiphenylene oxide on further nitration.

3,6-Dibromo-4,7-dinitrobiphenylene oxide (XV). 3,6-Dibromo-4-nitrobiphenylene oxide (0.7 g.) was heated for half an hour on the water-bath with a large excess of nitric acid ($d=1.45$), and the reaction product was recrystallized from acetone into colourless rectangular plates, m.p. 273–274° (corr.) (Yield 0.5 g. Found: N, 6.71; Br, 38.47. Calc. for $C_{12}H_4OBr_2(NO_2)_2$: N, 6.75; Br, 38.42%).

3,6-Dibromo-2,4,7-trinitrobiphenylene oxide (XVI). (i) 3,6-Dibromobiphenylene oxide (3.26 g.) was dissolved in warm nitric acid ($d=1.52$; 40 c.c.), and, after being kept on standing half an hour, the reaction mixture was diluted with water, then the colourless precipitates separated out. The reaction product (4.66 g.) was repeatedly recrystallized from acetone-methanol into colourless small hexagonal plates, m.p. 275–276° (corr.) (Yield 2.9 g. Found: N, 9.01; Br, 34.73. Calc. for $C_{12}H_3OBr_2(NO_2)_3$: N, 9.12; Br, 34.67%). It is readily soluble in acetone, benzene, chloroform and ethyl acetate, fairly in acetic acid and carbon tetrachloride, and sparingly in alcohols, ether and ligroin.

(ii) When 3,6-Dibromo-2,7-dinitrobiphenylene oxide (1 g.) was dissolved in warm nitric acid ($d=1.52$; 10 c.c.), and the reaction mixture was diluted with water, the colourless precipitates separated out. The reaction product (1.1 g.) was recrystallized from acetone-methanol into colourless hexagonal plates melting at 275–276° (corr.) (Yield 0.8 g. Found: N, 9.27; Br, 34.49. Calc. for $C_{12}H_3OBr_2(NO_2)_3$: N, 9.12; Br, 34.67%). It is identical in all respects with the corresponding compound obtained as described above by the direct nitration of 3,6-dibromobiphenylene oxide.

(iii) 3,6-Dibromo-4,7-dinitrobiphenylene oxide was dissolved in a large excess of warm nitric acid ($d=1.52$), and the reaction mixture was treated as in the case (i). The reaction product recrystallized from acetone-methanol is identical in all respects with the dibromotrinitrobiphenylene oxide which was obtained from 3,6-dibromo-2,7-dinitrobiphenylene oxide.

3,6-Dibromo-2,4,5,7-tetranitrobiphenylene oxide (XVII). 3,6-Dibromo-2,4,7-trinitrobiphenylene oxide (1 g.) was heated for 1 hour on the water-bath with nitric acid ($d=1.52$; 10 c.c.), and the reaction product (0.7 g.) separated out on dilution was recrystallized from acetone-ethanol into colourless needles melting at 352–354° (corr.) with decomposition, (Yield 0.5 g. Found: N, 10.95; Br, 31.42. Calc. for $C_{12}H_2OBr_2(NO_2)_4$: N, 11.07; Br, 31.59%). It is readily soluble in acetone, benzene and ethyl acetate, and sparingly in the other ordinary organic solvents.

3,6-Dibromo-1,2,8-trinitrobiphenylene oxide (XVIII). 3,6-Dibromo-1,8-dinitrobiphenylene oxide (1 g.) was dissolved in a large excess of warm nitric acid ($d=1.52$; 20 c.c.), and the reaction product (1.07 g.) separated out on dilution was recrystallized from acetone into colourless leaflets melting at 334–334.5° (corr.) with decomposition (Yield 1.0 g. Found: N, 8.99; Br, 34.79. Calc. for $C_{12}H_3OBr_2(NO_2)_3$: N, 9.12; Br, 34.67%). It is sparingly soluble in the ordinary organic solvents except acetone which dissolves it fairly.

(4) **Nitro-derivatives of 2,6-dibromobiphenylene oxide.** *2,6-Dibromo-3-nitrobiphenylene oxide* (XIX). When 2-Bromo-3-nitrobiphenylene oxide (2.92 g.) was heated for 20 hours with a large excess of bromine (4 g.) in boiling acetic acid (30 c.c.), the colour of bromine disappeared. The reaction product separated out on dilution was recrystallized from acetone-ethanol into yellow prisms melting at 205–206° (corr.) (Yield 3.5 g. Found: N, 3.75; Br, 43.20. Calc. for $C_{12}H_5OBr_2NO_2$: N, 3.78; Br, 43.08%). It is sparingly soluble in alcohols, and readily in the other ordinary organic solvents.

2,6-Dibromo-7-nitrobiphenylene oxide (XX). 2,6-Dibromobiphenylene oxide (1.63 g.) was dissolved in glacial acetic acid (25 c.c.), and, after addition of nitric acid ($d=1.52$; 2.5 c.c.), the mixture was heated on the water-bath. The reaction product separated out on dilution was recrystallized from ethanol into pale yellow needles melting at 209–210° (corr.) (Yield 0.9 g. Found: N, 3.80; Br, 43.21. Calc. for $C_{12}H_5OBr_2NO_2$: N, 3.78; Br, 43.08%). It is readily soluble in acetone, acetic acid, benzene, chloroform, carbon tetrachloride, ether and ethyl acetate, and fairly in alcohols and ligroin. When it was mixed with the dibromonitro-compound obtained by the bromination of 2-bromo-3-nitrobiphenylene oxide, its melting point was exceedingly depressed.

2,6-Dibromo-3,7-dinitro (or 3,7-dibromo-2,6-dinitro)-biphenylene oxide (XXI). (i) When 2,6-Dibromo-3-nitrobiphenylene oxide (1 g.) was treated for 10 minutes with warm nitric acid ($d=1.45$ c.c.), the crystalline form of the oxide completely changed. The reaction product was recrystallized from acetone into pale yellow hexagonal plates, m.p. 262–263° (corr.) (Yield 0.75 g. Found: N, 6.76; Br, 38.38. Calc. for $C_{12}H_4OBr_2(NO_2)_2$: N, 6.74; Br, 38.42%). It is fairly soluble in acetone, acetic acid, benzene, chloroform and ethyl acetate, and sparingly in alcohols, carbon tetrachloride, ether and ligroin.

(ii) 2,6-Dibromo-7-nitrobiphenylene oxide (0.6 g.) was heated for 3 hours on the water-bath with nitric acid ($d=1.45$; 10 c.c.), and the reaction product separated out on dilution was recrystallized from acetone into pale yellow hexagonal plates, m.p. 262–263° (corr.) (Yield 0.4 g.). It is identical with the corresponding compound obtained from 2,6-dibromo-3-nitrobiphenylene oxide.

2,6-Dibromo-3,5,7-trinitrobiphenylene oxide (XXII). 2,6-Dibromo-3,7-dinitrobiphenylene oxide (0.8 g.) was warmed with nitric acid ($d=1.52$; 10 c.c.) for 10 minutes on the water-bath, and the reaction product separated out on dilution was recrystallized from acetone-ethanol into colourless needles, m.p. 257–258° (corr.) (Yield 0.83 g. Found: N, 9.07; Br, 34.49. Calc. for $C_{12}H_3OBr_2(NO_2)_3$: N, 9.12; Br, 34.67%). It is readily soluble in acetone, fairly in acetic acid, benzene, chloroform and ethyl acetate, and sparingly in alcohols, carbon tetrachloride, ether and ligroin. This dibromotrininitro-compound hardly gives any higher nitro-derivative, even when it is boiled with fuming nitric acid ($d=1.52$).

(5) **Nitro-derivative of 1,8-dibromobiphenylene oxide.** *1,8-Dibromo-2,3,6-trinitrobiphenylene oxide* (XXIII). 1,8-Dibromo-3,6-dinitrobiphenylene oxide (0.5 g.) was treated for 1 hour with warm nitric acid ($d=1.52$; 10 c.c.), and the reaction mixture was diluted with water, and then colourless precipitates separated out. The reaction product (0.51 g.) was recrystallized from acetone-methanol into colourless rectangular plates, m.p. 297–298° (corr.) (Yield 0.45 g. Found: N, 9.03; Br, 34.52. Calc. for $C_{12}H_3OBr_2(NO_2)_3$: N, 9.12; Br, 34.67%). It is readily soluble in acetone, fairly in benzene and ethyl acetate, and sparingly in alcohols, acetic acid, chloroform, carbon tetrachloride, ether and ligroin.

(6) **Nitro-derivative of 2,3,6-tribromobiphenylene oxide.** *2,3,6-Tribromo-4,7-dinitrobiphenylene oxide* (XXIV). 2,3,6-Tribromobiphenylene oxide (3 g.) was dissolved in hot nitric acid ($d=1.45$), and the reaction product separated out on cooling was recrystallized from acetone ethanol into colourless needles or rhombic plates, m.p. 256–257° (corr.) (Yield 1.8 g. Found: N, 5.65; Br, 48.38. Calc. for $C_{12}H_3OBr_3(NO_2)_2$: N, 5.66; Br, 48.44%). It is readily soluble in acetone, benzene and ethyl

acetate, fairly in acetic acid and chloroform, and sparingly in alcohols, carbon tetrachloride, ether and ligroin.

(7) **Nitro-derivative of 2,3,6,7-tetrabromobiphenylene oxide.** 2,3,6,7-Tetrabromo-4,5-dinitrobiphenylene oxide (XXV). Finely pulverized 2,3,6,7-tetrabromobiphenylene oxide (1 g.) was treated for 1 hour with a large excess of boiling nitric acid ($d=1.52$) and the reaction product (1.18 g.) separated out on dilution was recrystallized from a large quantity of acetone into colourless rhombic plates or needles, m.p. $364-365^{\circ}$ (corr.) with decomposition, (Yield 0.9 g. Found: N, 4.86; Br, 55.54. Calc. for $C_{12}H_2OBr_4(NO_2)_2$: N, 4.88; Br, 55.69%). It is sparingly soluble in the ordinary organic solvents except acetone, benzene and ethyl acetate which dissolve it fairly.

(8) **Nitro-derivatives of 1,3,6,7-tetrabromobiphenylene oxide.** 1,3,6,7-Tetrabromo-2,5-dinitro (or 2,3,6,8-tetrabromo-4,7-dinitro)- and 1,3,6,7-tetrabromo-2,8-dinitro-biphenylene oxides (XXVI) and XXVII). When 1,3,6,7-Tetrabromobiphenylene oxide (0.7 g.) was treated for half an hour with warm nitric acid ($d=1.52$; 10 c.c.), the crystalline form of this compound completely changed. The reaction product was separated from the reaction mixture and extracted with acetone-ethanol. The residue was recrystallized from acetone, and two kinds of crystals were isolated by decantation. The one is colourless needles melting at $329-330^{\circ}$ (corr.) (Yield 0.3 g. Found: N, 4.97; Br, 55.51. Calc. for $C_{12}H_2OBr_4(NO_2)_2$: N, 4.88; Br, 55.69%), and the other is pale yellow compact prisms melting at $297-298^{\circ}$ (corr.) (Yield 0.15 g. Found: N, 5.05; Br, 55.47%). Both of these derivatives are sparingly soluble in the ordinary organic solvents.

Summary.

(1) Twenty seven higher nitro-derivatives of 2- and 3-bromo-, 2,6-, 3,6- and 1,8-dibromo-, 2,3,6-tribromo-, and 1,3,6,7- and 2,3,6,7-tetrabromobiphenylene oxides were newly obtained by nitrating the corresponding lower nitro-derivatives, and their constitutions were established.

(2) The absorption curves of those bromonitro-compounds were compared with each other, and also with those of the corresponding nitrobiphenylene oxides, to the confirmation of their constitutions as a consequence.

(3) In the nitration of the bromo- and bromonitro-biphenylene oxides, it was found that when the relative arrangements of the substituents at the 2- and 3-positions to the 1-position are the same as those of the same substituents at the 3- and 2-positions to the 4-position, the introduction of the nitro group more readily takes place at the 4-position than at the 1-position.

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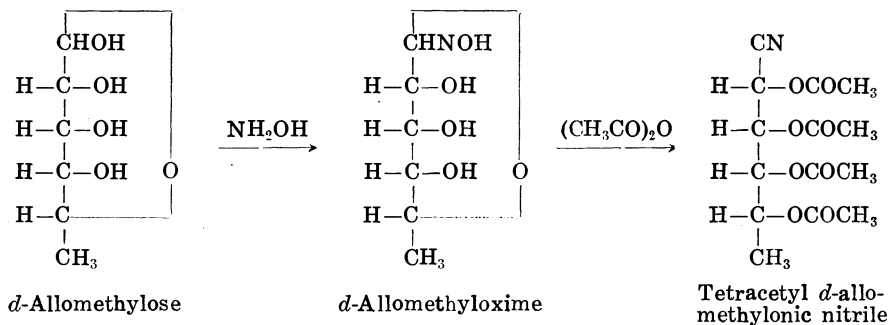
The Formation of *d*-Ribomethylose.

By Koichi IWADARE.

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About the formation of *d*-ribomethylose it was already reported by F. Micheel,⁽¹⁾ who prepared it by hydrolizing the sirupy diacetyl *d*-ribomethylose obtained from digitoxoseen diacetate. It was, however, obtained only in the form of osazones, the derivatives, which were the same as those of *d*-arabomethylose. In the course of our investigations on monoses,⁽²⁾ attempts were made to prepare this sugar. For this purpose, *d*-allomethylose, which is obtained from *l*-rhamnose by Levene's⁽³⁾ method, is used as the starting substance. That is, *l*-rhamnose is shaken with acetone, containing sulphuric acid, and 2,3-monoacetone *l*-rhamnose thus obtained is tosylated with *p*-toluene sulphonyl chloride to 5-tosyl 2,3-monoacetone *l*-rhamnose. And the latter is transformed into 2,3-monoacetone methyl *d*-allomethylloside by inversion with sodium methylate. It is purified by tosylation followed by detosylation, and hydrolized to *d*-allomethylose.

d-Allomethylose is degraded by Wohl's method⁽⁴⁾ to *d*-ribomethylose. Namely *d*-allomethylose is added to methyl alcohol containing hydroxylamine, and the mixture is warmed for a short while to dissolve the sugar, and filtered, if necessary, after being kept standing overnight, and concentrated under the diminished pressure to thick sirup. On adding a small quantity of methyl alcohol, it soon crystallizes into fine colourless needles, melting point, 146–146.5°C. (corrected). It mutarotates in aqueous solution. The specific rotatory power, $[\alpha]_D^{25}$, is +54° (6 minutes after being dissolved.) It changes to +5° after 2 hours and then to –4° after 4 hours (in equilibrium).

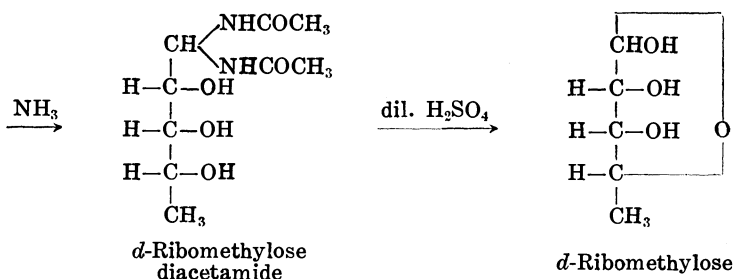


(1) F. Micheel, *Ber.*, **63**(1930), 347.

(2) K. Iwadare, S. Fukunaga, and B. Kubota, *This Bulletin*, **12**(1937), 116; K. Iwadare and B. Kubota, *Sci. Pap. Inst. Phys. Chem. Research*, **34**(1938), 183.

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d-Allomethyloxime is acetylated with acetic anhydride and anhydrous sodium acetate. Tetracetyl *d*-allomethylonic nitrile thus prepared is obtained in crystals, melting point, 166.5~167° (corrected). Ammonia water is added to the crystals and the mixture is warmed for a short time to obtain a clear solution, and, after being kept standing for 3 hours, concentrated under the diminished pressure to thick sirup, which is again dissolved in ammonia water and reconcentrated. On adding alcohol the sirup crystallizes into long colourless needles, melting point, 191° (corrected). The specific rotatory power, $[\alpha]_D^{20}$, of *d*-ribomethylose diacetamide is +7.4° in aqueous solution.

The equilibrium rotation of *d*-ribomethylose is determined by hydrolyzing the known quantity of *d*-ribomethylose diacetamide with 5% sulphuric acid. And the specific rotatory power $[\alpha]_D^{20}$ is found to be +20° *d*-Ribomethylose is obtained as sirup. On heating, it reduces Fehling's solution strongly, and, when heated with phenylhydrazine, phenylhydrazone, melting at 170°C., is obtained.

Experimental. *l*-Allomethylose. This substance was obtained by Levene's method⁽³⁾ from 2,3-monoacetone *l*-rhamnose which was prepared by E. Fischer⁽⁵⁾ from anhydrous *l*-rhamnose. But now more convenient method of preparing monoacetone *l*-rhamnose was suggested in this experiment. That is, 100 g. of *l*-rhamnose hydrate were added to 3.5 l. of acetone containing 35 c.c. of concentrated sulphuric acid, and the mixture was vigorously shaken for a short while to dissolve the sugar. Then, after 5 hours standing, the solution was neutralized with anhydrous sodium carbonate, and filtered. The filtrate was evaporated into a small volume at ordinary pressure and then into thick sirup in vacuum. The sirup (115 g.) thus obtained was dissolved in 1 l. of dry ether and the *l*-rhamnose, separated overnight, was filtered. The filtrate was evaporated into sirup and again dissolved in 500 c.c. of ether. To this solution, an equal volume of petroleum ether was added and the oily substance, which separated soon on adding, was removed. The solution was concentrated to sirup, which consisted mainly of 2,3-monoacetone *l*-rhamnose. This sirupy acetone-sugar (80 g.) was dissolved in 400 c.c. of dry pyridine, cooled at 0°C., and 80 g. of *p*-toluene sulphonyl chloride, dissolved in 200 c.c. of chloroform, was added to it. The mixture was kept at 0°C. for 1 hour and at room temperature overnight. Then, water (15 c.c.) was added to it and after half an hour the mixture was diluted with

(5) E. Fischer, *Ber.*, **28** (1895), 1162.

200 c.c. of chloroform, and washed twice with water, thrice with ice-cooled 10% sulphuric acid to remove pyridine, twice with ice-cooled saturated sodium bicarbonate solution and then twice with water. The chloroform solution was dried with calcium chloride and evaporated under the diminished pressure; toluene was added to it, and reconcentrated. The sirup was dissolved in a small quantity of toluene and petroleum ether was added to turbidity. Crystallization of 2,3-monoacetone 5-tosyl *l*-rhamnose began immediately, and it was filtered after being kept on standing overnight in a refrigerator. Yield, 33 g. And the oily substance (30 g.), which had been separated from ether solution of acetone-sugar on adding petroleum ether, was dissolved in 150 c.c. of ether and the equal quantity of petroleum ether was added. The separated oil was removed and the solution was concentrated into sirup. The sirup was treated in the same way as described above, and 8 g. of the tosyl derivative was obtained. Thus, the total yield of 2,3-monoacetone-5-tosyl *l*-rhamnose from 100 g. of *l*-rhamnose hydrate amounted to 41 g. This substance was treated just like Levene's method. Namely, 40 g. of it were dissolved in 800 c.c. of methanol which contained 12 g. of sodium methylate. After being kept on standing overnight, excess of methylate was decomposed with carbon dioxide and the solution was evaporated to dryness under the reduced pressure. The residue was extracted with ether and evaporated into sirup. This sirup (20 g.) was dissolved in 30 c.c. of pyridine and 30 g. of *p*-tosyl chloride was added to it. After being kept on standing overnight, 10 c.c. of water at first and then 200 c.c. of sodium bicarbonate solution were added. Separated crystals were filtered and recrystallized from methanol. Yield, 34 g.

5-Tosyl monoacetone methyl-*d*-allomethylofuranoside (30 g.) was dissolved in 1500 c.c. of 80% methanol and 600 g. of 2.5% sodium mercury amalgam was added to it in order to hydrolize it reductively to monoacetone methyl-*d*-allomethyloside. When the reaction ended, the mixture was separated from mercury, filtered, and evaporated to dryness. The residue was extracted with ether, dried, and distilled. The sirup of monoacetone methyl-*d*-allomethyloside (15 g.) was hydrolized by warming it with 300 c.c. of 1.5% sulphuric acid on a water-bath. It was neutralized with barium carbonate, filtered, and concentrated into sirup. On adding alcohol, crystallization occurred at once. Yield, 10 g.

d-Allomethyloxime. 5 g. of hydroxylamine hydrochloride were dissolved in 3 c.c. of hot water, and neutralized (phenolphthalein) with 6% sodium methylate solution. The mixture was cooled and filtered. 10 g. of allomethylose were dissolved in this solution. After being kept on standing overnight, it was filtered, if necessary, and evaporated into sirup. On adding methanol, it crystallized soon into colourless needles. It was recrystallized from 90% alcohol. Melting point, 146–146.5°C. (corrected). It showed mutarotation in aqueous solution. *d*-Allomethyloxime (0.1639 g.) was dissolved in water, and the volume of the solution was made up to 10 c.c. Its rotations were as follows:—

Time after dissolution	Direct reading	$[\alpha]_D^{18}$
6 min.	+0.88°	+54°
22 min.	+0.68°	+49°
2 hrs.	+0.08°	+ 5°
4 hrs.	-0.06°	- 4°
20 hrs. (in equilibrium)	-0.06°	- 4°

(Found: N, 7.98. Calculated for $C_6H_{13}O_5N$: N, 7.81%)

Tetracetyl-d-allomethyloxime nitrile. *d*-Allomethyloxime (2 g.) was dissolved in 3 c.c. of dioxane and 2 g. of anhydrous sodium acetate were added to the solution. To this mixture 10 c.c. of acetic anhydride was added in several portions. On adding each portion, the mixture was warmed on a water bath for a short while. After the whole quantity of acetic anhydride was added, the solution was warmed on a water-bath for 1 hour. Then it was poured over the cracked ice, and sodium bicarbonate solution was added in order to neutralize acetic acid. The mixture was extracted with ether, and, on evaporating the solvent, tetracetyl-*d*-allomethyloxime nitrile was obtained as yellow sirup. On adding alcohol, the sirup crystallized into big colourless plates, melting point 166.5–167°C. (Found: N, 4.57. Calculated for $C_{14}H_{19}O_8N$: N, 4.25%).

d-Ribomethylose diacetamide. Tetracetyl-*d*-allomethyloxime nitrile (2 g.) was dissolved in 40 c.c. of concentrated ammonia solution by warming it slightly on a water-bath at 50°C. After being kept on standing for 3 hours it was evaporated under the diminished pressure and the obtained sirup was redissolved in ammonia and reconcentrated. To remove water from the residue, alcohol was added to it and it was evaporated under the diminished pressure. The residue was obtained as crystalline mass. A small quantity of alcohol was added to it, and fine colourless needles were obtained. It was recrystallized from 95% alcohol. Melting point, 191°C. (corrected). The specific rotatory power, $[\alpha]_D^{18}$, of *d*-ribomethylose diacetamide is +7.4° in aqueous solution. (Found: N, 11.92. Calculated for $C_9H_{18}O_5N_2$: N, 11.96%).

Equilibrium rotation of d-ribomethylose. To get the equilibrium rotation of *d*-ribomethylose, known quantity of the *d*-ribomethylose diacetamide was hydrolyzed with 5% hydrochloric acid. Namely, 0.3056 g. of *d*-ribomethylose diacetamide was dissolved in about 5 c.c. of 5% hydrochloric acid, and warmed on a water-bath at 100°C for 1 hour. The hydrolyzed solution was made up to 10 c.c. with water, and the rotatory power of the solution was measured. Thus the specific rotatory power, $[\alpha]_D^{20}$, of *d*-ribomethylose was found to be +20° (calculated from the weight of *d*-ribomethylose formed, the direct reading being +0.36°).

d-Ribomethylose. *d*-Ribomethylose diacetamide (1 g.) was hydrolyzed with 0.8 N sulphuric acid by warming the solution on a water-bath at 100°C. It was continuously extracted with ether for 24 hours to remove acetic acid and neutralized with excess of barium carbonate. The mixture

was filtered, evaporated into sirup, and dissolved in absolute alcohol. The solution was filtered and evaporated. Thus the sirup of *d*-ribomethylose was obtained. On heating, it reduced Fehling's solution strongly. Its phenylosazone was obtained in usual method. Melting point, 170°C.

Summary.

d-Allomethylose is obtained from *l*-rhamnose by a little modification of Levene's method. And *d*-ribomethylose is prepared from *d*-allomethylose by Wohl's method of degradation, obtaining on the way *d*-allomethyloxime (melting point, 146–146.5°, and $[\alpha]_D^{18}$, +54°, 6 minutes after dissolution and –4° in equilibrium), tetracetyl *d*-allomethylonic nitrile (melting point 166.5~167°), and *d*-ribomethylose diacetamide (melting point, 191°, and $[\alpha]_D^{18}$, +7.4°). Equilibrium specific rotation, $[\alpha]_D^{20}$, of *d*-ribomethylose is found to be +20°.

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

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Über die innermolekulare Drehbarkeit bei einfacher Kohlenstoff-Kohlenstoffbindung.

Von San-ichiro MIZUSHIMA und Yonezo MORINO.

(Eingegangen am 11. November 1941.)

Problemstellung und Schluss. Zur Erklärung der Isomeriefälle hat die klassische Stereochemie die Vorstellung entwickelt, dass Molekülteile, die durch eine doppelte C=C-Bindung miteinander verknüpft sind, gegeneinander um die Achse dieser Bindung nicht verdrehbar sein sollen, während für die Bewegung um die Achse der einfachen C—C-Bindung "freie Drehbarkeit" postuliert wird. Die hinsichtlich der Doppelbindung gemachte Aussage ist eindeutig; dagegen lässt das chemische Material in Bezug auf die "freien Drehbarkeit" um die C—C-Achse noch drei Möglichkeiten offen, zwischen denen mit Hilfe chemischer Methoden noch nicht entschieden ist; nämlich dass

- 1) indifferente Rotation der beiden Molekülhälften stattfindet, oder dass
- 2) nur eine bestimmte Konfiguration in Frage kommt (völlig behinderte Rotation), oder dass

- 3) ein sich schnell einstellendes Gleichgewicht besteht zwischen mehreren Konfigurationen mit verschiedenem Azimut (Rotationsisomerie).

Seit 1932 haben wir das Problem auf Grund physikalischer Messungen (Dipolmoment und Ramaneffekt) angegriffen und den Schluss gezogen, dass für viele Moleküle bei tiefen und mittleren Temperaturen

im festen Zustand die obige Auffassung 2, und
im flüssigen oder gasförmigen Zustand die obige Auffassung 3

zutreffend ist. Im folgenden sollen die Messergebnisse und Diskussion kurz berichtet werden.

Dipolmoment. Unter den vielen von uns gemessenen Substanzen wollen wir hier nur Dihalogenäthane ($\text{ClH}_2\text{C}-\text{CH}_2\text{Cl}$, $\text{BrH}_2\text{C}-\text{CH}_2\text{Br}$, usw.) erwähnen, mit denen wir die wesentlichen Züge unserer Momentmessungen erklären können. Unsere Messergebnisse,^{(1) (2)} dass die im Gaszustand und in Lösungen gefundenen Momentwerte sich stark mit der Temperatur ändern, können mit der Auffassung der indifferenten Rotation oder der völlig behinderten Rotation nicht erklärt werden. Doch schliessen sie sich nicht direkt der Auffassung von der Koexistenz der mehreren diskreten Rotationsisomere an, da die Temperaturabhängigkeit des Momentes uns nur von der Änderung der durchschnittlichen Lage in Bezug auf die Verdrehung um die C—C-Achse und von der stabilsten Lage (bei Dihalogenäthan die Translage von Fig. 1 a) Kunde gibt. Aus diesem

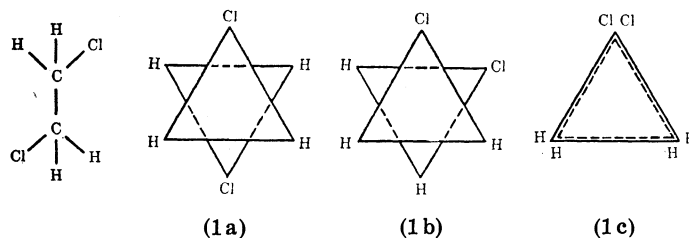


Fig. 1. Die Raumstruktur von $\text{ClH}_2\text{C}-\text{CH}_2\text{Cl}$ und ihre Projektion auf die Ebene senkrecht zu C—C-Achse.

Grunde wollen wir für die die Rotation behindernde Energie zuerst den einfachen Ansatz

$$U = \beta(1 - \cos \varphi) \quad (1)$$

machen, wobei φ der Verdrillungswinkel aus der stabilsten Translage ist und β eine Konstante, deren Grössenordnung mit derjenigen der Wärmebewegungsenergie vergleichbar sein soll. Dann ist das Quadrat des mittleren Momentes m

(1) Mizushima, Morino und Higasi, *Proc. Imp. Acad. (Tokyo)*, **8**(1932), 482; *Phys. Z.* **35** (1934), 905.

(2) Über die Messergebnisse anderer Autoren siehe z.B. "Dielektrische Polarisation" von Fuchs und Wolf, *Hand- und Jahrbuch der chemischen Physik*, Bd. 6/IB, 1935.

$$m^2 = 4\mu^2 \sin^2 \theta \frac{\int_{-\pi}^{+\pi} e^{-\frac{U}{kT}} \sin^2 \frac{\varphi}{2} d\varphi}{\int_{-\pi}^{+\pi} e^{-\frac{U}{kT}} d\varphi} = 2\mu^2 \sin^2 \theta \left[1 + \frac{iJ_1\left(i\frac{\beta}{kT}\right)}{J_0\left(i\frac{\beta}{kT}\right)} \right] \quad (2)$$

wobei μ (1.85×10^{-18} E.S.E.) das Dipolmoment der CH_2Cl -Gruppe und θ (70°) den Winkel zwischen μ und der C-C-Achse bedeutet.

Mit den in Tabelle 1 angegebenen Werten von β kann man die Momentwerte berechnen, die mit den gemessenen gut übereinstimmen.⁽⁴⁾

Tabelle 1.

Zustand	$\beta \times 10^{14}$
Gaszustand ⁽³⁾	10.93
Heptanlösung	7.83
Ätherlösung	6.65

Die Änderung des β -Wertes zeigt unmittelbar, dass die Wahrscheinlichkeit der Abweichung von der Translage in der Reihenfolge, Gaszustand, Heptanlösung, Ätherlösung, wächst.

Als die Ursache dieser Behinderungsenergie lässt sich elektrostatische Wirkung, Resonanzabstossung und von der Waalsche Kraft zwischen den beiden drehbaren Gruppen denken.

Wäre die elektrostatische Energie allein von Bedeutung, dann würde man bei $\text{BrH}_2\text{C}-\text{CH}_2\text{Br}$ einen fast gleichen Wert von β wie bei $\text{ClH}_2\text{C}-\text{CH}_2\text{Cl}$ finden, da das Bindungsmoment von C-Br demjenigen von C-Cl ungefähr gleich ist. Im Gegensatz dazu fanden wir bei $\text{BrH}_2\text{C}-\text{CH}_2\text{Br}$ einen wesentlich grossen Wert von β (16.85×10^{-14} im Gaszustand, 14.80×10^{-14} in Heptanlösung), woraus man ohne weiteres schliesst, dass die Resonanzabstossung eine wesentliche Rolle spielt. Dann darf man die Wechselwirkung zwischen Halogen- und Wasserstoffatome nicht mehr vernachlässigen (im Gegensatz zu der elektrostatische Wechselwirkung, wobei die C-H-Bindung nur einen verschwindenden Beitrag leistet). Von der berechneten Abstossungsenergie zusammen mit der van der Waalschen und elektrostatischen Energie erwartet man die Existenz des zweiten Minimums, dessen ungefähre Lage jenen zwei untereinander gleichwertigen räumlichen Formen entsprechen, d.h. den Zwischenformen von Fig. 1 b, die aus der Transform durch Verdrehung um etwa 120° hervorgehen. Den experimentellen Beweis für die Existenz dieses Minimums kann, aber, die Momentmessung uns nicht vorbringen, deren Ergebnisse durch die durchschnittliche Potentialkurve von Formel (1) befriedigend darstellen lassen.

Ramaneffekt. Um die Potentialkurve bei höherer Annäherung mit dem Beobachtungsmaterial in Zusammenhang zu bringen, haben wir die optische Messungen ausgeführt und zuerst bei verschiedenen Lösungen gefunden, dass die relative Intensitäten der Ramanlinien von Molekülen mit drehbaren Gruppen sich stark änderten.⁽⁴⁾ Zum Beispiel betrug die Intensitätsverhältnis $I(654)/(754)$ der beiden Linien von 654 und 754 cm^{-1} von $\text{ClH}_2\text{C}-\text{CH}_2\text{Cl}$: bei reiner Flüssigkeit 1:1.4, bei Alkohollösung 1:1.3, bei Ätherlösung 1:2, bei Hexanlösung 1:5.

(3) Neu gemessen (die näheren Angaben erscheinen demnächst).

(4) Mizushima, Morino, und Higasi, *Phys. Z.* **35** (1934), 905; *Sci. Pap. I.P.C.R.* (Tokyo), **25** (1934), 159.

Diese Tatsache läuft parallel mit der, welche wir bei der Momentmessung beobachteten und man kann das so auffassen, dass das Intensitätsverhältnis I (654)/(754) mit zunehmender Anzahl von Molekülen in der Translage abnimmt. Da die Linie 654 cm^{-1} , wie aus Fig. 2 ersichtlich, im festen Zustand vorständig verschwindet, kann man vermuten, dass fast alle Moleküle im festen Zustand sich in der Translage befinden.⁽⁵⁾ Dann sind alle in diesem Zustand beobachteten Ramanlinien den zum Symmetriezentrum der Transform (C_{2h}) symmetrischen Schwingungen zuzuordnen. Dass dies der Fall ist, konnten wir zeigen: einerseits durch die Berechnung der Normalschwingungen von Transmolekül⁽⁶⁾ und andererseits durch die Beobachtung des Isotopieeffektes.⁽⁷⁾ Für die letztere haben wir Tetradeuterio-Dibromäthan $\text{BrD}_2\text{C}-\text{CD}_2\text{Br}$ synthetisch

Tabelle 2.

Totalsymmetrischen Schwingungen des Transmoleküls.

$\text{BrH}_2\text{C}-\text{CH}_2\text{Br}$	$\text{BrD}_2\text{C}-\text{CD}_2\text{Br}$
190	188
660	607
1053	907
1255	991
1440	1154
2972	2183

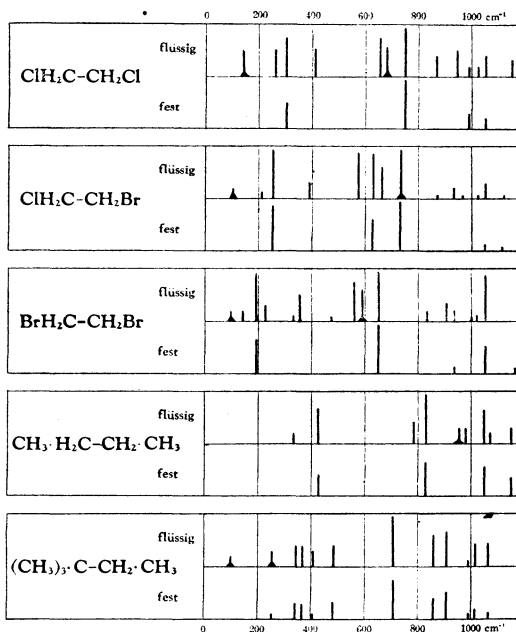


Fig. 2. Ramanspektren im Bereich tieferer Frequenz.

dargestellt und seine Spektren im flüssigen und im festen Zustand gemessen. Wir konnten zeigen, dass den totalsymmetrischen Schwingungen des Transmoleküls (vgl. Tabelle 2) die Produktregel von Redlich und Teller gilt, was die Richtigkeit unserer Zuordnung zeigt. Im festen Zustand kommt also nur eine einzige Molekülform in Frage, d.h. die innermolekulare Rotation ist eingefroren.

Es liegt nun nahe die nur im flüssigen Zustand oder in Lösungen erscheinenden Linien den Normalschwingungen der zweiten Form zuzuschreiben.⁽⁸⁾ Diese Form ent-

(5) Mizushima, Morino, und Mitarbeitern, *Sci. Pap. I.P.C.R.* (Tokyo), **29** (1936), 63; *Phys. Z.* **38** (1937), 459; *Proc. Ind. Acad. Sci.* **8** (1938), 315 (Raman Jubilee Volume).

(6) Mizushima und Morino, *Sci. Pap. I.P.C.R.* (Tokyo), **26** (1934), 1; Morino, *Bull. Chem. Soc. Japan*, **13** (1938), 189.

(7) Mizushima, Morino, Sugiura und Suzuki, *Proc. Imp. Acad.* (Tokyo), **14**, (1938), 250; *Sci. Pap. I.P.C.R.* (Tokyo), **36** (1939), 281.

(8) Bei Molekülen mit mehreren C-C-Achsen gehen mehr als zwei räumliche Formen hervor.

spricht dem obenerwähnten zweiten Minimum (Zwischenlage von Fig. 1 b), die im flüssigen Zustand oder in Lösungen eine wichtige Rolle spielt, wohl aber im festen Zustand wegen des Krystallfeldes ohne Bedeutung wird. Dass dieses Minimum auch im gasförmigen Zustand seine Wichtigkeit behalten soll, ist ohne weiteres klar aus dem von uns neuerdings gemessenen Ramanspektrum des gasförmigen Dichloräthans, dessen näheren Angaben demnächst erscheinen. Doch soll die Form der Potentialkurve im Gaszustand (d.h. der Potentialkurve des freien Moleküls) von derjenigen im flüssigen Zustand verschieden sein, da bei letztem Fall der Einfluss der Nachbarmoleküle eine wesentliche Rolle spielt.

Es ist wohl möglich einige von den "Flüssigkeitslinien" den antisymmetrischen Schwingungen der Transform zuzuschreiben, die wegen der innermolekularen Verdrillungsschwingung um diese Lage aktiv werden. Dass, aber, bei Molekülen wie $\text{ClH}_2\text{C}-\text{CH}_2\text{Br}$,⁽⁹⁾ $\text{CH}_3\text{CH}_2-\text{CH}_2\text{Cl}$, $\text{OHCH}_2-\text{CH}_2\text{Cl}$,⁽¹⁰⁾ u.s.w. auch das Verschwinden einiger starken Ramanlinien beim Übergang vom flüssigen nach dem festen Zustand beobachtet wurden (vgl. Fig. 2), macht die Existenz des zweiten Minimums höchst wahrscheinlich, da die Auswahlregel alle Frequenzen im Ramaneffekt erlaubt. Es folgt daraus, dass in flüssigen und gasförmigen Zuständen oder in Lösungen die ineinander umwandelbarer und im thermischen Gleichgewicht miteinander stehender Rotationsisomere koexistieren.

Indessen haben sich auch andere Autoren mit diesem Thema befasst. Unter ihnen haben Kohlrausch und Mitarbeitern,⁽¹¹⁾ den man erstmalige Verweisung auf die Koexistenz der Rotationsisomere verdankt, eine Reihe umfangreicher Arbeiten veröffentlicht. Da, aber, diese Autoren nur die Spektren im flüssigen Zustand gemessen haben, ist unsere Beobachtung für die festen und gasförmigen Zustände oder für die Lösungen von Bedeutung um den direkten experimentellen Nachweis dafür zu bekommen. Als die innermolekulare Lage für das zweite Minimum (z.B. bei Dihalogenäthanen, Butan, u.s.w.) denken sich diese Autoren die Cisstellung (vgl. Fig. 1 c) anstatt der oben erwähnten Zwischenlage. Um den ent-

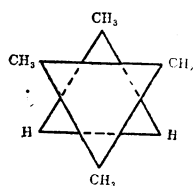


Fig. 3. Neohexan.

gültigen Schluss über die dem zweiten Minimum entsprechende Molekülform zu ziehen, haben wir neuerdings die Spektren einiger gesättigten Kohlenwasserstoffe sowohl im festen als auch im flüssigen Zustand gemessen.⁽¹²⁾ Nach unserer Ansicht soll Neohexan $(\text{CH}_3)_3\text{C}-\text{CH}_2\text{CH}_3$ nur eine einzige Molekülform haben, da die drei Minimumlage, wie aus Fig. 3 ersichtlich, der identischen räumlichen Form entsprechen; wohl aber nach anderer Ansicht (Cis-Trans-Isomerie) soll es zwei verschiedene Formen haben. In Überein-

stimmung mit unserer Meinung haben wir für diese Substanz keine Spektraländerung beim Übergang vom flüssigen nach dem festen Zustand

(9) Mizushima und Morino, *Sci. Pap. I.P.C.R.* (Tokyo), **29** (1936), 188; *Phys. Z.*, **38** (1937), 459.

(10) Mizushima, Morino und Nakamura, *Sci. Pap. I.P.C.R.* (Tokyo), **37** (1940), 205.

(11) Kohlrausch, "Der Smekal-Raman-Effekt," *Ergänzungsband*, (Springer), 1938; *Ber.* **71** (1938), 171.

(12) Mizushima, Morino und Takeda, *Sci. Pap. I.P.C.R.* (Tokyo), **38** (1941), 437.

gefunden (vgl. Fig. 2), während wir für n-Butan, n-Pentan, n-Hexan, n-Heptan, u.s.w., bei denen zwei oder mehr als zwei verschiedene Formen sich ausbilden sollen, die starke Spektraländerung immer noch bestätigen konnten.

Der obige Schluss wurde aus unseren Messungen des Dipolmomentes und des Ramaneffektes gezogen. Zu gleicher Zeit glauben wir, dass er mit den Folgerungen in anderen Gebieten (Ultrarotabsorption, Kerreffekt, Röntgen- und Elektronenbeugung) in Übereinstimmung gebracht werden kann.

Der Hauptteil dieser Mitteilung wurde eigentlich für die "Heisenberg-Festnummer" der Zeitschrift für Physik geschrieben und das Manuskript wurde schon vor sechs Monate nach Deutschland abgesandt. Da unter heutigen Umständen seine Ankunft an der Schriftleitung nicht festzustellen ist, wird es wegen unserer künftigen Arbeit hier abgedruckt.

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Elektronenbeugung und die Oberflächenstruktur der säurefesten Legierung (Fortsetzung): Fe-W in Salzsäure.

Von Shigeto YAMAGUCHI.

(Eingegangen am 11. November, 1941.)

Einleitung. Erst durch die vorliegende Forschung wurde vollständig bewiesen, dass die in HCl säurefest werdende Oberfläche einer Fe-W Legierung kompakt mit kleinen Kristallen von WO_2 (Wolframdioxyd) bedeckt ist. Dies ist ein augenscheinliches Beispiel der "selektive Oxydation", wie sie man schon an der Oberfläche von Duriron in Schwefelsäure erkannte.⁽¹⁾ Hier wurde auch die atomistische Struktur der Grenze zwischen dem Grundmetall und dem sich auf demselben bildenden Dioxyd deutlich.

Experimente. Zum Versuch wurde ein Stück der bearbeiteten Fe-W Legierung (W, 4%) verwandt. Wo es in Salzsäure (10%) bei Zimmertemperatur eingetaucht wurde, beobachtete man auf ihm die schwache Entwicklung von Gasblasen, die nur sehr vorübergehend war. Seine Oberfläche wird nach diesem Verfahren sowohl von grauer Farbe als auch säurefest, so dass nicht Metall an sich, sondern etwas Beständiges daran aufs neue dargestellt wäre. Auf diese Oberfläche wurden Elektronen angestrahlt, um die in Tab. 1 beschriebenen Gitterabstände, die dem Oberflächenprodukt charakteristisch sind, zu kennen. Dadurch, dass man sie

(1) S. Yamaguchi, *Sci. Pap. Inst. Phys. Chem. Res. (Tokyo)*, **38** (1941), 409; *Dies Bulletin*, **16** (1941), 332.

mit denen durch Röntgenstrahlenforschung bekannten aus WO_2 ,⁽²⁾ WO_3 ,⁽³⁾ W ,⁽³⁾ Fe_2O_3 ,⁽³⁾ FeO ,⁽³⁾ Fe_3O_4 ⁽³⁾ vergleicht, konnte nachgewiesen werden, dass es nichts anderes als WO_2 (Wolframdioxyd) ist (vid. Tab. 1).

Tabelle 1.

Gitterabstände WO_2 -Kristalls nach Röntgenmethode	Beobachtete Gitterabstände	Millersche Bezeichn.	Beobachtete Intensität
3.44	3.44	110	schwach
2.78	2.77	001	mässig
2.41	2.41	101	mässig
2.16	2.16	111	schwach
1.72	1.725	220	stark
1.71	1.72		
1.62	1.62	300	sehr sch.
—	1.28 (diffus)	—	sehr sch.

Ein Elektronenbeugungsversuch wurde wieder für die Oberfläche angestellt, die nur sehr kurz in das Ätzmittel (HCl , 10%) eingetaucht wurde, den eigenen metallischen Glanz also noch nicht verlor. Dieses Beugungsbild bestand aus denjenigen Ringen, die das Vorhandensein reinen Eisens ($\alpha\text{-Fe}$ von körperzentriertem Raumgitter), d.h. Grundmetalls und sehr kleiner Menge von WO_2 wahrnehmen lassen (vid. Tab. 2).

Tabelle 2.

Gitterabstände von $\alpha\text{-Fe}$ ⁽⁴⁾	Beobachtete Gitterabstände	Millersche Bezeichn.	Substanz
—	2.42	101	WO_2
2.02	2.02	110	Fe
1.43	1.43	200	Fe
1.17	1.18	211	Fe
1.01	1.01	220	Fe

Diskussion und Konklusion. Chemisch bekannt ist bereits, dass Wolfram bei Zimmertemperatur in HCl jeder Konzentration unlöslich und auch bei 110°C . nur sehr wenig angegriffen ist.⁽⁵⁾ Eisen ist dagegen in HCl verhältnismässig löslich. Wie in dem vorhergehenden Bericht über Duriron ausgeführt, verlässt das Grundmetall in Ätzmittel der leicht angegriffene Bestandteil, während der säurefeste an derselben Stelle fest

(2) V. M. Goldschmidt, *Naturwiss.*, **14** (1926), 295.

(3) J. D. Hanawalt, H. W. Rinn und L. K. Frevel, *Indust. & Eng. Chem.*, **30** (1938), 457.

(4) E. A. Owen und E. L. Yates, *Phil. Mag.*, **15** (1933), 472.

(5) cf. Gmelins Handbuch der anorganischen Chemie, "Wolfram gegen Säure."

bleibt. Nach der vorliegenden Forschung, entspricht dem letzteren Wolfram, und es bleibt noch als WO_2 auf der Metalloberfläche stehen, wenn es die Korrosion durch Aetzmittel auch erlitten hat. Dies ist ganz ähnlich der Erscheinung (selektive Oxydation), die schon mit Duriron in H_2SO_4 beobachtet wurde.⁽¹⁾

Die Bildungswärme von WO_3 ist grösser als die von WO_2 ; ⁽⁶⁾ in der Tat, findet die Bildung des ersteren häufiger als die des letzteren statt. Allein in dem Falle tritt beständig WO_2 auf, wo dieses Oxyd im Berühren mit dem Grundmetall hergestellt wird. Es handelt sich daher darum, dass das W-Atom freilich sechs Valenzelektronen besitzt, und sich unter gewissen Bedingungen doch WO_2 bildet.

Die Tabellen oder Aufnahmeplatte sind imstande zu bedeuten, dass sich nur die Netzebene (101) von WO_2 -kristall zu Anfang bildet, bevor die anderen Netzebenen auf dem Grundmetall mit Wachsen desselben Kristalls vollendet aufgebaut worden sind. Das WO_2 -Kristall besitzt die tetragonale Struktur von Cassiterit (SnO_2) ⁽⁷⁾, wie sie man durch ihr Modell in Fig. 1 zeichnen darf. Die Netzebenen (101)ⁿ vermögen sich vor allem zu entwickeln, während sich noch keine anderen auf dem Grundmetall zeigen. Diejenigen, die an das Grundmetall grenzen, müssen mit

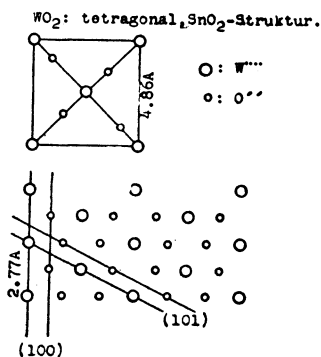


Fig. 1.

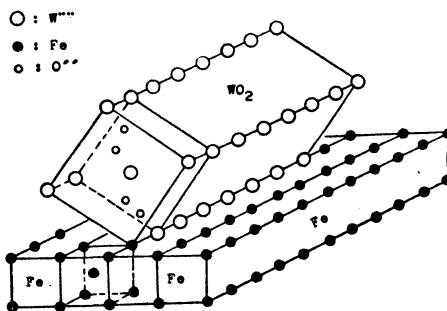


Fig. 2.

Notwendigkeit solche Ebenen sein, die mit den Millerschen Bezeichnungen ausser der (101) anzuweisen sind. Als solche sind zwar manche möglich, und unter ihnen ist doch die (100) die möglichste. Diese Netzebene ist bald nur aus Kation zusammengesetzt, bald aus Anion allein. Aus verschiedenen Gründen, besonders unter den gegenwärtigen Bedingungen ist nicht wahrscheinlich, dass die Anion-Schicht unmittelbar auf das Grundmetall stossen möge.* Die Netzebene (100) des WO_2 -Kristalls, die nur aus W⁺⁺⁺ besteht, kann unmittelbar mit der (100) von α -Fe fast genügend übereinstimmen, denn der erstere ist an der Gitterabstände (2.77 Å), d.h. an der Entfernung zwischen zwei W-Atomen in der (100), dem letzteren (2.86 Å) annähernd gleich. Diese Berührungsweise hilft wohl dem Grundmetall und dem Oxyd sich fest zu verbinden (vid. Fig. 2).

(6) J. A. M. Liempt, *Rec. Trav. Chim.*, **50** (1931), 343.

(7) R. W. G. Wyckoff, *The Structure of Crystals*, second edition, (1931), 231.

* Wenigstens gibt es keine Anziehungskraft zwischen Metall und O⁺⁺ von Neon-Struktur.

Das W^{5+} -Ion im WO_2 -Kristall besitzt noch zwei Valenzelektronen, um quantenmechanische Resonanz⁽⁸⁾ oder die metallische Bindung zu veranlassen, d.h., ihm ist die Bindung durch die unlokalisierten Elektronen mit Metall möglich. Die Bindungsart, wie sie in Fig. 2 gezeichnet wird, macht infolgedessen die Adhäsion des Oxyds mit dem Grundmetall (α -Fe) immer stärker. Dies darf man etwa "eine oberflächliche Legierung" nennen.

Zum Schluss sei es gestattet, Herrn Dr. Ichiro Iitaka und Herrn Prof. Takejiro Murakami für ihre Leitung dieser Arbeit Dank auszusprechen. Herrn Prof. S. Mizushima danke ich auch bestens für seine Interesse für diese Forschung. Bei dieser Gelegenheit möchte ich dafür meinen Dank zum Ausdruck bringen, dass diese Untersuchung von "Corrosion Committee" in "Nippon Gakuzyutsu Shinkokwai" finanziert wurde.

*Institut für physikalische und
chemische Forschung, Tokio.*

(8) L. Pauling, The Nature of the Chemical Bond, 1940, 401.

Nitroso-ethylbenzenes.

By Yojiro TSUZUKI.

(Received December 11, 1941.)

Derivatives of ethylbenzene are of great interest as the materials for investigating the electronic nature of alkyl radicals. But unhappily only little is known of these compounds in contrast with substituted methylbenzenes, probably because of the fact that pure ethylbenzene has not hitherto been an easily accessible compound.

The present author has now prepared *o*- and *p*- nitroso-ethylbenzenes with a view to compare their properties with those of nitroso-toluenes.⁽¹⁾ Among these compounds, however, *o*- nitroso-ethylbenzene is already obtained by R. E. Lutz and M. R. Lytton,⁽²⁾ who described it briefly as a substance melting at 61°, and being difficult to bring in the state of analytical purity.

The present author has synthesized nitroso-ethylbenzenes by the reduction of the corresponding nitro-compounds, obtained by the nitration of ethylbenzene.

(1) Y. Tsuzuki, T. Uemura and N. Hirasawa, *J. Chem. Soc. Japan*, **61** (1940), 1063; *Ber.*, **74** (1941), 616.

(2) *J. Org. Chem.*, **2** (1937), 68.

Nitration of Ethylbenzene.⁽³⁾ The mixture of 83 g. fuming nitric acid ($d=1.45$) and 81 g. concentrated sulphuric acid ($d=1.84$) was added drop by drop to 100 g. ethylbenzene (boiling point 133° , $n_D^{20}=1.49540$, $d_4^{20}=0.86644$, obtained by fractionating technical ethylbenzene) for several hours at 0°C ⁽⁴⁾ with mechanical stirring. Oil was separated from the layer of the acid, washed with water and distilled under reduced pressure with a Tichwinski fractionating column. The thrice repeated fractional distillation gave 30 g. pure *o*-nitro-ethylbenzene (boiling point $86-88^\circ$ (5 mm.), $n_D^{20}=1.53483$, $d_4^{20}=1.1139$) and 15 g. pure *p*-nitro-ethylbenzene (boiling point $101-102^\circ$ (5 mm.), $n_D^{20}=1.54585$, $d_4^{20}=1.1192$).

***o*- and *p*-Nitroso-ethylbenzenes.** The reduction of the nitro-ethylbenzenes into the corresponding nitroso-compounds was carried out in a similar way as described in the previous paper.⁽¹⁾ 7.5 g. nitro-compound were dissolved in 30 c.c. boiling ethyl alcohol, and 10 c.c. hot 2 *n*-ammonium chloride were added. To this solution 10 g. zinc dust were added in small portions in 10 minutes with vigorous shaking. After 5 minutes the residue was filtered off and a dilute ice-cold solution of 27 g. $\text{FeCl}_3+6\text{H}_2\text{O}$ was poured to the solution. The reaction product was subjected to steam distillation immediately, whereby the nitroso-compound was isolated and purified. Yield 2 g. (30% of the theory).

***o*-Nitroso-ethylbenzene:** colourless bright needles (from ethyl alcohol) melting at 61.5° . Found: N, 10.04. Calculated for $\text{C}_8\text{H}_9\text{NO}$: N, 10.37%. ***p*-Nitroso-ethylbenzene:** volatile green oil; it becomes very sticky at -30°C , but does not solidify even at -80°C ; it decomposes slowly on standing, and rapidly at 120°C . Found: N, 10.27. Calculated for $\text{C}_8\text{H}_9\text{NO}$: N, 10.37%.

The author wishes to thank Dr. K. Ohasi for supplying him ethylbenzene.

Musashi Higher School, Itabashiku, Tokyo.

(3) Cf. Beilstein and Kuhlberg, *Ann.*, **156** (1870), 206; Schultz and Flachsländer, *J. prak. Chem.*, [2] **66** (1902), 153; Cline and Reid, *J. Am. Chem. Soc.*, **49** (1927), 3150; Schreiner, *J. prak. Chem.*, [2] **81** (1910), 557; H. Kondo and S. Uyeo, *Ber.*, **70** (1937), 1091.

(4) Higher temperature was avoided, because it is expected that rising temperature increases the yield of the ortho isomer—the main product of the reaction—and decreases that of the para isomer, and also favours meta substitution. Cf. the work of Holleman and his co-workers on the nitration of toluene (Holleman and van den Arend, *Rec. trav. chim.*, **28** (1909), 408; Holleman, Vermeulen, and de Muoy, *Rec. trav. chim.*, **33** (1914), 1; further Holleman, *Chem. Rev.*, **1** (1925), 187; Rease, *Chem. Rev.*, **14** (1934), 55.

Über einen neuen Bestandteil von *Swertia japonica*, Makino (Gentianaceae).

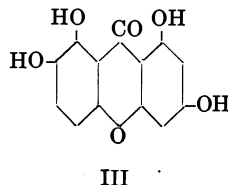
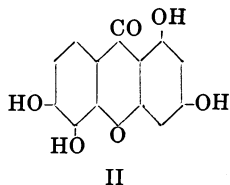
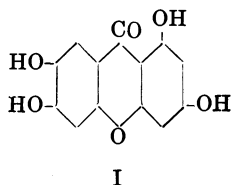
Von Yasuhiko ASAHINA, Juntaro ASANO und Yosio UENO.

(Eingegangen am 26. November, 1941.)

Kariyone u. Matsushima⁽¹⁾ isolierten aus dem Kraut von *Swertia japonica*, einer gebräuchlichsten Bitterdroge in Japan, ein Glukosid Swertiamarin $C_{16}H_{22}O_{10}$ und eine Säure „Swertiasäure $C_{27}H_{42}O_3$. Zu gleicher Zeit behauptete Nakaoki⁽²⁾, dass er noch darin Gentisin, teils frei teils in Form von Glukosid und eine Substanz „Swertisin“ $C_{13}H_{10}O_6$ gefunden hat. Kariyone u. Matsushima zeigten, dass das Swertiamarin, der eigentliche Bitterstoff der Droge, das Glukosid des Erythrocentaurins (von Méhu) ist. Die Swertiasäure wurde später von Kuwada und Matsukawa⁽³⁾ als Oleanolsäure $C_{30}H_{48}O_3$ erkannt.

Nun haben wir im alkoholischen Extrakt der Droge ein zweites, gelbgefärbtes, nur schwach bitterschmeckendes Glukosid $C_{20}H_{20}O_{11}$ (Swertianolin genannt) gefunden, welches bei der Hydrolyse nach der folgenden Gleichung gespalten wird: $C_{20}H_{20}O_{11} + H_2O = C_{14}H_{10}O_6 + C_6H_{12}O_6$.

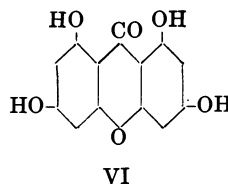
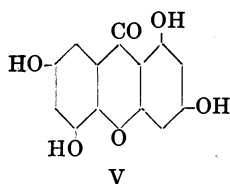
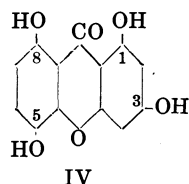
Das Aglykon $C_{14}H_{10}O_6$, das wir Swertianol nennen, bildet gelbe Prismen vom Schmp. 263° , existiert auch im Extrakt der Droge und wurde von Nakaoki für Gentisin gehalten. Es besitzt aber ein Atom Sauerstoff mehr als Gentisin, enthält ein Methoxyl und drei Phenolhydroxyle, von denen das eine mittels Diazomethans nicht, aber erst durch Jodmethyl und Silberoxyd methylierbar ist. Beim Erhitzen mit Jodwasserstoffsäure wird Swertianol entmethyliert und das so erhaltene Desmethylswertianol $C_{13}H_8O_6$ (Schmp. 317°) bildet Tetraacetyl-derivat, während bei der Einwirkung von Diazomethan nur drei Methyl-Gruppen (unter Bildung des Swertianol-dimethyläthers) aufnimmt. Da die chemische Eigenschaften des Desmethylswertianols, ganz besonders dessen Absorptionsspektrum des ultravioletten Lichtes, denen des Xanthons gut übereinstimmen, so darf man annehmen, dass es sich hier um ein Tetraoxy-xanthon handelt. Unter Berücksichtigung der Tatsache, dass das Desmethylswertianol bei der Kalischmelze Phloroglucin liefert, so kommt dafür folgende sechs Konstitutionsformeln in Betracht:



(1) *J. Pharmaceut. Soc. Japan*, **47** (1927), 133.

(2) *J. Pharmaceut. Soc. Japan*, **47** (1927), 142.

(3) *J. Pharmaceut. Soc. Japan*, **53** (1933), 680.



Ferner ruft das Desmethylswertianol, gleich wie Brenzkatechin und Hydrochinon, in kalter, alkoholischer Lösung durch Chloropentaammin-kobaltichlorid eine dunkelbraune Färbung hervor, was das Vorhandensein entweder von *ortho*- oder von *para*-ständigen Hydroxylen andeutet. Hierdurch darf man wohl V und VI ausschliessen. Neuerdings hat Tanase⁽⁴⁾ die oben aufgezählten Tetraoxyxanthone I, II, IV, V und VI synthetisiert und die Identität des Desmethylswertianols mit IV (1, 3, 5, 8-Tetraoxyxanthon) festgestellt. Da Swertianol selbst gegen Chloropentaammin-kobaltichlorid indifferent ist, so muss das Aether-Methyl entweder in 5- oder in 8-Stellung gebunden sein.

Was nun das von Nakaoki angegebene Gentisin anbetrifft, so haben wir uns durch Vergleich mit seinem originalen Präparat überzeugt, dass es nichts anderes als Swertianol ist.

Extraktion der Droge. Frische Kraut von *Swertia japonica* wird in kochendem Alkohol unter Zusatz von Calciumcarbonat in der Weise eingetragen, dass der Alkohol fortdauernd kochend bleibt. Nach 3 stündigem Digerieren wird es gepresst und das Filtrat zu dünnem Syrup eingedampft, wobei sich zunächst massenhaft Oleanolsäure dann eine hellgelbe, krystalline Substanz (Zp. 226°) ausscheiden. Da die letztere sich mit Salzsäure und Magnesium reduziert rot färbt, so scheint sie das sog. Swertisin von Nakaoki zu sein. Dann wird die Mutterlauge nach weiteren Einengen wiederholt mit Aether extrahiert, wobei das Swertianol darin aufgenommen wird. Der mit Aether gesättigte, wässrige Syrup fällt bei wochenlangem Stehen eine gelbe, krystalline Substanz, die wir Swertianolin nennen. In der letzteren Mutterlauge bleibt noch Swertiamarin, das wir hier nicht weiter untersucht haben.

Swertianolin. Zur Reinigung wird das Roh-Produkt zunächst mit Wasser gewaschen und dann je zweimal aus Eisessig und Methanol nach einander umgelöst. Die so gereinigte Substanz bildet gelbe Nadeln vom Schmp. 208°. Sie ist in meisten Solventien ziemlich schwer löslich, in warmem Eisessig leichter löslich. Alkalilauge löst die Substanz mit gelber Farbe. Die alkoholische Lösung färbt sich mit Eisenchlorid orangerot. (C₁₉H₁₇O₁₀(OCH₃): Ber. C 55.02 H 4.62 CH₃O 7.11. Gef. C 54.94 H 4.77 CH₃O 7.04).

Hexaacetyl-Derivat: Dargestellt durch Erwärmen in Acetanhydrid unter Zusatz von Pyridin. Farblose Krystalle vom Schmp. 226° (aus Eisessig). (C₃₂H₃₂O₁₇: Ber. C 55.79 H 4.69. Gef. C 56.12 H 5.09).

Hydrolyse des Swertianolins. Wird 1 g Swertianolin in 5% Schwefelsäure eine Stunde gekocht, so scheidet sich tiefer gelb gefärbtes Spaltungs-

(4) *J. Pharmacut. Soc. Japan*, **61** (1941), 341. (Japanisch).

produkt (Swertianol) aus. Dann wird das Filtrat mit Baryumcarbonat neutralisiert und das vom Baryumsulfat befreite Filtrat eingedampft. Der syrupöse Rückstand bildet mit Phenylhydrazin eine gelbe, krystalline Substanz vom Schmp. 205°. Eine Mischprobe mit dem Glucosephenyl-
osazon zeigte keine Schmp.-Depression.

Swertianol. Beim Umlösen aus Eisessig und Alkohol bildet das Swertianol tief gelbe Nadeln vom Schmp. 263°. Es ist in Aether schwer, in Alkohol ziemlich, in Eisessig leichter löslich. Die alkoholische Lösung färbt sich mit Eisenchlorid gelbgrün, wird durch Chloropentaammin-kobaltichlorid nicht geändert. Durch Kochen mit Salzsäure und Magnesium färbt es sich nicht. Kalilauge löst es mit gelber Farbe. ($C_{13}H_7O_5(OCH_3)$. Ber. C 61.31 H 3.68 CH_3O 11.32. Gef. C 61.79 H 3.69 CH_3O 11.65).

Triacetyl-derivat: Dargestellt durch Kochen im Acetanhydrid unter Zusatz von Natriumacetat. Farblose Nadeln vom Schmp. 228° (aus Eisessig). ($C_{14}H_7O_6(CO\cdot CH_3)_3$: Ber. C 59.98 H 4.03 CH_3CO 32.35. Gef. C 59.60 H 4.06 CH_3CO 33.22).

Dimethyläther: Dargestellt durch Zusatz von Überschuss Diazomethan in Aether-Aceton. Gelbe Nadeln vom Schmp. 204° (aus Alkohol). Die alkohol. Lösung färbt sich mit Eisenchlorid grün. ($C_{13}H_5O_3(OCH_3)_3$: Ber. C 63.55, H 4.67 CH_3O 30.81. Gef. C 63.14, H 4.55 CH_3O 30.39).

Trimethyläther: Dargestellt durch Kochen vom Dimethyläther in Jodmethyl unter Zusatz vom Silberoxyd. Farblose Nadeln vom Schmp. 209° (aus Alkohol). Eisenchlorid-Reaktion negativ. ($C_{13}H_4O_2(OCH_3)_4$: Ber. C 64.56 H 5.10 CH_3O 39.26. Gef. C 64.24 H 5.46 CH_3O 38.66.)

Monoacetyl-dimethyläther: Dargestellt durch Kochen vom Dimethyläther im Acetanhydrid unter Zusatz von Natriumacetat. Hellgelbe Nadeln vom Schmp. 223° (aus Alkohol). Eisenchlorid-Reaktion negativ. ($C_{18}H_{16}O_7$: Ber. C 62.77 H 4.69 CH_3O 27.05. Ger. C 63.12 H 4.64 CH_3O 27.05).

Desmethylswertianol. 0.5 g Swertianol werden in 30 ccm Jodwasserstoffsäure unter Zusatz von 0.5 g Phenol 2 Stunden gekocht. Dann wird das Produkt in Bisulfitlösung eingetragen und der Niederschlag abgesaugt. Gelbe Krystalle vom Zers.-P. 317° (aus Alkohol). Die Substanz ist in Alkohol und Aceton leicht, in Aether schwer löslich. Die alkohol. Lösung wird durch Eisenchlorid grünlichgelb gefärbt. Kalilauge löst sie mit braunroter Farbe. ($C_{13}H_8O_6$: Ber. C 59.98 H 3.10. Gef. C 60.02 H 3.48).

Tetraacetat: Dargestellt durch Kochen im Acetanhydrid unter Zusatz vom Natriumacetat. Farblose Nadeln vom Zers. p. 243–244°. ($C_{21}H_{16}O_{10}$: Ber. C 58.86 H 3.77. Gef. 59.02 H 3.66).

Methylierung des Desmethylswertianol: Wird eine Acetonlösung des Desmethylproduktes mit Diazomethan versetzt und übernacht stehen gelassen, so entsteht ein Methyl-Derivat vom Schmp. 204°, welches beim Mischen mit Swertianoldimethyläther keine Schmp.-Depression zeigt.

Kalischmelze des Desmethylswertianols. 1 g. Desmethylswertianol wird mit 20 g. KOH, unter Zusatz von 4 ccm. Wasser 30 Minuten bei 200°

geschmolzen. Dann wird die Schmelze in Natriumsulfitlösung (10%) gelöst, angesäuert und ausgeäthert. Die so erhaltene Substanz bildet beim Umlösen aus Wasser bräunliche Krystalle vom Schmp. 206°, die die violettrote Fichtenspanreaktion zeigt. Auch eine Mischprobe mit dem Phloroglucin (Schmp. 207°) zeigte keine Depression.

Weder durch 6 stündigem Kochen von Desmethylswertianol in 50%iger Kalilauge im Wasserstoffstrom noch durch 10 stündigem Kochen in 35%iger, glycerinhaltiger Kalilauge wurde es gespalten.

Swertisin (?) Die aus dem alkoholischen Extrakt der Droge beim Einengen ausgeschiedene, Substanz von Zers. p. 226° bildet ein hell gelbes, krystallinisches Pulver, das sich beim Erhitzen im Capillarröhrchen schon gegen 195° verfärbt und erst bei 226° unter Aufbrausen zersetzt. Auch bei wiederholtem Umlösen aus Alkohol wurde dieser unscharfe Schmelzpunkt nicht verbessert. Die alkoholische Lösung färbt sich mit Eisenchlorid braunrot; durch Erhitzen mit Salzsäure und Magnesium entsteht eine rote Lösung. ($C_{23}H_{24}O_{11}$: Ber. C 57.97 H 5.07 CH_3O 6.50. Gef. C 57.54, 57.56 H 4.84, 5.38 CH_3O 6.53).

*Pharmazeutisches Institut der kaiserl. Univ. Tokyo und
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Studies on Amino-Acid and Related Compounds. XIV.* Action of Nitric Acid on Phenylalanine, Tyrosine, and *p*-Hydroxybenzoic Acid.

By Yoshitaro TAKAYAMA and Yasuji TSUBUKU.

(Received November 12, 1941.)

In Part XIII⁽¹⁾ it has been briefly described that picric acid was obtained by heating tyrosine with nitric acid under the suitable condition. In the present paper, the behaviour of nitric acid on phenylalanine, tyrosine, and *p*-hydroxybenzoic acid is going to be discussed in detail.

Mörner (1915)⁽²⁾ has obtained *p*-nitrobenzoic acid, picric acid, and oxalic acid as well as the several other substances by oxidising protein with nitric acid, and he pointed out that the parent substance of nitrobenzoic acid was phenylalanine and those of picric acid were tyrosine and phenylalanine which arose from the protein during the treatment with nitric acid. Mörner⁽²⁾ has also found that *p*-nitrobenzoic acid was not obtained by heating phenylalanine merely with 60% nitric acid, but that it could be obtained when phenylalanine was mixed with an equal weight of starch and the mixture was kept on standing for 24 hours in 10 times their weight of 60% nitric acid and then heated on a water-bath for 20 hours. In the same way, though without starch, picric acid was obtained also from tyrosine in a small yield of 8.4%.⁽³⁾

In the present experiments, phenylalanine was refluxed with 10 times its weight of 8N-NO₃H at 100° for a long time, and neither *p*-nitrobenzoic acid nor oxalic acid was obtained, but only *p*-nitrophenylalanine was isolated. It seemed, therefore, probable that in this case only nitration took place. On the contrary, when phenylalanine was refluxed with nitric acid containing a little of vanadium compound as a catalyser, both nitration and oxidation occurred and *p*-nitrobenzoic acid was obtained in good yield and a little of benzaldehyde as well as benzoic acid was also isolated. In this case, oxalic acid was not isolated, as the acid was completely destroyed by nitric acid in the presence of vanadium compound. In the case of tyrosine, it was refluxed with 8N-NO₃H containing a little of vanadium compound, for 3 hours, and from this solution picric acid (31.4%)⁽³⁾ and 3,5-dinitro-4-hydroxybenzoic acid (13.2%) were obtained. In this experiment, when the time of refluxing was shortened to 1 hour, the dinitrohydroxybenzoic acid was obtained as a main product, but to which concentrated nitric acid was still more added and refluxed further for 2 hours, and only the picric acid was obtained in good yield (about 45%). In the absence of the catalyser, on heating with 8N-NO₃H tyrosine gave picric and oxalic acids in small yields of 3.5% and of 4.1% respec-

* Translated by the authors from *J. Chem. Soc. Japan*, **62** (1941), 34.

(1) Part XIII, this Bulletin, **17** (1942), 53.

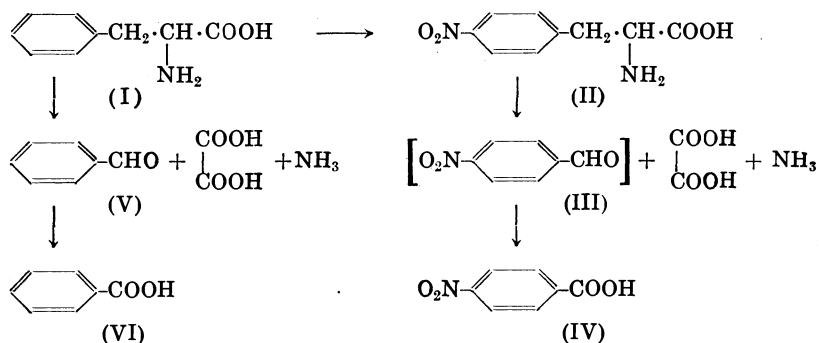
(2) C. Th. Mörner. *Z. physiol. Chem.*, **95** (1915), 265, 287.

(3) The percentages in this paper were expressed in molar per cent.

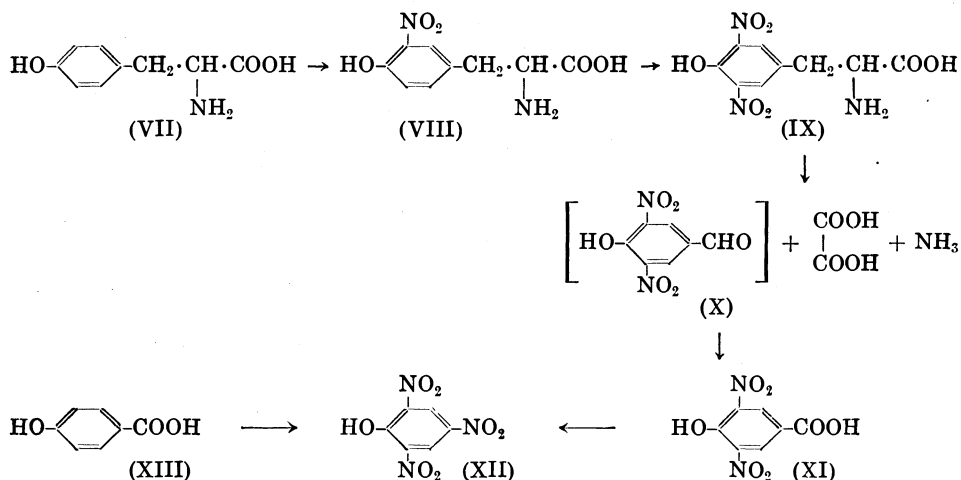
tively. From dinitrohydroxybenzoic acid by merely heating with 8N- NO_3H picric acid was easily obtained in a yield of 95%. Picric acid was also obtained in good yield, by heating dinirotyrosine with nitric acid in the presence of the catalyser, or by merely heating *p*-hydroxybenzoic acid with nitric acid without the catalyser.

From the facts described above, the behaviour of nitric acid on phenylalanine, tyrosine, and *p*-hydroxybenzoic acid may be represented as follows:

Phenylalanine



Tyrosine



Phenylalanine (I) was converted by nitration into *p*-nitrophenylalanine (II) and the latter gave rise to *p*-nitrobenzaldehyde (III), oxalic acid and ammonia by oxidation. This aldehyde was readily oxidised to *p*-nitrobenzoic acid (IV). This course of the reaction may be a main one, inferred from the yields of the final products. As a side reaction, phenylalanine was oxidised without nitration to benzaldehyde (V) and the aldehyde was oxidised readily to benzoic acid (VI) in small yield.

Tyrosine (VII) was converted by nitration into mononitrotyrosine (VIII) and then dinitrotyrosine (IX). The latter was oxidised with nitric acid in the presence of the catalyser to 3,5-dinitro-4-hydroxybenzaldehyde (X), oxalic acid, and ammonia. This aldehyde was readily oxidised to 3,5-dinitro-4-hydroxybenzoic acid (XI) and then picric acid (XII) in good yield. Picric acid was also obtained in good yield by merely heating *p*-hydroxybenzoic acid (XIII) with nitric acid. It appeared that the benzene nucleus of tyrosine, in this case, was somewhat attacked by nitric acid.

These methods⁽⁴⁾ for preparing *p*-nitrobenzoic and picric acids from phenylalanine and tyrosine respectively, may be applied for industrial purposes, as the crude phenylalanine and tyrosine are separated on the large scale from the by-products of the manufacture of sodium glutamate.

Experimental. *Action of nitric acid on phenylalanine.* Natural phenylalanine (3.325 g., 20.1 m. mols) was dissolved in 8N-NO₃H (30 c.c.) and refluxed at 100° for 8½ hours. From this solution needle crystals (1.4 g.) separated out on adding with sodium hydroxide solution until it gave weak acidic reaction. The crystals melted at 205°, and was submitted to analysis without further purification (Found: N, 11.33%). On concentrating the filtrate the second crops of the crystal (0.85 g.) were also obtained (Found: N, 11.36%). The combined crystals (10.7 m. mols, 53%) were recrystallised from water and analysed (Found: N, 11.67%. Calc. for NO₂C₆H₄·CH₂·CH(NH₂)·COOH·3/2 H₂O: N, 11.81%). The crystals thus obtained was identified as *p*-nitrophenylalanine.

The phenylalanine, therefore, was not oxidised and merely nitrated by the refluxing with nitric acid as described above. As oxalic acid was not found in the filtrate of *p*-nitrophenylalanine, the filtrate was extracted with ether. On distilling off the ether, a little of crystals (0.1 g.) was obtained and recrystallised from water in colourless needles, m.p. 122–123°. It was identified as phenyllactic acid by mixed melting point test. This acid arose from the phenylalanine by the action of nitrous acid formed by oxidation. In the same manner as 8N-NO₃H, phenylalanine was refluxed in 4N-NO₃H, and *p*-nitrophenylalanine (2.89 g.) was obtained (Found: N, 11.56%). It gave somewhat better yield (67.5%) than the case of 8N-NO₃H.

Oxidation of phenylalanine with nitric acid. Natural phenylalanine (10 m. mols) was dissolved in 8N-NO₃H (15 c.c.) containing vanadic acid (0.05 g.) and refluxed for 3 hours.

p-Nitrobenzoic acid. From the above-mentioned oxidised solution, yellow crystals (0.95 g.) separated out on cooling, and melted at 185–200°. The crystals were refluxed with benzene and separated into two parts, insoluble and soluble in benzene. The part insoluble (0.65 g., 39%) in benzene melted at 236°, after recrystallised from water, and it was identified as *p*-nitrobenzoic acid (Found: N, 8.45, 8.25%. Calc. for NO₂C₆H₄COOH: N, 8.38%).

Benzoic acid. From the part soluble in benzene, crystals were obtained, on distilling off the benzene. It was sublimed under reduced

(4) Japanese patent 129210; 129211 (picric acid).
134026 (*p*-nitrobenzoic acid).

pressure, yield 0.02 g., m.p. 122–122.5°. It was identified as benzoic acid by mixed melting point test.

Benzaldehyde. The mother liquor of *p*-nitrobenzoic acid was neutralised with sodium hydroxide solution and extracted with ether. From the ethereal solution, an oily substance which had an odour of benzaldehyde was obtained. It was converted into *p*-nitrophenylhydrazone as usual and recrystallised from dilute alcohol in reddish brown thin plates, m.p. 183–185°. It was identified as benzaldehyde by its *p*-nitrophenylhydrazone.

Ammonia. The volatile base was estimated as usual, 0.55 m. mol.

The effect of the concentration of nitric acid and the temperature of heating on the yields of *p*-nitrobenzoic acid from phenylalanine were also studied. Some data are shown in the following table.

Table 1.

Phenylalanine	Concentration of NO_3H	Time of heating	Yields of <i>p</i> -nitrobenzoic acid
10 m. mols	8N	3 hours (100°)	0.42 g. (25.2%)
10 m. mols	4N	3 hours (100°)	0.34 g. (20.4%)

Oxidation of tyrosine with nitric acid. Picric acid and dinitrohydroxybenzoic acid. Natural tyrosine (1.81 g., 10.03 m. mols) was dissolved in 8N- NO_3H (15 c.c.) containing vanadic acid (0.1 g.) and refluxed at 110° for 3 hours. After cooling the solution, yellow crystals (0.98 g.) were obtained, and on neutralising the mother liquor with potassium hydroxide, yellow crystals (0.11 g.) of potassium salt were obtained. The former crystals (0.98 g.) were dissolved in potassium hydroxide solution, and the potassium salt (0.73 g.) separated out on cooling. This salt was decomposed with dilute sulphuric acid and extracted with ether. From the ethereal extract, crystals were obtained and melted at 121–122°. The combined yield was 31.4%. It was identified as picric acid by mixed melting point test and by the determination of nitrogen. (Found: N, 18.22, 18.32%. Calc. for $(\text{NO}_2)_3\cdot\text{C}_6\text{H}_2(\text{OH})$: N, 18.33%). From the mother liquor of potassium salt (0.73 g.), the yellow crystals (0.3 g., 13.2%) separated out in thin plates, on addition of an excess of nitric acid. It melted at 240–242°. It was identified as 3,5-dinitro-4-hydroxybenzoic acid (Found: N, 12.46, 12.49%. Calc. for $(\text{NO}_2)_2\text{C}_6\text{H}_2(\text{OH})\cdot\text{COOH}$: N, 12.28%). Oxalic acid was not found in the oxidised solution.

Ammonia. The volatile base (NH_3) was distilled as usual, 2.0 mg. (1.2%).

Tyrosine (10 m. mols) was refluxed in 8N- NO_3H (15 c.c.) containing vanadic acid (0.1 g.) at 110° for 1 hour, then to the solution 13.7N- NO_3H (5 c.c.) was added and refluxed further for 2 hours. From the solution thus obtained, only picric acid was obtained in a yield of 45% without obtaining dinitrohydroxybenzoic acid. Under these conditions, but in the absence of the catalyser, the yields of picric acid, oxalic acid, and ammonia were 3.5%, 4.13%, and 0.3% respectively.

In order to obtain dinitrohydroxybenzoic acid the following procedure may be offered. Tyrosine (10 m. mols) was dissolved in 8N- NO_3H (15 c.c.) which contained vanadic acid (0.1 g.), and refluxed at 100–110° for 1 hour, and the separation of the oxidation products were made as described above. In this case the yield of dinitrohydroxybenzoic acid was 38%. When 4N- NO_3H , instead of 8N- NO_3H , was used and refluxed for 3 hours, the yields of dinitrohydroxybenzoic acid and picric acid were 39.9% and 17.6% respectively. Picric acid was also obtained in good yield (95%) when the dinitrohydroxybenzoic acid was refluxed in 10 times its weight of 8N- NO_3H .

Action of nitric acid on 3,5-dinitrotyrosine. Dinitrotyrosine (1.10 g., 3.8 m. mols) was dissolved in 8N- NO_3H (7 c.c.) containing vanadic acid (0.05 g.) and heated at 110° for 3 hours, and picric acid (0.44 g., 1.92 m. mols) was obtained. From the mother liquor potassium picrate (0.04 g., 0.15 m. mol) was also obtained. The combined yield of picric acid amounted to 54.5% of dinitrotyrosine used. In the above experiment, when the catalyser was omitted, picric acid was obtained only 9.75%, and oxalic acid (35.6%) as well as ammonia (1.1%) was also separated.

Action of nitric acid on p-hydroxybenzoic acid. p-Hydroxybenzoic acid (10 m. mols) was dissolved in 4N- or 8N- NO_3H (30 c.c.) and refluxed at 100° for 1–3 hours. From the oxidised solution picric acid (70%) was separated as described above, and oxalic acid (11–15%) was also separated as calcium salt by adding $\text{Ca}(\text{NO}_3)_2$ to the mother liquor.

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**On 7-Hydroxy-dihydro-codeine, 7-Hydroxy-dihydro-thebainol
and the corresponding (+)-Derivatives from Sinomenine.⁽¹⁾**

By Kakuji GOTO and Tatsuo ARAI.

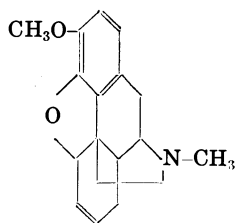
(Received November 11, 1941.)

In the 47th communication on sinomenine⁽²⁾, we have reported the formation of (+)-dihydro-codeine, (+)-dihydro-morphine and (+)-desoxycodine-C from sinomenine. By mild oxidation of (+)-desoxycodine-C (I) with potassium permanganate⁽³⁾, we obtained (+)-7-hydroxy-dihydro-codeine (II), which in turn could be racemised with (–)-7-hydroxy-dihydro-codeine, prepared from (–)-desoxy-codeine-C in the same way. The introduced two alcoholic groups have been demonstrated as dibenzoyl derivatives.

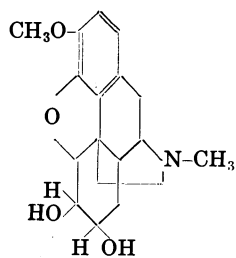
(1) The 50th Communication on Sinomenine.

(2) *Ann.*, **547** (1941), 194.

(3) Compare Cahn and Robinson, *J. Chem. Soc.*, **1926**, 908.

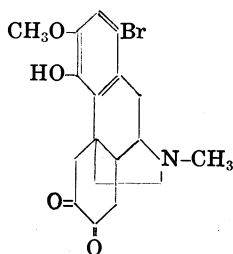


(I)

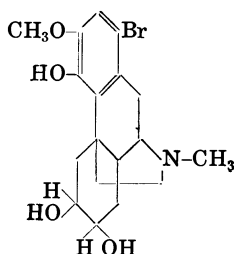


(II)

By reducing (+)-1-bromo-sinomeninone (III) with hydrogen gas in pyridine solution, using platin oxide as catalyst, the both ketonic groups were reduced and (+)-1-bromo-tetrahydro-sinomeninone (IV) was produced. By catalytic debromination of this substance in aqueous solution, we obtained tetrahydro-sinomeninone (V), namely (+)-7-hydroxydihydro-thebainol could be prepared from (–)-1-bromo-sinomeninone⁽⁴⁾ in the same process and the both were racemised. The three hydroxygroups in these substances have been made clear by the formation of triacetyl-derivatives, in which, however, the sign of rotation has been inverted remarkably enough.



(III)



(IV)

(V) (Br = H, in IV)

The racemisation trials of the above three substances (II, IV and V) were also successfully carried out with their respective methiodides.

Experimental. (+)-7-Hydroxy-dihydro-codeine (II). (+)-Desoxy-codeine-C (I; 1.5 g.) was dissolved in a small quantity of 10% hydrochloric acid and made up to 150 c.c. with distilled water. The solution was made slightly alkaline with 10% potassium hydroxyde and kept at 0°C by cooling and adding ice to it. The solution was stirred mechanically and 1% potassium permanganate solution (61 c.c.; 10% more than the calculated quantity) was added in half an hour. After the solution was saturated with carbon dioxide, it was stirred 15 minutes more and then filtered. The filtrate was evaporated down to 40 c.c. and extracted with ether, which removes unchanged desoxy-codeine-C. The aqueous layer was then saturated with potassium carbonate and extracted with chloro-

(4) Schöpf, Pfeifer, Hirsch: *Ann.*, **492** (1932), 213;
Goto, Shishido, Takubo: *Ann.*, **497** (1932), 293.

form. When evaporated, the chloroform yielded 0.5 g. of white, crystalline powder. This was washed with alcohol and recrystallised from chloroform+ethanol (1:1). Colourless flat prisms, m.p. 225°. Insoluble in alcohol or in ordinary organic solvents. (Calc. for $C_{18}H_{23}O_4N \cdot \frac{1}{2}H_2O$ (326): C=66.26; H=7.36; N=4.29%. Found: C=66.44, 66.24, 66.41; H=7.32, 7.43, 7.31; N=4.34%). Spec. rotatory power. Subst.=0.1097 g.; Chloroform+ethanol (1:1)=10 c.c.; 1 dm-tube, $\alpha=+1.42^\circ$. $[\alpha]_D^{21.5}=+129.4^\circ$.

Methiodide. Prepared by heating the both components+methanol in a stoppered bottle at 100°C for 30 minutes. The elongated leaflets from methanol. m.p. 252°. Yield 80%. Spec. rotatory power: Subst.=0.1012 g.; water=10 c.c.; 1 dm-tube. $\alpha=+0.91^\circ$. $[\alpha]_D^{18.5}=+89.9^\circ$

(-)-7-Hydroxy-dihydro-codeine. The preparation is same as above, except only from (-)-desoxy-codeine-C. m.p. 225°. (Found: C=66.77, 66.57; H=7.49, 7.53%). Spec. rotatory power: Subst.=0.1107 g.; ethanol+chloroform (1:1)=10 c.c.; 1 dm-tube. $\alpha=-1.42^\circ$. $[\alpha]_D^{22}=-128.3^\circ$.

Methiodide. The preparation is same as with (+)-substance. m.p. 252°. Spec. rotatory power: Subst.=0.1009 g.; water=10 c.c.; 1 dm-tube. $\alpha=-0.90^\circ$. $[\alpha]_D^{18.5}=-89.2^\circ$.

(d,l)-7-Hydroxy-dihydro-codeine. The above two solutions, used for the determination of spec. rotatory power, were combined and evaporated. The (d,l)-substance crystallised out at once. Prisms. m.p. 207°. $[\alpha]_D=\pm 0^\circ$.

d,l-Methiodide. The above two solutions, used for determination of spec. rotatory power were combined and evaporated. The residue was recrystallised from methanol. m.p. 238°. Plates. $[\alpha]_D=\pm 0^\circ$.

(-)-Dibenzoyl-7-hydroxy-dihydro-codeine. 7-Hydroxy-dihydro-codeine (0.1 g.) was dissolved in 1 c.c. pyridine and benzoylated by benzoyl-chloride (0.18 g.) at 0°C. By being kept on standing overnight, the dibenzoylated substance crystallised out from aqueous ammonium carbonate solution. Recrystallised from benzene, it forms colourless needles, melting at 128°. Yield 20%. (Calc. for $C_{32}H_{31}O_6N \cdot \frac{1}{2}H_2O$ (534): C=71.91; H=5.99, N=2.62%. Found: C=72.22; H=6.44; N=3.07%. Spec. rotatory power. Subst.=0.0485 g.; methanol=2.5 c.c.; 1 dm-tube. $\alpha=-3.18^\circ$. $[\alpha]_D^{24.5}=-163.9^\circ$.

Determination of benzoyl radicals. 0.0693 g. substance was hydrolysed by warm methanolic solution of potassium methylate, made acidic with phosphoric acid and steam-distilled. The distillate required 1.27 c.c. of 0.211 N NaOH, which corresponded to 0.0281 g. benzoyl, namely 40.5%. $C_{32}H_{31}NO_6$ (525) requires 40.0% benzoyl radical, calculated for two.

The simple titration gives nearly the same results, if we deduce the allowance for free dihydroxy-dihydro-codeine, using phenolphthaleine as indicator.

(+)-1-Bromo-tetrahydro-sinomeninone (IV). (+)-1-Bromo-sinomeninone (III 6.5 g.) in pyridine solution, added with platin oxide (0.3 g.), was reduced catalitically at 40°C., 2200 c.c. hydrogen were absorbed in 12 hours (calc. for $2H=740$ c.c. at 10°). Pyridine was then removed in the diminished pressure and the residue was recrystallised from acetone. Yield ca. 5.5 g. This was dissolved in methanol (30 c.c.), added with chloroform (100 c.c.) and shaken with water. The trioxy-derivative

crystallised into almost colourless prisms in chloroform-layer. This was collected and washed with acetone (1.7 g.). The chloroform gives 1.8 g. substance after the evaporation. The combined yield was almost 50%. Flat prisms. m.p. 136°. (Calc. for $C_{18}H_{24}BrNO_4$ (398): Br=20.10; N=3.52. Found: Br=20.79; N=3.27%). Spec. rotatory power. Subst.=0.1212 g., ethanol=10 c.c.; 1 dm-tube. $\alpha=+0.33^\circ$. $[\alpha]_D^{15}=+27.2^\circ$.

Methiodide. Prepared in the usual way. Prisms. m.p. 277° (from ethanol). Spec. rotatory power. Subst.=0.0718 g.; 50% Ethanol=2.5 c.c.; 1 dm-tube. $\alpha=+0.22^\circ$. $[\alpha]_D^{25}=+7.7^\circ$.

(-)-1-Bromo-tetrahydro-sinomeninone (=1-Bromo-7-hydroxy-dihydro-thebainol). The preparation is same as above. The pyridine solution gave the crystals of the product, when left overnight. Yield 4.2 g. Recrystallised from acetone, it forms flat prisms, melting at 137°. Spec. rotatory power. Subst.=0.1206 g.; ethanol=10 c.c.; 1 dm-tube. $\alpha=-0.32^\circ$. $[\alpha]_D^{16}=-26.5^\circ$.

Methiodide. m.p. 277°. Spec. rotatory power. Subst.=0.0718 g.; 50% ethanol=2.5 c.c.; 1 dm-tube. $\alpha=-0.21^\circ$. $[\alpha]_D^{25}=-7.3^\circ$.

(d,l)-1-Bromo-tetrahydro-sinomeninone. (+) and (-) substances (0.1206 g. each) were mixed in ethanol solution and evaporated. *d,l*-Substance crystallised out from acetone into needles. It melts at 117°, solidifies on further heating and decomposes at 195°. $[\alpha]_D=\pm 0^\circ$.

(d,l)-1-Bromo-tetrahydro-sinomeninone methiodide. The preparation is as above. Recrystallised from ethanol. Prisms m.p. 286°. $[\alpha]_D=\pm 0^\circ$.

(+)-Tetrahydro-sinomeninone (Br.=H, in IV). (+)-1-Bromo-tetrahydro-sinomeninone (2.5 g.) was dissolved in 80 c.c. 1% hydrochloric acid, added with 0.2 g. palladium chloride and 2 g. charcoal, and shaken in hydrogen atmosphere at 40°C. 175 c.c. of hydrogen were absorbed in 15 minutes (calc. for 1 mol., 140 c.c. at 10°). The filtrate was made alkaline with sodium carbonate and the base was taken up in chloroform. The chloroform residue was recrystallised from acetone. Needles. m.p. 157°. However, the acetone residue (0.8 g.) on being acetylated gives the same triacetyl-derivative as the crystal itself. (Calc. for $C_{18}H_{25}NO_4$ (319): C=67.71, H=7.84, N=4.39%. Found: C=67.45, 67.80; H=7.77, 7.76%, N=4.24%). Spec. rotatory power. Subst.=0.1500; ethanol=10 c.c.; 1 dm-tube. $\alpha=+0.36^\circ$. $[\alpha]_D^{20}=+24.0^\circ$.

Methiodide. Prisms. m.p. 290° (from ethanol). Spec. rotatory power. Subst.=0.0599 g.; 50% ethanol=2.5 c.c.; 1 dm-tube. $\alpha=+0.14^\circ$. $[\alpha]_D^{19.5}=+5.8^\circ$.

(-)-Tetrahydro-sinomeninone (=7-Hydroxy-dihydro-thebainol). Prepared in the same way as (+)-derivative. Yield 0.3 g. from 1.0 g. m.p. 157°. Spec. rotatory power. Subst.=0.1472 g.; ethanol=10 c.c.; 1 dm-tube. $\alpha=-0.35^\circ$. $[\alpha]_D^{20}=-23.8^\circ$.

Methiodide. m.p. 292°. Spec. rotatory power. Subst.=0.0599 g.; 50% ethanol=2.5 c.c.; 1 dm-tube. $\alpha=-0.13^\circ$. $[\alpha]_D^{19.5}=-5.4^\circ$.

(d,l)-Tetrahydro-sinomeninone (=d,l-7-hydroxy-dihydro-thebainol). The both optical antipodes (ca. 0.15 g. each) were mixed in ethanol and evaporated. The residue was recrystallised from acetone. Hexagonal prisms. m.p. 160°. $[\alpha]_D=\pm 0^\circ$.

(d,l)-*Tetrahydro-sinomeninone methiodide*. Prisms. m.p. 260° . $[\alpha]_D = \pm 0^{\circ}$.

(+)-*Triacetyl-tetrahydro-sinomeninone*. (+)-*Tetrahydro-sinomeninone* (1 g.) was boiled with acetic anhydride (10 c.c.) and sodium acetate (1 g.) for 3 hours. After the acetic anhydride was removed in the diminished pressure, the residue was dissolved in a small quantity of methanol and poured in 2% acetic acid (100 c.c.). The filtrate was made alkaline with soda and extracted quickly with ether. When ether was evaporated, the triacetyl substance crystallised out in beautiful prisms. It was washed with little cold methanol. m.p. 197° . Yield 60%. (Calc. for $C_{24}H_{31}NO_7$ (445): C=64.72; H=6.97; N=3.15%. Found: C=64.54; H=6.83; N=3.26%.) Spec. rotatory power. Subst.=0.1493 g.; ethanol=10 c.c.; 1 dm-tube. $\alpha = -0.31^{\circ}$. $[\alpha]_D^{18} = -20.8^{\circ}$.

Methiodide. Prepared in the usual way. Angular plates. m.p. 290° . Spec. rotatory power. Subst.=0.0772 g.; 60% ethanol=10 c.c.; 1 dm-tube. $\alpha = -0.22^{\circ}$. $[\alpha]_D^{25} = -29.5^{\circ}$.

Determination of acetyl-radicals in the methiodide. 0.1319 g. methiodide was dissolved in the mixture of 5 c.c. of 0.31 N alcoholic caustic potash (=7.75 c.c. 0.2 N) and 5 c.c. of 0.2 N aqueous caustic potash, warmed for an hour on steam-bath and left 20 hours at room temperature. The hydrolysed solution was neutralised with 9.5 c.c. of 0.2 N sulphuric acid. Acetyl radicals corresponded to 3.25 c.c. of 0.2 N sulphuric acid, namely 21.1%. Calc. for three acetyls 22.00%.

(-)-*Triacetyl-tetrahydro-sinomeninone* (Triacetyl-7-hydroxy-dihydro-thebainol). Preparation is same as above. m.p. 196° . Spec. rotatory power. Subst.=0.1478 g.; ethanol=10 c.c.; 1 dm-tube. $\alpha = +0.30^{\circ}$. $[\alpha]_D^{25} = +20.3^{\circ}$.

Methiodide. m.p. 292° from methanol. Spec. rotatory power. Subst.=0.0761 g.; 60% ethanol=10 c.c.; 1 dm-tube. $\alpha = +0.22^{\circ}$. $[\alpha]_D^{25} = +28.9^{\circ}$.

(d,l)-*Triacetyl-tetrahydro-sinomeninone*. The both optical antipodes were mixed in equal quantity in alcoholic solution and evaporated. It crystallises into prisms. m.p. 196° . $[\alpha]_D = \pm 0^{\circ}$.

Methiodide. Flat prisms from ethanol. m.p. 292° . $[\alpha]_D = \pm 0^{\circ}$.

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Hydrocarbons from Carbide (A) II.* Non-Catalytic Polymerization under Ordinary Pressure. Hydrogen Systems and General Experimental Details.

By Ryoji NEGISHI and Osamu KAMIKE.

(Received November 14, 1941.)

The acetylene molecule owes its unique reactivity to the unsaturated triple bond and high negative heat of formation. The unsaturated property enables it to polymerize readily into simple or complex molecules. When the nascent acetylene molecule is formed from calcium carbide by the action of water, it probably possesses more energy and reactivity than ordinary acetylene and it is even more capable of further polymerization. This extra reactivity would manifest itself in the lowering of the polymerization temperature, independent of its main reaction from the influence of environments, and it has actually increased the yield of products as compared with the results of ordinary acetylene reactions.

With the purpose of obtaining a maximum yield of liquid hydrocarbons, utilizing this excess reactivity of nascent acetylene, we have attempted the present series of investigations. In order to make the effect as evident as possible, we have tried non-catalytic experiments under the ordinary pressure. In our present discussion we shall neglect any catalytic effect⁽¹⁾ of such products of the reaction as calcium oxide, carbonate, and carbon. In fact, we have found their effects—if any—rather small. This point will be taken up again later.

In this paper, first, general methods of experimental procedure and analyses of the products are given sufficiently minutely in order to offer some information with regard to the probable sources of difficulty and errors and to the degree of accuracy of the results to be expected not only in this report but also in the whole series of investigations. Second, these experiments with hydrogen (and nitrogen) have been carried out somewhat in detail to determine the optimum conditions for liquid synthesis which will serve as a basis for the ensuing investigations with carbon dioxide, acetylene, and water gas.

* Hydrocarbons from Carbide, Thermodynamics by R. Negishi, O. Kimura, and O. Kamiike, *Rev. Phys. Chem., Japan*, **15** (1941), 31 will be henceforth referred to as Paper (A) I. (A) will be used in contradistinction to Papers from I to VI on the same subject which have been published in Japanese in *J. Soc. Chem. Ind., Japan*, (1941–1942). In those papers experimental details have been minutely given. In the present series of papers, which will appear in this Bulletin, most of the experimental details will be abridged, and only a minimum of them, pertinent to the discussion of the results, will be included.

(1) G. Egloff, *Reactions of Pure Hydrocarbons*, Reinhold Publish. Corp., N. Y. (1937); C. Ellis, *The Chemistry of Petroleum Derivatives*, Reinhold Publish. Corp., N. Y., Vols. I and II (1934 and 1937).

Experimental Details. (1) **Materials.** Carbide. A commercial product which had the following composition* was used:

Component	% by Weight
Acetylene	85-75
CaO	12-19
CaCO ₃	0.8-1.8
SiO ₂	1.7-2.5
CaS	0.3-1.2
Ca ₃ P ₂	0.2-0.5

Hydrogen. Commercial electrolytic hydrogen of which purity was rather inferior (about 97%, the rest being air) was used without any purification.

Nitrogen. A commercial product compressed in a cylinder was used without any purification.

The other gases used in the later investigations will also be given here.

Carbon Dioxide. A commercial product of about 99.5% purity was used without any purification.

Carbon Monoxide. It was prepared by the action of formic acid on hot concentrated sulphuric acid. It was partially purified by bubbling through a KOH solution (20%) and distilled water.

Acetylene. It was prepared by dropping the carbide grains of 1 to 2 mm size into excess of water. The gas was bubbled through several wash bottles containing distilled water. No further treatment was effected.

(2) **Apparatus.** The reaction gas was first collected into two 20-liter bottles so arranged that while one was being discharged, the other could be filled up simultaneously. By this means an uninterrupted flow of gas was possible. The gas was passed through a gas meter and then a water reservoir, or a saturator, maintained at a constant temperature (within $\pm 0.1^\circ\text{C}$) by means of a well insulated automatic regulated thermostat. The temperature of the bath, consequently that of the water in the saturator was so adjusted as to give a proper water vapor-gas ratio. The vapor and gas and their mixtures were assumed ideal in calculating their compositions. The saturated gas was passed from the top to the bottom through the carbide layers, sandwiched between those of glass wool, occupying about 50 cm. of a Terex glass reaction tube of 2.5-3 cm. diameter. By inserting the layers of glass wool, cracking and breaking of the reaction tube due to packing effect, caused by CaCO₃ formation, were prevented to some extent. Usually, 200 g. of the carbide grains per run was used. The reaction tube was heated by means of an automatically regulated electric furnace of 75 cm. length. The temperature could be easily maintained within $\pm 2^\circ\text{C}$ and most of the time within $\pm 1^\circ\text{C}$. The products were condensed, first, by a water-condenser and then by a trap cooled with a mixture of solid CO₂ and alcohol. The condensates in the condenser were designated as "condenser" and those in the trap "trap." The non-condensable gas was passed through a second gas meter and collected in a second set of two 20-liter bottles similarly arranged as the first. When one of the bottles was filled up, a gas sample was taken for analysis. Usually, a complete run required from 8 to 10

* The authors are grateful to Messrs. Kataoka, Kodama, Nakano, and Inaba for this as well as for most of the liquid and solid analyses given in this series of investigations; also to Messrs. Nagayoshi, Shimamura, and Maruyama for performing the experiments.

hours. The whole apparatus was made of Terex (similar to Pyrex) glass. Only where metal was connected to glass, rubber tubing was employed. The oil vapors never seriously came in contact with rubber at any point. The apparatus was equipped with by-pass from which nitrogen could be introduced to flush out the air in the reaction tube. A thermocouple was inserted from the bottom. It was so long as the temperatures at various points in the carbide reaction zone could be observed.

(3) *Methods of Analysis.* Since the detailed description of the methods of analysis used has been given in one of our papers⁽²⁾ it will not be repeated; however, as has been mentioned above, a minimum of it, indispensable to a fuller appreciation of the results discussed here and in the subsequent papers, will be given.

Carbide. Acetylene and carbonate contents were determined from the volumes of the gases developed by treating it with a 25% NaCl solution saturated with acetylene and with the above solution acidified with phosphoric acid, respectively. The gases were collected over the same solution. The total carbide analysis was made by alkali fusion, and Si, S and P were determined, respectively, as SiO_2 , SO_4 , and PO_4 .

Solid Residue. Any free, or decomposed, carbon and high polymers in the residue were determined together by elementary analysis after the carbonate and acetylene had been eliminated by the above method. The residue was extracted with chloroform when necessary.

Gas. Since our investigations were exploratory in nature, a large number of samples, containing complex mixtures of such components as CO_2 , C_2H_2 , olefins, O_2 , CO , H_2 , saturated gases, and nitrogen, had to be analysed. We finally adopted as the most suitable method for our purpose, both in speed and accuracy, a modified method of Schufftan, which in turn was a modification of Orsat's. Speed was gained at the expense of accuracy; accuracy of 5% must be considered satisfactory.

All of the gases, except hydrogen and the saturated ones, were determined by absorption with usual reagents. Hydrogen was determined by catalytic and selective combustion with copper oxide at 200–300°C; the saturated gases, by explosion. One of the most troublesome features and, at the same time, the source of the greatest uncertainty in our method was the absorption of acetylene in the CO_2 absorption medium. This was finally overcome by saturating the KOH solution with Na_2SO_4 , and passing the sample through the medium just once which was sufficient to absorb all of CO_2 and but slightly of acetylene. The results of Table 1 are instructive in this connection.

Liquid Products. The liquid products were subjected to elementary analysis, and usually the oxygen content was calculated by difference; however, direct oxygen determinations were made if necessary. In most of the cases calculation by difference was sufficient for our purpose. Combined products from different runs were subjected to distillation, and the various fractions were determined from their boiling ranges and other physical constants. The liquid products of these runs contained small amounts of sulphur, nitrogen, and oxygen as phenols and

(2) O. Kamiike, S. Kataoka, M. Nibayashi, and R. Negishi, Paper II.

Table 1. Solubility of Acetylene in KOH Solution.
(Purity of acetylene, 95.2).

No. of pass through absorb. medium	% C ₂ H ₂ Absorbed		
	KOH (1:2)	KOH (1:2)	
		Sat'd. with NaCl	Sat'd. with Na ₂ SO ₄
1	9.0	3.9	1.0
2	16.4	6.7	5.6
3	22.6	13.0	8.0
4	29.1	16.2	11.9
5	34.7	19.0	13.1
10	60.3	33.2	26.1

* If a sample contains less acetylene, the percentage absorbed will be less.

ethers. Alcoholic products, however, constituted the major portion of the oxygenated compounds in the product.

Results and Discussion. Since the experimental data on the formation of hydrocarbons directly from carbide^{(3) (4) (5)} is scarce, the authors have undertaken to conduct some experiments to find out the optimum conditions for the best yield of liquid products. Hydrogen (and nitrogen) saturated with the water vapour at about 80°C* has been first tried, and the results obtained are given in Table 2 for which some additional explanation may be necessary. In this paper (and also in this series of investigations), the time of contact has been calculated as follows:—the free space in c.c. of the carbide, taken equal to 1/2 of the total weight of the carbide charged, plus the glass wool space is multiplied by the total time in second and the product is divided by the total volume in c.c. at the reaction temperature of the hydrogen (or the reaction gas) introduced. The sum of the percentages in the Table is not necessarily equal to the figures given in the total carbon balance, since part of the carbide has been transformed into C₂H₆ and other products, and none of them has been included in the Table. The deviations of the total carbon and weight balances from 100 serve as a measure of reliability of the results found in the Table.

Effect of Temperature. In Fig. 1 the percentages of the products given in Table 2 are plotted against reaction temperatures. The various points at 300°C are less reliable than those at the other temperatures,

(3) G. L. Putman and K. F. Kobe, *Chem. Rev.*, **20** (1937) 131. This paper contains also other reactions than calcium carbide.

(4) H. Plauson and G. Tischenko, G. P. 346065 (1921); N. V. de Bataasche Petroleum Maatschappij, Holl. P. 22573 (1927); *Chem. Zentr.* 1931, I, 1356; F. Hansgirt, J. P. 127812, 134273, 134712.

(5) S. P. Gambarjan and L. S. Kasarjan, R. P. 41516; A. T. Babayan, *J. Gen. Chem.* (U.S.S.R.) **8** (1938) 602; *Chem. Abst.*, **33** (1939), 1269. In these references the carbide is reacted with acetone and ether to produce some hydroxy-yne compounds.

* At this temperature the ratio of the water vapor to gas is approximately 1 to 0.85. This proportion has been found to give nearly the best yield under our conditions.

Table 2. Hydrogen Systems.

Exp. No.	IL29	IL30*	IL34	IL35*	IL31	IL24	IL18**	IL16	IL25	IL27
Reaction Temp°C	300		340		380		420		460	
Time of Contact (sec.)...	12.3	14.1	18.1	18.5	12.6	7.8	10.9	10.6	7.3	5.4
Carbide Introd. (g.)	200	200	200	200	200	100	100	100	100	100
Liq.*** Carbon on React.										
Carbide Carbon (%) ..	15.5	16.0	21.8	13.5	18.4	20.6	11.4	15.3	9.4	10.4
CH ₄ (%)	2.1	0.0	3.5	7.3	10.4	5.4	11.8	6.8	9.3	9.7
CnH _{2n} (%)	1.5	0.8	0.6	3.2	4.7	2.1	5.6	4.6	4.5	4.6
C ₂ H ₂ (%)	20.5	24.8	26.7	34.3	23.8	26.8	7.4	19.8	12.6	13.2
(CO ₂ +CO) %	2.0	2.9	2.5	0.8	3.5	1.3	0.8	0.5	0.6	1.1
Decomp.+High Polym.										
(%)	11.8	7.3	20.7	48.9	26.8	26.7	49.8	23.8	39.4	44.8
Carbonate (%)	9.5	0.0	3.7	12.3	6.8	9.3	—	12.6	12.0	12.9
Total Carbon Balance ...	78.5	77.8	81.6	102.0	96.8	94.3	93.5	90.6	89.8	96.6
Total Weight Balance ...	99.4	96.0	99.8	100.6	99.8	100.2	98.3	98.1	99.8	99.2

* Nitrogen used. Data not plotted in Fig. 1.

** Data not used in Fig. 1.

*** % of produced carbon on reacted carbide carbon.

but in the general picture of the mechanism of the reactions, they seem to fit sufficiently to warrant their appearance in the Figure. For the sake

of convenience, the formations of the products will be discussed in their order of appearance on the 300°C line.

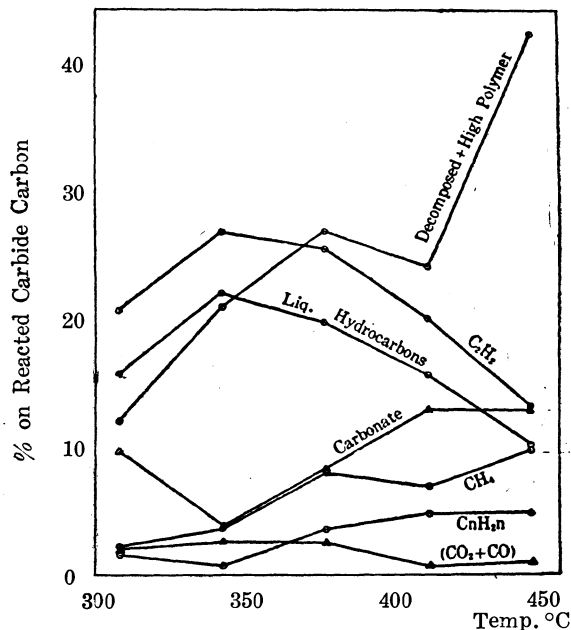


Fig. 1. Effects on Products of Carbide of Temperature.

The amount of free acetylene increases from 300 to 340°C, where it attains a maximum, and then decreases rapidly. There is no satisfactory explanation for this behavior, but from a considerably body of experimental data available from our runs, we may offer some suggestions. At lower temperatures (as at 250°C), we have obtained practically no liquid products, but a large amount of "yellow powder," or cuprene-like substance, and the efficiency of its formation at the temperature is much greater than that of

the liquid products at 340°C where the formation of the latter is the

highest. The one run made with hydrogen showed a conversion into the solid product of over 30%* as compared with 21.8% for the liquid. We might assume, therefore, that at lower temperatures the nascent acetylene molecules are in more favorable conditions as regards the effects of thermal agitation and cracking** and of the free energy of reaction⁽⁶⁾ for the solid polymerization. As the temperature is raised the sojourn of the acetylene molecules in the favorable positions becomes shorter, and an increased amount of free acetylene is resulted; at still higher temperatures the effects of thermal cracking become striking, and the concentration of it again decreases.

The yield of liquid products must also have a maximum. According to our thermodynamic considerations⁽⁶⁾, at lower temperatures the formation of solid polymers predominates, and, as the temperature is raised, the size of the polymers becomes less, and more liquid products are formed. With a further increase of temperature, the size of the molecules decreases further, and the amount of gaseous products increases at the expense of those of the liquid.

The residue is yellow at 250°C and becomes darker with the increase of temperature; at above 400°C it is black. At lower temperatures it may not contain any free carbon, but above 400°C some of it (or polymers with their hydrogens stripped off) is actually present.

The carbonate formation increases with the increase of temperature and is also dependent on the increasing formation of CO₂ with temperature. This CO₂ reacts with the freshly produced CaO from the carbide to form CaCO₃.

The sources of CO₂ and CO are not clear. We hesitate to make a definite statement on this point; however, it seems that the formation of CO₂ is intimately associated with CO. Some of the reactions, involving the substances found in the present systems, which may produce CO are given below:

Reaction	ΔF at 400°C
$C + \frac{1}{2}O_2 = CO$	- 40400
$C + CO_3 = 2CO^{(7)}$	+ 12800
$C + H_2O = CO + H_2$	+ 9500
$CH_4 + CO_2 = 2CO + 2H_2$	+ 17200
$CH_4 + \frac{1}{2}O_2 = CO + 2H_2$	- 36000
$CH_4 + H_2O = CO + 3H_2$	+ 13900
$CH_3OH = CO + 2H_2$	- 7400
$CO_2 + H_2 = H_2O + CO$	+ 3300

* With other gases like CO, CO₂, C₂H₂, the % conversion is from 35 to 65% of the reacted carbide carbon.

** At lower temperatures this effect is most pronounced. Since the reactions involving the carbide are highly exothermic, if the rate of reaction becomes sufficiently rapid, the accumulation of the heat of reaction far exceeds the dissipation of the same, and there may set in thermal decomposition and other complications.

(6) Paper (A) I.

(7) A. Semechkova and D. Frank-Kamenetzky, *Acta Physicochim.*, (U.R.S.S.) **12** (1940) 879. According to the investigators, the reaction is $C + CO_2 = CO + (CO)$, where (CO) is the adsorbed carbon monoxide, and this reaction takes place at 600°C.

In these reactions the source of oxygen may be that present in the original hydrogen, and CH_3OH has been identified as one of the products. These reactions may require much higher temperatures so that their rates become appreciable than the temperature range in our experiments. The fact, however, that (a) the actual temperature at the point of reaction is higher than that indicated*, (b) most of the reacting partners are in their nascent states, and (c) the products of reaction are removed continuously⁽⁸⁾ may induce some of these reactions to proceed as indicated above. Moreover, some of them may take place on the surface of the solid. In this connection the work of Kawakita⁽⁹⁾ on the decomposition of CO_2 into C and CO on reduced iron at temperatures as low as 300 to 400°C is suggestive.

The increase in the content of methane with the increase of temperature is as expected from thermodynamic considerations and is borne out by abundant experimental data.

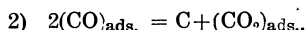
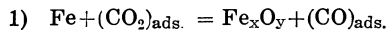
The increase in the formation of C_nH_{2n} with the increase of temperature may be due to partial cracking of the large molecules, on the one hand, and hydrogenation⁽¹⁰⁾ and polymerization^{(10) (11) (12)} of the acetylene molecules, on the other.

Effect of Time of Contact. Next, we shall consider briefly the effects of time of contact. Although the results are not complete, some information may be gathered from the relationship between the time of contact and the yield of liquid products for the hydrogen runs at 380°C. In these runs 100 g. of carbide grains was used. The results are shown in Fig. 2,

* At times the temperature at the reaction zone is nearly as much as 100°C higher than the average temperature (300°C) of the furnace.

(8) R. Negishi, a paper to be published in *Rev. Phys. Chem., Japan*, (1941). This precisely has been the case in the synthesis of iso-butyl alcohol in the presence of the carbide. By the continuous and rapid removal of the products of reaction, the equilibrium of the reaction is shifted sufficiently to counter-balance the effects of reduced pressure and temperature.

(9) According to K. Kawakita, *Rev. Phys. Chem., Japan*, **11** (1937), 75; *ibid.*, **12** (1938), 105; *ibid.*, **13** (1939), 87; *ibid.*, *ibid.*, **14** (1940), 1, the reaction is, on a reduced iron catalyst,

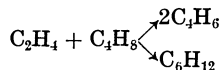


and these steps are repeated. This reaction can take place at a fairly low temperature range, 300 to 400°C.

(10) H. A. Taylor and A. van Hook, *J. Phys. Chem.*, **39** (1935), 811; J. B. Conn, G. B. Kistakowsky, and E. A. Smith, *J. Am. Chem. Soc.*, **61** (1939), 1868; A. Farkas and L. Farkas, *ibid.*, **61** (1939), 3396. The latter authors have shown that acetylene is first hydrogenated nearly completely to ethylene, and the ethylene then is hydrogenated to ethane.

(11) G. Egloff and E. Wilson, *Ind. Eng. Chem.*, **27** (1935), 917. They claim that ethylene is the key molecule for the polymerization of organic products, including the unsaturated.

(12) Storch, *J. Am. Chem. Soc.*, **56** (1934), 374. He has explained the formation of olefins with odd carbon number from ethylene by assuming a disproportionation to give a higher and a lower olefin, for example,



which is self-evident and requires no further remarks, especially when in lack of more complete data on the subject.

Finally, a comment will be made on the size of carbide grains. In some of the runs with powdered carbide which are not mentioned in this paper, there has been some evidence that the reaction becomes too rapid

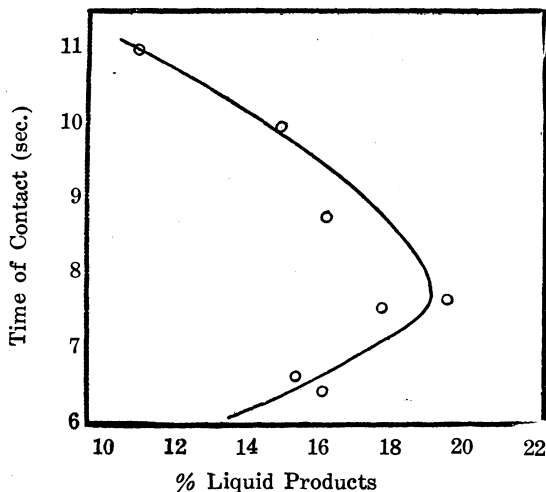


Fig. 2. Time of Contact and Yield.

the concentration of the water molecules is large, the yield of liquid products has been reduced by the heat of reaction involving the water molecules and the carbide.

With these informations on hand, studies on the synthesis of hydrocarbon liquids directly from the carbide have been continued, using such gases as CO_2 , C_2H_2 , water gas, and HCl , and their results will be given in the later papers which will appear also in this Bulletin.

Summary.

General experimental procedure, methods of analysis, and purification of materials have been given sufficiently in detail in order that the sources of difficulty and uncertainty in the results obtained not only in this paper but also in this series of investigations on the non-catalytic synthesis of hydrocarbon liquids directly from calcium carbide may be estimated.

Orientation and exploratory investigations have been made on hydrogen systems, and it has been found that a grain size of 1 to 2 mm, a saturation temperature of 80°C , and a reaction temperature of 340°C proved most suitable for the synthesis of liquid hydrocarbons under our experimental conditions.

The effects on the formations of the products of temperature have been discussed. These effects are intimately associated with the heat of reaction involving the carbide which is large.

due to local accumulation of the heat of reaction. The liquid yield, consequently, decreases markedly, and that of the decomposed carbon increases even more remarkably. If the size of the grains is too large, the surface available for reaction becomes less, and the concentration of the nascent acetylene molecules may become too small, and again the yield decreases. The same sort of concentration effect has been found when the saturation temperature is too low (about 65°C). On the other hand, when the temperature is above 85°C , and

The effects of the time of contact and of the grain size have been briefly mentioned in passing.

It is the authors' pleasure to thank Prof. T. Marusawa for his comment and encouragement throughout this work. They are also grateful to Dr. Sato, the director of this institute, for his permission for publication; to Dr. Fritz Hansgirk for suggesting the problem and with whom some interesting discussions have been held.

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Synthesis of Guanidine Compounds by the Cyanamide Condensation Method I. Preparation of Ethylenediguanidine and Tetramethylenediguanidine.* ** (Studies on some derivatives of calcium cyanamide. XI.⁽¹⁾)

By Kiitiro SUGINO, Kozo SHIRAI and Kiyoshi AOYAGI.

(Received November 17, 1941.)

Introduction and Outline of the Research.

In the previous communication, one of the authors⁽²⁾ (K. Sugino) studied the reaction of amine salts with dicyandiamide for guanidine preparation and the mechanism of this reaction was perfectly determined. For ammonium salt, this mechanism was outlined as follows:—

* A part of this report was given in the lecture at the general meeting of the Chemical Society of Japan, held in April, 1941.

** A part of this paper is one (Part II) of the papers of the series "Studies on Raw Materials of Synthetic Fiber". (Part I: *J. Soc. Chem. Ind. Japan*, **44** (1941), 706.)

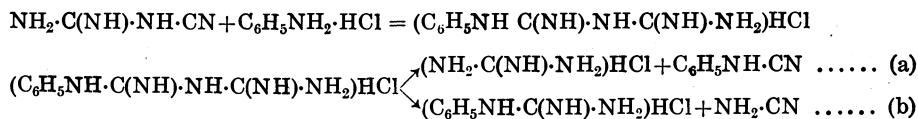
(1) The earlier papers of this series: I. Y. Kato, K. Sugino and K. Koizumi; *J. Electrochem. Assoc. Japan*, **2** (1934), 187; *Bull. Tokyo Univ. Eng.*, **3** (1934), 684; *Chem. Abst.*, **28** (1934), 7250. II. K. Sugino: *J. Electrochem. Assoc. Japan*, **4** (1936), 396. III. K. Sugino, T. Kobayashi and Y. Shibasaki: *J. Electrochem. Assoc. Japan*, **5** (1937), 390. IV. K. Sugino and M. Ogawa: *J. Electrochem. Assoc. Japan*, **6** (1938), 292; *Chem. Abst.*, **34** (1940), 7704. V. K. Sugino: *J. Chem. Soc. Japan*, **60** (1939), 111; *Bull. Tokyo Univ. Eng.*, **8** (1939), 84; *Chem. Abst.*, **34** (1940), 2795. VI. VII. K. Sugino: *J. Chem. Soc. Japan*, **60** (1939), 267, 351; *Bull. Tokyo Univ. Eng.*, **8** (1939), 99; *Chem. Abst.*, **34** (1940), 2273; **35** (1941), 5097. VIII. K. Sugino: *J. Chem. Soc. Japan*, **60** (1939), 411; *Bull. Tokyo Univ. Eng.*, **8** (1939), 151; *Chem. Abst.*, **35** (1941), 5097. IX. K. Sugino: *J. Chem. Soc. Japan*, **60** (1939), 507; *Bull. Tokyo Univ. Eng.*, **8** (1939), 195; *Chem. Abst.*, **35** (1941), 5098; *Chem. Zentr.*, (1939) II, 2638. X. K. Sugino and M. Kanayama: *J. Electrochem. Assoc. Japan*, **8** (1940), 250.

(2) Report VII of this series: *loc. cit.* (Foot note 1.)

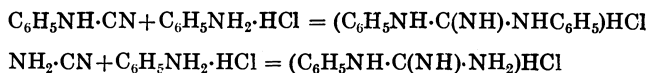
- (1) $\text{NH}_2\cdot\text{C}(\text{NH})\cdot\text{NH}\cdot\text{CN} + \text{NH}_3\cdot\text{HX} = (\text{NH}_2\cdot\text{C}(\text{NH})\cdot\text{NH}\cdot\text{C}(\text{NH})\cdot\text{NH}_2)\text{HX}$
 (2) $(\text{NH}_2\cdot\text{C}(\text{NH})\cdot\text{NH}\cdot\text{C}(\text{NH})\cdot\text{NH}_2)\text{HX} \begin{cases} \rightarrow (\text{NH}_2\cdot\text{C}(\text{NH})\cdot\text{NH}_2)\text{HX} + 1/2 \text{NH}_2\cdot\text{C}(\text{NH})\cdot\text{NH}\cdot\text{CN} \\ \rightarrow (\text{NH}_2\cdot\text{C}(\text{NH})\cdot\text{NH}_2)\text{HX} + \text{NH}_2\cdot\text{CN} \end{cases}$
 (2') $1/2 \text{NH}_2\cdot\text{C}(\text{NH})\cdot\text{NH}\cdot\text{CN} + 1/2 \text{NH}_3\text{HX} = 1/2 (\text{NH}_2\cdot\text{C}(\text{NH})\cdot\text{NH}\cdot\text{C}(\text{NH})\cdot\text{NH}_2)\cdot\text{HX} \rightarrow \text{reaction (2)}$
 (3') $\text{NH}_2\cdot\text{CN} + \text{NH}_3\cdot\text{HX} = (\text{NH}_2\cdot\text{C}(\text{NH})\cdot\text{NH}_2)\text{HX}$

The formation of biguanide monosalt, its thermal decomposition into guanidine salt and dicyandiamide or cyanamide and the reaction of latter compounds with parent ammonium salt take place successively and 2 mols of guanidine salt is obtained from 1 mol of dicyandiamide and 2 mols of ammonium salt.

The reaction of aniline hydrochloride with dicyandiamide was also found to take place according to this mechanism. But in this case, two reactions take place in the thermal decomposition of phenylbiguanide hydrochloride⁽³⁾. It is decomposed to (a) guanidine hydrochloride and phenylcyanamide and to (b) phenylguanidine hydrochloride and cyanamide.

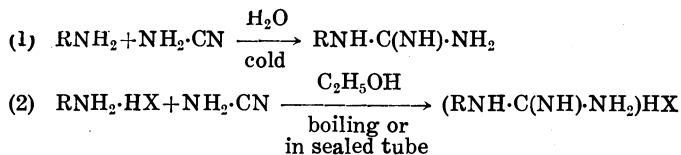


The cyanamides formed in nascent state react again immediately with aniline hydrochloride and the salts of diphenylguanidine and phenylguanidine are formed. (A part of cyanamides reacts together to give the phenyl derivatives of melamine.)



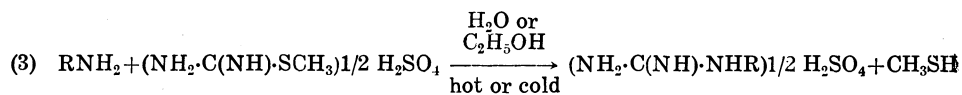
From these results, it was found that several kinds of guanidines were necessarily formed by the reaction of amine salt with dicyandiamide. Therefore, in order to convert the amine into corresponding simple guanidine, the older cyanamide method must be applied if calcium cyanamide is used as the starting material.

It has been well known that guanidine salt can be obtained by the action of cyanamide with amine salt. General methods of guanidine preparation using cyanamide may be summarized as follows:—

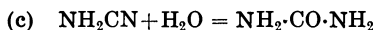
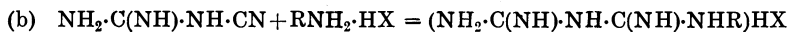


But recent guanidine literature indicates the popularity of methylisothiurea sulphate method (3) over the cyanamide condensation method.

(3) Report VIII of this series: *loc. cit.* (Foot note 1.)



This reason is not clearly known by the authors. But many disadvantages are found in the older cyanamide method. In that process, side reactions are possible in each instance. The three most common side reactions are the polymerisation of cyanamide to dicyandiamide (a), the condensation of this latter compound with the parent amine salt to give a biguanide salt (b) and the hydration of cyanamide to urea (c) (in aqueous solution). These may be outlined as follows:—



Therefore the yield of guanidines is very poor and the separation of guanidine salt from by-products and unchanged amine salt looks very difficult.

The cause of the above side reactions are probably due to the slowness of the rate of condensation for the guanidine salt. And it would appear that this method becomes practical when the rate of condensation absolutely exceeds that of side reactions.

The authors undertook to study this problem using the reactions of cyanamide with diamine salts. And it was found that corresponding diguanidine dihydrochloride was quantitatively obtained when diamine dihydrochloride was fused with the excess of cyanamide. At about 140°C, this reaction was completed for a short time and the probable side reaction was only the polymerisation of excess of cyanamide to dicyandiamide.

The reaction product contained diguanidine dihydrochloride and dicyandiamide. The separation of these two compounds was easily performed when the reaction product was refluxed with acetone. Dicyandiamide was soluble in hot acetone, but diguanidine dihydrochloride was not soluble. By this extraction, almost pure diguanidine dihydrochloride was obtained. If melamine (polymerisation product of 3 mols of cyanamide) existed, it was separated by the recrystallisation of diguanidine salt from alcohol.

From pure diguanidine dihydrochloride thus obtained, various salts of diguanidine were prepared and the properties of these compounds were compared with that cited in the literature.

Free alkylene diguanidines are not obtainable and not described in the literature. These compounds were also prepared by the action of metallic sodium with diguanidine dihydrochloride suspended in absolute alcohol and by evaporating the resulting alcoholic solution to almost dryness under the reduced pressure at low temperature. Beautiful crystals of alkylene diguanidine could be obtained when the concentrated alcoholic solution of diguanidine was mixed with a large amount of acetone and the resulting turbid mixture was allowed to stand for a long time. From the free alkylene diguanidine, many salts were also prepared.

Literature. About the synthesis of these diguanidine salts, only two literatures have as yet been published. Schenck⁽⁴⁾ prepared ethylenediguanidine dihydroiodide in alcoholic solution at room temperature from ethylenediamine hydrate and methylisothiurea hydroiodide and many salts of ethylenediguanidine were also derived from the dihydroiodide. Tetramethylenediguanidine salts were prepared by Kiesel⁽⁵⁾ by the reaction of cyanamide with tetramethylenediamine in aqueous solution at room temperature. (34% of the diamine could be converted to diguanidine and agmatine.) Tetramethylenediguanidine was also found by Kutscher, Ackermann u. Flössner⁽⁶⁾ in the muscle of *Arca Noae* and was named as Arcain.

Experimental materials. 1. *Ethylenediamine*. Commercial sample (Ethylenediamine hydrate) was used without purification. Its picrate melted at 230°C. From this, the hydrochloride was prepared. (Found Cl, 53.3. Calculated for $C_2H_8N_2 \cdot 2HCl$: Cl, 53.3%.)

2. *Tetramethylenediamine* (*Putrescine*). Tetramethylenediamine was prepared from ethyl alcohol by the following procedure.

Ethylene, made by passing the vapour of ethyl alcohol over Japanese acid clay at 380–390°C, was absorbed in bromine and the resulting ethylene dibromide (Yield: 90%) in alcoholic solution was refluxed with a slight excess of saturated aqueous solution of potassium cyanide according to the direction of Fauconnier⁽⁷⁾. Ethylene dinitrile (M.p. 53–54°C, B.p. 158–159°C/19 mm, 124°C/5 mm, yield: 52%) was obtained by distilling the reaction product under the reduced pressure. This was dissolved in absolute alcohol saturated with dry NH_3 gas and was reduced by metallic sodium. (The temperature was maintained below 20°C.) The reduction product was neutralized by conc. HCl and after removal of insoluble substances (NaCl, NH_4Cl etc.), the filtrate was evaporated to dryness to give the crude tetramethylenediamine dihydrochloride. For separation of ammonia from tetramethylenediamine, the crude diamine salt was converted to free diamine by the fractional distillation of the former compound with NaOH. Free tetramethylenediamine distilled was again neutralised by conc. HCl and evaporated to dryness. The residue was recrystallised from 85% alcohol. M.p. 317°C. (Found Cl. 43.8; N, 17.7. Calculated for $C_4H_{12}N_2 \cdot 2HCl$: Cl, 44.0; N, 17.4%.)

3. *Cyanamide*. Cyanamide was prepared from commercial calcium cyanamide according to the direction of one of the authors (K. Sugino) and M. Kanayama⁽⁸⁾ which was described in the previous paper. M.p. 44°C.

Reaction of cyanamide with alkylenediamine dihydrochloride. 1/100 mol of ethylenediamine- or tetramethylenediamine dihydrochloride (1.33 g, 1.61 g respectively) was thoroughly mixed with 2/100 mols (0.84 g, equimolecular amount) or 3/100 mols (1.26 g) of cyanamide and

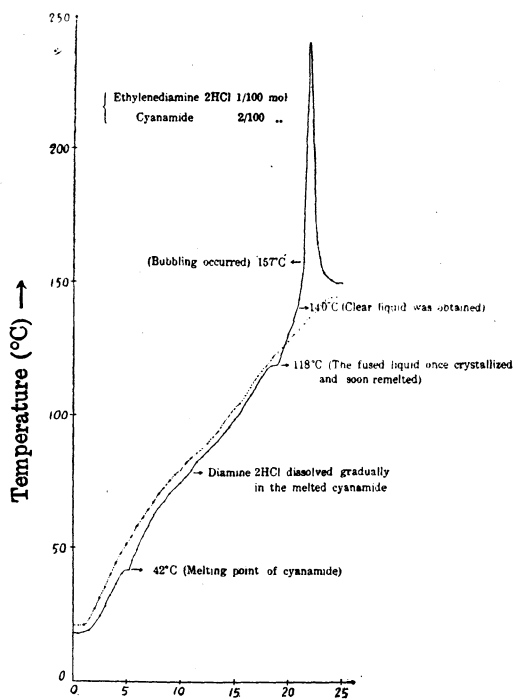
(4) *Z. physiol. Chem.*, **155** (1926), 306.

(5) *ibid.*, **118** (1921), 277.

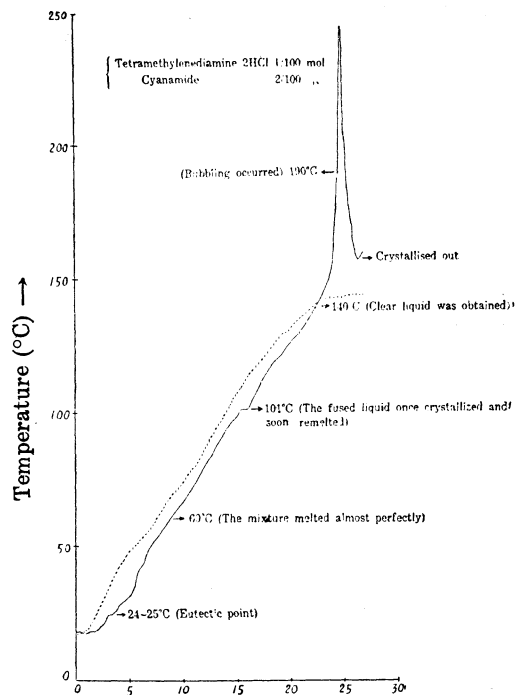
(6) *ibid.*, **199** (1931), 273.

(7) *Bull. soc. chim.*, [2], **50** (1888), 214.

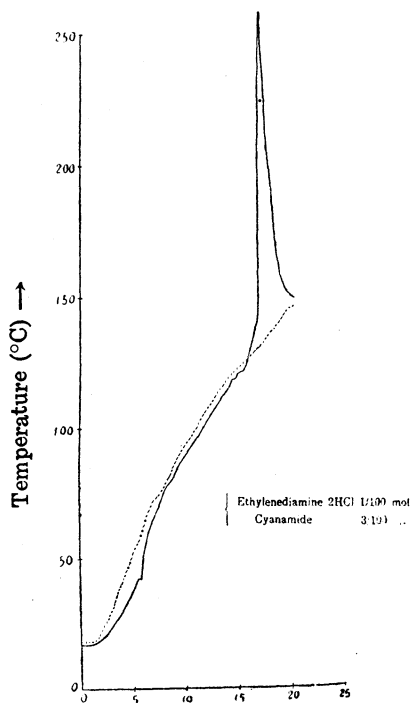
(8) Report X of this series: *loc. cit.* (Foot note 1.)



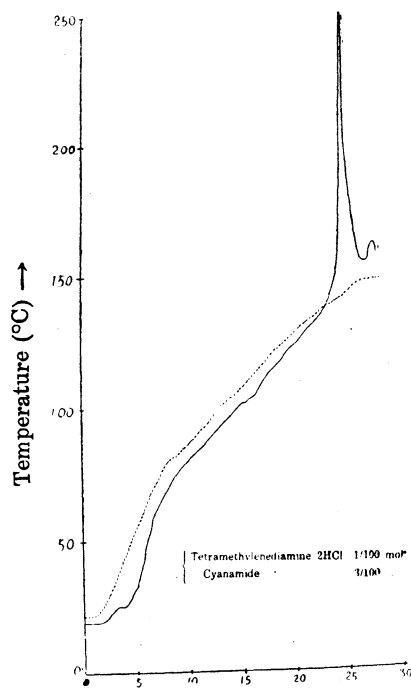
Time →
Fig. 1.



Time →
Fig. 2.



Time →
Fig. 3.



Time →
Fig. 4.

the mixture was heated in an oil-bath under fused state. The detail of the reactions was shown in the heating curves. (Fig. 1, 2, 3 and 4).

The evolution of heat due to the increase of the rate of condensation began at 135°C (ethylene-) and 155°C (tetramethylene) respectively and the temperature of the mixture reached about 240°C even if as small an amount of sample as 1/100 mol was used. This rise of the temperature induced the decomposition of diguanidine salts. In the case of ethylenediamine dihydrochloride, ethylenediguanidine dihydrochloride was obtained with a fair yield even at a high temperature. But in the case of putrescine dihydrochloride, the properties of the reaction product according to the heating curve (Fig. 2 or 4) was not identified with that of tetramethylenediguanidine dihydrochloride. So, for obtaining the alkylenediguanidine salt in pure state, it is essential that the temperature of the reaction is seriously regulated not to rise above 150°C at the highest. The influence of the reaction temperature and of the quantity of cyanamide on the yield of diguanidine was shown in Table 1.

Analytical method: Total reaction product (from 1/100 mol of diamine 2HCl and 2/100–3/100 mols of cyanamide) was dissolved in distilled water and the solution was made up to 250 c.c.. 50 c.c. of the aliquot portion was transferred to a beaker and about 150 c.c. of the saturated solution (20°C) of ammonium picrate and a few drops of conc. NH_4OH (NH_4OH dissolved the dipicrate of diamines) were added to it with constant stirring. (In the case of tetramethylenediguanidine, conc. NH_4OH was previously added to the ammonium picrate solution.) The precipitate was filtered off by suction with a gooch crucible of known weight and dried for 2–3 hrs. at 110°C and finally weighed as diguanidine dipicrate. The filtrate should be tested by adding more ammonium picrate solution. The solubility of ethylenediguanidine dipicrate in saturated ammonium picrate solution was found to be 0.0144 g./100 c.c. at 25°C.

Table 1.

Quantity of samples (mol)		Condition of the reaction	Yield of Diguanidine (%)	
Diamine 2HCl	Cyanamide		Ethylene	Tetramethylene
1/100	2/100	Fig. 1 & 2	71	77*
1/100	2/100	140~150°C, 30 mins	80	—
1/100	3/100	Fig. 3 & 4	87	91*
1/100	3/100	140~150°C, 30 mins	103	95

* In these cases, pure tetramethylenediguanidine could not be obtained as above mentioned. Therefore these data were calculated from the quantity of dipicrate which was assumed to be pure tetramethylenediguanidine dipicrate.

In the case of tetramethylenediamine dihydrochloride, agmatine (aminotetramethyleneguanidine) salt was not found in the reaction product even if 1 mol of cyanamide was used for 1 mol of diamine salt.

From these results, it is demonstrated that for converting the alkylenediamine dihydrochloride perfectly to corresponding diguanidine dihydrochloride, it is most favorable for 1 mol of diamine dihydrochloride, to be fused with 3 mols (1.5 times of equivalent amount) of cyanamide and the temperature of the reaction mixture cautiously maintained at about 140°C for less than 30 mins. This reaction is an exothermic one as above mentioned, so the regulation of the temperature is quite difficult

if a large amount of sample is used practically. But for small scale experiment, this is performed by a simple cooling.* In the case of large scale experiment, it is favorable that a small amount of water is previously used in the mixture of samples (or a small amount of water is added into the fused mass (140°C) from time to time) or an extremely concentrated aqueous solution of diamine dihydrochloride (1 mol) and cyanamide (3 mol) is heated in an autoclave at 140°C for 30–60 mins.

Ethylenediguanidine dinitrate and dihydroiodide were also prepared by fusion of 1/100 mol of ethylenediamine dinitrate and dihydroiodide with 3/100 mols of cyanamide according to the heating curves of Fig. 5 and 6. The yields of diguanidines were 60% and 70% of the theory respectively. The decomposition of the dinitrate at higher temperature was more rapid than that of the dihydrochloride. At 135–145°C, the yield of the dinitrate reached to 84% of the theory.

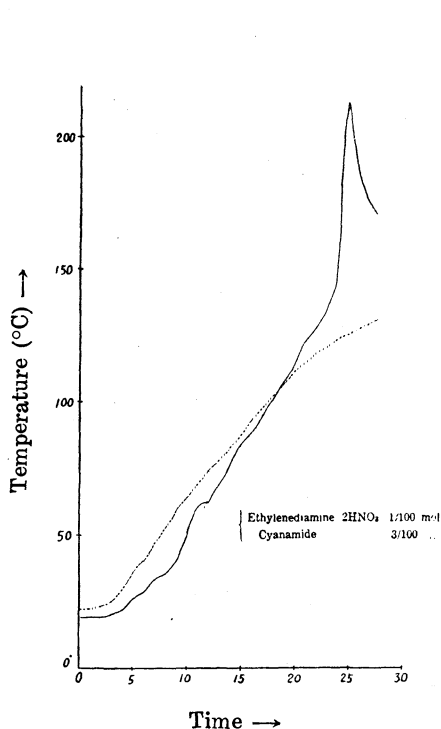


Fig. 5.

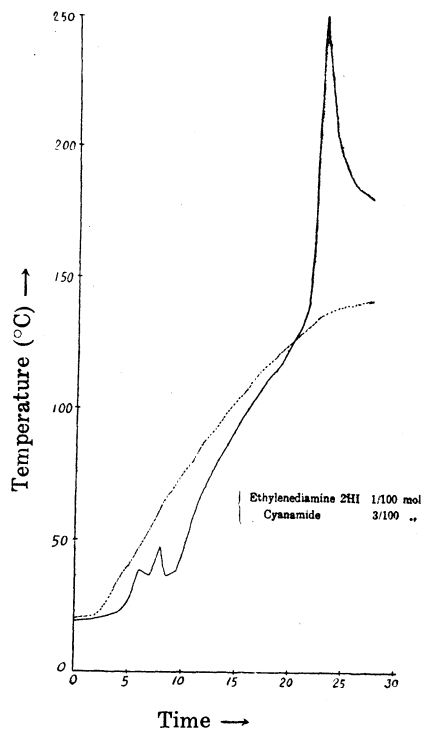


Fig. 6.

* The method of cooling in these experiments was as follows:—The reaction mixture was first heated according to the heating curves (Fig. 1 and 2) and when the temperature of the reaction reached 140°–150°C, the reaction vessel was taken away quickly from the oil bath. The temperature continued to rise by the heat of reaction, so the vessel was cooled by air or water. And when the temperature was depressed below 140°C by cooling, the vessel was again heated in the oil bath. These methods were repeated several times and after the evolution of heat ceased, the vessel was heated at about 140°C for a time.

Isolation of pure diguanidine dihydrochloride from the reaction product. By the above method, ethylenediamine- or tetramethylenediamine dihydrochloride could be converted perfectly to the corresponding diguanidine dihydrochloride. The possible impurities may be dicyandiamide and melamine due to the polymerisation of excess of cyanamide. For removal of dicyandiamide, the fused mass was pulverised by rubbing with a glass rod in a small portion of absolute alcohol and the powdered reaction product was refluxed with acetone for about 3 hrs. (100 c.c. of acetone was used for 5 g. of the crude diguanidine 2HCl .) Almost pure diguanidine dihydrochloride was obtained by a single extraction with acetone. Melamine probably does not exist when the reaction takes place at about 140°C , but if it exists, it is separated by the recrystallisation of the residue of acetone extract from alcohol. The properties and analytical results of pure alkylenediguanidine dihydrochloride were as follows:—
 Ethylenediguanidine dihydrochloride. M.p. 225°C . M.p. of its dipicrate 284°C . (Found Cl, 31.6; N, 39.6; $\text{C}_4\text{H}_{12}\text{N}_6$ (ethylenediguanidine, determined as dipicrate), 67.6. Calculated for $\text{C}_4\text{H}_{12}\text{N}_6 \cdot 2\text{HCl}$: Cl, 32.7; N, 38.7; $\text{C}_4\text{H}_{12}\text{N}_6$, 66.4%.)

Tetramethylenediguanidine dihydrochloride.

(1) Residue of acetone extraction. M.p. 228°C . M.p. of its dipicrate 253°C . (Found N, 34.8; $\text{C}_6\text{H}_{16}\text{N}_6$ (determined as dipicrate), 70.7. Calculated for $\text{C}_6\text{H}_{16}\text{N}_6 \cdot 2\text{HCl}$: N, 34.3; $\text{C}_6\text{H}_{16}\text{N}_6$, 70.2%.)

(2) 1 g. of sample (1) was refluxed with 20 c.c. of absolute alcohol. Soluble part (0.25 g.): M.p. $227\text{--}228^{\circ}\text{C}$. (Found N, 34.1. Calculated for $\text{C}_6\text{H}_{16}\text{N}_6 \cdot 2\text{HCl}$: 34.3%.) Insoluble part (0.70 g.): M.p. $233\text{--}234^{\circ}\text{C}$. (Found N, 35.0. Calculated for $\text{C}_6\text{H}_{16}\text{N}_6 \cdot 2\text{HCl}$: 34.3%.)

Ethylenediguanidine dinitrate was also purified by this method but not the dihydroiodide. For the salts of diguanidines which dissolve in acetone, this method cannot be applied.

Free alkylenediguanidines. Free alkylenediguanidines could be obtained in crystal form. The procedure was as follows:

In an alcoholic suspension of pulverised diguanidine dihydrochloride, a slightly less amount of clean sodium cuttings was added piece by piece with frequent shaking. (For example, 2.17 g. of ethylenediguanidine dihydrochloride (2.45 g. of tetramethylenediguanidine dihydrochloride) was suspended in 30–50 c.c. of absolute alcohol and 0.45–0.46 g. of metallic sodium was added.) After removal of the precipitate, the solution was evaporated under the reduced pressure at low temperature to a syrupy mass which was allowed to crystallise in a vacuum desiccator. In order to prepare a pure and beautiful crystal, absolute acetone was added to the concentrated solution until white turbidity occurred and was allowed to stand for 2 or 3 days. A beautiful and large crystal of ethylene- and tetramethylenediguanidine could be obtained.

Ethylenediguanidine. M.p. 163°C . M.p. of its dipicrate 285.5°C . (Found N, 59.1. Calculated for $\text{C}_4\text{H}_{12}\text{N}_6$: N, 58.3%.)

Tetramethylenediguanidine. M.p. 172°C . M.p. of its dipicrate 253°C . (Found N, 48.3. Calculated for $\text{C}_6\text{H}_{16}\text{N}_6$: N, 48.8%.)

Preparation of various salts of ethylenediguanidine and tetramethylenediguanidine. 1. *From the dihydrochloride* the dinitrate was

prepared by the addition of the theoretical amount of AgNO_3 to the solution of dihydrochloride. The dipicrate was precipitated from an aqueous solution of the dihydrochloride. The chloroplatinate and dichloroaurate were also precipitated from the dihydrochloride in aqueous solution. The melting point and other properties are shown in table 2.

Table 2.

1. Salts of ethylenediguanidine

Salts	M.p. (°C)	M.p. (given by Schenck) (°C)	Crystal form (under microscope)
$\text{C}_4\text{H}_{12}\text{N}_6 \cdot 2\text{HCl}$	225		Aggregate of small cubic crystal
$\text{C}_4\text{H}_{12}\text{N}_6 \cdot 2$ picrate	287*	284–285*	Long needlelike prism (brownish yellow)
$\text{C}_4\text{H}_{12}\text{N}_6 \cdot 2\text{HNO}_3$	252	252	Thin plate
$\text{C}_4\text{H}_{12}\text{N}_6 \cdot \text{H}_2\text{PtCl}_6$	253	255–258	Small granules (orange yellow)
$\text{C}_4\text{H}_{12}\text{N}_6 \cdot 2\text{HAuCl}_4$	255	258	Large plate (golden yellow)

* Schenck reported that this dipicrate decomposed without melting. But the dipicrate obtained by the authors melts at this temperature.

2. Salts of tetramethylenediguanidine

Salts	M.p. (°C)	M.p. (given by Kiesel) (°C)	Crystal form (under microscope)
$\text{C}_6\text{H}_{16}\text{N}_8 \cdot 2\text{HCl}$	228, 234		Aggregate of small plate-shaped crystals
$\text{C}_6\text{H}_{16}\text{N}_8 \cdot 2$ picrate	253	253–254	Long needle (brownish yellow)
$\text{C}_6\text{H}_{16}\text{N}_8 \cdot 2\text{HNO}_3$	242		Plate
$\text{C}_6\text{H}_{16}\text{N}_8 \cdot \text{H}_2\text{PtCl}_6$	224	224	Small platelike granule (deep yellow)
$\text{C}_6\text{H}_{16}\text{N}_8 \cdot 2\text{HAuCl}_4$...	173	173	Small needlelike granule (light yellow)

2. *From free diguanidine* the carbonate was precipitated by passing CO_2 saturated with water vapour in the absolute alcoholic solution of diguanidine. The carbonate was converted to the sulphate by the addition of dil. H_2SO_4 . The dihydroiodide, adipate and sebacate were also prepared from the absolute alcoholic solution of diguanidine by the addition of HI and the alcoholic solution of adipic acid or sebacic acid. The melting point and other properties are described in table 3.

Polymerisation of ethylene- and tetramethylenediguanidine adipate or sebacate.

Table 3.

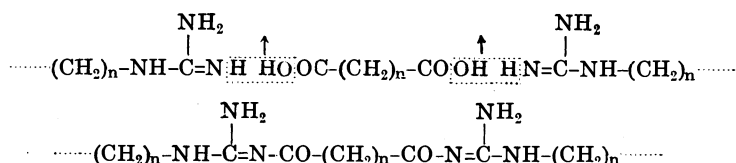
1. Salts of ethylenediguanidine

Salts	M.p. (°C)	M.p. (given by Schenck) (°C)	Crystal form (under microscope)
$\text{C}_4\text{H}_{12}\text{N}_6 \cdot \text{H}_2\text{CO}_3$	193		Long needle
$\text{C}_4\text{H}_{12}\text{N}_6 \cdot \text{H}_2\text{SO}_4$	278		Plate
$\text{C}_4\text{H}_{12}\text{N}_6 \cdot 2\text{HI}$	216	218–220	Large plate
$\text{C}_4\text{H}_{12}\text{N}_6 \cdot$ adipate	263		Small granules
$\text{C}_4\text{H}_{12}\text{N}_6 \cdot$ sebacate	217		Small granules

2. Salts of tetramethylenediguanidine

Salts	M.p. (°C)	M.p. (given by Kiesel) (°C)	Crystal form (under microscope)
$C_6H_{16}N_6 \cdot H_2CO_3$	202		Aggregate of small needlelike crystals
$C_6H_{16}N_6 \cdot H_2SO_4$	297	291	Spheric aggregate of small needle-shaped crystals
$C_6H_{16}N_6 \cdot 2HI$	199.5		Large plate
$C_6H_{16}N_6 \cdot \text{adipate}$	274		Fine blanching needle
$C_6H_{16}N_6 \cdot \text{sebacate}$	227		Small granules

Further, it was tested whether these diguanidine-dicarboxylic acid salts are able to form a fiber-forming polymer just as diamine-dicarboxylic acid salts by removal of the water formed in the reaction or not.



And it was found that this dehydration was difficult and imperfect compared with the case of diamine-dicarboxylic acid salts under same conditions and the thermal decomposition of diguanidine salt (into diamine salt and other comps.) occurred. (Heating in the absence of a solvent or diluent (fusion method) to reaction temperature (180–250°C) under the extremely reduced pressure (1 mm) or H_2 , N_2 atmosphere.)

The cause of this difficulty is probably due to the existence of the double bonds between carbon and salt-forming nitrogen in guanidine groups. According to preliminary experiments, the resulting polymers had fiber-forming property, but were somewhat soluble in hot water. (Ethylenediguanidine sebacate gave a polymer which was almost insoluble in water). These experiments are now being continued.

Summary.

(1) Ethylenediguanidine- and tetramethylenediguanidine dihydrochloride were prepared by the reaction of 3 mols of cyanamide with 1 mol of corresponding diamine dihydrochloride in fused state at about 140°C. The yield was about 100% of the theory.

(2) The dihydrochlorides were purified by the extraction with acetone which dissolved dicyandiamide.

(3) The method for preparing free diguanidines in crystal form is described.

(4) Various salts of these diguanidines were prepared from dihydrochlorides and free diguanidines and the melting point and other properties of these salts are also described.

In conclusion, the authors extend their thanks to the Department of Education and to Hattori Hoko Kwai for grants furnished to this research. Thanks are also due to Mr. M. Yamashita for carrying out the analytical work.

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Studies on Amino-Acids and Related Compounds. XV.* The Formation of Isovaleronitrile from Leucine by Electrolysis.

By Saburo MIDUNO and Yoshitaro TAKAYAMA.

(Received November 20, 1941.)

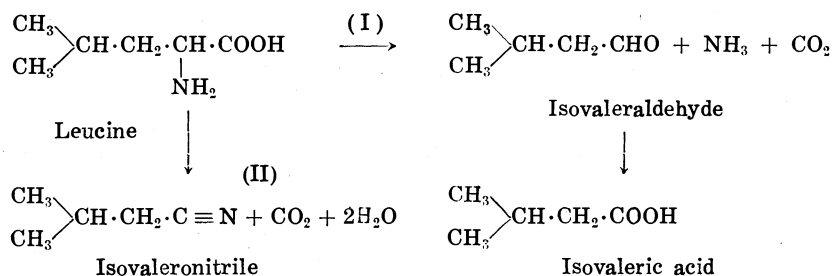
In Part XI⁽¹⁾ it was described that the electrolysis of leucine in dilute sulphuric acid at 100°, gave isovaleraldehyde as a main product and a little of isovaleric acid as well as a little of a neutral substance which had comparatively high boiling point. The present communication deals with the confirmation of the above-mentioned neutral substance as isovaleronitrile, and the conditions of its formation.

The neutral substance distilling over at 125–130° (as described in Part XI) was fractionated three times and the fraction, boiling at 128–129°, was collected. This fraction contained nitrogen on being hydrolised with sulphuric acid, and it gave isovaleric acid as well as ammonia and on being reduced with sodium and alcohol in toluene it gave isoamylamine.

From these facts the neutral substance was identified as isovaleronitrile, and the yield of the nitrile was only about 5% to isovaleraldehyde. Attempts were made to find the conditions which gave good yields of nitrile, and it was found that on the electrolysis of leucine in dilute sulphuric acid, mainly aldehyde was formed and the yield of the nitrile was small, while it was also found that the amount of the nitrile formed greatly increased, and gave the yield of about 30% of the nitrile to leucine⁽²⁾, when the acidity was kept as low as possible in the presence of sodium or ammonium sulphate.

It is known that amino-acids when oxidised by chloramine-T⁽³⁾ or sodium hypobromite⁽⁴⁾ give the corresponding nitriles. From the present experiments, it was found that also on electrolysis, leucine yielded isovaleronitrile and moreover gave good yields of nitrile under suitable conditions.

From these facts, it is quite probable that the electrolysis of leucine in dilute sulphuric acid proceeds in the following scheme (I and II).



* Translated by the authors from *J. Chem. Soc. Japan*, **62** (1941), 252.

(1) Part XI, this Bulletin, **12** (1937), 342.

(2) Japanese patent 134719.

(3) H. D. Dakin, *Biochem. J.*, **10** (1916), 319.

(4) A. H. Friedman and S. Morgulis, *J. Am. Chem. Soc.*, **58** (1936), 909.

See also Japanese patent 98556 (S. Komatsu).

In the electrolysis of leucine in dilute sulphuric acid, the aldehyde-formation (I) is the main reaction, but the electrolysis at an acidity as low as possible in the presence of sodium or ammonium sulphate is rather favourable to the nitrile-formation (II). These facts may be attributed to the amphoteric properties of the amino-acids. The formation of nitriles from other amino-acids by electrolysis will be reported in near future.

Experimental. It was already described in Part XI that when leucine was electrolysed in dilute sulphuric acid at 100°, yielded an oily substance. When this oil was extracted with alkali to remove isovaleric acid there remained a neutral part which consisted of mainly isovaleraldehyde and a little neutral substance boiling at 125–130°.

In the present experiments, the neutral substance (125–130°) was submitted to fractional distillation three times as shown in Table 1.

Table 1.

Fractions	Temperature (°C)	Distillate (g.)	Index of refraction n_D^{25}
1	125–127	2.1	
2	127–128	2.9	
3	128–128.2	8.0	
4	128.2–129	10.5	1.3904
5	129–130	5.1	1.3906

The fraction 3 had a sp. gravity $d_4^{19.5} = 0.79321$.⁽⁵⁾

1. Isovaleronitrile. Hydrolysis.—Formation of isovaleric acid and ammonia. The fraction 4 (0.2505 g.) boiling at 128.2–129, was refluxed in 20 c.c. of sulphuric acid (1:1) for 17 hours and distilled with addition of an excess of alkali to estimate nitrogen by Kjeldahl method (Found: N, 16.58%. Calc. for isovaleronitrile C_5H_9N : N, 16.80%).

The volatile base in the above distillate was identified as ammonia by the analysis of chloroplatinate (Found: Pt, 43.65%. Calc. for $(NH_4)_2PtCl_6$: Pt, 43.96%).

After the removal of the volatile base (NH_3) as described above, the residue was acidified with sulphuric acid and submitted to steam distillation to separate volatile acid. From the distillate silver salt was obtained as usual (Found: Ag, 51.87%. Silver isovalerate $C_5H_9O_2Ag$: Ag, 51.63%). Its anilide was also prepared, m.p. 111–112°. No lowering of melting point was observed when mixed with a pure specimen of the anilide of isovaleric acid.

Reduction.⁽⁶⁾—Formation of isoamylamine. Metallic sodium (10 g.) was melted in toluene (50 g.) on heating and a solution of the fraction 3 (6.1 g., b.p. 128–128.2) in absolute alcohol (12 g.) was added to it drop by drop with continual stirring. After 1 hour, absolute alcohol (12 g.) was added in the same way as above and then 97% alcohol (8 g.) was added to dissolve the excess of sodium. After adding water (7 g.), it was submitted to steam distillation. When concentrated hydrochloric acid (7 g.) was added to the distillate, an aqueous layer separated out. After distilling off the alcohol from the aqueous solution, the residue was evaporated up and hydrochloride (7.7 g.) was obtained. By the addition

(5) A. E. Arbusow, *Ber.*, **43** (1910), 2298 ($d_0^{20} = 0.7884$, b.p. 128.5).

(6) R. Adams and C. S. Marvel, *J. Am. Chem. Soc.*, **42** (1920), 314.

of alkali to the hydrochloride, free amine was obtained and fractionated as shown in Table 2.

Table 2.

Fraction	Temperature (°C)	Distillate (g.)
1	42-92	0.2
2	92-95	0.6
3	95-97	2.5
4	97	0.5
Total ..		3.8

The fraction 3 had a sp. gravity
 $d_4^{21.5} = 0.7483$.⁽⁷⁾

mine monooxalate $C_5H_{13}N \cdot C_2H_2O_4$: N, 7.90%).

From the facts described above, the neutral substance, boiling at 128-130°, was identified as isovaleronitrile. Its yield was about 5% to isovaleraldehyde.

2. Electrolysis of leucine under various conditions. To improve the yield of the nitrile, several attempts were made. For instance:

Leucine (25 g.) was dissolved in the mixture of $N-H_2SO_4$ (105 c.c., equivalent to leucine) and $N-Na_2SO_4$ (105 c.c.) and electrolysed at above 100°. The volatile oxidation products were collected in the distillate during the electrolysis as described in Part XI. The conditions of the electrolysis were as follows: Electrodes: lead peroxide anode (6.5×18.5 cm.), lead cathode (6.5×5 cm.). C. D.: 2 amps/dm.² Electric quantity: 4.7 F/mol. The voltage between electrodes: 3.1-3.3 volts.

The distillate consisted of an oily (10.3 g.)-and an aqueous (89 c.c.)-layers. The acidity of the electrolysed solution was 0.322N and its pH, 1.4. The content of the nitrile in oil (calculated from its nitrogen) was 28.5%. The oil (20 g.) of the distillate obtained by the same way as described above, was dissolved in ether and the corresponding aqueous layer was extracted with ether. The combined ethereal solution was treated with $N-NaOH$ to remove isovaleric acid and shaken with 30%- $NaHSO_3$ to remove isovaleraldehyde and then treated with 1% sodium carbonate. The ethereal solution thus obtained was dried over anhydrous sodium sulphate and submitted to fractional distillation as shown in Table 3.

The fraction 3 and 4 were combined and the nitrile was reduced to the isoamylamine by the same way as described above, and submitted to fractional distillation as shown in Table 4.

Isoamylamine oxalate was also prepared. It melted at 178°. The results of the electrolysis of leucine under various conditions are shown in Table 5.

(7) W. E. S. Turner and E. W. Merry, *J. Chem. Soc.*, **97** (1910), 2073 ($d_4^{20} = 0.7505$).

Isoamylamine-chloroplatinate and its oxalate. — Isoamylamine-chloroplatinate was prepared as usual. It decomposed at 215°. (Found: Pt, 33.20%. Calc. for $(C_5H_{13}N)_2H_2PtCl_6$: Pt, 33.41%). When the solution of anhydrous oxalic acid (0.35 g.) in ether (25 g.) was added to the ethereal solution of the amine (0.3 g.), white precipitate separated out. The precipitate was filtered, washed twice with ether, and recrystallised from 97% alcohol into plates, m.p. 178°. (Found: N, 7.76%. Calc. for isoamylamine monooxalate $C_5H_{13}N \cdot C_2H_2O_4$: N, 7.90%).

Table 3.

Fraction	Temperature (°C)	Distillate (g.)
1	44-110	0.4
2	110-126	1.0
3	126-128	3.9
4	128-128.3	0.5
5	residue	0.7
Total ..		6.5

The fraction 3 had sp. gravity
 $d_4^{30} = 0.7855$ (9)

Table 4.

Fraction	Temperature (°C)	Distillate (g.)
1	45-95.5	0.55
2	95.5-97	2.17
3	97	0.41
4	Residue	0.40
Total ...		3.50

The fraction 3 had sp. gravity
 $d_4^{30.5} = 0.7409$ (7)

Table 5.

No. of expt.	1	2	3	4	5	6
Electrolysate. (c.c.)	Sol. A. (200) + 2N-NaOH (15)	Sol. A. (133) + 2N-NaOH (20)	Sol. B. (220)	Sol. C. (220)	Sol. D. (210)	Sol. E. (210)
Leucine in the electrolysate. (g.)	19.19	11.24	24.6	26.7	24.9	22.45
Water added (c.c.)	91	100	100	85	91	—
C. D. (amps/dm ²)	2	2	2	2	2	2
F/mol.	3.67	6.25	2.86	2.63	4.70	5.28
Amp. × hours.	2.4 × 6	2.4 × 6	2.4 × 6	2.4 × 6	2.4 × 10	2.4 × 10
Volts.	4.0-4.5	4.7-5.0	3.3-3.4	4.1-4.0	3.1-3.5	3.4-3.8
pH (After electr.)	2.4	3.5	<1.0	2.0	1.4	—
H ₂ SO ₄ (N) (c.c.)	0.585 (210)	0.239 (215)	1.163 (215)	0.185 (197)	0.1675 (235)	— (206)
NH ₃ /T.N. (%)	95.5	98.0	82.2	83.6	100	—
Distillate oil (g.)	8.1	5.6	7.3	8.9	10.6	9.12
Percent to leucine. (%)	42.2	49.5	29.6	33.3	42.4	40.7
aq. layer (c.c.)	92	79	86	106	41	86
Nitrile (g.)	1.8	2.13	1.10	1.28	3.28 (3.60)*	2.96 (3.60)*
Percent to leucine. (%)	14.8	29.9	7.06	7.60	20.8 (24.0)*	20.8 (25.8)*

* and ** The quantity of isovaleronitrile or isovaleric acid in aqueous solution was combined.

Table 5.—(Concluded)

No. of expt.	1	2	3	4	5	6
Aldehyde (g.)	5.47	3.34	5.42	6.90	6.10	4.98
Percent to leucine. (%)	43.5	45.2	33.3	39.2	37.1	34.0
Isovaler. acid in oil. (g.)	0.83	0.125	0.785	0.725	0.24	1.18
Percent to leucine. (%)	5.57	1.40	4.08	3.95	5.95 (7.80)**	6.30 (10.5)**

Electrolysates:

Solution A.—To a solution of leucine (90 g.) in 2N-H₂SO₄ (305 c.c.) 2N-Na₂SO₄ (305 c.c.) was added.

Solution B.—Leucine (30 g.) was dissolved in 2N-H₂SO₄ (200 c.c.) and water (20 c.c.) was added to it.

Solution C.—Leucine (30 g.) was dissolved in N-H₂SO₄ (220 c.c.)

Solution D.—Leucine (60 g.) was added to 2N-H₂SO₄ (200 c.c.) and (NH₄)₂SO₄ (26.4 g., 0.2 mol) in water (200 c.c.) were mixed thoroughly and insoluble leucine (about 9 g.) was filtered off, then water (10 c.c.) was added. Thus, 444 c.c. of the solution was obtained. 210 c.c. of the solution contained 24.9 g. (0.19 mol) of leucine and the concentration of sulphuric acid was 0.922 N.

Solution E.—Leucine (52 g.) was dissolved in 2N-H₂SO₄ (200 c.c.) and Na₂SO₄ (32 g., 0.2 mol) in water (200 c.c.), was added and filtered. 210 c.c. of this solution contained 22.45 g. (0.17 mol) of leucine and the concentration of sulphuric acid was 0.913 N.

As it is shown in Table 5, the yields of the nitrile in the experiments, 1, 2, 3, 4, 5 and 6 were 14.8, 29.9, 7.06, 7.60, 20.8 and 20.8 respectively. The yields to 1 faraday per mol were 4.04, 4.78, 2.47, 3.05, 4.43 and 3.93% respectively. Thus, it was found that in the case of the higher acidity as in expt. 3, the yield was small, and in the case of the lower acidity, by the presence of Na₂SO₄ or (NH₄)₂SO₄ the yields were better. From the above experiments, it was found that the yields of isovaleronitrile could be increased if the electrolysis was carried out under suitable conditions.

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Studies on the Adsorption at the Solid—Liquid Interface. I. On the Adsorption of Some Fatty Acids by Glass.

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(Received November 25, 1941.)

Introduction. Numerous investigations have been carried out with regard to the adsorption of the solute molecules from solution on the solid surface, nevertheless, the information of the adsorption layer are rather scarce. The usual way of determining adsorption is to measure the amount of a dissolved substance which disappears from a known quantity of solution when it is brought into contact with the adsorbing powder. By such a method the adsorbed amount is estimated as the difference between two comparatively large quantities, and is, therefore, liable to be inaccurate unless the amount adsorbed is comparatively large. Investigators, consequently, have turned their attention principally to the adsorbents which have exceptionally great adsorbing power in order to simplify the experimental technique. Charcoal, or other porous substance such as silica gel has been used as the adsorbent in general. It is impossible, however, to interpret the results obtained on these substances, for practically nothing is known with the definiteness about surfaces of those substances. Moreover, the results obtained are considered to be composed of the overlapping of complex phenomena, that is the reason why called "sorption" instead of "adsorption."

The author has carried out some experiments with the hope that the phenomena may be treated as relatively simple matter, if a substance which has definite surface is used as adsorbent. As adsorbent which serves for such a purpose, powdered glass was used.⁽¹⁾

On the other hand, the problems of flotation, lubrication or the behavior of pigments suspended in oil, the informations of the adsorbed layer of a specific substance on the surface of solid materials are demanded for the practical purpose. On the surface of the general material, however, it is difficult to carry out the experiment on adsorption, since the amount adsorbed is too small.

The method hitherto used for this purpose consists of, e.g.⁽²⁾ the determination of the amount of solute by titration or weighing it directly after the complete evaporation of the solvent. As for such a method, the selection both for the solvent and the solute is limited.

The present author has determined the change of concentration of a solution before and after the adsorbing procedure, by measuring its

(1) The surface of the glass powder is not so simple as it has been expected at the beginning, and matters relating to this will be discussed in the next chance.

(2) Harkins and Gans, *J. Phys. Chem.*, **36** (1932), 86; Holmes and Thor, "Colloid Symposium Monograph. VII." 1930, p. 213; W. Ewing, *J. Am. Chem. Soc.*, **61** (1939), 1317.

density, using the float method. The float method⁽³⁾ of measuring density was used at the beginning, for the determination of the concentration of a binary solution. In recent years, however, it is used exclusively for measuring the amount of heavy water in common water, and the experimental technique has been improved by many investigators in connection with the studies of heavy water.

Experimental Procedure. A float, made of a boro-silicate glass, is put into the solution to be tested. By controlling the temperature of the solution, the float is made brought to suspension amid the solution. In this state, the density of the float and the solution is identical.

The apparatus is shown in Fig. 1. In this figure, S and S' are the thermostats, the temperature of the inner thermostat can be kept constant

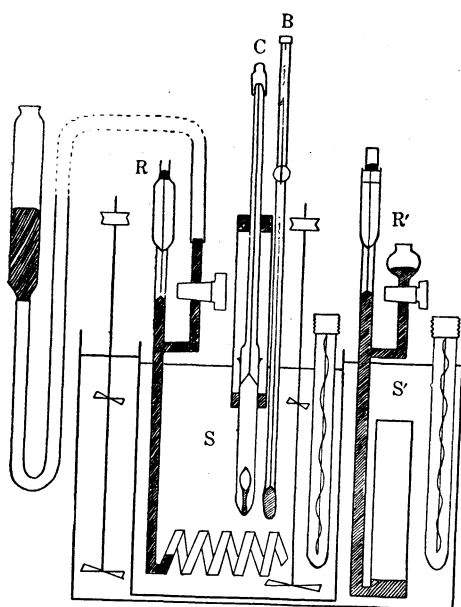


Fig. 1.

within the range of $\pm 0.002^{\circ}\text{C}$ by the regulator R. The temperature is controlled by increasing or decreasing the amount of mercury in the regulator which is connected to the mercury reservoir. C is the cell in which the solution to be tested and the float is contained. This cell and the float are made of boro-silicate glass (Terex glass). B is a Backmann thermometer. The motion of the float is observed through the telescope of a cathetometer. It is difficult to control just the temperature so as to keep the float in suspension amid the solution, and such temperature is found in the following way. Using a stop-watch the velocity of the float which moves up or down in the solution at a certain temperature is measured. From the temperature and the velocity curve, the temperature at

which velocity is zero will be found. This is the usual way of measuring the density of a solution by the float method.

When the liquid is benzene or toluene, owing to their large coefficient of expansion, the velocity of the motion of the float is relatively large even in the small range of the temperature. It is preferable that the length of the cell is long, on the other hand, the capacity of the cell is desired to be small for the saving of the solution used. From these reasons, the shape of the cell is quite slender and consequently the float too.

What we need is not the absolute value of the density of solution for the purpose of measuring the adsorption but only the relation between

(3) Richards and Shipley, *J. Am. Chem. Soc.*, **34** (1912), 599; Richards and Harris, *ibid.*, **38** (1916), 1000.

the concentration and the temperature at which the float stops in the solution. Practically this temperature is given by reading the Beckmann thermometer. By testing with a series of the solutions of known concentration, it has been found that there is a linear relation between the concentration and this temperature for a definite range of concentration. The experiment proceeds as follows, and its detailed description has been given in the preceding paper.⁽⁴⁾

A series of solutions of varying concentration is made. The density of each solution is measured and the relation between the density and the concentration is estimated. About 5 g. of adsorbent is taken in a test tube, and 10 c.c. of solution is introduced in the tube. The test tube is then hermetically sealed and is shaken at intervals. After about a week the upper liquid is taken out and separated thoroughly from adsorbent by the aid of centrifuge. The density of this upper liquid is measured and its concentration can be obtained from the known relation between the density and concentration. The amount adsorbed is given by the difference of the concentration of solution before and after the adsorbing procedure.

By the present method, as shown in the following section, it is possible to estimate the amount adsorbed in the order of 10^{-6} mol adsorbate per 1 g. of adsorbent. The accuracy will be better when the difference of the densities of components becomes larger.

In the present report, the experiments described are on the adsorption of some fatty acids from the toluene solution by the glass powder. The glass powder has been made by crushing the glass tubing, commonly used in the laboratory. The part between 100 and 140 mesh was selected and the small particles were removed by levigation. Then powder is washed with chromic acid mixture and consecutively with water. The powder thus obtained is designated as the "crushed" glass powder for the sake of convenience.

For each experiment, a part of this stock is taken and subjected to the following treatment. After washed in a Soxhlet apparatus with freshly distilled alcohol and then benzene, the powder is heated at 250–270°C. for about 6 hours under the reduced pressure by a rotary pump. The powder thus treated was used in the adsorption. The experiments were carried out at room temperature.

Results.

Results are shown in Table 1 and Fig. 2.

Table 1.

Solution	Weight of adsorbent (g.)	Initial concentration (g. in 100 c.c. solution)	Final concentration		Amount adsorbed by 1 g. adsorbent (Mol)
			(g. in 100 c.c. sol.)	Mol. in 1 l. sol.)	
Acetic acid/Toluen	5.724	0.1848	0.020	0.0033	4.8×10^{-5}
	6.873	0.3695	0.115	0.0192	6.2×10^{-5}
	6.989	0.739	0.360	0.0599	9.0×10^{-5}
	6.206	1.478	1.047	0.1744	11.6×10^{-5}

(4) H. Akamatu, *J. Chem. Soc. Japan*, **61** (1940), 470.

Table 1.—(Concluded)

Solution	Weight of adsorbent (g.)	Initial concentration (g. in 100 c.c. solution)	Final concentration		Amount adsorbed by 1 g. adsorbent (Mol)
			(g. in 100 c.c. sol.)	(Mol. in 1 l. sol.)	
Propionic acid/Toluene..	4.704	0.090	0.050	0.0068	1.1×10^{-5}
	4.690	0.180	0.133	0.0180	1.4×10^{-5}
	5.225	0.360	0.318	0.0429	1.1×10^{-5}
	4.356	0.478	0.466	0.0629	0.4×10^{-5}
	4.766	0.720	0.787	0.1063	-1.9×10^{-5}
	4.721	1.433	1.537	0.2076	-3.0×10^{-5}
Butyric acid/Toluene ...	4.773	0.1453	0.086	0.0098	1.4×10^{-5}
	5.473	0.2545	0.215	0.0244	0.8×10^{-5}
	5.438	0.2545	0.2025	0.0230	1.1×10^{-5}
	4.639	0.436	0.495	0.0562	-1.4×10^{-5}
	4.709	0.509	0.6125	0.0696	-2.5×10^{-5}
	4.314	1.018	1.1075	0.1258	-2.4×10^{-5}
Capric acid/Toluene ...	4.561	2.036	2.157	0.2449	-3.0×10^{-5}
	6.402	0.2218	0.035	0.0020	1.7×10^{-5}
	5.458	0.4435	0.292	0.0170	1.6×10^{-5}
	5.170	0.887	0.750	0.0436	1.5×10^{-5}
Palmitic acid/Toluene ..	5.296	1.774	1.708	0.0993	0.7×10^{-5}
	5.692	0.125	0.030	0.0012	0.7×10^{-5}
	4.915	0.250	0.085	0.0033	1.3×10^{-5}
	5.598	0.500	0.200	0.0078	2.1×10^{-5}
	5.671	1.000	0.720	0.0281	1.9×10^{-5}
Stearic acid/Toluene ...	4.989	2.000	1.675	0.0655	2.5×10^{-5}
	5.335	0.1085	0.077	0.0027	0.2×10^{-5}
	5.748	0.217	0.127	0.0045	0.6×10^{-5}
	5.439	0.434	0.220	0.0077	1.4×10^{-5}
Stearic acid/Toluene ...	6.027	0.868	0.360	0.0126	3.0×10^{-5}
	5.904	0.2663	0.197	0.0070	0.4×10^{-5}
	5.598	0.5325	0.487	0.0172	0.3×10^{-5}
	5.613	1.065	1.160	0.0411	-0.6×10^{-5}
	5.449	2.130	2.690	0.0953	-3.6×10^{-5}

Discussion. It is well known that, Traube's rule holds when fatty acids are adsorbed by charcoal (non-polar) from their aqueous solution (polar). However, on the other hand, the rule is reversed⁽⁵⁾ when they are adsorbed by silica gel (hetero-polar) from their solution in non-polar solvent such as toluene. The results given in this paper seem to have nothing to do with this rule. There seems to be three types of adsorption:—The type I, where the amount adsorbed increases with the increase of the concentration of the solution as in the case of acetic acid. The type II, where the adsorption is positive in the region of the low concentration of solution, while it is negative in the region of high concentration as in the case of propionic acid or butyric acid. The type III, where the

(5) Holmes and McKelvey, *J. Phys. Chem.*, **32** (1928), 1522; Bartell and Fu, *ibid.*, **33** (1929), 676.

amount adsorbed seems to be nearly saturated at some concentration of solution, as in the case of palmitic acid.

The type I and the type III are observed usually. The type III may be considered as the case of the monomolecular adsorption. If it is admissible to assume that the type III is the monomolecular adsorption, then the type I is the multi-layer ones. As to the type II, it can be expected that the propionic acid will be adsorbed positively from the solution of which solvent is non-polar liquid such as toluene. This is a case of

“polar and non-polar adsorption.” The type II is different also from the type of so-called “S” adsorption, for the transition happens in the region of very dilute concentration.

Primarily, the amount is given as only the difference of concentration of solutions before and after the adsorbing procedure, and consequently, in the case of the positive adsorption, the solvent molecules may be adsorbed with the solute molecules at the same time, and in the case of negative adsorption, the solute molecules may also be adsorbed with larger amount of the solvent molecules. The author, however, maintains the following opinion. It is plausible to think that, in the case of propionic acid and toluene, the layer directly contacts to the solid surface consists of propionic acid exclusively. When the adsorption layer of propionic acid is completed, however, the solid surface is covered by the electric double layers due to the dipoles of propionic acid, and consequently some other forces may be present on the adsorption of the second layer. So it is convenient to think about the first layer and the second layer separately with regard to the adsorbing forces. In the first layer, the adsorption proceeds in the relation directly between the solid surface and the adsorbate molecules, while in the second layer, between the first layer and the adsorbate molecules. In the latter case, the effect of the field due to the dipoles of the first layer may be considered as one of the causes of the adsorbing force. At all events, propionic acid is preferably adsorbed in the first layer directly and contacts to the solid surface, however, as soon as this first layer is completed, it will be another problem whether the solute molecules or the solvent molecules are adsorbed in the second layer. It must be noticed, in the results of this paper, that the positive adsorption always takes place at first which follows by the negative adsorption. It is also remarkable that the adsorption in the first layer takes place very readily still in the region of the low concentration of solution, except relatively large molecules such as palmitic acid or stearic acid.

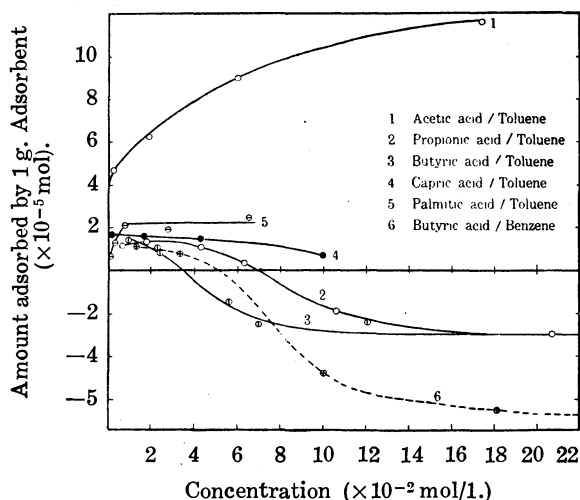


Fig. 2.

In the type I, acetic acid for example, the first, second and third layers etc. are all consisted of acetic acid. In the type II, propionic acid for example, after the first layer of the acid is completed, the solvent molecule, toluene, seems to be preferably adsorbed as the second layer. The results were similar, for the benzene solution instead of toluene. Table 2 shows the data obtained in the case of the solution of butyric acid in benzene, where the amount of the negative adsorption is somewhat greater than in the case of toluene solution.

Table 2. Butyric acid/Benzene.

Weight of adsorbent (g.)	Initial concentration (g. in 100 c.c. solution)	Final concentration		Amount adsorbed by 1 g. adsorbent (Mol.)
		(g. in 100 c.c. sol.)	(Mol. in 1 l. sol.)	
5.278	0.166	0.113	0.0128	1.1×10^{-5}
5.598	0.332	0.292	0.0332	0.8×10^{-5}
5.337	0.664	0.888	0.1008	-4.8×10^{-5}
5.174	1.328	1.625	0.1845	-6.5×10^{-5}
5.366	2.656	2.980	0.3384	-6.9×10^{-5}

If we assume that the negative adsorption is caused by the selective adsorption of the solvent molecules, then the adsorbed quantity of the solvent amounts enormously large to explain the results of Table 1 and 2. The amount, necessary to cover the surface of 1 g. of adsorbent is estimated roughly to be 2×10^{-5} mol. The calculation shows, from this figure, that the thickness of the adsorption layer of toluene, in the case of propionic or butyric acid solution, is about 100 molecular layers. For the solution of butyric acid in benzene, the corresponding figure attains 150 molecular layers. It is difficult to explain that such a large amount of solvent molecule is selectively adsorbed by a simple idea of the induction effect due to the field of dipoles in the first layer of propionic or butyric acid. No plausible explanation has yet been established.

In the type III, after the first layer is finished, neither the solute molecule nor the solvent molecule is adsorbed for the second layer. The type III may be constructed by the monomolecular adsorption. This assumption may not be far from the truth, since the author has carried out some investigations about the thickness of the adsorption layer and its description will be given in the next paper. In the case of palmitic acid, the effect of dipoles in the first layer will be too small to complete the second layer, for the length of hydrocarbon chain of the molecule is too long. Such an effect of the molecular length appears in the case of capric acid, where the negative adsorption proceeds in gradual manner. The satisfactory results have not been obtained by stearic acid, for its solubility in toluene is small. The solution of oleic acid in toluene belongs to the type II. In this case, oleic acid has a double bond in the middle part of the molecule, and seems to behave as a short molecule.

Summary.

(1) A method of determining relatively small amount of adsorption has been devised. To measure the change of concentration of solution

before and after the adsorbing procedure, the density determination using the float method is applied.

(2) The experiments are described on the adsorption of some fatty acids from the toluene solution by the glass powder.

In conclusion, the author wishes to express his sincere gratitude to Prof. Jitsusaburo Sameshima for his kind guidance and encouragement. The expense for the experiments has been defrayed by a grant given to Prof. Sameshima from Nippon Gakujutu Sinkokai (Japan Society for the Promotion of Scientific Research), to which the author's thanks are also due.

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Über die partielle Oxydation des Cholsäuremethylesters. (Untersuchungen über Sterine, XXVI.)

Von Satoru KUWADA und Syozo MORIMOTO.

(Eingegangen am 4. Dezember 1941.)

Bei der Dehydrierung des Cholsäuremethylesters mit Überschuss Aluminiumphenolat in kochendem Benzol-Aceton⁽¹⁾, konnten wir nur ein Dehydrierungsprodukt ($C_{25}H_{40}O_5$) vom Schmp. $171-172^\circ$ ⁽²⁾ erhalten. Es liefert ein Diacetat ($C_{26}H_{44}O_7$) vom Schmp. 193° , dessen Monoxim ($C_{26}H_{45}O_7N$) bei 178° schmilzt. Durch alkalische Verseifung der Kristalle vom Schmp. $171-172^\circ$ entsteht eine freie Säure ($C_{24}H_{38}O_5$, $[\alpha]_D^{25}$: $+37.20^\circ$) vom Schmp. 181° , aus der ein Diacetat ($C_{28}H_{42}O_7$) vom Schmp. 197° dargestellt wurde. Das Dehydrierungsprodukt des Cholsäuremethylesters ist daher der ein von den 3 theoretisch möglichen Monoketo-dioxy-cholansäuremethylestern.

Durch Chromsäure-Oxydation dieses Esters erhält man den bekannten Dehydrocholsäuremethylester vom Schmp. 239° und durch katalytische Reduktion den Cholsäuremethylester vom Schmp. 152° . Deshalb kann man sagen, dass während der obenerwähnten Dehydrierung keine sterische Umlagerung des Cholsäuremethylesters stattgefunden hat.

In der Literatur sind schon zwei Monoketo-dioxy-cholansäuren angegeben. Wie in der Tabelle 1 ersichtlich, stimmt aber unsere Monoketo-dioxy-cholansäure mit keinen bekannten Monoketo-dioxy-cholansäuren überein.

(1) *J. Pharmac. Soc. Japan*, **57** (1937), 247.

(2) Alle Schmelzpunkten sind unkorrigiert.

Tabelle 1.

Verbindungen	Freie Säure Schmp. u. $[\alpha]_D$	Acetat Schmp.	Acetyl-methyl- ester Schmp.
3.7-Dioxy-12-keto- cholansäure ⁽³⁾	218°, 219–220° +73–74°	221–222°	179°
3-Keto-7.12-dioxy- cholansäure ⁽⁴⁾	121–123°	197–198°	
Monoketo-dioxy-cholan- säure nach Kuwada und Mori.oto	181°, +37.20°	197°	191–193°

Das aus dem Monoketo-dioxy-cholansäuremethylester vom Schmp. 171–172° dargestellte Hydrazon wurde mit Kali-Pulver im Ölbad bei 150° erhitzt. Der durch Wasserzugabe ausgeschiedene Niederschlag wurde aus Essigester umgelöst, wobei die Nadeln ($C_{24}H_{40}O_4$, $[\alpha]_D^{25}$: +26.58–27.27°) vom Schmp. 206° entstanden. Diese Verbindung liefert einen Methylester vom Schmp. 151°, woraus einen Diacetyl-methylester vom Schmp. 146° entsteht. Die nach Kishner reduzierte Substanz ist also eine der Dioxy-cholansäuren. Mit keiner bekannten Dioxy-cholansäuren (Tabelle 2) stimmte aber die Säure vom Schmp. 206° überein, was wohl auf die verschiedene Konfiguration des Hydroxyls beruht.

Tabelle 2.

Verbindungen	Schmp. u. $[\alpha]_D$	Methylester Schmp.	Acetyl-methyl- ester Schmp.
Desoxycholsäure (3.12)	172° ^(5a)	95–97° ^(5b)	117° ^(5c)
α -Lago-desoxy- cholsäure (3.12) ⁽⁶⁾	156–157°, +80°	108°	
β -Lago-desoxy- cholsäure ⁽⁶⁾	213°, +37.4°	175°	
Iso-desoxy-cholsäure (7.12) ⁽⁷⁾	207–208°	54°	
β -Iso-desoxycholsäure (7.12) ⁽⁸⁾	226–227°	64°	
Cheno-desoxycholsäure (3.7) ⁽⁹⁾	140°, +11.1–13.2°		
Urso-desoxycholsäure (3.7) ⁽¹⁰⁾	203°, +44.5–51.1°		
Dioxy-cholansäure nach Kuwada und Morimoto	206°, +26.93°	151°	146°

Oxydiert man den Dioxy-cholansäuremethylester mit Chromsäure, so erhält man Diketo-cholansäuremethylester ($C_{25}H_{38}O_4$, $[\alpha]_D^{25}$: +15.96°)

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- (3) Borsche und Feske, *Z. physiol. Chem.* **176** (1928), 109.
 (4) Tai Sihk Sihn, *J. Biochem.* **27** (1938), 425.
 (5) a) Schlenck, *Z. physiol. Chem.*, **148** (1925), 223.
 b) Dane und Brady, *ibid.*, **244** (1936), 242.
 c) Wieland und Kapitel, *ibid.*, **212** (1932), 273.
 (6) Kishi, *ibid.*, **238** (1936), 210.
 (7) Wieland und Dane, *ibid.*, **210** (1932), 268 u. vgl. (2).
 (8) Wieland, Honold und Pascual-Vila, *ibid.*, **130** (1923), 326.
 (9) Windaus, Bohne und Schwarzenkopf, *ibid.*, **140** (1924), 167.
 (10) Kaziro, *ibid.*, **185** (1929), 151; **197** (1931), 206.

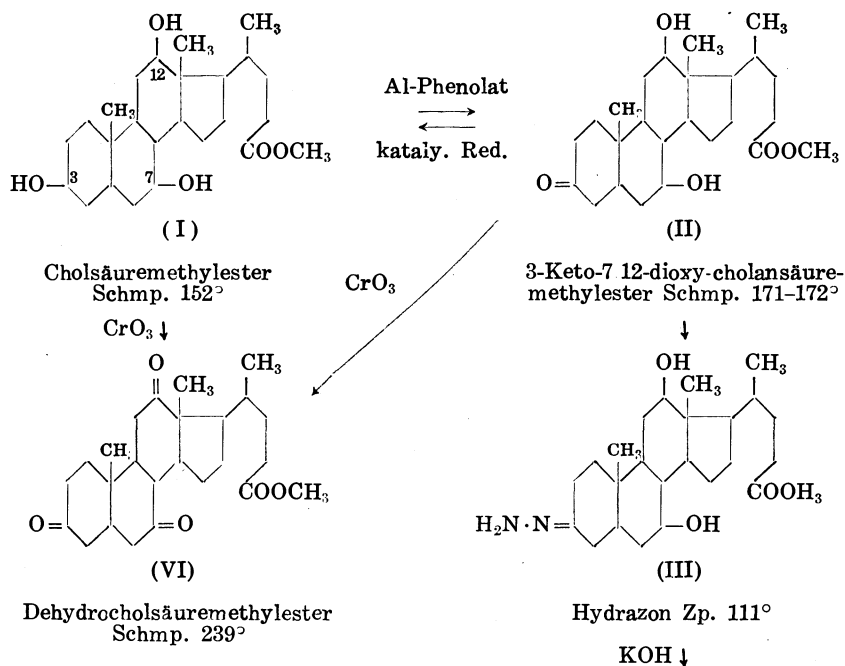
vom Schmp. 137–138°, der durch Verseifen eine freie Säure ($C_{24}H_{36}O_4$, $[\alpha]_D^{24}$: +16.10–16.36°) vom Schmp. 172° liefert. Die freie Säure bildet auch ein Dioxim vom Zp. 263°. Diese Diketo-cholansäure ist identisch mit 7.12-Diketo-cholansäure wie in der Tabelle 3.

Tabelle 3.

Verbindungen	Freie Säure Schmp. u. $[\alpha]_D$	Methylester Schmp. u. $[\alpha]_D$
3.7-Diketo-cholansäure	153° ⁽⁹⁾ 156° ⁽¹¹⁾ 161°, –33.6° ⁽¹⁰⁾	161–162°
3.12-Diketo-cholansäure ⁽¹²⁾	188–189°	136°
7.12-Diketo-cholansäure	176° ⁽¹³⁾ 171–172° ⁽⁸⁾ 176° ⁽¹⁴⁾	135°, +15.5°
Diketo-cholansäure nach Kuwada u. Morimoto	171–172°, +16.23°	137–138°, +15.95°

Aus diesen Ergebnissen wurde es sichergestellt, dass bei der Aluminiumphenolat-Dehydrierung des Cholsäuremethylesters nur die am C 3 ständige Hydroxylgruppe angegriffen wird und 3-Keto-7.12-dioxy-cholansäure-methylester entsteht.

Die vorliegende Arbeit wird daher schematisch wie folgt zusammengestellt:

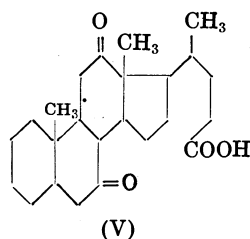


(11) Wieland und Jacob, *Z. physiol. Chem.*, **148** (1925), 232.

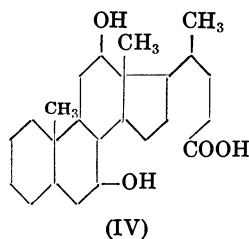
(12) Wieland und Borsche, *ibid.*, **106** (1919), 190.

(13) Borsche, *Ber.*, **52** (1919), 1352.

(14) Tschesche, *Z. physiol. Chem.*, **203** (1932), 263.



7,12-Diketo-cholansäure
Schmp. 172°



7,12-Dioxy-cholansäure
Schmp. 206°

Beschreibung der Versuche. *Cholsäuremethylester* (I). Die aus frischen Rindergallen isolierte Cholsäure wurde mit Methanol und konz. Schwefelsäure methyliert und der Methylester aus absol. Alkohol umgelöst. Schmp. 152° (Anhydrid). 47.7 mg Sbst., gelöst in Chloroform zu 3 ccm, 2 dm, 29°, α : +0.8°, $[\alpha]_D^{25}$: +25.15°.

Dehydrocholsäuremethylester (VI). Cholsäuremethylester wurde in Eisessig bei 35–40° mit 10%iger Chromsäure-Eisessiglösung oxydiert und das Oxydationsprodukt aus Essigester zweimal umkrystallisiert. Schmp. 239°.

Dehydrierung des Cholsäuremethylesters mittels Aluminiumphenolats: *3-Keto-7,12-dioxy-cholansäuremethylester* (II). 5 g Cholsäuremethylester wurden in 100 ccm Aceton gelöst und mit benzolischer Aluminiumphenolatlösung (dargestellt aus 3 g Aluminium-Amalgam und 15 g Phenol unter Zusatz von Spuren Sublimat und Jod) auf dem Wasserbade 10 Stdn. erhitzt. Die Reaktionslösung wurde dann nacheinander mit 10%iger Schwefelsäure und 10%iger Natronlauge geschüttelt. Beim Abdampfen des Benzols erhielt man einen krystallinischen Rückstand, der aus Aceton umgelöst wurde. Feine Säulen vom Schmp. 171–172°. ($\text{C}_{25}\text{H}_{40}\text{O}_5$. Ber. C 71.37, H 9.37, OCH_3 7.37. Gef. C 71.50, H 9.38, OCH_3 7.02.)

3-Keto-7,12-diacetoxy-cholansäuremethylester. Durch Erhitzen des 3-Keto-7,12-dioxy-cholansäuremethylesters mit Essigsäureanhydrid 3 Stdn. auf dem Drahtnetz erhielt man ein Diacetat, das aus Essigester in Nadeln vom Schmp. 193° krystallisiert. ($\text{C}_{29}\text{H}_{44}\text{O}_7$. Ber. C 69.00, H 8.79, OCH_3 6.14. Gef. C 69.05, H 8.46, OCH_3 6.09.)

3-Keto-7,12-dioxy-cholansäure. 3-Keto-7,12-dioxy-cholansäuremethylester wurde mit alkoholischen Kalilauge verseift und die freie Säure aus Essigester umgelöst. Schuppen vom Schmp. 181°. 0.0129 g Sbst., gelöst in absol. Alkohol zu 3 ccm, 2 dm, 29°, α : +0.32°. $[\alpha]_D^{25}$: +37.20°. ($\text{C}_{24}\text{H}_{38}\text{O}_5$. Ber. C 70.88, H 9.42. Gef. C 70.56, H 9.57.)

3-Keto-7,12-diacetoxy-cholansäure. Das durch Erhitzen der 3-Keto-7,12-dioxy-cholansäure mit Essigsäureanhydrid 2 Stdn. dargestellte Diacetat wurde aus Essigester umkrystallisiert. Nadeln vom Schmp. 197°. ($\text{C}_{28}\text{H}_{42}\text{O}_7$. Ber. C 68.52, H 8.63. Gef. C 68.38, H 8.75.)

Oxim des 3-Keto-7,12-diacetoxy-cholansäuremethylesters. 3-Keto-7,12-diacetoxy-cholansäuremethylester wurde in Alkohol mit Hydroxylaminacetat auf dem Wasserbad 2 Stdn. erwärmt. Nach der Wasserzugabe wurde der ausgeschiedene Niederschlag in Aether aufgenommen und der

Aetherrückstand aus Methanol umkrystallisiert. Nadeln vom Schmp. 178°. ($C_{29}H_{45}O_7N$. Ber. C 67.01, H 8.73, N 2.67. Gef. C 67.04, H 8.62, N 2.62.)

Chromsäure-Oxydation des 3-Keto-7.12-dioxy-cholansäuremethylesters: *Dehydrocholsäuremethylester* (VI). 3-Keto-7.12-dioxy-cholansäuremethylester wurde in Eisessig beim Zimmertemperatur mit Chromsäure oxydiert. Das Oxydationsprodukt krystallisiert aus Essigester in Nadeln vom Schmp. 239°. Sie zeigte bei der Misch-Schmp.-Bestimmung mit dem oben beschriebenen Dehydrocholsäuremethylester keine Schmp.-Erniedrigung. ($C_{25}H_{36}O_5$. Ber. C 72.06, H 8.72. Gef. C 71.83, H 8.33.)

Katalytische Reduktion des 3-Keto-7.12-dioxy-cholansäuremethylesters (II): *Cholsäuremethylester* (I). 1 g 3-Keto-7.12-dioxy-cholansäuremethylester und 1 g Platinoxid (nach Adams) wurden in 150 ccm Eisessig unter Wasserstoffstrom geschüttelt, wobei innerhalb 4 Stdn. 68 ccm Wasserstoff absorbiert wurden (theoretisch berechnet 53.3 ccm). Nach der Beendigung der Reduktion wurde die Eisessiglösung in Wasser hineingegossen, und der ausgeschiedene Niederschlag in Aether aufgenommen. Der Aetherrückstand wurde wiederholt aus absol. Alkohol umkrystallisiert. Säulen vom Schmp. 152°. 31.0 mg Sbst., gelöst in Chloroform zu 3 ccm, 2 dm, 29°, α : +0.52°, $[\alpha]_D^{25}$: +25.16°. ($C_{25}H_{42}O_5$. Ber. C 71.03, H 10.02. Gef. C 71.35, H 10.03.) Cholsäure.

Der obenerwähnte Ester wurde mit alkoholischen Kalilauge verseift, und das Verseifungsprodukt aus absol. Alkohol umgelöst. Säulen vom Schmp. 196°. 0.0843 g Sbst., gelöst in absol. Alkohol zu 10 ccm, 2 dm, 29°, α : +0.43°, $[\alpha]_D^{25}$: +25.50°. ($C_{24}H_{40}O_5$. Ber. C 70.53, H 9.87. Gef. C 70.76, H 10.18.)

Kishnersche Reduktion des 3-Keto-7.12-dioxy-cholansäuremethylesters: *7.12-Dioxy-cholansäure* (IV). 5 g 3-Keto-7.12-dioxy-cholansäuremethylester und 1 g Hydrazinhydrat wurden in 20 ccm absol. Alkohol 2 Stdn. auf dem Wasserbad erhitzt und beim Zimmertemperatur stehengelassen. Das ausgeschiedene rohe Hydrazon schmolz bei 111° (unter Zers.). 5 g Hydrazon wurden mit 10 g Kali-Pulver innig gemischt und im Ölbad unter Wasserstoffstrom bis 150° erhitzt, wobei die Entwicklung des Ammoniakgases deutlich bemerkt wird. Nach dem Aufhören der Ammoniak-Entwicklung wurde die Reaktionsmasse kaltgestellt und dann mit Wasser versetzt. Die Wasserlösung wurde angesäuert, der ausgeschiedene Niederschlag abfiltriert und in Aether aufgenommen. Aus Aceton, dann aus Essigester mehrmals umkrystallisiert, bildet der Aetherrückstand Nadeln vom Schmp. 206°. 23.70 mg, 18.70 mg Sbst., gelöst in absol. Alkohol zu 3 ccm, 2 dm, 21°, α : +0.42°, +0.34°, $[\alpha]_D^{25}$: +26.58°, +27.27°. ($C_{24}H_{40}O_4$. Ber. C 73.41, H 10.29. Gef. C 73.22, H 9.92.)

7.12-Dioxy-cholansäuremethylester. Der aus 7.12-Dioxy-cholansäure mit Methanol und konz. Schwefelsäure dargestellte Methylester wurde aus Methanol wiederholt umkrystallisiert. Nadeln vom Schmp. 151°. ($C_{25}H_{42}O_4$. Ber. C 73.83, H 10.42, OCH_3 7.62. Gef. C 74.06, H 10.28, OCH_3 7.30.)

7.12-Diacetoxy-cholansäuremethylester. Der nach der üblichen Weise mit Essigsäureanhydrid acetylierte 7.12-Dioxy-cholansäuremethylester krystallisierte aus Methanol als Nadeln vom Schmp. 145°. ($C_{29}H_{46}O_6$. Ber. C 70.97, H 9.45. Gef. C 70.71, H 9.33.)

Chromsäure-Oxydation des 7.12-Dioxy-cholansäuremethylesters:
7.12-Diketo-cholansäuremethylester. 3 g 7.12-Dioxy-cholansäuremethylester wurden in 30 ccm Eisessig gelöst und bei 27–31° unter Rühren innerhalb 1 Std. 10 ccm 10%iger Chromsäure-Eisessiglösung tropfenweise hinzugefügt und noch 1 Std. umgerührt. Der durch Wasserzugabe abgeschiedene Niederschlag wurde in Aether aufgenommen und der Aetherrückstand aus Methanol mehrmals umgelöst. Nadeln vom Schmp. 137–138°. 14.10 mg Sbst., gelöst in Chloroform zu 3 ccm, 2 dm, 25°, α : +0.15°, $[\alpha]_D^{25}$: +15.96°. ($C_{25}H_{38}O_4$. Ber. C 74.57, H 9.52, OCH_3 7.70. Gef. C 74.21, H 9.61, OCH_3 7.43.)

7.12-Diketo-cholansäure (V). 7.12-Diketo-cholansäuremethylester wurde mit alkoholischen Kalilauge verseift und das Verseifungsprodukt aus Alkohol umgelöst. Nadeln vom Schmp. 172°. 11.0 mg, 14.9 mg Sbst., gelöst in Chloroform zu 3 ccm, 2 dm, 24°, α : +0.12°, +0.16°, $[\alpha]_D^{25}$: +16.36°, +16.10°. ($C_{24}H_{36}O_4$. Ber. C 74.17, H 9.39. Gef. C 74.06, H 8.95.)

7.12-Diketo-cholansäure-dioxim. 7.12-Diketo-cholansäure wurde in Alkohol mit Hydroxylaminacetat erwärmt. Das durch Wasserzugabe ausgeschiedene Oxim wurde in Aether aufgenommen und der Aetherrückstand mehrmals aus Methanol umgelöst. Säulen vom Zp. 263°. ($C_{24}H_{38}O_4N_2$. Ber. C 68.85, H 9.15, N 6.69. Gef. C 68.88, H 9.19, N 6.95.)

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Untersuchungen über Flechtenstoffe. XCVII. Über ein neues Tridepsid „Hiascinsäure“.

Von Yasuhiko ASAHINA und Tunaharu KUSAKA.

(Eingegangen am 15. Januar 1942.)

Das Markgewebe der Flechte *Cetraria hiascens* Th. Fr. färbt sich sowohl mit Chlorkalk als auch mit Kalilauge purpurrot. Auf Grund ersterer Farbreaktion könnte man darin das Vorkommen eines Stoffs erwarten, welcher in seinem Molekül orcinähnlichen Kern besitzt. Beim Extrahieren der genannten Flechte aus Japan mit Aceton erhielten wir tatsächlich ein krystallinisches Produkt, welches jedoch nach der Mikro-Methode⁽¹⁾ geprüft, als Gemisch von wenigstens zwei Substanzen erkannt wurde. Durch den Krystall-Habitus unter Mikroskop wurde Gyrophor-

(1) Fortschritt der Chemie Organischer Naturstoffe, Bd. II, s. 53 (1939).

säure sicher nachgewiesen. Infolge wenig ausgeprägter Krystallform konnten wir aber den Rest mit keinem bekannten Flechtenstoff identifizieren.

Da das Krystallgemisch gegen Alkalien dem Oxyhydrochinon eigentlichen Farbreaktion aufweist, so lässt es sich schliessen, dass der zweite Bestandteil zum Oxyhydrochinon-Derivat gehört.

Dann haben wir das Depsid-Gemisch acetyliert und das Acetat-Gemisch aus Alkohol umgelöst, wobei wir im schwerlöslichen Anteil Tetraacetyl-gyrophorsäure und im leichterlöslichen Pentaacetyl-Derivat eines Tridepsids, welches um ein Sauerstoffatom mehr als Gyrophorsäure enthält, rein isolieren konnten. Wir nennen das neue Tridepsid „Hiascinsäure“; es ist nicht nur aus der Zusammensetzung $C_{24}H_{20}O_{11}$, sondern auch durch die Konstitutionsaufklärung der Zersetzungsprodukte als eine Oxy-gyrophorsäure anzusprechen. Die Trennung der freien Säuren lässt sich durch wiederholtes Umlösen aus Aceton bewerkstelligen, wobei sich die Hiascinsäure in der leichter löslichen Fraktion ansammelt.

Bei der Methanolyse nach Asahina und Akagi⁽²⁾ liefert die Hiascinsäure 5-Oxy-orsellinsäure-methylester (I, Schmp. 205°), Orsellinsäure-methylester (II, Schmp. 142°) und Orsellinsäure (III, Schmp. 185°). Vor kurzem liess Hiraiwa⁽³⁾ auf der von ihm zum erstenmal dargestellten 5-Oxyorsellinsäure Diazomethan nur kurze Zeit einwirken und hielt das so erhaltene Produkt vom Schmp. 154° für 5-Oxy-orsellinsäure-methylester von der Konstitution (I). Dies beruht auf einem Irrtum. Gegen Diazomethan ist die (4)-Hydroxylgruppe der 5-Oxyorsellinsäure fast ebenso reaktionsfähig wie Carboxylgruppe. Tatsächlich hat Hiraiwa 4-Methyläther-5-oxyorsellinsäuremethylester in Händen gehabt, was wir durch Synthese bewiesen haben.

Durch Einwirkung vom Ueberschuss Diazomethan nimmt Hiascinsäure fünf Methylene (statt sechs) auf und geht nur bis zum Tetramethyläthermethylester über. Das noch unangegriffen bleibende Hydroxyl widersteht den üblichen Methylierungsmitteln hartnäckig. Weder durch Jodmethyl und Kaliumcarbonat noch durch Jodmethyl und Silbercarbonat liess es sich methylieren. Bei der Hydrolyse des Tetramethylätherhiascinsäure-methylesters entstehen 2.4-Dimethyläther-5-oxy-orsellinsäure (IV, Schmp. 149°), Isoeverninsäure (V, Schmp. 149°) und Isoeverninsäure-methylester (VI, Schmp. 114°).

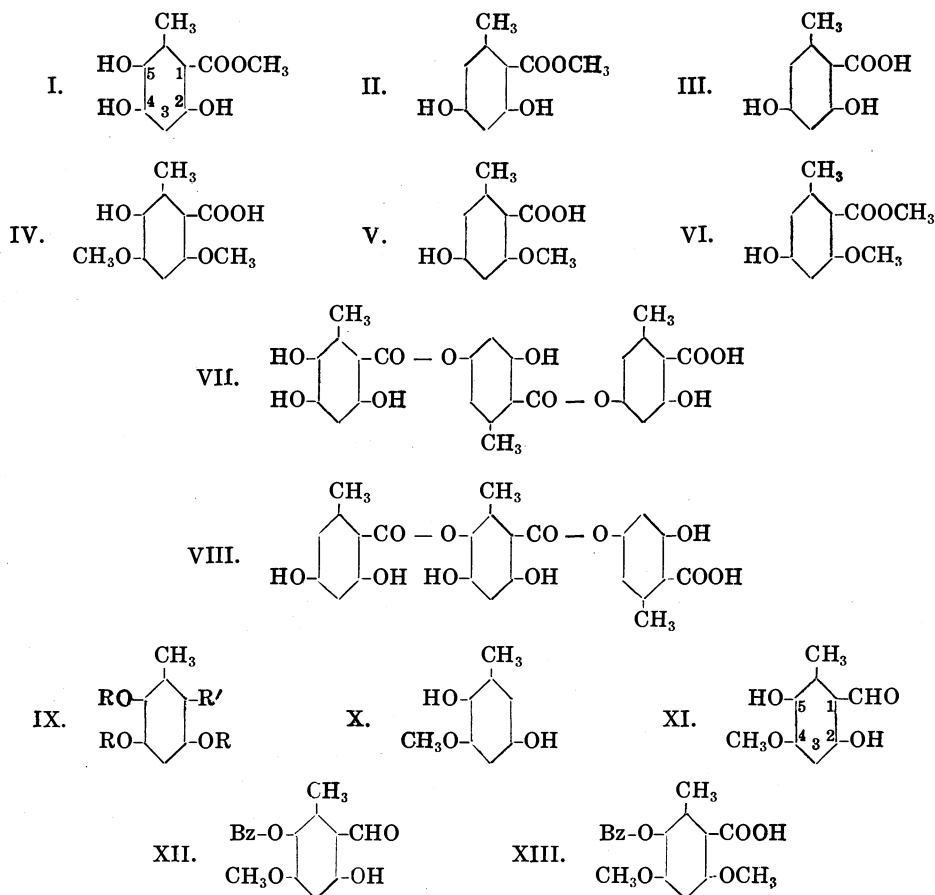
Hieraus folgt, dass sich die Hiascinsäure durch die Konstitution VII ausdrücken lässt. Eine alternative Formel VIII ist deshalb auszuschliessen, weil erstens die Hiascinsäure durch Barytlösung eine dem Oxyhydrochinon eigentümliche Farbenreaktion zeigt, zweitens der Tetramethyläther-methylester bei der Hydrolyse weder Dimethyläther-orsellinsäure noch Everninsäure liefert, welche sich aus VIII erwarten lassen.

Neulich hat der eine (Kusaka) von uns die Pentaacetyl- und Penta-carbäthoxy-hiascinsäure synthetisch dargestellt und die Konstitution VII für Hiascinsäure experimentell bewiesen.⁽⁴⁾

(2) *Ber.* **68** (1935), 1130.

(3) *J. Pharmaceut. Soc. Japan*, **60** (1940), 578.

(4) *J. Pharmaceut. Soc. Japan*, **61** (1941), 355.



Zur Synthese des 5-Oxy-orsellinsäure-methylesters (I) haben wir zunächst 5-Oxy-orsellinaldehyd (IX, R=H, R'=CHO) acetyliert, den so erhaltenen Triacetyl-oxy-orsellinaldehyd (IX, R=CH₃·CO, R'=CHO) zu Säure oxydiert und nach Veresterung mittels Diazomethans entacetyliert. Man kann auch die Hydroxyl-Gruppen des 5-Oxy-orsellinaldehyds mit Carbäthoxyl-Gruppen schützen, wobei aber die Ausbeute an Endprodukt weniger ausfällt. Andererseits um 2,4-Dimethyläther-5-Oxy-orsellinsäure darzustellen haben wir zunächst 3-Methyläther-2.3.5-trioxy-1-methylbenzol (X) nach Gattermann-Adams zum 4-Methyläther-5-oxy-orsellinaldehyd (XI) übergeführt. Wird nun der letztere nach dem Schützen der Hydroxyl-Gruppen oxydiert, so geht er in 4-Methyläther-5-oxy-orsellinsäure über, deren Methylester bei 154° schmilzt und mit dem von Hiraiwa⁽³⁾ für Methylester der 5-Oxyorsellinsäure gehaltenen identisch ist. Beim Benzoylieren geht der Aldehyd (XI) zum 5-Benzoyl-Derivat (XII) über, welches nach dem Methylieren und Oxydieren die Säure XIII liefert. Der Methylester der letzteren wird durch Entbenzoylieren in den Methylester der IV umgewandelt.

Extrahieren der Bestandteile von *Cetraria hiascens* Th. Fr. Beim Extrahieren von *Cetraria hiascens* gesammelt in Hokkaido: Daisetu-

Gebirge, mit Aceton wird ein krystallinisches Produkt erhalten. Ausbeute ca 4% bezogen auf Ausgangsmaterial. Löst man die Roh-Substanz unter Deckglas aus Glycerin-Eisessig um, so bemerkt man winzige Krystallwarzen, die in Gegenwart der Gyrophorsäure zum Vorschein kommen.

Wird das Krystall-Gemisch in Alkohol gelöst und mit einem kleinsten Tropfen Barytlösung versetzt, so färbt sich die Lösung rosarot, bei weiterem, vorsichtigem Zusatz von Barytlösung fällt einen grünen Niederschlag, der beim Umschwenken zu einer purpurroten Lösung aufgelöst wird.

Beim wiederholten Umlösen des Gemisches aus Aceton wurden zwei Hauptfraktionen erhalten.

Gyrophorsäure. Die in Aceton schwerer lösliche Fraktion besteht, nach der Mikro-Methode geprüft, aus Gyrophorsäure und einer anderen, noch unbekannten Substanz. Nun haben wir die Fraktion mittels Acetanhydrids unter Zusatz von Pyridin acetyliert und das Roh-Acetat wiederholt aus heissem Alkohol umgelöst. Das in Alkohol schwerer lösliche Acetat bildet, bei nochmaligem Umlösen aus Aceton farblose, feine Krystalle, die gleich wie Tetraacetyl-gyrophorsäure bei 228° unter Zersetzung schmelzen. Bei der Veresterung mittels Diazomethans in Aceton liefert das Acetat farblose Prismen vom Schmp. 202°. Eine Mischprobe mit dem Tetraacetylgyrophorsäure-methylester zeigte keine Schmp.-Depression. ($C_{33}H_{30}O_{14}$. Ber. C 60.88, H 4.65. Gef. C 60.97, H 4.81.)

In der von Tetraacetyl-gyrophorsäure befreiten, alkoholischen Mutterlauge verbleibt das Acetat der Hiascinsäure (s. u.).

Hiascinsäure. Die in Aceton leichter lösliche Fraktion des Krystallgemisches wurde so oft aus Aceton unter Wegschaffen des zuerst abzuschheidenden Anteils umgelöst, bis eine Probe unter Deckglas auf dem Objektträger aus Glycerin-Eisessig umkrystallisiert, keine Krystall-Aggregate der Gyrophorsäure mehr zeigte. Aus Alkohol umgelöst bildet die so gereinigte Substanz farblose, winzige Prismen, die bei 190.5° unter Zersetzung schmelzen. Sie ist in Aether, Benzol und Chloroform auch in der Wärme sehr schwer löslich, in Aceton und Alkohol in der Wärme leicht, in der Kälte schwer löslich. Die alkoholische Lösung wird durch Eisenchlorid blauviolett, durch Spuren Kalilauge rot gefärbt. Die oben citierte Reaktion durch Barytlösung wird mit derselben Lösung ausgeprägt hervorgerufen. Auch färbt sie sich mit Chlorkalk schön rot. ($C_{24}H_{20}O_{11}$. Ber. C 59.48 H 4.16. Gef. C 59.79, 59.40 H 4.54, 4.33.)

Methylester. Dargestellt durch Hinzufügen von berechneter Menge Diazomethan zur eiskalten Lösung von Hiascinsäure in Aceton-Aether und darauffolgendes Schütteln mit Bicarbonatlösung. Farblose Prismen vom Schmp. 144°. Die Farbenreaktion durch Alkalien sind dieselbe wie die freie Säure. ($C_{25}H_{22}O_{11}$. Ber. C 60.21 H 4.45 CH_3O 6.22. Gef. C 59.96 H 4.76 CH_3O 6.11.)

Pentaacetyl-hiascinsäure. Dargestellt durch Behandlung mit Acetonhydrid und Pyridin bei Zimmertemperatur. Farblose Prismen vom Schmp. 176–178° (u. Zers.) (aus Alkohol). ($C_{34}H_{30}O_{16}$. Ber. C 58.76 H 4.42. Gef. C 58.95 H 4.34. Mol. Gew.-Bestimmung nach Titrimethode. Ber. 694.2. Gef. 685.6, 702.5.)

Methylester der Pentaacetyl-hiascinsäure. Dargestellt durch Behandlung der acetylierten Säure mittels Diazomethans in Aceton. Farblose Prismen von Schmp. 213–214° (aus Alkohol). ($C_{37}H_{32}O_{16}$. Ber. C 59.28 H 4.55. Gef. C 59.38 H 4.59. Acetylbestimmung nach Pregl: Ber. 30.57. Gef. 30.68. Methoxyl-Bestimmung nach Mikro-Zeisel: Ber. 4.38. Gef. 3.97.)

Pentacarbäthoxy-hiascinsäure. Dargestellt durch Behandlung der Hiascinsäure mit Chlorkohlensäureäthylester in Aceton unter Pyridin-Zusatz. Farblose, rhombische Tafeln vom Schmp. 137° (aus Methanol); schwerlöslich in kaltem Aether, leicht löslich in Aceton und Benzol. ($C_{39}H_{40}O_{21}$. Ber. C 55.42 H 4.77. Gef. C 55.13 H 4.66.) Der Methylester bildet farblose, rhombische Tafeln vom Schmp. 175° (aus wasserhaltigem Aceton).

Tetramethyläther-hiascinsäure-methylester. Zunächst lässt man auf Hiascinsäure gelöst in Aceton Ueberschuss Diazomethan solange einwirken, bis sich eine Probe in Alkohol mit Eisenchlorid nicht färbt. Dann erhitzt man das Produkt gelöst in Aceton unter Zusatz von Jodmethyl und Kaliumcarbonat mehrere Stunden. Die so erhaltene Substanz bildet farblose, lange Tafeln vom Schmp. 212–213° (aus Alkohol). ($C_{29}H_{30}O_{11}$. Ber. C 62.78 H 5.45 CH_3O 27.98. Gef. C 63.02, 62.58 H 5.23, 5.28 CH_3O 28.31.)

Methanolyse der Hiascinsäure. Man löst 1.5 g Hiascinsäure in der Wasserstoffatmosphäre in 30 ccm 5 proz. methanolischer Kalilauge, lässt 2 Stdn. bei 40° stehen, säuert dann an und äthert aus. Man schüttelt den Aetherauszug mit Bicarbonatlösung und säuert die letztere sofort an, wobei sich eine Substanz (A) ausscheidet. Ausb. 0.5. Beim Verdampfen der entsäuerten, ätherischen Lösung bleibt ein nichtsaurer Bestandteil zurück (B). Ausb. 0.9 g.

Orsellinsäure (III): Das Spaltungsprodukt (A) bildet beim Umlösen aus verd. Methanol farblose Nadeln vom Schmp. 184–185° (u. Zers.). Der Methylester bildet farblose Prismen vom Schmp. 142°, der gemischt mit reinem Orsellinsäure-methylester keine Schmp.-Depression zeigte.

Orsellinsäure-methylester (II): Der nichtsaurer Bestandteil (B) wurde in 30 ccm warmem Benzol eingetragen und kurze Zeit digeriert, wobei ein Teil (C) ungelöst zurückblieb. Das benzolische Filtrat hinterliess beim Verdampfen einen Rückstand, der aus Methanol umgelöst farblose Prismen vom Schmp. 142° bildet und sich durch Misch-Schmp.-Bestimmung als Orsellinsäure-methylester erwies.

5-Oxy-orsellinsäure-methylester (I). Das in Benzol schwerlösliche Produkt (C) bildet beim Umlösen aus verdünntem Methanol farblose, hexagonale Tafeln vom Schmp. 205°. Die alkoholische Lösung entfärbt zunächst Eisenchloridlösung, färbt sich aber bei weiterem Zusatz der letzteren dunkelbraun. Bei vorsichtigem Zusatz von Barytlösung färbt dieselbe Lösung zunächst hellrot, fällt dann einen grünen Niederschlag, der beim Umschwenken zu einer roten Lösung aufgelöst wird. ($C_9H_{10}O_5$. Ber. C 54.55 H 5.05. Gef. C 54.31 H 4.95.)

Durch Vergleich wurde die Identität des Produktes (C) mit dem synthetischen 5-Oxy-orsellinsäure-methylester festgestellt. Das Triacetat des 5-Oxy-orsellinsäure-methylesters bildet farblose Prismen vom Schmp. 146–147° (aus Methanol). ($C_{15}H_{16}O_8$. Ber. C 55.56 H 4.97. Gef. C 55.63 H 4.91.)

Hydrolyse des Tetramethyläther-hiascinsäure-methylesters. 0.8 g Tetramethyläther-hiascinsäure-methylester werden in 10 g eiskalter, konz. Schwefelsäure gelöst, nach 1/4 stündigem Stehen mit Eiswasser übergossen und ausgeäthert. Der Aetherauszug wird mit Bicarbonatlösung geschüttelt, die Lösung angesäuert und ausgeäthert. Beim Verdampfen des letzteren Aetherextrakts verbleibt 0.52 g krystalliner Rückstand, der durch Digerieren mit 10 ccm warmem Benzol in zwei Bestandteilen getrennt. Ausb. des darin schwerlöslichen (B) 0.25 g, des leichterlöslichen (C) 0.18 g.

Der entsäuerte, primäre Aetherauszug hinterlässt beim Verdampfen einen Rückstand (A). Ausb. 0.25 g.

Isoeverninsäure-methylester (VI). Das Spaltungsprodukt (A) bildet beim Umlösen aus Petroläther farblose Prismen vom Schmp. 114°. Eine Mischprobe mit reinem Isoeverninsäure-methylester zeigte keine Schmp.-Depression. ($C_{10}H_{12}O_4$: Ber. C 61.19 H 6.17. Gef. C 61.14 H 6.17.)

Isoeverninsäure (V). Das Spaltungsprodukt (C) bildet beim Umlösen aus Essigester+Ligroin farblose Prismen vom Schmp. 175° (u. Zers.). ($C_9H_{10}O_4$. Ber. C 59.31 H 5.53. Gef. C 59.14 H 5.66.) Der daraus dargestellte Methylester schmolz bei 114°. Eine Mischprobe mit dem Isoeverninsäure-methylester zeigte keine Schmp.-Depression.

2-4-Dimethyläther-5-oxy-orsellinsäure (IV). Das in Benzol schwerlösliche Spaltungsprodukt (B) bildet bei wiederholtem Umlösen aus Benzol farblose Prismen vom Schmp. 147–149° (u. Zers.). In Alkohol und Aceton leicht, in heissem Benzol ziemlich löslich. Die alkoholische Lösung färbt sich mit Eisenchlorid nicht. ($C_{10}H_{12}O_5$. Ber. C 56.57 H 5.73. Gef. C 56.60 H 6.00.) Der Methylester (dargestellt durch Behandeln von (IV) mit Diazomethan) bildet farblose, lange Prismen vom Schmp. 114–115°. Er löst sich in Sodalösung nicht, wohl aber in Alkalilauge. Die alkohol. Lösung färbt sich mit Eisenchlorid nicht. ($C_{11}H_{14}O_5$. Ber. C 58.37 H 6.24. Gef. C 58.28 H 6.16.)

Trimethyläther-5-oxy-orsellinsäure-methylester. Beim Digerieren von (IV) in Aceton unter Zusatz von Jodmethyl und Kaliumcarbonat wird erst das noch intakt gebliebene Hydroxyl methyliert. Farblose Blättchen vom Schmp. 69–71° (aus Petroläther). In Alkohol, Aether, Aceton und Benzol leicht löslich, in kalter Kalilauge unlöslich. ($C_{12}H_{16}O_5$. Ber. C 59.96 H 6.71. Gef. C 60.03 H 6.59.)

Synthese der Derivate von 5-Oxy-orsellinsäure. *Trimethyläther-5-oxy-orsellinaldehyd* (IX, $R=CH_3$, $R'=CHO$): 3 g 2.4.5-Trioxy-6-methylbenzaldehyd. (1)⁽⁵⁾ werden in 15 ccm Methanol gelöst und in der Wasserstoffatmosphäre 13 g Dimethylsulfat und 24 ccm 20 proz. Natronlauge abwechselnd hinzugefügt. Das so ausgeschiedene Permethylyat (3 g)

(5) Hiraiwa, J. Pharmaceut. Soc. Japan, 60 (1940), 577.

bildet farblose Prismen vom Schmp. 104° (aus Methanol). Die alkohol. Lösung färbt sich mit Eisenchlorid nicht. ($C_{11}H_{14}O_4$. Ber. C 62.85 H 6.66. Gef. C 62.89 H 6.58.)

Trimethyläther-5-oxy-orsellinsäure (IX, $R=CH_3$, $R'=COOH$): Dargestellt durch Oxydieren von zugehörigen Aldehyd (s. o.) mittels Kaliumpermanganats in Aceton. Farblose, hexagonale Tafeln vom Schmp. $147-149^{\circ}$ (aus Benzol). Ziemlich schwerlöslich in Aether. ($C_{11}H_{14}O_5$. Ber. C 58.37 H 6.24. Gef. C 58.11 H 6.58.)

Der Methylester bildet farblose Blättchen vom Schmp. $69-71^{\circ}$ (aus Petroläther). Eine Mischprobe mit dem aus Tetramethyläther-hiascinsäure-methylester dargestellten zeigte keine Schmp.-Depression. ($C_{12}H_{16}O_5$. Ber. C 59.96 H 6.71 CH_3O 51.67. Gef. C 59.91 H 6.52 CH_3O 51.40.)

4-Methyläther-5-oxy-orsellinaldehyd (XI). 2.5 g 2-Methoxy-6-methylhydrochinon⁽⁶⁾ (X) werden in 30 ccm abs. Aether gelöst und unter Zusatz von 10 g Zinkcyanid mit trockner Salzsäuregas gesättigt. Beim Kochen mit Wasser scheidet sich der Aldehyd krystallinisch aus. Ausb. 2.4 g. Gelbe Prismen vom Schmp. 162° (aus Wasser oder Methanol). Ziemlich schwerlöslich in heissem Wasser. Die alkohol. Lösung färbt sich mit Eisenchlorid grün. ($C_9H_{10}O_4$. Ber. C 59.31 H 5.53. Gef. C 59.26 H 5.59.)

4-Methyläther-5-benzoyloxy-orsellinaldehyd (XII). 0.5 g Aldehyd (XI) werden in 5 ccm Aceton gelöst und unter Zusatz von 15 ccm n-NaOH und 0.5 g Benzoylchlorid (gelöst in 5 ccm Aceton) in der Wasserstoffatmosphäre geschüttelt. Man säuert die Lösung an, äthert aus und verdampft den mit Sodalösung gewaschenen Aether-auszug. Ausb. 0.5 g. Farblose Prismen vom Schmp. $142-143^{\circ}$ (aus Methanol). Die alkohol. Lösung färbt sich mit Eisenchlorid weinrot. ($C_{16}H_{14}O_5$. Ber. C 67.07 H 4.93. Gef. C 66.08 H 4.85.)

2.4-Dimethyläther-5-benzoyloxy-orsellinaldehyd. Dargestellt aus (XII) durch Behandlung mit Jodmethyl und Silberoxyd in Aceton. Farblose Prismen vom Schmp. $163-164^{\circ}$ (aus Methanol). Die alkohol. Lösung färbt sich mit Eisenchlorid nicht. Die Krystalle sind stark phototropisch, färben sich am Sonnenlicht gelb. ($C_{17}H_{16}O_5$. Ber. C 67.97 H 5.37. Gef. C 68.22 H 5.55.)

2.4-Dimethyläther-5-benzoyloxy-orsellinsäure (XIII). Dargestellt aus dem oben erhaltenen Aldehyd durch Oxydieren mit Permanganat in Acetonlösung. Farblose Prismen vom Schmp. 216° (aus Methanol). ($C_{17}H_{16}O_6$. Ber. C 64.53 H 5.11. Gef. C 64.41 H 5.44.) Der zugehörige Methylester bildet farblose, hexagonale Tafeln vom Schmp. $156-157^{\circ}$. ($C_{18}H_{18}O_6$. Ber. C 65.42 H 5.49. Gef. C 65.42 H 5.51.)

2.4-Dimethyläther-5-oxy-orsellinsäure-methylester (Methylester von IV). Man löst XIII in konz. Schwefelsäure, lässt bei 0° $1\frac{1}{2}$ Stunde stehen und giesst die Lösung ins Eiswasser. Farblose Prismen vom Schmp. $114-115^{\circ}$ (aus Ligroin). Identisch mit dem aus Tetramethyläther-hiascinsäure-methylester erhaltenen. ($C_{11}H_{14}O_5$. Ber. C 58.37 H 6.24. Gef. C 58.77 H 6.09.)

(6) Henrich, Nachtigall, Ber. **36** (1903), 894.

2.5-Diacetat des 4-Methyläther-5-oxy-orsellinaldehyds (1-Methyl-2.5-diacetoxy-benzol-1-aldehyd). Dargestellt durch Behandeln von (XI) mit Acetanhydrid und Pyridin. Farblose Prismen vom Schmp. 130–131° (aus Ligroin). ($C_{13}H_{14}O_6$. Ber. C 58.62 H 5.30. Gef. C 58.63 H 5.49.)

2.5-Diacetat der 4-Methyläther-5-oxy-orsellinsäure. Dargestellt durch Oxydieren von oben erhaltenem Aldehyd mit Permanganat in Aceton. Farblose Prismen vom Schmp. 160–161° (u. Zers.) (aus Benzol). ($C_{13}H_{14}O_7$. Ber. C 55.29 H 5.00. Gef. C 54.76, H 5.33.)

2.5-Diacetat des 4-Methyläther-5-oxy-orsellinsäure-methylesters. Dargestellt aus dem oben erhaltenen mittels Diazomethans. Farblose Blättchen vom Schmp. 170° (aus Methanol). ($C_{14}H_{16}O_7$. Ber. C 56.73 H 5.44. Gef. C 56.39 H 5.64.)

4-Methyläther-5-oxy-orsellinsäure-methylester. Man löst das oben erhaltene Diacetat des Methylesters in konz. Schwefelsäure, lässt bei 0° 20 Minuten stehen und giesst die Lösung ins Eiswasser ein. Farblose Prismen vom Schmp. 154° (aus Methanol). Die alkohol. Lösung färbt sich mit Eisenchlorid grün. ($C_{10}H_{12}O_5$. Ber. C 56.57 H 5.70 CH_3O 29.26. Gef. C 56.30 H 5.97 CH_3O 29.24.)

Triacetat des 5-Oxy-orsellinaldehyds. Dargestellt durch Behandeln von 5-Oxy-orsellinaldehyd mit Acetanhydrid und Pyridin. Farblose Blättchen vom Schmp. 109–110° (aus Benzol [2 Vol.] + Ligroin [1 Vol.]). Phototropisch, färbt sich am Licht gelb. ($C_{14}H_{14}O_7$. Ber. C 57.12 H 4.79. Gef. C 57.33 H 4.91.)

Triacetat der 5-Oxy-orsellinsäure. Dargestellt durch Oxydieren von oben erhaltenem Aldehyd mittels Permanganat in Aceton. Farblose Prismen vom Schmp. 146–147°. ($C_{14}H_{14}O_8$. Ber. C 54.17 H 4.54. Gef. C 54.41 H 4.39.)

Triacetat des 5-Oxy-orsellinsäure-methylesters. Dargestellt durch Einwirkung von Diazomethan auf dem oben erhaltenen Säure. Farblose Prismen vom Schmp. 146–147°. ($C_{15}H_{16}O_8$. Ber. C 55.56 H 4.97. Gef. C 55.24 H 5.17.)

5-Oxy-orsellinsäure-methylester (I). Man löst das oben erhaltene Triacetat des Methylesters in konz. Schwefelsäure, lässt bei 0° 30 Minuten stehen und giesst die Lösung ins Eiswasser ein. Farblose, hexagonale Tafeln vom Schmp. 205°. Die alkoholische Lösung färbt sich mit viel Eisenchlorid dunkelbraun, mit Spuren Barytwasser hellrot, fällt bei weiterem Zusatz des letzteren einen grünen Niederschlag, welcher beim Umschwenken zu einer roten Lösung aufgelöst wird. Eine Mischprobe mit dem aus der Hiascinsäure durch Methanolyse erhaltenen zeigte keine Schmp.-Depression. ($C_9H_{10}O_5$. Ber. C 54.55 H 5.05 CH_3O 15.66. Gef. C 54.36 H 5.20 CH_3O 15.87.)

Studies on the Adsorption at the Solid-Liquid Interface. II. On the Thickness of the Adsorption Layer.

By Hideo AKAMATU.

(Received November 25, 1941.)

Among many problems regarding the constitution of the adsorption layer, the problem on the thickness of the layer is still attractive. Since the theory of monomolecular adsorption was proposed by Langmuir, this is believed in general, notwithstanding the fact that the direct experimental proof is rather poor especially in the case of the solid-liquid interface. There are several investigations⁽¹⁾ which prove the monomolecular adsorption. However, most of them contain many assumptions in themselves. This problem may be solved if we know directly the surface area of the adsorbent and the adsorbed amount on that surface. Fortunately, the author has been able to measure relatively small amount of adsorption as well as the surface area of glass by making the glass powder of spherical particles.

Preparation of Adsorbent (Spherical Glass Powder). Spherical glass powder has been made by the method which was devised by Bloomquist and Clark,⁽²⁾ with some modifications.

The apparatus which is shown in Fig. 1, consists of two parts, i.e., the part in which the powder is heated with gas flame to melt the particles into spherical shapes, and the other part in which the powder is collected by a suction apparatus combined with an electric precipitator.

The glass powder has been made by crushing glass tubing commonly used in the laboratory. After the large particles have been roughly removed by levigation, the powder is thoroughly dried. A part of them is taken in a vessel, driven into gas flame with compressed air (Fig. 1.), and particles are melted into spherical shapes. Those particles are collected by a suction motor which is connected to an electric precipitator. The precipitator is made of L shaped glass pipe and its diameter is about 4 cm. By using a neon-transformer, electric potential is applied between a copper wire which is hanging in the pipe and a tin-foil which covers

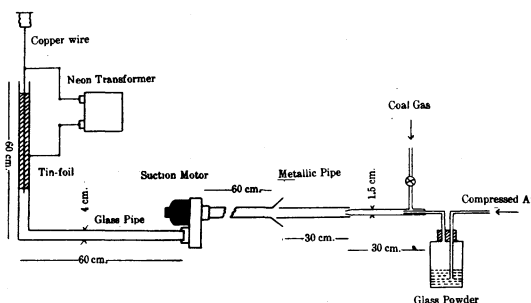
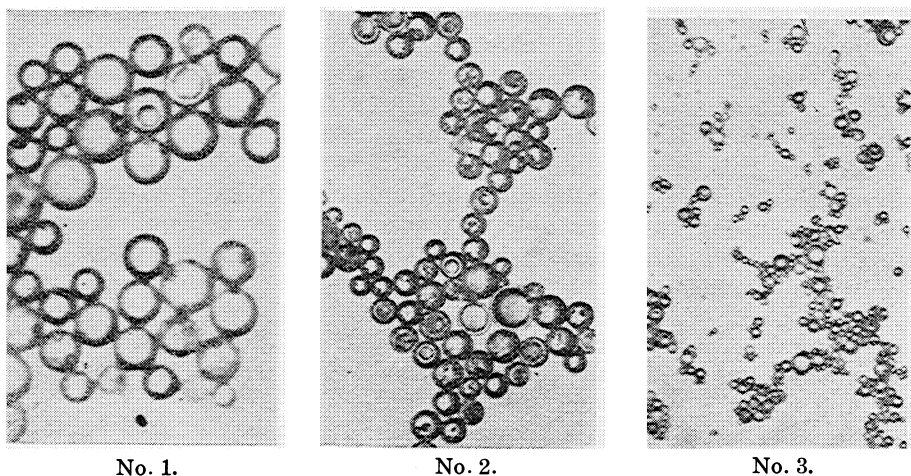


Fig. 1.

(1) Freundlich, "Kapillarchemie," 1930, P. 320; Harkins and Gans, *J. Phys. Chem.*, **36** (1932), 86; W. Ewing, *J. Am. Chem. Soc.*, **61** (1939), 1317; Fowkes and Harkins, *J. Am. Chem. Soc.*, **62** (1940), 3377.

(2) Bloomquist and Clark, *Ind. Eng. Chem.*, **12** (1940), 61.

a part of the pipe. After the particles have been captured, the precipitator is taken down, and the particles are poured out with water. In order to remove dust-like substances, the powder has been treated with dilute hydrochloric acid, then with chromic acid mixture and washed with water. As the powder consists of various size of particles, they have been collected in the following three parts by fractional levigation and used as adsorbents. No. 1 is the portion of which particles have settled in the water column, about 30 cm. in height, in 5–20 minutes, No. 2, in 20–40 minutes, and No. 3, in 40 minutes to 24 hours. Fig. 2 is the microscopic photographs of these three portions.



Microscopic photographs of glass powder. ($\times 300$)

Fig. 2.

The specific surface area (S) of the spherical powder is calculated by

$$S = 6 \sum D^2 / \rho \sum D^3,$$

where D is the diameter of each particle, and ρ , the density (2.50 for the glass used). The particle size was measured on the microscopic photograph, where the readings of the diameters of 550 particles for No. 1, 700 particles for No. 2, and 2000 particles for No. 3 were taken, and the average specific surface areas for 1 g. of powder were calculated as follows; No. 1: 1070 cm.², No. 2: 1810 cm.², No. 3: 4690 cm.².

For each experiment, the adsorbent is subjected to the following treatment. After washed with freshly distilled alcohol and benzene respectively, using a Soxhlet apparatus, the powder is heated at 250°–270°C for about 6 hours under the reduced pressure of a rotary pump.

Adsorption of Benzoic Acid. One of the methods of measuring the small amount of adsorption consists in determining the change of concentration of a solution before and after the adsorbing procedure by measuring its density, the float method being used. The description of

this method was given in the preceding paper.⁽³⁾ The accuracy of this method will be greater when the difference of the densities of components of solution used becomes larger. Expecting the so-called "polar and non-polar adsorption" to take place, benzoic acid is used as the solute while benzene as the solvent.

Benzoic acid used was the product designated "Kahlbaum to analysis" and benzene was purified in ordinary way. The experimental procedure was just like as described in the preceding paper. The experiments were also carried out at room temperature.

At first, the powder No. 1 was used as adsorbent, however, the density difference of solution before and after the adsorbing procedure was so small as in the order of the error of this method, and it might also be expected if the adsorption layer, in this case, be so thin as one molecular in thickness. To investigate the amount adsorbed by this method, larger surface area will be necessary. So, the powder No. 3 was next used as adsorbent, and the results obtained are shown in Table 1.

Table 1.

Adsorbent: Spherical glass powder No. 3.					
Solution : Benzoic acid/Benzene.					
Volume of Solution (c.c.)	Weight of adsorbent (g.)	Initial conc. (mol/l.)	Final conc. (mol/l.)	Amount adsorbed per 1 g. adsorbent (mol)	Area occupied by one molecule
10	5.244	3.56×10^{-2}	3.39×10^{-2}	3.1×10^{-6}	25 sq. Å
10	5.167	1.78 "	1.66 "	2.1 "	38 "
10	5.370	0.89 "	0.74 "	2.8 "	27 "

Adsorption of Palmitic Acid. Palmitic acid, as a typical surface active substance, has been chosen as the second adsorbate. But in this case, a good result in accuracy cannot be expected by the float method, for the difference of density between palmitic acid and benzene is not so large. The surface balance method has been devised instead of the float method to investigate smaller amount of change in concentration of solution before and after the adsorbing procedure.

The principle of the surface balance method is as follows. A definite volume of benzene solution of palmitic acid of known concentration is put on the surface of water. The solution spreads over the surface and, soon after, benzene will evaporate up leaving the monomolecular film of palmitic acid. The surface area of this film can be determined by the surface balance, under a certain surface pressure. Next, exactly the same volume of the solution of unknown concentration (e.g. the solution after the adsorbing procedure), is put on the surface of water and measure the area of the monomolecular film of palmitic acid under the same surface pressure as before. Then the concentration of the latter solution will be known from the ratio of these two values of surface area.

(3) H. Akamatu, this Bulletin, **17** (1942), 141.

In practice, it is preferable to measure the compression curve of the surface film under various surface pressures. In Fig. 3, A is the compression curve of a solution of which concentration is known (C), and

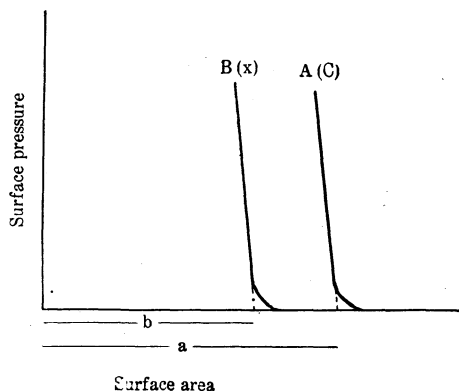


Fig. 3.

B is the one of which concentration is not known (x), a and b are the lengths of the abscissa axis by which the extrapolations of the curves cut the axis. The concentration of the solution B will be found from $x = C \times b/a$.

In this method, it is necessary to take exactly the definite volume of the solution to put on the surface of water, and this is easily attainable by using an automatic micropipette.

In practice, however, the favourable concentration and the volume of solution, which are put

on the surface of water, are limited within a certain range by the ordinal operation of the surface balance. For example, the most favourable concentration of benzene solution dissolving palmitic acid is in the order of 10^{-3} mol/l. In consequence, in the procedure of the adsorption, the concentration of the solution used is also demanded to be not far from this range. By this method, it is possible to investigate the amount adsorbed in the order of 10^{-7} mol or less adsorbate per 1 g. of adsorbent.

The experimental procedure is as follows. About 5 g. of adsorbent is taken in a test tube, and only 5 c.c. of solution is introduced into the tube. The test tube is then hermetically sealed and is shaken at intervals. After about a week, the upper liquid is taken out by using the automatic micropipette, after having been separated thoroughly from adsorbent by centrifuging.

The sample of palmitic acid from T. Schuchardt is recrystallized twice from alcohol. The experiments were carried out at room temperature. Results are shown in Table 2.

Table 2.

Adsorbent: Spherical glass powder No. 2.
Solution : Palmitic acid/Benzene.

Volume of Solution (c.c.)	Weight of adsorbent (g.)	Initial conc. (mol/l.)	Final conc. (mol/l.)	Amount adsorbed per 1 g. adsorbent (mol)	Area occupied by one molecule
5	4.124	3.2×10^{-3}	2.7×10^{-3}	5.9×10^{-7}	51 sq. Å
5	4.770	1.6 "	0.8 "	7.6 "	39 "
5	4.885	0.8 "	0.3 "	4.9 "	61 "
5	4.369	0.4 "	0.0 "	4.1 "	72 "

Discussion. In the 6th column of the table, the areas which one molecule of the adsorbate would occupy in the adsorption layer are shown,

assuming that the adsorption layer is one molecule in thickness. It is well known, from the information of the insoluble films on water, that in a tightly packed monomolecular film of normal long chain paraffin derivative, the smallest area which one molecule occupy is 20 sq. Å, and of benzene derivative, is 24 sq. Å. The observed values of the present investigation are 25–38 sq. Å for benzoic acid, and 40–70 sq. Å for palmitic acid. These values seem to indicate not only that the adsorption layer is monomolecular, but also in the case of benzoic acid, the complete monolayer has almost been saturated, while in the case of palmitic acid, the concentration of the solution has not been sufficient to form a complete monolayer, at the solid—liquid interface. However, considering that the apparent specific surface area which has been determined geometrically, cannot be larger than the true surface area of the adsorbent, it can be said with certainty that the adsorption layer is a type of monolayer, and in most case, the layer is not so closely packed in orientation as anticipated for the insoluble films on water.

Summary.

(1) The glass powder, each particle of which is spherical, was prepared, and their specific surface areas have been determined.

(2) Using this glass powder as adsorbent, the amounts of palmitic acid and benzoic acid, adsorbed from their benzene solutions, have been measured respectively.

(3) Two methods of determining adsorption, have been used. In the first method, the density determination by the float method is applied to determine the change of concentration of solution before and after the adsorbing procedure, and in the second method, the surface area of insoluble film on water has been measured by surface balance.

(4) It has been concluded that the thickness of the adsorption layer is monomolecular.

In conclusion the author wishes to express his hearty thanks to Prof. Jitsusaburo Sameshima for his kind guidance and encouragement. The cost of this research has been defrayed from the Scientific Research Encouragement Grant from the Department of Education, to which the author's thanks are due.

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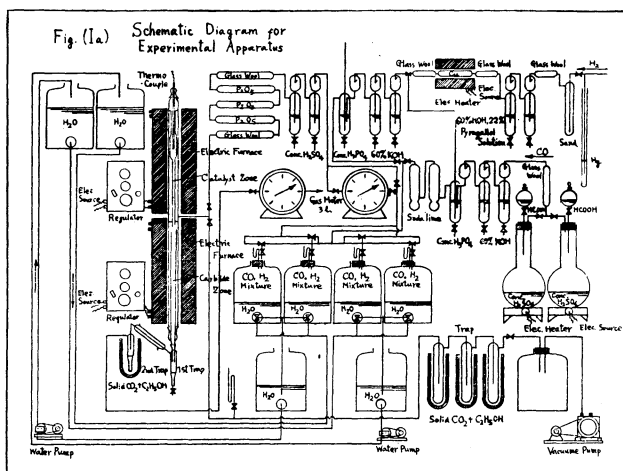
Physico-Chemical Investigations on Catalytic Mechanism. IV.⁽¹⁾ On the Fischer-Tropsch Synthesis of Hydrocarbons. (Experimental Series I⁽¹⁾).

By Senzo HAMAI, Shiro HAYASHI, Kiyoshi SHIMAMURA,
and Hiroshi IGARASHI.

(Received December 9, 1941.)

We have already published⁽²⁾ our newly proposed mechanism for the Fischer-Tropsch synthesis. In this paper we shall describe experimental aspects of this investigation, and some considerations on the experimental results will be made to substantiate our theory.

Experimental Apparatus⁽³⁾. The experimental apparatus is as shown in Fig. 1 a and 1 b. The main feature of the reaction vessel is its double walls. Owing to them, the gas mixture ($\text{CO} + 2\text{H}_2$), led in, can be heated before entering the catalyst zone into which the thermocouple well is thoroughly inserted to measure accurately even a slight variation of the temperature at which the reaction is occurring.



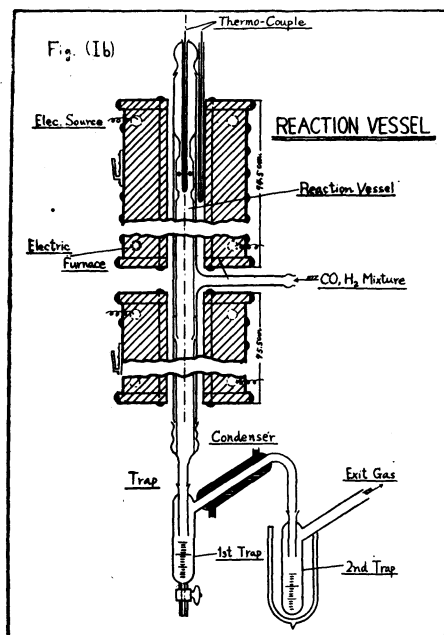
The double walled reaction vessel, 70 cm in length (the catalyst zone, about 60 cm.), is made of terex glass, and the diameter of the inner tube

(1) Report III in this series of Papers was published in *J. Soc. Chem. Ind. Japan*, **45** (1942), 313.

(2) (a) S. Hamai, *Jour. Chem. Soc. Japan*, **62** (1941), 516.

(b) S. Hamai, *This Bulletin*, **16** (1941), 213.

(3) The experimental apparatus shown here was specially designed as to have two reaction zones with the purpose of studying the two staged reaction with or without catalyst, and the combination reaction.—The detailed report for this series of investigations is to be given in our report subsequently published elsewhere.



is 1.4 cm and that of the outer tube, about 2.7 cm. A brief sketch is shown in Fig. 1 b. The temperatures of the electric furnaces are controlled by means of accurate regulators of potentiometric type. The catalysts which we have used are of Co type, of Fe and Co + Fe types with various promoters and kieselguhr. In this series of experiments we mainly employed the catalyst XII₁₆-I (Co type), which was prepared by the precipitation method from cobalt nitrate with potassium-carbonate, mixed adequately with various promoters and kieselguhrs; then thus prepared catalyst was made into tablet forms. The catalyst was reduced with hydrogen at 350°–375°C. just before we proceeded with the synthesis; so that there was not even a slight chance

of air being in contact with the catalyst before starting the experiment. Furthermore, no heat treatment was proceeded prior to H₂ reduction.

Preparations of Catalyst. For the preparation of the catalyst, the materials used were:

Co (NO ₃) ₂ · 6 H ₂ O	Extra pure, (Kojima)
Ce (NO ₃) ₃ · 6 H ₂ O	„ (Katayama)
Th (NO ₃) ₄ · 4 H ₂ O	„ (Kojima)
K ₂ O · 5 B ₂ O ₃ · 8 H ₂ O	Guaranteed reagent, (Kojima)
K ₂ CO ₃	Extra pure, (Kojima)
Kieselguhr	

Kieselguhr was purified by treating with HCl, HNO₃ and by heating at 500°C for 5–10 hrs. while the air was streamed through it, and these processes were repeated twice at least. Before the purification, its appearance was yellow, but when it was purified as such as mentioned above, it looked absolutely white.

These materials were taken in the calculated amount for the desired catalyst composition and then precipitated by 2N K₂CO₃ solution into carbonates, washed thoroughly with hot distilled water at least ten times until they became entirely free from the adsorbed nitrate ion and other possible impurities. Then they were dried at 100°–110°C. and finally made into small sized tablet forms by the tablet machine.

Preparations of Gases involved in the Reaction. *Hydrogen.* Hydrogen used was of commercial cylinder (electrolytic hydrogen) and was purified very carefully, as shown in the schematic flow diagram Fig. 1 a: firstly, by passing through two tubes of alkaline pyrogallol solution

(60% alkaline solution, 22% pyrogallol solution)⁽⁴⁾, then by heating in the tube which contained Cu gauze at 400°–500°C, and further through H₃PO₄, two tubes of concentrated H₂SO₄ and three tubes of P₂O₅.

Carbon Monoxide.⁽⁵⁾ Carbon monoxide was prepared by dropping air free formic-acid into concentrated sulfuric acid at 120°–150°C, as shown in the diagram, and passed over soda lime, H₂SO₄ and then P₂O₅.

Both hydrogen and carbon monoxide thus prepared were collected in the gas reservoir in an appropriate proportion so that we were able to pass these gas mixtures through the catalyst zone with a definite rate of flow at will.

Experimental Procedure. The catalyst was firstly reduced by streaming H₂ at some such temperatures as 350°–375°C at a definite rate of flow, just before we proceeded the reaction, at least for 5–10 hrs. When the catalyst zone was well ready for a run, the H₂–CO mixture (2:1) was passed through this catalyst zone at 200°C with a definite rate of flow (4–8 liters/hr.), and the gas contraction percentage was recorded from time to time by means of the readings in the gas meters installed as shown in our diagram. The amount of the catalyst used was 4 g. on the basis of the weight of Co.

The reaction products were collected in two separate portions, namely, in the first trap at which the vapor is condensed at room temperature, and with the water condenser and in the second trap with the solid CO₂–C₂H₅OH mixture. The reaction products thus obtained were later subjected to the determinations of physico-chemical constants such as refractive index, specific gravity, apparent molecular weight and elementary analysis, and if the amount was sufficient, the boiling points were also determined. The effluent gas was subjected to gas analysis, using a modified form of Orsat-gas-analysis—apparatus, to determine their constituents.

Experimental Results. Some of the experimental results are tabulated as follows:

Table 1.

Catalyst ⁽⁶⁾	XII ₁₆ –I			
	Co+15% CeO ₂ +15% ThO ₂ +10% B ₂ O ₃ +100% Kieselguhr			
Pretreatment	No heat treatment prior to H ₂ reduction.			
	H ₂ reduction at 350°C for 10 hrs.			
Exp. No.	FC ₇ –A	FC ₇ –B	FC ₇ –C	FC ₇ –D
Reaction Temperature (°C)	200	200	200	200
Rate of Flow (l/hr.)	4	4	4	4
Space Velocity	242	242	242	242
Average Gas Contraction (%)...	60	61.7	72.8	60.6
Oil Yield c.c./M ³ (c.c.)	28	111.3	125.4	125

(4) Treadwell and Hall, "Analytic Chemistry," Vol. II, P. 653, 1930.

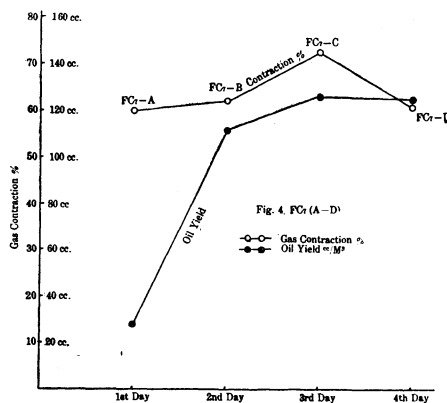
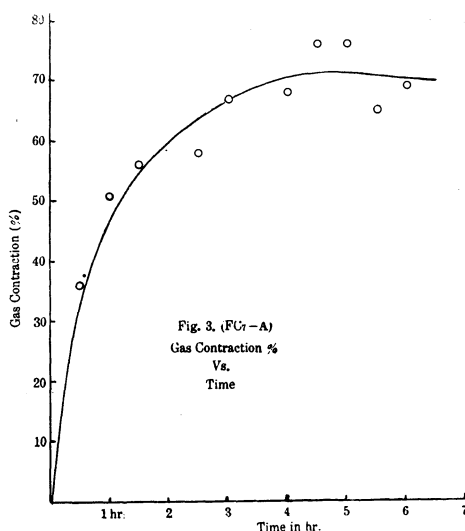
(5) Farkas and Melville, "Experimental Methods in Gas Reactions" P. 161, 1939.

(6) This catalyst was shown to be capable of yielding (171.7 c.c./M³) (in F₄₈–F).

Table 2. Gas Analysis Data.

Exp. No.	FC ₇ -A	FC ₇ -B	FC ₇ -C	FC ₇ -D
CO ₂	15.9	9.8	6.8	5.0
C ₂ H ₂	0.0	0.1	0.4	0.0
C ₂ H ₄	0.0	0.0	0.0	0.2
C _n H _{2n}	0.2	0.1	1.6	1.2
O ₂	0.2	0.4	0.3	0.6
CO	11.1	24.9	21.8	51.1
H ₂	15.5	20.4	42.3	20.8
CH ₄ ⁽⁷⁾	34.3	18.7	16.2	14.6
C ₂ H ₆	0.0	0.0	1.1	0.6
N ₂	20.8	24.6	9.5	6.0

As seen in Fig. 3, from the initial stage of the experiment, the gas contraction percentage gradually increases as far as to its contraction percentage for the presumably normalized reaction for which the contraction usually observed to be maintained at some such value as, say 60%;^(*) and furthermore, as it is noticed in Fig. 4, a steady contraction percentage was maintained as in the series of FC₇-A, FC₇-B, FC₇-C and FC₇-D, and each of which represents the result from the first day to the fourth day of the experiment. In Fig. 4 the relative oil yields as compared with each of the contraction percentage are plotted. This



apparently shows that the contraction percentage is not necessary to be parallel with the oil yield unless the reaction is normalized as such that the side reactions other than oil forming reactions are to be inhibited as time proceeds, as already pointed out in our previous paper⁽¹⁾; i.e., in the initial stage of the experiment CH₄ formation predominates and it

(7) CH₄ formation tends to be zero as time proceeds.

(*) It is unnecessary to be 60% always.

in turn always cuts down the oil formation. Once the catalyst is normalized, a steady contraction percentage is maintained and a good deal of oil formation is observed.

Durability of the Catalyst.⁽⁸⁾ Durability of the catalyst is of paramount importance, as well as its oil forming activity. We shall now

Table 3.

Exp. No.	Gas Contraction (%)	Oil Yield c.c./M ³
FC ₇ -A	60	28 cc.
FC ₇ -B	61.7	111.3 cc.
FC ₇ -C	72.8	125.4 cc.
FC ₇ -D	60.6	125 cc.
FC ₈ -(A-E) ⁽⁹⁾ . Ave.	60	149 cc.
FC ₉ -(A-C) ⁽⁹⁾ . Ave.	56.2	154 cc.
FC ₁₀ -(A-C) ⁽⁹⁾ . Ave.	58	123 cc.
FC ₁₁ -(A-N) ..	59	103 cc.

demonstrate that the catalyst we used here is well qualified for this purpose. The catalyst XII₁₆-I used in the series of FC₇ has been continuously used in FC₈(A-E), FC₉(A-C), FC₁₀(A-C) and FC₁₁(A-N).

As seen in Table 3, the contraction percentage are maintained practically about 60%, and the oil yields, however, are fluctuated; the catalyst was shown to be still in a usable form.

Reaction Products. The reaction products were collected in two separate portions as already mentioned. Those collected samples were subjected to the determination of their properties. They may be tabulated as follows:

Table 4.

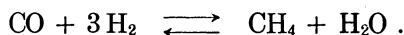
Exp. No.	FC ₇ (A-D)	
Reaction Temp.	200°C	
Catalyst No.	XII ₁₆ -I	
Catalyst Comp.	Co+15% CeO ₂ +15% ThO ₂ +10% B ₂ O ₃ +100% Kieselguhr	
Pretreatment	No heat treatment prior to H ₂ reduction.	
	H ₂ reduction at 350°C. for 15 hrs.	
Phys. Const.	1st trap oil (heavier)	2nd trap oil (lighter)
n _D ^{25°} , Ref. Ind.	1.4197 ^{25°}	1.3780 ^{25°}
d ₄ ^t , Sp. Gr.	0.7454 ^{20°}	0.6855 ^{25°}
Apparent M. W.	158.4	116.4
Elementary analysis		
C %	84.49	84.60
H %	15.42	15.39

(8) (a) F. Fischer and H. Koch, Brenn-Chem., **13** (1932), 61. Co+18% ThO₂ Catalyst was reported to be so durable that it was capable of being active for 1600 hrs., [(103 c.c./M³), 61.5% Gas Contraction]. (b) F. Fischer, Brenn-Chem., **16** (1935), 1.

(9) FC₈, FC₉, and FC₁₀ series are not pure Fischer reaction but a combination reaction with carbide about which details will be published later. Here, we just intend to show that the catalyst is still in useful and efficient condition, as shown in the FC₁₁ series.

Those results of other series under different conditions will be compared in our subsequent papers.

Some Considerations in Connection with Our Proposed Theory. In connection with our theory we have stated the fact that at the initial stage of the experiment, the methane formation predominates. This is due to the circumstance that the catalyst surface is not in a well arranged form, namely, not favorable for the oil forming activity, when various factors are taken into consideration which may influence the activity of the main reaction of liquid hydrocarbon formation, but they activate more or less the reaction of methane synthesis through



This reaction is well substantiated in our cited series of experiments, i.e., considering the results shown in Fig. 3-4 and Table 1-2, the activity of the catalyst as indicated in contraction percentage gradually builds up until a steady value of about 60% is attained and tends to remain, and, furthermore, from the values of FC₇-B, FC₇-C and FC₇-D, it is quite apparent that the contraction percentage is more or less maintained; and as already pointed out in our previous paper (Fig. II).^(2b) CH₄ formation in every set of experiments tends to be zero as time proceeds. All these observations well substantiate our explanations mentioned already.

Summary.

(1) The experimental apparatus and the experimental procedures were described for the investigations on the Fischer-Tropsch reaction with special reference to its catalytic mechanism.

(2) The durability of the catalyst used was discussed in connection with the investigation of catalytic activity as to its liquid hydrocarbons synthesis.

(3) Some properties of the reaction products were tabulated.

(4) Some consideration of CH₄ formation in connection with our proposed mechanism were presented and correlated with the experimental results.

In conclusion, the authors wish to express their thanks to Dr. T. Marusawa, Former Director of the Institute, and Dr. S. Sato, Director of the Institute, for their interests and the permission for this publication; also to their colleagues for their cooperation; and to Mr. I. Fujiwara who has willingly assisted us in this experimental investigation.

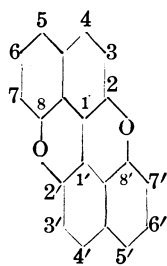
*The Central Laboratory,
South Manchuria Railway Company, Dairen.*

Studies on the Derivatives of Biphenylene Oxide. IX. General remarks.

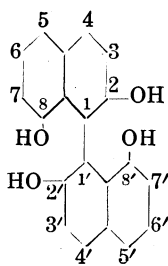
By Seishi YAMASHIRO.

(Received December 11, 1941.)

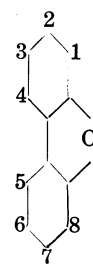
In the previous studies on the derivatives of 1,1'-dinaphthylene-2,8',-2,8'-dioxide (I), the following facts were recognized by the present author. When the dinaphthylene dioxide was heated only with concentrated nitric acid, it gave rise to a single hexanitro derivative, and when the same dioxide was treated first with nitric acid and then with a mixture of nitric and sulphuric acids, it gave the same hexanitro compound with an isomeric hexanitro derivative. And the former hexanitrodinaphthylene dioxide was rather readily soluble in caustic soda solution, and on hydrolysis yielded a corresponding nitro derivative of 2,2', 8,8'-tetrahydroxy-1,1'-dinaphthyl (II) quantitatively, while the latter one was much less soluble and gave nothing more than a brown amorphous substance as a hydrolyzed product. A more important fact is that the hydrolyzed product, obtained from the readily soluble dioxide, was reconverted without difficulty into the original dioxide when heated with acetic anhydride, but, on the contrary, that obtained from the less soluble dioxide did not regenerate the original dioxide in the same treatment.



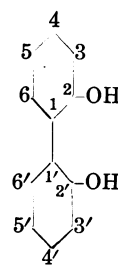
(I)



(II)



(III)



(IV)

Such different behaviours of those isomerides are obviously due to a certain difference in the relative positions of the nitro groups and the pyrone-rings of those compounds. Consequently, in the researches of the stability of such heterocyclic compounds and their hydrolyzed products, it is indispensable to make clear of the effects of substitution, exerted on the opening and closing of such rings.

Although a number of researches have been communicated with regard to the preparations of the nitro derivatives of the dinaphthylene dioxide, the constitutions of almost all the nitro compounds remain undetermined up to the present day. As far as the present author knows, only 5-nitro-⁽¹⁾ and 6,6'-dinitro-⁽²⁾ dinaphthylene dioxides were presumably established.

(1) I. S. Travkin, *Org. Chem. Ind. (U.S.S.R.)*, **2** (1936), 221-226.

(2) I. G. Farbenind. A.-G., Ger. Pat., 545,212, July 29, 1928.

The present author formerly exerted himself in establishing the constitutions of the isomeric hexanitrodinaphthylene dioxides, but he found it very difficult to establish them completely. For example, when the readily soluble hexanitro compound, mentioned above, was oxidized with potassium permanganate in caustic soda solution, a dinitro-hydroxy-phthalic acid was obtained and proved to be 4,6-dinitro-3-hydroxy-phthalic acid (1,2). It was impossible, however, to isolate the other components by which the positions of the other nitro groups could be determined. In addition, the higher nitro derivatives of the dinaphthylene dioxide, unfortunately, have no melting point and decompose explosively when heated. Therefore, it is also unfavourable to identify those compounds which could be obtained by synthesis.

Now, if the same isomeric phenomena be observed also in the derivatives of biphenylene oxide (III), it is desirable to study such effects of substitution exerted on the opening and closing of the furan-ring of this simple compound, because the preparation of the possible isomerides and the orientation of the substituents may be simpler in the derivatives of this compound than in those of the dinaphthylene dioxide.

In the early days of these studies on the derivatives of biphenylene oxide, however, the constitutions of some of the nitro derivatives which had been prepared by the other investigators were not yet rationally established, and besides many of the isomeric nitro compounds had not yet been obtained, so the present author occupied himself first with the establishment of the constitutions of the known nitrobiphenylene oxides and the preparation of the other nitro-derivatives. For these two objects, he employed two methods of preparation,⁽³⁾ one of which was the direct nitration of biphenylene oxide, and the other, the preparation of nitro-biphenylene oxides from the corresponding nitro derivatives of *o,o'*-biphenol (IV). The nitro compounds thus newly obtained and the amino, acetamino, nitroamino, and nitroacetamino compounds newly derived for the identification of those nitro compounds are as follows:

1-Nitro-biphenylene oxide	1,6-Diamino-biphenylene oxide
4-Nitro- " "	1,6-Bisacetamino- " "
1,6-Dinitro-biphenylene oxide	1,8-Diamino-biphenylene oxide
1,8-Dinitro- " "	1,8-Bisacetamino- " "
2,7-Dinitro- " "	1-Nitro-8-amino-biphenylene oxide
3,6-Dinitro- " "	1-Nitro-8-acetamino- " "
4,6-Dinitro- " "	2-Nitro-3-amino-biphenylene oxide
1,3,6-Trinitro-biphenylene oxide	2-Nitro-3-acetamino- " "
2,3,6-Trinitro- " "	7-Nitro-2,6-diamino-biphenylene oxide
2,3,7-Trinitro- " "	7-Nitro-2,6-bisacetamino- " "
2,4,6-Trinitro- " "	3-Nitro-2,7-diamino-biphenylene oxide
1,3,6,7-Tetranitro-biphenylene oxide	3-Nitro-2,7-bisacetamino- " "
2,3,6,7-Tetranitro- " "	2-Nitro-3,6-diamino-biphenylene oxide
2,4,6,7-Tetranitro- " "	2-Nitro-3,6-bisacetamino- " "
1-Amino-biphenylene oxide	3,7-Dinitro-2,6-diamino-biphenylene oxide
1-Acetamino- " "	3,7-Dinitro-2,6-bisacetamino- " "

(3) S. Yamashiro, *J. Chem. Soc. Japan*, **57** (1936), 714-718 (Part I); **59** (1938), 186-192 (Part II); **59**, 443-450 (Part III); **59**, 945-953 (Part IV); this Bulletin, **16** (1941), 61-69 (Part VI).

The properties of these compounds, especially the absorption spectra of those new nitro derivatives, were studied in comparison with those of the known nitro compounds. From the experimental results given in Parts I–IV and VI⁽³⁾ it was found that the nitrosubstitutions in a phenylene residue of biphenylene oxide and in the unsubstituted phenylene residues of nitrobiphenylene oxides take place in the orders of positions $2>3>4>1$, and $3>2>1$ and 4 (probably $1>4$) respectively. Consequently, the *o,p*-directing powers of the ring-forming oxygen atom, the phenylene residue and the nitrophenylene residue may be represented in the order $-C_6H_4->-O->-C_6H_3NO_2-$.

In Parts IV and VII,⁽⁴⁾ the nitro and bromonitro derivatives of biphenylene oxide were obtained from the corresponding derivatives of *o,o'*-biphenol by means of the intramolecular formation of a furan-ring. The present author accomplished this ring-closure successfully by heating *o,o'*-diacetoxydiphenyls with acid-removers. Many metallic oxides and carbonates were examined as such removers, but the carbonates only were found to be available for the closure of the furan-ring. And the orders of the availability among the carbonates are $Li_2CO_3>Na_2CO_3>K_2CO_3$ in alkali metals, and $BaCO_3>SrCO_3>CaCO_3>MgCO_3$ in alkaline earth metals. It was also found that influences of substituents exerted on the removal of the acetyl groups, and on the formation of the biphenylene oxides, too, are positive in the case of nitro group, though they are negative in the case of bromine, and that the both effects of those substituents come out remarkable in the same order of their relative positions, *ortho*>*para*>*meta*, to the acetoxy groups.

The reaction mechanisms in the formation of the biphenylene oxides and the reformation of the biphenols from the diacetoxydiphenyls can be reasonably explained as below on the basis of the electronic theory.⁽⁵⁾

When a negative ion such as oxygen ion acts upon an acetoxy group of a substituted diacetoxydiphenyl, the electromeric effects of the substituents are generally to show certain influences on the removal of the acetoxy group, though the same effect of the acetyl group in that acetoxy group induces the removal of the acetyl group itself. And the effects, which are exerted by the negative polar substituents such as nitro and carboxyl groups at certain positions, must be opposite to those exerted by such positive polar substituents like halogens at the same positions. With regard to the relative positions of those polar substituents to the acetoxy group, it can be said from an electromeric point of view that these substituents are considerably effective at the *o*- and *p*-positions, while they are scarcely so at the *m*-position. And the fact that they are most effective at the *o*-position can possibly be explained in no other way than that the acetoxy group is in this case at the nearest position to the origins of the electromeric effects which affect the elimination of that group.

Now, compare the above-mentioned influence of the acetyl group with the resultant of the influences of the substituents, within each one of the substituted acetoxyphenyl residues of the substituted diacetoxydiphenyl. Then the following inference may reasonably be drawn. That is to say,

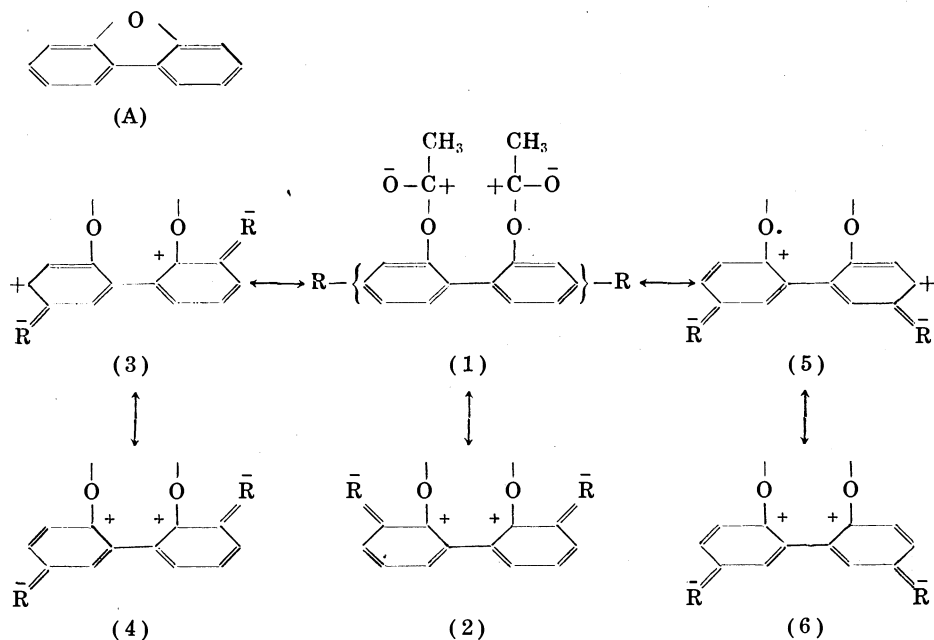
(4) S. Yamashiro, this Bulletin, **17** (1942),

(5) C. K. Ingold, *Chem. Rev.*, **15** (1934), 225.

if the former influence positively predominates over the latter, as in the examples I and II, the reaction product may be a biphenol, even if such a predominance occurs in *one* of those residues, as in the example III(i). On the contrary, moreover, if the latter positively predominates over the former in *both* of those residues, as in the example III(ii), a biphenylene oxide may be obtained.

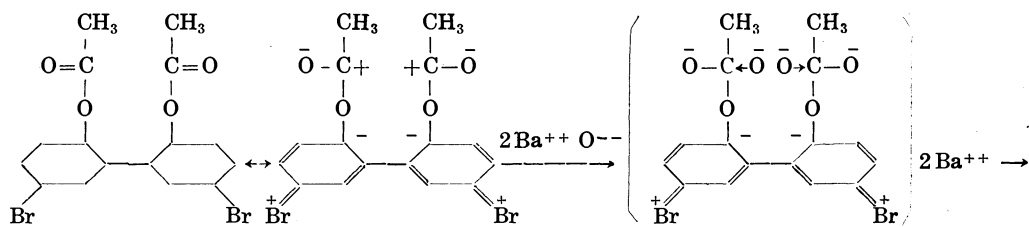
It may also be understood from the example III that when a certain derivative of the diacetoxydiphenyl exists in a special mesomeric state, the corresponding derivatives of both biphenol and biphenylene oxide are to be obtained simultaneously from that derivative.

The most stable structure of biphenylene oxide (formula A) has been previously established by K. Tatematsu and his co-worker⁽⁶⁾ who took into their account the minimum distortion of the natural valency-direction in the closure of the furan-ring according to Mill's hypothesis on the natural valency-angle. If this be the case, the biphenylene oxides are to be readily obtained from the corresponding diacetoxydiphenyls which have such arrangements of double bonds as those in the formulas (1), (2), (3), (4), (5) and (6).

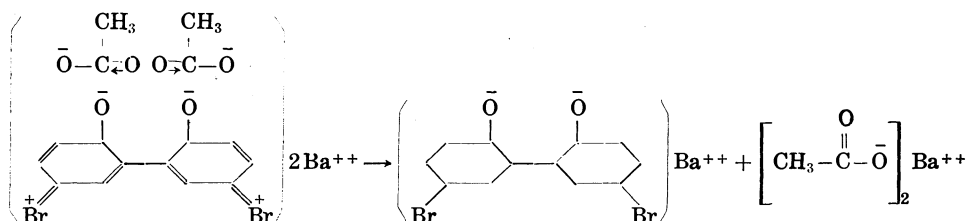


Three of them, i.e. (1), (3) and (5), however, cannot satisfy the above-mentioned necessary electronic conditions for the formation of the biphenylene oxides. Consequently, in the case of disubstituted compounds, the structural formulas (2), (4) and (6) should be available for the formation of the biphenylene oxides, while all other possible unperturbed structures, for that of biphenols.

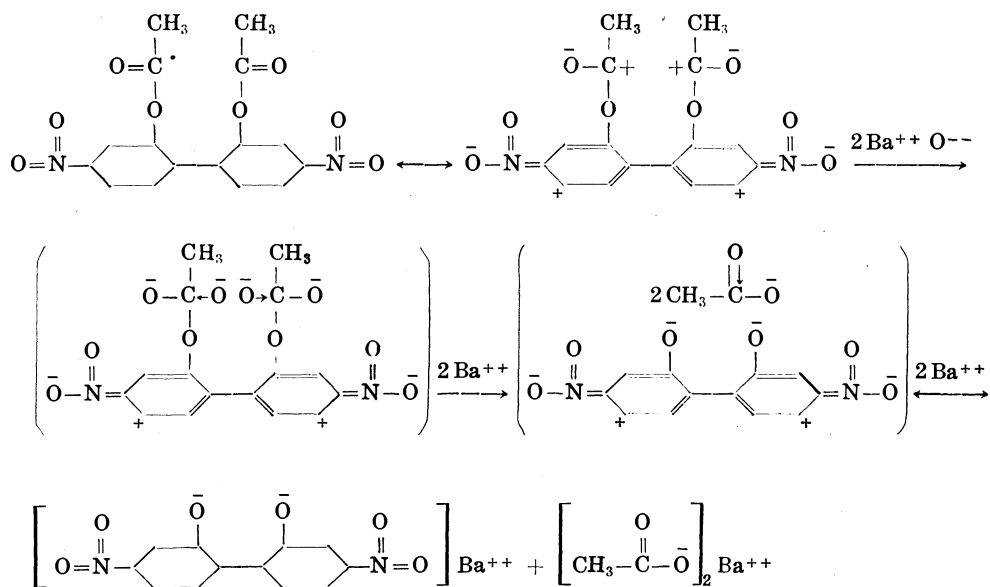
(6) K. Tatematsu and B. Kubota, this Bulletin, **9** (1934), 450.



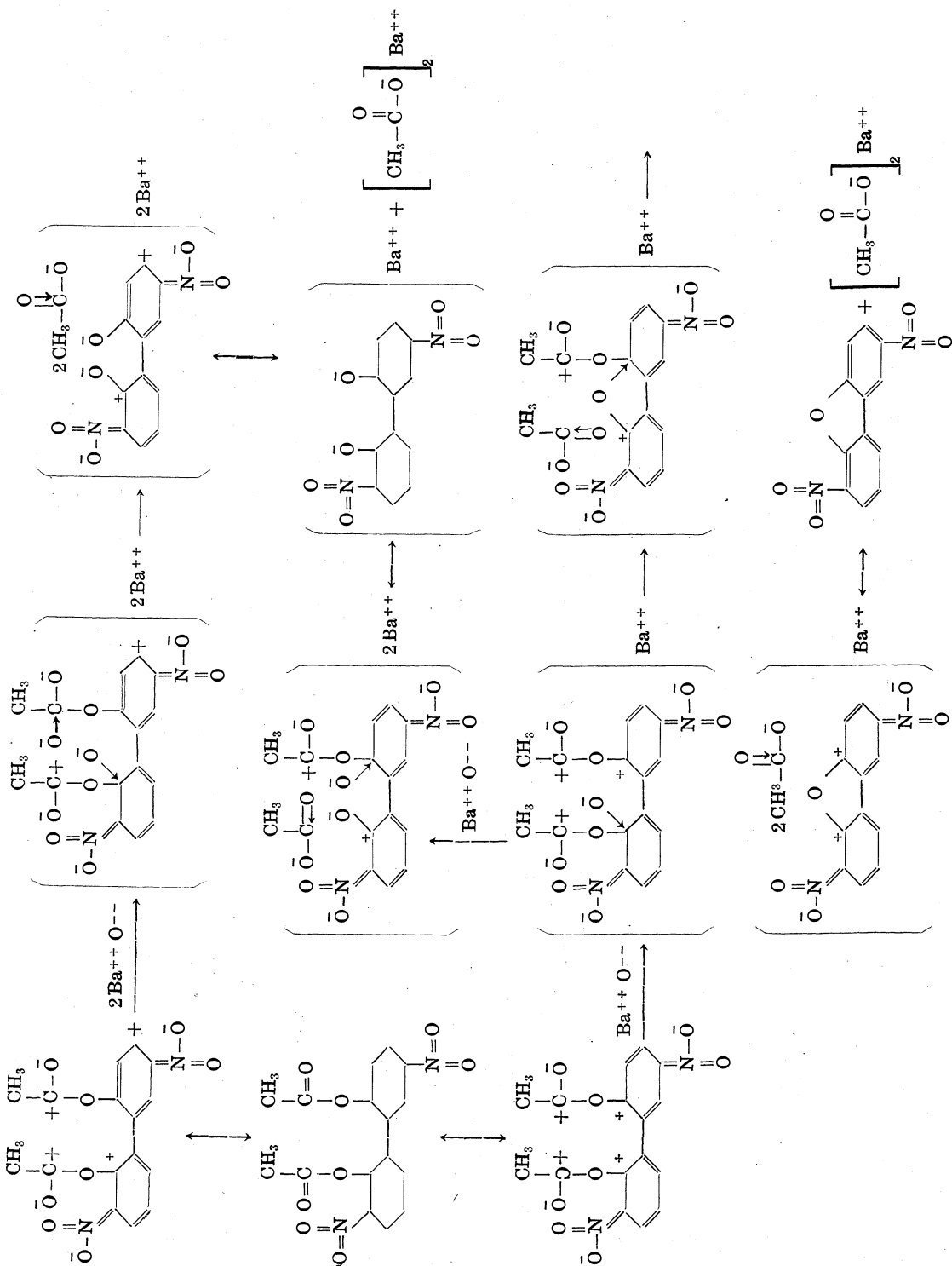
Example I.



Example II.



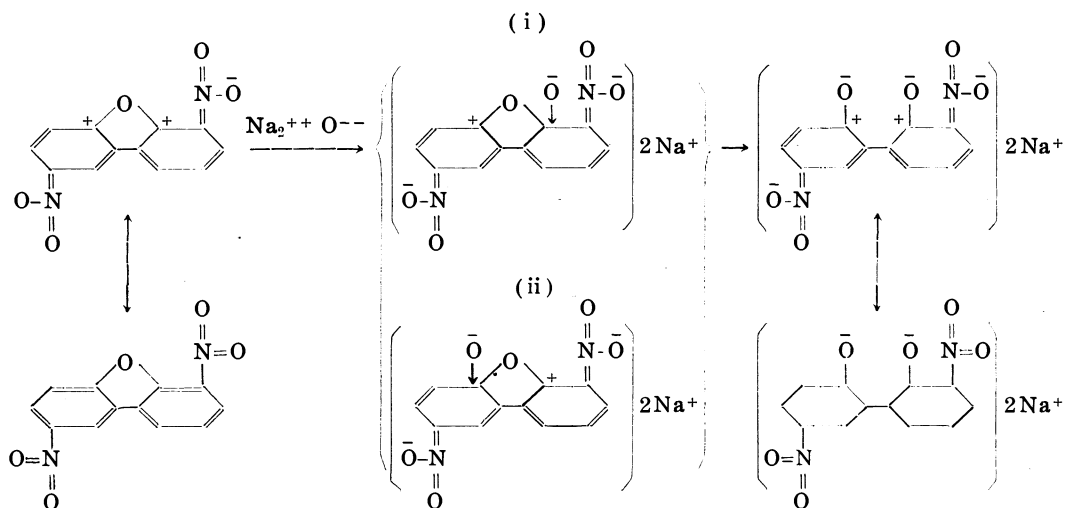
Example III.



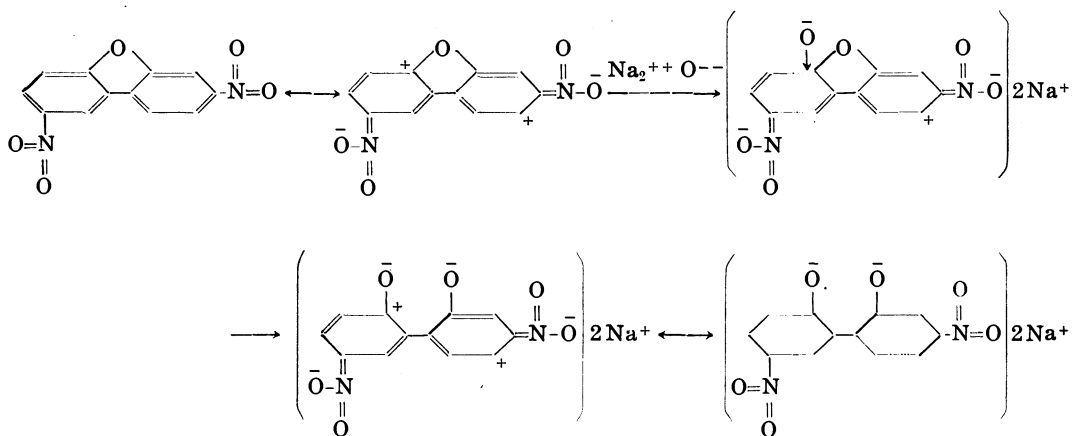
The opening of the furan-rings of the nitrobiphenylene oxides by caustic soda solution was examined in Part VII, and it was found that the tendency of this ring-opening is analogous to that of the ring-formation. That is to say, the increase in the number of the nitro group facilitates that opening, and the influence of the positions of the nitro groups is represented in the order ortho->para->meta-position relative to the ring-forming oxygen atom.

These experimental results can also be reasonably interpreted on the basis of the electronic theory as in the following examples.

Example IV.



Example V.



In the example IV, the main opening-reaction may proceed as in (i), because the positive electromeric effect of the nitrogroup is to be most

effective at the *o*-position to this group, as in the case of elimination of the acetoxyl groups from the diacetoxydiphenyls.

In conclusion, the author wishes to express his hearty thanks to Prof. R. Majima of Osaka Imperial University and S. Oba, the principal of Yonezawa Higher Technical School, for their kind advices and encouragements. The cost of these researches has been defrayed from the Japan Society for the Promotion of Scientific Research and from the Scientific Research Expenditure of the Department of Education, to which also the author wishes to record his thanks.

Yonezawa Higher Technical School, Yonezawa.

The Synthesis of Iso- and Normal Butyl Alcohols in the Presence of Calcium Carbide. (B)* III. Experimental Details and Preliminary Investigations on Methanol Catalysts in the Presence of the Carbide. Dry System.**

By Ryoji NEGISHI.

(Received December 16, 1941.)

In our investigations on the non-catalytic polymerization of nascent acetylene, or the synthesis of liquid products directly from calcium carbide under ordinary⁽¹⁾ and elevated⁽²⁾ pressures, traces of alcohols have been detected in the liquid products. From the fact that methanol is the common intermediate in all the mechanisms, though they themselves differ widely; so far proposed for the formation of higher alcohols⁽³⁾ from carbon monoxide and hydrogen, the possibility of synthesizing higher alcohols, particularly the butanols*, in the presence of carbide, from the same gases passed over a methanol catalyst has been conceived.

* R. Negishi, *Rev. Phys. Chem., Japan*, **15** (1941), 175; R. Negishi, *Rev. Phys. Chem., Japan* **15** (1941), 181 will be referred to as Papers (B) I and (B) II, respectively. (B) will be used to all the papers of this series in contradistinction to Papers I, II, etc., designated for the series of papers by the author on hydrocarbons from carbide, non-catalytic polymerization under ordinary and high pressures, and they will appear in *J. Chem. Soc. Ind., Japan*.

** This paper has been published by permission of Dr. S. Sato, the Director of the Central Laboratory, to whom the author's thanks are due.

(1) (a) R. Negishi, S. Kataoka, and O. Kamiike, *J. Soc. Chem. Ind. Japan*, **44** (1941), 1028; (b) O. Kamiike, S. Kataoka, M. Nibayashi, and R. Negishi, *ibid.* **44** (1941), 1030; (c-f) R. Negishi and O. Kamiike, *ibid.* **45** (1942), 133.

(2) (a) R. Negishi, M. Nibayashi, K. Sakon, and O. Kamiike, *ibid.*, (1942); (b-c) R. Negishi, M. Nibayashi, and O. Kamiike, *ibid.*, (1942).

(3) See Paper (B) II.

* The author is grateful to Mr. O. Kamiike who has actually identified iso-butyl alcohol by distillation; its details will appear later in this Bulletin in a collaborated paper.

Considering further that the synthesis of higher alcohols is invariably associated with the formations of water and carbon dioxide molecules⁽⁴⁾ and that the carbide has strong affinities for these molecules, its presence, therefore, would be of advantage. Moreover, thermodynamic calculations⁽⁵⁾ have shown that the presence of the carbide increases the free energy of butanol formations to quite a degree. All these factors have encouraged us to take up the problem. There has been a further impetus for the investigation; it is a new method of synthesizing the butanols.

In this paper I shall limit myself to the discussion of the experimental procedure, the effects of dry carbide on the activity of the catalyst, and to the tabulation of a considerable body of the experimental results obtained*. Their fuller discussion will be published in this Bulletin later. The experimental details will be given rather minutely in order that the probable sources of error, difficulty, and the reliability of the results, not only in this paper but also in the entire series of our investigations, may be estimated.

Experimental Details. The same three revolving horizontal autoclaves of approximately one liter capacity, designated as I, II, and III^(2a) were used. In later investigations an autoclave of entirely different design was employed.

In the dry systems investigated here, the carbide grains of 1 to 2 mm size and its acetylene content under the normal conditions of about 75 to 80% had been employed. The same gases as before^(2a) were used. The methods of charging, discharging, and analysing the products had also been given before^(2a). Gases and liquid products were analyzed, respectively, by a modified Schuften's method^{(1b) (2a)} and by elementary and distillation analyses.

Due to the limitations imposed upon the system by the construction of the autoclaves, it was not possible to maintain the total pressure of reaction at a constant value; so it was charged at the reaction temperature (or slightly lower, because the reaction is highly exothermic) to a predetermined value, and the gas was allowed to react until the pressure had decreased to a desired point. Then the gas was recharged to the original value. This was repeated as often as necessary until most of the carbide had reacted. Therefore, in all these runs it is not the reaction pressure but the reaction pressure range that is significant.

The volume of the charged gas was calculated from the blank determination made under the conditions as similar as possible to those of the actual runs. The volume of the gas after reaction was measured by means of a gas meter connected at the end of the condensing trains, which consisted of a water-cooling condenser and a trap cooled with solid CO₂-alcohol mixtures. The products condensed in the former was designated, as before, as "condenser" and those in the trap as "trap."

For these explorative and orientation runs, the liquid products were, as mentioned above, subjected to distillation, and the approximate alcoholic contents of the various fractions were determined. No special determinations of the hydrocarbons found in the fractions were made. In the more refined runs made later, the actual amount of iso-butyl alcohol was determined either by solvent analysis or by azeotropic distillation⁽⁶⁾.

(4) F. Fischer and H. Tropsch, *Die Umwandlung der Kohle in Oele*, **2** (1924), 246; P. K. Frolich and D. S. Cryder, *Ind. Eng. Chem.*, **22** (1930), 1051.

(5) R. Negishi, Paper (B) II.

* The author's thanks are due to Messrs. Sakon, Araki, Simono, and Kitakaze for making the autoclave runs; also to Messrs. Kataoka, Kodama, Nakano, and Inaba for analysing the products.

(6) R. Negishi and C. Isobe, this Bulletin, **16** (1941), 278.

Catalysts and their Preparation. The catalysts used in this series of runs, made in dry system, are designated as 15, 15b, 19, and 21. Their preparations will be briefly given. 15 and 15b were prepared under the same conditions by preparing 500 c.c. solutions containing 0.61 and 0.39 moles of chromium and zinc nitrates, respectively, and 150 g. of pumice grains of about 2 mm size was added to the mixture. The mixture was gradually dried at about 100°C; finally, it was calcined at 400°C in oxygen atmosphere for 4 and a half hours. Then it was reduced with H₂ at 400°C

for 5 hours. The activities of these catalysts were not so good, but sufficient for our purpose. Catalysts 19 and 21 were prepared under the same conditions, employing a method similar to that of Molstad and Dodge⁽⁷⁾. Solutions containing one mole per liter of chromium and zinc nitrates, both "Kojima" products, were mixed in the molal ratio of zinc to chromium as 0.39 to 0.61. It was then precipitated with an approximately 25% ammonium solution. Their activities were fair, but much more inferior to that given by the above investigators.

The activities of 19 and 21 were found to be greater than those of 15 and 15b, though without significant effects on the character of the gaseous and liquid products. A more complete set of data for the latter catalysts is given below.

The activity of a catalyst is of second importance in our present case, since in the presence of the carbide, which has large affinities for water and carbon dioxide molecules: the equilibrium of the reaction is so greatly shifted, especially in a static

Table 1_A.
Elementary Analysis of Liquid Product.

Component	Liquid in Trap	Liquid in Condenser	Methanol
C	37.17	34.49	37.50
H	12.99	12.16	12.50
O*	49.84	53.35	50.00

* by difference.

Table 1_B.
Analysis of Gaseous Product.

Component	Gas	
	Initial	After Reaction
CO ₂	3.3	6.4
C ₂ H _{2n}	0.0	0.0
O ₂	0.5	0.4
CO	31.5	28.4
H ₂	59.1	57.8
CH ₄	0.0	0.8
N ₂	5.6	6.1

system, by the continuous removal of the products. A catalyst with any activity has been found sufficient. However, the more active the catalyst is, the more rapidly the reaction comes to completion.

Effect on Activity of Carbide and of Reaction Products. The poisonous effects of carbide and of its reaction products on the activity of the catalyst do not seem to exist, as seen from Fig. 1, in which the results of run 97 (III_ASer. 93) and of run 110₃ (III_ASer. 100) are plotted together. In the former series 214 g. of catalyst 15 was used without carbide, and dp/dt, the rate of the total pressure change, of the last run of the series was plotted. In the latter series 212 g. of the same catalyst recovered after run 97 was mixed with 300 g. of the carbide, and dp/dt of one of the earlier runs in which the carbide had existed in excess and that of the last run, 110₃, of the series were plotted. In run 110₃, it might be assumed that no more carbide was present, as indicated by the absence of free acetylene when the residue was treated with water.

It is seen from the figure that the activity of the catalyst remains the same, within the accuracy of our measurements, even after 2500 minutes in contact with the

(7) M. C. Molstad and B. F. Dodge, *Ind. Eng. Chem.*, **27** (1935), 134.

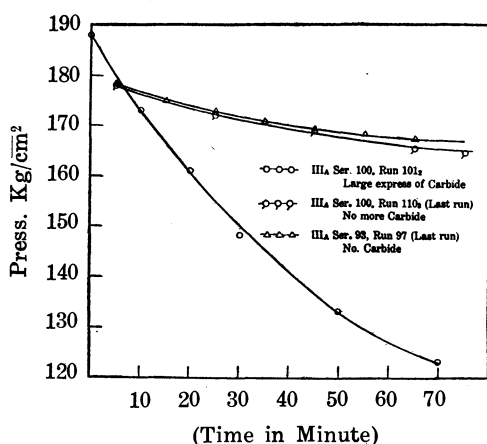


Fig. 1. Effect of Carbide on Activity of Catalyst XV.

carbide and its reaction products. Though not given in this paper, the same sort of results has been shown in the other runs.*

Results. We shall now tabulate the results of our dry systems in the following Tables and describe each run briefly. The Table will be constantly referred to in a later paper in which a fuller discussion of the results is given. Of the runs listed, III_A Ser. 113 and III_A Ser. 100 are accurate enough for a quantitative discussion. Its detail will be given in one of the later papers. The conditions of the runs are given in Table 2.

Table 2. Experimental Conditions.

Exp. No.	Catalyst and Wt. (g.)	Carbide (g.)	CO:H ₂	React. Temp. (°C.)	Press. Range Kg/cm².
III _A 111	216.5 (15b)	0	1:1.88	320	203
III _A Ser. 100	212 (15)	300	1:1.89	320	183-175
III _A Ser. 135** ..	119.2 (15)	200	1:1.89	320	130- 90
III _A Ser. 113	216 (15b)	300	1:1.85	280-320	165-135
IV _A Ser. 52	100(19+21)	500	1:2	305	200-100

* Autoclave II was used in every case. Catalyst was mixed with carbide.

** Catalyst placed "in cylinder," was supported at the center of the autoclave.

Run III_A 111. The purpose of this run was to see what would be formed from the catalyst. As mentioned already, it produced mainly methanol.

Run III_A Ser. 100 (runs 100 to 110). In every run two charges of gas were made to maintain a given range of pressure, and one complete discharge was made. For the last run, 110₃, three charges were made, because the reaction was quite slow, especially under the lower pressure. Each run required from 240 to 400 minutes. The total time of reaction was about 60 hours. The results of this run were quantitative and would be discussed in a later paper.

Run III_A Ser. 113 (runs 113 to 134). In this series the reaction temperature had been varied from 280 to 320°C., but most of the runs were made at 295 to 305°C. For the slower reactions a discharge was made for each charging, but, when the reactions were rapid (above 300°C.), two charges were made for each discharge. The total time of

* The longest run we have made is not over 150 hours.

reaction was 84 hours. These results were quantitative and would be discussed in a later paper.

Run III_A Ser. 135 (run 135 to 137). The catalyst was charged "in cylinder", and supported in the center of the autoclave. The purpose of this run was to investigate the effect of the catalyst not in contact with the carbide. From the results of the elementary analysis of the liquids and from the gas analysis, shown in Tables 3 and 4, respectively, it is obvious that the differences are small, but they are probably real. The fact that in III_A Ser. 100 there is less oxygen in the liquid products and more saturated gases seems to point to the same conclusion that the actual temperature in III_A Ser. 100 is higher than that of III_A Ser. 135. Similar evidence has been obtained in our synthesis of hydrocarbons directly from the carbide under the elevated pressure (2b, c).

Table 3. Elementary Analysis of Liquid Products.

Exp. No.	Liquids in the Condenser			Liquids in the Trap		
	C	H	O	C	H	O
Methanol	37.50	12.50	50.00	—	—	—
III _A 111	34.49	12.16	53.35	37.17	12.99	49.84
III _A Ser. 100	77.90	11.69	10.41	66.80	12.58	20.72
III _A Ser. 135	74.35	12.24	13.42	64.15	12.91	22.94
III _A Ser. 113	72.46	11.69	15.85	55.64	15.00	29.36
IV _A Ser. 52	75.49	11.73	12.78	70.51	12.60	16.89
Isobutanol	64.86	13.51	21.62	—	—	—

Run IV_A Ser. 52 (run 52 to 67). The reaction temperature was varied from 290 to 305°C., but most of the runs were made at 300 to 305°C. The purpose of this run was to investigate the effect of excessive carbide. Two pronounced effects were observed. One of them was a reduced oxygen content in the liquid products. This was ascribed as due to excessive dehydration by the carbide. It seemed that even some of the butyl alcohol synthesized from the methanol was dehydrated with a subsequent polymerization of the resulting unsaturated substances to form the hydrocarbon liquids with reduced oxygen content. The second effect was associated with the sudden increases, which we had designated as "jumps",^{(1),(2)} in both pressure and temperature. We are at a loss for a suitable explanation of this phenomenon. It was generally found that the apparent value of dp/dt reached a maximum only after a considerable amount of the carbide had reacted, and the rate again decreased until it finally reached that of the original value. Perhaps, the jumps are associated with this, but, as has been mentioned above, we are in the dark with regard to this phenomenon. These jumps also took place in Run III_A Ser. 40, in which 500 g. of the carbide was used. No jump had occurred when 300 g. or less of carbide was taken although the existence of a maximum in dp/dt was evident.

Table 4. Gas Analysis.

Exp. No. Auto. Run	III _A 135				IV _A 52**				III _A 113***					III _A 111		III _A 100□		
Run	135		136		57		59	64	115	124		128		111		100□□	104	
Gas	Orig.	React	React	Trap*	React	Trap	React	"Jump"	React	React	Trap	React	Trap.	Orig.	React	React	React	Trap
CO ₂	3.2	0.0	0.0	1.5	0.2	58.1	0.4	0.0	0.2	0.0	24.5	0.0	20.7	3.3	5.5	0.0	0.0	62.0
C ₂ H ₂	0.0	0.0	0.0	10.5	0.5	24.8	0.4	0.0	1.1	0.5	66.0	0.7	70.4	0.0	0.9	2.0	0.2	16.8
C ₂ H ₄	0.0	1.4	2.5	14.0	3.6	11.1	3.2	0.7	0.5	0.9	5.6	1.3	5.2	0.0	0.0	1.0	1.8	10.8
C _n H _{2n}	0.0	2.0	1.5	1.0	1.3	0.6	0.9	0.0	1.6	1.6	0.7	2.2	0.7	0.0	0.0	1.6	3.0	0.7
O ₂	0.5	0.6	0.5	0.5	0.5	0.0	0.5	0.7	0.7	0.5	0.5	0.4	0.4	0.5	0.5	0.7	0.5	0.3
CO	31.3	29.7	28.5	6.1	29.5	0.2	29.8	1.3	31.0	28.5	0.8	25.6	0.7	31.5	28.1	24.5	20.2	0.7
H ₂	59.2	54.3	55.9	1.5	61.3	0.2	52.3	11.0	57.3	58.2	0.0	58.4	0.0	59.1	27.8	50.8	53.3	0.9
CH ₄	0.3	3.3	2.9	2.8	0.0	0.0	9.7	71.2	0.5	0.7	0.0	2.1	0.0	0.0	0.8	7.6	9.0	0.0
C ₂ H ₆	0.0	1.7	1.7	17.1	0.0	2.2	0.0	11.5	0.5	2.3	0.0	1.2	0.0	0.0	0.0	3.9	5.2	5.0
C ₃ H ₈	—	—	—	—	—	2.5	—	—	—	—	—	—	—	—	—	—	—	1.0
N ₂	6.8	7.0	6.5	37.1	3.1	0.3	2.8	3.5	6.6	6.8	2.7	8.1	1.9	5.6	6.1	7.9	6.8	1.8
Reaction Temp. °C	320				305				290				306	320		320		

* Unreliable; probably air was mixed.

** Runs 57, 59, and 64 are the 5th, 6th, and 10th runs of the series (of 13 runs); Press. of jump was above 300 Kg/cm² (off scale).

*** 124 and 128 are the 12th and 16th runs of the series (of 22 runs); 115 is the 3rd.

□ 100 and 104 are, respectively, the 1st and 5th runs of the series (11 runs).

□□ The same gas as that of III_A 111 was used.

Some of the results of the gas analysis are shown in Table 4. Others were omitted simply because most of the results of the same series varied only slightly from run to run. Only what seems to be more or less typical has been given. Several interesting facts can be pointed out from the Table. The high content of saturated gases in run 64 is obviously associated with the jumps nearly $200^{\circ}\text{C}.$ in temperature and at least 150 Kg/cm^2 in pressure. Also in the same series, the results of runs 57 and 59, which have been made successively, show interesting effects for which no suitable explanation is found. In the former, and up to this run, there is no formation of saturated gases; but in 59, which has been made under about the same conditions as those of the former, there appears suddenly a rather large quantity of methane. Moreover, the methane formation of approximately this extent has been observed throughout the rest of the runs of the series. No such effect has been found with the other series; not even in III_A Ser. 40, which has been carried out at $310^{\circ}\text{C}.$ The results of Table 4 will be referred to again in the next paper when a discussion of the results of gas analysis of the runs made in liquid medium is taken up.

NOTE. Most of the results given in this paper and in the following (IV and V) were completed in 1939–1940, but the publication of them has been with-held.

Summary.

The experimental procedure and the preparations of the catalysts used are given in detail. The effects on the activity of the carbide and of the reaction products are found to be small—if at all.

The results of the runs in dry system are tabulated, and each run is briefly described. Short discussions on the results are also given. A fuller discussion on them is reserved for a subsequent paper.

The writer takes this opportunity to thank Professor T. Marusawa for his encouragement throughout the course of this investigation.

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Studies on the Reactions between Oxides in Solid State at Higher Temperatures. V.⁽¹⁾ The Reaction between Magnesium Oxide and Aluminium Oxide.⁽²⁾

By Yasuo TANAKA.

(Received December 16, 1941.)

Introduction. There exists only one addition compound, spinel ($\text{MgO} \cdot \text{Al}_2\text{O}_3$), in the system magnesium oxide and aluminium oxide. This compound belongs to the cubic system with a unit cell, consisting of 8 molecules of $\text{MgO} \cdot \text{Al}_2\text{O}_3$ and is able to contain an excess of aluminium oxide forming a solid solution. According to Hägg and Söderholm,⁽³⁾ the lattice constant of pure $\text{MgO} \cdot \text{Al}_2\text{O}_3$ is $a=8.056\text{\AA}$, and at the Al_2O_3 the richest limit of the solid solution with $\alpha\text{-Al}_2\text{O}_3$, which lies at about 67 mol % of Al_2O_3 , or corresponds approximately to $\text{MgO} \cdot 2\text{Al}_2\text{O}_3$, and it decreases to $a=7.968\text{\AA}$.⁽⁴⁾ They have stated further that the density of the solid solution is explained only under the assumption that the positions of the oxygen lattices are unchanged, and an excess of aluminium atoms exists by replacing the positions of the magnesium atoms and leaving a part of them unoccupied.

The solid reactions of the formation of $\text{MgO} \cdot \text{Al}_2\text{O}_3$ and those of the other spinel type compounds, especially those at lower temperatures, have been studied by many investigators.⁽⁵⁾ However, there is no report in which the velocity of their formations has been followed quantitatively. Also the composition of the solid solution, formed at the first stage, is not certain. The present research is carried out with a view to make these two points clear and, further, to compare the results with those of the reactions in the previous papers.⁽⁶⁾⁽⁷⁾⁽⁸⁾⁽¹⁾ The experimental procedure was almost the same as before.

I. Reaction products at 1400°. Mixtures of MgO and Al_2O_3 , corresponding to $\text{MgO}:\text{Al}_2\text{O}_3=2:1$, $1:1$ and $1:2$, were heated at 1400° for 10 hours; the amounts of free MgO of the products were determined and their X-ray photographs were taken. The results are given in Table 1.

(1) IV, This Bulletin, **17** (1942), 70.

(2) The main part of this paper has been published in Japanese in *J. Chem. Soc. Japan*, **62** (1941), 477.

(3) G. Hägg and G. Söderholm, *Z. physik. Chem.*, B, **29** (1935), 88.

(4) The limit of solubility differs somewhat with the temperature. It differs also with the modifications of Al_2O_3 , and the range of the unstable solid solution spreads to $\gamma\text{-Al}_2\text{O}_3$.

(5) For instance, W. Jander and W. Stamm, *Z. anorg. allgem. Chem.*, **199** (1931), 165; G. Hüttig and E. Zeidler, *Kolloid-Z.*, **75** (1936), 309; K. Hild, *Z. physik. Chem.*, A, **161** (1936), 317; W. Jander and H. Pfister, *Z. anorg. allgem. Chem.*, **239** (1938), 95.

(6) I, This Bulletin, **16** (1941), 428.

(7) II, This Bulletin, **16** (1941), 455.

(8) III, This Bulletin, **17** (1942), 64.

Since the reaction product, $\text{MgO} \cdot \text{Al}_2\text{O}_3$, as well as Al_2O_3 , heated at higher temperatures ($\alpha\text{-Al}_2\text{O}_3$), are insoluble even in concentrated acids, it is impossible to separate the reaction product from the unreacted Al_2O_3 .

Table 1. Reaction products at 1400° .

Mixing ratio $\text{MgO} : \text{Al}_2\text{O}_3$	Free MgO (%)	Lattice constant of the spinel formed. (Å)
2:1	21.18	8.05 ₁
1:1	3.06	8.03 ₈
1:2	0.72	8.00 ₇

It was understood that, with a mixture of $\text{MgO} : \text{Al}_2\text{O}_3 = 2:1$, the reaction was completed forming pure $\text{MgO} \cdot \text{Al}_2\text{O}_3$, because the calculated amount of free MgO was 22.08%,⁽⁹⁾ and the lattice constant of the spinel obtained coincided with that of pure spinel, given by Hägg and Söderholm.⁽³⁾ With a mixture of $\text{MgO} : \text{Al}_2\text{O}_3 = 1:2$, the lattice constant of the spinel became considerably smaller, and

the interference lines of $\alpha\text{-Al}_2\text{O}_3$ were observed distinctly at the same time.

II. Course of the reaction between 800° and 1200° . The course of the reaction was followed by determining free MgO of the products, and some of the products were studied by the X-ray method. Preparations were ignited before use.

As shown in Table 2, the reaction took place already considerably at 800° , but it was never completed even at 1200° . The lattice constants of the spinels in these products agreed approximately with that of pure $\text{MgO} \cdot \text{Al}_2\text{O}_3$, and the positions of the interference lines of MgO and of $\alpha\text{-Al}_2\text{O}_3$ were also unchanged.

Table 2. Free MgO (%) of the reaction products.

(1) $\text{MgO} : \text{Al}_2\text{O}_3 = 1:2$ (MgO = 16.51%).

Reaction time (hrs.)	0.5	1	3	6	10
Reaction temperature ($^\circ\text{C}$) ...	800	—	15.27	14.90	14.55
	900	—	13.43	13.08	12.19
	1000	12.96	10.94	10.00	8.85
	1100	7.38	6.60	5.73	5.29
	1200	4.85	4.17	3.56	3.08

(2) $\text{MgO} : \text{Al}_2\text{O}_3 = 1:1$ (MgO = 28.34%).

Reaction time (hrs.)	0.5	1	3	6	10
Reaction temperature ($^\circ\text{C}$) ...	800	—	26.49	26.03	25.81
	900	—	24.97	23.73	23.57
	1000	23.49	22.49	20.75	19.21
	1100	17.56	15.78	14.69	13.03
	1200	12.90	12.18	10.58	9.47

(9) Although free MgO obtained is slightly smaller than this value, its smaller value cannot be avoided when the amount of which is practically too much.

Table 2.—(Concluded)

(3) $\text{MgO}:\text{Al}_2\text{O}_3 = 1:2$ ($\text{MgO} = 44.17\%$).

Reaction time (hrs.)	0.5	1	3	6	10
Reaction temperature ($^{\circ}\text{C}$) ...					
800	41.71	41.17	40.61	40.77	40.39
900	39.98	39.40	38.40	37.87	37.21
1000	36.66	36.14	34.95	34.56	—
1100	31.61	29.89	28.16	27.20	—

III. Discussion of the results. It is obvious from the above experiments that pure $\text{MgO}\cdot\text{Al}_2\text{O}_3$, which is the richest in the basic component, MgO , within the possible range of the solid solution, is formed at the early stage of the reaction, whatever the mixing ratio of the components may be. It seems that, only with the mixtures containing an excess of Al_2O_3 , the solid solution, rich in Al_2O_3 , is formed after the greater part of MgO has been reacted to form $\text{MgO}\cdot\text{Al}_2\text{O}_3$. The tendency is quite reverse to that of the reaction between CaO and TiO_2 ,⁽⁷⁾ in which the composition of the solid solution, formed at first, is the richest in the acid component. While the lattice constant of the spinel, obtained with a mixture of $\text{MgO}:\text{Al}_2\text{O}_3=1:1$ at 1400° , is a little smaller than that of pure $\text{MgO}\cdot\text{Al}_2\text{O}_3$, it is considered that, even in a stoichiometric mixture, the solid solution, rich in Al_2O_3 , is formed locally where Al_2O_3 exists in excess toward the end of the reaction, leaving a part of MgO in free state.

As the lattice constant of the spinel, $a=8.007\text{\AA}$, obtained with a mixture of $\text{MgO}\cdot\text{Al}_2\text{O}_3=1.2$ at 1400° , is $0.044\text{\AA}$ smaller than that of pure $\text{MgO}\cdot\text{Al}_2\text{O}_3$, $a=8.051\text{\AA}$, it is calculated that the spinel in this case contains approximately the excess of 8.5 mol % Al_2O_3 , in forming a solid solution. Hägg and Söderholm⁽⁵⁾ confirmed the limit of the solid solution by fusing the components. It is also expected, by the solid reaction, that a solid solution with more Al_2O_3 is obtained when the reaction proceeds further.

In the present reaction, there exists a rapid initial reaction just as in the reactions between MgO or CaO and TiO_2 .⁽⁶⁾⁽⁷⁾ A further reaction seems to be controlled by the diffusion of the components through the reaction product; the energy of activation of the process with a stoichiometric mixture is calculated as $Q=41.1$ Kilocalories per mole, and the value is nearly equal to those of the above two reactions.

Finally, when the influence of the mixing ratio of the components on the rate of the present reaction is considered, it is found that the reaction takes place more readily with a mixture of $\text{MgO}:\text{Al}_2\text{O}_3=2:1$, namely, when MgO exists in excess, than with the other mixtures. This cause will be discussed in the next paper.

Summary.

(1) It has been found that pure $\text{MgO}\cdot\text{Al}_2\text{O}_3$ is formed at first in this reaction, and the solid solution rich in Al_2O_3 is formed gradually when an excess of Al_2O_3 is present.

(2) Although there exists a rapid initial reaction, the later reaction is controlled by the diffusion process with an energy of activation of 41.1 Kilocalories per mole.

(3) The reaction proceeds more easily with the mixtures containing an excess of MgO than with the other mixtures.

The author expresses his sincere thanks to Dr. R. Yoshimura, Director of the Department, for his interest in this work. He is also indebted to Mr. K. Oguro and Mr. T. Sugawa for their assistances with the experiments and to the Physics Section of the Laboratory for taking the X-ray photographs.

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**Der katalytische Isotopenaustausch des gasförmigen Sauerstoffs.
XII.⁽¹⁾ Die Austauschreaktion der Sauerstoffatome zwischen
Sauerstoff und Wasserdampf an der Oberfläche des Natrium-
und Kaliumcarbonats. (Auszug.)⁽²⁾**

Von Yosio OSUMI, Noriyoshi MORITA und Toshizo TITANI.

(Eingegangen am 7. Januar 1942.)

Inhaltsübersicht. Die Austauschreaktion der O-Atome zwischen gasförmigem Sauerstoff und Wasserdampf an der Oberfläche einiger Salze des Natriums und Kaliums wird untersucht. Dabei zeigt sich, dass an der Oberfläche des Natriumchlorids, Natriumsulfats und Natriumphosphats bis auf ziemlich hohe Temperaturen keine nennenswerte Austauschreaktion stattfindet. Dagegen tritt an der Oberfläche des Natrium- und Kaliumcarbonats oberhalb etwa 500° eine lebhafte Austauschreaktion ein und ihre Geschwindigkeit nimmt mit steigender Temperatur schnell zu. Die Reaktion wird mit Hilfe der Annahme erklärt, dass unter der Wirkung des Wasserdampfes aus dem Carbonat das Hydroxyd gebildet wird und durch die katalytische Wirkung des so gebildeten Hydroxyds die in Rede kommende Austauschreaktion herbeigeführt wird.

Austauschversuche. Die katalytische Austauschreaktion der O-Atome an der Oberfläche verschiedener Arten der Oxyde bzw. Hydroxyde ist bisher eingehend untersucht worden. Daran anschliessend wird in dem vorliegenden Versuch dieselbe Reaktion an der Oberfläche einiger Salze untersucht. Die Versuchsmethode und -anordnung ist genau dieselbe wie schon früher beschrieben wurde (vgl. z.B. die letzte Mittl. XI)⁽¹⁾. Das feinkörnige wasserfreie Salz wird als solches d.h. ohne Träger in das Katalysatorrohr eingeladen und auf einer bestimmten Temperatur erhitzt. Darüber wird nun das Reaktionsgasgemisch aus (an schwerem Sauerstoff angereichertem) schwerem Wasserdampf und elektrolytischem leichtem

(1) XI. Mittl.: erscheint aus Redaktionsgründe in fortlaufender Nummer dieses Bulletins.

(2) Y. Osumi und N. Morita, *J. Chem. Soc. Japan*, **62** (1941), 807. Y. Osumi und T. Titani, ebenda, **62** (1941), 812.

Sauerstoffgas langsam (bei Zimmertemperatur und unter atmosphärischem Druck gemessen 60 ccm pro Min.) geleitet. Das Gasgemisch besitzt die Zusammensetzung von $\text{H}_2\text{O}:\text{O}_2=1:2$. Der aus dem Katalysatorrohr zusammen mit dem Sauerstoffgas ausgeströmte Wasserdampf wird in einem Gefäß ausgefroren und gereinigt. Bezeichnet man den gewöhnlichen Wasser gegenüber gemessenen Dichteüberschuss des so behandelten schweren Wassers mit Δs_e und den, der das schwere Wasser vor dem Versuch besitzt, mit Δs_a , so lässt sich das prozentuale Austauschmass %A für die unter den angegebenen Versuchsbedingungen zwischen Wasserdampf und Sauerstoffgas stattgefundenen Austauschreaktion mit Hilfe der Gl. berechnen:

$$\%A = \frac{(\Delta s_a - \Delta s_e)}{(\Delta s_a - \Delta s_e)_\infty} \times 100.$$

In dieser Gl. drückt $(\Delta s_a - \Delta s_e)_\infty$ die Abnahme des Dichteüberschusses des schweren Wassers aus, die sich beim vollständigen Austausch ergeben würde. Dieser extreme Wert lässt sich aber mit Hilfe der relativen Menge des Wasserdampfes und Sauerstoffgases sowie ihrem resp. Dichteüberschuss, der lediglich auf die Anreicherung des schweren Sauerstoffs zurückgeführt wird, rechnerisch ermitteln. So ergibt sich beim vorliegenden Versuch $(\Delta s_a - \Delta s_e)_\infty = 29.1 \gamma$, wo der gesamte Dichteüberschuss des benutzten schweren Wassers 64.7γ betrug und davon 34.8γ auf die Anreicherung des schweren Sauerstoffs zurückgeführt wurde. Die Versuchsergebnisse sind in folgenden Tabellen 1 bis 5 zusammengestellt. Dabei entspricht jede Tabelle solch einer Versuchsreihe, die unter Verwendung eines frischen Katalysators d.h. Salzes ausgeführt wurde, dessen Menge in den Klammern hinter seinem Namen angegeben ist.

Tabelle 1. Natriumchlorid (7 g).

Versuchs- nr.	Temp. °C	$(\Delta s_a - \Delta s_e)$ in γ	%A
1	365	1.0	3
2	455	4.6	16
3	550	1.2	4
4	670	1.5	5

Tabelle 3. Natriumphosphat (10 g).

Versuchs- nr.	Temp. °C	$(\Delta s_a - \Delta s_e)$ in γ	%A
1	385	4.3	15?
2	475	1.7	6
3	595	1.8	6
4	720	2.2	8

Tabelle 2. Natriumsulfat (15 g).

Versuchs- nr.	Temp. °C	$(\Delta s_a - \Delta s_e)$ in γ	%A
1	385	1.0	3
2	450	0.0	0
3	540	0.0	0
4	700	-0.2	-1

Tabelle 4. Natriumcarbonat (8g).⁽³⁾

Versuchs- nr.	Temp. °C	$(\Delta s_a - \Delta s_e)$ in γ	%A
1*	350	1.2	4
2*	470	7.2	25
3	560	18.9	65
4	720	30.6	105

(3) Von Kahlbaum bezogen.

Tabelle 4. – (Fortsetzung)

Versuchs- nr.	Temp. °C	$(\Delta s_a - \Delta s_e)$ in γ	% A
1*	445	4.7	16
4	475	4.4	15
2	535	16.3	56
3	555	18.1	62

Versuchs- nr.	Temp. °C	$(\Delta s_a - \Delta s_e)$ in γ	% A
3	522	11.3	39
2	545	16.1	55
1	575	20.6	71

Tabelle 5. Kaliumcarbonat (10 g).⁽⁴⁾

Versuchs- nr.	Temp. °C	$(\Delta s_a - \Delta s_e)$ in γ	% A
1*	375	2.5	9
2*	445	4.8	17
3	535	6.2	21

Versuchs- nr.	Temp. °C	$(\Delta s_a - \Delta s_e)$ in γ	% A
2*	420	1.4	5
1	475	8.0	28
3	520	4.8	17
5	572	12.1	42
4	602	15.5	53
6	625	18.8	65

Aus den in Tabellen 1 bis 3 angegebenen Versuchsergebnissen darf wohl geschlossen werden, dass an der Oberfläche des Natriumchlorids, Natriumsulfats sowie Natriumphosphats keine nennenswerte Austauschreaktion stattfindet. Dagegen findet diese an der Oberfläche des Natriumcarbonats oberhalb etwa 450° und an der des Kaliumcarbonats oberhalb etwa 500° deutlich statt und ihre Geschwindigkeit nimmt mit steigender Temperatur stark zu, wie aus Tabellen 4 und 5 und noch deutlicher aus den nebenstehenden Abbn. 1a und 2a erkennbar ist.

In Abbn. 1b und 2b ist der Ausdruck $\log \left[-\log \left(1 - \frac{\% A}{100} \right) \right]$ gegen das Reziproke der absoluten Temperatur $1/T$ eingetragen. Die so eingezeichneten Punkte sollen aber auf einer geraden Linie liegen und aus der Neigung dieser geraden Linie lässt sich die Aktivierungsenergie A für die

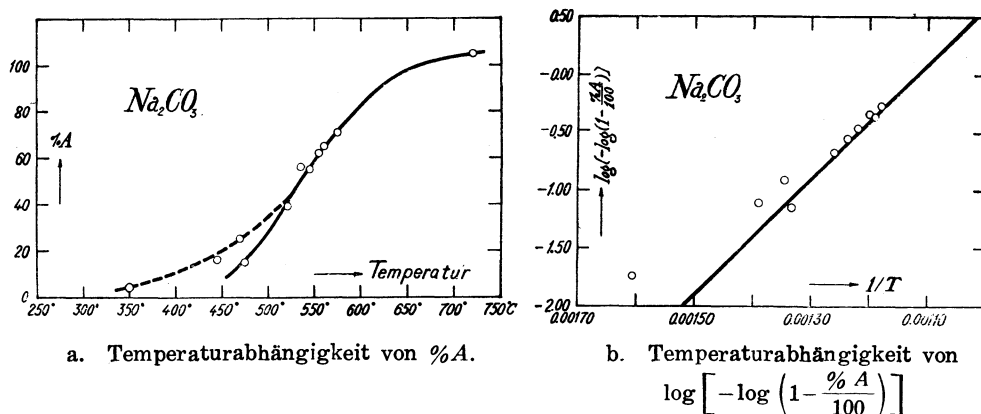


Abb. 1. Austauschreaktion zwischen gasförmigem Sauerstoff und Wasserdampf an der Oberfläche des Natriumcarbonats in Abhängigkeit von der Temperatur.

(4) Von Takeda bezogen. Dieses Präparat wies nach Beendigung der Versuche eine schwach bläuliche Färbung auf.

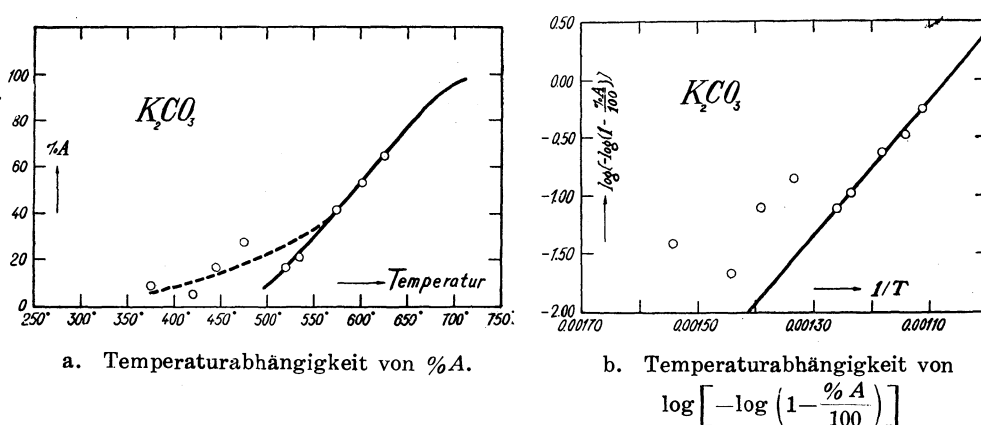


Abb. 2. Austauschreaktion zwischen gasförmigem Sauerstoff und Wasserdampf an der Oberfläche des Kaliumcarbonats.

betreffende Reaktion ermitteln.⁽⁵⁾ Mit Hilfe der Abbn. 1b und 2b wird nämlich gefunden, dass

$$A(Na_2CO_3) = 23 \text{ Kcal.} \quad \text{und} \quad A(K_2CO_3) = 27 \text{ Kcal.},$$

ist, obwohl einige Messresultate, die hauptsächlich am Anfang der einzelnen Versuchsreihen und besonders bei niedrigen Temperaturen gewonnen wurden, ziemlich stark auseinanderliegen.⁽⁶⁾ Die Austauschreaktion an dem weniger alkalischen Natriumcarbonat braucht also kleinere Aktivierungsenergie als an dem stärker alkalischen Kaliumcarbonat. Dementsprechend verläuft in der Tat die Austauschreaktion an dem Natriumcarbonat leichter als an dem Kaliumcarbonat, wie aus dem Vergleich der beiden Abbn. 1a und 2a ohne weiteres ersichtlich ist. Dieser Befund widerspricht aber auf den ersten Blick der aus den bisherigen Versuchen gefundenen Regel, dass die katalytische Wirksamkeit der ähnlich gebauten Oxyde bzw. Hydroxyde für die in Rede kommende Austauschreaktion mit der zunehmenden Alkalinität der betreffenden Oxyde bzw. Hydroxyde zunimmt. So verläuft z.B. die Reaktion an der Oberfläche des Kaliumhydroxyds, wie in dem letzten Versuche⁽⁷⁾ festgestellt wurde, leichter als an dem Natriumhydroxyd. Auf die Deutung für diese Diskrepanz sowie auf die Erklärung für die oben hingewiesene Streuung der Messresultate mit dem Alkalicarbonaten kommen wir später zurück.

Wirkung des Wasserdampfes auf das Natriumcarbonat. Da unter den untersuchten Arten der Salze nur die Carbonate messbare katalytische Wirksamkeit besitzen, liegt die Annahme nahe, dass die letztere mit den chemischen Eigenschaften der Carbonate in engem Zusammenhang steht. Wir haben weiter in dem letzten Versuche⁽⁷⁾ gefunden, dass das Natrium- und Kaliumhydroxyd für die in Rede kommende Austauschreaktion eine ausgezeichnete katalytische Wirksamkeit besitzt. So

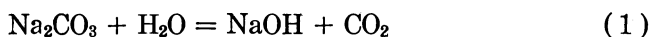
(5) N. Morita, dies Bulletin, **15** (1940), 306.

(6) Die so ausgestreuten Resultate sind in Tabellen 4 und 5 mit * bezeichnet.

(7) XI. Mittel.

ist durchaus möglich, dass das Carbonat unter der Wirkung des Wasserdampfes sich mindestens oberflächlich bis zum Hydroxyd verwandelt und das so gebildete Hydroxyd für die betreffende Austauschreaktion katalytisch wirkt. Um diese Annahme experimentell zu bestätigen, wird nun die chemische Wirkung des Wasserdampfes auf das Natriumcarbonat untersucht.

Das Katalysatorrohr wird mit etwa 30 g, d.h. eine etwa viermal so grosse Menge Natriumcarbonat wie die beim eigentlichen Austauschversuch benutzte (vgl. Tabelle 4), beladen und auf 300° bis 600° erhitzt. Über das so erhitzte Carbonat wird nun das reine Stickstoffgas und das Gasgemisch aus reinem Stickstoffgas und Wasserdampf abwechselnd, und zwar zunächst das Stickstoffgas und dann das Gasgemisch, langsam durchgeleitet. Das aus dem Katalysatorrohr ausgeströmte Gas wird nun jedesmal in eine frisch bereitete Barytlösung eingeleitet und die dabei austretende Trübung der Lösung miteinander verglichen. Dabei kommt zur Feststellung, dass bei der Durchleitung des reinen Stickstoffs fast keine bzw. nur sehr schwache Trübung auftritt. Wird dagegen der Stickstoffstrom durch das Gasgemisch aus Stickstoff und Wasserdampf ersetzt, so wird die Lösung ohne weiteres stark getrübt. Dass diese Trübung wirklich von der Zersetzung des Carbonats nicht aber von der Desorption der von vorn herein an ihm adsorbiert befindlichen Kohlensäure herrührt, davon können wir uns dadurch überzeugen, dass sogar nach fünfstündiger Durchleitung des reinen Stickstoffs, die fast keine Trübung aufwies, ohne weiteres eine starke Trübung auftrat, so bald als der reine Stickstoff durch das Gasgemisch aus Stickstoff und Wasserdampf ersetzt wurde. Die absolute Menge der Kohlensäure, die bei der Einwirkung des Wasserdampfes auf das Carbonat befreit wird, ist aber nicht so gross. Bei einem Sonderversuche, wo man etwa 15 g (=0.83 Mol) Wasserdampf auf 30 g (=0.28 Mol) Natriumcarbonat einwirken liess, wurden bei 438° etwa 0.00005 Mol und bei 623° etwa 0.003 Mol Kohlensäure in der Gasphase nachgewiesen. So liegt die Vermutung nahe, dass die durch die Reaktion:



entwickelte Kohlensäure grösstenteils an der Oberfläche des zu gleicher Zeit gebildeten Hydroxyds chemisorbiert beibehalten und nur ein kleiner Anteil in die Gasphase hinauskommt. Verläuft jedoch die oben angegebene Reaktion (1) an der Oberfläche einer bestimmten Menge des Carbonats nach beiden Seiten hin mit wohl messbarer Geschwindigkeit, so müssen die O-Atome des letzteren nach und nach gegen die des Wasserdampfes ausgetauscht werden. Dass dies wirklich der Fall ist, wird durch die in Tabelle 6 wiedergegebenen Versuche bestätigt. Bei diesem Versuch wird nämlich jedesmal 30 g (d.h. etwa viermal so viel wie beim eigentlichen Austauschversuch!) frisches Carbonat in dem Katalysatorrohr auf eine bestimmte Temperatur erhitzt und darüber wird 15 g an schwerem Sauerstoff angereicherten schweren Wasserdampfes zusammen mit reinem Stickstoffgas geleitet. Das letztere Gas wirkt als der Träger. Durch diese Behandlung nimmt nun der (gewöhnlichem Wasser gegenüber gemessene) Dichteüberschuss des schweren Wassers, der anfänglich $\Delta s_a = 64.7 \gamma$ beträgt, bis zu dem Wert Δs_e ab, der in der zweiten Spalte

der Tabelle 6 wiedergegeben ist. Der Dichteüberschuss des schweren Wasser vermindert sich also um den in der dritten Spalte der Tabelle angegebenen Betrag $(\Delta s_a - \Delta s_e)$.

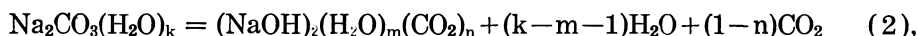
Tabelle 6. Austauschreaktion der O-Atome zwischen festem Natriumcarbonat und Wasserdampf.

Temp. °C	Δs_e in γ	$(\Delta s_a - \Delta s_e)$ in γ	%A
438	54.2	10.5	48
453	53.3	11.4	52
530	46.2	18.5	84
623	42.7	22.0	100

Eine einfache Rechnung zeigt, dass diese Abnahme der Dichte des schweren Wassers etwa 18 γ betragen sollte, wenn die in Rede kommende Austauschreaktion bis zum Gleichgewicht verlaufen würde. Da aber erstens diese Berechnung auf einer ziemlich groben Annäherung beruht und zweitens der in der am Ende der dritten Spalte der Tabelle 6 angegebene höchst gefundene Wert von $(\Delta s_a - \Delta s_e)$ d.h. 22.0 γ bei 623° sehr nahe dem oben angegebenen theoretischen Wert liegt, wird dieser gefundene Höchstwert von $(\Delta s_a - \Delta s_e)$ als der in Rede kommende Grenzwert angenommen. Das in der letzten Spalte der Tabelle angegebene prozentuale Austauschmass %A wird also mit Hilfe der Gl. gerechnet:

$$\%A = \frac{(\Delta s_a - \Delta s_e)}{22.0} \times 100.$$

Schluss und Diskussion. Aus dem oben angegebenen Versuche darf die Annahme wohl berechtigt erscheinen, dass die Austauschreaktion zwischen Wasserdampf und Sauerstoffgas an der Oberfläche des Natrium- bzw. Kaliumcarbonats in der Tat mit Hilfe der katalytischen Wirkung des Hydroxyds ausgeführt wird, das unter der Wirkung des Wasserdampfes aus dem Carbonat sekundär gebildet wird. Nimmt man weiter an, dass das wasserfreie Carbonat bei der Durchleitung des Wasserdampfes bis zu einem gewissen Grad hydratisiert wird und die daraus entwickelte Kohlensäure grösstenteils an dem zu gleicher Zeit gebildeten Hydroxyd chemisorbiert beibehalten wird, so können wir den ersten Schritt der in Rede kommenden katalytischen Austauschreaktion etwa folgendermassen formulieren:



In dieser Gln. drückt $\text{Na}_2\text{CO}_3(\text{H}_2\text{O})_k$ das einige Mole Wasser chemisorbiert verbundene Carbonat aus. Aus diesem hydratisierten Carbonat wird gemäss der Gl. (2) das ebenfalls hydratisierte und einige Mole Kohlensäure chemisorbiert verbundene Hydroxyd $(\text{NaOH})_2(\text{H}_2\text{O})_m(\text{CO}_2)_n$ gebildet und an der Oberfläche des so gebildeten Hydroxyds wird das Wassermolekül gemäss Gl. (3) aktiviert adsorbiert. Die Austauschreaktion der O-Atome zwischen dem so aktiviert adsorbierten Wassermolekül H_2O^* und dem Sauerstoffmolekül aus der Gasphase kann auf dieselbe

Weise, wie in dem letzten Versuche für die Austauschreaktion an der Oberfläche der Alkalihydroxyde angenommen wurde (vgl. Gl. 2 in XI. Mittl.), unter der Zwischenbildung des Peroxyds stattfinden.

Nimmt man nun an, dass unter den beiden Reaktionen (2) und (3) die letztere geschwindigkeitsbestimmend ist, so muss die erste Reaktion sich immer im Gleichgewicht befinden. Die Geschwindigkeit der ganzen Austauschreaktion wird also erstens durch die Gleichgewichtskonstante der Reaktion (2) und zweitens durch die Geschwindigkeitskonstante der Reaktion (3) beeinflusst. Unter diesen beiden Grössen muss die letztere d.h. die Geschwindigkeitskonstante der Reaktion (3), im Lichte der aus den bisherigen Versuche bestätigten allgemeinen Regel einen grösseren Wert für die stärker alkalische Kaliumverbindung besitzen als für die weniger alkalische Natriumverbindung. Was die Geschwindigkeitskonstante der Reaktion (3) anbetrifft, so ist hingegen durchaus möglich, dass sie für das weniger alkalische Natriumcarbonat vielmehr einen grösseren Wert besitzt als für das stärker alkalische Kaliumcarbonat. Dafür spricht z.B. die Tatsache, dass das Natriumcarbonat einen grösseren Zersetzungsdruck als das Kaliumcarbonat besitzt. Nimmt man deshalb an, dass der Einfluss dieser Gleichgewichtskonstante der Reaktion (2) auf die ganze Austauschgeschwindigkeit den der Geschwindigkeitskonstante der Reaktion (3) überwiegt, so folgt ohne weiteres, dass die betreffende Austauschreaktion an der Oberfläche des weniger alkalischen Natriumcarbonats viel schneller als an dem stärker alkalischen Kaliumcarbonat verläuft.

Mit Hilfe des eben angegebenen Reaktionsschemas können wir weiter die in Abbn. 1 und 2 gezeigte Tatsache wohl erklären, dass einige am Anfang einer Reihe der Versuche und besonders bei niedrigen Temperaturen gewonnenen Messresultate ziemlich stark auseinanderliegen. Da bei jeder Reihe der Versuche immer ein frisches Carbonat als Katalysator verwendet wurde, muss dieses Carbonat zuerst unter der Wirkung des Wasserdampfes mindestens oberflächlich bis zum Hydroxyd verwandelt werden, bis das erstere für die in Rede kommende Austauschreaktion genügend katalytisch aktiv wird. Dabei nimmt aber der Gehalt des durchströmenden schweren Wasserdampfes an schwerem Sauerstoff bis zu einem gewissen Grad ab, weil die eben angegebene Wechselwirkung zwischen dem Carbonat und dem Wasserdampf den Austausch der O-Atome zwischen den beiden Substanzen mit sich bringt, wie darauf schon oben hingewiesen wurde. Das am Anfang jeder Reihe der Versuche auftretende anormale grosse prozentuale Austauschmass $\%A$ rührt von diesem unmittelbaren Austausch zwischen dem Carbonat und dem Wasserdampf her. Die Abnahme der Dichte des schweren Wassers, die auf diesem Austausch zwischen dem Wasserdampf und dem Carbonat beruht, tritt aber bald hinter der eigentlichen katalytischen Austauschreaktion zwischen Wasserdampf und dem Sauerstoffgas vernachlässigend zurück, weil der erst genannte Austausch wegen der Kleinheit der beim eigentlichen Austauschversuche verwendeten Menge des Carbonats in kurzer Zeit bis zum Gleichgewicht kommt und das Carbonat mit dem schweren Sauerstoff abgesättigt wird. Nach dieser Absättigung des Carbonats an schwerem Sauerstoff findet die Abnahme der Dichte des schweren Wassers praktisch ausschliesslich durch die eigentliche katalytische Austauschreaktion zwischen dem Wasserdampf und dem Sauerstoffgas statt.

Zum Schluss möchten wir der Nippon Gakujutsu Shinkohkai (der Japanischen Gesellschaft zur Förderung der wissenschaftlichen Forschung) sowie der Hattori Hohkoku (der Hattori-Stiftung) für ihre finanzielle Unterstützung bei der Durchführung der vorliegenden Arbeit unsern Dank aussprechen.

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Eine Forschung über die Korrosion des Makromoleküls mit Elektronenbeugung (das Zersetzen von CdCl_2 -, CdBr_2 - und CdJ_2 -Makromolekülen durch Wasserdampf).

Von Shigeto YAMAGUCHI.

(Eigegangen am 12, Januar 1942.)

Einleitung. Beobachtet man „N-Beugungsbild“ bei Elektronenbeugung (nach Transmissionsmethode), so könnte man theoretisch vermuten, dass es einen zweidimensionalen Film als Quelle dieses Bildes gäbe⁽¹⁾. Der zweidimensionale Film, dessen Vorhandensein die Elektronenbeugungsmethode geschickt zu entdecken imstande ist, ist ein Einkristall, der sich längs einer gewissen Netzebene zweidimensional spaltet. Ein solches Spalten geschieht sehr häufig längs jenen Netzebenen, die nur durch die van der Waalschen Anziehungskräfte und Wasserstoff-Bindung locker verbunden sind⁽²⁾. Dass aus CdCl_2 -, CdBr_2 - und CdJ_2 -Kristallen mit Schichtengitter die N-Beugungsbilder erfolgen, erwartet man nicht nur theoretisch, sondern wird auch experimentell in dieser Forschung nachgewiesen. An den CdCl_2 - und CdBr_2 -Kristallen sind die Netzebenen (111), am CdJ_2 -Kristall (001), nur durch van der Waalsche Anziehungskräfte verbunden⁽³⁾ (vid. Abb. I). Denjenigen zweidimensionalen Film, der schon längs der Richtung (111) bzw. (001) gespalten wurde, kann man mit Recht als zu einem reinen Zustand isoliertes Makromolekül betrachten. Chemisch und physikalisch bedeutungsreich ist es, wenn man die Reaktion zwischen dem Makromoleküle und H_2O , als etwa eine von den einfachsten Reaktionen zwischen festem Körper und Gas behandelt.

(1) S. Kikuchi, *Proc. Imp. Acad. Japan*, **4** (1928), 271.

(2) S. Yamaguchi, *Nature*, **147** (1941), 296; *Sci. Papers Inst. Phys. Chem. Research* (Tokyo), **38** (1940), 142.

(3) L. Pauling, *Z. Krist.*, **74** (1930), 546; *The Nature of the Chemical Bond*, (1940), 189.

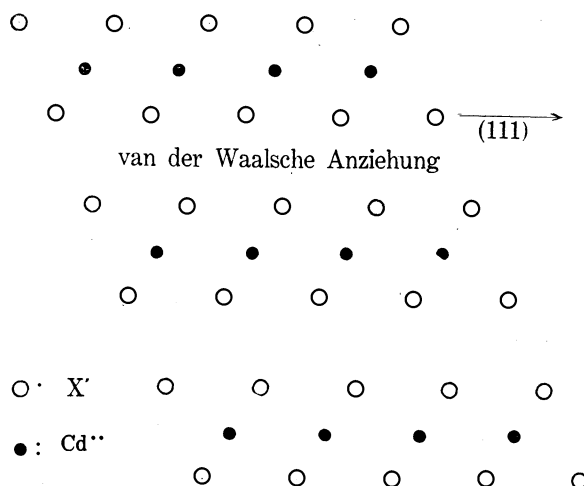


Abb. 1.

Experimente. CdCl_2 . In der vorliegenden Arbeit wurde zwar die „Netz-Methode“ benutzt,⁽⁴⁾ aber sie unterscheidet sich ein wenig von der bisherigen. In das geschmolzene CdCl_2 -Salz wurde ein Platindrahtnetz eingetaucht. Beim Herausziehen bildeten sich dann in allen Maschen des Netzes dünne Filme. Der auf diese Weise hervorgebrachte Film

diente erfolgreich als Versuchsprobe für Elektronenbeugung (vid. Photo. 1). Auch mit dem aus der wässrigen Lösung auf dem Platindrahtnetz kristallisierten Filme wurde ein Beugungsbild (vid. Photo. 2) aufgenommen, wie schon oft durch den Verfasser vorher durchgeführt wurde. Diese beiden Aufnahmen zeigen, dass die Versuchsprobe eine aus den pulverartigen CdCl_2 -Kristallen bestehende dünne Haut ist (vid. Tab. 1).

CdBr_2 . CdBr_2 wurde ebenfalls auf dieselbe Weise behandelt, die auf CdCl_2 verwandt wurde. Von Photo. 3 wird es an sich klar, dass der zweidimensionale Film aus dem geschmolzenen CdBr_2 -Salz mit dem Netz abgezogen werden kann. Die der Luft auszusetzende Ebene des CdBr_2 -Makromoleküls soll mit (111) indiziert werden, denn

$$\left\{ \begin{array}{l} d_{110} = 1.98 \text{ \AA} \\ \sqrt{3} d_{110} = 3.43 \text{ \AA} \end{array} \right. \quad (\text{nach Röntgenstrahlenmethode}^{(5)}),$$

und

$$\left\{ \begin{array}{l} d_{\text{beo}} = (110) = 1.98 \text{ \AA} \\ d_{\text{beo}} = 1.73(110) = 3.43 \text{ \AA} \end{array} \right. \quad (\text{nach der vorliegenden Arbeit})$$

(4) S. Yamaguchi, *Nature*, **146** (1940), 333.

(5) L. Pauling, *Proc. Natl. Acad. Sci.*, **15** (1929), 709.

(vid. Photo. 3 und Abb. 2). Da die Ausbreitungskugel annähernd das reziproke Gitter schneidet, das in Abb. 2 (oder Photo. 3) zu skizzieren ist, fällt rechtwinklig dem Ebene (111) der Elektronenstrahl. Photo. 4 und Tab. 2 zeigen, dass der Film aus dem Pulver von kleinen CdBr_2 -Kristallen besteht, wenn sie sich aus der wässrigen Lösung kristallisieren.

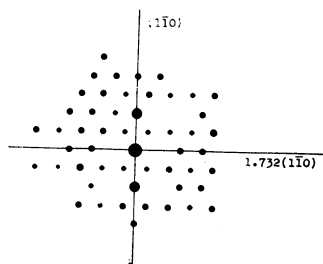


Abb. 2.

Tab. 2. (CdBr_2).

d_{beo}	d_R	hkl	I_{beo}
6.22 (Å)	6.22	111	s. sch.
3.37	3.37	100	s.
3.22	3.21 ₅	110	s.
3.11	3.11	222	s. sch.
2.52	2.52	221	sch.
2.07	2.07	333	s. sch.
1.98	1.98	110	s.

CdJ_2 . In diesem Falle ist es schwierig, jenes Salz zu schmelzen, weil es sich bei höheren Temperaturen leicht zum Zersetzen neigt. Also war dieser Versuch nicht passend, so war das Kristallisieren nur aus der wässrigen Lösung durchführbar. Das Beugungsbild, wie sie in Photo. 5 oder in Abb. 3

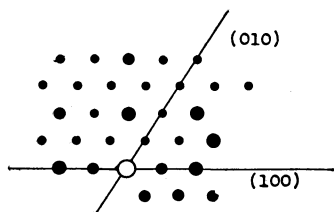


Abb. 3.

gezeigt wird, gibt dasjenige Makromolekül, auf dessen Oberfläche (001) der Elektronenstrahl annähernd rechtwinklig trifft, da

$$d_{100} = 3.68 \text{ Å} \quad (\text{nach Röntgenstrahlmethode})^{(6)}$$

$$d_{\text{beo}} = 3.68 \text{ Å} \quad (\text{nach der vorliegenden Arbeit})$$

diese zwei Werte völlig gleich sind.

Betrachtung 1. Nicht nur der aus dem geschmolzenen CdBr_2 -Salz isolierte dünne Film und die aus der Lösung gebildete CdJ_2 -Haut, sondern auch der auf dieselbe Weise hergestellte CdCl_2 -Film bieten deutlich einen charakteristischen Glanz, wenn man den letzteren nicht lange Zeit (weniger als 5 Minuten) in der Luft liegen lässt. Diesen bemerkenswerten Glanz liefern zweifellos die Spaltflächen (111) bzw. (001) von CdCl_2 -, CdBr_2 -, CdJ_2 -Einkristallen. Daher soll es einwandfrei sein, dass auch der CdCl_2 -Film in erster Linie wohl als zweidimensionaler Einkristall gespalten wird, aber CdCl_2 eigentlich so viel hygroskopischer ist als CdBr_2 und CdJ_2 , dass jenes sich sofort durch die Reaktion mit H_2O in der Luft zersetzt. Die van der Waalschen Kräften, wie sie die Ebenen (111) oder (001) schwach zusammenknüpfen, sind nach F. London⁽⁷⁾ mit $\Delta E a^2/R^6$ zu geben. Diese Anziehungskräfte sind von dem kleinsten Werte

(6) R. M. Bozorth, *J. Am. Chem. Soc.*, **44** (1922), 2232.

(7) F. London, *Z. phys. Chem.*, B **11** (1931), 222.

Tab. 3.

Makromolekül	$\propto \Delta E a^2 / R^6$
CdCl_2	1
CdBr_2	1.5
CdJ_2	2

bei CdCl_2 , von dem grössten bei CdJ_2 (vid. Tab. 3). Daher kann man unter ihnen CdCl_2 -Einkristall am leichtesten längs den van der Waalschen Bindungsebenen spalten. Die von aussen gegebene Wärmeenergie (kT) ist genügend, um diese Bindung locker zu machen. Wenn man dieses leicht zerfliess-

ende Makromolekül in der feuchten Luft, besonders unter hiesigem Klima liegen lässt, so verändert es sich sofort zu einer neuen Verbindung, d.h. zu $\text{CdCl}_2 \cdot \text{H}_2\text{O}$, die noch darunter stabil ist. Aber dieses Hydrat wittert in der Elektronenkamera aus, und der umkristallisierte CdCl_2 -Kristall, der sich pulverartig zeigt, wird wieder durch Elektronenbeugung beobachtet (vid. Photo. 1). Da sich beim Kristallisieren auf Zimmertemperatur aus der wässrigen Lösung von CdCl_2 einmal unvermeidlich CdCl_2 -Hydrat bildet, beobachtet man auch hier das CdCl_2 , das aus Auswitterung erfolgt, als Pulver der kleinen Kristallen (vid. Photo. 2). Auch in dem Falle, wo sich CdBr_2 -Kristall aus der wässrigen Lösung kristallisiert, läuft es auf dasselbe hinaus (vid. Photo. 4).

Dass CdJ_2 bei jeder Temperatur kein Hydrat darstellt, ist schon chemisch bekannt. Diese Tatsache hängt unmittelbar damit zusammen, dass sich aus der wässrigen CdJ_2 -Lösung CdJ_2 -Makromolekül aufbaut*.

Betrachtung 2.

CdJ_2 -Makromolekül.....	durch H_2O unangegriffen
CdBr_2 -Makromolekül.....	durch H_2O langsam angegriffen
CdCl_2 -Makromolekül.....	durch H_2O leicht angegriffen

Die obigen experimentellen Tatsachen können hier bequem aufgeklärt werden. Jedes Makromolekül setzt der Luft seine aus Anion allein

bestehenden zwei Schichten aus. Diese Schichten oder Oberflächen spielen bei CdJ_2 eine Rolle als dem Angriffe von H_2O widerstehende Barrikade, während sie bei CdCl_2 ganz impotent sind. Die Konfiguration dieser Schichten ist genau wie in Abb. 4 zu zeichnen. Die Abstände zwischen zwei Anionen sind bei CdCl_2 , CdBr_2 und CdJ_2 3.86 Å, 3.95 Å, bzw. 4.26 Å, und die Ionenradien von Cl' , Br' und J' sind 1.81 Å, 1.98 Å bzw. 2.16 Å.

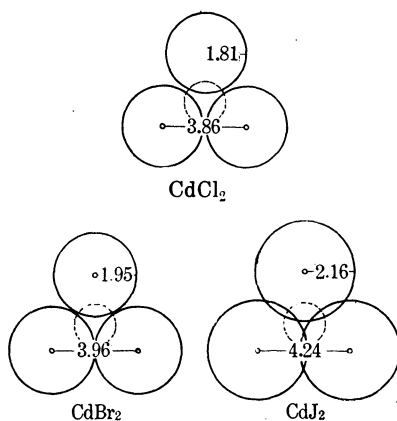


Abb. 4.

CdCl_2	$3.86 > 1.81 \times 2$
CdBr_2	$3.95 \approx 1.93 \times 2$
CdJ_2	$4.26 < 2.16 \times 2$

* Die van der Waalschen Anziehungskräfte unter CdJ_2 -Makromolekülen werden durch das stark polare Wasser vollends gehemmt.

Wie oben erkannt worden, ist bei CdCl_2 die gegenseitige Wirkung der Elektronenwolke des Cl' sehr schwach, indem sie bei CdJ_2 sehr bemerkenswert ist (vid. Abb. 4). In dem letzteren findet deutlich die quantenmechanische Resonanz unter den $J'-J'$ Banden statt. Zu einem Schluss können wir gelangen, dass Resonanz etwas zum Stabilisieren der Oberflächen des Makromoleküls und damit zum Hemmen des Angriffs von H_2O in der Luft dient. In dem Sinne, dass die quantenmechanische Resonanz die Oberfläche der Substanz stabil macht, dürfen sowohl die Säurefestigkeit der (Fe-W)-Legierung⁽⁸⁾ als auch die Wasserfestigkeit des CdJ_2 -Makromoleküls unter derselben Theorie behandelt werden.

Zusammenfassung.

(1) Stellt man die Kristalle von CdCl_2 - bzw. CdJ_2 -Struktur in Elektronenkamera als dünne Häute aus den wässrigen Lösungen her, so werden CdCl_2 - und CdBr_2 -Kristalle pulverartig, während sich CdJ_2 -Kristall als zweidimensionale Haut (Makromolekül) zeigt. Diese Erscheinungen sind davon abhängig, ob die obigen Salze stabile Hydrate besitzen oder nicht.

(2) Die Netz-Methode kann aus dem geschmolzenen CdBr_2 -Salz Makromolekül abschneiden.

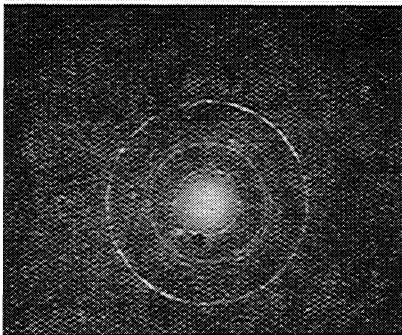
(3) Die Reaktionen zwischen den CdCl_2 -, CdBr_2 -, CdJ_2 -Makromolekülen und H_2O wurden hier originell behandelt.

Zum Schluss sei es gestattet, Herrn Dr. I. Iitaka und Herrn Prof. S. Mizushima für das Interesse an der vorliegenden Arbeit meinen herzlichen Dank auszusprechen. Diese Arbeit wurde von „Nippon Gakuzyutsu Shinkôkwai“ finanziert, wofür ich hier meinen Dank aussprechen möchte.

*(Institut für Physikalische und Chemische
Forschung in Tokio)*

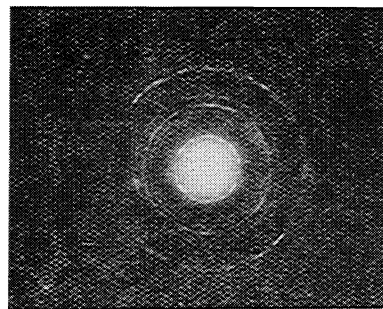
(8) S. Yamaguchi, dieses Bulletin, **17** (1942), 99.

Photo. 1.



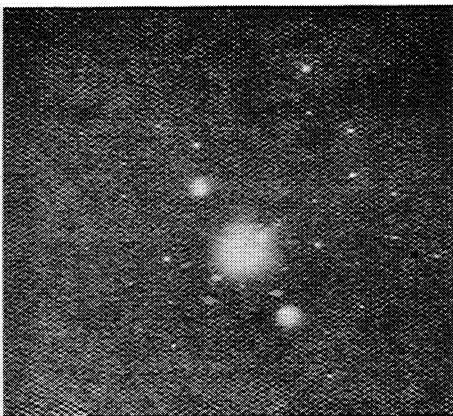
CdCl_2 -Haut aus dem geschmolzenen Salz.

Photo. 2.



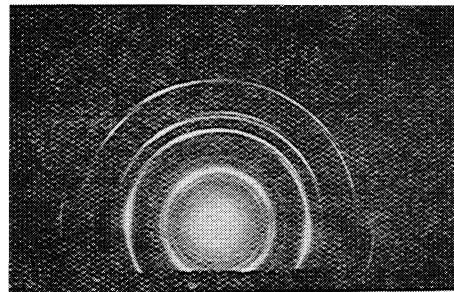
CdCl_2 -Haut aus der wässrigen Lösung.

Photo. 3.



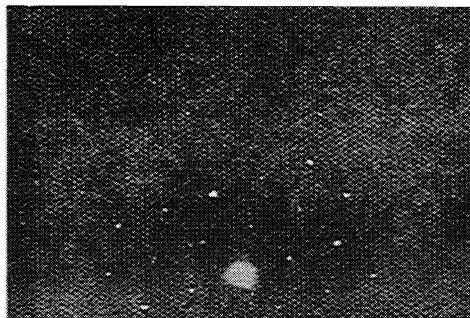
Zweidimensionale CdBr_2 -Haut aus dem geschmolzenen Salz.

Photo. 4.



CdBr_2 -Haut aus der wässrigen Lösung.

Photo. 5.



Zweidimensionale CdJ_2 -Haut aus der wässrigen Lösung.

Untersuchungen über Flechtenstoffe, XCVIII. Mitteil.: Über Lichexanthon, ein neues Stoffwechselprodukt der Flechte.

Von **Yasuhiko ASAHINA** und **Hisasi NOGAMI**.

(Eingegangen am 22. Januar 1942.)

Die Flechte *Parmelia formosana* Zahlbruckner, die nicht nur in Formosa, sondern auch in Kiusiu und Mittel-Hondo hie und da auftaucht, zeichnet sich durch die Eigenschaft aus, dass ihr Markgewebe beim Zutropfen von Alkalilauge weinrot gefärbt wird.

Beim Extrahieren der genannten Flechte mit Aether erhielten wir ein Produkt, welches sich als ein kompliziertes Gemisch von Stoffwechselprodukten erwies. Zur Trennung der einzelnen Bestandteile wurde der ätherische Auszug zunächst mit Bicarbonatlösung dann mit Alkalilauge ausgeschüttelt, und jede Fraktion für sich verarbeitet.

Der bicarbonatlösliche Bestandteil ist eine Phenolcarbonsäure vom Schmp. 200°, indem er in alkoholischer Lösung durch Eisenchlorid rotviolett gefärbt wird. Er wird aber durch Kalilauge nicht gefärbt.

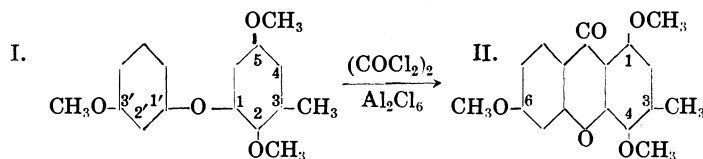
Der zweite, phenolische Bestandteil löst sich in Alkalilauge mit weinroter Farbe. Leider können wir ihn noch nicht in kristallinischem Zustand isolieren.

Die dritte, neutrale Bestandteil bildet gelbliche Prismen vom Schmp. 187°, deren Analysen-Werte der Formel $C_{16}H_{14}O_5$ entsprechen. Die Substanz ist in wässriger Alkalilauge unlöslich, wohl aber in alkoholischer Lauge. Die alkoholische Lösung färbt sich mit Eisenchlorid purpurrot. Durch Einwirkung von Essigsäureanhydrid liefert sie Monoacetat (Schmp. 192°). Mittels Diazomethans geht die Methylierung nicht glatt vor sich. Erst durch Behandeln mit Jodmethyl und Kaliumcarbonat in Aceton wird Monomethyläther (Schmp. 156°) erhalten. Beim Kochen mit Jodwasserstoffsäure spaltet das Naturprodukt zwei Mole Jodmethyl und geht in Desmethyl-Verbindung $C_{14}H_{10}O_5$ vom Schmp. 278° über. Da eine Auflösung des Monomethyläthers in konz. Schwefelsäure beim Belichten mit Quecksilber-Lamp blaugrün fluoresciert und eine salzsaure Lösung des Monomethyläthers durch Eisenchlorid ein Komplexsalz $C_{17}H_{17}O_5 \cdot FeCl_4$ liefert, so ist die Annahme berechtigt, den Naturstoff als ein Xanthon-Derivat und zwar ein Methyl-dimethoxy-oxy-xanthon anzusprechen. Da dasselbe ein in der Flechte zum erstenmal entdeckte Xanthon-Derivat ist, so nennen wir es „Lichexanthon“.

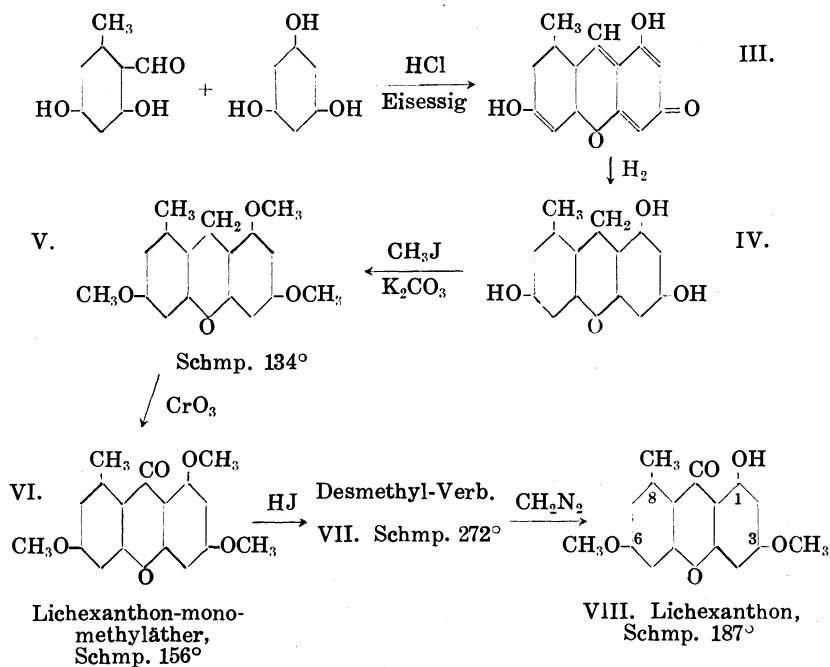
Früher haben Raistrick, Robinson und White⁽¹⁾ im Stoffwechselprodukte von einem Pilz, *Helminthosporium Ravenelii*, Ravenelin (3-Methyl-1,4,8-trioxy-xanthon) entdeckt. Beim Konstitutionsbeweis desselben haben sie 3-Methyl-1,4,6-trimethoxy-xanthon (Schmp. 157°) synthetisiert, dessen Entmethylierungsprodukt ein Isomeres des Ravenelins ist. Da der Schmp. des 3-Methyl-1,4,6-trimethoxy-xanthons mit dem des oben erwähnten Monomethyläthers fast übereinstimmt, so haben wir jenes

(1) Biochem., J., **30** (1936), 1903.

Xanthon synthetisiert. Hierzu wurde 2.5.3'-Trimethoxy-3-methyl-diphenyläther (I) ⁽²⁾ nach Asahina und Tanase ⁽³⁾ in Schwefelkohlenstoff unter Zusatz von Aluminiumchlorid mit Oxalylchlorid behandelt, wodurch das 3-Methyl-1,4,6-trimethoxy-xanthon (II) vom Schmp. 157° leicht erhalten wurde. Bei der Mischschmp.-Bestimmung mit unserem Monomethyläther wurde eine bedeutende Depression beobachtet, sodass von der Identität der beiden keine Rede ist.



Da aber unser Naturstoff bei der Kalischmelze, ausgeführt mit der kaum 200 mg. betragenden Substanz-Menge, eine Phenol gab, welches alle Farbenreaktionen von Orcin aufwies, so wird wohl der eine Kern des Naturstoffs Orcin sein. Unter dieser Annahme müssen die zwei restlichen Hydroxyle in anderen Kern sitzen derart, dass das eine dem Carbonyl benachbart ist, was aus positiver Fe-Reaktion und schwerer Methylierbarkeit mittels Diazomethans ersichtlich ist. Da andererseits die Desmethylverbindung des Naturstoffs in alkoholischer Lösung durch Zusatz von Chloropentaammincobaltchlorid gar nicht gefärbt wird, so stehen die zwei Hydroxyle im zweiten Kern weder in ortho- noch para, sondern in meta-Stellung zu einander. Also muss der zweite Kern Phloroglucin sein.



(2) Biochem. J., **30** (1936), 1310.

(3) Proc. Imp. Acad. (Tokyo), **16** (1940), 297.

Um dies synthetisch zu sichern, haben wir nach obigen Weise zunächst 8-Methyl-1,3,6-trimethoxy-xanthon (VI) dargestellt, welches sich als identisch mit dem Monomethyläther des Naturstoffs erwies. Durch dessen Entmethylierung entstand die Desmethylverbindung (VII), die durch Einwirkung von Diazomethan in den Naturstoff Lichexanthon, 1-Oxy-3,6-dimethoxy-8-methyl-xanthon (VIII) selbst überging.

Beschreibung der Versuche.

Extraktion von *Parmelia formosana* Zahlbr. 25 g. Flechtenthalli werden mit Aether erschöpfend extrahiert und der Aetherauszug mit 5 proz. Bicarbonatlösung geschüttelt, wobei sich zwischen Aether- und wasseriger Schicht eine ölige Substanz ausscheidet. Die letztere sammt der wässrigen Lösung wird vom Aether abgetrennt, angesäuert und ausgeäthert. Beim Verdampfen des letzteren verbleibt eine krystallinische Substanz (Säure A).

Der ursprüngliche, entsäuerte Aetherauszug wird dann mit 5 proz. Natronlauge geschüttelt, die letztere angesäuert und ausgeäthert (phenolische Substanz B).

Der von phenolischer Substanz B befreite Aetherauszug lässt beim Verdampfen eine krystallinische Substanz (Roh-Lichexanthon) zurück.

Säure A. Beim Umlösen aus verd. Alkohol bildet die „Säure A“ farblose Prismen vom Schmp. 200° u. Zers. Ausb. 200 mg. Sie ist in Alkohol, Aether und Aceton leichtlöslich. Ammoniakwasser und Alkalilauge lösen sie farblos. In warmer konz. Schwefelsäure löst sie sich mit grüner Farbe. Die alkohol. Lösung färbt sich mit Eisenchlorid violettrot, mit Chlorkalk nicht. 3.375 mg. Subst.: 8.020 mg. CO_2 , 1.990 mg. H_2O . 3.355 mg. Subst.: 2.410 mg. AgJ. 3.130 mg. Subst.: 0.61 ccm. 0.01-n-KOH (Indikator Bromthymolblau). $\text{C}_{27}\text{H}_{32}\text{O}_9$. Ber. C 64.77, H 6.45, CH_3O , 6.20, Mol. Gew. 500. Gef. C 64.81, H 6.60, CH_3O , 5.95, Mol. Gew. 513.

Methylester: Dargestellt durch Einwirkung von Diazomethan auf Säure A. Farblose Blättchen vom Schmp. 179° . Er löst sich in Alkalilauge farblos. Die alkohol. Lösung färbt sich mit Eisenchlorid nicht. 4.480 mg. Subst.: 10.740 mg. CO_2 , 2.690 mg. H_2O . 2.925 mg. Subst.: 2.680 mg. AgJ. $\text{C}_{28}\text{H}_{34}\text{O}_9$. Ber. C 65.34, H 6.66, $2\text{CH}_3\text{O}$, 12.07. Gef. C 65.38, H 6.72, CH_3O , 12.11.

Phenolische Substanz B. Die Phenolische Substanz bildet ein dicker Syrup. Sie löst sich in Alkalilauge mit weinroter Farbe. Wegen Mangel an Material konnten wir sie nicht weiter untersuchen.

Lichexanthon. Beim Umlösen aus Aceton bildet Lichexanthon gelbliche, lange Prismen oder feine, faserige Nadeln vom Schmp. 187° . Ausb. 0.45 g. Es ist in Alkohol und Aether ziemlich schwerlöslich, in Benzol und Aceton in der Wärme leichtlöslich. Es löst sich in wässriger Kalilauge nicht, wohl aber in alkoholischer Lauge. Beim Belichten mit Quecksilber-Lampe fluoresciert die alkoholische Lösung schwach orange-gelb; dieselbe Lösung färbt sich mit Eisenchlorid purpurrot. Eine Auflösung des Lichexanthons in Eisessig fluoresciert durch Zusatz von einem

Tropfen konz. Schwefelsäure grün. 3.820 mg. Sbst.: 9.370 mg. CO_2 , 1.800 mg. H_2O . 2.960 mg. Sbst.: 4.620 mg. AgJ. 0.200 mg. Sbst. gelöst in 2.770 mg. Campher, $\Delta=10.5^\circ$ (nach Rast). $\text{C}_{16}\text{H}_{14}\text{O}_5$. Ber. C 67.11, H 4.93, $2\text{CH}_3\text{O}$, 21.69, Mol. Gew. 286. Gef. C 66.90, H 5.27, CH_3O , 20.62, Mol. Gew. 276.

Mono-acetat: Dargestellt durch dreistündiges Kochen von 50 mg. Lichexanthon in 1 ccm. Acetanhydrid. Farblose Prismen vom Schmp. 192° (aus Aceton). 4.140 mg. Sbst.: 9.970 mg. CO_2 , 1.900 mg. H_2O . 6.980 mg. Sbst. neutralisieren 2.17 ccm. 0.01-n-KOH (Acetyl-Bestim. nach Wenzel). $\text{C}_{18}\text{H}_{16}\text{O}_6$. Ber. C 65.83, H 4.91, CH_3CO , 13.11. Gef. C 65.68, H 5.14, CH_3CO , 13.35.

Mono-methyläther: Dargestellt durch Kochen vom Lichexanthon in Aceton unter Zusatz von Jodmethyl und Kaliumcarbonat. Farblose Blättchen vom Schmp. 156° (aus Alkohol). Die alkohol. Lösung färbt sich mit Eisenchlorid nicht. Konz. Schwefelsäure löst ihn mit gelbgrüner Farbe; beim Belichten mit Quecksilberlampe fluoresciert die Lösung blaugrün. 3.915 mg. Sbst.: 9.790 mg. CO_2 , 1.800 mg. H_2O . $\text{C}_{17}\text{H}_{16}\text{O}_5$. Ber. C 67.98, H 5.37, Gef. C 68.20, H 5.14.

Eisenchlorid-Komplexsalz des Monomethyläthers: Man löst 30 mg. Monomethyläther in 5 ccm. konz. Salzsäure und fügt dazu Eisenchlorid (gelöst in konz. Salzsäure) hinzu. Der so erhaltene, gelbe Niederschlag bildet, beim Umlösen aus eisenchlorid- und salzsäurehaltigem Eisessig, gelbe Prismen vom Schmp. 195° (u. Zers.). 4.000 mg. Sbst.: 6.000 mg. CO_2 , 1.300 mg. H_2O u. 0.630 mg. Fe_2O_3 . $\text{C}_{17}\text{H}_{17}\text{O}_5 \cdot \text{FeCl}_4$: Ber. C 40.90, H 3.44, Fe 11.20. Gef. C 40.91, H 3.64, Fe 11.02.

Desmethyl-lichexanthon. Kocht man 50 mg. Lichexanthon in einem Gemisch von 3 ccm. Jodwasserstoffsäure ($d=1.7$) und 1 ccm. Acetanhydrid 3 Stunden, so wird es zunächst aufgelöst. Dann scheidet sich das entmethylierte Produkte aus, welches beim Umlösen aus verd. Alkohol und Sublimieren unter 3 mm. Druck (Bade-Temperatur $250-260^\circ$) gelbe Prismen vom Schmp. 272° bildet. Die Substanz ist in Alkohol und Aceton leicht löslich und die alkoholische Lösung färbt sich durch Zusatz vom Chloropentammincobaltichlorid nicht. $\text{C}_{14}\text{H}_{10}\text{O}_5$: Ber. C 65.10, H 3.91, Gef. C 64.67, H 3.90.

Kalischmelze des Lichexanthons. Man schmilzt 3 g. Kaliumhydroxyd unter Zusatz von 3 Tropfen Wasser bei 200° , fügt dazu 200 mg. Lichexanthon und erhitzt unter Umrühren bis gegen 330° . Man säuert die wässrige Lösung der Schmelze an, äthert aus und schüttelt die Ätherlösung nach einander mit 5 proz. Sodalösung und Natronlauge. Durch Ansäuern der letzteren Natronlauge und darauffolgendes Ausäthern wurde eine phenolische Substanz erhalten, die wir in krystallisiertem Zustand nicht überführen konnten. Die wässrige Lösung färbt sich mit Eisenchlorid violett, färbt Vanillin-Salzsäure tiefrot. Die alkalische Lösung färbt sich beim Kochen mit Chloroform rot und fluoresciert grün (Homofluorescein-Reaktion).

Synthese des 3-Methyl-1.4.6-trimethoxy-xanthons (II). 1 g. 2.5.3'-Trimethoxy-3-methyl-diphenyläther (I)⁽²⁾ wird mit 0.5 g. Oxalylchlorid

in 5 ccm. Schwefelkohlenstoff gelöst und unter Eiskühlung mit 1 g. Aluminiumchlorid in kleinen Portionen versetzt. Dann erhitzt man das Gemisch auf dem Wasserbad, bis das Salzsäure-Gas nicht mehr entweicht. Nun giesst man Schwefelkohlenstoff ab, rührt den schwarzen Rückstand mit Eiswasser um. Die so festgewordene Masse liefert bei wiederholtem Umlösen aus Alkohol zwei Produkte. Das in Alkohol schwerer lösliche bildet sandiges Krystallpulver vom Schmp. 178–179°, dessen Konstitution noch unbekannt ist. Das in Alkohol leichter lösliche bildet farblose Prismen vom Schmp. 157°, die sich durch Vergleich als identisch mit dem nach Raistrick u. a. ⁽¹⁾⁽²⁾ dargestellten 3-Methyl-1.4.6-trimethoxy-xanthon erwies. Eine Mischprobe mit dem Lichexanthonmethyläther vom Schmp. 156° zeigt eine Schmp.-Depression von ca 20°. 4.195 mg. Subst.: 10.455 mg. CO₂, 2.025 mg. H₂O. C₁₇H₁₆O₅. Ber. C 67.98, H 5.37. Gef. C 67.97, H 5.40.

Synthese des Lichexanthon (8-Methyl-1-oxy-3.6-dimethoxy-xanthon) (VIII).

1.6-Dioxy-8-methyl-fluoron (III): 6 g. Orsellinaldehyd und 5 g. Phloroglucin werden in einem Gemisch von 50 ccm. Eisessig und 16 ccm. konz. Salzsäure kurze Zeit gekocht, wobei sich das Chlorhydrat des Fluoron-Derivats in Form von roten Krystallen ausscheidet. Es bildet tiefrote Prismen, die sich gegen 260° verfärbt und gegen 320° unter Schwarzwerden zersetzt. Ausb. 8.3 g. Beim Schütteln mit Bicarbonatlösung verliert es Chlorwasserstoff und wandelt sich in blutrotem Pulver um. Beim Umlösen aus viel Alkohol bildet das Fluoron-derivat rote Prismen, die sich über 300° unter Verkohlung zersetzt. In meisten Solventien ist es schwer löslich.

1.3.6-Triox-8-methyl-xanthen (IV): 6.3 g. Fluoron (III) gelöst in 70 ccm. Alkohol absorbiert beim Schütteln in der Wasserstoffatmosphäre (Palladiumkohle als Katalisator) innerhalb 40 Minuten 1 Mol. Wasserstoffgas und wird farblos. Beim Verdampfen der Lösung verbleibt das orangegelb gefärbte Xanthen. Wegen seiner Empfindlichkeit gegen Luft-sauerstoff haben wir auf dessen Reinigung verzichtet.

1.3.6-Trimethoxy-8-methyl-xanthen (V): 5.5 g. 1.3.6-Triox-8-methylxanthen werden in 30 ccm. Aceton gelöst und unter Zusatz von je 22 g. Jodmethyl und Kaliumcarbonat 8 Stunden gekocht. Die mit Wasser verdünnte Reaktionsflüssigkeit wird ausgeäthert; der Aetherauszug wird nach Waschen mit verd. Natronlauge verdampft. Der so erhaltene Rückstand bildet beim Umlösen aus Alkohol farblose Prismen vom Schmp. 134°. Ausb. 3.5 g. 4.500 mg. Subst.: 11.720 mg. CO₂, 2.520 mg. H₂O. C₁₇H₁₈O₄. Ber. C 71.29, H 6.34. Gef. C 71.03, H 6.27.

1.3.6-Trimethoxy-8-methyl-xanthon (VI) (=Monomethyläther-liche-xanthon): 0.5 g. Xanthen (V) werden in 6 ccm. heissem Eisessig gelöst, mit 0.27 g. Chromsäureanhydrid versetzt und eine Stunde auf dem Wasserbad erwärmt. Dann wird das Reaktionsgemisch mit Wasser verdünnt und mit Essigester ausgeschüttelt. Der beim Verdampfen der Essigesterlösung verbleibende Rückstand bildet beim Umlösen aus Alkohol rote Blättchen vom Schmp. 158°, die sich durch Kohle nicht entfärben lässt. Ausb. ca. 50 mg. Erst bei wiederholtem Sublimieren im Hochvakuum (0.01 mm., Badtemperatur 180°) wurde die Substanz farblos und eine Mischprobe mit dem Lichexanthon-monomethyläther (Schmp. 156°)

zeigte keine Schmp.-Depression. 3.950 mg. Subst.: 9.740 mg. CO_2 , 1.840 mg. H_2O . $\text{C}_{17}\text{H}_{16}\text{O}_5$. Ber. C 67.98, H 5.37, Gef. C 67.25, H 5.21.

1.3.6-Trioxy-8-methyl-xanthon (VII) (=Desmethyl-lichexanthon): 40 mg. Trimethoxy-methyl-xanthon (VI) werden genau so wie bei natürlichem Lichexanthon mit Jodwasserstoffsäure unter Zusatz von Acetanhydrid gekocht. Die so gebildete Desmethyl-Verbindung bildet gelbe Prismen vom Schmp. 272° , die sich in jeder Hinsicht mit dem Desmethyl-lichexanthon identisch erwies.

1-Oxy-3.6-dimethoxy-8-methyl-xanthon (VIII) (=Lichexanthon): 20 mg. Trioxy-methyl-xanthon (VII) werden in 5 ccm. Aceton gelöst, mit ätherischem Diazomethan bis zum Gelbfärben der Lösung versetzt und übernacht stehen gelassen. Beim Verdampfen des Lösungsmittels verbleibt das partiell methylierte Produkt, welches beim Umlösen aus Aceton gelbliche, lange Prismen vom Schmp. 187° bildet. Eine Mischprobe mit dem natürlichen Lichexanthon zeigte keine Schmp.-Depression. 3.845 mg. Subst.: 9.440 mg. CO_2 , 1.700 mg. H_2O . $\text{C}_{16}\text{H}_{14}\text{O}_5$. Ber. C 67.11, H 4.93. Gef. C 66.96, H 4.95.

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Dimerisation von Styrol in schwerer Salzsäure. (Auszug).⁽¹⁾

Von Toiti YOSIDA.

(Eigegangen am 7. Februar 1942.)

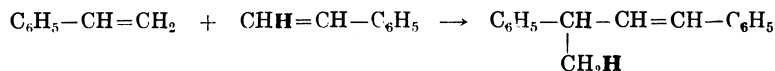
Inhaltsübersicht. Lässt man das Styrol durch die kräftige Schüttelung zusammen mit schwerer Salzsäure bei erhöhter Temperatur dimerisieren, so werden die D-Atome nicht nur im gebildeten Dimerisat, Distyrol, sondern auch im noch nicht dimerisiert bleibenden Styrol allmählich eingebaut. Aus der untersuchten Zeitabhängigkeit dieses Einbaus der D-Atome im Styrol und Distyrol sowie aus der ebenfalls beim vorliegenden Versuche festgestellten Tatsache, dass die in Rede kommende Reaktion nur durch Säure aber nicht durch Base katalysiert wird, lässt sich über den Mechanismus der Reaktion ein Schluss ziehen. Danach wird das Proton bzw. Deuteron zunächst an einem Styrolmolekül angelagert und durch die Verbindung des so gebildeten aktiven Moleküls mit dem neutralen Styrolmolekül wird ein labiler Zwischenkomplex gebildet. Das stabile Endprodukt, d.h. das Distyrol, entsteht aus diesem Zwischenkomplex durch die Abspaltung des Protons bzw. Deuterons. Unter diesen Teilprozesse muss aber der erste Schritt d.h. die Anlagerung des Protons bzw. Deuterons an einem Styrolmolekül, geschwindigkeitsbestimmend wirken.

Bei den Versuchen, wo die Kettenpolymerisation des Styrols in schwerem Alkohol untersucht wurde, haben wir gefunden, dass keine

(1) T. Yosida, *J. Chem. Soc. Japan*, **62** (1941), 970. Vorläufig mitgeteilt in T. Titani und T. Yosida, *Proc. Imp. Acad. Tokyo*, **17** (1941), 256.

D-Atome im gebildeten Polystyrol eingebaut werden⁽²⁾ und aus diesem Versuchsergebnis den Schluss gezogen, dass keine H-Atome im Styrol nicht nur beim Kettenstart sondern auch beim Kettenwachstums- sowie Kettenabbruchsprozess genügend frei bis zum Austausch gelockert bzw. umgelagert werden. Obwohl dieser letztere Schluss sehr plausibel erscheint, wäre es doch erwünscht den ähnlichen Versuch mit solch einer Reaktion auszuführen, bei der die Umlagerung der H-Atome von vorn herein mit grosser Wahrscheinlichkeit angenommen wird, und zu untersuchen, ob die D-Atome wirklich im Reaktionsprodukt eingebaut werden. Als solch eine Reaktion wählten wir nun die durch Salzsäure katalysierte Dimerisation des Styrols.

Schüttelt man nämlich eine Menge Styrol zusammen mit konzentrierter Salzsäure bei mässig hoher Temperatur (wie z.B. bei 150°), so wird das Styrol allmählich bis zu einem Dimerisat, zum Distyrol, verwandelt. Da aber das so gebildete flüssige Dimerisat des Styrols nach dem Versuch von Stobbe und Posnjak⁽³⁾ als 1,3-Diphenylbuten-(1) aufgefasst wird, liegt die Annahme nahe, dass im Verlauf der Reaktion ein H-Atom eines reagierenden Styrolmoleküls zum anderen umgelagert wird:



Lässt man deshalb dieselbe Reaktion statt in gewöhnlicher Salzsäure in schwerer d.h. D-haltiger Salzsäure vor sich gehen, so entsteht die Möglichkeit, dass die D-Atome im gebildeten Dimerisat eingebaut werden. Da aber der aus dieser Ansicht vorgenommene Versuch anzeigte, dass die

D-Atome nicht nur im gebildeten Distyrol sondern auch im noch nicht dimerisiert bleibenden Styrol eingebaut werden, haben wir diesen Einbau der D-Atome in den beiden Substanzen in Abhängigkeit von der Reaktionsdauer bzw. dem Umsatz des Styrols untersucht. Die Versuchsergebnisse sind in der nebenstehenden Abb. graphisch angegeben. In dieser Abb. wird an der oberen Abszisse die Versuchsdauer und an der unteren der prozentuale Umsatz des Styrols eingetragen. Hingegen drückt der auf der Ordinate eingezeichnete Wert Δs den gewöhnlichen Wasser gegenüber gemessenen Dichteüberschuss des

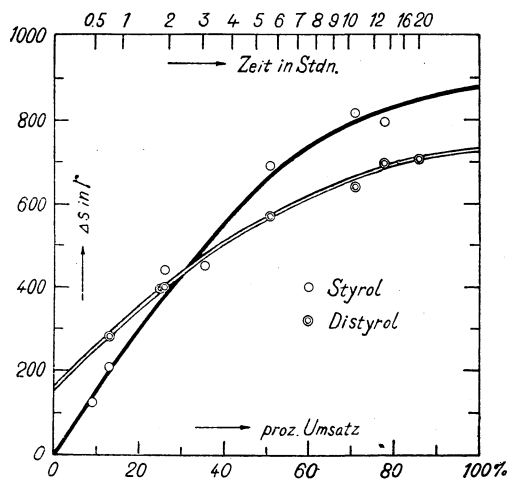


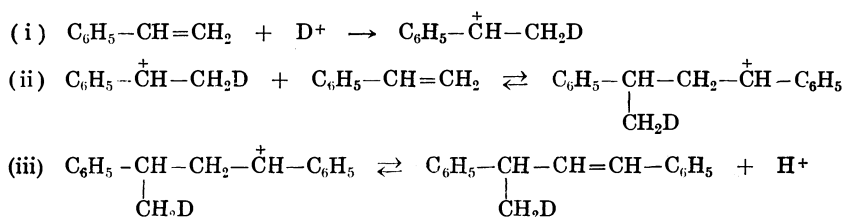
Abb. Der Dichteüberschuss Δs des Verbrennungswassers aus Styrol und Distyrol in Abhängigkeit vom prozentualen Umsatz des Styrols.

(2) T. Yosida und T. Titani, dies Bulletin, **16** (1941), 125. M. Koizumi und T. Titani, ebenda, **13** (1938), 304.

(3) H. Stobbe und G. Posnjak, *Ann.*, **371** (1909), 287. Vgl. dazu R. Fittig und E. Erdmann, *Ann.*, **216** (1883), 179.

Wassers aus, das aus der Verbrennung des gebildeten Distyrols bzw. des noch nicht reagiert bleibenden Styrols gewonnen wurde. Aus dieser Abb. wird ersehen, dass der D-Gehalt der beiden Substanzen mit dem zunehmenden Umsatz des Styrols allmählich gleich anwächst. Aber zugleich wird bemerkt, dass die Kurve von Styrol den Schnittpunkt der Ko-ordinaten durchläuft, während die von Distyrol die Ordinate bei einem endlichen Wert durchschneidet, der D-Gehalt des Styrols, der zum Nullumsatz extrapoliert wird, ebenfalls null ist, während der des Distyrols auch beim Nullumsatz endlichen Wert besitzt. Dies weist offensichtlich darauf hin, dass das Distyrolmolekül schon bei seiner Entstehung die D-Atome enthält, während das D-haltige Styrolmolekül erst durch die Zerlegung des so entstandenen D-haltigen Distyrolmoleküls gebildet wird.

Dieses Ergebnis kann nun mit Hilfe des von Whitmore⁽⁴⁾ für die säurekatalysierte Dimerisation der Olefine aufgestellten Mechanismus:



nur unter der zusätzlichen Annahme befriedigend erklärt werden, dass der erste Schritt (i) geschwindigkeitsbestimmend ist. Wäre nämlich dies nicht der Fall, d.h. würde diese Reaktion (i) nach beiden Seiten hin mit fast gleicher Geschwindigkeit umkehrbar verlaufen, so müssten die D-Atome schon bei diesem ersten Schritt im noch nicht dimerisierten Styrolmolekül eingebaut werden; der D-Gehalt des Styrols, der zum Nullumsatz extrapoliert wird, müsste einen endlichen Wert besitzen und das Distyrol, das offensichtlich aus dem so D-eingebauten Styrol gebildet wird, müsste immer einen grösseren D-Gehalt als das Styrol zeigen. Wird hingegen der erste Schritt (i) als geschwindigkeitsbestimmend angenommen, so können keine D-Atome bei diesem Schritt im Styrolmolekül eingebaut werden, weil dann die Reaktion (i) nur nach der rechten Seite hin verläuft und die Geschwindigkeit der Rückreaktion von (i), durch deren Verlauf die D-Atome im noch nicht reagierten Styrolmolekül eingebaut werden, vernachlässigbar so klein ist. In diesem Fall werden deshalb die D-Atome nur durch die reversible Zerlegung des aus Reaktion (iii) gebildeten D-enhaltenden Distyrolmoleküls d.h. durch die Rückreaktionen von (ii) und (iii) im Styrolmolekül eingebaut. So bleibt der D-Gehalt des Styrols mindestens am Anfang der Reaktion unterhalb des des Distyrols und besonders beim Nullumsatz, wo noch keine Distyrolmoleküle gebildet werden, muss der D-Gehalt des Styrols gleich Null sein.

Auf diese Weise geht die Kurve von Styrol, wie in der oben angegebenen Abb. gezeigt wird, vom Nullpunkt ab, während die von Distyrol die Ordinate bei einem endlichen Wert schneidet, weil das Distyrolmolekül, wie aus dem Reaktionsschema (iii) ohne weiteres ersichtlich ist, schon bei seiner Entstehung D-Atome enthält. Falls man nämlich die

(4) F. C. Whitmore, *Ind. Eng. Chem.*, **26** (1934), 94.

Reaktion in ganz reiner d.h. 100 prozentiger schwerer Salzsäure ausführt, wird am Anfang der Reaktion eben ein D-Atom in einem Distyrolmolekül eingebaut. Deshalb muss das Wasser, das aus der Verbrennung des so gebildeten Distyrols gewonnen wird, um 67200 γ dichter als gewöhnliches Wasser sein. Da wir uns aber beim wirklichen Versuch nur 4.5 prozentiger schwerer Salzsäure bedienen, soll der Dichteüberschuss des Verbrennungswassers aus dem Distyrol, das am Anfang der Reaktion gebildet wird, um 0.045 mal so klein wie der oben angegebene Extremwert d.h. 290 γ betragen. Dieser theoretische Wert ist aber fast doppelt so gross wie der aus der oben angegebenen Abb. durch Extrapolation gefundene: die Kurve von Distyrol schneidet die Ordinate bei solch einem Punkt, wo Δs nur 150 γ beträgt. Diese Diskrepanz ist aber nicht so bedenklich, wenn man die folgende Tatsache in Rechnung zieht. Unter den vorliegenden Versuchsbedingungen wird nämlich das D-Atom bzw. Deuteron aus dem Deuteroniumion der Form $D^+ \cdot H_2O$ aufgenommen, während das H-Atom bzw. Proton aus dem gewöhnlichen Hydroxoniumion $H^+ \cdot H_2O$ aufgenommen wird. Da aber die Nullpunktsenergie der Bindung $D^+ \cdot H_2O$ um einen gewissen Betrag niedriger als die der Bindung $H^+ \cdot H_2O$ liegt, muss die Aufnahmegeschwindigkeit des Deuterons ziemlich beträchtlich kleiner als die des Protons sein. Nimmt man z.B. diesen Unterschied der Nullpunktsenergie als etwa 500 cal an, so wird die Aufnahmegeschwindigkeit des Deuterons schon halb so klein wie die des Protons.

Auf diese Weise können wir die vorliegenden Versuchsergebnisse mit der oben angegebenen Annahme befriedigend erklären, dass die Anlageung des Protons bzw. Deuterons an einem reagierenden Styrolmolekül geschwindigkeitsbestimmend wirkt. Diese letztere Annahme steht aber auch mit dem auch beim vorliegenden Versuch festgestellten Befund sehr gut im Einklang, dass die in Frage kommende Dimerisationsreaktion des Styrols nur durch Säure aber nicht durch Base katalysiert wird. Schüttelt man nämlich das Styrol zusammen mit Salzsäure, so wird das Styrol mit wohl messbarer Geschwindigkeit dimerisiert. Hingegen konnten wir bei den Kontrollversuchen, wo derselbe Versuch unter Benutzung der ebenfalls konzentrierten Natronlauge und sonst unter den genau denselben Versuchsbedingungen wie bei der Salzsäure ausgeführt wurde, keine Anzeichen für die Dimerisation des Styrols ausfindig machen, wie weiter unten im experimentellen Teil ausführlich gezeigt wird. Dieses Ergebnis weist aber im Lichte der von Horiuti⁽⁵⁾ aufgestellten Theorie der Säure-Base-Katalyse darauf hin, dass der geschwindigkeitsbestimmende Prozess der in Rede kommenden Reaktion solch ein Teilprozess sein soll, wo das Proton an irgendeinem reagierenden Molekül angelagert wird.

Experimentelles. Die zum Versuch benutzte schwere Salzsäure wird durch die Absättigung des verdünnten schweren Wassers mit getrocknetem Chlorwasserstoffgas bereitet. Ihre Dichte war 1.125 und der Gehalt an D betrug 4.3%. Etwa 2 ccm der so bereiteten Salzsäure wird zusammen mit etwa 5 ccm frisch destilliertem Styrol sowie einer kleinen Menge

(5) J. Horiuti, Sammlung der Vorlesungen des 13. kleinen Komitees der Japanischen Gesellschaft zur Förderung der wissenschaftlichen Forschung, Nr. 1, (1940), 15.

(etwa 0.015 g.) Hydrochinon in einem Glasrohr (ohne Luftabschluss) eingeschmolzen. Das letztere wird mit dem Zweck zugesetzt, um die sonst immer bis zu einem gewissen Grad stattfindende Polymerisation des Styrols möglichst vollständig zu unterdrücken. Das so beladene Glasrohr wird nun in einem elektrisch geheizten Luftthermostat immer konstant bei $150 \pm 2^\circ$, aber verschiedener Zeitlänge kräftig geschüttelt. Nach Beendigung der Erwärmung wird die Salzsäure von der Styrolschicht abpipettiert und die letztere, nachdem sie durch die kräftige Schüttelung mit konzentrierter Sodalösung von der übrig bleibenden Salzsäure möglichst vollständig befreit und dann mit Chlorcalcium getrocknet worden ist, zur fraktionierten Destillation im Vakuum unterworfen. Da aber dabei das nicht dimerisierte Styrol schon bei etwa 40° , hingegen das Distyrol erst bei etwa 200° abdestillierte, konnten die beiden Verbindungen verhältnismässig leicht und vollständig abgetrennt werden. Das so abgetrennte Styrol und Distyrol wird nun zunächst in der Lösung von Schwefelkohlenstoff unter Benutzung des freien Broms separat bromiert, und das dadurch gewonnene Bromstyrol und das Bromdistyrol kommen in einem Verbrennungsrohr separat bis zu Wasser zur Verbrennung. Diese Massnahmeregel d.h. die Bromierung des Styrols und Distyrols ist insoweit zweckdienlich, als dadurch die letzten Spuren der schweren Salzsäure, die an den betreffenden Substanzen hartnäckig angehaftet waren, vollständig beseitigt wurden. Der Schmelzpunkt des dabei gewonnenen Bromstyrols und Bromdistyrols, der gut übereinstimmend mit den veröffentlichten Daten resp. 72° und $102 \sim 103^\circ$ beträgt, weist weiter darauf hin, dass die beiden Verbindungen genügend rein waren. Die Verbrennung des so bereiteten Bromstyrols und Bromdistyrols geht in einem mit Kupferoxyd gefüllten elektrisch geheizten Rohr im Luftstrom vor sich und der dabei zusammen mit dem Wasserdampf entwickelte Bromdampf sowie der Dampf des Kupfer(1)-chlorids wird unter Benutzung des Bleichromats beseitigt. Der Dichteüberschuss d.h. der D-Gehalt des dadurch gewonnenen Wassers wird, nachdem es auf geeignetem Weg gereinigt worden ist, mittels eines kleinen Glasschwimmers im Vergleich mit gewöhnlichem Wasser gemessen. Die Messgenauigkeit liegt innerhalb $\pm 2 \gamma$. Die Messresultate sind in Tabelle 1 zusammengestellt, wo die Versuchsnur. in der ersten Vertikalreihe die zeitliche Reihenfolge der einzelnen Versuche anzeigt. Dasselbe Ergebnis haben wir auch in der oben angegebenen Abb. graphisch wiedergegeben.

Tabelle 1. Dimerisation des Styrols in schwerer Salzsäure.

Versuchs- nr.	Versuchs- dauer in Stdn.	Umsatz des Styrols in %	Δs des Wassers aus Styrol in γ	Δs des Wassers aus Distyrol in γ
8	0.8	9	123	—
9	1.2	13	202	284
4	1.5	25	—	396
6	1.5	26	440	401
1	3.0	33	451	—
2	6.5	51	687	570
7	10.0	71	823	640
5	13.5	78	793	695
3	20.0	86	—	703

Dass die in Rede kommende Reaktion d.h. die Dimerisation des Styrols nur durch Säure aber nicht durch Base katalysiert wird, davon überzeugten uns die Versuche, die in Tabelle 2 wiedergegeben sind. Bei diesen

Tabelle 2. Vergleichsversuche in Salzsäure und in Natronlauge (150°).

Reaktion in HCl-Lösung			Reaktion in NaOH-Lösung		
Normalität von HCl	Versuchs- dauer in Stdn.	Umsatz des Styrols in %	Normalität von NaOH	Versuchs- dauer in Stdn.	Umsatz des Styrols in %
8.50	10	70	—	—	—
4.25	7	56	4.25	6	0
2.12	4	45	2.12	7	0

Versuchen wird nämlich eine Menge (etwa 5 ccm) gereinigten Styrols entweder mit einer bestimmten Menge (etwa 2 ccm) Salzsäure von verschiedener Konzentration oder mit derselben Menge Natronlauge von ebenfalls verschiedener Konzentration beide bei einer bestimmten Temperatur (150°) aber verschiedener Zeitlänge geschüttelt.⁽⁶⁾ Die Versuchsergebnisse sind aus Tabelle 2 ohne weiteres klar: das Styrol wird nur beim Vorhandensein der Salzsäure mit wohl messbarer Geschwindigkeit dimerisiert, während mit Natronlauge fast keine Anzeichen für die Dimerisation des Styrols ausfindig gemacht werden konnten, obwohl die Konzentration der Reagenz, die Versuchsdauer sowie die Versuchstemperatur in beiden Fällen fast bzw. ganz dieselben waren.

Zum Schluss möchte ich Herrn Prof. T. Titani für seine Anregung zu dieser Arbeit verbindlichst danken. Der Sumitomo Denki-Kogyo K.K. (den Sumitomo Elektrischen Industrie-Werken), die uns das Styrol zur Verfügung gestellt hat, sowie der Nippon Gakujutsu Shinkokai (der Japanischen Gesellschaft zur Förderung der wissenschaftlichen Forschung) und der Hattori-Hohkokhai (der Hattori-Stiftung), die uns beide finanziell unterstützt haben, bin ich auch zu grösstem Dank verpflichtet.

Osaka Teikoku Daigaku Rigaku-bu Kagaku Kyoshitsu
(Chemisches Institut der wissenschaftlichen
Fakultät der Kaiserlichen
Universität Osaka)

(6) In jedem Fall wird eine kleine Menge (etwa 0.015 g) Hydrochion zum Reaktionsgemisch zugesetzt, um die sonst bis zu einem gewissen Grad stattfindende Polymerisationsreaktion völlig zu vermeiden.

Vanadin-, Chrom- und Molybdängehalt einiger Mineralquellen Japans.

Von Kazuo KURODA.

(Eingegangen am 20. Februar 1942.)

Der Vanadin-, Chrom- und Molybdängehalt einiger Mineralquellen Japans wurde vor einigen Jahren von dem Verfasser berichtet.⁽¹⁾ Derselbe hat neulich noch einige andere Mineralquellen studiert und ihren Vanadin-, Chrom- und Molybdän gehalt bestimmt.

Das Kusatubad ist eine der berühmtesten heissen Quellen Japans. Nach der Analyse des Chemisch-Hygienischen Laboratoriums des Volkswohlfahrtsministeriums zu Tokyo im Jahre 1934, gehören diese Quellen zu den sauren Alaun- Vitriolquellen. Die höchste Temperatur liegt über 60°C, und hat den pH-Wert 1.5. Die Quellen liegen ungefähr 1200 m über dem Meeresspiegel. Das Mineralwasser quillt aus dem vulkanischen Gestein. Masutomi ist eine der berühmtesten radioaktiven Mineralquellen Japans. Der Radongehalt dieses Mineralwassers wurde im letzten Jahre von Nakai⁽²⁾, Oana und dem Verfasser⁽³⁾ gemessen. Der Radiumgehalt wurde von Nakai⁽²⁾ im Jahre 1938 mitgeteilt, und kürzlich vom Verfasser noch einmal bestimmt. Die Resultate der Analyse werden in kurzer Zeit berichtet werden. Die Mineralquellen von Masutomi gehören zu den Kochsalzquellen. Sie enthalten jedoch eine bemerkenswerte Menge von Kohlensäure. Die Thermalquellen von Takayu in der Provinz Yamagata und die Thermalquellen von Numaziri in der Provinz Hukusima gehören zu den sauren Alaun-Vitriolquellen. Diese Mineralquellen haben den pH-Wert 1-2. Die Thermalquellen von Sukayu in der Provinz Aomori gehören zu den sauren Quellen und die Thermalquellen von Kirisima in der Provinz Kagosima zu den Schwefelquellen. Diese Thermalquellen haben den pH-Wert 2-3. Das Arimabad ist eine der berühmtesten heissen Quellen Japans. Nach der Analyse des Chemisch-Hygienischen Laboratoriums des Volkswohlfahrtsministeriums zu Tokyo gehört diese Quelle zu den Kochsalzquellen. Die Thermalquellen von Kawazi gehören zu den einfachen warmen Quellen. Die katalytische Wirkung dieses Mineralwassers wurde von K. Okabe⁽⁴⁾ im letzten Jahre genau untersucht.

Die Bestimmung ergab die in nachfolgenden Tabelle verzeichneten Resultate (Tabelle 1).

(1) Kuroda, dies Bulletin, **14** (1939) 307; **15** (1940) 65.

(2) Nakai, dies Bulletin, **15** (1940), 333. *J. Chem. Soc. Japan* **58** (1937), 638. **59** (1938), 1181.

(3) Oana und Kuroda, dies Bulletin, **15** (1940), 485.

(4) Okabe, *J. Chem. Soc. Japan*, **62** (1941), 537.

Tabelle 1. Vanadin-, Chrom- und Molybdängehalt einiger Mineralquellen Japans.

Nr.	Name der Quellen	Provinz	(mg/L)			% (Abdampfrückstand)		
			V	Cr	Mo	V	Cr	Mo
1	Wasinoyu, Kusatu	Gumma	0.33	0.040	0.006	0.011	0.0013	0.0002
2	Tiyonoyu, Kusatu	Gumma	0.33	0.035	0.008	0.013	0.0014	0.0003
3	Sirahatanoyu, Kusatu	Gumma	0.32	0.032	0.003	0.011	0.0011	0.0001
4	Sekinoyu, Kusatu	Gumma	0.31	0.038	0.003	0.011	0.0013	0.0001
5	Matunoyu, Kusatu	Gumma	0.29	0.020	0.003	0.010	0.0007	0.0001
6	Zizōnōyu, Kusatu	Gumma	0.25	0.024	0.007	0.0085	0.0008	0.0002
7	Takayu	Yamagata	0.25	0.038	0.007	0.0068	0.0010	0.0002
8	Numaziri	Hukusima	0.11	0.00	0.003	0.0053	0.000	0.0001
9	Yagendō, Arima	Hyōgo	0.05	0.00	0.000	0.0005	0.000	0.0000
10	Tuganerō Nr. 1							
	Masutomi	Yamanasi	0.05	0.00	0.000	0.0007	0.000	0.0000
11	Higasiobi, Masutomi	Yamanasi	0.05	0.00	0.000	0.0005	0.000	0.0000
12	Hienoyu, Sukayu	Aomori	0.05	0.00	0.000	0.005	0.000	0.0000
13	Netunoyu, Sukayu	Aomori	0.05	0.00	0.000	0.005	0.000	0.0000
14	Iōsen, Kirisima	Kagosima	0.00	0.00	0.000	0.000	0.000	0.0000
15	Ikaho	Gumma	0.00	0.00	0.00	0.000	0.000	0.0000
16	Zizōkōsen, Akagi	Gumma	0.00	0.00	0.00	0.000	0.000	0.0000
17	Komotiyu, Kawazi	Totigi	—	—	0.016	—	—	0.0042

In Abb. 1 wurde der Zusammenhang zwischen den pH-Werten und dem Vanadiningehalt des Mineralwassers gezeigt. Die Mineralquellen enthalten je saurer sie reagieren desto mehr Vanadin. In Abb. 2 wurde

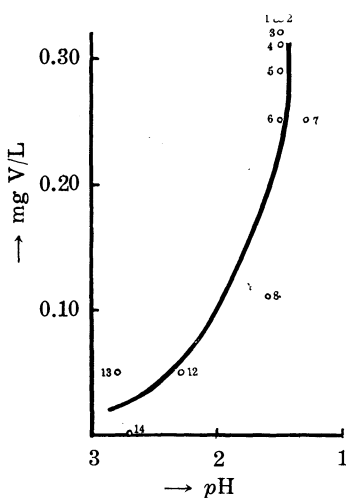


Abb. 1. Vanadiningehalt und pH.

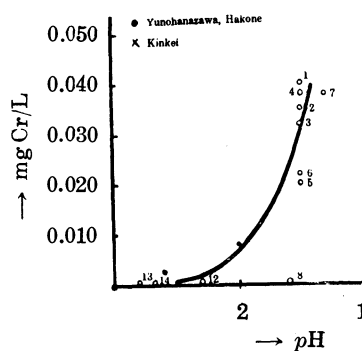


Abb. 2. Chromgehalt und pH.

der Zusammenhang zwischen den pH-Werten und dem Chromgehalt gezeigt. Der Zusammenhang ist ganz ähnlich. Der Molybdängehalt war jedoch unregelmässig und kein Zusammenhang wurde gefunden. Sehr interessant ist der hohe Molybdängehalt des Mineralwassers von Kawazi.

Tabelle 2.

	Clarke'sche Zahl	Durchschnittszahl von 32 Wasserproben. % (Abdampfückstand)
Cr	0.02	0.00045
V	0.015	0.0055
Mo	0.0013	0.000039

Tabelle 2 vergleicht die Clarke'sche Zahl des Vanadin-, Chrom- und Molybdäns, welche neulich von Prof. Dr. Kimura revidiert wurde, mit der Durchschnittszahl des Vanadin-, Chrom und Molybdängehalts von 32 Wasserproben Japans, welche in

Tabelle 1 dieser Mitteilung und in der vorhergehenden berichtet wurden. Die Durchschnittszahl des Vanadin-, Chrom- und Molybdängehaltes der Thermalquellen Japans ist beträchtlich kleiner als die Clarke'sche Zahl dieser Elemente.

Zusammenfassung.

(1) Der Vanadin- Chrom- und Molybdängehalt einiger Mineralquellen Japans wurde bestimmt.

(2) Die Mineralquellen enthalten je saurer sie reagieren desto mehr Vanadin und Chrom.

Ich möchte hiermit Herrn Prof. Kenjiro Kimura für seine freundliche Anleitung und steten Ratschläge, die mir bei der Ausführung dieser Arbeit zuteil geworden sind, meinen herzlichsten Dank aussprechen. Dem Unterrichtsministerium sei gedankt für die Gewährung einer Unterstützung zur Anregung wissenschaftlicher Forschung. Der Kaiserlichen Akademie der Wissenschaft sind wir für ihre finanzielle Unterstützung zu grossem Dank verpflichtet.

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Der katalytische Isotopenaustausch des gasförmigen Sauerstoffs. XI.⁽¹⁾ Die Austauschreaktion der Sauerstoffatome zwischen Sauerstoff und Wasserdampf an der Oberfläche des Natrium- und Kaliumhydroxyds. (Auszug.)⁽²⁾

Von Yosio OSUMI und Noriyoshi MORITA.

(Eingegangen am 7. Januar, 1942.)

Inhaltsübersicht. Die katalytische Austauschreaktion der O-Atome zwischen gasförmigen Sauerstoff und Wasserdampf an der Oberfläche des Natrium- und Kaliumhydroxyds wird unter Benutzung des an schwerem Sauerstoff angereicherten schweren Wassers untersucht. Dabei wird festgestellt, dass an Natriumhydroxyd von 360° ab und an Kaliumhydroxyd von 290° ab eine lebhaftere Austauschreaktion stattfindet und oberhalb 450° das Austauschgleichgewicht schnell erreicht wird. Die Reaktion wird mit Hilfe der Annahme erklärt, dass an der Oberfläche des in Rede kommenden Hydroxyds eine Art Peroxyd gebildet und durch den Zerfall dieses Peroxyds die Austauschreaktion herbeigeführt wird.

Einleitung. Aus den bisher von einem von uns ausgeführten Versuche kamen wir zu dem Schluss, dass die katalytische Wirksamkeit der Oxyde bzw. Hydroxyde für die Austauschreaktion zwischen gasförmigem Sauerstoff und Wasserdampf mit der zunehmenden Gruppennummer der Elemente der Oxyde bzw. Hydroxyde zunimmt, so lange als die betreffenden Elemente sich in derselben Horizontalreihe des periodischen Systems befinden und die Gruppennummer kleiner als vier bleibt.⁽³⁾ So wird z.B. gefunden, dass die in Rede kommende Austauschreaktion an der Oberfläche des Oxyds des Titans, das zur 4. Gruppe a der 4. Horizontalreihe gehört, erst von 590° ab, hingegen an der Oberfläche des Calciumoxyds, das zur 2. Gruppe derselben Horizontalreihe gehört, schon von 390° ab bemerkbar wird. Extrapoliert man diese Werte, so soll die Reaktion an der Oberfläche des Kaliumhydroxyds schon von etwa 300° ab merklich stattfinden, obwohl diese Reaktion oder im allgemeinen die Reaktion an der Oberfläche der Alkalihydroxyde noch nicht direkt experimentell untersucht wurde. Die vorliegenden Versuche wurden deshalb ausgeführt, um die betreffende Austauschreaktion an der Oberfläche der beiden typischen Alkalihydroxyde nämlich des Natrium- und Kaliumhydroxyds direkt experimentell zu untersuchen.

Versuchsmethode und -ergebnisse. Die Versuchsanordnung ist im grossen und ganzen dieselbe wie die schon früher beschriebene.⁽⁴⁾ Das Reaktionsgasgemisch von der Zusammensetzung $\text{H}_2\text{O}:\text{O}_2=1:2$ wird aus dem an schwerem Sauerstoff angereicherten schwerem Wasser und dem elektrolytischen Sauerstoff hergestellt und dieses Gasgemisch über das in einem Katalysatorrohr befindliche und auf einer bestimmten Tem-

(1) X. Mitteil.: dies Bulletin, **15** (1940), 298.

(2) Y. Osumi und N. Morita, *J. Chem. Soc. Japan*, **62** (1941), 802.

(3) Vgl. Abb. 2 IV. Mittl. (dies Bulletin, **14** (1939), 15).

(4) N. Morita und T. Titani, dies Bulletin, **13** (1938), 357.

peratur erwärmte Alkalihydroxyd langsam (bei Zimmertemperatur gemessen 60 ccm pro Min.) geleitet. Dabei wird das Alkalihydroxyd wegen seiner verhältnismässig leichten Schmelzbarkeit nicht als solches sondern in Verbindung mit einer Menge Asbest benutzt. Etwa 2 g von vorn herein gut gereinigter Asbest wird in 50 ccm 5 normaler Ätzalkalilösung zum Sieden erwärmt und der so mit dem betreffenden Alkali getränkte Asbest wird in dem Katalysatorrohr unter Durchleitung des Sauerstoffgases auf 400° bis zum Trocknen erhitzt.

Der aus dem Katalysatorrohr zusammen mit dem Sauerstoffgas ausgeströmte Wasserdampf wird durch Abkühlung kondensiert aufgefangen und nachdem er auf geeignetem Weg gereinigt worden ist, sein Dichteüberschuss dem gewöhnlichen Wasser gegenüber schwebemetrisch bestimmt. Bezeichnet man den so bestimmten Dichteüberschuss des schweren Wassers nach dem Versuche mit Δs_e und den vor dem Versuch d.h. ohne Austausch mit Δs_a , so lässt sich das prozentuale Austauschmass %A für die Austauschreaktion, die unter den angegebenen Versuchsbedingungen zwischen Wasserdampf und Sauerstoffgas stattfand, mit Hilfe der Gl. ohne weiteres berechnen:⁽⁵⁾

$$\%A = \frac{(\Delta s_a - \Delta s_e)}{(\Delta s_a - \Delta s_e)_\infty} \times 100.$$

In dieser Gl. drückt $(\Delta s_a - \Delta s_e)_\infty$ solch eine Abnahme des Dichteüberschusses des schweren Wassers aus, die sich beim vollständigen Austausch ergeben würde. Dieser extreme Wert der Dichteabnahme des schweren Wassers $(\Delta s_a - \Delta s_e)_\infty$ kann aber nun unter Benutzung der Zusammensetzung des Reaktionsgasgemisches sowie des Gehaltes des Sauerstoffgases und Wasserdampfes an schwerem Sauerstoff rechnerisch ermittelt werden. So ergab sich unter den vorliegenden Versuchsbedingungen⁽⁶⁾ $(\Delta s_a - \Delta s_e)_\infty = 29.1 \gamma$. Das prozentuale Austauschmass %A in der letzten Spalte der Tabellen 1 bis 3 wird deshalb mit Hilfe der Gl. berechnet:

$$\%A = \frac{(\Delta s_a - \Delta s_e)}{29.1} \times 100.$$

Tabelle 1. Natriumhydroxyd
(Präparat A).

Versuchs- nr.	Temp. °C	$(\Delta s_a - \Delta s_e)$ in γ	%A
1	435	26.5	91
2	460	28.7	99
3	505	29.0	100
4	685	30.7	106

Jede Reihe der Versuche, die in Tabelle 1 bis 3 wiedergegeben ist, wird unter Benutzung des frischen Hydroxyds ausgeführt und die Versuchsnr. in jeder Tabelle gibt die zeitliche Reihenfolge der einzelnen Versuche an. Nach der Beendigung der Versuche wurde bemerkt, dass der mit Natrium-

(5) Vgl. Gl. (1) in I. Mittl. (dies Bulletin, **13** (1938), 362).

(6) Das zum Versuch benutzte schwere Wasser wurde mit Hilfe der fraktionierten Destillation des gewöhnlichen Wassers hergestellt. Deshalb rührte vom gesamten Dichteüberschuss des benutzten Wassers, der 64.7 γ betrug, 34.8 γ von der Anreicherung des schweren Sauerstoffs. Der Rest kann auf die Anreicherung des schweren Wasserstoffs zurückgeführt werden. Dagegen war der zum Versuch benutzte elektrolytische Sauerstoff um 1.6 γ leichter als der gewöhnliche Wassersauerstoff.

Tabelle 2. Natriumhydroxyd
(Präparat B).

Versuchs- nr.	Temp. °C	$(\Delta s_a - \Delta s_e)$ in γ	%A
1	360	1.9	7
2	395	10.4	36
3	415	21.1	73

Versuchs- nr.	Temp. °C	$(\Delta s_a - \Delta s_e)$ in γ	%A
2	375	4.8	17
1	398	16.9	58
3	405	24.3	84
5	426	29.3	101
4	434	29.9	103

Tabelle 3. Kaliumhydroxyd.

Versuchs- nr.	Temp. °C	$(\Delta s_a - \Delta s_e)$ in γ	%A
1	310	5.0	17
2	385	23.0	79
3	535	29.9	103
4	655	30.6	105

Versuchs- nr.	Temp. °C	$(\Delta s_a - \Delta s_e)$ in γ	%A
1	320	5.7	20
2	345	9.7	33
3	380	18.2	63

hydroxyd getränkte Asbest schwach bräunlich und der mit Kaliumhydroxyd getränkte schwach bläulich gefärbt war.

Diskussion der Ergebnisse. Die in Tabellen 1 bis 3 angegebenen Ergebnisse sind in nebenstehender Abb. 1 graphisch eingezeichnet. Wie daraus ersichtlich ist, findet die Austauschreaktion an der Oberfläche des Kaliumhydroxyds viel leichter als beim Natriumhydroxyd statt; die Temperatur $t(10\%)$, wo das prozentuale Austauschmass %A erst 10% erreicht, liegt beim Natriumhydroxyd bei 360°, dagegen beim Kaliumhydroxyd bei 290°. Dieser letztere Wert stimmt aber mit dem oben in der Einleitung angegebenen erwarteten Wert (300°) sehr gut überein.

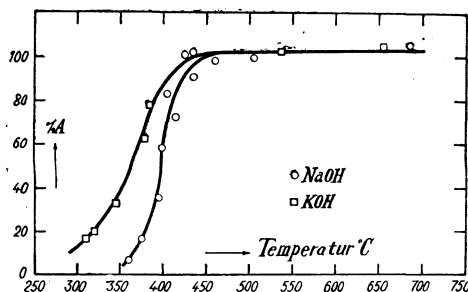


Abb. 1. Das prozentuale Austauschmass %A zwischen gasförmigen Sauerstoff und Wasserdampf an der Oberfläche des Natrium- und Kaliumhydroxyds in Abhängigkeit von der Temperatur.

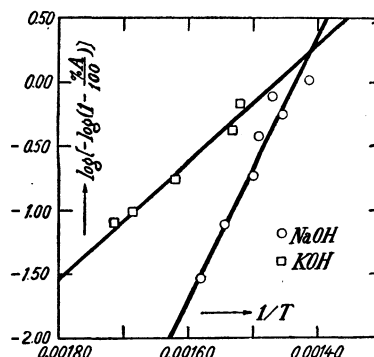


Abb. 2. Ermittlung der Aktivierungsenergie.

Der Unterschied der katalytischen Wirksamkeit zwischen Natrium- und Kaliumhydroxyd drückt sich aber noch deutlicher in der Aktivierungsenergie der betreffenden Reaktion aus. Um diese Energie zu ermitteln, wird in Abb. 2 der Logarithmus des Ausdrucks $\left[-\log\left(1 - \frac{\%A}{100}\right)\right]$ gegen das Reziproke der absoluten Temperatur $1/T$ eingetragen, da dieser erstere Ausdruck der Reaktionsgeschwindigkeit proportional sein soll.⁽⁷⁾

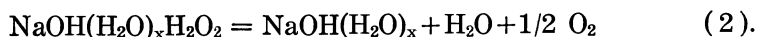
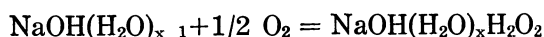
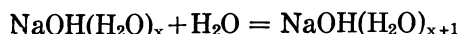
(7) N. Morita, dies Bulletin, **15** (1940), 176.

Aus der Neigung der in Abb. 2 angegebenen beiden geraden Linien ergibt sich die in Rede kommende Aktivierungsenergie:

$$A(\text{NaOH}) = 47 \text{ Kcal.} \quad \text{und} \quad A(\text{KOH}) = 21 \text{ Kcal.} \quad (1).$$

Gut übereinstimmend mit der aus den bisherigen Versuchen bestätigten allgemeinen Regel braucht also das weniger alkalische Natriumhydroxyd mehr Aktivierungsenergie als das stärker alkalische Kaliumhydroxyd.

Bei der Austauschreaktion an der Oberfläche der Erdalkalihydroxyde kamen wir zu dem Schluss, dass die aktivierte Adsorption des Wasserdampfes an der Oberfläche der betreffenden Hydroxyde massgebend wirkt.⁽⁸⁾ Zieht man nun die Tatsache in Rechnung, dass der Wasserdampf an Alkalihydroxyde ebenso stark oder noch stärker als an Erdalkalihydroxyde adsorbiert wird, so ist durchaus möglich, dass die Austauschreaktion an der Oberfläche der Alkalihydroxyde nach dem ähnlichen Mechanismus wie bei den Erdalkalihydroxyden verläuft. So kann z.B. die Reaktion an Natriumhydroxyd durch folgendes Schema dargestellt werden:



Die katalytische aktive Substanz ist also kein „trocknes“ Hydroxyd NaOH sondern das an diesem einige Moleküle Wasser halbchemisch verbundene „nasse“ Hydroxyd bzw. eine Art Polyhydrat $\text{NaOH}(\text{H}_2\text{O})_x$. An diesem Polyhydrat wird das Wasserdampfmolekül aktiviert adsorbiert. Verbindet das so aktiviert adsorbierte Wassermolekül das Sauerstoffmolekül aus der Gasphase an sich, so wird eine peroxydartige Verbindung gebildet und bei der Abspaltung dieses Peroxyds werden die O-Atome des Sauerstoffgases gegen die des Wassers ausgetauscht.

Zum Schluss möchten wir Herrn Prof. T. Titani für die Anregung zu dieser Arbeit verbindlichst danken. Der Nippon Gakujutsu Shinkokai (der Japanischen Gesellschaft zur Förderung der wissenschaftlichen Arbeit) sowie der Hattori Hohkoku (der Hattori-Stiftung) für ihre finanzielle Unterstützung sind wir auch zu grossem Dank verpflichtet.

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(8) N. Morita, dies Bulletin, **15** (1940), 128.

Untersuchungen über Flechtenstoffe. XCIX. Synthese der Dimethyläther-olivetonssäure und des Dimethyläther-olivetonids.^(*)

Von Yasuhiko ASAHINA und Hisasi NOGAMI.

(Eingegangen am 17. Februar, 1942.)

Wie wir in einer vorläufigen Mitteilung⁽¹⁾ dargethan haben, ist die Jerdansche Orientierung⁽²⁾ der Carboxyl-Gruppen in Dioxy-homophthalsäure und Dioxy-homo-teraphtalsäure (entstanden aus Orcin-tricarbonsäuretriäthylester durch Abspaltung eines kernständigen Carboxyls) im umgekehrten Sinne zu berichtigen. Bei der Darstellung der Orcin-tricarbonsäure-triäthylesters (I) nach Cornelius und Pechmann⁽³⁾ entsteht zugleich Orcin-tricarbonsäure-diäthylester (II) vom Schmp. 141°, den Jerdan durch Kondensation von Aceton-dicarbonsäure-diäthylester in Gegenwart des Chloressigsäureäthylesters mittels Magnesiumpulvers erhielt. Derselbe Diäthylester vom Schmp. 141° lässt sich auch aus dem Orcin-tricarbonsäure-triäthylester durch konz. Schwefelsäure darstellen. Hierbei ist aber die Ausbeute sehr gering.

Wird der Diäthylester vom Schmp. 141° (II) mit Kalilauge erhitzt, so wird Orcin-dicarbonsäure-monoäthylester (III, R=H) vom Schmp. 190° erhalten. Vor einiger Zeit hat der eine von uns (H.N.)⁽⁴⁾ denselben Monoäthylester über Dimethyläther-mono-äthylester-chlorid (IV, R=Cl) in Dimethoxy-carbäthoxy-phenacetyllessigsäure-äthylester (V, R=H) übergeführt. Bei der Ketonspaltung des letzteren entstand die niedrigere Homologe der Dimethyläther-olivetonssäure (VI, R=H) und des Dimethyläther-olivetonids (VII, R=CH₃). Die Desmethyl-Verbindung der ersteren kommt nach Oxyford und Raistrick⁽⁵⁾ im Stoffwechselprodukt von *Penicillium brevis-compactum* vor. Die Bildung solchen Enollaktons spricht dafür, dass die Dicarbonsäure (III), nicht ein Homoterephtalsäure-Derivat (wie Jerdan glaubte), sondern ein Homophthalsäure-Derivat sein muss. Zu demselben Schluss gelangt man durch die Bildung des Orsellinsäure-äthylesters aus (III, R=H) beim Decarboxylieren.

Wird nun die Natriumverbindung des γ -(3,5-Dimethoxy-2-carbäthoxy-phenyl)-acetessigsäure-äthylester (V, R=Na) mit n-Butyljodid umgesetzt und das so erhaltene Butyl-Derivat (V, R=nC₄H₉) der Ketonspaltung unterworfen, so entsteht eine Ketosäure (VI, R=nC₄H₉), die sich als identisch mit Dimethyläther-olivetonssäure erweist. Beim Erhitzen mit Ameisensäure geht die letztere leicht in Dimethyläther-olivetonid (VII, R=C₅H₁₁) über.

Anderseits lässt sich die Orcin-dicarbonsäure vom Schmp. 198° (VIII), die nach Jerdan⁽²⁾ aus Orcin-tricarbonsäure-triäthylester durch

(*) Asahina u. Asano, *Ber.*, **65** (1932), 475.

(1) *Proc. Imp. Acad. Tokyo*, **16** (1940), 119; *Chem. Zentr.*, **1940** II, 1419.

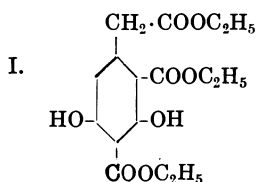
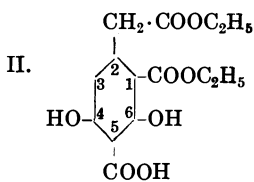
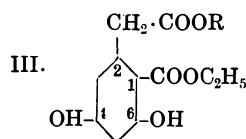
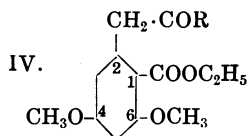
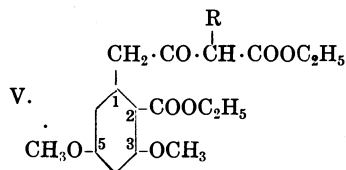
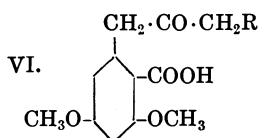
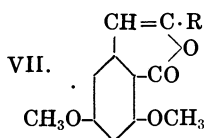
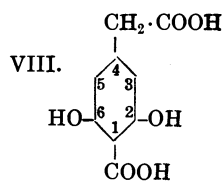
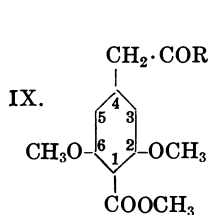
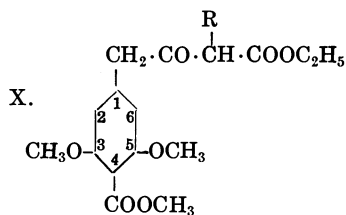
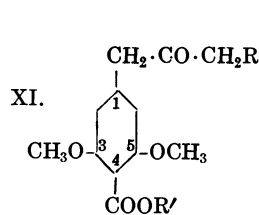
(2) *J. Chem. Soc.*, **75** (1899), 808.

(3) *Ber.*, **19** (1886), 1448.

(4) *J. Pharmaceut. Soc. Japan*, **61** (1941), 56.

(5) *Biochem. Journ.* **27** (1933), 634; *Chem. Zentr.*, **1934** II, 3515.

starke Kalilauge entsteht, nach folgender Umwandlung als 2.6-Dioxyhomoterephtalsäure charakterisieren. Der daraus dargestellte Dimethylätherdimethylester (IX, $R = OCH_3$) (Schmp. $72-73^\circ$) liefert bei der partiellen Verseifung 3.5-Dimethoxy-4-carbäthoxy-phenylessigsäure (IX $R = OH$), deren Säurechlorid (IX, $R = Cl$) mit Natrium-acetessigester gekuppelt wird. Beim Desacetylieren des Kuppelungsprodukts bildet sich 3.5-Dimethoxy-4-carbäthoxyphenylacetyl-essigsäure-äthylester (X, $R = H$) welcher bei der Ketonspaltung die Verbindung (XI, $R = R' = H$) giebt. Zufälligerweise stimmt der Schmp. der letzteren mit demjenigen des Dimethyläthers von der Raistrickschen Verbindung (VI, $R = H$) überein. Unsere Substanz liefert aber in keiner Weise Enollakton. Auch die aus der Verbindung (X, $R = C_4H_9$) erhaltene Ketonssäure (XI, $R = C_4H_9$, $R' = H$) erwies sich als nicht identisch mit Olivetonsäure und lieferte kein Enollakton.

Schmp. 98° .Schmp. 141° . $R = H$, Schmp. 190° . $R = C_2H_5$, Schmp. 108° . $R = OH$, Schmp. 103° . $R = Cl$, Öl. $R = H$, Schmp. 38.5° . $R = n \cdot C_4H_9$, Öl. $R = H$, Schmp. $139-141^\circ$. $R = n \cdot C_4H_9$, Schmp. 93° . $R = CH_3$, Schmp. 155.5° . $R = C_5H_{11}$, Schmp. 94° .Schmp. 198°  $R = OCH_3$ Schmp. $72-73^\circ$. $R = OH$, Schmp. 147.5° . $R = H$, Schmp. 115° . $R = n \cdot C_4H_9$, Öl. $R = H$, $R' = H$, Schmp. $139-140^\circ$. $R = n \cdot C_4H_9$, $R' = H$, Schmp. 137° .

Beschreibung der Versuche.

Kondensation von Acetondicarbonsäure-diäthylester mittels $\frac{1}{2}$ Natriums.⁽¹⁾ Man fügt 2 g. Natrium zu 200 g. abgekühltem Aceton-dicarbonsäure-diäthylester hinzu und erhitzt nach Auflösen des Metalls im Oelbad 4 Stdn. auf 140–150°. Dann schüttelt man das beim Erkalten erstarrte Produkt mit viel Benzol, wobei die Verbindung (II) teilweise ungelöst verbleibt. Um die letztere vom Triäthylester vollständig zu trennen wird die Benzollösung mit gesättigter Bicarbonatlösung (A) geschüttelt.

Orcin-tricarbonsäure-triäthylester (I): Scheidet sich beim Verdampfen der Benzollösung krystallinisch aus. Umgelöst aus Alkohol bildet er farblose Prismen vom Schmp. 98°. Ausbeute 45–50 g.

Orcin-tricarbonsäure-diäthylester-(1.2) (II): Das in Benzol schwer lösliche Kondensationsprodukt wird mit dem aus der angesäuerten Bicarbonatlösung (A) ausgeschiedenen vereinigt und aus Alkohol umgelöst. Die so erhaltene Substanz bildet farblose undurchsichtige Prismen vom Schmp. 141°. In Chloroform sehr leicht, in Alkohol und Benzol in der Wärme leicht, in Petroläther schwerlöslich. Die alkoholische Lösung färbt sich mit Eisenchlorid rotviolett, mit Chlorkalk orange. Eine Mischprobe mit dem nach Jerdan⁽²⁾ dargestellten Präparat zeigte keine Schmp.-Depression. 3.605 mg. Subst.: 7.140 mg. CO₂, 1.695 mg. H₂O. C₁₄H₁₆O₈. Ber. C 53.84 H 5.15. Gef. C 54.02 H 5.26

Derselbe Orcin-tricarbonsäure-diäthylester entsteht auch aus dem Triäthylester durch viertägiges Stehenlassen einer Lösung von 5 g. Triäthylester in 40 ccm. konz. Schwefelsäure. Man giesst die Schwefelsäure-Lösung im Eiswasser, extrahiert das ausgeschiedene mit Aether und schüttelt die Aether-Lösung mit Bicarbonatlösung. Im Aether bleibt 1.6 g. Ausgangsmaterial zurück. Die Bicarbonatlösung fällt beim Ansäuern ein Säure-Gemisch, woraus sich beim Fraktionieren aus Alkohol etwa 0.5 g. Orcin-tricarbonsäure-diäthylester vom Schmp. 141° isolieren lässt. In der Mutterlauge desselben befindet sich eine bei 173° schmelzende Substanz von unbekannter Struktur.

Bildung des Orsellinsäure-äthylester aus dem 4,6-Dioxy-homophtalsäure-monoäthylester-(1) (III), R=H). 0.35 g. Verb. (III R=H) werden mit 0.1 g. Kupfer-bronze in 4 ccm. Chinolin eingetragen und 15 Minuten auf 200–210° erhitzt. Das so erhaltene decarboxylierte Produkt bildet beim Umlösen aus kochendem Wasser farblose Prismen vom Schmp. 131–2°. Eine Mischprobe mit dem Orsellinsäure-äthylester zeigt keine Schmp.-Depression.

Dimethyläther-olivetonensäure und -olivetonid. γ -(3,5-Dimethoxy-2-carbäthoxy-phenyl)- α -n-butyl-acetessigsäure-äthylester (V, R=n C₄H₉): 1.67 g. γ -(3,5-Dimethoxy-2-carbäthoxy-phenyl)-acetessigsäure-äthylester (V, R=H) werden in 10 ccm. Alkohol gelöst und unter Zusatz von 0.11 g. Natrium (gelöst in 6 ccm. Alkohol) und 1.4 g. n-Butyljodid 4 Stdn. gekocht. Dann wird das Lösungsmittel abdestilliert, der Rückstand mit Wasser umgerührt und ausgeäthert. Das beim Verdampfen des Aethers verbleibende, rohe n-Butyl-Derivat bildet ein Oel, dessen alkohol. Lösung sich mit Eisenchlorid nicht färbt. Ausb. 1.5 g.

Dimethyläther-olivetonensäure (VI, R=n-C₄H₉): Man kocht 0.5 g. oben erhaltenes n-Butyl-Derivat ca. 2 Stdn. in 20 c.c. Alkohol (90%) unter Zusatz von 1 g. Kaliumhydroxyd, destilliert den Alkohol im Vakuum, löst den Rückstand im Wasser, säuert die Lösung an und äthert das so oelig ausgeschiedene Produkt aus. Beim Umlösen zunächst aus Ligroin, dann aus Benzol-Petroläther (1:1) bildet es farblose Prismen vom Schmp. 93°. Eine Mischprobe mit der aus Mikrophyllinsäure erhalten Dimethyläther-olivetonensäure⁽⁶⁾ zeigte keine Schmp.-Depression. 3.820 mg. Subst.: 9.095 mg. CO₂, 2.505 mg. H₂O. C₁₆H₂₂O₅. Ber. C 65.27 H 7.54 Fef. C 64.92 H 7.34.

Dimethyläther-olivetonid (VII, R=C₅H₁₁): 0.1 g. VI (R=C₄H₉) wird in 5 ccm. Ameisensäure (95%) gelöst, 2 Stdn. gekocht und im Vakuum verdampft. Der Rückstand wird in Aether gelöst, die Lösung mit Bicarbonatlösung geschüttelt und ver-

dampft. Das so erhaltene, neutrale Produkt bildet beim Umlösen aus Alkohol farblose Prismen vom Schmp. 94°. Eine Mischprobe mit dem Dimethyläther-olivetonid aus der Mikrophyllinsäure zeigte keine Schmp.-Depression. 3.925 mg. Sbst.: 9.990 mg. CO₂, 2.570 mg. H₂O. C₁₆H₂₀O₄. Ber. C 69.52, H 7.30. Gef. C 69.42, H 7.33.

Derivate der 2,6-Dioxy-homoterephthalsäure (VIII) und deren Umwandlungen. 2,6-Dioxy-homoterephthalsäure-dimethylester: Dargestellt durch Einwirkung von Diazomethan auf 2,6-Dioxy-homo-terephthalsäure von Schmp. 198°, die Jerdan⁽²⁾ aus Orcinticarbonsäure-triäthylester beim Kochen mit konz. Kalilauge erhielt und für Dioxyhomophthalsäure hielt. Farblose Prismen vom Schmp. 77° (aus Alkohol). C₁₁H₁₂O₆. Ber. C 54.98 H 5.04. Gef. C 55.04, H 5.02.

2,6-Dimethoxy-homoterephthalsäure-dimethylester (IX, R=OCH₃). Dargestellt durch Kochen von oben erhaltenen Dioxy-dimethylester mit Jodmethyl und Kaliumcarbonat in Methyläthylketon. Farblose Blättchen von Schmp. 72–73° (aus Alkohol). C₁₄H₁₆O₆. Ber. C 58.18 H 6.01. Gef. C 57.98 H 5.98.

2,6-Dimethoxy-homoterephthalsäure-monomethylester-(1) (IX, R=OH). Dargestellt durch einstündigem Kochen von IX (R=OCH₃) in alkohol. Kalilauge. Farblose Blättchen vom Schmp. 147.5° (aus Benzol). C₁₂H₁₄O₆. Ber. C 56.67 H 5.55. Gef. C 56.98 H 5.29.

2,6-Dimethoxy-homoterephthalsäure-chlorid-(4)-methylester-(1) (IX, R=Cl). Dargestellt durch Lösen von IX (R=OH) in Phosphor-trichlorid, Abgiessen nach gelindem Erwärmen und längerem Stehen von abgeschiedener Phosphorigsäure und Fällen durch Zusatz von Petroläther. Farblose Krystalle, die ohne weiteres zur folgenden Umwandlung verwendet wird.

γ-(3,5-Dimethoxy-4-carbomethoxy-phenyl)-acetessigsäure-äthylester-(1) (X, R=H). Man kuppelt das oben erhaltene Säurechlorid mit Natriumacetessigester und entacetyliert das Kupplungsprodukt mittels Ammoniaks in Gegenwart von Ammonchlorid. Farblose Tafeln vom Schmp. 115°. Die alkohol. Lösung färbt sich mit Eisenchlorid weinrot. C₁₆H₂₀O₇. Ber. C 59.23 H 6.22. Gef. C 59.19 H 6.05.

3,5-Dimethoxy-4-carbomethoxy-benzyl-methyl-keton (XI, R=H, R'=CH₃). Dargestellt durch einstündigem Kochen von X (R=H) in alkoholischer Kalilauge. Farblose Prismen vom Schmp. 100.5° (aus Petroläther). C₁₃H₁₆O₅. Ber. C 61.87 H 6.40. Gef. C 61.83 H 6.31.

3,5-Dimethoxy-4-carboxy-benzyl-methyl-keton (XI, R=H, R'=H). Dargestellt durch Lösen von XI (R=H, R'=CH₃) in konz. Schwefelsäure und Fällen nach 5 stündigem Stehen mit Wasser. Farblose Nadeln vom Schmp. 139–140° (aus Benzol). Auch bei 3 stündigem Kochen mit Acetanhydrid ändert es sich nicht. C₁₂H₁₄O₅. Ber. C 60.48 H 5.93. Gef. C 60.24 H 5.93.

γ-(3,5-Dimethoxy-4-carbomethoxy-phenyl)-α-n-butyl-acetessigester (X, R=n-C₄H₉). Man kocht die Natriumverbindung (X, R=Na) mit n-Butyljodid in Alkohol. Farbloses Öl, unlöslich in wässriger Kalilauge, färbt sich nicht mit Eisenchlorid.

3,5-Dimethoxy-4-carbomethoxy-benzyl-n-amylketon (XI, R=n-C₄H₉, R'=CH₃). Dargestellt durch Ketonspaltung von X (R=n-C₄H₉) mittels alkoholischer Kalilauge. Syrup.

3,5-Dimethoxy-4-carboxy-benzyl-n-amylketon (XI, R=n-C₄H₉, R'=H). Dargestellt durch Lösen von XI (R=n-C₄H₉, R'=CH₃) in konz. Schwefelsäure und Fällen mit Wasser. Man kann auch die Verseifung mit alkohol. Kalilauge bewerkstelligen. Farblose Prismen vom Schmp. 137° (aus Benzol). C₁₆H₂₂O₅. Ber. C 65.27 H 7.54. Farblose Prismen vom Schmp. 137° (aus Benzol). C₁₆H₂₂H₅. Ber. C 65.27 H 7.54.

(Pharmazeutisches Institut der kaiserl. Universität Tokyo.)

Über den Nachweis von nativem Eiweiss mit pH-Indicatoren. II.⁽¹⁾

Von Morizo ISHIDATE und Takeichi SAKAGUCHI.

(Eingegangen am 7. März 1942.)

Um den Mechanismus der Nachweisreaktion von nativem Eiweiss mit Farbstoffen näher zu studieren, haben wir nun von neuem etwa 30 verschiedene Farbstoffen, welche in bestimmtem pH-Bereiche einen deutlichen Farbumschlag aufweisen, mit derselben Reaktionsbedingung wie vorher untersucht. Hierbei erweisen sich die halogenierten Fluorescein-abkömmlinge, Eosin, Cyanosin, Erythrosin, Phloxin, Rose Bengale, und die halogenierten Oxyphenylmethanderivate wie Tetrabrombenzaurin und Tetrabromrosolsäure, und noch dazu Hexanitrodiphenylamin (Aurantia) als hoch empfindliche Indikatoren gegen Eiweissklassen. Dagegen auf Pepton, Aminosäuren sowohl auch auf die anderen makromolekularen Substanzen zeigen sie weit geringere Affinität, weshalb sie fast ebenso wie das Feiglschen Reagenz (Tetrabromphenolphthaleinäthylester) zweckmässige Eiweissindikatoren darstellen (vergl. Tafel 1 bezw. 2). Die Anwendbarkeit dieser Farbstoffe zum Nachweis der Eiweissstoffe ist damit eng verbunden, dass sie bekanntlich zum Färben von Seide und zum Wolldruck Verwendung finden.

Es wird dieses Mal auch angenommen, dass die reaktionsfähigen Farbstoffe ihre Umschlagsgebiete ausnahmslos in saurerer Seite besitzen. So ist es nicht verwunderlich, dass unter den Phenolphthaleinabkömmlingen Phenolphthalein selbst (pH=8.3–10.0), sein Methylester (8.0–9.4) und Tetrabromphenolphthalein (6.8–7.8) (I) gegen Eiweiss ganz negative Reaktion ergeben, dagegen Tetranitrophenolphthalein (1.6–3.0) (III) wie auch sein Ester (1.6–3.2) (IV) eine deutliche positive Reaktion aufweisen, und Tetrabromphenolphthalein-äthylester sowie methylester (3.5–4.9) (II) sehr wertvolle Indikatoren darstellen. Dieselbe Verhältnisse weisen auch die Fluorescein-derivate und die Oxyphenylmethanfarbstoffe auf. Also in Gegensatz zu Fluorescein (3.6–5.6) und seinen Methylester (4.0–6.2) bezw. Benzaurin (6.5–8.6) und Rosolsäure (6.9–8.0) sind ihre halogenierte Abkömmlingen Eosin (VI), Eosinmethylester (VII), Cyanosin, Erythrosin u.s.w. bezw. Tetrabrombenzaurin (V) und Tetrabromrosolsäure stark reaktionsfähiger.

Der Eintritt von Halogenen bezw. Nitrogruppen in die zwei Phenolkern e befördert die Dissoziation des betreffenden Phenols, infolgedessen wird der Farbumschlag des Farbstoffs stark nach der saueren Seite hin verschoben. Wenn einmal eines der beiden Hydroxyle methyliert wird, so wandelt sich der Farbstoff in einen reaktionslosen Stoff um. Es ist daher höchst wahrscheinlich, dass dieser geförderte Dissoziationsgrad des phenolischen Hydroxyls zur Funktion der Eiweissreaktion eine wesentliche Rolle spielt. Ob das Carboxyl am Phthalsäurereste frei oder methyl-

(1) M. Ishidate und T. Sakaguchi, *Ber.*, **74** (1941), 163.

Tafel 1.

Nr.	Indikator	Umschlagsgebiet (pH)		Grenzkonzentration (%)				Verratlösung des Indik. (A = Alkohol, W = Wasser) und der geign. Säure.
		Sauer	Alkalisch	Casein	Hämog- lobin	Oval- bumin	Gelatin	
1.	Tetrabromphenol- phthaleinmethyl- ester (Aut.)	3.5 gelb	— 4.9*) blau	0.004	0.004	0.005	0.004	0.1% A 0.2 N CH ₃ COOH
2.	Eosin (Merck)	0.0 orange	— 3.0 rosarot	0.0025	0.0025	0.005	0.005	0.1% W 0.1 N HCl
3.	Phloxin (Merck)	1.4 farblos	— 3.6*) rot	0.0005	0.0025	0.005	0.0025	0.05% W 0.1 N HCl
4.	Cyanosin (Grüber)	1.5 farblos	— 3.0 rot	0.0005	0.0025	0.005	0.005	0.05% W 0.1 N HCl
5.	Erythrosin (Merck)	0.0 farblos	— 3.6*) rot	0.001	0.005	0.005	0.0025	0.05% W 0.1 N HCl
6.	Rose Bengale (Grüber)	2.2 farblos	— 2.8*) rot	0.001	0.0025	0.005	0.005	0.05% W 0.1 N HCl
7.	Eosinmethylester (Aut.)	1.4 farblos	— 3.0*) rot	0.005	0.005	0.005	0.005	0.1% W 0.1 N HCl
8.	Jodeosin (Takeda)	0.5 orange	— 5.5*) rot	0.01	0.005	0.005	0.01	0.1% W 0.1 N HCl
9.	Tetranitrophenol- phthalein (Aut.)	1.6 farblos	— 3.2*) gelb	0.02	0.02	0.02	1.0	0.1% W 0.2 N CH ₃ COOH
10.	Tetranitrophenol- phthaleinmethyl- ester (Aut.)	1.6 farblos	— 3.2*) gelb	0.05	0.02	0.05	0.2	0.1% W 0.2 N CH ₃ COOH
11.	Tetrabrombenz- aurin (Aut.)	3.9 gelb	— 5.4*) blau	0.005	0.01	0.005	0.02	0.1% A 0.2 N CH ₃ COOH
12.	Tetrabromrosol- säure (Aut.)	2.7 gelb- orange	— 5.2*) violett	0.01	0.01	0.005	0.005	0.04% W 0.2 N CH ₃ COOH
13.	Aurantia (Grüber)	1.5 gelb	— 2.8*) orange	0.001	0.0025	0.005	0.005	0.05% W 0.1 N HCl

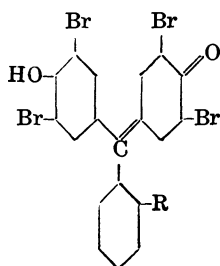
*) Das Umschlagsgebiet wurde von uns colorimetrisch mit der Pufferlösung bestimmt.

Tafel 2.

Indikator		Grenzkonzentration (%)								
		Pepton	Glycyl- glycin	Glyko- koll	Phenyl- alanin	Tyro- sin	l-Trypto- phan	Seife	Gummi- arabi- cum	Stärke Agar-Agar u. Lecithine
1		0.2	0.5	5.0	0.5	0.1	0.25	0.5	2.0	(—)
2		0.2	1.0	2.0	1.0	0.7	0.05	0.5	0.5	(—)
3		0.05	0.25	1.0	1.0	0.1	0.25	1.0	0.25	(—)
4		0.05	0.1	0.5	0.5	0.25	0.05	0.5	0.25	(—)
5		0.05	0.5	2.0	1.0	0.3	0.25	0.5	0.25	(—)
6		0.05	0.25	1.0	1.0	0.25	0.25	0.5	0.5	(—)
7		0.05	2.5	2.0	1.0	0.1	0.1	0.5	0.5	(—)
8		0.1	5.0	2.0	1.0	0.25	0.1	2.5	2.0	(—)
11		0.25	2.0	5.0	1.0	1.0	1.0	1.0	1.0	(—)
12		0.1	1.0	1.0	1.0	1.0	0.5	0.2	0.5	(—)
13		0.1	0.5	1.0	1.0	0.025	0.05	0.5	0.5	(—)

(—): Zeigt eine ganz negative Reaktion bei der betreffenden Konzentration.

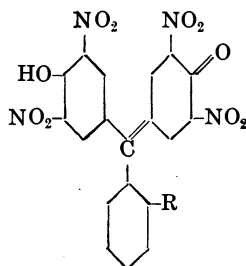
iert, ob der Phthalsäurerest halogeniert ist oder nicht, übt keinen nennenswerten Einfluss auf das Wesen der Reaktion, mit der Voraussetzung davon, dass durch Esterifizierung des Carboxyls der Umschlagsbereich des betreffenden Farbstoffs sich nicht weiter hin verschiebt, was in der Regel der Fall ist. Überdies dass das Vorhandensein von der Carboxylgruppe am Phthalsäurerest funktionell wenige Bedeutung hat, ist daraus ersichtlich, dass bromierte Benzaurin und Rosolsäure sich auch als die stark reaktionsfähigen Farbstoffe vorstellen.



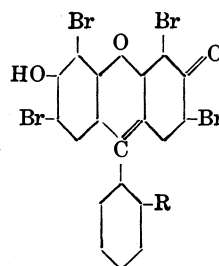
I: R = COOH

II: R = COOCH₃

V: R = H



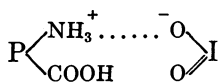
III: R = COOH

IV: R = COOCH₃

V: R = COOH

VII: R = COOCH₃

In der vorigen Abhandlung⁽¹⁾ haben wir schon die Annahme geäußert, dass die Reaktionsintensität zwischen Protein und Indikatoren viel mehr mit dem dissoziierten Anteil des gelösten Proteinmoleküls als mit der gesamten Konzentration der beiden Komponenten in Zusammenhang steht. Hiermit kann man den Mechanismus der Reaktion so erklären, dass sich der alkalisch gefärbte Farbstoff vornehmlich an der Stellung seines dissoziierten Anions (Phenolanion und derartigen) mit dem kationischen Zentrum des dissoziierten Eiweissmoleküls verbindet, wobei die Bindung genug beständig ist, in mässig saurer Lösung noch einen ursprünglichen alkalischen Farbton zu behalten. Die Bindungsform dürfte wohl folgendermassen als eine ionische Verbindung angesehen werden sein, die einen verhältnismässig schwachen Dissoziationsgrad besitzen.



P: Proteinrest

I: Indikatorrest

Bei der Ausführung der Tüpfelreaktion sauert man in der Regel das Gemisch von Eiweisslösung und Farbstoffen an. Sauert man dagegen Eiweisslösung zuerst an und fügt dann Farbstoffe hinzu, so wird die Empfindlichkeit der Reaktion stark verringert. Diese Tatsache würde für die erwähnte Erklärung eine wertvolle Stütze liefern können.

Fast alle genannten Eiweissindikatoren zeigen auch eine ähnliche Affinität sowohl gegen kolloidale Silber-halogenide und -cyanide, als auch gegen Silberion selbst. Es ist bekannt, dass Flourescein,⁽²⁾ Dichlorfluorescein⁽³⁾ und Eosin⁽²⁾ bei Argentmetrie zum Adsorptionsindikator Anwen-

(2) Fajans u. Wolff, *Z. anorg. allg. chem.*, **137** (1924), 221.

(3) Kolthoff u. Laur, *J. Am. Chem. Soc.*, **51** (1929), 3273.

dung finden und zwar die letzteren zwei wohl in schwach saurerer Lösung verwendet werden. Die Eiweissindikatoren lassen sich ohne weiteres in mehr oder weniger saurerer Lösung als geeignete Adsorptionsindikatoren aufweisen, was darauf beruht, dass die am Titrationsende entstehende Verbindung $(\text{AgCl}.\text{Ag})^+ \cdot (\text{I})^-$ bzw. $(\text{Ag})^+ \cdot (\text{I})^-$ in mässig saurem Medium recht beständig ist, folglich die Lösung bzw. die Fällung am Titrationspunkt scharf angefärbt wird. Über deren praktische Anwendung werden wir später eingehend berichten. Dieses Verhalten der Farbstoffe gegen Silbermizellen würde die Annahme weiter stützen, dass bei der Eiweissreaktion der aktive Stellung im Proteinmolekül eine positiv geladene Stickstoffgruppe ist.

Endlich wollen wir noch zufügen, dass diese Affinität des Proteinmoleküls mit Farbstoffen, wenn auch in schwächeren Grad, auch nach Desaminieren mittels Salpetrigrsäure erhalten bleibt.

Beschreibung der Versuche.

1. **Bestimmung der Grenzkonzentration der Eiweissarten (Tafel 1).** Die Bestimmung wurde wie vorher mittels der Tüpfelreaktion durchgeführt. Tetrabromphenolphthalein (Umschlagsgebiet $\text{pH}=6.8-7.8$), Phenolphthaleinmethylester (8.0-9.4), Fluorescein (3.6-5.6), Fluoresceinmethylester (4.0-6.2) lassen sich gegen 0.2% Ovalbumin, Casein und 1% Gelatin-lösung, und Benzaurin (6.5-8.6), Rosolsäure (6.9-8.0) und Dichlorindophenol (4.2-6.3) gegen 1% Ovalbumin, Casein, Hämoglobin und 5% Gelatin als reaktionsnegativ erweisen. Bei den folgenden Farbstoffreihen, die in einer sauren oder alkalischen Seite ein Umschlagsgebiet besitzen, wurde die Reaktion gegen 0.2% Ovalbumin auch als wirkungslos nachgewiesen: Alizarinrot, Anilinbraun, Benzpurpurin B, Brilliant-Kresilblau, Buttergelb, Chrysoidin, Cyanin, Hämatoxylin, Indigocarmin, Neutralviolett, Nilblau A, Orang G, Patentblau A, Protsil Sol. Pyronin G, Säurefuchsin und Wasserblau.

2. **Tafel 2.** ergibt die Grenzkonzentration des Peptons und der einigen Aminosäuren, und auch die Empfindlichkeiten gegen den einigen kolloidalen Lösungen. Wobei zeigt Pepton verhältnismässig höhere Affinität, was möglich darauf zurückzuführen ist, dass das Präparat noch gewissermassen Eiweiss enthält.

3. **Darstellung der Farbstoffen.** *Tetrabromphenolphthalin:* Dargestellt nach Baeyer⁽⁴⁾. Die farblose Kristalle, umgelöst mehrmal aus Alkohol, schmelzen bei 294° . (nach Baeyer: Schmp. $220-230^\circ$). $\text{C}_{20}\text{H}_{10}\text{O}_4\text{Br}_4$ Ber. Br 50.44, Gef. Br 50.48, 50.58.

Kaliumsalz des Tetrabromphenolphthaleinmethylesters: Hergestellt durch Oxydation des Tetrabromphenolphthaleinmethylester mit alkalischen Ferricyankalium. Es stellt ein tief blauviolett, in Wasser schwer lösliches Pulver dar. Das Ausgangsmaterial Tetrabromphenolphthalinesters wurde durch Bromierung des Phenolphthaleinesters in Eisessig dargestellt. Es stellt prismatische Kristalle von Schmp. 193° ($\text{C}_{21}\text{H}_{12}\text{O}_4\text{Br}_4$: Ber. Br 49.18, Fef. Br 49.38).

chinoid-Tetrabromphenolphthaleinmethylester-monomethyläther: Dargestellt durch Einwirkung von Diazomethan mit Tetrabromphenolphthalein methylester in der Aetherlösung. Das Substanz der Reinigung schwer zugänglich, schmilzt bei etwa $130-135^\circ$ u. Zers., $\text{C}_{22}\text{H}_{14}\text{O}_4\text{Br}_4$: Ber. Br 48.29, Gef. Br 44.14.

Tetranitrophenolphthaleinmethylester. Phenolphthaleinmethylester wurde mit konz. Schwefelsäure und Salpetersäure behandelt. Beim Zusatz von Wasser scheidet der Nitrokörper ab, der beim Umlösen aus Eisessig einen gelblichen feinen Kristall von Schmp. 266° liefert. $\text{C}_{21}\text{H}_{12}\text{O}_{12}\text{N}_4$ Ber. N 10.94, Gef. N 11.26.

(Pharmazeutisches Institut der kaiserl. Universität Tokio.)

(4) Ber., 9 (1876), 1231.

Studies on the Reactions between Oxides in Solid State at Higher Temperatures. VI.⁽¹⁾ Discussion of the Reaction Mechanism with a Special Reference to the Effect of Particle Size on the Reactions.

By Yasuo TANAKA.

(Received January 7, 1942.)

Introduction. In the present series of investigations, the author has studied several examples of the addition reactions between so-called basic and acidic oxides in the solid state at relatively high temperatures. The experiments have been carried out with the mixtures of two components, consisting of fine powders. The method of investigations was as follows: after the addition compounds, formed by the solid reactions, had been confirmed, the courses of the reactions were followed analytically by the difference of solubility of the components as well as that of the reaction products, and the results were checked by means of the X-ray method. Since the course of the reaction between MgO and TiO₂ had been proved to be the same under various experimental conditions, the other reactions were studied only with the pressed bodies of the powder mixtures. As these reactions take place only at high temperatures, it is difficult to follow the course of reaction quantitatively by the so-called Tubandt's method,⁽²⁾ which determines the exchanged amount at the contact plane of the two solid substances after the reaction and which has been applied for the reactions between metals or between certain salts.

As for reaction between solid substances, it has been considered in the first report⁽³⁾ that an amorphous layer of the mixture of the components is formed at first at their contact surface; that a new reaction product crystallizes out easily from this mixture, so long as the reaction temperature is sufficiently high; and that the later reaction proceeds by the diffusion of the components through this crystalline layer.⁽⁴⁾ If the surface reaction takes place rapidly enough, comparing with diffusion, the step that determines the rate of the whole reaction lies in the diffusion process, and many solid reactions have been regarded to be controlled by this process.⁽⁵⁾

The mechanisms of the present reactions had been discussed to some extent in the first report as well as in the others, and it was estimated that the rates of these reactions were also determined chiefly by the dif-

(1) V, *this Bulletin*, **17** (1942), 186.

(2) Cf. C. Tubandt, "Handbuch der Experimentalphysik," Bd. XII, 1. Teil, Leipzig (1932).

(3) I, *this Bulletin*, **16** (1941), 428.

(4) Cf., for instance, W. Jost, "Diffusion und chemische Reaktion in festen Stoffen," 39, 180, etc., Dresden and Leipzig (1937).

(5) Cf. G. F. Hüttig, *Z. angew. Chem.*, **49** (1936), 882; W. Jander, *Z. angew. Chem.*, **49** (1936), 879; J. A. Hedvall, "Reaktionsfähigkeit fester Stoffe," 146, etc., Leipzig (1938).

fusion process. However, these reactions were proved to have their own characteristics, and it was expected that there existed something different in their reaction mechanisms.

The present paper aims at dealing with the mechanism of these reactions in more detail, by studying theoretically as well as experimentally the effect of the particle size of each of the components on the reactions.⁽⁶⁾ Further, the mechanism of sintering due to the solid reactions is discussed.

I. Types of Reactions. The main characteristics of the reactions studied are summarized in Table 1. Though each of the characteristics has been explained on separate occasions, some of them will be repeated here.

Table 1. Main Characteristics of the Reactions in the Present Investigations.

Reaction system	Addition compound	Solid solution range	Compound or solid solution formed at first	"Reaction temperature" (°C)	Initial reaction	Heat of activation Kcal./mole
MgO—TiO ₂ ⁽³⁾	$\left\{ \begin{array}{l} 2\text{MgO} \cdot \text{TiO}_2 \\ \text{MgO} \cdot \text{TiO}_2 \\ \text{MgO} \cdot 2\text{TiO}_2 \end{array} \right\}$	—	MgO·2TiO ₂	725 ⁽¹⁰⁾	rapid	36
CaO—TiO ₂ ⁽⁷⁾	CaO·TiO ₂	$\left\{ \begin{array}{l} 3\text{CaO} \cdot 2\text{TiO}_2 \\ \sim \text{CaO} \cdot \text{TiO}_2^* \\ (+\text{TiO}_2) \end{array} \right\}$	CaO·TiO ₂ * (+TiO ₂)	675 ⁽¹⁰⁾	rapid	30.3
MgO—Al ₂ O ₃ ⁽¹⁾	MgO·Al ₂ O ₃	$\left\{ \begin{array}{l} \text{MgO} \cdot \text{Al}_2\text{O}_3 \\ \sim \text{MgO} \cdot 2\text{Al}_2\text{O}_3 \end{array} \right\}$	MgO·Al ₂ O ₃	< 800	rapid	41.1
MgO—SnO ₂ ⁽⁸⁾	2MgO·SnO ₂	—	—	950	slow	100
CaO—SnO ₂ ⁽⁹⁾	$\left\{ \begin{array}{l} 2\text{CaO} \cdot \text{SnO}_2 \\ \text{CaO} \cdot \text{SnO}_2 \end{array} \right\}$	—	CaO·SnO ₂	900	no	85

* Contains a slight excess of TiO₂.

** Of the formation of the first reaction product.

When a reaction is controlled by diffusion, there exists approximately a relation,⁽¹¹⁾

$$d\xi/dt = k'/\xi \quad \text{or} \quad \xi^2 = 2k't + \text{const.}, \quad (1)$$

where ξ is the thickness of the reaction product and t , the reaction time. If the reaction, with powder mixtures, is assumed to proceed uniformly on the particles of a spherical substance with a radius of r ,

(6) It may not be amiss to mention here that the author's purpose is not to present in this paper unique and quantitative discussions, but rather to offer some suggestive mechanisms of the reactions which are consonant to the experimental results obtained.

(7) II, this Bulletin, **16** (1941), 455.

(8) III, this Bulletin, **17** (1942), 64.

(9) IV, this Bulletin, **17** (1942), 70.

(10) G. Tammann, *Z. anorg. allgem. Chem.*, **149** (1925), 68.

(11) H. Braune, *Z. physik. Chem.*, **110** (1924), 147; W. Jost, *loc. cit.*, 15, 30.

$$1 - \sqrt[3]{1-x} = \xi/r$$

hold between ξ and x , the reaction amount per unit substance at a given time.⁽¹²⁾ Therefore, we obtain

$$\{1 - \sqrt[3]{1-x}\}^2 = \frac{2k'}{r^2} t, \quad (2)$$

or

$$\{1 - \sqrt[3]{1-x}\}^2 = 2kt. \quad (3)$$

The rates of the main parts of these reactions were expressed by this equation, and accordingly it was pointed out, as above mentioned, that they were controlled by diffusion.

However, in the three systems, MgO-TiO_2 , CaO-TiO_2 and $\text{MgO-Al}_2\text{O}_3$, the reaction proceeded within a half an hour from the commencement of the reaction, more rapidly than the rate expressed by equation (3); the reaction between MgO and SnO_2 proceeded slowly at first, especially at lower temperatures, namely, rather an induction period was observed in this case; while in the reaction between CaO and SnO_2 , the above equation was held from the beginning.

Further, when the energy of activation, Q , of the diffusion process was calculated from the temperature coefficient of the velocity constant according to

$$k = Ae^{-Q/RT}, \quad (14)$$

it was found that the values for the three former reactions lay approximately between 30 and 40 Kilocalories per mole, while those for the last two were 100 and 85 Kilocalories, respectively. Thus the energies of activation of the last two reactions were twice to three times greater than those of the former ones.

The effect of temperature on these reactions can also be seen dis-

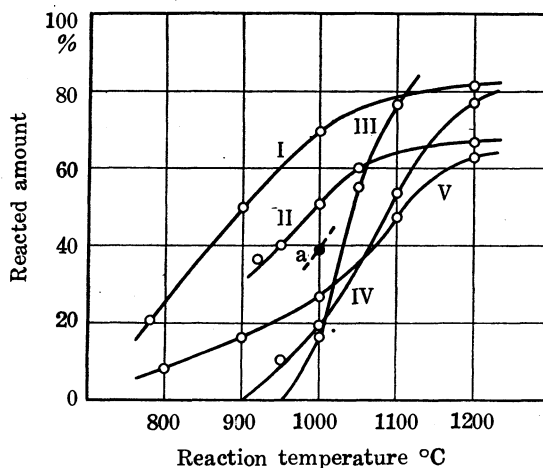


Fig. 1. Reacted amounts at various temperatures.

Curve I: The amount at a half an hour with a mixture, $\text{MgO}:\text{TiO}_2 = 1:2$, calculated from unreacted TiO_2 .^{(3) (13)}

Curves II-V: The amounts at three hours, respectively, with the mixtures, $\text{CaO}:\text{TiO}_2 = 1:1$, calculated from free CaO ; ⁽⁷⁾ $\text{MgO}:\text{SnO}_2 = 2:1$ ⁽⁸⁾ and $\text{CaO}:\text{SnO}_2 = 1:1$, ⁽⁹⁾ calculated from soluble SnO_2 ; and $\text{MgO}:\text{Al}_2\text{O}_3 = 1:1$, calculated from free MgO .⁽¹⁾

(12) W. Jander, *Z. anorg. allgem. Chem.*, **163** (1927), 1.

(13) As the preparations were used without heat treatment in this experiment, the reaction took place very easily. Under similar conditions as in the other reactions, the reacted amount at 3 hours falls on the point a.

tinctly from the reaction amounts at a certain reaction time given in Figure 1. The reaction takes place moderately already at as low as 800° in the systems, MgO-TiO_2 , CaO-TiO_2 and $\text{MgO-Al}_2\text{O}_3$, while the reaction temperature,⁽¹⁰⁾ or the temperature at which the first evidence of the reaction is observed, of the systems MgO-SnO_2 and CaO-SnO_2 , lies at 950° and 900° , respectively; nevertheless, the increase of the reaction rate with the temperature is very remarkable in the latter two reactions.

From these facts, the reactions studied here can be classified into two types: (1) the reactions of the three systems, MgO-TiO_2 , CaO-TiO_2 and $\text{MgO-Al}_2\text{O}_3$, in which a rapid initial reaction and a small energy of activation are observed, and (2) those of the systems, MgO-SnO_2 and CaO-SnO_2 , which have an induction period rather than a rapid initial reaction and a large energy of activation. It is easily expected that there should exist a certain relationship in the differences of the initial states of these reactions and their energies of activation.

II. Considerations on the Initial States of the Reactions. Surface Diffusion and Inner Diffusion. The initial states of these reactions will be considered at first. It is true, as has been stated in the first report,⁽³⁾ that the reaction heat is one of the causes for a rapid initial reaction, but an induction period can not be explained from this consideration. The difference in the initial states may be interpreted as follows:

Although the relation (3) is derived approximately by assuming that a reaction with powder mixture proceeds uniformly on a spherical substance, the experimental conditions do not strictly correspond to the assumption, because the particles of the components are by no means in contact with each other completely at the commencement of the reaction, however fine the preparations may be. The reaction begins only at the contact points of the components, and therefore, it takes place but slightly at the beginning. As the reaction proceeds, the product is formed from these contact points in the particles of both components. At the same time, however, the product tends to diminish its own surface area, because the crystals of the product at this stage are not yet fully developed, or in a state of disorder and have a large surface energy;⁽⁵⁾ a diminution of the surface area results in the increase of the interface of the components, and consequently the reaction rate increases gradually.

Now we shall consider a mixture of components, A and B, consisting of spherical particles in which all particles of A are surrounded completely by B, e.g., a mixture with a large excess of B. The total surface of A is covered more rapidly with the reaction product than that of B; and after the thickness of the product on A becomes approximately uniform, a further reaction proceeds with a constant rate. Then equation (3) becomes valid for A, or generally, for the component of which surface area is smaller.⁽¹⁴⁾ Thus an induction period should be observed at the beginning of the reaction. Assuming that a volume change due to the reaction is to be neglected and that the product is formed in both component particles with nearly equal quantities, the course of reaction is represented schematically in Figure 2 as t_1 , τ and t_2 .

(14) The total surface area of a given component in an unit reaction mixture will be frequently denoted simply as "surface area".

The present investigations have been carried out with the mixtures, compositions of which are corresponding to, or not too far from those of the reaction products. With these mixtures, if the particles of both components are assumed to be of equal size, about a half of the particles which surround each particle of a given component consists of its own; therefore, it should require a longer time before the particles are covered completely with the reaction product and the reaction begins to proceed uniformly. However, if the particles consist of different sizes, as it occurs practically, they will be in contact with each other more closely, and a uniform reaction may be observed comparatively readily. This condition is especially well satisfied in the present experiments, because they have been carried out with the pressed bodies. In these instances, equation (3) would be approximately applicable for both of the components.

So far it has been considered that the diffusion takes place only through the reaction product; however, it occurs also in another way, namely, one of the components can migrate on the surface of the reaction product as well as that of the other component. These two kinds of dif-

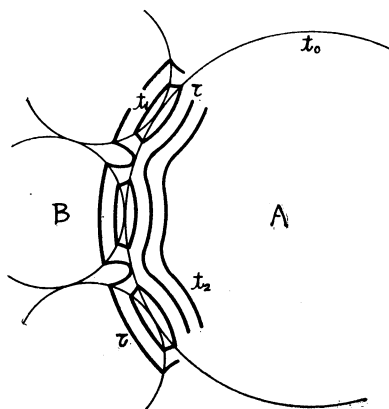


Fig. 2. Course of the reaction without surface diffusion (model).

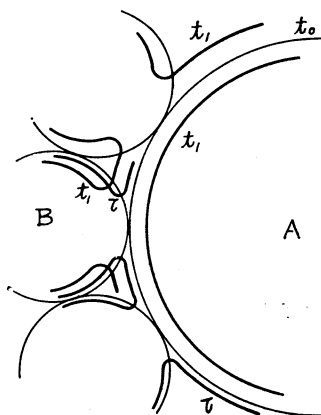


Fig. 3. Course of the reaction with a rapid surface diffusion (model).

fusion may be termed as the inner diffusion and the surface diffusion. It has been known that in metals the surface diffusion takes place more readily than the inner diffusion.⁽¹⁵⁾ Moreover, there are many instances of the solid reactions between oxides which take place smoothly in the temperature range still lower than that of the present experiments, and they have been regarded to proceed chiefly by the surface diffusion at these temperatures.⁽¹⁶⁾

Therefore, let us consider a reaction in which the component B migrates on the reaction product, and, further, on A far more readily than it suffers the inner diffusion. When the components consist of very fine powders, as have been used in the present experiments, the reaction

(15) I. Langmuir, *Chem. Rev.*, **13** (1933), 147; *J. Franklin Inst.*, **217** (1934), 543.

(16) J. A. Hedvall and G. Cohn, *Kolloid Z.*, **88** (1939), 224.

proceeds considerably at its early stage of the reaction owing to the surface diffusion. After the surface of A is covered completely by B, the inner diffusion proceeds uniformly on A; and, as the step that determines the rate lies also in the inner diffusion, equation (3) holds for A, or the diffused component.⁽¹⁷⁾ In this case, therefore, a rapid initial reaction should be obtained. (It is considered that the part of a particle of A which is not surrounded by B, and even a particle which is not at all in contact with B, is covered gradually by B.) The course is shown schematically in Figure 3. In this case, the size of A particles increases with the reaction, while that of B decreases and disappears finally.

According to the above considerations, a rapid initial reaction rate, found in the reactions of the three systems, MgO-TiO₂, CaO-TiO₂ and MgO-Al₂O₃, may be explained as to be due to the rapid surface diffusion; and the induction period of the reaction between MgO and SnO₂, as the absence of the distinct surface diffusion. There may exist such an intermediate case in which the surface diffusion takes place slowly and compensates the induction period of the inner diffusion, and equation (3) holds apparently from the beginning of the reaction. The reaction between CaO and SnO₂ is probably an example of this case.

III. Discussions on the Effect of Particle Size of the Components on the Reactions. The relation between the surface phenomenon and the inner diffusion can be more distinctly understood when the effect of particle size of the components on the reactions is considered.⁽¹⁸⁾

There exists the relation (2) between the reaction amount and the particle size, and, by the reaction between BaCO₃ and SiO₂ with a mixture of BaCO₃:SiO₂=1:10, Jander⁽¹²⁾ has proved experimentally the validity of the relation by changing the particle size of BaCO₃.⁽¹⁹⁾ However, as it is discussed in the last section, equations (2) and (3) should hold for the component with a smaller surface area when only the inner diffusion occurs, and for the diffused component when the rapid surface diffusion takes place; and there exists a rapid or a slow initial reaction period before these relations become applicable.

We shall discuss the effect of particle size on these reactions, taking the different cases into consideration. The radii of the two components are denoted as r_A and r_B , and for convenience, let r_B be constant, r_{B0} .

§ 1. *The Case in which no Surface Diffusion exists.* The following two instances will be discussed.

(a) The particles of A are surrounded completely by those of B:—In the normal reaction period⁽²⁰⁾ equation (2) holds for A. In the

(17) In this paper, "diffused" component means the component into which the other diffuses. The component that diffuses into the other will be referred to as the "diffusing" component. In Fig. 3, A is the "diffused", while B is the "diffusing" component.

(18) When we consider a powder mixture of the two components with a definite composition, their total surface areas are inversely proportional to their particle sizes.

(19) The existence of a slight induction period, which he explained in a different way from that of this paper, was observed in his experiment.

(20) The period in which the reaction proceeds owing to the inner diffusion according to equations (2) and (3) will be mentioned as the normal reaction period.

region where the reaction does not proceed too far, since the relation between the reaction amount and the thickness of the product can be expressed approximately by

$$x = 3\xi/r_A,$$

equation (2) becomes

$$x^2 = \frac{k''}{r_A^2} t. \quad (5)$$

Let τ be the initial reaction period, x_τ be the reaction amount produced in this period, and the reaction time from the commencement of the reaction be denoted as t , then we obtain from (5)

$$x = \frac{k}{r_A} \sqrt{t - \tau} + x_\tau. \quad (6)$$

In the induction period, ξ also increases according to the relation (1), while x changes with ξ and can be expressed as

$$x = \frac{1}{r_A} \int k(\xi) d\xi, \quad (7)$$

or

$$x = \frac{1}{r_A} \int k(t) dt. \quad (8)$$

However, since r_B is constant, as seen from Figure 2, it is admitted that the reaction amount per one particle of A increases with ξ , or with t nearly in the same way, unless r_A is not very small; namely, in (7) and (8), $k(\xi)$ and $k(t)$ may be assumed to be independent of the particle size of A. Then τ becomes also constant, and we have

$$x_\tau = \frac{k_\tau}{r_A} \sqrt{\tau},$$

and equation (6) becomes

$$x = \frac{k}{r_A} \sqrt{t - \tau} + \frac{k_\tau}{r_A} \sqrt{\tau}. \quad (9)$$

Therefore, the whole course of the reaction is expressed approximately by (8) and (9), and, throughout the induction and the normal reaction periods, there exists a relation,

$$x = K/r_A, \quad (10)$$

between x and r_A . In other words, the reaction amount at any reaction time should be inversely proportional to the particle size of the component A.

(b) Equal amounts of A and B exist:—⁽²¹⁾ When $r_A \gg r_{B0}$, since A becomes surrounded completely by B, the conditions in (a) are satisfied and equation (10) holds for A. Similarly, when $r_A \ll r_{B0}$, the same relationship holds for B, and in this case x is constant whatever r_A may be, because r_B is constant. With a medium sized particle of A, for instance, $r_A = r_{B0}$, as it is discussed in the last section, the particles of the two components are in contact with about a half of their own component; therefore, the reaction amount in the induction period is smaller than that which is discussed in (a), and it takes a longer time until the induction period is completed.

In this case, therefore, the curve in which x is plotted against $1/r_A$ at a certain reaction time changes gradually from $x = K/r_A$ to $x = \text{const.}$ in the neighbourhood of $r_A = r_{B0}$.

§ 2. *The Case in which remarkable Surface Diffusion occurs.*

(a) B diffuses on A, which is surrounded completely by B:—If we neglect the reaction amount due to the inner diffusion in the initial reaction period, the condition becomes just as discussed in § 1 (a), although the reaction amount in the initial stage is, of course, very much and this period is completed rapidly. Therefore, the course of reaction is expressed approximately by (8) and (9), and the relation (10) holds at any reaction time.

(b) Equal amounts of A and B exist:—When B diffuses on A, the above relations hold approximately, whatever the relation between r_A and r_B may be. Similarly, when A diffuses on B, equation (10) holds for B, and x becomes constant, whatever r_A may be. However, when r_A and r_B differ too much far and the surface area of the diffused component is far larger than that of the diffusing component, it needs a longer time until the total surface of the former is covered completely, and therefore the reaction amount at a certain reaction time, especially at the beginning of the reaction, is smaller than what is discussed above. In an extreme case, no normal reaction period is attained.

IV. Results of the Experiments on the Effect of Particle Size.

The above discussions seem to have proved experimentally for the reactions of the systems, MgO–SnO₂, MgO–Al₂O₃ and CaO–TiO₂; the details of which are described in the experimental part (sections VII–IX). The experiments have been carried out with the mixtures corresponding to the addition compounds.

The results of the experiment on the reaction between MgO and SnO₂ correspond to the case of § 1 of the last section; therefore, it is concluded that the reaction proceeds, as it is expected, mainly by the inner diffusion. However, a slight tendency of diffusion of MgO on the surface of SnO₂ is also observed.

As for the reaction between MgO and Al₂O₃, it is concluded that Al₂O₃ diffuses rapidly on MgO at first, and a further reaction takes place uniformly on the surface of MgO. In the last report,⁽¹⁾ it was found

(21) The argument is carried out for the equal volume amounts of the components, but it is valid to a first approximation for equi-molar mixtures or for the mixtures corresponding to the addition compounds.

that this reaction proceeded more readily with the mixtures containing the excess of MgO than with the other mixtures. As the particles used at that occasion were very fine and could be regarded as nearly of equal size, the total surface of MgO per unit mixture became larger when MgO existed in excess. Since Al_2O_3 diffuses on the surface of MgO, it is understood that the reaction proceeds rapidly in this condition.

By the reaction between CaO and TiO_2 , it is considered that CaO diffuses on TiO_2 , while at the same time the inner diffusion takes place comparatively readily; and indeed, as it is clear from the experiment in the second report,⁽⁷⁾ the reaction amount in the initial stage of this reaction is not so much as compared with those of the reactions, $\text{MgO}-\text{Al}_2\text{O}_3$ and $\text{MgO}-\text{TiO}_2$. It is of some interest to note that Al_2O_3 , the acidic component, migrates on MgO in the reaction between MgO and Al_2O_3 , while the basic component, CaO, diffuses on TiO_2 in this reaction.

In analogy to these experiments, it is admitted that the other two reactions, $\text{MgO}-\text{TiO}_2$ and $\text{CaO}-\text{SnO}_2$, proceed, respectively, as discussed in section II; and the component which migrates on the surface of the other may be regarded as MgO and CaO, respectively.

The technical importance of the effect of particle size on the reactions will be mentioned here. The solid reaction in which the surface diffusion takes place rapidly, for instance, the reaction between MgO and Al_2O_3 , proceeds more readily when the diffused component is very fine; therefore, in order to obtain a certain addition compound with ease, we should endeavour to pulverize the diffused component as fine as possible rather than *vice versa*. This is particularly well understood from Figure 6 (in section VIII), where the reaction proceeds more rapidly when MgO, the diffused component, (and Al_2O_3 , not necessarily) is very fine. When no distinct surface diffusion exists, it is desirable that both of the components are pulverized equally well, because the reaction rate is then controlled by the particle size of the component with a smaller surface area (or with a greater particle size); only when one of the components exists in a small quantity, this component should be fine.

V. Further Considerations on the Diffusion Mechanism. As it has been stated in the first report, Wagner⁽²²⁾ considered that the reactions in solid state proceed frequently by the exchange of the components in the form of ions (generally smaller metal ions), or by the "ionic diffusion", through the reaction product in which electrical neutrality is always preserved. He proved this point experimentally for the reaction between AgI and HgI_2 ⁽²³⁾ and supposed further that the analogous mechanism may hold for the formations of silicates and spinels,⁽²²⁾ but the experimental confirmations for the latter reactions are still lacking. On the contrary, Hedvall and Cohn⁽¹⁶⁾ stated that the diffusion in such a compound as silicates or spinels, the formation of which takes place smoothly already at so low temperatures that no distinct ionic conductivity is observed, could hardly be considered as ionic; and that these reactions proceed probably by the migration of the neutral atoms, or atom groups,

(22) C. Wagner, *Z. physik. Chem.*, B, **34** (1936), 309.

(23) E. Koch and C. Wagner, *Z. physik. Chem.*, B, **34** (1936), 317.

through the defect positions of the crystals, which exist owing to the incompleteness of the crystal growth,⁽²⁴⁾ or on the "inner surface" of the crystals. This mechanism may be mentioned as the "non-ionic diffusion". Thus, no conclusion has been given on the kinds of the elementary particles which migrate in these reaction products.

It is considered that the similar solid reactions can never be explained by a single mechanism; and, indeed, by studying the exchange reactions of certain wolframates and molybdates with a group of divalent metal oxides as well as their electric conductivities, Jander⁽²⁵⁾ has considered that some of these reactions proceed by the ionic diffusion while others by the migration of the neutral acid anhydride, i.e., WO_3 or MoO_3 .

Also the two types of the reactions found in the present investigations will probably be due to the differences in the nature of the reaction products as well as in their diffusion mechanism, and the author would like to explain, at present, these differences as follows:

Although the ionic conductivities of these reaction products are not yet certain, it may be assumed that they are very small at the temperature as low as 800° . The three reactions, MgO-TiO_2 , CaO-TiO_2 and $\text{MgO-Al}_2\text{O}_3$, are then to proceed, at least lower than 800° by the non-ionic migration of the components through the product. The surface diffusion in these instances may also be explained by a similar mechanism. On the other hand, for the other two reactions, MgO-SnO_2 and CaO-SnO_2 , which begin to take place at 950° and 900° respectively, the interpretation of the ionic diffusion may be possible. It is considered, namely, that the crystals of these reaction products are (when once formed) well developed, and it is difficult for the neutral atoms, or atom groups, to diffuse through them; and that they begin to dissociate with the increasing temperature, and the ions thus produced become to be able to exchange with each other. In these systems, the possibility of the ionic surface diffusion might be expected at higher temperatures; however, as Hedvall has stated,⁽¹⁶⁾ the exchange of ions at the surface of the ion crystals is hardly in question.

The energies of activation obtained in the latter two reactions may be regarded as that of the ionic diffusion. At higher temperatures, the ionic diffusion in the former three may also be possible; however, it is considered that the controlling steps are still the non-ionic diffusion, and that the energies of activation obtained, which are smaller than those of the latter ones, will be those of the non-ionic diffusion.

In this way, the differences in the energies of activation of the two types of the reactions as well as the existence of the surface diffusion in the former cases can well be interpreted. However, the final conclusion on this problem should be drawn only after more examples of similar reactions have been accumulated, and especially after the physical properties of the products have been made clearer.

VI. Sintering due to Solid Reactions. The phenomenon of sintering, i.e., a phenomenon in which a solid substance shrinks and reduces its porosity when it is heated within such a temperature range as it does

(24) At lower temperatures, the existence of the defect positions of this type is well understood.⁽¹⁶⁾

(25) W. Jander, *Z. anorg. allgem. Chem.*, **192** (1930), 295.

not melt completely,⁽²⁶⁾ has been utilized widely in the ceramic industry. Of course, the formation of a liquid phase, owing to the low melting eutectics, is one of the causes of sintering; however, the phenomenon occurs also in pure solid state and it is especially remarkable when a solid reaction takes place. Hedvall⁽²⁷⁾ called the phenomenon as "Trocken-sinterung" and, indeed, "Trockensinterung" of metals has recently been developed into so-called powder metallurgy.⁽²⁸⁾

For the use of refractories, which are exposed to high temperatures, it is desirable that the high melting substances are selected, and in the course of their manufacture, they should be sintered at relatively low temperatures without forming any liquid phase. Now magnesium oxide, which has a very high melting point and is well qualified as a basic refractory, sinters at a lower temperature than its melting point; and while it has been known that the existence of such oxides as Fe_2O_3 or Al_2O_3 is, probably owing to the formation of an addition compound, effective for its sintering, the author⁽²⁹⁾ has recently found further that the addition of a small quantity of TiO_2 is very effective in this connection. For instance, when

the pressed bodies of the various mixtures of MgO and TiO_2 were ignited at 1400° , their porosities diminished as shown in Figure 4.⁽³⁰⁾

In this system the sintering is particularly remarkable by the mixtures in which $2\text{MgO} \cdot \text{TiO}_2$ is formed. While MgO belongs to the cubic system, $2\text{MgO} \cdot \text{TiO}_2$ has also a cubic spinel structure; and it is easily expected that the spaces among the crystals become smaller when the particles of the same crystal system are packed most closely to each other than in the other cases. Fe_2O_3 and Al_2O_3 , too, form with MgO addition compounds with the spinel structure.

However, the addition of SnO_2 (which belongs, as well as TiO_2 , to the fourth group of the periodic system and also forms with MgO the

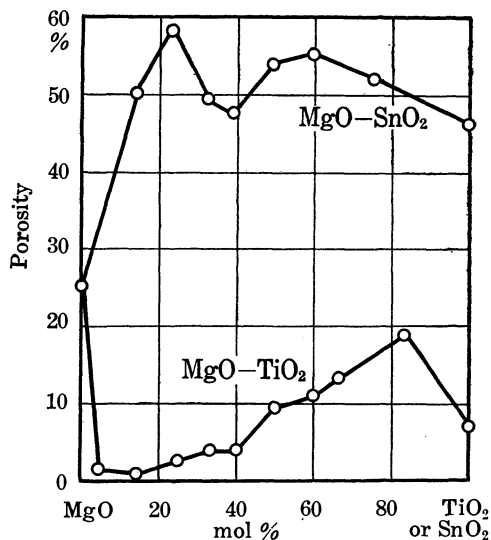


Fig. 4. Porosities of the ignition products at 1400° of the systems MgO-TiO_2 and MgO-SnO_2 .⁽³¹⁾

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However, the addition of SnO_2 (which belongs, as well as TiO_2 , to the fourth group of the periodic system and also forms with MgO the

(26) While the meaning of sintering is not certain, it is defined here as above.

(27) J. A. Hedvall, *loc. cit.*, 81.

(28) Cf., for instance, W. D. Jones, "Principles of Powder Metallurgy," London (1937); W. Seith, "Diffusion in Metallen," Berlin (1939).

(29) Y. Tanaka, *J. Soc. Chem. Ind. Japan*, **42** (1939), 387, 202B; 390, 204B; Y. Tanaka and T. Takagi, *J. Soc. Chem. Ind. Japan*, **42** (1939), 874, 405B.

(30) *J. Chem. Soc. Japan*, **60** (1939), 212.

(31) Let W be the weight of a porous solid substance, V be its total volume and s , its specific gravity, then the porosity, P , is calculated from

$$P = \frac{s - W/V}{s} \times 100\% .$$

spinel type compound, $2\text{MgO}\cdot\text{SnO}_2$) is not effective at all for the sintering of MgO ; the porosities of this system at 1400° are also given in Figure 4.^{(32) (33)} Therefore, it is easily conceivable that sintering, due to the solid reaction, depends not only on the structure of the addition compound but also on the reaction mechanism.

As for the above two systems, the following discussions may be given. Namely, by the reaction between MgO and TiO_2 , MgO migrates on the surface of TiO_2 and, as seen from Figure 3, the particles of MgO are deformed and their sizes decrease gradually. Therefore, the total body shrinks and, furthermore, it is considered that the crystal growth of MgO is accelerated by the stress due to its deformation; thus the body sinters by the reaction. On the other hand, by the reaction between MgO and SnO_2 , the surface diffusion occurs but slightly and the reaction takes place chiefly in the neighbourhood of the contact points of the components, and especially, as shown in Figure 2, if it is assumed that the components exchange each other with nearly equal quantities,⁽³⁴⁾ the particle sizes of the two components are unchanged; therefore, the vacant spaces remain as before and no sintering should be observed. The reaction between MgO and Al_2O_3 belongs to the former case, and the body sinters actually.

The author would like to point out, further, that the existence or non-existence of the surface diffusion and the phenomenon of sintering may play an important rôle in manufacturing mixed catalysts.

Experiments on the Effect of Particle Size.

VII. The Reaction between Magnesium Oxide and Stannic Oxide. The effect of particle size of the components on the reaction between MgO and SnO_2 , where no distinct surface diffusion has been considered to take place, was studied at first. With a mixture corresponding to the addition compound, $\text{MgO}:\text{SnO}_2=2:1$, the particle size of one of the components was kept constant, as 150 to 200 meshes to the inch, and that of the other component was changed.

Although it was difficult to obtain coarse particles from commercial preparations of MgO and SnO_2 (and of other oxides also) which were very fine powders, this was achieved by the following method: as the preparations were hardened moderately when they were kneaded with some water, dried and heated at 1200° to 1300° , they were crushed carefully and passed through different sieves. Although these particles consisted by no means of single crystals and were different in shape, they were assumed to be spherical, and their "mean radii" were estimated approximately as given in the second column of Table 2.

The amounts of free MgO and those of SnO_2 , soluble in $4N$ HCl , of the reaction products at 1100° are given in Table 2. The reaction proceeded slowly within a half an hour and after 3 or 6 hours it seemed to have proceeded normally. The reacted amounts were calculated from the percentage of soluble SnO_2 based on the theoretical value of total SnO_2 though it contained, as it was stated in the third report,⁽⁸⁾ some amorphous SnO_2 .⁽³⁵⁾

(32) *J. Chem. Soc. Japan*, **61** (1940), 1023.

(33) As the sintering of TiO_2 and SnO_2 themselves are different from each other, the comparison is not strict; however, the tendency is obvious.

(34) When the reaction proceeds by the ionic diffusion, this condition is satisfied.

(35) Since mixing of the components containing coarse particles can hardly be executed completely homogeneous, to calculate the reacted amount from free MgO will introduce much uncertainty. Ideally, a total analysis should be made with each reaction product.

Table 2. Effect of Particle Size on the Reaction
between Magnesium Oxide and Stannic Oxide.
 $\text{MgO}:\text{SnO}_2=2:1$ ($\text{SnO}_2=65.14\%$), 1100° .

Particle size of MgO		Particle size of SnO ₂ Meshes/ inch	Free	SnO ₂	Free	SnO ₂	Free	SnO ₂
Mesches'	Mean		MgO	Soluble	MgO	Soluble	MgO	Soluble
inch	radius		(%)	in 4N	(%)	in 4N	(%)	in 4N
	(mm)		HCl	HCl				HCl
Reaction time (hrs.)			0.5		2		6	
32- 48	0.20	150-200	33.13	4.16	32.12	6.90	31.59	7.98
65-100	0.09	"	32.80	4.75	31.32	8.27	30.37	10.46
150-200	0.04 ₅	"	32.73	4.98	30.60	10.57	29.08	13.65
200-*	0.02 ₅	"	32.60	5.27	30.27	11.05	27.99	15.08
150-200	0.04 ₅	32- 48	33.86	2.60	33.53	3.52	32.48	5.38
"	"	65-100	33.33	3.93	31.77	8.79	30.81	10.02
"	"	200-*	32.46	5.68	29.96	11.13	27.68	16.70

* Pulverized with an agate mortar as fine as possible.

As shown in Figure 5, the curves in which the reacted amounts are plotted against the reciprocals of the mean radii of MgO or SnO_2 particles at each reaction time turn out just as discussed in §1(b) of section III. However, the effect of the size of SnO_2 is a little greater than that of MgO which indicates that MgO migrates to some extent on the surface of SnO_2 .

VIII. The Reaction between Magnesium Oxide and Aluminium Oxide.

As in the above experiment, with a mixture of $\text{MgO}:\text{Al}_2\text{O}_3=1:1$, the effect of particle size on the reaction between MgO and Al_2O_3 was studied at 1200° . The reacted amounts were expressed by the percentage of combined to total MgO, which was, in case of the mixtures containing coarse particles, determined by total analysis.

The results are given in Table 3, and the relation between the reacted amounts and the reciprocals of the particle sizes are shown in Figure 6. Contrary to the results of the reaction between MgO and SnO_2 , the effect of the particle size of MgO is far greater than that of Al_2O_3 . Namely, when the particle size of Al_2O_3 is constant, the reacted amounts are nearly proportional to the reciprocals of the mean radii of MgO particles, or to the surface area of MgO; while the effect of the size of Al_2O_3 is not so remarkable unless its size is not very coarse. This agrees with the discussion of §2 of section III.

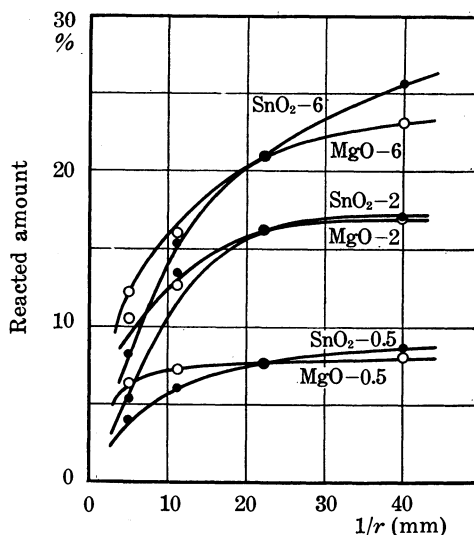


Fig. 5. Relations between the reacted amounts and the reciprocals of the mean radii of the components by the reaction between MgO and SnO_2 at 1100° .

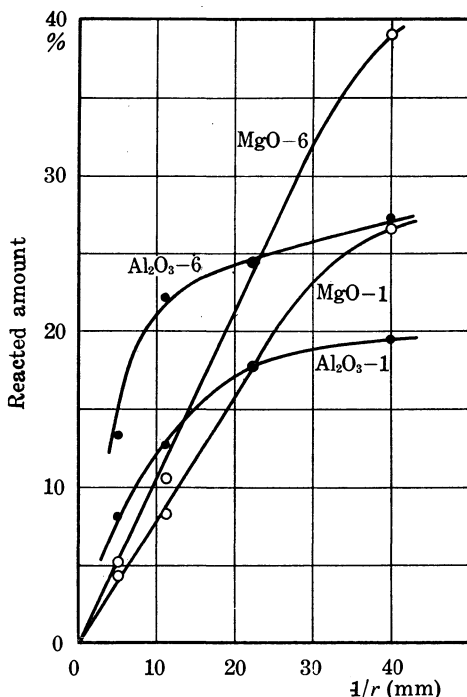
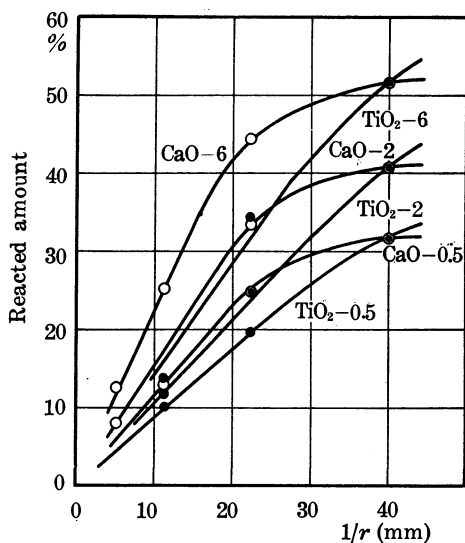
SnO_2 -2 means, for instance, the reacted amounts at two hours with varying the particle size of SnO_2 .

Table 3. Effect of Particle Size on the Reaction between Magnesium Oxide and Aluminium Oxide.

MgO:Al₂O₃=1:1 (MgO=28.34%), 1200°.

Particle size of MgO Meshes/inch	Particle size of Al ₂ O ₃ Meshes/inch	Reaction time (hrs.)		Reacted amount (%)	
		1	6	1	6
32- 48	150-200	4.30	5.19		
65-100	"	8.29	10.59		
150-200	"	17.78	24.45		
200-*	"	26.60	38.99		
150-200	32- 48	8.17	13.33		
"	65-100	12.70	22.20		
"	200-*	19.47	27.30		

* Very fine.

Fig. 6. Relations between the reacted amounts and the reciprocals of the mean radii of the components by the reaction between MgO and Al₂O₃ at 1200°.Fig. 7. Relations between the reacted amounts and the reciprocals of the mean radii of the components by the reaction between CaO and TiO₂ at 950°.

IX. The Reaction between Calcium Oxide and Titanium Oxide. The results of the experiment with a mixture of CaO:TiO₂=1:1 at 950° are shown in Table 4 and in Figure 7. The reacted amounts were calculated from the percentage of combined to total CaO.⁽³⁶⁾

(36) As the combined CaO was calculated from free CaO, the existence of some uncertainty was unavoidable. Moreover, since one of the components was kept constantly to be very fine powders, smaller than 200 meshes to the inch, the results were not so clear.

Table 4. Effect of Particle Size on the Reaction
between Calcium Oxide and Titanium Oxide.

CaO:TiO₂=1:1 (CaO=41.24%), 950°.

Particle size of CaO Meshes/inch	Particle size of TiO ₂ Meshes/inch	Reacted amount (%)		
		0.5	2	6
32-38	200-*	8.7	8.0	12.6
65-100	"	12.9	14.3	25.2
150-200	"	24.8	33.4	44.4
200-*	"	31.7	40.7	51.6
200-*	65-100	10.1	11.8	13.6
"	150-200	19.7	25.2	34.4

* Very fine.

Although the effect is not so distinct as in the reaction between MgO and Al₂O₃, it is obvious as far as that the effect of the particle size of TiO₂ is greater than that of CaO, and that a linear relationship between the reacted amounts and the reciprocals of the particle sizes holds approximately for the former. It seems that the inner diffusion takes place comparatively easily in this reaction.

Summary.

(1) The main characteristics of the solid reactions between the oxides, studied in the present investigations, have been summarized. These reactions can be classified into the following two types: (1) the reactions of the systems, MgO-TiO₂, CaO-TiO₂ and MgO-Al₂O₃, which have a rapid initial reaction period and a small energy of activation, and (2) those of the systems, MgO-SnO₂ and CaO-SnO₂, in which no rapid initial reaction and a large energy of activation are observed.

(2) The rapid initial reaction is probably due to the existence of a rapid surface diffusion, and when the reaction proceeds chiefly by the inner diffusion, no rapid initial part may be observed.

(3) The effect of the particle size of each of the components on these reactions has been discussed. In the reactions without distinct surface diffusion, the effect of the particle size of the component, of which total surface area is smaller, should be great, while that of the diffused component becomes remarkable when the surface diffusion takes place rapidly.

(4) For the three reactions, MgO-SnO₂, MgO-Al₂O₃ and CaO-TiO₂, the above discussions have been proved experimentally by changing the particle size of each of the components.

(5) Technical importance of the effect of particle size on solid reactions has been stated.

(6) Some further considerations on the diffusion mechanism have been given, and the difference in the energies of activation has been interpreted.

(7) Finally, the phenomenon of sintering due to solid reactions has been discussed. It is considered that the sintering occurs by the reactions in which a rapid surface diffusion takes place.

In conclusion, the author wishes to express his sincere thanks to Dr. R. Yoshimura for his interest, to Mr. K. Hirota for criticizing and discussing the problem willingly, and also to Dr. R. Negishi and to the other colleagues. He is also indebted to Messrs. S. Takasago and T. Sugawa for their assistances in the experiments.

Further the author takes this occasion to express his hearty gratitude to Prof. Y. Shibata of Tokyo Imperial University, to Prof. T. Marusawa, the former Director of the Central Laboratory, and to Dr. M. Sato, the present Director, for their keen interests and constant encouragement in carrying out the present series of investigations.

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Hydrocarbons from Carbide (A) III.* Non-catalytic Polymerization under Ordinary Pressure. Carbon Dioxide-, Carbon Monoxide-, and Hydrogen Chloride-Calcium Carbide Systems.**

By Ryoji NEGISHI and Osamu KAMIKE.

(Received January 12, 1942.)

In our first paper⁽¹⁾ of the present series, we have reported on the results of the orientation runs made with hydrogen and, with the informations gained therefrom, we have made a series of runs with carbon dioxide, water gas, and hydrogen chloride, singularly or with their mixtures, to increase further the yield of liquid products. Their results will be given in this paper. We shall reserve a fuller discussion on the results and on the mechanisms of the reaction in question for the third and final paper of this series of investigations on the non-catalytic polymerization under ordinary pressure.

I—Carbon Dioxide System.

We have chosen this system first, because we are reasonably certain that there will be no oil formation⁽²⁾ from the gas itself which probably

* This paper has been published by permission of Dr. M. Sato.

** The experimental details of these systems have been given in a series of papers published in Japanese in *J. Soc. Chem. Ind. Japan*, **44** (1941), 1028; *ibid.*, **45** (1942), 133.

(1) R. Negishi and O. Kamiike, Paper (A) II, this Bulletin, **17** (1942), 118.

(2) F. Fischer, *Brennstoff-Chem.*, **10** (1929), 279. According to him, when acetylene is mixed with 10% CO₂, the yield of liquid products increases, but there is no reaction involving CO₂, except that only about 0.27% of it is transformed into CO and traces of water.

would not be the case with acetylene or with water gas, and we can ascribe the whole mechanism of the oil formation to nascent acetylene.

In this section of the paper, only those runs with carbon dioxide alone and its mixture with hydrogen will be dealt with, and the runs with hydrogen chloride will be given at the time the latter system is discussed.

Most of the runs were made at 340°C and some at higher temperatures only when the supplementary data were necessary. Experimental conditions are given in Table 3.* The apparatus, the procedure of run, and the materials used have already been given.⁽¹⁾ In this and the subsequent investigations of the series, however, "desorption," (so designated for want of a better term) has been effected as follows: after the reaction had been conducted for a given period of time, the reaction gas** was switched over from the saturator to the by-pass, and the dried gas was introduced into the reaction zone. The temperature of the furnace was then raised. When the temperature was raised above 400°C, the effect of desorption was evident, as shown by a large amount of condensation along the cooler parts of the reaction tube. When the amount of condensation became small, the temperature was lowered to the original point, and the gas was switched back to the saturator. This process was repeated as often as necessary, but usually two per run sufficed.

Table 1. Carbon Dioxide-Carbide System.

Exp. No.	I _L 37	I _L 40	I _L 41	I _L 57	I _L 59	I _L 60
React. Temp. (°C) . . .	380-400	340-380	340-380	340	380	420
Gas	CO ₂	CO ₂ +H ₂	CO ₂ +H ₂	CO ₂	CO ₂	CO ₂
Saturation temp. °C . .	80	80	72	80.3	80.3	80.3
Ratio Gas to Water (partial Press.) . . .	1:0.85	CO ₂ :H ₂ :H ₂ O 2:1:2.67	CO ₂ :H ₂ :H ₂ O 1:1:1	1:0.86	1:0.87	1:0.87
Time of Contact (sec.) .	15.6	22.2	16.7	22.1	18.8	16.1
Liq. Prods. (g.)*** . .	13.95	14.7	17.2	27.9	21.5	10.3
Water	10.9	13.0	3.8	9.0	29.4	18.8
Oil on Reacted (%)						
Carbide Acetylene . .	35.5	32.7	33.6	43.3	38.8	23.9
Oil on Reacted (%)						
Carbide Carbon . . .	31.20	29.6	31.1	41.0	35.7	22.21
Carbon Balance	96.6	98.5	95.6	99.6	97.7	—
Wt. Balance	98.1	98.3	99.7	99.3	100.2	95.0

200 g. of carbide was used in every run.

Results and Discussion. Out of a large number of runs, only those which are sufficiently accurate to give either the total weight balance or the carbon balance more than 95% are shown in Table 3. The results of the first three runs are less comparable, because they are more or less explorative in nature, and the reaction temperatures have been varied over a wide range. Those of the last three runs are, however, quite

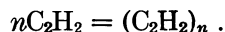
* The numbering of the Tables and Figures are consecutive throughout the whole series of papers, from (A) II to the final one.

** When a different gas, for example, H₂ or CO₂, was used to effect desorption, the reaction gas was shut off, and the dry gas in question was introduced from the by-pass.

*** Hydrocarbons.

comparative, and some interesting and suggestive results are possible from them. As has been the case with our first report,⁽¹⁾ the maximum yield of liquid products is again at 340°C* and at higher temperatures it diminishes. The ratio of liquid products to water seems to decrease with an increase of temperature, even when the extent to which the carbide has reacted is taken into consideration.

The percentage of the liquid products have been calculated on two different bases, namely, one on the reacted carbide acetylene and the other on the reacted carbide carbon. This sort of calculation has been performed, because we are really interested in the total amount of the liquid products which can be obtained from the carbide, or acetylene, (it is what becomes of the acetylene that is pertinent). There is also another reason for making this calculation. If the products are hydrogenated, the percentage of the liquid products will increase in proportion to the degree of hydrogenation, since the total weight of the liquid products is considered on the acetylene basis, while on the carbon basis, it will remain the same. Therefore, by comparing the two sets of percentages, we can obtain some idea as to the extent to which the products are hydrogenated and some information with regard to the mechanism of the reaction. If the two sets of values are the same, it means that there is no hydrogenation, or that there is no product of which H/C ratio is greater than that of acetylene; in other words, the reaction is simply



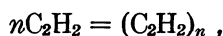
It is obvious from the results of Table 3 that the yield, calculated on acetylene, is always larger than that on the carbon. It may mean several things: either the whole products contain slightly more hydrogen than that in acetylene molecule or the majority of the products has about the same H/C ratio as that of acetylene, but there is present a small quantity of a substance with a very much higher H/C ratio. The data are not sufficiently accurate nor copious to decide which of the two is most probable, but the results of the elementary analysis in Table 4 are suggestive. It is rather surprising that the products contain so much oxygen. If it is assumed that most of it is due to methyl alcohol, which has been identified, we get some interesting results, as illustrated by I_L 57. Let us take the trap condensates of which elementary analysis gives the following results:

$$C = 74.98, \quad H = 9.37, \quad O = 15.65, \quad H/C = 0.1250.$$

Now, if we assume that all of this oxygen is due to methyl alcohol and make correction accordingly, the final H/C becomes 0.0853, while that of acetylene is 0.0833. The ratios of the percentages based on acetylene to those based on carbon are practically constant and greater than unity but slightly. From these facts we may assume reasonably that the majority of the products has a H/C ratio which is very nearly equal

* This seemed to be the case in the whole series of runs made under the ordinary pressure with the gases which are not themselves capable of polymerizing into liquid products. This point will become more clear when the results with other gases, especially acetylene, are reported later in this Bulletin.

to that of acetylene, but a small amount of substance with a higher ratio is also present. The main reaction of the nascent acetylene molecules, therefore, seems to be



whether H_2 (and CO_2) is present in the system or not.

Tabele 4. Gas Analysis (Carbon Dioxide-Carbide System).

Gas	I _L 37 (%)	I _L 40 (%)	I _L 41 (%)	I _L 57 (%)	I _L 59 (%)	I _L 60 (%)
CO ₂	72.8	33.5	30.5	56.6	64.6	72.8
C ₂ H ₂	10.5	17.4	8.4	18.8	22.2	12.1
C ₂ H ₄	0.9	0.6	0.6	0.2	0.4	0.4
C _n H _{2n}	0.0	—	0.0	0.1	0.7	0.6
O ₂	0.6	0.8	0.9	0.4	0.6	0.2
CO	0.6	0.6	0.6	0.3	0.8	0.4
H ₂	7.4	41.2	50.4	18.3	5.8	8.3
CH ₄	3.5	2.2	1.9	2.2	2.4	3.3
N ₂	4.0	3.5	3.9	4.0	2.8	2.4

The first striking thing about the results of elementary analysis in Table 4 is, as has been mentioned above, the high content of oxygen in the products, especially in the trap. Just what sort of oxygen we have here is at present difficult to say, but some evidence indicates that it is predominantly alcoholic. When the last three results in Table 4 are compared, it is interesting and may be of significance, that, both in the trap and condenser, the carbon content increases, while H/C ratio and the oxygen content decrease, respectively, with increasing temperature. When the analysis of the liquid products becomes more complete, we may be able to give a proper interpretation of the results.

In Table 5 the results of gas analysis are given. They should be considered qualitatively rather than quantitatively, since they do not represent the real compositions of the effluent reaction gas, owing to the fact that part of the effluent gas during desorption is invariably mixed with the effluent reaction gas. As for example, a high content of hydrogen in I_L 57 is due, undoubtedly, to the circumstance that desorption has been effected with hydrogen. Even with this limitation, a general trend in the change of the composition with temperature is as has been found in Paper (A) II⁽¹⁾ when the last three runs are compared.

There may remain some doubt as to the real significance of desorption, as defined in this paper, and in order to remove it I_L60 has been made. It became clearer from the results of this paper and those of a number of unpublished data that most of the liquid products were desorbed at near 420°C. If the apparent increase in the yield at the time of desorption is due rather to the increase in the oil formation at higher temperatures, the total yield should be higher for the reaction made at about 420°C than at lower temperatures. The data in Table 3 clearly indicate that the increase in the yield is due to a more efficient liquid formation

at lower temperatures plus the effect of desorption, and not due to that of higher reaction temperature.

Table 5. Elementary Analysis (Carbon Dioxide System).

Element	I _L 37 Com- bined	I _L 40		I _L 41		I _L 57		I _L 59		I _L 60	
		Trap	Cond.	Trap	Cond.	Trap	Cond.	Trap	Cond.	Trap	Cond.
C (%)	.. 81.23	78.66	84.92	83.02	84.02	74.62	83.19	77.43	85.75	80.56	86.59
H "	.. 8.62	9.93	8.53	10.10	8.46	9.96	8.76	10.24	8.60	9.76	8.49
C "	.. 10.15	11.41	6.35	6.88	7.52	15.42	8.05	12.32	5.65	9.68	4.92

Finally, the results of the present work indicate that the only reaction in which carbon dioxide is involved is that of the formation of carbonate, in agreement with the observations of Fischer⁽²⁾. Run I_L40 illustrates this point effectively. In this calculation the following have been assumed: (a) only acetylene forms the liquid, higher polymers, other gases (olefines and saturated), and free carbon; (b) the originally contained carbonate does not take part in any reaction. The results of calculation are gratifying.

Introduced		Found							Balance
		Free Gas (g.)	Decomp. + High Polym. (g.)	Carbonate (g.)	Liquid (g.)	Other Gases (g.)	Un-reacted (g.)	Sum (g.)	
C ₂ H ₂	62.92	13.84	12.64	—	12.36	1.49	21.28	61.61	1.31
CO ₂	30.10	13.30	—	16.76	—	—	—	30.06	0.04
Carbonate	1.17	—	—	1.17	—	—	—	1.17	(0.0)

II—Carbon Monoxide System.

In this system we have investigated the effect of a carrier gas which is itself capable of forming liquid products. From the studies of the hydrogen and of the carbon dioxide systems, we have obtained some indications that the main reaction of nascent acetylene is not influenced by carrier gases. It has been hoped, therefore, that it may be possible to effect a typical Fischer-Tropsch reaction (in the absence of a catalyst for the reaction) in parallel with the main reaction of the carbide.

The experimental results are given in Table 6 in which I_L62, of which weight balance deviates by more than the usual limit, $\pm 5\%$, has been included for the sake of comparison. It must be added here that we have had a great deal of experimental difficulty with this system. Quite frequently the reaction tube cracked without any warning, and although we had made quite a number of runs with CO alone and with its mixtures, only the two, given in the Table, appeared sufficiently quantitative. It may also be mentioned that for every run that appears in the Table, at least five runs have been made that are not sufficiently quantitative and are, therefore, not shown in the Table. Recourse to them, however, will be freely made in our discussion.

Table 6. Carbon Monoxide-Carbide System.
Hydrogen Chloride-Carbide System.

Exp. No.	I _L 44	I _L 50	I _L 64	I _L 65	I _L 62
Reaction Temp.(°C) .	340	340	340	340	380
Gas	CO	CO+H ₂	CO ₂ +HCl	CO ₂ +HCl	H ₂ +HCl
Saturation Temp.(°C)	80.1	72.5	79.3	80	90.5
Ratio Gas to Water (Partial Press.) . .	CO:H ₂ O 1:0.85	CO:H ₂ :H ₂ O 2:4:3	HCl:CO ₂ :H ₂ O 0.1:409:347	CO ₂ :H ₂ O* 1:0.86	HCl:H ₂ :H ₂ O 174:311:275
Time of Contact (sec.)	19.0	29.3	21.4	26.7	23.9
Liq. Prods. (g.) . . .	6.4	5.2	23.7	19.2	7.7
Water (g.)	3.0	0.4	17.2	13.6	27.15**
Oil on Reacted (%)					
Carbide Acetylene.	10.3	22.0	39.9	38.9	31.6
Oil on Reacted (%)					
Carbon (Carbide) .	10.2	20.3	33.2	35.1	27.6
Carbon Balance . . .	102.0	98.3	97.4	96.5	—
Weight Balance . . .	100.6	100.5	98.3	96.1	81

200 g. of calcium carbide grains was used in every run.

* Traces of HCl.

** H₂O+23.9% HCl.

Before we made the experiments, we had hoped, according to our thermodynamic calculations⁽³⁾, that we might obtain a larger total yield of liquid products by using water gas as a carrier gas, but our experimental results seemed to point otherwise. In fact, they indicated that the gas not only failed to form any liquid,* but had actually decreased** the yield, as shown in Table 6. The small yield might have been due to the fact that in these runs no desorption has been effected, but this can account only for a small part, since it is shown that the effect is appreciable only when CO₂ is involved as in I_L64. We are at present unable to offer a comforting explanation for the harmful effect of carbon monoxide or water gas on the direct synthesis of hydrocarbon liquids from the carbide.

The results of gas analysis in Table 7 should be considered rather qualitatively than quantitatively for the same reasons given in connection with CO₂ system. The results of semi-quantitative calculation, based on the gas analyses of I_L44 and I_L50, showed that part of the original CO had reacted to form CO₂ (eventually it produced calcium carbonate) and methane, but no liquid products.

(3) R. Negishi, O. Kimura, and O. Kamiike, *Rev. Phys. Chem., Japan*, **15** (1941), 31, Paper (A) I.

* I_L47 was made to see whether the carbide had any effect on a dry CO+H₂ mixture of 1:2 proportion or not. The temperature was varied from 150°C to 450°C, but there was no liquid formation; moreover, there was but slight reaction of any sort, as indicated by the negligible change in the weight of the carbide before and after the reaction (from 200 to 200.5 g.) and by the results of gas analysis (gas at 300°C) shown in Table 7. The original composition was about the same as that of I_L50.

** For I_L52, made under the same conditions as those of I_L50, the yield of liquid was 20.0%.

Table 7. Gas Analysis.

Gas	I _L 44		I _L 50		I _L 64 (%)	I _L 65 (%)	I _L 62 (%)	I _L 47 (%)
	Reacted (%)	Introd. (%)	Reacted (%)	Introd. (%)				
CO ₂	0.67	0.9	0.47	—	71.26	76.7	2.48	1.8
C ₂ H ₂	8.75	—	6.20	—	15.68	16.9	6.77	1.0
C ₂ H ₄	0.37	—	0.43	—	0.58	0.4	0.64	0.4
C _n H _{2n}	0.30	—	0.37	—	0.37	0.2	0.50	0.0
O ₂	0.51	—	0.80	—	0.32	0.4	0.94	1.4
CO	71.34	99.2	23.88	31.6	0.48	0.2	0.54	28.2
H ₂	9.28	—	60.54	61.9	6.90	2.3	80.89	58.8
CH ₄	3.75	—	1.70	—	2.33	1.2	4.74	2.0
N ₂	5.15	—	6.00	6.3	2.58	2.4	2.34	6.4

III—Hydrogen Chloride System.

Hydrogen chloride has been used to investigate the effect on the yield of the destruction of the basic substances produced in the reaction and the catalytic effect—if any—of the acid.

The effect of hydrogen chloride vapors seemed but slight. Although there was some difference in the physical appearance of the liquid products in runs I_L62 and I_L64, it might very well be accounted for by other effect than that of the acid concentration.* We hesitate to make a definite conclusion as to the effect on the yield of liquid products of the acid and also of the carbonate, but the results of Tables 8 and 9 are suggestive.

Table 8. Carbonate Carbon in Residue.

Exp. No.	Wt of Residue (g.)	CO ₃ Carbon in Residue (g.)	CO ₃ Carbon on React. CaC ₂ Carbon (%)
I _L 64	288.1	27.46	47.5
I _L 62	277.4	2.67	10.4
I _L 65	283.3	23.43	47.5
I _L 57	389.9	25.91	46.3

Table 9. Effect of Acid on Liquid Yield (at 340°C).

Exp. No.	HCl Conc. Wt. (%) Average	Vap. Press. mm Hg			Liquid Carbon on React. Carbide Carbon (%)
		HCl	H ₂ O	CO ₂	
I _L 62*	26	174	267	324*	28
I _L 64	3.5	0.1	347	409	33.2
I _L 65	0.58	Trace	350	410	35.1
I _L 57	0.0	0.0	350	410	41.0

* At 380°C; instead of CO₂, H₂ was used.

* The concentration of HCl in the saturated vapor was computed from the partial vapor values given in Int. Crit. Tables, Vol. III (1928), 301. Its concentration in the vapor phase was expressed in mm Hg and that in the liquid by weight percent, determined by titration with Na₂CO₃.

In Table 10 the results of elementary analysis of the liquid products are given. It seems that the products formed in the presence of CO contain less oxygen while those formed in the presence of the acid contain larger amounts than those with carbon dioxide. A proper explanation also awaits for this peculiar effect, if real.

Table 10. Elementary Analysis.

Element	I _L 44		I _L 50	I _L 64		I _L 65		I _L 62	
	Trap	Cond.	Combined	Trap	Cond.	Trap	Cond.	Trap	Cond.
C(%)	82.02	84.60	85.20	74.29	79.79	67.70	84.96	—	81.63
H "	9.71	8.69	8.76	10.10	8.78	10.48	8.85	—	8.20
O "	8.27	6.71	6.04	15.61	11.43	21.82	6.19	—	10.17

Summary.

The effects on the synthesis of hydrocarbon liquids directly from calcium carbide, in the temperature range of 340 to 420°C, of carbon dioxide, carbon monoxide, hydrogen chloride, and their mixtures have been studied. The present results are in general agreement with those of the hydrogen system, and it has been found that the main reaction of the nascent acetylene molecules is but slightly affected by the carrier gases.

In the carbon dioxide system the yield of liquid products has been found as high as 43% of the total reacted acetylene. The only reaction in which carbon dioxide takes part is the formation of calcium carbonate. The presence of hydrogen seems to have no effect on the character of the liquid products.

It has been shown that while carbon dioxide has favourable, carbon monoxide has unfavourable effects, and hydrogen chloride has none at all, or but slight, on the liquid yield.

In the presence of the carbide and its reaction products, carbon monoxide with hydrogen does not effect a Fischer-Tropsch synthesis; however, it reacts to produce some carbon dioxide and methane.

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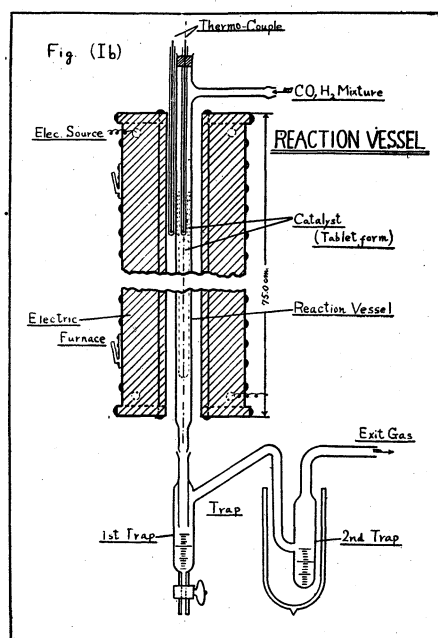
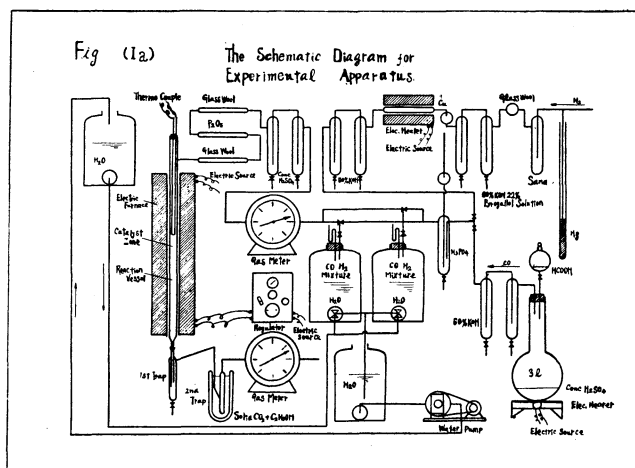
**Physico-Chemical Investigations on Catalytic Mechanism. (V).
On the Fischer-Tropsch Synthesis of Hydrocarbons.
(Experimental Series II*).(1)**

By Senzo HAMAI, Shiro HAYASHI and Kiyoshi SHIMAMURA.

(Received January 14, 1942.)

In a previous paper⁽¹⁾ we described the experimental apparatus by which a series of investigations concerning the catalytic mechanism has been studied. In this paper we shall attempt to report some of our further experimental results obtained from similar series of the experiments, made by using other set of apparatus; hereafter, for our convenience we shall call this series II.

Experimental Apparatus. The principal features of the apparatus are practically the same as before, except a few details of the reaction vessel. They are shown in Fig. 1 a and Fig. 1 b.



The main feature of the reaction vessel is, as shown in Fig. 1 b, a tube of all terex glass of which dimension is 1.4 cm. in diameter and

* Most of the results given in this paper were obtained and completed in 1939-1940, but the publication of them has been with-held.

(1) S. Hamai, S. Hayashi, K. Shimamura and H. Igarashi, *Bull. Chem. Soc. Japan*, **17** (1942), 166 (Report IV).

94 cm. in length, and the thermocouple well is well inserted to the tube as far as the middle part of the catalyst zone so as to enable us to record even a slight variation of temperature during a run.

Electric furnace was controlled by means of an accurate regulator of potentiometric type.

Catalyst. The catalysts which we have employed are of Co, of Fe, and of Co-Fe types with various promoters and Kieselguhr.

In this series of experiments we used mainly the catalysts shown in Tables 1-3 (Co type), and they were prepared by the precipitation method from cobalt nitrate with potassium carbonate (2N) with an adequate

Table 1.

Effects of Promoters (CeO_2) on the Gas Contraction
Reaction Temperature 200°C .

Exp. No.	Catalyst No.	Catalyst Composition (%) $\text{Co} + \text{CeO}_2 + \text{Kieselguhr}$			Average Gas Contraction (%)
F ₃₀ (A-G)	XII ₁ -1	100	5	100	51
F ₃₁ (A-G)	XII ₂ -1	100	10	100	54
F ₃₂ (A-E)	XII ₄ -1	100	20	100	35
F ₃₃ (A-D)	XII ₅ -1	100	30	100	24
F ₃₆ (A-D)	XII ₃ -1	100	15	100	56
F ₃₅ (A-D)	XII ₈ -1	100	48	100	17

Table 2.

Effects of Promoters (ThO_2) on the Gas Contraction
Reaction Temperature 225°C .

Exp. No.	Catalyst No.	Catalyst Composition (%) $\text{Co} + \text{ThO}_2 + \text{Kieselguhr}$			Average Gas Contraction (%)
F ₄	1 ₁ -1	100	15	100	40
F ₅	1 ₂ -1	100	20	100	70
F ₆	1 ₃ -1	100	30	100	70
F ₉	1 ₅ -1	100	10	100	6
F ₁₂	1 ₅ -1	100	10	100	5
F ₁₃	1 ₆ -1	100	48	100	60

Table 3a.

Effect of ThO_2 on the Gas Contraction Reaction
Temperature 200°C .

Exp. No.	Catalyst No.	Catalyst Composition (%) $\text{Co} + \text{CeO}_2 + \text{ThO}_2 + \text{Kiesel.}$				Average Gas Contraction (%)
F ₃₀ (A-D)	XII ₁ -1	100	5	—	100	51
F ₃₇ (A-D)	XII ₇ -1	100	5	5	100	35
F ₄₀ (A-G)	XII ₁₁ -1	100	15	15	100	34
F ₃₆ (A-D)	XII ₃ -1	100	15	—	100	56

Table 3b.

Effect of Cu on the Gas Contraction Reaction
Temperature 200°C.

Exp. No.	Catalyst No.	Catalyst Composition (%) Co + CeO ₂ + Cu + Kiesel.					Average Gas Contraction (%)
F ₃₀ (A-D)	XII ₁ -1	100	5	—	100		51
F ₃₈ (A-H)	XII ₆ -1	100	5	5	100		25

mixing of various promoters and Kieselguhr as a carrier, and were made into small tablet forms. (For a more detailed description for the preparation of the catalyst, see our report IV⁽¹⁾).

Preparation of Gases involved in the Reactions. Hydrogen and carbon monoxide were prepared and purified in the same way as already described⁽¹⁾.

Experimental Procedure. As described previously in our report IV, the main features of experimental procedure are the same except that they were carried out in various different conditions.

The reaction products were collected in two separate portions—similar to those of Series I and subjected to the determinations of physico-chemical properties.

The effluent gas was analyzed, using a modified form of Orsat Gas Analysis Apparatus for their constituents.

Experimental Results. In the present paper, we concern ourselves especially with different catalysts and their various influences on their activities and attempt to correlate with our theory of Fischer-Tropsch synthesis. Some of the illustrative results are tabulated as follows:

Table 1 and 2 show the influences of CeO₂^{(2) (3)} and ThO₂^{(3) (4) (5)} in various percentages, and the characteristic behaviours of each catalyst are illustrated in Fig. 1 and 2. As seen in these graphs, it is more or less recognizable that the influences of CeO₂ and ThO₂ are not similar but quite distinct; namely in the case of CeO₂, the gas contraction percentage is higher with about 15–10% of this promotor, while if it exceeds 15% such as 20% or over, the gas contraction decreases distinctly. In the case of ThO₂, the gas contraction percentage is higher with about 20–30% of the oxide and below this it is not so favorable with regard to its activity, and one of the interesting points is that the relatively high percentage of ThO₂ content does not influence the activity as much as that of the relatively low one. However, an evenmore interesting point is that if the points of the maximum activity in both cases are traced and the contents of ThO₂ and CeO₂ are expressed respectively in the moral

(2) S. Kodama, *J. Soc. Chem. Ind. Japan*, (Suppl.) **33**, (1930) 202b.

(3) F. Fischer and H. Koch, *Brenn-chem.*, **13** (1932), 61.

(4) S. Tsutsumi, *J. Chem. Soc. Japan*, **59** (1938), 1412.

(5) S. Tsutsumi, *J. Chem. Soc. Japan*, **57** (1936), 685.

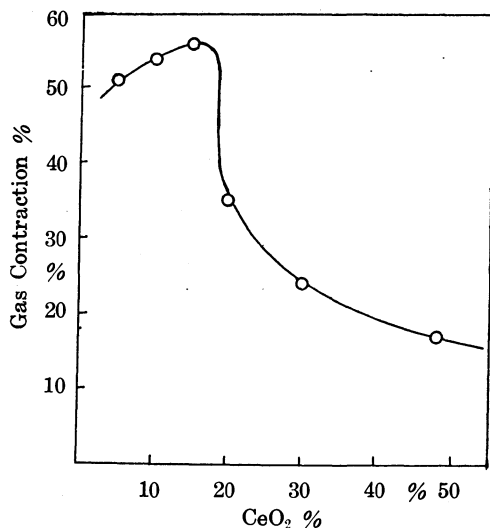


Fig. 1. Effect of CeO₂ % on The Gas Contraction %.

(Relatively High Yield of oil and Less Yield of CH₄)

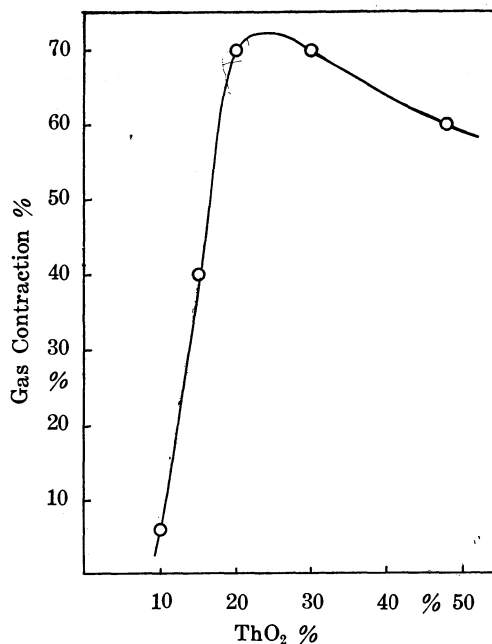


Fig. 2. Effect of ThO₂ on The Gas Contraction %.

(Relatively High yield of CH₄)

ratio^(*) instead of the usual weight percentages, strange as they seem, they happen to be about the same, namely Co:ThO₂=1:0.0513 (23~25%), Co:CeO₂=1:0.0513 (15%), [Co:ThO₂, 1:0.0557 (25%)]. These observed facts may be considered to be rather important from the stand point that in connection with the action of promoters, such as ThO₂ or CeO₂, the active centers to which the molecules of the promoters are distributed, are existing in such a manner as they seem to give the definite ratio. The interpretation of these phenomena may be very suggestive in regards to the theory of the promoter action, although such argument should not be put forward too far. At any rate, these facts, may possibly give a consequence fruitful in establishing the theory of promoter action.

Some investigators^{(3) (6)} have stated that the activity fell to zero when ThO₂ content was as high as 48%; but in our case the gas contraction percentage has been found to be as high as 60% with the same composition and it showed an activity almost as good as those of 20 and of 30%. These contradictory evidences show clearly that, as far as the catalytic activity is concerned, such a statement as cited in^{(3) (6)} does not have so much significance unless such facts are found absolutely reproduceable. This in turn implies that the investigation of catalytic mechanism, especially the catalytic activity, cannot be so easily discussed, even though the ex-

(*) Chemical properties are usually more closely connected with the molal ratio and better to be expressed in terms of molal properties of the system.

(6) S. Tsuneoka, "Synthetic Liquid Fuel" p. 65, (in Japanese).

perimental facts themselves might not be denied. But from these facts not only a clear-cut conclusion cannot be so easily drawn nor should be hastily deduced. Such experimental results themselves only tell a story of one side but not of general. Therefore, we can safely state that such evidence as the gas contraction percentage has true significance only for a definite reproducible condition.

The other interesting point is that, in the series of the catalysts containing CeO_2 , a relatively high yield of oil and low yield of CH_4 are found even at the initial stage⁽⁷⁾ of the run; while in the case of ThO_2 , a relatively high yield of CH_4 and low yield of oil.

Table 3 shows some of the influences of ThO_2 as found on the average gas contraction and the effects of Cu.⁽⁸⁾⁽³⁾ As seen in Table 3, when CeO_2 percentage is relatively low, the addition of ThO_2 is found to lower the activity; while if CeO_2 is as high as 15%, the addition of 15% ThO_2 does not much improve the gas contraction, but it remains practically the same; so that the addition of ThO_2 does not seem to improve the activity as much as expected.

As regards the oil formation, it was found that in $\text{F}_{36}(\text{A-D})$, in which the contraction percentage was 56%, the yield of oil was approximately estimated to be 121.3 c.c./ M^3 .

Some of the typical gas analysis data are tabulated as follows:

Table 4.

Exp. No.	Gas Analysis Date					
	$\text{F}_{30}-\text{A}$	$\text{F}_{30}-\text{B}$	$\text{F}_{20}-\text{C}$	$\text{F}_{30}-\text{D}$	$\text{F}_{31}-\text{G}$	$\text{F}_{32}-\text{E}$
CO_2	12.8	0.3	0.0	0.5	1.4	0.3
C_2H_2	0.0	0.0	0.0	0.0	0.0	0.0
C_2H_4	0.5	0.2	0.3	0.5	1.4	0.4
C_nH_{2n}	0.0	0.0	0.0	0.0	0.0	0.0
O_2	0.4	0.4	0.3	0.3	0.3	0.4
CO	6.1	31.8	31.5	31.6	29.4	31.5
H_2	39.8	65.2	66.0	65.4	66.1	65.3
CH_4	37.1*	0.0	0.0	0.0	0.0	0.0
C_2H_6	1.4	0.0	0.0	0.0	0.0	0.0
N_2	1.9	2.1	1.9	1.7	1.4	2.1

* Initial Stage.

(7) See: S. Hamai, *Bull. Chem. Soc. Japan*, **16** (1941), 213; Report IV, S. Hamai, S. Hayashi, K. Shimamura and H. Igarashi, *Bull. Chem. Soc. Japan*, **17** (1942), 166; E. F. G. Herington and L. A. Woodward, *Trans. Faraday Soc.*, **35** (1935), 958; *Brenn.-Chem.*, **20** (1939), 319.

(8) (a) F. Fischer, *Brenn.-Chem.*, **11** (1930), 489.

(b) K. Fujimura, *J. Chem. Ind. Japan*, **35** (1932), 532.

(c) S. Tsutsumi, *Report of the Fuel Research Institute, Japan*, **31** (1935).

(d) S. Tsuneoka and Y. Murata, *J. Chem. Ind. Japan*, **41** (1938), 95.

(e) F. Fischer and K. Meyer, *Brenn.-Chem.*, **12** (1931), 225.

Table 4.—(Continued)

Exp. No.	Gas Analysis Data					
	F ₃₃ —D	F ₃₅ —D	F ₃₆ —A	F ₃₆ —B	F ₃₆ —C	F ₃₆ —D
CO ₂	0.5	0.2	3.5	0.9	0.3	1.4
C ₂ H ₂	0.0	0.0	0.0	0.0	0.0	0.0
C ₂ H ₄	0.3	0.4	0.9	0.5	0.6	0.7
C _n H _{2n}	0.0	0.0	0.0	0.0	0.0	0.0
O ₂	0.2	0.3	0.6	0.3	0.3	0.4
CO	32.5	30.1	16.0	23.3	30.0	30.5
H ₂	64.8	67.5	56.8	66.6	67.0	64.9
CH ₄	0.0	0.0	19.6*	6.5*	0.0	0.0
C ₂ H ₆	0.0	0.0	0.0	0.0	0.0	0.0
N ₂	1.7	1.5	2.6	1.9	1.8	2.1

Table 5.

Exp. No.	Gas Analysis Data						
	F ₄	F ₅	F ₆	F ₉	F ₁₀	F ₁₂	F ₁₃
CO ₂	1.0	8.0	0.7	0.2	0.0	0.4	8.5
C ₂ H ₂	0.3	0.3	0.2	0.4	0.0	0.3	0.7
C ₂ H ₄	0.2	0.4	0.2	0.0	0.5	0.2	0.0
C _n H _{2n}	0.5	0.3	0.0	0.0	0.3	0.0	0.0
O ₂	0.4	0.3	0.3	0.4	0.4	0.3	0.4
CO	27.1	16.7	26.3	31.7	30.9	30.2	0.4
H ₂	68.4	59.0	70.8	65.5	66.3	67.3	46.0
CH ₄	0.0	12.8*	0.0	0.0	0.0	0.0	41.2*
C ₂ H ₆	0.0	0.9	0.0	0.0	0.0	0.0	1.1
N ₂	2.1	1.3	1.5	1.7	1.7	1.3	1.6

* Initial Stage.

As seen in these tables, CH₄ formation was observed at the initial stage⁽⁷⁾ (F₃₀—A), F₃₆(A—B). In the case of F₁₃ where ThO₂ content was 48%, the relatively high gas contraction percentage might be due to this abnormally high yield of CH₄.

As regards the influence of Cu on the activity of F₃₀(A—D) and F₃₈(A—H), it might be stated that, as far as these series of experiments are concerned, the addition of Cu seemed to lower the activity as evidenced by the average gas contraction. However, we must be cautious about drawing a general conclusion.

Thus far, we have shown some of typical results which indicate the various influences on the catalytic activity as caused by various amounts of promoters such as CeO₂, ThO₂ and Cu, along with the gas analysis data.

In Table 6 we have shown some of the physical and chemical properties of 1st and 2nd trap oils for the respective experiments.

Table 6.

Exp. No.	Reac- tion Temp. (°C)	Catalyst No.	Catalyst Comp. Co+ThO ₂ + Kieselguhr	Pretreat- ment hrs. °C	Physico-Chem. Properties					
					Ref. Ind.	Sp. Gr.	App. M. W.	Elem. Anal.		
								C %	H %	
F ₄ 1st trap oil	225	I ₁ -1	100 15 100	2 400 5 350	1.4350 ^{25°}	0.7747 ^{20°}	169	85.32	14.75	
F ₄ 2nd trap oil	"	"	" " "	"	—	0.7286 ^{20°}	113	85.92	14.83	
F ₄ Wax	"	"	" " "	"	1.4340 ^{85°} m. p. (58.6°-64.4°)	—	328	84.87	15.19	
F ₅ 1st trap oil	225	I ₂ -1	100 20 100	2 400 5 350	1.4211 ^{20°}	0.7542 ^{20°}	144	84.98	15.04	
F ₅ 2nd trap oil	"	"	" " "	"	—	0.6622 ^{20°}	85	85.18	15.44	
F ₃₀ (A-D) 1st trap oil	200	XII ₁₁ -1	100 5 100	5 400 5 350	1.4319 ^{20°}	0.7542 ^{25°}	154	85.41	15.05	
F ₃₀ (A-D) 2nd trap oil	"	"	" " "	"	1.4090 ^{20°}	—	102	84.45	15.55	
F ₃₁ (A-G) 1st trap oil	200	XII ₂ -1	100 10 100	5 400 5 350	1.4239 ^{20°}	0.7462 ^{25°}	149	84.87	14.84	
F ₃₁ (A-G) 2nd trap oil	"	"	" " "	"	—	0.7072 ^{25°}	—	84.74	14.87	
F ₃₂ (A-E) 1st trap oil	200	XII ₁ -1	100 20 100	5 400 5 375	1.4317 ^{20°}	0.7622 ^{25°}	167	85.05	14.50	
F ₃₂ (A-E) 2nd trap oil	"	"	" " "	"	—	—	—	—	—	
F ₃₃ (A-D) 1st trap oil	200	XII ₅ -1	100 30 100	5 400 5 375	1.4320 ^{20°}	0.7652 ^{25°}	166	84.53	14.97	
F ₃₃ (A-D) 2nd trap oil	"	"	" " "	"	—	—	—	—	—	
F ₃₅ (A-D) 1st trap oil	200	XII ₈ -1	100 48 100	5 400 5 375	1.4297 ^{20°}	—	—	84.50	15.16	
F ₃₆ (A-D) 1st trap oil	200	XII ₃ -1	100 15 100	5 400 5 375	1.4229 ^{20°}	0.7452 ^{25°}	143	85.56	15.00	
F ₃₆ (A-D) 2nd trap oil	"	"	" " "	"	1.4030 ^{22°}	0.6682 ^{25°}	90	84.19	15.51	
F ₃₇ (A-D) 1st trap oil	200	XII ₇ -1	100 5 100 +5% ThO ₂	5 400 5 375	—	—	—	—	—	
F ₃₇ (A-D) 2nd trap oil	"	"	"	"	—	—	—	—	—	
F ₃₈ (A-H) 1st trap oil	200	XII ₆ -1	100 5 100 +5% Cu	5 400 5 375	1.4313 ^{20°}	—	—	84.71	15.25	

Table 6.—(Concluded)

Exp. No.	Reaction Temp. (°C)	Catalyst No.	Catalyst Comp. CO+ThO ₂ + Kieselguhr	Pretreatment hrs. °C	Physico-Chem. Properties				
					Ref. Ind.	Sp. Gr.	App. M. W.	Elem. Anal.	
								C %	H %
F ₃₈ (A-H) 2nd trap oil	„	„	„	„	1.3980 ^{20°}	0.685 ^{20°}	85	84.24	15.62
F ₄₀ (A-G) 1st trap oil	200	XII ₁₁ -1	100 15 100 +15% ThO ₂	5 400 5 375	1.4319 ^{20°}	0.766 ^{20°}	153	85.69	14.42
F ₄₀ (A-G) 2nd trap oil	„	„	„	„	1.4071 ^{20°}	0.702 ^{20°}	90	85.08	15.23

Fifth Column; Indicates heat treatment prior to H₂ reduction and temperatures of H₂ reduction, respectively, in the order as written from the top.

Refractive index was determined by using Pulfrich refractometer, and the apparent molecular weights were determined by means of the freezing-point lowering method. The specific gravity was measured by using an ordinary pycnometer whose size was conveniently made as suitable to its respective amount of specimen.

Summary.

(1) Experimental apparatus for studying the catalytic mechanism for the Fischer-Tropsch synthesis with various different types of catalysts has been described and discussed (Series II).

(2) Influences of the CeO₂ content on the cobalt type catalyst as well as ThO₂ content along with the effect of Cu on the catalytic activity, as estimated by the average gas contraction, have been investigated.

(3) Typical gas analysis data for the effluent gas for each of these runs have been tabulated.

(4) Some of the physico-chemical properties of the reaction products have been determined and tabulated.

In conclusion, the authors take this occasion to express their sincere thanks to Dr. T. Marusawa, former Director of the Institute, and Dr. M. Sato, Director of the Institute, for their interests and encouragement during these series of investigations and also for the permission of the publication and we thank Messrs. Kuwabara, Igarashi, Fujiwara and Konoha who have assisted us willingly in the experimental part of this investigation.

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Studies on the Adsorption at the Solid—Liquid Interface. III. Note on the Polar and Non-polar Adsorption.

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On the Dielectric Theory of the Adsorption. Some relations between the adsorption and the dielectric nature of substances have already been known. It is about twenty years since the electrostatic theory concerning the force of the adsorption of gases or vapours has been proposed, and, since then, the theory has also been applied to the adsorption from the solution by many investigators.

According to the electrostatic theory⁽¹⁾ of the adsorption of vapour, the vapour molecules polarize the lattice of the adsorbent, and the certain molecules, which are near the surface of the adsorbent, is bound by the image force of itself in the lattice. In this case, the field induced by the adsorbent is not considered in general. In the case of the interface between the liquid and the solid, however, the potential difference between those two phases will vary widely as it depends on the dielectric structures of them. By the adsorption from the solution, moreover, the solvent molecules will be adsorbed, with the solute molecules at the same time, and therefore the amount of the adsorption will be given from the difference of these two amounts. In the dilute solution, with regard to a certain solute, the adsorption will increase, as less the adsorption of the solvent molecules is. Considering the electrostatic theory, the adsorption of the solvent molecules will be associated with their dipole moments. The adsorption will decrease, as greater the dipole moment of the solvent is. The adsorption of a certain solute are affected by the polarity of the solvent, and such phenomena were investigated by Nekrassow,⁽²⁾ Heymann and Boye,⁽³⁾ and Sata.⁽⁴⁾ On the other hand, the solute will be more adsorbed from a certain solvent, as greater the dipole moment of itself is. From such a view-point, studies were also carried out by Tamamushi,⁽⁵⁾ and Sata.⁽⁴⁾ However, the general relation has not yet been found.

In the case of the adsorption from the solution, the phenomena depend on the combination of the solute, the solvent and the adsorbent, and the electrical natures are also affected by their combinations. So things are complex and the definite results has not been found, notwithstanding, there are many qualitative relations between the adsorption and the dielectric natures. The present author thinks that to use charcoal as the adsorbent for the sake of convenience of the experimental technique is one of the reasons for such confusions. For charcoal is a typical

(1) Debye, *Physica*, **1** (1921), 362; Lorenz and Lande, *Z. anorg. Chem.*, **125** (1922), 47; E. Hückel, "Adsorption und Kapillarkondensation," 1928, Leipzig, p. 83.

(2) Nekrassow, *Z. physik. Chem.*, **136** (1930), 18.

(3) Heymann and Boye, *Z. physik. Chem.*, A **150** (1930), 219.

(4) N. Sata, *Kolloid-Z.*, **49** (1929), 275; *J. Chem. Soc. Japan*, **53** (1932), 617.

(5) B. Tamamushi, this Bulletin, **6** (1931), 74.

non-polar substance. Considering the electrical field of the interface, more general substance must be used as the adsorbent. The famous Traube's rule, i.e. fatty acid which has longer chain will be adsorbed more from the aqueous solution by charcoal than the one which has shorter chain is reversed⁽⁶⁾ when silica gel (polar) is used as the adsorbent and toluene (non-polar), as the solvent. Freundlich and Heller⁽⁷⁾ have shown that trans-azobenzene is adsorbed more by charcoal from the solution in methyl alcohol than cis-azobenzene, while, cis-form is adsorbed more than trans-form by aluminium oxide from the solution in petroleum ether. It is recognised, in general, that the non-polar adsorbent, such as charcoal, adsorbs well from the polar solvent, while the polar (or hetero-polar) adsorbent adsorbs well from the non-polar solvent, and such cases are called the "polar and non-polar adsorption."

To investigate the adsorption at the solid-liquid interface, and to consider the polar and non-polar adsorption also the present author has carried out some experiments on the behaviours of the molecules at the interface between glass (hetero-polar) and benzene or toluene (non-polar). The amount adsorbed by glass, though made into the fine powder, is so small that the method of the measurement must be specially devised. For such a purpose, the float method and the surface balance analysis were applied. In the preceding paper, the behaviours of fatty acids were reported (Part I),⁽⁸⁾ and it was also reported that the adsorption layer is one molecular in thickness in the case of palmitic acid and benzoic acid (Part II).⁽⁹⁾

Adsorption of Some Benzene-derivatives by the Glass Powder. Some of benzene-derivatives have large dipole moments and it is anticipated, from the electrostatic theory, that they would be readily adsorbed at the glass-benzene interface. Nevertheless, among benzoic acid, nitrobenzene, aniline and chlorobenzene which were studied by the present author, benzoic acid alone was adsorbed by the glass-benzene interface, and the other compounds were not adsorbed, or the amount adsorbed might be too small to be measured by the present method. Results are shown in Table 1 and Fig. 1.

The adsorbent was the same glass powder ("crushed" glass powder) as reported in the preceding paper (Part I), also the experimental conditions were the same. To determine the amount of the adsorption, the float method was applied. By this method, the difference of the concentration of the solution, before and after the adsorbing procedure, is determined from the change of the density, which is measured by a float. In Table 1, the notation of "Reading of Beckmann" means the arbitrary reading of the scales of a Beckmann thermometer, that indicate the temperature at which the density of the solution is identical with that of the float. The identity of this values before and after the adsorbing procedure shows that no measurable adsorption has taken place. In the case of aniline and chlorobenzene, things were just like as the case of nitro-

(6) Holmes and McKelvey, *J. Phys. Chem.*, **32** (1928), 1522.

(7) Freundlich and Heller, *J. Am. Chem. Soc.*, **61** (1939), 2228.

(8) H. Akamatu, this Bulletin, **17** (1942), 141.

(9) H. Akamatu, this Bulletin, **17** (1942), 161.

Table 1. Adsorption of Benzene-derivatives by the "Crushed" Glass Powder.

Volume of Solution (c.c.)	Weight of Adsorbent (g.)	Initial Concentration		Final Concentration		Amount adsorbed by 1 g. of Adsorbent (mol)
		(mol/l.)	Reading of Beckmann	(mol/l.)	Reading of Beckmann	
Benzoic acid / Benzene						
10	4.958	0.92×10^{-2}	3.200	0.28×10^{-2}	3.107	1.3×10^{-5}
10	5.003	1.84×10^{-2}	3.465	1.13×10^{-2}	3.259	1.4×10^{-5}
10	4.936	3.67×10^{-2}	4.000	2.99×10^{-2}	3.791	1.4×10^{-5}
10	4.759	7.35×10^{-2}	5.054	6.65×10^{-2}	4.854	1.5×10^{-5}
Nitrobenzene / Benzene						
10	4.812	1.27×10^{-2}	0.933	1.28×10^{-2}	0.934	0
10	4.407	2.55×10^{-2}	1.282	2.52×10^{-2}	1.278	0
10	5.258	5.10×10^{-2}	1.978	5.11×10^{-2}	1.981	0
10	4.616	10.20×10^{-2}	3.375	10.23×10^{-2}	3.380	0

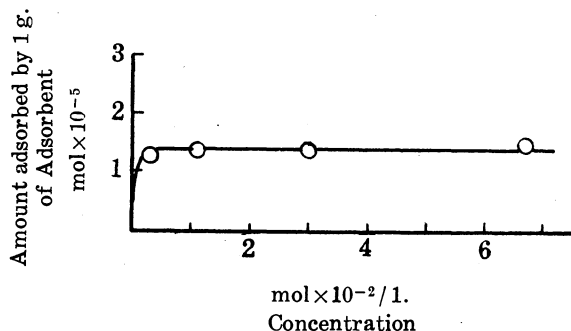


Fig. 1. Adsorption of Benzoic acid.

benzene, where the concentration of the solution which has been studied was in the region of 0.145 mol/l. and 0.089 mol/l. respectively for aniline and chlorobenzene.

Essentially, this method is not so acute when the difference of densities of the solute and the solvent is not large. However, when the densities of the compounds are much larger than benzene (solvent), it is expected that the change of the concentration would be observed acutely by measuring the density. Considering the result of the preceding paper (Part II), and the curve of Fig. 1, it is plausible to consider that the adsorption layer of benzoic acid is monomolecular in thickness. By this method, we can investigate the adsorption even when the adsorption layer is less than the monomolecular one. To make sure the above results, the adsorption measurement was carried out using the "spherical" glass powder⁽⁹⁾ of which specific surface area has been known in the case of nitrobenzene. However, no measurable adsorption also could be found.

It seems plausible to the present author to consider that nitrobenzene, aniline and chlorobenzene are not adsorbed at the glass-benzene interface, in the region of the concentration of the solution which has been studied. This fact is also deduced by the qualitative facts which are described in the following section.

On the Lateral Movement of the Float in the Solution. By the float method of density measurement, a float which was made of a boro-silicate glass was used. It is put in the solution to be tested, and the velocity of the motion of the float up and down at a certain temperature was observed. In this experiment a peculiar behaviour of the float has attracted notice of some investigators, namely, the float moves occasionally toward the wall of the cell and attaches to it. Sometimes this may be an accident caused, for instance, by the vibration of the stirrer, or the electrical charge of the float, etc. By the present author's experiences, however, it always occurs when the liquid is non-polar one such as benzene or toluene. Robinson and Smith⁽¹⁾ have reported that they had been troubled by this phenomenon in the case of silicon tetrachloride. On the other hand, the float never attach to the wall in the case of benzene or toluene dissolving fatty acid, or benzoic acid, while the float attach to the wall in the case of dissolving such as nitrobenzene or chlorobenzene as well as pure benzene. To prevent this behaviour of the float, it is necessary to take care not to be clean the float or the cell too much. Usually, the float is washed with benzene freshly distilled using a Soxhlet apparatus, and the cell is washed with chromic acid mixture, then with distilled water, and dried in an electrical drying oven, at each measurement. In those cases, however, the cell must be exposed in the open air for a long time (overnight, for instance) before the use, or the washing of the float must be neglected to prevent the adhering of the float to the wall.

The cause of such peculiar behaviour of the float may be the electrical charge (by the friction, for instance), or the heterogeneous contamination at the surface of the float. During the measurement of the density by the float method, the density of the float is almost identical to that of the solution. Consequently, the float can be moved by a very small force. The nature of this force is not known yet. The float does not attach to the wall of the cell when there exists any adsorption layer at the surface of the float or the wall,—it may be solvation, the contamination or the adsorption of a certain substance from the solution. The fact that the occurrence of this peculiar behaviour of the float in benzene solution dissolving nitrobenzene or chlorobenzene, corresponds to the non-adsorption of these compounds by the glass surface.

Adsorption of Alcohols and Esters. Alcohols are also adsorbed by glass from benzene solution. The results shown in Table 2 and Fig. 2 are also obtained by the float method.

Methyl alcohol and ethyl alcohol were much adsorbed, as the concentration of the solution was increased. The behaviours of alcohols seem to be alike to the fatty acids. In the case of fatty acids, however, the adsorption takes place still in the region of the low concentration of the solution, on the other hand, in the case of alcohols, no considerable adsorp-

(10) Robinson and Smith, *J. Chem. Soc.*, **1926**, 2162.

Table 2. Adsorption of Alcohols and Esters by the
"Crushed" Glass Powder.

Volume of Solution (c.c.)	Weight of Adsorbent (g.)	Initial Concentration (g./100 c.c.)	Final Concentration		Amount adsorbed by 1 g. of Adsorbent (mol)
			(g./100 c.c.)	(mol/l.)	
Methyl alcohol/Benzene					
10	5.557	0.1065	0.0998	0.031	0.4×10^{-5}
10	5.615	0.213	0.190	0.059	1.3×10^{-5}
10	4.960	0.426	0.400	0.125	1.6×10^{-5}
10	5.222	0.852	0.808	0.252	2.6×10^{-5}
10	5.950	1.704	1.635	0.510	3.6×10^{-5}
Ethyl alcohol/Benzene					
10	5.657	0.0912	0.0875	0.019	0
10	5.137	0.1823	0.170	0.037	0.5×10^{-5}
10	5.607	0.3645	0.3175	0.069	1.8×10^{-5}
10	5.240	0.729	0.646	0.140	3.4×10^{-5}
10	5.103	1.458	1.365	0.296	4.0×10^{-5}
Propyl alcohol/Benzene					
10	4.811	0.266	0.265	0.044	0
10	4.693	0.532	0.530	0.088	0
10	5.307	0.761	0.752	0.109	0.3×10^{-5}
10	4.767	1.064	1.038	0.173	0.9×10^{-5}
10	5.186	1.308	1.287	0.214	0.7×10^{-5}
10	4.572	1.522	1.505	0.251	0.6×10^{-5}
10	5.080	2.128	2.125	0.354	0
Tetradecyl alcohol/Benzene					
10	5.768	0.526	0.526	0.025	0
10	5.903	1.052	1.052	0.049	0
10	5.218	2.104	2.017	0.094	0.8×10^{-5}
Butyl acetate/Toluene					
10	4.356	0.138	0.113	0.010	0.5×10^{-5}
10	4.333	0.275	0.240	0.021	0.7×10^{-5}
10	5.267	0.551	0.517	0.045	0.5×10^{-5}
10	4.942	1.101	1.080	0.093	0.4×10^{-5}
10	4.299	2.202	2.20	0.189	0
Tripalmitine/Toluene					
10	7.158	0.461	0.461	0.006	0
10	5.995	0.923	0.923	0.012	0
10	6.489	1.845	1.845	0.023	0

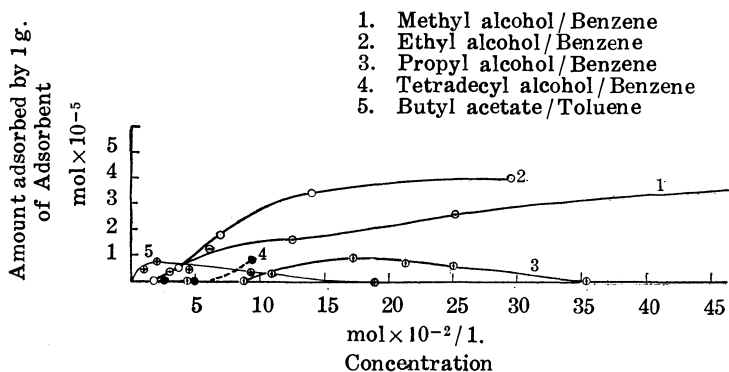


Fig. 2. - Adsorption of Alcohols and Butyl acetate.

tion takes place until the concentration of the solution increases beyond a certain range. This is a remarkable fact that the range of the concentration of the solution, at which any considerable adsorption be observed, is narrow in the case of propyl alcohol, and it seems that some negative adsorption takes place at the higher concentration. For tetradecyl alcohol, this range of the concentration is also limited, because it has the limited solubility.

For butyl acetate and tripalmitine, the amount adsorbed were small. Especially, in the case of tripalmitine, the change of the concentration of the solution was not observed before and after the adsorbing procedure. However, there are many qualitative evidences to consider that tripalmitine is adsorbed. The density difference of tripalmitine and toluene is rather small, and moreover, the size of the molecule of tripalmitine is large, so the numbers of molecule necessary to cover the surface of the adsorbent will be small, and the amount of the adsorption may not be observed by this method. The surface balance analysis was used instead of the float method, since tripalmitine makes a good monomolecular film on the surface of water. Moreover, the "spherical" glass powder of which specific surface area has been known, was used as the adsorbent. The results are shown in Table 3.

Table 3.

Adsorbent: "Spherical" glass powder No. 2. (of which specific surface area is 1810 cm².)
Solution: Tripalmitine/Benzene.

Volume of Solution (c.c.)	Weight of Adsorbent (g.)	Initial conct. (mol/l.)	Final conct. (mol/l.)	Amount adsorbed by 1 g. Adsorbent (mol)	*Area occupied by one molecule.
5	5.328	0.44×10^{-3}	0.40×10^{-3}	0.4×10^{-7}	747 sq. Å
5	5.229	0.88×10^{-3}	0.80×10^{-3}	0.8×10^{-7}	353 "
5	4.709	1.77×10^{-3}	1.51×10^{-3}	2.8×10^{-7}	108 "

* In the tightly packed monomolecular film on the surface of water, the smallest area which one molecule of tripalmitine occupies, is about 66 sq. Å.

From this result, it seems that tripalmitine is hardly adsorbed in the region of the low concentration of the solution. But at the higher concentration of the solution, the adsorption layer approaches to the monomolecular one.

On the Surface of the Glass Powder. As reported in the preceding paper, the amount of benzoic acid adsorbed by 1 g. of the "spherical" glass powder, of which specific surface area is 4700 cm.^2 , is determined to be about 3×10^{-6} mol. By the "crushed" glass powder, as reported in the present paper, this amount is about 1.4×10^{-5} mol. The shape of the particles of this powder are broken and irregular, and the surface area cannot be known. The particle size of this powder was estimated roughly by measuring the sedimentation velocity. As the result, it was found that the radius of the particles are distributed in the range of 3.5–7.5 micron, if the shape of the particle is assumed to be spherical. Taking the average radius to be 5.5 micron, the specific surface area is roughly assumed to be about 2180 cm.^2 . It must be deduced, from the results, that the "crushed" glass powder adsorbs benzoic acid ten times as much as the "spherical" glass powder, with the same surface area. The surface of the "spherical" glass powder went once melted through the melting process, in the course of its preparation, while the surface of the "crushed" glass powder, was left as they have been made by the crushing. The surface area of the "crushed" powder, was estimated to be 2180 cm.^2 which was calculated under the assumption that the shape of the particle is spherical. The true surface area must be, of course, larger than this value owing to the irregularity or the brokenness. The estimation of the area, considering the geometrical shape of the particles, however, may not be larger than three or four times of the value estimated from the assumption that the shape of particles is spherical. Consequently, the two or three times out of the ten times larger adsorbability by the "crushed" powder, might be caused by the great adsorbability at the edges or the points, or otherwise, the existence of crevices and wrinkles has to be assumed. In the case of the adsorption of palmitic acid by the "crushed" powder and by the "spherical" powder, things are also alike to the case of the adsorption of benzoic acid.

It can be supposed, frequently, that the chemical as well as physical natures of the surface of glass might be varied by their treatment, for instance, natural or not (polished or melted). Nevertheless, the experimental informations are scarcely known. The adsorbability by the glass surface reported in the present paper is an example of such cases.

Note on the Results. Results investigated show that carboxylic acids are always and readily adsorbed at the glass-benzene interface, even in the low concentration of the solution. Alcohols are also adsorbed, but they are not so easily adsorbed like carboxylic acid, and the adsorption does not take place until the concentration of the solution increases beyond a certain range. Nitrobenzene, aniline and chlorobenzene are not adsorbed at the glass-benzene interface when the concentration of the solution is as large as about 0.1 mol/l. If the adsorption takes place as the result of the orientation of the adsorbate molecules at the interface, caused by the tendency of the molecules intending to moderate the potential gap, nitrobenzene, aniline and chlorobenzene will be the most adsorbable com-

pounds, since they have large dipole moments⁽¹¹⁾ or the molecular polarizations.

Considering that alcohols and esters are also adsorbed, it cannot be assumed simply that, the adsorption by glass is a kind of the chemical reaction between the acid and the base in the usual sense. It seems a certain radical of a molecule, rather than the dipole moment as a whole, that associates with the adsorption. If the molecule be adsorbed by being approached closely to the atoms or molecules of the adsorbent, the cause of the attraction will not be the moment as a whole, but the local polarity in the molecule. Then, ultimately, the force of the adsorption is not far from the valency force. Among the forces which can be considered, the attraction⁽¹²⁾ caused by the hydrogen bridge between oxygen of glass and —OH radical, for instance, is also possible, but it is not beyond a speculation at present.

It must be noticed that, the substances which can be adsorbed by glass are rather limited and the amount of the adsorption is relatively small, while various substances are adsorbed in much quantity by charcoal, silica gel or alumina gel. It is probable that the mechanism of the adsorption is quite different for the case of the porous substance and the substance of compact surface, and it will not be caused simply by the surface area being large or small.

In conclusion the author wishes to express his hearty thanks to Prof. Jitsusaburo Sameshima for his kind guidance and encouragement. The cost of this research has been defrayed from the Scientific Research Encouragement Grant from the Department of Education, to which the author's thanks are due.

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(11) The dipole moments of benzene derivatives are as follows:—benzoic acid, 1.0; nitrobenzene, 3.90; aniline, 1.52; chlorobenzene, $1.52(\times 10^{-18}$ e.s.u.) (from the appendix of *Trans. Faraday Soc.*, **30** (1934)).

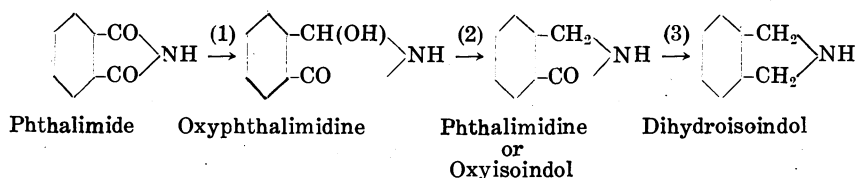
(12) The application of the hydrogen-bridge theory to the sorption by silica gel, was done recently by Elder and Springer. (*J. Phys. Chem.*, **44** (1940), 943.)

Electrolytic Reduction of Isatin and Its Derivatives. I. Reduction of Isatin.

By Buhei SAKURAI.

(Received February 23, 1942.)

In the previous communication⁽¹⁾ it was reported that the electrolytic reduction of phthalimide and its derivatives was found to proceed in the manner represented in the following scheme:



When reduced in a sulphuric acid solution with copper cathode one of the two carbonyls is reduced so as to give oxyphthalimidine, while with lead cathode the reduction goes further on and gives phthalimidine. For the reduction of another carbonyl the cathode with much stronger reducing power, such as zinc amalgam must be used. By using zinc amalgam cathode, powerful reducing action of which has previously been affirmed by Prof. M. Matsui and his collaborators, and by carefully controlling current density and temperature even a complete reduction may, without much difficulty, be achieved. Dihydroisoindol, which could not be obtained by purely chemical reduction of phthalimide, may thus be prepared. In the present experiment the author tried to make investigation on isatin, isomer of phthalimide.

Now, the author deemed it to be very interesting to see how isatin, an isomer of phthalimide, behaves toward the similar reduction process. In phthalimide both carbonyls are situated just in symmetrical position, each combining with carbon and nitrogen in similar manner. But in isatin, though one carbonyl is in combination with carbon and nitrogen as in phthalimide, another carbonyl has rather ketonic structure, combining only with carbon. The main object of this experiment was to ascertain how this difference of structure between phthalimide and isatin influences on their behaviours toward electrolytic reduction.

In purely chemical reduction, hitherto conducted by various authors, isatin was reduced to dioxyindol and further to oxyindol. But in no case the reduction of oxyindol to dihydroindol seems to have as yet succeeded. Spaeth and Breusch⁽²⁾ reported that they obtained dihydroindol by reducing isatin with lead electrode in 50% sulphuric acid. But even in this case the yield of dihydroindol was not more than 4%.

(1) *This Bulletin*, **5** (1930), 184; **7** (1932), 155.

(2) *Monatsch.*, **50** (1928), 349.

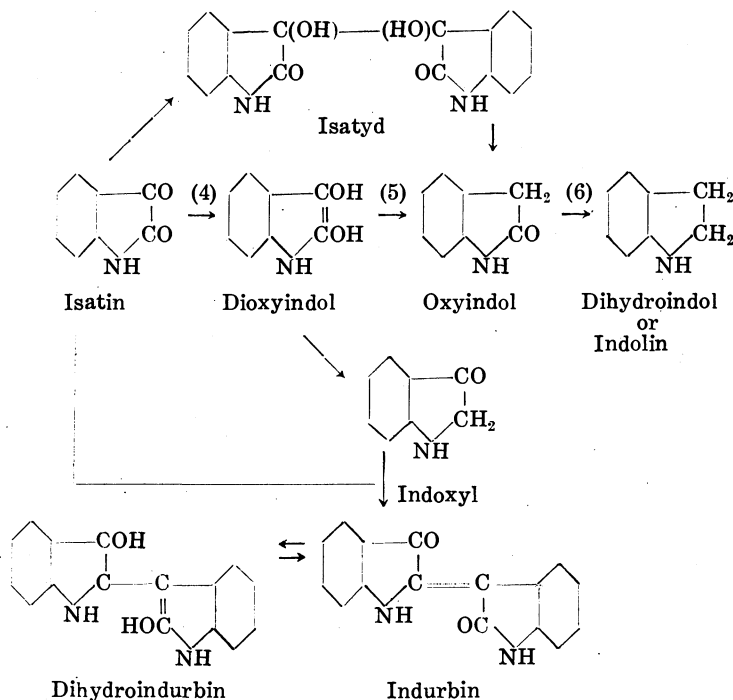
Now taking into consideration what causes had hitherto made the reduction of oxyindol to dihydroindol impossible or at least very unsatisfactory, the author tried to find favourable conditions by which both carbonyls in isatin could be reduced smoothly to $>\text{CH}_2$ group.

According to the author's experiment, weak alkaline solution is more suitable than acid solution for reducing isatin to dioxyindol, and especially the use of sodium bicarbonate seems to render very smooth and constant reduction. As such conditions may be deemed to act favourable in the case of electrolytic reduction too, the author tried to reduce isatin, suspended in the mixture of saturated sodium bicarbonate solution and alcohol, with lead cathode, constantly neutralizing the alkali, produced in the course of electrolysis with carbon dioxide. pH value of the electrolyte remained almost constant at 8.8–9.0. The yield of dioxyindol was satisfactory.

Next, dioxyindol was found to be easily reduced to oxyindol with sodium amalgam. In this case the pH value of solution gives considerable influence on the progress of reduction; if the solution is acidic, no reduction takes place and even if it is alkaline, pH value must be maintained between 7.2 and 7.4. In order to keep electrolyte in this condition, the use of sodium sulphate is most preferable and the alkali produced in the course of electrolysis should be neutralized with sulphuric acid, testing the pH value from time to time by means of test paper. In the electrolysis thus carried out with mercury cathode, oxyindol was produced with a pretty good yield. As it is rather impracticable to keep pH at a constant value by neutralizing alkali from time to time through a long course of electrolysis, an automatic neutralization method was sought, and the use of solid carbon dioxide was at last found to give the best results. It also serves at the same time as a cooling agent. When dioxyindol was reduced under the same condition as with isatin, a great deal of isatyd is produced together with oxyindol, and gradually changes into oxindol through electrolysis. Isatyd may thus be considered as an intermediate product which is produced when isatin is reduced to oxyindol. As dihydroindol is a substance of greater negativity, an acid solution may be regarded as suitable electrolyte for its production. From this consideration 50% sulphuric solution was used and under nearly the same conditions as in (2) electrolysis was conducted with greater current density. The results were satisfactory, producing the complete reduction product with 20% yield. As is apparent from what mentioned above, each intermediate substance, which is produced in the electrolysis of isatin, differently behaves towards electrolytic reduction and especially differs in the pH value, suitable for its reduction. This clearly explains the reason for the failure of the predecessors who attempted to obtain the final reduction product of isatin by using only one and same electrolyte.

When isatin or dioxyindol is reduced under the condition of (5), at the temperature above 20° , the electrolyte assumes red colour on the surface. This coloured substance may be extracted with ether, but its quantity is comparatively small, and is mixed with oxyindol so as to make its isolation difficult. It is, however, doubtlessly indurbin. Indoxyl, being extremely unsuitable, changes into indurbin in the moment it is produced by combining with isatin.

It was found out that indoxyl, though small in quantity, is produced in company with oxyindol, both of which are the immediate reduction products of dioxindyndol. The synopsis of the process of the reduction is formulated as follows:



Experimental.

(1) **Reduction of Isatin to Dioxindyndol.** For this purpose electrolysis was carried out under such conditions as follows:

Cathode: lead plate 100 sq. cm.; Cathodic solution: 60 c.c. of a saturated solution of sodium bicarbonate and 40 c.c. of alcohol, in which 5 g. of isatin were suspended; Anode: lead plate; Anodic solution: a saturated solution of sodium bicarbonate; Current density: 2.5 amp. per 100 sq. cm.; Time of electrolysis: 2.5 hours; Current quantity: 6.8 Faraday per mol.; Temperature: 16°-20°.

Here the pH value of the catholyte was kept constantly between 9-10 by passing CO₂ gas into the catholyte for neutralization. As the electrolysis advanced, isatin turned brown by degree, and in an hour and a half its colour disappeared almost completely. After 2.5 hours' electrolysis the deposit was filtered, and re-crystallized from acetone, whereupon yellow-brown needle-like crystals, melting at 168°, were obtained. This was dioxindyndol. The yield (4.6 g.) was calculated to be 85%. When the filtrate was made acidic and extracted with ether, a bit of red needle-like crystals of isatin were isolated from the ether extract.

When copper, silver, or nickel is substituted for lead as cathode, electrolysis takes much longer time and the yield lowers slightly, but

dioxyindol can be obtained easily. For instance, when copper or silver was used as cathode with the other conditions unchanged, electrolysis took 2.5 hours until the red colour of isatin had completely disappeared and the yield of dioxyindol was 75% and 41.5% respectively. Higher temperature of the electrolyte, lowers the yield. Perhaps it brings forth evolution of carbon dioxide and makes it difficult to keep the pH of the catholyte at favourable value.

(2) **Reduction of Isatin to Oxyindol.** In the reduction of isatin to oxyindol the use of electrode, which has a strong reducing power or of high current density, is by no means helpful, if reduction is conducted with sodium bicarbonate solution. When sulphuric acid solution is employed as electrolyte, the results are still worse, giving no appreciable progress of reduction. Accordingly electrolysis was performed with neutral Na_2SO_4 solution using mercury as cathode and carefully neutralizing the alkali, thereby produced. The electrolysis was conducted as follows:

Cathode: mercury 1 cm. dip and 16 sq. cm. of surface area; Cathodic solution: mixture of 90 c.c. of 10% sodium sulphate solution and 10 c.c. of alcohol, in which 5 g. of isatin were suspended; Anode: lead plate; Anodic solution: 10% solution of sodium sulphate; Current density: 15.6 amp. per 100 sq. cm.; Time of electrolysis: 6 hours; Current quantity: 16.3 Faraday per mol.; Temperature: 17°–20°.

The electrolysis was carried out by cooling the electrolytic bath from outside with ice and stirring it vigorously. In order to neutralize alkali in the course of electrolysis, about 10% dilute sulphuric acid was added drop by drop from the capillary tube prepared at one end of a separating funnel and the pH value was kept between 7.2 and 7.4 testing it constantly by means of brom-thymol-blue paper. In two hours the catholyte turned from orange-yellow gradually to yellow-brown. The amount of the sulphuric acid, required for neutralization, was small at first in spite of the constant current density, but gradually increased till at last it became almost constant.

The electrolyte, taken out after electrolysis, contained yellow-brown deposit, which was filtered (1.0 g.) and re-crystallized from acetone. This melted at 170° and was confirmed to be dioxyindol, the yield of which amounts to 19.7%. The ether extract of the filtrate coloured reddish. From this extract 0.4 g. of red crystals, melting at 120°, was obtained. This was examined on the microscope and found to be a mixture of colourless and red crystals. This was put in a crystal dish covered with the bottom of a flask filled with water and was slowly heated on a sand-bath, when colourless plate first, and then a small amount of red needle crystals were obtained. The former was oxyindol, melting at 126°, and the latter was doubtlessly indurbin, inferring from the fact that it was hard to melt but readily soluble in alcohol or ether, and when reduced with sodium amalgam, it became colourless. When shaken with ether, it gradually dissolves in the ether, thereby resuming red colour. Now the filtrate was slightly acidic with sulphuric acid, extracted with ether, when 1.0 g. of oxyindol was procured. The amount of total oxyindol was calculated to correspond to 31%.

Next, the remaining slightly acidic electrolyte was evaporated to dryness on the water-bath, and the residue was extracted with acetone, when 1.0 g. of yellow crystals was obtained after the evaporation of the solvent. This substance, melting at 243° , was evidently isatyd obtained through the reduction of isatin by ammonia sulphate. This was reduced to oxindol electrolytically under the same condition as in the case of isatin.

As the composition of electrolyte greatly influences the manner of reduction, a series of experiments were carried out by varying the composition of electrolyte, the results of which are summarized as follows:

Composition of Cathodic Solution (c.c.)		Reduction Product (%)		
10% soln. of Na_2SO_4	alcohol	dioxyindol	oxyindol	isatyd
90	10	19.7	31.0	20.1
80	20	59.9	11.1	15.3
70	30	64.9	4.4	10.0
60	40	67.5	3.0	5.8
50	50	69.1	2.6	4.5

As this experiment is rather time-wasting, another convenient method was adopted, in which solidified carbon dioxide (ordinary dry ice) was thrown into the catholyte, thereby performing neutralization and cooling at the same time. This brought in almost as good results as the former.

(3) **Reduction of dioxyindol to oxyindol.** 5 g. of dioxyindol was electrolyzed under the same condition as in the reduction of isatin to oxyindol. 1.7 g. (38%) of oxyindol were obtained after 1.5 hours' electrolysis.

(4) **Reduction of oxyindol to dihydroindol.** In order to reduce oxyindol further to dihydroindol, zinc amalgam was used as cathode and sulphuric acid was employed as electrolyte. Electrolysis was carried out under the following conditions:

Cathode: zinc amalgam 1.58 sq. cm.; Cathodic solution: mixture of 50 c.c. of 50% sulphuric acid and 50 c.c. of alcohol, in which 2 g. of oxyindol were dissolved; Anode: lead plate; Anodic solution: 50% sulphuric acid; Current density: 68.8 amp. per 100 sq. cm.; Temperature: 23° ; Time of electrolysis: 6.0 hours; Current quantity; 327 F. per mol.

Electrolysis was conducted by cooling the electrolyte chamber from outside by putting it in a water-bath full of ice water, and from inside by passing cold water through a spiral lead tube inserted to the catholyte, thereby preventing the rise of temperature. The catholyte was always kept vigorously stirring. In three hours oxyindol had completely dissolved. The electrolyte was taken out after electrolysis, and when it was made alkaline with caustic soda, ammonia-like smell came out; thereupon it was subjected to steam distillation, collecting the distillate in dilute hydrochloric acid solution as long as it continued to react alkaline. The hydrochloric acid solution was then evaporated to dryness, when 0.52 g. of white substance, melting at 218° , was left as residue. On the other hand, a part of the electrolyte was made alkaline with a caustic soda solution and its ether extract was treated with picric acid, when needle-like

colourless crystals, melting at 169° , were obtained. These two products are evidently the chloride, and the picric, of dihydroindol respectively, and the yield was found to be 20%.

In connection with this research the author expresses his sincere thanks to Dr. Matsui, Professor emeritus of the Kyoto Imperial University for his unsparing suggestions and also to the Japan Society for the Promotion of Scientific Research for their kindness of giving him a part of his research expense.

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The Oxygen Effect in the Hydrogen Bromide Catalysis of the Addition Reaction of Bromine to Cinnamic Acid in Carbon Tetrachloride Solution.

By Osamu SIMAMURA.

(Received March 27, 1942.)

The addition reaction of bromine to ethenoid compounds is affected by a number of factors, e.g., the nature of walls of reaction vessels, exposure to light, and presence of oxygen, hydrogen bromide, etc.; therefore, a rigid control of experimental conditions is required to secure any significant results. The discovery by D. M. Williams and T. C. James⁽¹⁾, that hydrogen bromide, eliminating the induction period observed in addition reactions of bromine to certain ethenoid compounds, accelerates the reactions to a great extent, is of general importance, for at least some of the irregularities often observed in the bromine addition under apparently identical conditions could be attributed to the effect of hydrogen bromide present as an impurity or produced by accompanying substitution reaction in the course of the addition reactions. S. V. Anantakrishnan and R. Venkataraman⁽²⁾ have tentatively suggested for the catalysis a mechanism involving the polarisation of the double bond and the activation of the bromine molecule by hydrogen bromide. This is far from satisfactory especially because the nature of the proposed activation is yet to be explained.

On the other hand, oxygen was found to inhibit the photochemical addition of chlorine to tetrachloroethylene in gas phase⁽³⁾ and in carbon

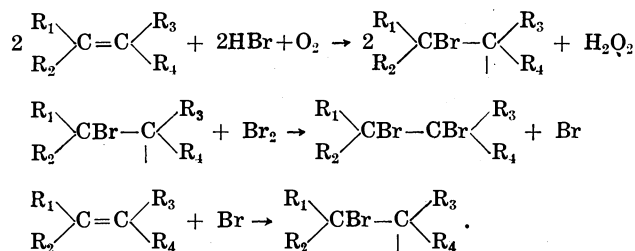
(1) D. M. Williams and T. C. James, *J. Chem. Soc.*, **1928**, 343.

(2) S. V. Anantakrishnan and R. Venkataraman, *ibid.*, **1939**, 224.

(3) R. G. Dickinson and J. L. Carrico, *J. Am. Chem. Soc.*, **56** (1934), 1473.

tetrachloride solution⁽⁴⁾; and subsequently W. H. Bauer and F. Daniels⁽⁵⁾ showed that also in the dark oxygen exerts an inhibitory effect on the bromine addition to cinnamic acid in carbon tetrachloride. Y. Urushibara and M. Takebayashi⁽⁶⁾ investigated the reaction with varying amounts of oxygen: the rate decreased sharply as the amount of oxygen increased. They also found an accelerating influence of benzoyl peroxide. The inhibitory effect of oxygen in the photochemical bromination is now explained⁽⁷⁾ as the result of capture by oxygen of free bromo radicals which would otherwise react with bromine to propagate the chains started by the action of light.

Earlier investigators in the field of the addition reactions of bromine paid no attention to the effect of oxygen and worked in the presence of air, although some of them excluded light deliberately to avoid the incursion of the photochemical process. In view of the inhibitory effect of oxygen the induction period is considered to be in all probability due to oxygen and it seemed that hydrogen bromide might not be in itself a catalyst for the addition of bromine, but its role might consist in the removal of oxygen inadvertently present in the reacting solution, thus restoring the reaction to its normal course. There was, however, an alternative: The researches⁽⁸⁾ in this laboratory on the oxygen effect in the addition of hydrogen bromide to ethenoid compounds have revealed that hydrogen bromide reacts with oxygen in the presence of ethenoid compounds, free bromo radicals being intermediately formed. If bromine is allowed to add in the presence of hydrogen bromide and oxygen, it will react with the bromo radical thus produced to yield the final product of the addition reaction and a bromine atom, which will attach itself to a molecule of the ethenoid compound regenerating another bromo radical, and this in turn will react with bromine to continue the chain reaction:



The chains propagated by these radicals and atoms are essentially identical with those generally postulated for photochemical addition reactions. Thus, in this mechanism oxygen and hydrogen bromide will co-operate in causing a rapid addition reaction. The latter possibility has been proved

(4) R. G. Dickinson and J. A. Leermakers, *J. Am. Chem. Soc.*, **54** (1932), 3852; J. A. Leermakers and R. G. Dickinson, *ibid.*, **54** (1932), 4648.

(5) W. H. Bauer and F. Daniels, *ibid.*, **56** (1934), 2014.

(6) Y. Urushibara and M. Takebayashi, this Bulletin, **12** (1937), 356, 499.

(7) R. F. Brown and F. Daniels, *J. Am. Chem. Soc.*, **62** (1940), 2820; W. Bockemüller and L. Pfeuffer, *Ann.*, **537** (1939), 178.

(8) Y. Urushibara, *J. Chem. Soc. Japan*, **60** (1939), 717; Y. Urushibara and O. Simamura, this Bulletin, **14** (1939), 323; O. Simamura, *ibid.*, **15** (1940), 292.

to be the case in the bromine addition of cinnamic acid in carbon tetrachloride solution as will be discussed in the present paper on the basis of the experiments conducted with due consideration for the effects of oxygen and hydrogen bromide.

Materials. Commercial bromine of chemically pure grade was shaken with water,⁽⁹⁾ refluxed with aqueous potassium bromide, and distilled. It was then dried by shaking with concentrated sulphuric acid and finally fractionated under reduced pressure. Cinnamic acid was purified by recrystallisation from hot water and then from aqueous alcohol.

Carbon tetrachloride was refluxed with an alkaline permanganate solution, dried with anhydrous calcium chloride, and distilled through a Widmer column. The boiling range was less than 0.1°. Then it was shaken with phosphorus pentoxide and distilled, the middle fraction being collected.

Hydrogen bromide was generated by dropping bromine to hot tetralin, passed through a washing bottle containing cold tetralin and then through a tube filled with anthracene. The gas was dried with phosphorus pentoxide and collected in a tube cooled with liquid air. Then the condensed hydrogen bromide was subjected to repeated melting and solidification followed by evacuation to eliminate traces of incondensable gases and finally to fractionation, the middle portion being used.

Hydrogen chloride was generated by dropping concentrated hydrochloric acid to concentrated sulphuric acid, bubbled through concentrated sulphuric acid, collected in a bulb cooled with liquid air, and purified in the same way as hydrogen bromide.

Experimental Procedure. The general procedure was as follows: In a glass tube with a capacity of 57 c.c. a small sealed bulb containing an accurately weighed amount of bromine (0.13–0.15 g.) was placed and a measured quantity of a carbon tetrachloride solution (about 20 c.c.) of cinnamic acid (the concentration, 0.034 mol./l.) was introduced from a burette so that, when the bulb with bromine was broken, a solution containing 0.045 mole of bromine per litre might result. The level of the meniscus of the solution was marked on the tube by labelling a strip of paper and 5 c.c. of carbon tetrachloride was added. The tube was connected to the vacuum line and evacuated. Carbon tetrachloride was distilled off until the meniscus reached the mark, the tube was then cooled with liquid air and further evacuated with a mercury diffusion pump. Such a procedure of removing oxygen dissolved in the carbon tetrachloride solution was adopted in preference to repeated solidification of the solution by cooling with liquid air, followed by evacuation and melting, because the former was far more rapid, although it involved a slight but unimportant sacrifice of accuracy in the concentration of the solution. Then a measured volume of hydrogen bromide gas was condensed on the top of the solidified mixture, oxygen was introduced to a specified pressure, and the tube was sealed off and taken out of the liquid air bath. It was protected from light throughout the procedure after the admission of hydrogen bromide. When the contents of the tube melted, which took usually 45 minutes, the reaction was started by breaking the bulb containing bromine by shaking the sealed tube. The tube was left in the dark at room temperature (10 to 12°) for eleven hours and twenty minutes. Then its tip was broken in a two percent aqueous solution of potassium iodide and the liberated iodine was titrated with decinormal thiosulphate.

The Uncatalyzed Addition and the Effect of Oxygen. Typical examples of the results are summarized in the accompanying table. Extent of addition in the last column denotes the percentage of the cinnamic acid which reacted with bromine in eleven hours and twenty minutes as calculated from the decrease in the amount of bromine. The reaction in the absence of added substances was not reproducible, the extent of addi-

(9) P.C.E.M. Terwogt, *Z. anorg. Chem.*, **47** (1905), 203.

tion ranging from 45 to 55% (Exp. 22 and 35). It is not certain whether this was caused by small traces of oxygen which may have been still present in the reaction mixture or by any other disturbing factors which escaped experimental control. Nevertheless, it is clear that the reaction occurred much faster in the absence of oxygen than in the presence, as 0.13

Table. The Addition of Bromine to Cinnamic Acid in Carbon Tetrachloride Solution in the Dark. Reaction temperature, 10–12°C; reaction time, 11 hours 20 minutes; bromine (0.13–0.15 g.), 0.045 mol./l.; cinnamic acid, 0.034 mol./l.

Exp. No.	Added Substances (millimole)	Extent of Addition (%)
22	None	45.3
35	None	55.1
2*	O ₂ , 0.11	11.1
11	O ₂ , 0.13	8.1
17	HBr, 0.92	32.8
18	HBr, 0.92	35.4
40	HBr, 0.92	36.4
25	HBr, 0.18	25.0
39	HBr, 0.18	22.2
19	HBr, 0.92; O ₂ , 0.02	89.7
20	HBr, 0.92; O ₂ , 0.05	99.2
26	HBr, 0.20; O ₂ , 0.02	98.0
27	HBr, 0.20; O ₂ , 0.09	96.8
28	HBr, 0.20; O ₂ , 0.21	94.5
31	HCl, 0.18	27.4
32	HCl, 0.92	14.6
33	HCl, 0.18; O ₂ , 0.11	2.6
34	HCl, 0.92; O ₂ , 0.11	3.6
36	Catechol, 5 mg.	27.3†
42	Catechol, 5 mg.; HBr, 0.18; O ₂ , 0.02	30.5†
23	Tetrabromohydroquinone, 20 mg.	5.5
29	Tetrabromohydroquinone, 25 mg.; HBr, 0.37; O ₂ , 0.11	94.1
37	H ₂ O, 2.3 mg.	41.0
38	H ₂ O, 2.3 mg.; HBr, 0.18	47.5

* The reaction time 17 hours 40 minutes.

† Apparent extent of addition.

admitted, the extent of addition being distinctly less with a smaller amount of hydrogen bromide (Exp. 25 and 39) than with a larger amount (Exp. 17, 18, and 40). The observed facts may be due to the contamination of hydrogen bromide or other reagents with traces of oxygen, the simultaneous presence of hydrogen bromide and oxygen accelerating the addition reaction as will be discussed below. Oxygen, however, must have been present in a very small amount, because the

millimole of oxygen admitted (of which 0.018 millimole is dissolved in the solution⁽¹⁰⁾) diminished the extent of addition to 8% (Exp. 11). These values are considered to be reasonable in comparison with those obtained by Y. Urushibara and M. Takebayashi⁽⁶⁾, if differences in the experimental conditions, especially in temperature and reaction time, are taken into account.

Effect of Hydrogen Bromide. Contrary to the expectation from existing experimental data it was found that in the presence of hydrogen bromide the reaction never proceeded faster than in the absence. It appears rather to exert a retarding effect. Complication arises, however, because the retardation did not increase with the amount of hydrogen bromide

(10) Calculated from the distribution coefficient of oxygen given by J. Horiuti, *Sci. Papers Inst. Phys. Chem. Research* (Tokyo), **17** (1931), 213.

retardation due to hydrogen bromide was overcome only partly in spite of the strong accelerating effect of oxygen and hydrogen bromide; it seems that the retardation by hydrogen bromide increases not so sharply with the amount of hydrogen bromide as the counteracting acceleration by oxygen and hydrogen bromide does. The hypothesis suggested by S. V. Anantakrishnan and R. Venkataraman⁽²⁾ that hydrogen bromide activates the reactants is no longer tenable.

Combined Action of Hydrogen Bromide and Oxygen. Experiments were carried out with 0.20 to 0.92 millimole of hydrogen bromide and 0.02 to 0.21 millimole of oxygen. The extents of addition were greater than 90% under these experimental conditions, showing that the reaction proceeds faster in the presence of both hydrogen bromide and oxygen together than in the absence of either or even both of them. This demonstrates convincingly the anticipated co-operation of hydrogen bromide and oxygen in causing a rapid addition reaction; and the possibility already referred to, that hydrogen bromide might be effective by merely eliminating the inhibiting oxygen, is excluded. On the basis of the data obtained, however, nothing can be said with regard to how the extent of addition is influenced by variation in amounts of the admitted gases.

Influence of Hydrogen Chloride. In contrast with the experiments with hydrogen bromide and oxygen, when hydrogen chloride was substituted for hydrogen bromide, no acceleration was observed at all, the pronounced inhibition being due to oxygen. If traces of oxygen which might still be present in the hydrogen chloride purified by fractionation in vacuum were not sufficient to reduce the rate of addition markedly, the fact that the extent of addition in Exp. 32 was found lower than Exp. 31 may be considered to indicate a retardation by hydrogen chloride. Its failure to co-operate with oxygen shows that the role of hydrogen bromide is as unique here in the bromine addition as in the addition of hydrogen bromide to ethenoid compounds in the presence of oxygen⁽¹¹⁾ and in the cis-trans isomerisation⁽¹²⁾ caused by the joint action of hydrogen bromide and oxygen; consequently a natural inference is that a common mechanism is in operation in all these reactions.

Effect of Antioxidants. A further evidence to support this view is afforded by the experiments in which the effects of antioxidants were examined. When 5 mg. (4.6×10^{-5} mole) of catechol was added to the reaction mixture, the extent of addition was diminished to about 30% whether both hydrogen bromide and oxygen were present or not. The extent of addition was only apparent in this case, because catechol consumed bromine. A separate experiment showed that one mole of catechol reacted with two moles of bromine in three hours and with a little more in seven hours, the concentrations of the reactants being the same as those obtaining in the addition reaction, whereas Zincke⁽¹³⁾ stated that he

(11) A series of papers by Y. Urushibara and M. Takebayashi beginning with this Bulletin, **11** (1936), 692. Cf. reference 8.

(12) Y. Urushibara and O. Simamura, this Bulletin, **12** (1937), 507; **13** (1938), 566. O. Simamura, *ibid.*, **14** (1939), 294.

(13) Th. Zincke, *Ber.*, **20** (1887), 1777.

obtained tetrabromocatechol by the action of bromine on catechol in chloroform. On the assumption that one mole of catechol reacted with two moles of bromine, the extent of addition for Exp. 36 and 42 are to be corrected to 13.6 and 18.5%, respectively. If the action of bromine on catechol in the reaction mixture yielded tetrabromocatechol, the corrected values should be zero and 3.1%, respectively. In any case the effectiveness of catechol in repressing the joint action of hydrogen bromide and oxygen has been demonstrated beyond doubt. Catechol represses the oxygen effect also in the addition of hydrogen bromide and in the cis-trans isomerisation. The similarity in this respect substantiates the view that a common mechanism is operating.

Tetrabromohydroquinone, with no nuclear hydrogen to react with bromine, was examined. Twenty mg. of it added to the reacting solution, though the greater part remained undissolved, was found to retard the uncatalyzed reaction of bromine, but it could not repress the rapid reaction caused by hydrogen bromide and oxygen. Its ineffectiveness may be attributed to its low solubility in carbon tetrachloride.

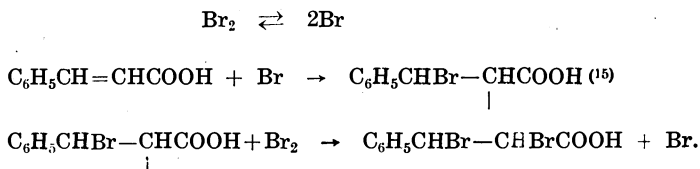
A significance to be attached to the retardation of the uncatalyzed reaction by catechol and tetrabromohydroquinone will be discussed below.

Effect of Water. In the reaction of hydrogen bromide and oxygen in the presence of the ethenoid compound water is one of the final products⁽⁸⁾; therefore, the effect of traces of water had to be investigated to ascertain that it would not be an important agent in the catalysis by hydrogen bromide and oxygen. Water was introduced into the reaction tube, which had been evacuated and cooled with liquid air as described above, by heating sodium sulphate decahydrate, contained in an amount to yield 1.3×10^{-4} mole of water in a tube connected to the vacuum line. This amount of water nearly saturated the carbon tetrachloride solution.⁽¹⁴⁾ Now, water was found to exert no conspicuous effect on the addition of bromine in the absence of any other added substances, but it compensated partly the slight retardation by hydrogen bromide. Inasmuch as the amount of water introduced here is much greater than what would have been produced by the complete conversion of the oxygen admitted (0.02 millimole) in Exp. 26, for which the extent of addition was 98.0%, it is concluded that the enormous effect caused by the joint action of oxygen and hydrogen bromide cannot be attributed to the action of water to be ultimately formed from them.

Conclusion. On the basis of the observations fully discussed above the nature of the hydrogen bromide catalysis in the addition of bromine to cinnamic acid has been elucidated. Thus, in order that hydrogen bromide can exert a catalytic action, the co-operation of oxygen is necessary. They start the chain reaction involving bromine atoms and free radicals just as exposure of the reaction mixture to light does. A generalisation of the proposed mechanism will no doubt be feasible in view of numerous instances of "the hydrogen bromide catalysis in the addition reaction of bromine" recorded in the literature.

(14) Cf. Rosenbaum and Walton, *J. Am. Chem. Soc.*, **52** (1930), 3571.

The effectiveness of antioxidants, such as catechol and tetrabromohydroquinone, in preventing the uncatalysed addition of bromine in the dark in carbon tetrachloride solution as well as that of oxygen is understandable if it is assumed that the chain mechanism as shown in the following scheme is predominantly in operation also in the dark and that they inhibit the reaction by functioning as chain breakers.



The view is favoured by the theoretical consideration by A. Sherman, O. T. Quimby, and R. O. Sutherland⁽¹⁷⁾, who, on the basis of the semi-empirical calculation of activation energies, were led to expect that the addition of bromine to an ethenoid double bond might follow the course involving bromine atoms and free radicals rather than that involving the bimolecular combination of bromine with a double bond. The calculation applies only to the reaction in gas phase, but it is not unreasonable to assume that carbon tetrachloride as a solvent would cause no appreciable change in the activation energies of the reaction.

Summary.

It has been found that a joint action of hydrogen bromide and oxygen accelerates the addition of bromine to cinnamic acid in carbon tetrachloride solution in the dark, whereas the reaction is retarded by either of them. The catalyzed reaction is prevented by catechol, and hydrogen chloride cannot be substituted for hydrogen bromide without the disappearance of the accelerating effect. On the basis of these observations the nature of the alleged catalysis of the addition of bromine by hydrogen bromide has been elucidated. The elimination of the induction period, which is certainly attributable to the inhibitory action of oxygen, is not due to the removal of the latter. The explanation offered is that hydrogen bromide and an ethenoid compound in co-operation with the very oxygen starts a rapid chain reaction involving bromine atoms and free radicals. Also for the uncatalyzed addition of bromine to cinnamic acid in carbon

(15) In this scheme the bromine atom is assumed to attach itself to the β carbon atom of cinnamic acid, because crotonic acid has been found to add hydrogen bromide to yield β -bromobutyric acid even in the presence of oxygen, i.e., under the conditions where the mechanism involving bromine atoms is operative,⁽¹⁶⁾ and cinnamic acid is known to give always β -bromohydrocinnamic acid.⁽¹⁷⁾

(16) O. Simamura, shortly published in this Bulletin.

(17) A. Michael, *J. Org. Chem.*, **4** (1939), 123.

(18) A. Sherman, O. T. Quimby and R. O. Sutherland, *J. Chem. Phys.*, **4** (1936),

tetrachloride a possibility of a mechanism involving chains has been suggested.

The author expresses his sincere thanks to Prof. Y. Urushibara for his kind guidance and encouragement throughout this work. Thanks are also due to the Imperial Academy for a grant.

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On the Metallo-organic Compounds. XI. Trialkyltin Sulphide, $R_3SnSSnR_3$.

By Taichi HARADA.

(Received March 31, 1942.)

Recently Kraus and Sessions⁽¹⁾ have shown that the trimethyltin group combines slowly with sulphur in benzene solution to form trimethyltin sulphide. The method, however, is disadvantageous for the preparation because the process is troublesome and gives a poor yield, therefore, the present investigation was carried out.

Trialkyltin sulphide is easily obtained from alcoholic solution by the following reaction.



R = alkyl group, X = halogen

Trialkyltin sulphide is a colourless liquid in general and soluble in ordinary organic solvents but insoluble in water. It reacts with a strong mineral acid, such as hydrochloric acid, to form trialkyltin chloride with evolution of hydrogen sulphide according to the equation:



Table. Physical Properties of Trialkyltin Sulphides.

	$((CH_3)_3Sn)_2S$	$((C_2H_5)_3Sn)_2S$	$((n-C_7H_7)_3Sn)_2S$
b.p.	118 ¹⁸ mm	187—188 ²⁰ mm	215—219 ¹⁸ mm
m.p.	7	colourless liquid	colourless liquid
Sp. g. at 35°	1.6392	1.4216	1.2110
R. I. at 18°	1.5592	1.5470	1.5290

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

Experimental. Trimethyltin Sulphide: Trimethyltin iodide was treated with Na_2S in absolute alcohol and the solvent was distilled off. The residue was treated with ether after the addition of water. The ethereal solution was dried with anhydrous Na_2SO_4 and finally it was subjected to vacuum distillation. Trimethyltin sulphide thus prepared is a colourless oily liquid with a strong disagreeable odour; b.p. $118^{18\text{mm}}$; m.p., 7°C .

It is soluble in ether, petroleum ether, benzene but insoluble in water. It reacts with hydrochloric acid with evolution of hydrogen sulphide and produces the acid derivative, trimethyltin chloride.

Anal. Subs., 0.3095: SnO_2 , 0.2597.

Calcd. for $\text{C}_6\text{H}_{18}\text{Sn}_2\text{S}$: Sn, 66.02.

Found: Sn, 65.91.

Triethyltin Sulphide: This compound was prepared in the same way as trimethyltin sulphide. It is a colourless liquid (b.p. $187\text{--}188^{20\text{mm}}$). It is soluble in ordinary organic solvents and insoluble in water.

Anal. Subs., 0.5355: SnO_2 , 0.3644 and BaSO_4 , 0.2727.

Calcd. for $\text{C}_{12}\text{H}_{30}\text{Sn}_2\text{S}$, Sn and S, 53.51 and 7.20.

Found: Sn, 53.60 and S, 7.03.

(1) M.W. of the Subs. in Benzene (Cryoscopic Method)

Subs.	Conc (%)	ΔT	$\text{C}_6\text{H}_6(\text{c.c.})$ at 20°C	Obs. M.W.
0.7566	3.328	0.397	25	425
"	2.107	0.243	40	425
"	1.582	0.178	55	431

(2) M.W. of the Subs. in Naphthalene (Cryoscopic Method)

Subs.	Conc (%)	ΔT	C_{10}H_8 (g.)	Obs. M.W.
0.8142	3.809	0.631	20.30	439
"	2.708	0.431	29.25	446
"	1.859	0.296	42.99	442

Calcd. for $((\text{C}_2\text{H}_5)_3\text{Sn})_2\text{S}$. M.W., 443.7.

Tri-*n*-propyltin Sulphide. This compound was prepared in the same way as trimethyltin and triethyltin sulphides. It is a colourless liquid (b.p., $215\text{--}219^{18\text{mm}}$) and is soluble in organic solvents but insoluble in water.

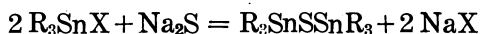
Anal. Subs., 0.4034: SnO_2 , 0.2300; BaSO_4 , 0.1777.

Calcd. for $\text{C}_{18}\text{H}_{42}\text{Sn}_2\text{S}$: Sn, 44.98 and S, 6.07.

Found: Sn, 44.90 and S, 6.05.

Summary.

Trialkyltin sulphide has been prepared according to the reaction:



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On the Metallo-organic Compounds. XII. Dialkyltin Sulphide R_2SnS (or tri-thio-anhydro-tris-dialkylstanne-dithiol $(R_2SnS)_3$).

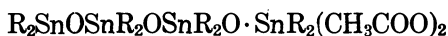
By Taichi HARADA.

(Received March 31, 1942.)

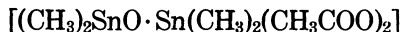
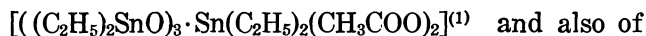
In the previous papers⁽¹⁾ the author described that dialkyltin halide and the diacetate combined with dialkyltin oxide in the ratio 1:3 to form the complex compounds.



(where R' represents the alkyl radical or hydrogen of the solvent alcohol or water) and



The formation of $R'OSnR_2OSnR_2OSnR_2OR'$ and $SnR_2OSnR_2OSnR_2O$ in the compounds may be regarded as the condensation product of three molecules of $R_2Sn(OR')(OH)$ formed previously by the interaction of R_2SnO with $R'OH$ under a given condition. It is pointed out, therefore, that tri-anhydro-tris-dialkylstanne-diol is the product formed by the elimination of one molecule of water from di-anhydro-tris-dialkylstanne-diol $H(R_2SnO)_3OH$. The correctness of this assumption is supported further by the results of molecular weight determination of



described below. The latter compound is very slightly soluble in such organic solvents as alcohol, benzene, naphthalene, etc., but fairly soluble when they are hot; hence the molecular weight of this compound was determined in naphthalene by its freezing-point method.

In a concentrated solution the determination gives a value which indicates that the compound is in a trimolecular form while as the solution becomes dilute the value decreases to a certain extent, indicating dissociation; that is, at 2.906, 1.672 and 1.396% concentrations the depressions were 0.113, 0.113 and 0.128°C. respectively. As these figures give molecular weights of 1268, 882 and 763 respectively (Calcd. for the trimolecular one



Therefore, dialkyltin oxide might have the six-membered hetero-cyclic structure:



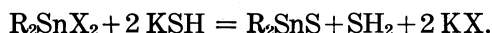
(1) T. Harada, *Sci. Papers Inst. Phys. Chem. Research* (Tokyo), **35** (1939), 290; **36** (1939), 497; **38** (1940), 146.

It is difficult, however, to determine the molecular weight of the compound owing to its insolubility in all solvents.

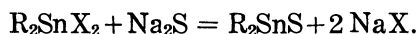
Dialkyltin sulphide resembles dialkyltin oxide in the type of reactions and in its constitution: that is, the compound is regarded as one wherein the oxygen is replaced by sulphur, and therefore, many similarities might be expected to exist between them. Contrary to the insolubility of the former, the latter is soluble in certain organic solvents. We expected that the result of the molecular weight determination of the sulphide will give a notion regarding the structure of the oxide. For this purpose the present investigation was carried out.

Recently Kotscheschkow⁽²⁾ obtained dimethyltin sulphide as a precipitate by saturating the aqueous solution of dimethyltin dichloride with hydrogen sulphide. The nature of the compound, however, is not disclosed except the melting point 148°C.

Dialkyltin sulphide is easily prepared by treating dialkyltin dihalide with KSH in absolute alcohol saturated with H₂S, therefore, the reaction may be represented as follows:



Both dimethyltin sulphide and diethyltin sulphide are colourless crystals, and the former melts at 149°C., the latter at 24°C. These compounds are also formed when the dialkyltin dihalide is treated with Na₂S in boiling alcohol according to the reaction:



The compound reacts with a strong mineral acid such as hydrochloric acid for example, producing the dialkyltin dihalide with evolution of hydrogen sulphide. The structure of these sulphides must be represented as the six-membered hetero-cyclic one



since the molecular weight determination in benzene and in naphthalene becomes three times the mono-molecular one. Therefore, the structure of the dialkyltin oxide (R₂SnO)₃ in



must be represented in a similar way. However, the sulphide has no tendency to combine with the corresponding dihalide or diacetate to form a complex compound as in the oxide. This is expected to be unlike the nature of oxygen which makes them able to extend secondary valencies producing complex compounds.

Experimental. Dimethyltin sulphide or tri-thio-anhydro-tris-dimethyltin-dithiol: Dimethyltin diiodide was treated with KSH in absolute alcohol saturated with H₂S, then the solution of the mixture was

extracted with ether after the addition of water. On evaporation of ether, colourless crystals were formed, m.p., 149°C .

(2) Dimethyltin diiodide was dissolved in absolute alcohol and was treated with Na_2S by heating until the solution indicated to be neutral or alkaline. The solvent was evaporated and a large amount of water was added. In this way a white substance separated out. The substance was extracted with ether. On evaporation of the solvent after filtration, a crystalline compound was formed which was identical with the compound formed by method I. Dimethyltin sulphide is difficultly soluble in hot alcohol but easily soluble in ether, benzene, naphthalene, etc.

Anal. Subs., 0.2749: SnO_2 , 0.2288, BaSO_4 , 0.3558.

Subs., 0.4430: SnO_2 , 0.3701, BaSO_4 , 0.5522.

Calcd. for $\text{C}_4\text{H}_6\text{SnS}$, Sn and S, 65.65 and 17.73.

Found: Sn, 65.66, S, 17.78, Sn, 65.77, S, 17.35.

(1) M.W. of the Subs. in Benzene (Cryoscopic Method)

Subs.	Conc. (%)	ΔT	C_6H_6 (c.c.) at 20°	Obs. M.W.
0.7566	5.191	0.505	25	543
"	3.309	0.315	40	543

(2) M.W. of the Subs. in Naphthalene (Cryoscopic Method)

Subs.	Conc. (%)	ΔT	C_{10}H_8 (g.)	Obs. M.W.
0.9208	4.403	0.610	19.99	541
"	3.262	0.430	27.31	541
"	2.705	0.355	33.12	542

Calcd. for $(\text{CH}_3)_2\text{SnS}$, M.W., 180.8 and for $((\text{CH}_3)_2\text{SnS})_3$, M.W., 542.4.

Diethyltin sulphide or tri-thio-anhydro-tris-diethyltin-dithiol: Diethyltin dibromide was treated with Na_2S in absolute alcohol. Then water was added; a heavy liquid separated out. The liquid was extracted with ether. The ethereal solution was dried with anhydrous Na_2SO_4 , then the solvent ether was removed in the usual way. In this way an impure amber coloured liquid was obtained. It was purified by vacuum distillation (b.p., $219\text{--}221^{\circ}\text{C}$ mm, m.p. 24°C). Its specific gravity was found to be 1.7264 at 35°C . The compound reacts with a strong acid, e.g. hydrochloric acid, forming the acid derivative with evolution of hydrogen sulphide. Diethyltin sulphide is soluble in ordinary organic solvent such as ether, benzene, etc. and insoluble in water.

Anal. Subs., 0.3964: SnO_2 , 0.2862, BaSO_4 , 0.4322.

Calcd. for $\text{C}_4\text{H}_{10}\text{SnS}$:Sn and S, 56.85 and 15.35.

Found: Sn, 56.87 and S, 14.98.

M.W. of the Subs. in Benzene (Cryoscopic Method)

Subs.	Conc. (%)	ΔT	C_6H_6 (c.c.) at 20°	Obs. M.W.
0.7065	3.115	0.256	25	615
"	2.245	0.180	35	625
"	1.755	0.140	45	625

Calcd. for $(C_2H_5)_2Sn S$, M.W., 208.8 and for $((C_2H_5)_2 Sn S)_3$ M.W., 626.5.

Summary.

Dialkyltin sulphide has been prepared by treating dialkyltin dihalide with KSH in absolute alcohol, saturated with hydrogen sulphide. The six-membered hetero-cyclic structure



and the term tri-thio-anhydro-tris-dialkylstanne-dithiol are suggested for the compound from the results of the molecular weight determination.

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Thermal Diffusion in Dilute Alcoholic Solutions (A Preliminary Report).

By Kozo HIROTA.

(Received May 12, 1942.)

Thermal diffusion of various aqueous solutions by using the thermal diffusion column has been studied by the present author, and it has been found that there exist some regularities in the separation of these solutions⁽¹⁾⁽²⁾. On the other hand, researches in alcoholic solutions are also going on in order to clarify the behaviour of the ions in solutions. Some of the experimental results will be reported here preliminarily.

The experimental method and the apparatus used are the same as described in a previous report. The data in the cases of NaCl solution and HCl solution (0.5 normal), containing 8~9 mole% of ethyl alcohol, are described in Table 1 together with the data of the corresponding aqueous solution (1 normal) for the sake of comparison. The separation

(1) This Bulletin, **16** (1941), 232, 473; **17** (1942), 42.

(2) *J. Chem. Soc. Japan*, **62** (1941), 480; **63** (1942), 105.

ratio is the quantity defined as the concentration at the bottom reservoir divided by that at the top reservoir.

Table 1. Experimental Results.

Experimental Conditions:			{ Distance of the annular space, 1.5 mm; Higher Temperature, 76°C; Lower Temperature, 20°C.		
Solute.	Normality.	Alcohol % in mole.	Separation Ratio of the Solute at		
			1 hr.	2 hrs.	infinite hrs.
HCl	1	0.0	1.20	1.22	1.25
	0.5	8.5	1.11	1.11	—
NaCl	1	0.0	1.04	1.05*	1.05
	0.5	8.8	1.01	1.02	—

* Interpolated value.

It has been shown from the decrease of the separation ratio that the velocity of the thermal diffusion became smaller by two or three times by adding ethyl alcohol to both solutions. In each run, the concentration change of alcohol was also estimated approximately by the refractometrical method, and it was found that only a small separation (within 6%) occurred. Such being the case, the diminution thus found is too small to be explained, if we assume that the added alcohol into the aqueous solution plays only the rôle of a diluting agent in the thermal diffusion of electrolytes. The present author considers that the change of the degree of hydration seems to have some connection with the phenomenon.

In conclusion, the author wishes to express his sincere thanks to Dr. R. Yosimura, Director of the Department, and to Dr. Tanaka for their interest and encouragement in carrying out this research.

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Katalytische Oxydation des Kohlenoxyds mittels schweren Sauerstoffs an der Oberfläche des Kupferoxyds. (Auszug).⁽¹⁾

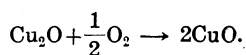
Von Toshizo TITANI, Sigeo NAKATA und Akira KANOME.

(Eingegangen am 24 April, 1942.)

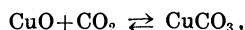
Inhaltsübersicht. Die katalytische Oxydation des Kohlenoxyds an der Oberfläche des Kupferoxyds wird unter Benutzung des schweren Sauerstoffs als "Spürer" untersucht. Der Versuch ergab,

(1) dass die Oxydation, unter den benutzten Versuchsbedingungen, von etwa 150° ab lebhaft stattzufinden beginnt und oberhalb etwa 400° das Kohlenoxyd praktisch vollständig bis zum Kohlendioxyd oxydiert wird.

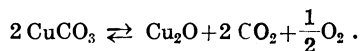
(2) Dabei wird die Reaktion durch die abwechselnde Reduktion und Oxydation des Kupferoxyds mittels des Kohlenoxyds und Sauerstoffgases nach dem Schema ausgeführt:



(3) Überschreitet aber die Temperatur etwa 400°, so tritt die Reaktion ein:



(4) und oberhalb etwa 500° verläuft daneben auch die Reaktion:



Um über den Mechanismus der katalytischen Oxydation des Kohlenoxyds mittels gasförmigen Sauerstoffs an der Oberfläche des Kupferoxyds Kenntnis zu gewinnen, wird die Reaktion unter Benutzung des an schweren Isotope angereicherten Sauerstoffs untersucht. Die dabei benutzte Apparatur ist im grossen und ganzen dieselbe wie die von einem von uns früher beschrieben wurde⁽²⁾, und die ganzen Versuche können zweckmässig in vier Teile abgeteilt werden: (1) die Bestimmung des Oxydationsgrades des Kohlenoxyds in Abhängigkeit von der Temperatur, (2) die Austauschreaktion der O-Atome zwischen Sauerstoffgas und Kupferoxyd, die mit der Oxydation des Kohlenoxyds stattfindet, (3) die Austauschreaktion der O-Atome zwischen dem Reaktionsprodukt, d.h. Kohlendioxyd und Kupferoxyd und (4) die Austauschreaktion der O-Atome zwischen dem Sauerstoffgas und dem Kohlendioxyd an der Oberfläche des Kupferoxyds.

Versuch 1. Die Bestimmung des Oxydationsgrades des Kohlenoxyds in Abhängigkeit von der Temperatur. Das aus etwa 50 g. fein granuliertem Kupfer von Merck und Bombensauerstoff (elektrolytischem Sauerstoff!) hergestellte Kupferoxyd wird in einem Katalysatorrohr auf verschiedene

(1) *J. Chem. Soc. Japan*, **63** (1942), 36, 41.

(2) S. Nakata und N. Morita, dies Bulletin, **16** (1941), 463.

Temperatur erhitzt und darüber wird das Reaktionsgasgemisch aus gleichen Volumen Kohlenoxyd und Sauerstoffgas mit der konstanten Geschwindigkeit von 48 ccm pro Min. geleitet. Das Katalysatorrohr wird aus Pyrexglas konstruiert und besitzt 30 cm. Länge und 2 cm. 1.W. Das aus Dem Rohr herauskommende Gas wird auf übliche Weise nach seinem Gehalt an Kohlenoxyd analysiert und der Oxydationsgrad des letzteren gemäss der Gl. berechnet:

$$\text{Oxydationsgrad} = \frac{\text{oxydierte Menge von CO}}{\text{verwendete Menge von CO}} \times 100.$$

Tabelle 1 und Kurve I in der unten angegebenen Abb. gibt einige Messresultate wieder. Dabei darf man aber keine grosse Genauigkeit der einzelnen Zahlenwerte beanspruchen, die insbesondere bei niedrigen

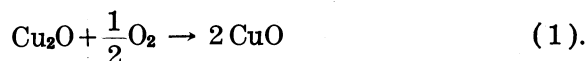
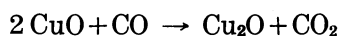
Tabelle 1. Oxydationsgrad des Kohlenoxyds in Abhängigkeit von der Temperatur.

Temp. (°C)	Oxydationsgrad in %.	Temp. (°C)	Oxydationsgrad in %.
100	1.2	250	81
140	3.1	280	88
160	5	300	92
180	21	350	98
200	58	380	100
220	68	400	100

Temperaturen gefunden wurden, weil der Oxydationsgrad wegen der grossen Wärmeentwicklung bei der Reaktion durch die Versuchsbedingungen stark beeinflusst wird. Aber in jedem Fall darf wohl geschlossen werden, dass die Oxydation von etwa 150° ab lebhaft stattzufinden be-

ginnt und oberhalb etwa 400° das Kohlenoxyd praktisch vollständig bis zu Kohlendioxyd oxydiert wird.

Versuch 2. Austauschreaktion der O-Atome zwischen Sauerstoffgas und Kupferoxyd, die mit der Oxydation des Kohlenoxyds stattfindet. Auf Grund der anderen ähnlichen Reaktionen wie z.B. der katalytischen Oxydation des Wasserstoffs an der Oberfläche des Kupferoxyds⁽³⁾ liegt die Annahme nahe, dass die in Rede kommende Reaktion durch die abwechselnde Reduktion und Oxydation des Kupferoxyds mittels des Kohlenoxyds und Sauerstoffgases nach dem Schema ausgeführt wird:



Verläuft aber die Reaktion wirklich nach diesem Schema, so ist durchaus möglich, dass die O-Atome des Kupferoxyds im Laufe der Reaktion gegen die des Sauerstoffs ausgetauscht werden. Um diese Möglichkeit experimentell zu bestätigen, werden im vorliegenden Versuch entweder die O-Atome im Sauerstoffgas oder die im Kupferoxyd mit schwerem Sauerstoff "labeliert" und ihre Wanderung während des Verlaufes der Reaktion

(3) J. Okayama, *Z. Elektrochem.*, **34** (1928), 294.

analytisch verfolgt. Die dabei benutzten Versuchsbedingungen sowie die Ergebnisse sind in Tabelle 2 zusammengestellt.

Tabelle 2. Austauschreaktion der O-Atome zwischen Sauerstoffgas und Kupferoxyd, die mit der Oxydation des Kohlenoxyds stattfindet.

1	2	3	4	5	6	7	8	9	10
Ver- suchs- nr.	Herstellung von CuO			Oxydation von CO			Temp. (°C)	Versuchs- dauer in Stdn.	D. Ü. von O ₂ nach dem Versuch in γ
	Menge von Cu in g	Menge von O ₂ in l	D. Ü. von O ₂ in γ	Menge von CO in l	Menge von O ₂ in l	D. Ü. von O ₂ in γ			
I	250	9.0	— 1	20	16	+35	290–300	10	+ 5
II	250	7.5	— 1	20	16	+35	120–140	10	+ 4
III	250	7.0	+35	25	20	— 1	120–130	12	+29

D. Ü. = Dichteüberschuss.

Bei Versuch I (vgl. Tabelle 2) wird 250 g. fein granuliertes Kupfer mittels Bombensauerstoffs (elektrolytischen Sauerstoffs), dessen Dichte, in der Form von Wasser gemessen, um 1 γ kleiner als gewöhnlicher Wassersauerstoff war, bis zu Kupferoxyd oxydiert. Dazu brauchten wir 9.0 l. Sauerstoffgas (vgl. Spalte 2 bis 4). Das so hergestellte Kupferoxyd wird nun in einem Katalysatorrohr auf 290° bis 300° möglichst konstant erhitzt und darüber wird das Reaktionsgasgemisch aus 20 l. Kohlenoxyd (aus Ameisensäure und konz. Schwefelsäure) und 16 l. schweren Sauerstoffgas, dessen Dichte, in der Form von Wasser gemessen, um 35 γ grösser als gewöhnlicher Wassersauerstoff war, mit der Geschwindigkeit von 62 ccm. pro. Min. geleitet (vgl. Spalte 5 bis 8). Nach der Beendigung des Versuchs, der etwa 10 Stunden dauerte (vgl. Spalte 9), wird der ganze Sauerstoff, der im Kupferoxyd chemisch verbunden ist, unter Benutzung des Bombenwasserstoffs bis zu Wasser rekombiniert. Die letzte 10. Spalte der Tabelle 4 gibt den Dichteüberschuss des Sauerstoffs im so rekombinierten Wasser gewöhnlichem Wassersauerstoff gegenüber an. Der Dichteüberschuss des Sauerstoffs im Kupferoxyd hat also vom anfänglichen –1 γ (vgl. Spalte 4) bis auf +5 γ (vgl. Spalte 10) und folglich insgesamt um 6 γ zugenommen. Diese Zunahme des Dichteüberschusses d.h. des Gehaltes an O¹⁸ des im Kupferoxyd verbundenen Sauerstoffs muss offensichtlich auf die erwartete Austauschreaktion der O-Atome zwischen dem schweren Sauerstoffgas und dem Kupferoxyd zurückgeführt werden.

Versuch II in Tabelle 4 wird unter den ähnlichen Versuchsbedingungen wie Versuch I ausgeführt bis auf die Versuchstemperatur, die bei Versuch II um etwa 150° niedriger als bei Versuch I liegt (vgl. Spalte 9). In diesem Versuch II wird aber auch genau so wie bei Versuch I eine untrügliche Zunahme des Dichteüberschusses des Sauerstoffs im Kupferoxyd festgestellt. Beim letzten Versuch III wird nun im Gegensatz der beiden anderen Versuche das schwere Kupferoxyd unter Benutzung des schweren Sauerstoffs hergestellt und darüber wird das Gemisch aus Kohlenoxyd

und gewöhnlichem Bombensauerstoff (elektrolytischem Sauerstoff) mit derselben Geschwindigkeit wie bei den Versuchen I und II geleitet. Dieser Fall ergibt dementsprechend eine Abnahme des Dichteüberschusses des im Kupferoxyd enthaltenen Sauerstoffs, wie aus dem Vergleich der Spalte 4 und 9 der letzten Horizontalreihe der Tabelle 4 ohne weiteres ersichtlich wird.

In jedem Fall wird also festgestellt, dass die O-Atome des Kupferoxyds im Laufe der katalytischen Oxydation des Kohlenoxyds an seiner Oberfläche allmählich gegen die des Sauerstoffgases ausgetauscht werden. Da aber nach dem Versuch von Morita und Titani⁽⁴⁾ die O-Atome des festen Kupferoxyds bis zu ziemlich hohen Temperaturen (mindestens bis auf 900°!) nicht direkt gegen die des Sauerstoffgases ausgetauscht werden können, darf wohl geschlossen werden, dass die gefundene Austauschreaktion mit der katalytischen Oxydation des Kohlenoxyds nach dem oben angegebenen Schema (1) ausgeführt wird. Eine einfache Rechnung zeigt, dass unter den benutzten Versuchsbedingungen die O-Atome des Kupferoxyds innerhalb zehn Stunden bis zur Tiefe von etwa 10^{-4} cm. gegen die des Sauerstoffgases ausgetauscht werden.

Versuch 3. Austauschreaktion der O-Atome zwischen Kohlendioxyd und Kupferoxyd. Nach den oben angegebenen Versuchen 1 und 2 wird das Kohlenoxyd gemäss des Mechanismus (1) praktisch vollständig bis zu Kohlendioxyd oxydiert, wenn die Reaktionstemperatur oberhalb von etwa 400° liegt. Da aber das so gebildete Kohlendioxyd saueren hingegen das Kupferoxyd basischen Charakter besitzt, können sich diese beiden Substanzen mindestens temporär miteinander verbinden:



Verläuft nun diese Reaktion nach beiden Seiten hin mit wohl messbarer Geschwindigkeit, so können die O-Atome des Kupferoxyds weiter gegen die des Kohlendioxyds ausgetauscht werden. Dass solch eine Austauschreaktion wirklich bei erhöhten Temperaturen stattfindet, wird dadurch bestätigt, dass der Gehalt an schwerem Sauerstoff des Kupferoxyds, das unter Benutzung des schweren Sauerstoffgases hergestellt worden ist, allmählich abnimmt, wenn darüber das gewöhnliche d.h. leichte Kohlendioxyd unter Erhitzung langsam geleitet wird. Zu diesem Zweck wird nämlich 150 g. Kupfer mit etwa 8 l. (30% der Theorie) schweren Sauerstoffgas (dessen Dichteüberschuss dem gewöhnlichen Wassersauerstoff gegenüber 35.2 γ beträgt) oxydiert und darüber wird eben das gleiche Volumen d.h. 8 l. gewöhnliches Kohlendioxyd (aus Marmor und Salzsäure) mit der Geschwindigkeit von 72 ccm. pro. Min. geleitet. Liegt dabei die Versuchstemperatur oberhalb etwa 400°, so zeigte sich eine untrügliche Abnahme des Dichteüberschusses des im Kupferoxyd verbundenen schweren Sauerstoffs, der nach der Beendigung des Versuchs durch die Reduktion mit Bombenwasserstoff in Form von Wasser sich wiedereinstellt. Die zweite Vertikalreihe der Tabelle 3 gibt diese Abnahme des Dichteüberschusses Δs des im Kupferoxyd enthaltenen Sauerstoffs nach dem Versuch an.

(4) N. Morita und T. Titani, dies Bulletin, **13** (1938), 656.

Tabelle 3. Austauschreaktion
der O-Atome zwischen
Kohlendioxyd und
Kupferoxyd.

Temp. (°C)	Δs in γ	% A
430	1.9	15
530	6.1	48
580	5.3	42
630	5.6	44

Diese Abnahme des Dichteüberschusses Δs des im Kupferoxyd enthaltenen Sauerstoffs soll aber, wie aus einer einfachen Rechnung sich ergibt⁽⁵⁾, 12.6 γ betragen, wenn die benutzten Mengen Kohlendioxyd und Kupferoxyd ihre O-Atome gegeneinander vollständig austauschen würden. Das prozentuale Austauschmass %A, das in der letzten Spalte der Tabelle 3 angegeben ist, wird deshalb gemäss der Gl. berechnet:

$$\% A = \frac{\Delta s_{\text{gef.}}}{12.6} \times 100$$

und seine Temperaturabhängigkeit mit Kurve II in der nebenstehenden Abb. wiedergegeben.

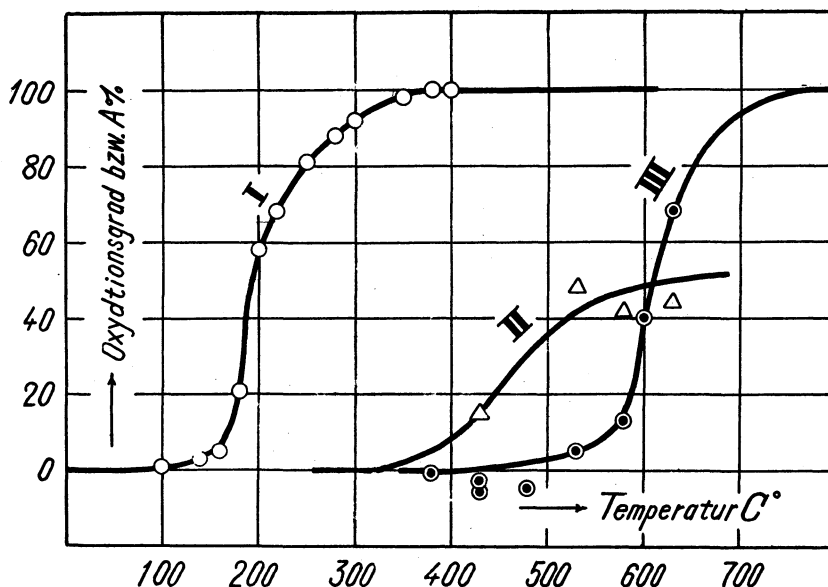


Abb. Temperaturabhängigkeit des Oxydationsgrades des Kohlenoxyds (I),
der Austauschreaktion zwischen Kohlendioxyd und Kupferoxyd (II)
und der zwischen Sauerstoffgas und Kohlendioxyd (III).

(5) Zur Herstellung des Kupferoxyds wurden 8 l. schweren Sauerstoffgases verbraucht und über das so hergestellte Kupferoxyd wurde eben das gleiche Volumen Kohlendioxyd geleitet. Da aber das benutzte schwere Sauerstoffgas um 35.2 γ , hingegen der Sauerstoff des mit gewöhnlichem Wasser im Austauschgleichgewicht befindlichen Kohlendioxyds bekanntlich um 10 γ , beide in der Form von Wasser gemessen, dichter als gewöhnlicher Wassersauerstoff ist, muss der Dichteüberschuss der beiden Arten Sauerstoff gleich $(35.2 + 10) / 2 = 22.6 \gamma$ betragen, wenn die angegebenen Mengen Sauerstoff und Kohlendioxyd ihre O-Atome gegeneinander vollständig austauschen würden. Der Dichteüberschuss des im Kupferoxyd verbundenen Sauerstoffs nimmt also bei diesem vollständigen Austausch um $35.2 - 22.6 = 12.6 \gamma$ ab.

Die Austauschreaktion zwischen Kohlendioxyd und Kupferoxyd findet also von etwa 400° an ziemlich lebhaft statt. Das dabei gefundene prozentuale Austauschmass %A erreicht doch auch bei hohen Temperaturen kaum 100%, d.h. das Austauschgleichgewicht wird kaum erreicht. Dieses letztere Ergebnis kann aber durch die Annahme wohl erklärt werden, dass die Geschwindigkeit der in Rede kommenden Austauschreaktion durch die Diffusionsgeschwindigkeit des Sauerstoffs im festen Kupferoxyd bedingt wird.

Versuch 4. Austauschreaktion der O-Atome zwischen Sauerstoffgas und Kohlendioxyd an der Oberfläche des Kupferoxyds. Bei diesem Versuch wird zunächst das Reaktionsgasgemisch aus gleichen Volumen Kohlenoxyd und schwerem Sauerstoffgas, dessen Dichteüberschuss dem gewöhnlichen Wassersauerstoff gegenüber 35.2 γ beträgt, über das aus gewöhnlichem Bombensauerstoff hergestellte Kupferoxyd geleitet. Die Strömungsgeschwindigkeit des Gasgemisches beträgt 48 ccm. pro. Min. und die Versuchstemperatur liegt bei 380° und 430°. Da aber unter diesen Versuchsbedingungen das Kohlenoxyd, wie aus Versuch 1 ersichtlich wird, praktisch vollständig oxydiert wird, bleibt gerade die Hälfte der benutzten Mengen Sauerstoffgas nicht reagiert übrig. Dieses übrig gebliebene Sauerstoffgas wird nun, nachdem es vom zu gleicher Zeit gebildeten Kohlendioxyd abgetrennt worden ist, mittels des Bombenwasserstoffs bis zu Wasser verbrannt und der Dichteüberschuss des so gewonnenen Wassers (dem gewöhnlichen Wasser gegenüber) mit dem Wasser verglichen, das zur Kontrolle aus demselben Sauerstoffgas und Bombenwasserstoff ohne weiteres d.h. ohne Reaktion mit Kohlenoxyd hergestellt wird. Der Versuch ergab, dass diese beiden Arten des Wassers innerhalb des Messfehlersbereiches (dem gewöhnlichen Wasser gegenüber) immer denselben Dichteüberschuss besitzt, so lange als die Versuchstemperatur unterhalb 430° liegt. Dies weist offensichtlich darauf hin, dass der Dichteüberschuss und folglich der O¹⁸-Gehalt des schweren Sauerstoffgases sogar nach der vollständigen Oxydation des Kohlenoxyds keine nennenswerte Änderung erleidet. Dieses Ergebnis erscheint jedoch im Lichte des oben angegebenen Versuchs 2 auf den ersten Blick merkwürdig, weil unter den angegebenen Versuchsbedingungen mindestens ein Teil der O-Atome des Sauerstoffgases, wie dort festgestellt wurde, gegen die des Kupferoxyds ausgetauscht werden müssen. Aber das ist kein Wunder, wenn man die Tatsache in Rechnung zieht, dass die im vorliegenden Versuch 4 benutzten Mengen Kupferoxyd viel weniger (fünf Mal so wenig) als die in Versuch 2 benutzten waren, obwohl die sonstigen Versuchsbedingungen d.h. die Zusammensetzung sowie die Strömungsgeschwindigkeit des Reaktionsgasgemisches in beiden Fällen nicht stark verschieden sind. Unter den im vorliegenden Versuch 4 benutzten Versuchsbedingungen liegt also die Abnahme des Dichteüberschusses des Sauerstoffgases, die wegen der Austauschreaktion gegen Kupferoxyd bis zu einem gewissen Grad stattfinden soll, wohl unterhalb des Messfehlersbereiches. Auf die experimentale Tatsache, dass das Sauerstoffgas unterhalb etwa 900° seine O-Atome nicht direkt gegen die des Kupferoxyds austauscht, wird schon oben in Versuch 2 hingewiesen. Ebenso wenig wahrscheinlich werden die O-Atome des Sauerstoffgases direkt gegen die des Kohlen-

dioxyds ausgetauscht, so lange als die Temperatur nicht so hoch liegt. Würde deshalb irgendeine nennenswerte Abnahme des Dichteüberschusses des Sauerstoffgases unter den angegebenen Versuchsbedingungen ausfindig gemacht, so soll diese Abnahme vielmehr auf die katalytische Austauschreaktion der O-Atome zwischen dem Sauerstoffgas und Kohlendioxyd zurückgeführt werden, die an der Oberfläche des Kupferoxyds stattfindet. Solch eine katalytische Austauschreaktion wurde tatsächlich dabei gefunden, als das Gemisch aus gleichen Volumen schweren Sauerstoffgases und gewöhnlichen leichten Kohlendioxyds mit der oben angegebenen Strömungsgeschwindigkeit d.h. 48 ccm. pro Min. über das auf 530° bis 630° erhitzte Kupferoxyd geleitet wurde, das aus 50 g. Kupfer und gewöhnlichem Bombensauerstoff dargestellt worden war. Die dabei gewonnenen Versuchsergebnisse sind in Tabelle 4 zusammengestellt, wo die zweite Vertikalreihe Δs die Abnahme des Dichteüberschusses des Sauerstoffgases, das man nach dem Versuch durch die Reakombination mit Bombenwasserstoff als Wasser wiederbekam.

Tabelle 4. Die katalytische Austauschreaktion der O-Atome zwischen Sauerstoffgas und Kohlendioxyd.

Temp. (°C)	Δs in γ	% A
430	-0.7	- 6
480	-0.6	- 5
530	0.6	5
580	1.7	13
600	5.0	40
630	8.6	68

Diese Abnahme des Dichteüberschusses des Sauerstoffgases soll aber, wie eine einfache Rechnung zeigt⁽⁶⁾, 12.6 γ betragen, wenn die verwendeten Mengen Sauerstoffgas und Kohlendioxyd ihre O-Atome gegeneinander vollständig austauschen würden. Das prozentuale Austauschmass %A, das in der letzten Spalte der Tabelle 4 angegeben ist, wird deshalb gemäss der Gl. berechnet:

$$\% A = \frac{\Delta s_{\text{gef.}}}{12.6} \times 100$$

und seine Temperaturabhängigkeit mit Kurve III in der oben angegebenen Abb. wiedergegeben.

Die katalytische Austauschreaktion der O-Atome zwischen Kohlendioxyd und Sauerstoffgas an der Oberfläche des Kupferoxyds tritt also oberhalb etwa 550° ein und bei hohen Temperaturen kann sie sogar ziemlich leicht bis zum Austauschgleichgewicht verlaufen⁽⁷⁾. Als erster Schritt der Reaktion kommt nun die Bildung der Oberflächenverbindung zwischen Kohlendioxyd und Kupferoxyd in Frage, deren umkehrbare Bildung und

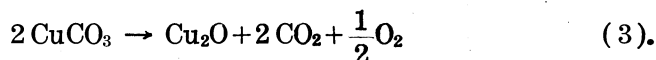
(6) Das benutzte Sauerstoffgas war um 35.2 γ , hingegen der Sauerstoff des mit gewöhnlichen Wasser im Austauschgleichgewicht befindlichen Kohlendioxyds um 10 γ , beide in der Form von Wasser gemessen, dichter als gewöhnlicher Wassersauerstoff. Da aber diese beiden Gase in gleichen Volumen, d.h. in Bezug auf Anzahl der O-Atome miteinander äquivalenten Mengen vermischt wurden, soll der Dichteüberschuss des Sauerstoffs in den beiden Gasen gleich $(35.2+10)/2=22.6$ γ betragen, wenn sie ihre O-Atome gegeneinander vollständig austauschen würden. Der Dichteüberschuss des Sauerstoffgases nimmt also beim vollständigen Austausch um $35.2-22.6=12.6$ γ ab.

(7) Diese verhältnismässig grosse Geschwindigkeit der Reaktion kann auch als eine Stütze für die Annahme aufgefasst werden, dass die in Rede kommende Austauschreaktion hauptsächlich zwischen Gasen stattfindet. Falls die Reaktion zwischen Gasen und festen Phasen verlief, würde die Geschwindigkeit der Reaktion nicht so gross sein können, wie dies z.B. beim letzten Versuch 4 der Fall war.

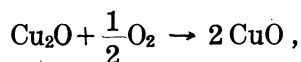
Zerlegung an der Oberfläche des erhitzten Kupferoxyds im letzten Versuch 4 festgestellt wurde. Verläuft aber der Zerfall der Verbindung, wie dabei angenommen wurde, ausschliesslich nach dem Schema:



so führt es wohl zum Austausch der O-Atome zwischen dem Kohlendioxyd und dem Kupferoxyd, nicht aber zu dem in Frage kommenden Austausch zwischen dem Kohlendioxyd und dem Sauerstoffgas. Um die letztere Reaktion zu erklären, muss deshalb angenommen werden, dass beim Temperaturbereich, wo die in Rede kommende Austauschreaktion merklich stattfindet, mindestens ein Teil der Dissoziation auch nach dem Schema verläuft:



Verläuft diese Reaktion nach beiden Seiten hin mit wohl messbarer Geschwindigkeit oder, was noch wahrscheinlicher ist, wird das in Reaktion (3) gebildete Kupferoxydul durch das Sauerstoffgas wieder bis zu Kupferoxyd oxydiert:

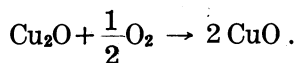
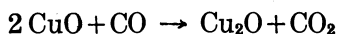


so entsteht die Möglichkeit, dass die O-Atome des Kohlendioxyds und Sauerstoffgases dadurch ihre Plätze gegeneinander wechseln. Kurve III in der oben angegebenen Abb. gibt also die Temperaturabhängigkeit der Geschwindigkeit der Reaktion (3) wieder.

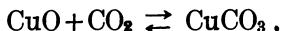
Zusammenfassung.

Die in den vorliegenden Versuchen 1 bis 4 gefundenen Tatsachen können kurz wie folgt zusammengefasst werden.

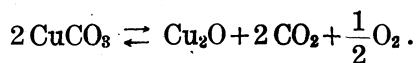
(1) Die katalytische Oxydation des Kohlenoxyds mittels gasförmigen Sauerstoffs an der Oberfläche des Kupferoxyds wird durch die abwechselnde Reduktion und Oxydation des Kupferoxyds mit Kohlenoxyd und Sauerstoffgas ausgeführt:



(2) Überschreitet die Temperatur etwa 400°, so tritt die Reaktion zwischen dem Kupferoxyd und dem primär gebildeten Kohlendioxyd ein:



(3) und oberhalb etwa 550° verläuft daneben auch die Reaktion:



Zum Schluss möchten wir der Nippon Gakujutsu Shinkohkai (der Japanischen Gesellschaft zur Förderung der wissenschaftlichen Arbeit)

sowie der Hattori Hohkohkai (der Hattori-Stiftung) für ihre finanzielle Unterstützung bei der Durchführung der vorliegenden Arbeit unseren besten Dank aussprechen.

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***d*-Altromethylose.**

Von Koichi IWADARE.

(Eingegangen am 27. März 1942.)

Von den sechzehn theoretisch möglichen Isomeren der Aldomethylpentosen mit normaler Kette waren zwölf Monosaccharide schon bereiteten worden. *l*-Altromethylose, der Antipode der hier mitgeteilten Monose, wurde von K. Freudenberg und Mitarbeiter⁽¹⁾ durch die Hydrierung des Diaceton-*d*-galaktoseens-(5,6) und die nachfolgenden mühsamen Trennungen über Hydrazonderivate hergestellt. Da wir für andere Zwecke⁽²⁾ über eine grössere Menge *d*-Allomethylose verfügten, so wurde ein Teil derselben zu *d*-Allomethylonsäure oxydiert und in *d*-Altromethylonsäure und *d*-Altromethylose übergeführt. *d*-Allomethylose, die als das Ausgangsmaterial zur Gewinnung der *d*-Altromethylose angewandt wurde, wurde unter geringer Variation⁽²⁾ der Vorschrift von P. A. Levene und J. Compton⁽³⁾ dargestellt, d. h. *l*-Rhamnosehydrat wurde mechanisch mit dem Schwefelsäure enthaltenden Aceton geschüttelt, erhaltene 2,3-Monoaceton-*l*-rhamnose mit *p*-Toluolsulfochlorid zu 2,3-Monoaceton-5-toluolsulfo-*l*-rhamnose esterifiziert, und diese mit Natriummethylat zu 2,3-Monoaceton-methyl-*d*-allometylosid umgelagert. Und die gereinigte Metylosid wurde zu *d*-Allomethylose hydrolisiert.

d-Allomethylose wurde mit Brom oxydiert, und das erhaltene Lakton aus Aceton in farblosen Blättchen umkristallisiert, die bei 133.5–134.5° schmelzen und eine spezifische Drehung von $[\alpha]_D^{20} = -24^\circ$ ($c = 3.47$ in Wasser nach 3 Minuten) zeigen. *d*-Allomethylonsäurelaktone zeigt wenige Mutarotation, $[\alpha]_D^{20} = -23.5^\circ$ (nach 24 Stunden). Es wurde in Wasser gelöst, mit Bariumcarbonat erhitzt, und Barium *d*-Allomethylonat wurde hergestellt, das eine spezifische Drehung von $[\alpha]_D^{20} = -8.3^\circ$ (in Wasser) zeigt. Das Amid und Phenylhydrazid der *d*-Allomethylonsäure wurden

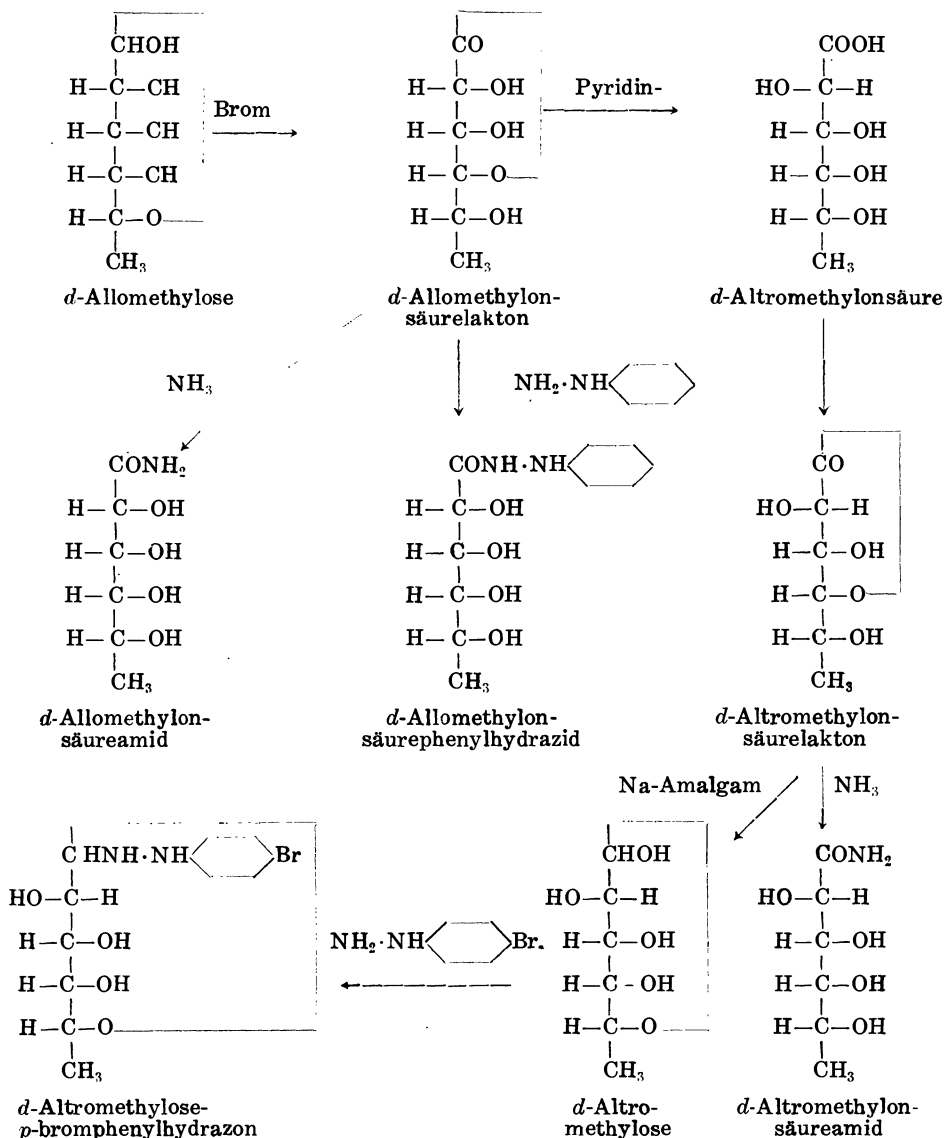
(1) K. Freudenberg und K. Raschig, *Ber.*, **62** (1929), 378.

(2) K. Iwadare, *Dieses Bulletin*, **17** (1942), 90.

(3) P. A. Levene und J. Compton, *J. biol. Chem.*, **116** (1936), 169.

nach den gewöhnlichen Methoden dargestellt. *d*-Allomethylonsäureamid kristallisierte in farblosen Oktaedern, die bei 142.5–143° schmelzen und eine spezifische Drehung von $[\alpha]_D^{25} = +9^\circ$ (in Wasser) zeigen. *d*-Allomethylonsäurephenylhydrazid kristallisierte in farblosen Nadeln, die bei 163–163.5° schmelzen und eine spezifische Drehung von $[\alpha]_D^{25} = +20^\circ$ (in Wasser) zeigen. Das Brucinsalz der *d*-Allomethylonsäure wurde durch Erhitzung von wässrige Lösung des *d*-Allomethylonsäurelaktens mit Brucin dargestellt. Es kristallisierte sehr langsam aus Alkohol in feinen farblosen Nadeln, die bei 115° sintern und bei 123° schmelzen und eine spezifische Drehung von $[\alpha]_D^{25} = -22.5^\circ$ ($c=1.02$ in Wasser) zeigen.

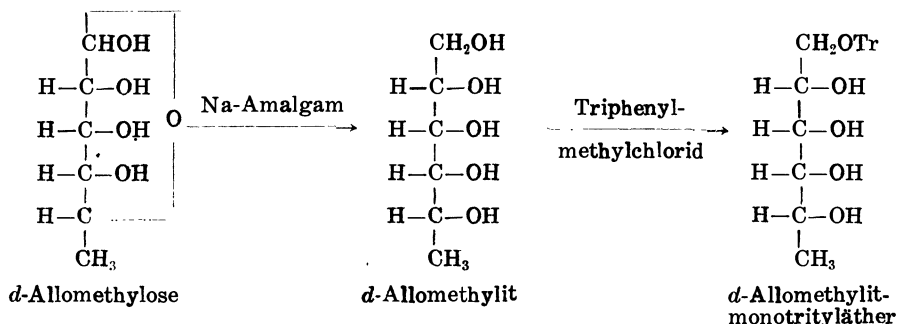
d-Allomethylonsäurelaktone wurde in Wasser gelöst und durch Erhitzen mit Pyridin epimerisiert. Für diesen Zweck wurde das Gemisch im



geschlossenen Rohr 40 Stunden bei 110° erhitzt, denn durch die Erhitzung bei 150–160° nach der Methode von Fischer⁽⁴⁾ wurde eine grössere Menge von harzigem Material gewonnen, und die Ausbeute wurde daher beträchtlich erniedrigt. Für die Isolierung der *d*-Altromethylonsäure aus dem epimerisierten Gemisch diente das Brucinsalz, denn die Kristalle des *d*-Altromethylonsäuren Brucins scheiden sich viel leichter als die des *d*-Allomethylonsäuren Brucins. *d*-Altromethylonsäurelaktone wurde aus dem Brucinsalz durch Befreiung mit Natronlauge hergestellt. Daraus wurde *d*-Altromethylonsäureamid nach der gewöhnlichen Methode hergestellt, das bei 147.5–148° schmilzt.

d-Altromethylonsäurelaktone wurde im Wasser gelöst und mit Natriumamalgam zum Zucker reduziert. Die sirupöse *d*-Altromethylse wurde mit *p*-Bromphenylhydrazin zum *d*-Altromethylse-*p*-bromphenylhydrazon übergeführt, das bei 177–177.5° schmilzt und spezifische Drehungen von $[\alpha]_D^{20} = +8^\circ$ (nach 7 Minuten) und von $[\alpha]_D^{20} = +7^\circ$ (nach einem Tage) zeigt. Das *d*-Isomer schmilzt bei 178° (spezifische Drehung, nicht mitgeteilt), und *d*-Allomethylse-*p*-bromphenylhydrazon⁽³⁾ schmilzt bei 145–146° und zeigt eine spezifische Drehung von $[\alpha]_D = -21.9^\circ$ (in Pyridin). Durch Erhitzung mit Benzaldehyd wurde *d*-Altromethylse-*p*-bromphenylhydrazon zur freien *d*-Altromethylse zersetzt, die nicht zum Kristall führen konnte.

Beiläufig wurde *d*-Allomethylse mit Natriumamalgam zu *d*-Allomethylit reduziert, das in farblosen, hygroskopischen Nadeln kristallisierte. *d*-Allomethylit schmilzt bei etwa 62–63° und zeigt eine spezifische Drehung von $[\alpha]_D^{20} = -11^\circ$ ($c = 4.68$ in Wasser). Monotrityl-*d*-allomethylit kristallisierte in prachtvollen Tafeln, die bei 177–178° schmelzen.



Beschreibung der Versuche.

d-Allomethylse. *d*-Allomethylse wurde genau nach der in der letzten Mitteilung⁽²⁾ beschriebenen Methode dargestellt. Aus 200 g. *l*-Rhamnosehydrat wurden 24 g. *d*-Allomethylse hergestellt.

d-Allomethylonsäurelaktone. 10 g. *d*-Allomethylse wurden in 60 ccm. Wasser gelöst und 20 g. Brom hinzugegeben. Dasselbe löste sich beim öfteren Umschütteln im Laufe von mehreren Stunden. Die Mischung blieb 3 Tage bei Zimmertemperatur stehen und das Brom wurde dann

(4) Die Gewinnung von *l*-Isorhamnonsäure aus *l*-Rhamnonsäure, E. Fischer und H. Herborn, *Ber.*, **29** (1896), 1961.

unter dem verminderten Druck weggetrieben. Die farblose Lösung wurde mit Silbercarbonat geschüttelt, bis das Bromwasserstoff gänzlich gefällt war. Das Filtrat wurde durch Schwefelwasserstoff vom Silber befreit und filtriert. Das Filtrat wurde unter dem verminderten Druck verdampft, wobei es sich nicht färbt. Bei genügender Konzentration scheidet sich das *d*-Allomethylonsäurelaktone in farblosen Kristallen ab. Zur völligen Reinigung genügt einmaliges Umkristallisieren aus heissem Aceton. Der Smp. war 133.5–134.5° und die spezifische Drehung $[\alpha]_D^{20} = -24^\circ$ ($c=3.47$ in Wasser, nach 3 Minuten) und -23.5° (im Gleichgewicht). (Gefunden: C 44.28, H 6.20. Berechnet für $C_6H_{10}O_5$: C 44.44, H 6.17%).

d-Allomethylonsäurebariumsalz. 0.2 g. *d*-Allomethylonsäurelaktone wurde in Wasser gelöst und mit überschüssigem Bariumcarbonat erhitzt. Das Gemisch wurde filtriert, das Filtrat verdampft und mit Alkohol versetzt. Der entstandene schuppige Niederschlag wurde filtriert und mit wässriger Alkohol gewaschen. Er zeigt eine spezifische Drehung von $[\alpha]_D^{20} = -8.3^\circ$ (in Wasser). Ausbeute, 0.2 g. (Gefunden: C 28.74, H 4.81, Ba 27.89. Berechnet für $C_6H_{11}O_6 \frac{Ba}{2}$: C 29.07, H 4.47, Ba 27.71%).

d-Allomethylonsäureamid. 0.2 g. *d*-Allomethylonsäurelaktone wurde in 2 ccm. Alkohol gelöst und mit trockenem Ammoniakgas versetzt. Die Lösung wurde verdampft und *d*-Allomethylonsäureamid kristallisierte in farblosen Oktaedern. Ausbeute, 0.18 g. Der Smp. war 142.5–143° und die spezifische Drehung $[\alpha]_D^{20} = +9^\circ$ (in Wasser). (Gefunden: C 40.06, H 7.36, N 7.97. Berechnet für $C_6H_{13}O_5N$: C 40.22, H 7.31, N 7.82%).

d-Allomethylonsäurephenylhydrazid. Das Phenylhydrazid der *d*-Allomethylonsäure entstand beim einstündigen Erhitzen der wässrigen Lösung von 0.2 g. *d*-Allomethylonsäurelaktone mit 0.2 g. Phenylhydrazin im Wasserbade. Das überschüssige Phenylhydrazin lässt sich durch Waschen mit Äther entfernen. Zur Reinigung wurde das Phenylhydrazid aus heissem Alkohol umkristallisiert. Ausbeute, 0.13 g. Die so erhaltenen, farblosen Nadeln schmelzen bei 163–163.5° und zeigen eine spezifische Drehung von $[\alpha]_D^{20} = +20^\circ$ in Wasser. (Gefunden: C 53.27, H 6.47, N 10.50, Berechnet für $C_{12}H_{18}O_5N_2$: C 53.33, H 6.67, N 10.37%).

Brucinsalz der d-Allomethylonsäure. 0.2 g. *d*-Allomethylonsäurelaktone wurde mit 2 ccm. Wasser und 0.5 g. Brucin 40 Minuten gekocht und die filtrierte Lösung unter dem verminderten Druck zum Sirup verdampft. Dazu wurde eine wenige Menge Alkohol hinzugefügt. Die Kristallisation des *d*-Allomethylonsäurebrucinsalzes begann langsam in einigen Tagen. Es kristallisierte in farblosen, feinen Nadeln, die bei 115° sintern und bei 123° schmelzen, und eine spezifische Drehung von $[\alpha]_D^{20} = -22.5^\circ$ ($c=1.02$ in Wasser) zeigen. Ausbeute, 0.22 g. (Gefunden: C 57.10, H 6.97, N 4.82. Berechnet für $C_6H_{12}O_6 \cdot C_{23}H_{26}O_4N_2 \cdot 2H_2O$: C 57.04, H 6.93, N 4.59%).

Brucinsalz der d-Altromethylonsäure. 5 g. *d*-Allomethylonsäurelaktone wurden in 20 ccm. Wasser gelöst und nach Zusatz von 2.5 ccm. Pyridin im geschlossenen Rohr 40 Stunden bei 110° erhitzt. Die Flüssigkeit war dann hellbraun. Sie wurde mit etwas mehr als der berechneten Menge Barythydrat, welches in heissem Wasser gelöst war, bis zum Verschwinden des Pyridins gekocht, dann der Baryt genau durch Schwefelsäure aus-

gefällt und die Mischung schliesslich durch Kochen mit Tierkohle entfärbt. Das Filtrat hinterliess beim Verdampfen unter dem verminderten Druck 4 g. Sirup, welcher nach 24 Stunden nur sehr wenige Menge Kristalle abschied. Daher wurde das Gemisch (3 g.) mit 30 ccm. Wasser und 7.5 g. Brucin 30 Minuten gekocht und die filtrierte Lösung unter dem verminderten Druck verdampft. Der hierbei bleibende Sirup erstarrte beim Erkalten zu schönen glänzenden Nadeln. Die Kristallmasse wurde zunächst zur Entfernung des überschüssigen Brucins mit kaltem Alkohol sorgfältig ausgelaugt und der Rückstand zweimal aus Methanol umkristallisiert. Smp. 152.5–153°. $[\alpha]_D^{25} = -24.4^\circ$. (Gefunden: C 57.62, H 6.71, N 4.88. Berechnet für $C_6H_{12}O_6 \cdot C_{23}H_{26}O_4N_2 \cdot 2H_2O$: C 57.04, H 6.93, N 4.59%).

d-Altromethylose. Zur Umwandlung in die Säure wurde das Brucinsalz (3 g.) in heisser wässriger Lösung mit Bariumhydroxyd zerlegt und das ausgeschiedene Brucin nach dem Erkalten abfiltriert. Die Mutterlauge wurde zur Trockne verdampft und der Rückstand wiederholt mit Alkohol extrahiert, um den Rest des Brucins vollends zu entfernen. Dann wurden die Bariumverbindungen wieder in Wasser gelöst, durch Schwefelsäure das Metall genau ausgefällt und das Filtrat zum Sirup verdampft. Derselbe war ein Gemenge von *d*-Altromethylonsäure mit ihrem Laktone. Dieses Gemisch wurde 2 Stunden im Vakuum auf 90° erwärmt. Der verbleibende dicke Sirup wog 0.6 g. Er wurde in 10 ccm Wasser gelöst und unter starkem Rühren mit Kältemischung gekühlt. Sobald die Temperatur auf 0° gesunken war, wurden 20 g. Natriumamalgam (2.5-proz.) in einigen Portionen eingeworfen. Durch Zutropfen von 20 proz. Schwefelsäure wurde die Lösung immer knapp sauer gehalten, so dass Kongopapier eben grau angefärbt wird. Nach einer Stunde war die Reduktion beendet. Das Quecksilber wurde abgetrennt und die wässrige Lösung mit Natronlauge so weit abgestumpft, dass sie nur noch auf Lackmus, aber nicht mehr auf Kongo sauer reagierte. Sie wurde dann im Vakuum eingedampft, bis sich Natriumsulfat auszuschcheiden begann. Es wurde mit 20 proz. Schwefelsäure auf Kongo angesäuert und mit 20 fachen Mengen Alkohol versetzt. Das ausfallende Sulfat wurde abgenutscht und mit Alkohol gewaschen. Die alkoholische Lösung wurde sofort mit Wasser verdünnt und im Vakuum verdampft, um alle Alkoholreste zu vertreiben. Die verbleibende Lösung wurde mit reinem Bariumcarbonat heiss neutralisiert. Es wurde filtriert und das Filtrat zum dünnen Sirup eingedampft. Derselbe wurde mit Methanol versetzt und das ausfallende *d*-Altromethylonsäurebariumsalz abgenutscht. Die Methanollösung wurde zum Sirup eingedampft, mit gleicher Menge *p*-Bromphenylhydrazin versetzt, und das Gemisch im Alkohol gelöst und 15 Minuten erwärmt. Die Lösung wurde verdampft und der zurückbleibende Sirup einigemal mit Benzol extrahiert, um das verbleibende *p*-Bromphenylhydrazin zu entfernen. Der Rückstand wurde mit Alkohol versetzt. *d*-Altromethylose-*p*-bromphenylhydrazon kristallisierte in feinen Prismen, die bei 177.0–177.5° schmelzen und $[\alpha]_D^{20} = +7^\circ$ (im Gleichgewicht) zeigen. (Gefunden: C 42.89, H 5.12, N 8.84. Berechnet für $C_{12}H_{17}O_4N_2Br$: C 43.25, H 5.14, N 8.41%). Durch die Zersetzung von *d*-Altromethylose-*p*-bromphenylhydrazon mit Benzaldehyd wurde der freie Zucker als Sirup erhalten.

d-Altromethylonsäureamid. *d*-Altromethylonsäureamid wurde aus *d*-Altromethylonsäurelaktone durch die gewöhnliche Methode dargestellt. Smp., 147.5–148°. (Gefunden: C 40.09, H 7.05. Berechnet für $C_6H_{13}O_5N$: C 40.22, H 7.31 %).

d-Allomethylit. 1 g. *d*-Allomethylose wurde in 10 ccm. Wasser gelöst, mit der verdünnten Schwefelsäure angesäuert und mit 25 g. 2.5 proz. Natrium-amalgam in mehreren Portionen versetzt. Es war zweckmässig, das Gemische immer schwach sauer zu erhalten. Nachdem das Natrium-amalgam gänzlich benutzt wurde, wurde die Lösung mit Alkali neutralisiert und wieder mit Natriumamalgam portionsweise versetzt, bis die Lösung nicht mehr die Fehlingsche Lösung reduzierte. Das Quecksilber wurde abgetrennt und die wässrige Lösung mit Schwefelsäure genau neutralisiert. Sie wurde dann im Vakuum eingedampft, bis sich Natriumsulfat auszuschcheiden begann. Sie wurde dann mit 20 fachen Mengen Alkohol versetzt und das ausfallende Sulfat abgenutscht. Die alkoholische Lösung wurde im Vakuum zum Sirup verdampft, derselbe im Alkohol gelöst und mit einer wenige Menge Äther versetzt. *d*-Allomethylit kristallisierte in farblosen, hygroskopischen Nadeln, die bei 62–63° schmelzen und eine spezifische Drehung von $[\alpha]_D^{10} = -11^\circ$ zeigen. (Gefunden: C 43.70, H 8.67. Berechnet für $C_6H_{14}O_5$: C 43.37, H 8.43 %).

d-Allomethylitmonotrityläther. 0.5 g. *d*-Allomethylit wurde in 3 ccm. Pyridin gelöst und 1.0 g. Triphenylmethylchlorid zugefügt. Die prachtvolle Kristalle von *d*-Allomethylitmonotrityläther erschien langsam aus der Lösung. Sie wurden aus Benzol umkristallisiert. Smp., 177–178°. $[\alpha]_D^{10} = 0$ ($c=1.0$ in Alkohol). (Gefunden: C 73.62, H 7.08. Berechnet für $C_{25}H_{28}O_5$: C 73.51, H 6.91 %).

Zum Schluss möchte ich Herrn Professor B. Kubota für seine freundlichen Ratschläge und seine Hilfe bei der vorliegenden Arbeit meinen herzlichsten Dank aussprechen.

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Geochemische Untersuchungen der Vulkane in Japan. XXV. Dichtemessungen des Wassers aus Fumarolen von dem Vulkan Yakedake. II.

Von Shinya OANA.

(Eingegangen am 27. März 1942.)

In der XVIII. Mitteilung von geochemischen Untersuchungen der Vulkane in Japan⁽¹⁾ habe ich berichtet, dass die Dichte des durch die Kondensation von Fumarolendämpfen erhaltenen Wassers beträchtlich grösser ist als die des Leitungswassers der Stadt Tokio. Vom geochemischen Standpunkt betrachtet, wird es nicht weniger interessant sein darauf zu bestätigen, dass dieser Zustand entweder immer unverändert bleibt oder nach den meteorologischen Umständen etwaige Abweichung zeigt.

Im Juli 1939 und im August 1940 habe ich wiederum die Wasserproben aus denselben Fumarolen durch Kondensation der Dämpfe gesammelt. Diese Wasserproben wurden sorgfältig gereinigt und die Dichteunterschiede zwischen diesen und dem Leitungswasser der Stadt Tokio wurden nach der Schwimmermethode bestimmt.⁽²⁾ Die gewonnenen Resultate sind in Tabelle 1 angegeben.

Tabelle 1. Dichteunterschied zwischen dem Wasser aus Yakedake-Fumarolen und dem Leitungswasser der Stadt Tokio.

Bezeichnung der Fumarole	im Jahre 1939			im Jahre 1940		
	Datum	Temperatur (°C)	Dichteunter- schied (γ)	Datum	Temperatur (°C.)	Dichteun- terschied (γ)
A ₁	27. Juli	185.5	+3.4 ₄	8. Aug.	166.4	+1.7 ₇
A ₂ **	"	***	+3.5 ₅	"	164.2	+2.4 ₅
B	"	209	+3.6 ₃	"	195.3	+1.2 ₀
C	28. Juli	81.4	-1.4 ₇	"	80.7	-1.2 ₈
D	27. Juli	93	+1.4 ₂	"	92.0	-0.2 ₃
E ₁ **	28. Juli	93	-1.5 ₀	****	—	—
E ₂ **	"	93	-1.8 ₇	****	—	—

* Nahe der Fumarole A₁, die in der XVIII. Mitteilung mit A bezeichnet wurde, gibt es eine andere, die hier mit A₂ bezeichnet wird.

** Die Fumarolen E₁ und E₂ befinden sich am zweiten Teich beim Krater.

*** Wegen der Beschädigung des Thermometers wurde die Temperatur nicht gemessen.

**** Diese Fumarolen waren im Aug. 1940 so schwach tätig, dass die Dämpfe nicht mehr kondensiert wurden.

(1) Dieses Bulletin, **14** (1939), 279.

(2) Die Methoden der Kondensation des Dampfes, der Reinigung des Wassers und der Dichtebestimmung sind dieselbe wie in den IX. und XVIII. Mitteilungen.

Zum Vergleich habe ich weiter die Dichtemessungen der verschiedenen Arten der natürlichen Wässer in der Umgebung von Yakedake bewerkstelligt und die Resultate in Tabelle 2 angegeben.

Tabelle 2. Dichteunterschied zwischen natürlichen Wässern und dem Leitungswasser der Stadt Tokio.

Art des Wassers	Datum	Temperatur (°C)	Dichteunterschied (γ)
Erster Teich neben bei dem Krater	27. Juli 1939	17.8	-1.0 ₅
Zweiter Teich neben bei dem Krater ...	28. Juli 1939	—	-0.6 ₃
Regenwasser*	27. Juli 1939	—	-1.4 ₂
Regenwasser**	28. Juli 1939	—	-0.9 ₉
Flusswasser***	"	10.1	-1.6 ₄
Flusswasser****	13. Aug. 1940	9.9	-0.8 ₀
Schneereste*****	"	—	+0.2 ₉
Kamikōti-Therme	28. Juli 1939	44.5	-1.4 ₀

* Bei der Berghütte Yakedakegoya frisch gesammelt.

** Regenwasser, geschöpft aus einem Regenfass bei der Berghütte.

*** } Aus dem Fluss Adusagawa bei der Brücke Kappabasi.

**** }
***** } Aus dem Firn von Karasawa.

Diskussion der Ergebnisse. Wenn man etwas über juveniles Wasser bearbeiten möchte, so wird das Fumarolenwasser am bequemsten dafür benutzt werden, weil das letztere wahrscheinlich durch vulkanische Aktivität unmittelbar aus Magma auf die Erdoberfläche heraufgebracht wird. Unter den Fumarolen, deren Wasserdichte bisher von mir gemessen wurden, sind A und B im Vulkan Yakedake (Tab. 1) am lebhaftesten tätig, wie ihre hohen Temperaturen hinweisen; somit scheint es, dass sie verhältnismässig reichliche Menge juvenilen Wassers enthalten. Die Dichtemessungen der Wasserproben, die von diesen Fumarolendämpfen kondensiert wurden, zeigen, dass die Konzentration des schweren Wassers vom August 1938 zum Juli 1939 und weiter zum August 1940 immer geringer wurde. Es muss hier erwähnt werden, dass die meteorologischen Bedingungen bei der Sammlungen solcher Wasserproben ganz verschieden waren. Gesammelt wurden nämlich die Wasserproben aus den Fumarolen im August 1938 nach dem lang gewährten trockenen Klima und im Juli 1939 an einem gelegentlichen trockenen Tag dieses regenreichen Sommers, dagegen im August 1940 an einem heiteren Tag nach täglichen Regenfällen. Wie man in Tab. 1 sieht, sind die Temperaturen der Fumarolen zwar von diese meteorologischen Umständen abhängig, d.h. im August 1938 zeigten die Fumarolen die höchsten Temperaturen und im August 1940 die niedrigsten. Aus dieser Tatsache könnte man wahrscheinlich den Schluss ziehen, dass die Wasserprobe von 1938 die grösste Menge des juvenilen Wassers enthält und solche von 1940 dagegen mit der reichlichsten Menge von vadosem Wasser beigemengt ist. Andererseits, wie man in der Resultate meiner Dichtemessungen von Regen-, Fluss- und Teichwasser in Tab. 2 ersieht, sind die Wässer von vadoser Arten immer bedeutend leichter als das Fumarolenwasser.

Deshalb könnte man wohl annehmen, dass das schwere Wasser im juvenilen Wasser mehr konzentriert sei als im vadosen.⁽³⁾ Nach den bisherigen Untersuchungen ist erwiesen, dass die Dichte des Thermalwassers immer den schwankenden Wert zwischen dem des juvenilen und vadosen Wassers nimmt. Dies beruht natürlich auf der Tatsache, dass die beiden Arten von Wasser auf verschiedener Weise in Thermalwasser beigemischt, sind, obgleich der Anteil des juvenilen Wassers in letzterem vielleicht viel geringer als in Fumarolenwasser sein dürfte. Auf jeden Fall ist es eine interessante Aufgabe die Mengenverhältnisse zwischen juvenilem und vadosem Wasser in den verschiedenen natürlichen Gewässern zu ermitteln, und ich werde diese Frage in der folgenden Mitteilungen weiter behandeln.

Es sei mir gestattet, Herrn Prof. Yuji Shibata und Herrn Prof. Kenjiro Kimura für ihre freundliche Anleitung und ihre Ratschläge und der Kaiserlichen Akademie der Wissenschaft für ihre finanzielle Unterstützung bei der Ausführung dieser Arbeit meinen herzlichen Dank auszusprechen.

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(3) M. Dole, *J. Chem. Phys.*, **4** (1936), 778; M. Harada, T. Titani, *Dieses Bulletin*, **10** (1935), 206.

Abbau von 1-Brom-methyl-sinomenin.⁽¹⁾

Von **Kakuji GOTO** und **Tatsuo ARAI**.

(Eingegangen am 30. März 1942.)

Durch Methylierung von 1-Brom-sinomenin mit Diazomethan haben wir 1-Brom-methyl-sinomenin in guter Ausbeute darstellen konnten. Damit wurden fast alle Reaktionen geprüft, die wir vorher mit Sinomenin, 1-Brom-sinomenin und Methyl-sinomenin ausgeführt haben, aber im Allgemeinen mit etwas grösseren Schwierigkeiten. Die Umsetzungen werden Einfachheit halber unten schematisch abgebildet und die Einzelheiten sollen im Versuchsteil auseinandergesetzt werden.

1-Brom-methyl-sinomenin (I) und sein Hofmannscher Abbau. 5 g. 1-Brom-sinomenin wurden in ätherischer Lösung von Diazomethan (bereitet aus 5 g. Nitrosomethyl-harnstoff) eingetragen. Die Methylierung wurde durch Zusatz von Methanol sehr beschleunigt. Nach drei Tagen, wenn der abdestillierte Äther keine gelbe Farbe mehr zeigte,

(1) LI Mitteilung über Sinomenin.

Jodmethylat. Krystallisiert beim Erwärmen beider Komponenten in Äthanol. Schmp. 228° (od. 241°). Ausbeute quantitativ. Halochromie in konz. H_2SO_4 gelbgrün mit rotem Stich.

Anal.: Subst.=0.0621; AgJ =0.0249 g. Ber. für $\text{C}_{21}\text{H}_{26}\text{O}_4\text{NBr}\cdot\text{JCH}_3$ (578): J =21.97%. Gef.: J =21.65%. Spez. Drehung. 0.0482 g. Subst., 10 ccm. 20% Methanol, 1-dm-Rohr. α = -0.23° . $[\alpha]_{\text{D}}^{28}$ = -47.7° .

1-Brom-4-methyl-sinomenol (III). 1.7 g. obigen Jodmethylates wurden mit 34 ccm. 5 proz. Natronlauge 30 Minuten gekocht. Der isolierte Phenanthren-körper wurde aus Eisessig umgelöst. Schmp. 134° . Ausbeute 0.2 g.

Anal.: Subst.=4.031; CO_2 =8.312; H_2O =1.380 mg. Ber. für $\text{C}_{17}\text{H}_{15}\text{O}_4\text{Br}$. (363): C =56.20; H =4.13%. Gef.: C =56.24; H =3.83%.

Acetylieren. 50 mg. dieses Phenanthrens wurden mit 6 ccm. Acetylanhydrid und wenig Na-acetat in gewöhnlicher Weise acetyliert. Die Acetyl-Verbindung krystallisiert aus Äther beim Verdampfen. Schmp. 168° (Auch Mischprobe mit dem folgenden).

Acetolyse von 1-Brom-methyl-sinomenin-jodmethylat. 1-Brom-4-methyl-6-acetylsinomenol.

0.9 g. des Jodmethylates wurden mit 13 ccm. Acetylanhydrid + 0.9 g. Na-acetat 6 Stunden lang in offenem Kolben gekocht. Nach Abdestillieren des Anhydrides i.V., wurde der Rückstand in Methanol gelöst und in viel 3 proz. Essigsäure eingegossen. Der unlösliche Teil wurde in Äthanol gelöst und in viel Äther eingetragen. Der mit Wasser wohl gewaschene Äther lässt beim Abdampfen 0.4 g. Phenanthren hinter. Es kann dann aus Methanol umgelöst werden. Schmp. 168° . Ausbeute 50 mg.

Dieser Abbau kann in Schliessrohr mit etwas besserem Resultat durchgeführt werden.

Anal.: Subst.=3.028; CO_2 =6.246; H =1.112 mg. Subst.=7.563; AgJ =13.326 mg. Ber. für $\text{C}_{19}\text{H}_{17}\text{O}_5\text{Br}$ (405): C =56.30; H =4.20; $3\text{CH}_3\text{O}$ =22.96%. Gef.: C =56.26; H =4.11; CH_3O =23.29%.

1-Brom-methyl-sinomeninon (IV). 3.2 g. 1-Brom-methyl-sinomenin wurden mit 10 facher Menge 15 proz. Salzsäure eine halbe Stunde bei 100° erhitzt. Die daraus befreite Base beginnt sich schon aus Äther in rhombischen Platten krystallisieren. Leicht löslich in meisten Lösungsmitteln. Schmp. 110° . Eisenchlorid-Reaktion in Methanol rot (Dienol).

Anal.: Subst.=3.908; CO_2 =8.017; H_2O =1.777 mg. Subst.=6.890 mg.; N_2 =0.206 ccm. (769.5 mm. 23.0°). Subst.=0.0290; AgJ =0.0323 g. Ber. für $\text{C}_{19}\text{H}_{22}\text{O}_4\text{NBr}$ (408): C =55.88; H =5.39; N =3.43; $2\text{CH}_3\text{O}$ =15.20%. Gef.: C =55.95; H =5.05; N =3.42; CH_3O =14.71%. Spez. Drehung. 0.0638 g. Subst. 2.5 ccm. Chloroform, 1 dm-Rohr. α = $+2.02^{\circ}$. $[\alpha]_{\text{D}}^{26}$ = $+79.2^{\circ}$.

Jodmethylat. Schmp. 251° . Anal.: Subst.=0.0468; AgJ =0.0197 g. Ber. für $\text{C}_{19}\text{H}_{22}\text{O}_4\text{NBr}\cdot\text{JCH}_3$ (550): J =23.09%. Gef.: J =22.73%. Spez. Drehung. 0.1816 g. Subst., 10 ccm. Wasser, 1 dm-Rohr. α = $+0.42^{\circ}$. $[\alpha]_{\text{D}}^{21.5}$ = $+23.1^{\circ}$.

Dioxim. Krystallisiert beim Schütteln der wässrigen Suspension mit Äther. Schöne Nadeln. Schmp. 235° . Ausbeute 1.5 aus 2 g. Diketon.

Anal.: Subst.=4.483; CO_2 =8.556; H_2O =2.198 mg. Subst.=2.370 mg.; N_2 =0.194 ccm. (767.5 mm. 24°). Ber. für $\text{C}_{19}\text{H}_{24}\text{O}_4\text{N}_3\text{Br}$. (438): C =52.05; H =5.48;

N=9.59%. Gef.: C=52.05; H=5.49; N=9.31%. Spez. Drehung. 0.1200 g. Subst. 10 ccm. Chloroform + Äthanol, 1 dm-Rohr. $\alpha = +1.58^\circ$. $[\alpha]_D^{21.5} = +131.7^\circ$.

1-Brom-methyl-sinomeninon-furazan (V). 0.5 g. des obigen Dioxims wurde mit 20 ccm. 25 proz. Kalilauge $1\frac{2}{3}$ Stunden gekocht. Das gebildete Furazan wurde abfiltriert und aus Methanol umgelöst. Nadeln. Schmp. 152° . Ausbeute sehr schlecht.

Das Dioxim erleidet nicht den Furazanringschluss mit 15 proz. Kalilauge⁽¹⁾.

Anal.: Subst.=2.472; CO₂=4.931; H₂O=1.143 mg. Subst.=2.463 mg.; N₂=0.213 ccm. (768.3 mm. 24°). Ber. für C₁₉H₂₂N₃O₃Br. (420): C=54.29; H=5.24; N=10.00%. Gef.: C=54.4; H=5.17; N=9.85%. Spez. Drehung. 0.0351 g. Subst., 10 ccm. Methanol, 1 dm-Rohr. $\alpha = +0.33^\circ$. $[\alpha]_D^{26} = +94.0^\circ$.

1-Brom-methyl-sinomeninsäure (VI)⁽²⁾. 1,3 g. 1-Brom-methyl-sinomeninon wurden mit 0.35 g. Perhydrol (30%) und 5 ccm. Eisessig 5.5 Stunden bei 100° erhitzt. Nach dem Verjagen des Eisessigs, i.V., wurde 0.2 g. amorpher Substanz aus methanolischer Lösung gewonnen. Dies wurde in verdünntem Ammoniak gelöst und mit BaCl₂ ins Ba-Salz. (Nadeln; Schmp. $>320^\circ$) umwandelt. Die von Ba durch berechneter Menge 0.1 N-H₂SO₄ befreite Säure wurde noch einmal in Ammoniak gelöst und mit Essigsäure gefällt, um etwa anhaftende Schwefelsäure wegzunehmen. Schmp. 271° (aus 20 proz. Methanol). Ausbeute ca. 60 mg. Es dreht die Polarizationsebene nach rechts.

Anal.: Subst.=2.314; CO₂=4.360; H₂O=1.060 mg. Subst.=2.625 mg.; N₂=0.079 ccm. (764.4 mm. 27.3°). Ber. für C₁₉H₂₄O₆NBr. (442): C=51.58; H=5.43; N=3.17%. Gef.: C=51.26; H=5.14; N=3.37%.

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(1) Vergleiche Dieses Bulletin, **6** (1931), 197.

(2) *Ann.* **494** (1932), 1.

Über die unregelmässige Reihe der kolloiden Lösungen durch Elektrolyten. VI. Die vergleichenden Versuche der Koagulationskurven verschiedener Sulfidsole.⁽¹⁾

Von Naoyasu SATA und Sigeru ITÔ.

(Eingegangen am 20. April 1942.)

(1) **Einleitung.** Wir haben schon die unregelmässige Reihe des HgS-Sols von recht mannigfaltigen Seiten untersucht. Dadurch erklärt sich, dass diese Erscheinung an allen untersuchten HgS-Solen ohne Ausnahme nachweisbar ist, d.h. die Ausgangsmaterialien, beigemischte Fremdionen, die Beständigkeit, die Reinheit usw. des Sols haben mit der unregelmässigen Reihe nicht viel zu tun.

Nun haben wir infolgedessen noch eine Frage aufgeworfen, ob sie eine spezielle Eigenschaft des HgS-Sols ist oder bei allen mit H₂S stabilisierten Sulfidsole eine allgemein erkennbare Erscheinung ist, welche sich durch genau gleiche Methode herstellen lässt. Es ist nämlich die Herstellungsmethode von HgS-Sol nach Winssinger prinzipiell an allen Sulfidsole anwendbar, wenn man ein geeignetes Salz als Ausgangsmaterial findet. Daraus können wir vielleicht annehmen, dass die Oberflächenstruktur oder der Stabilisierungsmechanismus der Teilchen der nach gleicher Winssinger-Methode hergestellten Sulfidsole voneinander sehr ähnlich sein möge. Somit wäre das Adsorptionsverhalten des AgNO₃ auf diesen *strukturell* verwandten Sulfidsole auch wahrscheinlich ähnlich, da die Adsorption eine Oberflächenerscheinung ist. Schliesslich wurde konstatiert, dass die nach Winssinger-Methode hergestellten verschiedenen Sulfidsole allgemein die unregelmässige Reihe zeigen. Von diesen Gesichtspunkten aus haben wir nachstehend zuerst die Anwendbarkeit der Winssinger-Methode an verschiedenen Sulfidsol-Darstellungen untersucht und dann das Vorhandensein der unregelmässigen Erscheinung bei der Koagulation so hergestellter Solen geprüft.

(2) **Die Herstellung verschiedener Sulfidsole.** Von der Verwandtschaft mit Quecksilber haben wir zuerst als Sulfid-Material Cadmium und Zink ausgewählt.

Herstellungsvorschriften und Sol-Eigenschaften sind folgende.

(i) *CdS-Sol.* CdS-Sol nach Winssinger-Methode wurde schon von E. Prost⁽²⁾ untersucht. Er hat das Sulfid aus CdSO₄-Lösung unter Zusatz von Ammoniak gefällt, was vielleicht zu vollkommenem Niederschlagen der Cd-Ionen geführt hat und wovon die Sol-Beständigkeit in gewissem Sinne abhängig gemacht wird. Wir haben den Versuch unter verschiedenen Bedingungen ausgeführt.

(1) N. Sata u. Y. Niwase, *Kolloid-Z.*, **84** (1938), 314; N. Sata u. S. Itô, dieses Bulletin, **15** (1940), 271; N. Sata u. K. Môri, ebendort, **16** (1941), 139; N. Sata u. S. Itô, ebendort, **17** (1942), 4.

(2) The Svedberg: Herstellung kolloider Lösungen anorganischer Stoffe. (Dresden und Leipzig, 1922) S. 391, 404.

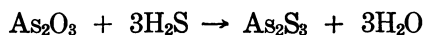
- (a) Von 100 ccm. 2.5% CdSO_4 -Lösung wurde das CdS mit H_2S gefällt unter Zusatz von 15 ccm. 6N- NH_4OH . Den Niederschlag wäscht man durch Dekantieren (3-mal). Die Suspension wurde peptisiert mit abermaligem H_2S -Durchleiten. Überschüssiger H_2S wurde mit H_2 ausgetrieben. Beständigkeit ist gut. Der Koagulationswert mit $\text{NaCl}=50$; $\text{CaCl}_2=0.6$; $\text{AlCl}_3=0.8$ Millimol./Lit.
- (b) Das CdS -Sol wurde hergestellt wie oben, aber ohne NH_4OH -Zusatz. Der Niederschlag liess sich nicht vollkommen peptisieren und lässt etwas Bodensatz zurück. Die Beständigkeit ist nicht so gut wie beim vorigen Fall, so z.B. setzt sich der Ko. W. (Abkürzung für Koagulationswert.) mit NaCl zu 2 Millimol./Lit. herab.
- (c) Das CdS -Sol (i), (a) wurde dialysiert für 11 Tage (nach 4 Tagen ist es koaguliert) und dann wieder mit H_2S peptisiert. Es ist doch viel beständiger als das CdS -Sol (i), (b), welches ohne Ammoniak hergestellt ist.
- (ii) *ZnS-Sol*. Das Sol ist auch von C. Winssinger⁽³⁾ hergestellt. Verschiedene Herstellungsmöglichkeiten haben wir untersucht. In diesem Fall ist NH_4OH unentbehrlich zum Peptisieren; d.h. aus ZnSO_4 unmittelbar gefälltes Sulfid lässt sich nicht mit H_2S peptisieren. Sondern man musste zuerst mit NH_4OH gefälltes Zn -Hydroxyd durch H_2S -Leiten in Sulfid umwandeln und gleichzeitig kolloidal peptisieren lassen.
- (a) Einer 100 ccm. 2.5% ZnSO_4 -Lösung wurde 6 ccm. 6N- NH_4OH zugesetzt. Ausscheidung von weissem, flockigem Zn -Hydroxyd-Niederschlag. Man leitet H_2S durch diese Hydroxyd-Suspension, um sie zur Sulfid-Suspension zu verwandeln. Da diese Suspension schwer absetzbar ist, musste man sie vor der Reinigung durch Dekantieren zentrifugieren, was nur 2-mal zu gestatten war. Vor dem dritten Dekantieren ist die Suspension automatisch peptisiert, ohne abermaliges H_2S -Durchleiten vollkommen, nur durch Umrühren eines Glasstäbchens. Noch übriggebliebenes H_2S wurde mit Durchleiten von H_2 ausgetrieben.
- (b) Das ZnS -Sol (ii), (a) kann man durch Erhitzen (98°C) koagulieren. Nach dem Dekantieren, peptisiert der grösste Teil des Niederschlags sich wieder durch einfaches Umrühren mit von neuem zugefügten Wasser. Diese Behandlung—Koagulieren durch Erhitzen, Zentrifugieren, Dekantieren und Peptisieren—wiederholt man 8-mal. Durch die Suspension wurde zuletzt zum vollständigen Peptisieren H_2S durchgeleitet.
- (c) Das ZnS -Sol (ii), (a) wird dialysiert für 7 Tage. (Nach 3 Tagen ist es koaguliert.) Danach wurde die Suspension wiederum mit H_2S peptisiert. In der Lösung NH_4 - und SO_4 -Ionen nicht nachweisbar. Tabelle 1 ergibt die Koagulationswerte dieser Sole in Millimol./Lit.

Tabelle 1.

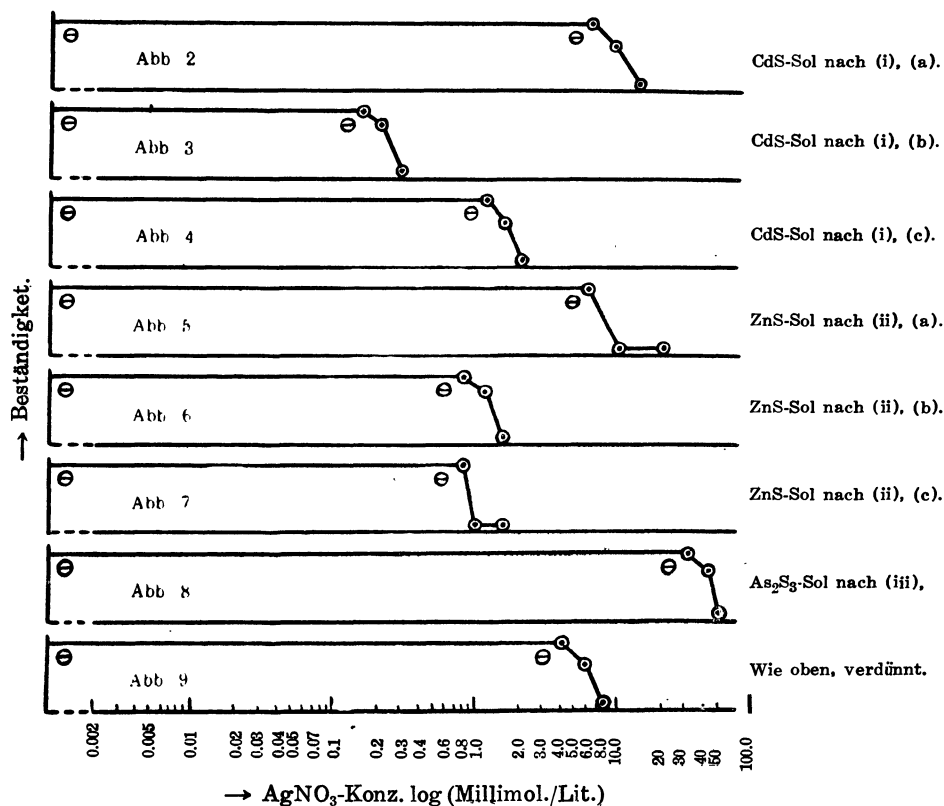
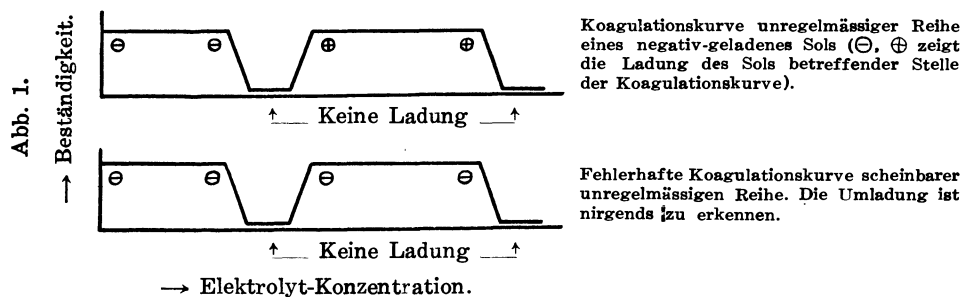
	Elektrolyt	NaCl	CaCl_2	AlCl_3
(ii), (a)	2-mal dekantiert	20	0.4	0.3
(ii), (b)	8-mal dekantiert mit Wärmeanwendung.	10	0.2	0.1

(3) *loc. cit.* (2), S. 299.

(iii) As_2S_3 -Sol. Zur Kontrolle haben wir auch As_2S_3 -Sol als einen Versuchsgegenstand ausgewählt. Bei diesem Sol ist besonders darauf zu achten, dass bei ihm ausser stabilisierenden H_2S keine beigemischten Fremdsubstanzen zu ahnen sind, wie die Reaktionsformel es zeigt:



(3) Die Koagulationsversuche. Die Koagulationsversuche, mit $AgNO_3$ als Elektrolyt, wurden dann an oben erhaltenen verschiedenen Sulfidsolen ausgeführt. Wie schon erwähnt, ist der Koagulationsversuch dieser Art ein sehr heikles Experiment. So haben wir diesmal die Koagulation nicht nur durch Trübung oder Flockenbildung entschieden, sondern



noch dazu durch Elektrophorese die Teilchenladung nachgesehen. Auf diese Weise kann man die Koagulationskurve vor einem Versuchsfehler garantieren. Bei dem Koagulationsversuche kommt manchmal eine fehlerhafte Koagulation vor, welche durch unerwartete Verunreinigungen in Versuchsgefäßen usw. ganz zufälligerweise hervorgerufen wird. In diesem Fall könnte die Koagulationskurve wie eine unregelmässige Reihe verlaufen, doch in Wirklichkeit ist gar keine, zur unregelmässigen Reihe charakteristische Umladung zu erkennen, was nur durch kataphoretische Untersuchung zu unterscheiden ist. Abb. 1 macht den Vorgang schematisch ersichtlich. Abb. 2–9 sind die Koagulationskurven der verschiedenen Sulfidsole.

(4) **Erörterung.** Das sogenannte nach „Winssinger Methode“ bekannte Herstellungsverfahren des HgS-Sols ist prinzipiell bei verschiedenen Sulfidsoleen allgemein anwendbar. Da in diesem Fall der H_2S zum Stabilisieren die Hauptrolle zu spielen hat, könnte man für alle Teilchen dieser Sulfidsole ganz gleiche oder wenigstens sehr ähnliche Oberflächenstruktur annehmen, wie aus Abb. 10 zu ersehen ist.⁽⁴⁾ Unter weiteren Annahme, dass solche ähnlich konstruierten Teilchen mit gleichem Elektrolyt (AgNO_3) auch gleicherweise die unregelmässige Koagulation wie HgS-Sol zeigen würde, haben wir obenstehende Untersuchung angestellt. Wie die Versuchsergebnisse aus den Abb. 2–9 erkennen lassen, erweist sich diese Vermutung als völlig haltlos, denn keins von den untersuchten Sulfidsoleen zeigt die unregelmässige Reihe. Daraus wird konstatiert, entweder die Oberflächenstruktur der Teilchen verschiedener Sulfidsole

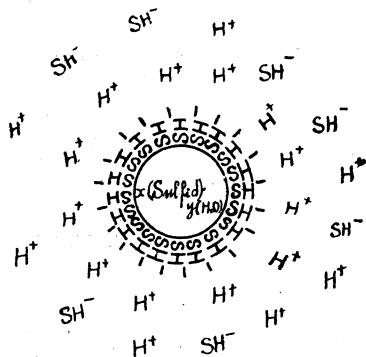


Abb. 10.

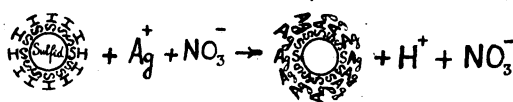


Abb. 11.

nicht ganz ähnlich anzunehmen ist, oder das HgS-Sol allein besitzt eine eigenartige Adsorptionseigenschaft mit AgNO_3 die unregelmässige Koagulation hervorzurufen. Wir haben schon bestätigt, dass die unregelmässige Reihe des HgS-Sols von beigemischten Fremdionen, die von verschiedenen Ausgangsmaterialien stammen, nicht beeinflusst wird. Noch dazu, weil der HgS-Niederschlag vor dem Peptisieren durch Dekantieren genügend gereinigt ist, könnte man leicht auf den Gedanken kommen, dass die

(4) H. B. Weiser, "Inorganic Colloid Chemistry," Vol. III, S. 212.

übriggebliebenen Fremdionen nach dem Peptisieren hauptsächlich auf der Teilchenoberfläche oder in ihrer diffusen Schicht verteilt worden sind. Dass diese Fremdionen auf der Teilchenoberfläche zur Entstehung der unregelmässigen Reihe nichts zu tun haben, legt uns die Vermutung nahe, dass die Ursache in der Verbindungsart von AgNO_3 an HgS -Oberfläche zu suchen ist. Ausserdem bei der Ausführung der Koagulationsversuche, konnten wir nachweisen, dass das anfangs neutrale HgS -Sol nach dem Zusatz der auch neutralen AgNO_3 -Lösung sauer geworden ist, woraus man die Wahrnehmung machen kann, dass hier eine polare Adsorption stattgefunden hat. Mitunter verstehen wir, dass zwischen SH -Ionen auf der Teilchenoberfläche und Ag -Ionen eine Austauschadsorption geschieht, wie aus Abb. 11 schematisch ersichtlich ist.

Wir kommen somit zum Schluss, dass eine weitere Überlegungsmöglichkeit hinsichtlich der Spezifität der unregelmässigen Reihe von HgS -Sol noch von der Seite des Adsorptionsproblems her zu finden ist. Die endgültige Diskutierung ist aus den Resultaten vergleichender Adsorptionsversuche von AgNO_3 an verschiedenen Sulfiden zu erwarten, welche schon im Gang ist.

Zusammenfassung.

(1) Um die Entstehung der unregelmässigen Reihe bei verschiedenen Sulfidsolen zu prüfen, wurde zuerst die Anwendbarkeit der sogenannten „Winssinger Methode“ zur Herstellung verschiedenen Sulfidsolen untersucht.

(2) Das Sulfidsol von Zn , Cd und As wurde nach dieser Methode unter variirenden Bedingungen hergestellt und ihre kolloidwissenschaftlichen Eigenschaften untereinander verglichen.

(3) Es wurden die Koagulationsversuche, mit AgNO_3 als Elektrolyt, an so erhaltenen, verschiedenen Sulfidsolen angestellt.

(4) Die unregelmässige Koagulationsreihe liess sich bei keinem Sulfidsol, ausser HgS -Sol, nachweisen.

(5) Dadurch wurde konstatiert, dass die unregelmässige Reihe auf eine spezielle Adsorptionseigenschaft von Ag - bzw. NO_3 -Ionen an HgS -Teilchen zurückzuführen ist.

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Geochemische Untersuchungen der Vulkane in Japan. XXVI. Dichtemessungen des Flusswassers. I.

Von Shinya OANA.

(Eingegangen am 21. Mai 1942.)

Einleitung. Es ist heutzutage äusserst schwierig, in irgend einem natürlichen Wasser die Mengenverhältnisse der schweren Sauerstoff- und Wasserstoffisotopen durch direkte Methoden genau zu ermitteln, obwohl gerade diese Frage im Gebiete der Geochemie von hohem Interesse ist. Man muss sich in der Gegenwart damit begnügen, dass man den Unterschied der summierten Konzentrationen der schweren Wasserisotopen in zwei verschiedenen Proben aus natürlichen Gewässern bestimmen kann. Die Dichte des Wassers steigt in dem Masse, in dem sich die Konzentrationen der schweren Wasserisotopen vergrössern. Wenn wir den Dichteunterschied zweier Proben vollständig gereinigten Wassers bis zu einer Genauigkeit von 0.1γ bestimmen (0.1γ ist die bis heute erreichte kleinste Fehlergrenze bei diesen Arbeiten), so können wir damit einen geringsten Unterschied der summierten Konzentrationen der schweren Wasserisotopen von 0.00009% der Atomanzahl erfassen. Es ergibt sich die Notwendigkeit, den Untersuchungen hinsichtlich der Dichte unveränderliches Wasser als Standard-Wasser zu Grunde zu legen. Wegen der Bequemlichkeit der Beschaffung habe ich das Leitungswasser der Stadt Tokio seit dem Anfang meiner Arbeit über Wasserisotopen als Standard gewählt. Etwa einmal im Jahre wird das Standard-Leitungswasser in grosser Menge bereitet. Zwischen den bis heute hergestellten Portionen des Standard-Leitungswassers konnte ich keinen Dichteunterschied beobachten. Worauf beruht diese Unveränderlichkeit der Dichte?

Um dieses Problem zu lösen, habe ich den Fluss Tamagawa entlang, der mein Standard-Leitungswasser liefert, eine Reihe von Wasserproben gesammelt und durch Schwimmermethode ihre Dichte bestimmt. Diese, die an dem Oberlauf sehr klein ist, wird im weiteren Laufe des Tamagawa-Flusses grösser, um schliesslich von einem gewissen Ort des Unterlaufs an den Wert 0γ zu erreichen und unveränderlich beizubehalten.

Ich habe auch bei anderen Flüssen entsprechende Verhältnisse beobachtet. Über diese Erscheinung wird weiter unten näherer berichtet.

Methoden der Versuche. Die Reinigungsprozesse des Wassers und die Methoden der Dichteunterschiedsbestimmung zwischen natürlichen Wässern und dem Leitungswasser der Stadt Tokio wurden in früheren Mitteilungen⁽¹⁾ beschrieben.

Ergebnisse der Versuche. Bis heute liegen vier Portionen des Standard-Leitungswassers vor, das jedesmal in einer Menge von etwa 20 l. in einer Glasflasche aufbewahrt wird und bei den Dichtemessungen eines natürlichen Wassers als Standard dient. Die Dichteunterschiedsbestim-

(1) S. Oana, Dieses Bulletin, **14** (1939), 279.

mungen zwischen den früheren drei Standards und dem letzten sind in Tabelle 1 wiedergegeben.

Tabelle 1. Dichteunterschiede zwischen verschiedenen Portionen des Standard-Leitungswassers.

Datum	Dichteunterschied, γ
15. Apr. 1936.....	0.0 ₀
10. Nov. 1938.....	-0.0 ₉
13. Mai 1940.....	+0.0 ₄
31. Jan. 1941.....	Standard

Aus dem Tamagawa-Fluss, der obengenannte Standards geliefert hat, wurden an verschiedenen Stellen seines Laufs 9 Wasserproben entnommen und geprüft. Die gewonnenen Resultate enthält Tabelle 2.

Die genannten Orte sind in Abb. 1 eingezeichnet.

Ein gleicher Versuch wurde bei einem anderen

Flusse, dem Adusagawa durchgeführt. Die gewonnenen Ergebnisse sind in Tabelle 3 enthalten.

Tabelle 2. Dichteunterschied zwischen dem Flusswasser von Tamagawa und dem Standard-Leitungswasser.

	Entfernung vom Ursprung, km.	Tageszeit, am 22. Sept. 1941	Luft- tem- peratur, °C.	Fluss- tem- peratur, °C.	pH	Dichte- unter- schied, γ
1 Taba	17.....	17 ^h (am 21.)	16.2	13.1	7.0	-1.0 ₅
2 Yuba	31.....	5 ^h 40	11.2	13.0	7.4	-1.3 ₂
3 Bentenkio	41.....	7 ^h 5	12.3	13.4	7.1	-0.5 ₃
4 Nipparagawa (17).... bei Hikawa		7 ^h 40	13.0	12.6	7.7	-0.7 ₀
5 Hikawa	41.5 ...	8 ^h 10	15.2	13.0	7.5	-0.8 ₃
6 Mitake	53.....	9 ^h 20	16.0	14.2	8.1	0.0 ₀
7 Hamura	70.....	12 ^h 10	21.5	16.1	7.4	-0.1 ₈
8 Oberes Sammelbecken des Leitungswassers bei Murayama		14 ^h 50	22.0	20.0	7.5	-0.1 ₃
9 Unteres Sammelbecken.		15 ^h 0	21.2	21.2	7.4	-0.0 ₄

4. Nipparagawa ist ein Nebenfluss, der bei Hikawa in den Tamagawa einmündet, und die Laufstrecke des ersteren bis hierher beträgt 17 km.

7, 8, 9. Das Leitungswasser wird von Hamura bis zum oberen Sammelbecken bei Murayama durch eine Röhre aus Zement geleitet und dann aus dem unteren Becken der Stadt Tokio geliefert, nachdem es bereits im oberen von suspendierten Stoffen befreit wurde.

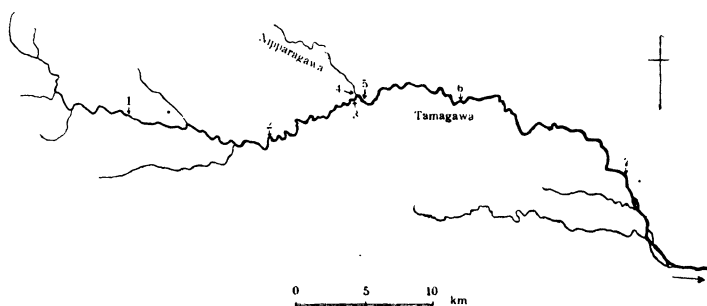


Abb. 1. Tamagawa-Fluss.

Tabelle 3. Dichteunterschied zwischen dem Flusswasser von Adusagawa und dem Standard-Leitungswasser.

Herkunft der Wasserprobe		Entfernung vom Ursprung, km
10	Schneereste vom Karasawa-Firn	(0)
11	Bächlein bei der Berghütte Karasawagoya	(0)
12	Nebenfluss Karasawa bei der Brücke Hondanibasi	(1.5)
13	Nebenfluss Karasawa bei der Felsengrotte von Yokoo	(4)
14	Adusagawa vor der Mündung des Karasawa	6
15	Adusagawa nach der Mündung des Tokusawa	10
16	Adusagawa bei der Brücke Kappabasi	15.5
17	Adusagawa bei Nakanoyu-Therme	22
18	Adusagawa bei der Bahnstation Simasima	49

Tageszeit, am 19. Aug. 1941		Lufttem- peratur, °C.	Flusstem- peratur, °C.	pH	Dichte- unterschied, γ
10	8 ^h 50	17.0	—	6.2	+0.2 ₉
11	8 ^h 30	17.0	14.1	5.8	-1.8 ₄
12	9 ^h 55	21.6	6.7	8.6	-1.7 ₅
13	10 ^h 30	20.8	7.0	7.4	-1.3 ₆
14	11 ^h 0	22.1	11.9	7.0	-1.0 ₅
15	12 ^h 30	22.3	11.1	6.9	-1.0 ₁
16	14 ^h 20	23.7	11.3	6.6	-1.4 ₀
17	16 ^h 25	23.4	18.1	7.0	-1.0 ₅
18	19 ^h 10	25.0	16.2	7.0	-0.3 ₁

Von 10 bis 13: Einzugsgebiet des Karasawa, der 4.5 km. von seinem Ursprung entfernt in den Adusagawa mündet.

Die genannten Orte zeigt Abb. 2.

Daneben ist eine Folge von Dichtemessungen an verschiedenen Flusswässern, die ich bei Studienreisen nach Thermal- oder Mineralquellen gesammelt habe, in Tabelle 4 aufgeführt.

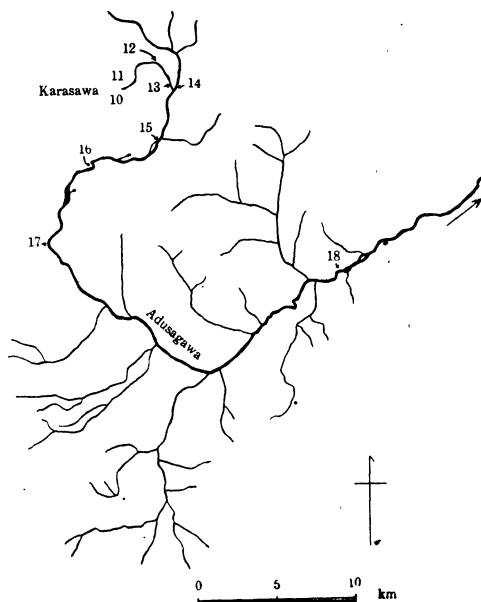


Abb. 2. Adusagawa-Fluss.

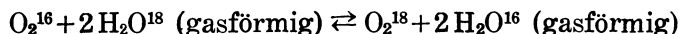
Tabelle 4. Dichteunterschiede zwischen Bach- und Flusswässern und dem Standard-Leitungswasser.

Name des Gewässers	Ort	Entfernung vom Ursprung, km
19 Bächlein	bei Fumarole von Shonnazawa ⁽²⁾	0
20 Bächlein	bei kohlensäurehaltiger Mineralquelle Ippōsui ⁽¹⁾	1
21 Sendatugawa	bei Ganiba-Therme ⁽²⁾	4
22 Hontanigawa	bei Mineralquelle A ₅ von Masutomi ⁽³⁾	6
23 ebenda	ebenda	6
24 Kamasegawa	bei Mineralquelle E von Masutomi ⁽³⁾	7
25 Gamadagawa	bei Hotaka-Therme ⁽¹⁾	11
26 ebenda	bei Yarimi-Therme ⁽¹⁾	12.5
27 Adusagawa	bei der Brücke Kappabasi	15.5
28 ebenda	ebenda	15.5

Zeit	Wassertemperatur, °C.	Dichteunterschied, γ
19 24. Mai 1939, 13 ^h	—	— 0.9
20 4. Aug. 1938	14.7	— 1.3
21 24. Mai 1939, 16 ^h	8.0	— 1.1
22 8. Juli 1939, 11 ^h	16.0	— 0.4
23 20. Okt. 1940, 17 ^h	10.9	— 0.6
24 19. Okt. 1940, 17 ^h	12.5	— 0.4
25 3. Aug. 1938	11.5	— 1.3
26 ebenda	14.0	— 1.9
27 28. Juli 1939	10.1	— 1.6
28 13. Aug. 1940	9.9	— 0.8

(2) S. Oana, *J. Chem. Soc. Japan*, **60** (1939), 1008.(3) S. Oana, ebenda, **15** (1940), 485.

Erörterung der Ergebnisse. Bei der Behandlung des vadosen Wassers gehen wir vom Wasserdampf in der Atmosphäre aus. Er weist eine verhältnismässig geringe Konzentration an schweren Wasserisotopen auf. Nach M. Dole beträgt sein Dichteunterschied -1.95γ und wird auf die Austauschreaktion zwischen O^{18} im Wasserdampf und O_2^{16} in der Luft zurückgeführt.⁽⁴⁾ Das heisst, bei dem sich ergebenden Gleichgewichte wächst die Gleichgewichtskonstante, die bei $0^\circ C$. 1.048 ist, mit dem Fallen der Temperatur⁽⁵⁾; demnach soll der Dichtewert bei tieferen Temperaturen in den oberen Luftschichten wahrscheinlich sein.



Wasserdampf kondensiert in der Luft in verschiedenen Formen. Er erscheint uns als Wolke, Nebel, Schnee oder Regen u.a.m. Auf dem Berggipfel von Fujisan, der sich 3776 m. über dem Meeresspiegel erhebt, wurden zwei Rauhreifproben gewonnen, die auf Grund meiner Prüfung die in Tabelle 5 mitgeteilten Werte zeigten.

Tabelle 5. Dichteunterschied zwischen dem Rauhreif und Standard-Leitungswasser.

Rauhreif	Zeit der Entstehung	Lufttemperatur, °C.	Luftdruck, mm Hg.	Dichteunter- schied, γ
Rauhrost	von 15 ^h am 16. Dez. 1941 bis 9 ^h am 17. Dez.	-18.6	496	-1.84
Rauheis	alt	erheblich höher		-0.39

Wenn unterkühlte Wassertropfen an irgend einen Körper anstossen, so entsteht Rauhreif. Bei tieferer Temperatur gebildeter Rauhreif ist undurchsichtig, weil er eine grosse Anzahl von kleinen Luftblasen enthält, und wird Rauhrost genannt, während bei höherer Temperatur gebildeter eine durchsichtige Masse von Eis ist. Der letztere wird Rauheis genannt. Infolge der Schmelzwärme können sich die Wassertropfen in diesem Fall aber nicht vollständig in Rauhreif verwandeln, ein gewisser Anteil wird vielmehr stets als Wasserdampf an die Luft abgegeben. Mit steigender Lufttemperatur nimmt dieser fliehende Anteil zu. Dies ist wohl die Ursache dafür, dass Rauhrost leichter ist als Rauheis, da bei der Tieftemperaturverdampfung Fraktionierung der Wasserisotopen in beträchtlicherem Grade stattfindet. Es ist deshalb über alle Erwartung schwierig, die Dichte des Wasserdampfes in der Luft durch Rauhreif zu ermitteln.

Wie verhält sich Schnee- oder Regenwasser? Am östlichen Abhang des Berges Norikuradake in Sinano-Provinz, sich etwa 1700 m. über die Meeresfläche erhebend, befindet sich eine kleine Hütte, die der Kaiserlichen Universität zu Tokio gehört. Ich habe im Vorgarten dieser Hütte Gelegenheit gehabt, den Schnee, der vom Nachmittag am 31. Dezember im Jahre 1941 bis zum Morgen am 2. Januar im Jahre 1942 bei Windstille gefallen war und 26.4 cm. hoch lag, in zwei gleich dicke Schichten getrennt

(4) M. Dole, *J. Chem. Phys.*, **4** (1936), 778.

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

zu gewinnen. Die Dichtewerte der Oberschicht und der Unterschicht zeigt Tabelle 6.

Tabelle 6. Dichteunterschied zwischen Schnee und Standard-Leitungswasser.

Zeit des Schneefalls		Lufttemperatur, °C.	Art der Schicht	Dichteunterschied, γ durchschnittlich	
Schnee am	vom Nachmittag des	zwischen	obere 13.2 cm	—3.5 ₅	—2.7 ₉
Abhang von	31. Dez. 1941 bis	—8.3			
Norikuradake	zum Morgen des 2. Jan. 1942	und —11.0	untere 13.2 cm	—2.0 ₂	

Der Dampfdruck des Eises ist bei tiefer Temperatur ausserordentlich klein und beträgt bei -10°C. nur 1.95 mm. Hg. Die in Tabelle 6 angegebene Dichte $-2.7_9 \gamma$ können wir deshalb natürlich als die des Wasserdampfes in der Luft betrachten, weil der Schnee bei dem Fallen durch den Luftraum fast allen Wasserdampf aufnehmen muss. Die Ursache dafür, dass die obere Schicht leichter ist als die untere, wird wohl durch Fraktionierung der Wasserisotopen bei der Bildung des Schnees zu erklären sein. Es ist möglich, dass sich schwerere Wasserisotopen früher kondensieren als leichtere. Dass die Dichte des Regenwassers gegen Ende des Regenfalles geringer wird, wurde tatsächlich in Osaka bei einem Regenfalle beobachtet.⁽⁶⁾

Beim Regenwasser sind die Dichteverhältnisse ebenso verwickelt wie beim Rauheif. Als Dichte des Regenwassers wurden von jedem Autor bisher verschiedene Werte angegeben.⁽⁷⁾ Sie liegen zwischen -0.4γ und -2.3γ .

Flusswasser wird von obengenannten verschiedenen Niederschlägen geliefert, und seine Dichte ist in der ersten Laufstrecke klein, wie die Tabellen 2, 3 und 4 zeigen. Die Dichte nimmt dann mit der Länge der zurückgelegten Laufstrecke zu. Dieser Umstand dürfte auf die Fraktionierung der Wasserisotopen bei der Verdampfung des Flusswassers zurückzuführen sein. Es ist durchaus zu erwarten, dass sich die Konzentrationen der schweren Wasserisotopen im Wasser durch Verdampfung vergrössern, weil der Dampfdruck der schweren Wasserisotopen kleiner als der von H_2O^{16} ist. Die Dichte des Tamagawa-Flusswassers erreicht 0γ nachdem es sich etwa 53 km. von seinem Ursprunge entfernt hat. Dass in der Tabelle 2 Nr. 1 schwerer als Nr. 2 ist, wird dadurch erklärt, dass bei Nr. 1 im Vergleich mit Nr. 2 Verdampfung in höherem Grade wirksam war, da Nr. 1 am Abend Nr. 2 jedoch früh am Morgen entnommen wurde.

Warum bleibt dieser Wert 0γ im weiteren Flusslaufe nunmehr unverändert? Im Flusswasser wird wohl zwischen O^{18} im Wasser und O_2^{16} in der Luft eine durch folgende Formel gezeigte Austauschreaktion stattfinden.⁽⁵⁾

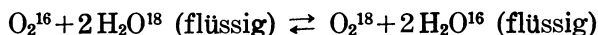
(6) M. Harada und T. Titani, Dieses Bulletin, **10** (1935), 206.

(7) Ebenda.

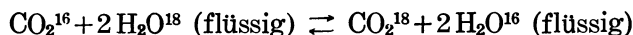
Y. Shibata, K. Noguchi und S. Kaneko, *J. Chem. Soc. Japan*, **58** (1937), 1013.

N. Parraaano, "Atti del X° Congr. Intern. Chimica", II.

S. Oana, *J. Chem. Soc. Japan*, **60** (1939), 1005.



Die Gleichgewichtskonstante ist bei 0°C. 1.020 und bei 25°C. 1.012. Daneben wird wohl auch die Austauschreaktion, die zwischen O^{18} im Wasser und CO_2^{16} in der Luft nach folgender Formel stattfindet, mitwirken⁽⁵⁾.



Die Gleichgewichtskonstante ist bei 0°C. 1.033 und bei 25°C. 1.028. Diese Austauschreaktionen verkleinern die Dichte des Flusswassers. Sie werden offenbar umso stärker wirksam, je länger der Flusslauf ist, weil sich die Substanz, die bei diesen Austauschreaktionen als Katalysator wirkt, nach dem Unterlauf hin vermehrt. Ich meine, dass die Dichte des Flusswassers in demjenigen Zustand, in dem die Zunahme der Dichte durch Verdunstung und die Abnahme der Dichte durch Austauschreaktionen sich gegenseitig ausgleichen, 0 γ ist.

Flusswasser fließt schliesslich ins Meer hinein. Hier unterliegt es einer Verdunstung grössten Ausmasses, die den weitaus überwiegenden Anteil des atmosphärischen Wasserdampfes liefert. Die Dichte des Meerwassers ist deshalb gross, weil ihre Abnahme durch Austauschreaktion gegenüber der dauernden Zunahme durch Verdunstung fast wirkungslos bleibt. Tabelle 7 bringt den Dichtewert des Meerwassers, das von der Japanischen Ozeanographischen Gesellschaft (Nippon Kaiyô Gakkai) für Standard-Meerwasser festgesetzt wurde.⁽⁸⁾

Tabelle 7. Dichteunterschied zwischen Standard-Meerwasser und Standard-Leitungswasser.

	Dichteunterschied
Standard-Meerwasser Nr. 16	+4.2 ₈ γ

Vorliegende Erörterung über Dichtewerte verschiedener vadoser Wässer zeigt, dass vom atmosphärischen Wasserdampf ausgehend und den Flusslauf folgend bis ins Meer die Wasserdichte sich vergrössert. Aus dieser Mitteilung folgt weiter, dass Flusswasser bei Dichtemessungen —jedenfalls in Japan—als Standard brauchbar ist, nachdem es vom Ursprunge des Flusses etwa 50 km. Laufstrecke zurückgelegt hat.

Es sei mir gestattet, Herrn Prof. Yuji Shibata und Herrn Prof. Kenjiro Kimura für ihre freundliche Anleitung und ihre Ratschläge und der Kaiserlichen Akademie der Wissenschaft für ihre finanzielle Unterstützung bei der Ausführung dieser Arbeit meinen herzlichen Dank auszusprechen.

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Die Kinetik der Umlagerung der Cis-Trans-Isomeren im Gaszustand (Dritte Mitteilung). Die Umlagerung der Dichloräthylene unter Einwirkung der Gefäßwand und metallischen Katalysatoren.

Von Bunichi TAMAMUSHI.

(Eingegangen am 21. Mai 1942.)

Die Frage über die Homogenität der Umlagerungsreaktion von Cis-Dichloräthylen in Trans-Dichloräthylen bzw. der Gegenreaktion von Trans-Dichloräthylen in Cis-Dichloräthylen im Gaszustand ist in bisherigen Untersuchungen teilweise beantwortet aber quantitativ noch nicht erschöpfend dargelegt worden. R. Büll⁽¹⁾ hat in seiner grundlegenden Arbeit gezeigt, dass die Umlagerungsreaktion von Cis-Dichloräthylen in Trans-Dichloräthylen im Gaszustand von den angesetzten kleinen Glaskugeln, sowie von Platinschnitzeln bei der Temperatur 300°C. kaum katalysiert wird, sodass die Reaktion praktisch als homogen angesehen werden kann, während sich die Gegenreaktion von Trans-Dichloräthylen in Cis-Dichloräthylen auch bei niedrigeren Temperaturen gegen katalytische Einflüsse von Glaswänden als viel empfindlicher erweist. Neuerdings kamen Jones und Taylor⁽²⁾ in ihrer kinetischen Untersuchung der thermischen Isomerisierung von Trans-Dichloräthylen in Cis-Dichloräthylen zur Schlussfolgerung, dass diese Reaktion möglicherweise zu einem gewissen Teil heterogen verläuft, aber doch annähernd als homogen angesehen werden kann, während die Nebenreaktion—die thermische Zersetzungsreaktion—weitgehend empfindlich gegen den Einfluss von der Gefäßwand ist. Als Fortsetzung und Erweiterung unserer Untersuchungen⁽³⁾ über die Kinetik der Umlagerung der Cis-Trans-Isomeren im Gaszustand haben wir nun in der vorliegenden Arbeit die Kinetik der Umlagerung von Cis-Dichloräthylen in Trans-Dichloräthylen sowie der Gegenreaktion von Trans-Dichloräthylen in Cis-Dichloräthylen im Gaszustand unter Einwirkung von der Gefäßwand und metallischen Katalysatoren (Platin-Netz, Platinschwarz) untersucht. Die dabei erhaltenen Ergebnisse sollen in Bezug auf die Frage der Homogenität der genannten Reaktionen quantitative Angaben darbieten.

Die kinetischen Messungen wurden hier bei einer tieferen Temperatur, nämlich, bei 200°C. bzw. 180°C. durchgeführt, wodurch man die Möglichkeit bekam, die Pyrolyse der Reaktionsteilnehmer auszuschliessen. Zur kinetischen Messung wurde die statische Methode angewandt, worüber die vorhergehende Mitteilung berichtet hat. Das Reaktionsgefäß von

(1) L. Ebert und R. Büll, *Z. physik. Chem.*, A **152** (1931), 451; R. Büll, Dissertation. Würzburg, 1936.

(2) J. L. Jones und R. L. Taylor, *J. Am. Chem. Soc.*, **62** (1940), 3480.

(3) B. Tamamushi und H. Akiyama, *Z. Elektrochem.*, **45** (1939), 72; B. Tamamushi, H. Akiyama und K. Ishii, ebenda, **47** (1941), 340.

Terexglas betrug etwa 1 oder 2 Liter Inhalt, einmal ohne und ein anderesmal mit vielen Glasröhrchen oder mit einem Platin-Netz oder mit einer kleinen Menge von Platinschwarz. Ein Gefäß mit innerlich versilberter Wand wurde auch zur Messung verwendet. Der Druck des reagierenden Stoffes im Reaktionsgefäß wurde gleich etwa 30 mm. bzw. 40 mm. Hg. gesetzt.

Das zur Untersuchung verwendete Material wurde folgenderweise hergestellt: Cis- und Trans-Dichloräthylen wurden aus Dichloräthylen des Handels (Präparat von Schering-Kahlbaum) durch wiederholte Fraktionierung mittels einer Youngschen Kolonne dargestellt. Die getrennten Fraktionen hatten folgende physikalische Konstanten.

Tabelle 1. Physikalische Konstanten der isomeren Dichloräthylene.

	Trans-Isomer	Cis-Isomer
Siedepunkt	48-49° (752 mm.)	59.5 60.1° (760 mm.)
Dichte d_4^{25}	1.1187	1.1417
Brechungsindex n_D^{25}	1.44316	1.44607
Dipolmoment	0.77×10^{-18}	1.81×10^{-18}

Das Platinschwarz wurde nach der Methode von Ramsay, Mond und Shields⁽⁴⁾ hergestellt, dessen Aktivität man im voraus mit Hilfe der Hydrierungsreaktion von Benzol in Zylohexan festgestellt hatte.

Das verwendete Platin-Netz hatte eine Dimension von 56.26 cm.² und das Oberfläche-Volum-Verhältnis von dem von Glasröhrchen freien Gefäß und von dem mit Glasröhrchen gefüllten war 0.364 cm.⁻¹ bzw. 9.96 cm.⁻¹

Das Reaktionsprodukt wurde nach der Reaktionszeit in einer mit dem Reaktionsgefäß verbundenen Ampoule mittels Kohlendioxyd-Toluol-Gemisch möglichst rasch kondensiert und dann auf den Gehalt von Cis- oder Trans-Verbindung hin analysiert, indem man hierzu die Bestimmung der Dielektrizitätskonstante der benzoligen Lösungen anwendete. Die Standard-Beziehung zwischen der Dielektrizitätskonstante (abgekürzt DK) und den Zusammensetzungen ist schon in unserer vorhergehenden Mitteilung⁽⁵⁾ angegeben worden.

Die untersuchten Reaktionen: Cis $\rightarrow$ Trans sowie Trans $\rightarrow$ Cis erreichen ein bestimmtes Gleichgewicht und zwar bei der hier gewährten Temperatur, nämlich bei 200°C. langsam nach mehr als 50 Stunden. Die Gleichgewichtslage konnte man nach den bisherigen Angaben wie unten annähernd abschätzen. Die Geschwindigkeitskonstante k (Cis $\rightarrow$ Trans) bzw. k' (Trans $\rightarrow$ Cis) hat man demgemäss mit Hilfe der folgenden Gleichungen:

$$k = \frac{K}{t(1+K)} \ln \left[\frac{100}{100 - \left(1 + \frac{1}{K}\right)c'} \right]$$

$$k' = \frac{K'}{t(1+K')} \ln \left[\frac{100}{100 - \left(1 + \frac{1}{K'}\right)c} \right]$$

(4) W. Ramsay, L. Mond und J. Shields, *Phil. Trans.*, **186 A** (1895), 661.

(5) *loc. cit.* (3).

berechnet, wobei t die Reaktionszeit, K bzw. K' die Gleichgewichtskonstante ($K = \text{Trans}_\infty / \text{Cis}_\infty$, $K' = \text{Cis}_\infty / \text{Trans}_\infty$), und c (%-Cis) bzw. c' (%-Trans) das Gewichtsprozent des entstandenen Reaktionsproduktes bedeutet. Hierbei wurde natürlich angenommen, dass die beiden Cis $\rightarrow$ Trans und Trans $\rightarrow$ Cis Reaktionen unimolekular verlaufen.

Nach den Angaben unserer vorhergehenden Untersuchung wird die Gleichgewichtslage bei 200°C. als etwa 60%-Cis-Verbindung ermittelt, während sie nach den neuen genaueren Angaben von Wood und Stevenson⁽⁶⁾ als 63.38%-Cis bei 185°C. und 62.2%-Cis bei 215°C. festgelegt ist. Wir haben demnach hierfür einen wahrscheinlichen Wert 62%-Cis dementsprechend $K=38/62$ bzw. $K'=62/38$ bei 200°C. angenommen. Die Ergebnisse der Messungen werden in folgenden Tabellen zusammengestellt.

Tabelle 2. Die Kinetik der Reaktion: Cis $\rightarrow$ Trans bei 200°C.

Versuchs-Nr.	Zeit in Stunden	Druck des Substrates (mm.)	DK	Reaktionsprodukt (%-Trans)	$k \cdot 10^6$ sek. $^{-1}$
<i>Im Gefäß ohne Katalysator.</i>					
70'	3	29	2.496	8.0	7.88
71'	5	29	2.490	11.0	7.22
72'	9	29	2.478	16.5	6.68
20	3	40	2.495	8.5	8.91
19	5	40	2.485	13.0	8.84
					(8.07)
<i>Im Gefäß mit Glasröhrchen.</i>					
60	3	40	2.500	7.5	7.75
59	5	40	2.485	13.0	8.84
61	9	29	2.473	18.6	7.89
					(8.16)
<i>Im Gefäß mit Platin-Netz.</i>					
10	4	40	2.491	11.0	9.02
12	6	40	2.485	13.0	7.37
11	8	40	2.473	18.6	8.87
14	10	40	2.469	21.4	8.74
					(8.50)
<i>Im Gefäß mit versilberter Wand.</i>					
40	2	40	2.502	5.8	8.00
38	4	40	2.493	9.4	7.50
41	6	40	2.485	14.0	7.54
					(7.68)
<i>Im Gefäß mit Platinschwarz (bei 180°C).</i>					
82	1	40	2.483	13.9	48.1
84	2	40	2.480	15.8	28.4
83	3	40	2.475	18.5*	23.5
					(33.3)
<i>Im Gefäß mit Platinschwarz (bei 200°C).</i>					
81	1/2	40	2.478	16.0*	123
80	4	40	2.430	39.0*	—

* Es trat dabei die Pyrolyse hervor.

(6) R. E. Wood und D. P. Stevenson, *J. Am. Chem. Soc.*, **63** (1941), 1650.

Tabelle 3. Die Kinetik der Reaktion: Trans $\rightarrow$ Cis bei 200°C.

Versuchs-Nr.	Zeit in Stunden	Druck des Substrates (mm.)	DK	Reaktionsprodukt (%-Cis)	$k' \cdot 10^6 \text{ sek.}^{-1}$
<i>Im Gefäss ohne Katalysator.</i>					
85'	10	27	2.351	24.5	8.66
83'	24	27	2.382	39.0	7.11
84'	50	28	2.425	59.0	10.33
1	2	40	2.314	6.5	9.54
3	4	40	2.323	11.0	8.41
2	6	40	2.332	14.8	7.83
					(8.84)
<i>Im Gefäss mit Glasröhrchen.</i>					
5	2	40	2.312	5.5	8.00
7	4	40	2.323	11.0	8.41
6	6	40	2.340	18.5	10.16
8	8	40	2.343	20.3	8.54
					(8.78)
<i>Im Gefäss mit Platin-Netz.</i>					
13	2	40	2.314	5.5	8.00
17	4	40	2.332	14.8	11.8
16	6	40	2.340	18.5	10.16
15	8	40	2.347	22.1	9.49
18	10	40	2.360	27.8	10.5
					(9.99)
<i>Im Gefäss mit versilberter Wand.</i>					
49	2	40	2.316	7.5	11.1
46	6	40	2.341	19.4	10.8
47	8	40	2.355	25.9	11.6
48	10	40	2.351	24.2	8.5
					(10.5)
<i>Im Gefäss mit Platinschwarz (bei 180°C).</i>					
88	1/2	40	2.326	12.0*	74
86	1	40	2.371	33.2*	132
87	2	40	2.408	50.8*	148
					(118)

* Es trat dabei die Pyrolyse hervor.

In Anbetracht dessen, dass man bei der Analyse des Reaktionsproduktes einen merklichen experimentellen Fehler nicht umgehen kann, so schwanken die k -Werte mehr oder weniger in einer Messungsreihe. Die Genauigkeit des Experiments könnte doch noch erhöht werden, es mangelte uns aber leider das Versuchsmaterial um den Versuch zu wiederholen.

Vergleicht man nun die oben erhaltenen k -Werte (Mittelwerte in jeder Messungsreihe) in den verschiedenen Messungsreihen miteinander, indem man den möglichen experimentellen Fehler in Betracht zieht, so muss man schliessen, dass die Reaktion: Cis-Verbindung $\rightarrow$ Trans-Verbindung durch die Einfüllung von Glasröhrchen oder durch die Versilberung der Gefässwand praktisch kaum beeinflusst wird, sodass die Reaktion als genügend homogen angesehen werden kann. Die katalytische Einwirkung vom Platin-Netz ist auch unbemerkt, dagegen ist die Ein-

wirkung von aktivem Platinschwarz ganz bedeutend. Beim Zusatz von Platinschwarz tritt ausserdem die thermische Zersetzungsreaktion sogar bei der untersuchten Temperatur 200°C. hervor, was man durch die plötzliche Druckerhöhung im Reaktionsgefäss oder durch die Feststellung von entstandenem HCl im Reaktionsprodukt erkennen konnte. Bei 180°C. trat die Nebenreaktion in geringerem Masse auch bei Vorhandensein von Platinschwarz hervor.

Aus Tabelle 3 sieht man, dass auch die Reaktion: Trans-Verbindung → Cis-Verbindung unter Zusatz von Glasröhrchen nicht merklich beeinflusst wird, sodass man sie auch praktisch als homogen betrachten kann.

Diese letzte Reaktion scheint allerdings nach den oben erhaltenen Angaben gegen Platin sowie gegen Silberwand einigermassen empfindlich zu sein; ihre katalytische Einwirkung ist aber noch nicht sicher festzustellen. Die katalytische Wirkung von Platinschwarz ist auch in diesem Fall sehr bedeutend und zwar tritt die Zersetzungsreaktion schon bei 180°C. sogar auch in kürzerer Reaktionszeit hervor. Es ist also wahrscheinlich, dass der Isomerisierungsprozess an sich auch in diesem Fall praktisch genügend homogen ist, während die Nebenreaktion durch die Gefässwand oder metallische Katalysatoren weitgehend katalysiert wird⁽⁷⁾.

Zusammenfassung.

Die Umlagerungsreaktion von Cis-Dichloräthylen in Trans-Dichloräthylen und ihre Gegenreaktion wurden unter Einwirkung von der Gefässwand sowie von metallischen Katalysatoren im Gaszustand bei 200°C. kinetisch untersucht.

Es wurde festgestellt, dass sowohl die Reaktion von Cis-Verbindung in Trans-Verbindung als auch die Reaktion von Trans-Verbindung in Cis-Verbindung durch die Einfüllung von Glasröhrchen oder einem Platin-Netz in Reaktionsgefäss sowie durch die Versilberung von der Gefässwand nicht merklich beeinflusst werden, woraufhin diese beiden Reaktionen praktisch als homogen betrachtet werden können.

Durch aktives Platinschwarz werden die beiden Umlagerungsreaktionen weitgehend katalysiert, wobei gleichzeitig die thermische Zersetzung der Reaktionsteilnehmer als Nebenreaktion stattfindet. In der Reaktion von Trans-Dichloräthylen in Cis-Dichloräthylen ist diese Nebenreaktion besonders empfindlich gegen den Katalysator.

Das Experiment in dieser Untersuchung wurde unter eifriger Mitwirkung von Herrn H. Akiyama und später von Herrn K. Ishii durchgeführt, den beiden Herren ich hier meinen warmen Dank aussprechen möchte. Herrn Prof. Dr. J. Horiuti (Sapporo) bin ich für seine wertvollen Ratschläge zu grossem Dank verpflichtet.

Es sei auch an dieser Stelle dem Nippon Gakujitsu Shinkokai für die Stipendien aufs wärmste gedankt.

Tokyo, Itabasiku.

Musashi Hochschule, Nedzu Chemisches Laboratorium.

(7) Vergl. Jones u. Taylor, *loc. cit.* (2).

The Addition of Hydrogen Bromide to Crotonic Acid in Carbon Tetrachloride Solution and the Oxygen Effect.

By Osamu SIMAMURA.

(Received April 17, 1942.)

Recent investigations on the addition of hydrogen halides to ethenoid compounds have centred in the abnormal addition of hydrogen bromide, in which oxygen, organic peroxides, and ferromagnetic metals such as reduced nickel and iron reverse the direction of addition which should otherwise follow the Markownikoff rule. The works in this field have been reviewed by J. C. Smith⁽¹⁾ from one point of view and by F. R. Mayo and C. Walling⁽²⁾ from another. The view⁽³⁾ developed in this laboratory concerning the oxygen effect on hydrogen bromide reacting with ethenoid compounds is supported by a series of the experimental facts which have been obtained with a variety of substances⁽⁴⁾. It has been established that a bromine atom delivered from hydrogen bromide by the action of oxygen in the presence of an ethenoid compound causes an abnormal addition by a chain mechanism, attaching itself to the double bond of the ethenoid compound to yield a free bromo radical, which reacts then with hydrogen bromide to give the final product of the addition reaction with regeneration of another bromine atom. In many cases of the abnormal addition the bromine atom is oriented to the carbon atom which would take up hydrogen in the normal addition, thus giving rise to the formation of an abnormal product different from the normal one. There are, however, no theoretical grounds to expect that such will be the case in all ethenoid compounds.

The nature of the substitution at the double bond is no doubt a factor to determine the direction of addition. Although the mechanism of the normal addition is still in controversy, if it is assumed that hydrogen halides behave as polar molecules when they add to olefins, the direction of addition will depend on the polarity of the double bond. According to Smith⁽⁵⁾, R. Robinson suggested that the direction of addition of hydrogen bromide to olefins could be predicted from a knowledge of the directive powers of the relevant groups when attached to the benzene nucleus: As the ortho and para directing groups not conjugated with the benzene nucleus all force electrons towards the nucleus, they should do so in compounds of the type $\text{CH}_2=\text{CHX}$, where consequently the normal product should be CH_3CHBrX , which agrees with the Markownikoff rule. With meta directing groups the reverse should be the case.

(1) J. C. Smith, *Chem. and Ind.*, **56** (1937), 833; **57** (1938), 461; *Ann. Reports*, **36** (1940), 219.

(2) F. R. Mayo and C. Walling, *Chem. Rev.*, **27** (1940), 351.

(3) Y. Urushibara, *J. Chem. Soc. Japan*, **60** (1939), 717.

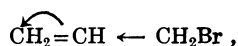
Y. Urushibara and O. Simamura, *this Bulletin*, **14** (1939), 323.

(4) O. Simamura, *ibid.*, **15** (1940), 292.

(5) J. C. Smith, *Chem. and Ind.*, **57** (1938), 461.

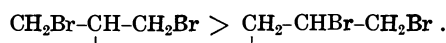
This hypothesis seems to have been substantiated by a great number of experimental facts. However, M. S. Kharasch, E. H. Rossin and E. K. Fields⁽⁶⁾ recently obtained 1,1,1,2-tetrachloropropane by adding hydrogen chloride to trichloromethylethylene, although they could not add hydrogen bromide under antioxidant conditions. This result agrees with the Markownikoff rule, but is not in accordance with what is predicted from Robinson's hypothesis, trichloromethyl being considered a meta directing group⁽⁷⁾.

The orientation of the bromine atom in the abnormal addition is a different matter, perhaps more complex. It may reasonably be assumed that a free bromine atom is directed towards the carbon atom with the higher electron density⁽⁸⁾. Thus, for example, in allyl bromide, which is considered to be polarised as indicated below, in the symbols of the English school,



a bromine atom is directed towards the γ carbon atom to yield finally 1,3-dibromopropane, the abnormal product. The hypothesis is the more attractive in so far as it brings, in conjunction with the polarisation of the double bond as postulated by Robinson, the orientation of the hydrogen bromide in the normal addition and the reversal of it in the abnormal addition into a consistent correlation. That the hypothesis of the greater reactivity of the carbon atom with the higher electron density may sometimes fail is shown by the instance of trichloromethylethylene cited above. As the trichloromethyl group is meta directing when attached to the benzene nucleus, it attracts electrons to itself; therefore, according to the hypothesis the product should be 1,1,1-trichloro-2-bromopropane when the mechanism involving bromine atoms is in operation, whereas 1,1,1-trichloro-3-bromopropane was really obtained under oxidant conditions.⁽⁶⁾

Another view is suggested by F. R. Mayo and C. Walling⁽²⁾ with additional advantages. The point of attack by the bromine atom is little affected by the polarity of double bond, but depends upon the relative stability of the two bromo radicals which may be formed. To exemplify the theory, allyl bromide gives 1,3-dibromopropane in the abnormal addition because the order of the stabilities is as follows,



However, why the former radical is more stable than the latter remains to be explained. Perhaps the idea of hyperconjugation⁽⁹⁾, i.e., conjuga-

(6) M. S. Kharasch, E. H. Rossin and E. K. Fields, *J. Am. Chem. Soc.*, **63** (1941), 2558.

(7) A. F. Holleman, J. Vermeulen and J. de DeMooy, *Rec. trav. chim.*, **33** (1914), 1. K. Lauer, *J. prakt. Chem.*, **142** (1935), 252.

(8) M. S. Kharasch, H. Engelmann and F. R. Mayo, *J. Org. Chem.*, **2** (1937), 288.

(9) See, for example, R. S. Mulliken, C. A. Rieke and W. G. Brown, *J. Am. Chem. Soc.*, **63** (1941), 41.

tion with saturated groups, would account for the assumed order of decreasing stabilities of aliphatic free radicals, tertiary > secondary > primary. In the tertiary radical the free valency electron can conjugate with three groups, while in the secondary one it can do so with two groups at most, thus the former being more stable by the energy acquired through the extra conjugation with the third additional group. From the same argument it is concluded that the secondary radical is more stable than the primary one.

The hypothesis of the radical stability could most satisfactorily explain the observations with crotonic acid⁽¹⁰⁾ which gives always β -bromobutyric acid irrespective of the conditions of addition, because the β -bromo radical $\text{CH}_3\text{CHBrCHCOOH}$ should be more stable than the α -isomeride, $\text{CH}_3\text{CHCHBrCOOH}$, by virtue of the conjugation of the free valency electron with the carboxyl group. The formation of β -bromobutyric acid as a normal product is in accord with the prediction from Robinson's hypothesis.

Propenylbenzene⁽¹¹⁾ and cinnamic acid⁽¹²⁾ are stated to give with hydrogen bromide always 1-phenyl-1-bromopropane and β -bromohydrocinnamic acid, respectively. Although a discussion of these findings seems to be rather hasty as the full experimental details are not available, they may be considered to indicate on the basis of the theory of the radical stability that the radicals $\text{C}_6\text{H}_5\text{CHBrCHCH}_3$ and $\text{C}_6\text{H}_5\text{CHBrCHCOOH}$ should be more stable than $\text{C}_6\text{H}_5\text{CHCHBrCH}_3$ and $\text{C}_6\text{H}_5\text{CHCH}_2\text{COOH}$, respectively. This is unexpected because theoretically the latter radicals should be more stable as the conjugation of the free valency electrons with phenyl groups would contribute much more to the stabilisation of the free radicals. Attention must be paid to another factor determining the orientation of hydrogen bromide in the abnormal addition. It concerns the reaction between the free bromo radical and hydrogen bromide where the final addition product and a bromine atom are yielded. When a free radical stabilised by the conjugation of the free valency electron with some groups reacts with hydrogen bromide, it would require a greater activation energy and consequently would react slower than when such stabilisation is absent. Then the reactivity of the free bromo radicals may be a predominant factor to determine the direction of addition of hydrogen bromide. Thus, those olefins with a phenyl group in conjugation with double bond may give results apparently contradictory to the theory of radical stability.

At this stage of development, where the problem of the orientation of hydrogen bromide has not reached a complete solution, accumulation of more experimental data is desirable.

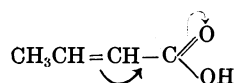
Addition of hydrogen bromide to crotonic acid has already been studied⁽¹⁰⁾ with results that β -bromobutyric acid is the only product obtainable irrespective of the conditions of addition and there seems to

(10) C. Walling, M. S. Kharasch and F. R. Mayo, *J. Am. Chem. Soc.*, **61** (1939), 2693. D. C. Grimshaw, J. B. Guy and J. C. Smith, *J. Chem. Soc.*, **1940**, 68.

(11) Unpublished work of M. S. Kharasch, P. C. White and F. R. Mayo cited by F. R. Mayo and C. Walling, *Chem. Rev.*, **27** (1940), 351.

(12) A. Michael and G. H. Shadinger, *J. Org. Chem.*, **4** (1939), 128.

be no indication of the accelerated reaction under oxidant conditions. Walling, Kharasch, and Mayo suggested that the chain mechanism might not operate when the double bond is conjugated with a carboxyl group, but they did not exclude the possibility that both mechanisms, normal and abnormal, yield the identical product. Smith and co-workers⁽¹⁰⁾ are of the opinion that bromine is not attracted to the α -carbon atom of crotonic acid since there is no accumulation of electrons in that position, the mesomeric polarisation in the molecule being such as represented by the formula.



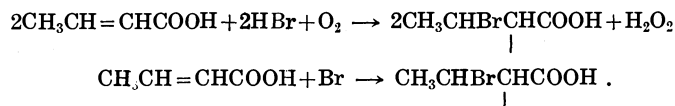
As the action of the mixture of hydrogen bromide and oxygen on allvl bromide and certain other ethenoid compounds has proved to be a very useful method for elucidating the mechanism of the abnormal addition⁽³⁾⁽⁴⁾, the same method has now been applied to crotonic acid to determine whether a similar chain mechanism operates when hydrogen bromide is added to this acid under oxidant conditions.

Into a suspension of 10 g. of crotonic acid in 50 c.c. of carbon tetrachloride the mixture of hydrogen bromide and oxygen was passed in the dark. The reaction vessel was cooled with ice water throughout the passage of the gas mixture. At the end of three hours the reaction mixture was found to have deposited a few c.c. of a pale brown oil, which on treatment as described in the experimental part yielded α -hydroxy- β -bromobutyric acid, m.p. 97–98°C. The carbon tetrachloride layer was colourless and on removal of the solvent 17 g. of an oil was obtained. It was distilled under diminished pressure and the first fraction, which passed over at 122–127° at 18 mm., was redistilled to yield 4.85 g. of β -bromobutyric acid, b.p. 94–98° at 4 mm., n_D^{20} 1.4782. When this was solidified by cooling with ice and then gradually warmed, the last pieces of crystals disappeared at 14°. If any α -bromobutyric acid was formed, it would be present in the head fraction as it boils lower than the β -isomeride, and as this fraction melted at 14°, whereas the α -bromo-acid melts at –4°⁽¹³⁾, it seems to have contained no appreciable amount of the α -isomeride. In the first distillation, as the temperature of the bath was raised, the thermometer reading rose continually from 127° and, when it reached 148°, the distillation was stopped as the distilling liquid solidified to a crystalline mass filling the arm of the distilling flask. The crystals were identified as crotonic acid dibromide, m.p. 86–88°. The residue in the flask also solidified on cooling to crystals of the same substance embedded in viscous oil. Thus the reaction products remaining in carbon tetrachloride were found to consist mainly of β -bromobutyric acid and crotonic acid dibromide. That α -bromobutyric acid was not detected is in accord with the findings of the foreign workers⁽¹⁰⁾. The formation of some substances of peroxidic nature is certain, although they were not identified, as the carbon tetrachloride solution and the brown oil liberated iodine from aqueous potassium iodide, while any of the three compounds isolated was found not to do so even when acidified with hydrochloric acid. Fur-

(13) Lespieau, *Compt. rend.*, **139** (1904), 739.

ther, crotonic acid dissolved in carbon tetrachloride and placed in diffuse light for a day developed no coloration with ferrous ammonium sulphate and ammonium thiocyanate. Thus it is concluded that reactions of the same type occurred as when the gas mixture was allowed to react with allvl bromide⁽³⁾. The formation of crotonic acid dibromide is a convincing evidence in support of the view that the reaction involved bromine atoms, which, in reacting with crotonic acid, must have attacked the β -carbon atom, as no α -bromobutyric acid or its derivatives were detected.

Isolation of α -hydroxy- β -bromobutyric acid was unexpected. If hydrogen peroxide or an organic peroxide formed⁽³⁾ in the course of the reaction should yield with crotonic acid α , β -epoxybutyric acid, this would readily react with hydrogen bromide to give the hydroxybromobutyric acid as described in the experimental part. However, the observed formation of the hydroxybromobutyric acid may be adduced in substantiation of the view that the reaction involved the formation of the bromine atom and that the bromine atom attached itself to the β -carbon atom of crotonic acid. Then the formation of the hydroxybromo-acid is interpreted as follows: In the first place a β -bromo radical acid is formed by the combined action of hydrogen bromide and oxygen or by the action of a bromine atom on crotonic acid



This radical acid then reacts with oxygen or hydrogen peroxide formed to yield finally the acid under consideration.

Oxygen having been shown to cause the reaction involving bromine atoms, it was expected that it might more or less accelerate the addition reaction, and its effect on the rate was examined. Hydrogen bromide (0.0135 mole) was allowed to react with crotonic acid (0.0128 mole) in carbon tetrachloride (10 c.c.) in a glass tube with a capacity of 60 c.c. for three hours in the dark at room temperature either in presence or in absence of oxygen. From the reaction mixture carbon tetrachloride and the unreacted hydrogen bromide were removed under reduced pressure and the remaining oil was treated with a sodium hydroxide solution and analysed for liberated bromide ion. The extent of reaction of crotonic acid was calculated on the assumption that the liberated bromide ion gives the amount of β -bromobutyric acid formed and no other products were yielded at all. It is obvious from the results tabulated below, that, contrary to the expectation, oxygen did not exert any perceptible influence on the rate of the reaction when the amount of oxygen admitted was small. The extent of addition decreased slightly as the amount of oxygen was increased. That in these cases the side reaction involving oxygen as has been described above took place appreciably was demonstrated by the turbid appearance of the reaction mixture when the greater part of the solvent was removed. No acceleration by oxygen of the addition of hydrogen bromide to crotonic acid might be taken to indicate that the bromo radical acid reacts readily with oxygen but not with hydrogen bromide to continue the chain reaction, which would superpose itself on the rapid

normal addition. There is indeed an incipient formation of chains by the joint action of hydrogen bromide and oxygen but they cannot develop to a noticeable abnormal addition reaction.

Table.

The Addition of Hydrogen Bromide to Crotonic Acid in the Presence of Oxygen in Carbon Tetrachloride Solution in the Dark.

Experiment Series	No.	Oxygen admitted mm. Hg	Crotonic acid reacted %	Temp.	Method of analysis*
I	{ 1	0	66.9	19-20	a
	{ 2	0	66.5		a
	{ 3	36†	68.5		a, b
II	{ 4	0	68.0	20	b
	{ 5	47	68.2		b
	{ 6	63	68.1		b
III	{ 7	0	69.8	20	b
	{ 8	157	66.7		b
	{ 9	274	62.5		b

Crotonic acid, 0.0128 mole; hydrogen bromide, 0.0135 mole; carbon tetrachloride, 10.0 c.c. Reaction time, three hours. Experiments belonging to the same series were conducted in quick succession.

* As regards the methods of analysis adopted see the experimental part.

† The amount of oxygen is 0.092 millimole.

Experimental Part.

Materials. Hydrogen bromide was generated by dropping bromine on hot tetralin, passed through a bottle containing cold tertalin and then through a tube filled with anthracene. It was dried by passage through a tube filled with glass wool sprinkled with phosphorus pentoxide and was conducted into a reaction vessel after mixing with oxygen which was taken from a cylinder and dried with phosphorus pentoxide. When the effect of oxygen on the extent of addition was investigated, the hydrogen bromide dried with phosphorus pentoxide was collected in a tube cooled with liquid air. It was melted, solidified again, and the tube was evacuated with a mercury diffusion pump. The process was repeated three times and the hydrogen bromide was fractionated, the middle portion being used. Crotonic acid was recrystallised from petroleum ether and the purified sample melted at 72-73°. Carbon tetrachloride was refluxed with an alkaline permanganate solution, dried with anhydrous calcium chloride, and fractionated after desiccation with phosphorus pentoxide.

The Action of the Mixture of Hydrogen Bromide Gas and Oxygen on Crotonic Acid in Carbon Tetrachloride in the Dark. The essential part of the experiment has already been described above. The pale brown oil which was deposited from the reaction mixture weighed 4.2 g. and, when a little water was added, complete solution took place. This was extracted with ether and the ethereal solution was dried with anhydrous sodium sulphate. On removing the ether under reduced pressure hexagonal plates insoluble in carbon bisulphide and very soluble in cold water were obtained. The product crystallized from water was dissolved in ether and by adding a little petroleum ether crystals melting at 97-98° were obtained; yield, 0.5 g. (Found: Br, 43.8. Calculated for $C_4H_7O_3Br$: Br, 43.6%). Its properties coincide with those

described for α -hydroxy- β -bromobutyric acid. According to P. Melikoff⁽¹⁴⁾, when the sodium salt of α -hydroxy- β -halocarboxylic acid is boiled in aqueous solution, carbon dioxide splits off and aldehyde or ketone results according to the constitution of the original acid. The substance obtained here was dissolved in a dilute sodium carbonate solution and heated, when the characteristic odour resembling that of acetaldehyde evolved. Although it was not characterized by the formations of derivatives, there is no doubt that propionaldehyde was formed. The melting point of the substance was not depressed on admixture with an authentic specimen of α -hydroxy- β -bromobutyric acid prepared by the action of hydrogen bromide on α , β -epoxybutyric acid (methylglycidic acid).

α -Hydroxy- β -bromobutyric Acid from Methylglycidic Acid. Methylglycidic acid (0.3 g.) prepared from α -bromo- β -hydroxybutyric acid following the direction given by Melikoff⁽¹⁵⁾ for α -chloro- β -hydroxybutyric acid was suspended in 25 c.c. of carbon tetrachloride and the mixture of hydrogen bromide and oxygen⁽¹⁶⁾ was passed for an hour and a half. The acid changed into a sticky mass. The carbon tetrachloride was decanted and the product was crystallized from water, m.p. 96–98°.

The Effect of Oxygen on the Addition of Hydrogen Bromide to Crotonic Acid in Carbon Tetrachloride in the Dark. In a glass tube with a capacity of 60 c.c. 1.1 g. of crotonic acid and 10 c.c. of carbon tetrachloride were placed and the tube was connected to the vacuum line. To remove the oxygen the contents of the tube were solidified by cooling with liquid air and the tube was evacuated with a mercury diffusion pump. The contents were then melted, again solidified, and the tube evacuated. The procedure was repeated three times. Then 0.0135 mole of hydrogen bromide (0.5 c.c. of liquefied hydrogen bromide at the temperature of solid carbon dioxide) was condensed on the top of the solidified mixture and oxygen was introduced to a specified pressure. The tube was sealed off and shaken manually as uniformly as possible. After three hours the capillary tip of the reaction tube was connected to a pump by means of a piece of rubber tubing, the tip was broken by crushing it from outside and the remaining hydrogen bromide and the greater part of carbon tetrachloride were removed. The remaining oily product was transferred to a 50 c.c. Erlenmeyer flask, which was then placed in a desiccator containing potassium hydroxide and scraps of paraffin. The desiccator was evacuated for three hours and left overnight. The product (0.2–0.3 g.) was treated with 5 c.c. of 1N sodium hydroxide solution, heated for thirty minutes on a water-bath, and by adding silver nitrate to the solution acidified with dilute nitric acid silver bromide was precipitated and weighed. This method of analysis is referred to as (a) in the accompanying table. Another method (b) consisted in heating the sample with 5 c.c. of 1N sodium hydroxide solution for five minutes and titrating the liberated bromide ion by the Volhard method. Both methods were found to give the identical value when applied to the product of Exp. No. 3.

Summary.

(1) Hypotheses suggested to explain the orientation of hydrogen bromide in the addition to the ethenoid compound have been briefly reviewed and criticized.

(2) Allowing the mixture of hydrogen bromide and oxygen to react with crotonic acid in carbon tetrachloride, three products, β -bromobutyric

(14) P. Melikoff and Petrenko-Kritschenko, *Ann.*, **266** (1891), 370; *Chem. Zentr.*, **1890**, I, 524.

(15) P. Melikoff, *Ber.*, **16** (1883), 1270.

(16) For the preparation oxygen is not necessary.

acid, crotonic acid dibromide and α -hydroxy- β -bromobutyric acid, have been isolated.

(3) Oxygen has been found not to accelerate the addition of hydrogen bromide to crotonic acid in carbon tetrachloride solution in the dark.

(4) It is concluded that in the addition of hydrogen bromide to crotonic acid in the presence of oxygen, this participates in the reaction producing free bromo-radical acid and bromine atoms, the latter being attached to the β -carbon atom of crotonic acid, but that the chains involving these cannot develop because of the ready reaction of the bromo radical acid with oxygen rather than with hydrogen bromide.

The author expresses his sincere thanks to Prof. Y. Urushibara for his kind guidance and encouragement throughout this work. Thanks are also due to the Imperial Academy for a grant.

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Studies on the Adsorption at the Solid-Liquid Interface. IV. Relations among the Adsorption, the Oiliness and the Flocculation of the Powder.

By Hideo AKAMATU.

(Received April 24, 1942.)

Introduction. When the surface of a solid contacts with a liquid or some powder is immersed in a liquid, the property of the surface of solid is changed by the solvation or the adsorption of a certain substance from the solution. There are many phenomena which depend on such property of the surface of solid. The action of the lubricant or the flotation process is the example of the application of such phenomena. To explain those phenomena we always assume the adsorption layer on the surface of the solid material. In practice, however, it is troublesome to find the method of investigating the adsorption layer, for the amount of the substance adsorbed is very small and the effect is very sensitive. We get the informations, in many cases, by the indirect method or by the analogy to some other cases, for instance, by the behaviour of the monomolecular film on the surface of water.

In our laboratory, the effects of the liquids on the friction coefficient of the glass surface have been studied,⁽¹⁾ and moreover, some results were

(1) J. Sameshima and coworkers, this Bulletin, **11** (1936), 659, 791; **12** (1937), 96, 127; **13** (1938), 127, 134; **14** (1939), 270, 297; **15** (1940), 288, 467. J. Sameshima, H. Akamatu and T. Isemura, *Rev. Phys. Chem. Japan*, **14** (1940), 55.

obtained regarding the adsorption by glass.⁽²⁾ The relations between those phenomena will be considered in the present report.

Summary of the Results on the Adsorption by Glass. The adsorptions by the glass powder of such substances as carboxylic acids, esters, nitrobenzene, aniline and chlorobenzene from their solutions dissolved in a non-polar solvent such as benzene or toluene were studied in the preceding papers.⁽²⁾ The adsorbing behaviours can be classified into the following three groups.

(I) The compounds having carboxyl radicals were adsorbed selectively from their benzene or toluene solution by glass, and the adsorption took place readily in the region of the low concentration of the solution (e.g. in the order of 10^{-3} mol/l.). In these cases, the adsorption layer seemed to approach to the monomolecular layer and then saturate, except the compound having small molecular weight such as acetic acid, which was much adsorbed.

(II) Alcohols did not show such strong selective adsorption as carboxylic acids, and no remarkable adsorption has been observed in the region of the low concentration. When the concentration of the solution, however, was beyond a certain range (e.g. 10^{-2} mol/l.), the selective adsorption took place, and things were like to the case of carboxylic acids.

(III) In the case of nitrobenzene, aniline and chlorobenzene, notwithstanding their large dipole moments, any considerable selective adsorption was not observed even in the range of the pretty high concentration of the solution. Those results are shown schematically in Fig. 1.

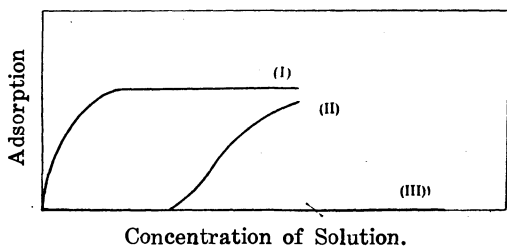


Fig. 1.

The relations between those results of the adsorption and the oiliness of liquids, and the flocculation or the apparent sedimentation volume of the powder in liquids will be discussed in the following sections.

Adsorption and Oiliness. The mechanism of the oiliness of the lubricant has not yet been understood thoroughly. However, two things, at least, are considered to be necessary. The first is the protecting action by the molecules of the lubricant combining with the surface of the solid. When the lubricant is pure liquid, this is caused by the solvation, and if the lubricant is a solution, it is necessary that the selective adsorption of a certain molecules take place. The adsorption is a necessary condition to reduce the friction, though it is not a sufficient one for good oiliness. For the second condition, the adsorption layer at the friction surface must have a special property to reduce the friction. As for this property, however, there is no definite theory. With regard to a certain homologous series of the lubricant, the larger the molecule, especially having the long

(2) H. Akamatu, this Bulletin, **17** (1942), 141, 161, 260.

hydrocarbone chain, the better the oiliness is. This is the most remarkable and suggestive fact. Things which are considered from this fact are as follows. (1) The shape of the molecule is associated with the good oiliness. Especially the flexibility of a molecule attracts the attention of the investigators. (2) The good orientation of molecules in the adsorption layer is necessary for good oiliness. As the lateral force between molecules oriented is greater, the adsorption layer will be more stable, by which the friction surface will be covered homogeneously. (3) The large molecules have the effect to separate the friction surfaces from each other. All of those things have the parallelism with the size or the length of the molecules. In the practical lubricating action, all of those things may be involved at the same time.

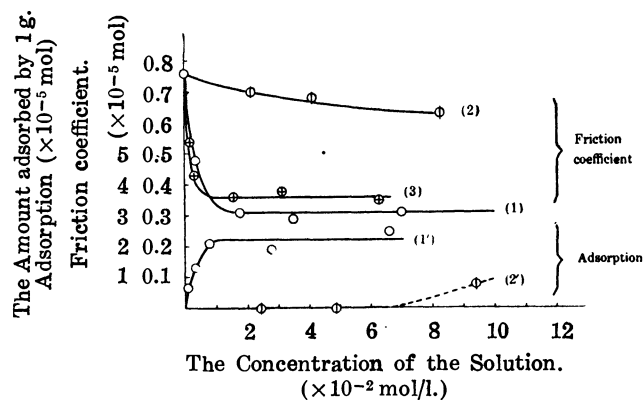
The adsorption is not a sufficient condition for good oiliness, while it is a necessary condition at least. For instance, fatty acids are readily adsorbed by glass in general. Among them, acetic acid seems to be most readily adsorbed, and consequently, it reduces more or less the friction coefficient of the glass surface, though it shows no remarkable oiliness. The friction coefficient of glass without any lubricant is almost unity. In the case of using acetic acid as lubricant, the friction coefficient is reduced to about 0.6; on the other hand, with more favourable fatty acids having long hydrocarbon chains, the values are far more small, with oleic acid, for instance, this value is 0.24.

Molecules, consisted of the hydrophilic radical and the hydrophobic radical at the same time, orient themselves at the surface of water in such a manner as their hydrophilic radical sets in water. This idea has been expanded to the surface of hydrophilic solid instead of water, and it is assumed that such molecules also orient themselves anchoring their polar groups on the solid surface and the adsorption takes place as the results. However, such an assumption cannot be applied imprudently to the case of the glass surface, at least, as mentioned above.

Among the polar radicals, the carboxyl radical is most readily adsorbed by the glass surface. This fact is consistent with the carboxylic acid, especially fatty acids, have much or less good oiliness. The fact⁽³⁾ that the oiliness of toluene or xylene solution dissolving small quantity of fatty acid, was identical with the oiliness of the fatty acid itself independent on the solvent, has been understood by the assumption that the fatty acid is selectively adsorbed by the friction surface and that the friction depends on it only. This assumption is consistent with the experimental results that the fatty acids are always preferentially adsorbed by glass. Hydroxyl radicals, on the other hand, are not selectively adsorbed by glass so strongly as carboxyl radicals. The alcohols are adsorbed from their benzene solutions only at the high concentration of the solution. This relation has also been investigated from the oiliness of the solution containing alcohol. For instance, in the case of the xylene solution dissolving palmitic acid, the oiliness is pretty good in the range of the low concentration of the solution and as the concentration increases the oiliness approaches to a saturated value. On the other hand, the oiliness is not good in the case of the toluene solution containing tetradecyl alcohol, not-

(3) H. Akamatu, this Bulletin, **13** (1938), 127.

withstanding the good oiliness being anticipated from the molecular structure of tetradecyl alcohol. The reason is that tetradecyl alcohol does not adsorbed preferentially at the glass surface as palmitic acid. This relation is shown in Fig. 2. The considerable adsorption of tetradecyl alcohol does not take place until the concentration of the solution approaches to the saturation.



- (1): Palmitic acid/Xylene (1'): Palmitic acid/Toluene
 (2): Tetradecyl alcohol/Toluene (2'): Tetradecyl alcohol/Benzene
 (3): Oleic acid/Toluene

Fig. 2.

Notwithstanding that the fatty acids and the alcohols have much or less good oiliness, their esters⁽⁴⁾ have rather poor oiliness. This is also understood from their small adsorbability.

With regard to nitrobenzene, aniline and chlorobenzene, no notable selectivity against benzene has been observed, from the adsorption experiment.

Table 1.

Lubricant	Friction Coefficient
Benzene	0.78
Toluene	0.76
Xylene	0.76
Nitrobenzene	0.84
Aniline	0.73
Chlorobenzene	0.81
Xylene solution dissolving Benzoic acid (2%)	0.59

For the bad oiliness of those substances, the deficiency in the flexibility of those molecules has been assumed by many investigators, however, this may be also caused by their bad adsorbability to the surface. Since benzoic acid is selectively adsorbed by glass and the xylene solution dissolving benzoic acid has also much or less good oiliness as compared with xylene itself. Friction coefficients of those substances are shown in Table 1.

In the case when the lubricant is consisted of many components, the fact⁽³⁾ that the oiliness of such a system depends on only a certain material alone, may understood from the consideration of the selective adsorption.

(4) T. Isemura, this Bulletin, **14** (1939), 270.

(5) T. Isemura, this Bulletin, **15** (1940), 288.

Adsorption and Flocculation of the Powder. It is well known that the stability or the swelling of the colloidal system depends on the nature of the dispersion medium. In the case when relatively large particles (microscopic) are suspended or sedimented in the liquid, the phenomena that the property of the system is affected by the nature of the liquid medium attract the attention of the investigators,⁽⁶⁾ not only because of its importance for the application, but also the fact that the system may be considered as a model of a colloidal system.

It is remarkable that the flocculation and the sedimentation volume of the powders in various kinds of liquids varied with the nature of the liquid.⁽⁷⁾ If the powder is hydrophilic, it is not liable to flocculate in the polar liquid, and the particles are dispersed, and consequently the sedimentation velocity is slow and the apparent sedimentation volume is small. On the other hand, in the non-polar liquid, the particles aggregate each other and become coarse particles, and consequently the sedimentation velocity is fast and the apparent sedimentation volume is large.

If the adhesion forces between the particles are strong, they aggregate each other by their contact points, and as the whole system they will take the loose packing, so the sedimentation volume will be large. On the other hand, if the adhesion forces are weak, the aggregation or the flocculation does not take place, and they will take the close packing as the whole system, and consequently the sedimentation volume will be small.

The aggregation of the particles may be prevented by the addition of some substances to the liquid even in the case of non-polar solvent, and as the results, the sedimentation volume of the system will be reduced. This phenomenon is remarkable and the addition of the substance to the solvent is analogous to the protecting action of the colloidal system. Taking the glass powder, for instance, this relation will be seen in Table 2.

Table 2.

Solvent	Solute	The ratio of the sedimentation volume of 1g. powder.
Toluene	—	1.00
Benzene	—	1.00
Toluene	Oleic acid (1%)	0.79
"	Palmitic acid (2%)	0.82
"	Tripalmitine (1%)	0.82
"	Benzoic acid (1%)	0.88
"	Acetic acid (5%)	0.94
Benzene	Palmitic acid (0.02 mol/l.)	0.84
"	Nitrobenzene (0.07 ")	1.00
"	Chlorobenzene (0.07 ")	1.00

(6) Wo. Ostwald and W. Haller, *Kolloidchem. Beihefte*, **29** (1929), 354; P. Reh binder, *Z. physik. Chem.*, A **146** (1930), 63; Bloomquist and Schutt, *Ind. Eng. Chem.*, **32** (1940), 827; K. Suzuki, *J. Chem. Soc. Japan*, **62** (1941), 888; B. Tamamushi and S. Tomatsu, this Bulletin, **17** (1942), 23.

(7) H. Akamatu, this Bulletin, **13** (1938), 456.

In those cases, when the substance added to the solvent can be adsorbed selectively by glass, there are much or less reducing effect of the sedimentation volume. Nitrobenzene or chlorobenzene has no effect. This relation is quite like the case of the oiliness. The preventing action of the aggregation of the particles and the reducing action of the friction of the solid surface by the so-called surface active substances is quite parallel in each other. This fact shows that the adhesion force between the particles is the same sort with the friction force. A series of the studies by Búzagh⁽⁸⁾ on the "Abreisswinkel" also showed the analogous results.

The peculiar behaviour of the float, frequently experienced during the density measurement by the float method, seems to have some relation to the adhesion force between particles. As already described in the preceding paper,⁽⁹⁾ this phenomenon is as follows. In the non-polar liquid such as benzene or in the solution dissolving the non-adsorbable solute, the float occasionally moves laterally toward the wall of the cell and attaches to it. In the benzene solution dissolving the surface active substance, however, this behaviour does not occur in general. This phenomenon seems to be related to the aggregation of the particles of the powder. We may suppose, from this fact, that the aggregation takes place not only when the particles collide each other by the chance, but also when they approach each other by some attraction force in the liquid such as benzene or toluene.

In conclusion the author wishes to express his hearty thanks to Prof. Jitsusaburo Sameshima for his kind guidance and encouragement. The cost of this research has been defrayed from the Scientific Research Encouragement Grant from the Department of Education, to which the author's thanks are due.

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(8) A. von Búzagh, "Kolloidik", 1936, Dresden, p. 158; *Kolloid-Z.*, **85** (1938), 318.

(9) H. Akamatu, this Bulletin, **17** (1942), 260.

Physico-Chemical Investigations on Catalytic Mechanism. VI. On the Fischer-Tropsch Synthesis of Hydrocarbons. (Experimental Series II)^{***} (2).

By Senzo HAMAI.

(Received January 14, 1942.)

The present paper being a further report of the series of investigations⁽¹⁾, we shall omit the experimental aspects, but we attempt to describe the results concerning the effects of promoters on the Co type catalyst. Experimental apparatus and detailed experimental procedures have been fully presented in our previous paper⁽²⁾.

One of the most interesting problems in the catalytic mechanism which have not yet been settled is the role of promoters in the catalytic activity in general. Bearing these in mind, we have carried out the experiments which may possibly throw some light in correlation with the catalytic activity; furthermore, these experimental results clear the way for the systematic explanations of the mechanism. So far many investigators⁽³⁾ have undertaken the task and contributed much, but on account of the fundamental difficulty to get reproducible results, most experimental results can hardly be considered as reliable as to give a clear-cut, general conclusion. In this sense, we are justified to say that, in such chaotic conditions of numerous results, we are confronted practically with a hopeless situation. For such reasons, the author considers that every bit of experimental results has to be correlated in some such systematic manner as to enable us to get hold of a clear vision of the catalytic mechanism out of such chaotic mass of numerous investigations.

We mainly present the effects of B_2O_3 in our new catalyst and of Cu, the combined effects of ThO_2 and CeO_2 , as well as those of pre-treatments of the catalysts.

Experimental Results. The catalyst which we had employed was a series of the catalysts of Co with various promoters such as CeO_2 , ThO_2 , B_2O_3 , and Cu and Kieselguhr as a carrier (support), as shown in our tables; and the method of preparation and experimental procedures were exactly similar to those, already described in our report IV⁽⁴⁾.

(***) Most of the results given in this paper was obtained and completed in 1939-1940, but the publication of them has been withheld.

(1) Our reports; I, II, III, IV, and V.

(I) *J. Chem. Soc. Japan*, **62** (1941), 516;

(II) This Bulletin, **16** (1941), 213;

(III) *J. Soc. Chem. Ind. Japan*, **45** (1942), 313;

(IV) This Bulletin, **17** (1942), 166;

(V) This Bulletin, **17** (1942), 252.

(2) Report IV, this Bulletin, **17** (1942), 166.

(3) Series of papers by the schools of Fischer, Kita, and others.

(4) Report IV, this Bulletin, **17** (1942), 166.

Tables 1-4 indicate typical results out of various experiments. As seen in Table 1, the effects of B_2O_3 on the average gas contraction as an approximate measure of the catalytic activity are well detectable. It seemed that the addition of B_2O_3 improved the activity as well as the quality of the products⁽⁵⁾; i.e., in $F_{40}(A)$ - $F_{40}(G)$ series where the catalyst

Table 1.

Exp. No.	Catalyst No.	Effects of B ₂ O ₃						Average Contraction (%)
		Catalyst Composition (%)					Reaction Temp. (°C.)	
		Co +	CeO ₂ +	ThO ₂ +	B ₂ O ₃ +	Kieselguhr		
F ₃₉ (A-I)	XII ₁₂ -1	100	15	15	5	100	200	64
F ₄₁ (A-E)	XII ₁₂ -1	"	"	"	"	"	"	49
F ₄₀ (A-G)	XII ₁₁ -1	"	"	"	0	"	"	34
F ₄₅ (A-H)	XII ₁₆ -1	"	"	"	10	"	"	49
F ₄₉ (F)	XII ₁₆ -1	"	"	"	10	"	"	42

Table 2.

Effects of B ₂ O ₃ in the Presence of Cu									
Exp. No.	Catalyst No.	Catalyst Composition (%)					Kieselguhr	Reaction Temp. (°C.)	Average Contraction (%)
		Co	CeO ₂	ThO ₂	B ₂ O ₃	Cu			
F ₄₈ (A-F)	XII ₁₉ -1	100	15	15	10	5	100	200	10
F ₄₃ (A-I)	XII ₁₄ -1	"	15	15	5	"	"	"	45
F ₄₇ (A-E)	XII ₁₈ -1	"	18	18	10	"	"	"	25
F ₄₄ (A-D)	XII ₁₅ -1	"	18	18	5	"	"	"	15

Table 3.

Exp. No.	Catalyst No.	Effects of Cu							Average Contraction (%)
		Catalyst Composition (%)					Kiesel- guhr	Reaction Temp. (°C.)	
		Co	+ CeO ₂	+ ThO ₂	+ B ₂ O ₃	+ Cu			
F ₄₈ (A-F)	XII ₁₉ -1	100	15	15	10	5	100	200	10
F ₄₅ (A-H)	XII ₁₆ -1	"	"	"	"	0	"	"	49
F ₄₇ (A-E)	XII ₁₈ -1	"	18	18	"	5	"	"	25
F ₄₆ (A-G)	XII ₁₇ -1	"	"	"	"	0	"	"	65
F ₄₃ (A-I)	XII ₁₄ -1	"	15	15	5	5	"	"	45
F ₃₉ (A-I)	XII ₁₂ -I	"	"	"	"	0	"	"	64

(5) Concerning this point, we shall present the results in our subsequent paper to be published elsewhere. (There is some good evidence that the products seem to contain branched chain hydrocarbons.)

Table 4.

Combined Effects of the ThO ₂ and CeO ₂ Contents									
Exp. No.	Catalyst No.	Catalyst Composition (%)					Kieselguhr	Reaction Temp. (°C.)	Average Contraction (%)
		Co	CeO ₂	ThO ₂	B ₂ O ₃	Cu			
F ₄₄ (A-D)	XII ₁₅ -1	100	18	18	5	5	100	200	15
F ₄₃ (A-I)	XII ₁₄ -1	"	15	15	"	"	"	"	45
F ₄₁ (A-E)	XII ₁₂ -1	"	"	"	"	0	"	"	49
F ₄₂ (A-I)	XII ₁₃ -1	"	18	18	"	"	"	"	"
F ₄₆ (A-G)	XII ₁₇ -1	"	"	"	10	"	"	"	65
F ₄₅ (A-H)	XII ₁₆ -1	"	15	15	"	"	"	"	49
F ₄₇ (A-E)	XII ₁₈ -1	"	18	18	"	5	"	"	25
F ₄₈ (A-F)	XII ₁₉ -1	"	15	15	"	"	"	"	10

contained no B₂O₃, the activity was estimated as 34%, while in F₃₉ (A)–F₃₉ (I) series, 64%, and in F₄₁ (A)–F₄₁ (E), 49%, in both of which the catalyst contained 5% B₂O₃. Furthermore, in F₄₅ (A)–F₄₅ (H) and F₄₉ (F) where the B₂O₃ content amounts to 10%, respectively, the activities have been observed to be 49% and 42%, respectively.

Therefore, we might say that the effect of B₂O₃ on Co+15% CeO₂+15% ThO₂+100% Kieselguhr catalyst is well detectable, as observed in Table 1; but as regards the suitable amount of B₂O₃, since 5% and 10% B₂O₃ give the effects practically to the same extent, it would be better to use a lesser amount of B₂O₃.

While in the presence of Cu, it has been observed that in the series of 18% CeO₂ and ThO₂, 10% B₂O₃ seemed to be better, but in the series of 15% CeO₂ and ThO₂, 5% B₂O₃ appeared to be better.

As regards the effect of Cu⁽⁶⁾ on those series, shown in Table 3, regardless of the respective percentage of CeO₂, ThO₂, and B₂O₃, those catalysts without Cu seemed to give much higher activity.

The combined effects of ThO₂ and CeO₂, with or without Cu, in the presence of 10% B₂O₃, 18% series have been observed to be better, while in the presence of 5% B₂O₃, both 15% and 18% series appeared to be practically the same. As to the influence of Cu, here, also the negative effect is definitely shown, as already discussed in connection with Table 3.

Table 5 shows some of the typical results of the influences of pre-treatment on the catalyst XII₁₆-1, Co+15% CeO₂+15% ThO₂+10% B₂O₃+100% Kieselguhr, such as temperature and the duration of heat treatment prior to H₂ reduction and of temperature and the duration of H₂ reduction on the catalytic activity as measured by the average gas contractions.

(6) (a) See also our report V, this Bulletin, **17** (1942), 252.

(b) Fischer, *Brenn-Chem.*, **11** (1930), 489, and the others mentioned in our Report V.

(c) S. Hamai, *J. Chem. Soc. Japan*, "Letter to the Editor" **63** (1942), 88

Table 5.

Effects of Pre-Treatments on the Catalysts

XII₁₆-1, Co + 15%CeO₂ + 15%ThO₂ + 10%B₂O₃ + 100%Kieselguhr

Exp. No.	Heat Treatment Prior to H ₂ Reduction		H ₂ Reduction		Reaction Temp.	Average Contraction
	(°C.)	(hrs.)	(°C.)	(hrs.)		
F ₄₅ (A-H)	400	5	375	5	200	49
F ₄₉ (F)	"	"	"	"	"	42
F ₅₀ (A-J)	"	"	300	"	"	34
F ₅₁ (A-F)	"	"	400	"	"	15
F ₅₂ (A-H)	"	"	350	"	"	43
FC ₇ (A-D)	No heat treatment		"	10	"	64

Table 6 demonstrates the contraction percentage as affected by various factors. These results show clearly that whenever we speak of the catalytic activity, every influencing factor must be carefully mentioned, otherwise it is practically meaningless to speak of the catalytic activity.

Table 6.

Contraction percentage as affected by various factors.

Exp. No.	Catalyst No.	Catalyst Composition				Pre-Treatment				React. Temp.	Ave. Contraction
						Heat-treatment		Temp. at the Reduction Prior to Heating			
		Co+ThO ₂ +CeO ₂ +Kieselguhr	(°C.)	(hrs.)	(°C.)	(hrs.)	(°C)	(%)			
F ₄	I ₁ -1	100	15	—	100	400	5	350	5	225	40
F ₁₄	"	"	"	—	"	"	2	"	"	"	25
F ₃₄ (A-B)	XII ₁₃ -1	"	—	15	"	"	5	375	"	200	22
F ₁₀	I ₄ -1	"	18	—	"	"	4	350	"	225	20
F ₅	I ₂ -1	"	20	—	"	"	2	"	4	"	70
F ₁₇	"	"	"	—	"	"	"	"	5	"	15
F ₁₈	"	"	"	—	"	"	"	"	"	"	"
F ₃₂ (A-E)	XII ₁₄ -1	"	—	20	"	"	5	375	"	200	35
F ₆	I ₃ -1	"	30	—	"	"	"	350	2	225	70
F ₃₃ (A-D)	XII ₁₅ -1	"	—	30	"	"	"	375	5	200	24
F ₁₃	I ₈ -1	"	48	—	"	"	2	350	"	225	60
F ₃₅ (A-D)	XII ₈ -1	"	—	48	"	"	5	375	"	200	17
F ₉	I ₅ -1	"	10	—	"	"	2	350	"	225	6
F ₁₂	"	"	"	—	"	"	"	"	"	"	5
F ₃₁ (A-G)	XII ₂ -1	"	—	10	"	"	5	"	"	200	54

Table 7 summarizes some of the possible correlations among the types of catalysts, their pre-treatments, the gas contraction percentage, oil yields, and gaseous products. As seen in this table, it cannot be so easily generalized that a parallelism between the gas contraction percentage and the oil yield, as evidenced by F₄₉ (F), where the oil yield amounts to 171.7 c.c./m.³ with 42% contraction, while F₃₉ (A-I) gives 121 c.c./m.³ with 64% contraction; F₄₅ (A-H), 124.4 c.c./m.³ with 49% contraction, F₄₆ (A-G), 127.1 c.c./m.³ with 65% contraction; and FC₇ (A-D), 129.4 c.c./m.³ with 64% contraction, respectively, although it

Table 7.

Exp. No.	Catalyst No.	Catalyst Composition (%)						Pre-treatment				Ave. Contraction (%)	Gaseous Products			Oil-yield cc/M ³	Space Velocity
								Heat-treat. (°C.) (hrs.)		H ₂ Reduction (°C.) (hrs.)			CH ₄ (%)	C ₂ H ₆ (%)	Olefins (%)		
	Co+CeO ₂ +ThO ₂ +B ₂ O ₃ +Kieselguhr + Cu																
F ₃₉ (A-I)	XII ₁₂ -1	100	15	15	5	100	—	400	5	375	5	64	10	0.9	1.2	121	330
F ₄₀ (A-I)	XII ₁₁ -1	"	"	"	—	"	—	"	"	"	"	34	0	0	0.5	75	280
F ₄₁ (A-E)	XII ₁₂ -1	"	"	"	5	"	—	"	"	"	"	49	"	"	0.7	78	330
F ₄₂ (A-I)	XII ₁₃ -1	"	18	18	"	"	—	"	"	"	"	"	3.9	"	1.5	98	231
F ₄₃ (A-I)	XII ₁₄ -1	"	15	15	"	"	5	"	"	"	"	45	5.5	"	0.2	93.2	233
F ₄₄ (A-D)	XII ₁₅ -1	"	18	18	"	"	"	"	"	"	"	15	0	"	0.4	21.7	239
F ₄₅ (A-H)	XII ₁₆ -1	"	15	15	10	"	—	"	"	"	"	49	11.5	"	0.5	124.4	244
F ₄₆ (A-G)	XII ₁₇ -1	"	18	18	"	"	—	"	"	"	"	65	6.7	1.2	1.7	127.1	220
F ₄₇ (A-E)	XII ₁₈ -1	"	"	"	"	"	5	"	"	"	"	25	0	0	0.3	67.2	237
F ₄₈ (A-F)	XII ₁₉ -1	"	15	15	"	"	"	"	"	"	"	10	"	"	0.2	26.5	242
F ₄₉ (F)	XII ₁₆ -1	"	"	"	"	"	—	"	"	"	"	42	"	"	0.0	171.7	248
F ₅₀ (A-F)	"	"	"	"	"	"	—	"	"	300	"	34	—	—	—	95.1	246
F ₅₁ (A-F)	"	"	"	"	"	"	—	"	"	400	"	15	0	0	0.5	51.9	239
F ₅₂ (A-H)	"	"	"	"	"	"	—	"	"	350	"	43	3	2.4	0.7	63.1	242
FC ₇ (A-D)	"	"	"	"	"	"	—	—	—	"	10	64	16.2	1.1	1.6	129.4	"

(*) CH₄ formation tends to zero as time proceeds.

might be said that 50–65% gas contraction usually gives 120–130 c.c./m.³ in these series of catalysts.

Thus far we have tabulated some of the typical results of the investigations concerning the effects of promoters on the Co type catalyst, with respect to the gas contraction percentage as a measure of the catalytic activity, also with regard to the oil yield as well; and also we pointed out that the fundamental difficulty as to get a general statement concerning the gas contraction percentage as related to the oil yield—which is so far simply considered as somewhat parallel—but actually it is not so simple as expected. Some authors have just considered these problems as the simplest case, i.e., a parallelism exists between the gas contraction and the oil yield, regardless of the amount of gaseous products formed, such as CH₄, C₂H₆ or C₂H₄. It is quite evident that, whenever CH₄ formation predominates, the contraction percentage is enormously high and the oil yield is not so appreciable—usually, when CH₄ formation is very much appreciable, the oil yield is negligibly small, as we often pointed out⁽⁵⁾ previously. Concerning suitable conditions for the synthesis of liquid hydrocarbons, it may probably be stated that the catalyst must be so rearranged that CH₄ formation is so restricted, or inhibited, as to direct the reaction of the liquid hydrocarbon synthesis on the catalytic surface, as required by our mechanism⁽⁷⁾, previously discussed.

Summary.

(1) The effects on the Co type catalyst of such promoters as B₂O₃ and Cu, and the combined effects of ThO₂ and CeO₂ on the catalytic activity have been investigated and discussed.

(2) The effects of the pre-treatment on the catalytic activity have been investigated and discussed.

(3) It has been shown that there is a fundamental difficulty to generalize a parallel relationship between the gas contraction and the oil yields.

(4) In discussing the catalytic activity, that the CH₄ formation must be carefully segregated whenever we speak of the catalytic activity as to its oil forming ability has been pointed out as of paramount importance.

In conclusion, the author takes this occasion to express his sincere thanks to Dr. T. Marusawa, Former Director of the Institute and Dr. M. Sato, Director of the Institute, for their interests and encouragement during these series of investigations and also for the permission of the publication; also he thanks to colleagues for their cooperation and to Messrs. Hayashi, Shimamura, Kuwabara, Igarashi and Fujiwara who have been willing to assist him in the experimental part of this investigation.

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(7) Report II, this Bulletin, **16** (1941), 213.

Hydrocarbons from Carbide (A) IV. Non-Catalytic Polymerization under Ordinary Pressure. Acetylene-Carbide System and General Remarks.

By Ryoji NEGISHI and Osamu KAMIKE.

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This paper will conclude our investigations on the non-catalytic direct synthesis of hydrocarbon liquid products from calcium carbide under ordinary pressure. The paper consists of two parts: the first part deals with the studies on acetylene-carbide system and the second gives a supplementary discussion and, at the same time, a resumé of the results of the entire series of investigations, consisting of the following systems:

Hydrogen—carbide,
Carbon dioxide—carbide,
Carbon monoxide (and water gas)—carbide,
Hydrogen chloride—carbide, and
Acetylene—carbide.

With the accumulation of the results with various gases, we feel more confident that we are now in a better position to picture the true affairs of the polymerization of nascent acetylene molecules, even in a system where the carrier gas itself may undergo polymerization. In fact, we have hoped that the total liquid yield may be increased by the polymerization of the very gas introduced, and for this reason, we have attempted to study the effects of acetylene and its mixtures with hydrogen or carbon dioxide. We have further hoped that by the introduction of acetylene, the formation of free acetylene from the carbide may be prevented, or suppressed, and thereby the nascent acetylene may be made more available for liquid synthesis.

In this paper we have made most of the runs at 340°C., which seems to be the most satisfactory temperature, and one run at 420°C. to make more clear the real effect of the carrier gas on the total yield of liquid products. Preparation of acetylene and experimental method have been already given in Paper (A) II⁽¹⁾.

Results and Discussion. Results are given in Table 11.* The first question that may be raised is whether the introduction of acetylene suppresses the formation of free acetylene from the carbide or not. Our data given in Table 12, seem to indicate it positively. In the table the results of only those experiments have been considered** in which except for

(1) R. Negishi and O. Kamiike, this Bulletin, **17** (1942), 118; also R. Negishi and O. Kamiike, *J. Soc. Chem. Ind., Japan*, **45** (1942), 135.

* Numbering of the Tables and Figures is consecutive from (A) II to the final paper.

** Percentage of free C₂H₂ varied from 20.3 to 36.1 for all the other runs at 340°C. involving mixtures of gases.

Table 11. Acetylene Systems.

Experimental No.	I _L 70	I _L 75	I _L 68	I _L 71	II _L 22
Reaction Temp. (°C.)	340	340	340	340	420
Gas	C ₂ H ₂	C ₂ H ₂ +H ₂	C ₂ H ₂ +CO ₂	C ₂ H ₂ +CO ₂	C ₂ H ₂
Saturation Temp. (°C.)	79.7	79.8	78.8	79.8	65.5
Ratio Gas to Water (Partial Press.)	C ₂ H ₂ :H ₂ O 1:0.86	C ₂ H ₂ :H ₂ :H ₂ O 1:1:2.67	C ₂ H ₂ :CO ₂ :H ₂ O 1:3:4	C ₂ H ₂ :CO ₂ :H ₂ O 1:3:4	C ₂ H ₂ :H ₂ O 2.7:1
Time of Contact (sec.)	25.9	28.9	18.3	22.9	23.7
Liquid Products (g.)	22.4	17.5	22.9	18.8	8.3
Water (g.)	1.5	0.7	7.2	3.8	1.0
Oil % on Reacted Carbide Carbon	40.6	34.5	36.9	30.0	130
Oil (total Wt.) % on Reacted Carbide C ₂ H ₂	47.2	38.0	40.7	33.6	137
Carbon Balance	102.3	96.0	95.8	104.5	99.0
Weight Balance	102.2	98.8	100.4	99.5	99.3

Table 12.

Exp. No.	I _L 34	I _L 35	I _L 44	I _L 57	I _L 65	I _L 70	I _L 68	I _L 71	I _L 75
Gas	H ₂	N ₂	CO	CO ₂	CO ₂ +HCl	C ₂ H ₂	C ₂ H ₂ +CO ₂	C ₂ H ₂ +CO ₂	C ₂ H ₂ +H ₂
Free C ₂ H ₂ (%)	+36.1	+26.7	+34.3	+27.8	+28.3	-8.4	+16.6	-42.2	-15.7

acetylene and HCl systems pure gases are used. The plus sign means that free acetylene has been formed while the minus means that the introduced acetylene has reacted; in other word, it is equivalent of saying that there is no formation of free acetylene. Minus 42.2% is definitely too high, and plus 16.6 is difficult to explain.*

Another question that may arise is whether or not the total liquid yield, based on the reacted carbide acetylene (and carbon), increases in these systems. The answer is again positive but with certain reservations. The results of Table 11 indicate that the effect of acetylene on the total yield is striking only when its concentration is relatively high, as for example, I_L-70 and II_L-22. When acetylene is diluted with an inert gas, such as H₂ or CO₂, and its concentration becomes relatively low, its effect on the total liquid yield disappears, as shown by I_L-75, I_L-68, and I_L-71. However, the presence of acetylene, even in a small concentration, has a striking effect on the suppression of the formation of free acetylene, as has been mentioned in the preceding paragraph. These effects, coupled with the fact that some of the introduced acetylene is actually used up, suggest that the role of the introduced acetylene is to form principally gaseous products, which in the absence of the acetylene are formed at the expense

* It may be added here that the results of I_L-68 are less reliable.

of the carbide, or that of the nascent acetylene molecules. It is interesting that the liquid yield at 420°C. is much larger than at 340°C., quite contrary to the results of the other systems, although the effect of the acetylene concentration cannot be entirely dismissed. Nevertheless, this point is in accord with the fact that the liquid formation by non-catalytic acetylene polymerization becomes appreciable only above 400°C. and optimum in the range, 500 to 700°C.⁽²⁾

The effect on the liquid yield of a diluent gas is small, and the final yield is mainly determined by the concentration of the water vapor. It may be added, however, that there exists an optimum concentration of the water vapor. A ratio not differing too far from 0.8 to 1.0 seems most favorable under our experimental conditions.

The results of elementary analysis are given in Table 13. The results of gas analysis are given in Table 14, and here, again, they should be considered, as in a previous paper⁽³⁾, qualitatively rather than quantitatively. In spite of the fact that some of the hydrogen used in effecting desorption

Table 13. Elementary Analysis.

Exp. No.	I _L 68		I _L 70		I _L 71		I _L 75		II _L 22	
	Trap.	Cond.	Trap.	Cond.	Trap.	Cond.	Trap.	Cond.	Trap.	Cond.
Element C....	74.98	84.69	67.98	86.27	79.76	82.66	79.69	86.72	74.10	81.96
" H....	9.37	8.62	10.21	8.73	9.97	8.61	9.01	9.26	10.30	8.19
" O....	15.65	6.69	21.81	5.00	10.27	8.73	11.20	4.01	15.60	9.85

Table 14. Gas Analysis (Average values).

Exp. No. Gas	I _L 68	I _L 70		I _L 71			I _L 75		II _L 22	
		Reacted	Desorp.	Reacted	Desorp.	Orig.	Reacted	Orig.	Reacted	Orig.
CO ₂	38.2	2.4	0.6	36.5	4.0	74.3	1.0	0.8	1.6	6.9
C ₂ H ₂	34.4	79.2	22.1	47.7	14.1	24.7	30.8	45.5	75.4	92.9
C ₂ H ₄	0.1	0.2	0.6	0.2	0.4	—	0.6	0.0	0.5	—
C _n H _{2n}	0.2	0.6	1.1	0.4	0.7	—	0.8	0.0	0.9	—
O ₂	0.7	0.6	0.6	0.6	0.5	—	0.8	1.0	0.5	—
CO	0.3	0.3	0.4	0.3	0.3	—	0.3	0.0	0.3	—
H ₂	21.3	9.6	62.3	8.8	70.3	—	57.4	47.9	12.4	—
CH ₄	1.7	4.0	8.7	1.7	7.0	—	4.1	0.4	6.1	—
N ₂	2.0	3.3	3.1	3.8	3.0	1.0	3.7	4.2	1.0	0.2

is mixed in the effluent reacted gas, the hydrogen contents in runs I_L-70 and I_L-71, which are at 340°C., are lower than that of II_L-22, which is at 420°C. and in which no desorption has been effected. A similar situation exists for the methane contents of these runs, and these facts are consonant with the effect ascribable to the difference in the reaction temperatures.

(2) G. Egloff, "The Reactions of Pure Hydrocarbons," Reinhold Publishing Corp., N.Y., (1937); C. Ellis, "The Chemistry of Petroleum Derivatives," Reinhold Publishing Corp., N.Y., Vols. I and II, (1934 and 1937).

(3) R. Negishi and O. Kamiike, this Bulletin **17** (1942), 244.

When the contents of methane in the effluent gas of desorption in I_L-70 and I_L-71 are considered, it is evident that they are higher than those in the respective effluent gases during the normal course of reaction. The difference must be real. When the temperature is increased to effect desorption, quite an appreciable amount of water is always condensed out along with the liquid products, even when a dry gas is used. The source of this water is not clear, but that is of no consequence in our present discussion. What appears significant is that this water reacting with the carbide, produces acetylene which probably is then transformed into methane more effectively at higher temperature. As has been mentioned before⁽³⁾, the effect of desorption is apparent only in I_L-71 in which carbon dioxide is present.

This system will conclude the experimental work on the non-catalytic direct synthesis of hydrocarbons from calcium carbide under ordinary pressure, and in the next section of this paper, we shall treat the subject from a broader perspective to give more coherence to the isolated facts obtained in the individual systems so far investigated.

Concluding Remarks. As we have already seen, hydrogen and nitrogen are without effect⁽¹⁾; carbon dioxide has a pronounced beneficial effect⁽³⁾ while carbon monoxide has rather harmful ones⁽³⁾; acetylene increases the total yield owing to the circumstance that it itself polymerizes under certain conditions; and, finally, hydrogen chloride has shown to give somewhat harmful effects only when its concentration is high⁽³⁾. We have also seen that desorption shows effects only when CO_2 (and its mixtures) is used as a carrier gas. Although these gases have varied in their effects on the total liquid products, they are without appreciable influence on the character of the products. This point has been briefly mentioned elsewhere⁽³⁾, but it becomes quite plausible in the light of the more complete set of data, which are shown in Table 15.

As can be readily seen from Table 15, the oxygen contents of the condensates in the condenser and in the trap differ widely, as is also the case with their H/C ratios. When the average ratios of H/C, 0.1309 and 0.1028, for the liquid in the trap and the condenser, respectively, are compared, there will be a difference of 27% between them, provided no correction for the oxygen content is taken into account; when corrected, the corresponding values are 0.0959 and 0.0890, and the difference is about 8% which is a notable reduction from that of the uncorrected. Moreover, the individual ratios for the corrected values differ from the average less markedly. This is interesting, because it gives some support to the validity of our assumptions that the oxygen is principally alcoholic and that the gases used are without influence on the character of the products.

The results of elementary analysis of the condenser condensates* also give good supporting evidence for the independence of nascent acetylene

* The results of the trap are not so uniform as those of the condenser, but this is due to the fact that the amount of the condensates in the former is very much smaller (at times, less than 10% of the condenser, or about 1 c.c.), and the results of analysis are less accurate. There is another probable source of error, which is more pronounced in the trap than in the condenser. It is the amount of water which may have dissolved in the respective condensates. A larger H/C ratio of trap as compared with that of condenser is suggestive.

Table 15.

Exp. No.	Gas Used	Elementary Analysis		H/C Ratio				On Reacted Carbide Carbon (%)		
		Analysis		Found		Correct. for MeOH Oxygen		Methane C in Reacted Gas	De-comp. + Poly. Carbon in Residue	
		Trap	Cond.	Trap	Cond.	Trap	Cond.			
I _L 35*	N ₂	C	74.79	86.57	0.1295	0.099	0.100	0.0894	3.5	20.7
		H	9.96	8.61						
		O	13.25	4.82						
I _L 34	H ₂	C	75.36	85.99	0.1355	0.0975	0.1024	0.0862	6.1	18.8
		H	10.22	8.39						
		O	14.40	5.62						
I _L 57	CO ₂	C	74.98	83.19	0.1250	0.1053	0.0853	0.0864	3.9	23.1
		H	9.37	8.76						
		O	15.65	8.05						
I _L 41	CO ₂ + H ₂	C	83.02	84.02	0.1214	0.1000	0.1070	0.0841	2.3	24.5
		H	10.10	8.47						
		O	6.88	7.52						
I _L 44	CO	C	82.02	84.60	0.1182	0.1027	0.1008	0.0881	7.3	48.9
		H	9.71	8.69						
		O	8.27	6.71						
I _L 50	CO + H ₂	C		85.20	Combined	0.1025	Combined	0.0898	3.4	43.1
		H	Combined	8.76						
		O		6.04						
I _L 64	HCl, 3.5 + CO ₂	C	74.29	79.79	0.1360	0.1100	0.0989	0.0833	3.5	23.4
		H	10.10	8.78						
		O	15.61	11.43						
I _L 65	HCl, Dil. + CO ₂	C	67.70	84.96	0.1550	0.1042	0.1020	0.0957	2.3	28.3
		H	10.48	8.85						
		O	21.82	6.19						
I _L 70	C ₂ H ₂	C	67.98	86.27	0.1500	0.1015	0.0923	0.0906	12.5	44.63
		H	10.21	8.73						
		O	21.81	5.00						
I _L 75	C ₂ H ₂ + H ₂	C	79.69	86.72	0.1130	0.1070	0.0871	0.0937	6.4	41.50
		H	9.01	9.26						
		O	11.20	4.01						
I _L 68	C ₂ H ₂ + CO ₂	C	74.98	84.69	0.1250	0.1015	0.0862	0.0873	3.8	28.4
		H	9.37	8.62						
		O	15.65	6.69						
Average				0.1309	0.1029	0.0959	0.0890			

* Least reliable.

polymerization, which we shall henceforth refer to as the specificity of nascent acetylene polymerization. As evident from Table 15, the results are quite similar in every case except for those of I_L-64. The fact that a ratio of H/C is near that of C₂H₂ but always larger is probably real and significant. The meaning of this is, among others, first, the mechanism of the main reaction of the nascent acetylene molecules may be written as

$$n(\text{C}_2\text{H}_2) = (\text{C}_2\text{H}_2)_n,$$

second, there is a slight amount of hydrogenation of the products, even in the absence of any catalyst. This is what we have anticipated in one of our papers⁽⁴⁾. At the instance the carbide reacts with water, there may exist some rather reactive hydrogen molecules or atoms, some of which may take part in hydrogenation⁽⁵⁾. The ratio of the average value of H/C to that of acetylene gives a measure of the degree of hydrogenation; it is 1.07, or about 7% is hydrogenated.

We cannot draw a conclusion as to the mechanism of the main reaction merely from the circumstance alone that the ratio of H/C is near that of acetylene, since it is quite possible that the average value of elementary analysis of the numerous components* contained in the products may be that of acetylene as far as its H/C ratio is concerned. However, it may be carried to the conclusion by a combination of the following evidences. Properly controlled low-temperature polymerization of acetylene⁽⁷⁾ will convert it into monovinylacetylene; a dimer, divinylacetylene; a trimer⁽⁸⁾; and a tetramer⁽⁹⁾⁽⁵⁾. Spark, Rosen, and Frolich in their interesting paper⁽¹⁰⁾, "Dimerization of Petroleum Hydrocarbons," have assumed that complicated hydrocarbons can be built up by a series of dimerizations involving the well-known 1, 3 rearrangement of hydrogen and have applied this principle to acetylene. According to them a dimer, vinylacetylene, is formed which may undergo either to vinyldivinylacetylene, $\text{CH}_2\text{-CH=C}\equiv\text{C-CH=CH-CH=CH}_2$, or to styrene by ring closure. Styrene has been identified⁽⁶⁾⁽¹¹⁾. Recently, butadiene has been

(4) R. Negishi, O. Kimura, and O. Kamiike, *Rev. Phys. Chem., Japan*, **15** (1941), 31.

(5) H. A. Taylor and A. Van Hook, *J. Phys. Chem.*, **39** (1935), 811. They have concluded from their homogeneous thermal polymerization of acetylene and its hydrogenation in the temperature range 495 to 535°C. that the principal processes (polymerization and hydrogenation) are interpreted as bimolecular with energies of activation of 40,500 and 42,000 calories, respectively. The efficiency of the association is high, but in the presence of excess of hydrogen, the hydrogenation process becomes predominant.

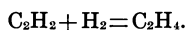
* Indicated by the absence of sharp breaks in the distillation curve and by the large number of the products, as shown in Table 16, identified by Schlapher and Stadler⁽⁶⁾ in their analysis of the cuprene-tar, the liquid products obtained during the formation of cuprene.

(6) Schlapher and Stadler, *Helv. Chim. Acta*, **9** (1926), 185.

(7) C. Ellis, Ref. 2, Vol. II, p. 701 ff. (1937).

(8) Acetylenebivinyll, $\text{CH}_2=\text{CHCH}=\text{CHC}\equiv\text{CH}$, another trimer of acetylene has been obtained by A. K. Klebanskii, U. A. Dranitzina, and I. M. Dobromil'skaya, *Compt. rend. acad. sci., (URSS)*, **2** (1935), 229.

(9) Pease, *J. Am. Chem. Soc.*, **51** (1929), 3470. He concludes that the rate determining process is the primary reaction involving two molecules of acetylene, and the major reaction involves four molecules of acetylene giving a tetramer. Taylor and Van Hook (*loc. cit.*) assume that the main reactions of acetylene in the presence of hydrogen are



(10) W. J. Spark, R. Rosen, and P. K. Frolich, *Trans. Faraday Soc.*, **35** (1939), 1040.

(11) M. E. Cupery and W. H. Carothers, *J. Am. Chem. Soc.*, **56** (1934), 1625.

prepared directly from acetylene⁽¹²⁾. In the light of the foregoing evidences, it is not unreasonable to assume that the main mechanism of the nascent acetylene polymerization is as written above; moreover, it becomes probable that some sort of chain-compounds are formed first which are then transformed into aromatic and condensed hydrocarbons⁽¹³⁾. In connection with this transformation, a recent paper by Thom  s, Egloff, and Morrell⁽¹⁴⁾ is highly suggestive.

We shall say a word concerning the beneficial effect of carbon dioxide in passing. It is difficult to point out definitely what the effect is but we believe that it is associated, to no small extent, with the destruction

Table 16. Physical Constants of Cuprene-Tar.

Compound	Formula	d ₂₀	Boiling Pt. �C at 760 mm.	Mol. Wt.	H/C
Hexenes	C ₆ H ₁₂	0.681–0.6938	64.1–68.1	84	0.167
Octene	C ₈ H ₁₆	0.7155	123	112	0.167
Benzene	C ₆ H ₆	0.8707	80.08	78	0.0833
Toluene	C ₇ H ₈	0.8658	110.5	92	0.0952
Xylenes	C ₈ H ₁₀	0.8612–0.8745	138.4–144.4	106	0.1041
Ethylbenzene	C ₈ H ₁₀	0.8669	136.1	106	0.1041
Styrene	C ₈ H ₈	0.9074	146	104	0.0833
Methylstyrene	C ₉ H ₁₀	—	—	118	0.0927
Trimethylbenzenes	C ₉ H ₁₂	0.8634–0.895	164.64–176.1	120	0.1112
Ethylmethylbenzenes	C ₉ H ₁₂	0.862–0.873	162–162.5	120	0.1112
Propylbenzenes	C ₉ H ₁₂	0.862–0.864	152–159.45	120	0.1112
Naphthalene	C ₁₀ H ₈	1.145	217.9	128	0.0666
Methylnaphthalenes	C ₁₁ H ₁₀	1.052–1.029	242–245	142	0.0758
Ethyl��naphthalene	C ₁₂ H ₁₂	1.059	258 (decomp)	156	0.0833
Dimethylnaphthalenes	C ₁₂ H ₁₂	1.001–1.008	261–266	156	0.0833
Anthracene	C ₁₄ H ₁₀	1.025	354–5	178	0.0596
Hexahydronaphthalene	C ₁₀ H ₁₄	0.934	168.7–180	134	0.1166
Butylbenzenes		0.862–0.8673			
Cymenes		0.8510–0.876			
Propyltoluenes		0.864			
Diethylbenzenes		0.860–0.865			
Dimethylethylbenzenes		0.861–0.877			
Tetramethylbenzenes		0.880–0.901			

of Ca(OH)₂ (and CaO). According to Berl and Hofmann⁽¹⁵⁾, CaO is unfavorable to acetylene polymerization and turns the reaction toward the formation of methane, hydrogen, and carbon. When our results in

(12) A. A. Balandin, Ya. T. Eidus, and E. M. Terent'eva, *Compt. rend. acad. sci.*, (URSS), **27** (1940), 343.

(13) E. Bergman, *Trans. Faraday Soc.*, **35** (1939), 1025; G. B. Kistiakowsky and W. W. Ransom, *J. Chem. Phys.*, **7** (1939), 725.

(14) C. L. Thomas, G. Egloff, and J. C. Morrel, *Chem. Rev.*, **28** (1941), 1. This interesting paper summarizes the reactions of hydrocarbons in electrical discharges, but the mechanism of acetylene polymedization in general is also included.

(15) E. Berl and K. W. Hofmann, *Z. angew. Chem.*, **44** (1931), 259.

Table 15 are examined, whenever CO_2 is used, a ratio of methane carbon, as well as that of free carbon, to carbide carbon is smaller.*

Hydrogen chloride seems without appreciable effect, and this is probably due to the fact that it may not react with CaO but slightly. In $\text{I}_L\text{-62}$ (Table 6⁽³⁾), where the average concentration of the acid is 26% by weight, the carbonate carbon in the residue is 10.4% while that in the hydrogen system⁽¹⁾ is from 3.7 to 12.9%; in $\text{I}_L\text{-75}$ (Table 11) in which a mixture of acetylene and hydrogen is used, it is 8%. Since HCl seems without effect on the carbonate, it may neither have any effect on CaO **.

The facts that the presence of the carbide increases the magnitude of $-\Delta F$ ⁽⁴⁾ and that the nascent acetylene molecules possess high reactivity might lead to a conclusion that there would be an improvement in the yield of hydrocarbon liquids. The answer to this point is hinted at when the results of $\text{I}_L\text{-57}$ (Table 3⁽³⁾) are compared with those obtained by Shiomi and Iwamoto⁽¹⁶⁾ and Amemiya⁽¹⁷⁾, as shown in Table 17. As can be seen from Table 17, under the respective optimum conditions the polymerization of nascent acetylene gives, even in the absence of catalyst, the highest yield both in volume and weight. The fact that the lower the reaction temperature, the lighter are the products is probably due to the predominance of catalytic effect over that of $-\Delta F$, or the chemical tendency, which favors the formation of heavier products in the carbide reactions⁽⁴⁾.

Table 17. Comparison between Polymerizations of Ordinary and Nascent Acetylene.

Experimenter	Catalyst	Temp. (°C.)	Max. Yield		Approx. Density
			c.c./cbm.	gr./cbm.	
Shiomi and Iwamoto ..	$\text{Co:Ni:Cr}_2\text{O}_3$ Acid clay	208	405	320	0.778*
Amemiya	Fe:Ni Kieselguhr	290	455.6**	389	0.855
Negishi and Kamiike..	None	340	486	460	0.9-1.0

* For the fraction boiling between 170 and 200°C.

** The more recent result by him is (ref. 17b), under the following conditions: Catalyst $\text{Fe:Ni:Co:Kieselguhr}$ (90:5:5:1000) + 2% K_2CO_3 , 3 g. as metal; reaction gas $\text{C}_2\text{H}_2:\text{H}_2=1:4$; flow rate 200 c.c./min.; reaction Temp.°C. (270?), 478.5 c.c./cbm.

In Shiomi and Iwamoto's experiment, given in Tables 18 and 19,, it is obvious that the fraction boiling up to 300°C. is about twice as large and the densities of various fractions are much less than ours. In their investigations they have obtained only 26.9% aromatic; similarly, Amemiya has obtained about 23% * aromatic for the fractions boiling up to 350°C. In ours, on the other hand, we are quite reasonable in assuming,

* High polymers and free carbon are determined together, and there is some uncertainty in the values of the individual components.

** Since the results of $\text{I}_L\text{-62}$ are least reliable, this argument must be taken with certain reservations.

(16) Shiomi and Iwamoto, *J. Soc. Chem. Ind., Japan*, **41** (1938), 831.

(17) T. Amemiya, *ibid.*, **42** (1939), 692; (b) *J. Fuel Soc., Japan*, **21** (1941), a45.

*** Calculated from his data given in Ref. 17b, pp. a56 and a57.

Table 18. Results of Distillation.

Negishi and Kamiike			Shiomi and Iwamoto	
Distillation Range Temp. (°C.)	Vol. (%)	Density at 25°C.	Range of Distillation	Fraction Vol. (%)
<100	1.8	—	—	—
100–150	5.7	0.837*	<150	28.7
150–200	7.8	0.9084	150–200	15.5
200–250	22.3	0.957	200–270	23.6
250–300	10.1	0.971	270–300	11.5
300–326	25.4	—	Above 300	19.6
Residue.....	22.1 (Wt. %)			

* For fraction below 150°C.

Table 19. Density of Products.

Temp. Range (°C.)	< 110	110–140	140–170	Above 170	Experimenter
Density ²⁰	0.685	0.739	0.749	0.778	Shiomi and Iwamoto
Temp. Range	Below 150		150–200		Negishi and Kamiike
Density at 25°C.	0.837		0.9084		

judging from the boiling ranges and densities, that the major fraction of the products is aromatic. This assumption becomes more plausible in the light of the identification made by Schlapher and Stadler⁽⁶⁾ of the cuprenetar (Table 16). The physical constants of the substances identified, as well as some of the unidentified substance having the empirical formula, $C_{10}H_{14}$, in the Table have been taken from the Science of Petroleum⁽¹⁸⁾.

Finally, we may say that many of our observations in this series of investigations are without adequate interpretation; to mention a few, the real effects on the liquid yield of carbon monoxide, hydrogen chloride, and desorption and the real nature of the individual components in the product. The role of a catalyst must be made clear in near future, but at this stage of progress, we may say with some confidence that in these reactions involving the carbide, it is not the question of the activation of the reactants, but of the selectivity, or the specificity, of the catalyst that is most pertinent.

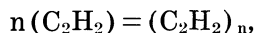
Summary.

It has been shown that when acetylene is used as a carrier gas, the percentage of the total liquid products, based on the reacted carbide acetylene (or carbon), increases owing to the polymerization of the carrier gas itself, provided its concentration is sufficiently high. If the concentration is low, the effect of the introduced acetylene appears limited merely to the suppression of the formation of free acetylene.

(18) The Science of Petroleum, Vol. 11 (1928), Oxford Press.

An explanation for a higher content than in the reacted gas of methane in the effluent gas used for desorption has been given for the acetylene system.

The supplementary data in support and evidence for the reasonableness of the over-all mechanism of nascent acetylene polymerization, which may be written



have been given.

It has been indicated that the efficacy of the synthesis of hydrocarbon liquids directly from calcium carbide is higher than even the catalytic polymerization, so far reported in literature, of ordinary acetylene.

*The Central Laboratory,
South Manchuria Railway Company, Dairen.*

Hydrocarbons from Carbide (A) V. Non-catalytic Polymerization under Elevated Pressures⁽¹⁾. Comparison between Ordinary and Elevated Pressure Reactions.

By Ryoji NEGISHI and Osamu KAMIIKE.

(Received April 6, 1942.)

In Papers (A) II to IV⁽²⁾, inclusively, we have given rather in detail the results of non-catalytic direct synthesis of hydrocarbon liquids from calcium carbide under ordinary pressure, and with the valuable informations gained therefrom, we have now attempted the same synthesis but under elevated pressures. The experimental results and discussions have been already given in Japanese⁽¹⁾, and in this paper we shall summarize only the main features of the three original papers, including also the additional discussions which are not found in the above papers⁽¹⁾. The treatment of the general subject, the synthesis of hydrocarbon liquid products directly from calcium carbide, will be made as complete as possible, however, always in harmony with the reliability and completeness of our experimental results which, we must admit, are not quite satisfactory at places.

Under elevated pressures we have limited our investigations to hydrogen-carbide, carbon monoxide-carbide, and a few preliminary runs with carbon dioxide-carbide systems. What prompted us to study these systems were the following questions: (1) Would the products from the carbide contain more hydrogen when they are prepared in excess of it? (2) What would be the behaviour of nascent acetylene towards hydrogen? (3) What are the effects of carbon monoxide (and water gas) particularly on the total liquid yield? (4) What differences exist between the runs under low and elevated pressures?

Before answering these questions, it would be of advantage to touch on some of the experimental details which are necessary for understanding and appreciating the difficulty involved and for estimating the reliability to be expected of the results.

For these high pressure experiments, three one liter autoclaves, which could be only used for static experiments, had been used. As a practical means of furnishing the necessary water for the carbide reactions, aluminum hydroxide, which gave up most of its water in the temperature range, 200 to 300°C, was used. Because of these limitations, the results obtained were limited both in scope and significance.

(1) This subject will be presented by the authors and M. Nibayashi in detail in Japanese in a series of Papers I to III, which will appear in *J. Soc. Chem. Ind., Japan*, **45**(1942). In the present paper most of the experimental details and tables will be omitted and only the high-lights of the three papers, which will henceforth be referred to as Papers I, II, and III, will be summarized.

(2) R. Negishi and O. Kamiike, this Bulletin, **17**(1942), 118; *ibid.*, **17**(1942), 44; *ibid.*, **17**(1942) to be published.

Some of the difficulties and uncertainties involved in these experiments will be mentioned briefly. First of all, heating of the autoclave had to be very carefully controlled to maintain the temperature in the range where aluminum hydroxide gave up most of its water. Since the reactions between calcium carbide and water are rapid and highly exothermic, if the release of the water is too rapid, there are apt to occur sudden "jumps" both in temperature and pressure. One example given below illustrates the "jumps" effectively. Initially, carbide grains of 2–3 mm. diameter and 100 kg/cm². of hydrogen were employed.

Exp. No.	Just before Jump		Just after Jump		C/H in Residue	Vol. % of CH ₄ +C ₂ H ₆
	Temp. (°C.)	Press. (kg./cm ² .)	Temp. (°C.)	Press. (kg./cm ² .)		
I _A –7	260	163	433	279	19	57.6

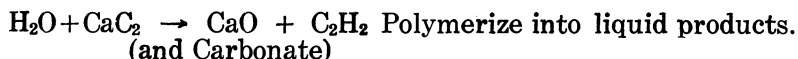
If powdered carbide is used, the jumps are more pronounced. They take place in less than one minute. When they occur, no liquid products, but saturated gases mostly of low molecular weight, and a large amount of free carbon in the residue are formed. Jumps were prevented to a large extent by using grains and by separating the hydroxide catalyst from the carbide by charging the former in a cylinder supported at the center of the autoclave. The hydroxide catalyst thus charged will be referred to as "in cylinder".

The second difficulty encountered was in obtaining satisfactory weight and carbon balances. Needless to say, our runs under elevated pressures were less refined than those under ordinary pressure, but besides this difference in the experimental refinement, there were at least two outstanding sources of difficulty. One of them was associated with the fact that the autoclaves had to be opened and closed after each run, and small leakage was often undetected. This probably accounted for the chief uncertainty in the weight balance. Uncertainty in the residue analysis was presumably the largest factor which gave unsatisfactory results in the carbon balance.

The residue consisted of free carbon, very high polymers, unreacted carbide, carbonate, calcium oxide, and small quantities of sulfur and other compounds. We found no satisfactory method of analysis. Our method was to extract the residue with chloroform and then to react it with water to determine the unreacted carbide; then with either dilute HCl or acetic acid to determine the carbonate content. The acetate or the chloride formed was dissolved with excess of water, and after drying, the residue was subjected to elementary analysis. It was quite difficult to oxidize the residue completely, and often very severe conditions, which were not without harm to the reagents in the combustion tube, had to be employed. Evidence of incomplete combustion of the sample was often noticeable.

While our blank runs indicated that below 400°C autoclaves II and III, which were used in most of the runs of our series, were practically

without any catalytic effect* for carbon monoxide and hydrogen mixtures, autoclave I was appreciably catalytic already at lower temperatures for the reduction of CO into methane and H₂O. Above 400°C the catalytic effect of each autoclave was more apparent, but the character of the reactions remained the same. When CO and H₂ were mixed with carbide alone, some hydrocarbon liquid products were obtained, but this was accounted for by the reactions:



Under similar conditions similar results were obtained, and the less the catalytic effect, the more reproducible were the results. These facts indicated that most of our runs were sufficiently reliable, and most of the differences in the carbon and weight balances were due to the factors considered above. It may be inferred, therefore, that when the total weight balance does not deviate a great deal from 100%, the results are, except for the residue analysis, nearly correct, regardless of what the corresponding total carbon balance may indicate. For the comparison of the gaseous and liquid products, therefore, it is the total weight balance, and not necessarily the carbon balance, that serves as a guide as to the reliability of the data. Our temperature readings are probably good to about $\pm 5^\circ\text{C}$ and the pressure within $\pm 5 \text{ kg/cm}^2$. In our present investigations, accuracy of 5% would be as satisfactory as might be hoped for, and even an order of 10% must be considered rather satisfactory.

Discussion. The results of blank runs on the catalytic effects of the autoclaves have been reported in Paper I, and those of the systems, hydrogen-carbide and carbon oxides-carbide, have been given in Paper II. We shall not retabulate the results here, but immediately avail ourselves of answering the questions raised at the beginning of this paper. The answers will not be given in the order of the questions.

(A) Effects of Pressure and Temperature. (1) *On the Yield of Products.* Results under various total initial pressures of the runs made with hydrogen, carbon monoxide (or water gas), and carbon dioxide are given in Table 20. Most of our runs were made in the neighborhood of 100 atmospheres, since it was evident from the hydrogen system that at about this pressure, a maximum in the total liquid products (free of gases condensed and dissolved in the trap and extractable products from the solid residue) was found. The existence of this maximum may have some connection with the concentration of the acetylene available. Although the total liquid products seem to be a direct function of the total pressure, the yields of saturated gases** are rather a function of the partial pressure of hydrogen. This is to be expected. The percentage yield of liquid products based on the

* For a more detailed description of the effect, see Ref. 1, particularly Paper I.

** Those of olefins and acetylene are small and the results are less definite.

Table 20. Effect of Pressure and Temperature on Products.

(Max. Reaction Temp. $\simeq 450^{\circ}\text{C}.$)

Exp. No.	Total Initial Press. kg./cm ² . at Room Temp.	Partial H ₂ Press.	% Calculated on Reacted CaC ₂ Carbon			Wt. (g.) Carbonate Carbon in Residue*	Note	Gas
			Methane+ Ethane Carbon	Residue Carbon	Liquid Carbon			
I _A 14	25	25	16.9	55**	23.6	< 3.8 ^Ω	"in cylinder"	H ₂
I _A Ser. 26	50	50	29.3	27.6**	26.6	< 17 ^Ω		
I _A Ser. 37	50	50	19.7	25.6**	28.4	< 15 ^Ω		
I _A Ser. 16	100	100	42.0	5.8	32.8	2		
II _A Ser. 38	100	100	32.6	4.4	33.3	1.3		
I _A 1	200	200	49.5	7.3**	24.9	< 4 ^Ω	Calcd. on 200 grs.	
II _A 15	70	53	27.6	6.7	22.1	4.3		CO+H ₂
II _A 11	70	50	25.2	13.8	22.2	9.3		
II _A Ser. 21	100	56	22.7	10.6	23.1	23.1		
I _A Ser. 51	100	∞ 80	23.2	21.4	36.8	25.8		CO+H ₂
II _A Ser. 18	70	∞ 55	10.1	17.2	12.6	14.4	405°C.	CO+H ₂
III _A Ser. 57	180-150***	∞ 50	24.4	12.7	25.0	26.7	370°C.	

* Calculated on 60 grams of reacted carbide carbon.

** Contains carbonate carbon.

^Ω Contains residue carbon.

*** At 370°C.

reacted carbide carbon of the elevated pressure runs are appreciably higher than the corresponding ones of ordinary pressure. We believe that this apparent increase in the yield is due to temperature effects than to any change in the reaction mechanism. In the autoclave runs any solid products, such as the yellow powder formed at lower temperatures and heavy liquid products adsorbed on the solid, are either decomposed into liquid or distilled out at higher temperatures, e.g., 450°C. On the other hand, in the runs under ordinary pressure, any such products will remain in the residue. Support for this argument is found in the relatively small amounts of carbon in the solid residues of the runs of high as compared with those of the low pressure, as shown in Table 15 (Paper (A) IV) and Table 20. Another evidence of this can be got from the results of II_A-Ser. 18 in which the highest temperature is 405°C. There, the percentage of liquid products is very much smaller, but the residue contains about 15 g. of extractable liquid as compared with a few grams from the others at 450°C. The results of III_A-Ser. 57, which will be discussed further in detail later, illustrate the same point.

(2) *On Hydrogenation.* In Table 21 the ratios of H/C, corrected and not corrected for methanol oxygen (Paper (A) III), of the condenser condensates of the runs under low and high pressures are given. In the last row of the table, percentages of hydrogenation based on the H/C ratio of acetylene for the different gases used are shown. It is evident

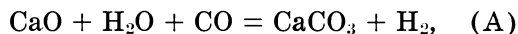
Table 21. Degree of Hydrogenation of Condenser Condensates.

System	Low Pressure			Elevated Pressure		
	H ₂	CO+H ₂	CO ₂ +H ₂	H ₂	CO+H ₂	CO ₂ +H ₂ **
H/C×10 Found	1.101	1.026	1.018	1.173	1.276	1.122
H/C×10 Corrected* ..	0.905	0.890	0.858	0.973	1.091	0.833
% Hydrogenated based on H/C of Acetylene.	8.7	6.8	3	17.5	31.0	0

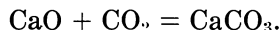
* Corrected for methanol oxygen.

** Result of one run.

that under elevated pressures, the percentages are higher. It is very much higher for CO+H₂ system while it is, within our experimental accuracy, about the same for CO₂+H₂ system. Furthermore, it seems that in the latter system the pressure has practically no effect. The fact that among the runs under high pressure, the degree of hydrogenation is almost independent of the pressure, within the range investigated, seems to strengthen our belief that the mechanism of the nascent acetylene polymerization is highly specific and but slightly—if at all—affected by pressure. The apparent increase in the percentages must be due to an increase in the time of contact. While in the runs under ordinary pressure it is about 20 sec, in the autoclave runs the substances remain in contact with hydrogen over 100 minutes. A particular increase in the H/C ratio for CO+H₂ system may be due to a slight formation of liquid product from water gas under elevated pressures. This statement appears paradoxical to what we have mentioned in Paper I that the gas itself does not form any liquid products. Since the conditions involved in the blank and present runs are quite different in such factors as the time of contact, the reaction products, it may be quite possible that a negligible amount in the blank runs could have become a bit more appreciable in the present runs, where especially any catalytic tendency will be greatly enhanced by the presence of the carbide⁽³⁾. Or it may be in some way connected with the presence of the reactive hydrogen* produced by some such reaction⁽⁴⁾ as



which is a combination of



We have seen that both of these reactions take place readily in our systems. According to Ellis⁽⁴⁾, the first reaction, (A), so-called "lime process", takes place most readily under elevated pressures and at about

(3) R. Negishi, O. Kimura, and O. Kamiike, *Rev. Phys. Chem., Japan*, **15**(1941), 31.

(4) C. Ellis, "Hydrogenation of Organic Substances," 3rd Ed., 738, D. Van Nostrand Co., N. Y., (1930).

* We have seen the same sort of evidence in the runs under low pressure (2).

450–600°C. The fact that $\text{CO} + \text{H}_2$ may have reacted under elevated pressures to produce some liquid products becomes more probable, though not necessarily more conclusive, in the light of the results of III_A Ser. 57. In this run the reaction temperature was constant at 370°C, and water gas was charged 5 times at the reaction temperature to maintain the total pressure to 160–180 kg/cm². The time of reaction was 1600 minutes. A liquid product condensed at 370°C was over 9 g. and 25% of the total reacted carbon, assuming that all the carbon had come from the carbide.* These values represent in percent and in the absolute amount a maximum at such a low temperature. A word should be added that in this run a catalyst, which was, however, found quite inactive,** had been used, and this fact cannot be entirely over-looked in the above discussion.

(B) **Products.** (1) *Liquid.* The combined liquid products from the runs under high pressure were separated into three groups: those obtained when aluminum hydroxide was in contact with the carbide, the hydroxide "in cylinder", and those obtained with water gas mixtures.

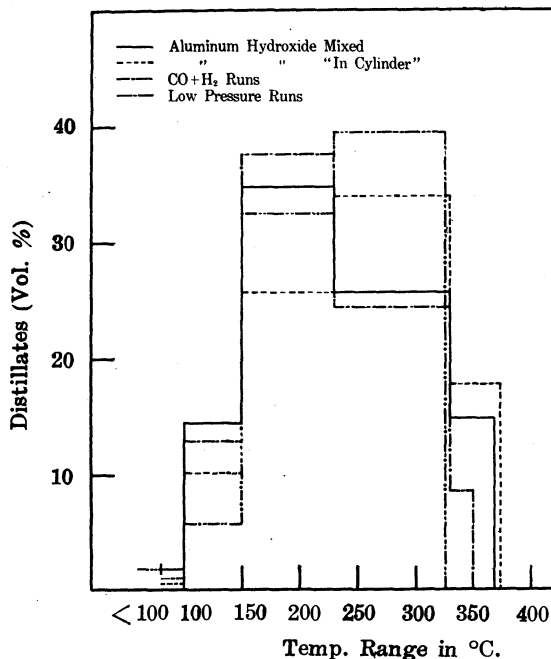


Fig. 3. Distillation Curves.

Their distillation curves and a similar one for the runs under low pressure are shown in Fig. 3. It is interesting that the curves for the runs under low pressure and the hydroxide "in cylinder" are alike in many respects. This is probably due to the temperature effect. This is in accord with thermodynamic considerations⁽³⁾. When the hydroxide and the carbide are separated, i.e., the hydroxide is "in cylinder", the water vapor released must diffuse through the atmosphere of the gas and the concentration of the water molecules must be uniformly distributed throughout by the time they react with the carbide. If, however, the hydroxide is in

intimate contact with the carbide, the concentration of the water molecules may not be uniform, but may be larger at places, and there the temperature may be higher than the average of the system. This explanation seems

* This assumption seems reasonable (Papers (A) III and II).

** As will be explained in one of the subsequent papers to be published elsewhere that even a slightly active catalyst may become rather active in the presence of the carbide.

to suffice for the shape of the curve for the liquid obtained when the hydroxide is in mixture with the carbide. The fact that its curve is similar to that of the water gas system may be accidental. As has been mentioned in a preceding section, CO and H₂ may have formed some liquid products which boil at lower temperatures. III_A Ser. 57 is a good example.

No detailed chemical analysis of the products has been made, but from some of the physical constants determined, they are chiefly aromatic and condensed in nature, as in the case of the runs under low pressure. From what has been said above, it seems quite probable that the main reaction of the nascent acetylene molecules under elevated pressures (under our present limited conditions) is the same as that under ordinary pressure runs, and the minor differences are ascribable to temperature and side effects, such as the formation of liquid products from the carrier gas itself, independently of the main reaction. The elementary analyses of the products are given in Tables 5, 7, and 9 in Paper II.

So far in these papers, we have reported only those runs made with aluminum hydroxide, but we have made some with zinc hydroxide as well. The results of the latter will be now given briefly. The yield of liquid products was about as satisfactory, and the products appeared more stable than those with aluminum hydroxide; their colour* did not change on standing, even over a year, and they appeared to be more hydrogenated. It seemed that zinc hydroxide had some catalytic effects⁽⁵⁾.

(2) *Gas*. The results of gas analysis of the runs are given in Tables 2, 3, 6, 9 and also in Paper II. It may be of some interest to mention that in some of the runs, especially when the total pressure of the system is low, the gaseous products** (at room temperature) found in the trap may be as high as 1/4 of the total original condensates (gaseous products condensed in trap and liquid products), as in runs II_A-13, II_A-11, and I_A Ser. 23; about 1/5 for I_A Ser. 37***. The analyses of the gases found in the trap are given in the same tables. It may be of some interest to note that their compositions are chiefly propane, butane, and olefines.

(3) *Residue*. The carbon content of the residue was small in every case when hydrogen was used and was also rather small for the other systems when that due to the carbonate carbon was taken account of. It is significant that the carbonate carbon contents are small in the hydrogen system, larger in the carbon monoxide (or water gas) system, and

* Amber, reddish, clear, and less dark than with aluminum hydroxide.

(5) A. J. Lozovoi, *Gen. Chem.* (USSR) 1(1931), 717. He had found that zinc oxide showed some catalytic effect in the polymerization of ordinary acetylene molecules, and it produced a liquid product at 370°C while aluminum oxide was much less catalytic and it did not reduce the ordinary temperature (500-600°C) of liquid formation.

** Condensed and dissolved in the trap cooled with alcohol-solid carbon dioxide.

*** Conditions of Runs.

Run	Gas	Total Press. kg./cm ² . (Room Temp.)
II _A 13	CO and H ₂	37
II _A 11	"	70
I _A Ser. 23	H ₂	25
I _A Ser. 37	H ₂	50

its value is, indeed, about the same as that of the carbon dioxide system when the time of contact is sufficiently long. As has been said before, the yield of liquid products increases at the expense of the carbon content in the residue. This is evident in Table 20.

(C) **Limitations of the Results.** As has already been mentioned in Paper I, the results obtained here are limited both in scope and significance because of the limitations imposed on the experimental conditions. Since aluminum hydroxide gives up most of its water at 200 to 300°C, the main reaction of the water vapor and the carbide is the formation of yellow powder⁽⁶⁾, or a cuprene-like substance, the formation of which is influenced only slightly by the variation in the gases employed. Above 300°C the apparent formation of the liquid products is due to a sort of distillation effect which is again only a little affected by the species of the gases. On account of these factors, it is but natural that the differences owing to pressure, temperature, and species of gases are not as clearly marked as they would be if a proper choice in the apparatus has been made. Since we now possess an autoclave in which the water vapors can be made to react with the carbide under any desired temperature and pressure, we are certain that more significant results are possible.

The carbide reactions are characterized by a large evolution of the heat of reaction, and this heat must be taken away rapidly and effectively in order to obtain a maximum benefit from the use of carbide. Problems concerning the utilization of the heat of reaction will be the subject of a subsequent paper.

(D) **Conclusion.** The use of nascent acetylene to bring about more effective polymerization, and the use of the carbide as a means of promoting and accelerating many organic syntheses which otherwise would be thermodynamically improbable are new problems that have not been heretofore investigated at all, or but slightly.

Therefore, in this series of investigations it has been the intention of the authors to study these problems rather broadly, but still sufficiently in detail to obtain data which are of fundamental interest and to see further what practical possibilities are open to them.

The polymerization of nascent acetylene has been made under ordinary pressure in dynamic system and under elevated pressure in static system. The data obtained are somewhat fragmentary because of the explorative nature of the investigation, of the extensiveness of the field to be covered, and finally of the limitation imposed on the experimental conditions; but they are, nevertheless, sufficient to draw some general conclusions.

First of all, it is safe to conclude that the efficacy of the polymerization into liquid products of nascent acetylene is higher than that, even in the presence of an active catalyst, of the ordinary acetylene—a manifestation of very high reactivity of nascent acetylene. For this reaction, the apparatus necessary is quite simple, and the need of a catalyst is dis-

(6) R. Negishi, M. Nibayashi, S. Kataoka, and O. Kamiike, *J. Soc. Chem. Ind., Japan*, **45**(1942), in print.

pensed with. However, the reaction has certain limitations. The final products are almost exclusively aromatic or condensed, as shown by their high densities and boiling points, and they are too diversified to be easily separated into individual components. The course of its polymerization cannot be controlled but with difficulty because of the extreme reactivity and specificity of the reactions of nascent acetylene. It seems to the authors that the production of the paraffin series, as the main products directly from calcium carbide, is not likely unless a catalyst of high selectivity is found. The heat of reaction involving the carbide is enormous, and this factor must be well considered; otherwise, harmful rather than favorable effects of the carbide will take place.

The specificity of nascent acetylene polymerization seems uninfluenced by the presence of foreign substances, and this fact makes possible the use of carbide as a means of clarifying the mechanism of a reaction in which even a catalyst may be present, without the fear of introducing undesirable side reactions involving acetylene and the reactants of the desired reaction. However, the fact that the commercial carbide almost invariably contain sulphur and phosphorus compounds as impurities must not be overlooked when a catalyst is used.

Because of the fact that calcium carbide is a powerful deoxygenating agent by virtue of its strong affinities for water and carbon dioxide molecules, it may be used with advantage in the preparation of deoxygenated products. As an example, it can take off the oxygen from alcohols readily. Butyl alcohols may be prepared from either methanol or ethanol, or both⁽⁷⁾, and completely deoxygenated compounds can also be formed from them. Thermodynamically, it is possible to deoxygenate practically all organic compounds, and this should be of great interest as a means of preparing such materials as olefines, unsaturated compounds, ethers, and other useful for organic syntheses.

The introduction of calcium carbide opens up the possibilities of organic syntheses enormously by virtue of its large increase in the free energy of reaction and the shift in the equilibrium owing to its great affinities for water and carbon dioxide molecules, which are not infrequently the by-products of organic reactions. By a proper choice of catalyst and experimental conditions, unlimited number of desirable substances may be synthesized.

Finally, this will conclude a series of investigations on the direct synthesis of hydrocarbons from calcium carbide. Due to circumstance, we are unable to pursue further this investigation and, with regret, we must leave many of the unsolved problems as they are. It is hoped that we shall be able to take up again this investigation from where we must leave off now.

What have been reported by us in a number of papers⁽¹⁾⁽²⁾ are the results of the culminating efforts of the following members, Messrs. Araki, Hayashi, Inaba, Kano, Kodama, Masunaga, Nagayoshi, Nakano, Sakon, Shimamura, and Shimono. To them our thanks are due. We are grateful to Dr. S. Hamai, Messrs. Nibayashi, Isobe, and Kataoka for their hearty co-operation.

(7) R. Negishi, *Rev. Phys. Chem., Japan*, **15**(1941), 127; *ibid.*, **15**(1941), 171.

The authors acknowledge with pleasure their indebtedness to Prof. T. Marusawa and to Dr. F. Hansgirk for their constant interest throughout this work; to Dr. M. Sato, the director of the institute, for his encouragement and permission for the publication.

Summary.

The effects on the character and yield of liquid products synthesized directly from calcium carbide under elevated pressures, of the species of gases, pressure, and temperature have been summarized. It has been found that the yield of liquid products increases with increasing total pressure of the system up to about 100 atmospheres and then decreases with further increase in the pressure.

The apparent characteristics of the products in carbon monoxide (or water gas) system seem different from the others, and an explanation for this has been given. As in the low pressure runs, carbon monoxide has rather harmful effects while, on the other hand, carbon dioxide has beneficial effects on the yield of liquid products.

There have been found slight differences in the yields and the properties of the products under elevated and ordinary pressures, and these differences have been explained as due rather to the effects of the time of contact and temperature than to any change in the mechanism of the polymerization reaction.

The limitations and the significance of the synthesis of hydrocarbon liquids directly from calcium carbide and several unique properties of the carbide which may be useful in organic syntheses have been pointed out and discussed.

*The Central Laboratory,
South Manchuria Railway Company, Dairen.*

The Synthesis of Iso- and Normal Butyl Alcohols in the Presence of Calcium Carbide (B) IV*. Synthesis in Liquid Paraffin. Static System.

By Ryoji NEGISHI.

(Received May 12, 1942.)

It has been shown in one of my papers that a large amount of heat is evolved when calcium carbide reacts⁽¹⁾. In dry system the localization and accumulation of heat result, augmenting unfavourable side reactions.

* This paper will appear in Japanese in *Rev. Phys. Chem. Japan*, **16**(1942).

(1) Under certain tolerable assumptions, the heat of reaction evolved at 310°C for autoclave run III_A Ser. 113 has been calculated to be about 114 kcal./mole of 70% carbide reacted.

In order to mitigate these effects, I have attempted to carry out the synthesis of butanols in the presence of calcium carbide in a liquid medium, and the results obtained are presented here. A comparison of these results and those of the dry systems⁽²⁾ will be given in my next paper, and here, I shall be concerned more with the gaseous products.

Experimental Details⁽³⁾. (1) *Method.* The same one-liter revolving autoclave used in the dry systems was again employed. A mixture of carbide and catalyst, both of 60 mesh powders, was charged; liquid paraffin was then added, and the components were mixed. The air in the autoclave was flushed out several times with the reaction gas (or hydrogen), and the temperature was raised to a desired point. The reaction gas was then charged and recharged as often as necessary to maintain the pressure range within the proper limits. Usually, two or three chargings, at or at slightly lower than the reaction temperature, were made for each discharge. Except for the final discharge of the final run of a series, the products were discharged to two or three atmospheres in order to prevent, to a maximum degree, a loss of the medium. The products were condensed as before⁽²⁾.

(2) **Materials.** (a) *Carbide.* Its final acetylene content, under the standard conditions, was from 70 to 75%. A typical analysis showed:

Subst.	CaC ₂	CaO	SiO ₂	Al ₂ O ₃	Fe ₂ O ₃	Others*
Weight (%)	72	14.5	3.5	2.4	0.6	7.1

* They contained CaCO₃ and some sulphur and phosphorus compounds.

(b) *Liquid Paraffin.* A commercial product was distilled under 5 mm Hg pressure in CO₂ atmosphere⁽¹⁾, and all the light boiling substances, which distilled out when the liquid temperature in the flask was maintained constant at 250°C, were eliminated. Under the standard conditions, the temperature of the liquid corresponded to 430°C, and the maximum vapour temperature attained was 410°C. The whole apparatus was of Terex glass. The elementary analysis of the liquid, designated as Paraffin Oil III, showed:

C=85.55, H=14.08, O=0.37 (by difference).

(c) *Gases.* Water gas was prepared by a technical method. It was used without purification. Hydrogen was a commercial product of about 98% purity. No purification was effected.

(d) *Catalysts.* The catalyst used are given in Table 1. Their preparations were the same as those given in Paper (B) III⁽²⁾.

Some effects on the catalytic activity of thorium will be mentioned briefly. As Fig. 1 indicates, a small concentration of thorium increases the total yield, and there is an optimum content which lies in the range,

(2) R. Negishi, Paper (B) III, this Bulletin, 17(1942), 179.

(3) The writer is grateful to Messrs. Sakon, Araki, Simono, and Kano for their experimental assistance.

Table 1.
Methanol Catalysts, their Composition.
(Reduced with H_2 at $400^\circ C.$ for 4 hours.)

Catalyst No.	Composition in Mole Ratio	Precipitating Agent	Activity*
18ab	Zn:Cr:Th 1:1:0.05	6 molal K_2CO_3	Good
21	Zn:Cr 39:61	25% NH_3	Fair
36a	Zn:Cr:Th 1:1:0.2	40% K_2CO_3	Good
25	Zn:Cr 39:61	28% NH_3	Fair

* Relative, based on the total liquid products, including water, and higher boiling substances.

reaction period was 95 hours, extending over 12 days.

We shall continue to investigate the effect of thorium and soon we may be able to state with more assurance the real effect of it. At this stage of progress, however, we can merely say that a small amount of thorium seems beneficial, as far as the total yield⁽⁵⁾, but not necessarily methanol, is concerned.

(3) *Analysis*⁽⁶⁾. Gaseous, liquid, and solid products were analysed as before⁽⁷⁾⁽⁸⁾. The solid residue was separated from the medium by washing with ether and filtering under vacuum. The amount of the medium was then determined by evaporating off the ether under reduced pressure. The acetylene and carbo-

0.05 to 0.20 moles⁽⁴⁾. The effect on the character of the products of thorium seems but slight, as may be seen from the results given in Table 2.

Autoclave runs VIII_A Ser. 6 and VIII_A Ser. 11 were made, respectively, in the closed autoclaves II and III and both runs extended over 40 hours in 15 days. II_{CA} Ser. 68 was made with a catalyst in pellets (50 g. of which occupied about 40 c.c.), packed in a reaction tube of 2.5 cm. diameter and with space velocities varying from 3000 to 13500; the

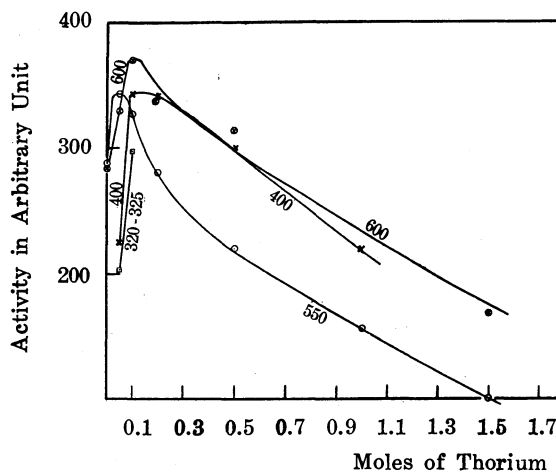


Fig. 1. Activity vs. Thorium Content (Temp. $^\circ C.$ of Reduction Indicated in Fig.)

(4) No effect of the temperature of reduction has been taken into account, but it is evident in the Fig.

(5) This is important, since in our case, not only the formation of the butanols but also that of hydrocarbons, as by-products, is not undesirable.

(6) The writer's thanks are due to Mr. O. Kamiike and to his assistants.

(7) O. Kamiike, S. Kataoka, M. Nibayashi, and R. Negishi, *J. Soc. Chem. Ind., Japan*, **44** (1941), 1030.

(8) R. Negishi, M. Nibayashi, K. Sakon, and O. Kamiike, *ibid.*, (1942), 366.

Table 2. Methanol from Various Catalysts.

(Water gas used without purification; CO:H₂ about 1:1.25)

Exp. No.	Catalyst No. and Composition*	Vol. Methanol*** (%)	Vol. Other Prods.** (%)	Reaction Conds.	
				Temp. (°C.)	Press. Kg./cm ² .
Auto. VIIIA Ser. 6	66, Cr:Zn 1:1	88.5	2.7	320	200-170
Auto. VIIIA Ser. 11	67, Cr:Zn:Th 1:1:0.1	86	3.5	320	200-170
II _{CA} Ser. 68 (t8-86)****	II _{CA} Cr:Zn:Th 0.4:0.6:0.05	85-88	10	330	200

* Mole ratio.

** Consist mostly of water and hydrocarbons; distillation losses not included.

*** Based on total liquid products.

**** Runs 68 and 69 not included. These runs were made at space velocities of 1000 and 2000, respectively. Their methanol vol. % was about 81, much less than the others made at higher space velocities (3000-13500).

nate contents of the residue were determined by taking average results of a large number of samples of the residue mixture, as discharged (including the medium), which were treated with warm water alone and with phosphoric acid, respectively. Blank tests have shown that this method is not reliable more than to 5% which is, however, sufficient for our present purpose. Lack of accuracy is partially compensated by the simplicity of the method.

Results and Discussion. The experimental conditions and some of the results obtained in the liquid system are shown in Tables 3, 4, 5, and 6. In agreement with what has been found⁽¹⁾ at 330°C but a slight amount of the medium is cracked, as shown in Table 3. It is rather startling that so much condensates have been obtained in the condenser, even at 300°C, in the presence of the carbide. A plausible explanation of this seems that a part of the medium has been forced out rather than cracked and distilled out. This has been definitely the case with runs 82 and 98. There is a trend in the amounts of condenser condensates with the reaction temperatures, but there may be no real significance in this parallelism. However, there is no reason to doubt that the presence of the carbide increases cracking of the medium⁽¹⁾, as seen from the results of IV_A Ser. 139 and IV_A Ser. 124⁽⁹⁾. In the latter run there is 41.7 c.c. of the fractions boiling lower than the original, as compared with only 6.7 c.c. in the former in which no carbide is present.

The results of Table 4 indicate that the lower the reaction temperature, the larger is the amount of the fraction boiling below 230°C. The same sort of relationship exists between the yield of iso-butyl alcohol and the temperature, as seen from Table 5. With decreasing temperature, however, the rate of reaction becomes quite slow.

(9) The results of this series are sufficiently reliable, and their quantitative discussion will be reserved for the next paper to be published in this Bulletin.

Table 6 gives the summarized results of gas analysis. There is no trend in the formations of the gases, except for methane, with temperature. It is of some interest to note that, as in all our carbide reactions, large amounts of ethylene, propane, and butane are present in the condensable gases (the gases condensed and dissolved in a trap cooled with

Table 3. Experimental Conditions.

Exp. No.*	Ser. 178	Ser. 139	Ser. 124	Ser. 58	Ser. 82	Ser. 98			
Autoclave Used	II	II	II	III	III	II			
CO:H ₂	1:1.23	1:1.35	1:1.3	1:2	1:1.75	1:1.7			
Catalyst No. and Wt (g.) .	36a, 45	None	18ab, 45	21, 22	21, 30	25, 30			
Carbide (g.)	300	None	300	220	300	301			
Paraffin (g.)	300	303	300	220	301	300			
Temp. (°C.)	300	330***	330	350	360	340-365			
Press. Range Kg./cm ² . ..	200-150	200	200-160	198-130	200-120	200-120			
Time (Min.)	1870	1995	2220	1840	1840	2145			
Condensates {	Cond. {	c.c. .	26	2.6	52.2	94.4†	253.2†	258.6†	
			g. ...	—	2.1	40.4	73.6	205.9	208.7
				c.c. .	21.1	0	35.4	37.4	31.4
			Trap. {		g. ...	17.7	0	24	25.5
Paraffin in the Residue (g.)	—	292		288		160	102	85	
Liquid boiling below									
Original (c.c.)	—	6.7	41.7	6.7	—	—			
Condensed and Dissolved									
Gas** (g.)	2.3	—	15.7	26.5	11.5	8.0			

* Autoclave run series IV_A tabulated; Paraffin Oil III used.

** Condensed and dissolved gas found in the trap, cooled with alcohol and solid CO₂, connected to the autoclave.

*** The first 150 minutes at 350°C.

† Probably due to forcing out of the medium.

Table 4. Distillation Analysis* (Vol. %).

Temp. Range (°C.)	IV _A Ser. 124	IV _A Ser. 178	IV _A Ser. 82
<100	18.8	11.5	2.5
100-150	35.4	43.5	13.7
150-230	27.6	29.0	25.0
230-270	Began to crack at 216°C		13.4
270-300	—	—	12.2
Residue	10.8	—	24.0
Loss	7.4	—	9.2

* Made by Mr. O. Kamiike. The author takes this occasion to thank him for his co-operation.

Table 5. Effect on the Yield of Iso-butanol of Temperature.

Exp. No.	Vol. of Crude Isobutanol* (103–110°C.) (%)	Reaction Temp. (°C.)
IV _A Ser. 178	18	300–305
IV _A Ser. 124	16	330
IV _A Ser. 82	1.8	360

* Based on the total liquid condensates, exclusively of the condensates found in the trap.

alcohol and solid carbon dioxide). The presence of ethylene may be qualitatively accounted for by the results of Taylor and Van Hook⁽¹⁰⁾ or of Farkas and Farkas⁽¹¹⁾ that the hydrogenation of acetylene to form ethylene is quite rapid and complete. The formations of butane and propane may be explained by the consideration of Egloff⁽¹²⁾ that ethylene is the key molecule for the synthesis of hydrocarbons. He assigns to

Table 6. Gas Analysis*, **.

Temp. (°C.) and Exp. No.	300	330	330	340	350		360	
	178	139***	124	98	58		82	
					React.	Trap.	React.	Trap.
CO ₂	0.2	3.3	0.0	0.3	0.0	29.8	0.3	4.2
C ₂ H ₂	1.5	0.0	0.7	0.7	0.0	18.9	0.6	6.8
C ₂ H ₄	3.0	0.3	1.2	1.0	3.0	17.3	1.7	22.0
C _n H _{2n}	0.8	0.0	1.1	0.2	0.3	0.0	0.4	3.0
O ₂	0.4	0.4	0.3	0.5	0.5	0.0	0.9	0.4
CO	40.1	38.0	40.7	30.8	26.9	0.0	28.1	0.5
H ₂	47.5	33.4	50.0	55.5	50.6	0.0	27.8	0.0
CH ₄	3.7	2.1	4.3	6.5	15.4	0.0	34.1	0.0
N ₂	2.8	2.5	1.7	3.5	2.3	0.0	6.1	1.8
C ₃ H ₈	—	—	—	—	—	14.6	—	13.8
C ₄ H ₁₀	—	—	—	—	—	18.7	—	47.1
Run No.	185	142	131	98	73		89	

* Since CO:H₂ varied for different runs, comparison cannot be quantitative.

** Approximately the middle run of each series taken.

*** No carbide is present.

the reaction, $2\text{CH}_2=\text{CH}_2 \rightarrow \text{CH}_3\text{CH}_2\text{CH}=\text{CH}_2$, which takes place quite readily according to various investigators^{(10) (12) (13)}, the activation energy of 35–37.7 kcal. per mole. In a closed system here employed, with excess of hydrogen, it is conceivable that the butylene thus formed is hydrogenated to butane. To account for the formation of propane, we shall

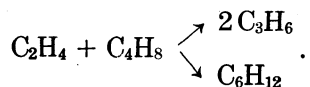
(10) H. A. Taylor and A. Van Hook, *J. Phys. Chem.*, **39**(1935), 811.

(11) A. Farkas and L. Farkas, *J. Am. Chem. Soc.*, **61**(1939), 3396. According to them, the activation energy is 12–17 kcal. on platinum surface, and according to Ref. (5), it is about 42 kcal./mol. in gas reaction.

(12) G. Egloff and E. Wilson, *Ind. Eng. Chem.*, **27**(1935), 917.

(13) Storch, *J. Am. Chem. Soc.*, **56**(1934), 374.

seek an additional explanation in the results of Storch⁽¹³⁾ in which ethylene has been polymerized at 377°C and 141.5 mm. For the contact times less than 2 hours the formation of butene predominates, but for 3 hours that of propene becomes largest. He has explained the presence of the olefines with odd number of carbon atoms by assuming a disproportionation to give a higher and a lower olefine, taking one of his examples,



It seems reasonable that this propene⁽¹⁴⁾ is then hydrogenated to propane in our case.

The question as to whether ethane is present or not in these experiments made in liquid medium is, from our available data, not possible to be answered.

In our gas analysis the components of the saturated gases in a mixture have been calculated from the volume decrease and the volume of carbon dioxide produced after explosion. If the mixture contains more than two components, there will be a freedom of choice of any two components from the lot. This introduces uncertainty, as seems to be indicated by the results of the analysis of the gases found in the trap of IV_A Ser. 124 shown in Table 6B. Though there is this shortcoming in the method of analysis, it seems quite unlikely that it is a matter of chance that no ethane (or very slight) is found in the results of all the runs made in liquid medium while there is abundance of it in dry.

From theoretical considerations, however, the absence of ethane in excess of ethylene and hydrogen may not be entirely out of order. The following considerations are suggestive in this connection.

First, according to the work of Wood (quoted from Egloff⁽¹²⁾), the temperature for the initial appearance and the maximum formation of products in the thermal reactions of ethylene are as shown in Table 7.

Second, according to the results of Moore and Taylor⁽¹⁵⁾, in their work on the mercury photosensitized hydrogenation of olefines, with about 40 mm. of olefine plus six fold excess of hydrogen, there is a significantly

(14) According to Ellis, "The Chemistry of Petroleum Derivatives," Vol. I, 80, The Chem. Catalog Co., Inc., N. Y., 1934, the results of Schneider and Frolich and of Lenher indicate that reactions of the type, $3\text{C}_2\text{H}_4 = 2\text{C}_3\text{H}_6$, e.g., the transformation of ethylene to propylene and not to butylene, can also take place although the mechanism of such reactions is still very obscure.

(15) W. J. Moore, Jr. and H. S. Taylor, *J. Chem. Phys.*, **8**(1940), 504.

Table 7.

Products	Temperature (°C.)	
	Initial Appearance	Maximum Formation
C_4H_8 , C_4H_6	350-400	650-750
C_2H_6	450-500	700
CH_4	500	1000
C_2H_2	650-700	1400
Aromatics	650	800-850

greater formation of propane and of butane from the respective olefines than that of ethane from ethylene. Their table is reproduced in Table 8.

Third, from the consideration of the energy of activation, it is of interest to note that the energy of activation of ethylene polymerization is less than that of hydrogenation, 35-37.7

Table 8.

Olefine Used	Olefine to Saturated Products (%)						
	CH_4	C_2H_6	C_3H_8	C_4H_{10}	C_5H_{12}	C_6H_{14}	C_8H_{18}
C_2H_4	2	14	—	84	—	—	—
C_3H_6	2	1	26	5	2	64	—
C_4H_8	3	1	1	29	—	—	66

kcal./mole as against 43.2 to 51.5 kcal./mole⁽¹²⁾ for the latter. Among ethylene, propylene, and butylene, the magnitude of the energy of activation of hydrogenation decreases with increasing molecular weight, as seen from the results obtained by Twigg⁽¹⁶⁾ on the exchange and hydrogenation reactions between deuterium and the olefines on reduced nickel at 55-120°C. His results are given in Table 9. Toyama⁽¹⁷⁾ and Kiyama⁽¹⁸⁾ obtained a similar relative order of the activation energies of hydrogenation for the hydrogenation of ethylene, propylene, and isobutene also on reduced nickel at about the same temperature range.

From what has been mentioned above, the absence of ethane in our experiments may not be out of harmony with the experimental facts already existing; but these considerations do not still completely explain why ethane is present in dry system while not in liquid medium⁽¹⁹⁾.

Table 9.

Olefine	Activation Energy kcal./Mol.
Ethylene	8.2±0.5
Propylene	6.0
Butene-2	3.3
Isobutene	3.3

(16) G. H. Twigg, *Trans. Faraday Soc.*, **35**(1939), 934.

(17) O. Toyama, *Rev. Phys. Chem. Japan*, **11**(1937), 353; **12**(1938), 115; **14**(1940), 86.

(18) R. Kiyama, *Rev. Phys. Chem. Japan*, **15**(1941), 137.

(19) Localization and accumulation of the heat of reaction in dry system may be the cause, but in lack of more definite evidence, this argument should not be pushed too strongly. The difference in the rates of polymerization in the two systems may not be entirely neglected from consideration.

Summary.

The synthesis of isobutyl alcohol in the presence of calcium carbide and a methanol catalyst has been made in liquid paraffin. It has been found that the reaction proceeds more smoothly, though not necessarily more effectively, than in dry system.

The effect of thorium on the catalytic activity of methanol catalyst has been investigated briefly. It has been found that 0.05 to 0.2 mole of it will increase the total yield of liquid products, but will not affect appreciably that of methanol.

The preponderate formations of ethylene, propane, and butane and the absence of ethane, even in the presence of excess ethylene and hydrogen, have been qualitatively explained.

The writer is grateful to Prof. T. Marusawa and to Dr. M. Sato for their interest and encouragement in this work. He is also grateful to Prof. H. Horiba for his comments on the paper prior to publication.

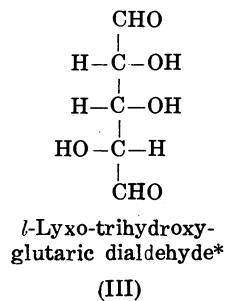
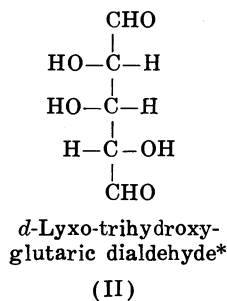
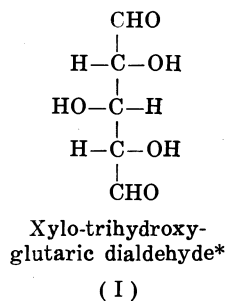
*The Central Laboratory,
South Manchuria Railway Company, Dairen.*

The Formation of Polyhydroxy-dialdehydes. III. *l*-Lyxo-trihydroxy-glutaric Dialdehyde and its Derivatives.

By Koichi IWADARE.

(Received June 8, 1942.)

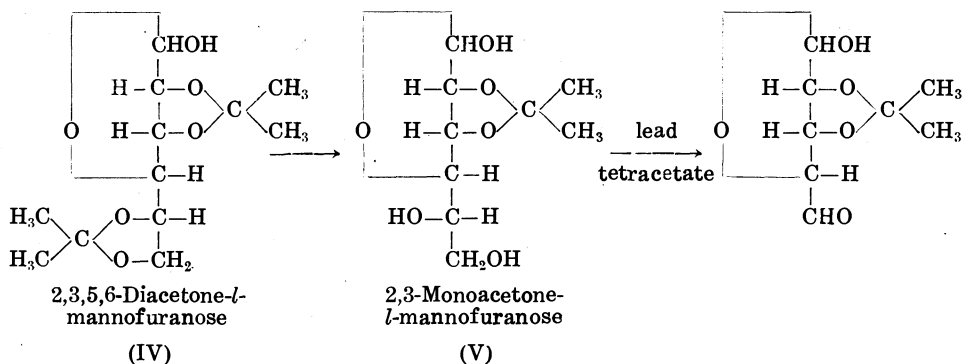
Theoretically there should exist four dialdo-pentonoses, that is, trihydroxy-glutaric dialdehydes, and, among them, xylo- and *d*-lyxo-trihydroxy-glutaric dialdehydes (I and II) were reported in the first and second papers. This communication is concerned with the formation of *l*-lyxo-derivatives (or *l*-arabo-derivatives) (III).



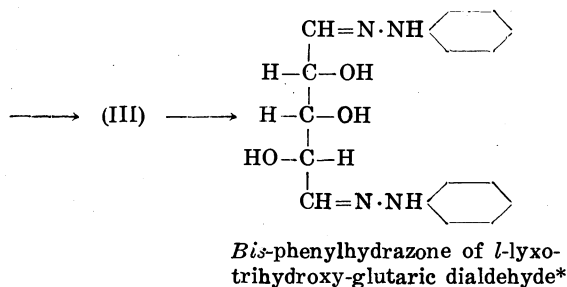
(1) K. Iwadare, I, this Bulletin, **16**(1941), 40; II, *ibid.*, **16**(1941), 144.

* These formulas are described arbitrarily in chain.

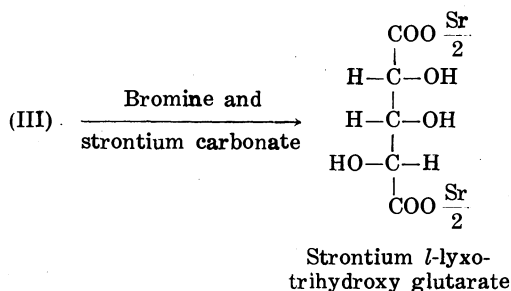
For obtaining *d*-lyxo-trihydroxy-glutaric dialdehyde, 2,3-monoacetone-*d*-mannofuranose was used as the starting substance, therefore it is plain that *l*-lyxo-trihydroxy-glutaric dialdehyde would be obtained from 2,3-monoacetone-*l*-mannofuranose. *l*-Mannose is obtained by cyanhydrin synthesis from *l*-arabinose⁽²⁾, and shaken mechanically with acetone which contains a small quantity of concentrated sulphuric acid. 2,3,5,6-Diacetone-*l*-mannofuranose thus obtained crystallizes into colourless needles, m.p. 122°–122.5°, and has specific rotatory power, $[\alpha]_D$, of -27° in acetone. It is dissolved in biphthalate buffer solution (pH 4.4), and the solution is distilled by heating in an oil-bath at 140–150° for 1.5 hours, the necessary quantity of water being added during the distillation to keep the volume of the solution constant. Then the buffer solution containing diacetone-*l*-mannose and monoacetone-*l*-mannose which is obtained by partial hydrolysis of diacetone-derivative is neutralized (phenolphthalein) and evaporated to small volume under the diminished pressure, and extracted with ether for 72 hours. The ether extract is evaporated to thick sirup and thoroughly washed with boiling petroleum benzine to remove diacetone-mannose. The remaining sirup of 2,3-monoacetone-*l*-mannofuranose is dissolved in benzene and oxidized with lead tetracetate. The reaction mixture is filtered, the filtrate evaporated under the diminished pressure, and the remaining sirup is hydrolyzed by warming with dilute sulphuric acid. On adding phenylhydrazine to the solution, *bis*-phenylhydrazone of *l*-lyxo-trihydroxy-glutaric dialdehyde precipitates immediately. It is recrystallized from acetone on adding petroleum ether and then from alcohol. It crystallizes into colourless needles, m.p. 165–165.5° (corrected, decomposing). $[\alpha]_D = +73^\circ$ in pyridine. *l*-Lyxo-trihydroxy-glutaric dialdehyde is obtained as sirup by decomposing the above-mentioned *bis*-phenylhydrazone with benzaldehyde. The specific rotation of this dialdehyde is calculated by directly measuring the rotation of its aqueous solution, which is obtained by decomposing the known quantity of its *bis*-phenylhydrazone, on the assumption that the conversion is quantitative. Thus, the specific rotatory power of *l*-lyxo-trihydroxy-glutaric dialdehyde, $[\alpha]_D^{10}$, is found to be -17° . *Bis-p*-nitro-phenylhydrazone of *l*-lyxo-trihydroxy-glutaric dialdehyde is obtained by adding the acidic aqueous solution of *p*-nitro-phenylhydrazine to the aqueous solution of the dialdehyde. Orange leaflets, m.p. 203.5–204° (decomposing).



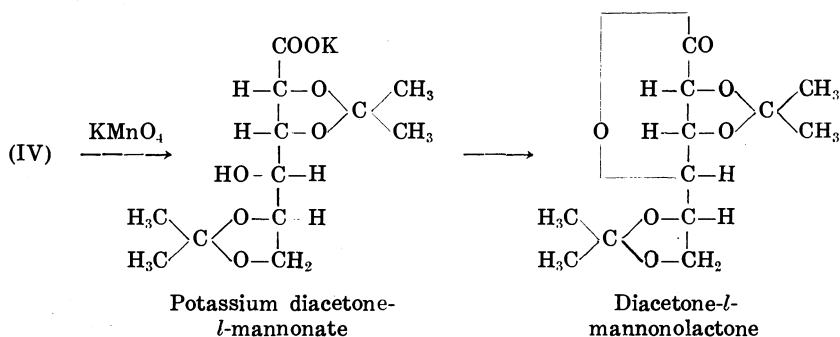
(2) E. Fischer, *Ber.*, **23**(1890), 370; **24**(1891), 2683.



By oxidizing the aldehyde groups of *l*-lyxo-trihydroxy-glutaric dialdehyde with bromine in the presence of strontium carbonate, strontium *l*-lyxo-trihydroxy glutarate is obtained.



By the way, diacetone-*l*-mannose is oxidized with potassium permanganate in alkaline solution, and potassium salt of diacetone-*l*-mannonic acid is obtained. This salt is converted into diacetone-*l*-mannonolactone, m.p. 124–124.5°, which agrees with that of *d*-isomer⁽³⁾.



Experimental. *2,3,5,6-Diacetone-l-mannofuranose.* Thirty grams of *l*-mannose, prepared from *l*-arabinose by cyanhydrin synthesis, were mechanically shaken for 6 hours with 1,200 c.c. of acetone containing 27 cc of concentrated sulphuric acid. The solution was neutralized with excess of anhydrous sodium carbonate and filtered. The filtrate, now coloured in light lemon-yellow, was concentrated to dryness under the

(3) Ohle and Berend, *Ber.*, **58**(1925), 2591.

diminished pressure. The crystalline residue was recrystallized from benzene. Yield, 28 g. It was recrystallized from ether by adding petroleum ether. Colourless needles, m.p. 122–122.5°. $[\alpha]_D = -27^\circ$ in acetone ($c=1.84$). (Found: C, 55.49; H, 7.67. Calculated for $C_{12}H_{20}O_6$: C, 55.37; H, 7.73%).

Monoacetone-l-mannofuranose. Diacetone-*l*-mannose (5 g) was dissolved in 125 cc of biphthalate buffer solution of pH 4.4, and the mixture was distilled by heating in an oil-bath at 140–150° for 1.5 hours, the necessary quantity of water being added from time to time to maintain the initial volume. Then the solution was cooled, neutralized to phenolphthalein, evaporated to about 15 cc under the reduced pressure, and extracted continuously with ether for 72 hours. The ether extract was concentrated to sirup. In order to remove diacetone-derivative from the sirup, 30 cc of petroleum benzene (70–90°) was added to it, and the mixture was heated on a boiling water-bath, and stirred mechanically for 30 minutes. Benzene extract was removed by decantation, and the remaining sirup was again extracted with benzene just like as above. This procedure was repeated ten times and monoacetone-*l*-mannofuranose remained as sirup.

Bis-phenylhydrazone of l-lyxo-trihydroxy-glutaric dialdehyde. Benzene (30 cc) was added to monoacetone-*l*-mannose (1.4 g), the mixture was warmed at 60° and lead tetracetate (3 g) was added to it. After warmed 5 minutes, it was cooled, filtered and washed with acetone. The combined filtrate and washings were evaporated in vacuum to sirup. The remaining sirup was dissolved in 50 cc of N/20-sulphuric acid, and warmed on a water-bath for half an hour. It was evaporated in vacuum to remove the isolated acetone, filtered if necessary, and phenylhydrazine (2 g) was added to it. A considerable quantity of precipitate soon appeared from the mixture. It was filtered, dried, and dissolved in acetone. Acetone solution was filtered, if necessary, and *bis*-phenylhydrazone was precipitated by adding petroleum ether. It was recrystallized from alcohol into fine colourless needles, m.p., 165–165.5° (corrected, decomposing). $[\alpha]_D = +73^\circ$ in pyridine ($c=0.47$). (Found: C, 62.41; H, 6.27; N 17.41. Calculated for $C_{17}H_{20}O_5N_4$: C, 62.18; H, 6.14; N, 17.06%).

l-Lyxo-trihydroxy-glutaric dialdehyde. The equilibrium rotatory power of *l*-lyxo-trihydroxy-glutaric dialdehyde was calculated from the rotatory power of its aqueous solution obtained by decomposition of the known quantity of its *bis*-phenylhydrazone. That is, 0.412 g of *bis*-phenylhydrazone was suspended in 6 cc of water and decomposed by benzaldehyde as mentioned above. The aqueous solution was made up to 10 cc by adding water and its rotatory power was measured with 1 dm tube. $\alpha_D = -0.32^\circ$. As 0.186 g of free dialdehyde should be obtained from 0.412 g of its *bis*-phenylhydrazone, the specific rotatory power, $[\alpha]_D$, of *l*-lyxo-trihydroxy-glutaric dialdehyde is -17° .

Bis-p-nitro-phenylhydrazone of l-lyxo-trihydroxy-glutaric dialdehyde. Obtained just as *d*-isomer described in the previous paper⁽¹⁾, m.p., 203.5–204° (decomposing). (Found: N, 20.41. Calculated for $C_{17}H_{18}O_7N_6$: N, 20.09%).

Strontium l-lyxo-trihydroxy-glutarate. Obtained just as *d*-isomer described in the previous paper⁽¹⁾. (Found: Sr, 33.34. Calculated for $C_6H_6O_7Sr$: Sr, 32.98%).

Potassium salt of diacetone-l-mannonic acid. Diacetone-*l*-mannose (1.5 g) was dissolved in 150 cc of water, and 0.33 g of potassium hydroxide and 0.65 g of potassium permanganate were added. After being kept on standing overnight, the mixture was filtered, the filtrate was neutralized with carbon dioxide, and evaporated under the reduced pressure. The residue was washed with ether and then extracted with cold alcohol. The alcohol extract was evaporated to small volume and ether was added to it. Fine needles appeared gradually. Yield, 1.25 g. They were recrystallized from acetone by adding benzene. $[\alpha]_D^{10} = +32.2^\circ$ in water ($c=1.34$). (Found: K, 12.02. Calculated for $C_{12}H_{19}O_7 \cdot K \cdot H_2O$: K, 11.76%).

Diacetone-l-mannonolactone. Potassium salt of diacetone-*l*-mannonic acid (0.65 g) was dissolved in 2.2 cc of N-sulphuric acid, and the solution was at once extracted with ether. The ether extract was washed with water, dried with anhydrous sodium sulphate, and evaporated in vacuum. The residue was crystallized from petroleum benzene into colourless needles. M.p., 124–124.5°. (Found: C, 55.68; H, 6.81. Calculated for $C_{12}H_{18}O_6$: C, 55.80; H, 7.02%).

Summary.

Following compounds were obtained in crystals: 2,3,5,6-Diacetone-*l*-mannofuranose, m.p., 122–122.5° and $[\alpha]_D = -27^\circ$ (in acetone). *Bis*-phenylhydrazone of *l*-lyxo-trihydroxy-glutaric dialdehyde, m.p., 165–165.5° and $[\alpha]_D = +73^\circ$ (in pyridine). *Bis-p*-nitro-phenyl-hydrazone of *l*-lyxo-trihydroxy-glutaric dialdehyde, m.p., 203.5–204°. Potassium diacetone-*l*-mannonate, $[\alpha]_D^{10} = +32.2^\circ$ (in water). And diacetone-*l*-mannopolactone, m.p. 124–124.5°.

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

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Geochemische Untersuchungen der Vulkane in Japan. XXVII. Dichtemessungen der Solen aus Gas- und Petroleumbohrlöchern auf Taiwan (Formosa).

Von Shinya OANA.

(Eingegangen am 21. Mai 1942.)

Erdgase und Petroleum sprudeln aus Bohrlöchern manchmal mit Sole zusammen. Ich habe den Dichteunterschied zwischen den Solen aus Gas- und Petroleumbohrlöchern auf Taiwan und dem Standard-Leitungswasser mittels Schwimmermethode bestimmt. Diese Solen enthalten im allgemeinen Kohlenwasserstoffe. Diese werden beim gewöhnlichen Reinigungsprozesse nicht vollständig beseitigt. Dafür hat sich das folgende Verfahren bewährt: 100 ccm. Sole wird mit 10 g aktiver Kohle unter Rückflusskühler 30 Minuten lang gekocht. Nachdem die Sole bis auf Zimmertemperatur abgekühlt ist, wird die aktive Kohle abfiltriert. Das Filtrat wird als Wasserdampf über Kupferoxyd, das auf 500°C. erhitzt ist, geleitet. Dadurch werden die Kohlenwasserstoffe vollständig beseitigt. Diese Probe wird dann nach dem gebräuchlichen Reinigungsprozesse weiter behandelt. Der Dichteunterschied gegen das Standard-Leitungswasser wird mittels Schwimmermethode bestimmt. Die gewonnenen Resultate sind in Tabelle 1 angegeben.

Tabelle 1. Dichteunterschied zwischen den Solen aus Gas- und Petroleumbohrlöchern auf Taiwan und dem Standard-Leitungswasser.

Bezeichnung der Bohrung	Ort		Tiefe, m	
R 78 W	Petroleumbohrloch	Syukkōkō, Sintiku Provinz	957–1040	
R 87 W	"	"	1202–1234	
R 90 W	"	"	1113–1502	
R 16 W	Gasbohrloch	Kinsui	1407	
R 10 W	"	"	1438	
R 8 W	"	Usiyama, Tainan-Provinz	714	
R 6 W	"	Rokuzyūkei "	956	

	Temperatur (°C)	Ergiebigkeit, hl/Tag	Cl ⁻ , g/l	Dichteunter- schied, γ
R 78 W	(15.5)	100.8	7.172	+ 0.6
R 87 W	(18.3)	12.0	7.794	+ 1.1
R 90 W	(45)	130.0	9.207	+ 2.0
R 16 W	—	—	0.3203	+ 0.6
R 10 W	26	21.8	14.20	+ 2.3
R 8 W	35	268	10.82	+ 3.5
R 6 W	55	4360	6.947	+ 3.8

Die eingeklammerten Temperaturen wurden an den Ausgängen der Bohrlöchern gemessen.

Dass die Behandlungen mit aktiver Kohle und Kupferoxyd die Isotopenverhältnisse des Wassers nicht ändern, ist in folgender Weise bestätigt worden. Drei Proben des gleichen Standard-Leitungswassers wurden nach obengenanntem Verfahren folgendermassen behandelt; die erste mit aktiver Kohle, die zweite mit Kupferoxyd, die dritte mit aktiver Kohle und danach auch mit Kupferoxyd. Die Dichteunterschiede zwischen diesen Proben und dem Standard-Leitungswasser wurden gemessen, nachdem sie dem gebräuchlichen Reinigungsprozesse entsprechend weiter behandelt worden waren. Die gewonnenen Resultat sind in Tabelle 2 angegeben.

Tabelle 2. Dichteunterschied zwischen drei verschiedenen behandelten Proben des Standard-Leitungswassers und dem unbehandelten Standard-Leitungswasser.

Ausgangssprobe	Behandlung	Dichteunterschied, γ
Standard-Leitungswasser	aktive Kohle	— 0.0
"	Kupferoxyd	— 0.1
"	aktive Kohle und Kupferoxyd	— 0.1

Zum Vergleich habe ich auch Solen aus Petroleumbohrlöchern der japanischen Hauptinsel nach demselben Verfahren gereinigt, ihre Dichteunterschiede bestimmt und in Tabelle 3 zusammengestellt.

Tabelle 3. Dichteunterschied zwischen Solen aus Petroleumbohrlöchern der Hauptinsel und Standard-Leitungswasser.

Herkunft der Probe	Ort	Cl ⁻ , g/l	Dichteunterschied, γ
Petroleumbohrloch	Takamati, Etigo-Provinz	7.597	+ 2.6
"	Haraiti, Kōduke-Provinz	13.04	+ 4.2
Mineralquelle*	Isobe, "	8.946	+ 2.4

* Die Mineralquelle von Isobe ist hier, obgleich sie keine Petroleumquelle ist, aufgeführt, weil sie in der nächsten Umgebung des Petroleumbohrlochs von Haraiti (etwa 2.1 km entfernt) entspringt.

Erörterung der Ergebnisse. Die Dichte der Solen aus Gas- und Petroleumbohrlöchern ist ausnahmslos höher als die Dichte des Standard-Leitungswassers. Wenn Proben benachbarter Herkunft in dieser Hinsicht miteinander verglichen werden, so ergibt sich eindeutig, dass die Wasserdichte mit der Chlorionenkonzentration steigt. Eine Ursache für Erhöhung der Konzentrationen der schweren Wasserisotopen im natürlichen Gewässer besteht in allmählicher Verdunstung des Wassers. Deshalb ergeben sich für Meerwasser und mineralisches Kristallwasser stark positive Dichtewerte. Dass die Dichteunterschiede der Solen aus Gas- und Petroleumbohrlöchern gross sind, deutet wohl auf Verdunstungsvorgänge oder auf Zusammenhänge zwischen Erdgas- und Petroleumvorkommen mit dem Meerwasser in geologischer Vorzeit hin. Schwere Wasserisotopen dürften danach ebenso wie Chloroionen oder andere Elemente durch Verdunstung konzentriert worden sein.

Es sei mir gestattet, Herrn Prof. Yuji Shibata und Herrn Prof. Kenjiro Kimura für ihre freundliche Anleitung und ihre Ratschläge, Herrn Toyojiro Ogura in dem Erdgas-Forschungsinstitut des Generalgouvernements von Taiwan für die lebenswürdige Überlassung der Proben und der Kaiserlichen Akademie der Wissenschaft für ihre finanzielle Unterstützung bei der Ausführung dieser Arbeit meinen herzlichen Dank auszusprechen.

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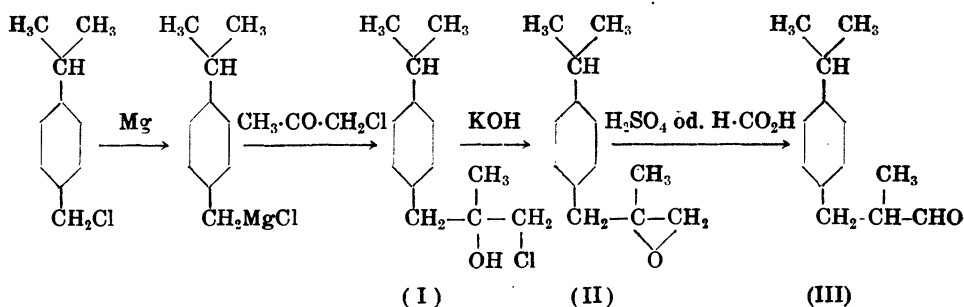
Synthese des *p*-Isopropyl- α -methylhydrozimtaldehyds.

Von Masataro YAMASHITA und Tokiyoshi MATSUMURA.

(Eingegangen am 17. Juni 1942.)

Vor kurzem⁽¹⁾ haben wir zwei verschiedenen Methoden zur Synthese des *p*-Isopropyl- α -methylhydrozimtaldehyds (sog. Cyclamenaldehyd), eines wichtigen synthetischen Riechstoffs, aus Cuminylnchlorid veröffentlicht. Wie wir damals bemerkten, ist jedoch dieses Aldehyd schon früher von Knorr, Weissenborn⁽²⁾ und Société des Usines Chimiques⁽³⁾ synthetisiert worden.

Nuerdings haben uns auch die Synthese dieselben Aldehyds durch einen neuen Weg gelungen: Die durch Einwirkung von Mg auf Cuminylnchlorid dargestellte Grignard-Verbindung wurde von Chloraceton in 2-Cuminyln-2-oxy-1-chlorpropan (I), dann von alkoholischer Kalilauge in 2-Cuminyln-2-methyläthlenoxyd (II) verwandelt. Schliesslich wurde das letzteres durch Schwefelsäure oder Ameisensäure zu dem Aldehyde (III) isomerisiert. Der oben erwähnte, von Verfassern aufgefundene Weg lässt sich folgendermassen veranschaulicht.



(1) M. Yamashita u. T. Matsumura, dies Bulletin, 16(1941), 413.

(2) A. P. 1844013 (1932).

(3) F. P. 833644 (1938).

Beschreibung der Versuche. *2-Cuminy-2-oxy-1-chlorpropan (I).* In einen Kolben, der mit einem Kühler versehen ist und in der sich eine Mischung aus 12.5 g. Mg-späne, einige Körnchen Jod und 300 ccm. Äther befindet, wurde allmählich eine Lösung von 85 g. (0.5 Mol) Cuminychlorid (dargestellt aus Isopropylbenzol, Paraformaldehyd, Zinkchlorid und Salzsäure) in 300 ccm. absol. Äther zugesetzt. Nachdem sich die Grignard-Verbindung gebildet hat, versetzte man, unter Kühlung mit Eis-Kochsalzmischung auf -5° , tropfenweise mit einer Lösung von 46 g (0.5 Mol) Chloraceton in 50 ccm. Äther, was etwa 50 Min. beanspruchte. Zum Schluss liess man noch der Kolbeninhalt in Eis über Nacht stehen. Das Reaktionsgemisch wurde nun mit Eis und verd. Essigsäure zersetzt, die ätherische Lösung mehrmals mit Wasser gewaschen, mit wasserfreiem Natriumsulfat getrocknet und man destillierte den Äther auf dem Wasserbad bei 50° ab. (I) bildet hellgelbes Öl. Ausbeute 94 g. Infolge Unbeständigkeit gegen Erhitzen wurde es, ohne gereinigt zu werden, weiter verarbeitet.

2-Cuminy-2-methyläthylenoxyd (II). 44 g. Öl (I) in 100 g. 95 proz. Alkohol versetzte man, auf -10° gekühlte, unter Rühren allmählich mit 25 proz. alkoholischer Kalilauge. Nach einstündigen Rühren neutralisierte man mit 10 proz. Essigsäure, filtrierte den Niederschlag ab und destillierte den Alkohol ab. Das zurückbleibende Öl wurde mit Äther verdünnt, getrocknet und fraktioniert. (1) $60-105^{\circ}$ (3 mm.) 12 g. (2) $105-135^{\circ}$ (3 mm.) 20 g. (3) der Rückstand 40 g.

Die (2) Fraktion, in welcher sich das gesuchte Oxyd befindet, wurde von neuem fraktioniert, wobei das Oxyd bei $111-113^{\circ}$ (3 mm.) überging. Ausbeute 16 g. Es bildet hellgelbes Öl n_D^{15} 1.5094, d_4^{15} 0.9735, $[R_L]_D$ 58.39 (Berechnet für $C_{13}H_{18}O_3$: 58.08).

Diacetat.—Mit Essigsäureanhydrid acetyliert. Sdp. $153-156^{\circ}$ (4 mm.). 1 g. Acetat: 20.60 ccm. N/2 KOH (Berechnet für $C_{13}H_{18}O_2$ $(COCH_3)_2$: 20.99 ccm.

p-Isopropyl- α -methylhydrozimtaldehyd (Cyclamenaldehyd) (III). Nach dem man das Oxyd tropfenweise mit 60 g. 95 proz. Ameisensäure (od. mit 6N Schwefelsäure) versetzt hat, kochte man das Gemisch 2 Stunden im Ölbad. Das Reaktionsgemisch wurde mit Wasser und Äther geschüttelt, die Ätherschicht mit verd. Soda-Lösung, dann mit Wasser gewaschen und mit wasserfreiem Natriumsulfat getrocknet.

Die getrocknete Äther-Lösung wurde schliesslich fraktioniert. Cyclamenaldehyd ging bei $135-140^{\circ}$ (10 mm.) über. Ausbeute 8 g. Es bildet hellgelbes Öl mit charakteristischem Geruch. Semicarbazon: Farblose Blättchen aus verd. Alkohol. Schmp. $169-170^{\circ}$. Mit dem von Verfasser früher⁽¹⁾ dargestellte Semicarbazon gemischt zeigt es keine Schmelzpunkterniedrigung.

Zum Schluss sind wir den Herrn S. Sawayama für seine Hilfe zu unseren besten Dank verpflichtet.

Die Veränderung der chemischen Zusammensetzung der Thermalquellen unter dem Einfluss der Gezeiten.

Von Kazuo KURODA.

(Eingegangen am 23. Juni 1942.)

Einleitung.

Die Zusammenhänge zwischen den Thermalquellen und den Gezeiten sind von einigen Forschern bemerkt und vor allem vom geophysikalischen Standpunkt aus genau untersucht worden. Über die Veränderung der chemischen Zusammensetzung von Thermalquellen unter dem Einfluss von Ebbe und Flut sind jedoch bisher nur wenige Tatsachen bekannt, und wenn auch das Thermalwasser in seltenen Fällen analysiert wurde, so war die Analyse meist unvollkommen und ungenau. Keine Regelmässigkeiten in den Erscheinungen konnten bisher gefunden werden. Wir haben kürzlich die regelmässige Veränderung der Zusammensetzung der Thermalquellen von Ito, in der Provinz Sizuoka, beobachtet und ihre Abhängigkeit von Ebbe und Flut festgestellt. Die tägliche und zeitliche Veränderung ist erstaunlicherweise regelmässig und sehr gross. Wir fanden dabei eine unerwartete Tatsache: eine Thermalquelle hat ihre maximale Konzentration bei der Ebbe, ihre minimale Konzentration bei der Flut. Wir beabsichtigen ferner unsere Untersuchungen an anderen Thermalquellen, in verschiedenen Gegenden und bei verschiedenen Gezeitenverhältnissen vorzunehmen. Wir werden die Zusammenhänge zwischen See-, Grund-, und Thermalwasser klar zu machen, und ferner den Mechanismus der Thermalquellen zu erklären suchen. In dieser Abhandlung möchten wir jedoch die bis jetzt von uns erzielten Ergebnisse mitteilen.

Die Thermalquellen von Ito. Die Thermalquellen von Ito liegen an der östlichen Seeküste der Izu-Halbinsel. Sie sind sehr berühmt durch die grosse Zahl ihrer Quellen und ihre hohe Ergiebigkeit. Fukutomi und Fujii⁽¹⁾ haben im Jahre 1936 diese Thermalquellen geophysikalisch untersucht, und Temperatur, Ergiebigkeit, und Wasserniveau gemessen, sowie viele Quellen analysiert. Im Jahre 1940, hat T. Nakai⁽²⁾ den Radiumgehalt der 20 Thermalquellen von Ito bestimmt und zeigt, dass die Radiumgehalte mit der Fukutomi'schen Theorie, nach der die Thermalquellen von Ito durch die Mischung von zwei verschiedenen Arten von Urthermalwasser und einem kalten Grundwasser gebildet werden, erklärt werden können. K. Okabe⁽³⁾ hat kürzlich diese Quellen spektroskopisch analysiert und die Gegenwart von Silber und Gold in dem Thermalwasser nachgewiesen.

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- (1) K. Fukutomi und Z. Fujii, *Bull. Earthq. Res. Inst.*, **15**(1937), 506–535.
K. Fukutomi, *Zisin*, **12**(1940), 404.
 - (2) T. Nakai, *dies Bulletin*, **15**(1940), 377.
 - (3) K. Okabe, Noch unveröffentlicht.

Die Gegenwart dieser Elemente ist nicht so unwahrscheinlich, da es in der Nachbarschaft von Ito einige Goldminen gibt. Okabe untersucht weiter die katalytische Wirkung dieser Thermalquellen. Einige Thermalquellen sind schon früh im Jahre 1889 vom chemisch-hygienischen Institut analysiert worden⁽⁴⁾. Die Radioaktivität wurde von R. Ishizu und Y. Kinugasa im Jahre 1913⁽⁴⁾ und von dem Verfasser im März 1942 gemessen.

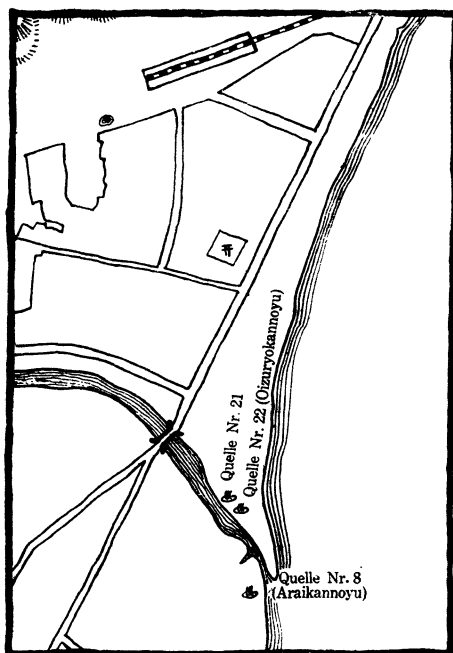


Abb. 1.

Analysenmethode. Eine hohe Genauigkeit der Analyse ist die notwendige Vorbedingung für unsere Untersuchung. Da eine grosse Zahl von Analysenresultaten notwendig ist, muss die Analysenmethode möglichst einfach und schnell sein. Die mühsame gravimetrische Methode ist unbrauchbar, wenn sie auch sehr genau ist. Wir haben deshalb hauptsächlich die volumetrische Methode angewandt.

(a) Temperaturmessung. Die Temperature wurde mit dem Maximum-Thermometer gemessen.

(b) pH-Messung. pH wurde kolorimetrisch mit Phenolrot als Indikator gemessen.

(c) Ergilbigkeitsmessung. Die Zeit, die zur Füllung eines 8-l-Eimers notwendig war, wurde gemessen.

(d) Atmosphärendruck. Mit einem Barometer gemessen.

(e) Abdampfdruckbestimmung. 100 ccm Thermalwasser auf einem Wasserbad abgedampft, 1 Stunde bei 110°C getrocknet, und gewogen.

(f) Chlor. Zu 20 ccm Wasserprobe wurden 0.5 ccm K_2CrO_4 Lösung (10%ig) addiert, und mit N/10 $AgNO_3$ Lösung titriert. N/10 $AgNO_3$ Lösung: 16.9888 g $AgNO_3$ in 1 Liter Wasser gelöst. 1 ccm von dieser Lösung entspricht 3.5457 mg Cl'.

(g) Sulfat. Zu 100 ccm Wasserprobe wurde Benzidinhydrochloridlösung addiert, 5 Minuten mit einem Rührstock gerührt, durch 5A Toyo-Filterpapier filtriert, 2 mal mit je 10 ccm kaltem Wasser gewaschen. Der Niederschlag von Benzidinsulfat und das Filterpapier wurden in einen Becher gebracht, 100 ccm Wasser addiert, bis 60°C erwärmt, und nach Zusatz von etwa 2 ml Phenolphthaleinlösung mit N/10 NaOH bis zur bleibenden Rotfärbung titriert.

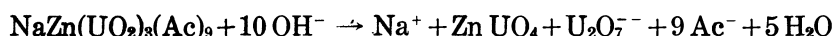
(4) R. Ishizu, "The Mineral Springs of Japan," 71, Tokyo (1915).

Benzidinlösung:⁽⁵⁾ Zur Herstellung der Benzidinlösung löst man 6.7 g reine Benzidinbase in 20 ml HCl (D=1.12) und verdünnt mit Wasser zu 1 Liter.

(h) Bestimmung von Calcium. Zu 50 ccm Wasserprobe addiert man 5 ccm NH₄OH (5:95) und kocht die Lösung. 10 ccm Ammoniumoxalat-lösung (gesättigt) wurde addiert und 3 Minuten gekocht, 1 Stunde stehen gelassen und filtriert. Der Niederschlag wurde mit kaltem Wasser 5 mal gewaschen, dann in 20–30 ccm heissem H₂SO₄ (1:3) gelöst, und bei 60–70°C. mit N/10 KMnO₄ Lösung titriert:

1 ccm N/10 KMnO₄ Lösung entspricht 2.004 mg. Ca.

(i) Bestimmung von Natrium. (a) Volumetrische Methode⁽⁶⁾. 10 ccm Wasserprobe wurden vorsichtig bis auf 5 ccm abgedampft. 35 ccm Zink-Uranyl-Acetat Reagens addiert. 5 Min. gerührt, 1 Stunde stehen gelassen und durch ein Glasfilter filtriert. Sodann 4 mal mit je 2 ccm absolutem Alkohol gesättigt mit dem Niederschlag von Zn·Na·(UO₂)₃ (C₂H₃O₂)₉ gewaschen. Der Niederschlag wurde in 100 ccm Wasser gelöst und mit N/2 NaOH bis Rotfärbung von Phenolphthalein eintrat, titriert. Dann wurde die Lösung gekocht, und wenn die Lösung farblos geworden, 5 ccm N/2 NaOH addiert und 5 Min. gekocht. Diese Operation wurde wiederholt bis zur bleibenden Rotfärbung. Dann titriert man den Basenüberschuss mit N/2 HCl. Die Reaktion verläuft wie folgt:



Wir müssen zuerst die Beziehung zwischen der Natriummenge und dem Volumen der N/2 NaOH Lösung mittels Natriumchlorid Normallösung feststellen. (b) Gravimetrische Methode⁽⁷⁾. Obenerwähnte volumetrische Methode ist jedoch nicht so genau. Wenn eine hohe Genauigkeit der Analyse erwünscht ist, müssen wir die gravimetrische Methode anwenden.

Der Niederschlag von Zn·Na·(UO₂)₃ Acetat wurde durch ein Glasfilter filtriert, mit Alkohol gewaschen, bei 110°C. 30 Min. getrocknet und gewogen.

Experimentalresultat.

I. Zeitliche Veränderung des Chlorgehaltes der Quelle Nr. 13 (Araikanoyu) am 15. März, 1942.

Die Quelle Nr. 13 liegt sehr nahe an der Seeküste (ungefähr 50 m), in der Nähe des Ufers des Ito-Okawa Flusses.

Die Quelle ist 90.90 m. tief. Sie wurde im Jahre 1919 ausgebaut. Der Besitzer sagt, dass diese Thermalquelle beträchtlich durch Ebbe und Flut beeinflusst wird.

(5) Kurtenacker, "Analytische Chemie der Sauerstoffsäuren des Schwefels," 24, Stuttgart (1938).

(6) Dobbins und Byrd, *J. Am. Chem. Soc.*, **53** (1931), 3288.

(7) Caley und Foulk, *J. Am. Chem. Soc.*, **51** (1929), 1664.

Der Verfasser war am 15. März 1942 in Ito gewesen, und hat je 1 Stunde, Temperatur und Chlorgehalt dieser Quelle gemessen. Das Resultat ist in Tabelle 1 angegeben (Tabelle 1).

Tabelle 1. Quelle Nr. 13.
15. März 1942.

Zeit	Temp. der Quelle °C	Cl' (g/L)
10 _h . 10	41.5	1.4410
11 _h . 10	41.5	1.4374
12 _h . 10	41.5	1.4566
13 _h . 5	41.7	1.4717
14 _h . 5	41.7	1.4916
15 _h . 5	41.5	1.5178

Tabelle 2.

Flut		Ebbe	
Zeit	Niveau (cm)	Zeit	Niveau (cm)
4 _h . 15	138	10 _h . 00	59
15 _h . 45	138	22 _h . 25	14

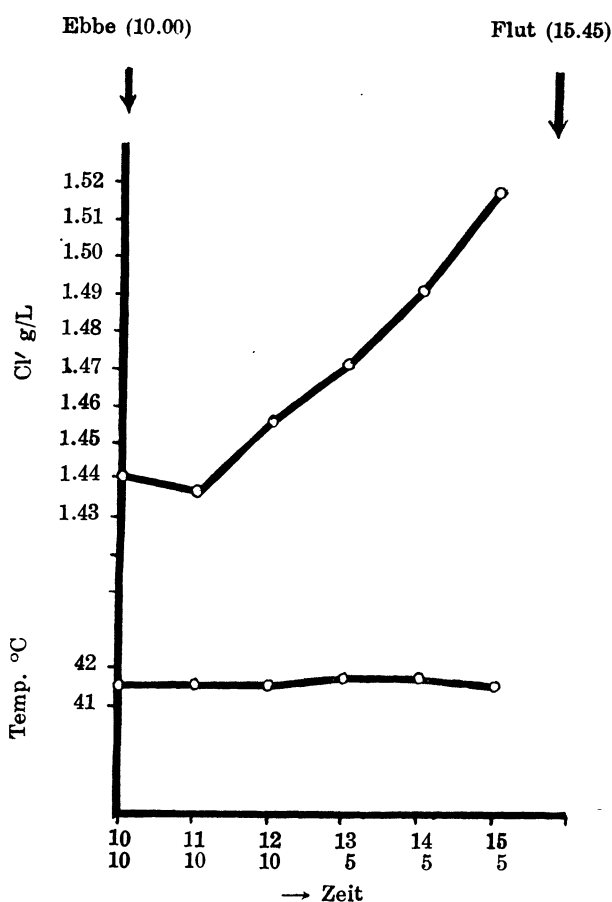


Abb. 2. Quelle Nr. 13. 15. März 1942.

Die Temperatur bleibt beinahe konstant, der Chlorgehalt vergrößert sich indes merkwürdigerweise regelmässig. Die Zeit von Ebbe und Flut in Ito war am 15. März 1942, wie folgt (Tabelle 2).

Wie man aus Abb. 2 ersieht, gehen Niveau und Chlorgehalt parallel zueinander. Es kann nicht bezweifelt werden, dass die regelmässige Veränderung des Chlorgehalts dieser Quelle von Ebbe und Flut verursacht wird. Die Experimente wurden leider nicht lange fortgesetzt, so dass wir das Resultat nicht ausführlich diskutieren können.

II. Zeitliche Veränderung des Chlorgehaltes der Quelle Nr. 13 (Araikannoyu) am 30. März 1942.

Am. 30. März 1942 wurden wieder die Chlorbestimmung, Temperatur- und pH Messung durchgeführt. Das Resultat war

sehr ähnlich wie am 15. März 1942. (Tabelle 3).

Wie man aus Abb. 3 ersieht, wird das Niveaumaximum um 15_h 20 erreicht, um 16_h 00 zeigt sich jedoch ein höherer Gehalt an Chlor als um

15_h 00. Der Zusammenhang zwischen Niveau und Chlorgehalt scheint etwas verschoben.

Tabelle 3. Quelle Nr. 13.
30. März 1942.

Zeit	Temp. der Quelle °C (Lufttemperatur °C)	pH	Cl' (g/L)
13 _h . 00	41.5 (18.3)	7.45	1.4339
14 _h . 00	41.5 (19.1)	7.45	1.4522
15 _h . 00	41.6 (19.0)	7.45	1.4636
16 _h . 00	— (—)	7.45	1.4771

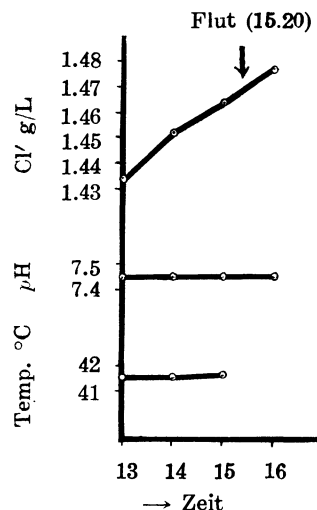


Abb. 3. Quelle Nr. 13.
30. März 1942.

III. Zeitliche Veränderung der chemischen Zusammensetzung der Quelle Nr. 21 von 30. bis 31. März 1942.

Diese Quelle liegt an der anderen Seite des „Ito-Okawa“, ungefähr 100 m von der Seeküste entfernt.

Ort der Quelle: 178–18, Kuzumihara, Matubara, Ito, Takata-Gun. Sizuoka-Ken (Provinz Sizuoka).

Besitzer: Herr T. Kitamura.

Verwalter: Herr M. Saito.

Tiefe der Quelle: 205.5 m (bis 52 m Eisenrohr).

Die Quelle soll beträchtlich von Ebbe und Flut beeinflusst werden. Die Quelle wird auch von dem Niveau des Flusswassers beeinflusst.

Wir haben vom 30. bis 31. März 1942, 24 Stunden an dieser Quelle, Temperatur, pH, Ergiebigkeit, Cl', SO₄', Na', und Ca'' gemessen.

Die Zeit von Ebbe und Flut in Ito am 30.–31. März 1942 war, wie folgt (Tabelle 4):

Das Resultat ist in Tabelle 5 und in Abb. 4 angegeben.

Tabelle 4.

	Flut		Ebbe	
	Zeit	Niveau (cm)	Zeit	Niveau (cm)
30. März	3 _h . 35	138	9 _h . 35	51
"	15 _h . 20	137	21 _h . 55	20
31. März	4 _h . 5	143	10 _h . 10	36
"	16 _h . 15	147	21 _h . 35	19

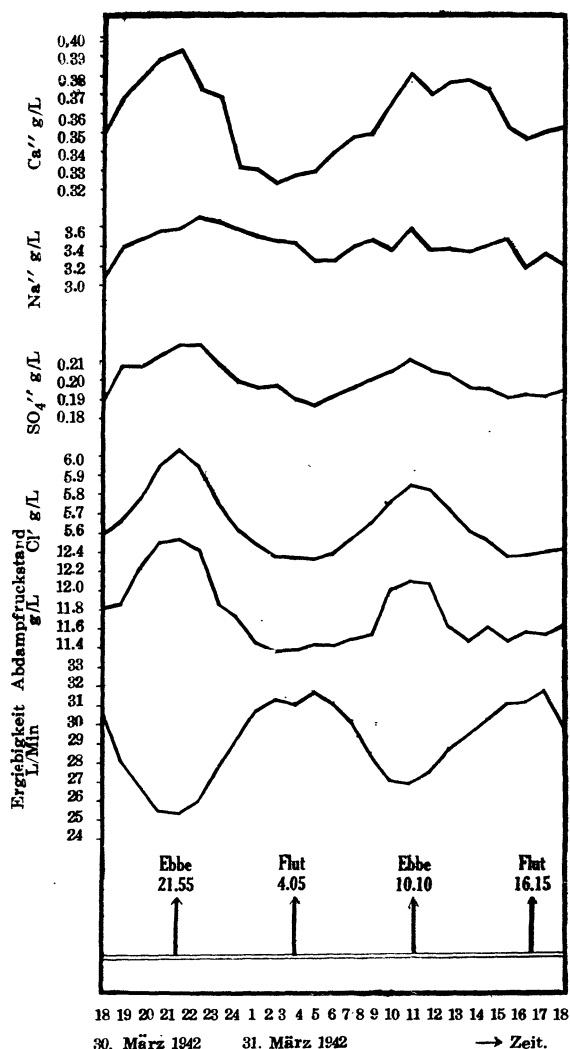


Abb. 4. Quelle Nr. 21. 30-31. März 1942.

24. April um 9_h (Flut Zeit 9.20) und am 25. April um 2_h (Flut-Zeit 0.45). Die Veränderung des Sulfates war nicht sehr regelmässig, weil die Analysenmethode von Sulfat nicht so genaue Messungen ermöglicht wie bei Chlor. Wir konnten daher bei dem Sulfatgehalt die zu erwartenden kleinen Veränderungen nicht feststellen. Die Neigung scheint jedoch ähnlich zu sein. Die Ergiebigkeit war ebenfalls etwas unregelmässig.

Die Zeit von Ebbe und Flut in Ito am 24.-25. April 1932 war, wie folgt (Tabelle 6).

V. Zeitliche Veränderung der chemischen Zusammensetzung der Quelle Nr. 22. (Oizuryokannoyu) vom 24. bis 25. April 1942.

Diese Quelle sprudelt ganz in der Nähe der Quelle Nr. 21, jedoch näher der Küste. Die Quelle ist auch ungefähr 100 m von der Seeküste entfernt. Tiefe der Quelle: 156 m (Eisenrohr 73 m).

Die Beziehung ist in diesem Fall ganz merkwürdig. Niveau und Ergiebigkeit verlaufen ganz parallel, Cl^- , SO_4^{2-} , Na^+ , Ca^{2+} usw. verändern sich jedoch umgekehrt. Die maxima von Cl^- , SO_4^{2-} , Na^+ , Ca^{2+} , usw. stimmen mit den Minima von Niveau und Ergiebigkeit überein.

IV. Zeitliche Veränderung der chemischen Zusammensetzung der Quelle Nr. 21 vom 24. bis 25. April 1942.

Wir haben vom 24.-25. April 1942, d.h. in einer Halbmondnacht, bei dieser Quelle wieder dasselbe Experiment durchgeführt. Es wurde erwartet, dass in dieser Nacht das Niveau beinahe konstant und dementsprechend die Zusammensetzungsänderung auch nicht so gross ist. Das Resultat entsprach unserer Erwartung. Die Veränderungen von Temperatur, pH, Ergiebigkeit, Chlor, und Sulfat sind sehr gering, Maxima von Chlorgehalt traten zweimal auf, am 24. April um 17_h und am 25. April um 7_h, Minima traten ebenfalls zweimal auf, am

Tabelle 5. Quelle Nr. 21. 30-31 März 1942.

Zeit	Luft-temp. (°C)	Temp. der Quelle (°C)	pH	Er-giebig-keit (L/Min)	Ab-dampf-rück-stand (g/L)	Cl' (g/L)	SO ₄ '' (g/L)	Na' (g/L)	Ca'' (g/L)
18 _{h.} 00	17.0	45.0	7.3	33.5	11.80	5.582	1.890	3.09	0.3486
19 _{h.} 00	16.4	45.0	7.2	28.2	11.84	5.659	2.070	3.41	0.3667
20 _{h.} 00	17.6	45.0	7.3	25.7	12.22	5.780	2.061	3.48	0.3783
21 _{h.} 00	16.0	45.0	7.3	23.0	12.48	5.954	2.122	3.57	0.3880
22 _{h.} 00	15.5	45.0	7.4	22.8	12.52	6.032	2.171	3.59	0.3923 ← Ebbe
23 _{h.} 00	14.7	45.0	7.3	24.0	12.40	5.936	2.180	3.72	0.3711 (21.55)
24 _{h.} 00	14.2	45.0	7.3	27.7	11.85	5.748	2.072	3.68	0.3680
1 _{h.} 00	13.7	45.0	7.3	30.6	11.71	5.610	1.982	3.59	0.3305
2 _{h.} 00	13.1	45.0	7.3	33.6	11.44	5.535	1.951	3.52	0.3293
3 _{h.} 00	12.7	45.0	7.3	34.8	11.37	5.475	1.965	3.47	0.3229
4 _{h.} 00	12.7	45.0	7.3	34.2	11.38	5.464	1.893	3.45	0.3265 ← Flut
5 _{h.} 00	12.2	44.9	7.3	35.5	11.43	5.461	1.863	3.26	0.3285 (4.05)
6 _{h.} 00	12.3	44.9	7.3	34.2	11.42	5.489	1.916	3.26	0.3386
7 _{h.} 00	12.5	45.0	7.3	32.4	11.49	5.578	1.960	3.41	0.3466
8 _{h.} 00	12.4	45.0	7.3	29.0	11.53	5.656	2.005	3.48	0.3474
9 _{h.} 00	13.5	45.0	7.3	26.2	12.02	5.762	2.042	3.37	0.3659
10 _{h.} 00	15.0	45.0	7.3	25.9	12.09	5.840	2.100	3.59	0.3763 ← Ebbe
11 _{h.} 00	15.1	45.0	7.4	27.0	12.06	5.815	2.048	3.37	0.3695 (10.10)
12 _{h.} 00	13.8	45.0	7.4	29.5	11.60	5.713	2.029	3.38	0.3759
13 _{h.} 00	12.0	45.0	7.3	30.9	11.44	5.606	1.952	3.35	0.3769
14 _{h.} 00	11.9	45.0	7.3	32.5	11.60	5.557	1.948	3.42	0.3614
15 _{h.} 00	17.7	45.0	7.3	34.3	11.44	5.472	1.900	3.50	0.3514
16 _{h.} 00	17.0	45.0	7.3	34.3	11.55	5.479	1.912	3.19	0.3458 ← Flut
17 _{h.} 00	15.8	45.0	7.3	35.5	11.53	5.493	1.905	3.33	0.3498 (16.15)
18 _{h.} 00	14.0	45.0	7.3	32.0	11.61	5.514	1.942	3.21	0.3522

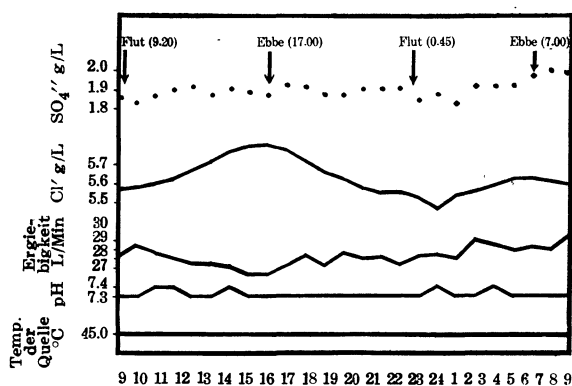


Abb. 5. Quelle Nr. 21. 24.-25. April 1942.

Tabelle 6.

	Flut	
	Zeit	Niveau (cm)
24. April	9.20	105
25. April	0.45	120
	11.40	103
	Ebbe	
	Zeit	Niveau (cm)
24. April	5.00	94
	17.00	45
25. April	7.00	86
	18.35	47

Das Experimentalresultat ist in Tabelle 8 angegeben. Die Neigung war ganz dieselbe wie bei Quelle No. 21. Die Veränderung war jedoch etwas kleiner. Die Ursache dafür ist vielleicht darin zu suchen, dass diese Quelle ein längeres Eisenrohr als die Quelle Nr. 21 hat. Die Quelle sprudelt unter der Badeanstalt hervor, die Probeentnahme war infolgedessen sehr schwer. Wir haben deshalb die Temperatur in der Badeanstalt

Tabelle 7. Quelle Nr. 21. 24-25. April 1942.

Zeit	Luft-Temperatur (°C)	Luft- druck (mm)	Temp. der Quelle (°C)	pH	Ergiebig- keit (L/Min)	Cl' (g/L)	SO ₄ '' (g/L)
9 _h . 00	18.5	760	45.0	7.3	28.2	5.567	1.857 ← Flut (9.20)
10 _h . 00	19.5	760	45.0	7.3	29.4	5.575	1.830
11 _h . 00	22.1	758	45.0	7.4	28.7	5.590	1.868
12 _h . 00	23.0	758	45.0	7.4	28.1	5.613	1.900
13 _h . 00	23.4	758	45.0	7.3	27.6	5.669	1.915
14 _h . 00	23.7	758	45.0	7.3	27.7	5.707	1.872
15 _h . 00	22.1	757	45.0	7.4	27.4	5.760	1.905
16 _h . 00	24.0	757	45.0	7.3	26.5	5.790	1.888
17 _h . 00	21.8	757	45.0	7.3	26.4	5.798	1.875 ← Ebbe (17.00)
18 _h . 00	19.2	757	45.0	7.3	27.3	5.772	1.922
19 _h . 00	15.0	758	45.0	7.3	28.4	5.707	1.913
20 _h . 00	12.1	758	45.0	7.3	27.3	5.650	1.871
21 _h . 00	12.8	757.5	45.0	7.3	28.6	5.613	1.871
22 _h . 00	11.1	757.5	45.0	7.3	28.0	5.567	1.904
23 _h . 00	10.3	758	45.0	7.3	28.2	5.541	1.902
24 _h . 00	9.5	758	45.0	7.3	27.4	5.544	1.901
1 _h . 00	9.5	759	45.0	7.3	28.4	5.514	1.845 ← Flut (0.45)
2 _h . 00	8.8	758	45.0	7.4	28.6	5.465	1.878
3 _h . 00	8.3	758	45.0	7.3	28.1	5.533	1.829
4 _h . 00	8.2	758.5	45.0	7.3	30.0	5.556	1.911
5 _h . 00	8.0	758.5	45.0	7.4	29.5	5.582	1.919
6 _h . 00	9.7	759	45.0	7.3	28.9	5.613	1.920
7 _h . 00	13.0	759	45.0	7.3	29.3	5.620	1.978 ← Ebbe (7.00)
8 _h . 00	18.3	759	45.0	7.3	29.1	5.605	2.000
9 _h . 00	21.3	759	45.0	7.3	30.6	5.598	1.991

Tabelle 8. Quelle Nr. 22.
24-25. April 1942.

Zeit	Temp. der Quelle (°C)	pH	Cl' (g/L)
9 _h 20	45.0	7.5	4.744 ← Flut (9.20)
10 _h . 30	45.0	7.5	4.733
11 _h . 30	45.0	7.5	4.748
12 _h . 30	45.0	7.5	4.752
13 _h . 30	45.0	7.6	4.752
14 _h . 30	45.0	7.5	4.793
15 _h . 30	45.1	7.5	4.793
16 _h . 30	45.1	7.5	4.797
17 _h . 30	45.1	7.6	4.786 ← Ebbe (17.00)
18 _h . 30	45.0	7.6	4.759
19 _h . 30	45.0	7.6	4.759
20 _h . 30	45.0	7.6	4.733
21 _h . 30	45.0	7.5	4.729

gemessen. Hier fanden wir eine um 1°C. niedriger liegende Temperatur. Die richtige Temperatur der Quelle liegt also mit 46°C., etwas höher als die der Quelle Nr. 21.

Diskussion. K. Honda und T. Terada⁽⁸⁾ bemerkten bei den Thermalquellen von Atami schon im Jahre 1906 eine regelmässige Hebung und Senkung des Wasserniveaus. Eine Thermalquelle, die in der Nähe der Oyu-Quelle (Geiser) liegt, verändert ihr

(8) K. Honda und T. Terada, Publications of the Earthquake Investigation Committee No. 22A(1906), 51.

Tabelle 8.—(Fortsetzung)

Zeit	Temp. der Quelle (°C)	pH	Cl' (g/L)
22 _{h.} 30	45.0	7.5	4.714
23 _{h.} 30	45.0	7.6	4.710
24 _{h.} 30	45.0	7.5	4.695 ← Flut (0.45)
1 _{h.} 30	45.0	7.5	4.684
2 _{h.} 30	45.0	7.6	4.702
3 _{h.} 30	45.0	7.5	4.695
4 _{h.} 30	45.0	7.5	4.695
5 _{h.} 30	45.0	7.5	4.718
6 _{h.} 30	45.0	7.5	4.736
7 _{h.} 30	45.0	7.6	4.740 ← Ebbe (7.00)
8 _{h.} 30	45.0	7.6	4.729
9 _{h.} 30	45.1	7.7	4.721

Niveau unter dem Einfluss des Geisers, und ein Thermalquelle, die in der Nähe der Seeküste liegt, unter dem Einfluss von Ebbe und Flut. Obige Autoren haben jedoch gar nichts über die Veränderung der chemischen Zusammensetzung der Thermalquellen geschrieben. R. Nomitu⁽¹⁰⁾ hat bei den Thermalquellen von Bepu in der Provinz Oita den Einfluss der Gezeiten auf die Thermalquellen

studiert. Er schreibt, dass die Ergiebigkeit sich parallel zu Ebbe und Flut verändert, die elektrische Leitfähigkeit der Thermalquellen aber genau umgekehrt ist. Dies ist eine sehr interessante Erscheinung, die wir chemisch noch einmal genau studieren müssen. K. Maeda⁽⁹⁾ hat bei den Thermalquellen von Asamusi in der Provinz Aomori diese Erscheinung wieder vom geophysikalischen Standpunkt aus genau untersucht. Er schreibt über die Veränderung des Chlorgehalts nur sehr kurz wie folgt: „Der Chlorgehalt der Thermalquellen wurde bestimmt, genügende Ergebnisse konnten jedoch noch nicht erzielt werden.“

Fukutomi hat vom 5.–26. November 1937 siebzehn Thermalquellen in Ito untersucht. Er schreibt in seiner Mitteilung wie folgt:⁽¹⁾ „Die Ergiebigkeit der Thermalquellen von Ito verändert sich, die Temperatur und der Chlorgehalt aber bleibt immer beinahe konstant“. In seiner Abhandlung über die Thermalquellen von Yatu schreibt Fukutomi wieder wie folgt⁽¹⁰⁾: „Die Veränderung der Ergiebigkeit der Thermalquellen von Yatu beträgt 2/3 der Ergiebigkeit des Durchschnittsniveaus der Gezeiten. Die Temperatur und der Chlorgehalt ändert sich jedoch nur um 1/30. Wir können daher daraus schliessen, dass die Temperatur und der Chlorgehalt immer konstant war. Dies ist eine bemerkenswerte Erscheinung, und wir möchten annehmen, dass der Einfluss von Ebbe und Flut auf die Ther-

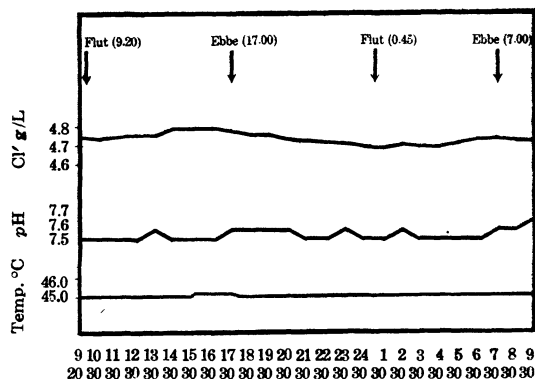


Abb. 6. Quelle Nr. 22. 24.–25. April 1942.

(9) K. Maeda, *Zisin*, 8(1936), 1.(10) Fukutomi, *Zisin*, 8(1936), 457.

malquellen nicht durch die Mischung von Seewasser und Thermalwasser verursacht wird, sondern nur der Veränderung des Gezeitendrucks auf den Wasserdruck im Thermalquellenwasserweg zuzuschreiben ist“. Meine neue Untersuchung zeigt jedoch, dass diese Fukutomi'sche Theorie nicht immer gültig ist. Meine Ergebnisse können nicht erklärt werden, ohne die Mischung von Thermalwasser und anderem Wasser in Betracht zu ziehen. Die Veränderung des Chlorgehaltes der Quelle Nr. 13 (Araikanoyu) kann durch die Mischung von Seewasser und Thermalwasser leicht erklärt werden. Die regelmässige Veränderung der chemischen Zusammensetzung der Quelle Nr. 21 ist jedoch etwas schwer zu erklären. Die maximale Ergiebigkeit und minimale Konzentration stimmen immer überein. Es ist kaum anzunehmen, dass diese Erscheinung durch die Verzögerung des Einflusses der Gezeiten verursacht wird. Wir müssen also die Vermischung mit Grundwasser berücksichtigen. Dasselbe ist weit stärker verdünnt als das See- und Thermalwasser. Seine Temperatur ist uns noch nicht bekannt.

Weil die Temperaturveränderung jedoch immer weniger als 0.1°C . betrug, müssen wir daraus schliessen, dass die Mischung schon in der Tiefe geschieht oder dass die Temperatur des Grundwassers und des Thermalwassers ganz gleich war. In letzteren Fall, können wir die Vermischung in der Nähe der Erdoberfläche vermuten. Wir können dies schematisch darstellen (s. Abb. 7). Das Grundwasser strömt durch ein in der Nähe der Erdoberfläche liegendes Loch in das Eisenrohr ein. Bei der Ebbe ist das Niveau des Grundwassers unter diesem Loch, bei der Flut über diesem Loch. Es ist indes unwahrscheinlich, dass es in der Nähe der Erdoberfläche ein Loch in dem Rohr gibt, und dort die Temperatur des Grund- und Thermalwassers gleich ist. Es ist viel wahrscheinlicher und leichter zu erklären, dass die Vermischung in der Tiefe geschieht. Ein derartiges Modell wird in Abb. 8 gezeigt. In diesem Fall wirkt das

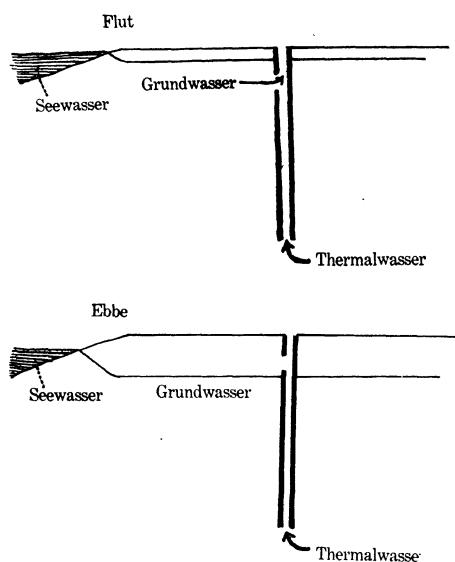


Abb. 7.

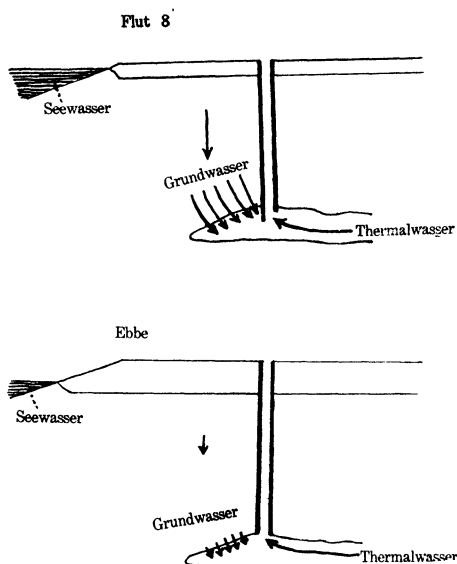


Abb. 8.

Seewasser nur druckgebend, d.h. das Seewasser fliesst gar nicht in das Thermalwasser ein, sondern drückt nur das Grundwasser ins Thermalwasser. Bei der Flut erreicht dieser Druck ein Maximum und die grösste Menge von verdünntem Grundwasser fliesst in das Thermalwasser; deshalb hat die Thermalquelle ihre minimale Konzentration bei der Flut. Der Druck erreicht sein Minimum bei der Ebbe, aus diesem Grunde ist auch die in die Thermalquelle fliessende Grundwassermenge am geringsten; deshalb hat die Thermalquelle ihre maximale Konzentration bei der Ebbe.

Um diese Ansicht zu bestätigen, ist die Temperaturmessung in der Tiefe des Thermalquellenrohrs notwendig. Der Verfasser hat den Plan, die Temperatur mit einem Widerstandthermometer zu messen. Die Ergebnisse seiner Experimente werden später berichtet werden.

Zusammenfassung.

(1) Die Veränderung der chemischen Zusammensetzung der Thermalquellen von Ito unter dem Einfluss der Gezeiten wurde untersucht.

(2) Die zeitliche Veränderung der chemischen Zusammensetzung einiger Thermalquellen von Ito ist erstanunlicherweise gross und regelmässig.

(3) Die Thermalquelle Nr. 21 hat ihre maximale Konzentration bei der Ebbe und ihre minimale Konzentration bei der Flut.

(4) Diese Erscheinungen können nicht erklärt werden, ohne die Vermischung von Thermalwasser mit anderem Wasser in Betracht zu ziehen. Wir müssen die Vermischung mit Grundwasser berücksichtigen.

Ich erlaube mir hiermit Herrn Prof. Kenjiro Kimura für seine freundliche Anleitung und steten Ratschläge, die mir bei der Ausführung dieser Arbeit zuteil geworden sind, meinen herzlichsten Dank aussprechen. Ferner möchte ich Herrn T. Hanya für seine eifrige Hilfe und Herrn Kumanosuke Kataoka, von der Thermalquellen-Vereinigung Ito, und Herrn M. Saito für ihre Freundlichkeit, herzlichst danken. Dem Unterrichtsministerium sei gedankt für die Gewährung einer Unterstützung zur Anregung wissenschaftlicher Forschung. Der Kaiserlichen Akademie der Wissenschaft sind wir für ihre finanzielle Unterstützung zu grossem Dank verpflichtet.

*Chemisches Institut der Naturwissenschaftlichen Fakultät,
Kaiserliche Universität zu Tokio.*

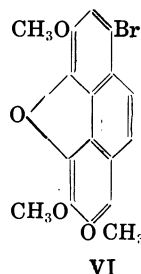
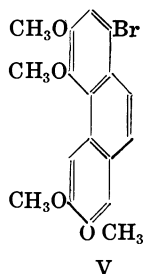
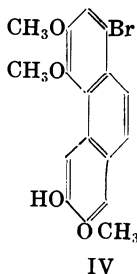
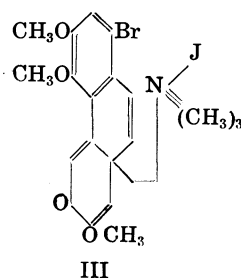
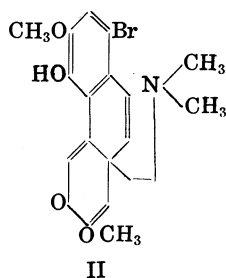
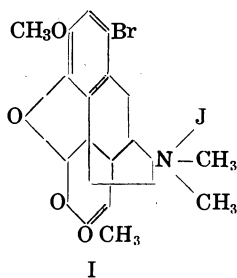
Abbau von 1-Brom-sinomenein-jodmethylat mit Alkali.⁽¹⁾

Von Kakuji GOTO, Tatsuo ARAI und Tatsuo ODERA.

(Eingegangen am 7. Juli 1942.)

Ueber den Abbau von 1-Brom-sinomenein-jodmethylat (I) mit Dimethylsulfat und Alkali haben wir schon in der XXXVII. Mitteilung berichtet⁽²⁾. Dort haben wir 1-Brom-3-methyl-6,7-dimethoxy-morphenol (VI) als Hauptprodukt und daneben 1-Brom-dimethyl-sinomenol (V) in geringer Ausbeute erhalten. Bei Wiederholung dieser Reaktion haben wir indessen gefunden, dass in manchen Fällen das letzt genannte Phenol das einzige Produkt darstellte und das gesuchte Morphenol gar nicht isoliert worden war. Dieser Umstand führte uns das Verhalten dieses Jodmethylates gegen Alkali genauer zu untersuchen.

Wenn das 1-Brom-sinomenein-jodmethylat bei Zimmertemperatur mit der berechneten Menge sehr verdünnter Natronlauge behandelt wird, so wird es zuerst ein brauner Niederschlag gebildet, der sich schnell darin wieder auflöst. Chloroform extrahiert daraus ein gelbes Produkt, welches aus Methanol in schönen langen Prismen umkristallisiert wird. Wir wollen diesem Produkt nach der Analyse und seinem Verhalten die Konstitution II erteilen und es als des-N-Methyl-1-brom-dehydro-meta-sinomenin bezeichnen⁽³⁾.



(1) LII. Mitteilung über Sinomenin. Alle Mischproben in dieser Arbeit wurden mit den entsprechenden Substanzen aus 1-Brom-4-methyl-sinomenin (LI. Mitteilung, dieses Bulletin, 17(1942), 304) ausgeführt.

(2) Dieses Bulletin, 8 (1933), 366.

(3) Für das Wort "meta" siehe Schöpf und Borkowsky, *Ann.*, 458(1927), 148.

Die Hauptgründe, welche beim Aufnahme der obigen Struktur in Betracht gezogen wurden, sind folgende.

(i) In dieser Substanz muss der originale Oxydring gespalten worden sein, da sie in verdünntem Alkali löslich ist und eine grüne Eisenchlorid-reaktion gibt. Bei der Methylierung mit Dimethylsulfat und Alkali nimmt sie nur einen Methyl auf. Der gebildete Monomethyl-äther wurde als Jodmethylat (III) isoliert.

(ii) Sie muss eine des-N-Base sein, weil sie sich in konz. Schwefelsäure in stark blauer Farbe löst und bei der Acetolyse 1-Brom-diacetyl-sinomenol in einer quantitativen Ausbeute gibt.

(iii) Die hydrolytische Spaltung des Oxydringes muss mit dem Verlust eines Molekules Wasser verknüpft worden sein. Dies ist durch Analyse klar gezeigt.

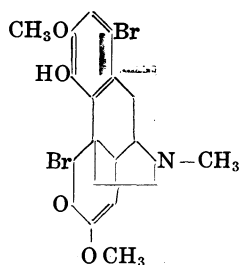
(iv) Sie muss sehr wahrscheinlich eine chinoide Struktur besitzen, da die freie Base gelb gefärbt ist und ein stark rotes Natriumsalz bildet. Dies bedingt die Eliminierung von Wasser aus C(5) und C(13) mit der Verschiebung von N-haltigen Seitenkette.

(v) Die Verschiebung muss nach C(14) geschehen, weil, sonst, die Seitenkette nicht so leicht bei der Acetolyse weggenommen werde.

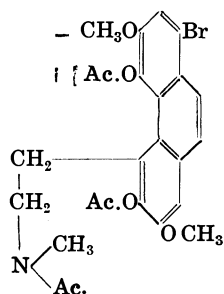
Es ist merkwürdig, dass eine solche verwickelte Umwandlung so schnell durch so verdünntes Alkali bei der Zimmertemperatur vollgezogen wird. Doch scheint es uns, dass dieses Verhalten des 1-Brom-sinomenein-jodmethylates die Ursache der äusserst unstabilen Natur des ähnlich gebauten Kodeinonjodmethylates, wie schon lange von Knorr⁽⁴⁾ bemerkt worden war, teilweise erklärt. Tatsächlich haben wir durch die ähnliche Behandlung von Kodeinonjodmethylat eine entsprechende des-N-Base (des-N-Methyl-dehydro-meta-thebainon) einmal erhalten. Aber, da diese letztere Reaktion trotz zahlreicher Wiederholung nie seither wieder glücklich hat, wollen wir die Untersuchung in der Zukunft vorbehalten.

Da einmal die stark labile Natur des 1-Brom-sinomenein-jodmethylates erklärt worden war, ist die Gewinnung von 1-Brom-3-methyl-6,7-dimethoxymorphenol leichter geworden. Die Methylierung von der freien Base und das stärkere Erwärmen (bis 90°) sind die Hauptbedingungen (siehe Versuchsteil). Daraus ersieht man, dass in dieser Beziehung das Methyl-methosulfat viel beständiger als das Jodmethylat ist.

Schliesslich sei es erwähnt, dass 1,5-Dibrom-sinomenin (VII) bei der Acetolyse 1-Brom-triacetyl-sinomenenin (VIII) gibt. Diese Tatsache beweist klar, dass in der letzteren Substanz auch der Oxydring geöffnet worden ist.



VII



VIII

(4) Ach und Knorr, *Ber.*, **36** (1903), 3073.

Versuche

Des-N-methyl-1-brom-dehydro-meta-sinomenin (II). *Abbau von 1-Brom-sinomenein-jodmethlat (I).* I) *Mit sehr verdünntem Alkali.* 0.55 g (1 Mol) dieses Jodmethlates wurde in 30 ccm Wasser gelöst und bei 20°, mit 8 Tröpfchen (=ca. 2/5 ccm; 1 Mol) 10 proc. Natronlauge versetzt. Die Lösung trübt und färbt sich braun, aber in einigen Minuten wieder erklärt. Chloroform extrahiert daraus gelbe Nadeln, die, aus Methanol umkrystallisiert, bei 199–201° schmilzt.

Wenn man obige braune Lösung in einem Bad von 80° zehn Minuten erwärmt, so gewinnt man ohne weiteres die Krystalle von freier Base. Ausbeute 0.18 g d. h. 50%.

II) *Mit stärkerem Alkali.* 1 g des Jodmethlates wurde in einem Kolben mit 12 ccm 11 proc. Natronlauge in einem Wasserbad von 80° zehn Minuten eingetaucht. Das Jodmethlat wird zuerst gelöst, die Lösung nimmt braune Farbe an, und schliesslich wird das Ganze in einer dicken Krystallbrei umgewandelt. Das rote Phenolat wird auf Glasfilter gesammelt und mit 10 proc. Natronlauge wohl gewaschen. Aus dem Filtrat isoliert man noch etwa 1/3 der Gesamtausbeute, nachdem man es soda-alkalisch macht und mit Chloroform extrahiert. Befreien des Phenolates geschieht wie gewöhnlich. Ausbeute 0.55 g d.h. 70%. Schmp. 199–201°.

Diese Substanz zeigt eine grüne Eisenchlorid-Reaktion, löst sich in verdünntem Alkali mit roter Farbe, die sich aber beim Ansäuern gelb umschlägt. In konz. Schwefelsäure löst sich zuerst rot, dann braun und schliesslich violett (beständig). Gefunden: C, 57.08; H, 5.10. Berechnet für $C_{20}H_{22}BrO_4N$ (420): C, 57.14; H, 5.24%. Spez. Drehung. Subst. = 0.0421 g, Methanol = 10 ccm, 0.5 dm-Rohr, $\alpha = +0.38^\circ$, $[\alpha]_D^{25} = +180.5^\circ$.

Chlorhydrat-krystallisiert in gelbe Nadeln. Schmp. 130°. Jodmethlat krystallisiert nicht. Oxim ist sehr schwer zu erhalten durch gewöhnliche Methode.

Alkalyse. Keine krystallisierende Substanz.

Acetolyse. Ausbeute an 1-Brom-diacetyl-sinomenol ist fast quantitativ.⁽⁵⁾

Des-N-methyl-1-brom-4-methyl-dehydro-meta-sinomeninjodmethlat (III). Des-N-methyl-1-brom-dehydro-meta-sinomenin (II) wird mit Dimethylsulfat und Alkali bei 68–80° methyliert. Bei dieser Temperatur wird das methylierte Methyl-methosulfat durch Zusatz von KJ als Jodmethlat niedergeschlagen. Centimeterlange Nadeln aus Wasser. Ausbeute 80%. Schmp. 182°–183° (zers.; sintern ab 175°). Keine Eisenchlorid-reaktion. Es färbt sich mit konz. Schwefelsäure zuerst braun, dann grün und nach einigen Minuten reinblau (beständig). Gefunden: C, 44.82; H, 4.83; N, 2.71; CH_3O , 16.00; J, 21.37. Berechnet für $C_{22}H_{27}NO_4BrJ$ (576): C, 45.83; H, 4.69; N, 2.60; CH_3O , 16.15; J, 22.05%.

Spec. Drehung. Subst. = 0.1102 g; Methanol = 10 ccm; $\alpha = +1.11^\circ$, $[\alpha]_D^{25} = +100.7^\circ$.

(5) Dieses Bulletin, 8(1933), 368.

Alkalischer Abbau. 1 g dieses Jodmethyldes wurde mit 20 ccm 16 proc. Natronlauge eine halbe Stunde gelinde gekocht (starker Amingeruch). Nach Verdünnen mit 180 ccm Wasser, wurde das Filtrat angesäuert und mit Äther extrahiert. Der Ätherrückstand gab 120 mg schöne Krystalle, die sich aus Methanol umkristallisieren lassen. Schmp. 135° (auch die Mischprobe). Alle Eigenschaften sind identisch mit denen des 1-Brom-4-methyl-sinomenols (IV). Daneben bei dieser Alkalyse entsteht immer ein alkali-unlösliches Phenanthren, welches bei 156° schmilzt. Dies wurde nicht zur Zeit untersucht. Methylieren des obigen Phenanthrens (Schmp. 135°) mit Dimethylsulfat und Alkali hat 1-Brom-dimethyl-sinomenol (V; Schmp. 144.5°, auch die Mischprobe) gegeben. Acetylieren durch Kochen mit Essigsäureanhydrid gab denselben 1-Brom-3-methyl-6-acetyl-sinomenol, wie man bei Acetolyse von 1-Brom-4-methyl-sinomenin isoliert hat. Schmp. 168° (aus Methanol). Auch die Mischprobe.

Acetolyse. Durch Acetolyse von des-N-Methyl-1-brom-4-methyl-dehydro-meta-sinomenin (1 g; 20 ccm Anhydrid + 1 g Na-acetat; 7.5 Stdn.) gewinnt man 1-Brom-4-methyl-6-acetyl-sinomenol in 10 proc. Ausbeute. Anfangs schmolz es bei 159°. Durch wiederholtes Umkristallisieren aus Methanol, wurde der Schmp. zu 167° erhöht. Die Mischprobe blieb unverändert.

1-Brom-3-methyl-6,7-dimethoxy-morphenol (VI)⁽⁶⁾.

Die beste Arbeitsweise, dieses Phenol aus 1-Brom-sinomenin zu gewinnen, ist folgende:

0.5 g 1-Brom-sinomenin wird in 5 ccm sehr verdünnter Salzsäure gelöst und mit Alkali fein gefällt. Der Kolben wird in einem Bad von 60–70° eingetaucht und mit je 5 ccm Dimethylsulfat und 33 proc. Natronlauge methyliert (innere Temperatur bleibt etwa 50°). Schliesslich wird die Badtemperatur auf 90° zehn Minuten erhalten, um das Abspalten der Seitenkette zu vervollständigen. Das Brom-morphenol wird mit Äther ausgeschüttelt. Ausb. 120 mg. Umgelöst aus 15 g kochendem Methanol, stellt es lange, haarige Nadeln dar. Schmp. 139°. In konz. Schwefelsäure löst es sich rein orange mit grüner Fluoreszenz.

Katalytische Reduktion. 200 mg dieses Morphenols wurden in Eisessig mit 1 g Pd-Kohle (=0.1 g Pd) in Wasserstoff geschüttelt. Die berechnete Menge von Wasserstoff wurde in 3 Stdn. verbraucht. Das entbromte Produkt, 3-Methyl-6,7-dimethoxy-morphenol, krystallisiert in rhombischen Prismen und schmilzt bei 94°. Beilstein-Reaktion negativ. Ausb. nur 35 mg. Gefunden: C, 71.40; H, 5.49. Berechnet für $C_{17}H_{14}O_4$ (=282); C, 72.34; H, 4.96%.

1-Brom-triacetyl-sinomenin (VIII).

4 g Sinomeninchlorhydrat (1 Mol) wurden mit 2 Mol Brom an seinen C(1) und C(5) bromiert. Nach vollständigem Verjagen der Essigsäure i.V., wurde der Rückstand mit 40 ccm Essigsäureanhydrid und 8 g Na-acetat vier Stdn. gekocht. Das Anhydrid wurde i.V. abdestilliert, der Rückstand in wenig Methanol gelöst und in viel 3 proc. Essigsäure ein-

(6) Ann., 489(1931), 93. Der hier angegebene Schmp. 143° war zu hoch.

gegossen. Der unlösliche Teil wurde mit 7 g Aethanol umkrystallisiert. Prismen. Schmp. 135° (aus Methanol). Löst sich gelb in Eisessig, aber die Farbe nimmt langsam einen grünen Stich an. In konz. Schwefelsäure löst es sich braunrot, aber die Farbe umschlägt dick-grün nach zehn Min. Alle sonstigen Eigenschaften zeigten, dass hier dieselbe Substanz vorliegt, die in 37. Mitt. als 1-Brom-diacetyl-sinomenenin bezeichnet worden war. Die dort angegebene Analysenwerte⁽⁷⁾ an C, H, N und zwei hydrolysierbare Acetyls stimmt sehr gut mit der Formel $C_{25}H_{26}NO_7Br$ (532) überein. Die lang offen gelassene Frage, ob in dieser Substanz der Oxydring intakt bleibt, oder geöffnet worden ist, wurde durch diese Darstellungsweise zugunsten der letzteren entschieden. Der Wegnahme des Bromatoms aus C(5) benötigt natürlich Einführung von einer Doppelbindung in Kern III, welcher sich mit der Enolisierung des Ketons vollständig aromatisieren muss. Dies bedingt die Umlagerung der Seitenkette nach C(5) oder C(8). Wir ziehen nach Analogie mit Thebeninumlagerung C(5) vor. Wenn die Seitenkette nach C(8) umgelagert wird, dann wird ein Aporphinskelett gebildet, der natürlich zu der acetolytischen Spaltung von C-N-Verkettung einen Widerstand zeigen muss.

Kitasato Institut, Tokyo.

(7) Dieses Bulletin, 8(1933), 368.

Geochemische Untersuchungen der Vulkane in Japan. XXVIII. Geochemische Untersuchungen an den Mineralquellen von Masutomi. II.

Von Shinya OANA und Kazuo KURODA.

(Eingegangen am 28. Juli 1942.)

Die Mineralquellen von Masutomi in Yamanasi-Ken (Kai-Provinz) sind, seitdem *R. Ishizu* und seine Mitarbeiter im Jahre 1914 den Radongehalt ihrer Wässer bestimmten,⁽¹⁾ wegen der starken Radioaktivität berühmt. Genannte Autoren teilten ausserdem Ergebnisse chemischer Analysen von einigen Quellwässern mit.⁽¹⁾ *T. Nakai* führte im Oktober 1936 und im April 1937 Radon- und weiter Radiumbestimmungen aus.⁽²⁾ Diese Bestimmungen steigerten das Interesse an genannten Quellen beträchtlich. Wir haben seit dem Juli 1939 bis jetzt schon vier Studienreisen nach Masutomi unternommen und einen Teil unserer Untersuchungsergebnisse, hauptsächlich über den Radongehalt, in der letzten Mitteilung veröffentlicht.⁽³⁾ Wir berichten nachstehend über unsere gesamten Er-

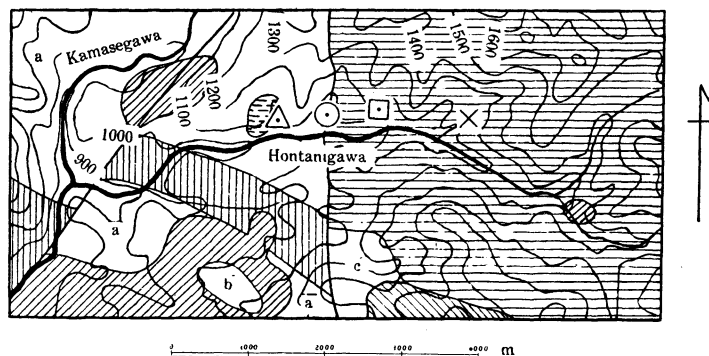
(1) *R. Ishizu*, "The Mineral Springs of Japan," (1915), 85.

(2) *T. Nakai*, dies Bulletin, 15 (1940), 363.

(3) *S. Oana* und *K. Kuroda*, ebenda, 15 (1940), 485.

gebnisse und erörtern anschliessend die Herkunft der Radioaktivität in diesen Quellwässern.

Geologie der Umgebung. Die Masutomi-Quellen entspringen im Hontanigawa Tale an den Ufern des gleichnamigen Flusses. In den Abb. 1 und 2 findet man eine Verwerfung, die den Fluss Hontanigawa senkrecht schneidend von Norden nach Süden verläuft. Östlich dieser Verwerfung steht Granit an und westlich Sandstein. Diejenigen Quellen, die nahe der Verwerfung aus Granit entspringen, haben wir zur Gruppe A, diejenigen, die in grösserer Entfernung von der Verwerfung längs des Yuzawa, eines Nebenflusses des Hontanigawa, zu Tage treten zur Gruppe D zusammengefasst. Aus der Verwerfung selbst brechen in Nachbar-



Erklärung zu Abb. 1.

	Grobkörniger Granit		Tonschiefer
	Granitporphyr		a, Sandstein
	Tuffbreccie		b, Hornblendedacit
	Tuffbreccie aus zwei Arten des Pyroxenandesits		c, Porphyrischer Granit

Gruppe A

Gruppe B

Gruppe C

Gruppe D

Gruppe E

Die gleichen Zeichen werden auch in den anderen Abbildungen gebraucht.

Abb. 1. Geologischer Plan von Masumoti.⁽⁴⁾

(4) M. Ichiki, *Bull. Earthquake Research Inst. Tokyo Imp. Univ.*, 7 (1929), 380.

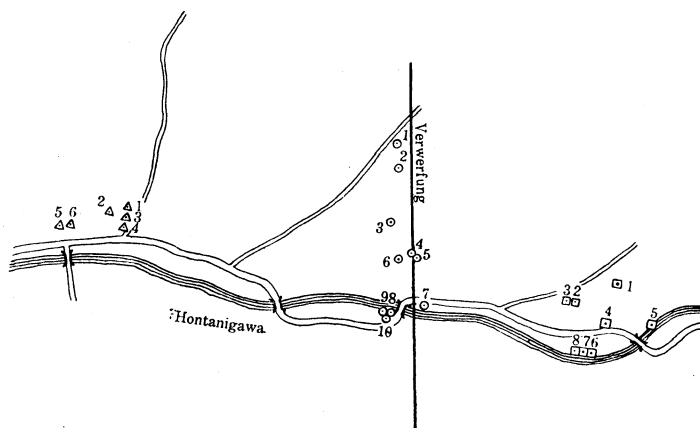


Abb. 2. Lageskizze der Quellen.

schaft des Hontanigawa mehrere Quellen hervor, die wir als Gruppe B bezeichnen. Die Sandsteinschicht, die die westliche Seite der Verwerfung bildet, enthält eine Quellgruppe, die mit C bezeichnet wird. Im Tale des Kamasegawa, eines Flusses, der sich bei Siokawa mit dem Hontanigawa vereinigt, treten zwei Quellen zu Tage, die als Gruppe E aufgeführt werden. Eine Übersicht über alle genannten Quellen vermittelt Tabelle 1.

Physikalische und chemische Eigenschaften der Quellwässer. 1. *Austrittstemperatur.* Tabelle 2 enthält alle bisher bestimmten Austrittstemperaturen. Die aus der Tabelle 2 zu entnehmenden kleinen Schwankungen haben praktisch keine Bedeutung, weil einerseits selbst innerhalb einer Quelle gewisse räumliche Temperaturunterschiede auftreten können und weil anderseits nicht geeichte Quecksilberthermometer zur Messung gebraucht wurden.

2. *pH.* Alle bisher bestimmten pH-Werte sind in Tabelle 3 enthalten. Bemerkenswert ist die überaus geringe Veränderlichkeit der pH-Werte. Die pH-Bestimmung wurde stets in der Nähe der Quelle an quellfrischen Proben kolorimetrisch vorgenommen. Wegen der gelösten Kohlensäure reagieren die Wässer schwach sauer. Wenn man die Wasserprobe stark schüttelt, so entweicht die Kohlensäure zum Teil und damit erhöht sich der pH-Wert mehr oder weniger. Bei Quelle B₇ steigt der pH-Wert z.B. von 6.3 bei quellfrischer Probe nach kräftigen Schütteln auf 6.7.

3. *Hauptbestandteile.* Chemische Analysen der Hauptbestandteile einiger Masutomi-Wässer wurden von *Ishizu* und seinen Mitarbeitern durchgeführt. Das Analysenergebnis von der Quelle B₁ bringt Tabelle 4.

4. *Abdampfrückstand.* 50 ccm jeder Wasserprobe wurde in Platinschale im Wasserbade abgedampft. Dieser Abdampfrückstand wurde weiter im elektrischen Thermostaten bei 120°C. bis zum konstanten Gewicht getrocknet und gewogen. Tabelle 5 zeigt diese Resultate. Die Zahlen sind nicht sehr genau, weil die Wasserproben nach der Entnahme monatelang in Glasflaschen aufbewahrt wurden und in dieser Zeit er-

Tabelle 1. Übersicht über die Quellen von Masutomi.

Gr.	Name	Anmerkungen	Bad
A ₁	Kinsentō		+
A ₂	Tuganerō No. 1		+
A ₃	Tuganerō No. 2		+
A ₄	Totikubo No. 1	entspringt aus einer Spalte in fossilem Kalksinter.	—
A ₅	Hiuke-sui	entspringt unmittelbar aus einer Spalte im Granit.	—
A ₆		nahe am rechten Hontanigawa-Ufer am Fuss fossiler Sinterterrassen. Dieser Austritt wurde im Jahre 1942 zum ersten Male beobachtet. In unmittelbarer Nähe flussabwärts entspringen zwei weitere kleine Quellen (A ₇ und A ₈).	—
B ₁	Nibuzawa	Dieses Mineralwasser wurde früher abgefüllt und verhandelt. Die Schüttungsmenge betrug 2.5 l/Min. (10. Juli 1939).	—
B ₂	Sio-no-sawa-tugane-yu		—
B ₃	Gantō-hunsen		—
B ₄	Kuridaira No. 1		+
B ₅	Kuridaira-tennen-buro		+
B ₆	Kuridaira No. 3		—
B ₇	Higasiobi-no-izumi	seit langem bekannte Quelle in alter brunnenartiger Staufassung. Die Schüttungsmenge betrug: 1.41 l/Min. (8. Juli 1939) 1.85 " (18. Okt. 1940) 2.16 " (20. Mai 1942)	—
B ₈	Wadegawara No. 1	B ₈ , B ₉ und B ₁₀ befinden sich in Hochwasserbett des Flusses, und sind nicht mehr als 1 m von einander entfernt.	—
B ₉	Wadegawara No. 2		—
B ₁₀			—
C ₁	Ginsentō-kami-no-yu		+
C ₂	Ginsentō-huru-yu	früher +,	—
C ₃	Ginsentō-naka-no-yu		+
C ₄	Ginsentō-simo-no-yu	kalt und deshalb als besonders schmackhaft beliebt.	—
C ₅	Ōsiba		—
C ₆			—
D ₁ bis D ₁₂		entspringen aus Spalten im Flussbett des Yuzawa, das aus nacktem festem Granit besteht.	
E ₁	Wada-matuba-kōsen	dicht an Kamasegawa.	+
E ₂	Siozawa-kuromori-kōsen		+
W ₁		Flusswasser aus Hontanigawa bei A.	
W ₂		Flusswasser aus Kamasegawa bei E.	

Erklärung zu Tabelle 1.

Gr. = Gruppenbenennung der Quelle.

Name = Quellbezeichnungen, die z.T. volkstümlicher Herkunft sind und von *Nakai* gebraucht wurden.

Bad = Auswertung der Quelle für Bad (+) oder Quelle unbenutzt (—).

Tabelle 2. Austrittstemperaturen der Mineralquellen von Masutomi, °C.
(Die eingeklammerten Zahlen bezeichnen den Tag, an dem
jeweils eine Wasserprobe entnommen wurde.)

	Okt. 1936 ⁽²⁾ (Apr. 1937)	Juli 1939	Okt. 1940	Okt. 1941	Mai 1942
A ₁	31.0	31.0 (7)	31.7 (17)	31.5 (19)	31.4 (20)
A ₂	28.0	29.6 (6)	32.3 (17)	30.0 (18)	—
A ₃	30.8	30.1 (6)	30.7 (17)	30.5 (18)	29.4 (20)
A ₄	27.0	28.0 (7)	27.5 (17)	—	—
A ₅	(11.2)	14.7 (11)	13.5 (20)	13.0 (17)	—
A ₆	—	—	—	—	27.0 (16)
B ₁	24.0	24.0 (10)	24.2 (20)	24.5 (19)	24.3 (20)
B ₂	20.0	20.9 (10)	19.0 (20)	19.0 (19)	—
B ₃	20.0	26.0 (10)	16.5 (20)	17.0 (19)	—
B ₄	22.0	21.2 (10)	22.3 (18)	21.2 (19)	20.6 (20)
B ₅	23.2	23.6 (10)	21.3 (18)	22.0 (19)	—
B ₆	—	21.4 (10)	20.0 (18)	19.0 (19)	—
B ₇	25.0	24.5 (8)	25.0 (18)	24.7 (19)	24.1 (20)
B ₈	18.0	22.0 (9)	19.0 (18)	18.3 (21)	—
B ₉	19.5	20.5 (9)	18.8 (18)	15.8 (21)	—
B ₁₀	—	—	—	12.0 (21)	—
C ₁	28.5	28.5 (10)	25.9 (19)	25.0 (21)	—
C ₂	31.0	30.0 (10)	31.3 (19)	31.3 (21)	—
C ₃	22.0	27.0 (10)	21.9 (19)	22.0 (21)	—
C ₄	17.0	— (10)	19.4 (19)	17.8 (21)	18.0 (20)
C ₅	22.5	22.6 (10)	23.2 (19)	22.5 (20)	—
C ₆	—	29.1 (10)	22.0 (19)	25.2 (20)	—
D ₁	—	11.3 (9)	11.2 (20)	—	—
D ₂	(11.5)	14.7 (9)	12.0 (20)	—	—
D ₃	(13.7)	11.8 (9)	11.2 (20)	—	—
D ₄	(18.5)	11.9 (9)	—	—	—
D ₅	—	14.1 (9)	—	—	—
D ₆	—	14.4 (9)	14.0 (20)	—	—
D ₇	(13.7)	17.8 (9)	18.0 (20)	—	—
D ₈	—	18.0 (9)	—	—	—
D ₉	—	15.5 (9)	—	—	—
D ₁₀	—	14.0 (9)	—	—	—
D ₁₁	—	16.5 (9)	—	—	—
D ₁₂	—	16.1 (9)	—	—	—
E ₁	13.0	11.5 (10)	12.5 (19)	12.0 (18)	—
E ₂	12.0	—	—	11.2 (18)	—
W ₁	—	16.0 (8)	10.9 (20)	9.9 (17)	9.1 (20)
W ₂	—	—	13.3 (19)	10.0 (18)	—

kennbare Niederschläge ausgeschieden haben. Die Grösse des Fehlers kann nicht einwandfrei bestimmt werden.

5. *Chlor.* Wir titrierten je 10 ccm der Wasserprobe mit etwa n/10-Silbernitratlösung gegen Kaliumchromat als Indikator. Die Resultate enthält Tabelle 6.

6. *Sulfat.* Sulfat wurde kolorimetrisch mit Pulfrich-Photometer (C. Zeiss) bestimmt. Dabei wurde die Konzentration des aus Bariumchromatbrei durch 25 ccm Untersuchungswasser befreiten Chromat-Ions

Tabelle 3. pH-Werte der Quellwässer von Masutomi.

	Juli 1939	Okt. 1940	Okt. 1941	Mai 1942
A ₁	6.3	6.2	6.2	6.2
A ₂	6.4	6.3	—	—
A ₃	6.4	6.5	—	—
A ₄	6.3	6.3	—	—
A ₅	—	6.0	—	—
A ₆	—	—	—	6.4
B ₁	—	6.6	7.0	—
B ₂	—	6.0	6.1	—
B ₃	—	6.2	6.3	—
B ₄	6.0	5.9	5.9	—
B ₅	6.4	6.5	6.5	—
B ₆	—	6.0	6.1	—
B ₇	6.3	6.3	6.3	—
B ₈	6.5	6.5	6.3	—
B ₉	6.2	6.0	6.1	—
B ₁₀	—	—	5.6	—
C ₁	6.5	6.9	6.9	—
C ₂	6.5	6.5	6.5	—
C ₃	6.7	6.7	6.5	—
C ₄	—	6.4	6.4	—
C ₅	6.4	6.4	—	—
C ₆	6.6	6.5	—	—
D ₁	3.8	—	—	—
D ₂	5.4	5.4	—	—
D ₃	3.8	3.8	—	—
D ₄	4.0	—	—	—
D ₅	4.0	—	—	—
D ₆	5.8	5.6	—	—
D ₇	6.0	5.6	—	—
D ₈	5.9	—	—	—
D ₉	5.5	—	—	—
D ₁₀	3.7	—	—	—
D ₁₁	5.6	—	—	—
D ₁₂	5.5	—	—	—
E ₁	6.4	6.5	—	—

kolorimetriert. Die Resultate sind in Tabelle 7 enthalten. Nur die Zahlen in der Reihe vom Oktober 1941 wurden gravimetrisch bestimmt.

7. *Gesamtkohlensäure.* Um die Gesamtkohlensäure in natürlichen Gewässern an Ort und Stelle zu bestimmen, titriert man Bikarbonat-Kohlensäure mit einer titrierten Salzsäure gegen Methylorange und dann freie Kohlensäure mit einer titrierten Natriumkarbonatlösung gegen Phenolphthalein. Bei letzterem Verfahren ist es nicht selten schwierig oder fast unmöglich, einen scharfen Farbumschlag zu erzielen. Infolgedessen leidet die Genauigkeit bei der Bestimmung der Gesamtkohlensäure beträchtlich. Daher entwickelten wir die folgende Analysenmethode: Man bringt 25 ccm Probenwasser in einen 100 ccm-Kolben, dessen Hals an zwei Stellen verengt ist. Nachdem Bariumhydroxyd-

lösung im Überschuss durch Filtrierpapier zugesetzt wurde, schmilzt man den Hals des Kolbens zu, wodurch eine Ampulle entsteht. Diese wird im Laboratorium weiter verarbeitet. In der Ampulle setzt sich die Gesamtkohlensäure in Bariumkarbonat um. Falls daneben Sulfat-Ion auftrat, so entsteht auch Bariumsulfat. Auch ursprünglich vorhandenes Calciumkarbonat wird unter Bildung von Calciumhydroxyd vollständig in Bariumkarbonat umgewandelt. Diese Vorgänge konnten wir mittels spektroskopischer Analyse des im Kontrollversuche hergestellten Niederschlags bestätigen. Der Bariumniederschlag wird abfiltriert und mit kohlensäurefreiem Wasser gewaschen. Zum Rückstande fügt man im Überschuss verdünnte Salzsäure hinzu. Das aus dem Filtrat mit Schwefelsäure gefällte und abfiltrierte Bariumsulfat wird gewogen. Die Gesamtkohlensäure im Probenwasser ist damit ohne weiteres zu berechnen.

Tabelle 5. Abdampfrückstandswerte
der Quellwässer von Masutomi, g/l.

		Okt. 1936(?)	Juli 1939	Okt. 1941
Tabelle 4. Ionentabelle der Quelle B ₁ ⁽¹⁾ , g/l.		A ₁	7.49	7.56
		A ₂	8.53	7.50
		A ₃	8.99	—
		A ₄	9.42	—
		A ₅	—	6.78
Kationen	B ₁	7.25	16.20	7.28
K ⁺	0.13861	B ₂	4.89	4.41
Na ⁺	2.45086	B ₃	2.92	4.14
NH ₄ ⁺	0.00107	B ₄	3.62	2.94
Ca ⁺⁺	0.23843	B ₅	8.56	8.42
Mg ⁺⁺	0.02100	B ₆	7.65	6.35
Fe ⁺⁺	0.00141	B ₇	9.69	9.85
		B ₈	3.25	7.10
		B ₉	7.12	7.32
		C ₁	9.64	9.35
Anionen		C ₂	10.30	11.18
Cl ⁻	3.16877	C ₃	9.72	10.35
SO ₄ ⁻⁻	0.47317	C ₄	9.78	9.95
HCO ₃ ⁻	1.48800	C ₅	9.40	9.16
		C ₆	—	9.78
		D ₁	—	—
		D ₂	—	—
HBO ₂	0.17028	D ₃	—	—
H ₂ SiO ₃	0.16880	D ₄	—	—
		D ₅	—	—
Freie		D ₆	—	—
		D ₇	—	—
Kohlensäure	0.26617	D ₈	—	—
		D ₉	—	—
		D ₁₀	—	—
		D ₁₁	—	—
		D ₁₂	—	—
		E ₁	13.34	13.90
		E ₂	4.46	4.81

Wenn man daneben die Bikarbonat-Kohlensäure mit titrierter Salzsäure gegen Methylorange titriert, so kann man freie und Bikarbonat-Kohlensäure trennen. Nach genanntem Verfahren ermittelte Werte der Gesamtkohlensäure sind in Tabelle 8 aufgeführt.

8. *Radium*. Für die Bestimmung von Radium wurde der im Jahre 1936 und 1937 von *Nakai* benutzte Apparat verwendet. Radium wurde nach der Radon-Methode mit Hilfe des Präzisionselektroskops von Riken (Physikalisch-chemisches Institut in Tokio) gemessen. Die Analysenmethode ist ausführlich in der Mitteilung von *Nakai* beschrieben.⁽²⁾ Ein kleiner Unterschied besteht jedoch darin, dass wir die im Untersuchungswasser entstandenen Niederschläge mit Natriumkarbonat schmolzen und dann in Salzsäure lösten und diese Lösung zusammen mit dem Quellwasser in eine Curie-Flasche einschmolzen, während *Nakai* das Quellwasser und

Tabelle 6. Chlor-Gehalt der Quellwässer von Masutomi, g/l.

	Juli 1939	Okt. 1940	Okt. 1941
A ₁	3.195	3.306	3.212
A ₂	3.786	4.207	3.244
A ₃	3.931	4.034	—
A ₄	3.934	4.037	—
A ₅	2.599	3.289	2.574
B ₁	3.360	3.576	3.350
B ₂	1.935	2.101	1.991
B ₃	1.692	1.910	1.774
B ₄	1.365	1.742	1.294
B ₅	3.722	4.129	3.779
B ₆	2.731	2.740	2.825
B ₇	4.183	4.236	4.231
B ₈	3.032	3.181	3.011
B ₉	—	2.056	3.288
C ₁	4.488	4.564	4.175
C ₂	4.601	4.626	4.427
C ₃	4.399	4.567	4.574
C ₄	4.225	4.606	4.596
C ₅	4.225	4.198	4.032
C ₆	4.413	4.340	4.282
D ₂	—	0.046	—
D ₆	—	0.019	—
D ₇	—	0.399	—
E ₁	—	7.656	6.963
E ₂	—	—	2.141
W ₁	0.0167	0.0070	—
W ₂	—	0.0169	—

die Niederschläge in zwei Curie-Flaschen getrennt einnahm. Die gewonnenen Ergebnisse sind in Tabelle 9 enthalten.

9. *Radon*. Den Radongehalt der Quellwässer massen wir mittels IM-Fontaktoskops an der Quelle selbst. Wenn das Quellwasser grosse Mengen Radon enthielt, wurde die Wasserprobe mit destilliertem, radonfreiem Wasser so verdünnt, dass die Konzentration des Radons etwa 40×10^{-10} Curie/1 betrug. Die von uns so ermittelten Werte sind zusammen mit denen *Ishizu's* und *Nakai's* in Tabelle 10 angeführt.

Es ist selbstverständlich, dass der Radongehalt eines Quellwassers durch etwaige Niederschläge mehr oder weniger verändert werden kann. Die in der Tabelle 10 für die Quellen A₄, B₉ und C₄ erkennbaren grossen Schwankungen des Radongehaltes

überschreiten jedoch den Umfang so verursachter Veränderungen weitaus. In nächster Umgebung genannter drei Quellen liegt eine Anzahl weiterer Austritte. Wenn man aus den Radongehalten und Schüttungsmengen aller benachbarten Quellen die gesamte Radon-Förderung in der Zeiteinheit berechnet, so dürfte unseres Erachtens dieser Wert immer annähernd konstant bleiben.

10. *Schweres Wasser*. Wir bestimmten die Dichteunterschiede zwischen vollständig gereinigten Quellwässern und dem in gleicherweise gereinigten Standard-Leitungswasser der Stadt Tokio mittels Schwimmermethode⁽⁵⁾ und zeigen die Resultate in Tabelle 11.

11. *Vanadium, Chrom und Molybdän*. Der Vanadium-, Chrom- und Molybdän-Gehalt der Quellen A₂ und B₇ wurde mit der Sandell'schen kolorimetrischen Methode bestimmt. In beiden Proben wurden ungefähr 50 γ Vanadium pro Liter Wasser nachgewiesen, während Chrom und Molybdän noch nicht einmal in Spuren zu finden waren. Wenn die Analysenresultate der genannten Elemente bei vielen bisher untersuchten Wässern statistisch betrachtet werden, so kommen wir zum Schlusse, dass

(5) Y. Shibata, K. Noguchi und O. Kaneko, dies Bulletin, 14 (1939), 274.

Tabelle 7. Sulfat-Gehalt der Quellwässer von Masutomi, g/l.

	Juli 1939	Okt. 1940	Okt. 1941
A ₁	0.535	0.572	0.569
A ₂	0.535	0.583	0.481
A ₃	0.576	0.576	—
A ₄	0.705	0.759	—
A ₅	0.800	0.759	0.794
B ₁	0.478	0.510	0.484
B ₂	0.282	0.310	0.279
B ₃	0.248	0.310	0.251
B ₄	0.180	0.246	0.183
B ₅	0.510	0.556	0.549
B ₆	0.407	0.368	0.401
B ₇	0.535	0.571	0.667
B ₈	0.441	0.431	0.478
B ₉	0.330	0.288	0.465
C ₁	0.556	0.556	0.562
C ₂	0.583	0.572	0.605
C ₃	0.551	0.535	0.610
C ₄	0.556	0.545	0.570
C ₅	0.535	0.530	0.569
C ₆	0.561	0.514	0.529
D ₂	—	0.078	—
D ₃	—	0.048	—
D ₆	—	0.052	—
D ₇	—	0.320	—
E ₁	0.006	0.003	0.000
E ₂	—	—	0.003
W ₁	0.024	0.016	—
W ₂	0.006	—	—

Tabelle 8. Gesamtkohlensäure-Gehalt der Quellwässer von Masutomi im Okt. 1940, g/l.

A ₁	1.447
A ₂	1.934
A ₃	1.628
A ₄	0.756
A ₅	0.887
B ₁	0.833
B ₂	0.022
B ₃	0.775
B ₄	1.767
B ₅	1.098
B ₆	1.194
B ₇	1.202
B ₈	—
B ₉	0.964
C ₁	1.040
C ₂	0.866
C ₃	0.816
C ₄	1.577
C ₅	0.527
C ₆	1.278
D ₃	0.019
D ₆	0.101
D ₇	1.089
E ₁	2.615

Tabelle 9. Radiumgehalt der Quellwässer von Masutomi.

	Okt. 1936 ⁽²⁾ (Apr. 1937)		Juli 1939	
	10 ⁻¹² g/l	10 ⁻¹² g Ra/g Abdampfrückstand	10 ⁻¹² g/l	10 ⁻¹² g Ra/g Abdampfrückstand
A ₁	29.30	3.91	21.97	2.64
A ₂	64.53	7.56	24.61	2.62
A ₃	29.39	3.27	30.31	3.14
A ₄	32.62	3.46	26.95	8.78
A ₅	(39.16)	—	28.71	7.09
B ₁	6.22	0.86	7.73	0.48
B ₂	2.46	0.27	0.58	0.13
B ₃	2.46	0.84	1.74	1.74
B ₄	0.77	0.21	1.46	0.39
B ₅	26.01	3.04	14.06	1.57
B ₆	6.56	0.86	5.56	0.83
B ₇	35.65	3.68	18.89	1.86
B ₈	6.76	2.05	8.20	1.46
B ₉	11.62	1.63	8.20	1.12
B ₁₀	—	—	0.58	0.06

Tabelle 9.—(Fortsetzung)

	Okt. 1936 ^(*) (Apr. 1937)		Juli 1939	
	10 ⁻¹² g/l	10 ⁻¹² g Ra/g Abdampfrückstand	10 ⁻¹² g/l	10 ⁻¹² g Ra/g Abdampfrückstand
C ₁	7.35	0.76	5.68	—
C ₂	9.39	0.91	6.50	0.58
C ₃	0.43	0.05	0.58	0.06
C ₄	3.42	0.35	2.05	0.18
C ₅	2.68	0.28	1.93	—
C ₆	—	—	7.83	0.77
D ₁	—	—	0.46	2.1
D ₂	(0.00)	—	0.46	1.3
D ₃	(0.00)	—	<0.5	—
D ₄	(1.76)	—	<0.5	—
D ₅	—	—	<0.5	—
D ₆	—	—	<0.5	—
D ₇	(71.81)	—	1.74	1.10
D ₈	—	—	1.22	0.73
D ₉	—	—	<0.5	—
D ₁₀	—	—	0.58	0.19
D ₁₁	—	—	1.04	0.28
D ₁₂	—	—	1.33	3.24
E ₁	82.66	6.19	84.36	5.60
E ₂	11.57	2.60	—	—

Tabelle 10. Radongehalt der Quellwässer von Masumi, 10⁻¹⁰ Curie/l.

	Aug. 1914 ⁽¹⁾	Okt. 1936 ^(*) (Apr. 1937)	Juli 1939	Okt. 1940	Okt. 1941	Mai 1942
A ₁	8.0	11.9	7.5	5.2	8.8	8.0
A ₂	—	17.8	15.7	15.3	16.0	—
A ₃	—	14.5	12.6	9.5	9.3	—
A ₄	—	93.2	58.6	15.4	—	—
A ₅	—	—	—	—	—	—
A ₆	—	—	—	—	—	600.
B ₁	1430.	1203.	—	—	—	—
B ₂	859.	701.	—	—	—	—
B ₃	—	39.5	—	—	—	—
B ₄	2140.	2097.	—	2320.	2060.	2020.
B ₅	—	27.1	—	17.4	26.9	—
B ₆	—	—	849.	939.	997.	—
B ₇	—	32.4	33.0	32.8	37.1	38.9
B ₈	2390.	2139.	—	2470.	2380.	1530.
B ₉	3010.	4889.	3970.	4370.	2240.	265.
B ₁₀	—	—	—	—	945.	—
C ₁	—	378.	—	111.	312.	—
C ₂	375.	556.	—	481.	414.	—
C ₃	—	42.0	—	116.	73.5	—
C ₄	—	153.	—	830.	1250.	1490.
C ₅	1010.	1318.	—	1550.	1190.	—
C ₆	—	—	—	62.2	67.7	—
D ₆	—	—	—	9.6	—	—
D ₇	—	(58.4)	—	10.1	—	—
E ₁	—	17.4*	—	12.7	—	—
E ₂	—	7.1*	—	—	—	—

* Im Laboratorium bestimmte Werte.

Tabelle 11. Dichteunterschiede zwischen den Quellwässern von Masutomi und dem Standard-Leitungswasser der Stadt Tokio, γ .

	Juli 1939	Okt. 1940
A ₁	+0.0 ₄	$\pm 0.0_0$
A ₂	+0.5 ₅	-0.3 ₈
A ₃	+0.5 ₅	+0.4 ₃
A ₄	+0.2 ₁	+0.2 ₆
A ₅	+0.1 ₇	-0.1 ₃
B ₁	-0.3 ₈	+0.2 ₆
B ₂	-0.5 ₈	-0.0 ₉
B ₃	-1.0 ₅	-0.0 ₄
B ₄	-0.3 ₀	-0.1 ₃
B ₅	+0.5 ₁	-0.0 ₉
B ₆	-0.1 ₇	-0.1 ₃
B ₇	+0.2 ₉	-0.2 ₁
B ₈	—	$\pm 0.0_0$
B ₉	-0.0 ₄	-0.3 ₄
C ₁	+0.7 ₇	+0.2 ₁
C ₂	—	+0.2 ₅
C ₃	+0.7 ₂	-0.0 ₉
C ₄	+0.4 ₇	-0.5 ₁
C ₅	+0.0 ₄	-0.0 ₄
C ₆	+0.1 ₇	+0.3 ₀
E ₁	—	+0.3 ₄
W ₁	-0.4 ₃	-0.6 ₀
W ₂	—	-0.8 ₉

Vanadium und Chrom in mineral-sauren Quellwässern höhere Konzentrationen aufweisen, während sie in nicht sauren Wässern gewöhnlich nur in geringsten Mengen vorkommen. Die Mineralquellen von Masutomi gehören zu den vanadium-, chrom- und molybdän-armen Mineralquellen, wie man aus Tabelle 12 ersieht.

Nach der kürzlichen Revision K. Kimura's betragen die Clarke'schen Zahlen für Cr 0.02, für V 0.015 und für Mo 1.3×10^{-3} .⁽⁶⁾ Danach liegt also der Gehalt der Quellwässer von Masutomi an diesen Elementen beträchtlich niedriger als ihre Clarke'sche Zahl.

12. Kupfer, Blei und Zink. Nur in Spuren auftretende Schwermetalle werden nach der polarographischen Methode bestimmt.⁽⁷⁾ Die Mengen von Kupfer, Blei, Zink und verschiedenen anderen Schwermetallen in Quellwässern sind meistens sehr gering. Nach der polarographischen Methode können wir daher diese Elemente nicht unmittelbar genau so bestimmen, wie dies für die Alkalimetalle mittels der Majer'schen

Tabelle 12. Vanadium-, Chrom- und Molybdän-Gehalt der Quellwässer von Masutomi.

	mg/l			% des Abdampfrückstands		
	V	Cr	Mo	V	Cr	Mo
Durchschnittswerte von 32 japanischen Quellwasserproben	0.122	0.011	0.0025	0.0055	0.00045	0.000029
A ₂ und B ₇	0.05	0.00	0.000	0.0006	0.0000	0.00000

Methode geschehen kann.⁽⁸⁾ Vielmehr macht sich stets folgendes Extraktions- und Konzentrierungsverfahren auf der Basis von Diphenylthiocarbazon (Dithizon) erforderlich.⁽⁹⁾ Nach diesem Verfahren wurden zusammen 19 Wasserproben vom Oktober 1936 und vom Juli 1939 bearbeitet. Kupfer und Blei waren nicht mit Sicherheit nachzuweisen. Wir müssen daraus folgern, dass der Gehalt an Kupfer und Blei in den

(6) K. Kimura, revidiert 1938, noch nicht veröffentlicht.

(7) K. Heller, G. Kuhla und F. Machek, *Mikrochem.*, **23** (1937), 78.

(8) V. Majer, *Z. anal. Chem.*, **92** (1933), 321.

(9) K. Kuroda, dies Bulletin, **15** (1940), 88, 153; **16** (1941), 69.

untersuchten Proben aus Masutomi—wie überhaupt in Quellwässern—unter $50\gamma/1$ liegt. Dass jedoch ausnahmsweise auch ein höherer Kupfergehalt vorkommen kann, zeigten unsere Untersuchungen einer in der weiteren Umgebung von Masutomi am Ufer des Kitanogawa (nahe dem Mizukaki-Berge) entspringenden Mineralquelle. In ihrer Schüttung wiesen wir mittels der Dithizon-Methode einen ungefähren Kupfergehalt von $100\gamma/1$ nach.⁽¹⁰⁾ Dagegen ergaben alle Proben schöne polarographische Zink-„Stufen“, die quantitative Bestimmungen ermöglichten. Die Ergebnisse bringt Tabelle 13. Für die Bearbeitung der Proben vom Oktober 1940 wurde folgende Grundleistung benutzt: $n/10$ -Ammoniumacetat, $n/40$ -Kaliumrhodanid, pH 4.6.

Tabelle 13. Zink-Gehalt der Quellwässer von Masutomi.

	Okt. 1936		Juli 1939		Okt. 1940
	$\gamma/1$	% des Abdampfrückstands	$\gamma/1$	% des Abdampfrückstands	$\gamma/1$
A ₁	80	0.0011			
A ₂	26	0.0003			
B ₃	35	0.0012			
B ₄	215	0.0060			
B ₇	39	0.0004			
B ₉	64	0.0009			
C ₂	80	0.0008			
C ₃	78	0.0008			
D ₁			224	0.10	102
D ₂			88	0.025	
D ₃			164	0.060	
D ₄			102	0.051	
D ₅			126	0.11	
D ₆			80	0.021	
D ₇			102	0.0065	40
D ₈			60	0.0036	
D ₉			64	0.0042	
E ₁	113	0.0008			

Erörterung der Ergebnisse. (1) *Langfristige Konzentrationsveränderungen einiger Elemente.* Unsere Beobachtungen in den letzten 3 bis 4 Jahren führen uns zu der Auffassung, dass sich chemische Eigenschaften der Quellschüttungen keineswegs unabhängig von einander sondern vielmehr in klar ausgeprägten wechselseitigen Abhängigkeiten—und zwar sowohl hinsichtlich der einzelnen Elemente wie auch hinsichtlich der einzelnen Quellen und Quellgruppen—verändern. Für die Jahre 1939 bis 1941 zeigt Abb. 3 für die einzelnen Quellgruppen ermittelte Durchschnittswerte des Chlor- und Sulfat-Gehalts sowie des Dichtewertes und daneben—mit unterbrochenen Linien—die entsprechenden Werte sowie die festgestellten Schüttungsmengen der Quelle B₇.

Die Schüttungsmenge von B₇ stieg vom Juli 1939 bis zum Oktober 1940 um 31% an. Im gleichen Zeitraume fiel der Dichtewert ab. Der

(10) K. Kuroda, dies Bulletin, 15(1940), 439.

Dichtewert aller Quellwässer von Masutomi ist stets grösser als der des Flusswassers (Tab. 11). Die in dieser Gegend aus der Tiefe emporsteigenden Schüttungen enthalten grössere Anteile schweren Wassers als die dortigen Oberflächengewässer. Der als Träger der Wärme und der Kohlensäure vermutlich aus grösster Tiefe stammende Schüttungsanteil darf mengenmässig als konstant angesehen werden. Danach ist die Beimischung von Wässern aus geringeren Tiefen im Oktober 1940 wahrscheinlich grösser als im Juli 1939. Die Niederschlagssumme für den Juli 1939 ist grösser als die für den Oktober 1940. Dahingegen ist die Schüttungsmenge von B₇ im Oktober 1940 grösser als im Juli 1939. Dieser scheinbare Widerspruch beruht darauf, dass die Wirkungen von Niederschlägen auf eine Quelle eine mehr oder weniger grosse Verzögerung erleiden. Denn das Niederschlagswasser benötigt eben eine gewisse Zeit, um in die Tiefe zu sinken und sich dort dem Quellstrome beizumischen, mit dem es dann wieder an der Oberfläche erscheint.

Der Gehalt der Quellwässer an Chlor und Sulfat nimmt vom Juli 1939 bis zum Oktober mit einziger Ausnahme bei der Gruppe C zu. Vom Oktober 1940 bis zum Oktober 1941 nimmt der Sulfat-Gehalt zu, während der Chlor-Gehalt im gleichen Zeitraume abnimmt. Die einzige Ausnahme bildet dabei die Gruppe A. Dass der zeitliche Verlauf des Chlor- und Sulfat-Gehaltes nach der Zeit übereinstimmende oder entgegengesetzte Neigung zeigt, deutet wieder eine Verzögerung und den Unterschied der Herkunft der beiden Bestandteile in Quellwässern an.

Um diesen scheinbaren Widerspruch zu erklären, scheint es angebracht, hier folgende hydrologische Anmerkungen, die uns von G. H. Schwabe anlässlich einer mündlichen Erörterung über unsere gemeinsamen Untersuchungen in Masutomi in kurzer Fassung zur Verfügung gestellt wurden, wiederzugeben:

„Reihenbeobachtungen über quantitative Veränderungen einzelner physikalischer und chemischer Faktoren einer Quelle oder einer Quellgruppe führen erfahrungsgemäss häufig zu scheinbar widersprechenden Ergebnissen. Ein solcher hydrologisch aufschlussreicher Fall liegt hier vor. Die von den Verfassern festgestellten quantitativen Veränderungen

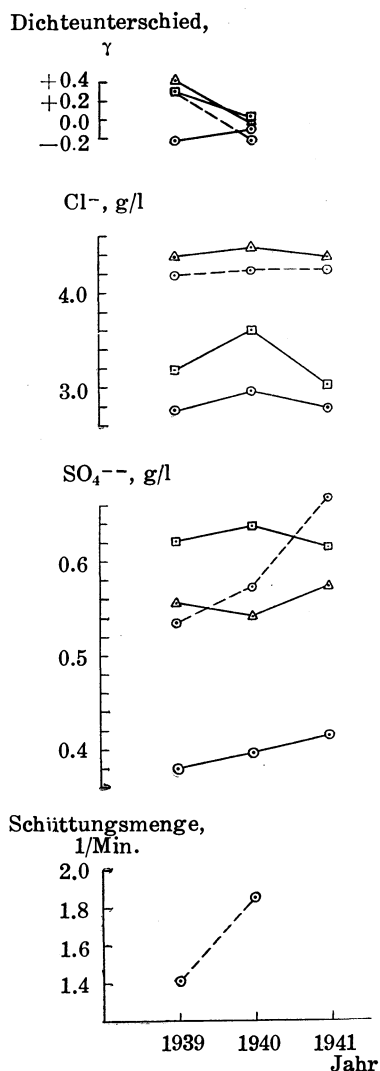


Abb. 3.

des Dichtewerts und der Gehalte an Chlor und Sulfat sind zweifellos letztenendes auf Niederschlagswirkungen zurückzuführen. Dass diese Veränderungen nicht gleichsinnig zu verlaufen scheinen, kann nur im hydrologischen Charakter des Quellgebiets und im Quellmechanismus selbst begründet sein. In Kürze ist dazu folgendes zu erwägen:

1. Dass sich Niederschlagswirkungen auf einzelne Faktoren einer Quellschüttung nicht gleichzeitig und nicht im gleichen Masse auswirken, ist durch Beobachtungen mehrfach bestätigt. Ein theoretisch einfaches, in Chile beobachtetes Beispiel, über das demnächst ausführlicher berichtet werden soll, bieten die Thermen von Puyehue (Provinz Osorno). Im Boden absinkendes Niederschlagswasser dringt in verhältnismässig grösser Tiefe in den thermalen Quellstrom ein. Dieser Quellstrom durchquert in vielfach verzweigtem Gerinne, also weiträumig, ein Trümmergestein. Im Austritt ist daraufhin anfangs eine Steigerung der Schüttungsmenge bei gleichbleibender oder u.U. gar ansteigender Temperatur und unveränderten pH- und Alkalitätswerten zu beobachten. Wahrscheinlich treten in diesem ersten Stadium auch keine nennenswerten chemischen Änderungen ein, weil das in der Tiefe zudringende Fremdwasser zuerst nur druckerhöhend auf den Quellstrom wirkt und das im klüftigen Gestein befindliche Thermalwasser in den aufsteigenden Strom hineindrängt. Erst später machen sich, meist mit absinkender Temperatur verbunden, Vermischungserscheinungen beider Wässer durch chemische Veränderungen der Schüttung bemerkbar.

Wenn somit erfahrungsgemäss und theoretisch wohl begründet die Wirkungsverzögerungen für einzelne Schüttungsfaktoren verschieden sind, ist es kaum möglich aus zahlenmässig kleinen Serien ein klares Bild vom einzelnen Quellmechanismus zu gewinnen. Vor allem bleibt, wenn die zeitlichen Abstände der Beobachtungstermine grösser sind, verborgen, welche Veränderungen der einzelne Faktor zwischen diesen Terminen durchläuft.

2. Unter Beachtung vorstehender Verhältnisse könnte man in hydrologischer Hinsicht die Befunde der Verfasser etwa folgendermassen deuten: Absinkendes Niederschlagswasser verdrängt in grösserer Tiefe aus einem verzweigten Spaltensystem das dort befindliche Quellstromwasser. Durch Druckerhöhung steigt die Schüttungsmenge, ohne dass chemische Veränderungen eintreten. Sodann mischt sich in der gleichen Zone dem Quellstrome das Fremdwasser bei, nachdem es aus Quellstromwasser stammendes und vielleicht adsorptiv an das Gestein gebundenes Chlor in sich aufgenommen hat. (Man muss ferner u.U. auch an eine Chloranreicherung infolge Verdampfung denken, der im klüftigen oder spaltenreichen Gestein längere Zeit ruhendes Quellwasser ausgesetzt sein kann.) Eine unter solchen Umständen stattfindende Mischung hat zur Folge, dass sich der Dichtewert der Schüttung stärker verringert als der Chlor-Gehalt. Wenn nun letzterer sogar eine gewisse Erhöhung zeigt, so ist zu beachten, dass infolge erhöhten Druckes im Quellstrom (grössere Schüttungsmenge) sonst in geringerer Tiefe zudringendes Fremdwasser nunmehr weitgehend ausgeschaltet wird.“

(2) *Beziehungen zwischen den Gehalten an verschiedenen Elementen.* Die Parallelität zwischen Chlor-Gehalt und Abdampfrückstand leuchtet in Abb. 4 unmittelbar ein. Dabei ist zu beachten, dass, wie bereits erwähnt

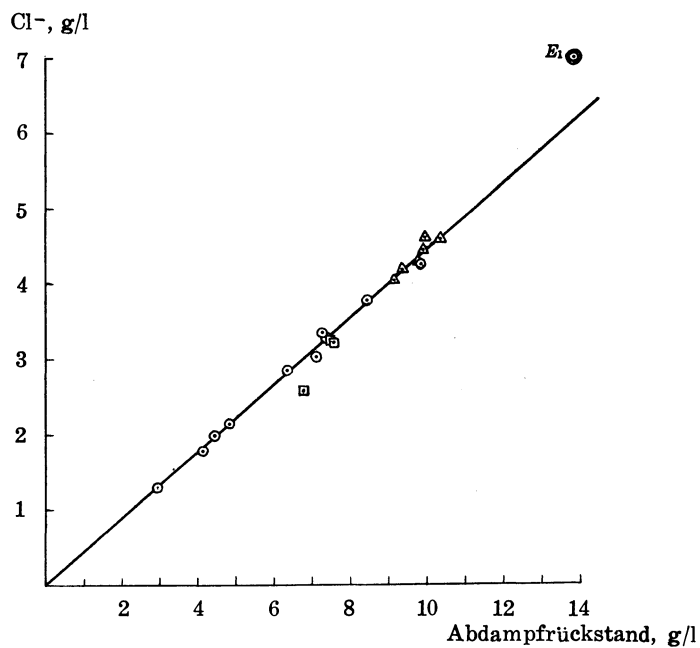


Abb. 4. Abdampfrückstand und Chlor-Gehalt im Okt. 1941.

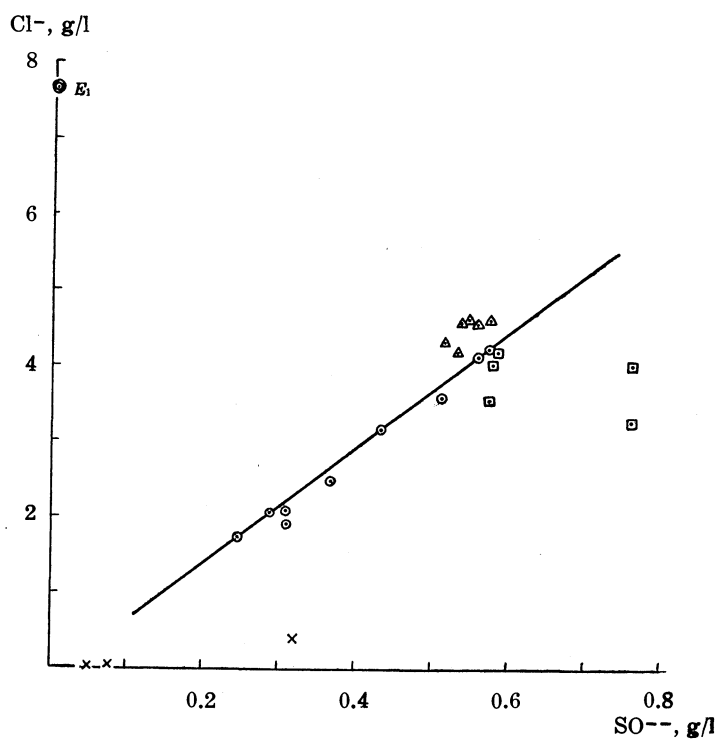


Abb. 5. Sulfat- und Chlor-Gehalt im Okt. 1940.

wurde, die Werte für den Abdampfückstand keinen Anspruch auf hohe Genauigkeit erheben können. Wie sich jedoch trotzdem ergibt, dann in Masutomi der Chlor-Gehalt als ein Massstab für die Gesamtkonzentration des Quellwassers betrachtet werden.

Auch zwischen Chlor- und Sulfat-Gehalt besteht, wie Abb. 5 belegt, eine geradlinige, wenn auch nicht so streng ausgeprägte Proportion. Am weitesten weichen die Gruppen A und D durch ihren im Vergleich mit dem Chlor-Gehalte unverhältnismässig hohen Sulfat-Gehalt vom durchschnittlichen Werte der Proportion ab. Man muss daraus schliessen, dass wenigstens ein Teil des Sulfat-Gehaltes anderen Ursprungs ist als der Chlor-Gehalt. Nur so wird verständlich, warum die verhältnismässig chlor-reiche Schüttung von E₁ fast kein Sulfat enthält.

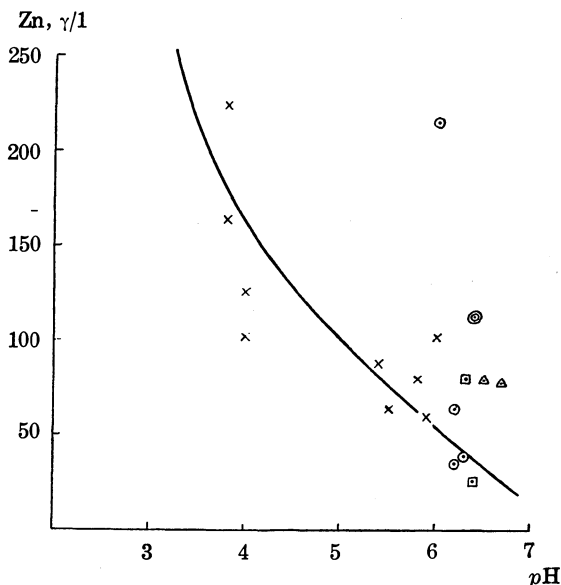


Abb. 6. pH-Wert und Zink-Gehalt.

Der Zink-Gehalt nimmt in Masutomi im allgemeinen mit fallenden pH der Schüttung zu. Die Abweichungen von dieser Regel können, wie Abb. 6 zeigt, ziemlich grosse Ausmasse erreichen. Durch unverhältnismässig hohen Zink-Gehalt fällt, wie auch Tabelle 13 zeigt, die Gruppe D auf. Während bei den anderen Gruppen der Sulfat-Gehalt 0 bis 9.1 % des Abdampfückstandes beträgt, enthalten die Schüttungen der Gruppe D 13 bis 22%. Daraus muss geschlossen werden, dass zwischen der Herkunft des Sulfats und der des Zinks ursächliche Zusammenhänge bestehen oder dass sogar beide

gleicher Herkunft sind. Es besteht durchaus die Möglichkeit, dass in dieser Gegend in verhältnismässig geringer Tiefe schwefel- und zinkhaltige Erze vorkommen. Durch Nachweis solcher Erze wäre unsere Annahme leicht zu bestätigen.

Zwischen Chlor- und Radiumgehalt einerseits und den Dichtewerten der Quellwässer andererseits bestehen, wie die Abb. 7 und 8 erkennen lassen, gerade Proportionen. Deshalb muss auch zwischen den Gehalten an Chlor und Radium ein entsprechendes Verhältnis bestehen. Wie Abb. 9 zeigt, ist diese Proportion jeweils nur innerhalb der einzelnen Quellgruppe nachzuweisen. Man muss sich stets vor Augen halten, dass die absoluten Mengen des Radiums im Quellwasser—vor allem auch im Vergleich mit den anderen bearbeiteten Bestandteilen—ausserordentlich gering sind. Infolgedessen müssen sich gerade auf den Radiumgehalt jene Faktorenkomplexe verhältnismässig sehr stark auswirken, die den chemischen Charakter eines Quellwassers vorzüglich bestimmen: 1. Die ursprünglichen chemischen und physikalischen Eigenschaften des „Tiefen-

wassers“, zu denen zweifellos der Radiumgehalt gehört und 2. die chemischen und physikalischen Eigenschaften der vom Quellstrom durchquerten Schichten, die den ursprünglichen Charakter des Wassers abwandeln. Diese Überlegung erklärt, warum gerade beim mengenmässig so geringen Radiumgehalt örtlich bedingte und damit für die einzelnen Quellgruppen eigentümliche Abwandlungen sichtbar werden müssen.

In gleicher Weise ist der aus Abb. 8 ersichtliche Sachverhalt zu deuten. Es zeigt sich hier, dass ein höherer Radiumgehalt einen höheren Dichtewert des Wassers voraussetzt, während umgekehrt der Dichtewert allein noch keinen Anhaltspunkt für den tatsächlichen Radiumgehalt bietet. Diese einseitige Abhängigkeit ist widerspruchsfrei zu erklären, sofern man annimmt, dass die Herkunft beider Faktoren im „Tiefenwasser“ liegt. Auf dem Wege zum Austritte wird durch örtliche Bedin-

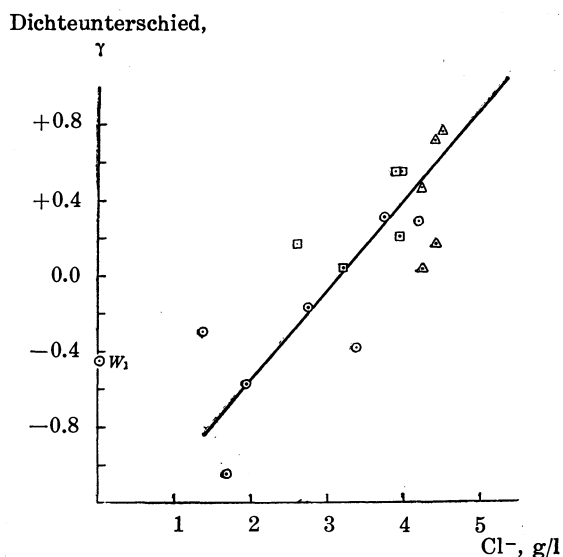


Abb. 7. Chlor-Gehalt und Dichteunterschied im Juli 1939.

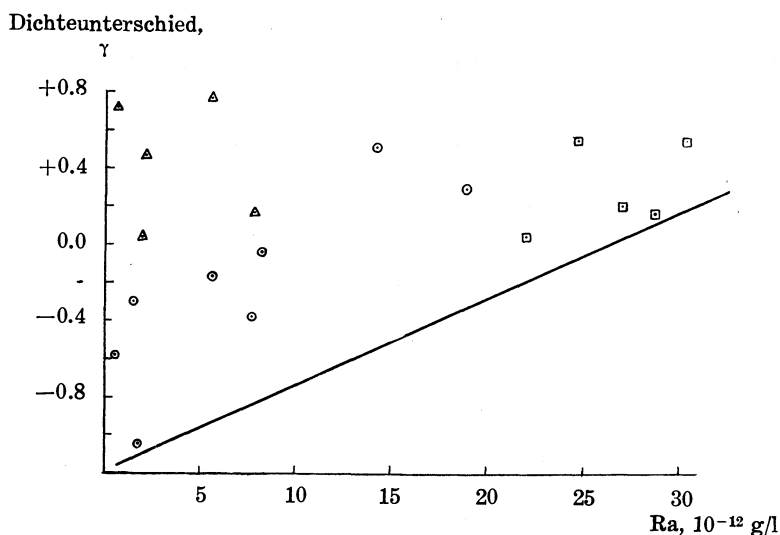


Abb. 8. Radiumgehalt und Dichteunterschied im Juli 1939.

gungen der Radiumgehalt in verschiedenem Ausmasse vermindert, wohingegen der Dichtewert keine derartigen Veränderungen erleidet. Auch

das Chlor im Quellwasser dürfte überwiegend aus dem „Tiefenwasser“ stammen.

Aus den vorstehenden Tabellen und Abbildungen ergibt sich, dass die eingangs nach geologischen Gesichtspunkten geordneten Quellgruppen

Ra, 10^{-12} g/l

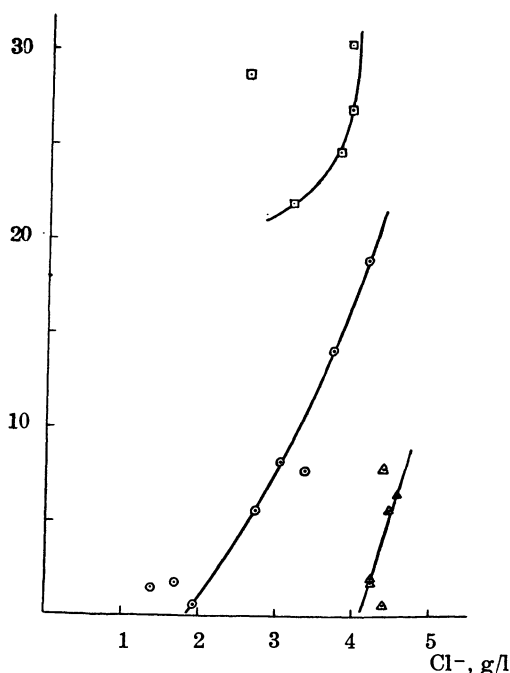


Abb. 9. Chlor- und Radium-Gehalt im Juli 1939.

dampfrückstand legten wir Werte vom Juli 1939 zu Grunde und für Zink Werte vom Oktober 1936 und vom Juli 1939. Da es sich hier lediglich um einen vergleichenden Überblick handelt, dürften als Unterlagen zu verschiedenen Zeiten gewonnene Werte zulässig sein, zumal deren verhältnismässig geringe Schwanungsbreite aus vorstehenden Tabellen hervorgeht.

Durch Radium- und Radongehalt unterscheiden sich die einzelnen Quellgruppen besonders scharf von einander. Die grössten Radiummengen finden sich in den Gruppen E und A, während die Gruppen B und C bei weitem am radon-reichsten sind.

Da im Allgemeinen radium- und radon-reiche Quellen aus Granitgrund entspringen, darf auch für das Masutomi-Gebiet angenommen werden, dass diese beiden Bestandteile hauptsächlich aus dem Granit stammen. Der Quellstrom löst aus der Berührungsfläche einen winzigen Anteil des dort vorhandenen Radiums. Dagegen wird die Gesamtmenge des in diesen Zonen durch Radium-Zerfall entstehenden Radons vom Quellwasser aufgenommen und gelöst. Daher ist der Radongehalt der Quellwasser mit $10-5000 \times 10^{-10}$ Curie/1 ausserordentlich viel grösser als aus

in mehr oder weniger von einander abweichenden chemischen und physikalischen Eigenschaften der Schüttungen ihre Bestätigung finden. Um diese Verhältnisse anschaulich darzustellen, haben wir in Tabelle 14 für die Gruppen A, B, C, D und E Durchschnittswerte und Extremwerte angeführt. Natürlich hat jeder einzelne Faktor für jede Quelle einen anderen Wert, der sich im Laufe der Zeit mehr oder weniger stark ändert. Trotzdem aber ist Tabelle 14 geeignet, die Quellgruppen miteinander zu vergleichen. Für die Berechnung der Durchschnittswerte benutzten wir Bestimmungsergebnisse von den Quellen, A₁, A₂, A₃, A₄, B₄, B₅, B₆, B₇, B₈, B₉, C₁, C₂, C₃, C₄, C₅, C₆, D₆, D₇ und E₁ im Oktober 1940, weil diejenigen der anderen Quellen nicht vollzählig sind. Für die angegebenen Extremwerte gilt diese Beschränkung nicht. Für Radium und Ab-

Tabelle 14. Gruppen-Durchschnitts- und -Extremdaten der Quellschüttungen von Masutomi im Oktober 1940.

Quellgruppe	A	B	C	D	E
Austrittstemperatur, °C	30.6 (13.5-32.3)	21.1 (16.5-25.0)	24.0 (19.4-31.3)	16.0 (11.2-18.0)	12.5
pH-Wert	6.3 (6.0-6.5)	6.2 (5.9-6.6)	6.6 (6.4-6.9)	5.6 (3.8-5.6)	6.5
Abdampfdruckstand, g/l (1939)	7.60 (3.07-9.66)	7.07 (3.72-16.20)	10.82 (10.15-11.33)	0.99 (0.11-3.70)	15.06
Chlor, g/l	3.896 (3.289-4.207)	3.014 (1.742-4.236)	4.482 (4.198-4.626)	0.209 (0.019-0.399)	7.656
% des Abdampfdruckstands	51.2	42.6	41.	21.1	50.8
Sulfat, g/l	0.623 (0.572-0.795)	0.410 (0.288-0.571)	0.542 (0.514-0.572)	0.186 (0.048-0.320)	0.003
% des Abdampfdruckstands	8.2	5.8	5.0	18.8	0.0
Gesamtkohlensäure, g/l	1.441 (0.756-1.934)	1.245 (0.022-1.767)	1.017 (0.527-1.577)	0.595 (0.019-1.089)	2.615
Radium, 10 ⁻¹² g/l (1939)	26.0 (21.97-30.31)	9.4 (0.58-18.89)	4.1 (0.58-7.83)	1.1 (< 0.5-1.74)	84.36
10 ⁻¹² g Ra/g Abdampfdruckstand	3.42	1.33	0.38	1.11	5.60
Radon, 10 ⁻¹⁰ Curie/l	11.4 (5.2-15.4)	1692. (17.4-4370)	525 (62-1550)	9.9 (0.6-12.7)	12.7
Zink, γ/l (1936 und 1939)	53 (26-80)	88 (35-215)	79 (78-80)	91 (60-224)	113
% des Abdampfdruckstands	0.0007	0.0015	0.0008	0.0092	0.0008
Dichtewert, γ	+0.0 ₈ (-0.3 ₈ ~ +0.4 ₃)	-0.1 ₅ (-0.3 ₄ ~ +0.2 ₆)	+0.02 (-0.5 ₁ ~ +0.3 ₀)	—	+0.3 ₄

dem errechneten Gleichgewichte mit dem tatsächlich im Quellwasser vorhandenen Radium zu erwarten wäre. Die im Wasser von uns bestimmte Radiummenge kann nach dem Gleichgewichtsgesetze lediglich einen Radongehalt von $1-10 \times 10^{-12}$ Curie/1 bedingen. Der tatsächlich vorhandene vielfache Mehrbetrag muss also aus dem Untergrunde stammen. Die Quellströme der Gruppen A und E durchqueren Granit, die der Gruppen B und C Granit und Sandstein. Der Radiumgehalt beträgt im Granit $0.63-2.72 \times 10^{-12}$ g/g,⁽¹¹⁾ der im Sandstein $0.21-1.13 \times 10^{-12}$ g/g.⁽¹²⁾ Mithin ist für die Gruppen E und A ein höherer Radiumgehalt zu erwarten als für B und C.

In den Gruppen A und E sind die Berührungsflächen der Quellströme mit dem Gestein (Granit) vermutlich verhältnismässig klein. Da die Aufnahme des Radons nur durch diese Berührungsflächen erfolgen kann, muss in ihren Schüttungen die Radonmenge naturgemäss in engen Grenzen bleiben. Die durch die Verwerfung verursachte Zertrümmerung des Untergrundes im Gebiet der Gruppen C und ganz besonders B bedingt eine ausserordentliche Vergrösserung der Berührungsflächen des in Nebenspalten ruhenden mineralischen Grundwassers. Wir setzen hier selbstverständlich diejenigen schmalen Spalten voraus, durch die sich darin vorhandenes Grundwasser nicht fortbewegt und zwar durch die Radon, wegen seines gasförmigen Wesens, ohne weiteres diffundiert. Damit wird für diese Quellwässer der Raum, aus dem sie Radon empfangen können, entsprechend vergrössert. Da Radon dauernd neu gebildet und angereichert wird, kann es auch aus ruhenden Grundwasserkörpern in die Quellströme übergehen, während diese Möglichkeit für das Radium nicht besteht. Daher scheinen Radon- und Radium-Gehalt der Masutomiwässer weitgehend unabhängig von einander zu sein.

Aus vorstehenden Betrachtungen ergibt sich, dass Schüttungen benachbarter Quellen in ihrem chemischen Charakter erhebliche Unterschiede aufweisen können, obwohl ein einheitlicher Ursprung ihrer Quellströme angenommen werden darf. Als Ursachen für solche Unterschiede sind mengenmässig verschiedene Zuschüsse von Oberflächenwässern zum Quellstrom und chemische und physikalische Eigenschaften des von diesem durchquerten Gesteins anzusehen.

Es sei uns gestattet, Herrn Prof. Yuji Shibata und Herrn Prof. Kenjiro Kimura für ihre freundliche Anleitung und ihre Ratschläge und der Kaiserlichen Akademie der Wissenschaft für ihre finanzielle Unterstützung bei der Ausführung dieser Arbeit unseren herzlichen Dank auszusprechen.

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Kaiserliche Universität zu Tokio.*

(11) J. Hatsuta, *Mem. Coll. Sci. Kyoto Imp. Univ.*, B 12(1936), 1.

(12) R. D. Evans und C. Goodman, *Bull. Geol. Soc. Am.*, 52 (1941), 459.

A Note on the Catalytic Isomerization of Dimethyl Maleate to Dimethyl Fumarate.

By **Bun-ichi TAMAMUSHI.**

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The catalytic effect of a paramagnetic substance on the cis-trans isomerization of ethylene compounds has been first discussed by R. Kuhn,⁽¹⁾ who at the same time qualitatively demonstrated that some paramagnetic metals (alkali metals, platinum, palladium, etc.) and gases (especially NO₂) are really effective in accelerating the isomerization of dimethyl maleate and cis-stilbene. Further quantitative studies on such catalytic effect have been carried out in our laboratory both in gaseous and liquid states of the reacting substance (dimethyl maleate and cis-dichlorethylene).⁽²⁾ In the course of these studies, we made some complementary experiments on the isomerization of dimethyl maleate to dimethyl fumarate in the presence of some paramagnetic and other catalysts, the results of which may also be worth while to be reported.

Experiment 1. Dimethyl maleate was distilled in a small Claisen flask under the pressure of 7 mm. and 760 mm. Hg, in contact with a catalyst—copper wire, platinum wire, platinum black, metallic sodium—the catalyst being placed in the vapour phase. No conversion, which would be detected by the subliming fumarate, was observed in each case.

Experiment 2. The maleic ester was heated to 200°C. in a small Terex flask for about 3 hours with the same catalysts as used in the experiment 1, which now being placed in the liquid phase. There happened no remarkable conversion with copper or platinum wire, while it took place to a striking degree with platinum black (30% -fumarate) and with metallic sodium (80% -fumarate). The analysis of the reaction product was done by determining its crystallization temperature, the previously obtained standard relation between the crystallization temperature and the composition of mixtures of the cis and trans compounds being here applied.

Experiment 3. The maleic ester was kept in an Erlenmeyer flask with a stopper at 110–120°C. for 30–40 minutes in contact with a gas mixture of oxygen and nitrogen oxide prepared by the action of nitric acid on copper. The liquid became soon pale blue, while the isomerization proceeded so far as to give 40% dimethyl fumarate, large crystals of the fumarate subliming on the wall of the flask.

(1) R. Kuhn, "Stereochemie," herausgeg. von K. Freudenberg, Leipzig (1933), p. 913.

(2) B. Tamamushi, H. Akiyama and K. Ishii, *Z. Elektrochem.*, **43** (1937), 156; **45** (1939), 72; **47** (1941), 340; this Bulletin, **12** (1937), 382; **17** (1942), 321.

Experiment 4. The maleic ester was maintained at the temperature of 150°C. in a quartz flask, once without catalyst and then with metallic phthalocyanines (copper-, magnesium- and iron phthalocyanines)—0.01 g. catalyst in 3 c.c. of the reacting substance—for 3, 5, 7 hours; the product was then analysed. The results obtained are as follows:

Time (hrs.)	3	5	7
Without catalyst	0.85	1.5	2.7%-fumarate
With copper phthalocyanine	1.1	1.8	2.8
With magnesium phthalocyanine	0.95	1.5	2.7
With iron phthalocyanine	1.4	2.2	3.1

Iron phthalocyanine is, therefore, proved to be more or less effective in accelerating the isomerization, whereas copper and magnesium phthalocyanines are practically ineffective.⁽³⁾ The similar results were obtained in the experiment at 170°C.

Experiment 5. The maleic ester was heated to boiling under the normal pressure and the vapour was made to flow over a catalyst—platinum black, iron or copper phthalocyanine—in a Terex reaction tube maintained at 300°C. in an electric furnace at the flow rate of 1 c.c. of the liquid per 30 minutes. The product was condensed in an ampoule and analysed. The following results were obtained:

	Fumarate formed (%)
Without catalyst	1.9
With platinum black (0.5 g.)	4.9
With iron phthalocyanine (1 g.)	8.0
With copper phthalocyanine (1 g.)	4.2

Experiment 6. The maleic ester was vapourized into a reaction flask of Terex glass under the pressure of about 40 mm. Hg. at the temperature of 300°C. in contact with platinum black. After the reaction time of 3–7 hours, the product was taken out in an ampoule by condensation and analysed. The fumarate content was found to be 3–17%, while the reaction without catalyst under the same conditions gave 1.7–3% of the fumarate. The platinum black was found to be also effective in accelerating the reverse reaction, namely, the isomerization of dimethyl fumarate to dimethyl maleate. It is to be noticed that the cis-trans isomerization of dichlorethylene in gaseous state is also remarkably catalysed in the presence of platinum black.⁽⁴⁾

Materials used in the Experiments. Dimethyl maleate: prepared by the method of Walden.⁽⁵⁾ B.p. 83–84° (11 mm.), n_D^{20} 1.4445.

(3) The magnetic susceptibilities of metallic phthalocyanines have not yet been extensively determined. After the measurement of Klemm and Senff, however, iron and manganese phthalocyanines have greater susceptibilities than other metallic phthalocyanines. *J. prakt. Chem.*, **154** (1939), 73.

(4) B. Tamamushi, *this Bulletin*, **17** (1942), 321.

(5) P. Walden, *Z. physik. Chem.*, **20** (1896), 377.

Platinum black: prepared by the method of Ramsay, Mond and Shields.⁽⁶⁾ Copper-, magnesium-, and iron phthalocyanines: prepared and kindly afforded by Mr. H. Akiyama of Nippon Yushi Company, to whom my sincere thanks are due. The samples were purified by sublimation in a high vacuum.

I express my warm thanks for Messrs. K. Ishii, K. Fuse and S. Tohmatsu for their help in the experiment.

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(6) W. Ramsay, L. Mond and J. Shields, *Phil. Trans.*, **186 A** (1895), 661.

Determination of the Minute Quantities of Silver in Mineral Waters by the Dithizone Method.

By Kazuo KURODA.

(Received July 28, 1942.)

Silver is fairly widely distributed in various minerals and it is almost invariably found in the sulphide ores of lead, copper and zinc. As has already been reported, acid springs in Japan always contain a considerable amount of copper and zinc, and the author is of the opinion that the source of copper and zinc in mineral springs is usually their sulphide ores. From this it may be deduced that silver is geochemically associated with copper and zinc and that the minute traces of silver are present in acid springs.*

In the previous papers,⁽¹⁾ volumetric and polarographic methods using diphenylthiocarbazone (dithizone) for determining the minute quantities of copper in large amounts of iron, were studied and these methods were applied to the determination of the element in some mineral springs in Japan. The occurrence of copper in a large number of mineral springs in Japan has recently been found by Prof. Kimura,⁽²⁾ and the presence of silver associating with copper in many mineral springs was also found by him.

In the present paper the author has studied the method and found that the minute traces of silver down to 5 γ per litre of spring waters could easily be determined by the dithizone method as in the case of the determination of copper in the mineral waters.

* The silver content of sea water is believed today to be 0.3 γ per litre, and if the spring waters contain ten times a larger amount of silver than sea water, it is not so difficult to estimate the amount by suitable methods.

(1) Kuroda, this Bulletin, **15** (1940), 439; **16** (1941), 69.

(2) Not yet published.

I. *Determination of the minute Quantities of Silver by the Dithizone Method.* According to H. Fischer⁽³⁾, volumetric determination of silver by the dithizone method in the presence of copper, lead, zinc, cadmium, arsenic, antimony, bismuth, mercury, gold, etc. gives a satisfactory result. The volumetric procedure is very tedious, however, when the spring water contains a considerable amount of iron. The author has found in the present work that when a large amount of iron is present, it could be removed by ammonia and ammonium carbonate, as in the case of copper which was described in the previous papers, though the analytical procedure becomes rather troublesome.

(a) *When iron is absent.* Add nitric acid to the mineral water, adjust to pH 3 and titrate with a carbon tetrachloride solution of dithizone in a separating funnel, shaking vigorously each time. The orange yellow colour of the carbon tetrachloride layer indicates the presence of silver. When silver is absent and copper is present, the carbon tetrachloride layer turns to the green colour of itself or reddish violet colour of copper.

The amount of silver is obtained from the volume of the carbon tetrachloride solution of dithizone which is used to extract the orange yellow dithizone complex of silver.*

(b) *When a large amount of iron is present.* Add nitric acid to a 500 c.c. portion of the mineral water and boil to oxidize the iron to the ferric condition. Add ammonium hydroxide (1:1) to slight excess and then 5 c.c. of saturated ammonium carbonate solution.** Warm and filter the solution. Wash the residue with a warm mixture of 10 c.c. of water, 1 c.c. of ammonium hydroxide (1:1) and 1 c.c. of saturated ammonium carbonate solution. Dissolve the precipitate in 5 c.c. of nitric acid (1:5) and precipitate as above. Combine the filtrates, and render them acid with dilute nitric acid and evaporate to dryness. Dissolve the residue in nitric acid, adjust to pH 3 and titrate with a carbon tetrachloride solution of dithizone.

The efficacy of the method was tested by the following experiments.

(1) A known amount (10~100 γ) of silver and copper was added to dilute nitric acid solution (pH 3) and titrated with the carbon tetrachloride solution of dithizone.

(2) A known amount (10~60 γ) of silver was added to the sulphate solution which contained 100 mg. of iron and the solution was submitted to the complete process of the separation of iron and the volumetric determination of silver by the carbon tetrachloride solution of dithizone.

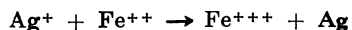
The following results were obtained. (Tables 1 and 2).

(3) Fischer, Leopoldi, and Uslar, *Z. Anal. Chem.*, **101** (1935), 1.

* Each c.c. of the dithizone solution used by the author corresponded to 8.3 γ of silver.

** Silver remains in the solution as complex silverdiamine salt: $\text{Ag}(\text{NH}_3)_2^+$ ions are formed. (Treadwell, Hall, "Analytical Chemistry" I, p. 101.)

As is described in Treadwell's "Analytical Chemistry", ferrous sulphate precipitates gray metallic silver from boiling solutions.



It is considered, however, that this precipitated silver is redissolved by nitric acid.

Table 1. Volumetric Determination of Silver and Copper.

No.	Added (γ)		Found (γ)		Error (γ)	
	Silver	Copper	Silver	Copper	Silver	Copper
(1)	100	50	97	52	-3	+2
(2)	50	50	54	48	+4	-2
(3)	20	50	22	47	+2	-3
(4)	100	10	99	8	-1	-2

Table 2. Determination of Minute Amounts of Silver in Large Amounts of Iron.

No.	Iron added γ	Silver added (γ)	Silver found (γ)	Error (γ)
(1)	100000	10	13	+3
(2)	100000	20	19	-1
(3)	100000	40	40	0
(4)	100000	50	53	+3
(5)	100000	60	56	-4

Down to 5γ of silver could be detected, and the results described in Table 2 show that 10γ of silver in 100 mg. of iron could be quantitatively determined by this method.

The spectroscopic test showed the presence of silver in some of the reagents, but the author could not detect it by the dithizone method. The amount of silver derived from the reagents is therefore considered to be less than 5γ . The dithizone solution was purified as was described in the previous paper. Silver was not detected in distilled water, but the presence of copper, lead and zinc was often found in it. (Table 3)

Table 3.

No.	(γ /l.)			
	Cu	Pb	Zn	Ag
(1) Tap Water of Tokyo	28	13	65	<1
(2) Distilled Water	< 1	2	28	<1
(3) Redistilled Water	< 1	< 1	2(?)	<1

II. Silver Content of Some Mineral Springs in Japan.

(a) Arc Spectrographic Detection and Estimation of Silver.

Nitric acid (0.20 c.c.) was added to suitable quantities (100 to 200 c.c.) of the mineral water and the heavy metals were extracted with the carbon tetrachloride solution of dithizone. Sodium nitrate (10 mg.) was added to the carbon tetrachloride solution and evaporated to dryness. The residue was subjected to arc excitation, a Hilger spectrograph of E 2 type being used.

The following lines were found:

Table 4.

No.	Mineral Spring	Prefecture	Spectral Lines of Silver	
			3280.68 Å	3382.89 Å
(1)	Netunoyu, Sukayu	Aomori	W	W
(2)	Hienoyu, Sukayu	Aomori	W	W
(3)	Iron Spring No. 1, Sinyu, Sukayu..	Aomori	W	F
(4)	Iron Spring No. 2, Sinyu, Sukayu..	Aomori	W	F
(5)	Gongenyu, Yunohanazawa, Hakone..	Kanagawa	—	—
(6)	Sea Water, Senami	Niigata	—	—

Pure silver nitrate was dissolved in water and the solutions containing 1, 0.1, 0.01, 0.001 and 0.0001 mg. of silver per c.c. were prepared. Sodium nitrate (10 mg.) was added to 1 c.c. of each solution, and evaporated to dryness. Then it was placed on the lower graphite electrode and subjected to arc excitation. The charges actually placed on the lower electrodes contained 1, 0.1, 0.01, 0.001 and 0.0001 mg. of silver respectively. The spectral lines observed at different concentrations are described in Table 5. In this Table, VS signifies that the line in question is very strong, S, that it is strong, W, weak, and F, faintly visible.

Table 5. Spectral Lines of Silver at Different Concentrations.

λ (Å)	1 mg.	0.1 mg.	0.01 mg.	0.001 mg.	0.0001 mg.
3280.68	VS	S	S	W	W
3382.89	VS	S	S	W	F

Table 5 shows that 0.001 to 0.0001 mg. of silver was contained in 100 c.c. of the mineral water of Sukayu, and less than 0.0001 mg. in 100 c.c. of the Gongenyu spring and 200 c.c. of sea water. Therefore, the silver content of the hot springs of Sukayu is considered to be from 1 γ to 10 γ per litre and that of the Gongenyu spring and sea water, less than 1 γ per litre.

(b) *Silver Content of the Hot Springs of Sukayu.* Eleven samples of mineral springs in Japan were tested by this dithizone method, but the presence of silver was detected only in the hot springs of Sukayu, in Aomori Prefecture. The results of analysis are shown in Table 6.

Table 6.

	Ag (γ /l.)
(1) Iron Spring No. 1, Sinyu, Sukayu.....	12
(2) Iron Spring No. 2, Sinyu, Sukayu.....	15

Netunoyu and Hienoyu were not analysed by this dithizone method, but the silver content of these springs is also considered to be about 10 γ Ag per litre from the results of spectroscopic estimation described in (a). According to the analysis by the hygienic laboratory in Tokyo. Netunoyu and Hienoyu belong to acid springs, and Sinyu to bitter springs containing gypsum. The water samples used in this series of experiments were

usually collected by the author himself, except the mineral waters of Sukayu which were presented by the owner of the hot spring.

Summary.

(1) Volumetric and spectroscopic methods, using dithizone for determining the minute quantities of silver in the mineral waters, were studied.

(2) The amount of silver in mineral springs was estimated by the dithizone method. The occurrence of silver in the hot springs of Sukayu was spectroscopically detected and estimated to be about 10γ per litre. The dithizone method gave $12\sim 15\gamma$ Ag per litre.

The author expresses his hearty thanks to Prof. Kenjiro Kimura for his kind guidance in the course of this study. The cost of this research has been defrayed from the Scientific Research Encouragement Grant from the Department of Education, to which the author's thanks are due.

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The Synthesis of Iso- and Normal Butyl Alcohols in the Presence of Calcium Carbide (B) V.* Comparison of the Results in Dry and Liquid Systems.

By Ryoji NEGISHI and Osamu KAMIIE.

(Received July 6, 1942.)

Because the results of autoclave runs III_A Ser. 100, III_A Ser. 113, and IV_A Ser. 124 are quantitative and they (especially III_A Ser. 100) are the first runs in which conclusive evidence of the formation of iso-butyl alcohol has been obtained; and, furthermore, because of the circumstance that these results have proven invaluable for the later investigations on the synthesis of butyl alcohols, they will be given here in some detail. An attempt will be made in this and the following papers, to delve into the mechanism of the reaction as deeply as possible, still keeping within the propriety of the reliability of the data. Since the experimental procedure and methods of analysis have been given⁽¹⁾, they will not be repeated. We shall begin immediately with the discussion of the results which are summarized in Tables 1 to 4 and in Fig. 1 to 5.

* This paper has been published by permission of Dr. M. Sato.

(1) R. Negishi, Papers (B) III and IV, this Bulletin, 17(1942), 179; 17(1942), 364.

Table 1. Summarized Results of Runs III_A Ser. 113, III_A Ser. 100, and IV_A Ser. 124. (Catalyst mixed with carbide).

Experimental Number . .	III _A Ser. 113	III _A Ser. 100	IV _A Ser. 124
Paraffin Oil Introd. (g.) .	None	None	300
Residue liq. Recovered (g.)	—	—	288
Carbide (g.)	300 (grains)	300 (grains)	300 (60 mesh)
CO:H ₂	1:1.85	1:1.89	1:1.3
Reaction Temp. (°C.) . .	295–305	320	330
Press. Range, kg/cm ² at Reaction Temp. °C. . .	165–135	183–175	200–160
Catalyst No. and Wt. (g.) .	15b 216	15, 212	18ab, 45
Liquid Products	c.c. g.	c.c. g.	c.c. g.
Condenser	46.5 38.8	35.8 30.1	52.2 40.4
Trap	53.3 41.0	50.0 36.2	35.4 24.0
Extract	— 17.1	— 3.9	— —
Condensable Gas (trap)	— 45.7	— 37.6	— 15.7
Total carbide carbon Introd. (g.)	79.05	79.05	83.85
Total Carbide Carbon React. (g.)	79.05	79.05	68.00
Total reacted Carbon (g.) .	198.6	181.7	160.9
Total Liq. Carbon (without Extract) on Total React. Carbon (%)	25.6	26.4	27.5
Gaseous and Residue Car- bons (g.)+ % on Total reacted Carbon	Carbon (%)	Carbon (%)	Carbon (%)
CH ₄	5.30 2.7	17.59 9.7	} 10.71** 6.7
C ₂ H ₆	9.19 4.6	16.16 8.6	
C ₂ H ₄	10.17 5.2	7.82 4.3	8.85 5.5
C _n H _{2n} *	19.82 10.0	11.82 6.5	6.45 4.0
C ₂ H ₂	32.98 16.6	9.79 5.4	4.03 2.5
Carbonate	36.41 18.4	38.91 21.4	33.4 20.8
Hi Polym. and Decomp. .	11.86 6.0 (15.0)***†	32.37 17.8 (41)***	16.07 10.0 (0)***†
Total Carbon Balance† . .	96.6	102.1	91.2†
Total Weight Balance . .	98.3	100.0	96.5

* Calculated as C₃H₆.

** Mostly Methane.

*** If all free carbon is from carbide.

† Contains large amount of "yellow powder".

‡ The real accuracy of the results is not as good as what it appears to be. What we are really interested in is the absolute amount of the carbon unaccounted for, and in this series it amounts to 47 g. It is difficult to say how this "unaccounted-for" carbon is distributed among the products given in the Table.

Table 2. Elementary Analysis of Liquid Products.

Exp. No.	Liquid in Condenser			Liquid in Trap		
	C	H	O	C	H	O
III _A Ser. 100	77.90	11.69	10.41	66.80	12.58	20.72
III _A Ser. 113	72.41	11.69	15.85	55.64	15.00	29.36
IV _A Ser. 124	(Cond.+Trap)			68.53	13.10	18.37

Table 3. Distillation Analysis of Condensate.

" Condenser "			
Temp. Range (°C.)	Volume (%)		
	III _A Ser. 113	III _A Ser. 100	IV _A Ser. 124*
<100	17.5**	8.4	18.8
100-150	41.6***	24.7	35.4
150-230	27.1	30.1	27.6
230-297.3	11.2	18.3	At 216°C began to crack
Residue	10.7	12.2	10.8
Loss	—	6.3	7.4
Total	108.1†	100	100
Sample Taken (c.c)	42	28.7	—

" Trap "		
Temp. Range (°C.)	Volume (%)	
	III _A Ser. 113	III _A Ser. 100
<60	25.35	48.6
60 - 70	22.5	12.4
70 -105	10.5	3.2
105-120	19.8‡	7.0
Residue	7.0	3.4
Total	84.75	74.6
Loss	15.25§	25.4§
Sample (c.c.)	40.0	44.8

* Condenser + Trap.

** Contains some acetone.

*** 44.7% of the cut is isobutyl alcohol (16% of the total "condenser.")

† Due probably to cracking.

‡ 92% of the cut is isobutyl alcohol (18% of the total "Trap.")

§ Dissolved gases.

Table 4. Effect of Temperature and of Carbide on the Formation of Butyl Alcohol.

Exp. No.	System	Reaction Temp. (°C.)	Crude Isobutanol Vol. %* (103-110°C.)	Wt. of Carbide Used (g.)
III _A Ser. 113	Dry	295-305	21.1	300
IV _A Ser. (40+50)	Dry	300-305	8.8	500
III _A Ser. 100	Dry	320	7.1	300
IV _A Ser. 178	Paraffin	300-305	18	300
IV _A Ser. 124	Paraffin	330	16	300
IV _A Ser. 82	Paraffin	360	1.8	300

* Volume (%) based on Total condensates, corrected for the medium forced out.

Discussion. Autoclave run III_A Ser. 100 is the first series of runs in which the main object has been to investigate whether or not butyl alcohols could be definitely prepared from mixtures of carbon monoxide and hydrogen in the presence of a methanol catalyst and calcium carbide. From the previous experiences that, when water vapour is passed over carbide, the optimum temperature for the liquid synthesis is about

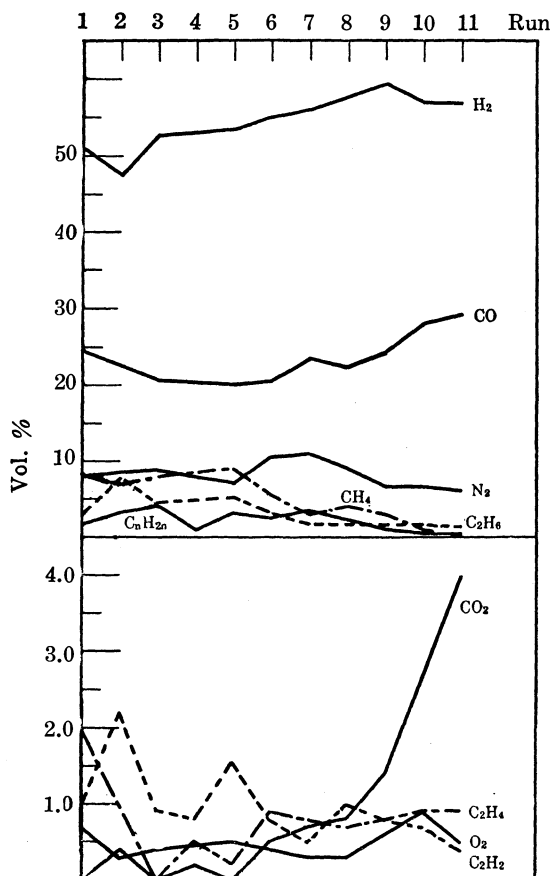


Fig. 1. Gas Composition vs Run
(III_A Ser. 100).

definitely too high. This is evident from the results of gas analysis given in Table IV in Paper (B) III and in Fig. 1 in this paper and from the high content of decomposed carbon in the residue, as shown in Table I. With this valuable information on hand, we have made autoclave runs III_A Ser. 113 at lower temperatures (and under lower pressure due to circumstances) and IV_A Ser. 124 at higher temperatures but in a liquid medium, which has the same sort of effect as lowering of the reaction temperature, to distribute and dissipate rapidly the excessive heat of reaction. Their

340°C⁽²⁾; the reaction involving the carbide is exceedingly exothermic; and finally, the lower the temperature, the greater is the carbon monoxide conversion into methyl alcohol, we have at first tried 320°C. The choice of the pressure was perforce determined by circumstances. The effect of pressure, however, is not so important in the static system, especially in the presence of the carbide which possesses large affinities for water and carbon dioxide molecules, by-products of the reaction. The removal of the reaction products shifts the equilibrium sufficiently so that its effect substantially overcomes that of the reduced pressure.

As shown in the tables, the formation of iso-butyl alcohol (practically all iso- and no normal) was not large, but they gave indications that in the closed system here employed, the effect of the temperature appeared rather important, and in this case the temperature seemed

(2) R. Negishi and O. Kamiike, Papers I to VI, *J. Soc. Chem. Ind. Japan*, **44** (1941), 1028; **45** (1942), 137.

results are also given in the tables and figures. The yields of butyl alcohol, on the one hand, have increased appreciably, while those of the saturated gases of lower molecular weights, as well as of the decomposed carbon, on the other hand, have decreased. This is good supporting evidence for the correctness of the assumption that the reaction temperature in III_A Ser. 100 has been too high.

When the results of III_A Ser. 100 and of III_A Ser. 113 are compared with those of non-catalytic, direct synthesis of hydrocarbon liquids from the carbide in dry system, several noticeable differences come to light. First, much larger quantities of hydrocarbon liquids are formed in the present series. In the high pressure non-catalytic reactions⁽³⁾, at temperatures as low as 310 to 320°C. such a large quantity of liquid products is not possible from the carbide. Neither is it probable even in the ordinary pressure reactions⁽²⁾ in which fairly large amounts of liquid products have been obtained at 340°C. The products found in the low pressure runs are dark, viscous, and dense, but those in the present series are for the "condenser", light greenish brown and clear with a "crab-like" odour and for "trap", colourless and transparent. Second, the results of the analysis of the gases found in the trap are different in the present and the non-catalytic runs. In the former a large amount of carbon dioxide was found, while it was absent in the latter; no butane⁽⁴⁾ in the former, while it was found

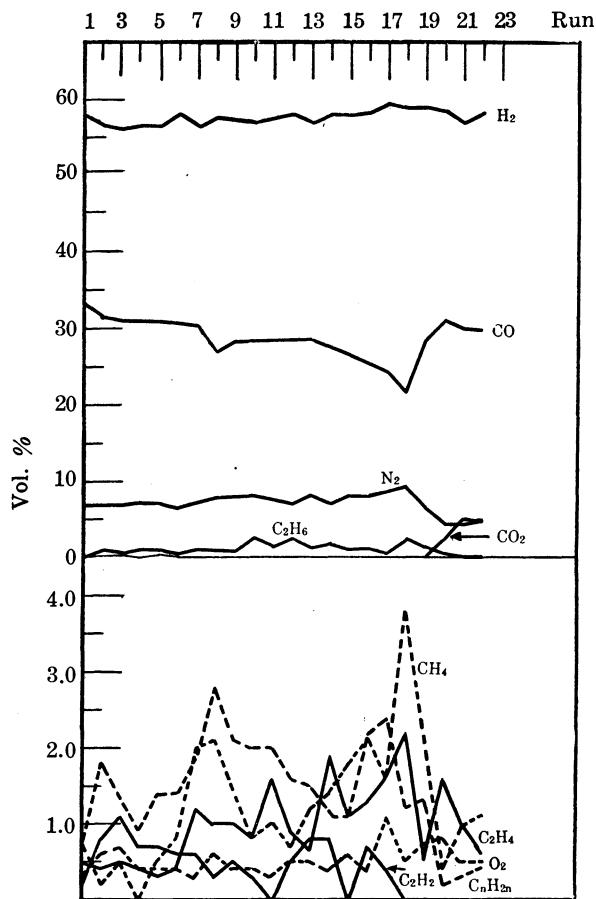


Fig. 2. Gas Composition vs Run (III_A Ser. 113).

(3) R. Negishi, M. Nibayashi, and O. Kamiike, Papers I-III, to be published in Japanese in *J. Soc. Chem. Ind. Japan*, **45** (1942).

(4) Butane is found in the series of runs carried out in liquid medium at higher temperatures, 350-360°C. It seems suggestive that the temperature has a great deal to do with the appearance of butane, but with our present limited data, nothing more can be said.

in some of the latter runs which were carried out at higher temperatures⁽⁴⁾.

We can offer no adequate explanation for these differences. As to the increased formation of liquid products, the results of the formation

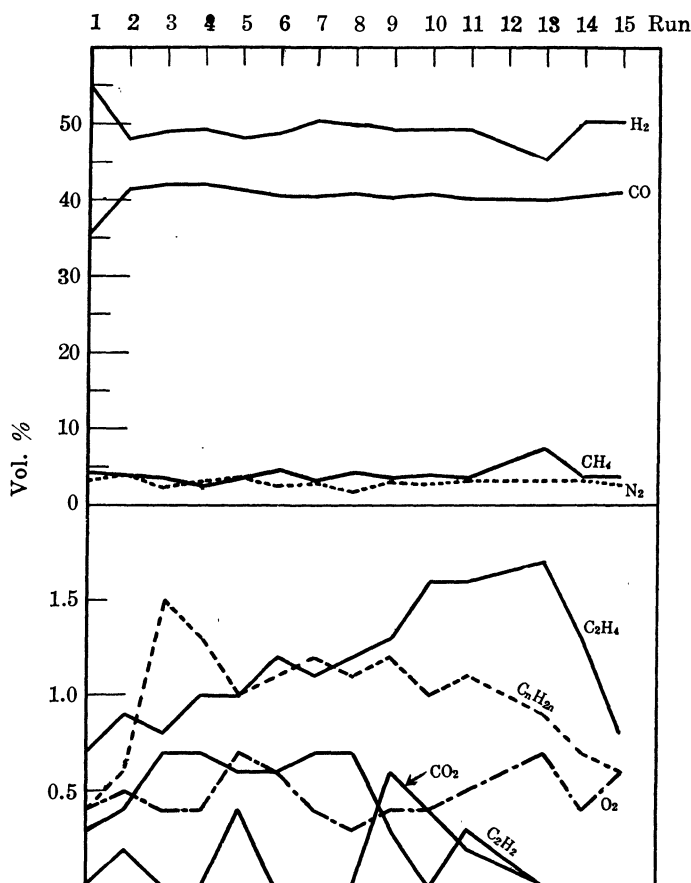


Fig. 3. Gas Composition vs Run (IV_A Ser. 124).

of butanols from methanol⁽⁵⁾ in the presence of the carbide are suggestive. We have found that a considerable amount of the methanol introduced has disappeared inexplicably. Probably, part of this methanol has formed hydrocarbon liquids; there are qualitative indications that such is the case. It seems more probable, in our case, that the liquid products are formed rather from the alcohols, methanol and butanol produced, than directly from $\text{CO} + \text{H}_2$ ⁽⁶⁾ or from acetylene⁽⁷⁾. In connection with the last point, a rough estimate based on the results of III_A Ser. 113 indicates that most of the carbide acetylene has escaped as such or has formed C_nH_{2n} and the "yellow powder", and only about 10% of the carbide has been actually transformed into liquid products. The role

(5) R. Negishi, *Rev. Phys. Chem. Japan*, **15** (1941), 171.

(6) Tsutsumi, *J. Fuel Soc. Japan*, **16** (1937), 481; F. Fischer and H. Kuester, "Gesammelte Abhandlung zur Kenntnis der Kohle," Band 11, 459; H. Pichler and H. Bufflet, *Brennstoff-Chem.*, **21** (1940), 257, 273, 285. According to them, under proper conditions, hydrocarbon liquids of paraffin series and waxes can be synthesized from carbon monoxide and hydrogen under elevated pressures.

(7) H. A. Taylor and A. Van Hook, *J. Phys. Chem.*, **39** (1935), 811; A. Farkas and L. Farkas, *J. Am. Chem. Soc.*, **61** (1939), 3396; G. Egloff and E. Wilson, *Ind. Eng. Chem.*, **27** (1935), 917. According to these investigators, acetylene is readily hydrogenated to ethylene, and the latter has a lower activation energy of polymerization than that of hydrogenation and, furthermore, it is the key molecule for the hydrocarbon synthesis. These facts, therefore, cannot be entirely over-looked in our case.

of the carbide in this series has been to dehydrate the methanol synthesized to produce not only the butanols⁽⁵⁾ but also some hydrocarbon liquid products. The fact that most of the carbide acetylene has escaped free may be of great practical importance.

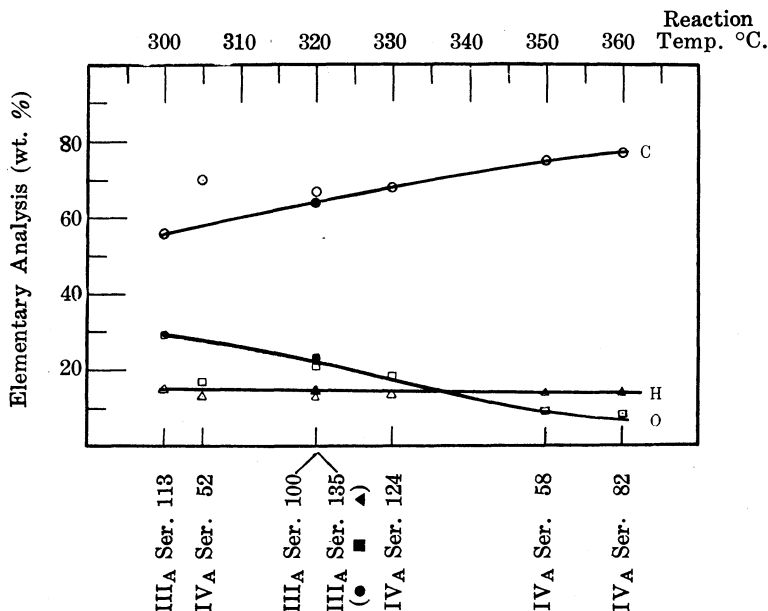
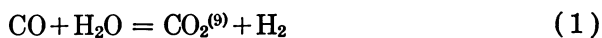


Fig. 4. Effect of Reaction Temperature on Trap Condensates.

As for the second difference mentioned above, i.e., the difference in the composition of the gases found in the trap, we are again without a suitable explanation and can only offer suggestions. The presence of a large amount of CO_2 in the runs, in which a catalyst (oxides of Zn and Cr) has been used, may be correlated with the fact that the following reaction⁽⁸⁾ also takes place:



and CO_2 more than sufficient to react with CaO may be produced. Our calculation indicates that the source⁽¹⁰⁾ of the water involved in reaction (1) is likely the reduction of carbon monoxide to form methane and ethane.

We shall now compare the results obtained in dry and liquid systems. Although we lack a conclusive support, a considerable body of experimental results we have gathered indicates that the role played by the carbide in the mechanism of the formations of the products in these two

(8) P. K. Frolich and D. S. Cryder, *Ind. Eng. Chem.*, **22** (1930), 1051.

(9) We have found no definite indications that $2\text{CO} = \text{CO}_2 + \text{C}$ takes place under our conditions.

(10) Water may be produced from the decomposition of methanol. We have no indication that CO_2 has been reduced to produce water in our case.

systems are essentially the same. The over-all mechanism of the reaction may be summarized as follows:

- (a) Synthesis of methanol from CO and H₂.
- (b) Dehydration by the carbide of the methanol to form isobutyl alcohol.⁽⁵⁾
- (c) More complete dehydration by the carbide of the alcohols followed by polymerization to produce hydrocarbon liquids.
- (d) Polymerization, hydrogenation, and escape of acetylene molecules.

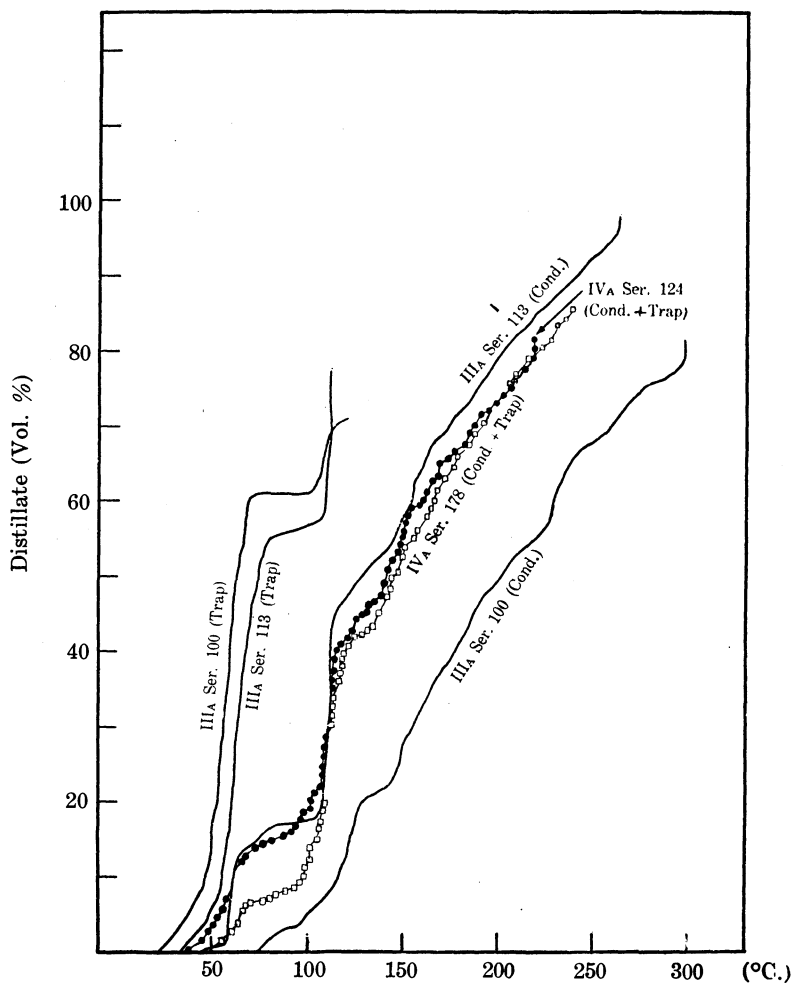


Fig. 5. Distillation Curves.

The differences observed in the systems are rather due to the effects of the heat of reaction involving the carbide; but such differences as no formation of ethane, the lesser amounts of olefins and free acetylene (see Table I) in liquid medium may not be so simply explained.⁽¹¹⁾

(11) As in Paper (B) IV, these differences may also be connected with the relative rates of polymerization reactions both in dry and liquid mediums.

Tables 2 and 3 show the results of elementary and distillation analyses of the products formed from the two systems. The results of Table 4 summarize the effect on the butanol yield of temperature, and the distillation curves for some of the runs are shown in Fig. 5. In spite of the fact that IV_A Ser. 124 has been made at 330°C, as compared with 320°C for III_A Ser. 100, the yield of butanol in the former is very much greater. This is an excellent example of the advantage of carrying out highly exothermic reactions in a liquid medium where the accumulation of excessive heat of reaction is less likely, and a better distribution of heat is effected. There is another advantage in using a liquid medium which may readily crack.* As is seen in Table I, the residue of IV_A Ser. 124 contains no free carbon; on the other hand, a part of the medium has cracked to give lower boiling substances, as the results of the distillation of the liquid medium separated from the residue of the series show. When it was distilled under the following conditions:

Maximum liquid temperature (in flask) °C	429**
Maximum vapor temperature	398**
Distillation pressure, p mm. Hg	5

approximately 41 c.c. of products boiling below the original paraffin oil (III) was obtained, as compared with 6.7 c.c. in IV_A Ser. 139 in which the medium alone had been treated at 330°C for nearly 2000 minutes. In the former series the decomposition of the carbide had been avoided at the expense of that of the medium. This fact may be of practical significance.

Among the series of the same system, the observed differences are effected by the variation in the temperature, the time of contact, and the amount of the carbide used, just to mention a few. The difference, for example, in the yield of butanol, as in III_A Ser. 52 and III_A 113, which have been carried out at about the same temperature, is probably due to the difference in the amounts of the carbide used. In the former 500 g. while only 300 g. has been used in the latter. Dehydration must have been more complete in the excess of the carbide, as indicated by the results of elementary analysis in Table 2 of Paper (B) III⁽¹⁾ and in Fig. 4. The difference between the yields of butanol, as is also the case with the relative amounts⁽¹²⁾ of saturated gases, olefins, free C₂H₂ and free carbon, as shown in Table 1, for III_A Ser. 113 and III_A Ser. 100 is, no doubt, due

* Usually cracking reactions are endothermic.

** Corrected to normal conditions.

(12) A similar sort of relationship was obtained when the first 13 runs of IV_A Ser. 124 were compared with IV_A Ser. 178, which contained just 13 runs. The results (the amount of carbon (g.)) are shown in the Table A. (Condensable gases, i.e., the gases found in the trap, are not included).

Table A.

Exp. No.	C ₂ H ₂	C ₂ H ₂	C _n H _{2n} (as C ₃ H ₆)	Methane
Ser. 178	4.84	11.2	6.22	3.64
Ser. 124	2.16	4.47	5.46	7.70

to the temperature. The effect of the temperature becomes clearer when IV_A Ser. 178 and IV_A Ser. 82 are compared. It is of some note that increasing the temperature has a similar sort of effect as increasing the amount of carbide, as seen from the results of IV_A Ser. 52 and III_A Ser. 100. The decreasing oxygen contents with increasing temperature means, among others, that dehydration reactions become more important with temperature. It is of significance that in our case the reaction temperatures are quite low, and 350°C already seems too high, even in a liquid medium. In most of the direct synthesis of butanols from CO and H₂, the temperature of reaction must be at least above 350°C⁽¹³⁾ and usually well over 400°C.

The usual assumption that the average temperature of the reaction vessel is not a true indication of the actual temperature of the reaction is interestingly, though perhaps without much significance, illustrated by Fig. 4 in which the results of the elementary analysis of the trap condensates of the series of runs made both in dry and liquid systems are plotted against the reaction temperatures. When a smooth line is drawn through all the carbon points, it passes through, at 320°C, the point obtained when the catalyst is placed "in cylinder", supported at the center of the autoclave, and finally, through the point obtained at 300°C in dry system. The same sort of behavior is apparent, though to a lesser extent, for the oxygen and hydrogen lines. The carbon and the oxygen points at 320°C in III_A Ser. 100 (in which the catalyst is mixed with the carbide) are above and below the extended lines, respectively. All these relationships show that the actual temperature in III_A Ser. 100 is higher than the average of the system. It is not surprising that the points of III_A Ser. 135 and III_A Ser. 113, though carried out in dry system, would fall on the lines. It has been found that when the catalyst is separated⁽³⁾ from the carbide, the reaction takes place less rapidly, and the accumulation of heat is not so excessive. At 300°C we have seen that the reaction proceeds rather slowly and, again, we should expect no abnormal effect of the heat of reaction. The points at 305°C do not at all fall on the curves, and this is due to the fact that, in the presence of a large amount of carbide, excessive dehydration takes place; therefore, the conditions of the series are not strictly comparable with the others. The relative positions of the points with respect to the curves are as expected from the above considerations.

In Figs. 1, 2, and 3, the results of gas analysis of each run of the series (III_A Ser. 100, III_A Ser. 113, and IV_A Ser. 124) are given graphically. In Figs. 1 and 2 the CO₂ contents suddenly increase and they become larger than the original value (3.3%). This is good evidence that the water gas reaction also takes place. The content of CO₂ in the gas serves as a fair guide as to the amount of carbide still present in the system. When the carbide exists in sufficient quantities, the content of CO₂ remains practically constant (and very small), while a sudden increase indicates that the carbide has been used up considerably.

This paper will complete the reports on the series of experiments made in our static system. The date and the discussion presented in this

(13) P. K. Frolich and W. K. Lewis, *Ind. Eng. Chem.*, **20**(1928), 285.

series of papers are, at places, fragmentary and incomplete, but we have decided to publish them, because they are sufficiently interesting in themselves, and because the synthesis of butyl alcohols in the presence of calcium carbide is new and has not heretofore been reported in the literature. The next series of investigation will be made with an autoclave into which the reaction gases can be continuously charged. Their results will appear later also in this Bulletin on appropriate occasions.

Summary.

The results of autoclave runs III_A Ser. 100, III_A Ser. 113 in dry and IV_A Ser. 124 carried out in liquid paraffin have been compared and discussed rather quantitatively.

It has been found that the main reactions involving the carbide are the same in the two systems. The differences found are attributable to the accumulation of the heat of reaction, while those among the series of the same system are, in addition, due to such secondary effects as the time of contact and the amount of the carbide present.

From a considerable body of experimental results, it has been indicated that the role of the carbide is to dehydrate the methanol synthesized from carbon monoxide and hydrogen to produce isobutyl alcohol, and with further dehydration of the alcohols, hydrocarbon liquids are produced. Under certain conditions the principal fraction of the carbide acetylene may escape as free or form olefines and yellow powder, with only a slight formation of liquid products.

It has been shown that cracking of the carbide acetylene is avoided at the expense of that of the medium.

It is the authors' pleasure to express their sincere thanks to Professor T. Marusawa for his keen interest and encouragement throughout this series of investigations.

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Die Veränderung der Chemischen Zusammensetzung der Thermalquellen unter dem Einfluss der Gezeiten. II. Mitteilung. Weitere Untersuchungen der Thermalquellen von Ito.

Von Kazuo KURODA.

(Eingegangen am 28. Juli 1942.)

In der vorhergehenden Mitteilung⁽¹⁾ wurde über die regelmässige Veränderung der chemischen Zusammensetzung der Thermalquellen von Ito (Provinz Sizuoka) berichtet. Der Verfasser hat kürzlich noch einige andere Thermalquellen in Ito untersucht. Zwei Thermalquellen zeigten keine Veränderung der Zusammensetzung, eine andere wurde jedoch durch Ebbe und Flut beträchtlich beeinflusst. Die Einflüsse der Gezeiten auf die chemische Zusammensetzung der Thermalquellen sind bei einzelnen Quellen sehr verschiedenartig. Die Stellen der untersuchten Thermalquellen sind in Abb. 1 gezeigt.

I. Die Veränderung der chemischen Zusammensetzung der Quelle Nr. 10 (Azumaya-Ryokan-no-yu).

Es gibt zwei Quellen in Azumaya (Hotel Azuma); (Quellen Nr. 10A und Nr. 10B). Die Quelle Nr. 10A, die ungefähr 500 m von dem Hotel entfernt ist, und zu diesem mittels Rohr geleitet wird, hat höhere Temperatur als die Quelle Nr. 10B, die im Hotel selbst ist. Da beide Quellen sehr tief liegen, muss das Wasser hochgepumpt werden. Der Verfasser hat an einem bestimmten Tage (erster Tag) von 19^h 30 bis 24^h 00 je 30 Minuten den Chlorgehalt und pH dieser Quellen gemessen. Dieses Resultat ist in Tabelle 1 gezeigt. Die Zeit der Ebbe und Flut ist in Tabelle 2 angegeben.

Tabelle 1a. Quelle Nr. 10A
(Azumaya-Ryokan-no-yu)

Zeit	Cl' (g/L)	pH
19 ^h 30	1.0229	7.4
20 00	1.0233	7.4
20 30	1.0219	7.4
21 00	1.0212	7.4
21 30	1.0240	7.4
22 00	1.0233	7.4
22 30	1.0261	7.4
23 00	1.0233	7.4
23 30	1.0233	7.4
24 00	1.0247	7.4

Tabelle 1b. Quelle Nr. 10B
(Azumaya-Ryokan-no-yu)

Zeit	Cl' (g/L)	pH
19 ^h 30	0.2943	7.4
20 00	0.2932	7.4
20 30	0.2939	7.4
21 00	0.2939	7.4
21 30	0.2939	7.4
22 00	0.2939	7.4
22 30	0.2942	7.4
23 00	0.2942	7.4
23 30	0.2936	7.4
24 00	0.2947	7.4

(1) dies Bulletin, 17(1942), 381.

Tabelle 2.

Zeit der Ebbe und Flut des
betreffenden Tages.

	Zeit	Wasserniveau (cm)
Flut	15 ^h 50	151
Ebbe	21 20	91

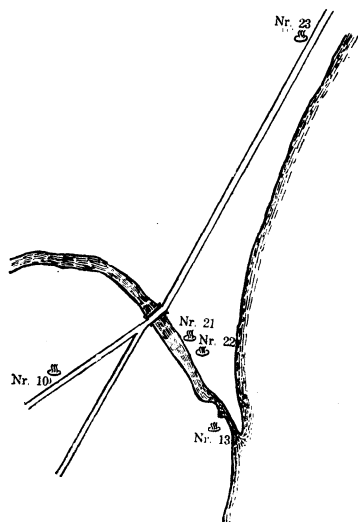


Abb. 1.

Die Zeit von Ebbe und Flut ist in Tabelle 3 angegeben.

Tabelle 3.

	Flut		Ebbe	
	Zeit	Niveau (cm)	Zeit	Niveau (cm)
Zweiter Tag	2 ^h 40	154	9 ^h 45	5
	16 45	160	22 15	91
Dritter Tag	3 30	159	10 45	-3

Das Sprudeln dieser Quelle endete um 8^h 30 am zweiten Tag. Dann wurde die Senkung des Wasserniveaus in dem Rohr beobachtet. Das Minimum des Wasserniveaus wird um 10^h 15, d.h. 30 Minuten nach der Zeit der Ebbe (9^h 45) erreicht. Die Wassertemperatur, die in der Oberfläche des Wassers gemessen, sinkt ziemlich schnell herab. Das Sprudeln der Quelle begann wieder um 11^h 16. Die Periode der Suspension des Sprudelns ist also 2 Stunden und 46 Minuten. Das Thermalwasser wurde zuerst um 11^h 45 am zweiten Tag entnommen. Danach wurden Temperatur, pH und der Chlorgehalt der Quelle einmal pro Stunde gemessen. Danach erzielten wir folgendes Resultat. (s. Tabelle 4).

Der Chlorgehalt der Quelle Nr. 10A veränderte sich zwischen 1.0212–1.0261 g per Liter. Die Veränderung ist weniger als 5/1000. Deshalb können wir annehmen, dass die chemische Zusammensetzung dieser Quelle beinah konstant bleibt. Der Chlorgehalt der Quelle Nr. 10B veränderte sich zwischen 0.2932–0.2947 per Liter. Die Veränderung ist also ungefähr 5/1000. Solch kleiner Unterschied kann vielleicht ein experimentaler Fehler sein.

II. Die Veränderung der chemischen Zusammensetzung der Quelle Nr. 23 (Suzuki-Ryokan-no-Yu).

Die Quelle Nr. 23 liegt ungefähr 60–70 m von der Seeküste entfernt. Die intermittierende Erscheinung dieser Thermalquelle ist sehr interessant. Während der Ebbe sprudelt diese Quelle nicht, jedoch soll diese Erscheinung nur am Tage selbst, bzw. kurz vor und nach dem Vollmond oder Neumond, beobachtet worden sein.

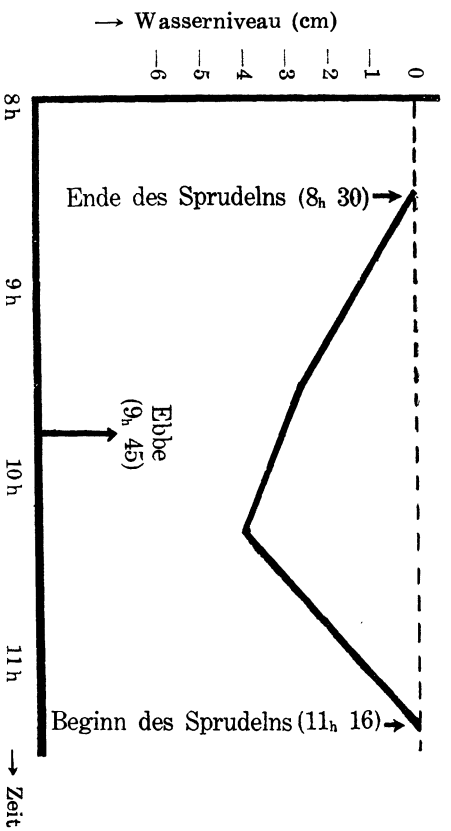


Abb. 2. Veränderung des Wasserniveaus.

Tabelle 4. Quelle Nr. 23 (Suzuki-Ryokan-no-yu).

Zeit	Atom. Druck (mm)	Luft- Temp. (°C)	Wasser- Temp. (°C)	pH	Cl (g/L)	Energie- bigkeit. (L/Min.)
11h 45	762	26	36.5	7.4	3.8364	—
12 00	762	26	42.1	7.4	3.7549	1~5
12 15	762	27.2	42.5	7.4	3.7053	1~5
12 30	762	27.0	43.1	7.4	3.7762	1~5
12 45	762	27.0	43.6	7.4	3.8364	10
13 45	762	27.3	44.3	7.3(?)	3.8542	15
14 45	762	27.5	44.5	7.4	3.8577	20
15 45	762	27.5	44.5	7.4	3.8435	30
16 45	762	27.7	44.5	7.4	3.8400	35 Flut
17 45	762	27.3	44.5	7.4	3.8294	25 (16.45)
18 45	762	27.0	44.6	7.4	3.8294	20
19 45	762	26.9	44.3	7.4	3.8294	15
20 45	762	26.8	44.3	7.4	3.8400	10~15
21 45	762	26.2	44.3	7.4	3.8471	15
22 45	762	24.7	44.3	7.4	3.8471	7 Ebbe
23 45	762	26.1	44.2	7.4	3.8577	10 (22.15)
24 45	762	24.3	44.3	7.4	3.8364	10~15
1 45	762	25.5	44.4	7.4	3.8400	15
2 45	762	25.9	44.5	7.4	3.8400	25
3 45	763	25.5	44.5	7.4	3.8329	25 Flut
4 45	763	25.3	44.6	7.4	3.8471	30 (3.30)
5 45	764	25.0	44.5	7.4	3.8471	20
6 45	764	24.2	44.4	7.4	3.8542	15
7 45	764	23.8	44.1	7.4	3.8577	10
8 45	764	23.7	43.5	7.4	3.8187	5

Die Veränderung der Ergiebigkeit ist sehr gross und regelmässig, die der Temperatur am Anfang und Ende sehr bemerkenswert, sonst jedoch kein grosser Unterschied. Der Maximumwert trat 1 oder 2 Stunden nach der Flut, und der Minimumwert nach der Ebbe auf. Die Veränderung des Chlorgehaltes ist am Anfang sehr merkwürdig. Der Minimumwert tritt um 12^h 15 (ungefähr 1 Stunde nach dem Beginn des Sprudeln) auf. Die Ursache ist vielleicht darin zu suchen, dass sich zu Anfang kaltes Grundwasser mit dem Thermalwasser vermischt. Demnach bleibt der

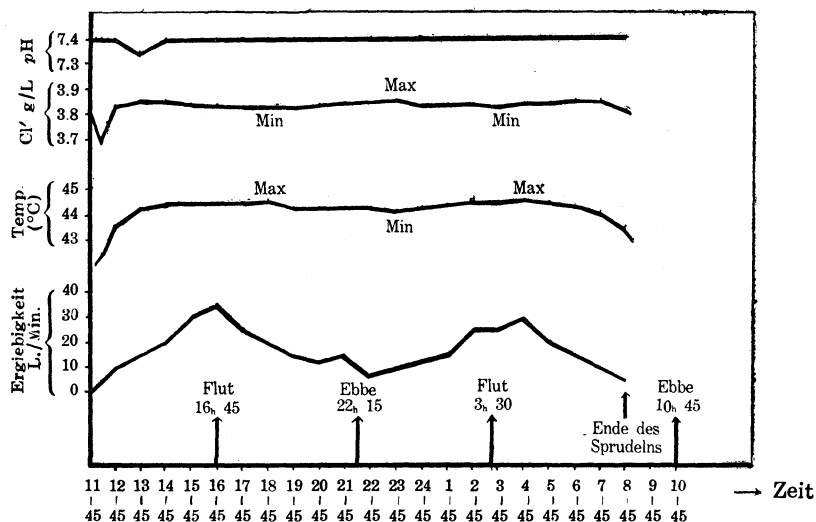


Abb. 3. Quelle Nr. 23 (Suzuki-Ryokan-no-Yu).

Chlorgehalt der Thermalquellen beinahe konstant. Wenn man die Analysenresultate vorsichtig betrachtet, treten bei Flut Minima und bei Ebbe Maxima auf. Diese Neigung ist der Quelle Nr. 21 sehr ähnlich, die in der vorhergehenden Untersuchung studiert worden ist. Die pH-Werte bleiben beinahe konstant, und man kann keine regelmässige Veränderung bemerken.

Erörterung. Die Veränderung der Ergiebigkeit und Temperatur der Quelle Nr. 23 kann man mit Hilfe der Fukutomi'schen Theorie, die sagt, dass der Einfluss von Ebbe und Flut auf die Thermalquellen nicht durch die direkte Mischung von Seewasser und Thermalwasser verursacht wird, sondern nur der Veränderung des Gezeitendrucks auf den Wasserdruck im Thermalquellenwasserweg zuzuschreiben ist, gut erklären. Um die Veränderung des Chlorgehaltes zu erklären, möchten wir eine geringe Vermischung von kaltem chlorarmen Grundwasser und Thermalwasser betrachten. Die Zusammenhänge zwischen Thermalwasser, Seewasser und Grundwasser sind bei dieser Thermalquelle ganz gleich wie bei den Quellen Nr. 22 und 21, die in der vorhergehenden Mitteilung schematisch gezeigt worden sind.

Zusammenfassung.

Die Veränderung der chemischen Zusammensetzung von 3 Thermalquellen in Ito (Provinz Sizuoka) wurde untersucht. 2 Quellen zeigten keine Veränderung von Temperatur, pH und Chlorgehalt. Eine Quelle wurde jedoch beträchtlich durch Ebbe und Flut beeinflusst. Maxima von Ergiebigkeit und Temperatur, Minima von Chlorgehalt treten 1 oder 2 Stunden nach der Flut auf. Diese Quelle sprudelt während der Ebbe ungefähr 3 Stunden lang nicht.

Ich erlaube mir hiermit Herrn Prof. Kenjiro Kimura für seine freundliche Anleitung und steten Ratschläge, die mir bei der Ausführung dieser Arbeit zuteil geworden sind, meinen herzlichsten Dank aussprechen. Herrn Dr. Yasuo Miyake möchte ich für seine freundliche Ratschläge, Herrn Kigosi für seine eifrige Hilfe herzlich danken. Dem Unterrichtsministerium sei für die Gewährung einer Unterstützung zur Anregung wissenschaftlicher Forschung gedankt. Der Kaiserlichen Akademie der Wissenschaft sind wir für ihre finanzielle Unterstützung ebenfalls zu grossem Dank verpflichtet.

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Über die Acetolyse von 1-Brom-sinomenein-ke-ton.⁽¹⁾

Von Kakuji GOTO, Ryo-zo MORI* und Tatsuo ARAI.

(Eingegangen am 31. Juli 1942.)

Wir haben vor einigen Jahren über die Acetolyse von 1-Bromsinomenein-ke-ton⁽¹⁾ berichtet⁽²⁾. Die äusserst schlechte Ausbeute an Phenanthren-körper (1-Brom-3-methoxy-4,6,7-triacetoxy-phenanthren) hat uns veranlasst schon dabei unsere Achtung auf dem stickstoff-haltigen Produkt zu richten.

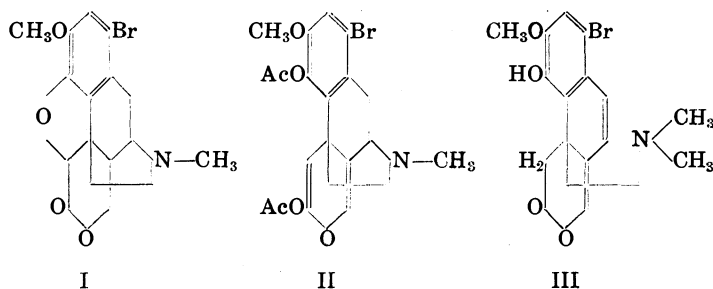
Um das letztere zu isolieren, wurde das Acetolysat, nach Verjagen des Anhydrides, in Methanol gelöst und in 3 proc. Essigsäure eingegossen. Das klare, gelbe Filtrat wurde dann mit Soda alkalisiert und schnell in Aether aufgenommen. Der Aether-Rückstand wollte sich nicht krystallisieren, aber beim Zusatz von Methyljodid wurde er sofort in ein wohl

(1) LIII. Mitteilung über Sinomenin.

* Herr Ryo-zo Mori hat kurz vorher durch einen Unfall sein Leben zum Vaterland geopfert. Wir bedauern seinen Tod, aber sein lieber Charakter wird in dem Gedächtnis von seinen Freunden ewig fortleben.

(2) Diese Bulletin, 8 (1933), 369.

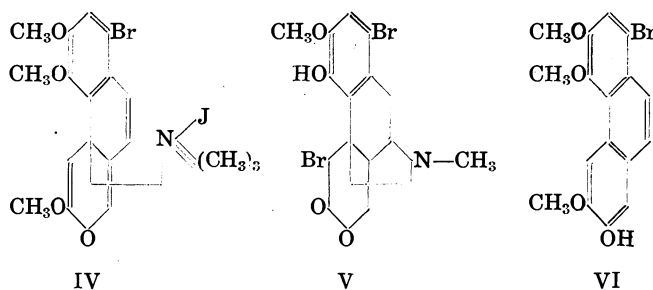
krystallisierendes, gelbes Jodmethylat von einer Base (II) umgewandelt, die wir aus folgenden Gründen als Diacetyl-1-brom-dehydro-sinomeninon bezeichnen wollen.



Das Jodmethylat schmilzt bei 203° und besitzt die Bruttoformel $C_{23}H_{25}NO_6BrJ$, enthält das originale Methoxyl, zwei leicht hydrolysierbare Acetoxyle und zeigt nur fade braune Farbe mit konz. Schwefelsäure.

Behandelt man dieses Jodmethylat mit Dimethylsulfat und Alkali, so werden die zwei Acetyle gegen zwei Methyl- getauscht, geöffnet an seiner C-N-Bindung und es entsteht eine des-N-Base. Die letztere wurde als Jodmethylat in schönen Krystallen erhalten, besitzt die Molekularformel $C_{22}H_{29}NO_4BrJ$, schmilzt bei 201.5° und gibt mit konz. Schwefelsäure sofort eine schöne blaue Farbe. Die zugrunde liegende freie Base ist als des-N-Methyl-dimethyl-1-brom-dehydro-sinomeninon (IV) zu bezeichnen.

Die Frage, ob in Diacetyl-1-brom-dehydro-sinomeninon der Oxydri- ring geöffnet worden ist, wurde durch die Acetolyse von 1,5-Dibrom-sinomeninon (V) in bejahender Weise beantwortet. Dabei haben wir dieselbe Diacetyl-1-brom-dehydro-sinomeninon erhalten, wie aus 1-Brom-sinomenoneinketon. Der Mischschmelzpunkt der Jodmethylate aus beiden Quellen bleibt auch unverändert.

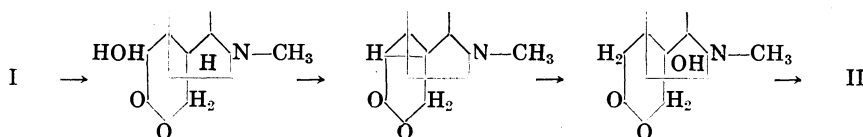


des-N-Methyl-dimethyl-1-brom-dehydro-sinomeninon-jodmethylat (IV) gibt beim Kochen mit 16.5 proc. Natronlauge zwei Phenanthrenkörper, davon einer ist alkali-löslich und der andere nicht. Der erstere ist besonders das Hauptprodukt, wenn man den Abbau in wässrigalkoholischem Alkali ausführt. Dieses Phenanthren enthält drei Methoxyle und ein Hydroxyl. Das Bromatom bleibt intakt. Die Stellung von diesen vier sauerstoffhaltigen Substituenten muss ganz gleich wie in Sinomenol selber

sein, weil dieses 1-Brom-oxy-trimethoxy-phenanthren sich sehr leicht zu 1-Brom-dimethyl-sinomenol methylieren lässt.

Acetylierung von diesem Brom-oxy-phenanthren führte, aber zu einem Acetyl-derivat, das ganz verschieden von dem 1-Brom-3,4,7-trimethoxy-6-acetoxy-phenanthren ist, welches man durch Acetolyse von 1-Brom-4-methylsinomenin gewonnen hat⁽³⁾. Dieser Unterschied lässt sich auch in den entbromten, benzoyleierten Derivaten beider Phenanthrene feststellen. Da die durch Öffnen von Oxydring entstandene, 4-ständige Phenolgruppe erfahrungsgemäss leicht methylierbar sein muss, suchen wir die Ursache des Unterschiedes dieser zwei Brom-phenanthrene in der umgekehrten Stellung von 6-Acetoxy- und 7-Methoxygruppen. Wenn diese Annahme richtig ist, dann muss das in Frage kommende Produkt 1-Brom-7-oxy-3,4,6-trimethoxy-phenanthren (VI) sein.

Diese Deutung passt wohl die angenommene chinoide Formel (II) von Diacetyl-1-brom-dehydro-sinomeninon. Eine der Keton-gruppen in dieser Substanz ist in der Stellung (7), wo die Enolisierung vollständig verhindert ist. Alkalyse von einer Substanz von der Konstitution IV wird natürlich zu dem Phenanthren (VI) führen. Das Zustandekommen der chinoiden Substanz II aus 1-Brom-sinomenein-keton (I) ist leicht verständlich wenn man annimmt dass beim Öffnen des Oxydringes, ein dreigliedriger Ring unter C(5), C(13) und C(14) oder ein vier-gliedriger Ring unter diesen drei und C(8) gebildet und dann dieser drei-oder vier-gliedriger Ring wieder hydrolytisch geöffnet wird, eine Doppelbindung in 8~14 Stellung hinterlassend, wie etwa in den folgenden Formelbildern gezeigt wird.



Eine Stütze für die chinoide Struktur dieser Diacetyl-base (II) ist die Tatsache dass sie eine tief rote Farbe zeigt, wenn sie mit kaustischem Alkali desacetyliert. Die Farbe schlägt beim Ansäuern gelb um. Die des-N-Methyl-dimethyl-base (IV) hat kein salz-bildendes Ort und zeigt natürlich diese Farbenänderung nicht.

Versuche. (–)-Diacetyl-1-brom-dehydro-sinomeninon-jodmethylat (II). (a) Durch Acetolyse von 1-Brom-sinomenein-keton. 30 g 1-Brom-sinomenein wurden durch einstündiges Erhitzen mit 50 ccm konz. HCl + 100 ccm Wasser bei 100° ins Diketon (I) umgewandelt. Die Lösung wurde zuerst allein und dann dreimal mit Methanol i. V. abgedampft. Der Rückstand wurde mit 200 ccm Essigsäure-anhydrid und 10 g Na-acetat vier Stunden gelinde gekocht. Nach dem Verjagen des Anhydrides i. V., wurde der Rückstand in Methanol gelöst und in 600 ccm 3 proc. Essigsäure eingegossen. Das Filtrat wurde, nach Alkalisieren mit Natrium-carbonat, schnell mit Aether geschüttelt und der Aether mit Natrium-sulfat getrocknet. Der Aether-rückstand wollte sich nicht krystallisieren, aber

(3) LI. Mitteilung, dieses Bulletin, 17(1942), 306.

verwandelte sich beim Zusatz von Jodmethyl unter Erwärmung ins Kryallbrei. Rohe Ausbeute 33 g, d.h. 66% d.T. Dieses Jodmethylat lässt sich aus Methanol umlösen. Dann stellt es wohl gebildete Nadeln oder kurze Prismen dar. Schmp. 203°. In konz. Schwefelsäure löst es sich fade rosa.

(b) Durch Acetolyse von 1,5-Dibrom-sinomeninon (V). 3.2 g Sinomeninon wurden, in 60 ccm Eisessig gelöst, mit 3.2 g (=2 Mol.) Brom, verdünnt ebenso mit 60 ccm Eisessig, an seinem C(1) und C(5) bromiert. Nach Abdampfen des Eisessigs, wurde der Rückstand ganz in der Weise wie unter (a) angegeben, behandelt. Das Jodmethylat wog ca. 2 g d.h. 50% d.T. Aus Methanol krystallisiert es in achteckigen Plättchen und schmilzt bei 198° (auch die Mischprobe). Gefunden: C, 44.05; H, 4.35; N, 2.30; Br, 13.18; J, 19.98; CH₃O, 5.18. Berechnet für C₂₃H₂₅NO₆BrJ (618): C, 44.66; H, 4.05; N, 2.27; Br, 12.92; J, 20.71; CH₃O, 5.02%.

Acetyl-bestimmung. 0.3000 g Jodmethylat, gelöst in 30 ccm Methanol und versetzt mit 10 ccm N/5-NaOH. Nach Erwärmen bei 100° fünf Minuten, wurde mit destilliertem Wasser stark verdünnt und mit N/5-H₂SO₄ titriert, Lackmus und Phenolphthalein als Indikator. Verbraucht wurden 5.4 ccm N/5-H₂SO₄, also $(10-5.4) \times 41 \div 5000 = 0.03772$ g Acetyl. Ber. 13.27%, Gef. 12.57%. Spec. Drehung. Subst.=0.0942 g; 50% Methanol=10 ccm; 1 dm-Rohr; $\alpha = -0.21^\circ$; $[\alpha]_D^{18} = -22.3^\circ$.

(+)-Diacetyl-1-brom-dehydro-sinomeninon-jodmethylat (II). 1 g (-)-1-Brom-sinomeninon (aus (-)-Dihydro-thebainon) wurde mit 1 Mol Brom bromiert und dann wie in (b) acetolysiert und behandelt. Ausbeute 0.3 g. Schmp. 203° (aus Methanol). Alle anderen Eigenschaften sind gleich mit dem (-)-Jodmethylat aus Sinomenin, ausgenommen der spec. Drehung. Spec. Drehung. Subst.=0.0958 g; 50% Methanol=10 ccm; 1 dm-Rohr; $\alpha = +0.21^\circ$; $[\alpha]_D^{19} = +21.9^\circ$.

d,l-Diacetyl-1-brom-dehydro-sinomeninon-jodmethylat. Durch Vereinigen und Abdampfen der obigen beiden Lösungen. Flache Prismen aus Methanol. Schmp. 193°, $\alpha = \pm 0^\circ$.

Der N-freie Anteil ist, wie schon berichtet, 1-Brom-3-methoxy-5,6,7-triacetoxy-phenanthren. Dieses Phenanthren wird durch Acetolyse dieses Diacetyl-jodmethyلاتes (II) in 80 proc. Ausbeute erhalten.

1-Brom-dehydro-sinomeninon-chlorhydrat. (ableitet von II). 9.2 g des Aether-rückstandes, beschrieben in (2), wurden mit 17 ccm 10 proc. Salzsäure über Nacht stehen gelassen. Dann wandelte die ganze Lösung in Krystallbrei von desacetyliertem Chlorhydrat um. Zersp. 203° (wasserfrei; Sintern ab 190°). Eisenchlorid-Reaktion rotbraun. Gelbrote Farbe mit konc. Schwefelsäure. Gefunden: C, 50.56; H, 4.70; Cl, 8.46. Berechnet für C₁₈H₁₉O₄NBr·HCl (429.5): C, 50.29; H, 4.42; Cl, 8.29%. Spec. Drehung. Subst.=0.1180 gr; Wasser=10 ccm; 1 dm-Rohr. $\alpha = -0.06$; $[\alpha]_D^{18} = -5.10^\circ$.

des-N-Methyl-1-brom-dehydro-sinomeninon (III). 1.5 g Diacetyl-1-Brom-dehydro-sinomeninon-jodmethylat (II) wurden in 40 ccm Wasser gelöst (eventuell filtriert) und nach Zusatz von 5 ccm 33 proc. NaOH eine Stunde bei 50~60° erwärmt. Die Lösung färbt sich stark gelbbraun. Nachdem das freie Alkali mit CO₂ fixiert wurde, versetzte man 40 ccm Methanol und mit Chloroform wiederholt geschüttelt. Der Chloroform-

Rückstand krystallisierte beim Zusatz von Methanol. Gelbe Prismen, die an der Luft verröten. Schmp. 184–187°. Jodfrei. Eisenchloridreaktion zuerst rot (Diketon), nach einigen Tagen grün. Stark blaue Halochromie in konz. Schwefelsäure (des-N-Methyl-base). Gefunden: C, 55.63; H, 5.15; N, 3.31. Berechnet für $C_{19}H_{20}NO_4Br$ (406): C, 56.15; H, 4.92; N, 3.45%. Spec. Drehung. Subst.=0.0937 g; 2% HCl=10 ccm; 0.5 dm-Rohr; $\alpha=+1.33^\circ$; $[\alpha]_D^{12}=+283.9^\circ$.

Durch Acetolyse gibt diese Substanz (III) das 1-Brom-3-Methoxy-4,6,7-triacetoxy-phenanthren in einer guten Ausbeute.

(-)-*des-N-Methyl-dimethyl-1-brom-dehydro-sinomeninon-jodmethylat* (IV). 4 g Diacetyl-1-brom-dehydro-sinomeninon-jodmethylat (II) wurden in 35 ccm Wasser gelöst und mit wechselseitigem Zusatz von 10 ccm 33 proc. Natronlauge und 10 ccm Dimethyl-sulfat methyliert. Die Temperatur muss am Ende bei 70–75° gehalten werden. Durch Zusatz von 4 g Kaliumjodid zu der noch warmen Lösung wird das Jodmethylat dieser des-N-Methyl-dimethyl-base zur Krystallisation gebracht. Umgelöst aus zehnfacher Menge Wasser, stellt es gelbe Prismen dar, die bei 201.5° unter Zers. schmelzen. Ausbeute 2 g. Blaue Halochromie in konz. Schwefelsäure (des-N-Methylbase). Gefunden: C, 45.21; H, 5.24; N, 2.31; Br, 13.65; J, 22.80; CH_3O , 15.72. Berechnet für $C_{22}H_{20}NBrJO_4$ (578): C, 45.69; H, 5.02; N, 2.42; Br, 13.84; J, 21.97; $3CH_3O$, 16.09%. Spez. Drehung. Subst.=0.0684 gr. Methanol=10 ccm; 1 dm-Rohr. $\alpha=-1.16^\circ$; $[\alpha]_D^{22.5}=-169.6^\circ$.

(+)-*des-N-Methyl-dimethyl-1-brom-dehydro-sinomeninon-jodmethylat* (IV). Darstellung aus (+)-Diacetyl-jodmethylat (II; S. oben) in der ganz ähnlichen Weise wie bei (-)-Substanz. Schmp. 199°. Ausbeute ca 50%. Spec. Drehung. Subst.=0.0675 g; Methanol=10 ccm; 1 dm-Rohr. $\alpha=+1.17^\circ$. $[\alpha]_D^{22.5}=+170.4^\circ$.

d,l-Substanz. Die beiden Lösungen, die man bei der optischen Messung gebraucht hat, wurden vereinigt und verdampft. Kurze, hexagonale Prismen (ebenso aus Wasser). Schmp. 224°. $\alpha=\pm 0$.

Hofmannscher Abbau von des-N-Methyl-dimethyl-1-brom-dehydro-sinomeninon-jodmethylat.

4 g dieses Jodmethylates (IV) wurden mit 30 ccm 11 proc. Natronlauge 15 Minuten und dann, nach Zusatz von 30 ccm 5 proc. Natronlauge, noch eine halbe Stunde gelinde gekocht. Aus der mit Wasser verdünnten alkalischen Lösung gewann man mittelst Chloroform ein Phenanthren von Schmp. 178° (umgelöst aus Aethanol; Ausbeute 0.3 g), welches, aber, zur Zeit nicht untersucht wurde. Die Alkali-lösung wurde dann mit Kohlensäure gesättigt und wieder mit Chloroform extrahiert. Das alkali-lösliche Phenanthren krystallisiert dann in Prismen von Schmp. 161° (auch aus Aether). Ausbeute 1 g Leicht löslich in org. Lösungsmitteln. Eisenchlorid-Reaktion grün. Gefunden: C, 56.01; H, 4.24. Berechnet für $C_{17}H_{15}O_4Br$ (363): C, 56.19; H, 4.13%.

Methylieren. Durch Methylieren dieses Phenanthrens mit Dimethyl-sulfat und Alkali wurde 1-Brom-dimethyl-sinomenol (Schmp. 114.5°; auch Mischprobe) gewonnen. Dies beweist klar dass die Umlagerung der O-haltigen Gruppen nicht stattgefunden hat.

Acetylieren. 0.4 g des Phenanthrens + 0.1 g Na-Acetat + 10 ccm Essigäthydrat wurden eine Stunde gekocht. Das 1-Brom-3,4,6-trimethoxy-7-acetoxypheanthren schmilzt bei 132° (aus Eisessig). Ausbeute 0.3 g. Gefunden: C, 56.29; H, 4.24. Berechnet für $C_{19}H_{17}O_5Br$ (405): C, 56.29; H, 4.19%.

Dasselbe Acetylphenanthren wurde auch durch Acetolyse von des-N-Methyl-dimethyl-1-brom-dehydro-sinomeninon-jodmethylat (IV) erhalten. Schmp. 129°; Ausbeute 30%. Dieses Produkt wurde desacetyliert und mit Dimethylsulfat und Alkali methyliert. Das entstandene 1-Bromdimethylsinomenol schmilzt bei 143° (auch die Mischprobe).

Benzoylieren. Das Phenanthren (VI) wurde in 4 proc. Natronlauge gelöst (Ausscheidung von Phenolat), und nach Schotten-Baumann mit Benzoylchlorid benzoyliert. Das 1-Brom-3,4,6-methoxy-7-benzoyloxyphenanthren krystallisiert in Nadeln aus Methanol. Schmp. 177°. Gefunden: C, 61.75; H, 4.07. Berechnet für $C_{24}H_{19}BrO_5$ (467): C, 61.67; H, 4.07%.

3,4,6-Trimethoxy-7-benzoyloxyphenanthren. Das Bromphenanthren (VI) wurde katalytisch entbromt. Weder das bromfreie Phenol noch dessen acetylierte Produkt war krystallin. Das nach Schotten-Baumann benzoylierte Oxyphenanthren war, indessen, wohl krystallisierend. Schmp. 141.5°. Gefunden: C, 73.82; H, 5.25. Berechnet für $C_{24}H_{20}O_5$ (388): C, 74.22; H, 5.15%.

Benzoyl-Bestimmung. Hydrolyse mit 0.25 N alkoholischem Kali und Rücktitrieren mit 0.2 N Schwefelsäure. Ber. 27.01%. Gef. 29.91%.

3,4,7-Trimethoxy-6-benzoyloxyphenanthren. Zum Vergleich, wurde das letztere Phenanthren durch Kalischmelze von Methylsinomenin und darauffolgende Benzoylieren des auch nicht krystallisierenden Oxyphenanthrens dargestellt. Schmp. 139°. Gefunden: C, 73.71; H, 5.39%.

Die Mischprobe der beiden Trimethoxybenzoyloxyphenanthrene schmolz aber, bei 134° (mit vorherigem Sintern ab 120°).

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The Glow Electrolysis and its Mechanism. (II).⁽¹⁾ On the Study of the Formation of Basic Salts.

By Yohei YAMAGUCHI and Akinori MUTA.

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Introduction. The study of the mechanism of glow electrolysis, in which one of the electrodes of the ordinary electrolysis is drawn up in the atmosphere and the electric current is flowed by the glow discharge between this electrode and the surface of the solution, has been investigated by the following authors.

Since 1887, Gubkin⁽²⁾ studied the glow discharge of the solutions of zinc sulphate, silver nitrate and platinic chloride and obtained zinc oxide, metallic silver and metallic platinum, respectively; Günther-Schulze⁽³⁾, Makowezki⁽⁴⁾, Haber⁽⁵⁾, Klemenc⁽⁶⁾, Corbino⁽⁷⁾, Cousin, Jolivois⁽¹⁰⁾, Fichter and Keslenholz⁽⁹⁾ studied on various sorts of salt solutions and obtained oxides and hydroxides. Many of them often observed that the current efficiency was about 120% or more, especially for the solutions of copper, zinc, and lead salts. And they attributed the anomalous current efficiency to the photochemical action or adsorption without quantitative analyses of the products.

Yamaguchi and Shiba⁽¹⁾ previously studied on the glow electrolyses for various salt solutions and discussed the experimental results with the theory dissociation of water molecules by the impacts of electrons. Yasuda⁽¹¹⁾ reported that colloidal solutions were obtained by the similar process.

In the present experiment, the products of the glow electrolyses for cupric sulphate and zinc sulphate solutions at various concentrations were carefully examined by the quantitative analysis, etc. It was found that many products were composed of such basic salts as $2\text{CuSO}_4 \cdot 5\text{Cu}(\text{OH})_2 \cdot \text{H}_2\text{O}$; $\text{CuSO}_4 \cdot 3\text{Cu}(\text{OH})_2$; $\text{ZnSO}_4 \cdot 3\text{Zn}(\text{OH})_2$, and the glow electrolysis gave one of the new methods of formation of basic salts. The abnormal discrepancy of the actual current efficiency from that calculated by Faraday's law is attributed to the formation of basic salts.

(1) Y. Yamaguchi and A. Muta, *J. Electrochem. Assoc. Japan*, **10**(1942), 232; Y. Yamaguchi and T. Shiba, this Bulletin, **9**(1934), 83.

(2) J. Gubkin, *Pogg. Ann.*, **32**(1887), 114.

(3) A. Günther-Schulze, *Z. Elektrochem.*, **31**(1925), 187.

(4) A. Makowezki, *Z. Elektrochem.*, **17**(1911), 217.

(5) F. Haber and A. Klemenc, *Z. Elektrochem.*, **20**(1914), 485.

(6) A. Klemenc, *Z. Phys. Chem.*, **130**(1927), 378; **A 154**(1931), 385; **A 166**(1933), 313; **B 27**(1935), 339; **A 179**(1938), 1; **A 182**(1938), 91; **B 40**(1938), 252; *Z. Elektrochem.*, **37**(1931), 742.

(7) O. M. Corbino, *Atti. Acad. Lincei. Roma*, **6.5**(1927), 377.

(8) M. P. Jolivois, *Ber.*, **71**(1938), 73; *Bull. soc. chim.*, [5] **5**(1938), 1429.

(9) F. Fichter and K. Kestonholz, *Helv. Chim. Acta*, **23**(1940), 209.

(10) M. P. Jolivois, *Helv. Chim. Acta*, **23**(1940), 405.

(11) S. Yasuda, *Japan. Assoc. Advancement*, **15**(1940), 327.

Apparatus. The apparatus is shown in Fig. 1. The discharge cell is a U-tube of 5.5 cm. in diameter, the cathode of platinum wire is held in gas phase and the anode is immersed in the solution. The diameter of the platinum wire is 1.4 mm. and the distance between the tip of the platinum wire of the cathode and the surface of the solution is about 5 mm. The pressure of gas phase is always kept at 5 to 10 mm. Hg., and the voltage of the glow electrolysis is held at 300 to 600 V. The apparatus is put in a mixture of ice and salt. The diagram of circuit is shown in Fig. 2.

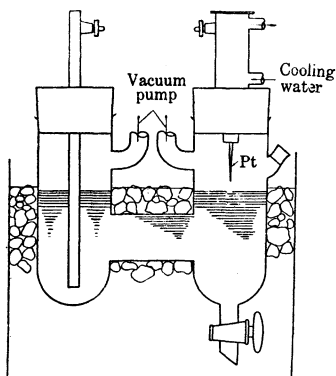


Fig. 1.

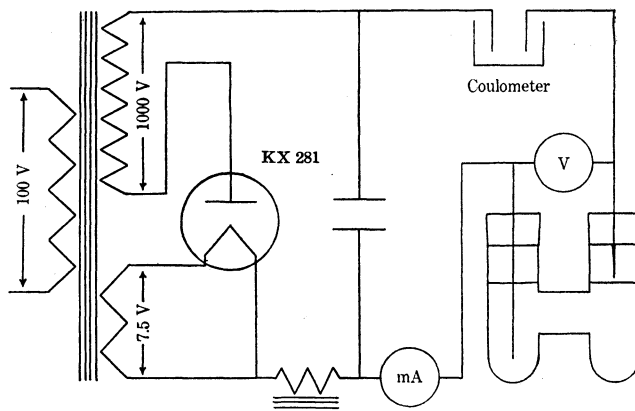


Fig. 2.

Experimental. (1) In the case of the glow electrolysis of zinc sulphate solution, white thin membrane of precipitate is generally formed from the concentrated solution, and white colloid is generally from comparatively dilute one, while white colloid is always formed from the solution which is stirred by bubbles of air.

After the precipitate was filtered, and washed until there was no reaction of SO_4 , it is dried between $100^\circ\text{--}110^\circ\text{C.}$ and weighed. It is then dissolved in NaOH solution and electro-analysed at 50°C. , 4.4V and 0.8A for 2 hours. The total weight of zinc is weighed, and compared with the weight of copper from copper coulometer. Thus the current efficiency of zinc is determined, and the weight per cent of zinc in the precipitate is also obtained.

Table 1.

No.	Conc. (mol./l.)	V	MA	mm. Hg	Current Efficiency (%)	Zn (%)
1	2.00	560	38	51	110	55.5
2	1.79	500	58	26	110	54.9
3	1.02	520	44	28	117	55.7
4	0.77	540	44	26	115	55.5
5	0.46	556	41	56	106	55.4
6	0.062	540	60	31	118	55.5
7	0.046	520	42	30	109	55.5
8	0.032	621	30	68	89	56.3
9	0.031	600	30	27	104	55.7
10	0.013	624	26	55	97	54.5

From Table 1 we can see that the products are in the same composition in these regions of concentration.

Quantitative Analysis. As stated above, the total weight of the precipitate and Zn are weighed, and the weight of SO_4^{--} is also determined by BaCl_2 . From these results the proportion of ZnSO_4 to $\text{Zn}(\text{OH})_2$ also is known as 1 to 3 as shown in Table 2. Water of crystallization is also examined by heating. There is found only 29.2% of loss in weight, which will be obtained by the reaction $\text{ZnSO}_4 \cdot 3\text{Zn}(\text{OH})_2 \rightarrow 4\text{ZnO}$. Therefore, the precipitates have no water of crystallization.

Table 2.

No.	Concentration mol/l.	Total Weight (g.)	Zn (g.)	SO_4^{--} (g.)	$\text{ZnSO}_4 : \text{Zn}(\text{OH})_2$
11	2.77	0.0810	0.0460	0.0172	1:3.06
12	0.02	0.1321	0.0725	0.0326	1:3.02

(2) *Very Dilute Zinc Sulphate Solution.* When a very dilute solution of 8.04×10^{-6} mol./l. is electrolysed at 1000V, 4mA, and 9 mm. Hg. white colloidal solution is obtained. The product is found to be of the composition $\text{Zn}(\text{OH})_2$ by quantitative analysis and crystalline by the Debye-Sherrer photograph.

(3) *Cupric Sulphate Solution.* (a) *Current efficiency.* The green precipitates are formed by the glow electrolysis. The total weight of the precipitate is determined by the same treatment as in the case of zinc sulphate. It is then dissolved in nitric acid and electrolysed with 2.2V and 0.6A for 3 hours at 75°C. The weight of the deposited Cu is determined and the current efficiency is calculated.

Table 3.

No.	Concentration (mol./l.)	V	MA	mm. Hg	Current Efficiency (%)	Cu (%)
1	0.775	610	41	28	111	51.0
2	0.412	660	32	23	103	49.6
3	0.016	680	38	28	—	51.2
4	0.015	680	36	26	—	50.4
5	0.011	620	37	26	118	50.9
6	0.009	580	39	19	113	51.0
7	0.005	600	27	19	109	51.0
8	0.004	660	29	23	125	55.0
9	0.002	630	24	19	120	55.2
10	0.002	755	24	—	—	54.1

It is shown in Table 3 that there are two kinds of precipitates which are separately deposited by the different condition of the concentration. The condition will be varied by temperature.

(b) *Quantitative Analysis.* The quantity of SO_4^{--} is determined by BaCl_2 and that of crystalline water is measured by red heating. The analytical data of the precipitates of 51 and 55% of Cu are shown in Tables 4 and 5 respectively.

Table 4.

No.	Concentration (mol./l.)	Total Weight (g.)	Cu (g.)	SO_4^{--} (g.)	$\text{CuSO}_4:\text{Cu}(\text{OH})_2$
1	0.775	0.1061	0.0541	0.0233	1:2.52
2	0.015	0.1275	0.0641	0.0300	1:2.51
3	0.009	0.1354	0.0745	0.0261	1:2.47

Table 5.

No.	Concentration (mol./l.)	Total Weight (g.)	Cu (g.)	SO_4^{--} (g.)	$\text{CuSO}_4:\text{Cu}(\text{OH})_2$
8	0.002	0.2192	0.1207	0.0451	1:3.04

46.5% of water is driven off by red heat, and 45.6% is expelled by the reaction: $\text{CuSO}_4 \cdot 3\text{Cu}(\text{OH})_2 \rightarrow 4\text{CuO}$.

(4) *Very Dilute Cupric Sulphate Solution.* Greenish blue colloidal solution is obtained from 5.4×10^{-6} mol./l. solution of CuSO_4 by the glow electrolysis with 820V and 18mA at 23 mm. Hg. The greenish blue product is known as $\text{CuO} \cdot 2\text{H}_2\text{O}$ by red heat. By heating the green colloidal solution soon changes into black colloid, which is $6 \text{ CuO} \cdot \text{H}_2\text{O}$.

Discussion. As these experiments, basic salts are formed by the glow-electrolysis of zinc and cupric sulphate solutions. The basic salt is formed by the secondary reaction, while the hydroxide is formed by the primary reaction as seen on very dilute solutions.

Basic salts of cupric and zinc sulphate have been usually formed by the following two methods, the one is that an insufficient quantity of alkali is added to a concentrated salt solution, the other is that metal or oxide powders are suspended in a concentrated salt solution. The reaction velocity in the former is much faster than in the latter. By the glow-electrolysis the formation of basic salt is soon observed after the electrolysis, as then it is in the former case. Thus, quantity of zinc combined as zinc hydroxide is in proportion to the amount of coulomb. And the hydroxide is in proportion to the amount of coulomb. And the hydroxide combines secondarily with sulphate in the solution to form basic salts. Hence the current efficiency of total zinc becomes larger than that calculated from the coulometer by Faraday's law, and often over 100%.

If a known amount of zinc oxide is suspended one month in a saturated solution of zinc sulphate and the basic salt formed is weighed, the weight of the basic salt is the sum of the weights of the zinc oxide, and of the zinc sulphate and water combined, as shown in Table 6.

Table 6.

ZnO (g.)	ZnSO ₄ ·3Zn(OH) ₂ ·H ₂ O (cal.)	ZnSO ₄ ·3Zn(OH) ₂ ·H ₂ O (obs.)
0.3665	0.5730	0.5725

This fact will verify the above explanation of the current efficiency which is often over 100%.

The basic salt is formed immediately, when an insufficient quantity of alkali is added to cupric sulphate solution,⁽¹²⁾ then the activation energy of the following reaction is small, and the heat of reaction is as shown by the following equation,



Hence it is very reasonable that there is the formation of basic salt which is more stable than simple hydroxide.

Current efficiency. From these facts, it is clear that the true current efficiency of product corresponds to the weight of metal of hydroxide in basic salt.

The calculated true current efficiencies are shown in Table 7.

Table 7.

Precipitate		Current Efficiency Calculated	
		As Basic Salt (apparent) (%)	Hydroxide only (true) (%)
No. 5	ZnSO ₄ ·3Zn(OH) ₂	118	88.5
No. 5	2CuSO ₄ ·5Cu(OH) ₂ ·H ₂ O	118	84.5
No. 8	CuSO ₄ ·3Cu(OH) ₂	125	94.0

When we make allowance for the dissolution of anode metal, its current efficiency is to be comparable to the current efficiency (85%) of the product CuO·2H₂O formed in a very dilute solution of cupric sulphate

Weights of Cu anodically dissolved per coulomb are shown in Table 8. It is known that the current efficiency are almost 100%.

Table 8.

	Precipitate	Current Efficiency (%)
No. 1	2CuSO ₄ ·5Cu(OH) ₂ ·H ₂ O	98.9
No. 2	"	101.0
No. 7	CuSO ₄ ·3Cu(OH) ₂	100.0
	CuO·2H ₂ O	91.0

From these results, it is unable to consider that there is the reaction which deposits metal at cathode and lets free SO₄⁻⁻, over the number of coulomb passed.

(12) M. P. Sabatier, *Compt. rend.*, **125**(1897), 301. M. O. Binder, *ibid.*, **193**(1934), 653.

(13) M. P. Sabatier, *Compt. rend.*, **125**(1897), 101.

The weight of copper anodically dissolved is somewhat greater than that of metal in hydroxide, cathodically formed. This discrepancy is attributed to the existence of the reaction $\text{Cu} \rightarrow \text{Cu}^+$ in some extent, together with the main reaction $\text{Cu} \rightarrow \text{Cu}^{++}$, when copper is anodically dissolved, as the ordinary electrolysis.⁽¹⁴⁾

The Effect of the Temperature. For the reason that the glow electrolysis gives metallic compounds, it can be suspected that there is an effect of heat, caused by the impacts between electrons and metallic ions or water molecules. From the above experiment, it is known that the product in a very dilute solution of cupric sulphate by the glow electrolysis is $\text{CuO} \cdot 2\text{H}_2\text{O}$ and not $6\text{CuO} \cdot \text{H}_2\text{O}$ and the reaction $\text{CuO} \cdot 2\text{H}_2\text{O} \rightarrow 6\text{CuO} \cdot \text{H}_2\text{O}$ takes place in an aqueous suspension at 77°C .⁽¹⁵⁾ From these facts there is no need to suppose the effect of heat for the formation of the metallic compounds.

From the result of the studies on the state of the deposits, it was found that in zinc sulphate solution by the glow-electrolysis, the deposit becomes the more colloidal the more dilute the solution is. The size of the particle is known as 10^{-5} to 10^{-6} cm. by the Debye-Sherrerr Method.

Summary.

(1) It has been said that oxides are formed by the glow-electrolysis of zinc sulphate solution. From the above studies, however, it is known that $\text{ZnSO}_4 \cdot 3\text{Zn}(\text{OH})_2$ is formed, and the colloidal solution of zinc hydroxide is obtained with very dilute solution, as 8.04×10^{-6} Mol.

(2) It has been said that oxide or hydroxide is formed in the cupric sulphate solution. From the above researches, however, the basic salt, $2\text{CuSO}_4 \cdot 5\text{Cu}(\text{OH})_2 \cdot \text{H}_2\text{O}$, is obtained from its concentrated solution of over 0.002 mol., and $\text{CuSO}_4 \cdot 3\text{Cu}(\text{OH})_2$ is obtained from under 0.002 mol. and colloidal solution of simple hydroxide, $\text{CuO} \cdot 2\text{H}_2\text{O}$, is formed with the very dilute solution of 5×10^{-6} mol./l.

(3) The reason for the abnormally large current efficiency such as about 120% has not been cleared. From the following facts, it is cleared that this is the result of the secondary formation of the basic salt.

- (a) The comparison of the ordinary method of formation of the basic salt with its formation by the glow electrolysis.
- (b) The agreement between the current efficiency of hydroxide contained in basic salt as a constituent and that of hydroxide produced in a very dilute solution.
- (c) The weight of copper anodically dissolved shows the current efficiency of about 100%.
- (d) The weight of the basic salt, $\text{ZnSO}_4 \cdot 3\text{Zn}(\text{OH})_2 \cdot \text{H}_2\text{O}$ which is formed from ZnO, is the sum of the weight of ZnO taken and the weights of ZnSO_4 and water combined.

(14) F. Fischer, *Z. Elektrochem.*, **10**(1904), 427.

(15) W. Spring and L. Lucion, *Z. anorg. Chem.*, **2**(1892), 195; D. Tommasi, *Bull. soc. chim.*, **37**(1882), 197.

(4) For the mechanism of the glow-electrolysis, there is no need to consider the effect of heat caused by impacts between electrons and ions, etc., because the green $2\text{CuO}\cdot\text{H}_2\text{O}$ which is obtainable at ordinary temperature is formed in a very dilute solution and it changes to black $6\text{CuO}\cdot\text{H}_2\text{O}$ by heating over 77°C .

In conclusion, the authors wish to express their hearty thanks to Dr. K. Baba and the late Dr. K. Kasai, Director and former Director of the Hitachi Central Research Laboratory, for their kind advice and encouragement. A part of the expense of this investigation has been defrayed from the Scientific Research Encouragement Grant from the Department of Education to which the authors' thanks are due.

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**Physico-Chemical Investigations on Catalytic Mechanism. VIII.
On the Fischer-Tropsch Synthesis of Hydrocarbons with Special
Reference to the Durability of Catalyst.
(Experimental Series II.) (4).**

By Senzo HAMAI, Shiro HAYASHI and Kiyoshi SHIMAMURA.

(Received August 1, 1942.)

Introduction. In a previous paper⁽¹⁾, we reported the experimental results relating to the durability and pretreatment of catalyst. In this paper we shall attempt to report some of our earlier experimental data for the durability of catalyst. We have been calling attention to the prime importance of durability of catalyst which may possibly depend on various factors, such as the method of preparation, history of pretreatment, constituents of the catalyst, as well as the type of promoters present and numerous others. For a systematic research for this type of investigation, the question of revivification is often taken up side by side, since the experimental investigation for the durability without revivification takes too much of the time although such data must be very essential, especially for developing a theory, as related to the catalytic activity and durability.

Here, in this paper we shall present some of our durability records for the catalyst I₁-1, Co+15% ThO₂+100% Kieselguhr and V₁-1, Co+12% U₃O₈+2.5% Cu+100% Kieselguhr. Preparations of the catalysts

(1) Report VII, S. Hamai, *J. Chem. Soc. Japan*, **63**(1492), in press.

were similar to those already described in our earlier papers⁽²⁾. Experimental procedure was also analogous to those already mentioned in our previous papers. The catalyst I₁-1 and V₁-1 were pretreated by air at 400°C. for 2 hours prior to H₂ reduction at 350°C. for 5 hours, and after these pretreatments, the regular synthesis was proceeded by passing a CO+H₂ mixture (CO:H₂=1:2), 4 l./hr. at 225°C. The gas contraction percentage was taken as a measure of the activity, and the variation of the composition of the effluent gas was analyzed from time to time by using a modified form of the Orsat Gas Analysis Apparatus; in reality the gas samples were taken at the intervals of about 2 hours and analyzed.

Experimental Results and Discussions. Table 1 is more or less self explanatory. In Table 2, those gas analysis data for the effluent gas for F₄ in which the catalyst I₁-1, CO+15%ThO₂+100%Kieselguhr has been employed are shown. As seen in this table, after a certain period the synthesis reaction seemed to be normalized and in such a case more or less, no methane formation was observed⁽³⁾. In Table 3, those data for F₁₄ for the same catalyst and similar pretreatment and experimental conditions are shown. Here we also noticed that after a certain period the

Table 1.

Exp. No.	Catalyst No.	Catalyst Comp.						Pretreatment		Exp. Durat. (hrs.)	React. Temp. (°C.)	Cont. Per- cent- age (%)
		Co+ThO ₂ +U ₃ O ₈ +Cu+Kies.						Heat. Treat. (°C.) (hrs.)	H ₂ Reduct. (°C.) (hrs.)			
F ₄	I ₁ -1	100	15	—	—	100		400 2	350 5	65	225	40
F ₁₄	"	"	"	—	—	"		" "	" "	"	"	15
F ₁₉ (A-K)	V ₁ -1	"	—	12	2.5	"		" 5	" 5	129 ² / ₃ *	"	45-35
F ₁₉ (L)	"	"	—	"	"	"		— —	270 2	6	190-250	70
F ₁₉ (M)	"	"	—	"	"	"		— —	— —	13	250	40
F ₁₉ ** (N)	"	"	—	"	"	"		— —	— —	"	225	25
F ₁₉ (O)	"	"	—	"	"	"		— —	— —	10½	"	16
F ₁₉ (P)	"	"	—	"	"	"		— —	300 2	4	225-300	22
F ₁₉ (Q)	"	"	—	"	"	"		400 2	270 5	13½	225	8
F ₁₉ (R)	"	"	—	"	"	"		— —	— —	12	230	44
F ₁₉ (S)	"	"	—	"	"	"		— —	— —	13	235	"

* Total hrs. for F₁₉(A-K)

** Rate of gas flow, 6-4 l./hr.

(2) IV, this Bulletin, 17(1942), 166.

V, this Bulletin, 17(1942), 252.

VI, this Bulletin, 17(1942), 339.

(3) Samples 22, 24 and 28 show a few percent of CH₄; this is probably due to the local variation of reaction temperature on the particular part of the catalyst which might possibly have caused the CH₄ formation (i.e., temperature rises locally owing to the possible fluctuation of the gas flow which in turn causes the insufficient conducting of the heat.).

Table 2.

(F₁₄) Catalyst I₁-1, Co+15% ThO₂+100% Kieselguhr.Heat treatment prior to H₂ Reduction, 400°C., 2 hrs.H₂ Reduction, 350°C., 5 hrs.

Duration of Experiment, 65 hrs.

Reaction temperature, 225°C.

Rate of Gas Flow, 4 l./hr., CO:H₂=1:2.

Gas Analysis Data											
Sample No.	1	2	3	4	5	6	7	8	9	10	11
CO ₂	0.1	0.2	5.0	12.7	7.0	4.2	2.5	2.0	2.6	2.6	2.5
C ₂ H ₂	0.0	0.0	0.0	0.2	0.3	0.0	0.3	0.0	0.7	0.3	0.0
C ₂ H ₄	0.3	0.2	0.0	0.3	0.8	0.7	0.5	1.0	0.7	0.4	0.5
C _n H _{2n}	0.0	0.3	0.2	0.2	0.2	0.5	0.7	0.2	0.0	0.8	0.4
O ₂	0.6	0.4	0.3	0.4	0.4	0.6	1.0	0.3	0.4	0.3	0.6
CO	14.8	20.5	14.1	7.6	16.4	21.1	25.6	26.5	25.6	26.7	28.5
H ₂	81.3	76.9	70.0	56.8	62.9	64.1	64.0	65.4	64.8	64.1	64.7
CH ₄	0.0	0.0	6.5	19.2	8.0	5.6	0.0	2.7	3.0	2.8	0.0
C ₂ H ₆	0.0	0.0	0.0	0.6	2.2	0.9	0.0	0.0	0.0	0.0	0.0
N ₂	2.9	1.5	3.9	2.0	1.8	2.3	4.5	1.9	2.3	2.1	2.8
Sample No.	12	13	14	15	16	17	18	19	20	21	22
CO ₂	3.0	1.1	0.6	0.4	0.0	1.0	1.3	1.0	1.1	0.0	1.1
C ₂ H ₂	0.4	0.2	0.0	0.2	0.0	0.3	0.3	0.2	0.4	0.6	0.3
C ₂ H ₄	0.6	0.5	0.5	0.8	0.5	0.2	0.4	0.3	0.5	0.3	0.3
C _n H _{2n}	0.3	0.2	0.4	0.6	0.2	0.5	0.2	0.5	0.5	0.2	0.2
O ₂	0.4	0.5	0.3	0.3	0.4	0.4	0.3	0.4	0.2	0.7	0.2
CO	27.5	30.3	30.9	28.7	30.2	27.1	30.3	30.4	30.4	31.2	30.9
H ₂	61.9	65.1	65.7	66.2	66.8	68.4	65.5	65.3	65.8	64.4	64.8
CH ₄	3.6	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.9
C ₂ H ₆	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
N ₂	2.4	2.1	1.6	1.8	1.9	2.1	1.7	1.9	1.1	2.6	1.4
Sample No.	23	24	25	26	27	28	29	30	31*		
CO ₂	1.1	1.4	1.2	1.3	1.1	1.4	1.2	1.1	0.0		
C ₂ H ₂	0.4	0.0	0.2	0.5	0.2	0.3	0.1	0.3	0.0		
C ₂ H ₄	0.5	0.6	0.6	0.7	0.7	0.5	0.7	0.4	0.0		
C _n H _{2n}	0.2	0.0	0.2	0.1	0.4	0.2	0.5	0.2	0.0		
O ₂	1.4	0.4	0.3	0.3	0.3	0.4	0.5	0.4	0.3		
CO	26.4	27.1	29.7	28.9	30.1	26.1	29.0	30.6	30.7		
H ₂	63.9	67.4	65.9	66.6	65.6	68.4	65.9	65.5	67.6		
CH ₄	0.0	0.8	0.0	0.0	0.0	0.4	0.0	0.0	0.0		
C ₂ H ₆	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0		
N ₂	6.1	2.3	1.9	1.6	1.6	2.2	2.1	1.5	1.4		

* Initial Gas Mixture.

Table 3.

(F₁₄) Catalyst I₁-1, Co+15%ThO₂+100% Kieselguhr.Heat Treatment prior to H₂ Reduction, 400°C., 2 hrs.H₂ Reduction, 350°C., 5 hrs.

Duration of Experiment, 65 hrs.

Reaction Temperature, 225°C.

Rate of Gas Flow, 4 l./hr., CO:H₂=1:2.

Gas Analysis Data											
Sample No.	1	2	3	4	5	6	7	8	9	10	11
CO ₂	0.0	0.2	2.4	2.0	0.4	0.8	0.6	0.5	0.7	0.3	0.4
C ₂ H ₂	0.2	0.2	0.2	0.3	0.6	0.2	0.1	0.3	0.2	0.3	0.3
C ₂ H ₄	0.0	0.0	0.4	0.3	0.4	0.5	0.3	0.2	0.3	0.7	0.5
C _n H _{2n}	0.0	0.1	0.5	0.2	0.0	0.0	0.0	0.0	0.2	0.0	0.0
O ₂	0.4	0.3	0.4	0.5	0.3	0.4	0.4	0.3	0.5	0.4	0.4
CO	0.0	0.0	18.5	23.7	30.3	31.2	31.6	32.6	31.1	31.3	31.4
H ₂	97.9	86.2	67.6	70.2	66.1	65.1	65.1	65.5	64.9	65.2	65.1
CH ₄	0.0	10.5	7.9	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
C ₂ H ₆	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
N ₂	1.5	2.5	2.1	2.8	1.9	1.8	1.9	1.6	2.1	1.8	1.9
Sample No.	12	13	14	15	16	17	18	19	20	21	22
CO ₂	0.2	0.4	0.4	0.6	0.2	0.3	0.3	1.2	0.8	1.1	0.5
C ₂ H ₂	0.2	0.2	0.3	0.3	0.3	0.0	0.2	0.1	0.3	0.0	0.2
C ₂ H ₄	0.3	0.3	0.3	0.2	0.2	0.5	0.3	0.0	0.4	0.7	0.3
C _n N _{2n}	0.0	0.0	0.0	0.0	0.3	0.2	0.0	0.0	0.3	0.2	0.1
O ₂	0.2	0.3	0.4	0.3	0.2	0.5	0.3	0.2	0.3	0.6	0.4
CO	32.3	31.8	31.5	31.1	31.1	30.7	30.4	30.6	29.2	29.0	29.6
H ₂	65.1	65.6	65.4	65.9	66.4	65.4	66.7	66.5	67.0	65.7	66.9
CH ₄	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
C ₂ H ₆	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
N ₂	1.2	1.4	1.7	1.6	1.3	2.4	1.8	1.4	1.7	2.7	2.0
Sample No.	23	24	25	26	27	28	29	30	31	32	33
CO ₂	0.6	0.5	0.3	0.0	0.4	0.6	0.2	0.4	0.3	0.3	0.4
C ₂ H ₂	0.0	0.1	0.1	0.2	0.3	0.2	0.3	0.3	0.3	0.2	0.3
C ₂ H ₄	0.1	0.5	0.0	0.4	0.2	0.3	0.2	0.2	0.0	0.3	0.2
C _n H _{2n}	0.3	0.3	0.4	0.2	0.2	0.2	0.3	0.0	0.2	0.0	0.1
O ₂	0.2	0.3	0.3	0.2	0.3	0.4	0.3	0.5	0.3	0.4	0.2
CO	30.5	26.0	26.1	31.7	33.0	31.3	31.6	31.3	32.3	32.4	33.8
H ₂	67.0	70.7	71.5	66.2	64.4	64.3	65.9	65.1	65.3	64.7	64.0
CH ₄	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
C ₂ H ₆	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
N ₂	1.3	1.6	1.3	1.1	1.2	1.7	1.5	2.2	1.3	1.7	1.0

synthesis reaction was definitely normalized so that no CH_4 formation was observed as long as the catalyst surface remained suitable to the normalized reaction. We noticed almost without exception that the formation of C_2H_4 was observed and furthermore C_2H_4 percentages seemed to be, more or less, about the same. This very fact is consistent with the view already discussed⁽⁴⁾ that the role played by CH_2 during the normal synthesis of the Fischer-Tropsch reaction is no longer doubtful, as it is evidenced by

Table 4.

F_{19} -(A-K) Catalyst V_1 -1.

$\text{Co} + 12\% \text{U}_3\text{O}_8 + 2.5\% \text{Cu} + 100\% \text{ Kieselguhr}$.

Heat Treatment Prior to H_2 Reduction, 400°C ., 5 hrs.

H_2 Reduction, 350°C ., 5 hrs.

Space Velocity 342.

Reaction Temperature 225°C .

Duration of Experiment, 19 days F_{19} -(A-S).

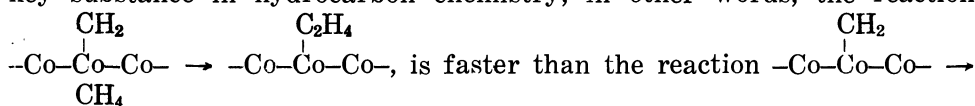
Oil Yield 180 cc./m³.

Rate of Gas Flow 4 l./hr., $\text{CO}:\text{H}_2=1:2$.

Exp. No.	Exp. Duration (hrs.)	Ave. Gas Contraction (%)	Remarks
F_{19} -A	6	45	Oil Yields
F_{19} -B	12	45	180 c.c./m. ³ (A-E)
F_{19} -C	12	40	
F_{19} -D	12	40	
F_{19} -E	13	40	
F_{19} -F	13	35	
F_{19} -G	12	35	
F_{19} -H	$11\frac{2}{3}$	30	Oil Yields
F_{19} -I	13	35	100-80 c.c./m ³ (F-K)
F_{19} -J	13	35	
F_{19} -K	12	35	
F_{19} -L	6	70	Reduction at 270°C . by H_2 for 2 hrs.
			Reaction at 190° - 250°C .
F_{19} -M	13	40	Reaction at 250°C .
F_{19} -N	13	25	Reaction at 225°C .
			Rate of Gas Flow 6-4 l./hr.
F_{19} -O	$10\frac{1}{2}$	16	Reaction at 225°C .
F_{19} -P	4	22	Reaction at 225° - 300°C .
			After Rereduction at 300°C . for 2 hrs.
F_{19} -Q (225°C .)	$13\frac{1}{2}$	8	Heat Treatment at 400°C for 2 hrs.
			H_2 Reduction at 270°C for 5 hrs.
F_{19} -R (230°C .)	12	44	
F_{19} -S (235°C .)	13	44	

(4) S. Hamai, this Bulletin, 16(1941), 213.

various accumulated facts in hydrocarbon chemistry in general⁽⁵⁾, and starting from CH₂, if polymerized to C₂H₄, various reactions, including polymerization and hydrogenation, leading to higher hydrocarbons are quite easily attained, as pointed out by Egloff, Schaad and Lowry⁽⁶⁾, furthermore, Egloff and Wilson⁽⁷⁾ pointed out that C₂H₄ acts as the key substance in hydrocarbon chemistry, in other words, the reaction



$-\text{Co}-\text{Co}-\text{Co}-$ in the normalized reaction, while the formation of CH₄ at the initial stage predominates via different paths and its formation is faster at the initial stage,⁽⁸⁾ and as the reaction becomes normalized the reaction of CH₄ formation at the initial stage must be restricted, or prohibited, as we have already pointed out⁽⁹⁾.

In Table 4, the results for the catalyst V₁-1, Co+12% U₃O₈+2.5% Cu +100% Kieselguhr, are shown. Pretreatment by air at 400°C. for 5 hours and H₂ reduction at 350°C. for 5 hours and the reaction was proceeded at 4 l./hr. and 225°C. and various other conditions are indicated in the table. Here we tabulated experimental duration, average gas contraction percentages and oil yields. Table 5 gives the gas analysis data for F₁₉-A—F₁₉-K. Here also we noticed that the methane formation at the initial stage and C₂H₄ formation in every gas sample are consistent with the explanation already mentioned. Table 6 is for F₁₉-L, where the catalyst was rereduced by H₂ at 270°C. for 2 hours then it proceeded the regular synthesis at 190–250°C. When the reaction temperature was as

Table 5. Gas Analysis Data.

F ₁₉ -(A-K)											
Exp. No.	F ₁₉ -A	F ₁₉ -B	F ₁₉ -C	F ₁₉ -D	F ₁₉ -E	F ₁₉ -F	F ₁₉ -G	F ₁₉ -H	F ₁₉ -I	F ₁₉ -J	F ₁₉ -K
CO ₂	2.3	0.3	1.0	1.5	0.8	0.7	1.1	0.7	0.8	0.8	0.8
C ₂ H ₂	0.3	0.0	0.5	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
C ₂ H ₄	0.4	0.3	0.7	1.1	1.6	0.5	0.6	0.4	0.9	1.0	1.1
C _n H _{2n}	0.0	0.4	0.0	0.0	0.2	0.0	0.3	0.0	0.0	0.0	0.0
O ₂	0.5	0.4	0.3	0.5	0.3	0.5	0.4	0.3	0.4	0.3	0.3
CO	20.5	30.2	29.5	30.4	30.9	30.3	31.8	30.6	30.6	30.7	31.2
H ₂	69.0	66.0	66.6	63.9	64.7	65.8	64.1	66.4	65.5	65.8	65.2
CH ₄	6.5	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
C ₂ H ₆	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
N ₂	2.5	1.9	1.4	2.7	1.5	2.2	1.7	1.6	1.7	1.4	1.4

- (5) (a) R. G. W. Norrish, *Proc. Roy. Soc. (London)*, A **150**(1925), 36.
 (b) L. S. Kassel, *J. Am. Chem. Soc.*, **54**(1932), 3949.
 (c) L. E. H. Bawn, *Trans. Faraday Soc.*, **34**(1938), 598.
 (d) D. E. W. R. Steacie, *Chem. Rev.*, **22**(1938), 311.
- (6) Egloff, Schaad and Lowry, *J. Phys. Chem.*, **35**(1931), 1825.
- (7) Egloff and Wilson, *Ind. Eng. Chem.*, **27**(1935), 917.
- (8) S. Hamai, S. Hayashi and K. Shimamura, this Bulletin, **17**(1942), 252.
- (9) S. Hamai, this Bulletin, **16**(1941), 213.

Table 6. Gas Analysis Data.

F ₁₉ -L,	Re-reduction by H ₂ at 270°C., for 2 hrs.				
Reaction Temp. (°C.)	190	190	225	250	250
Sample No.	1	2	3	4	5
CO ₂	0.2	0.4	0.0	9.2	13.6
C ₂ H ₂	0.0	0.0	0.0	0.0	0.2
C ₂ H ₄	0.0	0.0	0.4	0.5	0.2
C _n H _{2n}	0.0	0.0	0.0	0.0	0.0
O ₂	0.7	0.4	0.3	0.5	0.4
CO	7.1	27.2	30.7	17.8	12.1
H ₂	89.1	70.2	67.2	57.7	57.0
CH ₄	0.0	0.0	0.0	12.0	14.6
C ₂ H ₆	0.0	0.0	0.0	0.0	0.0
N ₂	2.9	1.8	1.4	2.3	1.9

high as 250°C., there we found definitely the formation of CH₄—also C₂H₄ formation. Table 7 shows the gas analysis data for F₁₉-M where the same catalyst as F₁₉-L was used but only the reaction temperature was varied 250–240°C. The formation of methane decreases distinctly with the decrease of the reaction temperature, as seen in the table. Table 8 shows the data of gas analyses for F₁₉-N where the reaction was proceeded at 225°C.; here again we observed that at the initial stage CH₄ was found, and as the reaction was normalized, the formation of CH₄ was completely restricted, while without exception C₂H₄ was observed.

Table 7. Gas Analysis Data.

F ₁₉ -M	Continued from F ₁₉ -L						
Reaction Temp. (°C.)	250	250	250	250	240	240	240
Sample No.	1	2	3	4	5	6	7
CO ₂	12.0	14.1	14.8	10.5	3.3	2.6	3.0
C ₂ H ₂	0.2	0.2	0.2	0.0	0.0	0.0	0.0
C ₂ H ₄	0.5	0.6	0.3	0.5	0.9	1.2	1.3
C _n H _{2n}	0.0	0.0	0.0	0.0	0.3	0.0	0.0
O ₂	0.3	0.3	0.4	0.5	0.4	0.3	0.4
CO	11.7	4.6	2.5	7.5	22.1	25.9	26.1
H ₂	51.8	52.2	57.9	57.9	65.2	64.6	63.5
CH ₄	18.5	25.1	18.2	17.8	4.5	2.8	3.8
C ₂ H ₆	2.6	0.0	4.0	3.2	1.4	1.2	0.5
N ₂	1.3	1.9	1.8	2.1	1.9	1.4	1.7

Table 8. Gas Analysis Data.

F ₁₉ -N		Continued from F ₁₉ -M					
Reaction } Temp. } (°C.) }	225	225	225	225	225	225	225
Sample } No. }	1	2	3	4	5	6	7
CO ₂	4.2	0.6	0.4	0.5	0.6	0.6	0.4
C ₂ H ₂	0.0	0.0	0.0	0.0	0.0	0.0	0.0
C ₂ H ₄	1.2	0.8	0.5	0.6	0.9	0.7	0.5
C _n H _{2n}	0.3	0.0	0.0	0.2	0.0	0.0	0.0
O ₂	0.3	0.3	0.5	0.4	0.4	0.3	0.5
CO	24.3	29.3	30.3	29.4	30.0	28.2	29.3
H ₂	59.4	66.9	66.0	67.1	66.1	69.5	67.0
CH ₄	8.9	0.0	0.0	0.0	0.0	0.0	0.0
C ₂ H ₆	0.0	0.0	0.0	0.0	0.0	0.0	0.0
N ₂	1.7	2.1	2.3	1.8	2.0	1.6	2.3

Table 9 shows the data for F₁₉-0. Here again we confirmed the methane formation at 270°C. and no CH₄ formation at 225°C.. Table 10 indicates the data for F₁₉-P where the catalyst was re-reduced at 300°C. for 2 hours by H₂ and the reaction was proceeded at 225°C.. Table 11 gives the data for F₁₉-Q where the same catalyst was pretreated by air at 400°C. for 2 hours and re-reduced by H₂ at 270°C. for 5 hours and then the reaction at 225°C.. Here also we see that during a certain initial period CH₄ formation was observed then it became null after the reaction

Table 9. Gas Analysis Data.

F ₁₉ -O		Continued from F ₁₉ -N					
Reaction } Temp. } (°C.) }		270	225	225	225	225	225
Sample } No. }	1	2	3	4	5	6	7
CO ₂	2.4	12.8	1.1	0.5	0.6	0.5	0.5
C ₂ H ₂	0.0	0.0	0.0	0.0	0.0	0.0	0.0
C ₂ H ₄	0.6	1.0	0.5	0.9	0.7	0.3	0.4
C _n H _{2n}	0.0	0.0	0.0	0.0	0.2	0.0	0.0
O ₂	0.5	0.3	0.3	0.4	0.3	0.4	0.3
CO	28.0	7.7	29.2	28.4	29.2	29.0	30.2
H ₂	66.2	59.0	67.2	67.4	67.6	68.1	66.9
CH ₄	0.0	14.4	0.0	0.0	0.0	0.0	0.0
C ₂ H ₆	0.0	1.7	0.0	0.0	0.0	0.0	0.0
N ₂	2.3	1.8	1.7	2.4	1.4	1.7	1.6

Table 10. Gas Analysis Data.

F ₁₉ -P Re-reduction at 300°C. for 2 hrs. by H ₂				
Reaction Temp. (°C.) } Sample No. }	225	225	225	225
CO ₂	0.0	0.2	0.4	0.6
C ₂ H ₂	0.0	0.0	0.0	0.0
C ₂ H ₄	0.0	0.4	0.6	0.7
C _n H _{2n}	0.0	0.0	0.0	0.0
O ₂	0.4	0.3	0.4	0.5
CO	0.0	0.7	24.6	28.2
H ₂	97.5	69.9	72.1	67.9
CH ₄	0.0	0.0	0.0	0.0
C ₂ H ₆	0.0	0.0	0.0	0.0
N ₂	2.1	1.7	1.9	2.1

Table 11. Gas Analysis Data.

F ₁₉ -Q, Heat treatment at 400°C. for 2 hrs. Re-reduction at 270°C. for 5 hrs. by H ₂ .							
Reaction Temp. (°C.) } Sample No. }	225	225	225	225	225	225	225
	1	2	3	4	5	6	7
CO ₂	0.2	4.0	2.0	0.9	0.5	0.5	0.4
H ₂ H ₂	0.0	0.0	0.2	0.0	0.0	0.0	0.0
C ₂ H ₄	0.2	0.3	0.3	0.5	0.5	0.6	0.6
C _n H _{2n}	0.0	0.0	0.0	0.0	0.0	0.2	0.2
O ₂	0.6	0.3	0.4	0.4	0.4	0.3	0.4
CO	0.0	2.8	24.3	29.4	30.1	30.7	29.4
H ₂	96.3	75.0	62.7	66.9	66.5	66.2	66.9
CH ₄	0.0	14.6	7.7	0.0	0.0	0.0	0.0
C ₂ H ₆	0.0	0.0	0.0	0.0	0.0	0.0	0.0
N ₂	2.7	2.1	1.9	1.8	2.0	1.5	2.1

attained so-called normalized condition. Table 12-13 indicate the data for the reaction temperatures 230°-235°C., respectively. Here once again, as far as the CH₄ formation and C₂H₄ formation are concerned, they are no exceptional cases, as already stated before. As seen in these data, the fact that the CH₄ formation predominates at the higher reaction temperature is probably due to the circumstance that the formation of CH₄ becomes faster and of comparable order with the normalized synthesis reaction. (Within the tested temperature ranges).

Table 12. Gas Analysis Data.

F ₁₉ -R		(Continued from F ₁₉ -Q)						
Reaction Temp. (°C.)	}	230	230	230	230	230	230	230
Sample No.		1	2	3	4	5	6	7
CO ₂		0.5	3.0	2.7	1.6	1.1	0.7	1.0
C ₂ H ₂		0.0	0.0	0.0	0.0	0.0	0.0	0.0
C ₂ H ₄		0.8	0.7	1.0	1.1	0.9	0.5	0.9
C _n H _{2n}		0.2	0.3	0.3	0.3	0.0	0.2	0.0
O ₂		0.5	0.3	0.4	0.4	0.4	0.5	0.4
CO		30.2	26.2	26.9	28.9	29.6	29.9	29.4
H ₂		65.4	61.1	61.7	61.7	66.2	66.0	65.2
CH ₄		0.0	7.1	5.3	4.4	0.0	0.0	0.0
C ₂ H ₆		0.0	0.0	0.0	0.0	0.0	0.0	0.0
N ₂		2.4	1.3	1.7	1.6	1.8	2.2	2.1

Table 13. Gas Analysis Data.

F ₁₉ -S		(Continued from F ₁₉ -R)						
Reaction Temp. (°C.)	} 235	235	235	235	235	235	235	235
Sample No.								
	} 1	2	3	4	5	6	7	8
CO ₂	0.9	3.7	4.4	2.8	2.5	2.6	1.6	1.2
C ₂ H ₂	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
C ₂ H ₄	1.1	1.2	0.9	0.9	0.8	0.8	0.6	0.7
C _n H _{2n}	0.2	0.0	0.4	0.3	0.3	0.4	0.2	0.0
C ₂	0.5	0.3	0.4	0.4	0.3	0.6	0.4	0.3
CO	27.3	26.1	25.6	27.6	27.4	25.5	28.7	29.5
H ₂	67.8	60.7	58.5	62.2	63.7	61.1	66.3	66.8
CH ₄	0.0	6.3	7.9	2.9	3.8	5.6	0.0	0.0
C ₂ H ₆	0.0	0.0	0.0	1.1	0.0	0.0	0.0	0.0
N ₂	2.2	1.7	1.9	1.8	1.2	2.4	2.2	1.5

Thus, we have demonstrated rather conclusively that the formation of CH₄ at the initial stage predominates and it gradually becomes null as the reaction surface is normalized, and these have been tested with various different pretreatments as well as different reaction temperatures. Furthermore, we also have shown that as the reaction temperature becomes higher the CH₄ formation definitely tends to become appreciable; and without exception, the C₂H₄ formation, with a fairly constant amount, can be observed even with the catalyst composition differing and with various different pretreatments.

Summary.

(1) The durability experiments with the catalysts, Co+15% ThO₂+100% Kieselguhr and Co+12% U₃O₈+2.5% Cu+100% Kieselguhr, are reported and tabulated.

(2) Following mainly the gas analysis data, the normalized reaction was discussed with special reference to the initial formation of CH₄.

(3) Some correlations with the formation of C₂H₄, in connection with our reaction mechanism already proposed, as well as the predominating tendency of CH₄ formation at higher reaction temperature have been given.

In conclusion, the authors wish to thank Dr. T. Marusawa, Former Director of the Institute, and Dr. S. Sato, Director of the Institute for their interest and encouragement in carrying out this investigation and for the permission for the publication; also to thank Messrs. Igarashi, Konoha, Kuwabara and Fujiwara who willingly assisted us in carrying out this experiment.

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Physico-Chemical Investigations on Catalytic Mechanism. IX. On the Fischer-Tropsch Synthesis of Hydrocarbons with Special Reference to Factors essential to the Particular Catalysts. (Experimental Series II) (5).

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(Received August 1, 1942.)

Introduction. We have been publishing a series of experimental results essential in correlating and systematizing factors which may possibly throw a light upon developing a theory of the reaction mechanism for the Fischer-Tropsch synthesis of hydrocarbons. The present paper, being one of these series, mainly deals with the results obtained with the catalysts^(*) composed of Co, U_3O_8 , Cu, Mn and Kieselguhr and especially those effects of the reaction temperatures, rate of gas flow, pretreatments and promoters, such as U_3O_8 , Cu and Mn, upon the catalytic activity.

Experimental Materials. Hydrogen and carbon monoxide involved in the reaction were prepared similarly as already described in our earlier papers⁽¹⁾.

The materials used in the preparations of the catalysts were nitrates of cobalt, uranium, copper and manganese of which quality is as follows:

$Co(NO_3)_2 \cdot 6H_2O$	Extra pure (Kojima)
$UO_2(NO_3)_2 \cdot 6H_2O$	" " "
$Cu(NO_3)_2 \cdot 3H_2O$	Guaranteed reagent (Kojima)
$Mn(NO_3)_2 \cdot 6H_2O$	" " (Katayama)
K_2CO_3	Extra pure (Kojima)
Kieselguhr	(Purified) ⁽²⁾

The calculated amount of these materials were taken for the specified catalyst composition, and precipitated by 2 N K_2CO_3 solution as carbonates, washed thoroughly with hot distilled water⁽³⁾ at least ten times until it became entirely free from the adsorbed nitrate ions and other possible impurities, then dried at 100–110°C. and finally made into small sized tablets by tablet machine.

(1) Our Reports, IV, this Bulletin, 17(1942), 166,
V, this Bulletin, 17(1942), 252,
VI, this Bulletin, 17(1942), 339,
VII, *J. Chem. Soc. Japan*, 63(1942), No. 11.
VIII, this Bulletin, 17(1942), 451.

(2) IV, this Bulletin, 17(1942), 166.

(3) S. Hamai, *Science* (Iwanami), 11(1941), 518.

(*) For this type of catalyst, see: S. Tsutsumi, *Report of the Fuel Institute, Japan*, No. 31, 1935.

Experimental Procedure. The catalyst thus made was pretreated as specified in the tables, and when the catalyst zone was ready for a run, a H_2 -CO mixture (2:1) was passed over it at the specified temperatures with a definite rate of gas flow (4-8l./hr.); and the gas contraction percentage was measured from time to time.

The reaction products were collected in two separate portions, similarly as those described in our previous papers⁽¹⁾. The reaction products obtained were later subjected to the determinations of physico-chemical constants such as refractive index, specific gravity, apparent molecular weight and elementary analysis. The effluent gas was subjected to gas analysis using a modified form of Orsat gas analysis apparatus, for their constituents.

Experimental Results and Discussions. Some of the experimental results are tabulated and graphically represented. Most of the tables are self-explanatory, but, for the sake of thoroughness, we shall explain them briefly. In Tables 1-8, the gas analysis data for the effluent gas from the typical runs for the specified condition of the catalyst V_1-1 , $Co+12\% U_3O_8+2.5\% Cu+100\%$ Kieselguhr are shown. From these data, we are convinced that at the initial stage, the methane formation predominates, as often we have called attention in our previous papers⁽¹⁾⁽⁴⁾; however, the duration in which CH_4 forms may differ depending on such experimental conditions as the reaction temperatures, rate of gas flow as well as pre-treatments. As regards the formations of CO_2 , we may

Table 1.

$F_{20}-A$, V_1-1 , $Co+12\% U_3O_8+2.5\% Cu+100\%$ Kieselguhr,
 Heat treatment, 400°C., 4 hrs., (Prior to H_2 Reduction).
 Reduction, 270°C., 5 hrs. by H_2 .
 Reaction Temp., 225°C., (4.5 hrs., Exp.).
 Contraction, 66%.
 Space Velocity, 346.
 Rate of Flow, 4 l./hr.; $CO:H_2=1:2$.

Gas Analysis Data.

	1	2	3
CO_2	0.0	2.0	9.4
C_2H_2	0.0	0.0	0.0
C_2H_4	0.2	0.0	0.4
C_nH_{2n}	0.0	0.0	0.2
O_2	0.4	0.5	0.4
CO	0.0	0.0	13.1
H_2	97.4	85.3	59.2
CH_4	0.0	9.7	15.2
C_2H_6	0.0	0.0	0.0
N_2	2.0	2.5	2.1

(4) VII, *J. Chem. Soc. Japan*, **63**(1942), No. 11.VIII, this Bulletin, **17**(1942), 451.

Table 2.

F₂₀-B, (Continued from F₂₀-A)Reaction Temp., 225°C., 13 hrs. Exp.
Contraction, 70%.

Gas Analysis Data.							
	1	2	3	4	5	6	7
CO ₂	5.7	7.7	13.8	13.8	12.0	9.6	9.6
C ₂ H ₂	0.0	0.0	0.0	0.0	0.0	0.0	0.2
C ₂ H ₄	0.6	0.0	1.3	0.7	0.8	1.2	1.2
C _n H _{2n}	0.3	0.0	0.3	0.4	0.2	0.0	0.0
O ₂	0.4	0.5	0.7	0.5	0.4	0.3	0.4
CO	18.5	21.2	18.3	14.6	15.1	18.2	18.6
H ₂	59.7	52.8	45.7	51.4	54.5	57.1	56.0
CH ₄	14.1	14.4	17.1	14.3	15.2	10.3	10.2
C ₂ H ₆	0.0	0.0	0.0	2.0	1.8	1.9	1.9
N ₂	1.6	2.3	2.8	2.3	1.8	1.4	1.9

Table 3.

F₂₀-C, (Continued from F₂₀-B)Reaction Temp., 200°C., 220°C.
Contraction, 12%, 68%, (12 hrs. Exp.).

Gas Analysis Data.						
	1	2	3	4	5	6
CO ₂	2.0	0.7	0.7	3.5	6.5	5.7
C ₂ H ₂	0.0	0.0	0.0	0.0	0.0	0.0
C ₂ H ₄	0.6	0.3	0.4	0.4	1.4	1.0
C _n H _{2n}	0.2	0.0	0.0	0.2	0.0	0.0
O ₂	0.6	0.4	0.3	0.3	0.5	0.4
CO	50.2	32.0	32.0	27.0	23.1	24.6
H ₂	63.6	64.8	65.2	62.4	58.3	59.5
CH ₄	0.0	0.0	0.0	4.6	5.1	5.7
C ₂ H ₆	0.0	0.0	0.0	0.0	2.0	1.3
N ₂	2.8	1.8	1.4	1.3	2.1	1.8
(200°C.)			(220°C.)			

Table 4.

F₂₀-D, (Continued from F₂₀-C),Reaction Temp., 210°C
Contraction, 35% (6 hrs. Exp.).

Gas Analysis Data.				
	1	2	3	4
CO ₂	5.4	2.6	1.0	0.9
C ₂ H ₂	0.0	0.0	0.0	0.0
C ₂ H ₄	1.3	0.8	0.8	0.7
C _n H _{2n}	0.0	0.0	0.2	0.0
O ₂	0.3	0.3	0.4	0.3
CO	25.0	28.8	29.9	30.3
H ₂	57.3	59.5	65.6	66.3
CH ₄	7.9	5.8	0.0	0.0
C ₂ H ₆	1.3	0.0	0.0	0.0
N ₂	1.5	2.2	1.9	1.5

Table 5.

F₂₀-E, (Continued from F₂₀-D)Re-reduction, 350°C., by H₂, 2 hrs.

Reaction Temp., 225°C. (4 l./hr.).

Contraction, 60%, (8 hrs. Exp.).

Gas Analysis Data.

	1	2	3	4	5
CO ₂	0.0	0.0	5.0	5.6	4.2
C ₂ H ₂	0.0	0.0	0.0	0.0	0.0
C ₂ H ₄	0.4	0.2	0.4	0.9	0.8
C _n H _{2n}	0.0	0.0	0.0	0.0	0.3
O ₂	0.3	0.3	0.4	0.3	0.4
CO	0.0	0.0	1.6	13.8	22.3
H ₂	97.4	81.4	76.9	64.0	58.0
CH ₄	0.0	5.6	4.3	11.6	12.1
C ₂ H ₆	0.0	0.0	5.7	2.1	2.4
N ₂	1.9	1.5	1.7	1.7	1.9

Table 6.

F₂₀-F, (Continued from F₂₀-E)

Reaction Temp. 225°C.,

Rate of Flow, 8 l./hr. 6 l./hr.

Contraction, 25% 25% (12 hrs. Exp.).

Gas Analysis Data.

	1	2	3	4	5	6	7
CO ₂	6.0	9.0	1.0	0.3	0.3	0.4	0.5
C ₂ H ₂	0.0	0.0	0.0	0.0	0.0	0.0	0.0
C ₂ H ₄	0.9	0.6	0.8	0.6	0.7	0.7	0.9
C _n H _{2n}	0.0	0.2	0.0	0.0	0.0	0.0	0.0
O ₂	0.4	0.5	0.4	0.2	0.3	0.4	0.2
CO	19.7	10.7	30.7	31.6	31.1	31.2	31.4
H ₂	59.2	58.5	65.1	65.9	66.1	65.6	65.7
CH ₄	8.8	17.6	0.0	0.0	0.0	0.0	0.0
C ₂ H ₆	3.2	0.0	0.0	0.0	0.0	0.0	0.0
N ₂	1.8	2.5	2.0	1.4	1.5	1.7	1.3
(8 l./hr.)				(6 l./hr.)			

Table 7.

F₂₀-G, (Continued from F₂₀-F)

Reaction Temp., 230°C.
 Rate of Flow, 8 l./hr., 6 l./hr.
 Constriction, 40%, 42% (13 hrs. Exp.).

Gas Analysis Data.

	1	2	3	4	5	6	7	8
CO ₂	2.0	2.4	2.0	1.2	1.4	1.3	1.8	1.0
C ₂ H ₂	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
C ₂ H ₄	0.8	1.1	1.4	1.0	1.2	1.4	1.9	1.2
C _n H _{2n}	0.0	0.2	0.0	0.3	0.3	0.0	0.2	0.5
O ₂	0.3	0.4	0.4	0.5	0.4	0.3	0.3	0.5
CO	30.0	27.4	28.5	29.4	29.8	30.7	29.5	30.0
H ₂	65.5	59.5	60.6	60.0	64.8	61.3	61.1	64.0
CH ₄	0.0	4.7	4.0	4.4	0.0	2.6	2.1	0.0
C ₂ H ₆	0.0	1.6	1.3	1.4	0.0	1.0	1.8	0.0
N ₂	1.4	1.7	1.8	1.4	2.1	1.4	1.3	2.8
	(8 l./hr.)				(6 l./hr.)			

Table 8.

F₂₀-H, (Continued from F₂₀-G)

Reaction Temp., 230°C. (4 l./hr.)
 Constriction, 50% (7 hrs. Exp.).

Gas Analysis Data.

	1	2	3	4
CO ₂	2.2	3.3	3.8	3.0
C ₂ H ₂	0.0	0.2	0.0	0.0
C ₂ H ₄	1.4	1.3	1.2	1.3
C _n H _{2n}	0.4	0.3	0.0	0.2
O ₂	0.5	0.4	0.4	0.3
CO	26.5	27.4	25.9	26.4
H ₂	60.2	59.6	60.7	60.4
CH ₄	5.0	4.3	5.0	5.4
C ₂ H ₆	0.5	1.3	1.2	1.4
N ₂	2.3	1.9	1.8	1.6

possibly state that they are somewhat parallel with the methane formations, as clearly shown in these tables; of course, a strict proportionality may not be expected, since the reaction system is quite complex and furthermore they are outcome of the combinations of the reactions, such as (1) $\text{Co} + 3\text{H}_2 = \text{CH}_4 + \text{H}_2\text{O}$ and (2) $\text{CO} + \text{H}_2\text{O} = \text{H}_2 + \text{CO}_2$ and of the combination of these two (3) $2\text{CO} + 2\text{H}_2 = \text{CH}_4 + \text{CO}_2$, as well as (4) $\text{CO}_2 + 4\text{H}_2 = \text{CH}_4 + 2\text{H}_2\text{O}$, and also of these reactions; the extents of the equilibria as well as the reaction speed are connected with various factors and expected to be inter-related. Judging these reactions and our results as regards

the formations of CH_4 and CO_2 as well as H_2O , the explanations seem to be rather reasonable, especially with regard to the initial stage of the reaction prior to normalization of the reaction system.

In Tables 9–11, the results are given for the effects of promoters, such as U_3O_8 , Cu in various different percentages, and of Mn. As seen in Table 9, for these particular catalysts, as far as the copper content is concerned, 2.5% Cu seemed to be optimal among those tested in this range of percentages. Here we also are convinced that the average gas contraction percentage may not necessarily be parallel with the order of

Table 9. Effects of Promoters.

Type of Catalyst, $\text{Co} + 12\% \text{U}_3\text{O}_8 + x\% \text{Cu} + 100\% \text{Kieselguhr}$ Rate of gas Flow; 4 l./hr.; $\text{CO}:\text{H}_2=1:2$

Cu (%)	React. Temp. (°C.)	Exp. No.	Ave. Gas Cont. (%)	Oil Yields c.c./m ³	Remarks			
					Heat Treat.		H ₂ Reduct.	
					(°C.)	(hrs.)	(°C.)	(hrs.)
					(400)	(4)	(270)	(5) (F ₂₀ -A)
2.5	200	F ₂₀ -C	12	28.5	—	—	—	—
	220	"	68	147	—	—	—	—
	210	F ₂₀ -D	36	26.9	—	—	—	—
	230	F ₂₀ -H	50	131.3	—	—	350	2
	225	F ₁₉ -E	40	173	400	5	350	5
5	200	F ₂₁ -B	52	18	400	2	250	5
	190	F ₂₁ -D	30	20	—	—	210	2
	225	F ₂₁ -E	70	46	—	—	350	2
	200	F ₂₁ -H	30	80	—	—	230	2
10	200	F ₂₂ -A	57	3.9	400	2	230	5
	"	F ₂₂ -B	32	56	—	—	300	2
					(400)	(5)	(270)	(5) (F ₂₃ -A)
0	200	F ₂₃ -E	20	46	—	—	370	2
	225	"	30	—	—	—	—	—
	"	F ₂₃ -G	24	63.3	—	—	300	2

Table 10. Effects of Promoters.

Type of Catalyst, $\text{Co} + x\% \text{U}_3\text{O}_8 + 2.5\% \text{Cu} + 100\% \text{Kieselguhr}$ Rate of gas Flow, 4 l./hr.; $\text{CO}:\text{H}_2=1:2$

U ₃ O ₈ (%)	React. Temp. (°C.)	Exp. No.	Ave. Gas Cont. (%)	Oil Yields c.c./m ³	Remarks			
					Heat Treat.		H ₂ Reduct.	
					(°C.)	(hrs.)	(°C.)	(hrs.)
					(400)	(4)	(270)	(5) (F ₂₀ -A)
12	225	F ₂₀ -B	70	123	—	—	—	—
					(400)	(5)	(270)	(5) (F ₂₆ -A)
15	"	F ₂₆ -C	66	93	—	—	—	—

Table 11. Effects of Promoters.

Type of Catalyst, Co+12% U₃O₈+5% Cu+x% Mn+100% Kieselguhr
 Rate of Gas Flow, 4 l./hr.; CO:H₂=1:2

Mn (%)	React. Temp. (°C.)	Exp. No.	Ave. Gas Cont. (%)	Oil Yields c.c./m ³	Remarks			
					Heat Treat.		H ₂ Reduct.	
					(°C.)	(hrs.)	(°C.)	(hrs.)
4	200	F ₂₀ -A	3	43	400	5	300	5
	270	F ₂₀ -B	66*	24	—	—	—	—
	250	F ₂₀ -C	40	45	—	—	—	—
					(400)	(2)	(250)	(5) (F ₂₁ -A)
0	190	F ₂₁ -D	30	20	—	—	210	2
	225	F ₂₁ -F	66*	7.1	—	—	300	2
	200	F ₂₁ -H	30	80	—	—	230	2

* Large amount of CH₄ formation.

oil yields, as often we have called attention in our earlier papers⁽⁵⁾. In Table 10, the results with 12 and 15% U₃O₈ are compared. In Table 11, the effects of Mn are compared. Although no definite conclusion may be drawn from these meager data, we may conservatively state that the effects of Mn is not distinct; however, as far as these data allow, a catalyst without Mn seems to be more desirable. In Table 12 the effects of a carrier, Kieselguhr, for this particular catalyst are compared.

Table 12. Effects of Carrier, Kieselguhr.

Type of Catalyst, Co+12% U₃O₈+2.5% Cu+x% Kieselguhr
 Rate of Gas Flow, 4 l./hr.; CO:H₂=1:2

Kiesel. (%)	React. Temp. (°C.)	Exp. No.	Ave. Gas Cont. (%)	Oil Yields c.c./m ³	Remarks			
					Heat Treat.		H ₂ Reduct.	
					(°C.)	(hrs.)	(°C.)	(hrs.)
100	225	F ₂₀ -A	66**	38.8	400	4	270	5
"	"	F ₂₀ -B	70	122.6	—	—	—	—
"	200	F ₂₀ -C	12	28.5	—	—	—	—
"	220	"	68	146.9	—	—	—	—
0	225	F ₂₄ -A	66*	3.4	400	5	300	5
"	"	F ₂₄ -B	66*	9.3	—	—	"	2
"	"	F ₂₄ -C	62*	14.5	—	—	350	"
"	"	F ₂₄ -D	64*	2.6	400	2	"	5
"	"	F ₂₅ -A	66*	0	400	5	270	"
"	"	F ₂₅ -B	64*	0	—	—	350	2

* Large amount of CH₄ formation.

** CH₄ formation at the initial stage.

(5) S. Hamai, S. Hayashi, K. Shimamura and H. Igarashi, this Bulletin, 17 (1942), 166; S. Hamai, this Bulletin, 17 (1942), 339.

Here we can see definitely the superiority of the catalyst with the carrier, and with the catalyst containing no Kieselguhr contributes almost nothing to the oil formation reaction but the methane formation. As far as the contraction percentage is concerned, both cases are of comparable order. These results clearly demonstrate the importance of segregation of catalytic activities due to each particular reaction, as that of methane formation and that of oil formation, when we discuss the catalytic activities as judged from the gas contraction alone. From these data, we can clearly see that the contraction percentages, namely, 66%, indicated for the catalyst with no Kieselguhr, is practically entirely due to the reaction (I) $\text{CO} + 3\text{H}_2 = \text{CH}_4 + \text{H}_2\text{O}$, forming a large amount of methane and water which in turn reacts with CO and gives $\text{CO} + \text{H}_2\text{O} = \text{H}_2 + \text{CO}_2$. Thus we see a large amount of CO_2 formation, somewhat in parallel with the methane formation. (The maximum contraction available from the reaction (I) alone is $66\frac{2}{3}\%$). Furthermore, in these cases practically no oil formation was observed, at least a very small amount—if any.

In Tables 13–17, those effects of the reaction temperature on the activity for various different catalysts as judged from the gas contraction percentages, oil yields, as well as principal gaseous products are compared at several different temperatures.

In main, when the temperature⁽⁴⁾ is higher, gaseous products, such as CH_4 and CO_2 , predominate for every catalyst tested, with a considerable magnitude of gas contraction and a very small amount of oil formation. This is very reasonable, considering that these reactions, mentioned already, predominate at these particular conditions, especially when the reaction system is not well normalized. Here we see also the optimal

Table 13. Effects of the Reaction Temperature on the Activity.

Type of Catalyst, $\text{Co} + 12\% \text{U}_3\text{O}_8 + 2.5\% \text{Cu} + 100\% \text{Kieselguhr}$ Rate of Gas Flow, 4 L./hr.. $\text{CO}:\text{H}_2=1:2$											
Exp. No.	React. Temp. (°C.)	Ave. Gas Cont. (%)	CO_2	C_2H_4	CH_4	C_2H_6	Oil Yields c.c./m ³	Remarks			
								Heat Treat.	H ₂	Reduct.	
								(°C.)	(hrs.)	(°C.)	(hrs.)
F ₁₉ -E	225	40	0.8	1.6	0.0	0.0	173	400	5	350	5*
F ₁₉ -L	250	70	9.2	0.5	12.0	0.0	103	400	5	270	2
								400	4	270	5**
F ₁₉ -R	230	44	0.7	0.5	0.0	0.0	—	—	—	—	—
F ₁₉ -S	235	44	1.6	0.6	0.0	0.0	—	—	—	—	—
								400	4	270	5†
F ₂₀ -B	225	70	9.6	1.2	10.2	1.9	123	—	—	—	—
F ₂₀ -C	220	68	0.7	0.3	0.0	0.0	147	—	—	—	—
F ₂₀ -D	210	36	0.9	0.7	0.0	0.0	27	—	—	—	—
										350	2‡
F ₂₀ -H	230	50	3.8	1.2	5.0	1.2	131.3	—	—	—	—

* (F₁₉-A); ** (F₁₉-Q); † (F₂₀-A); ‡ (F₂₀-E).

Table 14. Effects of the Reaction Temperature on the Activity.

Type of Catalyst, Co+12% U ₃ O ₈ +5% Cu+100% Kieselguhr											
Rate of Gas Flow, 4 l./hr., CO:H ₂ =1:2											
Exp. No.	React. Temp. (°C.)	Ave. Gas Cont. (%)	CO ₂	C ₂ H ₄	CH ₄	C ₂ H ₆	Oil Yields c.c./m ³	Remarks			
								Heat Treat.		H ₂ Reduct.	
								(°C.)	(hrs.)	(°C.)	(hrs.)
F ₂₁ -A	200	60*	15.3	0.2	38.9	2.7	0	400	2	250	5
F ₂₁ -C	190	22	0.2	0.5	0.0	0.0	54.4	—	—	230	2
	200	44	0.6	0.5	0.0	0.0	—	—	—	—	—
F ₂₁ -D	190	30	0.3	0.6	0.0	0.0	—	—	—	210	2
	200	32	0.5	0.5	0.0	0.0	20	—	—	—	—
	225	80	7.0	0.7	11.2	3.9	—	—	—	—	—
F ₂₁ -E	190	23	0.2	0.4	0.0	0.0	46.1	—	—	350	2
	200	30	0.5	0.2	0.0	0.0	—	—	—	—	—
	225	70	0.2	0.4	0.0	0.0	—	—	—	—	—
F ₂₁ -H	200	30	0.5	0.7	0.0	0.0	80.0	—	—	230	2
With 10% Cu											
								400	2	230	5**
F ₂₂ -B	200	32	0.2	0.5	0.0	0.0	56	—	—	300	2

* (F₂₂-A).

Table 15. Effects of the Reaction Temperature on the Activity.

Type of Catalyst, Co+12% U ₃ O ₈ +100% Kieselguhr											
Rate of Gas Flow, 4 l./hr., CO:H ₂ =1:2											
Exp. No.	React. Temp. (°C.)	Ave. Gas Cont. (%)	CO ₂	C ₂ H ₄	CH ₄	C ₂ H ₆	Oil Yields c.c./m ³	Remarks			
								Heat Treat.		H ₂ Reduct.	
								(°C.)	(hrs.)	(°C.)	(hrs.)
F ₂₃ -A	200	20	0.2	0.2	0.0	0.0	12	400	5	270	5
F ₂₃ -E	200	20	0.0	0.0	0.0	0.0	46	—	—	370	2
	225	30	0.2	0.2	0.0	0.0	—	—	—	—	—
F ₂₃ -F	225	32	0.3	0.2	0.0	0.0	22	—	—	300	2
F ₂₃ -G	225	24	0.2	0.2	0.0	0.0	63.3	—	—	—	—

Table 16. Effects of the Reaction Temperature on the Activity.

Type of Catalyst, Co+12% U ₃ O ₈ +2.5% Cu											
Rate of Gas Flow, 4 l./hr.; CO:H ₂ =1:2											
Exp. No.	React. Temp. (°C.)	Ave. Gas Cont. (%)	CO ₂	C ₂ H ₄	CH ₄	C ₂ H ₆	Oil Yields c.c./m ³	Remarks			
								Heat Treat.		H ₂ Reduct.	
								(°C.)	(hrs.)	(°C.)	(hrs.)
F ₂₄ -A	225	66*	17.7	0.2	62.2	0.0	3.4	400	5	300	5
F ₂₄ -B	"	66*	13.4	0.0	50.2	0.0	9.3	—	—	300	2
F ₂₄ -C	"	62*	12.1	0.0	47.1	0.0	14.5	—	—	350	2
F ₂₄ -D	"	64*	14.0	0.4	53.5	0.0	—	400	2	350	5
	200	15	1.1	0.2	0.0	0.0	2.6	—	—	—	—
F ₂₄ -E	200	2	0.2	0.3	0.0	0.0	2.2	—	—	—	—
F ₂₅ -A	225	66*	14.5	0.4	59.1	0.0	—	400	5	270	5
F ₂₅ -B	"	64*	14.1	0.4	54.4	0.0	—	—	—	350	2

* Large amount of CH₄ formation.** (F₂₂-A).

Table 17. Effects of the Reaction Temperature on the Activity.

Type of Catalyst, Co+12% U ₃ O ₈ +5% Cu+4% Mn+100% Kieselguhr											
Rate of Gas Flow, 4 l./hr.; CO:H ₂ =1:2											
Exp. No.	React. Temp. (°C.)	Ave. Gas Cont. (%)	CO ₂	C ₂ H ₄	CH ₄	C ₂ H ₆	Oil Yields c.c./m ³	Remarks			
								Heat Treat.		H ₂ Reduct.	
								(°C.)	(hrs.)	(°C.)	(hrs.)
F ₂₉ -A	200	3	0.0	0.2	0.0	0.0	43	400	5	270	5
F ₂₉ -B	270	66*	18.0	0.4	23.8	8.0	24	—	—	—	—
F ₂₉ -C	250	40	3.9	1.1	0.0	0.0	45	—	—	—	—
Co+15% U ₃ O ₈ +2.5% Cu+100% Kieselguhr											
F ₂₆ -A	225	70*	6.9	0.3	29.2	1.0	50	400	5	270	5
F ₂₆ -B	"	74	5.0	2.1	10.2	9.2	73	—	—	—	—
F ₂₆ -C	"	66	3.9	1.8	7.3	6.2	93	—	—	—	—
F ₂₆ -D	"	64*	5.1	1.9	15.4	3.3	52	—	—	—	—
F ₂₆ -E	"	32	0.2	0.3	0.0	0.0	48	400	5	350	5

* Large amount of CH₄ formation.

reaction temperature for the particular catalyst; among these data we may possibly state that 225°C. is the optimal for the majority of these catalysts except for those without Kieselguhr. This catalyst, as shown in Table 16, may not be considered as desirable as far as the oil formation is concerned although the activity for the formation of gaseous products, such as CH₄ and CO₂, is very high.

In Tables 18–23, those effects of various pretreatments upon the catalytic activity as judged by the average gas contraction, oil yields, and gaseous products, at several different reaction temperatures are shown. Regarding the initial reduction temperature, the presence of Cu seems to lower the reduction temperature. This is in concordance with the fact found in the literature⁽⁶⁾. For the catalyst, CO+12% U₃O₈+2.5% Cu+100% Kieselguhr, by the H₂ pretreatment at relatively low temperature such as 270°C., as compared with the initial pretreatment temperature 350°C., the once decayed activity may be restored as in the series of F₁₉; while in the series of F₂₀, the decayed activity equally is recovered with the reversed order of pretreatments, namely, initially at 270°C., 5 hrs. then at 350°C. 2 hrs., but we may find a difference in the formation of gaseous products, i.e., CH₄ and CO₂ formations are more persistent in the series of F₂₀.

As seen in Tables 19–20, we may say that there is some optimal pretreatment temperature to get a fairly good activity although in every case the methane formation may be found immediately after pretreatment.

(6) (a) F. Fischer and H. Koch, *Brenn-Chem.*, **13**(1932), 61.

(b) S. Tsutsumi, *Report of Fuel Research Institute, Japan*, No. 31 (1935).

(c) S. Tsuneoka, "Synthetic Liquid Fuel" (in Japanese) pp. 66, 67, 68, 86, 87 (1938).

Table 18. Effects of Pre-treatments.

Type of Catalyst, Co+12% U₃O₈+2.5% Cu+100% Kieselguhr
Rate of Gas Flow, 4 l./hr.; CO:H₂=1:2

Exp. No.	React. Temp. (°C.)	Pre-treatments				Ave. Gas Cont. (%)	Oil Yields c.c./m ³	CO ₂ (%)	C ₂ H ₄ (%)	CH ₄ (%)	C ₂ H ₆ (%)
		Heat Treat.		H ₂ Red.							
		(°C.)	(hrs.)	(°C.)	(hrs.)						
		400	5	350	5	(F ₁₉ -A)					
F ₁₉ -E	225	—	—	—	—	40	173	0.8	1.6	0.0	0.0
F ₁₉ -L	250	400	5	270	2	70	103	9.2	0.5	12.0	0.0
F ₁₉ -N	225	—	—	—	—	25	50	0.6	0.9	0.0	0.0
F ₁₉ -Q	225	400	2	270	5	22	—	0.5	0.6	0.0	0.0
F ₁₉ -R	230	—	—	—	—	44	—	0.7	0.5	0.0	0.0
F ₁₉ -S	235	—	—	—	—	44	—	1.6	0.6	0.0	0.0
		400	4	270	5	(F ₂₀ -A)					
F ₂₀ -B	225	—	—	—	—	70	123	9.6	1.2	10.2	1.9
F ₂₀ -C	220	—	—	—	—	68	147	6.5	1.4	5.1	2.0
F ₂₀ -E	225	—	—	350	2	64	70	4.2	0.8	12.1	2.4
F ₂₀ -H	230	—	—	—	—	50	131.3	3.8	1.2	5.0	1.2

Table 19. Effects of Pre-treatments.

Type of Catalyst, Co+12% U₃O₈+5% Cu+100% Kieselguhr
Rate of Gas Flow, 4 l./hr.; CO:H₂=1:2

Exp. No.	React. Temp. (°C.)	Pre-treatments				Ave. Gas Cont. (%)	Oil Yields c.c./m ³	CO ₂ (%)	C ₂ H ₄ (%)	CH ₄ (%)	C ₂ H ₆ (%)
		Heat Treat.		H ₂ Red.							
		(°C.)	(hrs.)	(°C.)	(hrs.)						
F ₂₁ -A	200	400	2	250	5	60	0	15.3	0.2	38.9	2.7
F ₂₁ -C	"	—	—	230	2	44	54	0.6	0.5	0.0	0.0
F ₂₁ -D	"	—	—	210	2	32	20	0.5	0.5	0.0	0.0
F ₂₁ -E	"	—	—	350	2	30	46	0.5	0.2	0.0	0.0
F ₂₁ -F	"	—	—	300	2	36	7	0.7	0.3	0.0	0.0
F ₂₁ -H	"	—	—	230	2	30	80	0.5	0.7	0.0	0.0

Table 20. Effects of Pre-treatments.

Type of Catalyst, Co+12% U₃O₈+10% Cu+100% Kieselguhr
Rate of Gas Flow, 4 l./hr.; CO:H₂=1:2

Exp. No.	React. Temp. (°C.)	Pre-treatments				Ave. Gas Cont. (%)	Oil Yields c.c./m ³	CO ₂ (%)	C ₂ H ₄ (%)	CH ₄ (%)	C ₂ H ₆ (%)
		Heat Treat.		H ₂ Red.							
		(°C.)	(hrs.)	(°C.)	(hrs.)						
F ₂₂ -A	200	400	2	230	5	57	4	14.0	0.3	1.9	0.0
F ₂₂ -B	"	—	—	300	2	32	56	0.2	0.5	0.0	0.0
F ₂₂ -C	"	—	—	350	2	16	2.4	0.3	0.2	0.0	0.0
F ₂₂ -D	"	—	—	270	2	20	35	0.0	0.2	0.0	0.0

Table 21. Effects of Pre-treatments.

Type of Catalyst, $\text{Co} + 12\% \text{U}_3\text{O}_8 + 100\% \text{Kieselguhr}$
 Rate of Gas Flow, 4 l./hr., $\text{CO}:\text{H}_2=1:2$

Exp. No.	React. Temp. (°C.)	Pre-treatments				Ave. Gas Cont. (%)	Oil Yields c.c./m ³	CO ₂ (%)	C ₂ H ₄ (%)	CH ₄ (%)	C ₂ H ₆ (%)
		Heat Treat.		H ₂ Red.							
		(°C.)	(hrs.)	(°C.)	(hrs.)						
F ₂₃ -A	200	400	5	270	5	20	12	0.2	0.2	0.0	0.0
F ₂₃ -B	"	—	—	300	2	15	19	0.2	0.2	0.0	0.0
F ₂₃ -C	"	—	—	350	2	10	18	0.0	0.3	0.0	0.0
F ₂₃ -D	"	—	—	400	2	10	5.5	0.0	0.0	0.0	0.0
F ₂₃ -E	"	—	—	370	2	20	46	0.0	0.0	0.0	0.0
F ₂₃ -F	225	—	—	300	2	32	22	0.3	0.2	0.0	0.0
F ₂₃ -G	"	—	—	—	—	24	63.3	0.2	0.2	0.0	0.0

Table 22. Effects of Pre-treatments.

Type of Catalyst, $\text{Co} + 12\% \text{U}_3\text{O}_8 + 2.5\% \text{Cu}$,
 Rate of Gas Flow, 4 l./hr.; $\text{CO}:\text{H}_2=1:2$

Exp. No.	React. Temp. (°C.)	Pre-treatments				Ave. Gas Cont. (%)	Oil Yields c.c./m ³	CO ₂ (%)	C ₂ H ₄ (%)	CH ₄ (%)	C ₂ H ₆ (%)
		Heat Treat.		H ₂ Red.							
		(°C.)	(hrs.)	(°C.)	(hrs.)						
F ₂₄ -A	225	400	5	300	5	66*	3.4	17.7	0.2	62.2	0.0
F ₂₄ -B	"	—	—	300	2	66*	9.3	13.4	0.0	50.2	0.0
F ₂₄ -C	"	—	—	350	2	62*	14.5	12.1	0.0	47.1	0.0
F ₂₅ -A	225	400	5	270	5	66*	0	14.5	0.4	59.1	0.0
F ₂₅ -B	"	—	—	350	2	64*	0	14.1	0.4	54.4	0.0

* An extraordinarily large amount of CH₄ formation was observed. The maximum contraction percentage due to $\text{CO} + 3\text{H}_2 = \text{CH}_4 + \text{H}_2\text{O}$ alone is 66 2/3%; considering these we may possibly say that our results indicate that the reaction is entirely due to the above reaction. Therefore, this catalyst is to be extraordinarily good for CH₄ formation, but not for oil formation under these conditions.

Table 23. Effects of Pre-treatments.

Type of Catalyst, $\text{Co} + 15\% \text{U}_3\text{O}_8 + 2.5\% \text{Cu} + 100\% \text{Kieselguhr}$
 Rate of Gas Flow, 4 l./hr.; $\text{CO}:\text{H}_2=1:2$

Exp. No.	React. Temp. (%)	Pre-treatments				Ave. Gas Cont. (%)	Oil Yields c.c./m ³	CO ₂ (%)	C ₂ H ₄ (%)	CH ₄ (%)	C ₂ H ₆ (%)
		Heat Treat.		H ₂ Red.							
		(°C.)	(hrs.)	(°C.)	(hrs.)						
F ₂₆ -A	225	400	5	270	5	70	50	6.9	0.3	29.2	1.0
F ₂₆ -B	"	—	—	—	—	74	73	5.0	2.1	10.2	9.2
F ₂₆ -C	"	—	—	—	—	66	93	3.9	1.8	7.3	6.2
F ₂₆ -D	"	—	—	—	—	64	52	5.1	1.9	15.4	3.3
F ₂₆ -E	"	400	5	350	5	32	48	0.2	0.3	0.0	0.0
F ₂₆ -F	"	—	—	—	—	13	0	0.3	0.2	0.0	0.0

In Table 21, we see that for the catalyst without Cu, the reduction temperature at the initial stage should be fairly high in order to get sufficient activity and the later pretreatment temperature has to be higher for getting a reasonable amount of oil formation.

As observed in Table 22, for the catalyst without Kieselguhr, regardless of differences of pretreatment temperatures, there we found no difference as to the activity in the oil formation, but in every case we found practically the same contraction percentage, with predominating tendency for CH_4 and CO_2 formations. These facts, with the fore-mentioned relations between the oil formation and the pretreatments, imply that there is some delicate connection between the pretreatments and the activity for the oil formation which may be sensitively affected by the porosity of materials as well as the surface structure as varied by these heat treatments. However, a more definite conclusion, though very desirable, cannot be obtained at the present stage.

The lowering of the initial reduction temperature when Cu is present in the catalyst again is demonstrated even for the catalyst which contains 15% U_3O_8 , and a fairly low temperature for pretreatment may be adopted for a sufficient activity. These are shown in Table 23.

In Table 24, some of the physico-chemical constants for the products in the series of F_{19} – F_{29} are compiled. In this table, the first trap oil indicates the heavier fraction and the second the lighter one condensed by solid CO_2 – $\text{C}_2\text{H}_5\text{OH}$ mixture.

Table 24. Properties of the Products.

Exp. No.	Ref. Ind. 25°C.	Sp. Gr. 25°C.	App. M. W.	Elem. Analysis	
				C %	H %
F_{19} (A–K) 1st trap	1.4259 ^{30°}	0.759	160	84.79	15.32
F_{19} (A–K) 2nd trap	1.3850 ^{30°}	0.677	88	83.63	15.82
F_{19} (L–P) 1st trap	1.4212 ^{30°}	0.770	179	84.97	15.01
F_{19} (L–P) 2nd trap	1.3868 ^{30°}	0.702	100	84.24	15.84
F_{20} (A–D) 1st trap	1.4222 ^{30°}	0.756	139	85.19	14.73
F_{20} (A–D) 2nd trap	1.3802 ^{30°}	0.685	84	84.39	15.58
F_{20} (E–H) 1st trap	1.4273	0.758	152	84.40	15.68
F_{20} (E–H) 2nd trap	1.3939	0.687	87	83.79	16.07
F_{21} (A–D) 1st trap	1.4219	0.749	130	84.66	15.28
F_{21} (A–D) 2nd trap	1.4034	—	94	83.69	16.21
F_{21} (E–H) 1st trap	—	—	—	83.82	15.81
F_{21} (E–H) 2nd trap	1.4010	0.701	81	83.02	16.76
F_{22} (A–F) 1st trap	1.4258 ^{30°}	—	—	84.33	15.14
F_{22} (A–F) 2nd trap	1.4080 ^{30°}	—	—	—	—
F_{23} (A–I) 1st trap	1.4273 ^{30°}	0.765	177	84.74	15.06
F_{23} (A–I) 2nd trap	1.4028 ^{30°}	0.711	111	83.92	15.20
F_{26} (A–D) 1st trap	1.4213 ^{30°}	0.748	139	85.04	15.29
F_{26} (A–D) 2nd trap	—	0.687	92	84.37	15.42
F_{26} (A–D) 1st trap	1.4381 ^{20°}	—	177	—	—

In Fig. 1, the results for the contraction percentages in the series of F_{20} as a function of the reaction temperature are plotted, while in Fig. 2, the results for the contraction percentages as a function of the rate of gas flow at 225°C. and 230°C., respectively, are plotted.

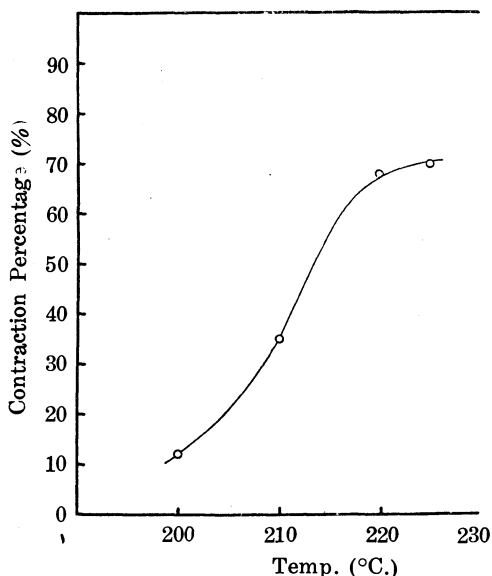


Fig. 1. Gas Contraction Percentage Vs. Reaction Temperature.

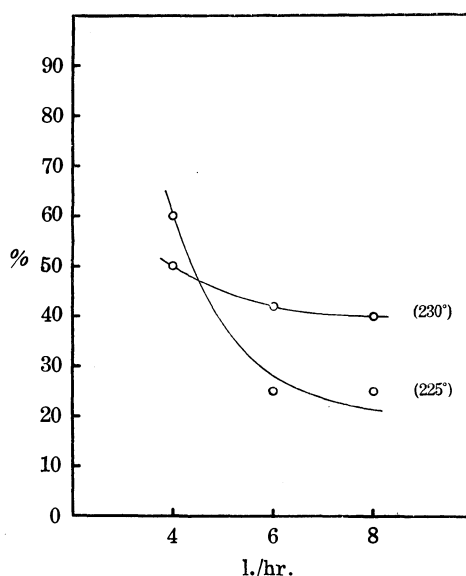


Fig. 2. Contraction % Vs. Rate of Flow.

Thus far, we have presented typical results for the series F_{19} – F_{29} , with respect to the gas analysis data, and the effects of reaction temperature, rate of gas flow, pretreatments, and of promoters. These results are correlated, and some explanations are offered with special reference to the reaction mechanism for the Fischer-Tropsch synthesis of hydrocarbons.

Summary.

(1) The experimental materials used in this investigation are briefly described along with the preparations of the catalysts.

(2) The experimental procedure with reference to our previous paper is presented.

(3) The typical results, as related to the catalytic activity and gaseous products, are tabulated and some correlations are offered.

(4) The effects of such promoters as U_3O_8 , Cu, and Mn along with those of a carrier, Kieselguhr, upon the catalytic activity are tabulated and discussed; furthermore, possible correlations with the oil formation are presented.

(5) The results of the effects of the reaction temperature, as well as of the pretreatment upon the activity, with special emphasis on the oil formations and gaseous products are presented and discussed rather thoroughly, and some possible correlations are given.

(6) Finally, the properties of the liquid products for the series of F_{19} – F_{29} for the type of catalysts, $\text{Co} + x\% \text{U}_3\text{O}_8 + y\% \text{Cu} + z\% \text{Mn} + w\% \text{Kieselguhr}$, such as refractive indices, specific gravities, apparent molecular weights and elementary analysis data are compiled in the table.

In conclusion, the authors express their hearty thanks to Dr. T. Marusawa, Former Director, and to Dr. S. Sato, Director of the Institute, for their interests and constant encouragement in carrying out this investigation and for the permission for this publication. Also the authors take this occasion, to extend their thanks to Messrs. Igarashi, Fujiwara and Kuwabara who have been willing to assist us in the experimental part of this investigation and to Messrs. Kataoka, Inaba, Kodama and Nakano who have helped us in the analytic work.

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An Empirical Equation for Calculating the Changes in the Boiling Points of Hydrocarbons with Small Changes in Pressure.

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In the separation by distillation of hydrocarbons for the purpose of identification, it is frequently necessary to calculate the change in the boiling point with pressure, even when the change in pressure may be less than 10 mm. The above statement may be fully appreciated when it is realized that a pressure change of 10 mm. corresponds to nearly 0.5°C . which is often as much as the difference between the boiling points of the compounds to be separated.

In the course of our investigations on hydrocarbon synthesis and separation of the products by distillation, we have found the following empirical equation,

$$dt_b \text{ }^{\circ}\text{C.}/dP_{\text{mm.}} = 0.0345 + 0.00011 t_b \quad (1)$$

in which t_b is the boiling point in centigrade, $P_{\text{mm.}}$ is the pressure expressed in mm. of Hg, quite convenient and sufficiently accurate for a large number of hydrocarbons commonly found in the gasoline boiling range.

The purpose of this paper is to illustrate the usefulness and the limitations of the above equation, and, at the same time, to indicate briefly justification for the linear form it assumes. A comparison of the equation with those found in the literature will be also considered.

From the thermodynamic relation,

$$(\partial S/\partial V)_T = (\partial P/\partial T)_V \quad (2)$$

in which S , P , T , V have the usual significance, the Clausius-Clapeyron equation,

$$dP/dT = \frac{\Delta L}{T(V_g - V_l)}, \quad (3)$$

may be readily derived. It expresses the change in the boiling point with pressure in terms of the temperature at which the heat of vaporization is ΔL and where the liquid with a volume V_l is completely changed into vapor with a volume V_g .

Equation (3) is general, and if ΔL , T , V_l , and V_g are known, dT/dP can be determined exactly. However, it would be more convenient if dT/dP (or dt/dP) can be expressed as a simple function of the boiling point of the pure substance. For the very purpose we have found equation (1) quite adequate. We do not intend to attach any theoretical significance to the equation; our sole purpose is, as has already been mentioned above, to give a simple empirical equation which may be of use in practical application. This equation is theoretically applicable for dT/dP only at $P=760$ mm., but for a change of ± 10 mm. from 760, it should still be fairly accurate.⁽¹⁾

Because of the simple form Trouton's relation takes, the Clausius-Clapeyron equation can be readily put in a much simpler form⁽²⁾ by its application, as will be illustrated below:

Writing the Clausius-Clapeyron equation in an equivalent form,

$$dP/dT = P\Delta L/RT^2 \quad (4),$$

where R is the gas constant and ΔL , P , T have the same significance as in (3), and by assuming the vapor to behave ideally, ΔL to be independent of the temperature, and the volume of the liquid to be negligible in com-

(1) D. B. Brooks, *J. Research, NBS*, **21**(1940), 847; E. R. Smith, *ibid.*, **26**(1941) 129. As is evident from the results, a change of 40 mm. gives a difference of 0.0016~

P mm.	dt/dP^*		Benzene
	n -Heptane	Iso-octane	
700	0.04779	0.04958	0.0456
760	0.04480	0.04649	0.0427
800	0.04304	0.04467	0.0411

* Calculated from dP/dT originally given in his Table.

0.0018 in dt/dP , or about $0.0004^\circ\text{C.}/10$ mm. Hg., which is well within the accuracy of experimental error.

(2) By use of Trouton's rule many relations, especially those involving the heat (or energy) of vaporization, can often be reduced to simpler forms. Kimura's (O. Kimura, *J. Chem. Soc. Japan*, **63**(1942), 98) derivation of his viscosity function, $\eta = Ae^{b/\theta}$ is a good example. However, his basic idea of deriving an expression for viscosity which is applicable to all substances of the same series (paraffin) independently of the properties of the individual members of the series in terms of the reduced absolute temperature, or in its equivalent forms; in other words, when η for the members are plotted against the proper functions of the reduced absolute temperatures, all viscosities will fall on the same line, is not original. It has already been mentioned by E. P. Irany (*J. Am. Chem. Soc.*, **61**(1939), 1734.)

parison with that of the vapor, and since P is always in the neighborhood of 760 mm., we readily obtain

$$dT_b/dP = KT_b \quad (5),$$

where T_b is the boiling point in the absolute temperature. Therefore, in terms of t_b , the boiling point in centigrade, the expression becomes

$$dt_b/dP = K(273.1 + t_b) = A + Kt_b,$$

which is the form relation (1) assumes.

We shall now show to what extent relation (1) is useful; at the same time a comparison will be made between it and other empirical equations for dt_b/dP found in the literature. Relation (1) has been obtained by changing the first term of the equation,⁽³⁾

$$dt_b/^{\circ}\text{C.}/dP_{\text{mm.}} = 0.0350 + 0.00011 t_b \quad (6),$$

which is the equation of the line drawn through the accurate dt_b/dP points given in Table 1.

Table 1. Change in Boiling Point with Small Change in Pressure.

Hydrocarbons ⁽⁶⁾	Formula	B.P. ($^{\circ}\text{C.}$) at 760 mm.Hg.	$dt_b/^{\circ}\text{C.}/dP_{\text{mm.}}$		Deviation Found— Calculated	Ref.
			Found	Calculated*		
3,3-Dimethyl-butene-1	C_6H_{12}	41.239	0.0397	0.0395	+0.0002	4
2,3-Dimethyl-butene-1	C_6H_{12}	55.615	0.0410	0.0411	—0.0001	4
2,3-Dimethyl-butene-2	C_6H_{12}	73.24	0.0414	0.0431	—0.0017	4
2,3,3-Trimethyl-butene-1	C_7H_{14}	77.874	0.0447	0.0436	+0.0011	4
2,3-Dimethyl-butane	C_6H_{14}	57.999	0.0412	0.0414	—0.0002	4
2,2-Dimethylbutane	C_6H_{14}	49.731	0.0407	0.0405	+0.0002	4
2,2,3-Trimethyl-butane	C_7H_{16}	80.879	0.0449	0.0439	+0.0010	4
3-Ethylpentane	C_7H_{16}	93.473	0.0446	0.0453	—0.0007	4
<i>n</i> -Heptane	C_7H_{16}	98.424	0.0449	0.0458	—0.0009	4
2,2,4-Trimethyl-pentane	C_8H_{18}	99.233	0.0465	0.0459	+0.0006	4
2,3,4-Trimethyl-pentane	C_8H_{18}	113.391	0.0479	0.0475	+0.0004	4
Benzene	C_6H_6	80.094	0.0427	0.0438	—0.0011	5
2,2,4,4-Tetramethylpentane	C_9H_{20}	122.281	0.0492	0.0485	+0.0007	6
Isopropylbenzene	C_9H_{12}	152.39	0.0507	0.0517	—0.0010	7
			$\pm 0.002^{**}$			

* From Eq. (6), $dt_b/^{\circ}\text{C.}/dP_{\text{mm.}} = 0.0350 + 0.00011 t_b$.

** Limits of experimental error. The writer (R.N.) is unable to ascertain whether it is ± 0.0020 or ± 0.0002 .

(3) C. Isobe and R. Negishi, *J. Soc. Chem. Ind., Japan*, **45**(1942).

(4) D. B. Brooks, F. L. Howard, and H. C. Crafton, Jr., *J. Research NBS*, **24**(1940), 33.

(5) E. R. Smith and H. Matheson, *ibid.*, **20**(1938), 641.

(6) F. L. Howard, *J. Research NBS*, **24**(1940), 677.

(7) J. D. White and F. W. Rose, Jr., *ibid.*, **21**(1938), 151.

(8) G. Egloff, ('Physical Constants of Hydrocarbons, Reinhold Publish. Corp., (1939, 1940); Science of Petroleum, Vol. II, (1938), 1302.

Table 2 shows the results of determination and calculation made by Lamb and Roper⁽⁹⁾ on dt_b/dP (originally dP/dT_b) of 35 hydrocarbons of the paraffin series. Their results seem fairly accurate, and they serve as a good basis for some interesting comparison between our empirical relation and theirs, either derived from the Clausius-Clapeyron equation or derived empirically to agree particularly with the data given in Table 2.

Lamb and Roper have derived the expression,

$$(dP/dT)_{T_b} = \frac{760 \times 20.85}{RT_b} = \frac{7975}{T_b}, \text{ or}$$

$$dt_b/dP = 0.03425 + 0.0001254 t_b \quad (7),$$

by combining the Clausius-Clapeyron equation, under the assumptions already mentioned above, with Trouton's rule, assuming 20.85 for the Trouton constant (the mean value for the 35 hydrocarbons listed in Table 2).

The line representing this equation is given in Fig. 1, where it is obvious that, even with the particular Trouton constant used, the deviation between the values of dt_b/dP calculated and found becomes appreciable at lower and higher temperatures. It clearly indicates that some of the simplifying assumptions involved in (7) are not justified.

On the other hand, relation (1) is in much better agreement with the observed values. In fact, it is even better than the equation⁽⁹⁾,

$$(dP/dT)_{T_b} = \frac{3634 \log_{10} T_b}{T_b} - 2.68 \quad (8),$$

which takes into account the trend⁽¹⁰⁾ in Trouton constant with the boiling point, and is about as good as their so-called "general" equation,⁽⁹⁾

$$(dP/dT)_{T_b} = \frac{3461 \log_{10} T_b}{T_b} - 1.77 \quad (9),$$

derived simply by altering the constants in relation (8) to agree better with the results in Table 2.

A comparison of the relative accuracies of the equations, (1), (7), (8), and (9) are given along with that of the "special" equation,

$$(dP/dT)_{T_b} = \frac{a_s \log_{10} T_b}{T_b} + b_s \quad (10)$$

proposed by Lamb and Roper⁽⁹⁾, in which a_s and b_s are the constants for the particular group of hydrocarbons, in the last columns of Table 2. The results require no explanation.

(9) A. B. Lamb and E. E. Roper, *J. Am. Chem. Soc.*, **62**(1940), 806.

(10) The fact that Trouton constant is not really a constant has long been recognized by numerous investigators, and a number of corrections—from purely empirical to semi-theoretical—have been proposed. One of the more exact and compatible with theory, yet quite simple in form, is what is known as Hildebrand's rule (J. H. Hildebrand, "Solubility," Reinhold Publish. Corp., 102(1936)).

Table 2.⁽⁹⁾ Change in Boiling Points with Pressure for Some of the Hydrocarbons in the Paraffin Series.

Hydrocarbons*	Formula	B.P. (°C.) at 760 mm.	dt_b/dP^{**} °C./mm.	Deviation Calculated-Found (%)				
				Eq. (1)	Eq. (7)	Eq. (8)	Eq. (9)	Eq. (10)
<i>n</i> -Alkanes								
Methane	C ₁ H ₄	-161.43	0.0163	-2.6	+16.5	+4.3	-3.5	-0.1
Ethane	C ₂ H ₆	-88.69	0.0244	-1.1	+5.6	+2.4	-0.5	-0.9
Propane	C ₃ H ₈	-42.12	0.0299	-0.1	+3.0	+3.0	+0.4	+0.3
Butane	C ₄ H ₁₀	- 0.68	0.0341	-0.8	-0.1	+1.7	-0.5	-0.3
Pentane	C ₅ H ₁₂	36.11	0.0388	+0.9	+0.2	+3.9	+1.4	+1.6
Hexane	C ₆ H ₁₄	68.74	0.0421	-0.0	-1.9	+2.0	-0.4	+0.8
Heptane	C ₇ H ₁₆	98.36	0.0447	-1.3	-4.0	+0.4	-0.8	-0.3
Octane	C ₈ H ₁₈	125.66	0.0482	-0.2	-3.5	+1.4	+0.8	+1.1
Branched-chain Alkanes								
2-Methylpropane	C ₄ H ₁₀	-12.10	0.0337	1.5	2.9	4.1	2.0	-0.1
2,2-Dimethylpropane	C ₅ H ₁₂	9.46	0.0363	1.9	2.3	4.6	2.4	0.4
2-Methylbutane	C ₅ H ₁₂	27.95	0.0380	1.1	0.7	3.5	1.6	-0.4
2,3-Dimethylbutane	C ₆ H ₁₄	57.99	0.0414	1.4	-0.2	0.8	1.9	-0.1
2,2,4-Trimethylpentane	C ₈ H ₁₈	99.23	0.0465	2.4	-0.4	4.2	2.9	1.0
2,5-Dimethylhexane	C ₈ H ₁₈	109.20	0.0466	0.1	-2.9	1.5	0.6	-1.3
2,6-Dimethyloctane	C ₁₀ H ₂₂	158.54	0.0521	0.4	-3.7	1.7	0.9	-0.8
<i>n</i> -Alkenes								
Ethene	C ₂ H ₄	-103.81	0.0226	-2.2	6.4	0.7	-1.1	0.4
Propene	C ₃ H ₆	-47.66	0.0291	-0.5	2.9	2.5	-0.1	0.5
1-Butene	C ₄ H ₈	- 6.30	0.0338	-0.1	0.9	2.5	0.3	0.1
Trans-2-butene	C ₄ H ₈	0.91	0.0350	1.0	1.8	3.7	1.5	1.2
Cis-2-butene	C ₄ H ₈	3.53	0.0339	-2.9	-2.3	-0.4	-2.4	-2.7
1-Heptene	C ₇ H ₁₄	93.78	0.0459	2.4	-0.1	4.4	3.0	1.2
Branched-chain Alkenes								
2-Methylpropene	C ₄ H ₈	- 7.12	0.0344	2.1	3.3	4.9	2.6	2.5
2-Methyl-2-butene	C ₅ H ₁₀	38.43	0.0389	0.4	-0.5	2.7	0.9	0.0
Dienes								
Propadiene	C ₃ H ₄	-33.64	0.0300	-2.7	-0.2	0.2	-0.8	-0.5
1,3-Butadiene	C ₄ H ₆	- 4.51	0.0340	-0.0	0.9	2.6	0.4	1.0
1,4-Pentadiene	C ₅ H ₈	26.06	0.0376	0.4	0.1	2.9	0.9	-0.4
2-Methyl-1,3-butadiene	C ₅ H ₈	34.08	0.0382	-0.2	-0.8	2.1	0.3	0.6
<i>n</i> -Alkynes								
Ethyne	C ₂ H ₂	-85.22	0.0229	-9.5	-2.6	-5.2	-8.0	-1.0
Propyne	C ₃ H ₄	-23.21	0.0299	-7.0	-4.7	-3.9	-6.2	-2.1
1-Butyne	C ₄ H ₆	9.05	0.0358	0.7	1.0	-3.2	1.1	3.9
2-Butyne	C ₄ H ₆	27.11	0.0363	-3.3	-3.6	-0.9	-2.8	-1.0
Miscellaneous								
1-Buten-3-yne	C ₄ H ₄	5.11	0.0338	-3.1	-3.1	-1.2	-3.2	—
1,3-Butadiyne	C ₄ H ₂	9.79	0.0351	-1.5	-1.2	1.0	-1.0	—
Cyclohexane	C ₆ H ₁₂	80.74	0.0438	1.0	-1.2	3.0	1.5	—
1,5-Hexadien-3-yne	C ₆ H ₆	83.50	0.0435	-0.4	-2.7	1.5	0.1	—
Means of Values for all Hydrocarbons Listed				1.7	2.5	2.5	1.7	0.9

* For name and carbon skeleton; see Ref. (8).

** Calculated from dP/dT .

In Fig. 1 are drawn and plotted the lines representing relations (1), (7), (9), and that representing the data given in Table 3⁽¹¹⁾, and dt_b/dP mm. values not only given in Table 2 but also in Table 4⁽¹²⁾⁽¹³⁾. Some of the compounds are given in Tables 2 and 4 to show how closely various investigators agree, or disagree, on dt_b/dP of the same substances. The "length" of the points roughly indicates the relative accuracy of the

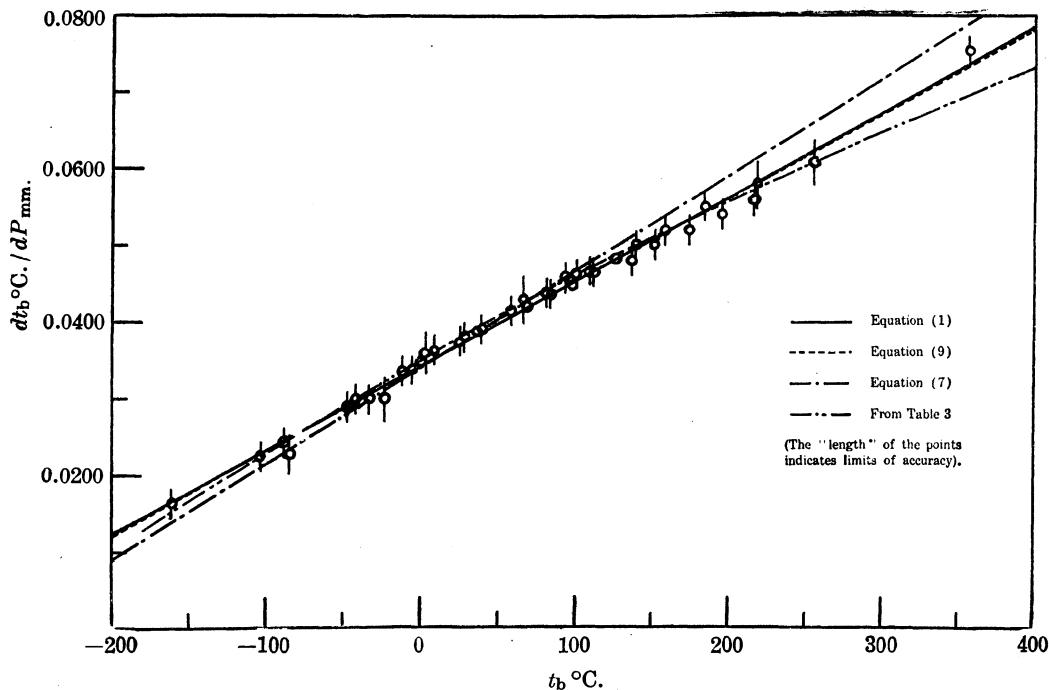


Fig. 1. $dt_b^\circ\text{C.}/dP_{\text{mm.}}$ Vs t_b .

Table 3. Correction Factors for the Boiling Point for Small Change in Pressure*.

B.P. at 760 mm.	Correction factor $^\circ\text{C./mm.}$	B.P. at 760 mm.	Correction factor $^\circ\text{C./mm.}$
-100	0.023	200	0.056
- 50	0.029	250	0.061
0	0.035	300	0.065
50	0.040	350	0.069
100	0.046	400	0.073
150	0.051		

* The correction factors can be regarded as accurate over a pressure range, 760 ± 50 mm Hg. (Ref. 11).

(11) E. S. L. Beale, Science of Petroleum, Vol. II, 1281 (1938).

(12) Landolt-Boernsteins Tabellen, 2427 (1936).

(13) Landolt-Boernsteins Tabellen, 1289 (1932).

Table 4. Change in Boiling Point with Small Change in Pressure.

Hydrocarbons	Formula	B.P. (°C.) at 760 mm.	$dt_b^{\circ}\text{C.}/dP_{\text{mm.}}$		Diff. Found- Calcula- ted	Ref.*
			Found	Calcula- ted		
<i>n</i> -Pentane	C_5H_{12}	{ 36.00 36.10	0.039	0.038	0.001	12
<i>i</i> -Pentane	C_5H_{12}		0.041	0.038	0.003	12
<i>n</i> -Hexane	C_6H_{14}	27.95	0.037	0.037	0.000	13
<i>n</i> -Heptane	C_7H_{16}	68.71	0.042	0.042	0.000	12
<i>n</i> -Octane	C_8H_{18}	98.35	0.045	0.045	0.000	12
<i>n</i> -Nonane	C_9H_{20}	125.59	0.048	0.048	0.000	12
<i>n</i> -Decane	$\text{C}_{10}\text{H}_{22}$	150.71	0.050	0.051	-0.001	12
<i>n</i> -Undecane	$\text{C}_{11}\text{H}_{24}$	174.06	0.052	0.054	-0.002	12
<i>n</i> -Dodecane	$\text{C}_{12}\text{H}_{26}$	195.84	0.054	0.056	-0.002	12
Hexene	$\text{C}_{12}\text{H}_{26}$	216.23	0.056	0.058	-0.002	12
Benzene	C_6H_6	65.92	0.043	0.042	0.001	16
Toluene	C_6H_6	80.122	0.0428	0.0433	-0.0005	13
<i>m</i> -Xylol	C_7H_8	{ 110.80 110.606	0.042	0.047	-0.005	13
			0.0464	0.0467	-0.0003	13
<i>m</i> -Xylol	C_8H_{10}	139.10	0.0490	0.0498	-0.0008	13
			0.0498	0.0498	0.0000	13
Ethylbenzene	C_8H_{10}	136.15	0.048	0.049	-0.001	13
Propylbenzene	C_9H_{12}	159.45	0.052	0.052	0.000	13
<i>n</i> -Butylbenzene	$\text{C}_{10}\text{H}_{14}$	183.10	0.058	0.055	0.003	13
Cyclohexane	C_6H_{12}	80.80	0.045	0.043	0.002	13
Methylcyclohexane	C_7H_{14}	101.20	0.048	0.046	0.002	13
1,2,4-Trimethyl-cyclohexane	C_9H_{16}	141.22	0.051	0.051	0.00	17
Diphenyl	$\text{C}_{12}\text{H}_{10}$	254.93	0.061	0.063	-0.002	16
Naphthalene	{ C_{10}H_8	218.	0.0592	0.0585	0.0007	16
		217.68	0.057	0.058	-0.001	16
		217.96	0.058	0.058	0.000	16

* Data given by Ref. 16 least reliable.

(17) J. D. White and A. R. Glasgow, Jr., J. Research NBS, **22**(1939), 137.

measurement. For the results given in Table 2, $\pm 0.002^{(14)}$ has been assumed except for normal pentane, hexane, heptane, and octane for which $\pm 0.0005^{(15)}$; for ethyne, propyne, and cis-2-butene ± 0.003 . Most of the results given in Table 4 are given a weight of $\pm 0.002^{(14)}$. From Fig. 1 it seems to the author that the values of dt_b/dP for decane, undecane, and dodecane, though given a relative accuracy of ± 0.002 , deviate much more than that, and they seem to be too low.

It may be of some interest to mention in passing that dt_b/dP observed and calculated by relation (1) for mercury, sulfur, and sodium are as given in Table 5.

(14) There is no real basis for the value assumed except for isopropylbenzene, $dt_b/dP = 0.0507 \pm 0.002$ (Ref. 7).

(15) The results of various measurements given in Tables 1, 2, and 4 do not differ more than ± 0.0005 from the mean.

Some of them are definitely lower than ± 0.002 ; probably ± 0.004 .

Table 5.

	B.p. (°C.)	dt_b/dP (°C./mm.)		Ref.*
		Obs.	Calc.	
Mercury	356.8	0.0754	0.0735	16
Sulfur	{ 444.53	0.0820	0.0830	16
	{ 444.55	0.0908		
Sodium	878	0.153	0.131	12

* Accuracy uncertain.

From the results given in this paper, some plausibility is lent to the following statements: (a) Relation (1) is, for practical purposes, accurate for expressing the change in the boiling point with a small change in pressure for most of the hydrocarbons over a wide range of temperature (from -160 to 300°C); (b) Relation (1) is just as accurate as the "general" equation, or (9), but it has the great advantage that its expression is very much simpler and linear; (c) The correction factors given in Table 3 are also quite good, but they seem to be inadequate at temperatures above 300°C .

The first constant term in relation (1) has been reduced by 0.0005 from the original 0.0350 found in (6) for the simple reason that, by this change, the deviations between calculated and observed for the hydrocarbons given in Table 2 are reduced materially. In view of the fact that the accuracy of the determination itself may not be greater than ± 0.002 , the above change may not be significant; however, there seems to be evidence from the results of Tables 1 and 2 that there is a real difference, which amounts to about 0.0005, between dt_b/dP for branched and unbranched compounds. Unfortunately the available data are not sufficiently accurate to warrant a further discussion on this point.

As is obvious from Fig. 1, the lines representing the "general" equation (9), and relation (1) almost coincide with each other although the former is not a linear equation. This is due to the circumstance that $\log_{10}T_b$ changes only from 2.23830 to 2.75820 for the change in T_b from 173.1 to 573.1°K .

$dt_b^\circ\text{C.}/dP_{\text{mm.}}$ for other compounds, containing halogen, nitrogen, and oxygen, have been similarly treated, and it is indicated that relation (1) is applicable not only to hydrocarbons but also to most of the substances without hydrogen bonding. A more detailed discussion of the problem will be given later.

Summary.

An empirical relation,

$$\frac{dt_b^\circ\text{C.}}{dP_{\text{mm.}}} = 0.0345 + 0.00011 t_b,$$

for calculating the change in the boiling point with a small change in

pressure has been derived. It has been found that the equation is applicable to most of the hydrocarbons, with their boiling points ranging from -160 to 300°C. , with a maximum deviation of about ± 0.002 .

A comparison of this equation with the others found in the literature has been made, and it has been found that the relation is just as accurate as some of the more complicated ones proposed.

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Electrolytic Reduction of Nitriles.

By Masaki OHTA.

(Received August 31, 1942.)

In order to study the electrolytic reduction of nitriles with platinum cathode covered with palladium, the present author attempted the reduction of typical compounds containing CN-group and found that they were readily reduced to the corresponding amines.

The electrolytic reduction of nitriles has been reported only by a few workers.⁽¹⁾ One example is described by Mr. T. Matukawa⁽²⁾ in the case of 2-methyl-4-amino-5-cyano-pyrimidine, which is reduced in acidic solution with platinum cathode covered with palladium to 2-methyl-4-amino-5-aminomethyl-pyrimidine hydrochloride. The author applied this method to other compounds containing CN-group and found that they were comparatively readily reduced. Moreover, some nitriles, e.g., malonitrile, ethylenecyanohydrin, cyanoacetic acid, which are difficult to reduce by the ordinary reduction methods, could be readily reduced with electrolytic reduction.

In Table 1, the nitrile used, and their reduction products and yields are summarized. The reduction products were identified as free bases, hydrochlorides or their suitable derivatives by comparing their melting points or boiling points with what is described in the literature and by analysis.

Among these, the reduction of malonitrile and ethylenecyanohydrin have never been attempted, but by electrolytic reduction the author obtained trimethylenediamine hydrochloride and γ -oxypropylamine respectively. β -Alanine has been obtained by Hofmann's reaction from succinimide⁽³⁾, but by electrolytic reduction it can be readily obtained from cyanoacetic acid and it seems to be an excellent method of preparing β -alanine.

(1) K. Ogura, *Memoirs of the College of Science of Kyoto Imperial University*, **12**(1929), 339.

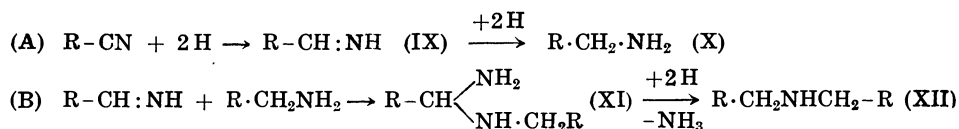
(2) T. Matukawa, *Jap. Pat. No.* 133464 (1939).

(3) Hoogewerff and Van Dorp, *Rec. trav. chim.*, **10**(1893), 4.

Table 1.

	Nitrile	Reduction products	Yield (%)
I	CH ₃ CN	CH ₃ CH ₂ NH ₂	100
II	<i>o</i> -CH ₃ ·C ₆ H ₄ CN	<i>o</i> -CH ₃ ·C ₆ H ₄ CH ₂ NH ₂	40
III	C ₆ H ₅ ·CH ₂ CN	C ₆ H ₅ ·CH ₂ CH ₂ NH ₂	75
IV	CN·CH ₂ ·CN	NH ₂ (CH ₂) ₃ NH ₂	50
V	CN·CH ₂ ·CH ₂ ·CN	NH ₂ (CH ₂) ₄ NH ₂	70
VI	CN(CH ₂) ₄ CN	NH ₂ (CH ₂) ₆ NH ₂	40
VII	CN·CH ₂ ·CH ₂ ·OH	NH ₂ ·CH ₂ ·CH ₂ ·CH ₂ ·OH	30
VIII	CN·CH ₂ ·COOH	NH ₂ ·CH ₂ ·CH ₂ ·COOH	40

In the present experiments the author adopted nearly the same condition, but it is obvious that the condition of electrode, current density, concentration of acid in catholyte, temperature etc. have great influences on the yield, and it is expected that the yield described in Table 1 might be greatly increased. Indeed, in some cases, the formation of ammonium chloride in the reduction products was observed. According to Braun,⁽⁴⁾ the mechanisms of reduction of nitrile are formulated as follows:



Nitrile is at first reduced to aldimine (IX) which is further reduced to primary amine (X). (X) may react with the aldimine yielding an addition compound (XI), which is unstable and by further reduction and loss of ammonia produced secondary amine (XII). Hartung⁽⁵⁾ reported that the formation of secondary amine can be suppressed by carrying out the reduction in the presence of hydrochloric acid which fixes the resulting primary amine as hydrochloride.

The author has also carried out the reduction in the presence of mineral acid; even when the formation of ammonium chloride was occasionally observed. Studies concerning the problem whether the formation of ammonium chloride is due to the above mentioned mechanisms or to the hydrolytic decomposition of nitrile are in progress.

Experimental.

General Procedure of Reduction. The apparatus for reduction consists of (i) a 200 c.c. beaker as an electrolytic bath; (ii) platinum wire net (150 cm.²) as cathode; (iii) platinum wire as anode; (iv) a porous unglazed porcelain cylinder as a diaphragm. Preparation of cathode: A mixture of 50 c.c. of water, 10 c.c. of concentrated hydrochloric acid and a solution of 0.5–1 g. of palladium chloride in a little dilute hydrochloric acid are used as catholyte and electrolyzed at room temperature (current density: 0.02 amp./cm.²). The colour of palladium chloride having disappeared, the catholyte was taken out and then reduction was carried out.

(4) v. Braun, *Ber.*, **56**(1923), 1988. Cf. T. Hoshino, *J. Soc. Chem. Ind. Japan*, **44**(1941), 1085.

(5) Hartung, *J. Am. Chem. Soc.*, **50**(1928), 3370.

A solution of a nitrile in dilute hydrochloric acid (when the nitrile was sparingly soluble in water, it was dissolved by adding glacial acetic acid) was used as catholyte and reduced electrolytically. The bath was cooled with ice water from outside. When the reduction was not smooth, a small amount of palladium chloride solution was added to the catholyte. Dilute hydrochloric acid was used as anolyte. After reduction the catholyte was taken out and evaporated to dryness in vacuum and the residual amine hydrochloride was identified as such or as a suitable derivative.

(I) Reduction of acetonitrile. Catholyte: 1 g. of acetonitrile was dissolved in 50 c.c. of 8% hydrochloric acid. Anolyte: dilute hydrochloric acid. Current density: 3 amp./dm.². Electrolysis was conducted at 15° for two hours. The electrolyte was taken out after electrolysis, and evaporated in vacuum. 2 g. of pure ethylamine hydrochloride was obtained. The yield was quantitative. The picrate melted at 169°.

(II) Reduction of *o*-tolunitrile. Catholyte: 1 g. of the nitrile was dissolved in a mixture of 50 c.c. of glacial acetic acid, 10 c.c. of concentrated sulphuric acid and a little water. Anolyte: 20% sulphuric acid. Current density: 2 amp./dm.². Temperature: 10°. After one hour and a half, the catholyte was concentrated in vacuum, made strongly alkaline with sodium hydroxide and extracted with ether. The ether extract was shaken with dilute hydrochloric acid. The hydrochloric acid solution was evaporated to dryness under reduced pressure. The residue was recrystallized from absolute alcohol by adding a little ether. 0.5 g. of *o*-tolubenzylamine hydrochloride was obtained, m.p. 217°. Found: N, 8.88. Calcd. for C₈H₁₂NCl: N, 9.07%.

(III) Reduction of benzylcyanide. Catholyte: 1 g. of benzylcyanide was dissolved in a mixture of 30 c.c. of glacial acetic acid, 10 c.c. of water and 10 c.c. of concentrated hydrochloric acid. Anolyte: 10% hydrochloric acid. Current density: 2 amp./dm.². Temperature: 10°. After two hours the catholyte was treated as described in general procedure. 1 g. of phenylethylamine hydrochloride was obtained. Yield 75%; m.p. 217°. Found: C, 61.05; H, 7.67. Calcd. for C₈H₁₂NCl: C, 60.95; H, 7.62%.

(IV) Reduction of malonitrile. Catholyte: 1 g. of malonitrile was dissolved in a mixture of 40 c.c. of water and 10 c.c. of concentrated hydrochloric acid. Anolyte: dilute hydrochloric acid. Current density: 3.5 amp./dm.². Temperature: 8–10°. After two hours' electrolysis the catholyte was evaporated under reduced pressure, the residue was fractionally crystallized from alcohol. 0.3 g. of ammonium chloride and 1.1 g. of trimethylenediamine hydrochloride (m.p. 243–4°) were obtained. Yield 50%. Found: N, 18.91. Calcd. for C₃H₁₂N₂Cl₂: N, 19.05%. Picrate: m.p. 216°, from dilute alcohol.

(V) Reduction of succinonitrile. Catholyte: 1 g. of nitrile was dissolved in 60 c.c. of 10% hydrochloric acid. Current density: 5 amp./dm.². Temperature: 10°. After one hour's electrolysis, the catholyte was treated as in the reduction of acetonitrile. 1.4 g. of tetramethylenediamine

hydrochloride was obtained, m.p. over 290° . Yield: 70%. Found: N, 17.27. Calcd. for $C_4H_{14}N_2Cl_2$: N, 17.33%.

(VI) **Reduction of adiponitrile.** The reduction was conducted under the same condition as in the reduction of succinonitrile. From 1 g. of the nitrile 0.7 g. (40%) of hexamethylenediamine hydrochloride was obtained, m.p. 246° . Found: N, 14.60. Calcd. for $C_6H_{18}N_2Cl_2$: 14.81%.

(VII) **Reduction of ethylenecyanohydrin.** Catholyte: 10 g. of ethylenecyanohydrin was dissolved in 90 c.c. of 7% hydrochloric acid. Current density: 4 amp./dm.². Temperature: ca. 10° . After nine hours' electrolysis, the catholyte was evaporated under reduced pressure and the residue was dissolved in absolute alcohol containing a little absolute ether. A small amount (0.9 g.) of ammonium chloride was filtered off and the filtrate was neutralized with alcoholic sodium hydroxide, filtered from sodium chloride and the solvent was distilled off. The residue was first distilled under reduced pressure. The fraction which distilled over at $105-110^{\circ}$ under 25 mm. was redistilled under ordinary pressure. 3 g. (30%) of γ -hydroxypropylamine was obtained. The boiling point was $185-189^{\circ}$.⁽⁶⁾ For the purpose of identification 1 g. of the hydroxyamine was dissolved in water, and shaken with 3 g. of phenylisocyanate. The reaction occurred instantly and white precipitate was produced. After ten minutes, the precipitate was collected and recrystallized at first from water, then from dilute alcohol, m.p. 140° . Found: N, 13.51. Calcd. for $C_6H_5NHCONHCH_2CH_2CH_2OCONHC_6H_5$: N, 13.41%.

(VIII) **Reduction of cyanoacetic acid.** Catholyte: 2 g. of cyanoacetic acid was dissolved in 60 c.c. of 10% hydrochloric acid. Current density: 2 amp./dm.². Temperature: $8-10^{\circ}$. After 3 hours, the catholyte was evaporated under reduced pressure, the residue was dissolved in a small amount of absolute alcohol, and ether was added. 1 g. of β -alanine hydrochloride (m.p. ca. 120°) was obtained. It was identified as a phenylisocyanate derivative as follows: 1 g. of the product was dissolved in sodium hydroxide solution (0.7 g. NaOH) and shaken with 1 g. of phenylisocyanate. White precipitate which was instantly produced was collected and recrystallized from hot water, m.p. 171° . Analysis shows that this is the known γ -ureidopropionic acid⁽⁷⁾. Found: N, 13.55. Calcd. for $C_{10}H_{12}O_3N_2$: N, 13.46%.

In connection with this research the author expresses his sincere thanks to Dr. T. Hoshino for his kind guidance and also to Mr. H. Kawasumi for analysis and to Mr. C. Koyama for his collaboration in this research.

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(6) According to Henry, *Ber.*, **33**(1900), 3169 the boiling point of γ -hydroxypropylamine is $187-188^{\circ}/756$ mm.

(7) Hoogewerff and Van Dorp, *Rec. trav. chim.*, **9**(1890), 60.

On the Radon Content of the Mineral Springs of Masutomi.

By Kazuo KURODA and Masaki NAKANISHI.

(Received November 10, 1942.)

In the previous papers,⁽¹⁾⁽²⁾ S. Oana and one of the present authors (K. Kuroda) reported the radon content of the mineral springs of Masutomi, Yamanashi Prefecture. In those papers they reported that the springs belonging to the group A contained a large amount of radium, but their radon content was always very low.⁽³⁾ The present authors, however, measured recently the radon content of the springs of group A, and found a number of springs containing an exceedingly large amount of radon.

There are several springs on the river Hontani (A6, A7, A8, A9, etc.). The springs issue from the granite and produce a splendid sinter in which, according to G. Schwabe,⁽⁴⁾ various organisms are found, and supposed to be deposited by the biological reactions. The author (Kuroda) measured the radon content of the spring A6 in May, 1942 and found that its radon content was 600×10^{-10} Curie per litre. The springs A7 and A8 were observed by G. Schwabe and found to be very interesting biologically. The author, however, did not measure their radon content, and determined only the temperature, pH, HCO_3' and CO_2 contents of the spring water.

The radon content of the springs A8 and A9 was measured on 1 November, 1942, a rainy day, and it was found that the radon content of both springs was larger than 1000 Mache. As it was rainy on that day, and moreover, there was a small spring quite near to the spring A9 which flows into this spring, it was supposed that the radon content of the springs A8 and A9 would be really larger than the value obtained at that time. We measured then the radon content of A92, a small spring flowing into the spring A9, and found that its radon content was about 663 Mache, considerably smaller than the radon content of A9 measured on the previous day.

The radon content of the spring A9 was therefore expected to be far larger than 1000 Mache, so we measured on the next day the radon content of the spring water of A9, which was not mixed by the water of A92.

A 10 c.c. portion of the spring water was diluted with distilled water to 500 c.c. and the radioactivity was measured by I. M. fontactoscope. The constant of the fontactoscope was 0.585 Mache radon per div. per

(1) S. Oana and K. Kuroda, this Bulletin, 15(1940), 485.

(2) S. Oana and K. Kuroda, this Bulletin, 17(1942), 397.

(3) S. Oana and K. Kuroda, this Bulletin, 17(1942), 414-415.

(4) The results of biological observations will be published shortly after in the „Mitteilungen der Deutschen Gesellschaft für Natur- und Völkerkunde Ostasiens“, together with our geochemical observations.

min. or 2.129×10^{-10} Curie radon per div. per min. The velocity of the foil of the fontactoscope was about 50 div. per min.

The radon content of this spring was found to be 1930 Mache or 7030×10^{-10} Curie per litre. This is the highest value ever observed in this country, and the fourth in the world.⁽⁵⁾

On the following day the radon content of this spring water was measured once more, and was found that its radon content diminished down to 1490 Mache. It is quite interesting to ascertain the phenomenon that such a large variation of the radioactivity of the spring water was caused by the effect of the rain. The experiments on such a phenomenon are now planned and the results will be reported later. The radon content of all the newly found springs of A group is very high.

The authors express their hearty thanks to Prof. Kenjiro Kimura for his kind guidance in the course of this study. The cost of this research has been defrayed from the Scientific Research Encouragement Grant from the Department of Education, to which the authors' thanks are due.

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(5) George Hevesy and F. A. Paneth, "A Manual of Radioactivity," London, (1938), 227.

Über die Oxydation von Camphen mit Bleitetraacetat.

Von Morizo ISHIDATE, Noboru INOUE und Hiroyuki FUKUSHIMA.

(Eingegangen am 23. September 1942.)

Vor kurzem haben Hückel und Hartmann⁽¹⁾ bei der Oxydation von Camphen mit Bleitetraacetat eine Carbonylverbindung als Enolacetat isoliert, welche sie ohne weiteres für Camphenilanaldehyd (VIII) hielten. Unabhängig von der Mitteilung haben wir uns gelegentlich mit derselben Untersuchung beschäftigt und den anderen Schluss erhalten.

Die Carbonylverbindung bzw. ihr Enolacetat, welche das Hauptprodukt der Oxydation darstellt, ist von keiner Aldehydnatur. Ihr Semicarbazon (Schmp. 223°) stimmt nicht mit dem bekannten Camphenilanaldehydsemicarbazon⁽²⁾ sowohl beim Mischproben als auch beim Vergleichen von den Röntgenaufnahmen überein. Beim Oxydation mit Permanganat liefert die Substanz keine Monocarbonsäure, sondern eine einzige zwei-basische Säure, die sich in aller Hinsicht mit Camphencamphersäure (IV) als identisch erweisen lässt. Hieraus folgt, dass die Carbonylverbindung ein ringerweitertes Keton d. h. ein Homocamphenilon, dem entweder die Formel III oder III' beigelegt wird, sein muss. Ein Homocamphenilon ist schon von Lipp und sein Mitarbeitern⁽³⁾ durch Alkalischemelz des ω -Bromcamphens erkannt worden. Die angegebene Konstanten der Derivate (Semicarbazon, Oxim und Bromderivat) sind aber von denen von unserem Homocamphenilon aus Camphen weit abweichend, obwohl das Ausgangsmaterial ebenfalls fast inaktiv war. Um die mögliche stereochemische Verwirrung auszuschliessen, haben wir das Keton aus vollkommen inaktivem ω -Bromcamphen hergestellt und unmittelbar zur Vergleichung gestellt, so dass die beide Ketone völlig identisch waren. Beim Kalischemelz des ω -Bromcamphens wurde neben dem genannten Keton, abgesehen von sogenanntem Dicamphenyläther, eine kleine Menge Aldehyd isoliert, der sich nach dem Mischproben und der Röntgenaufnahme seines Semicarbazons nicht anders als Camphenilanaldehyd erweisen lies. Also war Lippsche Homocamphenilon (Semicarbazon 210–212°) noch nicht ganz rein gewesen.

Aus der Tatsache, dass das Homocamphenilon durch Natriumamid keine Spaltung erleidet, haben Lipp und sein Schülern ihm die Formel VI wahrscheinlicher gemacht, denn wenn es die andere Formel VI' hätte, sollte diese Reaktion analog mit Fenchon und Camphenilon positiv verlaufen. Wir haben nun eine Versuche gemacht, ob das Homocamphenilonoxim ähnlich wie beim Campheroxim durch Schwefelsäure unter Ringsprung zwischen C₁ und C₂ eine ungesättigte Nitril bildet oder nicht, was aber nur vergebens war. Dabei wurde das ursprüngliche Keton regeneriert. Hiermit muss man annehmen, dass das erweiterte Ringketon viel

(1) *Ber.*, **70**(1937), 959.

(2) Siehe unten.

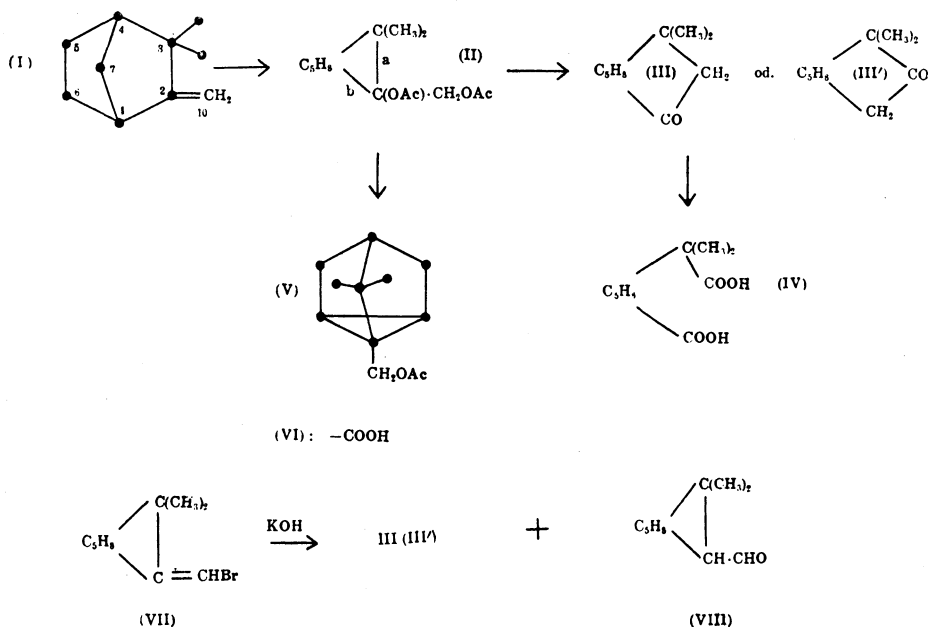
(3) *Ann.*, **453**(1927), 1; *J. prakt. Chem.*, **105**(1932), 63.

beständiger als Campher- oder Camphenilonskelette ist, folglich jene Reaktionen bei den Ringhomologen nicht immer in derselben Weise verlaufen können. Die Stellung des Carbonyls also bleibt noch unbestimmt.

Aus dem Verseifungsprodukt des Oxydationsgemisches wird neben dem Homocamphenilon eine kleine Menge von Nicht-Carbonylverbindung isoliert. Bei der Permanganatoxydation der letzteren erhält man eine Monocarbonsäure von Schmp. 151° . Die Säure wurde durch den direkten Vergleich mit dem bekannten α -Tricyclensäure (VI) als identisch festgestellt. Es besteht also kein Zweifel, dass die Säure aus α -Tricyclenalkohol im Oxydationsprodukte des Camphens herstammte.

Betrachtet von der Reaktionsmechanismus des Bleitetraacetats gegen Camphen, würde zuerst als Zwischenprodukt Camphenglykoldiacetat (II) gebildet. Erleidet der letztere eine Deacethylierung zwischen C_2 und C_6 , so entsteht der Tricyclenalkohol (V) bzw. dessen Acetat, während wenn die Deacethylierung zwischen C_2 und C_{10} verläufe, so die Bildung des Camphenilanaldehyds bzw. seines Enolacetats erwartet wird, was aber nicht der Fall. Viel günstiger dabei scheint eine Umlagerung unter Bildung von ringerweitertem Keton stattzufinden, wobei das Keton vorherrschend als Enolacetat vorhanden ist. Das daraus regenerierte Keton ist aber nicht mehr fähig, durch die übliche Acethylierung wieder zum Acetat umzuwandeln.

Weder Camphenilanaldehyd bzw. sein Enolacetat noch Camphenoxyd bei der Behandlung mit Kalilauge oder Acetanhydrid Homocamphenilon ergibt, so ist zur Bildung des letzteren der Camphenglykol bzw. dessen Diacetat als eine einzige wichtige Zwischenstufe betrachtet zu werden, wahrscheinlich auch bei der Reaktion des Kalischmelz des ω -Bromcamphens. Der Vorgang, aus dem Glykol das erweiterten Ringketon zu bilden, ist nur dadurch erklärlich, dass die endständige primäre Hydroxylgruppe ablöst und gleichzeitig die Bindung a (zwischen C_2 und C_3) bzw. b.



(zwischen C_2 und C_1) aufspringt und eine Semipinakolinumlagerung stattfindet. Es ist sehr merkwürdig, dass dabei die primäre Hydroxygruppe zur Umlagerung Anlass gibt.

Schliesslich sei es nochmals betont, dass der von Hückel und Hartmann angegebene Isocamphanol und seine Abkömmlingen ohne weiteres durch den Homocamphenilol und die betreffenden Derivaten ersetzt werden müssen.

Beschreibung der Versuche.

Camphen. Das als Ausgangsmaterial verwendete Camphen wurde aus *l*-Borneol über das Bornylchlorid und durch den folgenden Behandeln mit Anilin hergestellt, das optisch vollkommen inaktiv ist.

Oxydation von Camphen mit Bleitetraacetat. Eine Lösung von 40 g Camphen in 150 ccm Eisessig wurde mit 130 g Bleitetraacetat 10 Stdn. bei 70–80° unter Rühren erwärmt. Das Reaktionsprodukt wurde durch Vakuumdestillation von Eisessig befreit und mit Aether versetzt. Die ätherische Lösung wurde nach gründlichen Auswaschen mit Sodalösung getrocknet und im Vakuum fraktioniert. Die Hauptfraktion (35 g) geht unter 10 mm bei 95–120° über. Das ölige Destillat ergibt bei Einwirkung von Semicarbazid teilweise ein krystallinisches Semicarbazon (A). Nach vollständiger Abscheidung des Semicarbazon (10 g) wurde das Filtrat mit 10%iger methanolischer Kalilauge verseift, ausgeäthert und destilliert. Die hier erhaltene neutrale ölige Substanz wurde nochmal in der verdünnten alkoholischen Lösung mit Semicarbazid versetzt, so erhält man 20 g Semicarbazon (B). Die von Semicarbazon beseitigte Filtrat wurde mit Aether extrahiert. Der Aetherauszug wurde nach Waschen mit Sodalösung getrocknet und destilliert. Das gegen Carbonylreagenz indifferente Anteil ($Kp_{10} 90-95^\circ$) erwägt sich 1–2 g (Fraktion C).

Homocamphenilonsemicarbazon. Das erstere (A) und das letztere (B) Semicarbazon sind dieselbe Substanz von Schmp. 223° (aus Methanol), und lassen sich sowohl beim Vergleichen von den Röntgenaufnahmen, wie auch durch der Mischproben mit dem des racemischen Homocamphenilons als identisch erweisen, welches aus rac.- ω -Bromcamphen nach Lippschen Methode hergestellt wurde. Gefunden: N, 20.12. Berechnet für $C_{11}H_{19}ON_3$: N, 20.08%.

rac.-Homocamphenilon. Dargestellt durch Verseifen des Semicarbazon. $Kp_{10} 91^\circ$. Es löst sich nicht in Sulfitlösung und ist gegen Permanganatlösung indifferent. Gefunden: C, 78.83; H, 10.25. Berechnet für $C_{10}H_{16}O$: C, 78.94; H, 10.52%.

rac.-Camphencamphersäure. 2 g Homocamphenilon wurden in 5 % Kalilauge suspendiert und mit 60 ccm von 3 % Permanganatlösung oxydiert. Nach Durchwaschen des verbleibenden Ketons wurde die angesäuerte Lösung mit Aether extrahiert. Beim Abdampfen des Aethers bleibt ein krystallinischer Rückstand, der beim Umlösen aus Wasser ein farbloses Pulver von Schmp. 133.5° bildet. Gefunden: C, 59.70; H, 8.23; $(COOH)_2$, 44.33. Berechnet für $C_{10}H_{16}O_4$: C, 60.00; H, 8.50; $(COOH)_2$, 45.00%.

rac.-Monobrom-homocamphenilon. Dargestellt mit überschüssigem Brom in der Tetrachlorkohlenstofflösung. Lange Prismen vom Schmp.

71° aus Methanol. Gefunden: Br, 36.67. Berechnet für $C_{10}H_{15}Br$: Br, 34.60%.

rac.-Homocamphenilonoxim. Dargestellt mit Hydroxylamin in der alkoholisch-alkalischen Lösung. Blättchen vom Schmp. 75.5° aus Methanol. Gefunden: N, 8.58. Berechnet für $C_{10}H_{17}ON$: N, 8.49%.

3 g des Oxims wurden in 25% Schwefelsäure 1/4 Std. gekocht, und das Reaktionsprodukt mit Aether extrahiert und fraktioniert. Das Hauptdestillat (Kp.₁₂ 101°) wurde mit Homocamphenilon identisch nachgewiesen, während eine kleine Menge von stickstoffhaltigen Substanz (N, 7.34%) isoliert wurde, die aber beim langen Kochen mit 30% Kalilauge keine nennenswerte Säure ergab.

α-Tricyclensäure. Die Fraktion C wurde in einer kleinen Menge Aceton gelöst und mit der berechneten Menge Permanganatlösung (3%) in der Kälte oxydiert. Nach Waschen mit Aether wurde die Lösung dann angesäuert und mit Aether extrahiert. Beim Abdampfen des Aether erhält man eine Säure, die sich beim Umlösen aus Methanol als ein prismatischer Kristall von Schmp. 151° darstellt. Die Säure liess sich durch den Mischproben mit der bekannten α-Tricyclensäure als identisch erweisen. Gefunden: C, 73.68; H, 8.44. Berechnet für $C_{10}H_{14}O_2$: C, 72.24; H, 8.49%.

Kalischmelzen des rac.-ω-Bromcamphens. 15 g rac.-ω-Bromcamphen wurden nach Lipp und seinen Mitarbeitern mit 18 g Kaliumhydroxyd verschmelzt. Das Reaktionsprodukt wurde mit Wasserdampf destilliert und das Destillat mit Aether extrahiert. Der Aetherrückstand ergab beim Versetzen mit Semicarbazid etwa 4 g Semicarbazon vom Schmp. 221°. Dieses zeigte beim Mischschmelzen mit dem oben erhaltenen Homocamphenilonsemicarbazon (223°) eine deutliche Depression (bei 216°). Dann wurde das Semicarbazon mit Hilfe von heissem Aceton in zwei Teile getrennt. Der in Aceton schwerer lösliche Teil schmolz bei 223° und war mit dem des Homocamphenilons vollkommen identisch. Das in Aceton leichter lösliche Teil, umgelöst aus Alkohol, schmolz bei 196°, das mit Camphenilanaldehydsemicarbazon (s.u.) als identisch nachgewiesen wurde.

Verhalten des Camphenoxyds und des Camphenilanaldehyds gegen Säure und Alkali. Camphenoxyd wurde durch Oxydation von rac.Camphen mit Benzopersäure nach Pummer und Reindel dargestellt. Beim Erwärmen mit alkoholischem Alkali oder Eisessig geht das Camphenoxyd quantitativ zu Camphenilanaldehyd über, der als Semicarbazon (Schmp. 196°) und Camphenilansäure leicht charakterisiert wurde. Das Aldehyd liess sich andererseits mit der nach Bredt durch Einwirkung von Chromylchlorid auf Camphen erhaltenen Substanz als identisch erweisen. Sein Enolacetat wurde leicht durch das Erhitzen des Aldehyds mit Acetanhydrid und Natriumacetat erhalten. Dieser Enolacetat ging beim Kochen mit alkoholischer Kalilauge wieder zum betreffenden Aldehyd über, wobei keine Bildung von Homocamphenilon beobachtet wurde. Das Semicarbazon des Camphenilanaldehyds ist leichter löslich in Aceton, Essigester und Alkoholen als das Homocamphenilonsemicarbazon, was zur Trennung der beiden Komponenten gute Dienste leistet.

Untersuchungen über Flechtenstoffe. C. Mitteilung: Über Rangiformsäure (I).

Von Yasuhiko ASAHINA und Toyosaku SASAKI.

(Eingegangen am 29. September 1942.)

Hesse⁽¹⁾ hatte aus einem Exemplar von *Cladonia sylvatica* *d*-Usninsäure und eine nicht näher untersuchte Säure (Sylvatsäure) aber keine Fumarprotocetrarsäure isoliert. Da eigentliche *Cladonia sylvatica* Träger der bitterschmeckenden Fumarprotocetrarsäure ist, so müsste sein Material morphologisch der *Cl. sylvatica* fast übereinstimmende, aber nicht bitterschmeckende *Cl. mitis* gewesen sein. Später hatte Hesse auf Suche nach der sog. Sylvatsäure dieselbe Flechte wiederholt untersucht, konnte er aber jene Säure nicht mehr in genügender Menge fassen.⁽²⁾

Nach Hesse schmilzt die Sylvatsäure bei 100°, besitzt die Zusammensetzung $C_{21}H_{38}O_7$ und spaltet beim Kochen mit Jodwasserstoffsäure ein Methoxyl und geht in Norsylvatsäure (Schmp. 109°) über.

Bei der Extraktion von *Cladonia mitis* aus Japan haben wir nun darin ca 1% *d*-Usninsäure und eine Säure der Fett-Reihe (Roh-Ausbeute ca 0.27%) gefunden. Die letztere schmilzt bei 106°, ist rechtsdrehend und indifferent gegen Eisenchlorid, sowie Chlorkalk. Die Zusammensetzung der Säure entspricht $C_{21}H_{38}O_6$; sie besitzt ein Methoxyl, welches auch durch Alkali verseift wird. Dieses Verseifungsprodukt ist eine gesättigte Tricarbonsäure $C_{20}H_{36}O_6$ vom Schmp. 118°. All diese Eigenschaften stimmen mit denen der Rangiformsäure bzw. deren Verseifungsproduktes Norrangiformsäure⁽³⁾ gut überein.

Hieraus ist zu schliessen, dass die sog. Sylvatsäure von Hesse auch Rangiformsäure gewesen war. Die niedrigeren Schmelzpunkte der Sylvatsäure, sowie Norsylvatsäure sind wohl durch den Wassergehalt bedingt, was auch aus ihren Analysen-Werten ersichtlich ist.

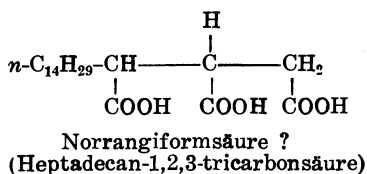
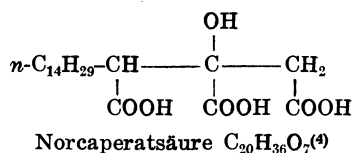
Je nach den Exemplaren schwankt jedoch die Ausbeute an Rangiformsäure sehr erheblich. Bei einigen konnten wir sogar nichts davon finden. Also ist es begreiflich, dass Hesse bei der späteren Untersuchungen keine nennenswerte Menge Sylvatsäure in Händen hatte, weil er gerade mit rangiformsäurefreien Sorten gearbeitet hätte.

Da alle bisher strukturell aufgeklärte Flechtenfettsäuren mit einander in genetischer Zusammenhang stehen, so schreiben wir vorläufig für Norrangiformsäure die Konstitution der Desoxy-Norcapersäure zu:

(1) *J. prakt. Chem.*, **76**(1907), 29.

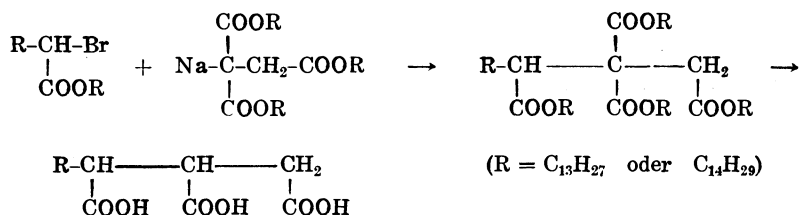
(2) Sandstedt, *Abh. Naturwiss. Verein Bremen XXV*, S. 106–107 (1922).

(3) Paterno, *Gazz. chim. ital.*, **1882**, 259; *Ber.*, **15**(1882), 2242; Hesse, *J. prakt. Chem.*, **57**, 275–280.



Hesse hatte für Rangiformsäure eine um H_2 weniger Formel gegeben. Da diese Säure gesättigt ist, so müsste dann eine monocyclische Verbindung sein, was man noch zu bestätigen hat.

Ferner haben wir nach der allgemeinen Methode der Tricarballylsäure-Synthese sowohl Hexadecan-1,2,3- als auch Heptadecan-1,2,3-tricarbonsäure dargestellt, von denen sich die letztere als nicht identisch mit der Norrangiformsäure, sondern als ein Isomer davon erwies. Dadurch ist aber die oben aufgestellte Konstitution der Norrangiformsäure ohne weiteres in Abrede zu Stellen. Abgesehen von optischer Inaktivität des synthetischen Produktes, treten hierbei verschiedene stereoisomere Verbindungen auf, deren Orientierung uns noch nicht gelingt.



Beschreibung der Versuche.

Extraktion von *Cladonia mitis* Sandst. 300 g Flechten-Thalli werden mit Aether erschöpfend extrahiert und der Extrakt eingengt, wobei sich die Usninsäure grösstenteils ausscheidet. Das Filtrat wird dann mit 3%iger Sodalösung geschüttelt, die letztere angesäuert und der dabei entstandene Niederschlag in Aether (A) aufgenommen. Beim Verdampfen des mit Sodalösung entsäuerten Aether blieb ein neutrales, Liebermannsche Reaktion gebendes Produkt zurück, welches wir nicht weiter verfolgten.

Usninsäure. Die Roh-Ausbeute der Usninsäure betrug 3 g (1%). Beim Lösen in Chloroform und Fällen durch Alkohol-Zusatz bildet sie gelbe Nadeln vom Schmp. 200° . 28 mg Subst. gelöst in Chloroform zu 3 ccm, $\alpha_D^{25} = +4.74^\circ$ (1 dm, 22°). Mithin $[\alpha]_D^{25} = +506^\circ$.

Rangiformsäure. Beim Verdampfen der ätherischen Lösung (A) bleibt einen Rückstand zurück, den man in wenig kaltem Alkohol löst, filtriert, entfärbt unter Kohle-Zusatz in der Wärme und verdampft (Rückstand 0.7 g). Bei wiederholtem Umlösen aus heissem Benzol bildet die Substanz farblose, feine Nadeln vom Schmp. 106° . Sie ist leicht löslich in Alkohol und Aether in der Kälte und in Benzol und Chloroform in der Wärme. Auch in heissem Petroläther ist sie ziemlich löslich. Die

(4) Asano und Ohta, *Ber.*, **66**(1933), 1020; *Ber.*, **67**(1934), 1842.

alkoholische Lösung färbt sich weder mit Eisenchlorid noch mit Chlorkalk. 0.0315 g Sbst. gelöst in Alkohol zu 1.5 ccm, $\alpha = +0.34^\circ$ (1 dm, 24°). Mithin $[\alpha]_D^{24} = +16.2^\circ$. 4.495 mg Sbst.: 10.750 mg CO_2 , 4.081 mg H_2O . 3.730 mg Sbst.: 8.968 mg CO_2 , 3.230 mg H_2O . 42.65 mg Sbst.: 25.3 mg AgJ (nach Zeisel). 56.8 mg Sbst.: 2.98 ccm 0.1 N-NaOH (Phenolphthalein). Gefunden: C, 65.22, 65.53; H, 10.16, 9.69; CH_3O , 7.83; Mol. Gew. 380.9 (als zweibasisch). Berechnet für $\text{C}_{21}\text{H}_{38}\text{O}_6$: C, 65.24; H, 9.91; CH_3O , 8.03%; Mol. Gew. 386.3.

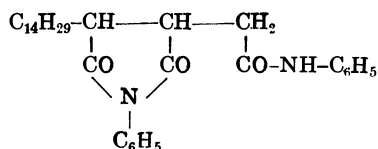
Verseifungszahl. 64.1 mg Sbst. verbrauchten in der Wärme 5.01 ccm 0.1 N-NaOH, woraus sich das Mol. Gew. (als Tricarbonsäure) 383.80 berechnen lässt.

Dimethylester. Dargestellt durch Einwirkung von Diazomethan in Aether. Farblose Nadeln vom Schmp. 46.5° (aus Methanol). 44.5 mg Sbst. gelöst in Alkohol zu 1.5 ccm, $\alpha_D = +0.28^\circ$ (1 dm, 22°). Mithin $[\alpha]_D^{22} = +9.4^\circ$. Gefunden: C, 66.96; H, 10.21; CH_3O , 22.25. Berechnet für $\text{C}_{23}\text{H}_{42}\text{O}_6$: C, 66.63; H, 10.22; $(\text{CH}_3\text{O})_2$, 22.46%.

Norrangiformsäure. Man verseift die Rangiformsäure mittels Natronlauge auf dem Wasserbade, dann säuert an und extrahiert mit Aether. Beim Umlösen des Verseifungsproduktes aus Eisessig bildet es farblose, winzige Kriställchen vom Schmp. 118° (schon gegen 100° etwas zusammensinternd). In Aether, Alkohol und Chloroform ist sie leicht löslich. 42.95 mg Sbst., gelöst in Alkohol zu 1.5 ccm, $\alpha_D = +0.37^\circ$ (1 dm, 18°). Mithin $[\alpha]_D^{18} = +12.9^\circ$. 3.727 mg bei $85-90^\circ$ getrocknete Sbst.: 8.810 mg CO_2 , 3.237 mg H_2O . Gefunden: C, 64.47; H, 9.75. Berechnet für $\text{C}_{20}\text{H}_{36}\text{O}_6$: C, 64.47; H, 9.72%.

Dianilid-anhydrid. Man erhitzt 0.3 g Rangiformsäure-dimethylester und 0.25 g Anilin in einem zugeschmolzenen Rohr 3 Stunden auf 200° , nimmt das Produkt in Aether. Nach Verjagen des Aethers wird der Ueberschuss Anilin im Vakuum entfernt. Die so verbleibende Substanz bildet beim Umlösen aus Petroläther farblose Nadeln die gegen 121° unscharf schmelzen. Sie sind in Aether, Alkohol und Benzol leicht löslich. In Alkalilauge unlöslich. Gefunden: C, 76.53; H, 8.59; N, 5.66. Berechnet für $\text{C}_{32}\text{H}_{44}\text{N}_2\text{O}_3$: C, 76.14; H, 8.79; N, 5.75%.

Wohl kommt dem Anilid die Konstitution zu:



Synthese der Hexadecan-1,2,3-tricarbonsäure.

Hexadecan-1,2,2,3-tetracarbonsäure-tetraäthylester. Man löst 0.7 g Natrium in 15 ccm abs. Alkohol, löst darin 7.1 g Aethenyltricarbonsäure-triäthylester⁽⁵⁾, setzt dann zur auf 80° erwärmten Lösung 10 g α -Brompentadecansäure hinzu und kocht das Gemisch 12 Stunden im Dampfbade, wobei sich das umgesetzte Bromnatrium teilweise ausscheidet. Die vom

(5) Bischoff, *Ann.*, **214**(1882), 38.

ausgeschiedenen Salz befreite, alkoholische Lösung wird stark eingengt und der Rückstand mit wenig Wasser umgerührt und ausgeäthert. Nach Verjagen des Aethers wird der ölige Rückstand zunächst zum Wegschaffen der zurückbleibenden Ausgangsmaterialien unter vermindertem Druck destilliert und dann der hoch siedende Anteil im Hochvakuum destilliert, wobei die Fraktion: Sdp. 0.03 209–210° besonders gesammelt wird. Ausb. 6.7 g. Gefunden: C, 64.62; H, 9.76. Berechnet für $C_{28}H_{50}O_8$: C, 65.32; H, 9.80%.

Hexadecan-1,2,3-tricarbonsäure. Man kocht 4 g oben erhaltenen Tetraäthylesters in 50 ccm Jodwasserstoffsäure ($d=1.7$) bis das Jodäthyl nicht mehr überdestilliert, was man sich durch Eintauchen der zurückgebogenen Spitze des Kühlrohrs im Wasser leicht überzeugt. Am Ende der Reaktion schäumt der Kolbeninhalt sehr stark, sodass man ein ziemlich geräumiges Gefäß anzuwenden hat. Beim Erkalten bildet sich das Verseifungsprodukt an der Oberfläche eine Kristallschicht. Aus Eisessig umgelöst bildet das Produkt farblose, feine Prismen, die erst nach Trocknen bei 105° einen Schmp. 135.5–136.5° aufweist. Es ist in Alkohol und Aether leicht löslich. Gefunden: C, 63.97; H, 9.49; Mol. 363.3 (als 3-basisch). Berechnet für $C_{19}H_{34}O_6$: C, 63.64; H, 9.56%; Mol. Gew. 358.3.

Der Trimethylester wird dargestellt durch Einwirkung von Diazomethan auf die Tricarbonsäure. Er bildet farblose Kristalle vom Schmp. 37° (aus Methanol), ist leicht löslich in meisten Solventien. Gefunden: C, 66.21; H, 9.73. Berechnet für $C_{22}H_{40}O_6$: C, 65.94; H, 10.07%.

Synthese der Heptadecan-1,2,3-tricarbonsäure.

Heptadecan-1,2,3-tetracarbonsäure-tetraäthylester: Man löst 1.2 g Natrium in 25 ccm abs. Alkohol, fügt dazu 12.8 g Aethenyl-tricarbonsäure-triäthylester und 19 g α -Brompalmitinsäure-äthylester nach einander und verfährt weiter genau so wie bei der Darstellung des Hexadecan-tetracarbonsäure-tetraäthylesters.

Das Kupplungsprodukt siedet unter 0.04 mm Druck zwischen 215–217°. Ausbeute ca 10 g. Gefunden: C, 65.97; H, 10.04. Berechnet für $C_{29}H_{52}O_8$: C, 65.86; H, 9.92%.

Heptadecan-1,2,3-tricarbonsäure. Man erhitzt 5 g Tetraäthylester in 90 ccm Jodwasserstoff ($d=1.7$) eventuell unter Zusatz von 5 ccm Essigsäureanhydrid und verfährt genau so wie bei der Darstellung der Hexadecan-1,2,3-tricarbonsäure. Das Verseifungsprodukt bildet farblose Kristalle vom Schmp. 142.5° (aus Eisessig). Gefunden: C, 64.18; H, 9.81; Mol. Gew. 379.5 (als dreibasisch). Berechnet für $C_{20}H_{36}O_6$: C, 64.47; H, 9.74%; Mol. Gew. 372.3.

Der Trimethylester wird dargestellt durch Einwirkung von Diazomethan auf die Tricarbonsäure. Er bildet farblose Kristalle vom Schmp. 45° (aus Methanol). Leicht löslich in meisten Solventien. Gefunden: C, 66.26; H, 9.94. Berechnet für $C_{23}H_{42}O_6$: C, 66.61; H, 10.21%.

Lead Content of the Calcareous Sinters.

By Kazuo KURODA.

(Received October 15, 1942.)

The calcium carbonate precipitated from hot-springs carries down a great variety of impurities characteristic to each hot-spring. In the calcareous deposits from the springs of Vichy, for example, J. Bouquet⁽¹⁾ found the presence of arsenic. W. P. Headden⁽²⁾ reported that tufa from the Doughty springs, in Colorado, probably contained traces of radium. The radium content of a number of sinter deposits from radioactive mineral springs in Japan was recently estimated by T. Nakai,⁽³⁾ and the thorium content of sinter from Masutomi by K. Shimokata.⁽⁴⁾ Hokutolite, found from the hot springs of Hokuto in Formosa for the first time, consists of barium and lead sulphate and is strongly radioactive. In the calcareous sinters, however, lead is rarely detected. E. Minami and K. Hirabayashi⁽⁵⁾ estimated the zinc content of sinters from a number of hot-springs in Japan by the polarographic method. These sinters contained a minute quantities of zinc (0.0000–0.0007%), but no samples contained a detectable amount of lead. The present author has studied the sinters from the hot-springs of Yunomata in the Japanese Northern Alps, which were collected and sent to us through the courtesy of Dr. S. Oana. The author was able to estimate the lead content by the polarographic method, though the presence of lead was not detected spectroscopically. (*)

The sinters were faintly rose coloured and was supposed to contain a considerable amount of manganese. One sample was gray coloured and Dr. Oana said that it contained iron sulphide. They dissolve quite readily in hydrochloric acid and have no visible insoluble residue.

5 g. of sample were dissolved in hydrochloric acid (distilled) and the solution was evaporated to dryness. The residue was carefully dissolved in water and the solution was made up to 10 c.c. A part of the solution was put in a small electrolysis vessel and then polarographically examined, using a 2-volts accumulator. The solution brought to the electrolysis vessel was yellow coloured and the current-voltage curve showed a large wave at the beginning (Fig. 1). Between the 5th and the 6th lines a fine "lead-wave" is seen. The height of this wave is about 5 mm. (sensitivity of the galvanometer=1/20) (Fig. 2). The height of

(1) J. Bouquet, *Ann. chim. phys.*, (3) **42**(1854), 332.

(2) W. P. Headden, *Proc. Colorado Sci. Soc.*, **8**(1905), 1.

(3) T. Nakai, this Bulletin, **15**(1940), 333.

(4) K. Simokata, *J. Chem. Soc. Japan*, **63**(1942), 1109.

(5) Not yet published.

(*) According to Prof. K. Kimura, less than 1 γ lead in 10 mg. sample can not be detected by usual spectroscopic method. As the lead content of this sinter is less than 0.01%, 10 mg. of sample contains less than 1 γ of lead. Therefore the presence of lead was not detected spectroscopically.



Fig. 1. Calcareous sinter from the hot springs of Yunomata.
Sensitivity of the galvanometer $1/5$.
2 volts accumulator.

Fig. 2. Calcareous sinter from the hot springs of Yunomata.
Sensitivity of the galvanometer $1/20$.
2 volts accumulator.

Fig. 3. Calcareous sinter from the hot springs of Yunomata.
A little lead nitrate solution was added.
Sensitivity of the galvanometer $1/20$.
2 volts accumulator.

Fig. 4. Pure calcium carbonate for analytical use.
Sensitivity of the galvanometer $1/5$.
2 volts accumulator.

the wave increased when a little lead nitrate solution was added (Fig. 3). The height of wave became 116 mm when 3.1 mg. of Pb was added. The lead content of this sinter is, therefore, considered to be 140 γ per 5 g., namely 0.0028%.

Pure calcium carbonate for analytical use was equally treated and polarographically examined. The presence of Zinc was detected and the amount was estimated to be about 0.0016%. Lead was, however, not detected in this sample. This experiment shows that the reagents which were used in this experiments did not contain lead.

As the radium content of the water and the calcareous sinter is not yet known, we can not discuss the relation between the content of lead and the radioactivity of the hot-spring in this paper. The radium content of this calcareous sinter will be reported shortly.

Summary.

The lead content of the calcareous sinter from the hot-springs of Yunomata in Northern Alps, Nagano Prefecture was estimated by the polarographic method.

The author expresses his hearty thanks to Prof. Kenjiro Kimura for his kind guidance and encouragement in the course of this study. It is also the author's pleasant duty to acknowledge the kind advice given by Prof. Eiiti Minami and Dr. Shinya Oana. The cost of this research has been defrayed from the Scientific Research Encouragement Grant from the the Department of Education, to which the author's thanks are due.

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Über die Mesomerie des Diazocamphers und deren Abbauprodukten: Die Bildung von 7-Oxoepifenchylalkohol.

Von Morizo ISHIDATE und Takashi ISSHIKI.

(Eingegangen am 31. Oktober 1942.)

3-Diazocampher ist rein isolierbar und verhältnismässig beständiger Körper. Durch dessen thermische Zersetzung isolierte zunächst Angelli⁽¹⁾ β -Pericyclocamphanon (sog. „Camphenon“) und daneben einen stickstoffhaltigen dimerisierten Körper Dicamphanonazin (sog. „Azocamphenon“). Später erhielten Bredt und Holz⁽²⁾ durch das Erhitzen unter Zusatz von Kupferbronz den ersteren mit guter Ausbeute. Eben nach unserer eigener Prüfung übertrifft es dabei an der Ausbeute nicht etwa 50%, und die andere Hälfte geht in Verharzen.

Merkwürdig ist die Tatsache, dass der Diazocampher sich bei einfacher Behandlung mit Eisessig unter fast quantitativer Stickstoffentwicklung stürmisch zersetzt. Das Reaktionsprodukt wird durch Destillation in drei Teilen getrennt. Die erste Fraktion ist als solches mit β -Pericyclocampanon identisch. Die dritte Fraktion, die verhältnismässig geringer ist, besteht hauptsächlich aus den Angellischen Dicamphanonazin von Schmp. 222°. Aus der mittleren Fraktion wird nach der Reinigung über den Semicarbazon ein stickstofffreier Körper von Schmp. 52° isoliert, dem die Zusammensetzung von $C_{10}H_{15}O \cdot OCOCH_3$ zukommt. Verseift man nun den Acetat mit Kalilauge, so wird kein definiertes Produkt isoliert, erst beim Erwärmen mit verdünnten Mineralsäuren wird das betreffende Oxyketon isoliert. Kocht man aber das Acetat-semicarbazon mit Salzsäure, so entsteht neben dem Oxyketon ein stickstoffhaltiger Körper, der einem Oxyketonsemicarbazon-dehydrat entspricht. Dieses Verhalten scheint darauf hinzuweisen, die Hydroxyl- und die Carbonylgruppe des Oxyketons einander in β -Stellung stehen. Das Oxyketon und die daraus durch Chromsäureoxydation erhaltene Diketoverbindung lassen sich mit keinem von den allen bekannten Oxycamphern bzw. Oxocamphern (3, 5 und 6-Oxycamphern bzw. den entsprechenden Oxo-Camphern) identifizieren. Hieraus kann man annehmen, dass das Oxyketon nicht mehr Camphan-skelett innehat, wohl aber unter der Ringisomerisation nach dem Schema IC-IV' eine Konstitution eines β -Oxyketons von Formel IV besitzen dürfte. Das neue Skelett ist als ein Epimer des Fenchan angesehen zu werden, so ist das Oxyketon als 7-Oxoepifenchylalkohol genannt zu werden. Durch dessen Wolffschen Reduktion wurde hier Epifenchylalkohol (VI), ferner durch die darauf folgende Oxydation Epifenchon erhalten.

Unter welchem Reaktionsmechanismus werden denn aus dem Diazocampher die erwähnten dreierlei Produkte abgeleitet?

(1) *Ber.*, **28**(1888), 819.

(2) *J. prakt. Chem.*, **101**(1917), 133.

Im Sinne der Elektronentheorie⁽³⁾ verdankt der Diazokörper seine treibende Kraft und die Beständigkeit der Ausbildung eines mesomeren Systems. Abgesehen von der Polarität des Carbonyls kommen als die hauptsächlichste Mesomerie des Diazocamphers die unter stehenden drei Grenzformeln (IA, IB, IC) in Absicht. Mit der Annahme dieser Mesomerieformeln dürfte der Bildungsvorgang der eben erhaltenen drei Abbauprodukten folgendermassen restlos erklärt werden.

1) Der Diazonium-Carbeniat⁽⁴⁾ IA besitzt in sich keine Oktettlücke, so ist er gegen anionische Substitution (z. B. CH_3COO^-) recht beständig. Dagegen ist das einsame Elektronenpaar des Carbeniats kann vermitteln, mit Proton oder mit dem Wasserstoff am C_5 koordinativ zu kuppeln. Also bei der Abspaltung von Stickstoff resultiert die Bildung von 3,5-Cyclocamphanon (II).

2) Der Ammonium-Azeniat IB erzeugt im Camphergerüste keine wesentliche Polarität, so kann keine Veränderung bzw. Substitution in dem Skelett auftreten. Das einsame Elektronenpaar des rechten N-Atoms vermag aber die Kupplung mit einer kationische Substituent zu vermitteln. Ist die Substituent dann der eine Oktettlücke besitzende Carbenium IC, so entsteht hierbei die symmetrische Dicamphanonazin (III); während wenn die Substituent der umgelagerte Carbenium von Typus IV' ist, so darf ein unsymmetrische Diketonazin entstehen. Auf dem Unterscheidung dieser beiden möglichen Isomerie kommen wir diesmal nicht eingehend.

3) Der Carbenium-Azeniat IC vermag an seiner Oktettlücke die Anionoid-Substituenten anzulagern. Die oben erwähnte Bildung von Dicamphanonazin stellt dafür ein Beispiel dar. Andererseits in Anwesenheit des Eisessigs ist hierbei eine Acetylierung auch möglich. Dabei addiert aber die Acetylanion nicht direkt an C_3 , sondern an der unter Ringisomerisation neu auftretenden Oktettlücke des C_4 -Atoms. Es resultiert also die Bildung des 7-Oxo-epifenchylacetats (IV). Die solche Ringisomerisation findet im Camphanskelette in der α -Stellung in Bezug auf C_2 -Atom oft statt, z. B. Isoborneol-Camphenhydrat-Umlagerung. Jetzt wird es gezeigt, dass dieselbe Umlagerung auch in der β -Stellung möglich ist.

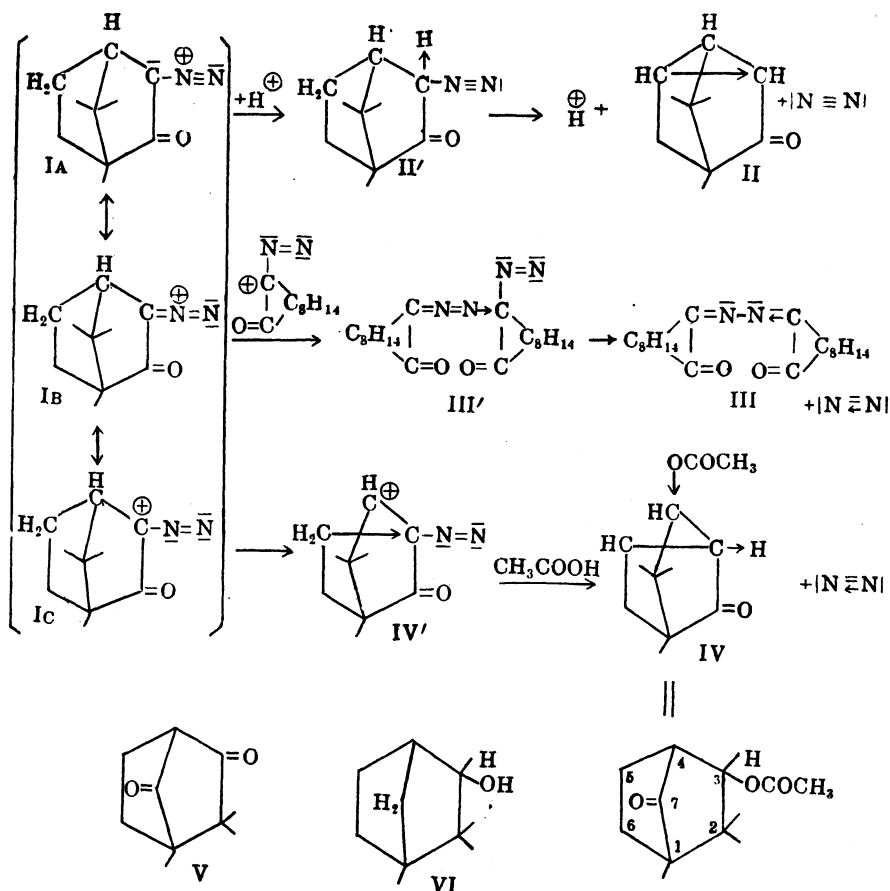
Dass die beiden Abbauprodukte, 7-Oxo-epifenchylacetat und Dicamphanonazin aus derselben Carbeniumform entstammen, wird auch aus der experimentelle Tatsache gestützt, dass die Ausbeute an den beiden Körpern je nach der Reaktionsbedingung relativ abwechselnd sind.

Zusammenfassung.

1. Durch Zersetzung des Diazocamphers mit Eisessig wurde ausser dem bekannten β -Pericylocamphanon und Dicamphanonazin eine neue Verbindung 7-Oxo-epifenchylacetat erhalten.

(3) Vergl. Eistert, *Ber.*, **86**(1936), 208; W. A. Noges und E. Meitzner, *J. Amer. Chem. Soc.*, **52**(1930), 5070.

(4) Die Nomenklatur ist nach der Vorstellung von B. Eistert, „Tautomerie und Mesomerie“, s. 27 Stuttgart (1938).



2. Die Ausbildung des theoretisch möglichen mesomeren Systems des Diazocamphers wurde tatsächlich aus deren Zersetzungsprodukten hingewiesen.

3. Oxy- und Oxo-derivate des neuen Skelettes „Epifenchan“ wurden dargestellt.

Beschreibung der Versuche.

Das Ausgangsmaterial Diazocampher wurde aus *d*-Campher nach der bekannten Methode über Campherchinon⁽⁵⁾ und dessen Monohydrat⁽⁶⁾ dargestellt. Aus 400 g wurden etwa 210 g reinen Diazocampher (Schmp. 74–5°) erhalten.

Zersetzung des Diazocamphers. 1 Teil Diazocampher wird in etwa 1.5 Teilen Eisessig portionsweise zugesetzt, wobei er unter der stürmischer Entwicklung von Stickstoffgas in Lösung geht. Nach einigen minutigen Erwärmen auf dem Wasserbade wird die Lösung mit Soda neutralisiert

(5) Evan, Ridgion und Simonsen, *J. Chem. Soc.*, 1934, 137.

(6) Bredt und Holz, *J. prakt. Chem.*, 95 (1917), 148.

und dann mit Aether extrahiert. Der Aetherauszug wird verdampft und das Rückstand in Vakuum in drei Teilen fraktioniert. Die erste Fraktion stellt farblose kristalle (β -Pericyclocamphanon), die zweite hellgelbe Flüssigkeit (7-Oxo-epifenchylacetat) und der dritte strohgelbe Kristalle dar.

Versuch 1:—Unter der heftigeren Reaktionsbedingung—12.517 g Diazocampher entwickelt bei 10°C, 1640 ccm N₂ (Ber N₂:1630 ccm), es entspricht 100.5% der Theorie. Die erste Fraktion erwiegt 4 g (Sdp₁₂ 98°), die zweite 4 g (Sdp_{9.5} 128–132°) und der dritte ganz wenig. Versuch 2:—Unter der milden Bedingung—23.2 g der Substanz: Gef. N₂ 2600 ccm (bei 10°C), d. h. 82.4% der Theorie. Die erste Fraktion wiegt 7.5 g (Sdp₄ 61–3°), die zweite, 6 g (Sdp₄ 108–110°), die dritte 5 g (Sdp₄ ca. 130°).

β -Pericyclocamphanon (II). Die erste Fraktion wird auf Tonplatte gepresst und aus Benzin umkristallisiert. Campherähnliche Kristalle von Schmp. 168°. Sein Semicarbazon schmilzt bei 243–4° (aus Alkohol).

Dicamphanonazin (III). Erhalten durch das Umlösen der dritten Fraktion aus Alkohol. Hellgelbe Blättchen von Schmp. 218° (Schmp. 222° nach Angeli). Gefunden: N, 8.81. Berechnet für C₂₀H₂₈O₂N₂: N, 8.54%.

7-Oxo-epifenchylacetat (IV). Er ist der Hauptbestandteil der zweiten Fraktion des Abbauprodukts des Diazocamphers. 4.240 mg Subst. (Sdp₄ 108–110°): 10.75 mg CO₂, 3.300 mg H₂O:—0.1129 g, 0.1874 g Subst. (Sdp_{9.5} 128° bzw. Sdp₄ 110–111°): verbr. 5.63 ccm bzw. 8.64 ccm 0.1 n-NaOH. Gefunden: C, 68.60; H, 8.60; CH₃CO, 21.47, 19.85. Berechnet für C₁₂H₁₈O₃: C, 69.15; H, 8.71; CH₃CO, 20.46%.

Die über sein Semicarbazon gereinigte und durch das folgende Verseifen mit Oxalsäure erhaltene reine Präparat stellt Kristalle vom Schmp. 50–2° (Sdp_{3.5} 101°) dar. Der Acetat ergibt aber beim Erwärmen mit Kalilauge kein definiertes Verseifungsprodukt.

7-Oxo-epifenchylacetat-semicarbazon. Dargestellt wie üblich. Farblose Nadeln von Schmp 224° (aus Alkohol). Gefunden: C, 58.67; H, 7.84; N, 15.70. Berechnet für C₁₃H₂₁O₃N₃: C, 58.40; H, 7.86; N, 15.73%.

7-Oxoepifenchylalkohol. 18 g von 7-Oxoepifenchylacetatsemicarbazon werden in 10%iger Salzsäurelösung 1/2 Stdn. zum Sieden erhitzt. Beim Erkalten und dem langen Stehen scheiden sich lange prismatische Kristalle (A) aus. Die von den Kristallen filtrierte Lösung wird mit Aether extrahiert. Beim Verdampfen des Aethers erhält man einen kristallinen Rückstand (6 g), der nach dem Umlösen aus Benzin bei 147° schmilzt. Er löst sich leicht in Wasser und es riecht campherähnlich. 0.131 g Subst. gelöst in abs. Alkohol zum 1 ccm, α =+1.13° (1 dm Rohr) $[\alpha]_D^{15}$ =+8.63°. Gefunden: C, 71.56; H, 9.34. Berechnet für C₁₀H₁₆O₂: C, 71.39; H, 9.59%. Beim Acetylierung mit Essigsäureanhydrid liefert der Alkohol wieder den ursprünglichen Acetat (Schmp. 50–2°, Sdp₁₂ 127°, und sein Semicarbazon: Schmp. 224–6°). So ist es klar, dass das Oxyketon durch Salzsäure keine Konstitutionsänderung erleidet.

3,5-Dinitrobenzoat. Dargestellt durch Erhitzen von 0.2 g 7-Oxo-epifenchylalkohol und 0.4 g 3,5-Dinitrobenzoylchlorid in 10 ccm Toluol unter Zusatz von einigen Tropfen Pyridin; lange Tafeln von Schmp.

120° (Mikromethode) aus Benzin. Gefunden: N, 7.68. Berechnet für $C_{17}H_{18}O_7N_2$; N, 7.74%.

7-Oxoepichylalkohol-semicarbazon. Schmp. 207–9° aus Aceton. Gefunden: N, 18.47. Berechnet für $C_{11}H_{19}O_2N_3$; N, 18.66%.

7-Oxo-epifenchylalkohol-semicarbazon-3-N-dehydrat. Scheidet sich beim Erhitzen des 7-Oxo-epifenchylalkoholsemicarbazon mit Salzsäure als prismatische Kristalle (Substanz A) ab. Nadeln aus Alkohol, Aceton oder Ligroin. Die Kristalle wandeln sich bei etwa 150° in Tafeln um und dann schmelzen bei 172–3°. Gefunden: C, 64.10; H, 8.04; N, 20.14. Berechnet für $C_{11}H_{17}ON_3$: C, 63.75; H, 8.27; N, 20.27%.

7-Oxo-epifenchon (V). 6 g 7-Oxo-epifenchylalkohol werden in 18 ccm Eisessig mit 4.2 g Natriumbichromat auf dem siedenden Wasserbade 1/2 Std. erhitzt. Dann wird die Lösung mit Soda neutralisiert und mit Aether extrahiert. Beim Abdampfen des Aethers erhält man eine Kristallmasse, die beim Umlösen aus Benzin bei 151° schmilzt. 0.470 g Subst.: gelöst in abs. Alkohol zum 5 ccm, $\alpha = +0.48^\circ$ (1-dm-Rohr, bei 17°); $[\alpha]_D^{17} = +5.11^\circ$.

7-Oxoepifenchon-disemicarbazon. Dargestellt wie üblich; das Rohprodukt wird mit Aether und Wasser ausgewaschen, und aus vielen Alkohol umkristallisiert, Pulvern von Schmp. 259° (u. Zer.). Gefunden: C, 51.47; H, 7.48; N, 29.86. Berechnet für $C_{12}H_{20}O_2N_6$: C, 51.42; H, 7.19; N, 29.97%.

Epifenchylalkohol (VI). 2 g 7-Oxo-epifenchylacetat-semicarbazon werden mit Natriumalkolat (2 g Na und 15 ccm abs. Alkohol) in Rohr 8 Stdn. bei 190° erhitzt. Dann wird das Produkt mit Essigsäure neutralisiert und mit Wasserdampf destilliert. Beim Extrahieren des Destillates mit Aether erhält man ein Oel von Sdp_{10.5} 104.5° (2.3 g aus 28 g Semicarbazon). Gefunden: C, 77.65; H, 11.92. Berechnet für $C_{10}H_{18}O$; C, 77.93; H, 11.69%.

Epifenchylalkohol-3,5-dinitrobenzoat. Dargestellt wie oben; ein gelbliches Blättchen von Schmp. 75° (unter Mikrobestimmung) nach Umlösen aus Benzin. Gefunden: N, 8.15. Berechnet für $C_{17}H_{20}O_6N_2$: N, 8.05%.

Epifenchon. Dargestellt durch die Oxydation des Epifenchylalkohols mit Bichromat in Eisessig auf dem siedenden Wasserbade. Die Oxydation ist beim Zimmertemperatur ganz träge. Farbloses Oel von Sdp₁₂ 93–4°. *Epifenchonsemicarbazon*: glänzendes Blättchen von Schmp. 209–210° (aus Alkohol). Gefunden: C, 63.21; H, 9.03; N, 19.96. Berechnet für $C_{11}H_{19}ON_3$: C, 63.12; H, 9.15; N, 20.07%.

Über die Polarität des C₇-Atoms in Camphermolekül.

Von Morizo ISHIDATE und Takashi ISSHIKI.

(Eingegangen am 31. Oktober 1942.)

In neuer Zeit haben Arndt und Eistert⁽¹⁾ in ihrem Studium über die Reaktion zwischen Diazomethan und Aldehyd darauf hingewiesen, dass ein Aldehyd, bei welchem das der Aldehydgruppe benachbarte C-Atom ein instabiles Oktett ($\delta+$) besitzt, bei der Einwirkung von Diazomethan vornehmlich ein Äthylenoxyd gibt; Aldehyd, bei welchem jenes C-Atom ein stabiles Oktett ($\delta-$) hat, mit Diazomethan hauptsächlich in das betreffende Methylketon übergeht. Diese Reaktion dürfte also das Mass der Polarität des mit der Aldehydruppe verbundenen C-Atoms zu schützen gestatten.

Mit dieser Annahme haben wir auf *trans*- π -Apocampher-7-aldehyd (*trans*- π -Oxocampher) (I) eine ätherische Diazomethanolösung unter Ausschluss von Alkoholen einwirken lassen. Dabei wurde einheitlich bloss das betreffende Methylketon (II) isoliert. Hieraus folgt, dass das C₇-Atom des Camphermoleküls ein stabiles Oktett besitzt, d. h. das Atom mehr oder weniger negativ polarisiert ist.

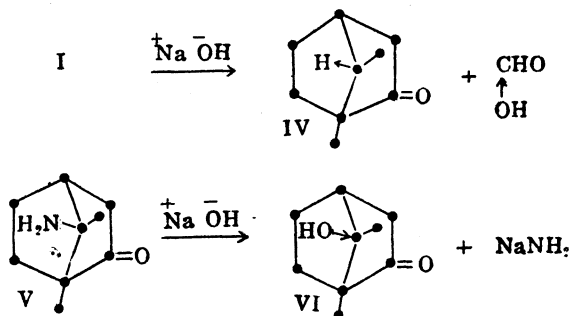
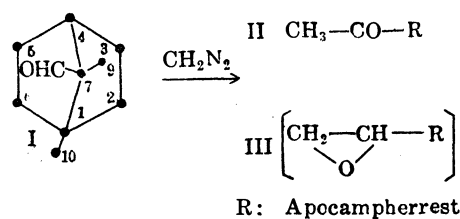
Induziert dieser Effekt über das C₁-Atom hinweg, so wird das Oktett des C₂-Atoms mehr oder weniger integriert ($\delta-$). Dieser induktive Effekt steht also dem Effekt des Schlüsselatoms O am C₂ entgegen. Diese Annahme stimmt mit der Erkenntnis überein, dass die Carbonylgruppe des Camphers überhaupt reaktionsträge ist. Dass sich die Bindungen zwischen C₇-Atom und C₄-Atom bzw. C₁-Atom trotz ihrer Spannung—aus dem Sachseschen Modell ersichtlich—gegen Reagenzien eine ausgesprochene Beständigkeit aufweisen, ist auch auf der Natur (stabiles Oktett) jenes C-Atoms zurückzuführen. Falls die Bindung überhaupt aufspringt, findet es im allgemeinen zwischen C₇ und C₁ statt,—z. B. die Bildung von Carvenon aus Campher durch Schwefelsäure—, was auf dem entgegenstehenden Effekt des Schlüsselatoms O zurückgeführt werden darf.

Vor kurzem haben Ishidate und Sano⁽²⁾ mitgeteilt, dass der *d-trans*- π -Oxo-campher unter Hydrolyse, doch in geringfügiger Grad, seine Aldehydgruppe als Ameisensäure abspaltet, und er selbst in *d*- π -Santenon (IV) übergeht, was mit der Hydrolyse des Chlorals analogisch verläuft. Diese Befunde stehen scheinbar mit der Ergebnisse, dass der π -Oxocampher mit Diazomethan hauptsächlich den Methylketon bildet, während Chloral bei der Einwirkung des Diazomethans nur den Äthylenoxyd⁽³⁾ ergibt, in Widerspruch. Die Hydrolyse der beiden Aldehyde geht aber quantitativ ganz anders vor. Beim π -Oxocampher ist die Hydrolyse ungeheuer langsam. Das C₇-Atom fungiert bei der Reaktion als Aninoid (Oktett

(1) Arndt und Eistert, *Ber.*, **68**(1935), 196; Eistert, *Angew. Chem.*, **54**(1941), 99.

(2) *Ber.*, **74**(1941); *J. Pharmaceut. Soc. Nippon*, **61**(1941), 350.

(3) Arndt und Eistert, *Ber.*, **61**(1928), 1118.



mit einem einsamen Elektronenpaar); es stellt nämlich eine „Krypto-ionische“ Reaktion dar, welche keine Konfigurationsänderung mit sich bringt. Beim Chloral geht die Hydrolyse fast quantitativ vor, so ist die C-C Bindung stark gelockert, d.h. besitzt das betreffende C-Atom das ausgesprochene instabile Oktett.

Der andere Fall, bei welchem der C₇-Atom als eine aufrichtige Oktett-lücke in der Reaktion eintritt, wurde schon von einer von uns und Tani⁽⁴⁾ bei der alkalische Hydrolyse des 7-Amino-*trans*- π -apocamphers (V) zum 7-Oxy-*trans*- π -apocampher (VI) gezeigt. Die Bindung zwischen C₇ und NH₂ des Moleküls ist wegen der einander abstossenden Polarität (δ -) stark gelockert, folglich spaltet sie an dieser Stelle leicht und quantitativ ab: und zwar tritt dabei das C₇-Atom als Sextett auf, was aus der Bildung der inactiven Derivate aus dem activen Körper wohl geschlossen wird.

Beschreibung der Versuche.

***trans*- π -Aprocampher-7-methylketon (II).** 15 g *d-trans*- π -Oxocampher (*d-trans*- π -Apocampher-7-aldehyd) werden in 300 ccm ätherischen Diazomethanolösung, hergestellt aus 32 g Nitrosomethylharnstoff, eingetragen. Nach 40 stündigem Stehen bei Zimmertemperatur wird Aether abdestilliert und der Rückstand wird mit gesättigter Bisulfitlösung gut geschüttelt. Der in Bisulfitlösung unlösliche Anteil wird mit Aether extrahiert und der Aether abgedampft. Das so erhaltene Reaktionsprodukt (ca. 6 g) schmilzt bei 80–90°, welches beim Umlösen aus Petroleumäther oder Wasser den Schmp. 85° (Sdp₇ 111–2°) zeigt. Der Körper erweist sich auf dem Legal-schen Proben auf Methylketon als stark positiv. Er ist schwer löslich

(4) Ishidate und Tani, *J. Pharmaceut. Soc. Nippon*, **62** (1942), 8.

in Wasser und leicht löslich in organischen Solventien. Gefunden: C, 73.57; H, 8.90. Berechnet für $\text{C}_{11}\text{H}_{16}\text{O}_2$: C, 73.30; H, 8.95%.

Semicarbazon. Dargestellt durch Zusammenbringen von je 3.3 g rohen methylketon, Semicarbazidhydrochlorid und Natriumacetat in verd. Alkohol. Ausbeute 3.3 g. Beim fraktionierten Kristallisation aus Alkohol oder Wasser wird immer ein einheitliches Semicarbazon von Schmp. 223° erhalten. Gefunden: C, 60.65; H, 8.32; N, 17.50. Berechnet für $\text{C}_{12}\text{H}_{18}\text{O}_2\text{N}_3$: C, 60.74; H, 8.07; N, 17.70%.

Da es ein Monosemicarbazon darstellt und zwar nun keine Legalschen Reaktion mehr aufweist, findet die Kondensation gewiss an dem neu auftretenden Keton statt.

Oxim. Dargestellt aus dem rohen Methylketon und Hydroxylaminhydrochlorid in alkohol. alkalischer Lösung. Es ergibt ein einheitliche Monoxim von Schmp. $137-8^\circ$ (aus Alkohol). Es zeigt auch keine Legalsche Reaktion auf Methylketon. Gefunden: N, 7.12. Berechnet für $\text{C}_{11}\text{H}_{17}\text{O}_2\text{N}$: N, 7.17%.

Prüfung auf der Aethylenoxydverbindung. Das rohe Methylketon wird einerseits mit konz. Salzsäure und andererseits mit 10% Schwefelsäure etwa $1/4$ Stdn. lang gekocht. Nach dem Erkalten wird die Lösung mit Aether extrahiert. Aus dem Aetherauszug konnten wir ausser dem Methylketon (Schmp. 85°) keine nennenswerte Produkte (Chlorhydrin- bzw. Glykol-derivate) isolieren.

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