



Koichi Matsubara.

PROFESSOR KOICHI MATSUBARA.

Professor Koichi Matsubara was born in Nagoya as the first son of Yasoichi Matsubara, a *samurai* of the Owari clan, on the 22nd day of the fifth month of the fifth year of Meiji in the then statutory lunar calendar, corresponding to June 27, 1872, in the Gregorian calendar. He came to Tokyo in his sixth year of age and received all his educations in Tokyo. Thus, in 1878, he was first sent to Nankai-Gakko and then to Shiba-Gakko, both municipal elementary schools in the city, and in 1884, he went to Tokyo Prefectural Middle School. In 1888, he was admitted to the First Higher Middle School, in whose dormitory he lived for five years. In 1893, he graduated from this school and was matriculated at the College of Science of the Imperial University of Tokyo, where he chose chemistry as his speciality and studied under Professors Divers, Sakurai, Haga, Yamagawa, Fujisawa, and Tsuruta. In 1896, he finished his university course, and continued his studies as a post-graduate student.

In 1897, he was appointed to the professorship at the Second Higher School in Sendai, and took the charge of chemistry in the preparatory courses for imperial universities, the main courses in the Higher Schools at that time. In the next year, he was transferred to the same post in the First Higher School in Tokyo. In 1899, he was appointed Assistant Professor of Chemistry in the College of Science of the Imperial University of Tokyo. Being sent to Europe, as a Government Research Fellow, for further study of organic chemistry, he spent two years, from 1903 to 1905, at Owens College of the University of Manchester, under Professor W. H. Perkin, working on nor-terpene, etc., and next one year at the University of Berlin, under Professor Emil Fischer, working on valine, etc. He came back to his *alma mater* in 1906, and the chair of organic chemistry in the College of Science was put in his care. This chair he held for twenty-seven years continuously since then. In 1909, he was promoted to the Professorship, and in 1913, the degree of D. Sc.

was conferred to him by the Minister of Education upon the recommendation of the President of the Imperial University of Tokyo. From 1913 to 1929, he gave the lectures on organic chemistry also to the students of the Department of Applied Chemistry in the College of Engineering of the University. He was elected by his Faculty a Member of the Library Committee of the University from 1913 to 1930, and was elected its Chairman in 1927 and 1929. In December of 1926, he was elected a Member of the University Council for three years, and in December of 1929, he was appointed the Dean of the Faculty of Science. May 22, 1932, being his sixtieth birthday, he retired from the Professorship and the Deanship on March 31, 1933, the end of the academic year, in accordance with the traditions concerning the age limit of professors in the Imperial University of Tokyo. Quite recently, the title of Honorary Professor of the Imperial University of Tokyo was conferred to him by Imperial command. He is in the Senior Third Court Rank, and is decorated with the Second Class of the Imperial Order of the Sacred Treasure. He was one of those whose meritorious services for the sake of education extending over thirty years were specially honoured by the Minister of State for Education on the 10th of November, 1928, the Coronation Day of the present Emperor.

Professor Matsubara was requested by the Ministry of Education to serve on several committees, some nominated by the Imperial Cabinet upon the recommendation of the Minister of Education and others nominated by the Minister.

Thus he was nominated by the Cabinet an Additional Member of the Committee for the Compilation of the Catalogue of Scientific Literature in 1901, and served as such for two years. He was again nominated an Ordinary Member of this Committee in 1917. This Committee is aiming to compile the catalogue of scientific literature published in Japan for the sake of the International Catalogue of Scientific Literature, originated by the Royal Society of London and administered by an International Council, commencing with literature of the year 1901. Although the work of this Committee was suspended in 1922, as the publication of the International Catalogue was temporarily stopped with the 14th issue owing to the

World War, the Japanese Committee is continued nominally even to the present time. In this relation, Professor Matsubara represented the Imperial Government at the Second International Convention of the International Scientific Catalogue held in London in 1905.

In 1923, Professor Matsubara was nominated by the Cabinet a Member of the National Research Council. This Council is an organization attached to the Ministry of Education and has been established in 1920 for the purpose of coordinating and encouraging activities at home in the various branches of science and its applications and also of cooperating with like institutions in other countries, with the view of promoting national and international researches in these fields, as the outcome of the conference of the representatives of the principal inter-allied Scientific Academies held in London and Paris in October and November of 1918, and the Constitutive Assembly of the International Research Council held in Brussels in July of 1919. Professor Matsubara, who was attached to the Division of Chemistry, was elected the Vice-Chairman of that Division in 1924, and the Chairman in 1930, and as such is also a member of the Division of General Affairs since 1924, besides the Chairman of the Publication Committee of this central Division and also that of the Division of Chemistry. In this connection he represented the National Research Council of Japan at the Extraordinary General Assembly of the International Research Council held in Brussels in June of 1926. This is the meeting at which it was resolved, after agreeing unanimously to omit from the Statutes of the International Council the words which have limited the membership of the Council to the allied and neutral countries, to invite Germany, Austria, Hungary and Bulgaria to join the International Research Council and the Unions attached to it. He represented the National Research Council of Japan also at the Seventh International Chemical Conference of the International Union of Pure and Applied Chemistry, held in Washington, September, 1926. As a Member of the National Research Council, he acted as General Secretary, together with the late Professor N. Yamasaki, for the Third Pan-Pacific Science Congress, held in Tokyo, October and November, 1926, under the auspices of the National Research Council of Japan.

Perhaps it may be added here that Professor Matsubara represented the Imperial Government at the Sixth International Congress of Applied Chemistry, held in Rome, April and May, 1906. He was one of the organizers of the Japanese Committee of the Pasteur Centenary Celebrations of 1922, and also of the Berthelot Centenary Celebrations of 1927, and gave memorial lectures in both of these occasions. He was also a member of several committees for the organization of the World Engineering Congress, held in Tokyo, October and November, 1929.

There is a Committee attached to the Ministry of Education for giving certificates for the teachers. Formerly the certificates for the teachers in secondary education only were concerned by this Committee. Professor Matsubara, after serving as an Examining Member of chemistry in 1907, 1910, 1911 and 1912, was appointed in 1913, by the Cabinet, one of the Standing Members of this Committee, to conduct all business connected with the testing of the qualifications of teachers for licenses, both by examination and without examination. When, in 1919, the certificates for the teachers of the Higher Courses of the Higher Schools, which are practically the preparatory courses for the universities and colleges, were determined to be given and to be controlled by this Committee, he was requested to act in the same capacity also for this section. He is still continuing to serve in both of these sections.

When School Books Investigation Committee was reorganized in 1920, Professor Matsubara was nominated, by the Cabinet, one of its Members. This Committee has to examine the textbooks for elementary schools, which relate to morals, Japanese language, arithmetic, Japanese history, geography, science, etc. Such textbooks are to be those for which the copyright is held by the State, and they are submitted to this Committee by the Minister of Education before their publication.

When, in 1907, Mr. (now Baron) Toranosuke Furukawa offered a sum of money to build a College of Science in Sendai, the Ministry of Education determined to establish the Tohoku Imperial University with this College of Science in Sendai and the College of Agriculture in Sapporo as its constituent colleges, and Professor Matsubara was nominated, by the Minister, a member of the Organization Committee of this College, which was opened in 1911.

Again, in 1927, the Post-Graduate Courses of the Higher Normal Schools of Tokyo and Hiroshima were to be reorganized each to a College of Literature and Science, according to a resolution of the Education Council passed in 1922, and Professor Matsubara was requested, by the Minister of Education, to be a member of the Organization Committee of these Colleges, which were opened in 1929.

When in 1921, the syllabus of "science" to be taught in the Literature Section of the Higher Courses of Higher Schools was to be discussed and fixed, the Ministry of Education requested Professor Matsubara to be a member of the drafting committee. Again in 1926, he acted in the same capacity when the syllabus of chemistry to be taught in the Science Section of the Higher Courses of Higher Schools was discussed and fixed. In 1924, when the syllabus of physics and chemistry to be taught in Middle Schools was revised, he also served in the revising committee.

From 1919 to 1931, Professor Matsubara acted as a consultant to the Naval Arsenal at Hiratsuka. He was a Councillor of the Institute of Physical and Chemical Research from 1930 to 1933, while he was the Dean of the Faculty of Science of the Imperial University of Tokyo. He acted as a Juror at the Tokyo Taisho Exhibition of 1914.

Professor Matsubara joined this Society, then the Tokyo Chemical Society, in 1894 as an Associate, and in 1896 as a Member. He was elected Editor of the Journal of the Society in 1899-1903, Member of the Council 1906-1907, Secretary 1907-1908, Editor 1908-1919, President 1919-1920, and Editor 1920-1926. Besides, he served on several committees of the Society, and was the centre of its activities for many years.

He joined the Society of Chemical Industry, of Japan, in 1898, and the Association of Chemical Industry, of Japan, in 1917, just after the establishment of both, and served in the Council of both of these institutions several times.

In 1908, he joined the Kogakukai (Society for the Promotion of Science), a society of some fifty people, publishing the *Toyo-gakugei-zasshi* (Oriental Journal of Science), a journal in the line of the "Nature" of London or the "Science" of New York, and acted as its editing secretary from 1911 to 1921.

Professor Matsubara was distinguished, through his whole course of education, by high standard of scholarship. One who ever knows him cannot help admiring his excellent memory and extreme carefulness in all details. His omnivorous stock of knowledge, and plain and impartial character made him a man who cannot be missed in all organizations in which he played always an important rôle. Indeed his meritorious and implicit contributions to the progress of sciences in Japan shall never be forgotten.

On the occasion of his retirement from the Professorship, his friends and pupils raised a considerable sum of money, which was transferred to the Chemical Society of Japan. The Society decided with gratitude to establish a fund to be used for the encouragement of the progress of chemistry, in association with the name of Professor Matsubara.

Yuji SHIBATA.

June, 1933.

BULLETIN OF THE CHEMICAL SOCIETY OF JAPAN

THE STICK ANTIMONY ELECTRODE FOR THE MEASUREMENT OF HYDROGEN ION CONCENTRATION⁽¹⁾

By Taku UEMURA and Hideo SUEDA.

Received November 12th, 1932. Published January 28th, 1933.

The usual hydrogen electrode method is undoubtedly the most accurate one of all the electrometric ways of estimating hydrogen ion concentration, but it cannot be applied to solutions containing reducible substances like ammine complex salts. We have already studied the above solution by using the quinhydrone electrode, but even in the limited range of its applications, our purpose was not attained. And, metal electrodes can be presented to these very reducible solutions for the determination of hydrogen ion concentration (pH). Several types of antimony electrode are thus reported for this purpose: Plated type, by Shukov and Aveyevich⁽²⁾, and Dropping type, by Roberts and Fenwick⁽³⁾. Franke and William⁽⁴⁾, Snyder⁽⁵⁾, Vlès and Vellinger⁽⁶⁾, Itano⁽⁷⁾, Parks and Beard⁽⁸⁾ are the principal investigators on the stick antimony electrode which has been favored because of its ease of preparation and use.

The experimental formulas given by these authors have a tolerable accuracy in their own studies, but it is difficult to find the uniformity in their results. When one wishes to determine pH values by using the antimony electrode, one must fully calibrate the metal electrode. Supposing that the disagreement of data is due to the different nature and treatment of the electrode, we have paid attention to the manipulation of the metal and principally adopted Vlès-Vellinger's idea of experiments.

(1) Read before the 8th Annual Meeting of the Japanese Association for the Advancement of Science (Nippon Gakujutsu-Kyôkai), held at Nagoya, Japan, October 16th, 1932.

(2) Shukov and Aveyevich, *Z. Elektrochem.*, **35** (1929), 349; **37** (1931), 771.

(3) Roberts and Fenwick, *J. Am. Chem. Soc.*, **50** (1928), 2125.

(4) Franke and William, *Ind. Eng. Chem.*, **20** (1928), 87.

(5) Snyder, *Soil Science*, **26** (1928), 107.

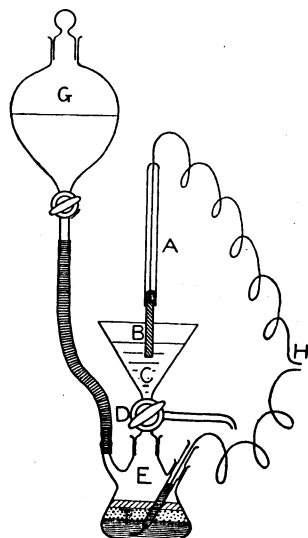
(6) Vlès and Vellinger, *Arch. phys. biol.*, **6** (1927), 38 and 92.

(7) Itano, *Ber. Ohara Inst. landw. Forsch. Japan*, **4** (1929), 273.

(8) Parks and Beard, *J. Am. Chem. Soc.*, **54** (1932), 856.

Experimental.

Apparatus. For the present determination of pH values, we have used the mode of glass vessel presented by Vlès and Vellinger⁽⁶⁾.



- A : Glass tube for protecting the antimony electrode.
- B : Antimony electrode.
- C : Sample for determining pH value.
- D : Three way stopcock.
- E : Saturated potassium chloride solution.
- F : Calomel electrode.
- G : Reservoir for potassium chloride solution.
- H : To potentiometer.

Fig. 1.

Dimension: Diameter of glass funnel..... 6 cm.
 Height of glass funnel..... 6 cm.
 Diameter of glass vessel (bottom) 5.5 cm.

Preparation of the Stick Antimony Electrode. A hard glass tube (about 7 mm. in inside diameter and 30 cm. in length) is filled with metallic antimony pieces to occupy at first from 10 to 15 cm. in length; and, held horizontally it is gently heated on a fish-tail formed Bunsen burner. When the antimony is sufficiently fused, the tube must be slowly moved to and fro to expel the air-bubbles in the metal. Next, the red-heated glass tube containing the fused antimony is drawn to keep a uniform diameter of about 4–5 mm., and is thrown into water for sudden cooling. If cooled gradually, in this case, the solidified antimony easily gets a cleavage surface along its cross section of the stick and becomes very brittle. To connect a copper wire with the prepared antimony stick, we apply direct electric current (70 volts; 2–3 amperes), taking the wire as cathode and the metal, as anode. We thus make an arc between the electrodes, and when the end of the stick is sufficiently

fused the wire is strongly put into the fused stick of antimony. As the joint of these two metals falls easily apart, even after it was completely cooled, we generally cover the electrode with a glass tube and its end is sometimes sealed with paraffine, de Khotinsky cement or bakelite varnish.

Different Treatments of Antimony Electrodes. According to the Vlès-Vellinger's publications⁽⁶⁾, the antimony electrode is influenced by different treatments, such as polishing with emery paper of various degrees. To study these effects more minutely, we have chosen several samples of electrodes variously prepared.

- A-electrode: Compact surface polished with No. 0000 emery paper.
- B-electrode: Compact surface polished with No. 00 emery paper.
- C-electrode: Surface not compact, (air-bubbles are leaving mark on the surface) polished with No. 00 emery paper.
- D-electrode: A-electrode containing a minute quantity of copper⁽⁹⁾.
- E-electrode: B-electrode containing a minute quantity of copper⁽⁹⁾.
- F-electrode: Polish with No. 00 emery paper and take the electrode as anode (platinum as cathode) and electrolyse water (acidified with a very small quantity of dilute sulphuric acid) from 2 to 3 minutes. Gray coloured.

All these electrodes, once polished, are again cleaned in distilled water, wiped with absorbent cotton and used.

Original Impurities detected in Antimony Pieces. We have used two kinds of antimony pieces for our present studies; one is of Japanese origin (labelled Kojima's Deer brand—Extra pure, Tokyo). By an application of the electric arc spectral method, we have detected some lines of foreign elements, thus:

Arsenic: 2349.88 Å, 2898.86 Å, 3860.60 Å
Copper: 4022.88 Å, 4062.91 Å
Lead: 3639.72 Å, 3683.62 Å
Tin: 3034.25 Å, 3175.16 Å, 3262.50 Å

Our second sample used for the preparation of the following two electrodes is the Merck's reagent where any lines of impurities can not be found, except those of arsenic.

- a-electrode: Compact surface polished with No. 0000 emery paper, and left in water for more than one hour.
- b-electrode: Compact surface polished with No. 0000 emery paper.

(9) About 0.1–0.01% of copper.

Buffer Solutions. We have prepared the following buffer solutions, whose pH values are defined by hydrogen electrode, to observe the accuracy of our stick antimony electrode.

pH	
1.25	(50 c.c. M/5 KCl; 64.5 c.c. M/5 HCl, dilute to 200 c.c.)
1.96	(50 c.c. M/5 KCl; 10.6 c.c. M/5 HCl, dilute to 200 c.c.)
2.97	(50 c.c. M/5 KH Phthalate; 20.32 c.c. M/5 HCl, dilute to 200 c.c.)
3.97	(50 c.c. M/5 KH Phthalate; 0.40 c.c. M/5 NaOH, dilute to 200 c.c.)
4.99	(50 c.c. M/5 KH Phthalate; 23.85 c.c. M/5 NaOH, dilute to 200 c.c.)
6.05	(50 c.c. M/5 NaH ₂ PO ₄ ; 5.70 c.c. M/5 NaOH, dilute to 200 c.c.)
7.07	(50 c.c. M/5 NaH ₂ PO ₄ ; 29.63 c.c. M/5 NaOH, dilute to 200 c.c.)
7.99	(50 c.c. M/5 H ₃ BO ₃ , M/5 KCl; 3.97 c.c. M/5 NaOH, dilute to 200 c.c.)
9.00	(50 c.c. M/5 H ₃ BO ₃ , M/5 KCl; 21.30 c.c. M/5 NaOH, dilute to 200 c.c.)
9.99	(50 c.c. M/5 NaH ₂ PO ₄ ; 46.80 c.c. M/5 NaOH, dilute to 200 c.c.)
10.59 ⁽¹⁰⁾	(100 c.c. Glycocoll solution ⁽¹¹⁾ ; 50 c.c. M/5 NaOH, dilute to 200 c.c.)
12.39 ⁽¹⁰⁾	(80 c.c. Glycocoll solution ⁽¹¹⁾ ; 60 c.c. M/5 NaOH, dilute to 200 c.c.)

The above mentioned buffer solutions are chosen in every one pH range and the chemicals used for the preparation have nearly the purity of reagents of the Kahlbaum's grade.

The Measured Electromotive Force (E.M.F.) Values. Table 1 shows that A- and B-electrodes, and D- and E-electrodes have respectively similar values while C- and F-electrodes show slightly different results from those of the former two pairs.

TABLE 1.

pH	Electrodes (Japanese origin)					
	A-	B-	C-	D-	E-	F-
1.25	65.3	67.7	73.0	66.0	65.8	63.2
1.96	106.7	105.5	107.5	105.7	105.5	108.4
2.97	162.5	161.6	161.6	158.5	159.5	158.9
3.97	212.2	211.3	212.8	211.6	212.8	210.6
4.99	267.9	268.5	269.1	266.9	267.7	266.7
6.05	329.6	329.6	330.9	329.8	328.0	326.8
7.07	383.4	382.0	383.7	382.7	383.0	382.1
7.99	428.3	428.1	430.6	427.6	427.8	427.1
9.00	473.9	474.9	476.5	476.5	476.7	475.4
9.99	524.3	522.8	525.6	524.4	525.9	525.7
10.59	557.0	556.0	557.6	557.5	556.5	555.9
12.39	687.0	687.1	694.7	686.0	687.1	682.6

(10) The last two solutions are mixed according to the Sørensen's indication, while the others are based on Clark and Lubs' standards.

(11) Our glycocoll (glycine) solution is prepared by dissolving 1.501 gr. glycocoll and 1.71 gr. NaCl in 200 c.c. H₂O.

Now, A- and B-electrodes, which have almost the same surface condition, have received a different mechanical treatment, and D- and E-electrodes are also polished with emery paper of different degrees, but to each is added a small and equal quantity of copper. And, the result given by these two pairs of electrodes shows that any mechanical treatment influences but slightly the E.M.F. values, while the surface condition and the chemical nature of the electrodes cannot be neglected for the measurement of E.M.F.

Our second results obtained from the electrodes prepared by the Merck's reagent are as follows:

TABLE 2.

pH	Electrodes		pH	Electrodes	
	a-	b-		a-	b-
1.25	79.8	80.5	7.03	403.4	404.7
1.99	112.1	112.1	7.93	435.8	438.0
2.99	159.0	159.2	8.91	492.5	491.3
3.97	223.3	223.3	10.05	553.4	552.4
4.99	283.0	283.3	10.77	595.3	591.8
5.95	339.8	335.0	11.97	693.5	697.9

Table 2 also shows that the slight difference of mechanical treatment has very little effect on the E.M.F. values.

Next, we have found the mean of observed values that nearly coincide with each other and have tabulated them in Table 3, comparing the calculated values from our empirical equation (see page 6-7) deduced from the experimental results.

TABLE 3.

pH	Mean values of				pH	Mean values of	
	A-B (obs.)	A-B (calc.)	D-E (obs.)	D-E (calc.)		a-b (obs.)	a-b (calc.)
1.25	66.5	66.6	65.9	65.4	1.25	80.2	71.8
1.96	106.1	104.8	105.6	103.8	1.99	112.1	113.2
2.97	161.9	159.1	159.0	158.2	2.99	159.1	169.2
3.97	211.8	212.9	212.2	212.2	3.97	223.3	224.1
4.99	268.3	267.8	267.3	267.3	4.99	283.2	281.2
6.05	329.6	324.7	328.9	324.6	5.95	337.4	335.0
7.07	382.7	379.7	382.9	379.7	7.03	404.0	395.5
7.99	428.2	429.2	427.7	429.3	7.93	436.9	445.9
9.00	474.4	483.5	476.6	483.9	8.91	491.9	500.8
9.99	523.6	536.8	525.2	537.3	10.05	552.9	564.6
10.59	556.5	569.0	557.0	569.8	10.77	593.6	604.9
12.39	687.1	665.9	686.9	666.9	11.97	695.7	672.1

Theoretical.

Many authors⁽¹²⁾ mention the theoretical side of the antimony electrode, and some of them declare that chemical changes occur on the surface of the metallic electrode, and they even give several constitutional formulas of intermediates which are supposed to be obtained. Assuming any metallic oxide whose solubility is very small, the next equation will be formed in the solution, and it shows that the metallic ion concentration of the solution is controlled by its hydrogen ion concentration.



M is, in this case, a divalent metal whose oxide is therefore MO. Supposing MO nearly insoluble, then we may have

$$[\text{M}^{++}] = K[\text{H}^+]^2.$$

Applying the Nernst equation,

$$E = e_0 + \frac{0.0577}{2} \log [\text{M}^{++}]$$

Putting $K [\text{H}^+]^2$ in place of $[\text{M}^{++}]$,

$$E = e_0 + \frac{0.0577}{2} (\log K + \log [\text{H}^+]^2),$$

$$E = e'_0 + 0.0577 \log [\text{H}^+],$$

$$E = e'_0 - 0.0577 \text{ pH (at } 17^\circ\text{C).}$$

From this, we conclude that the electrode potential (E) can be varied according to pH value. It goes without saying that this conclusion holds only when the small solubility of the metallic oxide is realised, and the equation is similarly derived in the case of a trivalent metallic oxide of very small solubility. One of the few metals that fulfill these conditions is antimony.

Applying the principle of least-square method, we have derived the following empirical equations from each set of the experiments whose data of E.M.F. have already been tabulated.

- (1) Equation derived from the mean values of A- and B-electrodes (see Table 3);

$$E = 53.8 \text{ pH} - 0.7 \dots\dots\dots (1)$$

(12) loc. cit.

- (2) Equation derived from the mean values of D- and E-electrodes (see Table 3);

$$E = 54.0 \text{ pH} - 2.1 \quad \dots\dots\dots (2)$$

- (3) Equation derived from C-electrode (see Table 1);

$$E = 54.0 \text{ pH} + 0.3 \quad \dots\dots\dots (3)$$

- (4) Equation derived from F-electrode (see Table 1);

$$E = 53.8 \text{ pH} - 1.8 \quad \dots\dots\dots (4)$$

- (5) Equation derived from the mean values of a- and b-electrodes (see Table 3);

$$E = 56.8 \text{ pH} + 1.8 \quad \dots\dots\dots (5)$$

With the theoretical values calculated from these empirical formulas and the observed results, we can make a diagram that represents the relation of pH and E.M.F. Of the two straight lines in the following

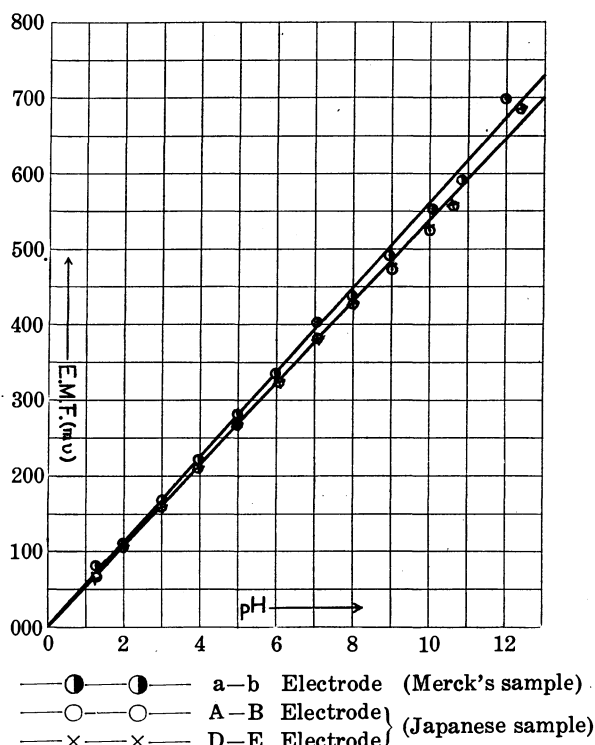


Fig. 2.

diagram (Fig. 2), the upper one shows the theoretical values deduced from the equation (5), obtained from the electrode of Merck's sample; the lower one shows the equations (1) and (2).

Next, in Tables 4 and 5, we give the maximum deviation of observed and calculated values of E.M.F. which are obtained from equations (1), (2) and (5); a percentage of the error, and the difference due to the determination of pH by hydrogen and antimony electrodes.

TABLE 4.
A-, B-, D- and E-Electrodes.

pH	Max. dev. of E.M.F. from calc. value (m.v.)		% of error from calc. value		pH—diff. (Sb to H ₂)	
	A-; B-	D-; E-	A-; B-	D-; E-	A-; B-	D-; E-
1.25	-1.3	+0.6	2.0	0.9	0.02	0.01
1.96	+1.9	+1.9	1.8	1.8	0.04	0.04
2.97	+3.4	+1.3	2.1	0.8	0.06	0.02
3.97	-1.6	±0.6	0.8	0.3	0.03	0.01
4.99	+0.7	±0.4	0.3	0.2	0.01	0.01
6.05	+3.9	+4.2	1.2	1.3	0.07	0.08
7.07	+3.7	+3.3	1.0	0.9	0.07	0.06
7.99	-1.1	-1.7	0.3	0.4	0.02	0.03
9.00	-9.6	-7.4	2.0	1.5	0.18	0.14
9.99	-14.0	-12.9	2.6	2.4	0.26	0.24
10.59	-13.0	-13.3	2.3	2.3	0.24	0.25
12.39	+21.2	+20.2	3.2	3.0	0.39	0.37

TABLE 5.
a- and b-Electrodes.

pH	Max. dev. of E.M.F. from calc. value (m.v.)	% of error from calc. value	pH—diff. (Sb to H ₂)
1.25	+8.7	12.1	0.15
1.99	-1.1	1.0	0.02
2.99	-10.2	6.0	0.18
3.97	-0.8	0.4	0.01
4.99	+2.1	0.8	0.04
5.95	+4.8	1.4	0.09
7.03	+9.2	2.3	0.16

Table 5.—(Continued)

pH	Max. dev. of E.M.F. from calc. value (m.v.)	% of error from calc. value	pH—diff. (Sb to H ₂)
7.93	—10.1	2.2	0.18
8.91	—9.5	1.9	0.17
10.05	—12.2	2.2	0.22
10.77	—13.1	2.2	0.23
11.97	+25.8	3.8	0.46

Part of the expenses of this study is defrayed with the Research Fund of the University, for which we desire to tender our gratefulness.

Summary.

As we have performed various kinds of experiments with the stick antimony electrode, changing their conditions of electrodes and external influences, we may summarise the results of our observations.

(1) The stick antimony electrode in an unstirred solution in contact with air at equilibrium gives a reliable measurement of pH values from pH 1 to 9 inclusive. Recognizing some decrease of accuracy in the results, we may of course apply this electrode for the determination of pH values above pH 9, up to 12.

(2) The value of E.M.F. (m.v.) with the electrode prepared by a Japanese sample and measured against the saturated calomel electrode is obtained by the equation $E = 53.8 \text{ pH} - 0.7$.

(3) We did not take the temperature as a calculating factor, but we always record it during our observation, and we know that E.M.F. value becomes invariably greater when the temperature rises. All our experiments have been made with a temperature varying between 10°C. and 25°C., and the mean error due to the temperature gradient, in this case, is, on an average, about 4%, which is comparable to other experimental errors easily inserted in the estimation of the hydrogen ion concentration.

(4) The surface of a polished antimony electrode is probably covered in a solution with an oxide whose colour is dependent on the pH value of the solution, and the change is more striking when the solution is more acidic. When the pH value of the solution is 1 to 8, the surface of the electrode immersed in the solution becomes black, but if the

solution is alkaline (pH is 9 to 12), the immersed part shows a whitish shade of colouring.

(5) When pH is small, i.e. acidic, we generally obtain a higher value of E.M.F. at the beginning of the experiment, and the value decreases and tends to a point of equilibrium; but the opposite takes place in the case of an alkaline solution whose pH is great. We may think that colour change on the surface of the electrode immersed in a solution has perhaps some relation to this transformation of the direction of E.M.F.

(6) The time to reach equilibrium is also dependent on the pH value of the solution. It is comparatively short when the solution is slightly alkaline and its pH value is about 8 to 9, and the colour on the surface of the electrode due to the immersion cannot easily be found in this range of pH. But when the solution is strongly acidic (small pH) or strongly alkaline (large pH), the surface of the electrode changes readily in colour, and the time to reach equilibrium becomes longer.

(7) As for the effect of stirring a solution, E.M.F. deviates to a higher side after it has once reached equilibrium. If we stir the solution from the beginning of the experiment (continuous stirring), E.M.F. thus obtained gives generally a higher value than it is unstirred but when we stop the vibration, E.M.F. value decreases.

(8) Mechanical treatment by the preparation of the stick antimony electrode (Ex. emery paper for polishing) is rather little influenced for obtaining the E.M.F. value, but the original minute impurities contained in an electrode, and the porousness of the electrode cannot be neglected in the determination of E.M.F.

(9) When we have once observed with a solution saturated with antimony oxide, results are obtained at equilibrium, and they are nearly similar to those of an ordinary case. We may, therefore, conclude that the chemical change of the electrode, often discussed by some authors, is not a great factor in the use of the antimony electrode.

(10) When we immersed two electrodes in the same solution but, at different times, the course followed to reach equilibrium are nearly parallel. If the equilibrium is once established by an electrode in a given solution, and we only change the electrode with a polished one, or use the same after polished it again, nearly the same course taken in the first case may also be followed to obtain an equilibrium value.

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RHYTHMIC PRECIPITATES.

By Toshizo ISEMURA.

Received November 28th, 1932. Published January 28th, 1933.

In the experiments on the diffusion of electrolytes in jellies, the author has found some new examples of rhythmic precipitates. In this communication the obtained results is reported briefly. The formations of rhythmic precipitates have been observed in the following cases: oxalates of calcium and strontium, copper hydroxide, and lead chromate in silica gel, and silver chromate in gelatine gel. The last mentioned case is, of course, the best known example of the rhythmic precipitate, yet it is described here because the author succeeded in making more beautiful and more sharp layers of silver chromate than ever obtained.

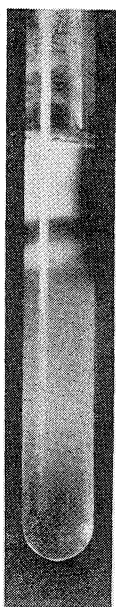
Calcium Oxalate in Silica Gel. To 5 c.c. of sodium silicate solution (density, 1.06) add 5 c.c. of a mixture of acetic and oxalic acid solutions (0.5 N., ratio of two acids: 1:1 or 1:3). This silica gel set in one night. Now ca. 5 c.c. of calcium chloride solution (10 to 25% solution) are poured on the gel. The banding readily forms which has an appearance like the opal. Clear spaces between bands are so narrow that the banding can better be seen by the transmitted light. Too large or too small quantity of oxalic acid prevents the formation of calcium oxalate band.

Strontium Oxalate in Silica Gel. To 5 c.c. of water glass solution (1.06) add equal volume of the mixed acid above described, and 0.01–0.02 gr. of potassium citrate. After setting the gel put 5 c.c. of 25% strontium nitrate solution on it. About a week later, the formation of the banding of strontium oxalate is found. When the solution of strontium nitrate is poured on the silica gel containing the soluble oxalate or oxalic acid only, no strata is formed. It has previously been found by Hatschek⁽¹⁾ that the addition of material indifferent to the reaction system often causes the formation of bands. It is moreover known that citrate of potassium or sodium accelerates the formation of nucleus of the crystals. If the jelly contains citrate the nucleus formation will be accelerated and, accordingly, the formation of strata will become easier. By adding a small quantity of potassium citrate to the mixture before setting, the author has found the formation of dense, white banding of strontium oxalate.

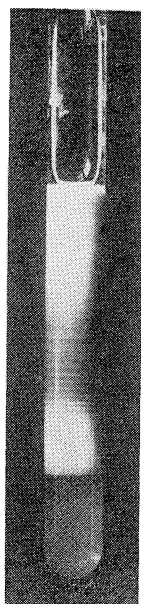
(1) Hatschek, *Kolloid Z.*, **27** (1920), 225; *Biochem. J.*, **14** (1920), 418.

The formation of periodic precipitate of barium oxalate in silica gel could not be observed whether the citrate was added or not. Without the addition of citrate the barium oxalate grows as beautiful dendrites or plumes. The addition of small amount of glucose gives the crystal of silky lustre and the crystals become larger. In the lower part of the test-tube grow crowds of thin long plates, composed of many needles just like asbestos, and each plate often measures more than 3–4 mm. When citrate is added in the silica gel, the dendrites or plumes are not formed but many small globules and crystals form. At the lower part of the test-tube considerably large well-defined crystals of barium oxalate are formed. It measures often 2–3 mm. long.

Copper Hydroxide in Silica Gel. To 5.5–6 c.c. of sodium silicate solution add 5 c.c. of 0.5 N. acetic acid. After setting the basic gel put 0.5 N. copper sulphate solution as outer electrolyte. Two or three large thick bluish white layers are formed. Besides, in the lower part of the test-tube faint layers are also formed. These precipitates are probably copper hydroxide. Fig. 1 is the photograph of it.⁽²⁾



Copper hydroxide
in silica gel
Fig. 1.



Lead chromate
in silica gel
Fig. 2.



Silver chromate
in gelatine gel
Fig. 3.

(2) The photographs were kindly taken by Mr. N. Asada, for which the writer expresses his hearty thanks.

Lead Chromate in Silica Gel. In 5 c.c. of sodium silicate solution dissolve 0.01–0.005 gr. of potassium chromate as inner electrolyte and 0.03–0.05 gr. of glucose. To this solution add an equal volume of a half normal solution of acetic acid. After setting 10% lead nitrate solution is poured on the gel as outer electrolyte. Ten or more days later, we find that many thin and crowded bands were formed. If too much potassium chromate are added, the dentrites are also formed simultaneously, and if too little, the bands become very vague.

It is said that lead chromate precipitates in bands in agar-agar gel but not in gelatine and in silica gel. In the author's experiment, however, the periodicity has also been observed in silica gel. In the periodic precipitates of mercuric iodide in silica gel H. N. Holmes⁽³⁾ has found that the presence of glucose in the gel makes the bands very much sharper. In the same manner, the author has found that the addition of glucose makes the periodic structure of the lead chromate much sharper. In this case, two periodicities exist just as the case of silver chromate banding in gelatine containing small amount of soluble chlorides. Larger periodicity is easily recognised while smaller one is often difficultly observable without using a magnifying glass. At the lower part of the tube, however, both can easily be recognised with the naked eyes. It is interesting that in this case the upper part of the jelly is coloured yellow, the subsequent layer orange and the lower brown. Under this part the banding appears and the lowermost part becomes yellow again. It seems that such colour change is caused by the size of crystals formed. The photograph is shown in Fig. 2.

Silver Chromate in Gelatine Gel. Banding of silver chromate in gelatine gel was first found by R. E. Liesegang⁽⁴⁾ and since then, many papers have been published on this subject. It is known that silver chromate does not deposit in bands in pure agar-agar gel, while S. C. Bradford⁽⁵⁾ succeeded in making bands in agar gel by addition of small amount of potassium citrate. According to Bradford, the existence of salts of polyvalent acids such as citrates increases, generally, the metastable limit of crystallization of silver chromate or dichromate, and accordingly, the deposited crystals will be smaller in size. And this condition favors the formation of banding.

In the case of gelatine jelly, the banding appears without the addition of any indifferent substance, though the formed silver chromate is

(3) See, Alexander, "Colloid Chemistry," Vol. I (1926), p. 803.

(4) Liesegang, *Naturwiss. Wochenschr.*, **11** (1896), 353.

(5) See, Alexander, "Colloid Chemistry," Vol. I (1926), p. 790.

fairly coarse. So, for the same reason, if citrate is added in the inner electrolyte, more beautiful and sharper layers of very fine crystals may be expected. The experiment has been conducted as follows.

Let 0.2 gr. of gelatine swell in 10 c.c. of water and then dissolve by warming on a water bath and filter, if necessary. Then add 0.01 gr. of potassium dichromate and 0.02 gr. of potassium citrate. After setting completely, 5 c.c. of 15% silver nitrate solution are poured on the gel and stand it in a dark cold place. The banding is obtained which is more beautiful and sharper than usual (Fig. 3).

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STUDIES ON PUTREFACTIVE PRODUCTS OF BEER YEAST.

By Kôtarô NISHIDA.

Received November 29th, 1932. Published January 28th, 1933.

Formerly, as putrefactive products of yeast, ethylamine, trimethylamine, isoamylamine, caprylamine and sepsin were isolated by Hesse,⁽¹⁾ Müller⁽²⁾ and Faust⁽³⁾; and recently the writer⁽⁴⁾ reported with Dr. Yoshimura on the occurrence of hypoxanthine, histamine, putrescine, cadaverine, tyramine and leucine in a putrefied yeast. In this experiment, the author isolated the phenylethylamine, adenine, hypoxanthine, histamine, putrescine, cadaverine, tyramine and leucine from putrefied beer yeast.

Experimental Part.

The beer yeast experimented was obtained by pressing and drying the settled yeast in the bottom of fermenting tunk after main-fermentation of beer; and the various forms of nitrogen in the dried sample were as follows:

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- (1) Hesse, *Jahresber. Fortschr. Chem.*, (1857) 403.
 - (2) Müller, *J. prakt. Chem.*, **70** (1859), 65.
 - (3) Faust, *Arschiv. exper. Path. Pharm.*, **51** (1904), 248.
 - (4) K. Yoshimura and K. Nishida, *J. Agr. Chem. Soc. Japan*, **8** (1932), 309.

	Moisture 9.64%	Dry matter 90.36%
	In 100 parts of dry matte	Ratio (Total N as 100)
Total N	10.153	100.0
Protein N	6.883	67.8
Non-protein N	3.270	32.2
In which :		
Ammonia N	0.097	1.0
Organic base N	1.481	14.6
Other N	1.692	16.6

In earthen pot, 9 kg. of the sample were allowed to stand in 36 liters of water for 28 days, stirring the mixture one time in every day. In this period, average of maximum temperature daily was 28.3°C., average of minimum temperature 10.0°C., and average of temperature at 10 a.m. daily 22.5°C. In the above conditions the putrefaction took place, and still the liquid was kept an acidic reaction.

The various forms of nitrogen in the filtrate of the putrefied substance were determined:

	In 100 parts of original sample	Ratio (Total N as 100)
Total N	8.277	100.0
Protein N	0.625	7.6
Non-protein N	7.652	92.4
In which :		
Ammonia N	1.192	14.4
Organic base N	2.370	28.6
Other N	4.090	49.4

Isolation and Identification of Organic Bases. To remove protein and other impurities, neutral- and basic-lead acetate were added to the above putrefied yeast; when the excess of lead was removed by sulphuric acid and the mother liquor from the lead sulphate was evaporated to a small volume, the considerable amounts of inorganic substances (ammonium- and potassium-sulphate) crystallised out. The filtrate from the preceding inorganic substances was diluted with 5% sulphuric acid, and then researches were carried out on the organic bases, fractionally precipitated by adding phosphotungstic acid to the above solution.

First Precipitate by Phosphotungstic Acid.

This precipitate was decomposed by baryta, and excess of baryta was removed by CO₂ and the solution was fractionated into five fractions.

I. Volatile Base (Phenylethylamine). The diluted solution of free bases obtained by the above treatment was distilled under reduced pressure, and the distillate was received into dilute hydrochloric acid, and then the alcohol soluble base was isolated as hydrochloride. The yield was 2.90 gr. The hydrochloride formed colourless thin plates of silky lustre, and melted at 215–216°C. (uncorr.). Its analytical results agreed with the hydrochloride of the compound having the formula $C_8H_{11}N$.

No.	Subst. mg.	CO ₂ mg.	H ₂ O mg.	C%	H%	N%	Cl%
(1)	3.261	7.270	2.350	60.80	8.06	—	—
(2)	3.854	8.620	2.807	61.00	8.15	—	—
(3)	4.545	0.335 c.c. N(22.5°C., 761. 8 mm.)				8.53	—
(4)	6.245	0.461 c.c. N(22.5°C., 761. 2 mm.)				8.54	—
(5)	4.780	4.245 mg. AgCl	—	—	—	—	21.98
(6)	6.720	5.970 mg. AgCl	—	—	—	—	21.98
Calc. for $C_8H_{11}N \cdot HCl$				60.93	7.68	8.89	22.50

The chloroaurate, readily soluble in water and alcohol, crystallised in yellow thin plates of pearly lustre.

Anal. : Subst. = 0.1088, 0.2470, 0.4952; Au = 0.0468, 0.1059, 0.2115 gr.

Found : Au = 43.01, 42.87, 42.71%.

Calc. for $C_8H_{11}N \cdot HCl \cdot AuCl_3$ (Phenylethylamine chloroaurate): Au = 42.76%.

The chloroplatinate of the base, hardly soluble in water and alcohol, crystallised in small bright golden yellow prisms and melted at 247–248°C. (uncorr.) with decomposition.

Anal. : Subst. = 0.2156, 0.1523, 0.0498; Pt = 0.0645, 0.0452, 0.0148 gr.

Found : Pt = 29.92, 29.68, 29.72%.

Calc. for $(C_8H_{11}N \cdot HCl)_2 PtCl_4$ (Phenylethylamine chloroplatinate): Pt. = 29.94%.

The hydrochloride was converted into picrate by adding Na-picrate to its aqueous solution. It formed yellow prisms and melted at 170°C. (uncorr.). From these results, the volatile organic base obtained from the putrefied yeast is no doubt phenylethylamine.

II. The Base Crystallised out as Nitrate (Adenine). The residual solution after the distillation of volatile base was slightly acidified with nitric acid and by evaporation of the solution 11.50 gr. of adenine nitrate were crystallised out. Analytical results of the nitrate are as follows.

Anal.: Subst. = 0.2348; H_2O = 0.0111 gr.

Subst. = 0.2491; Nitron nitrate = 0.4477 gr.

Found: H_2O = 4.73%; HNO_3 = 30.19%.

Calc. for $\text{C}_5\text{H}_5\text{N}_5 \cdot \text{HNO}_3 \cdot \frac{1}{2}\text{H}_2\text{O}$ (Adenine nitrate): H_2O = 4.35%; HNO_3 = 30.43%.

The picrate of characteristic hairy needles is yellow and sparingly soluble in water and it decomposes at 282°C . (uncorr.).

The chloroaurate, which was converted from the picrate, crystallised in yellow prisms and melted at 263°C . (uncorr.).

Anal.: Subst. = 0.1067, 0.0723; Au = 0.0505, 0.0341 gr.

Found: Au = 47.33, 47.16%.

Calc. for $\text{C}_5\text{H}_5\text{N}_5 \cdot 2\text{HCl} \cdot 2\text{AuCl}_3 \cdot \text{H}_2\text{O}$ (Adenine chloroaurate): Au = 47.35%.

III. Precipitate by Silver Nitrate (Hypoxanthine). The precipitate by silver nitrate was decomposed by hydrochloric acid. When the filtrate from AgCl was evaporated under reduced pressure, crystals of the hydrochloride of the base (13.70 gr.) separated out. Its chloroaurate forms yellow prisms and decomposes at $246\text{--}247^\circ\text{C}$. (uncorr.).

Anal.: Subst. = 0.3015; Au = 0.1246 gr. Found: Au = 41.33%.

Calc. for $\text{C}_5\text{H}_4\text{N}_4\text{O} \cdot \text{HCl} \cdot \text{AuCl}_3$ (Hypoxanthine chloroaurate): Au = 41.42%.

The hydrochloride was also analysed as its chloroplatinate.

Anal.: Subst. = 0.2309; Pt = 0.0658 gr. Found: Pt = 28.50%.

Calc. for $(\text{C}_5\text{H}_4\text{N}_4\text{O} \cdot \text{HCl})_2 \text{PtCl}_4$ (Hypoxanthine chloroplatinate): Pt = 28.62%.

The above results agree fairly well with the data of hypoxanthine derivatives.

IV. Precipitate by Silver Nitrate and Baryta. The precipitate, prepared by silver nitrate and baryta, was treated with hydrochloric acid and sulphuric acid to remove the silver and baryta. Then phosphotungstic acid was added to the above filtrate, and the precipitate was decomposed by baryta. The filtrate from barium phosphotungstate after removing the excess of baryta by carbon dioxide was concentrated to a small volume under reduced pressure; and then hydrochloric acid was added to the solution of free base obtained by the above treatment.

The hydrochloride freed from water was treated with cold absolute alcohol and was separated as follows:

(A) *Insoluble Portion in Absolute Alcohol (Histamine)*. From this portion 7.80 gr. of colourless hygroscopic substance were obtained, which gives intensive diazo-reaction. Its picrate formed rhombic plates of bright yellow and decomposed at $232\sim 233^{\circ}\text{C}$. (uncorr.).

The chloroaurate of the base prepared from the hydrochloride crystallised in yellow prisms and decomposed at 218°C . (uncorr.).

Anal.: Subst. = 0.4131; Au = 0.2061 gr. Found: Au = 49.89%.

Calc. for $\text{C}_5\text{H}_9\text{N}_3\cdot 2\text{HCl}\cdot 2\text{AuCl}_3$ (Histamine chloroaurate): Au = 49.85%.

(B) *Soluble Portion in Absolute Alcohol (Histamine)*. The yield of the base from the precipitate, which was formed by adding saturated alcoholic solution of HgCl_2 to this portion, was 1.30 gr. as hydrochloride. The hydrochloride was hygroscopic, colourless prisms and gave intensive diazo-reaction. The natures of its picrate and chloroaurate were as follows: The picrate formed yellow rhombic crystals and decomposed at 231°C . (uncorr.). The chloroaurate of the base crystallised in golden yellow prisms and melted at 218°C . (uncorr.) with decomposition.

Anal.: Subst. = 0.2936, 0.1876; Au = 0.1464, 0.0930 gr.

Found: Au = 49.86, 49.57%.

Calc. for $\text{C}_5\text{H}_9\text{N}_3\cdot 2\text{HCl}\cdot 2\text{AuCl}_3$ (Histamine chloroaurate): Au = 49.85%.

These results agree precisely with histamine derivative in all respects.

V. *Filtrate from Silver Nitrate- and Baryta-Precipitate*. The filtrate was treated with hydrochloric acid and sulphuric acid to remove an excess of silver and baryta. Then phosphotungstic acid was added to the above solution, and the precipitate obtained thus was decomposed by baryta. The filtrate from barium phosphotungstate after removing the excess of baryta by carbon dioxide was concentrated to a small volume under reduced pressure. The solution of free base obtained from the above treatment was converted into the hydrochloride by adding hydrochloric acid. And the hydrochloride freed from water was treated with cold absolute alcohol and was separated as follows:

(A) *Insoluble Portion in Absolute Alcohol (Tyramine)*. The yield was 2.30 gr. It was colourless plates of silky lustre and gave strong Millon's reaction. The picrate formed deep yellow prisms and melted at 203°C . (uncorr.). The chloroplatinate crystallised in orange yellow,

long prisms, hardly soluble in water, decomposed at 224–225°C. (uncorr.) and remarkably gave phenol odour by ignition.

Anal.: Subst. = 0.1131, 0.0762; Pt = 0.0323, 0.0216 gr.

Found: Pt = 28.56, 28.35%.

Calc. for $(C_8H_{11}NO \cdot HCl)_2PtCl_4$ (Tyramine chloroplatinate): Pt = 28.48%.

These results agree well with tyramine derivatives.

(B) *Soluble Portion in Absolute Alcohol.* The alcohol soluble portion gave a white precipitate by the addition of saturated alcoholic solution of mercuric chloride.

(a) *Precipitate by Mercuric Chloride (Putrescine).* When the mercury was removed by sulphuretted hydrogen and the liquid freed from mercuric sulphide was evaporated to a small volume, the hydrochloride of the base was crystallised out (1.10 gr.). The picrate formed greenish yellow prisms, hardly soluble in water, and decomposed at 252–253°C. (uncorr.). The hydrochloride was also analysed as its chloroaurate (Decomp. point = 231°C.).

Anal.: Subst. = 0.3055; Au = 0.1564 gr. Found: Au = 51.19%.

Calc. for $C_4H_{12}N_2 \cdot 2HCl \cdot 2AuCl_3$ (Putrescine chloroaurate): Au = 51.35%.

The chloroplatinate of the base formed glistening orange yellow prisms, and decomposed at 222–223°C. (uncorr.). The result of the analysis was as follows:

Anal.: Subst. = 0.1994; Pt = 0.0781 gr. Found: Pt = 39.17%.

Calc. for $C_4H_{12}N_2 \cdot 2HCl \cdot PtCl_4$ (Putrescine chloroplatinate): Pt = 39.13%.

(b) *Filtrate from $HgCl_2$ -precipitate (Tyramine).* The alcoholic solution filtered from the $HgCl_2$ -precipitate was evaporated and the residue was suspended in water, treated with sulphuretted hydrogen gas and the mercuric sulphide was filtered off. Then the hydrochloride of the base (2.40 gr.) was obtained from the above filtrate. It was colourless thin plates of silky lustre and gave strong Millon's reaction. The picrate prepared from the hydrochloride formed yellow prisms and decomposed at 203°C. (uncorr.). The chloroplatinate of the base crystallised in orange yellow prisms and decomposed at 223–224°C. (uncorr.). It gave remarkably odour of phenol by ignition, and the amount of platinum in it was as following.

Anal.: Subst. = 0.1557; Pt = 0.0438 gr. Found: Pt = 28.13%.

Calc. for $(C_8H_{11}NO \cdot HCl)_2PtCl_4$ (Tyramine chloroplatinate): Pt = 28.48%.

Second Precipitate by Phosphotungstic Acid.

I. Volatile Base (Phenylethylamine). Dilute solution of free bases prepared from the precipitate which was deposited by phosphotungstic acid was distilled under reduced pressure and the distillate was received into dilute hydrochloric acid, and then alcohol soluble base was separated as hydrochloride. The yield was 4.30 gr. It was colourless thin plates having silky lustre and its M.P. being 214°C. (uncorr.). The chloroaurate of the base crystallised in yellow thin plates of pearly lustre.

Anal.: Subst. = 0.1329, 0.3435, 0.4889; Au = 0.0564, 0.1470, 0.2083 gr.

Found: Au = 42.44, 42.79, 42.61%.

Calc. for $C_8H_{11}N \cdot HCl \cdot AuCl_3$ (Phenylethylamine chloroaurate): Au = 42.76%.

The chloroplatinate crystallised in golden yellow small prisms, hardly soluble in water and alcohol. It turned to black at about 230°C. and decomposed at 246–247°C. (uncorr.).

Anal.: Subst. = 0.1530, 0.2444; Pt = 0.0459, 0.0735 gr.

Found: Pt = 30.00, 30.07%.

Calc. for $(C_8H_{11}N \cdot HCl)_2PtCl_4$ (Phenylethylamine chloroplatinate): Pt = 29.94%.

II. Non-Volatile Bases. After the volatile base was removed, the concentrated residual solution was acidified with hydrochloric acid and evaporated to dryness on a water-bath. The residual mass was separated into soluble and insoluble portions by using absolute alcohol.

(A) *Insoluble Portion in Absolutè Alcohol (KCl).* The amounts of this portion obtained were 19.80 gr. It was colourless short prisms and gave violet flame reaction. The analysis of its chloroaurate is as follows.

Anal.: Subst. = 0.1957; Au = 0.1019 gr. Found: Au = 52.07%.

Calc. for $KCl \cdot AuCl_3$ (Potassium chloroaurate): Au = 52.15%.

(B) *Soluble Portion in Absolute Alcohol.* The alcoholic solution filtered from the above insoluble portion was treated with the saturated alcoholic solution of mercuric chloride.

(a) *Precipitate by Mercuric Chloride (Cadaverine).* From the precipitate by mercuric chloride, 4.10 gr. of colourless hygroscopic crystals were obtained as hydrochloride. The picrate formed bright yellow prisms, hardly soluble in water, and melted at 223°C. (uncorr.) with decomposition. The chloroaurate crystallised in deep yellow irregular prisms and decomposed at 225°C. (uncorr.).

Anal.: Subst. = 0.4743; Au = 0.2376 gr. Found: Au = 50.09%.

Calc. for $C_8H_{14}N_2 \cdot 2HCl \cdot 2AuCl_3$ (Cadaverine chloroaurate): Au = 50.38%.

The chloroplatinate of the base formed short prisms with glistening golden yellow colour.

Anal.: Subst. = 0.1417; Pt = 0.0542 gr. Found: Pt = 38.25%.

Calc. for $C_5H_{14}N_2 \cdot 2HCl \cdot PtCl_4$ (Cadaverine chloroplatinate): Pt = 38.06%.

(b) Filtrate from Mercuric Chloride-Precipitate (Tyramine). 7.70 Gr. of hydrochloride of the base were obtained from this portion. It was colourless thin plates of silky lustre and gave intensive Millon's reaction. The picrate formed yellow prisms and decomposed at $203^\circ C$. (uncorr.). The chloroplatinate of the base was orange yellow thin plates of pearly lustre, and it decomposed at $222^\circ C$. (uncorr.) and gave a strong odour of phenol by ignition.

Anal.: Subst. = 0.1470, 0.1164; Pt = 0.0415, 0.0334 gr.

Found: Pt = 28.23, 28.69%.

Calc. for $(C_8H_{11}NO \cdot HCl)_2 \cdot PtCl_4$ (Tyramine chloroplatinate): Pt = 28.48%.

Filtrate from Phosphotungstic Acid-Precipitate. (Leucine).

The filtrate from the second precipitate by phosphotungstic acid was alkaliified by adding the saturated solution of baryta, and the precipitates of Ba-sulphate and Ba-phosphotungstate were filtered off. Then the filtrate which was freed exactly from the excess of baryta with sulphuric acid was concentrated to a small volume and 324.90 gr. of crystals were obtained.

Anal.: Subst. = 0.1018; N = 0.01107 gr. Found: N = 10.87%.

Calc. for $C_6H_{13}NO_2$ (Leucine): N = 10.69%.

It was converted into copper salt and the content of copper was determined.

Anal.: Subst. = 0.0585, 0.0917; CuO = 0.0142, 0.0228; Cu = 0.01822, 0.01135 gr.

Found: Cu = 19.40, 19.87%.

Calc. for $(C_6H_{12}NO_2)_2Cu$ (Leucine copper): Cu = 19.64%.

In conclusion, the author wishes to express his thanks to Dr. K. Yoshimura, Director of the college, for valuable advice, and to Mr. A. Yamada for the kind assistance.

Summary.

The quantities of substances isolated from 9 kg. of the dried beer yeast by putrefaction were as follows:

Phenylethylamine (as hydrochloride)	7.20 gr.
Adenine (as nitrate)	11.50 „
Hypoxanthine (as hydrochloride)	13.70 „
Histamine (as hydrochloride)	9.10 „
Tyramine (as hydrochloride)	12.40 „
Putrescine (as hydrochloride)	1.10 „
Cadaverine (as hydrochloride)	4.10 „
Leucine	324.90 „
Ammonia	128.74 „

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November, 1932.

STUDIES ON MOLECULAR-REARRANGEMENTS OF α -GLYCOLS.
VIII. REDUCTION OF $\alpha\beta$ -DINAPHTHYL KETONE (AN
ATTEMPT TO COMPARE THE ELECTRO-
NEGATIVITIES OF α - AND β -
NAPHTHYL RADICALS).

By Masao MIGITA.

Received December 3rd, 1932. Published January 28th, 1933.

Skraup⁽¹⁾ has observed in his research on the affinity requirement of organic radicals, that in the two naphthyl radicals, the affinity requirement in α -position is stronger than in β -position.

In the studies on dissociation of hexa-aryl ethanes, Gomberg and his collaborators⁽²⁾ have found that α -naphthyl radical is more potent than β -naphthyl radical, in causing the dissociation of the ethane-molecules, e.g. di- α -naphthyl-tetraphenyl ethane dissociates into the monomer to 68% in benzene solution, while di- β -naphthyl-tetraphenyl ethane dissociates to 32.3%. If it is admitted to take the dissociation degree of hexa-aryl ethanes for a criterion of electronegativities of substituents in their molecules⁽³⁾, we can infer from these results that between α - and β -naphthyl radicals the former exceeds the latter in its electronegativity.

The author⁽⁴⁾ has attained to the same result, inferring the relative electronegativities of α - and β -naphthyl radicals indirectly from the fact

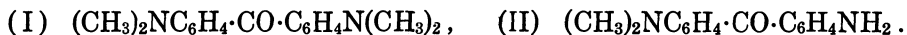
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- (1) Skraup, *Ber.*, **55** (1922), 1080.
 - (2) Gomberg, *Chem. Rev.*, **1** (1925), 104.
 - (3) Migita, this Bulletin, **7** (1932), 382.
 - (4) Migita, this Bulletin, **7** (1932), 378.

that in the rearrangement of sym. di-*p*-anisyl-di- α -naphthyl glycol⁽⁵⁾, α -naphthyl radical migrates, though to a lesser extent, as well as *p*-anisyl radical, while in the case of sym. di-*p*-anisyl-di- β -naphthyl glycol, migration of *p*-anisyl radical occurs almost exclusively.

Though it is intended, in the present work, to compare the electro-negativities of α - and β -naphthyl radicals directly by the pinacoline method from the rearrangement products of sym. $\alpha\alpha\beta\beta$ -tetranaphthyl glycol, all attempts to obtain this pinacone from $\alpha\beta$ -dinaphthyl ketone have proved unsuccessful.

Glacial acetic acid and zinc dust reduced this ketone to $\alpha\beta$ -dinaphthyl methane at higher temperature, and to $\alpha\beta$ -dinaphthyl carbinol at room temperature, as in the case of β -naphthyl-diphenyl ketone⁽⁶⁾. The author has also proved that the similar result is obtained under the same conditions in the case of α -naphthyl-diphenyl ketone. The formation of the corresponding methanes in the reduction of ketones by *zinc dust and glacial acetic acid* is considered to be rather anomalous, and the case of Michler's ketone⁽⁷⁾ is probably the only precedent found in literature.

In this anomalous reduction, negativities of the substituents are not deemed to be the directing factor, because ketones containing more negative radicals than naphthyl are not reduced to the methanes under the same conditions, as seen in the case of di-*p*-methoxy-benzophenone⁽⁸⁾ and *p*-methoxy-*p'*-ethoxy-benzophenone⁽⁹⁾. The author wishes to attribute this to the sterical influence of the substituents. The fact that Michler's ketone (I) is reduced to corresponding methane by zinc dust and acetic acid, while dimethyl-*p*-aminobenzophenone⁽⁹⁾ (II) is reduced to corresponding pinacone, seems to throw some hints on this problem.



$\alpha\beta$ -Dinaphthyl ketone remained unchanged by the action of absolute alcohol under direct sunlight, as in the case of *p*-anisyl- β -naphthyl ketone, presumably owing to its extremely small solubility in absolute alcohol.

When the ketone was reduced by magnesium and magnesium iodide, the reaction seemed to proceed for the desired direction, since evolution of heat and formation of ketyl solution with wine-colour were observed in the process of reduction. However, the reaction product was dark

(5) Bailar, *J. Am. Chem. Soc.*, **52** (1930), 3596-3603.

(6) Migita, this Bulletin, **7** (1932), 385-386.

(7) Votoček and Krauz, *Ber.*, **42** (1909), 1602.

(8) Migita, this Bulletin, **7** (1932), 335, 342.

(9) Willstätter and Goldmann, *Ber.*, **39** (1906), 3768.

coloured rosinous matter, of which purification from organic solvents was tried in vain by every means. On allowing the syrupy product to stand at room temperature for a long period, a minute quantity of granular crystals was obtained. But the yield was too poor to give a further investigation.

Experimental Part.

$\alpha\beta$ -Dinaphthyl Ketone. This ketone was prepared after Tschitschibabin and Korjagin⁽¹⁰⁾, from 30 gr. of α -bromo-naphthalene, 4 gr. of magnesium and 15 gr. of β -naphtho-nitrile. The product, purified from acetic ester, melts at 136–7°C. It dissolves in concentrated sulphuric acid with orange colour.

Reduction of $\alpha\beta$ -Dinaphthyl Ketone.

Reduction by Zinc Dust and Glacial Acetic Acid. (a) *At Boiling Temperature.* Two grams of the ketone were reduced by boiling with 8 c.c. of glacial acetic acid and 4 gr. of zinc dust, and the reaction product was usually poured into water. The resulting precipitates contained yellowish substance which is readily soluble in organic solvents imparting the solution green fluorescence, and were found freed from it only by repeated fractional crystallisation from hot ligroin. As this impurity separates out as yellowish rosinous matter from warm ligroin solution, the crude product was dissolved in hot ligroin and the solution was decanted from the rosin after full precipitation of it, and cooled quietly. White crystalline mass which deposited on the side of beaker, was gathered and recrystallised from ether. It forms thick prisms and melts at 96°C. It was identified by this melting point and elementary analysis as $\alpha\beta$ -dinaphthyl methane, prepared by Tschitschibabin⁽¹¹⁾ by reducing $\alpha\beta$ -dinaphthyl carbinol with hydrogen iodide in hot glacial acetic acid.

Anal.: Subst. = 0.0712; CO₂ = 0.2440; H₂O = 0.0396 gr.

Found: C = 93.6; H = 6.24%.

Calc. for C₂₂H₁₆ ($\alpha\beta$ -dinaphthyl methane): C = 94.0; H = 5.97%.

(b) *At Room Temperature.* To the solution of 2.2 gr. of the ketone dissolved in sufficient glacial acetic acid (ca. 400 c.c.) to keep it solution at room temperature, were added 10 gr. of zinc dust, and the reaction mixture was allowed to stand at room temperature for five days. The crude product, obtained after usual treatments, was found readily

(10) Tschitschibabin and Korjagin, *Chem. Centr.*, (1914), I, 1658.

(11) Tschitschibabin, *Ber.*, **44** (1911), 449.

soluble in organic solvents except ligroin and petroleum ether. It crystallises from a quantity of ligroin in fine white needles, grouped in burr-like masses, which melts at 112–3°C. to a colourless liquid⁽¹²⁾. It dissolves in concentrated sulphuric acid with pure blue colour. It was identified from these properties and the elementary analysis, as $\alpha\beta$ -dinaphthyl carbinol, prepared by Tschitschibabin⁽¹³⁾ from α -bromo-naphthalene and β -naphthaldehyde by Grignard's reaction. The yield was nearly quantitative.

Anal.: Subst. = 0.0684; CO₂ = 0.2219; H₂O = 0.0347 gr.

Found: C = 88.6; H = 5.70%.

Calc. for C₂₁H₁₆O ($\alpha\beta$ -dinaphthyl carbinol): C = 88.7; H = 5.64%.

Reduction by Absolute Alcohol under Direct Sunlight. Two grams of ketone and 50 c.c. of absolute alcohol were sealed in a tube and exposed to direct sunlight for about two months. Though the weather was not favourable, the net time of exposure amounted to 200 hours. During the exposure, the solution assumed brownish tint, but on opening the tube, formation of acetaldehyde was not observed and the crystals in the tube were identified as unchanged ketone which was recovered quantitatively.

Reduction by Magnesium and Magnesium Iodide. To 2 gr. of powdered magnesium, suspended in 20 c.c. ether and 30 c.c. of benzene were added 2 gr. of iodine and kept the solution boiling quite vigorously. The practically colourless solution of the magnesium iodide was cooled and to it were added 2 gr. of $\alpha\beta$ -dinaphthyl ketone dissolved in 10 c.c. of benzene. While the reaction mixture was shaken, heat was evolved and after few hours the solution assumed wine-colour. Shaking was continued until evolution of heat ceased and magnesium was uncoated. After twenty hours, the green solution was filtered from unchanged magnesium and was hydrolysed by dilute sulphuric acid with the addition of a pinch of sodium bisulphite. The benzene solution was dehydrated with sodium sulphate and the solvent was distilled off. Brown syrupy residue was easily soluble in organic solvents and purification from various organic solvents has been tried in vain. On allowing the syrupy mass to stand for about two weeks, some crystals were deposited on the side of beaker, which dissolved in concentrated sulphuric acid with intense green colouration. However, the yield was too poor to give a further investigation.

***p*-Bromo-Diphenyl.** *p*-Bromo-diphenyl was prepared after Gomberg and Bachmann⁽¹⁴⁾ by diazotizing *p*-bromo-aniline and coupling it with benzene. Purification of the crude product was, however, simplified by

(12) Tschitschibabin purified this carbinol from benzene and gave it a melting point 106–7°C. However, his sample is probably not in a reliably pure state, since benzene, in which this carbinol is rather easily soluble, is not taken for a suitable solvent for purification. The author has actually observed that the carbinol obtained by purifying the crude product from benzene, melted at 106–7°C. to a yellow liquid, while the product purified from ligroin melted at 112–3°C. to a colourless liquid.

(13) Tschitschibabin, *Ber.*, **44** (1911), 447.

(14) Gomberg and Bachmann, *J. Am. Chem. Soc.*, **46** (1924), 2339.

recrystallising it from hot ligroin with an addition of animal charcoal. It crystallises in white lamellar, melting $90-91^{\circ}\text{C}$. to colourless liquid, while the product purified by the original method⁽¹⁵⁾, melted to slightly coloured liquid at $89-90^{\circ}\text{C}$.

α -Naphthyl-Diphenyl-Ketone. This ketone was prepared from 14.4 gr. of *p*-bromo-diphenyl, 0.5 gr. of activated magnesium and 10 gr. of α -naphtho-nitrile. The resulting magnesium complex was hydrolysed and subjected to steam distillation alternately in acidic and alkaline reactions. Dark coloured product was treated with ether to remove colouring impurities, and then purified from a quantity of absolute alcohol. It crystallises in fine needles, melting at $140-141^{\circ}\text{C}$. It is sparingly soluble in cold organic solvents, especially in glacial acetic acid. It dissolves in concentrated sulphuric acid with reddish orange colouration. The yield of the purified product was about 3.5 gr.

Anal.: Subst. = 0.0627; CO_2 = 0.2055; H_2O = 0.0301 gr.

Found: C = 89.4; H = 5.38%.

Calc. for $\text{C}_{23}\text{H}_{16}\text{O}$ (α -naphthyl-diphenyl-ketone): C = 89.6; H = 5.19%.

α -Naphthyl-Diphenyl-Carbinol, $(\alpha\text{-C}_{10}\text{H}_7)(\text{C}_6\text{H}_5.\text{C}_6\text{H}_4)\text{CHOH}$. One gram of α -naphthyl-diphenyl ketone was dissolved in 300 c.c. of glacial acetic acid and was allowed to react with excess of zinc dust for four days at 25°C . The reaction mixture was treated as usual and the resulting raw product was recrystallised from ligroin. It crystallises in white microscopical prisms, melting at 131°C . to a glassy mass. It dissolves in concentrated sulphuric acid imparting the solution intense greenish blue colour. Its composition was found corresponding to carbinol or pinacone, but it was identified as the carbinol from the facts that the product gives the same colouration toward concentrated sulphuric acid, before and after fusion, and that the original ketone is reduced to corresponding methane by the same reducing agents but at the boiling temperature of the reacting mixture (See below).

Anal.: Subst. = 0.0649; CO_2 = 0.2107; H_2O = 0.0339 gr.

Found: C = 88.5; H = 5.86%.

Calc. for $\text{C}_{23}\text{H}_{18}\text{O}$ (α -naphthyl-diphenyl carbinol): C = 89.0; H = 5.81%.

The yield was practically quantitative.

α -Naphthyl-Diphenyl-Methane, $(\alpha\text{-C}_{10}\text{H}_7)(\text{C}_6\text{H}_5.\text{C}_6\text{H}_4)\text{CH}_2$. α -Naphthyl-diphenyl ketone was usually reduced in gently boiling glacial

(15) Alcoholic solution of the raw product was decolourized by zinc dust and concentrated hydrochloric acid. The solution was filtered and allowed to crystallise.

acetic acid solution with zinc dust. On pouring the reaction product into water, yellowish crystalline cakes separated and the solution turned milky. The precipitates were recrystallised twice from glacial acetic acid and finally from ligroin with an addition of animal charcoal. It crystallises in thick prisms, melting at 146°C . Purified product does not dissolve in concentrated sulphuric acid, while raw product gives greenish blue colouration toward it. This colouration is due to the presence of a small quantity of the carbinol, which is removed only by recrystallising from glacial acetic acid. The product was proved to be the corresponding methane, α -naphthyl-diphenyl methane, from its composition and molecular weight. The yield of the pure product did not exceed 40% of the theory.

Anal.: Subst. = 0.0635; CO_2 = 0.2177; H_2O = 0.0365 gr.

Found: C = 93.5; H = 6.41%.

Calc. for $\text{C}_{23}\text{H}_{18}$ (α -naphthyl-diphenyl-methane): C = 93.9; H = 6.10%.

Mole. weight: Subst. = 0.270; Camphor = 2.834 mgr.

Depres. of m.p. = 13.0°C :

Found: Mole. weight = 294. Calc. for $\text{C}_{23}\text{H}_{18}$: Mole. weight = 294.

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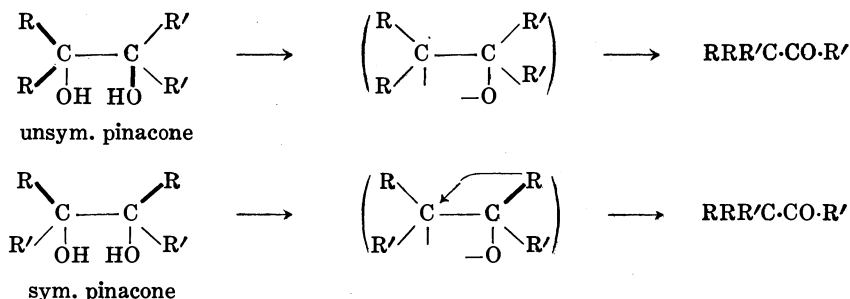
STUDIES ON MOLECULAR-REARRANGEMENTS OF α -GLYCOLS.
IX. CONCLUSION (THE PINACOLINE REARRANGEMENT
AS A METHOD OF ESTABLISHING RELATIVE ELECTRO-
NEGATIVITIES OF ORGANIC RADICALS).

By Masao MIGITA.

Received December 3rd, 1932. Published January 28th, 1933.

Migration Aptitudes of Organic Radicals. It was Meerwein⁽¹⁾ who explained the mechanism of pinacolone rearrangement by the theory of affinity requirement. His interpretation was originally intended to answer the question which hydroxyl group in *unsymmetrical* pinacone molecule is taken off, and it is impossible to explain why the radical with the larger affinity requirement has greater migration tendency in the rearrangement of a *symmetrical* pinacone.

(1) Meerwein, *Ann.*, **419** (1919), 121.



where thick bars denote larger affinity requirement.

Therefore, Tiffeneau and Lévy⁽²⁾ were obliged to conclude that a certain migratory aptitude is concerned to each radical, but this property is not necessarily concomitant with its saturation capacity. It must be specially mentioned here that they believed that each radical has its own migration tendency, since this idea has been and is still cherished by many organic chemists. Quite recently Bachmann⁽³⁾ has stated in his studies on rearrangement of unsymmetrical aromatic pinacones as follows: "The series representing the relative migration aptitudes of the groups in symmetrical pinacones does not hold for the unsymmetrical pinacones. The series for the latter type of molecule may be expressed as follows: $\text{C}_6\text{H}_5 > \text{CH}_3\text{C}_6\text{H}_4 > \text{CH}_3\text{OC}_6\text{H}_4$. It is especially striking that the *p*-anisyl group, which in the symmetrical pinacone migrates nearly exclusively with respect to the phenyl group, migrates to a lesser extent than the phenyl group when the two groups are in the unsymmetrical molecule."

The reason why Bachmann considered the above result "especially striking" consists in the fact that he understands the migration aptitude as a definite property concerned to each radical.

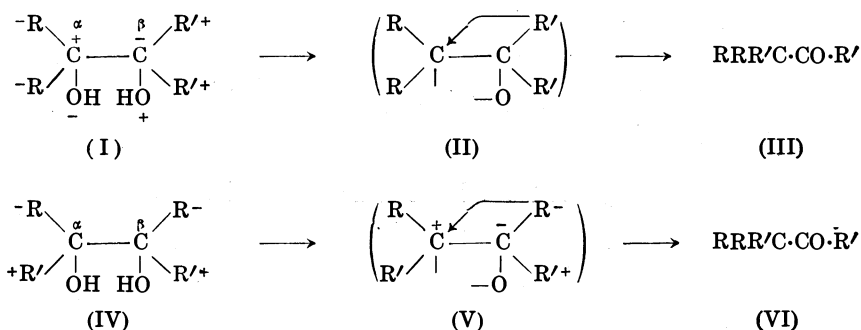
The present author⁽⁴⁾ has interpreted the pinacolone rearrangement from the electronic conception of valency and concluded that the order representing the migratory tendency of organic radicals is never constant but it may be reversed depending on the type of molecule subjected to rearrangement. By the author's theory it is quite possible to predict with certainty, the selective migration of radicals by pinacolone rearrangements irrespective of the type of pinacones. It is applicable not only to the rearrangements of pinacones, but also to those of tertiary

(2) Tiffeneau and Lévy, *Compt. rend.*, **176** (1923), 312.

(3) Bachmann, *J. Am. Chem. Soc.*, **54** (1932), 2112-18.

(4) Migita, this Bulletin, **3** (1928), 315-6.

aminoalcohols⁽⁵⁾ and of trisubstituted α -glycols⁽⁶⁾. For example, the rearrangements of *unsymmetrical* and *symmetrical* pinacones will be reviewed here, which are expressed schematically as follows:



where R is more negative than R'.

Strictly speaking, it is not selective migration of radicals, but selective elimination of two hydroxyl groups that comes into question in the rearrangement of *unsymmetrical* pinacones of the type $\text{R}_2\text{C}(\text{OH})\cdot\text{CR}'_2(\text{OH})$. As for the selective elimination of these hydroxyl groups, the author has logically deduced that the more negatively polarized hydroxyl group, that is the one bound to carbon atom combined with the more negative groups, should be more ready to be eliminated⁽⁷⁾. Thus, in formula I, the hydroxyl group attached to α -carbon atom will be more readily eliminated, which will result in formation of the fraction of molecule II. It is clear that the migration of a radical from β - to α -carbon atom in the fraction of molecule II can not be said selective, since the both radicals attached to β -carbon atom are the same. It appears, however, as if the more positive radical R' migrates with respect to the more negative radical R, when the constitution of the pinacolone formed is simply compared with that of the original pinacone.

In the rearrangement of *symmetrical* pinacones the fraction of molecule shown in formula V will be produced intermediately, in which the α -carbon atom has extremely positive polarity, since it has been deprived of a part of its bond-forming electrons with the elimination of the hydroxyl group. Therefore, if one of the two groups attached to β -carbon atom migrates to α -carbon atom in order to make least the

(5) Migita, this Bulletin, **3** (1928), 313-314.

(6) Migita, *ibid.*, **4** (1929), 57-65.

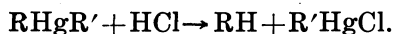
(7) Migita, *ibid.*, **3** (1928), 312-313.

disturbance of the affinity, the group that wanders should be the one that is more negative. Thus migration of the more negative group will chiefly take place in the rearrangement of symmetrical pinacones.

It is concluded that the electronegativities of the substituents in the molecules exert directing influence on the selective elimination of the two hydroxyl groups in the rearrangement of unsymmetrical pinacones and on the selective migration of radicals in the case of symmetrical pinacones.

Relative Electronegativities of Organic Radicals. If migration of radicals in the rearrangement of a pinacone can be predicted by their electronegativities, as shown above, conversely the relative electronegativities of any two radicals R and R' can be determined from the rearrangement products of the symmetrical or unsymmetrical pinacone containing the two radicals in question. For this purpose, it is sufficient to analyse organic acids produced by the hydrolysis of the rearrangement products. Thus a pinacoline rearrangement offers a simple method to compare electronegativities of organic radicals.

An interesting method to determine relative electronegativities of organic radicals has been given by Kharasch and Marker⁽⁸⁾, in which mercury is coupled with two organic radicals R and R' and the resulting compound is treated with hydrogen chloride. The reaction runs as follows:



It is plausible to assume that the more electronegative of the two radicals R and R' combines with H⁺ to form corresponding hydrocarbon.

Though this method exceeds the pinacoline method in its theoretical interest, it has some disadvantages for practical purpose. Firstly it is generally not so easy to prepare an organomercuric compound containing two given radicals as to prepare a pinacone with the same radicals, and secondly isolation and identification of a mixture of organomercuric chlorides will be in most cases more troublesome work than in the case of a mixture of organic acids⁽⁹⁾.

In the pinacoline method the pinacones of either symmetrical or unsymmetrical type which contain the two radicals to be compared may

(8) Kharasch and Marker, *J. Am. Chem. Soc.*, **48** (1926), 3130.

(9) Analysis of a mixture of organomercuric chlorides by its mercury content and that of organic acids by the silver value are applicable only when no high degree of accuracy is demanded.

be used⁽¹⁰⁾, but the symmetrical pinacone is preferable to the other on account of its easiness of preparation. It is especially so when the electronegativities of aromatic radicals are compared, since in this case a simple method is available as described below. Under certain conditions, we may obtain pinacolines, instead of pinacones, when certain aromatic ketones are reduced by glacial acetic acid and zinc dust. It has been proved experimentally as well as theoretically that this direct pinacolone formation from a ketone takes place when both radicals attached to carbonyl group are of high electronegativities⁽¹¹⁾. Therefore, if the ketone $\text{RCO.R}'$ is reduced to pinacolone, while the ketone $\text{RCO.R}''$ to pinacone, we can conclude that R' is more negative than R'' . Thus, we can compare the relative electronegativities of aromatic radicals simply from the reduction products of two suitable ketones.

In the foregoing works the author has attempted to compare electronegativities of several highly negative aromatic radicals by pinacolone method and obtained the following series,



which contains some supplements as well as confirmations to the series of electronegativities given by Kharasch and collaborators. Hithertofore, *p*-anisyl has been considered to be the most electronegative radical but it is found that *p*-ethoxyphenyl radical is by far more negative. β -Naphthyl radical is proved to be more positive than α -naphthyl radical and to rank nearly with diphenyl radical with respect to its negativity.

Dissociation of Pinacones. The criterion of the stability of a carbon-to-carbon bond is the affinity of the bound radicals for the binding electrons. When the electrons are closely held by both carbon nuclei, the bond is stable; when they are displaced away from one or both nuclei the bond is unstable. Therefore, we can distinguish two cases in unstable linkages between two carbon atoms, thus:

1. Linkage between two radicals of very slight electronegativities, in this case the binding electrons are displaced away from both carbon nuclei.
2. Linkage between an extremely electronegative organic radical and a weakly electronegative one, in which the bond-forming electrons are held at a distance from one nucleus.

(10) It must be remembered that the relation between migration aptitude and electronegativity is reversed in these two cases.

(11) Migita, this Bulletin, 7 (1932), 335, 342, 380.

Dissociation of hexa-aryl ethanes into free radicals and high reactivity of chlorine atom in triarylmethyl chlorides may be cited in illustration of the cases 1 and 2 respectively.

Aromatic pinacones bear close resemblance to hexa-aryl ethanes with respect to the negativities of substituents, and their molecules have unstable linkage of the first kind between the two carbon atoms in chain. Therefore they are naturally assumed to dissociate with production of free radicals under certain conditions, as in the case of hexa-aryl ethanes. This assumption has been confirmed experimentally⁽¹²⁾ by the fact that iodomagnesium ketyl radicals with tervalent carbon atoms, $RR'C\cdot OMgI$, are formed when aromatic ketones are reduced by binary mixture of magnesium and its iodide in benzene-ether solution. The formation of free ketyl radicals is recognized by the development of intense colourations, sensible toward oxygen, in the process of reduction.

Besides this, aromatic pinacones undergo another kind of dissociation, that is scission into ketones and carbinols, which is also attributable to the presence of unstable linkage in the molecule. According to literature, the dissociation of aromatic pinacones into ketones and carbinols takes place nearly exclusively at their melting points, tetra-*p*-bromobenzophenone⁽¹³⁾ is the only pinacone that undergoes rearrangement and this sort of dissociation simultaneously by the action of acetyl chloride. Being interested in this singular instance, the author has carried out close experiment with tetra-*p*-methoxy-benzopinacone under the same conditions, but dissociation into ketone and carbinol could not be observed.

The author has observed that the dissociation into ketone and carbinol takes place not only in aromatic pinacones, but also in $\alpha\alpha$ -dimethyl-

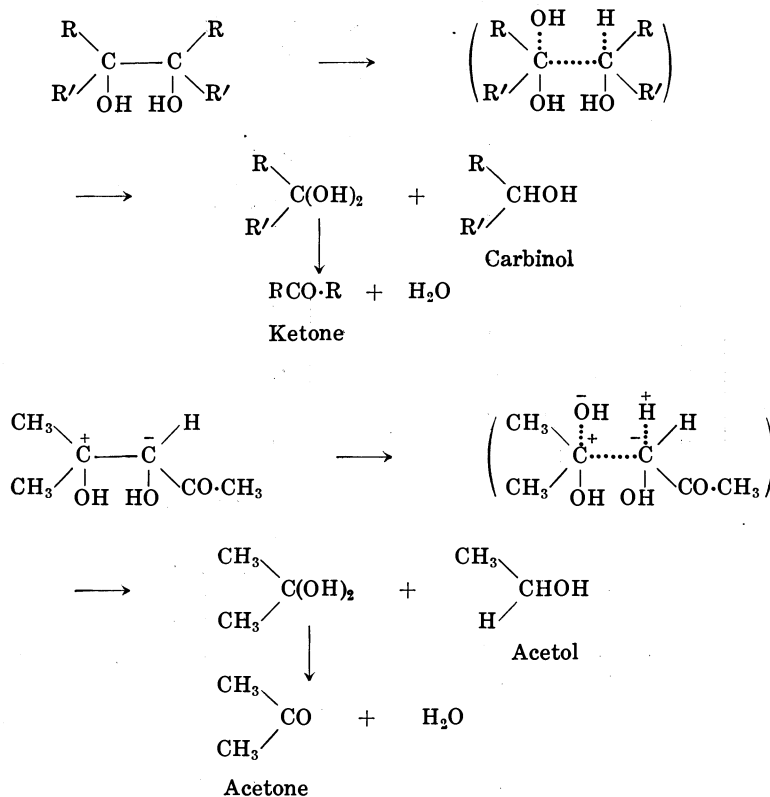
β -acetyl glycol, $\begin{array}{c} \text{CH}_3 \\ \diagup \\ \text{C} \\ \diagdown \\ \text{CH}_3 \end{array} - \begin{array}{c} \text{H} \\ \diagup \\ \text{C} \\ \diagdown \\ \text{OH} \end{array} - \text{COCH}_3$, an aliphatic glycol containing unstable linkage of the second kind, and that with far greater facility⁽¹⁴⁾.

The mechanism of dissociation into ketone and carbinol can be interpreted as follows: In the first stage of the reaction, addition of water takes place at the two adjacent carbon atoms with unstable linkages, which weakens more the bond between these carbon atoms and results in scission of the molecule at this point.

(12) Gomberg and Bailar, Jr., *J. Am. Chem. Soc.*, **51** (1929), 2229.

(13) Montagne, *Rec. trav. chim.*, **43** (1924), 126-142.

(14) Warming with dilute acid or alkali is sufficient to cause the scission of the glycol. Migita, this Bulletin, **4** (1929), 226-7.



Addition of water is naturally expected to occur easier when the polarities of the two carbon atoms are of different signs than when they are same. This is the reason why dimethyl-acetyl glycol with the second kind of unstable linkage exceeds aromatic pinacones with the first kind of unstable linkage in its facility of dissociation into ketone and carbinol.

Reduction of Aromatic Ketones with Highly Negative Groups. Aromatic pinacones are generally obtained by reducing corresponding ketones (i) with zinc dust and glacial acetic acid, (ii) with absolute alcohol under direct sunlight or (iii) with the binary mixture of magnesium and magnesium iodide in benzene-ether solution. The author has reduced several aromatic ketones with highly negative groups by these methods and found that the products are not necessarily pinacones, but they may be pinacolines, carbinols or hydrocarbons under certain conditions (See the Table below).

Reduction of some Aromatic Ketones with Highly Negative Radicals.

Ketone, RCO-R'		Reducing Agents.			
R•	R' •	Glacial acetic acid and zinc dust.		Absolute alcohol under direct sunlight.	Magnesium iodide and magnesium.
		At room temp.	At higher temp.		
CH ₃ O-	CH ₃ O-	R ₃ C·CO·R	R ₃ C·CO·R	R ₂ C(OH)·C(OH)R ₂	Rosinous matter.
CH ₃ O-	C ₂ H ₅ O-	—	RR' ₂ C·CO·R	RR' ₂ C·CO·R	—
CH ₃ O-		RR'/C(OH)·C(OH)RR'	R ₂ R'/C·CO·R'	Not reduced.	—
*CH ₃ O-		RR'/C(OH)·C(OH)RR'	R ₂ R'/C·CO·R'	Not reduced.	—
		RR'/CHOH	RR'/CH ₂	Not reduced.	Pinacone ?
		RR'/CHOH	RR'/CH ₂	—	—
		RR'/CHOH	RR'/CH ₂	Not reduced.	RR'/C(OH)·C(OH)RR'
		—	R ₂ C(OH)·C(OH)R ₂ ^{a)}	R ₂ C(OH)·C(OH)R ₂ ^{b)}	R ₂ C(OH)·C(OH)R ₂ ^{c)}
CH ₃ O-		RR'/C(OH)·C(OH)RR' ^{d)}	R ₂ R'/C·CO·R' ^{e)}	—	RR'/C(OH)·C(OH)RR' ^{d)}
CH ₃ O-	CH ₃ -	RR'/C(OH)·C(OH)RR' ^{d)}	R ₂ R'/C·CO·R' ^{d)}	—	RR'/C(OH)·C(OH)RR' ^{d)}
(CH ₃) ₂ N-	H ₂ N-	—	RR'/C(OH)·C(OH)RR' ^{f)}	—	—
(CH ₃) ₂ N-	(CH ₃) ₂ N-	—	R ₂ CH ₂ ^{g)}	—	RR'/C(OH)·C(OH)RR' ^{e)}

* Unpublished.

a) Zagumenni, *Ber.*, **14** (1881), 1402.

b) Ciamician and Silber, *Ber.*, **33** (1900), 2912.

c) Gomberg and Bachmann, *J. Am. Chem. Soc.*, **49** (1927), 249, 254.

d) Bachmann and Moser, *J. Am. Chem. Soc.*, **54** (1932), 1126.

e) Tiffeneau and Orékhoff, *Bull. Soc. chim.*, **37** (1925), 430.

f) Willstätter and Goldmann, *Ber.*, **39** (1906), 3768.

g) Votoček and Krauz, *Ber.*, **42** (1909), 1602.

(i) *Reduction by Zinc Dust and Glacial Acetic Acid.* Aromatic ketones containing highly negative groups are generally reduced by zinc dust and acetic acid to pinacones at ordinary temperature and pinacolines at higher temperature; however, if the negativities of the groups are extremely high, pinacolines are formed even at ordinary temperature as in the case of di-*p*-methoxy-benzophenone.

α -Naphthyl-diphenyl and β -naphthyl-diphenyl ketones and $\alpha\beta$ -dinaphthyl ketone give carbinols at room temperature and hydrocarbons at higher temperature. This behaviour is considered to concern with sterical problem, rather than with negativity problem.

(ii) *Reduction by Absolute Alcohol under Direct Sunlight.* This method seems inapplicable to ketones which are difficultly soluble in alcohol. It is highly interesting that *p*-methoxy-*p'*-ethoxy-benzophenone is not reduced to pinacone but to pinacoline by this method, while di-*p*-methoxy-benzophenone gives pinacone under the same conditions. We can see, here also, the influence of highly negative substituents on a pinacone in its reactivity.

(iii) *Reduction by Magnesium and Magnesium Iodide.* Reduction by this method has been reported not only to give an excellent yield such as from 75 to 100 percent, with many aromatic ketones, but also to be successful to the ketones to which all other methods fail. The present author has also experienced that β -naphthyl-diphenyl ketone is reduced to corresponding pinacone only by this method. However, this method seems to give less satisfactory results in the reduction of ketones containing *p*-anisyl radical, for example, Bachmann and Moser⁽¹⁵⁾ observed that 4-methoxy-, 4-methoxy-4'-methoxy-, and 4-methoxy-4'-phenyl-benzophenones were reduced to corresponding pinacones with the yields of 45, 2 and 35% respectively. The author did not succeed in reducing di-*p*-methoxybenzophenone by this method.

In conclusion, the author begs to tender his sincere thanks to Prof. K. Matsubara for his kind advices and encouragements throughout this work.

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(15) Bachmann and Moser, *J. Am. Chem. Soc.*, **54** (1932), 1126.

VEREINFACHUNG DER DARSTELLUNGSWEISE VON EINIGEN GLUCOSE-MONO-SCHWEFELSAURESSALZEN UND ÜBER IHRE OPTISCHE DREHUNGSVERMÖGEN.

Von Tokuro SODA.

Eingegangen am 21. Dezember, 1932. Ausgegeben am 28. Februar, 1933.

Wenn man nach der bisher bekannten Darstellungsweise die Metallsalze der Glucose-mono-schwefelsäure einheitlich gewinnen will, so muss man erst schön kristallisierbares Brucinsalz darstellen, weil sonst un-reagierter freier Zucker sich nicht von dem gebildeten Salz trennen lässt. Dann wird dieses Brucinsalz durch Ba-hydroxyd zum Ba-salz umgesetzt und dieses Ba-salz weiter mit sulfat der gewünschten Metallen behandelt, wobei die Menge des Sulfates genau dem Barium Gehalt entsprechen muss. Diese Prozesse sind etwas umständlich, besonders wenn man häufig z.B. K- oder Na-salz darzustellen hat, wie bei meinen Versuchen über Gluco-sulfatase⁽¹⁾ der Fall war. Es ist daher erwünscht die Darstellungsweise etwas zu vereinfachen.

Meine früheren Versuche⁽²⁾ zeigten dass Glucose-mono-schwefelsauresalze durch die Hefe nicht vergoren liessen. Daher sieht man leicht ein dass der nicht sulfonierte Zucker durch Vergärung beseitigt werden kann. Unter Berücksichtigung dieser Tatsache, habe ich die Darstellungsweise von Glucose-mono-schwefelsauresalzen in folgendermassen modifiziert: Der Veresterungsprozess ist im wesentlichen derselbe wie in früheren Mitteilung geschildert wurde.

20 gr. gut getrocknete Glucose wird in ein kleines kölbchen eingenommen und mit 75 ccm. Pyridin heiss gelöst. Die abgekühlte Lösung wird in ein Reagensglas, die sich mit einem Rührerwerk, einem Thermometer und einen Tropfentrichter versehen ist, eingegossen und mit Eiswasser gekühlt. Im Tropfentrichter bringt man ein Gemisch von 7 ccm. Chlorsulfonsäure und 18 ccm. Chloroform ein, und unter heftigem Rühren wird dieses Gemisch langsam ins Reagensglas tropfenweise zugesetzt, dabei beachtet man dass die Temperatur nicht über 10°C. steigt. Sobald das gesamte Gemisch zugesetzt ist, entfernt man die Kühlung und rührt etwa eine Stunde weiter. Nach Stehen über Nacht, setzt sich die sirupöse

(1) Soda and Hattori, dieses Bulletin, **6** (1931), 258; *J. Chem. Soc. Japan*, **54** (1933), 59.

(2) Soda, *Biochem. Z.*, **135** (1923), 623.

Reaktionsprodukt auf dem Boden ab. Sie wird von der oberen Pyridin Schicht durch Dekantieren abgetrennt und in wenig Wasser gelöst. Die Lösung wird erst im Vakuum abgedampft um Chloroform zu befreien, dann setzt man 80 gr. Bleioxyd Pulver zu und destilliert im Vakuum weiter ab bis Pyridin frei wird, dabei vermeidet man zu stark einzudicken. Man filtriert die Pyridin freie Lösung vom Rückstand ab. Das Filtrat ist frei von Sulfation, es enthält noch Bleisalz von Glucose-mono-schwefelsäure, freie Glucose, eine Spur von Chlorion und Bleihydroxyd. Das letztere kann durch Zuleiten des Kohlendioxyds leicht ausgefällt werden. Chlorion wird durch Zusatz von Silbersulfatlösung gefällt und mit Hilfe von Tierkohle völlig beseitigt. Das Filtrat wird nun mit Wasser auf ca. 600 ccm. verdünnt und danach leitet man Schwefelwasserstoff bis kein Niederschlag mehr gebildet wird. Der Überschuss von Schwefelwasserstoff wird dann durch Luftstrom entfernt. In dieser Weise erhält man die freie Glucose-mono-schwefelsäurelösung.

Es ist nun bereit mit beliebigen Base zu neutralisieren. Dabei ist es natürlich zweckmässig Carbonat oder Oxyd anzuwenden, falls sie unlöslich sind. Nun setzt man 20 bis 30 gr. Presshefe (Bäckereihefe von Fleishmann) zu und lüftet ein bis zwei Tage durch. Die ausgegorene Flüssigkeit wird abfiltriert, eingeengt im Vakuum (40°C.) und das Salz mit absolutem Alkohol ausgefällt.

Die direkt darstellbaren Salze durch dieses Verfahren sind natürlich beschränkt auf diejenige, die auf die Hefe nicht giftig wirken. Erfahrungsgemäss, sind K-, Na-, Ca- und Ba-salze in dieser Weise darstellbar. Li- oder Mg-salze sind nicht giftig aber ihre Salze scheinen beim Einengen teilweise sich zu zersetzen. Die Darstellungsweise dieser und auch anderer Salzen werden untersucht. Wenn die Metalle gegen die Hefe giftig sind, so muss man über das Ba-salz umgehen. Man könnte befürchten dass beim Abdestillieren des Pyridins in Gegenwart von Bleioxyd durch Bildung von Bleihydroxyd, die Konfigurationsänderung eintreten würde, und ob die Glucose auch im heissen Pyridin unverändert bliebe.* Deswegen habe ich das Brucinsalz aus der freien Glucose-mono-schwefelsäuren Lösung dargestellt und dieses mit dem durch das frühere Verfahren dargestellten Salz verglichen. Wie man aus den folgenden Experimente sieht, zeigt es sich dabei dass das neue Verfahren einwandfrei anwendbar ist.

* Man kann auch das Abdestillieren des Pyridins mit Bleioxyd in folgenderweise vermeiden: Das Pyridin wird erst durch Destillation mit Bariumcarbonat ausgetrieben, sodann fällt man das Barium mit Überschuss von Schwefelsäure aus. Ferner wird der Überschuss von Schwefelsäure durch Bleioxyd beseitigt und das gebildete Bleisalz von Glucose-mono-schwefelsäure wie üblich behandelt.

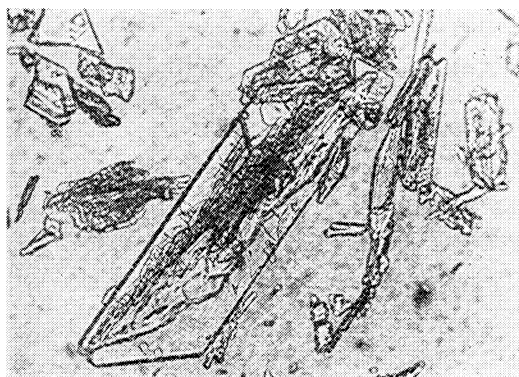
Darstellung des Brucinsalzes. Die freie Glucose-mono-schwefelsäurelösung wird, wie oben angegeben, erst dargestellt. Dabei wird der freie Säuren Gehalt vorher von der gefällten Menge des Bleisulfids geschätzt; dann wird ein kleiner Überschuss von alkoholischer Brucin-lösung in die Säure-lösung zugesetzt und im Vakuum (40 bis 45°C.) eingeeengt. Die erst ausgeschiedene weisse Masse ist freies Brucin; es wird daher beseitigt und weiter bis zum Sirup eingeeengt, der beim Erkalten erstarrt. Man löst ihn heiss auf dem Wasserbad in wenig Wasser und setzt absoluten Alkohol allmählich zu bis die Lösung sich schwach trübt. Beim Erkalten kristallisiert das Brucinsalz aus. Ausbeute: 12 gr.

Vergleich der Eigenschaften des nach neuem Verfahren dargestellten Brucinsalzes mit der des früheren Salzes

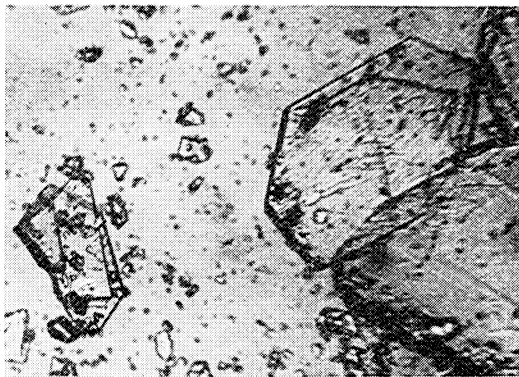
	Dargestellt nach dem neuen Verfahren	Dargestellt nach dem früheren Verfahren
1. Zersetzungspunkt	178°C.	178°, 180°C.
2. $[\alpha]_D$ (Anfangsdrehung)	-1.57° (nach 15')	-0.75° (nach 10') -2.53° (nach 20')
$[\alpha]_D$ (Enddrehung)	-5.69° (c. = 2.551; 15°C.)	-5.65° (c. = 2.654; 18.5°C.) -5.60° (c. = 2.766; 20°C.)
3. Schwefelgehalt	4.84%, 4.86% (Berechnet für $C_6H_{11}O_6SO_3H \cdot \frac{1}{2}H_2O$ 4.82%)	4.86%
4. Brechungssexponenten sind gleich für beiden Salzen:	$n_1 = 1.544$, $n_2 = 1.6555$	

Also sind die beiden Brucinsalze identisch.

Die Kristallform des Brucinsalzes



(aus Aceton und Wasser)



(aus Wasser)

Kalium Glucose-mono-schwefelsäure. Vom obigen Brucinsalz wurde erst das Ba-salz und danach durch Umsetzen mit Kaliumsulfat, das K-salz dargestellt. Es zeigte sich eine starke Mutarotation; nämlich, man beobachtete anfangs $[\alpha]_D^{25} = +23.4^\circ$; (nach 15'); nach 185', $+36.5^\circ$ ($c = 1.751$).

Aus dem zweiten Ansatz wurde nach oben angegebenem Verfahren zuerst die Lösung von freien Glucose-mono-schwefelsäure dargestellt, mit KOH neutralisiert und durch Hefe vergoren. Das Filtrat vom Gärgut wurde eingengt und aus absolutem Alkohol gefällt. Die Ausbeute beträgt 7 gr. Die nach dem Umfällen bis zur Gewichtskonstanz getrocknete Substanz (100°C. im Vakuum) ergab bei der Analyse folgende Werte:

Anal.: Subst. = 0.1173, 0.1047, 0.1869; $K_2SO_4 = 0.0347, 0.0309$;

$BaSO_4 = 0.1502$ gr.

Gef.: K = 13.27, 13.25; S = 11.03%.

Ber. für $C_6H_{12}O_6SO_3K$: K = 13.11; S = 10.75%.

Die wässrige Lösung dieses Salzes zeigt folgende Mutarotation: 0.489 gr. Substanz in 25 ccm. Wasser gelöst und polarisiert im 200 mm. Rohr (Temp. 14°C.).

Zeit (Min.)	α	$[\alpha]_{5461}$	$[\alpha]_D$
10	+1.08	+26.0	
30	1.36	34.7	
60	1.40	35.7	
135	1.50	38.3	
190	1.58	40.3	
250	1.63	41.6	
2830	1.72	44.0	+37.3

$[\alpha]_D$ berechnet aus $[\alpha]_{5461}$ durch den Rotationsdispersionsfaktor vom gewöhnlichen Zucker (1.181): $44.0 : 1.181 = 37.3$

Die spezifische Drehung von der freien Glucose-mono-schwefelsäure, berechnet aus der Drehung des K-salzes:

$$[\alpha]_D = \frac{37.3 \times 298}{260} = +42.8^\circ$$

Die zweite Beobachtung der Mutarotation: 0.9343 gr. Substanz 50 ccm. Wasser gelöst und polarisiert in 200 mm. Rohr (12°C.).

Min.	α	$[\alpha]_{5461}$
20	1.19	31.8
50	1.30	34.8
170	1.47	39.3
1610	1.64	43.9

Natrium Glucose-mono-schwefelsäure wird dargestellt nach gleichen Verfahren wie beim K-salz. Ausbeute: 9.5 gr. Dieses Salz verhält sich beim Ausfällen aus Alkohol etwas verschieden als die anderen Salze: nämlich, es wird nicht als ganz festes Pulver gefällt, sondern als zähe klumpige Masse, die sich allmählig erstarrt. Es enthält kaum Alkohol, aber reichliche Menge von Wasser. Es ist sehr hygroskopisch; erhitzt auf 80°C. im Vakuum, quillt es sich auf, und nach mehrere Tagen, verliert es etwa 20% seiner Gewicht. Auf 100°C. erhitzt, nimmt sein Gewicht weiter ab, jedoch mit Zersetzung. Die Analyse des auf 80°C. getrocknete Substanz zeigte folgende Zahlen:

Anal.: Subst. = 0.2154, 0.2038; $\text{Na}_2\text{SO}_4 = 0.0513$; $\text{BaSO}_4 = 0.1585$ gr.

Gef.: Na = 7.71; S = 10.69%.

Ber. für $\text{C}_6\text{H}_{11}\text{O}_6\text{SO}_3\text{Na} \cdot \text{H}_2\text{O}$: Na = 7.68; S = 10.65%.

Durch Aufbewahren auf längere Zeit (etwa 2 Monate) über Phosphor-pentoxyd im Vakuum verliert dieses Salz vollständig sein Wasser. 0.3523 gr. Substanz (Wasser frei) in 10 ccm. Wasser gelöst und in 100 mm. Rohr polarisiert:

Min.	α	$[\alpha]_{5461}$	$[\alpha]_D$ (ber.)	$[\alpha]_D$ (ber. für freie Säure)
10	+1.63	+46.3		
30	1.61	45.7		
70	1.56	44.3		
125	1.54	43.7		
24 Stde.	1.54	43.7	+37.0	40.1

Barium Glucose-mono-schwefelsäure ist durch Umsetzen des Bleisalzes dargestellt indem man in Bleisalzlösung in Gegenwart von BaCO_3 Schwefelwasserstoff leitet. Freie Glucose wird dann vergoren und wie üblich behandelt. Ausbeute: 11 gr. Das Ba-salz, getrocknet auf 80°C. im Vakuum, zeigte folgende Analysenwerte:

Anal.: Subst. = 0.1658, 0.1369; $\text{BaSO}_4 = 0.0552$, 0.0923 gr.

Gef.: Ba = 19.58; S = 9.28%.

Ber. für $(\text{C}_6\text{H}_{11}\text{O}_6\text{SO}_3)_2\text{Ba} \cdot \text{C}_2\text{H}_6\text{O}$: Ba = 19.55; S = 9.15%.

Das Drehungsvermögen der wässrigen Lösung war folgend: 0.3896 gr. Substanz wurde in 10 ccm. Wasser gelöst und im 100 mm. Rohr bei 17.5°C. polarisiert.

Min.	α	$[\alpha]_{5461}$	$[\alpha]_D$ (beobachtet)
20	1.63	41.8	
19 Stde.	1.50	+38.5	+32.6
$[\alpha]_D$ Wert berechnet aus $[\alpha]_{5461} = +32.6^\circ$			
$[\alpha]_D$ Wert für freie Säure umgerechnet = +43.7°			

Calcium Glucose-mono-schwefelsäure. Dieselbe Darstellungsweise wie beim Ba-salz ist anwendbar. Ausbeute beträgt 15 gr. Dieses Salz enthält reichliche Menge von Alkohol; sein Gewicht nimmt etwa 20% ab, wenn es im Vakuum auf 100°C. getrocknet wird.

Anal.: Subst. = 0.1275, 0.2163; CaSO_4 = 0.0272; BaSO_4 = 0.1527 gr.

Gef.: Ca = 6.28; S = 9.74%.

Ber. für $(\text{C}_6\text{H}_{11}\text{O}_6\text{SO}_3)_2\text{Ca} \cdot 2\text{C}_2\text{H}_5\text{O}$: Ca = 6.17; S = 9.85%.

Es zeigte folgende Mutarotation: 0.2678 gr. Substanz in 10 ccm. Wasser gelöst und in 100 mm. Rohr polarisiert (16°C.).

Min.	α	$[\alpha]_{5461}$	$[\alpha]_D$
10	+1.27	47.4	
20	1.22	45.5	
30	1.18	44.1	
40	1.17	43.7	
65	1.14	42.6	
65	1.10	41.1	
155	1.07	40.0	
215	1.05	39.2	
275	1.04	38.8	
395	1.03	38.5	
48 Stde.	1.02	38.1	32.3 (ber.)

Man rechnet daraus für die freie Säure um' $[\alpha]_D = +40.4^\circ$

Aus obigen Experimente geht es hervor, dass für die Rotationsdispersion der Glucose-mono-schwefelsäuresalzen $[\alpha]_{5461} : [\alpha]_D = 1.181$ ist; d.h. diese Salze haben dieselbe Rotationsdispersion wie die freien Zucker. Ferner, wenn man die spezifische Drehung $[\alpha]_D$ von freien Glucose-mono-schwefelsäure berechnet, so erhält man annähernd die gleichen Werte: $+42.8^\circ$ aus K-salz, $+40.1^\circ$ aus Na-salz, $+43.7^\circ$ aus Ba-salz und $+40.4^\circ$ aus Ca-salz. Der Einfluss von Metallionen scheint also nur gering zu sein.

Berücksichtigt man nun auf ihre Mutarotation, so bemerkt man dass die Mutarotation beim K-salz sehr stark zunehmend zeigt, während bei den anderen immer abnehmend zeigen. Diese Mutarotation verläuft nicht nach dem Schema der monomolekularen Reaktion, sondern ihre Anfangsgeschwindigkeit ist viel grösser, wie man aus folgenden Kurven sieht.

Die Mutarotation von Kalium Glucose-mono-schwefelsäure

Min.	$[\alpha]_{5461}$	$\alpha_\infty - \alpha$	$\log (\alpha_\infty - \alpha)$
10	26.0	18.0	1.25
15	27.7	16.3	1.21
20	31.8	12.2	1.08
30	34.7	9.3	0.97
50	34.8	9.2	0.96
60	35.7	8.3	0.92
135	33.3	5.7	0.76
170	39.3	4.7	0.67
190	40.3	3.7	0.57
250	41.6	2.4	0.38
∞	44.0		

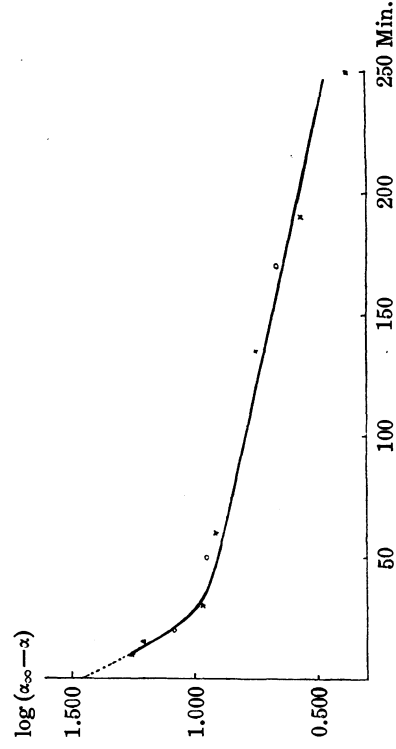


Abb. 1. K-Glucose schwefelsäure.

Die Mutarotation von Calcium Glucose-mono-schwefelsäure

Min.	$[\alpha]_{5461}$	$\alpha - \alpha_\infty$	$\log (\alpha - \alpha_\infty)$
10	47.4	9.3	0.968
20	45.5	7.4	0.869
30	44.1	6.0	0.778
40	43.7	5.6	0.748
65	42.6	4.5	0.653
95	41.1	3.0	0.477
155	40.0	1.9	0.279
215	39.2	1.1	0.041
275	38.8	0.7	-0.155
∞	38.1		

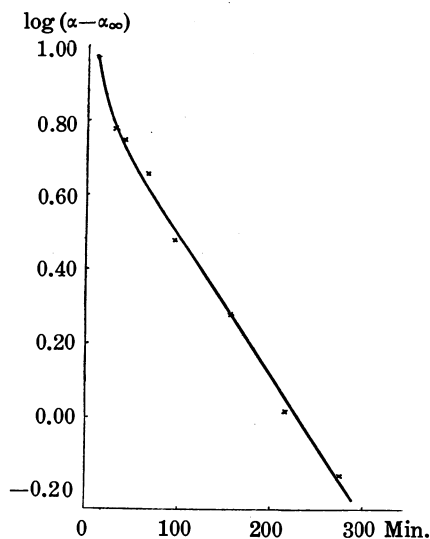


Abb. 2. Ca-Glucose schwefelsäure.

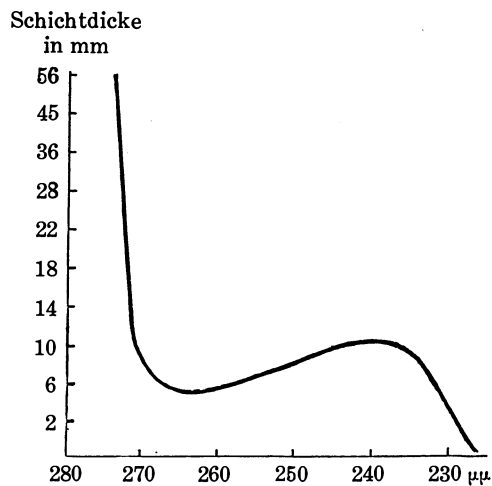


Abb. 3. Absorptionsband von K-Glucose-mono-schwefelsäure 0.560 Mol. (Wasser).

Nun, Ohle⁽³⁾ hat bewiesen dass bei unsre Glucose-mono-schwefelsäure ihre 6-te CH_2OH verestert sei; auch äussert er die Meinung dass der Pyranose-ring wegen des Einflusses der SO_3 -Gruppe sehr labil wird und vielmehr geneigt sei Furanose-ring zu bilden; infolgedessen ist in der Lösung reichliche Menge von Aldehydform existenzfähig. Für die Beweisführung der Aldehydform, hat Ohle fuchsinschwefligen Säure angewandt. Das Absorptionsspektrum des obigen K-salzes jedoch zeigt ein Absorptionsband gegen $263\mu\mu$; es ist also deutlich nach kurzwelligem Teil verschoben als das gewöhnliche CO-Band ($280\mu\mu$).

Ohle hat auch angemerkt dass Glucose-6-mono-schwefelsäure leicht in Fruktose-derivat übergehen kann, aber die obigen Präparate zeigen keine Ketosen-reaktion. Als Ketosen-reaktion fielen die Seliwanoffsche und Ekkertsche Proben ganz negativ aus. α -Naphthol-Probe die Z. Dische⁽⁴⁾ aufgeschlagen hat und die auch bei uns studiert und als sehr spezifische und empfindliche Reaktion (0.2 mg. Fruktose in 5 ccm. nachweisbar) erwiesen wurde, zeigte auch keine charakteristische blaue Färbung von der Fruktose. Also, das oben geschilderte Verfahren ist mild genug um die Gefahr von Übergang ins Fruktose-derivate zu entkommen.

(3) *Biochem. Z.*, **136** (1923), 446; *Z. angew. Chem.* **43** (1930), 217; *Chemie d. Monosaccharide und d. Glykolyse* (1931) 97, 99, 131.

(4) *Chem. Abstr.*, **23** (1929), 4766.

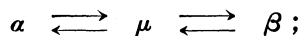
Wenn die Mutarotationskurve des K-salzes bis zu Zeit Null extrapoliert wird, so erhält man für die Anfangsdrehung ungefähr $[\alpha]_{5461} = +16^\circ$ oder $[\alpha]_D = +13.5^\circ$. Daraus wird $[\alpha]_D$ von Glucose Teil als 22.4° errechnet werden: $13.5 \times 298 : 180 = 22.4$, angenommen dass die substituierte $-\text{OSO}_3\text{H}$ Gruppe am C(6) nur geringen Einfluss auf der Drehung haben würde. Dieser Wert liegt sehr nahe der Drehung von β -Glucopyranose ($+20^\circ$).

Die Drehung der freien Glucofuranose ist noch nicht bekannt, aber neulich hat Haworth⁽⁵⁾ die Drehung von α - und β -Aethylglucofuranosid angegeben. Unten wird die bisher bekannten Drehungen tabuliert:

	Aethylglucosid		Glucose	
	α	β	α	β
Pyranose	+150.3	-33.4	+113	+20
Furanose	+ 98	-86	(+ 61)	(-32)
Differenz	52	53	52	52

Im Klammer sind die errechnete Drehungen der Glucofuranose (auf Grund der Annahme der Superposition der Drehungen) angegeben. Also, wenn obige Rechnungsweise statthaft wäre, so ist es wahrscheinlich dass in festem Zustand Glucose-6-mono-schwefelsaurensalz wesentlich aus Pyranose bestehe, obwohl dieser Pyranosering sehr labil sein würde, wie Ohle⁽⁶⁾ behauptet.

Nun ist eine Stufenreaktion bei der Mutarotation angenommen:



wenn μ sehr klein ist, wird diese Reaktion monomolekular. Der labile Pyranosering unsres K-salzes wird in der Lösung sehr rasch abgespalten; daher wird μ nicht mehr zu vernachlässigen sein. Man könnte wohl die obige Abweichung der Mutarotation von der monomolekularen Reaktion darauf zurückführen.

Man könnte doch gegen Pyranosering so einwenden dass dieses K-salz ein Gemisch von α - und β -Glucofuranose sei, und zufällig dieselbe Drehung wie die β -Glucopyranose angebe. Aber wir können aus den oben errechneten Drehungen von α - und β -Glucofuranose, die Mengen Verhältnis beider Isomeren berechnen: $61(1-x) - 32x = 22.4$, $x = 0.41$. Also etwa 41% β -Glucofuranose muss man darin annehmen. Dies steht im widerspruch mit der am Anfang sehr rasch aufsteigenden Mutarotation.

(5) *J. Chem. Soc.*, **1929**, 2796.

(6) loc. cit.

Die Mutarotation des Ca-salzes läuft anfangs sehr rasch ab wie man aus der Zeit-log($\alpha - \alpha_\infty$) Kurve sieht. Deshalb wird die Extrapolation des Anfangsdrehung sehr ungenau, aber ungefähr kommt der Wert von log($\alpha - \alpha_\infty$) für die Zeit Null zwischen 1.4 und 1.6. Wenn der Zuckerteil des Ca-salzes α -Glucopyranose ($+113^\circ$) wäre, so wird seine Anfangsdrehung folgenderweise berechnet:

$$\frac{\alpha \times 650}{180 \times 2} = +113, \quad \alpha = +62.6^\circ \text{ oder } [\alpha]_{5461} = 62.6 \times 1.181 = 74^\circ,$$

daher log(74–38) = 1.556. Also ist es wieder wahrscheinlich dass der Zuckerteil des Ca-salzes die α -Glucopyranose sei.

Die Enddrehung der Glucosemono-schwefelsäure ist im Mittel 41.75° . Daraus berechnet man $[\alpha]_D$ vom Glucose-teil:

$$\frac{41.75 \times 260}{180} = 60.02.$$

Nun hat Haworth⁽⁷⁾ Glucofuranose-5,6-mono-carbonat rein dargestellt und $[\alpha]_{5780} =$ zwischen $+15^\circ$ und $+18^\circ$ als Gleichgewichtswert angegeben. Daraus berechnet man: $[\alpha]_{5780}$ von Glucofuranose $16.5 \times 206 : 180 = +18.9^\circ$ ($[\alpha]_D$ Wert soll noch kleiner sein).

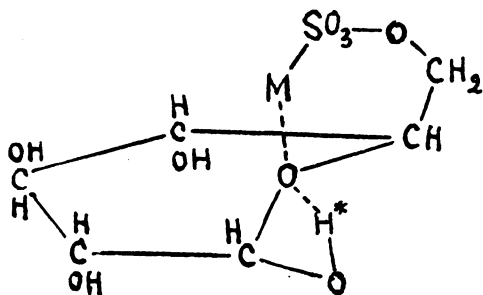
Also nehmen wir an dass Glucose-mono-schwefelsäure beim unsren experimentellen Bedingungen immer als Glucopyranose fungieren, so gehört das K-salz zum β -Glucopyranose-typ und Na-, Ca- und Ba-salz zum α -Glucopyranose-typ.

Wie soll diese eigentümliche Einflüsse der Metalle erklärt werden? Es ist wohl bekannt dass Glucose mit den Metallsalzen Molekularverbindungen bildet, zwar solche Verbindungen mit NaCl, CaCl₂, BaCl₂ aber merkwürdigerweise ist keine einzige Molekularverbindung mit KCl bisher beschrieben worden. Nach Matsuura⁽⁸⁾ bildet KCl keine Molekularverbindung mit Glucose. Daher liegt es die Annahme nahe dass K im Gegensatz zur anderen Metalle (Na, Ca, Ba) nur wenige Affinität gegen Glucose habe. Die Haftstelle des Metalles im Glucosemoleküle soll hauptsächlich das Ring-O sein, weil hier die Nebervalenz am stärksten ausgeprägt ist. Beim Erstarren des Metallsalzes von Glucose-mono-schwefelsäure, würden alle Metallatome um diese Restaffinität mit dem "beweglichen H-Atom"⁽⁹⁾ konkurrieren. Dies setzt die Gelegenheit des

(7) *J. Chem. Soc.*, **1929**, 2805.

(8) *Ber. d. Tech. Hochschule zu Hiroshima, Japan.* **1** (1929), Nr. 4, 217.

(9) Vgl. nachstehende Mitteilung: Eine Anschauung über die Umwandlungsmechanismus von α - und β -Formen der reduzierenden Zuckerarten. In folgender Abbildung ist das bewegliche H-Atom mit * bezeichnet.



beweglichen H-Atoms in β -Bindung überzugehen herab und veranlasst die Bildung von α -Modifikation. Dabei möge noch die abstossende Kraft von Metall mitspielen. Ausserdem wirken noch folgende Kräfte auf dem beweglichen H-Atom: Nebenvalenzkraft, elektrisches Moment von OH des C(2), und besonders sehr starke Anziehungskraft von SO_3 .

Es ist denkbar dass diese Anziehungskraft von SO_3 sehr enorm sein würde, besonders wenn das Metall nach dem Ring-O angezogen und damit auch SO_3 näher herangerückt wird. Bei solchem Falle wird diese Anziehungskraft alle andere α -Modifikationen begünstigende Einflüsse überwiegen, und das Gleichgewicht nach β verschieben, falls das Metall nicht zu stark am Ring-O verbunden ist. Deswegen erstarrt das K-salz stets in β -Isomer.⁽¹⁰⁾ Dagegen ist es beim Na, Ca oder Ba-salz anderes, da diese Metalle, wie oben schon erwähnt ist, sehr fest am Ring-O verbinden können, wird der Übergang des beweglichen H-Atom am Ring-O gesperrt und α -Isomer resultiert. Die Stärke der am Ring-O bindende Kraft von diesen Metalle sind wohl nicht gleich: z.B. die Mutarotation des Ba-salzes ist viel schwächer als die des Ca-salzes. Wahrscheinlich ist entweder im Ba-salz mehr β -Isomer beigemischt als im Ca-salz, oder die Mutarotation des Ba-salzes verläuft unmessbar schnell. Es scheint also als ob die Metallvalenz bei $\text{SO}_3\text{Ba-SO}_3$ viel vollkommener gesättigt sei als bei $\text{SO}_3\text{Ca-SO}_3$, und demgemäss ist die Bildung von β -Isomer beim Ba-salz weniger verhindert als beim Ca-salz. Dies hat wohl irgend einen Bezug auf dem Alkoholgehalt bei diesen Salzen: Ba-salz enthält 1 Mol. Alkohol, während Ca-salz 2 mol.; bemerkenswert ist dass das K-salz kein Lösungsmittel bei sich hat.

An dieser Stelle sei es erwähnt dass Ca- oder Ba-Glucose-6-phosphorsäure⁽¹¹⁾ auch eine kleine absteigende Mutarotation zeigt. Dies könnte man wohl ähnlicher Weise wie bei Ca- oder Ba-Glucose-6-schwefelsäure erklären.

(10) Während diese Mitteilung im Druck war, habe ich eine kleine Menge von Mg-salz erhalten. Es zeigte die aufsteigende Mutarotation: $[\alpha]_{5461}^{13} = +23.2 \rightarrow 46.5^\circ$ (0.1075 gr. in 10 ccm. Wasser). Seinem S-Gehalt nach muss das Salz der Formel $(\text{C}_6\text{H}_{11}\text{O}_6\text{SO}_3)_2\text{Mg}$ entsprechen. Anal.: Subst.=53.7; BaSO_4 =44.3 mg. Gef.: S=11.3%; Ber.: S=11.8%. Es enthält weder Wasser noch Alkohol wie beim K-salz, und ist nicht hygroskopisch. Die Molekularverbindung zwischen Glucose und MgCl_2 scheint auch unbekannt zu sein.

(11) Komatsu and Nodzu, *Mem. coll. sci. Kyoto Imp. Univ.*, **7** (1924), 277.

Das Brucinsalz von Glucose - mono - schwefelsäure zeigt auch eine absteigende Mutarotation:

Min.	$[\alpha]_D$	$\alpha - \alpha_\infty$	$\log (\alpha - \alpha_\infty)$
10	-0.75	4.90	0.690
15	1.57	4.08	0.611
20	2.53	3.21	0.494
45	2.98	2.67	0.426
65	3.40	2.25	0.352
90	3.62	2.03	0.307
140	3.96	1.69	0.228
150	4.30	1.36	0.130
∞	-5.65		

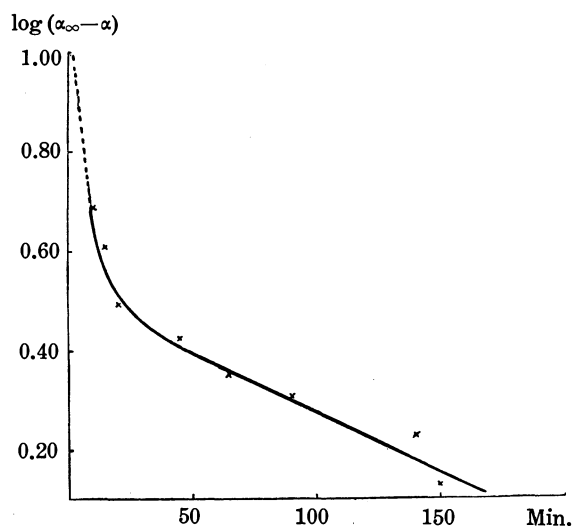


Abb. 4. Brucin-Glucose schwefelsäure.

Die Zeit- $\log(\alpha - \alpha_\infty)$ Kurve zeigt also keine gerade Linie, d.h. diese Reaktion ist nicht monomolekular wie beim Ca-salz. Das Strychninsalz im Gegenteil zeigt nach Ohle⁽¹²⁾ eine aufsteigende Mutarotation ($[\alpha]_D = -6.72^\circ \rightarrow -0.72^\circ$). Er hat daraus geschlossen dass Zuckerkomplex vom Brucinsalz zu α -Glucose und vom Strychninsalz zu β -Glucose sei. Hier begegnen wir wieder einem merkwürdigen Einfluss der Basen auf der α - und β -Konfiguration der Zucker. Könnte man auf diesem Falle die analoge Erklärung wie beim Ca- oder K-salz anwenden? Die chemische

(12) *Biochem. Z.*, **136** (1923), 446.

Konstitution der beiden Alkaloide ist sehr kompliziert und ist noch nicht klar gestellt; so weit ist es doch bekannt dass die beiden Alkaloide sehr nahe verwandten Konstitution haben sollen und nur mit der Anwesenheit von zwei Methoxylgruppen bei Brucin sich gegeneinander unterscheiden lassen. Sicherlich hat Methoxylgruppen mehr oder weniger Affinität gegen Ring-O. Deshalb könnte man annehmen dass Brucin mehr Affinität gegen Ring-O als Strychnin habe. Ob die Affinität des Brucins und des Strychnins vergleichbar mit der Affinität des Ca und K sein würde, ist nicht klar. Aber wenn der Fall wäre, dann würde man ganz einfach, analoger Weise wie beim Metallsalze, den merkwürdigen Unterschied der Mutarotation zwischen Brucinsalz und Strychninsalz verstehen.

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EINE ANSCHAUUNG ÜBER DIE UMWANDLUNGS- MECHANISMUS VON α - UND β -FORMEN DER REDUZIERENDEN ZUCKERARTEN.

Von Tokuro SODA.

Eingegangen am 21. Dezember, 1932. Ausgegeben am 28. Februar, 1933.

Die Erklärung des Mechanismus bei der Umwandlung von α - und β -Formen der reduzierenden Zuckerarten war früher umsonst, weil die Konfiguration von α - und β -Isomeren der Zucker meistens ungewiss war. Die Fortschritte der Zuckerchemie in letzter Zeit, jedoch scheint die Konfiguration der gewöhnlichen Zuckerarten aufgeklärt zu haben. Aber ob wir ohne Gefahr deren Umwandlungsmechanismus diskutieren können, ist allerdings noch fraglich. Die vorliegende Hypothese könnte deshalb noch sehr spekulativ sein, jedoch habe ich mich bemüht damit die bisher bekannten Tatsachen möglichst in Einklang zu bringen, weil gerade diese Frage mich sehr interessiert. Wenn sie irgend einen gesunden Kern enthält und sich weiter entwickeln lässt, so werde ich sehr erfreut sein.

Über die Mutarotation wurden schon früherher verschiedene Theorien angegeben: z.B. Hydrat-Theorie von Lowry,⁽¹⁾ Oxonium-Theorie von Armstrong,⁽²⁾ Oxo-Cyclo-Tautomerie-Theorie von Jacobson-Stelzner,⁽³⁾ ge-

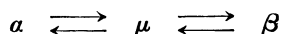
(1) *J. Chem. Soc.*, **83** (1903), 1316.

(2) *Loc. cit.*, **83** (1903), 1309.

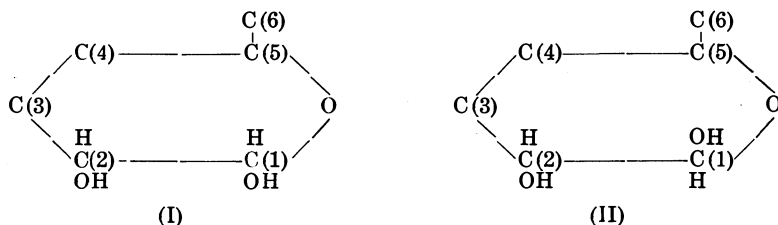
(3) „Lehrbuch d. org. Chemie,” **1** (2), 915.

stützt von Baker, Ingold und Thorpe⁽⁴⁾; Prototropie-Theorie von Lowry.⁽⁵⁾ Ohle⁽⁶⁾ hat neulich eine Theorie entwickelt, in welcher er die Mutarotation in weiterem Sinne behandelt, d.h. er rechnet nicht nur die Epimerisation sondern auch Ring-Tautomerie, Ring-Ketten-Tautomerie usw. mit.

Dass die Mutarotation nicht als echte monomolekulare Reaktion verläuft, ist heute wohl bekannt; sie verläuft nach der Stufen-Reaktion:



Die bisher entwickelten verschiedenen Mutarotationstheorien unterscheiden sich in der Konstitution dieser μ -Form und ihre Entstehungsmechanismen. Der Unterschied zwischen α - und β -Form ist bekanntlich von der Konfiguration C(1) abhängig, z.B. wenn α -Form (I) ist, dann muss β -Form (II) sein:



Die beiden Hydrat-Theorien von Lowry und von Armstrong sind Baker, Ingold und Thorpesche Theorie nach nicht allgemein gültig. Die Letztgenannten stützen Oxo-Cyclo-Desmotropie-Theorie, welche die Aldehydform als Zwischenzustand (μ) annimmt. Aber bisher ist keine einwandfreie Beweisführung für die Existenz des Absorptionsband der Carbonyl-gruppe angebracht worden, obwohl die Existenz der μ -Form in einigen Fällen sehr wahrscheinlich ist. Lowry⁽⁷⁾ als auch Ohle⁽⁶⁾ nehmen deshalb eine Nebenvaleanzbindung zwischen CO und OH vom C(5) oder C(4) an, um die complete Öffnung des Ringes zu vermeiden.

Nun scheint es mir aber noch eine etwas andere Zwischenform denkbar zu sein. Einfachheitshalber, beschränken wir vorläufig unsre Diskussion nur über die Epimerisation der Pyranosen.

(4) *J. Chem. Soc.*, **125**(1924), 268.

(5) *Chem. Rev.*, **4** (1927), 231.

(6) *Chemie d. Monosaccharide u. d. Glykolyse*, (1931) 116.

(7) *Rapports sur les Hydrates de Carbone* (10^{me} Conférence de l'Union Internationale de Chimie, 1930, p. 92).

Satz I. In einem spannungsfreien Pyranosering, liegt jedes Glied nicht auf einer Ebene⁽⁸⁾; der Ring nimmt etwa folgende Formen:

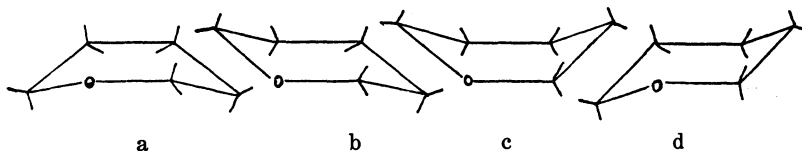


Abb. 1.

Man könnte annehmen dass in der Lösung diese verschiedenen molekularen Formen sich miteinander andauernd ändern, oder die Glieder des Ringmoleküls immer schwingen. Da Hexosen oder Methylpentosen das aus dem Ringe hervorstehende C(6) haben, so besitzen sie grössere Trägheit der Schwingung als Pentosen; d.h. die Vergrösserung oder Verkleinerung der Schwingungsweite der Pentoseringe wird leichter erreicht als die der Methylpentosen oder Hexosen. In wässriger Lösung haben Hexosen grössere Trägheit als Methylpentosen, weil CH_2OH der Hexosen hydratisierbar ist.

Aber diese Schwingung ist nicht eine einfache Schwingung wie z.B. Seitenschwingung oder Pendelschwingung. In Abb. 1. angegebene Formen sind alle im spannungsfreien Zustand, und um ihre Formen untereinander zu wechseln, müssen sie, wie beim Cyclohexan, durch einen gespannten Zwischenzustand gehen.

Die Potentialenergiekurve des Cyclohexan-ringes bei solcher Schwingung wird also etwa wie die Folgende sein:

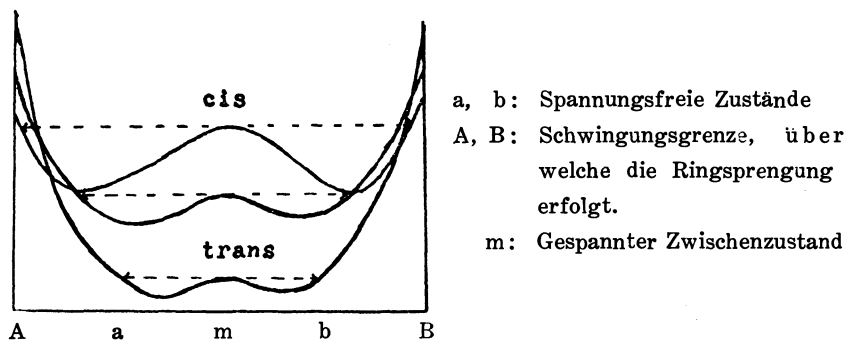


Abb. 2.

(8) Haworth, „Constitution of Sugars,” p. 91. Mohr, *J. pr. Chem.*, **98**(1918), 315.

Substituiert man, nun, H von benachbarten C-Atomen des Cyclohexans durch z.B. OH, so werden die Potentialenergie-kurven entweder ansteigen oder sinken je nach dem die Substitution cis oder trans ist. Wie man aus Abb. 2. sieht, sind die cis-substituierten Moleküle energiereicher und haben grössere Schwingungsweite als die trans-substituierten.

Satz II. Nehmen wir auch an, wie Ohle, dass H von OH des C(1) stark nach Ring-O-Atom angezogen sei, und dass Wasser, Basen, Säuren oder Hitze auf OH sein H dissozzierend wirken; also, dieses H kann indiesem Zustand, näher an Ring-O kommen. Je nachdem der Stellung des Ring-O, wird der Abstand zwischen OH des C(1) und C(5), wie unten gezeigt, einmal klein, andermal gross:

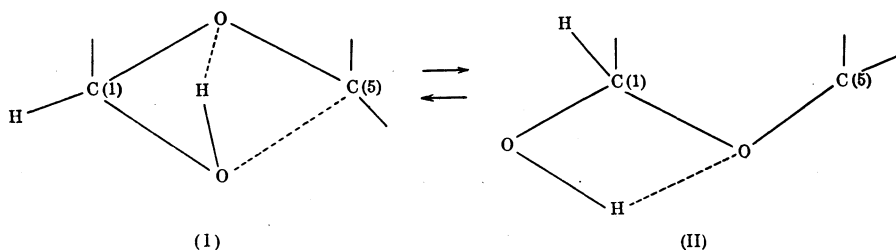


Abb. 3.

Da das Ring-O mit H von OH des C(1) durch seiner Nebervalenz verbunden ist, so ist die Bindung C-O-C etwas verlockert. Andererseits, wenn OH-Gruppe von C(1) ihr H-Atom teilweise dissoziiert, so muss dieses O-Atom mit seiner Nebervalenz irgendwohin einwirken. Dies könnte wohl am nächsten Lage stehenden C(5)-Atom (beim Schwingungszustand I) geschehen. Dann würde die polare Bindung C(5)-O immermehr geschwächt und somit die Nebervalenzbindung zwischen Ring-O und dissoziiertes H-Atom verstärkt. In diesem Zustand ist dies H-Atom sehr beweglich und wenn irgend ein Kraftfeld auf ihm seine Wirkung ausübt, so wird diese *bewegliche H-Atom* leicht nach seiner Richtung abgestossen. Wenn das *bewegliche H-Atom* sich am Ring-O heranrückt, so wird diese Nebervalenzbindung fest und andererseits die O-C(5) Bindung geschwächt und gleichzeitig geht das andere O-Atom durch seine Bindung mit C(5) ins Ring-O über (Abb. 4).

Also, denken wir den μ -Zustand als ein sehr verlockelter Zustand der C(5)-O Bindung, wo der Valenzwechsel zwischen Ring-O und OH des C(1) ermöglicht ist. Nach dieser Auffassung, werden die Zuckermoleküle in den μ -Zustand gebracht, wenn die Schwingung ihrer C(1) eine gewisse Grenze überschreitet, weil infolgedessen OH des C(1) sehr

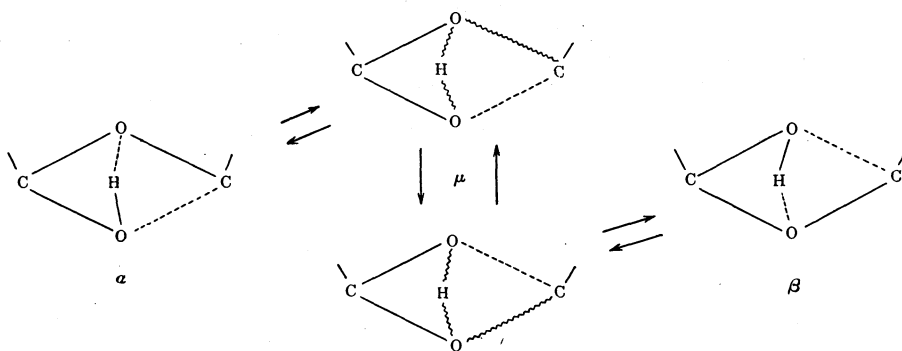


Abb. 4.

nahe an C(5) heranrückt und stark seine Nebenvalenz ausüben kann. Nach dieser Hypothese verläuft die Mutarotation über den μ -Zustand, zu welchem es nur erreichbar ist erst wenn H von C(1)OH sich beweglich machen kann. Da bei Methyl- oder Äthylglucoside kein bewegliches H-Atom gibt, so zeigen sie keine Mutarotation und erst nur durch besondere Katalysatoren sind sie fähig ihre Form zu ändern.

Satz III. Wir haben schon gesehen (Satz I) dass die cis-substituierten Moleküle des Cyclohexans grössere Schwingungsweite als die trans-substituierten besitzen. Natürlich, können wir dergleichen Einfluss beim Zucker erwarten. Beim Schwingen des Ringes, entsteht eine oscillierende Drehung der benachbarten Systemen H-C-OH in gegeneinander umgekehrter Richtung um die Valenzlinie der beiden C-Atome:

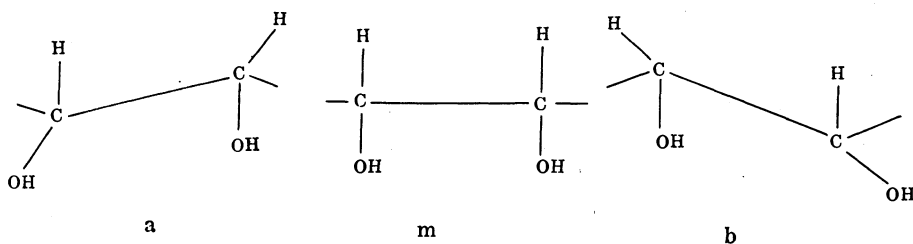


Abb. 5.

Daher, wenn H oder OH des C-Atoms nebeneinander in cis-Stellung vorkommen, dann wird die Schwingungsweite des Umdrehens vergrößert und wenn sie in trans-Stellung sind, dann wird diese verkleinert. Diese Einflüsse an der Ringschwingung wird am meisten ausgeprägt wo die Valenzbindung verlockert ist. Also, es sind C(1) bzw. C(5) die ihre

Schwingung bzw. Umdrehung am meisten vergrößert werden. Wegen der verlockerten Bindung von O-C(5) beim μ -Zustand, ist dieses O-Atom geneigt sich mit C(1) zu bewegen. Daher erbringt das Schwingen des C(1) mehr Gelegenheiten für den Valenzwechsel zwischen Ring-O und C(1)OH, weil damit das *bewegliche H-Atom* (Satz II) mehr dissozierbar sein würde und gleichzeitig die Nebenvalenz vom C(1)OH auch häufiger auf C(5) einwirken könnte als wenn das Letzte in Schwingung ist. Da 2, 3-cis-Konfiguration in Vergleich zur 3, 4-cis-Konfiguration grösseren Einfluss auf C(1) ausüben kann, so ist es zu erwarten dass bei 2, 3-cis-Konfiguration die Gelegenheit für den μ -Zustand mehr begünstigt sei als bei der Anderen.

Satz IV. Die moderne physikalische Chemie lehrt uns dass der Valenzwinkel des O-Atoms von Ring-glieder HCOH nicht 180° , sondern viel kleiner ist. Also beim Schwingen der Ring-C-Atome um ihre gemeinsamen Drehungsachsen werden die anhaftenden H und OH in einer etwa wie unten veranschaulichten Bewegung eingestellt: (vgl. Abb. 5.) und somit ist ihre mittlere Stellung etwa wie m, was zum

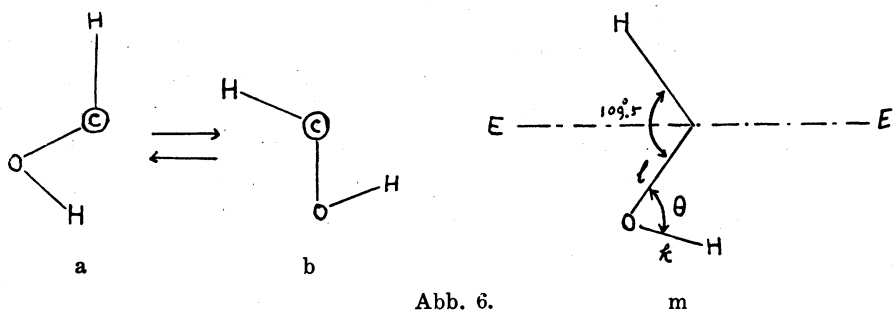


Abb. 6.

m

gespannten Zustand entspricht. Die Zahlenwerte von θ ist für Wasser zweierlei angegeben: der eine 64° und der andere 110° . Es ist schwer zuentscheiden welchen Wert wir annehmen sollen, obwohl man θ von Alkoholen beinahe gleich den des Wassers vermuten dürfte. Man könnte jedoch in folgendermassen die Richtung vom elektrischen Feld ungefähr schätzen: wenn $\theta = 110^\circ$ und $1 = k$ ist, so wird die Richtung vom elektrischen Felds beinahe parallel zur Ringebene EE' ; da aber $1 > k$ ist, so soll die elektrische Resultante etwas nach oben gerichtet sein. Es ist klar dass wenn man $\theta = 64^\circ$ setzt, dann diese Neigung nach oben noch grösser wird. Es ist auch wohl denkbar dass OH von allen Gliedern mit ihren H-Atomen nach Ring-O angezogen werden; daher richten die Resultanten der elektrischen Momente im ganzen nach dem Ring-O. Das *bewegliche*

H-Atom von C(1) (Satz II) wird demgemäss nach dieser Kraftfeldrichtung abgestossen. Das folgende Perspektiv wird diesen Zustand veranschaulichen; wenn man für θ den kleineren Wert annimmt, so kommt das *bewegliche H* zwischen C(1) und das O-Atom, wie man in Abb. 7

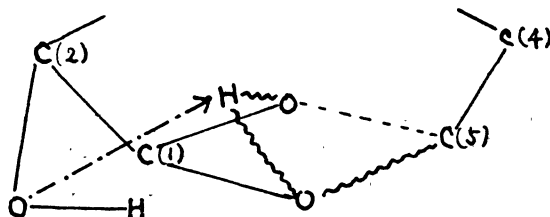


Abb. 7.

sieht. Daher wird die Feldstärke von OH, die auf das *bewegliche H*-Atom wirken, am stärksten beim C(2) und dann beim C(3) oder C(4) sein, je nachdem die Stellung des *beweglichen H*-Atom. Die Stellung von OH des C(6) liegt auch in der Nähe vom *beweglichen H*, aber da C(6) in der Lösung frei drehbar sein würde, übt dieses OH nur wenig Einfluss aus.

Satz V. Beim μ -Zustand könnte die Nebenvalenz von beiden labilen O-Atome—das Ring-O und das O-Atom von C(1)OH—in geeigneter Bedingung seine Anziehungskraft auch auf H von OH ausüben, falls das H sehr nahe von O-Atomen heranrücken können. Da die Abstände zwischen diesem O-Atome und OH des C(2) und C(6) beinahe gleich kommen könnte, ziehen wir diese zwei Fälle in Gedanken. Die OH-Gruppe des C(6) kann in die Nähe von OH des C(1) anrücken wenn Beide auf der gleichen Seite der Ringebene sitzen, aber die Ringschwingung begleitet immer die grosse Abstandsänderung zwischen beiden OH, weil das C(6) dabei nach innen und aussen bewegt; daher ist in der Lösung die stabile Nebenvalenzbindung zwischen diesen Beiden OH unmöglich.

Nun, wenn H von OH des C(2) nach O-Atom angezogen ist, so würde die Nebenvalenzbindung zwischen diesem O-Atom und C(5) geschwächt und dementsprechend die Neigung des anderen O-Atoms ins Ring-O überzugehen verstärkt, und somit auch seine Affinität zum *beweglichen H* geschwächt. Andererseits, das O vom C(2) könnte auch seine Nebenvalenz auf dem *beweglichen H* ausüben und zieht H zu sich an. Also, schliesslich befestigen sich OH des C(1) und C(2) durch ihre Nebenvalenzbindung in cis-Stellung, die Nebenvalenzbindung O---C(5) bricht ab und der Ring stabilisiert sich in cis-Form (Abb. 8).

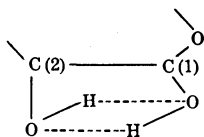


Abb. 8.

Aus dem was oben gesagt, sieht man dass die Anziehungskraft der Nebervalenz im entgegengesetzten Sinne zur Kraft des elektrischen Felds der OH-Gruppe (dem Satz IV gemäss) auf das *bewegliche H* wirkt. Die beiden Kräfte sind nicht stets ausgeglichen, sondern die Beziehung ist veränderlich, je nach der Bedingung. Während das elektrische Feld unabhängig von der Bewegung des H-Atoms oder OH-Gruppe entsteht, wird die Nebervalenzbindung gestört, wenn die Schwingungskraft des H-Atoms die Nebervalenzkraft überwiegt. In der Lösung, stört die Verdünnung oder Erhöhung der Temperatur die Nebervalenzbindung, und befähigt das Konzentrieren oder Erniedrigen des Temperatur diese Bindung. Wenn die Bedingung für diese Bindung eignet, so wird diese Bindungskraft stärker wirken als andere elektrische Kräfte, da die Nebervalenzbindung ganz direkter Natur ist. So wirkt das Konzentrieren, die cis-Konfiguration vermehrend, z.B. bei Glucose und Galaktose steigt ihre spezifische Drehung auf, während bei Mannose sie absteigt. (vgl. nachstehende Tabelle).

Die folgende Tabelle ist nach Hudson und Yanovsky⁽⁹⁾ so wie Haworth und Hirst⁽¹⁰⁾ zusammengestellt.

Zucker	α	β	I	II	III	δ	% Alkohol (III)
d-Fruktose	-21	-133(c)	0.082	36	51 (α)	+15	80
d-Lyxose	+ 5(t)	- 70	0.065	75	83 (α)	+ 8	90
l-Rhamnose	- 8(t)	+ 54	0.039	73	85 (α)	+12	70
d-Arabinose	-54	-175(c)	0.031	58	62 (α)	+ 4	80
d-Xylose	+92(c)	- 20	0.021	65	56 (β)	- 9	„
d-Mannose	+30	- 17(c)	0.0190	58	82 (α)	+24	„
d-Galaktose	+144(c)	+ 52	0.0102	69	58.2 (β)	-10.8	60
d-Glucose	+113(c)	+ 19.7	0.0065	66	55.3 (β)	-10.7	80

(c), (t)—gewöhnliche Modifikation: cis, trans.

Spalte I.—Koeffizient der Mutarotationsgeschwindigkeit im Wasser (20°C.)

Spalte II.—Prozente der trans-Modifikation im Wasser

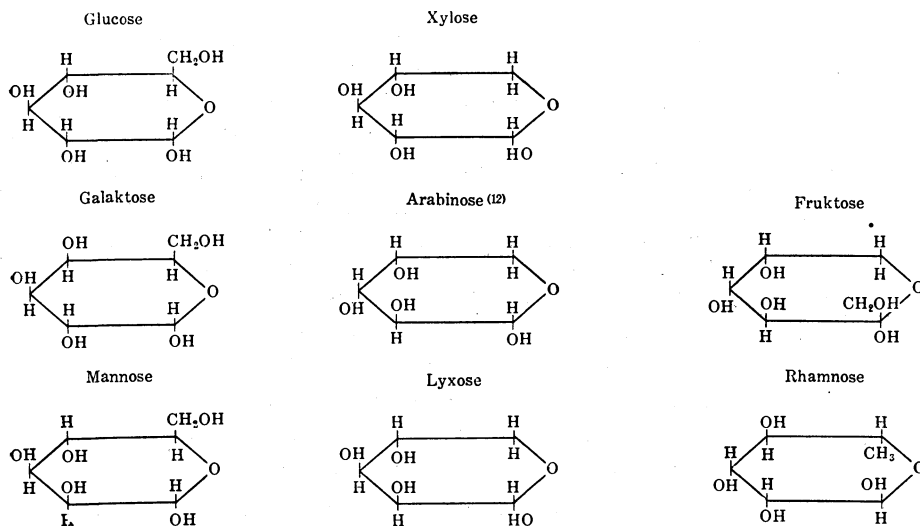
Spalte III.—Prozente der trans-Modifikation in wässrigen-Alkohol

δ —Differenz der Konzentration: (III)—(II).

(9) *J. Am. Chem. Soc.*, **39**, (1917).

(10) *J. Chem. Soc.*, **1928**, 1226.

Die Konfiguration der α -Modifikation der obigen Zucker (nach Haworth⁽¹¹⁾).



Erklärung der Tabelle. Wie man aus der Tabelle (Spalte I) sieht ist die Mutarotationsgeschwindigkeit bei Pentosen grösser als bei Hexosen. Dies kommt vor wegen der Anwesenheit des C(6) bei Hexosen, welches die Ringschwingung verzögern lässt und am μ -Zustand zu erzielen erschwert (nach Satz I). Der Einfluss von cis-OH, dem Satz III nach, ist auch hier klar zu sehen; nämlich, die Mutarotationsgeschwindigkeit ist am grössten bei den Zuckern, die 2, 3-cis Konfiguration haben und am kleinsten, bei denen ohne cis-Konfiguration. Der Unterschied zwischen Lyxose und Rhamnose könnte man als den Einfluss von CH₃ am C(5) erklären. Methylgruppe vergrössert wohl die Momente der Ringschwingung, aber da sie nicht hydratisierbar ist, zeigt sie viel kleineren Effekt als CH₂OH der Hexosen.

Die Mutarotationsgeschwindigkeit nimmt immer mit der Temperatur zu. Dieser Einfluss der Temperatur kommt davon dass das bewegliche H-Atom mehr dissoziiert und die Schwingung der Ring-glieder, besonders C(1), vergrössert wird. Andererseits, je mehr der Lösungsmittel Alkohol enthält, desto schwieriger läuft die Mutarotation. Dies folgt daraus dass Alkohol die Dissoziation des beweglichen H abdrückt.

(11) *Ber.*, **65**, (1932) (A), 43.

(12) Vogel gibt umgekehrte Konfiguration für α - und β -Arabinose an (Vogel-Georg, Tabellen d. Zucker u. ihrer Derivate 1931). Nach der Untersuchung von Helferich über Phenolglykosid-Spaltung durch Emulsin sind die obigen Konfigurationen für Glucose, Xylose, Galaktose, Arabinose und Mannose wahrscheinlich (*Z. physiol. Chem.* **208** (1932), 91; **209** (1932), 269).

Der Prozentgehalt der β -Modifikation in obiger Tabelle (Spalte II und III) ist berechnet worden, zwar angenommen dass in der Lösung nur α - und β -Modifikationen existieren. Aber diese Annahme ist heutzutage nicht mehr einwandfrei. Da es vielfach durch Experimente gestützt ist,⁽¹³⁾ will niemand wohl bezweifeln dass Zucker in ihren Lösungen auch als andere Formen als α oder β existieren. Nur ist es noch heute eine strittige Frage welche Form sie besitzen. So haben dafür Riiber und Minsaas⁽¹⁴⁾ die α - und β -Formen der γ -Zucker, Schlubach⁽¹⁵⁾ gleichfalls α - und β -Formen der h-Zucker, und Ohle allerlei mögliche Formen angenommen; während nach Lowry und Smith⁽¹⁶⁾ nur eine μ -Form genügt um ihre experimentellen Ergebnisse zu stützen, obwohl es damit nicht gesagt ist dass die Existenz der anderen Formen unmöglich sei. Die Menge dieser Zwischenformen in der Lösung reihen sich nach Schlubach in folgender Ordnung (vermutet aus dem Temperaturkoeffiziente der spez. Drehung): Fruktose > Mannose > Galaktose > Glucose. Man könnte auch diese Ergebnisse als Einflüsse von cis-OH aus Satz III erwarten, weil wir den Zwischenzustand als μ -Zustand betrachten wollen. Fruktose hat seine 4, 5-cis-OH neben der beweglichen 6-ten CH₂, daher würde seine Schwingungsweite sehr leicht vergrössern, und nach Satz I, wird dieser Zustand anhalten wegen dem Momente von 1-ste CH₂OH. Dadurch wird die Fruktose vielleicht zum μ -Zustand leicht erreichen und im Gleichgewicht würde, also, der grösste Teil der Fruktose als β - und μ -Formen vorhanden sein. Für die Pentosen nach obigen Hypothesen, soll die Reihenfolge Lyxose > Arabinose > Xylose sein.

Auf der Drehung von Glucose und Xylose hat die Temperatur fast keinen Einfluss. Also, die Ringschwingungsenergie dieser Zucker muss sehr klein sein und der μ -Zustand, schwer erreichbar. Dies könnte man nach Satz III erklären: nämlich, die beiden Zucker haben kein cis-OH und somit wird die Ringschwingung immer verpuffert. Deshalb brauchen wir keine merkliche Menge von μ -Zucker in dieser Lösung zu berücksichtigen, und können wir den Prozentgehalt der β -Form in obigen Tabelle (Spalte II) beinahe als richtig auffassen. In wässrig-alkoholischer Lösung wird die Nebenvaleanzbindung sich mehr ausprägen als im Wasser, da die Schwingung des C(1) wegen der Herabsetzung der Dissoziation vom beweglichen H schwächer wird, und daraus folgt nach Satz V dass cis-Form d.h. α -Modifikation in diesem Lösungsmittel zunimmt.

(13) Worley, Andrews, *J. physic. Chem.*, **32** (1928), 311.

(14) *Ber.*, **59** (1926), 2266.

(15) *Naturw.*, **20** (1932), 273.

(16) *J. Chem. Soc.*, **1928**, 666.

Bei anderen Zucker darf man nicht die Menge der μ -Form vernachlässigen, weil bei diesen wegen cis-OH ihre Schwingung lebhaft sein würde und somit die Nebenvalenzbindung nicht auftreten kann.

Nach Lowry und Smith⁽⁶⁾ sind die Prozentgehalte von α , μ und β -Formen der Galaktose in wässriger Lösung 28.5%, 12.0% und 59.5%, und daraus berechnet, wird die Drehung der μ -Form: $[\alpha]_{5461} = +58^\circ$ oder $[\alpha]_D = +49^\circ$ was sehr nahe von der Drehung der β -Form ($+52^\circ$) liegt. Daher, wenn man den Prozentgehalt der β -Form direkt aus der Gleichgewichtsdrehung berechnet wie $144(1-x) + 52x = 80.5$; $x = 69\%$, so soll in Wirklichkeit x ungefähr den Prozentgehalt von $\beta + \mu$ darstellen. Nun drückt Alkohol die Dissoziation des beweglichen H-Atom herab, deshalb würde in wässrig-alkoholischer Lösung die Menge der μ -Modifikation stark vermindert sein, und dadurch soll der Prozentgehalt der β -Form in diesem Medium (58.2%) ungefähr den wahren Wert Zeigen. Hier existiert doch noch etwas mehr trans-Form als cis-Form (58.2: 41.8). Dies bedeutet dass beim Gleichgewicht in der wässrig-alkoholischen Lösung, das elektrische Moment von C(2)-OH die gesamten Momente von 3, 4-cis-OH noch ein wenig überwiegt. Doch befindet sich 1.3% ($= 59.5 - 58.2$) weniger trans-Form in dieser Lösung als in wässriger Lösung und die μ -Form in wässriger Lösung stabilisiert sich alle in die α -Modifikation. Da die drei elektrischen Momente von OH gegen beweglichen H beinahe gegeneinander ausgeglichen sind und nur kleine Differenz zeigen, könnte hier ein schwaches Moment von OH des C(6) (siehe Satz IV) sich auf dem beweglichen H ausgeprägt sein. Dadurch werden die ganze μ -Form als auch ein kleiner Teil der β -Modifikation in die α -Modifikation stabilisiert.

Da die Konfiguration von Arabinose gleich der Galaktose ist, nur mit dem Unterschied dass bei der ersten C(6) fehlt, wird die Stabilisierung einfach in die trans-Form, allerdings nur gering, erfolgen. Bei Mannose, Lyxose und Rhamnose muss der Einfluss von 2, 3-cis-OH auf dem beweglichen H so stark sein dass andere Einflüsse fast vernachlässigt werden können. So besitzen alle drei Zucker in wässrig-alkoholischer Lösung einen sehr hohen Prozentgehalt der trans-Formen, zwar Rhamnose am höchsten. Dies kommt vielleicht aus dem abstossenden Einfluss der CH_3 -Gruppe auf dem beweglichen H-Atom. Fruktose gehört an Galaktose-Reihe, daher kann die trans-Form bei ihr nicht viel existieren. Aber im 80%-igen Alkohol bleibt vielleicht noch die μ -Form reichlich zurück, weil im 95%-igen Alkohol das Prozent der trans-Form noch bis auf 57% steigt.

Aus dem obigen Ergebnis von Galaktose sieht man dass der Prozentabfall von 59.5 bis 58.2 sehr gering ist wenn man ihn mit dem Abfall

von 69 bis 58.2 vergleicht. Also hier handelt es sich hauptsächlich um die Stabilisierung von μ -Form, und die Umformung von α in β ist nur gering (1.3%).

Wenn man annimmt dass die Analogie für anderen Zucker als Galaktose gültig sei, so würde die Differenz (δ) zwischen den Prozentgehalt in wässriger Lösung und denselben in wässrig-alkoholischer Lösung, der Konzentration ihrer μ -Form ungefähr proportional sein, wenn auch nicht gleich (vgl. Tabelle). Überblickt man die Tabelle dieser Ansicht nach, so findet man dass μ -Form der Pentosen in wässriger Lösung viel weniger als dieselbe bei der Hexosen vorhanden ist, was aber auch gleich durch den Satz I als Trägheit von C(6)OH erklärt wird.

Nun berechnen wir folgende Quotienten, so findet man eine Regelmässige Beziehung darunter:

$$\frac{\delta(\text{Galktose})}{\delta(\text{Arabinose})} = \frac{10.8}{4} = 2.7 ; \quad \frac{\delta(\text{Mannose})}{\delta(\text{Lyxose})} = \frac{24}{8} = 3.0 ;$$

$$\frac{\delta(\text{Glucose})}{\delta(\text{Xylose})} = \frac{10}{9} = 1.1$$

Die ersten zwei Quotienten sind beinahe gleich, während der dritte ganz verschieden ist. Wie schon erwähnt, treten δ (Glucose) und δ (Xylose) nur durch ihre Nebervalenzkraft auf, daher spielt hier C(6) fast keine Rolle und somit ist der Quotient gleich 1. Bei den anderen, in Gegenteil, muss der Einfluss von C(6) bemerkenswert sein und zwar gleich gross, wenn der Einfluss im Sinne Satz I sich wesentlich abspielen würde, und was gerade unsrem theoretischen Gedanken nach eine Zunahme von μ -Form bedeutet. Mannose, Lyxose und Arabinose haben die Konfiguration, welche dem Satz IV nach, die trans-Form begünstigt; deshalb sind alle δ positiv.

Wir haben bei der Galaktose den Einfluss von OH des C(6), obwohl sehr gering, auf der Umwandlung α in β im Sinne Satz IV berücksichtigt. In diesem Falle, stellen sich dem entgegen die Resultante der anderen elektrischen Kräfte, allerdings wenn auch sehr schwach. Deswegen wird die Wirkung von OH des C(6) etwas ausgeglichen. Aber bei Mannose wirken alle Kräfte von OH des C(2), C(3) und des C(6) in demselben Sinne, und somit kann auch die Letzte ihre Vollkraft ausprägen. Also, die Umwandlung des cis-Form in trans-Form könnte bei Mannose grösser sein als die des trans-Form in cis-Form bei Galaktose. Deshalb sind die beiden Quotienten etwas verschieden. Da bei Mannose ihre 2, 3-cis-OH die μ -Form (nach dem Satz III) sowie die trans-Form (nach dem Satz IV) zunehmend wirkt, so sollte auch in wässriger Lösung mehr trans-

Form vorhanden sein als bei Galaktose, angenommen dass der letzte Einfluss gross sei. Aber da es nicht der Fall ist, möge man denken dass δ von Mannose auch ungefähr die Konzentration ihrer μ -Form darstellt.

Hier haben wir noch zwei Quotienten welche beinahe gleich sind:

$$\frac{\delta(\text{Mannose})}{\delta(\text{Galaktose})} = \frac{24}{10.8} = 2.3 ; \quad \frac{\delta(\text{Lyxose})}{\delta(\text{Arabinose})} = \frac{8}{4} = 2.0$$

Durch Analogie würde bei Lyxose und Arabinose, ihre δ die Konzentration der μ -Form darstellen.

Bemerkenswert ist es dass gerade bei solchen Zucker deren δ positiv sind, ihre trans-Form dem α -Zucker entspricht wie man aus der Tabelle sieht.

Zum Schluss sei noch erwähnt dass die Reihenfolge der Konzentration in wässrig-alkoholischer Lösung gut nach dem Satz IV folgt, nur mit der Ausnahme von Glucose und Xylose. Dies kommt vor, weil gerade bei diesen zwei Zucker die Nebenvalenzbindung ausgeprägt ist. Wenn es uns daher erlaubt ist für die beiden Zucker die Werte in wässriger Lösung zu erborgen, da hier fast keine Nebenvalenzbindung angenommen wird, so ist der Satz IV jetzt einwandfrei anwendbar. In wässriger Lösung ist der Satz IV nur gültig für Pentosen, aber nicht mehr für Hexosen. Da pentosen, in ihrer wässrigen Lösung, nicht viel μ -Form enthalten, so werden ihre Drehungen auch nicht stark durch ihre Anwesenheit beeinflusst sein, und die Effekte vom Satz IV werden nicht geschleiert. Die aus der Drehungen von α - und β -Mannose oder Galaktose direkt berechneten Prozente (Spalte II) sind verschieden von den Werten, die Hudson⁽¹⁷⁾ aus der Drehung in wässrig-alkoholischer Lösung reduziert hat. Er hat nämlich 62% für Mannose, 64% für Galaktose errechnet, zwar in folgenderweise: Erst bestimmt man die $[\alpha]$ der α - und β -Zucker in wässrigem Alkohol (z.B. A%) durch Löslichkeitsexperimente. Sei es a° und b° . Sodann löst man eine bekannte Menge des Zuckers in $(100 - A)$ ccm. Wasser auf. Nachdem das Gleichgewicht erreicht ist, setzt man A ccm. absoluten Alkohol zu, und sogleich wird

(17) *J. Am. Chem. Soc.*, **39**, (1917), 1021.

ihre Drehung abgelesen. Sei diese $[\alpha] = c^\circ$. Da bei diesem Verfahren keine Formverschiebung denkbar ist, wird folgende Gleichung möglich sein:

$a(1-x) + bx = c$; hier ist x = der Bruchteil von β -Zucker in wässriger Lösung. Es ist wahrscheinlich, wie Hudson angenommen hat, dass α , β -Umwandlung sehr langsam erfolgen würde, aber die Stabilisierung der μ -Form in die α - oder β -Modifikation dürfte ziemlich schnell verlaufen. Es ist daher denkbar dass die μ -Formen teilweise in stabilen Formen während dieser Behandlung schon umgewandelt seien. Deshalb kommen die Werte welche Hudson berechnet hat näher an die wahren Werte.

Über die α - oder β -Formen der kristallisierten Zucker. Die gewöhnlichen kristallisierten Zucker werden aus sehr konzentrierten wässriger Lösung durch Zusatz von Alkohol dargestellt. Die als cis-Isomeren kristallisierenden Zucker sind: α -Glucose, α -Galaktose, α -Xylose, β -Mannose, β -Arabinose; dagegen kristallisieren α -Lyxose und α -Rhamnose als trans-Isomeren aus.

Es ist ganz klar dass bei solcher Behandlung die Nebenvalenzkraft sehr wichtige Rolle spielt. Beachtenswert ist doch dabei ob die Nebenvalenz stark genug ausgeprägt sein würde ehe noch der Sirup nicht ganz erstarrt und die Formänderung durch die Nebenvalenz noch ermöglicht bleibt. Über die günstige Konfiguration von Glucose und Xylose für die Entwicklung der Nebenvalenz ist schon aufmerksam gemacht worden, daher ist es selbstverständlich dass Glucose und Xylose in α -Modifikation kristallisieren. Galaktose und Arabinose haben 3, 4-cis-Konfiguration. Infolgedessen würden ihre μ -Zustände etwas lang lebzig sein, und die Formänderung würde bis zur zähen Konsistenz, worin Nebenvalenz sehr stark ausgeprägt sein kann, möglich sein. Ausserdem, sind die gesamten elektrischen Momente gegen die Nebenvalenzbindung, wie wir schon gesehen haben, nicht viel. Darum kristallisieren diese Zucker in cis-Form. Der μ -Zustand von Mannose, Lyxose und Rhamnose muss sehr lang lebzig sein und die elektrischen Momente wirken so stark zur Bildung der trans-Form dass die Nebenvalenzkraft bis Formstabilisierung nicht die elektrischen Kräfte überwiegen könnte. Deswegen kristallisieren Lyxose und Rhamnose in trans-Form. Bei Mannose, in sehr zäher Konsistenz, wirkt Nebenvalenz von OH des C(6) in gleichem Sinne wie OH des C(2), darum ist die gewöhnliche β -Mannose von cis-Isomer.

β -Glucose, β -Galaktose und β -Rhamnose können aus ihren gewöhnlichen α -Isomeren in folgenderweise dargestellt werden:⁽¹⁸⁾ die konzentrierte Lösung wird einiger Zeit heiss erhalten und verdampft bis zur trocknen Masse, welche beide α - und β -Zucker enthält. Sodann wird diese Masse in wenig kaltem Wasser gelöst und sogleich durch Zusatz von Alkohol gefällt; β -Glucose oder β -Galaktose kristallisiert erst aus, und leicht lösliches α -Isomer bleibt in der Lösung zurück. β -Rhamnose wird aus dieser Masse durch 80 %-igem Alkohol extrahiert, da diese löslicher als α -Isomer ist.

Interessant ist es dass gerade bei diesen drei Zuckern ihre cis-Modifikationen das Kristallwasser enthalten können. Das H vom Wasser wird durch das alkoholische O-Atom und zugleich das H von alkoholischen OH, durch das O-Atom vom Wasser angezogen. Also stellen wir es wie Abb. 9a schematisch dar:

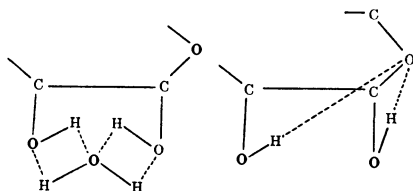


Abb. 9a.

b.

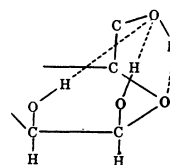


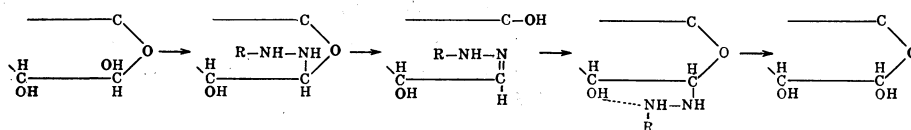
Abb. 10.

Aber solche Anziehungskräfte können wohl zwischen Ring-O und H existieren, wie in Abb. 9b gezeigt ist, sogar vielleicht stärker als solche des Wassers. Bei obigen drei Zuckern jedoch wird die Nebenvalenz von Ring-O durch CH_3 oder OH vom C(6) gerade abgesättigt, dadurch werden OH vom C(1) und C(2) mit Wasser in Verbindung gebracht. Da Methylgruppe im Vergleich mit OH nicht so stark die Nebenvalenz vom Ring-O absättigen kann, so enthält Rhamnose nur halb Mol. Kristallwasser. Pentosen enthalten kein Kristallwasser, weil das Ring-O mit seinem Vollkraft die Nebenvalenz von OH des C(1) und C(2) absperrt. Das OH des C(6) von Mannose wird zu Ring-O angezogen, und dementsprechend wird Nebenvalenz vom Ring-O abgesättigt. Aber zugleich rückt OH des C(6) näher an das OH des C(1) und des C(2), und beraubt wieder die Nebenvalenzkraft, welche sonst Kristallwasser anziehen würde. (Abb. 10). Daher hat β -Mannose kein Kristallwasser bei sich.

(18) Lippmann, Die Chemie der Zuckerarten; Tanret, *Bull. soc. chim. Paris*, (3) 13, 728; 15, 195.

β -Glucose kristallisiert nach Behrend⁽¹⁹⁾ aus ihrer Pyridin-Lösung, zwar als Additionsverbindung mit Pyridin, welches mit der Zeit zerfließt. Da Pyridin mit Ring-O oder mit andere dissozierende OH durch seine Nebenvalenz verbinden könnte, würden die Nebenvalenzbeziehungen zwischen OH untereinander und diegleiche zwischen OH des C(1) und Ring-O abgebrochen. Infolgedessen, kristallisiert der Zucker nach der Wirkung von elektrischen Momente in trans-Modifikation. Nach Levene,⁽²⁰⁾ ist α -Mannose auch auf solcher Weise darstellbar. Levene hat konzentriertes Ammoniak für dieselben Zweck angewandt, und es ist ihm gelungen β -Glucose und α -Mannose darzustellen. Da Ammoniak auch dergleichen Nebenvalenzbindung wie Pyridin bilden würde, könnte man wohl solche Resultate erwarten. Er empfiehlt auch Eisessig zur Gewinnung von trans-Isomeren. Eisessig mag wohl als Vorstufe der Acetylierung mit OH Nebenvalenzbindung ausbilden, demgemäss wird die Beziehung der Nebenvalenz von OH untereinander ausgeschaltet, und nur die Einflüsse der elektrischen Momente würden zurückbleiben. Daher wird hier wieder trans-Isomer gebildet.

Die bisher entwickelte Hypothese bezieht sich auf den freien Zucker. Wie diese Hypothese bei ihren Derivaten, z.B. Acetylzucker, Halogenose usw. modifiziert werden soll, werde ich zurzeit dahingestellt sein lassen.⁽²¹⁾ Es sei nur noch erwähnt dass Haworth⁽²²⁾ β -Lyxose aus α -Isomer über ihr p-Bromphenylhydrazon dargestellt hat, und diese Reaktionsmechanismus etwa wie folgend sein würde:



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(19) *Ann.*, **331** (1904), 359.

(20) *J. Biol. Chem.*, **57** (1923), 329.

(21) Wolfrom and Morgan (*J. Am. Chem. Soc.*, **54** (1932), 3390) behaupten eine Aldehyd-form als die Zwischen-form der Mutarotation. Ihre Experimente wurde aber mit Pentaacetylgalaktose ausgeführt.

(22) *J. Chem. Soc.*, **1928**, 1226.

GLUCO-SULFATASE. III.⁽¹⁾

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Received January 12th, 1933. Published February 28th, 1933.

We have reported in the preceeding communication⁽¹⁾ that our sulfatase exists not only in *Eulota* spp., but also in other mollusks, such as mud-snail (*Viviparus japonicus* Martens). It would be interesting, therefore, to investigate the existence of our sulfatase in wider ranges of the molluscan phylum.

Those materials investigated in the present researches were partially obtained from the market and others collected at the Misaki Marine Biological Station. The experimental manipulations are the same as described in the preceeding papers, that is, the enzyme solutions were prepared as usual from the ground contents of materials with a centrifuge and the hydrolysed sulphate was titrated by the benzidine-method.

The experimental data are summarized below in Table 1. In this table, (S) means the amount of sulphate in 1 c.c. as sulphur in miligram, and (%) means the percentage of this sulphur to the total sulphur (free sulphate and ethereal sulphate). Those data in brackets mean the corresponding controls.

Table 1.

Species \ Days	2	4	5	6	7	Date of collection
1. <i>Lymnaea</i>	{(S) 0.023 (0.008) (%) 1.2 (0.4)	0.049 (0.007) 2.6 (0.4)	0.088 (0.010) 4.7 (0.5)			Middle of May
2. <i>Paphia</i>	{(S) 0.039 (0.000) (%) 1.4 (0.0)	0.149 (0.000) 5.2 (0.0)		0.181 (0.024) 6.4 (0.8)		
3. <i>Ostrea</i>	{(S) 0.065 (0.042) (%) 2.3 (1.5)	0.077 (0.057) 2.7 (2.0)		0.088 (0.057) 3.1 (2.0)		
4. <i>Anadara</i>	{(S) 0.019 (0.016) (%) 0.7 (0.6)	0.042 (0.015) 1.5 (0.5)		0.060 (0.016) 2.1 (0.6)		

(1) Gluco-Sulfatase II, *J. Chem. Soc. Japan*, 54 (1933), 59.

Table 1.—(Continued)

Species	Days	2	4	5	6	7	Date of collection
5. <i>Turbo</i>	{ (S) 0.198 (0.079) (%) 7.0 (2.8)	0.230 (0.078) 8.1 (2.7)			0.284 (0.079) 10.0 (2.8)		End of June
6. <i>Corbicula</i>	{ (S) 0.013 (0.000) (%) 0.5 (0.0)	0.038 (0.000) 1.3 (0.0)			0.048 (0.000) 1.7 (0.0)		
7. <i>Meretrix</i>	{ (S) 0.195 (0.147) (%) 6.8 (5.2)	0.260 (0.151) 9.1 (5.3)			0.291 (0.202) 10.2 (7.1)		
8. <i>Haliotis</i>	{ (S) 0.230 (0.039) (%) 8.1 (1.4)	0.349 (0.036) 12.2 (1.3)			0.410 (0.055) 14.4 (1.9)		
9. <i>Rapana</i>	{ (S) 0.142 (0.091) (%) 5.0 (3.2)		0.182 (0.070) 6.4 (2.5)		0.231 (0.076) 8.1 (2.7)		Beginning of July
10. <i>Monodonta</i>	{ (S) 0.318 (—) (%) 11.2 (—)	0.436 (0.000) 15.3 (0.0)			0.537 (0.018) 18.9 (0.6)		
11. <i>Clava</i>	{ (S) 0.281 (0.066) (%) 9.9 (2.3)	0.344 (0.063) 12.1 (2.2)			0.483 (0.066) 16.9 (2.3)		Middle of July
12. <i>Coronatus</i>	{ (S) 0.338 (—) (%) 11.9 (—)	0.416 (0.000) 14.6 (0.0)			0.560 (0.000) 19.6 (0.0)		
13. <i>Charonia</i>	{ (S) 1.190 (0.152) (%) 41.8 (5.3)	1.923 (0.154) 67.5 (5.4)			2.130 (0.177) 74.8 (6.2)		End of July
14. <i>Onchidium</i>	{ (S) 0.148 (0.012) (%) 5.2 (0.4)	0.237 (0.007) 8.3 (0.2)			0.288 (0.024) 10.1 (0.8)		
13'. <i>Charonia</i>	{ (S) 1.160 (0.234) (%) 59.8 (12.0)	1.495 (0.228) 77.1 (11.7)			1.674 (0.231) 86.5 (11.9)		

Table 1.—(Concluded)

Species	Days	2	4	5	6	7	Date of collection
15. <i>Tetraclita</i>	{ (S) 0.049 (0.030) (%) 2.5 (1.5)	0.055 (0.037)			0.067 (0.052)		Middle of September
16. <i>Ischinochiton</i>	{ (S) 0.110 (0.022) (%) 5.7 (1.7)	0.222 (0.028)			0.305 (0.027)		
17. <i>Bathytoma</i>	{ (S) 0.133 (0.006) (%) 6.9 (0.3)	0.197 (0.006)			0.196 (0.006)		
18. <i>Strombus</i>	{ (S) 0.118 (—) (%) 6.1 (—)	0.274 (0.014)			0.369 (0.014)		
19. <i>Latrunculus</i>	{ (S) 0.062 (0.043) (%) 3.3 (2.2)		0.083 (0.048)			0.093 (0.046)	Middle of October
20. <i>Chicoreus</i>	{ (S) 0.135 (0.106) (%) 7.0 (5.4)		0.286 (0.096)			0.324 (0.096)	
			14.7 (4.9)			16.7 (4.9)	

The scientific names of the above forms are:

1. <i>Lymnaea japonica</i> Joy.	2. <i>Paphia philipinarum</i> Adams.
3. <i>Ostrea gigas</i> Thum.	4. <i>Anadara inflata</i> Reeve.
5. <i>Turbo cornutus</i> Solander.	6. <i>Corbicula leana</i> Prime.
7. <i>Meretrix meretrix</i> Linné.	8. <i>Haliotis gigantea</i> Gmelin.
9. <i>Rapana thomasi</i> Grosse.	10. <i>Monodonta labis</i> Linné.
11. <i>Clava kochi</i> Philippi.	12. <i>Turbo coronatus corensis</i> Recluz.
13. <i>Charonia lamps</i> Linné.	14. <i>Onchidium verruculatum</i> Cuvier.
15. <i>Tetraclita squamosa japonica</i> Pilsbry.	16. <i>Ischinochiton</i> .
17. <i>Bathyloma luhdorfi</i> Lischke.	18. <i>Strombus luhuanus</i> Linné.
19. <i>Latrunculus japonicus</i> Sowerby.	20. <i>Chicoreus sinensis</i> Reeve.

Now, let us rearrange the above experimental results in the order of the maximum hydrolysing power of the animals studied, and classify them according to taxonomy.

Table 2.

No.	Specific names (Japanese names in brackets).	Class.	Order.	Hydrolysed % of glucose-sulphate.
1.	<i>Charonia lampas</i> (Boshu-bora).	Gastropoda.	Prosobranchiata.	74.6% (2)
2.	<i>Viviparus japonicus</i> (Tanishi).	"	"	36.3%*
3.	<i>Turbo coronaus</i> (Sugai).	"	"	19.6%
4.	<i>Strombus luhuanus</i> (Magaki).	"	"	18.3%
5.	<i>Monodonta labis</i> (Ishidatami).	"	"	18.3%
6.	<i>Eulota</i> (Maimai).	"	Pulmonata.	17.0%*
7.	<i>Clava kochi</i> (Kanimori).	"	Prosobranchiata.	14.6%
8.	<i>Ischinochiton</i> (Hizaragai).	Amphieura.	Placophora.	14.3%
9.	<i>Haliotis gigantea</i> (Awabi).	Gastropoda.	Prosobranchiata.	12.5%
10.	<i>Chicoreus sinensis</i> (Kiebor).	"	"	11.8%
11.	<i>Bathytoma luhdorfi</i> (Shyazikugai).	"	"	9.8%
12.	<i>Onchidium verruculatum</i> (Isoawamochi).	"	Pulmonata.	9.3%
13.	<i>Turbo cornutus</i> (Sazae).	"	Prosobranchiata.	7.2%
14.	<i>Paphia philipinarum</i> (Asari).	Pelecypoda.	Eulamellibranchiata.	5.6%
15.	<i>Rapana thomasi</i> (Akanishi).	Gastropoda.	Prosobranchiata.	5.4%
16.	<i>Lymnaea japonica</i> (Monoaragi).	"	Pulmonata.	4.2%
17.	<i>Meretrix meretrix</i> (Hamaguri).	Pelecypoda.	Eulamellibranchiata.	3.1%
18.	<i>Latrunculus japonicus</i> (Baigai).	Gastropoda.	Prosobranchiata.	2.4%
19.	<i>Corbicula leana</i> (Shijimi).	Pelecypoda.	Eulamellibranchiata.	1.7%
20.	<i>Anadara inflata</i> (Akagai).	"	Filibranchiata.	1.5%
21.	<i>Ostrea gigas</i> (Kaki).	"	Pseudolamellibranchiata.	1.1%
22.	<i>Tetraclita squamosa</i> (Kurofujitsubo).	Crustacea.	Cirripedia.	0.8%

(*Viviparus* and *Lymnaea* are fresh water forms and *Eulota* terrestrial; others are marine animals).

* These data are from the preceding papers.

(2) During this communication under press, we have experienced that the enzyme of *Charonia* can hydrolyse 82.7% of the ester in 10 days. As another example of Gastropoda we have further investigated *Bursa bufo* Röding (*Naruto-bora*). Its enzyme decomposed 80.5% of the substrate in 10 days.

With a few exceptions, the activity of enzyme of Gastropoda is decidedly stronger than that of Pelecypoda. *Chiton* is the only exception in the first thirteen examples. It shows strong enzyme action but belong to Amphineura. The Amphineura are more primitive than Gastropoda.

From No. 14 to No. 22 no regularity can be found. But to discuss these small differences of activity of enzyme, the analytical data have to be fairly constant for all examples. Our analytical data, however, cannot fulfill this condition; its activity seems to vary by the metabolic condition of animals and the properties of protein of the enzyme solution are not always the same and seem to have some influence upon analytical data. Therefore we wish to leave this question of irregularity open for the future studies. Anyhow, so far as we have experienced, it can be said that the very active glucosulfatase is always found in Gastropoda, though it is not the case vice versa.

We wish to acknowledge our thanks to the staffs of the Misaki Marine Biological Station for their kind assistance in collecting materials.

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DAS VERHALTEN DES CYCLOHEXANS UND SEINER DERIVATE BEI ANODISCHER OXYDATION.

Von Moriaki YOKOYAMA.

Eingegangen am 5. Januar, 1933. Ausgegeben am 28. März, 1933.

Einleitung.

Dass das Benzol, der Grundkohlenwasserstoff der aromatischen Körper, unter Aufnahme von nascierendem oder katalytisch aktiviertem Wasserstoff unmittelbar in das Cyclohexan, den Grundkohlenwasserstoff der hydroaromatischen Körper, verwandelt wird, ist allgemein bekannt. Formell betrachtet ist also das Cyclohexan eine Hydroderivat des Benzols. Die physikalischen und chemischen Eigenschaften des Cyclohexans stehen allerdings mit jenen, die man a priori von einem "Benzolderivate" erwarten würde, recht wenig im Einklang. So zeigt das Cyclohexan bei der Einwirkung von Brom ein vom Benzol verschiedenes Verhalten. Z.B. bei der Einwirkung von überschüssigen Brom auf Benzol⁽¹⁾ entsteht schon beim Kochen im Dunkeln Brombenzol, *p*-Dibrombenzol und wenig *o*-Dibrombenzol, Cyclohexan⁽²⁾ hingegen wird kaum verändert; im Sonnenlicht bildet Benzol⁽³⁾ glatt mit Brom Hexabromanlagerungsprodukt, dagegen siedendes Cyclohexan⁽²⁾ Monobromcyclohexan, 1.2-Dibromcyclohexan neben geringen Mengen verschiedener Polybromderivate. Ferner erwies sich bei der Einwirkung von Aluminiumchlorid nach Friedel-Crafts Benzol als leicht substitutionsfähig durch Kohlenwasserstoffreste, während eine derartige direkte Substitution von Wasserstoffatomen, die an Kohlenstoff gebunden sind, durch Alkylreste im Cyclohexan nicht möglich ist.

Nun wird zu betrachten sein, ob die Aehnlichkeitsverhältnisse zwischen den zwei Körpern, wie sie bei der Bromsubstitutionsreaktion erkannt wurden, auch bei der elektrochemischen Oxydation in Erscheinung treten können. Doch finden sich nur lückenhafte Angaben, wenn man die Frage aufwirft, wie die Verhältnisse hierbei sind. Elektrochemische Oxydationen sind nur an aromatischen Kohlenwasserstoffen durchgeführt worden und zwar hauptsächlich von Fichter und seinen Mitarbeitern,⁽⁴⁾ welche

(1) F. Riese, *Ann.*, **164** (1872), 162, 176; Schramm, *Ber.*, **1** (1885), 606.

(2) F. Bodroux u. F. Taboury, *Compt. rend.*, **152** (1911), 1253; *Bull. Soc. Chim.*, [4] **9** (1911), 593.

(3) Faraday, der Entdecker des Benzols, kannte schon diese Reaktion.

(4) *J. Soc. Chem. Ind.*, **48** (1929), 325.

zeigten, wie die anodische Einwirkung auf den Wasserstoff im aromatischen Kern ist. Dagegen ist, soviel wir aus der Literatur ersehen konnten, bis jetzt kaum bekannt, wie das Verhalten von hydroaromatischen Kohlenwasserstoffen bei der elektrochemischen Oxydation ist.

Wir wollten deshalb einen Beitrag zu diesem Fragen-Komplex liefern, indem wir uns in der vorliegenden Arbeit die Aufgabe stellten, den Verlauf der elektrochemischen Oxydation an einigen Musterbeispielen zu studieren mit dem Zweck, auf Grund der Oxysubstitutionsreaktionen am Cyclohexan die Analogien und Verschiedenheiten von aromatischen und hydroaromatischen Kohlenwasserstoffen in ihrem Verhalten an der Anode festzustellen; wir hatten dabei die Hoffnung über die Oxydation der aromatischen Kohlenwasserstoffe einige Klarheit zu gewinnen.

Elektrochemische Oxydation des Benzols.

Ueber die elektrochemische Oxydation von Benzol wurden schon einige Untersuchungen veröffentlicht. E. Gattermann und F. Friedrichs⁽⁵⁾ elektro-oxydierten Benzol in alkoholisch-schwefelsaurer Lösung an Platinanoden und erhielten dabei Hydrochinon. Theodor Kempf⁽⁶⁾ zeigte die Entstehung von Chinon bei der Elektrolyse von Benzol, das in verdünnter Schwefelsäure emulsionartig verteilt war, an einer Bleidioxidanode. Fr. Fichter⁽⁴⁾ fand bei der Oxydation einer Suspension von Benzol in wässriger Schwefelsäure an Platin- oder Bleidioxidanoden neben Chinon und Hydrochinon untergeordnete Mengen von Maleinsäure und Brenzcatechin.

Da aber diese Arbeiten für unsere Zwecke nicht genügend Aufschluss boten, mussten manche der Versuche von Anfang an wiederholt werden. Eine Emulsion von 2.35 gr. (0.03 Mol.) Benzol (Kahlbaum; Sdp. 80°C. bei 757 mm; $D_4^{20} = 0.8801$; $n_D^{20} = 1.4976$) in 100 ccm n-Schwefelsäure wurde an einer cylindrischen Bleiblechanode (mit vorher frisch hergestelltem Bleidioxid-Ueberzug) mit 0.05 Amp./cm² anodischer Stromdichte unter lebhaftem Rühren (700 Touren pro Minute) in der Tonzelle oxydiert, wobei die Temperatur durch äussere Kühlung bei ca. 30°C. gehalten wurde. Der Katholyt war n-Schwefelsäure, die Kathode ein Platinblech, welches das Tondiaphragma umgab. Zur Kondensation des Benzols wurde ein kleiner Liebig'scher Kühler durch eine Bohrung des Stopfens hindurchgeführt. Die durchgesandte Strommenge betrug 10 F/Mol. Schon kurz nach Stromschluss nahm der Elektrolyt eine gelbliche Farbe an, die allmählich über gelb nach braun und dunkelrötlichbraun umschlug.

(5) *Ber.*, **2** (1897), 1942; vgl. auch Renard, *Compt. rend.*, **91** (1880), 175.

(6) D.R.P. 117251 (1899); Friedländer, **6**, 109.

A. Die gasförmigen Produkte. Die aus dem Anodenraum entwickelten Gase wurden nach der bei der elektrochemischen Oxydation von Pyridin⁽⁷⁾ erwähnten Methode möglichst sorgfältig analysiert. Denn die dauernde Kontrolle der qualitativen Beschaffenheit der Anodengase während des Verlaufes der Elektrolyse erschien geeignet, ein klares Bild von der Art des Verlaufes des ziemlich komplizierten Oxydationsprozesses zu vermitteln. Die Analysendaten sind in der folgenden Tabelle (1) zusammengestellt. In ein Diagramm (Fig. 1) eingetragen, ergaben die Werte dieser Tabelle die beistehend gezeichneten Kurven.

Tabelle 1.

Anode: Bleidioxyd; Temp.: 30°C.

Stromstärke: 2.5 Amp.; Stromdichte: 0.05 Amp./cm².

Stdn.	Sauerstoff-coulom. (ccm.)	Anodengas (ccm.)	Aufgefangene Gase						Stromausbeute %
			CO ₂		O ₂		CO		
			ccm.	%	ccm.	%	ccm.	%	
0.5	70.8	28.8	10.5	36.4	16.8	58.2	1.5	5.4	71.2
1	70.1	31.7	18.6	58.6	11.6	36.6	1.5	4.8	83.5
1.5	70.3	30.2	20.9	69.2	8.3	27.5	1.0	3.3	88.2
2	70.5	53.0	33.4	63.0	11.2	30.0	1.2	3.1	84.1
2.5	70.5	37.4	25.0	66.9	18.1	34.1	1.5	2.9	74.3
3.	70.2	58.2	32.6	56.0	22.9	39.3	2.5	4.7	67.5
3.5	70.0	64.0	31.0	48.5	30.4	47.5	2.6	4.0	56.7
4	70.7	68.1	31.0	45.5	34.4	50.5	2.7	4.0	51.4

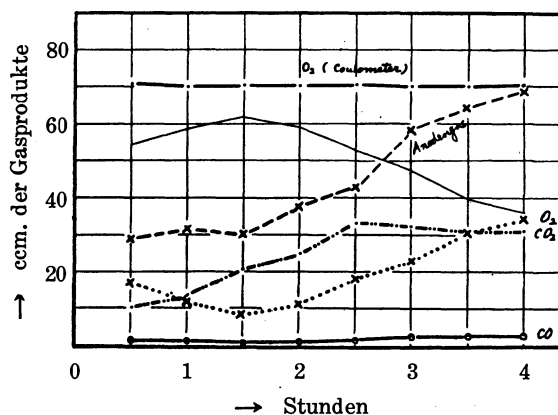


Fig. 1.

(7) Yokoyama u. Yamamoto, dieses Bulletin, 7 (1932), 28.

Wie die Tabelle (1) und die Figur (1) zeigen, werden Kohlendioxyd und Kohlenmonoxyd während der Elektrolyse gebildet, wobei ersteres sich am Anfang in verhältnismässig grösserer Menge entwickelt und im Laufe der Elektrolyse langsam eine stärkere Entwicklung zeigt, die aber dann wieder nachlässt, während Kohlenmonoxyd wenig und fast konstant im Verlaufe der Elektrolyse anfällt.

Die Menge des in der Zelle verbrauchten Sauerstoffs ist am Anfang gering, steigt aber deutlich sehr schnell bis zum Optimalpunkt und sinkt dann wieder langsam.

Zieht man den entweichenden Sauerstoff mit in den Bereich der Betrachtung und trägt die prozentische Zusammensetzung, wie sie sich am Schluss der einzelnen Analysenzeiten ergeben hat, in ein Diagramm (Fig. 2) ein, so stellt sich die Sauerstoffkurve als Spiegelbild der Kohlendioxydkurve dar, während die Kohlenmonoxydkurve der Abzissenachse nahezu parallel verläuft. Es geht daraus deutlich hervor, dass die im Verlaufe der Elektrolyse sinkende Sauerstoffentwicklung hauptsächlich auf Rechnung einer gesteigerten Kohlendioxydbildung zu setzen ist.

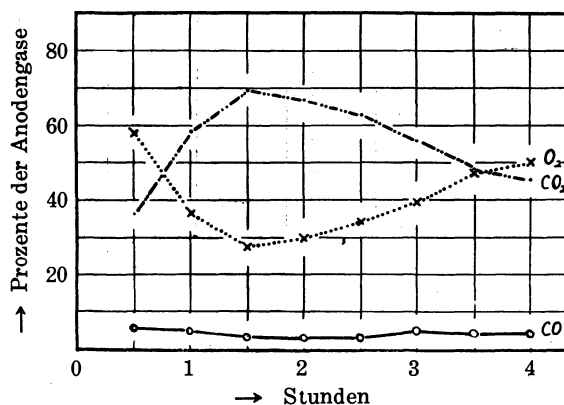


Fig. 2.

Einige Analysenresultate aus der grossen Reihe der durchgeführten Versuche, die zur Ermittlung der Einflüsse von Temperatur und Anodenmaterial bei verschiedenen Bedingungen durchgeführt worden sind, wurden in folgenden Tabellen (2, 3 und 4) zusammengestellt. Wie aus den Tabellen (1, 2, 3 und 4) und den entsprechenden Figuren (1, 3, 4 und 5) ersichtlich ist, sind die Stromausbeuten an der Bleidioxydanode viel besser als die an platinieren Platinanoden. Der Einfluss der Temperatur bei der Bleidioxydanode ist nicht so merklich, jedoch bei platinieren Platinanoden wesentlich höher. Der Temperaturkoeffizient, bezogen auf die Stromausbeute bei platinieren Platinanoden, ist um das Mehrfache grösser als der bei der Bleidioxydanode.

Tabelle 2.

Anode: Bleidioxid; Temp.: 70°C.
 Stromstärke: 2.5 Amp.; Stromdichte: 0.05 Amp./cm².

Stdn.	Sauerstoff-coulom. (ccm.)	Anodengas (ccm.)	Aufgefangene Gase						Strom- ausbeute %
			CO ₂		O ₂		CO		
			ccm.	%	ccm.	%	ccm.	%	
0.5	70.0	39.4	32.3	81.9	6.5	16.5	0.6	1.6	90.7
1	70.5	40.0	34.4	86.0	4.8	12.0	0.8	2.0	93.1
1.5	70.1	36.1	32.2	89.2	3.1	8.6	0.7	2.2	95.5
2	70.4	37.7	31.3	83.0	5.8	15.4	0.6	1.6	91.8
2.5	70.5	46.8	31.7	67.7	14.3	30.5	0.8	1.9	79.8
3	70.2	59.8	37.0	61.8	21.0	35.2	1.8	3.0	70.2
3.5	70.4	67.0	35.5	53.0	30.1	44.9	1.4	2.1	57.3
4	70.5	71.0	38.1	53.6	31.4	44.3	1.5	2.1	55.5

Tabelle 3.

Anode: Platiniertes Platin; Temp.: 30°C.
 Stromstärke: 2.5 Amp.; Stromdichte: 0.05 Amp./cm².

Stdn.	Sauerstoff-coulom. (ccm.)	Anodengas (ccm.)	Aufgefangene Gase						Strom- ausbeute %
			CO ₂		O ₂		CO		
			ccm.	%	ccm.	%	ccm.	%	
0.5	71.0	62.2	0.6	0.9	59.4	95.6	2.2	3.5	16.4
1	70.4	60.3	1.2	2.0	53.6	88.7	5.6	9.3	24.0
1.5	69.2	55.6	1.4	2.6	49.2	88.4	5.0	9.0	28.2
2	71.0	55.6	1.4	2.6	49.2	88.4	5.0	9.0	30.7
2.5	70.6	53.4	1.4	2.7	47.2	88.3	4.8	9.0	33.1
3	70.8	54.9	2.2	4.1	48.9	89.0	3.8	6.9	30.9
3.5	69.2	55.4	1.4	2.5	49.0	88.5	5.0	9.0	29.2
4	71.6	56.2	1.6	3.0	51.2	91.0	3.4	6.0	28.5

Tabelle 4.

Anode: Platiniertes Platin; Temp.: 70°C.
Stromstärke: 2.5 Amp.; Stromdichte: 0.05 Amp./cm².

Stdn.	Sauerstoff-coulom. (ccm.)	Anodengas (ccm.)	Aufgefangene Gase						Stromausbeute %
			CO ₂		O ₂		CO		
			ccm.	%	ccm.	%	ccm.	%	
0.5	71.6	42.6	7.3	16.9	35.2	82.7	0.2	0.4	50.9
1	71.5	39.6	7.2	18.1	32.2	81.3	0.2	0.5	54.9
1.5	70.2	41.6	7.0	16.8	34.3	82.3	0.3	0.9	51.2
2	72.4	47.9	9.1	19.0	38.8	80.7	0.2	0.3	46.5
2.5	72.8	52.0	10.4	20.0	41.4	79.6	0.2	0.4	42.5
3	71.2	55.7	11.8	21.2	43.6	78.2	0.3	0.6	38.8
3.5	70.0	54.9	10.4	18.9	44.3	80.8	0.2	0.3	36.1
4	70.6	60.0	11.2	18.7	48.6	81.0	0.2	0.3	31.1

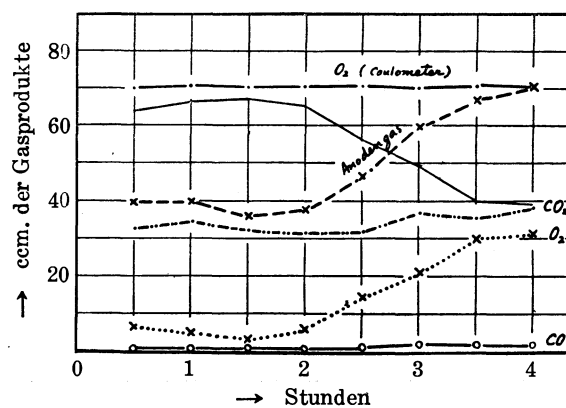


Fig. 3.

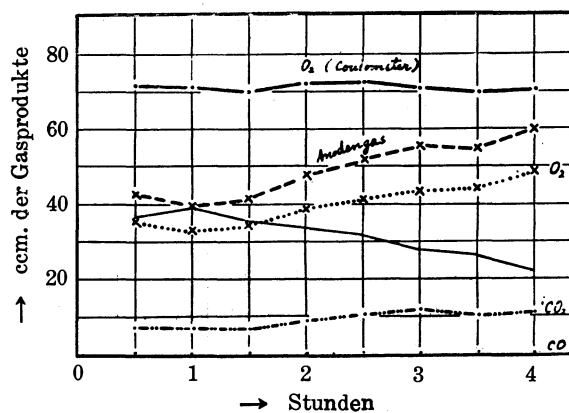


Fig. 4.

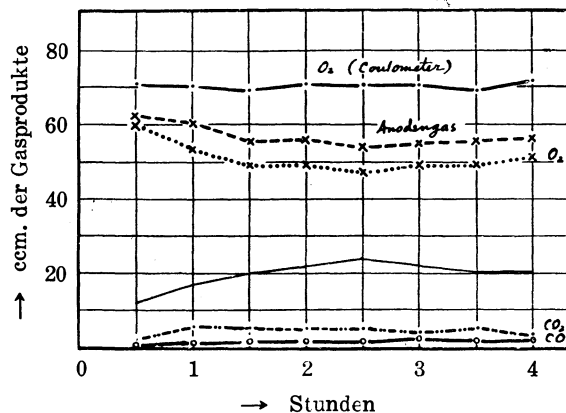


Fig. 5.

Auffällig ist die stets beobachtete Erscheinung, dass die im Anfang stark zunehmende Stromausbeute am Schluss deutlich sinkt. Es hat den Anschein, dass im Verlauf der Elektrolyse ein leicht oxydabler Körper entsteht, dessen Konzentration zunächst stark zu-, dann langsam abnimmt.

B. Behandlung der Anodenflüssigkeit. Auch bei den Versuchen über hydroaromatische Körper, bei denen der Anolyt Gegenstand der Untersuchung war, wurden die eingangs erwähnten Bedingungen grundsätzlich eingehalten.

(a) *Chinon*. Aus der stechend riechenden, rötlichbraunen Anodenflüssigkeit wurde zunächst durch Ausschütteln mit Benzol das entstandene Chinon (Schmp. 112°–115°C.) extrahiert und in der benzolischen Lösung durch Schütteln mit verdünnter Schwefelsäure und Zinkstaub in Hydrochinon übergeführt. Aus der Zinklauge wurden dadurch etwa 0.58 gr. Hydrochinon (Schmp. 168.5°–170°C.) erhalten (aus 3 Versuchen), auf Chinon umgerechnet 6.1% des Ausgangsmaterials.

Anal.: Subst. = 2.767; CO₂ = 6.619; H₂O = 1.419 mgr.

Gef.: C = 65.24; H = 5.74 %.

Ber. für C₆H₄O₂: C = 65.42; H = 5.50 %.

(b) *Ameisensäure und Brenzcatechin*. Die mit Benzol extrahierte Lösung des Anolyten wurde hierauf ausgeäthert; nach Abdestillieren des Aethers hinterblieb ein braungefärbter, stechend nach Ameisensäure riechender harzartiger Rückstand. Die ätherischen Destillate, nach der bei der elektrochemischen Oxydation von Tolu-*p*-chinon⁽⁸⁾ beschriebenen

(8) Yokoyama u. Ishikawa, dieses Bulletin, 6 (1931), 280.

Art auf Ameisensäure verarbeitet, ergaben etwa 0.01 gr. Bariumformiat (aus 2 Versuchen).

Der oben erwähnte Rückstand (Ausbeute sehr gering) wurde in wenig Wasser gelöst. Die wässrige Lösung reagierte gegen Lackmus sauer und gab mit Ferrichlorid eine typische intensive Grünfärbung, die nach Zusatz von Natriumcarbonatlösung über Violett in Rot überging; ferner liess sich durch Bleiessig ein amorphes Bleisalz ausfällen. Dem Verhalten nach handelt es sich wahrscheinlich um Brenzcatechin, das Fichte⁽⁴⁾ auch erhielt.

(c) *Maleinsäure*. Die mit Aether extrahierte Lösung des Anolyten (aus 4 Elektrolysen) wurde auf dem Wasserbade mit Bariumcarbonat gegen Lackmus neutralisiert und in der Wärme möglichst rasch abfiltriert. Das Filtrat wurde zur Trockne verdampft. Es hinterblieb ein schwach braun gefärbter Rückstand, der nach der Entfernung der gefärbten Stoffe durch Tierkohle aus Wasser zweimal umkrystallisiert wurde und dann kleine weisse Krystalle lieferte, die 0.15 gr. (0.4% der theoretischen Menge) wogen. Diese wurden nach dem Trocknen auf dem Toluolbade⁽⁹⁾ einer Barium-Bestimmung unterworfen.

Anal.: Subst. = 0.0782 gr. nach Abrauchen mit Schwefelsäure

BaSO₄ = 0.0681 gr.

Gef.: Ba = 51.25 %.

Ber. für C₄H₂O₄Ba + H₂O: Ba = 50.98%.

Bei dieser elektrochemischen Oxydation von Benzol an der Bleidioxyanode in verdünnter Schwefelsäure wurden die folgenden Oxydationsprodukte erhalten: Brenzcatechin, Chinon, Maleinsäure, Ameisensäure, Kohlendioxyd und Kohlenmonoxyd.

Elektrochemische Oxydation des Cyclohexans.

Im folgenden soll gezeigt werden, wie Cyclohexan unter dem Einfluss der anodischen Oxydation verändert wird, und ein Vergleich mit dem Benzol gezogen werden.

I. Oxydation in wässrig-schwefelsaurer Emulsion. Eine innige Emulsion von 2.523 gr. [(0.03 Mol.) ; Sdp.: 80.5°–82°C. (754 mm.) ; $D_4^{25} = 0.7727$] Cyclohexan, das aus Benzol durch katalytische Reduktion in Gegenwart von reduziertem Nickel hergestellt worden war, in 100 ccm n-Schwefelsäure wurde an einer cylindrischen Bleidioxyanode bei 0.05 Amp./cm². anodischer Stromdichte oxydiert, wobei ein elektrisch geheiztes Wasserbad die

(9) Büchner, *Ann.*, **49** (1844), 72.

Temperatur bei 70°C. hielt, während sonst die Bedingungen die gleichen waren wie beim Benzol.

Die Analyse der Anodengase während der Elektrolyse ergab die hier zusammengestellten Werte. Wie man aus den Tabellen (Tabelle 5, 6 u. 7) und den entsprechenden Diagrammen (Fig. 6, 7 u. 8) ersehen kann, ist die Menge des freigesetzten Sauerstoffs in diesen Versuchen ganz besonders gross und von Anfang an fast konstant, sowohl an der Bleidioxylanode als auch an der Platinanode, d.h. *die Menge des in der Zelle umgesetzten Sauerstoffs ist von Anfang an sehr klein und bleibt konstant* und die Stromausbeute dementsprechend sehr gering. So ist die Stromaus-

Tabelle 5.

Anode: Bleidioxyd; Temp.: 70°C.

Stromstärke: 2.5 Amp.; Stromdichte: 0.05 Amp./cm².

Stdn.	Sauerstoff-coulom. (ccm.)	Anodengas (ccm.)	Aufgefangene Gase						Strom- ausbeute %
			CO ₂		O ₂		CO		
			ccm.	%	ccm.	%	ccm.	%	
0.5	79.7	75.5	1.3	1.7	74.6	98.7	—	—	6.4
1	79.6	75.6	1.6	2.1	74.0	98.4	—	—	7.0
2	81.2	73.8	0.5	0.7	72.9	98.8	0.4	0.5	8.9
3	80.3	74.6	1.0	1.4	73.2	98.1	0.4	0.5	8.8
4	80.0	72.4	0.8	1.1	71.5	98.8	0.1	0.1	10.6

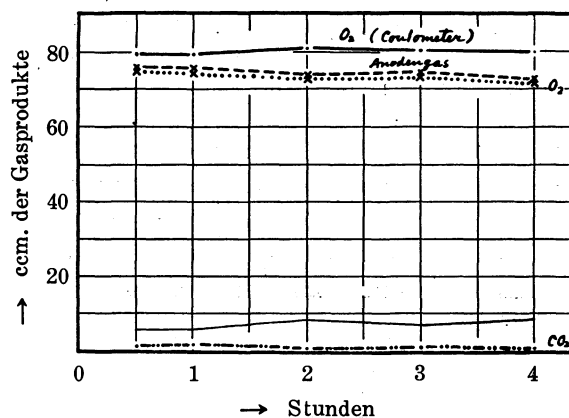


Fig. 6.

Tabelle 6.

Anode: Bleidioxyd; Temp.: 30°C.

Stromstärke: 2.5 Amp.; Stromdichte: 0.05 Amp./cm².

Stdn.	Sauerstoff-coulom. (ccm.)	Anodengas (ccm.)	Aufgefangene Gase						Strom- ausbeute
			CO ₂		O ₂		CO		
			ccm.	%	ccm.	%	ccm.	%	%
0.5	70.6	67.5	0.2	0.3	67.2	99.5	0.1	0.2	4.8
1	70.6	67.8	0.4	0.6	67.2	99.1	0.2	0.3	4.8
1.5	74.6	71.9	0.2	0.5	71.6	99.3	0.1	0.2	4.0
2	70.6	68.6	0.4	0.6	68.1	99.3	0.1	0.1	3.6
2.5	70.6	69.1	0.1	0.2	68.9	99.7	0.1	0.2	2.1
	70.4	68.6	0.3	0.4	68.3	99.5	0.1	0.1	3.0
3.5	69.4	68.4	0.4	0.6	68.0	99.4	—	—	2
4	73.6	71.6	0.2	0.3	71.4	99.6	0.1	0.1	3

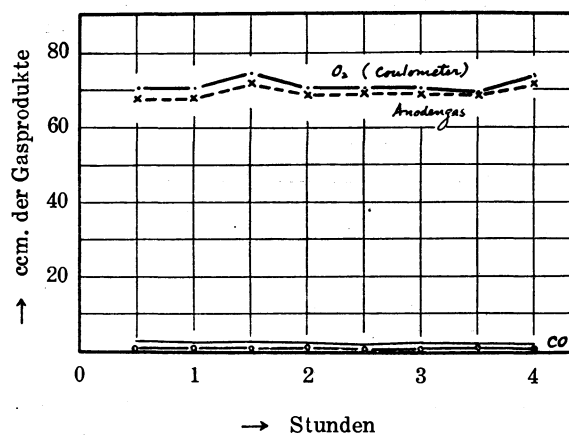


Fig. 7.

Tabelle 7.

Anode: Platiniertes Platin; Temp.: 70°C.
Stromstärke: 2.5 Amp.; Stromdichte: 0.05 Amp./cm².

Stdn.	Sauerstoff-coulom. (ccm.)	Anoden-gas (ccm.)	Aufgefangene Gase						Strom-ausbeute %
			CO ₂		O ₂		CO		
			ccm.	%	ccm.	%	ccm.	%	
0.5	79.8	80.8	3.2	4.0	77.6	96.1	—	—	2.8
1	80.0	80.7	2.2	2.8	78.5	97.4	—	—	1.9
2	78.6	79.7	2.3	2.9	77.4	97.2	—	—	2.9
3	80.1	80.1	1.7	2.1	78.4	97.8	—	—	2.1
4	80.1	80.0	1.7	2.1	78.3	97.7	—	—	2.2

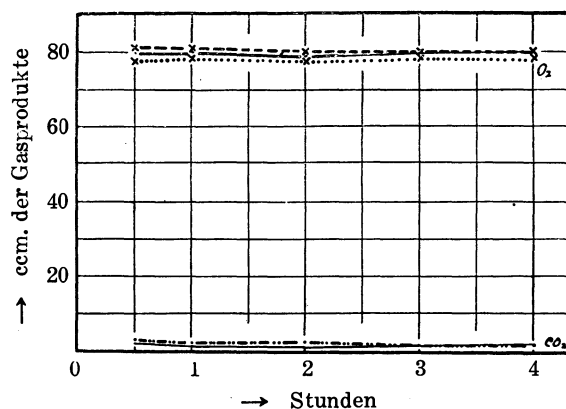


Fig. 8.

beute an Platinanoden bei niedriger Temperatur (30°C.) so gering, dass wir sie nicht einmal genauer feststellen konnten. Die Stromausbeute an Bleidioxidanoden zeigt deutlich bessere Werte als die an Platinanoden. Der Einfluss der Temperatur auf die Stromausbeute ist fast gleich bei beiden Anoden. Bei Anwendung der Bleidioxidanode wächst die Stromausbeute durch Erhöhung der Temperatur von 30°C. auf 70°C. auf etwa den doppelten Betrag. Die Einflüsse von Temperatur und Anodenmaterial sind daher quantitativ fast die gleichen wie beim Benzol.

Diese analytischen Daten lassen erkennen, dass das Cyclohexan im Vergleich zum Benzol sehr schwer elektrolytisch oxydierbar ist und dass ein wesentlicher Unterschied im Verlauf der elektrochemischen Oxydation beider Substanzen vorhanden sein muss.

Nach dem Schluss der Elektrolyse wurde der fast farblose Anolyt vom unveränderten Cyclohexan mit Hilfe des Scheidetrichters getrennt und von dem während der Elektrolyse an der Anode gefällten Bleisulfat durch Filtration befreit. Das Filtrat wurde mehrmals mit Aether ausgeschüttelt. Die ätherische Lösung hinterliess nach Entfernung des Aethers eine etwas gelb gefärbte Krystallmasse, die auf Ton getrocknet wurde und deren Ausbeute in diesem Fall sehr klein war (ca. 0.11 gr. aus 5 Elektrolysen). Die geringe Ausbeute kann man auch schon aus den gasanalytischen Daten in Tabelle (5) ersehen. (Wir werden darauf im Abschnitt 7 zurückkommen). Die Masse wurde nach der im nächsten Teil (T. II, Abschnitt 2) näher erwähnten Methode zuerst mit Benzol behandelt. Aus der in Benzol schwer löslichen Masse wurden Bernsteinsäure isoliert und eine Krystallmasse in geringer Menge, welche gegen Lackmus sauer reagierte und zwischen 142° und 157°C. schmolz; es handelte sich wahrscheinlich um ein Gemisch von Adipinsäure und Bernsteinsäure. Die isolierte Bernsteinsäure schmolz bei 178–179.5° und liess sich durch die Grünfluoreszenz nach der Behandlung mit Resorcin und konz. Schwefelsäure charakterisieren. Aus dem Benzolauszug wurde eine Säure mit dem Smp. 83–91°C. erhalten. Es handelte sich vielleicht um Glutarsäure; aber die Menge war zu gering um sich genau identifizieren zu lassen. Ausserdem konnten wir nach ähnlicher Methode wie vorher Ameisensäure als Bariumsalz erhalten, die aus Mercurichlorid Mercurochlorid abschied.

II. Oxydation des Cyclohexans in Aceton-Schwefelsäure. Wenn man Cyclohexan einfach in verdünnter Schwefelsäure emulgiert und bei Zimmertemperatur an der Bleidioxydanode elektrooxydiert, so wird es nur wenig angegriffen; besser gelingt der Versuch in der Wärme (70°C.), doch sind auch dann die Stromausbeuten gering, indem viel Sauerstoff unausgenutzt bleibt, wie aus der gasanalytischen Tabelle (5) ersichtlich ist. Daher haben wir in Aceton-Schwefelsäurelösung elektrolysiert.

8.2 ccm Cyclohexan (ca. 0.075 Mol.), 32 ccm 2n-Schwefelsäure und 120 ccm Aceton wurden an der Bleidioxydanode mit 0.05 Amp./cm². anodischer Stromausbeute bei ca. 30°C., unter Anwendung von 17.5 Amp.-Std. (21 F/Mol.) und lebhafter Rührung oxydiert, wobei die Platinkathode in n-Schwefelsäure das Tondiaphragma umgab. In diesem Versuch liess sich die Gasanalyse nicht durchführen, da die Analysenresultate durch die Anwesenheit des als Lösungsmittel benutzten Acetons, das auch an der Anode oxydiert wurde, gefälscht wurden.

Der Anolyt wurde während der Elektrolyse allmählich über gelblich nach gelbbraun gefärbt. Nach Beendigung der Elektrolyse und vor-

sichtigem Abdestillieren des Acetons und unveränderten Cyclohexans wurde mit Aether ausgeschüttelt. Das mit Aether extrahierte Gemisch von Stoffen war weit mehr als im vorigen Fall, dem Versuche in wässrig-schwefelsaurer Emulsion. Neben viel harzartigem Oel wurden nadel-förmige Krystalle erhalten und durch Abpressen auf Ton gereinigt. Die Menge betrug ca. 0.96 gr. für 4 Einzelversuche. Die getrocknete Substanz konnte zunächst mit wenig Benzol in einen schwer (α) und einen leicht löslichen Teil (β) getrennt werden.

(α). *Die in Benzol schwer lösliche Substanz.* (a) *Adipinsäure:* Die in Benzol schwer lösliche Substanz wurde mit einer kleinen Menge kalten Wassers behandelt. Der bei dieser Behandlung nicht in Lösung gehende Rest wurde nach dreimaliger Umkrystallisation aus heissem Wasser in Form reiner Adipinsäure (0.42 gr.; 0.53%) erhalten, die bei 148–149°C. schmolz.

Anal.: Subst. = 2.988; CO₂ = 5.436; H₂O = 1.872 mgr.

Gef.: C = 49.58; H = 7.01%.

Ber. für C₆H₁₀O₄: C = 49.29; H = 6.90%.

Um die Säure weiter zu charakterisieren, verwandelten wir sie nach der von Aschan⁽¹⁰⁾ angegebenen Methode vermittelt Phosphortrichlorid in das Chlorid und dieses in das Amid, dessen Schmelzpunkt 220°C. statt 223°C. war.

(b) *Bernsteinsäure:* Das in den wässrigen Mutterlaugen zurückgebliebene Gemisch von Stoffen wurde nach dem vollständigen Trocknen auf dem Wasserbade mit wasserfreiem Aether behandelt. Aus dem in Aether schwer löslichen Teil wurde Bernsteinsäure (etwa⁽¹¹⁾ 0.31 gr.; 0.8%) erhalten, die nach dem Umkrystallisieren aus Wasser, sowie aus Alkohol bei 181°–182.5°C. schmolz; der Mischschmelzpunkt mit einem käuflichen Präparat (von Kahlbaum) ergab keine Erniedrigung.

Anal.: Subst. = 3.645; CO₂ = 5.406; H₂O = 1.781 mgr.

Gef.: C = 40.55; H = 5.47%.

Ber. für C₄H₆O₄: C = 40.66; H = 5.13%.

(c) *Malonsäure:* Aus dem leicht in Aether löslichen Teile haben wir Malonsäure (0.09 gr.; 0.15%) erhalten, die nach vielmaligem Umkrystallisieren aus Aether, Wasser und Benzol bei 134°–136.5°C. schmolz. Die kleinen krystallinen Tafeln färbten sich beim Erwärmen mit Essig-

(10) Ber., **31** (1898), 2344; vgl. W. Borsche u. Wollemaun, Ber., **45** (1912), 3715.

(11) Infolge der starken Substanzverluste während der Reinigung haben wir bei allen diesen Versuchen nur Rohausbeutezahlen gegeben.

säureanhydrid gelbrot mit gelbgrüner Fluoreszenz. Auf Grund dieser Beobachtungen war der Stoff Malonsäure.

(β). *Die in Benzol lösliche Substanz.* (d) *Glutarsäure*: Der in das Benzol gegangene Anteil wurde nach dem Verjagen des Benzols in Wasser gelöst und mit Bariumhydroxydlösung vorsichtig gegen Lackmus neutralisiert, wobei das in Wasser schwer⁽¹²⁾ lösliche Bariumsalz der Malonsäure (wenig) und ein leicht lösliches Bariumsalz (etwa 0.05 gr.) entstanden. Nach der Entfernung des Bariums aus der Lösung des leicht löslichen Bariumsalzes mittels Schwefelsäure wurde das Filtrat auf dem Wasserbade getrocknet. Die hierbei erhaltenen Krystalle schmolzen bei 91.5–95°C.

Anal.: Subst. = 2.926; CO₂ = 4.835; H₂O = 1.538 mgr.

Gef.: C = 45.17; H = 5.91%.

Ber. für C₅H₈O₄: C = 46.43; H = 6.10%.

Es handelt sich wahrscheinlich um Glutarsäure. Eine genaue Identifizierung dieser Substanz liess sich infolge der ausserordentlich gering anfallenden Menge nicht durchführen. Die ölige harzartige Substanz haben wir nicht näher untersucht.

Bei der elektrochemischen Oxydation von Cyclohexan (15.138 gr.) in Aceton-Schwefelsäurelösung haben wir 0.42 gr. (0.53%) Adipinsäure, 0.31 gr. (0.8%) Bernsteinsäure, 0.09 gr. (0.15%) Malonsäure und wahrscheinlich Glutarsäure isoliert. Bei der Elektrolyse in Emulsionzustand (Teil I) haben wir aus 12.615 gr. Cyclohexan ca. 0.11 gr. Krystallmasse erhalten, in der dieselben Fettsäuren wie bei der Aceton-Schwefelsäurelösung nachgewiesen wurden.

Elektrochemische Oxydation von Cyclohexanol und Cyclohexanon.

Auf Grund der Untersuchung über die elektrochemische Oxydation des Cyclohexans kann man die intermediäre Bildung von Cyclohexanol und Cyclohexanon annehmen. Um diese Möglichkeit zu prüfen, haben wir jetzt auch den Verlauf der elektrolytischen Oxydation von Cyclohexanol und Cyclohexanon studiert.

I. Elektrochemische Oxydation des Cyclohexanols. 0.03 Mol. Cyclohexanol (Sdp. 159°–160°C.; $D_4^{25} = 0.9473$; $n_D^{25} = 1.4636$), aus Phenol durch katalytische Reduktion in Gegenwart von reduziertem Nickel dargestellt, wurde an Bleidioxidanoden unter den gleichen Bedingungen wie

(12) Roboul, *Ann. chim phys.*, (5) **14** (1878), 501.

Benzol elektrolysiert. Die angewandte Strommenge war 8 F/Mol. Die Farbe des Anolyten ging allmählich über gelblich in gelb über.

A. *Die gasförmigen Produkte.* Während der Elektrolyse wurden die Anodengase nach derselben Methode wie vorher sorgfältig analysiert und die Resultate in folgender Tabelle (8) niedergelegt. Wie aus der Tabelle (8) und Figur (9) leicht ersichtlich ist, stieg am Anfang der Elektrolyse die Menge des entwickelten Kohlendioxydgases, sank aber später wieder, während die Bildung von Kohlenmonoxyd gering, aber von Anfang an fast konstant blieb.

Tabelle 8.

Anode: Bleidioxyd; Temp.: 30°C.

Stromstärke: 2.5 Amp.; Stromdichte: 0.05 Amp./cm².

Stdn.	Sauerstoff-coulom. (ccm.)	Anodengas (ccm.)	Aufgefangene Gase						Stromausbeute %
			CO ₂		O ₂		CO		
			ccm.	%	ccm.	%	ccm.	%	
0.5	70.2	11.0	2.3	20.9	8.3	75.4	0.4	3.6	88.2
1	70.5	17.7	9.8	54.8	7.4	41.8	0.6	3.4	89.5
1.5	70.4	25.1	16.3	64.9	8.2	32.7	0.6	2.4	89.4
2	70.4	26.3	16.6	63.1	9.1	34.6	0.6	2.4	87.2
2.5	70.7	34.5	19.4	56.6	14.2	41.6	0.9	2.6	80.0
3	70.3	40.0	19.6	49.0	19.6	49.0	0.8	2.0	72.2
3.5	70.4	46.3	19.9	43.0	25.3	54.7	1.1	2.4	54.1
4	17.1	48.3	19.1	39.5	28.3	58.4	0.9	1.9	59.7

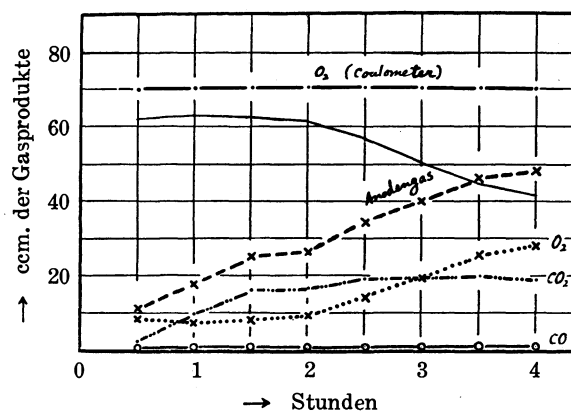


Fig. 9.

Die Stromausbeute ist in diesem Versuch verhältnismässig gut und beträgt etwa 87–90% in den ersten zwei Stunden, sinkt aber im Verlauf der Elektrolyse.

Es zeigt sich auch eine gewisse Proportionalität des Prozentgehaltes des Gases an Kohlendioxyd mit der Stromausbeute (Tabelle 8): Von 1 bis 1.5 Stunde steigt Kohlendioxydgehalt und Stromausbeute, in den folgenden Stunden sinken beide Werte. Daraus lässt sich ableiten, dass der nichtoxydable Körper, dessen Bildung die Stromausbeute erhöht, bei seinem Zerfall hauptsächlich Kohlendioxyd liefert.

B. *Behandlung des Anolyten.* (a) *Cyclohexanon*: Der etwas gelb gefärbte Anolyt wurde nach der Elektrolyse unmittelbar mit Aether mehrmals extrahiert. Nach dem Abdestillieren des Aethers aus der gelb gefärbten Aetherlösung hinterblieb ein Gemisch von weissen Krystallen und einem hellgelben Oel. Durch Filtration wurde die Krystallmasse vom Oel getrennt und ergab 0.17 gr. für eine Elektrolyse, während die Flüssigkeit 1.8 gr. wog. Das gelbe Oel wurde zunächst mit einer kleinen Menge von Aether verdünnt, und dann wurde durch Behandeln mit Natriumbisulfitlösung das Cyclohexanon in die Bisulfitverbindung übergeführt, die weiterhin mit Soda zersetzt und mit Aether geschüttelt wurde. Die so erhaltene Aetherlösung hinterliess nach dem Verdampfen ein Oel vom Sdp. 152–158°C. Zur Identifizierung des Cyclohexanons wurde auf übliche Weise sein Semicarbazon dargestellt, das nach dem Umkrystallisieren aus Methylalkohol zwischen 163° und 165°C. schmolz; dieser Schmelzpunkt stimmt mit dem zu 166°–167°C. für Semicarbazon des Cyclohexanons von Zelinsky⁽¹³⁾ angegebenen genügend überein.

Anal.: Subst. = 3.053; CO₂ = 4.607; H₂O = 1.401 mgr.

Gef.: C = 53.81; H = 7.61%.

Ber. für C₇H₁₂ON₃: C = 54.16; H = 8.45%.

Das Oel enthielt noch andere Substanzen, die keine Bisulfitverbindung bildeten.

(b) *Cyclohexen*: Wir haben daher das Oel von 3 Elektrolysen aufgesammelt. Das gesammelte Produkt (ca. 6 gr.) wurde durch fraktionierte Destillation in drei Fraktionen zerlegt

Fraktion I.	Sdp.: 80–90°C.	ca. 0.3 gr.
Fraktion II.	Sdp.: 150–165°C.	ca. 1.5 gr.
Fraktion III.	Sdp.: 210–240°C.	ca. 0.9 gr.

(13) Ber., ~~30~~ (1897) 1541.

Die erste Fraktion vom Sdp. 80–90°C. ($n_D^{18.6} = 1.4481$) erwies sich schon durch ihren eigentümlichen Geruch als Cyclohexen, das wahrscheinlich durch Wasserabspaltung⁽¹⁴⁾ aus Cyclohexanol entstanden war.

(c) *Bernsteinsäure*: Die zweite Fraktion von Sdp. 150–165°C. war der Hauptbestandteil des Destillates und bestand hauptsächlich aus Cyclohexanon und einer kleinen Menge von unverändertem Cyclohexanol, dessen Vorhandensein mit Phenylisocyanat bestätigt wurde. Aus dem Cyclohexanon wurde nach der im Teil (a) erwähnten Methode Semicarbazon (0.86 gr.) hergestellt, das zusammen mit dem im Teil (a) erhaltenen Semicarbazon (0.27 gr.) 1.12 gr. wog, entsprechend etwa 0.7 gr. (5.7%) Cyclohexanon.

Die dritte Fraktion vom Sdp. 210–240°C. (0.9 gr.) erstarrte nach dem Erkalten zum grössten Teil. Die Krystallmasse wurde nach Abpressen auf Ton getrocknet und wog 0.29 gr. Nach Umkrystallisieren aus Wasser schmolz sie bei 182–183.5°C. und erwies sich nach den folgenden Analysenresultaten als Bernsteinsäure.

Anal.: Subst. = 3.484; CO₂ = 6.874; H₂O = 2.368 mgr.

Gef.: C = 41.15; H = 5.11%.

Ber. für C₄H₆O₄: C = 40.66; H = 5.13%.

(d) *Dicyclohexyläther*(?): Wir erhielten eine noch höher siedende Fraktion vom Sdp. 260–280°C., allerdings in so geringer Menge, dass eine gründliche Untersuchung nicht auszuführen war. Wir nehmen an, dass es sich um Dicyclohexyläther⁽¹⁵⁾ handelte.

(e) *Adipinsäure*: Was bis 300°C. nicht überdestilliert war, bestand aus einem rötlichbraun gefärbten Oel, das nach dem Erkalten fast völlig erstarrte. Die Masse wurde auf Ton von dem dunkelbraunen harzartigen Oel befreit. Das erhaltene weisse Krystallpulver reagierte sauer und zeigte nach dem Umkrystallisieren aus Essigsäureester den Schmelzpunkt von 148.5–150°C., war also Adipinsäure (0.72 gr.).

Anal.: Subst. = 4.038, 4.763; CO₂ = 7.228, 8.463; H₂O = 2.345, 2.394 mgr.

Gef.: C = 48.81, 49.59; H = 6.50, 7.01%.

Ber. für C₆H₁₀O₄: C = 49.29; H = 6.90%.

Ausserdem haben wir nach der schon früher mitgeteilten Methode Ameisensäure erhalten.

Die im Teil (a) beschriebene, durch Filtration vom Oel getrennte Krystallmasse (0.59 gr. aus 4 Elektrolysen) wurde nach der beim Cyclo-

(14) Wasserabspaltung an der Anode ist schon beobachtet worden, z.B. von O. Dony-Henault, *Z. Elektrochem.*, **6** (1900), 541; u.s.w.

(15) S. Komatsu u. M. Masumoto, dieses Bulletin, **5** (1930), 241; vgl. T. Ogawa, dieses Bulletin, **6** (1931), 175.

hexan erwähnten Methode behandelt und dabei 0.29 gr. Adipinsäure, 0.23 gr. Bernsteinsäure gewonnen und Malonsäure als wahrscheinlich nachgewiesen.

Unter Zusammenfassung der bisherigen Beobachtungen bei der elektrochemischen Oxydation von Cyclohexanol wurden also aus 12 gr. Ausgangsmaterial 0.7 gr. Cyclohexanon (5.7%), 0.91 gr. Adipinsäure (5.2%), 0.52 gr. Bernsteinsäure (3.9%), Malonsäure (gering), 0.3 gr. Cyclohexen (2.8%), Kohlendioxyd und Kohlenmonoxyd erhalten.

II. Elektrochemische Oxydation des Cyclohexanons. 2.95 gr. Cyclohexanon (0.03 Mol.; Sdp.: 157°C.; $D_4^{25} = 0.9388$; $n_D^{25} = 1.4505$), das aus Cyclohexanol durch katalytische Oxydation mit reduziertem Nickel hergestellt wurde,⁽¹⁶⁾ wurden an Bleidioxidanoden unter denselben Bedingungen wie vorher elektro-oxydiert. Die durchgesandte Strommenge betrug 8 F/Mol. Der Anolyt färbte sich während der Elektrolyse gelblich.

A. Die gasförmigen Produkte. Im Verlaufe der Elektrolyse wurden die im Anodenraum entweichenden Gase wie vorher analysiert und die Daten in folgender Tabelle (9) wiedergegeben. Der Verlauf der Bildung von Kohlendioxyd und Kohlenmonoxyd und die Tatsache, dass Cyclohexanon ein sehr leicht oxydierbarer Körper ist, sind aus dieser Tabelle und dem Diagramm (10) zu ersehen. In diesem Versuch verhielt es

Tabelle 9.

Anode: Bleidioxyd; Temp.: 30°C.

Stromstärke: 2.5 Amp.; Stromdichte: 0.05 Amp./cm².

Stdn.	Sauerstoff-coulom. (ccm.)	Anodengas (ccm.)	Aufgefangene Gase						Stromausbeute %
			CO ₂		O ₂		CO		
			ccm.	%	ccm.	%	ccm.	%	
0.5	70.8	18.0	5.5	30.6	12.1	67.2	0.4	2.4	82.8
1	69.9	26.2	14.2	54.3	11.6	44.2	0.4	1.5	83.4
1.5	70.0	31.6	16.7	52.8	14.5	45.9	0.4	1.3	79.3
2	71.7	35.1	17.5	49.8	17.1	48.7	0.5	1.5	76.2
2.5	70.6	39.7	18.4	46.3	20.9	52.6	0.4	1.1	70.4
3	71.4	44.2	19.0	43.0	24.8	56.1	0.4	0.9	65.2
3.5	70.3	47.5	19.4	40.8	27.7	58.3	0.4	0.9	60.7
4	70.6	51.8	19.9	38.4	31.3	60.4	0.6	1.2	55.7

(16) S. Komatsu, S. Tanaka und T. Waida, noch nicht veröffentlicht.

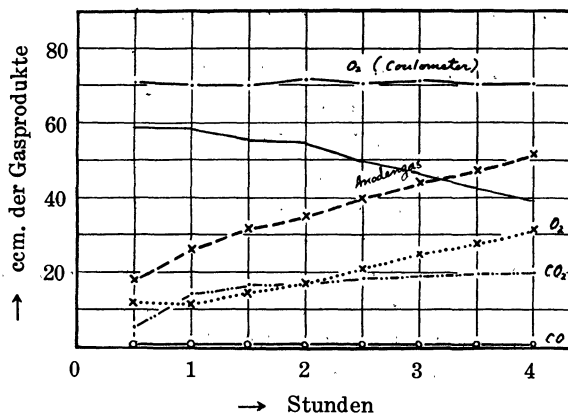


Fig. 10.

sich mit den an der Anode entwickelten Gasen sehr ähnlich wie beim Cyclohexanol. Die optimale Punkt für den Prozentgehalt an Kohlendioxyd und die Stromausbeute liegt zwischen 0.5 und 1 Stunde.

B. *Behandlung des Elektrolyten.* Die gelbliche Anolyt wurde mehrmals mit Aether ausgeschüttelt. Nach dem Abdestillieren des Aethers haben wir etwa 1.4 gr. weisse Krystallmasse und ca. 0.5 ccm. rötlich-braunes Oel erhalten. Aus der Krystallmasse wurden ca. 0.8 gr. (18% der Theorie) Adipinsäure (Smp. 149–150°C.), 0.14 gr. (3.9%) Bernsteinsäure (Smp. 181.5–183°C.) und 0.03 gr. (0.5%) Malonsäure (Smp. 133–134°C.) isoliert.

Für Adipinsäure: Anal. Subst. = 3.810; CO₂ = 6.833; H₂O = 2.345 mgr.

Gef.: C = 48.90; H = 6.92%.

Ber. für C₆H₈O₄: C = 49.29; H = 6.90%.

Für Bernsteinsäure: Anal. Subst. = 4.314; CO₂ = 6.406; H₂O = 1.858 mgr.

Gef.: C = 40.50; H = 4.82%.

Ber. für C₄H₄O₄: C = 40.66; H = 5.13%.

Für Malonsäure: Anal. Subst. = 2.662; CO₂ = 3.409; H₂O = 0.8336 mgr.

Gef.: C = 34.93; H = 3.51%.

Ber. für C₃H₄O₄: C = 34.61; H = 3.87%.

Das Oel bestand hauptsächlich aus unverändert gebliebenem Cyclohexanon.

Bei der elektrochemischen Oxydation des Cyclohexanons haben wir aus 2.95 gr. Cyclohexanon 0.8 gr. (18%) Adipinsäure, 0.14 gr. (3.9%) Bernsteinsäure, 0.03 gr. (0.5%) Malonsäure, Kohlendioxyd und Kohlenmonoxyd erhalten.

Elektrochemische Oxydation des Cyclohexens.

Nach der Untersuchung eines vollständig aromatischen Körpers, des Benzols, und eines vollständig hydroaromatischen Körpers, des Cyclohexans, machten wir zum Vergleiche eine Reihe von Versuchen mit einem Vertreter der ungesättigt-hydroaromatischen Körper, dem Cyclohexen.

2.47 gr. (0.03 Mol.) Cyclohexen ($D_4^{25} = 0.8064$; $n_D^{25} = 1.4434$) Sdp.: 81.5–83°C. (756 mm), hergestellt aus Cyclohexanol durch Wasserabspaltung mit Hilfe von $\text{SO}_4\text{H}_2 \cdot 3\text{H}_2\text{O}^{(17)}$, wurden in 100 ccm. n-Schwefelsäure emulgiert und in einem Tondiaphragma an einer cylindrischen Bleianode (mit vorher frisch hergestelltem Bleidioxyd-Ueberzug bei 0.05 Amp./cm² anodischer Stromdichte unter starker Rührung (ca. 700 Touren) oxydiert, wobei die Temperatur bei ca. 30°C. gehalten wurde. Die durchgesandte Strommenge betrug 10 F/Mol. Die Anodenflüssigkeit färbte sich nach dem Schluss der Versuche ziemlich gelb.

A. Die gasförmigen Produkte. Die aus dem Anodenraum entweichenden Gase wurden nach der gleichen Methode wie beim Benzol analysiert. Die Analysendaten sind in den folgenden Tabellen zusammengestellt. Wie die Tabellen (10, 11, und 13) zeigen, werden Kohlendioxyd und Kohlenmonoxyd während der Elektrolyse gebildet, wobei ersteres in verhältnismässig grosser Menge entsteht, von Anfang an im Verlauf der Elektrolyse fast konstant bleibt und später langsam weniger wird.

Aus den Tabellen und entsprechenden Diagrammen geht hervor, dass bei Verwendung von Bleidioxidanoden weit bessere Stromausbeuten erzielt werden als an platinieren Platinanoden. Der Temperaturkoeffizient bei der Elektrolyse mit Bleidioxyanoden ist viel kleiner als der für Platinanoden und beträgt nur etwa 1/3 dasselben. *Die Kurve für den bei der Elektrolyse verbrauchten Sauerstoff geht von Anfang an im Gegensatz zu der des Benzols langsam herunter.* Die anfänglich gute Stromausbeute sinkt im Verlaufe der Elektrolyse.

Aus den oben geschilderten analytischen Daten kann man daher so folgern, dass das Ausgangsmaterial und die am Anfang entstehende Substanz ein weit besserer Depolarisator ist als die im folgenden entstehenden Oxydationsprodukte. In dem Masse, wie sich dieser leichter oxydierbare Körper verringert, geht der Verbrauch an elektrolytisch entwickeltem Sauerstoff zurück.

B. Die in Aether lösliche Substanz. (a) *Ameisensäure:* Die Anodenlage wurde unmittelbar nach Beendigung der Elektrolyse mit

(17) S. Komatsu, S. Tanaka und T. Waida, noch nicht veröffentlicht.

viel Aether mehrmals (etwa 25 mal) ausgeschüttelt. Nach Verdunsten der ätherischen Lösung blieb eine stechend riechende gelblich gefärbte Flüssigkeit zurück, die bald zu einer krystallinischen Masse erstarrte. Die ätherischen Destillate, nach der bei der elektrochemischen Oxydation von Tolu-*p*-chinon beschriebenen Art auf Ameisensäure verarbeitet, ergaben 0.08 gr. Bariumformiat. Die krystallinische Masse wurde durch Abpressen auf Ton von öligen Beimengungen befreit. Die getrocknete Substanz (etwa 0.78 gr. für 3 Einzelversuche) wurde nach der beim Cyclohexan erwähnten Methode behandelt und dadurch die folgenden Substanzen erhalten.

Tabelle 10.

Anode: Bleidioxid; Temp.: 30°C.

Stromstärke: 2.5 Amp.; Stromdichte: 0.05 Amp./cm².

Stdn.	Sauerstoff-coulom. (ccm.)	Anodengas (ccm.)	Aufgefangene Gase						Stromausbeute %
			CO ₂		O ₂		CO		
			ccm.	%	ccm.	%	ccm.	%	
0.5	70.3	32.5	18.2	56.0	13.0	40.0	1.3	4.0	81.5
1	70.4	45.9	23.9	52.0	19.9	43.3	2.1	4.7	71.8
1.5	70.6	46.3	23.6	51.0	21.7	46.8	1.0	2.2	69.3
2	70.2	49.3	24.2	48.6	24.2	48.6	1.4	2.8	65.5
2.5	70.5	54.5	26.2	48.1	27.3	50.1	1.0	1.9	61.2
3	70.9	55.8	23.6	42.2	31.6	56.5	0.6	1.3	56.4
3.5	70.2	55.9	20.1	35.9	34.8	62.2	1.1	1.9	50.5
4	69.8	57.6	20.4	35.4	36.2	62.8	1.0	1.8	48.2

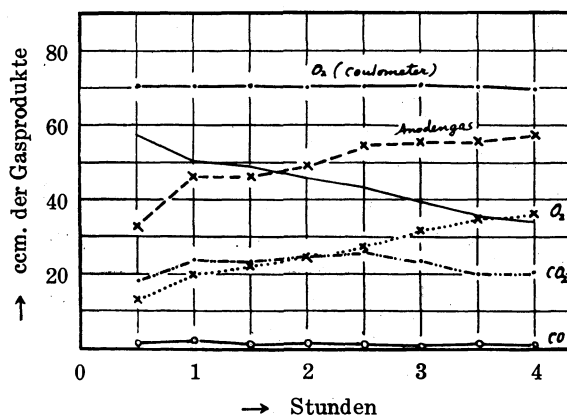


Fig. 11.

Tabelle 11.

Anode: Bleidioxyd; Temp.: 70°C.

Stromstärke: 2.5 Amp.; Stromdichte: 0.05 Amp./cm².

Stdn.	Sauerstoff-coulom. (ccm.)	Anodengas (ccm.)	Aufgefangene Gase						Strom- ausbeute
			CO ₂		O ₂		CO		
			ccm.	%	ccm.	%	ccm.	%	%
0.5	70.4	33.6	28.3	84.1	4.8	14.3	0.5	1.5	93.0
1	70.5	34.1	27.4	80.3	6.0	17.6	0.7	2.1	91.5
1.5	70.3	41.7	31.6	75.8	8.5	20.4	1.6	3.8	87.9
2	70.5	40.7	29.1	71.4	10.8	26.1	1.2	2.5	84.8
2.5	70.3	51.2	31.8	62.2	18.4	35.9	1.0	1.9	85.3
3	70.7	55.5	29.7	54.0	24.1	43.8	1.2	2.2	66.0
3.5	70.4	60.3	30.5	50.5	28.6	47.4	1.2	2.1	59.4
4	70.1	57.3	27.8	48.4	28.5	49.5	1.2	2.1	59.3

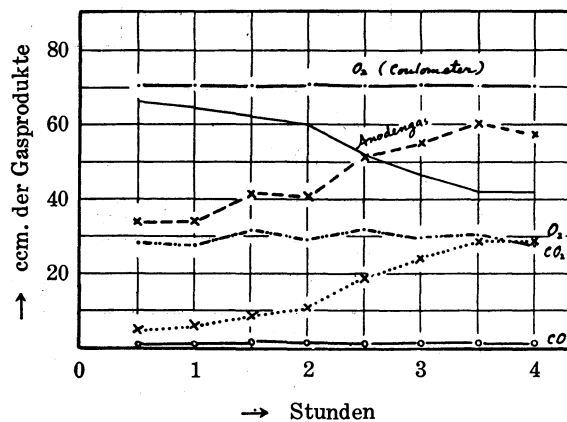


Fig. 12.

Tabelle 12.

Anode: Platiniertes Platin; Temp.: 70°C.

Stromstärke: 2.5 Amp.; Stromdichte: 0.05 Amp./cm².

Stdn.	Sauerstoff-coulom. (ccm.)	Anodengas (ccm.)	Aufgefangene Gase						Strom- ausbeute %
			CO ₂		O ₂		CO		
			ccm.	%	ccm.	%	ccm.	%	
0.5	71.9	34.6	1.5	4.5	32.5	93.9	0.6	1.8	54.2
1	71.1	36.0	1.5	4.2	34.5	95.3	0.2	0.5	51.5
1.5	70.3	44.5	2.8	6.3	41.6	93.3	0.1	0.4	41.7
2	72.9	51.1	3.4	6.8	47.4	92.8	0.2	0.4	34.1
2.5	70.2	53.6	4.4	8.3	49.0	91.3	0.2	0.4	31.4
3	70.2	56.1	4.4	7.9	51.5	91.8	0.3	0.3	27.6
3.5	70.8	56.7	4.7	8.3	51.8	91.5	0.2	0.2	26.9
4	70.6	57.5	4.9	8.6	52.4	91.2	0.2	0.2	25.8

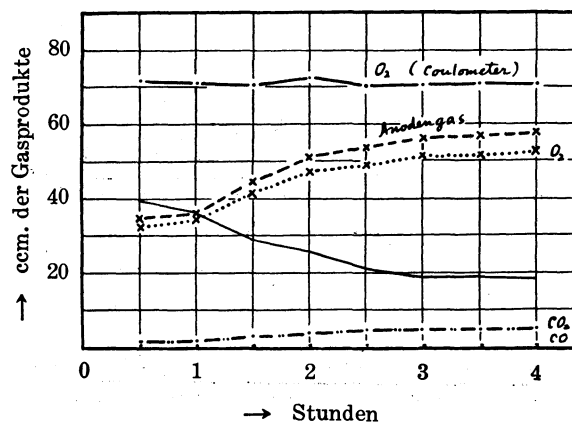


Fig. 13.

Tabelle 13.

Anode: Platiniertes Platin; Temp.: 30°C.
 Stromstärke: 2.5 Amp.; Stromdichte: 0.05 Amp./cm².

Stdn.	Sauerstoff-coulom. (ccm.)	Anodengas (ccm.)	Aufgefangene Gase						Strom- ausbeute %
			CO ₂		O ₂		CO		
			ccm.	%	ccm.	%	ccm.	%	
0.5	70.8	58.2	2.0	3.4	55.8	96.0	0.4	0.6	21.2
1	70.0	57.7	1.6	2.8	55.7	96.7	0.4	0.5	20.5
1.5	70.8	58.7	2.0	3.4	56.3	96.0	0.4	0.6	20.5
2	68.2	57.6	2.4	4.2	54.8	95.2	0.4	0.6	19.6
2.5	70.8	61.6	2.8	4.5	58.6	95.1	0.2	0.4	17.2
3	70.2	61.8	2.4	3.9	59.2	95.8	0.2	0.3	15.8
3.5	71.0	64.3	2.6	4.0	61.5	95.7	0.2	0.3	14.0
4	69.5	64.4	2.6	4.0	61.6	95.7	0.2	0.3	11.5

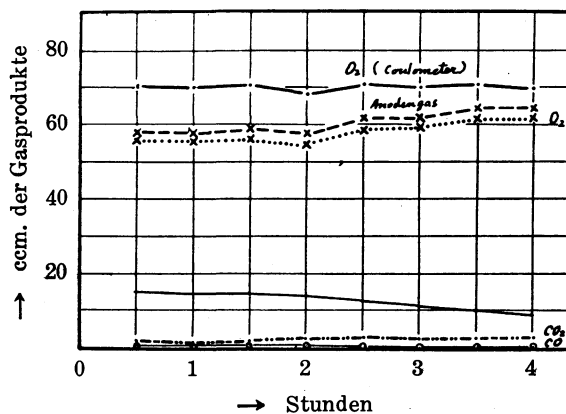


Fig. 14.

(b) *Adipinsäure*: Die Ausbeute betrug 0.87 gr., entsprechend 6.6% der Ausgangsmaterials. Der Körper schmolz nach der Umkrystallisation aus Wasser bei 148–149°C.

Anal.: Subst. = 3.375; CO₂ = 6.086; H₂O = 2.016 mgr.

Gef.: C = 49.18; H = 6.69%.

Ber. für C₆H₁₀O₄: C = 49.29; H = 6.90%.

(c) *Bernsteinsäure*: Die Ausbeute betrug 0.28 gr., entsprechend 2.9% der Theorie. Nach dem Umkrystallisieren aus Wasser und Alkohol schmolz die Substanz bei 178–181°C.

Anal.: Subst. = 3.946; CO_2 = 5.936; H_2O = 1.725 mgr.

Gef.: C = 41.02; H = 4.89%.

Ber. für $\text{C}_4\text{H}_6\text{O}_4$: C = 40.66; H = 5.13%.

Zur näheren Identifizierung wurde noch das Silbersalz hergestellt, dessen Silbergehalt analytisch ermittelt wurde:

0.1034 gr. Subst., getrocknet im Vakuum über Schwefelsäure, gaben nach dem Glühen 0.0679 gr. Silber.

Gef.: Ag = 65.67%.⁽¹⁸⁾

Ber. für $\text{C}_4\text{H}_4\text{O}_4\text{Ag}$: Ag = 65.03%.

(d) *Malonsäure*: Die Ausbeute betrug 0.07 gr., entsprechend 0.4% der Theorie. Nach vielmaligem Umkrystallisieren aus Aether, Wasser und Benzol schmolzen die Krystalle bei 131.5–132.5°C.

Anal.: Subst. = 2.424; CO_2 = 3.063; H_2O = 0.7427 mgr.

Gef.: C = 34.46; H = 3.43%.

Ber. für $\text{C}_3\text{H}_4\text{O}_4$: C = 34.61; H = 3.87%.

Das Bariumsals der Malonsäure, welches zur weiteren Charakterisierung dargestellt wurde, wurde nach dem Waschen und Trocknen im Vakuum über Schwefelsäure der Analyse unterworfen.

0.0905 gr. ergaben nach Abrauchen mit Schwefelsäure 0.0876 gr. BaSO_4 .

Gef.: Ba = 56.96%.

Ber. für $\text{C}_3\text{H}_2\text{O}_4\text{Ba}$: Ba = 57.40%.

(e) *Glutarsäure*: Die der beim Cyclohexan erhaltenen Glutarsäure entsprechende Säure (Ausbeute: sehr gering) wurde auch in diesem Versuch isoliert, und schmolz bei 88–95°C.⁽¹⁹⁾ Infolge der schlechten Ausbeute konnte ich keine nähere Charakterisierung durchführen.

C. Behandlung des wässrigen Anolyten. Der Anolyt wurde zur Entfernung der Sulfationen zunächst mit Bariumhydroxydlösung und schliesslich mit Bariumcarbonataufschlammung neutralisiert. Das Filtrat enthielt eine geringe Menge einer fruchteterartigen, angenehm riechenden Substanz, deren Sicherstellung aber bisher noch nicht gelang.

Das bei der Neutralisation der Schwefelsäure entstandene Barium-

(18) Der etwas zu hohe Ag-Gehalt muss auf schwer abtrennbare Verunreinigungen (Malonsäure u.s.w.) zurückgeführt werden.

(19) V. Meyer u. P. Jacobson, „Leh. Org. Chem.“ I, [1], Seite 382 (1913).

salz behandelten wir mit Salzsäure auf dem Wasserbade, um die Bariumsalze der elektrolytisch gebildeten schwer löslichen Carbonsäuren im Bariumchlorid zu verwandeln und die Carbonsäuren frei zu machen, und filtrierten ab. Das Filtrat wurde nach dem Trocknen mit absolutem Alkohol behandelt. Von den in Alkohol gelösten Substanzen konnten wir Malon- und Bernsteinsäure leicht nachweisen.

(f) *Cyclohexanon*: Nun wurde geprüft, welche Folgen eine verkürzte Versuchsdauer (5.7 Amp.-Std.) bei höherer Temperatur (70°C.) hat. Die sonstigen Bedingungen waren die gleichen wie in den vorherigen Versuchen. Nach beendeter Elektrolyse war die Anodenflüssigkeit leicht gelb gefärbt und eine kleine Menge eines gelb gefärbten Oels schwamm auf dem Elektrolyten. Das Oel wurde in einem kleinen Scheidetrichter abgetrennt (3.4 gr. für 4 Einzelversuche) und nach dem Trocknen fraktioniert destilliert. Es wurden hierbei folgende zwei Hauptfraktionen erhalten:

Fraktion I.	Sdp. 80–95°C.	ca. 2.8 gr.
Fraktion II.	Sdp. 140–160°C.	wenig.

Fraktion I. Diese Fraktion war der Hauptteil des Destillates und bestand fast völlig aus unverändertem Cyclohexen.

Fraktion II. Diese angenehm kampferartig riechende Fraktion, von der nur einige Tröpfchen erhalten wurden, wurde mit Semicarbazidchlorhydrat behandelt; das dabei erhaltene, in prismatischen Nadeln krystallisierende Semicarbazon schmolz nach dem Umkrystallisieren aus Alkohol bei 162–163°C. Eine Mischprobe mit Semicarbazon des Cyclohexanons zeigte keine Erniedrigung des Schmelzpunktes. Es handelte sich wahrscheinlich um ein Semicarbazon des Cyclohexanons von Zelinsky.⁽¹³⁾

Aus der wässrigen Schicht hatten wir durch Ausäthern (aus diesen 4 Elektrolysen) 0.22 gr. eines Gemisches von Säuren erhalten, wie oben schon geschildert wurde.

Bei der elektrolytischen Oxydation von Cyclohexen konnten wir somit aus 7.41 gr. Cyclohexen 0.33 gr. (6.6%) Adipinsäure, 0.16 gr. (2.9%) Bernsteinsäure, 0.07 gr. (0.3%) Malonsäure, Kohlendioxyd, Kohlenmonoxyd und eine geringe Menge von Cyclohexanon und Glutarsäure isolieren.

Elektrochemische Oxydation des Cyclohexandiols.

Um die Bildungsweise der gefundenen kleinen Mengen von Cyclohexanon bei der elektrochemischen Oxydation von Cyclohexen zu untersuchen, stellten wir die im weiteren geschilderten Versuche an.

0.03 Mol. (3.4224 gr.) Cyclohexandiol (Smp.: 99–101°C.), das aus Cyclohexen durch Oxydation mit Peressigsäure hergestellt wurde,⁽²⁰⁾ wurden in 100 ccm. n-Schwefelsäure unter kräftiger Rührung an der Bleidioxydanode bei einer Anodenstromdichte von 0.05 Amp./cm² bei 30°C. elektrolysiert. Die Strommenge betrug 6 F/Mol. Der Anolyt war nach beendeter Elektrolyse nur etwas gelblich gefärbt. Bei diesem Versuche liessen sich die Anodengase nicht analysieren, weil die Menge des Ausgangsmaterials zu gering war. Aber wir haben die Menge des im Anodenraum entweichenden Kohlendioxyds mit einem Kaliapparat gemessen und dabei 0.0203 gr. erhalten.

Nach der Elektrolyse wurde die Anodenflüssigkeit mit Aether etwa 20 mal ausgeschüttelt. Die Aetherlösung hinterliess nach dem Abdestillieren des Aethers ein kampferartig riechendes, gelblichbraun gefärbtes Oel, das viel weisse Krystalle enthielt. Durch Filtration wurde die Krystallmasse vom Oel getrennt; die erstere betrug 1.3 gr. und das letztere 0.7 gr. bei einer Elektrolyse.

A. Behandlung der Krystallmasse. (a) *Adipinsäure*: Nach dem Trocknen auf Ton wurde die Krystallmasse nach der beim Cyclohexan geschilderten Weise behandelt und dabei 0.763 gr. (17%) Adipinsäure (Smp. 148–149°C.) isoliert.

Anal.: Subst. = 3.923; CO₂ = 7.052; H₂O = 2.402 mgr.

Gef.: C = 49.03; H = 6.85%.

Ber. für C₆H₁₀O₆: C = 49.29; H = 6.90%.

Ausserdem haben wir nach der Behandlung wie vorher 0.04 gr. Bariumformiat, 0.11 gr. (3.1%) Bernsteinsäure (Smp. 179.5–181°C.) und 0.01 gr. (0.16%) Malonsäure (Smp. 132–133.5°C.) erhalten.

Für Bernsteinsäure: Anal. Subst. = 3.781; CO₂ = 5.694; H₂O = 1.737 mgr.

Gef.: C = 41.07; H = 5.14%.

Ber. für C₄H₆O₄: C = 40.66; H = 5.13%.

Für Malonsäure: Anal. Subst. = 3.240; CO₂ = 4.116; H₂O = 1.005 mgr.

Gef.: C = 34.65; H = 3.47%.

Ber. für C₃H₄O₄: C = 34.61; H = 3.87%.

B. Behandlung des Oels: Das bräunlich gefärbte Oel erstarrte beim Durchschütteln mit überschüssiger 40%iger Natriumbisulfitlösung unter Erwärmung zu einem Brei, der aus glänzenden Blättchen der abgeschiedenen Bisulfitverbindung bestand. Aus der so erhaltenen Bisulfitverbindung stellten wir nach der beim Cyclohexanol erwähnten Methode

(20) S. Komatsu, S. Tanaka und T. Waida, noch nicht veröffentlicht.

Semicarbazon dar, das nach dem Umkrystallisieren aus Alkohol bei 158–160.5°C. schmolz. Trotzdem wir die weitere Identifizierung dieser Substanz infolge der geringen Ausbeute nicht weiter durchführen konnten, nehmen wir an, dass das Oel wohl Cyclohexanon ist, das durch Umlagerung des Cyclohexandiols ohne elektrochemische Einwirkung lediglich durch Stromwärme und Schwefelsäure an der Anode entstanden sein dürfte.

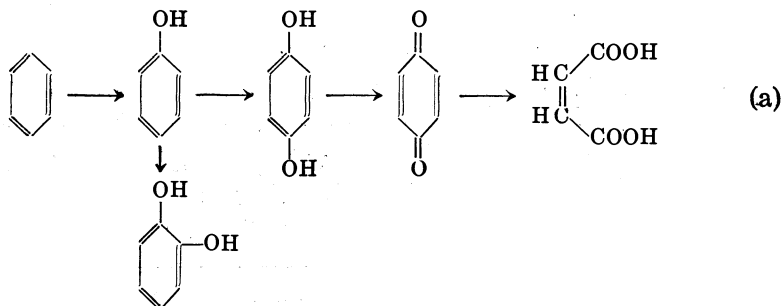
Bei der elektrochemischen Oxydation des Cyclohexandiols wurden also aus 3.4224 gr. Ausgangsmaterial 0.76 gr. (17%) Adipinsäure, 0.11 gr. (3.1%) Bernsteinsäure, 0.01 gr. (0.16%) Malonsäure, 0.0203 gr. Kohlendioxyd, 0.04 gr. Bariumformiat und Cyclohexanon (wenig) erhalten.

Einige Schlussbetrachtungen über die Versuchsergebnisse

I. Ueber den Reaktionsmechanismus. Wie Abschnitt (2) erwähnt, lieferte die zum Vergleich mit Cyclohexan elektrolytisch analog durchgeführte Oxydation von Benzol an der Bleidioxydanode in verdünnter Schwefelsäure als Kernoxydationsprodukte Benzochinon und Brenzcatechin, und als Abbauprodukte Maleinsäure, Ameisensäure, Kohlendioxyd und Kohlenmonoxyd.

Auf der einen Seite hatten schon Fr. Fichter und seine Schüler das Verhalten des Phenols an Platin- oder Bleidioxydanoden in verdünnter Schwefelsäure studiert und dabei Brenzcatechin, Benzo-*p*-chinon, Hydrochinon als kernoxydierte Produkte und Maleinsäure als Kernaufspaltungsprodukt erhalten. Auf der anderen Seite wurde die elektrolytische Oxydation des Chinons von R. Kempf an Bleidioxydanoden in 30%iger Schwefelsäure bei niedriger Stromdichte von 0.02 Amp./cm² durchgeführt und dabei Ameisensäure, Maleinsäure und Traubensäure als wichtigste Produkte sicher nachgewiesen.

Somit lässt sich der elektrochemische Oxydationsverlauf von Benzol (nach den Beobachtungen von Fichter, Kempf und uns) in folgendes Schema fassen.



Es erweist sich also deutlich, dass der oben gezeigte Oxydationsverlauf des Benzols parallel zu der Bromsubstitution des Benzols, wie sie schon in der Einleitung wiedergegeben wurde, verläuft.

Bei der elektrochemischen Oxydation des Cyclohexans in verdünnter Schwefelsäure und in aceton-schwefelsaurer Lösung an Bleidioxydanoden wurden die folgenden Oxydationsprodukte erhalten: sicher Adipin-, Bernstein-, Malon-, Ameisensäure und Kohlendioxyd, wahrscheinlich Glutarsäure und Kohlenmonoxyd. Die Entstehung dieser Substanzen wies deutlich auf die Aufspaltung des Cyclohexanrings bei der elektrochemischen Oxydation hin.

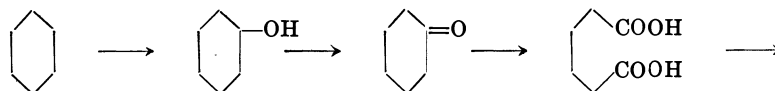
Um die Beziehungen zwischen Cyclohexan und seinen elektrochemischen Oxydationsprodukten aufzuklären und das Oxydationsschema von Cyclohexan zu vervollständigen, wurde nun der Verlauf der elektrolytischen Oxydation von Cyclohexanol und Cyclohexanon studiert.

Die elektrolytische Oxydation von Cyclohexanol an der Bleidioxydanode in verdünnter Schwefelsäure ergab Cyclohexanon; aus ihm entstanden als Abbauprodukte Adipin-, Bernstein-, Ameisen-, Malonsäure, (letztere wahrscheinlich), Kohlendioxyd und Kohlenmonoxyd. Ausserdem wurde aus Cyclohexanol durch Wasserabspaltung aus der Molekel sekundär Cyclohexen gebildet. Unter den gleichen Bedingungen wie beim Cyclohexanol oxydierten wir elektrolytisch das Cyclohexanon und erhielten dabei auch die gleichen, eben beim Cyclohexanol erwähnten Fettsäuren und gasförmigen Produkte.

Wenn wir nun unsere Beobachtungen und experimentellen Befunde über Cyclohexan, Cyclohexanol, und Cyclohexanon zusammenfassen, einen Vergleich ziehen zwischen der Aehnlichkeit der Reaktionsprodukte und ihren Ausbeuten und den Verhältnissen bei der Bildung von gasförmigen Produkten u.s.w., so kommen wir zu folgender Erklärung für den Reaktionsmechanismus bei der elektrochemischen Oxydation des Cyclohexans unter unseren Bedingungen.

In erster Linie wird Cyclohexan hydroxydiert; dabei entsteht Cyclohexanol, das zum Cyclohexanon weiter oxydiert wird, und das letztere wird oxydativ zur Adipinsäure aufgespalten. Die schlechte, aber konstante Stromausbeute lässt sich in folgender Weise zwanglos erklären. Sobald bei einem Cyclohexanmolekül trotz seiner grossen Beständigkeit einmal der oxydative Angriff eingeleitet ist, geht er an derselben Stelle noch weiter, während die übrigen Cyclohexanmoleküle unverändert bleiben. Nach Beendigung dieser gekoppelten Reaktion wird ein neues Molekül angegriffen u.s.w.

Unter Zusammenfassung dieser Ueberlegungen lässt sich auch ein Schema für den Oxydationsverlauf beim Cyclohexan aufstellen. Es lautet:



Man versteht leicht, dass der im obigen Schema gezeigte Mechanismus der elektrochemischen Oxydation des Cyclohexans ähnlich dem der Bromsubstitution von Cyclohexan sich abspielt.

Bei der Oxydation einer Emulsion von Cyclohexen in wässriger Schwefelsäure an Bleidioxidanoden fanden wir Cyclohexanon, Adipin-, Bernstein-, Malon-, Ameisensäure, Kohlendioxyd und Kohlenmonoxyd. Die elektrolytische Oxydation von Cyclohexandiol ergibt auch dieselben Produkte wie die von Cyclohexen.

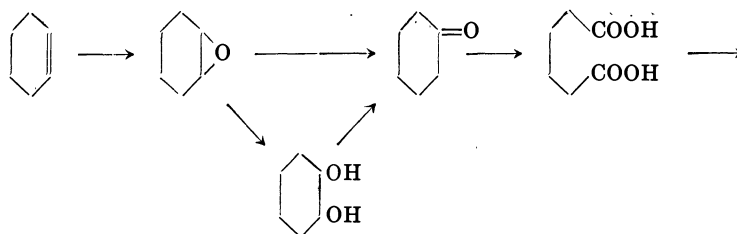
Nicht nur die Beobachtungen (vgl. die obigen Angaben), dass Cyclohexen durch Wasserabspaltung bei der elektrochemischen Oxydation von Cyclohexanol entsteht und Cyclohexandiol, Cyclohexanon und Cyclohexen einander analoges Verhalten an der Anode zeigen, sondern auch der rein chemische Vorgang⁽²¹⁾ dass sich Cyclohexen durch Persäuren glatt zu Cyclohexenoxyd oxydieren lässt und letzteres in Gegenwart von Säuren leicht in Cyclohexanon oder Cyclohexandiol verwandelt wird, lassen uns also die Oxydation des Cyclohexens folgendermassen auffassen.

Zuerst wird aus Cyclohexen durch die Perschwefelsäure, die an der Anode zunächst entstanden sein dürfte (siehe unten), Cyclohexenoxyd gebildet, das danach durch Umlagerung in Cyclohexanon verwandelt wird. Alle Versuche das Cyclohexenoxyd zu isolieren, waren aber vergeblich. Diese Umlagerung lässt sich vielleicht auf die Wirkung der anodischen Schwefelsäure zurückführen, da in unmittelbarer Nähe der Anode lokale Ueberhitzung und infolge der Entladung der Sulfationen eine weit höhere Schwefelsäurekonzentration herrschen wird als durchschnittlich im Elektrolyten.

Der Versuch über das Cyclohexandiol lässt erkennen, dass die Bildungsweise des beim Cyclohexen erhaltenen Cyclohexanons durch Umlagerung des Cyclohexandiols, welches durch Hydrolyse des Cyclohexenoxys entstanden sein dürfte, auch möglich ist. Das entstandene Cyclohexanon wird dann oxydativ weiter zu Adipinsäure u.s.w. gespalten.

Für die elektrochemische Oxydation des Cyclohexens bei unseren Bedingungen schlagen wir einstweilen daher folgendes Schema vor.

(21) vgl. S. Tanaka, J. Chem. Soc. Japan, **53** (1932), 669.



II. Der Vergleich zwischen dem Oxydationsmechanismus von Benzol und Cyclohexan. Beim ersten Blick erscheint das Oxydationsschema (a) für den aromatischen Kohlenwasserstoff, das Benzol, und das Oxydationsschema (b) für den hydroaromatischen Kohlenwasserstoff, das Cyclohexan, ähnlich, doch lässt sich bei näherer Betrachtung folgende Verschiedenheit feststellen.

Beim Benzol entsteht in der ersten Stufe bei der elektrolytischen Oxydation durch Addition von einem Sauerstoffatom Monosubstitutionsprodukt. In der zweiten Stufe finden Reaktionsvorgänge statt analog denen bei der Halogensubstituierung; es bilden sich demgemäss *p*- und *o*-Dioxysubstitutionsprodukte und in der dritten Stufe Diketoverbindung durch weitere Oxydation. Dann wird der Ring oxydativ aufgespalten und ergibt Maleinsäure.

Obgleich Cyclohexan, das doch viel weniger substituionsfähig ist als das Benzol, durch Addition von einem Sauerstoffatom in der ersten Stufe wie das Benzol in Monoxyverbindung verwandelt wurde, findet beim Cyclohexan im Gegensatz zum Benzol in der zweiten Stufe keine weitere Oxysubstituierung statt, sondern eine Oxydation zum Keton und es folgt dann die Ringaufspaltung wie beim Benzol und ergibt Adipinsäure.

Cyclohexan verhält sich also analog zum Benzol bei der elektrochemischen Oxydation in den folgenden Punkten; erstens, in der Einführung einer Hydroxylgruppe in der ersten Stufe; zweitens, in der Bildung der entsprechenden Säuren (Adipinsäure beim Cyclohexan und Maleinsäure beim Benzol) unter Aufspaltung des Ringes in der Nachbarschaft der Carbonylgruppe. Doch wird, wie oben geschildert, auch die Verschiedenheit von Benzol und Cyclohexan bei der elektrochemischen Oxydation nachgewiesen, die bei der Einleitung des Versuches über die Substitutionsreaktion erwähnt wurde.

Benzol wird daher diese Veränderung der chemischen Eigenschaften durch Verwandlung in die gesättigte Verbindung (das Cyclohexan) erleiden. Man wird damit diesen Unterschied der Substitutionsreaktion zwischen Benzol und Cyclohexan wie die anderen Reaktionen auf die An- und Abwesenheit des *aromatischen Charakters* zurückführen können.

III. Vergleich der elektrochemischen Oxydierbarkeit von Benzol, Cyclohexen und Cyclohexan. Wie aus der Molekularstruktur hervorgeht, haben Benzol, Cyclohexen und Cyclohexan einen aus sechs Kohlenstoffatomen aufgebauten Ring. Aber das den aromatischen Typ charakterisierende Benzol (I) hat drei symmetrisch angeordnete Doppelbindungen, das in wesentlichen Punkten wie ein Olefin sich verhaltende Cyclohexen (II) eine und das chemisch dem Verhalten der Paraffine entsprechende Cyclohexan keine.



Es ist interessant, die Stabilität der drei Verbindungen gegenüber der anodischen Einwirkung zu vergleichen und das Verhalten der Doppelbindung bei der elektrochemischen Oxydation zu studieren.

Zur Vergleich haben wir die Stromausbeuten benutzt. Wie in den folgenden Diagrammen (Fig. 15 u. 16) gezeigt wird, betragen die Stromausbeuten von Cyclohexen nach halbstündiger Elektrolyse an Bleidioxydanoden bei 30°C. etwa 81.5% und bei 70°C. 93%; an Platinanoden bei 30°C. 21% und bei 70°C. 54.2%. Dagegen sind die entsprechenden Werte von Cyclohexan bei 70°C. 6.4% (an Bleidioxydanoden), bei 30°C. 4.8%, bzw. bei 70°C. 2.8% (an Platinanoden), wie wir in einer Reihe von Versuchen beobachtet haben. Daher ist das Cyclohexan viel beständiger als das Cyclohexen gegenüber anodischer Einwirkung.

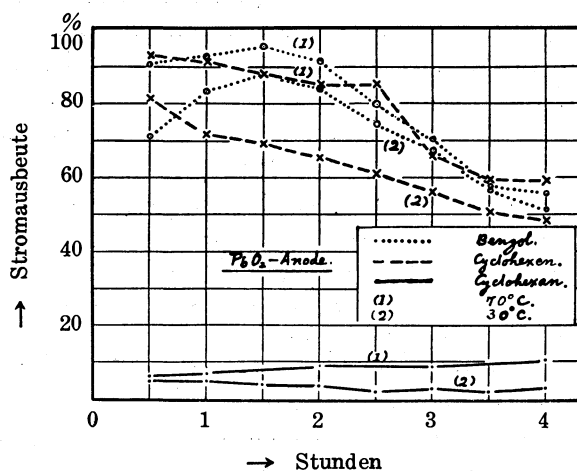


Fig. 15.

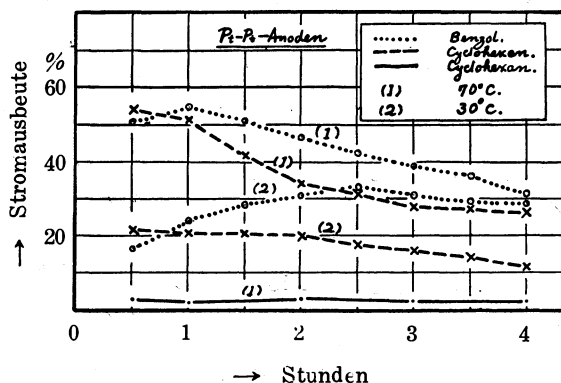
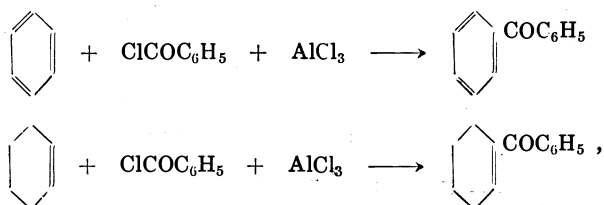


Fig. 16.

Da die Oxydationsprodukte mitsamt den Zwischenprodukten bei dem Cyclohexan und Cyclohexen dieselben und leicht oxydierbar sind, wie experimentell (in Tabellen 8 und 9) gezeigt wurde, ist der Unterschied in den Stromausbeuten bei der elektrochemischen Oxydation auf die unterschiedliche Beständigkeit der Ausgangsmaterialien selber zurückzuführen.

Die Stromausbeutekurve bei der elektrochemischen Oxydation von Benzol zeigt nun das unvermutete Resultat, dass die Stromausbeute in summa bei dem relativ gesättigten Benzol durchschnittlich grösser war als die beim typisch ungesättigten Cyclohexen. Dagegen lehrt ein Vergleich, dass die Stromausbeute des Cyclohexens (nach halbstündiger Elektrolyse bei 30°C. 10% und 70°C. 3% an Bleidioxidanoden, bzw. bei 30°C. 4% und bei 70°C. 3% an Platinanoden) höher als die entsprechende von Benzol ausfiel, also anfangs höher war als die von Benzol. Wie lässt sich aber dieses Verhalten erklären? Mit Hilfe folgender Ueberlegung könnte man sich dieses Phänomen so vorstellen: Cyclohexen ist ein besserer Depolarisator an der Anode als Benzol. Aus Benzol entsteht aber als primäres Produkt Phenol, das leichter oxydiert wird als das aus Cyclohexen entstehende Primär-Produkt. Das Phenol seinerseits liefert bei der weiteren Oxydation nebeneinander Brenzcatechin und Hydrochinon, die leichter oxydierbar sind als die entsprechende Substanz aus Cyclohexen. Daher kann man die durchschnittlich bessere Stromausbeute von Benzol auf die intermediäre Bildung von sehr leicht oxydierbarem Phenol zurückführen und das merkwürdige Ergebnis erklären, dass Benzol scheinbar unbeständiger ist als Cyclohexen. In Wirklichkeit ist Benzol natürlich trotz seiner drei Doppelbindungen stabiler als Cyclohexen bei der elektrochemischen Oxydation wegen seiner symmetrischen Struktur.

Betrachtet man nun die Formulierungen der Darzensschen Arbeit⁽²²⁾, wonach die Friedel-Craftssche Reaktion nach folgendem Schema beim Cyclohexen analog wie beim Benzol verläuft



so wird man bemerken, dass Benzol in chemischer Natur dem Cyclohexen ähnlich ist; Benzol ist demnach so reaktionsfähig wie Cyclohexen. Aber diese Reaktion lässt sich nicht auf Cyclohexan übertragen. Gemäss dem Darzensschen Befund und dem Vergleich mit unseren Stromausbeuten folgt, dass Benzol in der Stabilität gegenüber der anodischen Einwirkung hinter dem Cyclohexan zurücksteht.

Diese Verhältnisse kann man auch an den Stärkeunterschieden bei der Kohlendioxydbildung (Tabelle 1, 5 und 10) und aus der folgenden Ausbeutetabelle ersehen.

Tabelle 14.

Ausgangsmaterial	Angew. in Anodenraum		Anode	Stromdichte Amp./cm ²	F/Mol	Temp. (C)	Ausbeute (Prozente der Theorie)								
	K.W. (mol)	Elyt.					Maleinsäure	Adipinsäure	Bernsteinsäure	Malonsäure	Glutarsäure	Ameisensäure	Cyclohexanon	Chinon	Brenzcatechin
	0.03	100 ccm. n-H ₂ SO ₄	PbO ₂	0.05	10	30	0.46					gering		6.1	gering
	0.03	100 ccm. n-H ₂ SO ₄	PbO ₂	0.05	10	30		6.6	2.9	0.3	gering	gering	gering		
	0.075	32 cm ² 2n-H ₂ SO ₄ ; 120 cm ² Aceton	PbO ₂	0.05	21	30		0.53	0.8	0.15	gering	gering			

(22) *Compt. rend.*, **150** (1910), 707.

Die Tatsache, dass die Kurve des pro Zeiteinheit für die Oxydation in der Zelle verbrauchten Sauerstoffs beim Benzol (Fig. 1) ziemlich schnell ansteigt bis zu einem Optimalpunkt um langsam wieder heruntergehen, dass die Kurve beim Cyclohexan (Fig. 5) von Anfang an fast konstant bleibt und die des Cyclohexens (Fig. 10) gleich zu Beginn abfällt, lässt uns noch folgende Schlüsse ziehen.

Das Benzol, trotzdem es bei der elektrochemischen Oxydation schwer oxydierbar ist, wird schnell weiter oxydiert, wenn es einmal angegriffen ist. Dagegen zeigt Cyclohexan die Tendenz nur langsam weiter reagieren. Cyclohexen ist selbst sehr reaktionsfähig, doch stellen sich nach der ersten Reaktionsstufe die gleichen Verhältnisse ein wie beim Cyclohexan.

IV. Ueber die an der Anode oxydierend wirkende Substanz. Im Folgenden wird noch betrachtet, welcher Natur die an der Anode oxydierend wirkende Substanz bei diesen Versuchen sein dürfte.

Für den Mechanismus der Kolbeschen Kohlenwasserstoffelektrosynthese hat Fr. Fichter, gestützt auf zahlreich Versuche⁽²³⁾ nach den verschiedensten Richtungen, die Peroxyd - Persäuretheorie⁽²⁴⁾ vorgeschlagen, nachdem er festgestellt hatte, dass die zunächst an der Anode entstehenden Peroxyde und Persäuren eine wichtige Rolle als Zwischenprodukte bei der Elektrolyse der Fettsäuren und ihrer Salze spielen.

Bei der elektrolytischen Oxydation organischer Sulfosäuren⁽²⁵⁾ wurde auch nachgewiesen, dass die oxydierend wirkende Substanz wahrscheinlich Sulfopersäure und Sulfoperoxyd ist.

Nach diesen und anderen Beobachtungen kann man wohl überhaupt annehmen, dass die Oxydation der Kohlenwasserstoffe und ihrer Derivate z.B. in schwefelsaurer Lösung während der gesamten Elektrolyse nicht als direkte elektrochemische Einwirkung an der Elektrode anzusehen ist, sondern als eine sekundäre im Anodenraum stattfindende Reaktion rein chemischer Natur. Für so energische Oxydationswirkungen, wie sie für die Hydroxylierung des Kerns und die Aufspaltung des aus 6 Kohlenstoffatomen aufgebauten Ringes notwendig sind, scheinen nur Persäuren in schwefelsaurer Lösung geeignet zu sein. Wenn eine an der

(23) Ein reichhaltiges Beweismaterial bringen die Arbeiten Fichters und seiner Schüler in den *Helvetica Chimica Acta*.

(24) *Helv. Chim. Acta*, **1** (1918), 146; *Trans. Am. Electrochem. Soc.*, **45** (1924), 131.

(25) Fichter und Stocker, *Helv. Chim. Acta*, **7** (1924), 1064; Yokoyama, *Helv. Chim. Acta*, **12** (1929), 756; **13** (1930), 1257. Ueber Aethansulfonsäure (noch nicht veröffentlicht).

Anode leichter als Schwefelsäure zu Peroxyd oder Persäure sich umwandelnde Substanz im Anolyten anwesend sein sollte, so müsste natürlich die Peroxyverbindung dieser Substanz als oxydierend wirkendes Agens eine Rolle spielen; z.B. Xylolsulfopersäure bei der elektrochemischen Oxydation von Xylolsulfonsäure.

R. Kempf⁽²⁶⁾ äusserte die ähnliche Ansicht, dass die meisten elektrochemischen Oxydationen sich insofern auf indirekte rein chemische Prozesse zurückführen lassen, dass das primäre gebildete Peroxyd des Metalls als Sauerstoffüberträger wirkt, und stützte sich dabei auf seine Versuche über die Oxydation des Benzols und des Benzochinons mit Silberperoxyd. Aber Fr. Fichter⁽²³⁾ zeigte, dass an Graphitanoden in wässrig-schwefelsaurer Emulsion aus Benzol dieselben Oxydationsprodukte wie bei Verwendung von Bleidioxidanoden gebildet werden. Die Kempfsche Annahme, dass Metallperoxyd (z.B. Bleidioxyd) bei der elektrochemischen Oxydation als wirksames Agens beteiligt sein könnte, scheidet mithin aus.

Zur Diskussion steht auch die von K. Elbs⁽²⁷⁾ aufgestellte Hypothese, dass die an der Anode gebildete nascierende Perschwefelsäure als oxydierendes Agens bei der elektrochemischen Oxydation von aromatischen Verbindungen in schwefelsaurer Lösung in Betracht kommt. Ich halte diese Auffassung für die wahrscheinlichste bei unseren soeben geschilderten Elektrolysenbedingungen, weil die Oxydation mit überschwefelsauren Salzen bei organischen Verbindungen die gleiche Wirkung ausübt wie die Oxydation an der Anode in Gegenwart von Schwefelsäure. So erhielt z.B. H. A. Gordon⁽²⁸⁾, als er mit Essigsäure angesäuerte Acetatlösungen mit Perschwefelsäure oxydierte, als gasförmige Produkte Aethan, Acetylen, und Methan. Die Bildung von Aethan beweist, dass man imstande ist, mit Persulfat die Kolbesche Elektrosynthese auf rein chemische Weise nachzuahmen. Denn Methan bildet sich auch bei elektrochemischer Durchführung der Kolbeschen Aethansynthese unter bestimmten Bedingungen⁽²⁹⁾. In analoger Weise wurde die Oxydation von Nitrophenol von K. Elbs⁽³⁰⁾ u.s.w. sowohl elektrochemisch, als auch mit Persulfat durchgeführt, und hier war der qualitative Verlauf der Reaktion in allen entsprechenden Fällen derselbe.

(26) *Ber.*, **38** (1905), 3963; *Ber.*, **39** (1906), 3715.

(27) Moser, „Elektrolyt. Prozesse d. org. Chem.“, (1910) S. 67.

(28) *J. Phys. Chem.*, **18** (1914), 55.

(29) Fichter und L. Panizzon, *Helv. Chim. Acta*, **15** (1932), 998; vgl. N. Shukla, *Trans. Faraday Soc.*, **27** (1931), 35; E. Baur, *Z. Elektrochem.*, **29** (1923), 105.

(30) *Ibid.*; vgl. auch *J. prakt. Chem.*, **2 48** (1893), 179.

Fr. Fichter und seine Mitarbeiter⁽³¹⁾ haben häufig den Parallelismus zwischen der Oxydation an der Anode und der mit Wasserstoffperoxyd betont, was nicht verwunderlich erscheint, da Wasserstoffperoxyd die gleiche -O-O-Konfiguration aufweist wie Perschwefelsäure.

Eine weitere Unterstützung der Ansicht, dass in unseren Versuchen schon primär Perschwefelsäure entstanden war, gibt der Umstand, dass wir bei der Anodengasanalyse vor dem Zusatz unserer Ausgangsmaterialien immer die Ozonentwicklung beobachtet haben, die aber nach dem Zusatz derselben gleich aufhörte; Fr. Fichter und W. Bladergroen⁽³²⁾ haben bei ihren Versuchen über Fluorreaktionen die Ozonentwicklung im Verlaufe der Elektrolyse der Schwefelsäure auf das an der Anode entstehende SO_4 (oder S_2O_8) zurückgeführt, und dieser Stoff steht ja in naher Beziehung zur Perschwefelsäure.

Das erhaltene Cyclohexanon (in Abschnitt 6) beim Cyclohexen lässt erkennen, dass Cyclohexenoxyd als Zwischenprodukt entstanden ist. Diese Bildung von Cyclohexenoxyd ist eine Stütze für die Perschwefelsäure-Hypothese. Denn es ist ja vielfach festgestellt worden, dass bei der Oxydation von Aethylenverbindungen durch verschiedene Persäuren⁽²¹⁾ die zunächst gebildete Substanz Aethylenoxyd ist.

Im Sinne unserer obigen Ueberlegungen nehmen wir wenigstens bei unseren Versuchsbedingungen einstweilen an, dass die so energisch wirkende Oxydation eine sekundäre, *auf die an der Anode entstehende Ueberschwefelsäure zurückzuführen ist.*

Es sei mir an dieser Stelle gestattet, Herrn Prof. Dr. Shigeru Komatsu für die freundliche Beschaffung der Ausgangsmaterialien, die Anregung, die zahlreichen Ratschläge und die stets wohlwollende Unterstützung bei dieser Arbeit meinen herzlichsten Dank auszusprechen. Herrn Kiichiro Sata, der die Mikroelementaranalyse der bei den Versuchen erhaltenen Produkte durchführte, sei auch an dieser Stelle bestens gedankt.

Technische Hochschule zu Yokohama.

(31) *Z. Elektrochem.*, **27** (1926), 430; *Helv. Chim. Acta*, **9** (1921), 488, 491; u.s.w.

(32) *Helv. Chim. Acta*, **10** (1927), 358.

RHYTHMIC PRECIPITATES. II. ON THE INFLUENCE OF LIGHT AND THE EFFECT OF AGING.

By Toshizo ISEMURA.

Received January 14th, 1933. Published March 28th, 1933.

It is a well-known fact that light affects the formation of rhythmic precipitates and the aging of jellies before superimposing the diffusing solution has the remarkable effect on the formation of periodic structure. Many papers⁽¹⁾ on these subjects were published, but the results obtained by different authors show the lack of agreement.

These different results are probably caused by the complicated effects of both light and aging. Therefore, experiments on the influence of light must be carried out completely in the same condition (for instance, temperature, concentrations of inner and outer electrolyte, aging of gel) except that of light. And for the same reason, experiments on the effect of aging of gel must be carried out in the same condition excepting that of age. Irradiation with light affects the ring formation and even the diffused light in the room has considerable influence, so it is recommended that the experiment should be undertaken in the dark room. The experiments undertaken by present writer have been carried out on these precautions. The system of gelatine-silver chromate has been studied principally.

Effect of Complete Darkness. It is interesting to study, whether the rhythmic precipitates can be formed or not, in complete darkness. Küster⁽²⁾ states that no bands of silver chromate were formed while Davis⁽³⁾ obtained good bands in the dark. Blair⁽⁴⁾ reported that the bands formed in complete darkness show irregularity. The experiments carried out by the present author are as follows. Three samples of gelatine solutions were prepared, the first sample was made in complete darkness while the second and the third in an ordinary room. Let the first and the second set in the dark place and the third in the light. Three days later, silver nitrate solution was poured on these gels. After standing the former two in the dark and the latter in the light for a week, rhythmic precipitates of silver chromate were recognised in all three

(1) See Hedge, "Liesegang Rings," (1932), 17, 26.

(2) *Kolloid-Z.*, **13** (1913), 192.

(3) *J. Am. Chem. Soc.*, **44** (1922), 2698.

test-tubes and no irregularity was noticed. From this fact it has been asserted that the formation of bands is not affected by the darkness.

Influence of Visible Ray. According to Blair⁽⁴⁾ the bands become irregular when the gel has been irradiated with visible light. But recently Cluzet and Kofmann⁽⁵⁾ stated that the formation of rhythmic precipitates was unaffected by visible light. The present writer found that the radiation of visible ray has an important effect on the formation of bands though the bands do not become irregular even by the strong irradiation of direct sun light. The experiment was done as follows: allowed the gelatine gel containing potassium dichromate as an inner electrolyte to set in test-tubes and kept in a dark place. Then each of the test-tubes was exposed to direct sun light for different interval of time. To avoid the effect of heat ray, the day light was filtered through the layer of water. In this case, the number of the formed bands increases in proportion to the time of exposure. And when exceeded a certain time interval, the bands were formed too close to each other and the whole

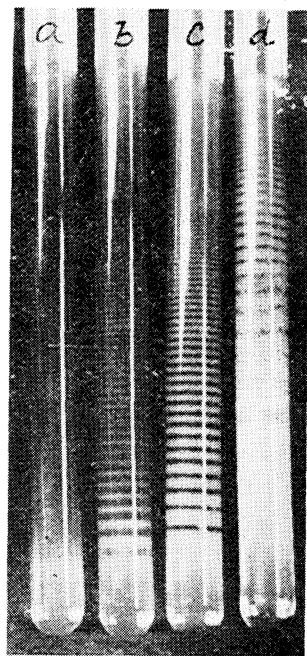


Fig. 1.

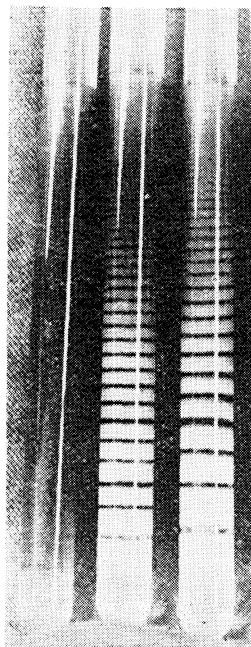


Fig. 2.

(4) *Phil. Mag.*, **49** (1925), 90.

(5) *Compt. rend. Soc. Biol.*, **104** (1931), 1001; *Brit. Chem. Abs.*, (1931), 694.

appeared as dark brown strip. Some of the results obtained are shown in Fig. 1. The samples in this photograph have been made from 2.5% gelatine sol containing 0.1% potassium dichromate, allowing to set in a dark. Sample (a) in the photograph was exposed ca. 3 hours, (b) 2 hours, (c) 1 hour and (d) kept in a dark throughout. Afterwards 15% silver nitrate solution was poured on the gels and the test-tubes were stood in a dark.

Analogous result was also obtained by the influence of diffused light which is shown by Fig. 2. Gelatine solution which was prepared as above described, was poured into three test-tubes and left to set. One was exposed about 5 hours to direct sunlight and the other kept in an ordinary room about 3 days long and the last kept in the dark throughout. Then 15% silver nitrate solution was poured on the gels, and kept all tubes in the dark. The left in the photograph is one exposed to direct sunlight, the middle to diffused light and the right is one which kept in a dark place.

From these results, we can conclude that visible light causes the number of bands to increase and the distance between bands to shorten. It seems that these changes which are caused by the exposure to light, are due to the transformation of gel structure and to the interaction of gelatine and potassium dichromate. After long exposure, gel becomes somewhat difficultly soluble and does no more reset. From this fact, it is probable that the gel changes somewhat in its structure or at least the micelle of gelatine suffers some changes.

The author conceives, from these facts, that at first the gelatine reacts with potassium dichromate on the exposure to light and moreover the micelle of gel changes to insoluble modification. This modification has a less protective action from crystallization of silver chromate than before. So the bands become closer and the number of them increases.

Blair studied the effect of visible light by the exposure to the radiation with $\frac{1}{2}$ watt lamp instead of sunlight, from very short distance (6 in. range), and recognised that the bands become irregular. In writer's opinion, by the radiation from a short distance as in Blair's experiment, the energy of light delivered to the gel system does not distribute equally as in the case of parallel ray as sunlight. Hence the irregular bands were formed.

Influence of Ultra-violet Ray. According to Blair, ultra-violet ray from quartz mercury lamp makes the formation of bands impossible even in a few hours, while Cluzet and Kofmann found that the formation of

Liesegang rings was retarded by ultra-violet light. The retardation of formation of rings is also recognised by the author's experiment. And rings became finer and closer each other than in the non-illuminated case. Some of the results obtained are shown in the photograph (Fig. 3). The same sol (6.5% gelatine, 0.1% potassium dichromate) was poured into three test-tubes of fused silica, one exposed about ten hours; the second about five hours and the third was kept in the dark. The lamp used for this experiment was an Acme mercury quartz lamp which was made by Shimazu Seisakusho. Input of the current applied to the apparatus was 108 volts and 10.2 amperes. Distance to the test-tubes from the lamp was about 30 cm. In the photograph the left is one which was exposed about ten hours and the middle about five hours and the right unexposed one.



Fig. 3.

In the case of copper chromate bands in silica gel the effect of irradiation with ultra-violet light was not recognised.

Effect of Aging. It is interesting that the banding is affected with the age of jellies before superimposing the diffusing solution. Schleussner⁽⁶⁾ recommended to keep a gelatine gel for twenty four hours before pouring the outer electrolyte. The most interesting observation which has ever been done, is that of Blair.⁽⁴⁾ He has made measurements which show that the distance of the last band from the upper end of jelly increases regularly with the age of gel. This result was also reproduced by the present author.

The writer has found another interesting fact. When the experiment was carried as follows, the effect of aging on the formation of bands did not appear. The gelatine solution was prepared and poured into several test-tubes and allow to set. Later, after different time intervals, each of the test-tubes excepting one, was warmed and the gel melted and allowed to reset. In this manner, the gels of different age were prepared. Then silver nitrate solution was poured on them. In this case, the formed bands in the respective tubes appeared quite equal and identical to that of unmelted gel, i.e. the most aged gel.

(6) *Kolloid-Z.*, **31** (1922), 347.

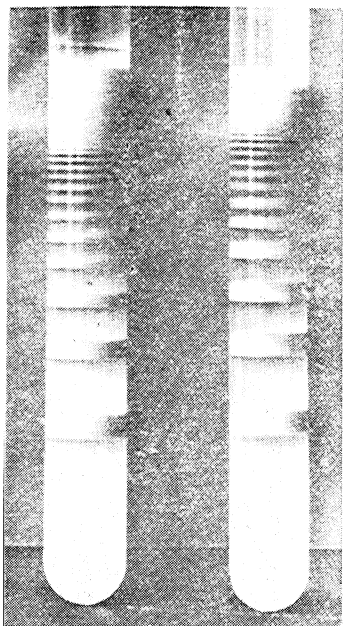


Fig. 4.

From these results the writer concludes that the aging effect of gel on the formation of Liesegang rings is not caused by the change of structure of gel as Blair considered, but by the change of modification of gelatine into the less protective one by an interaction of potassium dichromate and this change proceeds with the age. And it is considered also that the decrease of potassium dichromate after aging was not recognised as Blair observed, for this change of modification is probably caused by spending very small amount of potassium dichromate.

Effect of aging was also studied on the system of copper chromate in silicic acid gel within the range of three months. The remarkable results as in the case of silver chromate in gelatine was not seen. But in the aged gel the first band becomes generally thicker than that in the newly formed gel. And the second and other consecutive

bands become inversely thicker in fresh gel than in older ones. According to Koenig,⁽⁷⁾ a fresh silica gel gives the best bands, the effect becoming more and more irregular, the longer the gel is kept before diffusion begins. But in the author's experiment on copper chromate bands, the long aged silicic acid gel also gave good bands as shown in the photograph (Fig. 4). The gel in the left tube was one aged eighty days before diffusion started and the gel in the right test-tube one freshly prepared having the same composition. In both tubes very beautiful strata are recognised and show no irregularity.

In conclusion the writer expresses his hearty thanks to Prof. J. Sameshima of the Tokyo Imperial University for his kind advices on this paper.

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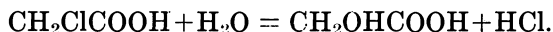
(7) *J. Phys. Chem.*, **24** (1920), 466.

THE VELOCITY OF SPLITTING OFF OF CHLORINE FROM MONOCHLORACETATE.

By Sinnosuke MATUURA.

Received February 13th, 1933. Published April 28th, 1933.

When monochloroacetic acid is acted on by water, it is partially converted into glycolic acid and hydrochloric acid, according to the equation



The velocity of this decomposition or hydrolysis is very slow, but that of the salt is rapid and especially accelerated by the presence of alkalis in excess.

Many investigations on this subject have been carried out. Buchanan⁽¹⁾ made a study of the velocity of decomposition by heating the solution of monochloroacetate. Lossen and Eihoff⁽²⁾ measured the velocity of decomposition at room temperature. After keeping the solution for 500 days, the quantity of decomposed product was determined. Euler⁽³⁾ repeated Schwab's⁽⁴⁾ experiment on the velocity of decomposition of monochloroacetate by the presence of sodium hydroxide at 65 and 80°C. Senter⁽⁵⁾ investigated the velocities of decomposition of monochloroacetic acid and its salts, with or without caustic soda at 74.4 and 102°C. Johanson⁽⁶⁾ measured the velocity of reaction of the barium salt with barium hydroxide, and of the sodium salt with sodium hydroxide respectively at 250°C. But their concentration of the solution was determined after a long interval from the start of reaction. Drushel and Simpson⁽⁷⁾ also measured the velocity of decomposition of sodium monochloroacetate at 70 and 90°C. Euler and Fahlander⁽⁸⁾ investigated the velocity of decomposition of sodium monochloroacetate with sodium hydroxide or with other catalysers. Hedelius⁽⁹⁾ determined the velocity of splitting off of chlorine from monochloroacetate, acting with sodium hydroxide at 55–90°C.

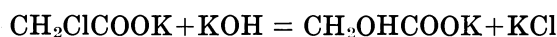
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- (1) *Ber.*, **4** (1971), 340, 863.
 - (2) *Ann.*, **342** (1905), 116.
 - (3) *Ber.*, **39** (1906), 2726.
 - (4) *Etades Dyn. chem.* 1884, 20.
 - (5) *Z. physik. Chem.*, **70** (1910), 511.
 - (6) *Z. physik. Chem.*, **79** (1912), 621.
 - (7) *J. Am. Chem. Soc.*, **39** (1917), 2456.
 - (8) *Z. physik. Chem.*, **100** (1922), 171.
 - (9) *Z. physik. Chem.*, **96** (1920), 343.

Thus many papers are published on this subject, yet in none of them can be found the determination of the course of reaction in earlier stage at lower temperature.

The author has made a research on the velocity of the reaction within about 3 hours with or without caustic alkali at 25–35°C. The results obtained are reported below.

Theoretical.

As above mentioned, monochloracetate is decomposed in aqueous solution with caustic alkali as the following:—



Assuming that a represents the initial concentration (in mols) of monochloracetate, b that of caustic alkali and x the decomposed amount of monochloracetate (or produced chloride) at the end of time t , the velocity of the reaction can be expressed by

$$\frac{dx}{dt} = k(a-x)(b-x),$$

k being the constant of velocity.

In case $a \neq b$, on integration, we obtain the expression

$$\frac{1}{a-b} \ln \frac{b(a-x)}{a(b-x)} = kt,$$

or

$$e^{(a-b)kt} = \frac{b(a-x)}{a(b-x)}.$$

As x and kt are small and the high powers of $\frac{x}{a}$ and $\frac{x}{b}$ can be neglected, we may write

$$1 + (a-b)kt = \left(1 - \frac{x}{a}\right) \left(1 + \frac{x}{b}\right).$$

then

$$1 + (a-b)kt = 1 - \frac{x}{a} + \frac{x}{b}.$$

Hence

$$k = \frac{x}{abt}$$

In case $a = b$, the equation becomes

$$\frac{dx}{dt} = k(a-x)^2,$$

which gives, on integration,

$$\frac{1}{a-x} - \frac{1}{a} = kt,$$

or

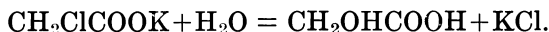
$$\frac{x}{a(a-x)} = kt.$$

As x is small, we may write

$$k = \frac{x}{a^2 t}.$$

In either case, the decomposed quantity of monochloracetate (or produced chloride) is proportional to the product of concentrations of both monochloracetate and caustic alkali at their initial state and the time. If monochloracetate has been decomposed partially at initial state, we must write $x = \alpha + \beta t$ instead of $x = kabt$, where α represents the decomposed monochloracetate at initial state and $\beta = k a b$.

In the case where only monochloracetate exists in the solution, the reaction may be as follows:—



As the reaction proceeds, the acidity of the solution increases. This reaction to some extent may be considered as monomolecular. Hence the velocity of the reaction can be expressed as follows:—

$$\frac{dx}{dt} = k(a-x)$$

where a is the concentration of monochloracetate at initial state, and x the decomposed quantity of this salt at time t . On integration, we have

$$\ln \frac{a}{a-x} = kt.$$

As x and kt are small, we may write

$$k = \frac{x}{at}.$$

Similarly as described above, in case monochloracetate has been decomposed partially at first, we may write $x = a + \beta t$ instead of $x = kat$, where $\beta = ka$.

If we measure the concentration of produced chloride and the time, we can calculate the velocity constant of the reaction.

Experimental.

The experiment is carried out as follows. The solutions of monochloracetic acid and caustic alkali are kept in a thermostat, and mixing the two solutions, a portion of the solution is drawn out at a certain time and a silver nitrate solution is added both to this sample acidified with nitric acid and to the standard solution of potassium chloride. The two solutions are compared by using the nephelometer of Clet Co.

The chemicals used are obtained from Kahlbaum. The results of the experiments are shown in Tables 1, 2 and 3.

Table 1.



Exp. No.	Temp. C.	Initial state (M.)	$\beta \times 10^4$	t . min.	$x \times 10^4$ (M.) obs.	$x \times 10^4$ (M.) calc.
1	20	$a = 0.3113$ $b = 0.2965$	0.02092	30	3.30	3.24
				60	3.82	3.87
				91	4.45	4.51
				125	4.94	5.23
				150	5.95	5.75
				180	6.61	6.38
				210	7.05	7.00
				240	7.53	7.63
				270	8.19	8.26
2	25	$a = 0.3000$ $b = 0.3000$	0.04195	20	2.68	2.51
				40	3.42	3.35
				60	3.89	4.19
				90	5.30	5.45
				150	8.08	7.96
				180	9.59	9.22
				210	10.20	10.48
3	25	$a = 0.3084$ $b = 0.4077$	0.07230	30	4.61	4.43
				60	6.85	6.60
				90	8.35	8.77
				120	10.65	10.94
				150	13.02	13.10
				180	15.63	15.27

Table 1.—(Concluded)

Exp. No.	Temp. C.	Initial state (M.)	$\beta \times 10^4$	t. min.	$x \times 10^4$ (M.) obs.	$x \times 10^4$ (M.) calc.
4	30	$a = 0.3000$ $b = 0.3000$	0.12117	40	4.54	3.79
				60	6.85	6.22
				90	8.46	9.85
				120	13.04	13.49
				150	17.44	17.12
				180	19.63	20.76
				210	25.66	24.39
5	30	$a = 0.4000$ $b = 0.3000$	0.13593	30	4.50	4.20
				45	6.16	6.24
				60	7.37	8.28
				90	12.73	12.36
				120	16.69	16.44
				150	19.24	20.52
				180	28.15	24.59
6	30	$a = 0.4000$ $b = 0.4000$	0.20095	210	26.47	28.67
				40	7.76	5.84
				60	10.00	9.85
				90	15.31	15.88
				120	21.44	21.91
				150	22.52	27.94
				180	36.88	33.97
7	30	$a = 0.5000$ $b = 0.5000$	0.29491	210	41.48	40.00
				40	14.65	15.18
				60	21.62	21.08
				90	30.26	29.93
8	30	$a = 0.3000$ $b = 0.3000$ $\text{KNO}_3 = 0.5000$	0.07226	120	38.43	38.77
				12	2.73	2.72
				25	3.47	3.66
				40	4.85	4.74
				60	6.13	6.19
				90	8.47	8.35
				120	10.38	10.52
				150	13.35	12.69
				180	14.20	14.86
				210	17.16	17.02

Table 2.



Exp. No.	Temp. C.	Initial state (M.)	$\beta \times 10^4$	t. min.	$x \times 10^4$ (M.) obs.	$x \times 10^4$ (M.) calc.
9	25	$a = 0.3000$ $b = 0.3000$	0.034472	10	1.08	1.07
				20	1.36	1.42
				40	2.07	2.11
				60	2.58	2.80
				90	3.87	3.83
				120	5.28	4.86
				150	5.93	5.90
				180	6.65	6.93
10	30	$a = 0.3000$ $b = 0.3000$	0.063324	30	2.59	2.23
				60	4.03	4.13
				90	6.09	6.03
				120	7.17	7.93
				180	12.19	11.73
11	35	$a = 0.3000$ $b = 0.3000$	0.19602	10	1.90	1.00
				30	4.72	4.92
				60	7.95	10.80
				90	18.32	16.68
				120	24.49	22.57
				150	27.05	28.45

Table 3.



Exp. No.	Temp. C.	Initial state (M.)	$\beta \times 10^4$	t. min.	$x \times 10^4$ (M.) obs.	$x \times 10^4$ (M.) calc.
12	25	0.3000	0.002512	20	1.62	1.69
				60	1.84	1.80
				90	1.88	1.87
				120	2.02	1.95
				150	2.07	2.02
				180	2.00	2.10
				210	2.17	2.17
13	30	0.5000	0.01849	30	1.74	1.67
				45	1.86	1.95
				60	2.22	2.23
				80	2.63	2.60
14	30	0.5000	0.01361	10	1.64	1.56
				25	1.70	1.76
				40	1.86	1.96
				70	2.43	2.37

β is calculated by the method of least squares and then k is obtained from $\beta = kab$ or $\beta = ka$.

In experiment No. 8, beside the reacting substances, potassium nitrate was added; it is shown that the reaction velocity is retarded by the presence of another salt with a common ion.

Tables 4 and 5 give the resumes of the values at each temperature. The results of calculation show a fair agreement with the theory which we assumed at first.

Table 4.

Exp. No.	Temp. C.	Initial conc. (M)		$\beta \times 10^4$	$k \times 10^4$ mean
		CH ₂ ClCOOK	KOH		
1	20	0.3113	0.2965	0.02092	0.227
2	25	0.3000	0.3000	0.04195	0.466
3	„	0.3084	0.4077	0.07230	0.575
4	30	0.3000	0.3000	0.12117	1.35
5	„	0.4000	0.4000	0.13593	1.13
6	„	0.4000	0.4000	0.20095	1.26
7	„	0.5000	0.5000	0.29491	1.13
8	„	0.3000	0.3000	0.07226	
			KNO ₃ = 0.5000		
Exp. No.	Temp.	CH ₂ COONa	NaOH	$\beta \times 10^4$	$k \times 10^4$
9	25	0.3000	0.3000	0.034472	0.381
10	30	0.3000	0.3000	0.063324	0.704
11	35	0.3000	0.3000	0.196020	2.18

Table 5.

Exp. No.	Temp. C	Initial conc. (M.) CH ₂ ClCOOK	$\beta \times 10^4$	$k \times 10^4$ mean
12	25	0.3000	0.002512	0.8372
13	30	0.5000	0.01849	3.698
14	30	0.5000	0.01361	2.72

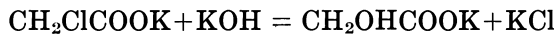
In conclusion the author expresses his thanks to Mr. Sigeru Kondô for his assistance.

Summary.

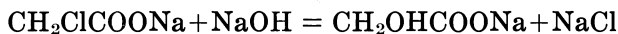
1. Assumed as monomolecular reaction, the velocity of the decomposition of potassium monochloracetate in aqueous solutions is measured,

$$k_{25^{\circ}} = 0.837 \times 10^{-6} \text{ and } k_{30^{\circ}} = 3.21 \times 10^{-6}$$

2. The velocities of the following reactions are measured,



$$k_{20^{\circ}} = 0.227 \times 10^{-4}, k_{25^{\circ}} = 0.521 \times 10^{-4} \text{ and } k_{30^{\circ}} = 1.23 \times 10^{-4}$$



$$k_{25^{\circ}} = 0.381 \times 10^{-4}, k_{30^{\circ}} = 0.704 \times 10^{-4} \text{ and } k_{35^{\circ}} = 2.18 \times 10^{-4}$$

The velocity constant of potassium salt is larger than that of sodium salt.

3. The reaction velocity of potassium monochloracetate with potassium hydroxide is retarded by the presence of another salt (i.e. KNO_3).

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ZUR THEORETISCHEN DEUTUNG DER FREUNDLICH- SCHEN ADSORPTIONSISOTHERME.

Von Bun-ichi TAMAMUSHI.

Eingegangen am 28. Februar, 1933. Ausgegeben am 28. April, 1933.

Es sind bisher manche Versuche,⁽¹⁾ die Freundlichsche Adsorptionsisotherme:

$$a = ac^{\frac{1}{n}} \dots\dots\dots (1)$$

theoretisch zu erklären. Einige von denen hatten Erfolg, obwohl sie noch nicht vollkommen befriedigend zu sein scheinen. Henry⁽²⁾ hat diese Isotherme aus der Gibbsschen Gleichung abgeleitet, wobei er die Änderung

(1) *J. Phys. Chem.*, **31** (1927), 251 Dort eine Übersicht.

(2) *Phil. Mag.*, 6, **44** (1922), 689.

der freien Oberflächenenergie des Adsorbens durch die monomolekular adsorbierten Moleküle in Betracht gezogen hat. Nach ihm, bedeutet der Exponent $\frac{1}{n}$ das Verhältnis von der osmotischen Arbeit zur gesamten Arbeit bei der Adsorption von a Mol Adsorptivs. Später hat Bancroft⁽³⁾ eine analoge, aber noch einfachere Herleitung dieser Isotherme angegeben. Die Herleitung solcher Art, die allerdings berechtigt angesehen werden kann, soll im folgenden noch anderweitig und zwar deutlicher ausgeführt werden, indem man hierbei für die adsorbierte Phase zweidimensionale Zustandsgleichung anwendet.

Die folgenden Betrachtungen beziehen sich auf die Grenzfläche fest-gasförmig, wo die Erscheinungen molekularkinetisch verhältnismässig leicht begreifbar sind. Die Anwendung der Gibbsschen Gleichung sowie der zweidimensionalen Zustandsgleichungen zur Grenzfläche fest-gasförmig soll aus jetzt vielfach erkannten Gründen erlaubt werden.

Man nimmt für die adsorbierte Schicht folgende Zustandsgleichung an:

$$(\sigma_0 - \sigma) \frac{1}{a} = iRT, \quad \dots\dots\dots (2)$$

worin σ_0 die Oberflächenspannung des reinen Lösungsmittels, σ die Oberflächenspannung der Lösung, a die adsorbierte Menge in Mol pro cm² der Oberfläche, R die Gaskonstante, T die absolute Temperatur, und i eine Konstante, deren physikalische Deutung bald angegeben wird, bedeutet. Aus dieser Gleichung und der Gibbsschen Gleichung, nämlich:

$$a = -\frac{c}{RT} \frac{\partial \sigma}{\partial c} \quad \dots\dots\dots (3)$$

folgt eine Beziehung zwischen a und c (die Konzentration im homogenen Raum):

$$a = kc^{\frac{1}{i}}, \quad \dots\dots\dots (4)$$

worin k eine Integrationskonstante bedeutet. Diese letzte Beziehung stimmt formal mit der empirisch angestellten Adsorptionsisotherme (1) überein.

Es wird nun dem Exponent $\frac{1}{i}$ bzw. $\frac{1}{n}$ seine physikalische Deutung angegeben. Man hat zuerst⁽⁴⁾ den Koeffizient i etwa versuchsweise in

(3) *J. Phys. Chem.*, **31** (1927), 1501.

(4) Tamamushi, *Dieses Bulletin*, **1** (1926), 185.

Gleichung (2) eingeführt, der sich aber eigentlich auf der Abweichung des Zustandes der adsorbierten Schicht von dem Zustande idealer Schicht beziehen soll. Diese Abweichung hat den Grund im allgemeinen in zwei Faktoren, nämlich, die Flächenbedürfnisse der adsorbierten Moleküle einerseits und die Molekularkräfte zwischen den adsorbierten Moleküle andererseits. Man kann also in diesem Sinne eine andere Zustandsgleichung aufstellen, die inhaltlich mit Gleichung (2) identisch sein soll, und die in Analogie zu der van der Waalsschen Zustandsgleichung der Gase lautet:⁽⁵⁾

$$\left(\pi + \frac{\alpha}{\Omega^2}\right)(\Omega - \beta) = RT, \quad \dots\dots\dots (5)$$

worin π (gleich $\sigma_0 - \sigma$) den Flächendruck, Ω (gleich $\frac{1}{a}$) die Oberfläche in cm^2 pro Mol des adsorbierten Stoffes, β das Flächenbedürfnis der adsorbierten Moleküle pro Mol und α eine Konstante, die sich auf Molekularkräfte bezieht, bedeutet.

Vergleicht man Gleichung (5) mit Gleichung (2), so bekommt man für den Koeffizient i folgenden Ausdruck:

$$i = 1 + \frac{\beta}{\Omega} - \frac{\alpha}{RT\Omega}, \quad \dots\dots\dots (6)$$

indem man dabei den höheren Glied $\frac{\alpha\beta}{\Omega^2}$ vernachlässigt.

Der Exponent $\frac{1}{i}$ ist somit abhängig von $\Omega \left(\frac{1}{a}\right)$ bzw. von der Dichte des Adsorptivs im homogenen Raum. Dieser Anspruch spricht aber der Erfahrung nicht wider, denn auch der Exponent $\frac{1}{n}$ in der Freundlichschen Isotherme von Dichte nicht streng unabhängig ist.⁽⁶⁾

Für kleine Dichten, soweit β sowie α vernachlässigt werden können, wird i annähernd gleich 1 sein. Dementsprechend bekommt man aus der Zustandsgleichung der idealen Schicht:

$$\pi\Omega = RT \quad \dots\dots\dots (7)$$

und der Gibbschen Gleichung folgende Beziehung

$$\alpha = kc, \quad \dots\dots\dots (8)$$

die den Henryschen Satz darstellt und die für genügend kleine Dichten auch empirisch bestätigt worden ist.

(5) Vgl. Magnus, *Z. anorg. u. allg. Chem.*, **158** (1926), 67.

(6) Vgl. Freundlich, „Kapillarchemie“ Bd. 1 (1930), 157.

Für grössere Dichten, hat man den Einfluss sowohl von β auch von α zu berücksichtigen. Der erste Einfluss wirkt immer derart, dass es den Wert von i grösser als 1 zu machen, aber der zweite wirkt verschieden, je nachdem α positiv oder negativ ausfällt. Die Zwischenmolekularkräfte könnten im Falle der adsorbierten Phase entweder anziehend oder abstossend sein, während sie sich im Falle der Gase stets anziehend wirkt.

Denkt man die Dipolmoleküle, deren elektrischer Dipol asymmetrisch im Molekül liegt, so werden sie an der Grenzfläche so orientiert, dass sie nicht nur miteinander parallel, sondern auch alle gleichgerichtet sind. Es ist klar, dass die Moleküle bei einer solchen Orientierung sich gegenseitig abstossen werden.⁽⁷⁾ In diesem Falle kommt i ohneweiteres grösser als 1 aus, da α negativ ausfällt.

Wenn aber die Orientierung der Moleküle an der Grenzfläche eine solche ist, dass sie zwischen ihnen ein Anziehungspotential bedingt, d. h. wenn der Wert von α positiv ausfällt, so wird i entweder grösser oder kleiner als 1 sein, je nachdem

$$\beta - \frac{\alpha}{RT} > 0, \quad \text{oder} \quad \beta - \frac{\alpha}{RT} < 0.$$

Bei mittleren oder hohen Temperaturen, dürfte im allgemeinen die erste Bedingung erfüllt werden und zwar stehen unsere meisten Beobachtungen (an der Grenzfläche fest-gasförmig) mit dieser Bedingung im Einklang. Erst bei genügend tiefen Temperaturen würde es folgen, dass der Einfluss der anziehenden Kräfte denjenigen der Raumversperrung übersteigt und somit die zweite Bedingung erfüllt wird. Die Realität solcher Verhältnisse müsste noch in bezug auf den „kritischen Zustand der adsorbierten Schicht“ diskutiert werden.⁽⁸⁾ Wenn aber, jedenfalls, solche Verhältnisse existierten, so müsste sich dies im Verlauf der Adsorptionsisotherme in der Weise äussern, dass sie bei grösseren Dichten nach der Dichte-Achse konvex sein werden, während sie anfänglich konkav nach dieser Achse oder eventuell linear verlaufen.

(7) Eine Abstossungskraft solcher Art ist von Magnus (loc. cit.) für Kohlendioxyd an Kohle angenommen worden.

(8) Hückel, „Adsorption u. Kapillarkondensation“ (1928), 195.

Nach der Potentialtheorie von Polanyi⁽⁹⁾ könnte solcher Verlauf, der zur Kondensationserscheinung entspricht, schon im Gebiete der mittleren Dichten realisiert werden. Ein einziger solcher Fall (Adsorption von Schwefeldioxyd an technischer Kohle) ist von Polanyi und Welcke⁽¹⁰⁾ beobachtet worden.

In meisten Fällen, ist es aber sehr wahrscheinlich, dass an der Grenzfläche fest-gasförmig der Einfluss der Raumversperrung denjenigen der anziehenden Kräfte übersteigt, denn die stärkeren aktiven Stellen der Oberfläche stufenweise abgesättigt werden. Es wird dann aus Gleichung (6) folgen, dass der Exponent $\frac{1}{i}$ bzw. $\frac{1}{n}$ kleiner als 1 ausfällt.

Diese Folgerung ist aber natürlich kein Beweis für die Erfahrungen, sondern etwa ein Vorbild, in dem man den wirklichen Verlauf der Adsorptionsisotherme einsehen könnte.

In Fällen, wo die aktiven Stellen der Oberfläche miteinander so weit entfernt sind, dass die Zwischenmolekularkräfte vernachlässigt werden, stellt man eine Zustandsgleichung auf, die lautet

$$\pi(Q-\beta) = RT. \quad \dots\dots\dots (9)$$

Aus dieser Gleichung und der Gibbsschen Gleichung wird die bekannte Isotherme von Langmuir:⁽¹¹⁾

$$c = \frac{Ka}{1-\beta a} \quad \dots\dots\dots (10)$$

hergeleitet, worin K eine Integrationskonstante bedeutet.

Man sieht weiter, dass sich der Exponent $\frac{1}{i}$ bzw. $\frac{1}{n}$ bei genügend hohen Temperaturen, wo sowohl β auch a vernachlässigt werden können, gegen 1 annähert. Solche Verhältnisse sind auch empirisch erkannt worden.⁽¹²⁾

In bezug auf die Konstante k in Gleichung (4) bzw. a in der Freundlich'schen Isotherme (1) wird hier nur kurz bemerkt, dass sie analog wie die Konstante K in der Langmuir'schen Isotherme (10) statistisch berechnet werden könnte,⁽¹³⁾ denn die beiden Isothermen aus der Gibbsschen

(9) *Verh. Deutsch. physik. Ges.*, **18** (1916), 55; *Trans. Faraday Soc.*, **28** (1932), 330.

(10) *Z. physik. Chem.*, **132** (1928), 321.

(11) Volmer, *Z. physik. Chem.*, **115** (1925), 253; auch Tamamushi, loc. cit.

(12) Vgl. Freundlich, loc. cit. s. 159.

(13) Kar, *Physik. Z.*, **26** (1925), 614.

Gleichung in ganz analoger Weise hergeleitet wurden und die beiden Konstanten k und K dabei eine Integrationskonstante bedeuteten.

Die Überlegungen, die oben angegeben worden sind, nehmen keine Rücksicht auf die Wirkung der in der ersten Schicht adsorbierten Moleküle auf die weiter von der Oberfläche entfernten. Es musste auch dabei abgesehen werden in Fällen, wo es sich um Kapillarkondensation handelt, wo der Verlauf der Isotherme ganz in anderer Weise zu deuten ist.

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STUDIES ON AMINO-ACIDS AND RELATED COMPOUNDS.
PART I. ELECTROLYTIC OXIDATION
OF GLUTAMIC ACID.

By Yoshitaro TAKAYAMA.

Received March 8th, 1933. Published April 28th, 1933.

Although the mechanism of the oxidative decomposition of some natural amino-acids has been studied to some extent by several investigators,⁽¹⁾ yet we have no satisfactory results in this line. The works published are still incomplete when viewed from the standpoint of organic chemistry, especially electro-organic chemistry.

With regards to the electrolytic oxidation of amino-acids, C. Neuberg⁽²⁾ has observed that amino-acids lose ammonia, and are converted into aldehydes with an atom of carbon less, when their dilute aqueous solutions are subjected to electrolysis with platinum electrodes.

Fr. Fichter⁽³⁾ and his collaborators pointed out that glycine and its allies undergo similar electrolytic oxidation, and their mechanisms are expressed by the following equations, glycine being taken as the type.

(1) H. D. Dakin, *J. Biol. Chem.*, **1** (1905), 171; **4** (1908), 63; *Biochem. J.*, **10** (1916), 319. K. Langheld, *Ber.*, **42** (1909), 2360. W. Denis, *J. Biol. Chem.*, **9** (1911), 365; **10** (1911), 73. H. Wieland u. E. Bergel, *Ann.*, **439** (1924), 196.

(2) C. Neuberg, *Biochem. Z.*, **17** (1909), 270; **24** (1910), 152.

(3) Fr. Fichter u. M. Schmid, *Helv. Chim. Acta*, **3** (1920), 704; Fr. Fichter u. F. Kuehn, *Helv. Chim. Acta*, **7** (1924), 167.

- 1) $\text{NH}_2\text{CH}_2\text{COOH} + \text{O} + 2\text{F} = \text{NH}_3 + \text{CH}_2\text{O} + \text{CO}_2$ (Initial reaction)
- 2) $\text{NH}_2\text{CH}_2\text{COOH} + 3\text{O} + 6\text{F} = \text{NH}_3 + 2\text{CO}_2 + \text{H}_2\text{O}$ (Final stage)

They also mentioned that the electrolytic oxidation of amino-acids may be fairly compared with the oxidative de-amination which these compounds undergo in the living organism, but is far more vigorous and profound.

Though the electrolytic oxidation of other amino-acids would be more complicated than the case above mentioned, the elucidation of the mechanism of these reactions would contribute not only to electro-organic chemistry, but also to biochemistry. From this point of view, a series of researches was instituted, and glutamic acid was selected as the first compound for investigation.

Concerning the oxidation of glutamic acid, several papers have been published. E. Ehrlich⁽⁴⁾ observed that glutamic acid produced succinic acid by alcoholic fermentation. H. D. Dakin⁽⁵⁾ found that succinic acid was a reaction product when glutamic acid was oxidised with hydrogen peroxide. U. Suzuki and Y. Matsuyama⁽⁶⁾ oxidised glutamic acid with nitric acid in the presence of vanadic acid and obtained succinic acid. But no adequate investigation has been reported on the electrolytic oxidation of this amino-acid.

The author has first examined the influence of anode material, current density, and diaphragm on the rate of oxidation of glutamic acid. When the anodic oxidation was carried out in an undivided cell under the same conditions, it was found that lead peroxide gave best current efficiency (considered from the yield of ammonia), out of the three kinds of anode materials, namely, carbon, platinum, and lead peroxide, as the following figures show.

Ammonia-Nitrogen to Total-Nitrogen

Pt: 3.9% C: 4.7% PbO₂: 48.5%.

With regards to current density, 2 amp./dm². was found to be most favorable for the formation of both ammonia and succinic acid, and no remarkable difference of the nitrogen distribution was found between the experiments in cells with and without diaphragm.

The Oxidation Products.—*d*-Glutamic acid in N.-sulphuric acid was oxidised at a lead peroxide anode with a current density of 2 amp./dm². The oxidised solution was subjected to steam distillation and acetic acid

(4) E. Ehrlich, *Biochem. Z.*, **18** (1909), 391.

(5) H. D. Dakin, *J. Biol. Chem.*, **5** (1909), 409.

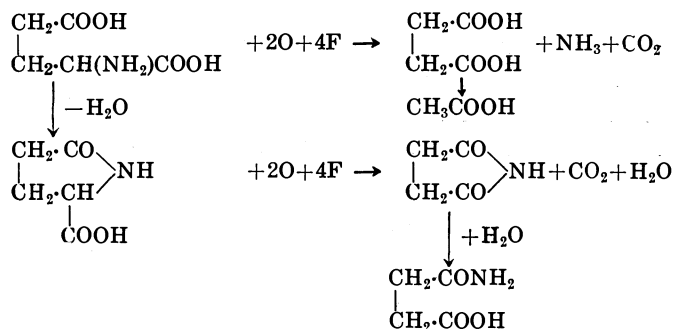
(6) Japanese patent No. 39210.

was obtained from the distillate. Large quantities of ammonium chloride and of succinic acid as well as unchanged glutamic acid were isolated from the residue of the steam treatments.

From the results of the nitrogen distribution in the solution, it seemed that the presence of some imino or amide compound might be possible. In fact, a small quantity of such a compound was isolated and identified as succinamic acid by comparison with the synthetic sample. The presence of this substance may be considered as derived from pyrrolidone-carboxylic acid. The latter acid was first formed from glutamic acid, then it was oxidised to succinimide, which on partial hydrolysis yielded succinamic acid. The formation⁽⁷⁾ of pyrrolidone-carboxylic acid in the solution of glutamic acid is quite probable, and it will be discussed fully in the next paper.

Acetic acid obtained from the electrolysate of glutamic acid was speculated as secondary oxidation product of succinic acid. This has been actually proved by the anodic oxidation of pure succinic acid.

Mechanism of the Reaction. The products obtained from glutamic acid in the above oxidation comprise succinic acid, acetic acid, succinamic acid, ammonia and carbon dioxide. Considering the isolation of these substances as the basis, the course of the oxidation can be explained to be as follows:



Experimental Part.

d-Glutamic acid, N = 9.56% (C₅H₉O₄N requires N = 9.50%), m.p. 209–210°C. $[\alpha]_D^{20} = +31.5^\circ$ (hydrochloride).

Apparatus. Cell: a 250 c.c. cylindrical glass vessel, provided with a rubber stopper, carrying a condenser, a thermometer, and two elec-

(7) F. W. Foreman, *Biochem. J.*, **8** (1914), 481.

trodes. As for the divided cell, a rectangular glass jar ($6.5 \times 4.1 \times 10$ cm.) was used, which was bisected vertically, parchment paper being inserted at its joint and tightly braced from outside.

Anode (3×6 cm.): platinum, carbon, or lead peroxide sheet.

Cathode (3×6 cm.): lead or carbon sheet.

The distance between the electrodes was 1.7 cm.

Copper coulometer was used for the determination of amount of electricity.

Influence of Anode Material, Current Density and Diaphragm. The experiments were carried out under the following conditions.

(a) *Without a Diaphragm.*—About two grams of glutamic acid was dissolved in 200 c.c. of N.-sulphuric acid and electrolysed at room temperature in the above cylindrical cells which were connected in series. The nitrogen distribution in the solution are summarised in Tables I and II.

Table I.
Influence of Anode Material.

Anode/Cathode	Glutamic acid in gr.	Amp./dm ² .	Amp. hrs.	NH ₃ -N/Total N (%)
Pt/C	1.989	2.30	1.186	2.18
C/C	1.995	„	„	1.97
PbO ₂ /Pb	1.996	„	„	31.70

Table II.
Influence of Anode Material and Current Density.
(NH₂-N was determined by van Slyke's method)

Anode/Cathode	Glutamic acid in gr.	Amp./dm ² .	Amp. hrs.	NH ₃ -N/Total N (%)	NH ₂ -N/Total N (%)
Pt/C	2.001	1.89	2.648	3.90	94.7
C/C	2.000	„	„	4.70	90.4
PbO ₂ /Pb	2.100	„	„	48.5	32.6
Pt/C	2.000	7.97	2.790	2.20	97.8
C/C	2.000	„	„	—	86.6
PbO ₂ /Pb	2.000	„	„	29.7	40.7

Above results clearly show that the best yield of ammonia is obtained in the case when lead peroxide anode was used with current density of 2 amp./dm².

(b) *With a Diaphragm.*—Anolyte: 70 c.c. of N.-sulphuric acid containing about 0.7 gr. of glutamic acid. Catholyte: 70 c.c. of N.-sulphuric acid. Anode (3×6 cm.): platinum, carbon, or lead peroxide sheet. Cathode (3×6 cm.): carbon or lead sheet. The results are given in Table III.

Table III.
Influence of Diaphragm.

Anode/Cath.	Glut. acid in gr.	Amp./dm ² .	Amp. hrs.	NH ₃ -N/Total N (%)			NH ₂ -N/Total N (%)		
				Anoly.	Cath.	Sum	Anoly.	Cath.	Sum
Pt/C	0.6984	1.86	0.977	2.2	1.5	3.7	88.6	10.2	98.8
C/C	0.6984	„	„	2.2	1.3	3.5	87.2	10.6	97.8
PbO ₂ /Pb	0.6987	„	„	40.8	6.1	46.9	23.8	6.3	30.1

The percentage of ammonia obtained in the cases tabulated in Table III are similar to those in Table II, that is to say, no remarkable difference is found between the results of divided and undivided cells.

(c) *Oxidation at a Lead Peroxide Anode.*—About 6 gr. of glutamic acid was dissolved in 160 c.c. of N.-sulphuric acid, and oxidised in undivided cells, with lead peroxide anode at different current densities varying from 2 amp./dm². to 13 amp./dm². The results are given in Table IV.

Table IV.
Oxidation at a Lead Peroxide Anode.

Glut. acid in gr.	Amp./dm ² .	Amp. hrs.	NH ₃ -N/Total N (%)	NH ₂ -N/Total N (%)	Temp.	Volts.
5.987	1.96	7.377	59.3	14.5	—	3.5
6.022	7.38	6.436	62.6*	17.0	35°	4.8
5.997	13.3	6.143	55.4	19.0	50°	6.3

* In Table II, the better current efficiency is secured in the case of 1.89 amp./dm². This contradiction may be due to the difference in concentration of glutamic acid. (The former, 1% solution; the present, 3.8%).

Referring merely to the formation of ammonia, the best result was secured in the case of 7.38 amp./dm². By taking the yield of other oxidation products into account, 2 amp./dm². was chosen throughout the series of these researches as the most suitable condition. The amount of total-N extremely exceeds the sum of ammonia-N and amino-N. The difference may be (at least partly) ascribed to the presence of succinamic acid.

Isolation of Oxidation Products. Fifty grams of glutamic acid was dissolved in 600 c.c. of N.-sulphuric acid. The solution was placed in two equal rectangular glass vessels connected in series, each of them provided with an ebonite lid carrying a condenser and a thermometer. The solution was electrolysed with a lead peroxide anode (5.6×7.4 cm.) and a lead cathode (5.6×7.4 cm.) under the following conditions: the distance between the anode and the cathode, 3 cm.; C.D., 2 amp./dm².; current quantities, 55.8 amp. hours; temperature, 25°C. After the electrolysis, the nitrogen distribution in the solution was determined.

Nitrogen Distribution.

Total-N	98.6%
Ammonia-N (MgO)	87.0
Ammonia-N (30% NaOH)	3.9
Amino-N (van Slyke)	6.2

The ammonia-N (MgO) was determined by distillation over magnesium hydroxide under reduced pressure, and an excess of 30% NaOH was added to the residue. To estimate ammonia-N (NaOH) it was distilled under ordinary pressure, and the distillate was received in N.-sulphuric acid. This nitrogen represents the amount of succinamic acid.

The oxidised solution was first submitted to steam distillation, the distillate (A) was neutralised with sodium hydroxide and redistilled. The first portion of the distillate (A₁) gave no iodoform reaction, and reduced neither Fehling's solution nor Tollens' reagent, but it gave only faint red colouration with fuchsin reagent. The original solution also showed no aldehyde reaction.

Volatile Acid.—Acetic Acid. The neutralised residue (A₂) was evaporated to dryness, an excess of syrupy phosphoric acid added, and it was redistilled. The volatile acid, obtained from the distillate (A₃), was identified as acetic acid by both ferric chloride and acetic ether reactions, and by its silver salt.

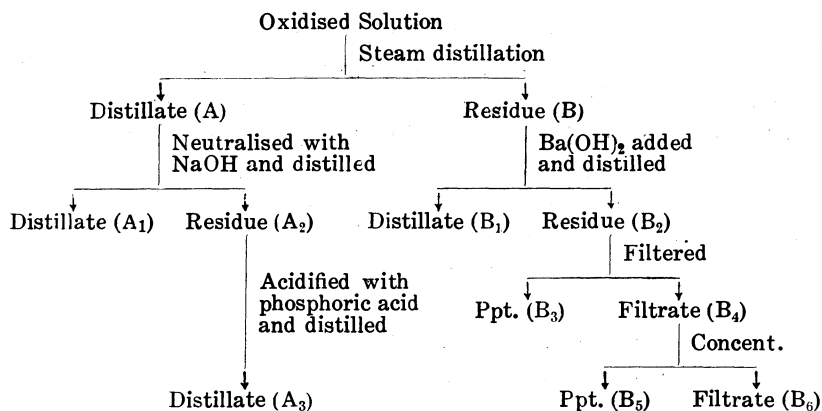
Anal.: Subst. = 0.2352; Ag = 0.1521 gr. Found: Ag = 64.66%.

Calc. for $C_2H_3O_2Ag$ (silver acetate): Ag = 64.64%.

The Volatile Base.—Ammonia. After making the residue (B) alkaline with barium hydroxide, it was submitted to distillation under reduced pressure, and a large quantity of ammonia was received in dilute hydrochloric acid (B_1). The ammonium chloride (8 gr.) thus obtained was identified as its platonic double chloride. Other bases were not present.

Anal.: Subst. = 0.0983; Pt = 0.0432 gr. Found: Pt = 43.94%.

Calc. for $(NH_4)_2PtCl_6$ (ammonium chloroplatinate): Pt = 43.96%.



Succinic Acid.—The residue (B_2) was filtered. The precipitate (B_3), consisting of barium hydroxide, barium sulphate and organic salts of barium, was treated with sulphuric acid to remove barium, and from the concentrated filtrate free succinic acid crystallised out. The filtrate (B_4) was concentrated and barium succinate (B_5) was obtained which was then converted into free acid as usual. The joined yield was 18 gr. from 50 gr. of glutamic acid. It melted at $183^\circ C$. and the melting point showed no lowering when mixed with pure succinic acid.

Anal.: Subst. = 0.1437 gr.; Required N./10-NaOH = 24.27 c.c.

Calc. for $C_4H_6O_4$ (succinic acid): N./10-NaOH = 24.33 c.c.

Subst. = 0.1010; CO_2 = 0.1502, H_2O = 0.0464 gr.

Found: C = 40.56; H = 5.14%.

Calc. for $C_4H_6O_4$ (succinic acid): C = 40.63; H = 5.12%.

The mother liquor (B_6) of barium succinate, free from barium and sulphuric acid, was concentrated when it yielded glutamic acid, its hydrochloride decomposing at $205-206^\circ C$.

Succinamic Acid.—Fifty grams of glutamic acid was dissolved in 560 c.c. of N-sulphuric acid and oxidised until one-half of the glutamic acid has been oxidised, the conditions being similar to those in previous cases of oxidation. The current applied amounted to 30.5 amp. hours.

The nitrogen distribution in the oxidised solution was as follows:—

Nitrogen Distribution.

Total-N	97.1%
Ammonia-N (MgO)	43.4
Ammonia-N (NaOH)	9.5
Amino-N (van Slyke)	44.0

The solution was made up to 1000 c.c. by adding water, and to isolate succinamic acid, half of the solution was neutralised with barium carbonate and barium hydroxide. The precipitate thus formed was filtered. The filtrate was concentrated to about 30 c.c. under reduced pressure at 50°C. and barium succinate formed was filtered. The filtered solution was treated with sulphuric acid to remove barium, and an excess of calcium hydroxide was added. Ammonia was driven off by distillation under reduced pressure and glutamic acid was recovered as its calcium salt.

After removing calcium as oxalate, the filtrate was concentrated to a syrup. The syrup was extracted with acetone. The crystals, formed after removal of acetone from the extract, was treated with ether to remove succinic acid, and it was recrystallised from acetone in colourless plate (0.7 gr.), m.p. 154–155°C. It was identified as succinamic acid⁽⁸⁾, by the determination of nitrogen, mixed melting point test and conversion into silver salt.

Anal.: Subst. = 0.1253 gr.; NH_3 = 10.65 c.c. of N./10- H_2SO_4 .

Found: N = 11.91%.

Calc. for $\text{C}_4\text{H}_7\text{O}_3\text{N}$ (succinamic acid): N = 11.96%.

Anal.: Subst. = 0.0498; Ag = 0.0239 gr. Found: Ag = 48.0%.

Calc. for $\text{C}_4\text{H}_5\text{O}_3\text{NAg}$ (silver succinamate): Ag = 48.18%.

Electrolytic Oxidation of Succinic Acid.—Separation of Acetic Acid. A solution of 20 gr. of succinic acid in 500 c.c. of N-sulphuric acid was electrolysed with a lead peroxide anode and a lead cathode under the following conditions: anodic current density 2 amp./dm², temperature 25°C., current quantity 20.0 amp. hours. The oxidised solution was submitted to steam distillation. The distillate gave neither aldehyde nor

(8) *Ann.*, **134** (1865), 136; **162** (1872), 174.

ketone reactions. It was converted into sodium salt, dried, treated with phosphoric acid and distilled. Acetic acid was obtained from the distillate. It was identified as its silver salt.

Anal.: Subst. = 0.1359; Ag = 0.0877 gr. Found: Ag = 64.55%.

Calc. for $C_2H_3O_2Ag$ (silver acetate): Ag = 64.64%.

In conclusion, the author expresses his hearty thanks to Prof. K. Matsubara for his kind inspection of this paper.

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ON THE COPPER AGE IN ANCIENT CHINA. II.
(ON THE TRANSITIONAL PERIOD BETWEEN THE COPPER
AND BRONZE AGE IN ANCIENT CHINA.)

By **Tsurumatsu DŌNO**

Received March 15th, 1933. Published April 28th, 1933.

In the previous paper, the present author reported⁽¹⁾ the results of chemical analyses of some metallic spear-heads of ancient China, which were made of almost pure copper. These specimens studied possess very primitive appearances and seem to belong to extremely antique species closely resembling to those relics unearthed from Yin Site in Honan. By this chemical investigation, the existence of the pure copper implements in ancient China being first confirmed, the author came to the conclusion that the real presence of the copper age in China preceding probably to the well known bronze age must be considered.

Encouraged by this discovery, the author has hereafter endeavoured to search for the specimens of the same kind as those recently analysed, in order to extend his study in this side. Fortunately several halberds in the type of those unearthed in Yin Site were put at his disposal by Mr. Sugimura in Peking, to whose kindness the author is very much indebted (compare Figs. I, II and III). According to the chemical study of these new specimens by the author, it was proved that one (A) of these three halberds contains so insignificant amount of tin that the arc spectral analysis was only able to detect the presence of this metal as several very

(1) Dōno, this Bulletin, 7 (1932), 347.

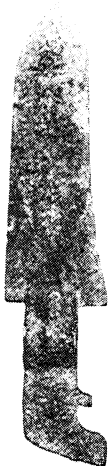


Fig. 1. Specimen A

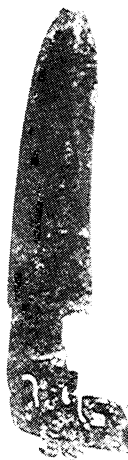


Fig. 2. Specimen B

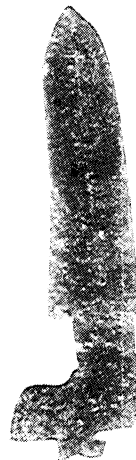


Fig. 3. Specimen C

faint lines, and consequently this specimen must be called the pure copper implement. The second one (B) involves tin in the amount detectable by an ordinary chemical analysis, namely about 0.60%⁽²⁾: even this, however, it must be classified in the copper implement from its very low contents in tin compared with ordinary bronze. As for the last specimen (C), it showed indeed a considerably high contents of tin ($\text{Sn} = 2.19\%$) and it will undoubtedly be called a bronze implement in spite of that this is in the same type with the other two.

From the latter interesting fact, it may easily be concluded that the specimen (C) should have been manufactured in the transitional period between the copper and bronze age, and further that the copper age in ancient China existed very probably closely before the bronze age. It may also be supposed that the bronze age in ancient China should have begun at the time in which these types of halberds were made use of.

Experimental Part.

The chemical analysis as well as the metallographical study were carried out in the usual way⁽³⁾ and the constituents, which are scarcely detected by the chemical methods, were found from their so called "raies ultimes" of the arc spectra. The results are given below.

(2) This low contents in tin must not be considered that this metal was added artificially.

(3) T. Dōno, *J. Chem. Soc. Japan*, **51** (1930) 463; **53** (1932), 100.

Wave-length of tin-lines	Specimen A	Specimen B	Specimen C
3175.16	doubtful	intense	intense
3262.50	„	„	„

Results of chemical
analyses

	Specimen A	Specimen B	Specimen C
Sample (gr)	0.4890	0.5016	0.5085
Copper (%)	77.20	97.60	83.85
Tin (%)	Trace	0.60	2.19
Lead (%)	15.08	0.58	5.85
Iron (%)	2.80	0.08	0.08
Arsenic (%)	—	—	Trace
Nickel (%)	0.03	0.04	—
Gold (%)	Trace	Trace	Trace
Silver (%)	0.04	0.03	0.06
Total (%)	95.15	98.93	97.03

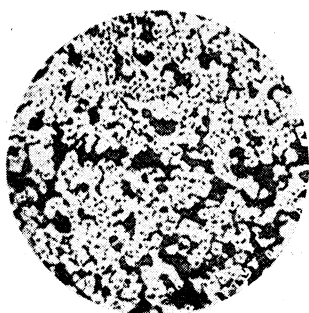


Fig. 4. Specimen A

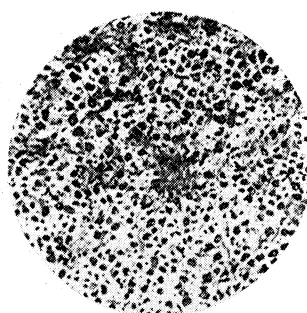


Fig. 5. Specimen A (etched)

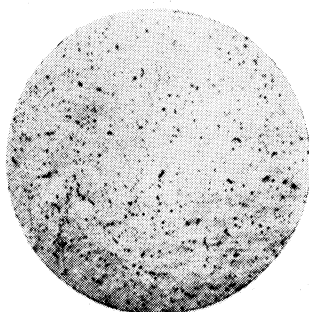


Fig. 6. Specimen B

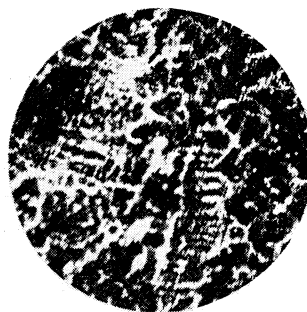


Fig. 7. Specimen B (etched)

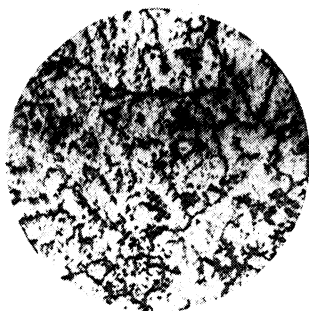


Fig. 8. Specimen C

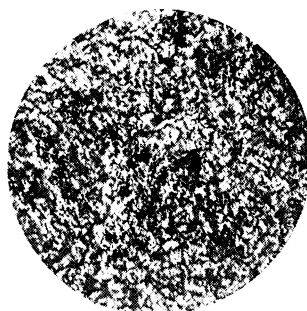


Fig. 9. Specimen C (etched)

As will be seen in the analytical results given above, the total values do not attain to 100%; this is, as was stated in the previous paper, due to oxygen which combined probably with metals during and after the manufacture of these weapons. As for the meaning of the existence of other metals was also already explained in the preceding paper.

Thus the author could add two more examples of pure copper implements in the ancient Chinese relics and was able to strengthen the recognition of the existence of the copper age in ancient China. The fact, that one of specimens now studied was of bronze, tells us that the beginning of the bronze age may be considered to have occurred at the time in which these types of halberds were made use of.

In conclusion, the author expresses his sincere gratitude to Prof. Dr. Shibata, Prof. Dr. S. Katō and Prof. Dr. K. Kimura for their kind guidances, and to Prof. Dr. Y. Harada, Dr. Y. Komai and Dr. N. Egami in the Archaeological Institute of the Faculty of Literature of Tokyo Imperial University, who gave valuable advices to his investigation from the standpoint of Archaeology and also to Prof. Dr. T. Mishima for the trouble of taking the metallographical photographs.

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STUDIES ON AMINO-ACIDS AND RELATED COMPOUNDS.
PART II. ELECTROLYTIC OXIDATION OF
PYRROLIDONE-CARBOXYLIC ACID.

By Yoshitaro TAKAYAMA.

Received March 27th, 1933. Published May 28th, 1933.

In the previous communication,⁽¹⁾ it was stated that succinamic acid was obtained from the electrolysate of glutamic acid, and its formation was ascribed to the anodic oxidation of pyrrolidone-carboxylic acid, which could be formed, apart from electrolysis, by the dehydration of glutamic acid.

The formation of pyrrolidone-carboxylic acid from glutamic acid is well known. Menozzi and Appiani⁽²⁾ first stated that glutamic acid is very easily converted by heating into its lactam, pyrrolidone-carboxylic acid. E. Abderhalden⁽³⁾ reported that *l*- and *dl*-pyrrolidone-carboxylic acids were obtained from glutamic acid when it was heated to 150–160°C. and 180–190°C. respectively. F. W. Foreman⁽⁴⁾ observed that glutamic acid was converted into its lactam when its aqueous solution was boiled for a certain length of time, and reversely, pyrrolidone-carboxylic acid was re-converted into glutamic acid by boiling with strong hydrochloric acid. C. Okinaka⁽⁵⁾ found that above reversible reaction occurred even in the absence of acid or alkali, and studied the equilibrium points of above reversible reactions at 120°, 130° and 140°C. He also mentioned that the rate of transformation into the lactam was increased as the temperature was raised or by the presence of dilute alkali, and it was retarded in the presence of an excess of strong acids or alkalies.

The author intended to ascertain that such a reversible reaction would occur actually even in the solution in normal sulphuric acid and at a lower temperature, and has undertaken the following experiments.

d-Glutamic acid and *l*-pyrrolidone-carboxylic acid were dissolved in N.-sulphuric acid, and kept at 35° and 50°C., and amounts of amino-N in their solution were determined from time to time. The changes of amino-N

(1) Y. Takayama, Studies on amino-acids and related compounds. Part I.

(2) Menozzi und Appiani, Abderhalden: „Biochem. Handlexikon” **4**, 615.

(3) E. Abderhalden und K. Kautzsch, *Z. physiol. Chem.*, **64** (1910) 447.

(4) F. W. Foreman, *Biochem. J.*, **8** (1914), 481.

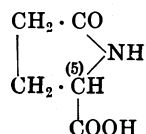
(5) C. Okinaka, “The Sexagint” (a collection of papers dedicated to Prof. Y. Osaka by his pupils in celebration of his 60th birthday) Kyoto, (1927), p. 27.

content thus obtained showed the degree of their conversions. The results obtained are tabulated in Fig. 1, Tables I and II.

From the above results it is clear that the reversible reaction proceeds even at such a low temperature as 35°C., and we can conclude that a solution of glutamic acid, kept under similar conditions as in the electrolytic oxidation, should contain a certain amount of pyrrolidone-carboxylic acid (i).

Next, in order to compare the rate of the electrolytic oxidation of glutamic acid with that of pyrrolidone-carboxylic acid, each of these acids was dissolved in N.-sulphuric acid and oxidised with a lead peroxide anode under the same conditions. The amounts of ammonia-N formed were determined at a certain interval of time. The results are given in Fig. 2, the curves representing ammonia-N/faradays per mol.

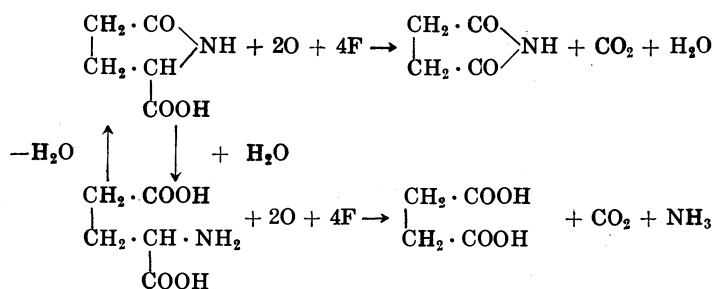
From these curves we see that the rate of oxidation of pyrrolidone-carboxylic acid is far greater than that of glutamic acid and the difference of the rates may be ascribed to the presence of the easily oxidisable carbon (5) in the former acid (ii).

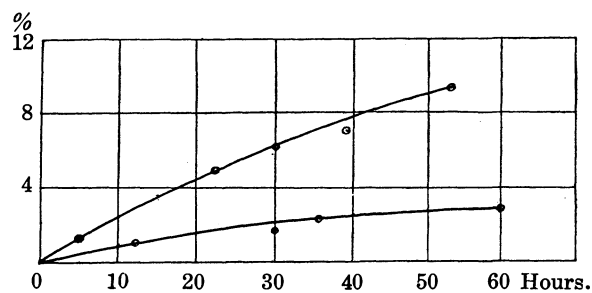


Pyrrolidone-carboxylic acid was dissolved in N.-sulphuric acid and oxidised at a lead peroxide anode. The oxidised solution contained a little of ammonia-N (MgO) and much of ammonia-N (NaOH), hence the presence of imino or amino compound is easily presumable (iii).

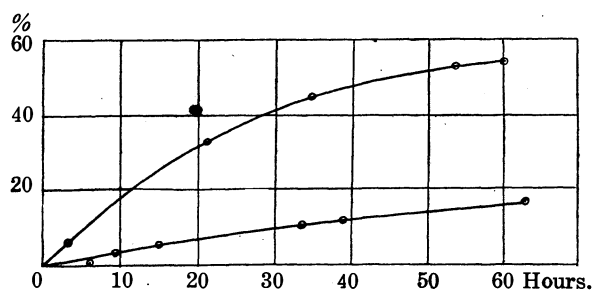
In fact, succinimide was isolated abundantly together with a small amount of succinic acid (iv).

From these facts, (i), (ii), (iii) and (iv), it is quite probable that the oxidation of pyrrolidone-carboxylic acid proceeds in the following scheme and that succinamic acid formed from glutamic acid is produced by the hydrolysis of succinimide.



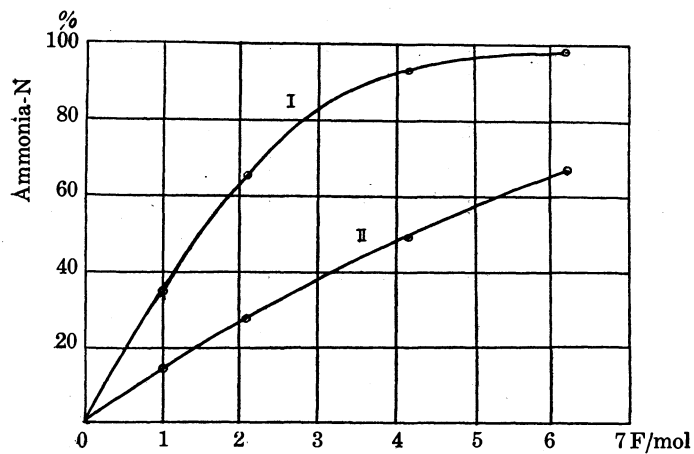


Glutamic Acid Changed.



Pyrrolidone-Carboxylic Acid Changed.

Fig. 1.



I = Pyrrolidone-Carboxylic acid.
 II = Glutamic acid.

Fig. 2.

Experimental Part.

Conversion of Glutamic Acid into Pyrrolidone-Carboxylic Acid and vice versa.

d-Glutamic acid ($N = 9.25\%$; calc. $N = 9.50\%$)

$[\alpha]_D^{20} = +30.5^\circ$ (as hydrochloride).

l-Pyrrolidone-carboxylic acid ($N = 10.67\%$; calc. $N = 10.85\%$)

$[\alpha]_D^{20} = -11.55^\circ$ (aqueous solution).

The solutions used: 5 gr. of glutamic acid in 50 c.c. of N.-sulphuric acid, and 5 gr. of pyrrolidone-carboxylic acid in 50 c.c. of N.-sulphuric acid.

The procedure: The solution to be examined was introduced into a stoppered flask and kept at 35° or 50°C . in a thermostat. After a certain interval of time, 2–5 c.c. of the solution were taken, and total-N as well as amino-N (van Slyke) in it were determined. The results of the experiment are shown in Tables I and II.

Table I.

Glutamic acid at 50°C .				
Time.	Total-N. in 100 c.c.	$\text{NH}_2\text{-N}$. in 100 c.c.	Glutamic acid.	Glutamic acid changed.
0 hrs.	0.8762 gr.	0.8694 gr.	99.2%	0 %
5	"	0.8578	97.9	1.3
23	"	0.8256	94.2	5.0
30	"	0.8175	93.3	5.9
39	"	0.8100	92.5	6.7
54	0.8798	0.7912	89.9	9.3
Glutamic acid at 35°C .				
6 hrs.	0.8896 gr.	0.8768 gr.	98.6%	1.4%
12	0.8932	0.8806	98.6	1.4
30	0.8861	0.8710	98.3	1.7
36	0.8896	0.8680	97.6	2.4
60	0.8896	0.8616	96.9	3.2

Table II.

Pyrrolidone-carboxylic acid at 50°C.			
Time	Total-N. in 100c.c.	NH ₂ -N (increased) in 100 c.c.	Pyrrolidone-carboxylic acid changed.
3 hrs.	1.052 gr.	0.0558 gr.	5.3%
21	„	0.3486	33.1
27	„	0.3828	36.4
35	1.045	0.4632	44.3
54	„	0.5645	54.4
60	1.055	0.5814	55.1
Pyrrolidone-carboxylic acid at 35°C.			
6 hrs.	1.029 gr.	0.0114 gr.	1.1%
9	1.030	0.0378	3.7
15	„	0.0597	5.8
33	„	0.1105	10.8
39	„	0.1323	12.8
63	„	0.1860	18.1

Rates of Oxidation of Glutamic Acid and Pyrrolidone-Carboxylic Acid.

A solution containing 14.714 gr. of glutamic acid in 280 c.c. of N.-sulphuric acid and a solution containing 12.921 gr. in 280 c.c. of N.-sulphuric acid were electrolysed in undivided cells which were connected in series under the following conditions: The electrodes are of equal size (4×5 cm.), anode: lead peroxide sheet, cathode: lead sheet, C.D.: 2 amp./dm², temperature: 19–20°C.

The process of investigation: In the course of electrolysis at every definite consumption of electricity, 10 c.c. of the solution were drawn out and the total ammonia-N (NaOH) in it was determined and its percentage to total-N was calculated, which denotes the percentage of amino-acid oxidised. The results of this experiment are shown in Table III.

Table III.

Faradays per mol.	Oxidised solution.	Glutamic acid oxidised N. in 10 c.c.	Pyrrolidone-carboxylic acid N. in 10 c.c.
1.00 F	0.100 mol 280 c.c.	Total-N, 47.80 mg. NH ₃ -N 6.68 14.0%	47.80 mg. 16.72 35.0%
2.07 F	0.093 mol 260 c.c.	Total-N, 47.40 mg. NH ₃ -N 12.90 27.4%	48.50 mg. 31.90 65.8%
4.07 F	0.0858 mol 240 c.c.	Total-N, 46.45 mg. NH ₃ -N 22.60 48.6%	48.80 mg. 45.40 93.0%
6.24 F	0.0786 mol 220 c.c.	Total-N, 45.70 mg. NH ₃ -N 31.10 68.1%	48.80 mg. 48.00 98.4%

Electrolytic Oxidation of Pyrrolidone-Carboxylic Acid. Separation of Oxidation Products. 6.45 Gr. of pyrrolidone-carboxylic acid was dissolved in 120 c.c. of N.-sulphuric acid and electrolysed with a lead peroxide anode and a lead cathode with an anodal current density of 2 amp./dm². The amount of electricity was 7.97 amp. hours, and the temperature was 23–28°C.

The nitrogen distribution of the oxidised solution was as follows:

Total-N	100.0%
Ammonia-N (MgO)	15.7
Ammonia-N (NaOH)	80.6

The solution was neutralised with barium hydroxide, and the precipitated barium sulphate was filtered off. The filtrate was evaporated to dryness under reduced pressure, and extracted with alcohol (A). The mass insoluble in alcohol was treated with acetone (B), after acidifying with hydrochloric acid. From (B) a small quantity of succinic acid, m.p. 181°C., was obtained.

On distilling off alcohol from (A), crystals were obtained which were found to be almost pure succinimide (3.2 gr.).

Similarly 6.45 gr. of pyrrolidone-carboxylic acid was oxidised with a current quantity of 8.0 amp. hours (at 24°C.). The oxidised solution was

neutralised with potassium hydroxide, evaporated to dryness under reduced pressure, and extracted with absolute alcohol. The crystals formed after removal of alcohol, were recrystallised from acetone in colourless crystals (3.4 gr.), m.p. 126°C., alone or when mixed with a pure sample of succinimide (Kahlbaum).

Anal.: Subst. = 0.1114, 0.0919; CO₂ = 0.1980, 0.1641; H₂O = 0.0489, 0.0406 gr.

Subst. = 0.2626; NH₃ = 26.56 c.c. of N./10-H₂SO₄.

Found: C = 48.49, 48.68; H = 4.89, 4.94; N = 14.17%.

Calc. for C₄H₅O₂N (succinimide): C = 48.48; H = 5.02; N = 14.15%.

From the residue, after separating succinimide, succinic acid, m.p. 183°C., was obtained.

Oxidation of Glutamic Acid. A solution consisting of 530 c.c. of N.-sulphuric acid and 50 gr. of glutamic acid was electrolysed with a lead peroxide anode, the amount of electricity applied being 32.8 amp. hours. The ammonia-N (NaOH) of the oxidised solution amounts to 12.3% of total nitrogen.

The solution was neutralised with barium carbonate, and filtered. The filtrate was evaporated to dryness, and extracted with acetone containing a little hydrochloric acid. The residue, after removal of acetone, was recrystallised from acetone and alcohol, succinamic acid being obtained (0.5 gr.) in colourless crystals, m.p. 154–155°C.

Anal.: Subst. = 0.1155; NH₃ = 10.10 c.c. of N./10-H₂SO₄.

Found: N = 12.26%.

Calc. for C₄H₅O₃N (succinamic acid): N = 11.94%.

The above attempt to obtain succinimide from the electrolysate of glutamic acid by the similar treatments as in the case of pyrrolidone-carboxylic acid was a failure, while a small amount of succinamic acid was obtained. This fact is explained as follows. A small amount of succinimide, perhaps once formed in the solution, may have been completely hydrolysed to succinamic acid during electrolysis and various treatments for its isolation.

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A NEW DITERPENE— γ -CAMPHORENE.

By Kinzô KAFUKU, Taichirô OYAMADA and Masura NISHI.

Received April 5th, 1933. Published May 28th, 1933.

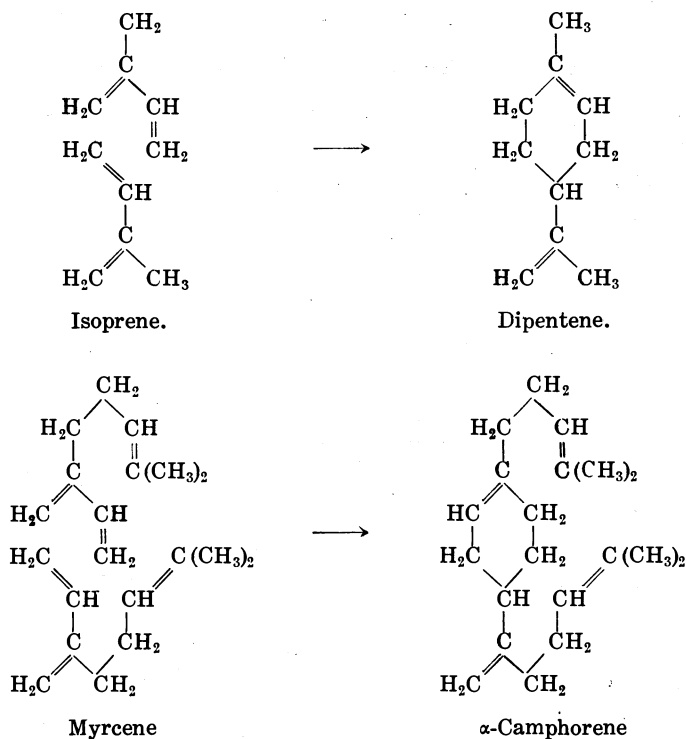
It was F. W. Semmler and Irene Rosenberg⁽¹⁾ who first liberated the diterpenes α - and β -camphorenes out of the high-boiling fraction of camphor oil, and shortly afterwards these were synthetically prepared by Semmler and K. G. Jonas⁽²⁾ from the aliphatic terpene myrcene by the action of heat and pressure on it. These diterpenes are regarded as monocyclic as they give tetrahydrochlorides as well as octahydro-compounds, and also as their molecular refractions accord with $C_{20}H_{32} \mid =_4$, but, as to their constitutional formulae, nothing exact is yet known. Only, L. Ruzicka and M. Stoll⁽³⁾ have suggested the following one for α -camphorene from considerations of its mode of formation from myrcene and of the oxidative destruction of its octahydro-derivative, taking into account that myrcene which represents isopentenyl-isoprene, ought to undergo an analogous polymerization as isoprene does to form dipentene, but this deduction is not rigorous enough.

One of the present authors (K), during his former experiments with Formosa lemongrass oil, proceeded with his terpene fraction exactly as described by Semmler and Jonas, in order to identify myrcene in it, and it was that his crude α -camphorene tetrahydrochloride appeared under the microscope to be a conglomerated mixture of two distinctly differently shaped crystals—the one representing thin hexagon plates, the other tiny needle-shaped prisms. Furthermore, he observed that pure α -camphorene tetrahydrochloride corresponding to the descriptions of Semmler and others could only be attained after several consecutive recrystallizations of this crude product from hot ethyl alcohol, and that at the pure stage, no more needle-like crystals were to be seen under the microscope except in very small amount. With a view to clear up the nature of this prismatic contamination, the present authors recently resumed the study in this field of research, and, after a series of experiments, at last arrived at the conclusion that among the diterpenes resulting from the polymerization of myrcene, there existed a hitherto unknown diterpene which leads to a new hydrochloride melting at 96–98°C., and which crystallizes

(1) *Ber.* **46** (1913), 768.

(2) *Ber.* **46** (1913), 1566; **47** (1914), 2077.

(3) *Helv. Chim. Acta*, **7** (1924), 271.



in prismatic needles. The reason why this diterpene slipped the elaborate hands of such renowned chemist as Semmler, is because this hydrochloride is readily decomposed by hot alcohol never to crystallize again. To this new diterpene, the authors propose the name " γ -camphorene."

γ -Camphorene has almost the same physical properties as the α -modification as can be seen from the following data:—

	α -Camphorene	γ -Camphorene
b. p. / 4.5 mm.	178°	176–178°
d	0.8864 _(21/4)	0.8875 _(19/4)
n_D	1.4998 ₍₂₁₎	1.5030 ₍₁₉₎
M. R.	90.7	90.6
Do. calc. as $C_{20}H_{32}$	90.48	

γ -Camphorene tetrahydrochloride is readily soluble in cold petroleum ether while α -camphorene tetrahydrochloride is not, and thus the two can easily be separated from each other. The γ -hydrochloride can be recrystallized from warm petroleum ether without decomposition, and the purified crystals melt at 96–98°C. The γ -hydrochloride, on treatment

with alcoholic potash, regenerates γ -camphorene and this regenerated hydrocarbon, on being acted on by dry hydrogen chloride gas, redeposits the needle-crystalline γ -camphorene tetrahydrochloride only, and no more plate crystals of α -camphorene tetrahydrochloride with it. By the action of hydrogen bromide gas, α -camphorene gives a tetrahydrobromide melting at 133–134°C., while γ -camphorene yields a corresponding hydrobromide melting at 111–114°C.

Experimental.

Myrcene. The starting material myrcene was obtained partly from Formosa lemongrass oil and partly from linalool. That from the former was prepared by carefully fractionating the crude oil dried over anhydrous sodium sulphate under 50 mm. pressure, and then shaking the terpene fraction thus obtained with 40% sodium bisulphite solution, and finally distilling the product over metallic sodium. The other portion from linalool was obtained in the following way: To pure linalool kept in a flask and heated to 100–120°C., iodine in form of fine powder was slowly added, when a violent reaction took place. The mass was distilled under 100 mm. pressure, and the process was repeated with the distillate until all linalool decomposed. Then the product was distilled over metallic sodium and was rectified under 12 mm. pressure. Myrcene thus obtained showed the following physical properties:—

b. p. / 12 mm.	55°C.
d	0.8030 _(19/4)
n_D	1.4680

Polymerization of Myrcene. Myrcene was heated in a sealed tube in a bomb furnace up to 240–260°C. for four hours. After cooling, the content of the tube was fractionated under 6 mm. pressure, when about 30% came over between 51° and 55°C., which turned out to be an isomerized monocyclic terpene with some unchanged myrcene, the properties of which are as follows:

b. p.	51–55°C. / 6 mm.
d	0.8420 _(22/4)
n_D	1.4680 ₍₂₂₎
M. R.	44.9
Do. calc. as $C_{10}H_{16}$ $\equiv_2$	44.90

The next 44% distilled between 162° and 176°C., and showed the following constant:

b. p.	162–176°C. / 6 mm.
d	0.9203 _(23/4)
n _D	1.4960 ₍₂₄₎
M. R.	88.3
Do. calc as C ₂₀ H ₃₂ ₄	90.48

These constants are in accordance with Semmler's data for crude camphorene.

α - and γ -Camphorene Tetrahydrochloride. The crude camphorene thus obtained was dissolved in its own volume of absolute ether and was saturated with dry hydrogen chloride gas and stood overnight in cold. The gruel-like mass of crystals thus produced was freed from the adhering liquid on porous porcelain and then it was boiled with light petroleum ether and filtered while warm. From the filtrate there precipitated on cooling the needle-like crystals of γ -camphorene tetrahydrochloride m.p. 96–98°C. The filtered crystals were washed with warm petroleum ether several times, dried, and then recrystallized from hot alcohol. The crop of crystals so obtained, on inspection under the microscope contained no more needle-shaped crystals of γ -camphorene tetrahydrochloride, and melted at 129–131°C., representing pure α -camphorene tetrahydrochloride.

Anal.: Crystals (m.p. 96–98°C.) = 2.730; AgCl = 3.762 mg.

Found: Cl = 34.17%. Calc. for C₂₀H₃₀Cl₄: Cl = 33.91%.

Crystals (m.p. 129–131°C.) = 3.386; AgCl = 4.480 mg.

Found: Cl = 33.50%. Calc. for C₂₀H₃₀Cl₄: Cl = 33.91%.

Regeneration of α - and γ -Camphorenes. Ten grams each of α - and γ -camphorene tetrahydrochlorides were separately dissolved in an excess of 10% alcoholic potash, boiled under reflux for seven hours on the water-bath, saturated with carbon dioxide, filtered from depositing solid matters, alcohol distilled off, and finally the residual substance was distilled in vacuo over metallic sodium. The yield of the ultimate product in each case amounted, in the case of α -camphorene to about 98%, and in that of γ -camphorene to about 75% of the theory, and each exhibited such properties as given in the preceding page. These, on treatment with hydrogen chloride, gave the respective hydrochlorides only, and not the mixture of the two hydrochlorides.

α - and γ -Camphorene Tetrahydrobromides. On treatment of these two diterpenes with hydrogen bromide gas, tetrabromides resulted. From α -camphorene lustrous scaly crystals crystallized out which after purification melted at 133–134°C., while from γ -camphorene, prismatic needle

crystals separated out with m.p. 111–114°C. Both could be recrystallized from petroleum ether, but the γ -modification was more soluble than the α -hydrobromide, and moreover, it exhibited a remarkable tendency to decompose on dissolving in hot alcohol.

Anal.: α -Hydrobromide = 5.910; AgBr = 7.500 mg.

Found: Br = 53.96%. Calc. for $C_{20}H_{36}Br_4$: Br = 53.66%.

γ -Hydrobromide = 4.937; AgBr = 6.180 mg.

Found: Br = 53.34%. Calc. for $C_{20}H_{36}Br_4$: Br = 53.66%.

Camphorene Octabromide. By the action of bromine, α - and γ -camphorenes give an undefined crystalline octabromide, seemingly identical. For this purpose, an ethereal solution of each hydrocarbon was treated by an excess of bromine, also in the same medium. The reaction mass was stood still in an ice chamber overnight, excess of bromine and ether expelled in vacuo, the residue which at first assumed a syrupy consistency, gradually solidified on keeping. Then, it was powdered, redissolved in ether, a little methyl alcohol added thereto, filtered, and evaporated in cold. Thus, from both hydrocarbons, a white crystalline powder was obtained which melted between 70° and 80°C., showing no lowering of the melting point by mixing with each other. Other methods of purification were tried to attain to a more definite melting point but in vain.

Anal.: Substance from α -camphorene = 6.105; AgBr = 10.026 mg.

Substance from γ -camphorene = 4.237; AgBr = 6.871 mg.

Found: Br = 69.91; 69.01%. Calc. for $C_{20}H_{32}Br_8$: Br = 70.17%.

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GLUCOSULFATASE. V.

By Tokuro SODA and Fujio EGAMI.

Received April 18th, 1933. Published May 28th, 1933.

Glucosulfatase⁽¹⁾ is regarded as an enzyme which hydrolyses glucose-monosulphate.⁽²⁾ Some of its properties, however, are still ambiguous. For instance, we do not know if: (1) it is simply a hydrolysing enzyme, (2) it can be obtained in pure state and (3) it can be obviously distin-

(1) T. Soda and C. Hattori, this Bulletin, **6** (1931), 258.

(2) T. Soda, *Biochem. Z.* **135** (1923), 623; this Bulletin, **8** (1933), 37.

guished from phenosulfatase. In the present paper we have chiefly dealt with these questions.

As experimental materials, we used at first the internal organs of *viviparus japonicus* (*tanishi*)⁽³⁾ and afterwards those of *charonia lampas* (*boshu-bora*),⁽⁴⁾ the liver of which is found to be the best material.⁽⁵⁾

Experiment A. I. The effect of the time of autolysis and the effect of CaCO_3 as a neutralising agent.

Enzyme solution. (a) Ten grams of the internal organs of *viviparus japonicus* dried with acetone were autolysed for 3 days in 60 c.c. of water at 35°C . in the presence of a little chloroform (we used it always as an antiseptic during the autolysis). The enzyme solution was then separated with a centrifuge. (b) Forty grams of the enzyme material were autolysed for 3 hours in 240 c.c. of water and the enzyme solution was obtained in the same way as in (a). **Substrate solution.** Solution of potassium glucose-monosulphate, 5 c.c. of which gave 0.0999 gr. BaSO_4 .

The compositions of the reaction mixture and of the controls were as follows:

Reaction mixture:	Enzyme solution	50 c.c.
	Substrate solution	50
	Chloroform	2
Controls:	(1) Enzyme solution	50 c.c.
	Chloroform	1
	With or without CaCO_3	
	(2) Substrate solution	50 c.c.
	Chloroform	1
	With or without CaCO_3	

These solutions were kept at room temperature (ca. 20°C .) and the controls (1) and (2) were mixed just before it was put to analysis.

The method of estimation: 10 c.c. of the reaction mixture (or 5 c.c. of each control) were mixed with 10 c.c. of 20% trichloroacetic acid and the protein-precipitate was separated with a centrifuge. Fifteen c.c. of the clear solution were mixed then with 10 c.c. of 5% BaCl_2 solution and 15 c.c. of 5% KOH solution. It was immediately separated again from the precipitate in the same way as before. Now 30 c.c. of the clear solution were hydrolysed by HCl and thus the substrate, which had not been previously decomposed by the enzyme, was determined in the form of BaSO_4 by the ordinary gravimetric method. Result of experiments:

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- (3) T. Soda and C. Hattori, *J. Chem. Soc. Japan*, **54** (1933), 59.
 (4) " " " " , this Bulletin, **8** (1933), 65.
 (5) " " " " , *J. Chem. Soc. Japan*, **54** (1933), 377.

Table 1.

	Enzyme	CaCO ₃	1 day	5 days	9 days	13 days
No. 1.	a	with	29.1%	44.7%	44.7%	46.0%
No. 2.	b	with	5.6	22.9	37.3	43.6
No. 3.	b	without	9.0	25.0	26.2	26.2
Control	b	with	—	—	—	0.4
„	b	without	—	—	—	0.2

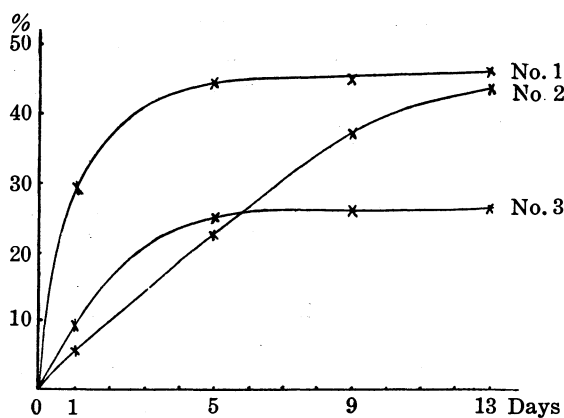


Fig. 1.

The percentage in this table expresses the rate of decomposition of the substrate. From these experiments we see that the enzyme solution (a) (autolysed for 3 days) was in the beginning much more active than that of (b) (autolysed for 3 hours). And we see from No. 2. and No. 3. that CaCO₃ is available for this kind of experiment as a neutralising agent.

II. The evidence of simply hydrolytic nature of the enzyme.

In order to ascertain that this enzyme actually hydrolyses glucose-monosulphate in the following way:



and has no other action than this, we tried to estimate the quantity of glucose produced by glucosulfatase. For this purpose the glucose thus produced was fermented by yeast and the volume of CO₂ obtained was approximately determined with the apparatus of Lunge and Rittener.⁽⁶⁾

(6) *Z. angew. Chem.*, **19** (1906), 1849.

Now, if we assume that the hydrolysis by the enzyme and the fermentation by yeast have been complete, 10 c.c. of the reaction mixture in the above experiment (I) would give at normal state

$$2 \times 22412 \times \frac{0.0999}{\text{BaSO}_4} = \frac{2 \times 22412 \times 0.0999}{233.5} = 19.18 \text{ c.c. of CO}_2$$

according to the equation of ordinary fermentation:



As for the blank test, we have ascertained that the mixture of 5 gr. yeast, 5 c.c. enzyme solution and 45 c.c. of water, on standing, evolved no CO_2 . From the mixture of 5 gr. yeast, 10 c.c. of sample No. 2. in the forgoing article (hydrolysed for 9 days) and 40 c.c. water evolved 7.83 c.c. CO_2 , at the atm. pressure (P) = 757.8 mm., the temperature (t) = 22.3°C . and vapour tension of water (p) = 20.3 mm. The volume of CO_2 at N.S. (V) has been calculated from the observed volume (v) by the following formula:

$$V = v \cdot \frac{273.1}{273.1 + t} \cdot \frac{760}{P - 0.8p} \quad (7)$$

From the above data we have $V = 7.06$ c.c. Therefore the percentage of glucose hydrolysed by the enzyme can be calculated as follows:

$$7.06/19.18 \times 100 = 36.8\%$$

The percentage obtained from the determination of $\text{SO}_4 = 37.3\%$, as is shown in Table 1. This coincidence of both percentages could be regarded as the proof that glucosulfatase is simply a hydrolysing enzyme. After 20 days the same experiment as above was repeated. The blank test, however, gave this time 2.29 c.c. of CO_2 therefore this amount was subtracted from the volume 16.65 c.c. of CO_2 evolved by fermentation, and we obtain $v = 14.36$ c.c. at $t = 25.5^\circ$, $P = 756.2$ mm., $p = 24.5$ mm. Consequently $V = 12.73$ c.c., and the enzymic hydrolysis expressed in percentage is $12.73/19.18 \times 100 = 66.4\%$. The corresponding percentage calculated from the determination of SO_4 is 64.2%.

Experiment B. Adsorption and purification of the enzyme.

The dry enzyme preparations were made from *charonia lampas* in the same way as in Experiment A. The substrate solution was either

(7) The factor "0.8" in this formula is to reduce the vapour pressure of pure water to that of saturated NaCl-solution or of KOH-solution (1:2).

sodium or barium salt of glucose-monosulphate of 0.0709 N.⁽⁸⁾ The experiments were always carried out at 30.0°C. in a thermostat.

I. Adsorption by kaolin.

Enzyme solution: No. 1. 20 Gr. of the dry enzyme preparation were autolysed for a day in 100 c.c. of water at 32°C. and the clear enzyme solution was separated with a centrifuge. No. 2. 8 Gr. of kaolin were added to 25 c.c. of the above enzyme solution (No. 1), and it was clarified again as above and made up to 25 c.c. by adding water to it (kaolin here used was that of Merck heated for about 2 hours at 200°C.).

Substrate solution: Solution of sodium glucose-monosulphate.

Reaction mixture: Substrate solution 30 c.c.
 Enzyme solution 20
 Water 10
 Chloroform and CaCO₃

Controls: (1) Substrate solution 30 c.c.
 Chloroform and CaCO₃
 (2) Enzyme solution 20 c.c.
 Water 10
 Chloroform and CaCO₃

The experiment procedure: same as is described in Experiment A. Result of experiments:

Enzyme	1 day	2 days
No. 1.	13.4%	20.1%
No. 2.	1.3	1.5
Control (No. 1.)	—	3.6

We see that the enzyme was almost perfectly adsorbed by kaolin. The 3.6% hydrolysis observed in the control is probably due to the presence of some unknown ethereal sulphate in the enzyme preparation.

Two c.c. of both enzyme solutions were dried separately in vacuum over CaCl₂. The weight of No. 1. and No. 2. after being dried were 0.0918 gr. and 0.0324 gr. respectively. From these data we have attempted to calculate the concentration of glucosulfatase. Assuming that the reaction proceeds as monomolecular (on this point we shall deal later on) the velocity constant (k) was calculated as follows:

$$k = \frac{1}{t} \log \frac{a}{a-x} = \log \frac{100}{100-13.4} = 0.0625 \quad (\text{Enzyme No. 1.})$$

(8) Concentration of substate solutions is always of the same normality if not otherwise stated.

As 20 c.c. of enzyme solution were diluted with 10 c.c. of water, the actual dried weight of 2 c.c. of the enzyme solution should be

$$m = 0.0918 \times 2/3 = 0.0612 \text{ gr.}$$

If we express the concentration of our glucosulfatase as "G-Sulf." (Glucosulfatase-fähigkeit), so the concentration of Enzyme No. 1. is: G-Sulf = $k/m = 1.0$; Enzyme No. 2.: G-Sulf = 0.3.

II. Adsorption experiments with BaSO_4 and aluminium hydroxide gel.⁽⁹⁾

Enzyme solution: No. 1. 15 Gr. of the dry enzyme preparation were autolysed for 2 days in 80 c.c. of water at 32°C. and the enzyme solution was separated with a centrifuge.

No. 2. Ten c.c. of aluminium hydroxide gel were added to 25 c.c. of the enzyme solution No. 1, and the clear enzyme solution No. 2 was separated by means of a centrifuge.

No. 3. Five c.c. of 10% BaCl_2 solution were added to 25 c.c. of the enzyme solution No. 1 which contained some inorganic sulphate. Then the enzyme solution No. 3 was separated from the precipitate (which contained proteins and BaSO_4) with a centrifuge.

Substrate solution: Solution of sodium glucose-monosulphate.

Reaction mixture:	Substrate solution	20 c.c.
	Enzyme solution	20
	Chloroform and CaCO_3	

Result of experiments:

Enzyme	Rate of hydrolysis in 2 days	Weight of 2 c.c. enzyme solution dried	Concentration of enzyme (G-Sulf)
No. 1.	24.4%	0.0595 gr.	1.0
No. 2.	22.7	0.0398	1.4
No. 3.	75.7	—	—

From the above result, it is obvious that aluminium hydroxide gel adsorbs scarcely the enzyme, but it removes the impurities fairly well.

(9) Preparation of aluminium hydroxide gel: saturated solution of $\text{AlCl}_3 \cdot 6\text{H}_2\text{O}$ (20 gr.) was added to 500 c.c. of warm ammonium hydroxide solution (5%). Then the solution was boiled for about 7 hours keeping its volume as constant as possible. It was then dialysed for several weeks. Two c.c. of the gel thus obtained, after being dried in vacuum over CaCl_2 , weighed 0.0138 gr., and after ignition it weighed 0.0091 gr. as Al_2O_3 .

The most remarkable fact is the increase of activity by the treatment with BaCl_2 (Enzyme No. 3). We have, therefore, studied the purification of the enzyme by applying these two methods and found very effective as is described in the next article.

III. Purification of the enzyme with BaCl_2 and $\text{Al}(\text{OH})_3$ gel.

Enzyme solution: 10 Gr. of the dry enzyme preparation were autolysed for 2 days in 50 c.c. of water at 32°C . Then it was separated with a centrifuge. Ten c.c. of 10% BaCl_2 solution were added to it and again separated as before. The solution was then treated with 5 c.c. of $\text{Al}(\text{OH})_3$ gel and subsequently centrifuged. A quite clear enzyme solution was thus obtained.

Substrate solution:	Solution of barium glucose-monosulphate with an excess of BaCl_2 .	
Reaction mixture:	Substrate solution	20 c.c.
	Enzyme solution	20
	Chloroform and CaCO_3	

The method of estimation: As the enzyme solution thus obtained was almost free from proteins, the treatment with trichloroacetic acid was omitted and the procedure was simplified as follows:

Ten c.c. of the filtered reaction mixture were decomposed by HCl and the amount of substrate was determined as usual in the form of BaSO_4 . Result of the experiment: The amount of hydrolysis in a day = 82.0%, $k = 0.745$; the weight of 2 c.c. enzyme solution dried = ca. 0.11 gr. (in which some excess of BaCl_2 is contained; therefore the original weight must be less than this). From these data we have: G-Sulf. = 7.

IV. Adsorption experiment with charcoal.

Enzyme solution: 30 Gr. of the dried liver were autolysed for 2 days in 120 c.c. water at 32°C . It was separated with a centrifuge and 4 c.c. of Na_2SO_4 solution (saturated at 15°C .) and 12 c.c. of 10% solution of BaCl_2 were successively added to it. Then it was centrifuged again. Ten c.c. of $\text{Al}(\text{OH})_3$ gel were added to it. After centrifuging off the gel, the solution was treated with 5 gr. of charcoal and subsequently filtered. This enzyme solution was perfectly clear.

Substrate solution:	Solution of barium glucose-monosulphate with an excess of BaCl_2 .	
Reaction mixture:	Substrate solution	30 c.c.
	Enzyme solution	30
	Chloroform and CaCO_3	

Result of the experiment:

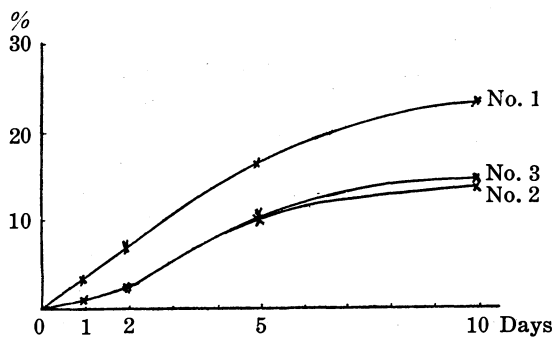


Fig. 2.

According to these results, glucose and galactose inhibit the action of glucosulfatase and indeed in about same degree.

II. Effects of inorganic sulphate and phosphate and magnesium carbonate.

The inhibiting action of phosphate upon phosphatase has been studied by many biochemists. Recently E. Jacobsen⁽¹⁰⁾ studied also this problem and he explained the mechanism of this inhibition by the affinity between the phosphate and the enzyme. Therefore it would be interesting to study the action of sulphate ion upon glucosulfatase in the analogous way.

According to C. Hommerberg,⁽¹¹⁾ phosphate has also inhibiting action upon phenosulfatase and therefore we must remove phosphate ion, if we want to obtain very active phenosulfatase.

The effect of magnesium salt, an activator of phosphatase,⁽¹²⁾ upon phenosulfatase has also been studied. Neuberg and Linhardt⁽¹³⁾ tried to use MgCO_3 instead of CaCO_3 as a neutralising agent, whereas C. Hommerberg⁽¹⁴⁾ used MgCl_2 in order to examine the effect of Mg-ion. According to them, Mg-ion has always a remarkable inhibiting action upon phenosulfatase. It would be, therefore, also significant to examine the actions of phosphate and MgCO_3 upon glucosulfatase.

Enzyme solution: 20 Gr. of the dry liver of *charonia lampas* were autolysed for 2 days in 80 c.c. of water at 32°C. Crude enzyme solution was separated with a centrifuge and 4 c.c. of Na_2SO_4 solution and 12 c.c.

(10) *Biochem. Z.*, **249** (1932), 21.

(11) *Z. physiol. Chem.*, **200** (1931), 79.

(12) Erdtman, *Z. physiol. Chem.*, **177** (1928), 211.

(13) *Biochem. Z.*, **142** (1923), 192.

(14) *Z. physiol. Chem.*, **200** (1931), 80.

of 10% BaCl_2 solution were successively added. The precipitate was centrifuged off and the solution was shaken with 2 gr. of charcoal, thereafter it was filtered and dialysed.

Substrate solution: Solution of sodium glucose-monosulphate.

Reaction mixtures: Substrate solution 30 c.c.
 Enzyme solution 10
 Buffer solution (acetate buffer, pH: 7) 10
 Water 5
 1. Water 5
 or (a) Sulphate solution: 12% Na_2SO_4
 or (b) Phosphate solution:
 $\text{NaH}_2\text{PO}_4 + \text{Na}_2\text{HPO}_4$, pH = 7;
 6% as P_2O_5
 2. Water and CaCO_3 or Water and MgCO_3 5

Method of estimation: Ten c.c. of the reaction mixture were treated with 6 c.c. of 10% BaCl_2 solution and 4 c.c. of 1% KOH solution and it was then filtered. Fifteen c.c. of the filtrate were put to analysis as already described (Experiment B, III).

Results of experiments:

		The rate of hydrolysis in 2 days
1.	Water	27.6%
	Sulphate (a)	13.6
	Phosphate (b)	0.0
2.	CaCO_3	16.6
	MgCO_3	9.2

The inhibiting action of phosphate is enormously strong; that of sulphate and MgCO_3 is also evident.

Experiment D. On glucosulfatase and phenosulfatase in the liver of *charonia lampas*.

I. Comparison of the activities of glucosulfatase and phenosulfatase.

Enzyme solution: 10 Gr. of the liver dried with acetone were auto-lysed for 2 days in 50 c.c. of water at 32°C ., and from this the enzyme solution was prepared after the procedure described in Experiment B, III.

Substrate solutions: No. 1. solution of barium glucose-monosulphate with an excess of BaCl_2 . No. 2. solution of sodium phenolsulphate with an excess of BaCl_2 . Both solutions had the same normality. (0.0769 N).

Reaction mixture: Enzyme solution 20 c.c.
 Substrate solution 20 c.c.
 Chloroform and CaCO_3

Result of experiment:

Substrate	The rate of hydrolysis in a day
No. 1. (Gl)	78.8%
No. 2. (Ph)	75.6

Neuberg and Simon⁽¹⁵⁾ as well as Hommerberg⁽¹⁶⁾ tried to prepare phenosulfatase from some mammalian organs. The former could extract the enzyme but with only weak activity (8% hydrolysis in several days), while the latter did not succeed to prepare it. Phenosulfatase obtained from the liver of *charonia lampas* has probably the strongest activity ever extracted from animal organs (almost comparable to that of Taka-diastase).

II. Adsorption of glucosulfatase and phenosulfatase by kaolin.

Enzyme solution: No. 1. 30 Gr. of the dried liver were autolysed for 2 days in 120 c.c. of water 32°C. and further treated as in Experiment B, III (10% BaCl₂: 20 c.c., Al(OH)₃: 20 c.c.).

No. 2. 15 Gr. of kaolin were added to 60 c.c. of the enzyme solution (No. 1.) and it was separated with a centrifuge. The clear solution was diluted with water to 60 c.c.

No. 3. The kaolin which adsorbed the enzyme was washed with water.

Substrate solutions: No. 1. solution of barium glucose-monosulphate with an excess of BaCl₂. No. 2. solution of sodium phenolsulphate with an excess of BaCl₂.

Reaction mixtures:

No. of enzyme	No. 1.	No. 2.	No. 3.
Substrate solution	70 c.c.	20 c.c.	20 c.c.
Enzyme solution	70	20	20 c.c. water+6 gr. kaolin with enzyme

Chloroform and CaCO₃ were added.

Result of experiments:

(15) *Biochem. Z.*, **156**(1925), 372.

(16) *Z. physiol. Chem.*, **200**(1931), 69.

Subst.	Enzyme	3 hours	6 hours	21 hours	58 hours
(a) No. 1.	No. 1.	17.6%	33.1%	73.9%	75.1%
(b) {	No. 1.	—	—	—	1.6
	No. 2.	—	—	—	2.5
(c) {	No. 1.	—	—	—	29.5
	No. 2.	—	—	—	49.3

The reaction velocity constants calculated as monomolecular reaction from data of experiment (a) are:

Hours	3	6	21	58
<i>k</i>	0.028	0.029	0.028	0.012

Therefore the reaction is monomolecular at least for first 20 hours. Both enzymes are adsorbed well by kaolin with about the same ratio as in the solution. It seems hopeless to separate these two enzymes by the adsorption method such as described above.

III. Evidence that the phenosulfatase and the glucosulfatase are not one and the same enzyme.

We have seen that the glucosulfatase always hydrolyses also phenol-sulphate. We do not know, however, whether the glucosulfatase can by itself hydrolyse phenolsulphate or it is always mixed with the phenosulfatase which had been studied by Neuberg and his co-workers. In this experiment, we attempted to distinguish these two enzymes by their different stability against weak alkali and also by the inhibiting action of glucose upon both enzymes.

Enzyme solution: The enzyme solution (A) was prepared in the same way as described in Experiment C, II, but without dialysis.

No. 1. Forty c.c. of the enzyme solution (A) were diluted with 4 c.c. of water. No. 2. To 20 c.c. of the enzyme solution (A) 1 c.c. of 2 N. ammoniumhydroxide solution was added and kept for 16 hours. Then it was neutralised by 2 N. acetic acid.

Substrate solution: solutions of barium glucose-monosulphate and sodium phenol-sulphate both with an excess of BaCl₂.

Reaction mixture:	Substrate solution	15 c.c.
	Enzyme solution	10 c.c.
	Water or glucose solution (10%)	5 c.c.
	Chloroform and CaCO ₃	

Results of experiment:

Substrate	Enzyme	Water or glucose soln.	The rate of hydrolysis in a day
Glucose-sulphate	No. 1.	water	70.1%
"	No. 2.	"	13.6
"	No. 1.	glucose	61.1
Phenol-sulphate	No. 1.	water	29.0%
"	No. 2.	"	36.6
"	No. 1.	glucose	27.8

The above data show that the action of glucosulfatase is strongly inactivated by weak alkali while that of phenosulfatase is rather activated by it. Moreover, glucose which has remarkable inhibiting action upon glucosulfatase scarcely inhibits the action of phenosulfatase. These facts may serve for the evidence that glucosulfatase and phenosulfatase are not one and the same enzyme.

The difference of activities of glucosulfatase and phenosulfatase in this experiment is very remarkable compared with that observed in Experiment D, I. Charcoal seems to adsorb phenosulfatase.

Summary.

1. Glucosulfatase is a simply hydrolysing enzyme.
2. It is almost perfectly adsorbed by kaolin.
3. It can not be adsorbed by BaSO_4 , aluminium hydroxide gel and charcoal. These adsorbents can be used for the purification of the enzyme. Thus a perfectly clear enzyme solution is obtainable. A solid preparation of very active glucosulfatase was obtained. Its purity (G-Sulf) is 11.6 while the original value was 1.0.
4. The enzyme action is inhibited by: glucose, galactose, MgCO_3 , inorganic sulphate and phosphate.
5. Glucosulfatase always contains phenosulfatase but they are not one and the same enzyme.

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ON NIGAKI OIL.

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Received April 18th, 1933. Published May 28th, 1933.

"Nigaki" (literally, "bitter tree"), *Picrasma quassioides* Benn. (*Simarubaceae*), is a shrub or tree grown in hills and fields, and has yellowish-green blossoms from May to July; the fruits are of the size of a pea. The plant has an intense bitter taste, and the bitter substance in the ligneous parts is used as a stomachic, and the decoction sap as an insecticide. The plant is distributed in Japan and China, and also in the Himalaya; in Chôsen (Corea) it is found in almost all mountaineous districts.

No mention of nigaki oil is found in the literature. The oils from the *Simarubaceae* mentioned in the literature have mostly been obtained from tropical plants. It is interesting to note that tariri fat obtained from the genus *Picramnia* belonging to the *Simarubaceae* has been reported to contain a peculiar acid called "tariric acid." The acid melts at 50.5°C., has the formula $C_{18}H_{32}O_2$, and is thus an isomer of linolic acid; but the acid contains a triple bond, its constitutional formula being $CH_3.(CH_2)_{10}.C:C.(CH_2)_4.COOH$, and resembles in this respect to stearolic acid.⁽¹⁾

In our study of nigaki oil, a particular attention has been directed as to the occurrence of tariric acid in the oil, but with negative result. On the other hand we have confirmed that the oil contains a large proportion of petroselinic acid, an isomer of oleic acid.

Experimental Part.

(1) **General Properties of Nigaki Oil.** The nigaki fruits used for this experiment were procured from Chûsei-Nandô, Chôsen. They were of a nearly spherical form, and had rumples on the rinds. Most of them had a brown colour, while the others were brownish-yellow or brownish-green. As the fruit shell rather easy to be stripped off, it was not difficult to separate it from the kernel. The kernels were dark yellow and had brown spots. The weight of 50 c.c. of the fruits was 230 gr., and 610 fruits weighed 50 gr. The ratio of the shell to the kernel was about 45:55. On analysis the following figures were obtained:

(1) Arnaud, *Bull. Soc. Chim.*, 1892, (3), 7, 233.

	Moisture	Oil
Shell	7.49%	38.36%
Kernel	5.96%	46.57%

From 2240 gr. of the fruits, 660 gr. of the oil were obtained by pressing.

There are three kinds of nigaki oil, viz., obtained (1) from the whole fruit, (2) from the fruit shell, and (3) from the kernel. The nigaki oil mentioned in this paper represents the oil obtained from the whole fruit as mentioned above, but the other two oils have also been prepared and their properties examined.

Nigaki oil was a brownish-yellow, viscous liquid at the room temperature of 26°C., and deposited a large amount of crystalline solid in winter. It had a bitter taste and an unpleasant odour. Its characteristics, etc., were determined as follows:

d_4^{20}	0.9322	Iodine value (Wijs)	76.7
n_D^{20}	1.4712	Reichert-Meißl value	1.21
Acid value	19.0	Acetyl value	28.70
Saponification value	200.5	Unsaponifiable matter	1.48%

On cooling to 0°C., the oil did not solidified in an hour, but at -20°C. it solidified to a salve-like mass, which regained its mobility at 15°C.

The fatty acids had a brownish-yellow colour, and consisted of liquid and solid substances at 26°C. They showed the neutralisation value 207.0 and the iodine value 79.5. By the lead-salt-ether method, 76.7% of liquid and 23.3% (by difference) of solid acids were obtained; they had the following properties:⁽²⁾

	Melt. pt.	Neutr. v.	Iodine v.	n_D^{20}
Solid acids	57.5-58°C.	219.6	14.0	—
Liquid acids	—	200.6	93.8	1.4613

On bromination the liquid (unsaturated) acids produced a small amount of precipitate in petroleum ether solution; in ether only a very small amount of precipitate was formed.

(2) **Examination of the Composition of the Fatty Acids.** The oil was heated with an equal weight of methyl alcohol containing 2.5% of hydrogen chloride on a water bath for about 12 hours. The fractional

(2) This experiment was performed in summer season. At lower temperature (ca. 10°C.) lead petroselinate is sparingly soluble in ether. As petroselinic acid is solid at the ordinary temperature, the designation of "liquid" acids would be incorrect, and is used here only conventionally.

distillation of 500 gr. of the methyl esters thus prepared under 15 mm. pressure gave the following result:

	Yield		Appearance	Saponif. value	Iodine value	n_D^{20}
	gr.	%				
(1) Until 180°	5.9	1.2	Pale yellow liquid	265.8	45.0	1.4420
(2) 180-190°	5.5	1.1	„	258.2	48.3	1.4444
(3) 190-200°	16.4	3.3	„	230.1	55.6	1.4469
(4) 200-210°	155.0	31.0	Light orange-yellow liquid	199.8	68.0	1.4493
(5) 210-215°	215.9	43.2	„	193.5	85.1	1.4519
(6) 215-216°	35.8	7.2	„	192.4	93.3	1.4540
(7) Residue	ca. 65	ca. 13	Dark brown viscous liquid	—	—	—

The distillation nearly ceased at 216°C. The comparatively large amount of the residue was probably due to somewhat incomplete esterification, and possibly also to the presence of some high boiling compounds in the shell oil.

The above result showed that the chief constituents are the esters of C_{18} acids boiling between 200-216°C. under 15 mm. pressure, which amounted to more than 80%.

On saponifying the fractions (1), (2), and (3), the fatty acids were separated into solid and liquid parts by the lead-salt-ether or lead-salt-alcohol method. From the solid acids palmitic acid was identified. From the fraction (1), an acid of the neutralisation value of 282 was obtained, which appeared to be impure lauric acid. Although not isolated, myristic acid was likely to be present. Of the liquid (unsaturated) acids, the presence of the lower acids (C_{12} to C_{16}) was not ascertained, but those from the fraction (3) consisted of C_{18} acid (probably petroselinic acid).

The fractions (4), (5), and (6) were used for the identification of C_{18} acids. As a preliminary test, a mixture of the corresponding amounts of (5) and (6) was re-fractionated under 15 mm. pressure, and the fatty acids obtained from the fraction boiling at 212-214°C. were treated by the lead-salt-ether method. After the separation of the solid acids (chiefly palmitic), the unsaturated acids were changed into lithium salts and dissolved in 80% alcohol. The salt deposited on cooling was decomposed with hydrochloric acid, and free acid separated. The acid had the neutralisation value 199 and the iodine value 87. As it was liquid in summer season, the presence of tariric acid, a solid of comparatively high melting point, seemed to be excluded. At first we considered the substance to be

ordinary oleic acid, but by the elaidin test, an acid of m.p. 50°C. was obtained. Also the original substance solidified to a crystalline mass at a lower temperature. So we were convinced that the substance consists of a solid octadecenoic acid.

To prepare a larger amount of the acid, the fractions (4)-(6) and the residue (re-esterified) were mixed and fractionated. The fraction 206–212°C. (14–15 mm.) was similarly treated as above, and the crude octadecenoic acid recrystallised from dilute acetone by ice-cooling, and finally the admixed saturated acids were removed as far as possible by means of magnesium acetate. The acid thus purified formed a crystalline mass, melted at 29–29.5°C., and had the neutralisation value 199.7 and the iodine value 86.0 (calc. for $C_{18}H_{34}O_2$, neutr. value 198.8, iodine value 89.9). Judged from the iodine value, it still contained a small proportion of saturated acids. On hydrogenation the acid was changed into stearic acid. By the elaidin reaction, an elaidic acid of m.p. 53°C. was produced. The hydroxy-acid obtained by Hazura's method melted at 121–121.5°C. From these results, the octadecenoic acid appeared to be petroselinic acid.

A small amount of a liquid octadecenoic acid was found to accompany petroselinic acid; it probably consisted of oleic acid.

In the above experiment, the free acids obtained from the filtrate of the lithium salts in alcohol had the iodine value 114. On bromination they gave insoluble precipitates in petroleum-ether and ether solutions; so linolic and linolenic acids were likely to be present. The presence of the latter was highly probable by the melting point (178°C.) of the ether-insoluble bromide.

(3) Confirmation of Petroselinic Acid. Although the octadecenoic acid described above appeared in all probability to be petroselinic acid, its constitution has been confirmed by the oxidation method with potassium permanganate.⁽³⁾

20 Gr. of the methyl ester of the acid were dissolved in 200 c.c. of acetone and oxidised with 80 gr. of potassium permanganate. On dissolving the precipitated manganese oxide with sodium bisulphite and dilute sulphuric acid, the product was repeatedly extracted with ether (total 3000 c.c.). The ether solution was concentrated and treated with 20% aqueous solution of sodium carbonate to dissolve out acidic compounds. On evaporating off the ether, 4.6 gr. of the "neutral" substance were obtained. It formed a crystalline mass, and had the saponification

(3) E. F. Armstrong and T. P. Hilditch, *J. Soc. Chem. Ind.*, **44** (1925), 45T.

value 244, the acid value 134, and the iodine value 15. So it contained, besides neutral substance, still an appreciable amount of acidic product. The latter on isolation was found to consist chiefly of white crystals, which melted at 35°C. and had the neutralisation value 279.6. It was recognised to be impure lauric acid.

The soda extract was saponified with caustic potash and on acidifying shaken with ether. The residue obtained on evaporating off the ether was then treated with petroleum ether, and separated into the soluble and insoluble parts in it.

(1) *Petroleum Ether Soluble Part.* Yield 10.2 gr.; white crystals with a marked odour of lower fatty acids; neutralisation value 304.4. 9 Gr. of this substance were fractionated under 15 mm. pressure as follows:

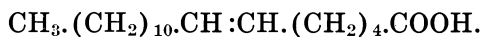
	Yield (gr.)	Appearance	Neutr. v.
(a) Until 170°C	0.2	Colourless liquid	—
(b) 170–180°C.	6.3	White crystals	308.1
(c) 180–185°C.	1.5	„ „	309.6
(d) Residue	0.5	Pale orange-yellow crystals	—

The boiling point of the chief fraction (b) corresponded to those of lauric acid. The high neutralisation value was due to admixed lower acids formed by the secondary reactions. On recrystallising the mixture of (b) and (c) from 70% alcohol by ice-cooling, 4 gr. of the refined substance were obtained. It was white crystals of m.p. 40°C. and had the neutralisation value 283.6. No depression of melting point was observed by the mixed test with lauric acid (Kahlbaum). So the substance was confirmed to be lauric acid $C_{12}H_{24}O_2$ (m.p. 43.6°C., neutr. v. 280.3).

The acids contained in the mother liquor were converted into barium salts and deposited from hot alcohol. The analysis of the salts gave Ba 26.89% (calc. for $(C_{12}H_{23}O_2)_2Ba$, Ba 25.64%) and showed that they consisted mainly of barium laurate.

(2) *Petroleum Ether Insoluble Part.* Yield 4.9 gr.; white crystals; neutr. value 755.9. On recrystallisation from acetic ether, first crop, 2.3 gr., m.p. 150.5–151°C., neutr. value 772.8; second crop, 0.6 gr., m.p. 148–148.5°C., neutr. value 773.1. So they were recognised to be adipic acid $C_6H_{10}O_4$ (m.p. 151°C., neutr. value 768.2).

The above experiments have shown that the oxidation products of the octadecenoic acid from nigaki oil are lauric and adipic acids, so that its constitution corresponds to those of petroselinic acid as follows:



Petroselinic acid was discovered by E. Vongerichten and A. Köhler⁽⁴⁾ from the seed oil of parsley, *Petroselinum sativum*. The content of the acid in the mixed fatty acids of the oil has been stated to be about 76%. Further the acid occurs in the seed oil of *Hedera helix* (up to 62%).⁽⁵⁾

We have found petroselinic acid in the oil of a tree quite different from the above two plants.

(4) **Nigaki Shell and Kernel Oils.** Besides the nigaki oil mention-above, we have examined the shell and kernel oils separately.

The shell oil was a brownish-yellow liquid mixed with solid constituents at 20°C.; it became clear on warming to 29°C. It had a bitter taste.

The kernel oil was a yellow liquid at 20°C.; at the room temperature of 13°C., it mostly solidified to a white crystalline mass. The oil had also a bitter taste.

	Shell oil	Kernel oil
Sp. gr.	d_4^{30} 0.9580	d_4^{15} 0.9217
Ref. index	d_D^{20} 1.4710	n_D^{20} 1.4705
Acid value	44.5	4.8
Saponif. value	219.7	190.4
Iodine value (Wijs)	50.6	93.9

The shell oil had a high saponification value and a low iodine value; it appeared to contain chiefly the comparatively lower saturated acids (mainly palmitic). Whether the oil contains petroselinic acid or not, has not yet been ascertained.

The kernel oil contained petroselinic acid as the chief constituent. The ether solution of the lead salts of the fatty acids of the oil gave a large amount of precipitate at 10°C., which did not wholly dissolve at 15°C. The precipitate consisted mostly of lead petroselinate. The liquid acids isolated from the ether-soluble lead salts at 15°C. had the iodine value 104, a fact indicating the occurrence of the higher unsaturated acids (linolic and linolenic) in the oil.

Summary.

(1) The properties and composition of the nigaki oil (a mixture of the shell and kernel oils) obtained from the whole fruit of "nigaki," *Picrasma quassioides* Benn., have been examined.

(4) Ber. 42 (1909), 1638.

(5) Grün-Halden, „Analyse der Fette u. Wachse", II, 324.

(2) As the chief constituent of the fatty acids of the oil, the occurrence of petroselinic acid, $C_{18}H_{34}O_2$ ($\Delta^{6:7}$ octadecenoic acid), has been ascertained.

(3) As the other constituent, palmitic acid has been identified from the saturated acids; lauric acid appears also to be present. Of the unsaturated acids, oleic, linolic, and linolenic acids are likely to be present.

(4) The shell and kernel oils have also been examined separately. The former contains an appreciable proportion of saturated acids, while the latter has been found to contain petroselinic acid as the chief constituent.

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STUDIES ON AMINO-ACIDS AND RELATED COMPOUNDS. PART III. ELECTROLYTIC OXIDATION OF ARGININE.

By Yoshitaro TAKAYAMA.

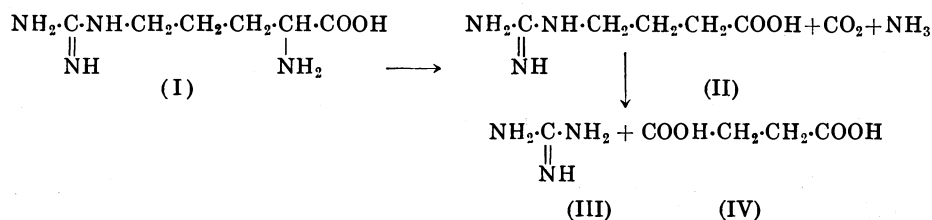
Received March 27th, 1933. Published June 28th, 1933.

In the previous communications the electrolytic oxidations of glutamic acid and its lactam, pyrrolidone-carboxylic acid, were discussed. In the present paper the study on arginine is to be reported, which possesses a guanidine group as its characteristics.

Arginine is considerably unstable towards alkali. When it is boiled with barium hydroxide solution, its guanidine group is easily attacked, yielding urea and ornithine.⁽¹⁾ On the other hand, on treating with an oxidising agent, such as barium permanganate, the guanidine group seems to be rather more stable than the amino-group, and guanidine, succinic acid and guanidine-butyric acid⁽²⁾ are obtained as oxidation products. Agmatine, $\text{H}_2\text{N}\cdot\text{C}\cdot\text{NH}\cdot\text{CH}_2\cdot\text{CH}_2\cdot\text{CH}_2\cdot\text{CH}_2\cdot\text{NH}_2$, the decarboxyl derivative

$\begin{array}{c} \text{NH} \\ \parallel \\ \text{NH}_2\cdot\text{C}\cdot\text{NH}\cdot\text{CH}_2\cdot\text{CH}_2\cdot\text{CH}_2\cdot\text{CH}\cdot\text{COOH} \\ | \\ \text{NH}_2 \end{array}$

of arginine, also yields above three compounds when it is oxidised with calcium permanganate.⁽³⁾ Fr. Kutscher, the investigator of the above two reactions, has expressed the oxidation of arginine as follows. Arginine (I) is first attacked at its amino-group and is changed to guanidine-butyric acid (II), which yields guanidine (III) and succinic acid (IV) on further oxidation.



(1) E. Schulze u. E. Winterstein, *Z. physiol. Chem.*, **26** (1898), 1; *Ber.*, **30** (1898), 2879.

(2) E. Benech u. Fr. Kutscher, *Z. physiol. Chem.*, **32** (1901), 278; Fr. Kutscher, *Z. physiol. Chem.*, **32** (1901), 413.

(3) R. Engeland u. Fr. Kutscher, *Ber.*, **43** (1910), 2882; Abderhalden, "Handbuch d. biolog. Arbeitsmethoden," I, 7 (1922), p. 238.

In the case when the β -oxidation is possible, γ -guanidine-butyric acid will be converted into guanidine-acetic acid, of which the methyl derivative is creatine, $\text{H}_2\text{N}\cdot\text{C}\cdot\text{N}\cdot\text{CH}_2\cdot\text{COOH}$. Thus it is said⁽⁴⁾ that arginine



bears close relation to the formation of creatine in the living organism.

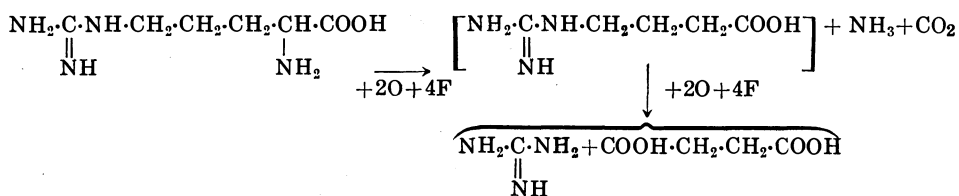
An attempt to obtain guanidine and succinic acid from arginine by the electrolytic oxidation has never been reported before. The author separated arginine from the hydrolysate of gelatine and purified it as hydrochloride and then changed it to sulphate. The dilute sulphuric acid solution of the sulphate was oxidised under the same conditions as described in the previous papers. The temperature was 25–26°C. during the electrolysis.

The oxidation has been carried out by the following different ways:—

- 1) Applying sufficient amount of electricity (10F/mol);
- 2) Applying insufficient amount of electricity (4F/mol), with the purpose of obtaining the intermediate product, if possible.

The oxidation products were separated almost in the same way as mentioned by Kutscher.⁽⁵⁾ The precipitate formed by the addition of phosphotungstic acid was decomposed by barium hydroxide as usual, and ammonia and guanidine were obtained as volatile and nonvolatile bases respectively. The latter was isolated as picrate in considerable amount. Guanidine-butyric acid, contrary to the author's expectation, could not be isolated even at moderate electric quantity. The filtrate from phosphotungstate always contained succinic acid, which was isolated and its silver salt was analysed. The yield of guanidine was 15% of arginine used in the case of 10F/mol and 32% in the case of 4F/mol. As to the yield of succinic acid it was rather worse, though that acid seemed to be stable towards oxidation. This may be considered as due to the loss caused at the precipitation of phosphotungstates and barium sulphate.

Assuming that guanidine-butyric acid is particularly unstable to anodic oxidation, the mechanism of oxidation in this case may be represented in the same way as Kutscher described.



(4) Dakin, "Oxidations and Reductions in the Animal Body," (1922), p. 82.

(5) loc. cit.

Experimental Part.

d-Arginine hydrochloride was prepared by the method of K. Felix and K. Dirr⁽⁶⁾ and it was recrystallised from alcohol. It melted at 223°C.

Anal.: Subst. = 0.1848; 0.1708 gr.; NH_3 = 35.05, 32.03 c.c. of N./10- H_2SO_4 .

Found: N = 26.57, 26.47%.

Calc. for $\text{C}_6\text{H}_{14}\text{O}_2\text{N}_4$, HCl (arginine hydrochloride): N = 26.61%.

Four grams of above sample were dissolved in 120 c.c. of N- H_2SO_4 and sufficient water was added to it. It was distilled under reduced pressure to drive off hydrochloric acid. The above treatments were repeated several times until the residue showed no trace of hydrochloric acid. The solution was made up to 120 c.c. and electrolytically oxidised.

Electrodes: lead peroxide-lead (4×5 cm.); distance of them 2.5 cm.: C.D.: 2 amp./dm²; electric quantity applied: 4.80 amp. hours. The temperature showed 25°C.

Phosphotungstic acid was added to the oxidised solution and the precipitate formed (A) was separated from the filtrate (B).

Phosphotungstate (A). It was decomposed by barium hydroxide and the solution was distilled at a temperature as low as possible and the distillate (A_1) was received in hydrochloric acid. 0.1 Gr. of hydrochloride of a base was obtained from the distillate. It was found to be ammonia by the analysis of its platinic double chloride.

Anal.: Subst. = 0.1007; Pt = 0.0442 gr. Found: Pt = 43.90%.

Calc. for $(\text{NH}_4)_2\text{PtCl}_6$: Pt = 43.95%.

After removal of barium exactly, the residue (A_2) was concentrated under reduced pressure, but it was impossible to bring it into crystallisation. The concentrated solution was treated with sodium picrate, and the base was precipitated as the picrate (A_3), which was separated from filtrate (A_4). The picrate (0.8 gr.), recrystallised from alcohol, melted at 315°C. with decomposition coinciding with that of guanidine picrate. It was thoroughly extracted with ether, after acidifying with hydrochloric acid.

Anal.: Picrate = 0.3068; Picric acid obtained = 0.2441 gr.

Found: Picric acid = 79.58%.

Calc. for CN_3H_5 , $\text{C}_6\text{H}_2(\text{NO}_2)_3\text{OH}$: (picric acid) = 79.45%.

(6) K. Felix und K. Dirr, *Z. physiol. Chem.*, **176** (1928), 38.

A picrolonate was prepared from the above hydrochloric acid solution. It was found to be guanidine picrolonate by its melting point 274°C . An auric double chloride was also prepared and its gold content was determined as follows.

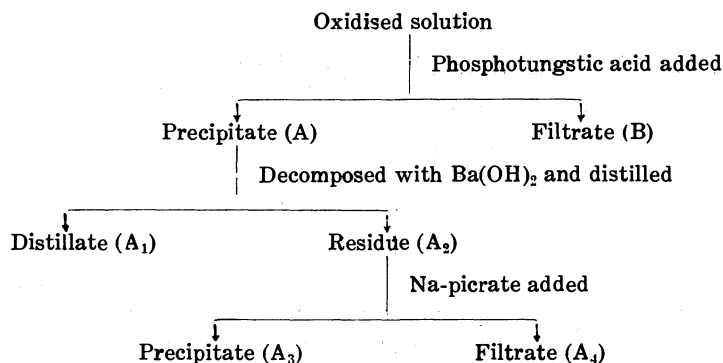
Anal.: Subst. = 0.2680; Au = 0.1315 gr. Found: Au = 49.07%.

Calc. for CN_3H_5 , HAuCl_4 : Au = 49.35%.

Picric acid being removed by extraction with ether, the filtrate (A_4) was treated with phosphotungstic acid as usual, but the attempt to precipitate guanidine-butyric acid as its phosphotungstate was not successful. The small amount of chloroplatinate was got from the above solution, but the analysis of platinum did not coincide with that of the expected compound. It may have been probably that of guanidine.

Anal.: Subst. = 0.0533; Pt = 0.0197 gr. Found: Pt = 36.97%.

Calc. for $(\text{CN}_3\text{H}_5)_2$, H_2PtCl_6 : Pt = 36.96%.



Filtrate (B). The solution, after removing barium with carbon dioxide, was concentrated under reduced pressure and a barium salt was obtained. It was converted into free acid. The free acid, after recrystallisation from water, melted at 183°C . and no lowering of melting point was observed when mixed with a pure sample of succinic acid. Its silver salt was analysed.

Anal.: Subst. = 0.1150; Ag = 0.0747 gr. Found: Ag = 64.95%.

Calc. for $\text{C}_4\text{H}_4\text{O}_4\text{Ag}_2$ (silver succinate): Ag = 65.04%.

An acid was again obtained from the filtrate of barium succinate, which was found to be nothing else than succinic acid. The total yield of this acid amounted to 0.25 gr.

The electrolytic oxidation was repeated with different amount of electricity. It was reduced to 4.27F/mol. 10 Gr. of arginine hydrochloride were dissolved in 100 c.c. of water and hydrochloric acid was removed by shaking with 8 gr. of silver sulphate. By adding N.-H₂SO₄, the solution was made up to 300 c.c. (total content of nitrogen was equal to 2.311 gr.) and was electrolysed.

Phosphotungstate (A). Guanidine was isolated as its picrate. It weighed 4.4 gr. After recrystallisation from water, 3.7 gr. of pure sample were obtained. The project to get guanidine-butyric acid even under this condition was a failure.

Filtrate (B). 0.3 Gr. of succinic acid was obtained. It was identified by mixed melting point test.

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STUDIES ON AMINO-ACIDS AND RELATED COMPOUNDS.
PART IV. ELECTROLYTIC REACTIONS
OF LEUCIC ACID.

By Yoshitaro TAKAYAMA.

Received March 27th, 1933. Published June 28th, 1933.

l-Leucic acid is one of the physiologically interesting hydroxy-acids and has a close relation with leucine. It is easily obtained by the action of nitrous acid upon natural leucine. H. D. Dakin⁽¹⁾ has described briefly that leucic acid, when oxidised with hydrogen peroxide yielded acetone, isovaleraldehyde, and a mixture of acids which were probably isovaleric acid and isobutyric acid. Fr. Fichter and Fr. Kuhn⁽²⁾ reported that leucine gave several oxidation products, when its solution in sulphuric acid was electrolysed with platinum electrodes.

The author undertook the present work with the intention of comparing the oxidation products of leucic acid with those of leucine. Leucic acid in N.-sulphuric acid was electrolysed in an undivided cell with a lead peroxide anode and a lead cathode. During the progress of the electrolysis, a yellowish oily layer separated out on the surface of the electroly-

(1) H. D. Dakin, *J. biol. Chem.*, **4** (1908), 91-100.

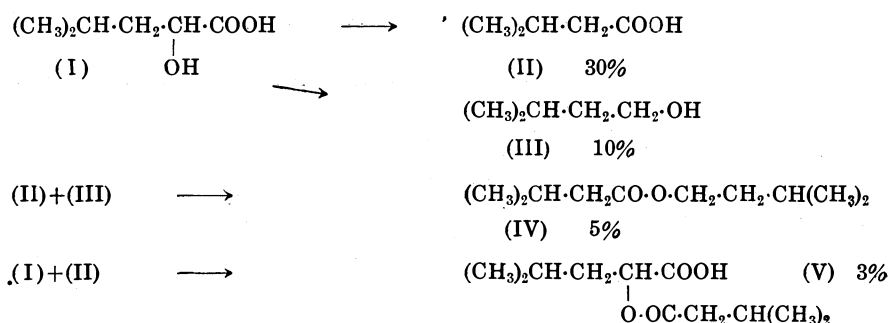
(2) Fr. Fichter and Fr. Kuhn, *Helv. chim. Acta*, **7** (1924), 167.

sate. It was found that the oily layer consisted of isovaleric acid (10%), isovaleryl-leucic acid (3%) and isoamyl ester of isovaleric acid (5%). From the aqueous solution isoamyl alcohol (5%) and isovaleric acid (20%) as well as unchanged leucic acid were isolated. In short, the oxidation products were isovaleric acid (II), isoamyl alcohol (III), isoamyl isovalerate (IV) and isovaleryl-leucic acid (V), but the lower fatty acids were not found. The gaseous oxidation products were not examined.

It is known that leucine is vigorously attacked by anodic oxidation and yields isovaleraldehyde, acetone, isovaleric, isobutyric, acetic and formic acids, as well as ammonia and carbon dioxide. As mentioned above, the oxidation products of leucine and those of leucic acid vary from each other; and it may be concluded that they behave quite differently on oxidation, though they only differ at their α -substitution group, the former having amino and the latter having hydroxyl group.

Identification of the oxidation products: Amyl alcohol was identified by conversion into isovaleric acid and into crystalline isoamyl α -ester of 3-nitrophthalic acid,⁽³⁾ m.p. 164–165°C. To identify isovaleryl-leucic acid, it was hydrolysed with alkali and the two components formed were isolated. The boiling point of this acyl-oxy-acid is concordant with that of the synthetic sample, which was prepared from leucic acid and isovaleryl chloride.

The electrolytic reaction of leucic acid may be briefly represented as follows (excepting the gaseous products):



The similar examples of the formation of esters during electrolysis are frequently met with in the literature.⁽⁴⁾ Isoamyl alcohol might be formed by the cathodic reduction of isovaleryl aldehyde.

(3) This ester is easily obtained from its components when heated together, and it seems to be a suitable compound for identification of isoamyl alcohol.

(4) P. Askenasy, R. Leiser und N. Grünstein, *Z. Electrochem.*, **15** (1909), 846, 852. C. J. Brockman, "Electro-organic Chemistry," (1926) p. 81, 84.

Experimental Part.

Apparatus. Cell: A cylindrical glass vessel (dia. 6 cm., height 9 cm.) provided with a rubber stopper carrying a condenser, a thermometer and two electrodes. Anode (4×5 cm.): lead peroxide sheet; cathode (4×5 cm.): lead sheet, the distance between anode and cathode was 1.5 cm.

l-Leucic acid $(\text{CH}_3)_2\text{CH}.\text{CH}_2.\text{CH}(\text{OH}).\text{COOH}$, m.p. 78°C ., was prepared from natural *l*-leucine and nitrous acid. 13.20 Gr. (1/10 mol) of leucic acid were dissolved in 120 c.c. of N.-sulphuric acid and electrolysed in an undivided cell, under the following conditions, C. D.: 2 amp./dm²., temperature: 38.5°C . quantity of electricity: 12.0 amp. hours.

Separation of Oxidation Products. During the progress of the electrolysis an oily layer separated on the surface of the electrolysate. The oily layer was treated with a saturated solution of sodium bicarbonate, and extracted with ether to separate the neutral part (B) from the acidic part (A). The sodium bicarbonate solution of the latter was acidified with sulphuric acid and submitted to steam distillation, the distillate (A_1) was neutralised with sodium hydroxide, evaporated to dryness and distilled after adding phosphoric acid. The distillate was redistilled and separated into (1) the first running (165 – 172°C .) and (2) the main fraction (172 – 174°C .). Each fraction was converted into silver salt and analysed.

Anal.: Subst. (1) = 0.2241; Ag = 0.1154 gr.

„ (2) = 0.3080; Ag = 0.1593 gr.

Found: Ag (1) = 51.52; Ag (2) = 51.71%.

Calc. for $\text{C}_6\text{H}_9\text{O}_2\text{Ag}$ (silver isovalerate): Ag = 51.64%.

From these analyses and boiling point, it may be said that the fraction (1) as well as the fraction (2) consisted of isovaleric acid without lower members of fatty acids.

After the steam distillation of (A), a portion of the oil (A_2) separating in the flask was converted into silver salt and analysed. Thus the oil (A_2) was speculated as an acyl-oxy-acid formed from isovaleric and leucic acids, and the attempt of distillation under reduced pressure was successful. The oil passed over at 165 – 175°C . under 24 mm. with slight decomposition. Another portion of this oil was heated with concentrated solution of sodium hydroxide on the water bath for several hours and distilled in steam. From this distillate isovaleric acid was obtained.

Anal.: Subst. = 0.2608; Ag = 0.1346 gr. Found: Ag = 51.60%.

Calc. for $C_5H_9O_2Ag$ (silver isovalerate): Ag = 51.64%.

The residue of steam treatments was extracted with ether. After removal of ether, the crystals formed were identified as leucic acid.

Anal.: Subst. = 0.2023; Ag = 0.0912 gr. Found: Ag = 45.08%.

Calc. for $C_6H_{11}O_3Ag$ (silver leucinate); Ag = 45.14%.

As the distillate was contaminated with its decomposition products, it was purified by steam treatment and by washing with water, then it was converted into silver salt.

Anal.: Subst. = 0.2203; Ag = 0.0728 gr. Found: Ag = 33.05%.

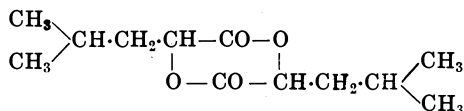
Calc. for $C_{11}H_{19}O_4Ag$ (isovaleryl-leucic acid): Ag = 33.41%.

To establish a positive proof, the same compound was synthesised from isovaleryl chloride (1.5 mol) and leucic acid (1 mol) by heating on the water bath. The reaction product distilled at 165–175°C./24 mm. The distillate was treated as above and its silver salt was analysed.

Anal.: Subst. = 0.3342; Ag = 0.1110 gr. Found: Ag = 33.21%.

Calc. for $C_{11}H_{19}O_4Ag$ (isovaleryl-leucic acid): Ag = 33.41%.

During the distillation of this acid a small quantity of crystals separated out from the distillate, which were identified as di-isobutyl glycolide (the dehydration product of leucic acid), m.p. 169–170°C., by comparison with a pure synthetic specimen.



Anal.: Subst. = 0.0935, 0.1125; CO_2 = 0.2164, 0.2614;

H_2O = 0.0699, 0.0844 gr.

Found: C = 63.16, 63.37; H = 8.36, 8.39%.

Calc. for $C_{12}H_{20}O_4$ (di-isobutyl glycolide): C = 63.11; H = 8.83%.

Neutral Part (B). The residue, after removal of ether, gave no aldehyde and ketone reaction. It was distilled under ordinary pressure, two fractions being obtained, b. p. 130–140°C. (1.2 gr.) and 190–195°C. (1.1 gr.). The former fraction smelt of amyl alcohol and was identified as such by conversion into isovaleric acid and by the separation of mono-amyl α -ester of 3-nitrophthalic acid, m. p. 164–165°C.

Oxidation of amyl alcohol to isovaleric acid: 0.7 gr. of alcohol was oxidised with a mixture of 3 gr. $\text{K}_2\text{Cr}_2\text{O}_7$, 5 gr. H_2SO_4 and 15 c.c. H_2O , alcohol being converted into acid (4.86 c.c. of N.-NaOH).

Anal.: Subst. = 0.2712; Ag = 0.1406 gr. Found: Ag = 51.83%.
 Calc. for $C_5H_9O_2Ag$ (silver isovalerate): Ag = 51.64%.

Nitrophthalic acid ester⁽⁵⁾: The crystalline mass formed by heating the mixture of 1 gr. of alcohol and 2 gr. of 3-nitrophthalic anhydride was recrystallised from benzene in yellow crystals melting at 164–165°C.

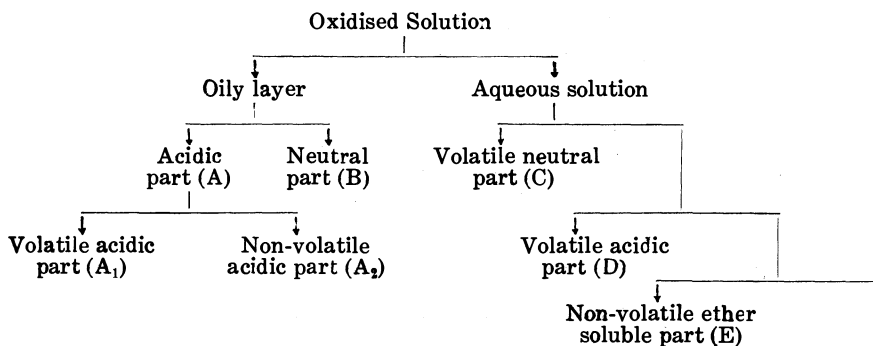
Anal.: Subst. = 0.1039, 0.1092; CO_2 = 2127, 0.2236;
 H_2O = 0.0489, 0.0529 gr.
 Found: C = 55.84, 55.85; H = 5.27, 5.42%.
 Calc. for $C_{13}H_{15}O_5N$ (monoisoamyl ester of 3-nitrophthalic acid): C = 55.49;
 H = 5.38%.

The fraction (190–195°C.) on hydrolysis with 40% NaOH yielded isovaleric acid and amyl alcohol. The former was identified by its silver salt.

Anal.: Subst. = 0.4212; Ag = 0.2159 gr. Found: Ag = 51.25%.
 Calc. for $C_5H_9O_2Ag$ (silver isovalerate): Ag = 51.64%.

The latter was identified as amyl alcohol by conversion into acid as described above.

Anal.: Subst. = 0.1373, Ag = 0.0710 gr. Found: Ag = 51.71%.
 Calc. for $C_5H_9O_2Ag$ (silver isovalerate): Ag = 51.64%.



Aqueous Solution. The aqueous part was neutralised with sodium hydroxide and submitted to steam distillation to separate the neutral volatile part (C). From (C) amyl alcohol was obtained, but no ester was found. The former was identified as usual.

Anal.: Subst. = 0.2628; Ag = 0.1356 gr. Found: Ag = 51.57%.
 Calc. for $C_5H_9O_2Ag$ (silver isovalerate): Ag = 51.64%.

(5) MacKenzie, *J. Chem. Soc.*, **79** (1901), 1135.

The residue of (C) was again distilled with steam, after acidifying with sulphuric acid to separate volatile acidic part (B). (D) gave only isovaleric acid in considerable amount (20%).

Anal.: Subst. = 0.3171; Ag = 0.1632 gr. Found: Ag = 51.46%.

Calc. for $C_5H_9O_2Ag$ (silver isovalerate): Ag = 51.64%.

After the separation of (D), the solution was again neutralised, concentrated and extracted with ether. From the ethereal extract unchanged leucic acid was recovered (E).

Anal.: Subst. = 0.3673; Ag = 0.1650 gr. Found: Ag = 44.94%.

Calc. for $C_6H_{11}O_3Ag$ (silver leucinate): Ag = 45.14%.

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STUDIES ON AMINO-ACIDS AND RELATED COMPOUNDS.
PART V. ELECTROLYTIC OXIDATION OF TYROSINE
AND PHENYLALANINE.

By Yoshitaro TAKAYAMA.

Received March 27th, 1933. Published June 28th, 1933.

Among various researches on the oxidation of amino-acids, the allied subjects with the present communication are treated in the following ones.

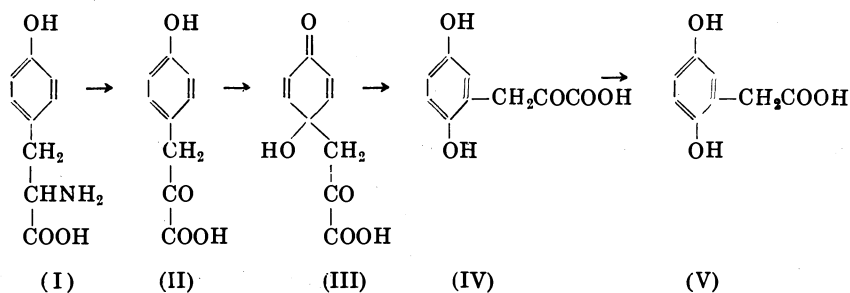
C. Neuberg⁽¹⁾ electrolysed 1-5% solution of several amino-acids with platinum electrodes and observed that the aldehydes having an atom of carbon less were formed from all amino-acids which he dealt with. In the cases of tyrosine and phenylalanine the formation of corresponding aldehydes was assumed from indirect grounds.* The formation of black flocculent precipitates was also observed by him in both of these cases.

* The electrolysate of tyrosine reduced Fehling's solution and gave a crystalline precipitate with phenylhydrazine or *p*-nitrophenylhydrazine and also showed a purple reaction with ferric chloride. The electrolysate of phenylalanine smelt of phenylacetaldehyde and reduced alkaline silver solution.

(1) C. Neuberg, *Biochem. Z.*, **17** (1909), 270.

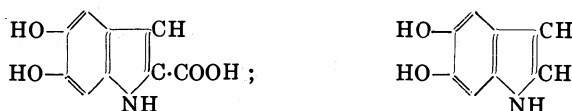
W. Denis⁽²⁾ oxidised a small quantity of tyrosine with alkaline potassium permanganate and obtained ammonia, carbon dioxide and oxalic acid. He also reported that acetic acid, nitric acid and *p*-hydroxybenzoic acid might be formed.

Views⁽³⁾ diverge widely as to the metabolism of these amino-acids in the living organism, but the following scheme is generally accepted. Tyrosine (I) is oxidised up to homogentisic acid (V), through *p*-hydroxyphenylpyruvic acid (II) and two other stages (III, IV).



In normal organism, homogentisic acid is completely oxidised with the breakdown of benzene nucleus, while in cases of alkaptonuria much of this acid is excreted in urine. Phenylalanine is said, on oxidation in vivo, to be converted into homogentisic acid also.

A tyrosine oxidising enzyme, tyrosinase, produces from tyrosine a pink or red pigment, which on further action changes to a brown or black substance. The latter resembles in all respects with the melanin obtained by usual method. Recently Raper⁽⁴⁾ identified the following intermediate precursors of the black pigment (isolated as their methoxy derivatives) and established a certain definite facts concerning the reaction.



On the other hand, a similar melanin was prepared from tyrosine by a pure chemical method. O. Adler⁽⁵⁾ oxidised tyrosine with hydrogen

(2) W. Denis, *J. Biol. Chem.*, **10** (1911), 73.

(3) See H. D. Dakin, "Oxidations and reductions in the animal body," (1922), P. 84-87 and H. H. Mitchell and T. S. Hamilton, "The biochemistry of amino-acids," (1929), p. 403-406.

(4) H. S. Raper, *Biochem. J.*, **20** (1926), 735; **21** (1927), 89; **24** (1930), 239.

(5) O. Adler, *Biochem. Z.*, **141** (1923), 304-309.

peroxide and ferric chloride, and obtained a black amorphous powder, which he named tyrosine-melanic acid. On heating it was converted into so-called tyrosine-melanin. K. Kurono⁽⁶⁾ isolated the black pigments (soyamelanin, soyamelanic acid) from soy and says that the pigments have the resemblance to Adler's melanins. Prof. Y. Shibata⁽⁷⁾ recently published an interesting paper concerning the asymmetric oxidation of dihydroxyphenylalanine by means of metallic complex salts.

As to the electrolytic oxidation of these amino-acids no detailed study has ever been tried before. The author intends to elucidate the mechanism of electrolytic oxidation of these amino-acids by seizing all of the oxidation products. The oxidation was carried out under the same conditions as in the previous communications.

Comparison of Nitrogen Distribution. Dilute sulphuric acid solutions of tyrosine and phenylalanine were electrolysed with lead peroxide anode

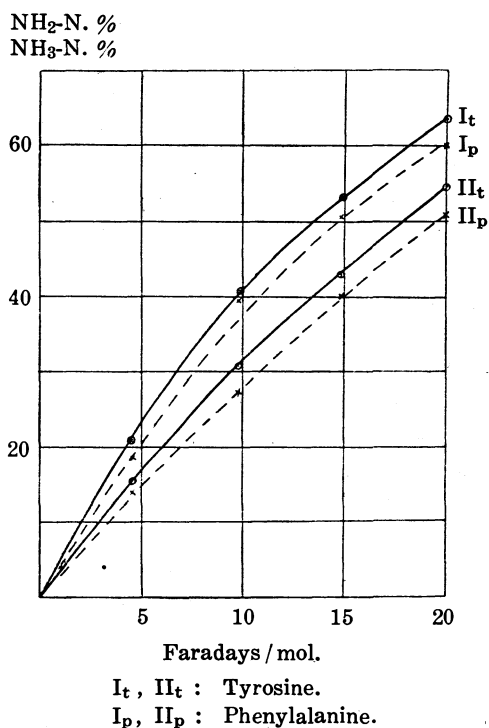


Fig. 1.

under the same current conditions. At every definite consumption of electricity (5F/mol), the electrolysis was interrupted and the decrease of amino-nitrogen and amount of ammonia formed were determined. Two couples of curves in Fig. 1 show the courses of reaction.

From Fig. 1 we may conclude the following two facts. First, if by oxidative deamination all of the freed nitrogen was entirely changed to ammonia, the curves representing decrease of NH_2-N (I_t and I_p) and increase of NH_3-N (II_t and II_p) must superpose upon each other. In reality a certain discrepancy is observed, which may partly be ascribed to the formation of melanin and its precursors.

Second, the disparity between I_t and I_p shows that the oxidation of

(6) K. Kurono and Katsume, *J. Soc. Brewing, Japan*, **21** (1926) No. 2, p. 13; No. 3, p. 8.

(7) Y. Shibata and R. Tsuchida, *this Bulletin*, **4** (1929), 142.

phenylalanine required much more current quantity than that of tyrosine. This fact agrees with a theory on phenylalanine metabolism remarked by some biochemists—phenylalanine is first converted into tyrosine, preceding to further oxidation.—Though it might be mere coincidence, the last stage of oxidation of these amino-acids do not show marked diversity.

Large amount of tyrosine in 2N.-sulphuric acid solution was electrolysed with lead peroxide anode, current quantity being 15F/mol. The electrolysate assumed yellowish tint, and then changed to brownish black as the electrolysis proceeded. The electrolysate was thoroughly extracted with ether. The part soluble in ether was separated into neutral, phenolic, and acidic parts by usual treatments.

Phenolic part mainly consisted of hydroquinone. From the acidic part of the first extraction a small quantity of *p*-hydroxyphenylacetic acid was isolated. It was identified as such by comparison with the synthetic sample by means of polarising microscope. Succinic acid was also obtained from the acidic part. The part insoluble in ether was concentrated to a small volume and a large amount of tyrosine was recovered. On treating the filtrate of tyrosine with barium hydroxide, ammonia was isolated as the only volatile base. No definite compound was isolated from the residue of the distillation of ammonia.

Volatile Part—The electrolysate was distilled in steam. Small amount of acetic acid, benzoquinone and a liquid of phenolic nature were obtained from the distillate.

When the electrolysate was allowed to stand for a length of time, a brownish black melanin-like substance was formed. A similar substance was also obtained from other electrolysate, from which the part soluble in ether had been previously removed. The latter sample was washed and dried to a constant weight and was analysed. As already mentioned, three kinds of melanin were isolated by Raper, Adler and Kurono with different treatments. The author's result has nearer approach to that of Adler than to either of the other two.

Melanin from tyrosine electrolysate: C = 62.44; H = 4.28; N = 6.25%.

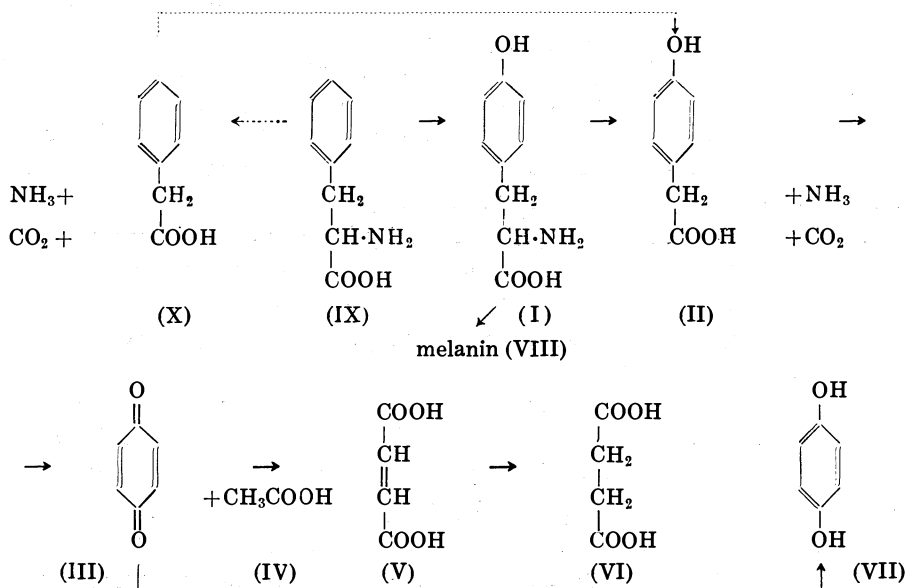
Tyrosine melanin (Adler): C = 60.30; H = 2.77; N = 12.45%.

Tyrosine melanic acid (Adler): C = 54.40; H = 3.46; N = 6.54%.

Electrolysate of phenylalanine gave the analogous oxidation products. Hydroquinone, succinic acid, acetic acid, ammonia, carbon dioxide and melanin were isolated.

The electrolytic oxidation of tyrosine may be represented as follows: The amino-group of tyrosine (I) is first split off and *p*-hydroxyphenylacetic acid (II) as well as ammonia and carbon dioxide are formed. *p*-

Hydroxyphenylacetic acid, on further oxidation, gives quinone (III) and acetic acid (IV). Quinone may be converted into succinic acid (VI) as Kempf⁽⁸⁾ and Fichter⁽⁹⁾ have pointed out. Hydroquinone (VII) is to be formed by the cathodic reduction of quinone.



As to the oxidation of phenylalanine two possible processes can be conceived. First, it (IX) is converted into tyrosine, and then proceeds the course of the oxidation of the latter. Second, the side chain of phenylalanine is first attacked and phenylacetic acid (X) is formed, which is converted into *p*-hydroxyphenylacetic acid (II). In fact, it can not be determined which course the reaction has taken.

Experimental Part.

Sample of tyrosine: N = 7.71% (calc. 7.74%)

$[\alpha]_D^{20} = -13.0^\circ$ (5 gr. in 100 c.c. of 4% HCl)

$[\alpha]_D^{20} = -8.4^\circ$ (5 gr. in 100 c.c. of 21% HCl)

(8) R. Kempf, *J. pr. Chem.*, **83** (1911), 329.

(9) Fr. Fichter and E. Schlager, *Helv. chim. Acta*, **10** (1927), 406.

Raper: tyrosine melanin, N = 8.65%.

Kurono: Soya melanin, C = 56.18; H = 2.46; N = 7.48%.

Soya melanic acid C = 54.82; H = 2.87; N = 7.23%.

Sample of phenylalanine: $N = 8.43\%$ (calc. 8.49%)

$[\alpha]_D^{20} = -32.5^\circ$ (2% solution). Decomposition point 265°C .

Both of them⁽¹⁰⁾ were prepared from the hydrolysate of wheat gluten.

Rate of Oxidation of Tyrosine and Phenylalanine. Sulphuric acid solutions of tyrosine (9.055 gr. ca. 1/20 mol in 120 c.c. of 2N.- H_2SO_4) and of phenylalanine (8.255 gr. ca. 1/20 mol in 120 c.c. of 2N.- H_2SO_4) were electrolysed in undivided cells which were connected in series under the following conditions.

Cells: 200 c.c. capacity glass cylinders. Electrode (4×5 cm.) lead peroxide—lead, C.D.: 2.0 amp./dm². Potential diff. between electrodes: 2.5–2.6 volts. Temperature was kept at 35°C . by immersing the cell in a thermostat.

Process of investigation: In the course of electrolysis, at every definite consumption of electricity (5F/mol) a part of the solution was drawn out and the nitrogen distribution was determined as follows:

Total-N in 5 c.c. by Kjeldahl method;

$\text{NH}_3\text{-N}$ (NaOH) and $\text{NH}_2\text{-N}$ in 15 c.c. by van Slyke method.

After each set of determinations the volume of the solution is diminished by 20 c.c. The current quantity applied before next determination was reduced to such an extent as 5F/mol is maintained in relation to the original volume of the solution. The four sets of determinations were carried out and the total current quantity applied amounted to 20F/mol. The results are tabulated in Table I and Table II.

Table I.

Faradays per mol.	Substance	Total-N mg.	$\text{NH}_3\text{-N}$ mg.	$\text{NH}_2\text{-N}$ mg.
6.449 A.H.	Tyrosine	81.56 (15 c.c.)	12.42 (15 c.c.)	64.86 (15 c.c.)
4.67F/mol	Phenylalanine	82.68 (")	12.06 (")	67.35 (")
$\frac{6.449}{5.663}$	Tyrosine	69.20 (")	20.87 (")	41.07 (")
12.112 A.H.				
9.75F/ "	Phenylalanine	69.88 (")	19.67 (")	42.14 (")

(10) Both of the purified samples were obtained from Mr. R. Nakamura of Suzuki & Co., for whose kindness the author is very grateful.

Table I.—(Concluded)

Faradays per mol.	Substance	Total-N mg.	NH ₃ -N mg.	NH ₂ -N mg.
12.11 4.71 16.82 A.H.	Tyrosine	57.36 (15 c.c.)	24.45 (15 c.c.)	27.07 (15 c.c.)
14.82F/ „	Phenylalanine	59.33 („)	23.82 („)	29.07 („)
16.82 3.85 20.67 A.H.	Tyrosine	46.34 („)	25.06 („)	16.81 („)
20.05F/ „	Phenylalanine	49.85 („)	25.36 („)	20.06 („)

Table II.

Faradays per mol.		4.67 F		9.75 F		14.82 F		20.05 F	
Subst.		Ty.	Ph.	Ty.	Ph.	Ty.	Ph.	Ty.	Ph.
$\frac{\text{NH}_3\text{-N}}{\text{Total-N}}$	(1)	15.23%	14.58%	30.16%	28.15%	42.62%	40.15%	54.08%	50.87
$\frac{\text{NH}_2\text{-N}}{\text{Total-N}}$	(2)	79.52	81.45	59.36	60.30	47.19	48.99	36.27	40.25
NH ₂ -N decreased	(3)	20.48	18.55	40.64	39.70	52.81	51.01	63.73	59.75
Melanin-N + loss	(4)	5.25	3.97	10.48	11.55	10.19	10.86	9.65	8.85

Ty. = Tyrosine, Ph. = Phenylalanine. (3) = 100%—(2), (4) = (3)—(1).

Separation of Oxidation Products.

90.6 Gr. (0.5 mol) of tyrosine were dissolved in 1200 c.c. of 2N.-sulphuric acid. The solution was placed in two cells of equal size, which were connected in series.

Electrodes (10×12 cm.): lead peroxide anode and lead cathode. C.D.: 2 amp./dm²., Current quantity applied: 100.8 amp. hrs. for each cell, Temp: 36°C.

Nitrogen Distribution in the Oxidised Solution.

NH ₃ -N (MgO+NaOH)	40.3 %
NH ₂ -N (van Slyke)	41.3 %
Melanin-N+loss (difference)	18.4 %

(A) **Separation of the Part Soluble in Ether.** The electrolysate was thoroughly extracted with ether. The first extraction showed reddish yellow colour, while the last part was almost colourless. Ether was expelled, 3.1 gr. of crystalline residue remaining. It was separated into three parts, namely phenolic, acidic and neutral as usual.

(a) *Phenolic Part.* After decolourisation with animal charcoal and sulphur dioxide gas, it was recrystallised from water and drained on porous plate. It weighed 1.5 gr. (melting point 155–165°C.). Recrystallisation was repeated until the melting point attained 169°C. It was found to be hydroquinone by elementary analysis and mixed melting point test.

Anal.: Subst. = 0.1026, 0.1020; CO₂ = 0.2468, 0.2453;

H₂O = 0.0496, 0.0532 gr.

Found: C = 65.60, 65.58; H = 5.41, 5.83%.

Calc. for C₆H₆O₂ (hydroquinone): C = 65.39; H = 5.49%.

(b) *Acidic Part (p-Hydroxyphenylacetic Acid; Succinic Acid).* From first part of the extraction a viscous liquid was obtained, which gradually changed to a crystalline mass. On recrystallisation from water it separated out in needles melting at 146–147°C. It was readily soluble in water and showed slight purple black colouration with ferric chloride. No lowering of melting point was observed when mixed with a pure specimen of *p*-hydroxyphenylacetic acid (m.p. 147–148°C.).

Synthesis of p-Hydroxyphenyl-acetic Acid.⁽¹¹⁾ One gram of *p*-hydroxybenzyl cyanide (Takeda) was hydrolysed by boiling with 5 c.c. of concentrated hydrochloric acid under reflux condenser. After cooling the solution was extracted with ether. Ether was expelled, and then remaining crystals were recrystallised from water. Thus, 0.8 gr. of pure sample melting at 147–148°C. was obtained. Its silver salt was analysed with following result:

Anal.: Subst. = 0.1213; Ag = 0.0505 gr. Found: Ag = 41.64%.

Calc. for C₈H₇O₃Ag: Ag = 41.66%.

Crystalline Form and Optical Properties of p-Hydroxyphenyl-acetic Acid. Crystals: rhombic prisms, crystallised from water in needles or rods, sometimes tablets on a slide glass (Fig. 2).

Optical properties: extinction straight; sign of elongation positive, sometimes negative. Crystals always elongated parallel to Y-axis. Z was perpendicular to tablets (elongation positive).

(11) H. Salkowski, *Ber.*, **17** (1884), 506.

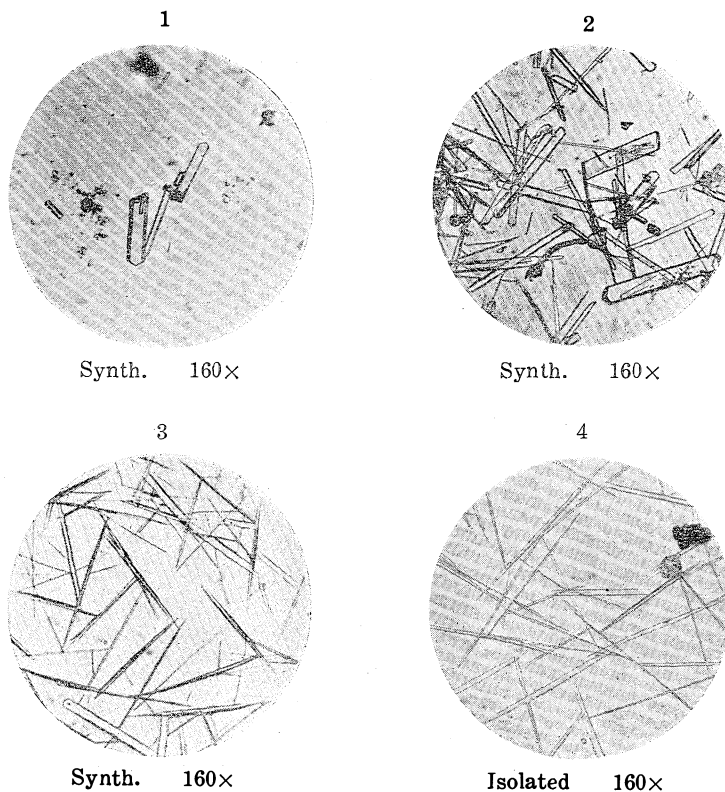


Fig. 2.'

Index of refraction: $\alpha = 1.547 \pm 0.002$; $\beta = 1.596 \pm 0.001$; $\gamma = 1.639 \pm 0.002$.

Refractive indices were measured by the immersion method: α was measured in the mixture of chlorobenzene and nitrobenzene, β in (bromobenzene-bromoform), and γ in (chloronaphthalene-bromonaphthalene).

Identification: The crystalline substance with m.p. $146-147^\circ\text{C}$., which was separated from the oxidation products of tyrosine, was identified as *p*-hydroxyphenylacetic acid by immersing in the liquid $n = 1.596$, comparing its other optical properties with the synthetic sample, as well as the mixed melting point test.

Last part of the extraction consisted of nearly pure succinic acid. After recrystallisation from water it (0.2 gr.) melted at 183°C . It was converted into silver salt.

Anal.: Subst. = 0.1915; Ag = 0.1239 gr. Found: Ag = 64.71%.
Calc. for $\text{C}_4\text{H}_4\text{O}_4\text{Ag}_2$ (silver succinate): Ag = 65.04%.

(c) *Volatile Part (Acetic Acid; Benzoquinone)*. 90.6 Gr. (1/2 mol) of tyrosine were electrolysed just in the same way as above. The filtered electrolysate was subjected to steam distillation. The total quantity of acid in the distillate was determined by titration, the amount being 0.0448 mol per 1 mol of tyrosine. The distillate was neutralised with sodium carbonate, and phenolic and neutral parts were removed by extraction with ether. The residue was evaporated to dryness. The presence of acetic acid in it was confirmed by acetic ether as well as ferric chloride reactions and the silver salt was prepared, but the amount was too small for analysis. From the above ethereal extract a yellow oil was obtained, from which yellow crystals separated out after a certain time. After being drained on porous plate it melted at 115°C. and showed the same melting point when mixed with a pure sample of benzoquinone. It also gave the iodine reaction, characteristic to quinone, when treated with potassium iodide and chloroform.

(B) *Part Insoluble in Ether*. Barium hydroxide was added to it until neutral to congo red. Barium sulphate was filtered off and the filtrate was boiled with dilute hydrochloric acid. After removing barium the filtrate was concentrated to a syrup. No definite compound was isolated from the syrup (containing 1.44 gr. of nitrogen).

From the filtrate of barium sulphate the crystals (13.3 gr.) were obtained, which were identified as tyrosine by the determination of nitrogen.

Anal.: Subst. = 7.150 mg. NH_3 = 2.65 c.c. of 0.01522 N.- H_2SO_4 .

Found: N = 7.90%. Calc. for $\text{C}_9\text{H}_{11}\text{O}_3\text{N}$ (tyrosine): N = 7.74%.

(a) *Volatile Base*. The total amount of nitrogen in the mother liquor of tyrosine amounted to 2.338 gr. To a part of it an excess of barium hydroxide was added and distilled under reduced pressure. The distillate was received in hydrochloric acid. Hydrochloride of a base was obtained. It was identified as ammonia by the analysis of its platinic double chloride.

Anal.: Subst. = 0.1924; Pt = 0.0843 gr. Found: Pt = 43.81%.

Calc. for $(\text{NH}_4)_2\text{PtCl}_6$: Pt = 43.95%.

(b) *Melanin-like Substance*. From the part insoluble in ether brownish precipitate was formed after it was allowed to stand for a month. It was collected on a filter and washed until the washing was free from SO_4 and dried over lime under reduced pressure. The sample was dried again to a constant weight over calcium chloride at 100°C. and analysed. 0.4 Gr. of the sample was obtained from 90.6 gr. of tyrosine. It was found to be amorphous under polarising microscope and is readily soluble

in sodium hydroxide solution and reprecipitated by acid. The sample can be heated in a capillary up to 310°C. without any alteration.

Anal.: Subst. = 0.1003; CO₂ = 0.2296; H₂O = 0.0384 gr.
Subst. = 0.1249; N₂ = 6.82 c.c. (18.4°C., 757.2 mm.).
Found: C = 62.44; H = 4.28; N = 6.25%.

The other sample obtained without separation of the part soluble in ether has darker shade and the content of nitrogen amounted to 4.7%.

Electrolytic Oxidation of Phenylalanine.

82.6 Gr. of phenylalanine were dissolved in 1200 c.c. of 2N.-sulphuric acid and were oxidised in the same way as in the case of tyrosine. The current quantity applied was 202.2 amp. hrs. (15F/mol). The formation of melanin-like substance was also observed in this case.

The investigation of oxidation products was carried out just in the same way as in the case of tyrosine.

(a) **Phenolic Part:** 0.9 Gr. of hydroquinone was isolated; m.p. 169°C.

Anal.: Subst. = 0.0770; CO₂ = 0.1843; H₂O = 0.0380 gr.
Found: C = 65.27; H = 5.52%.
Calc. for C₆H₆O₂ (hydroquinone): C = 65.39; H = 5.49%.

(b) **Acidic Part:** 1.6 Gr. of succinic acid were isolated, m.p. 183°C.

Anal.: Subst. = 0.0634; CO₂ = 0.0942; H₂O = 0.0295 gr.
Found: C = 40.52; H = 5.20%.
Calc. for C₄H₆O₄ (succinic acid): C = 40.63; H = 5.12%.

(c) **Volatile Part:** The presence of acetic acid was examined by conversion into acetic ether when it gave the other smell, reminding that of ethyl benzoate. But benzoic acid could not be isolated.

(d) **Volatile Base.** Ammonia was isolated.

Anal.: Subst. = 0.2100; Pt = 0.0921 gr. Found: Pt = 43.86%.
Calc. for (NH₄)₂PtCl₆, Pt = 43.95%.

Neither *p*-hydroxyphenylacetic acid nor phenylacetic acid were isolated. Further study on this line will be done in near future.

In conclusion, the author wishes to express his sincere thanks to Prof. K. Matsubara for his kind encouragement and invaluable advice given throughout these works.

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STUDIES ON AMINO-ACIDS AND RELATED COMPOUNDS.
PART VI. ELECTROLYTIC OXIDATION OF
IMIDAZOLYL-PROPIONIC ACID.

By Yoshitaro TAKAYAMA.

Received April 13th, 1933. Published July 28th, 1933.

In the previous communications,⁽¹⁾ it was stated that pyrrolidone-carboxylic acid was easily oxidised at anode and yielded considerable amount of succinimide. This fact shows that this heterocyclic nucleus is particularly unstable towards anodic oxidation. Some amino-acids possess heterocyclic nuclei, which may undergo more or less individual change by the anodic oxidation. In the present paper, the study on imidazolyl-propionic acid is to be reported. Before trying some experiments on histidine, the above acid was selected, because it has similar structure as histidine, and differs only at one point, the lack of α -amino-group. It seems to be more plain in this case than in the case of histidine itself to investigate the mechanism of oxidation of imidazol nucleus.

As to the oxidation of imidazol derivatives, two reports are cited in the literatures. Wyss⁽²⁾ oxidised imidazol with chromic acid and potassium permanganate. In the former case, no definite compound was isolated, while in the latter, formic acid was obtained. On the other hand Radziszewski⁽³⁾ isolated oxamide and oxamic acid (?) when he oxidised imidazol with 3 per cent. solution of hydrogen peroxide.

Little definite information has been given relating to the electrolytic oxidation of heterocyclic compounds. Fr. Fichter and his collaborator⁽⁴⁾ have electrolytically oxidised several compounds having pyrazolone nucleus (antipyrine and its allies) and obtained products which were not the same as those obtained by pure chemical methods. But in none of these cases the rupture of pyrazolone nucleus was found to occur.

Imidazolyl-propionic acid was oxidised under the same conditions as in the previous experiments. The temperature was kept at 30°C. by immersing the cell in the thermostat. The electrolysate assumed yellowish tint as the electrolysis proceeded, but the formation of melanin-like substances was not observed. The amount of electricity applied was about 6F./mol.

(1) Y. Takayama, this Bulletin, **8** (1933), 125, 137.

(2), (3) Br. Radziszewski, *Ber.*, **17** (1884), 1289.

(4) Fr. Fichter and H. D. Montmollin, *Helv. chim. Acta*, **5** (1922), 256.

Nitrogen Distribution in the Electrolysate.

NH ₃ -N (MgO)	65.8 %
NH ₃ -N (NaOH)	12.3 %

From this result the presence of amide type compounds can be presumed. The electrolysate was thoroughly extracted with ether. Parts soluble (a) and insoluble (b) in ether were treated separately.

Part Soluble in Ether (a). When ether was expelled there remained a certain amount of crystalline residue, which was separated from a small bulk of the mother liquor. After recrystallisation from water, it melted at 184°C. and was found to be succinic acid by elementary analysis. The further crop* of this acid was obtained from (b) by other treatments. The joined yield of succinic acid amounted to 30.4% of imidazolyl-propionic acid used.

The mother liquor of succinic acid showed fuchsin reaction and silver mirror reaction. *p*-Nitrophenylhydrazone was prepared from it. The hydrazone, after recrystallisation from alcohol, melted at 172–174°C. The aldehyde was found to be succinic acid semialdehyde by the analysis of this hydrazone.

Part Insoluble in Ether (b). An excess of barium hydroxide was added to it and the solution was distilled under reduced pressure until the final distillate showed no reaction of ammonia. The distillate was received in hydrochloric acid, from which ammonia was obtained. It was confirmed by the analysis of its platonic double chloride. The residue was freed from barium, and concentrated under reduced pressure to a small bulk (c), then the estimation of urea was carried out by the following methods.

(1) *Xanthydrol Method.* The definite volume of the solution (c) was taken and the methyl alcohol solution of xanthydrol (Kahlbaum) $\text{O} < \begin{smallmatrix} \text{C}_6\text{H}_4 \\ \text{C}_6\text{H}_4 \end{smallmatrix} > \text{CHOH}$ was added to it. Urea could be quantitatively precipitated as dioxanthyl urea.

(2) *Urease Method.* Urease was added to the same definite volume. The amount of urea was estimated by the titration of ammonia formed by the enzymatic action of urease.

The results obtained from (1) and (2) fairly coincided with each other and the yield of urea was 1.3% of imidazolyl-propionic acid used. The result of nitrogen distribution shows that the total amount of the

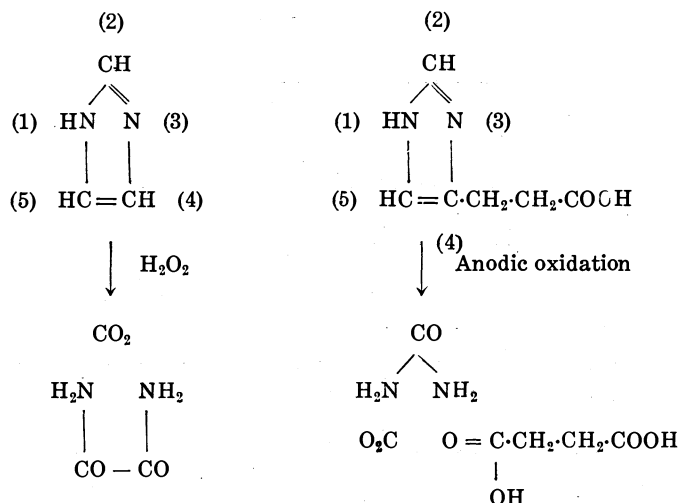
* Though sufficient quantity of ether was used, the extraction of succinic acid was not complete owing to its small solubility in that solvent.

amide compounds amounted to 12.5%. The discrepancy of the results obtained by different determinations may be ascribed to the presence of other compounds of amide type, such as oxamide or oxamic acid. But the project to obtain them from the solution was not successful. The difference is probably caused by the hydrolysis of urea during many treatments for its isolation.

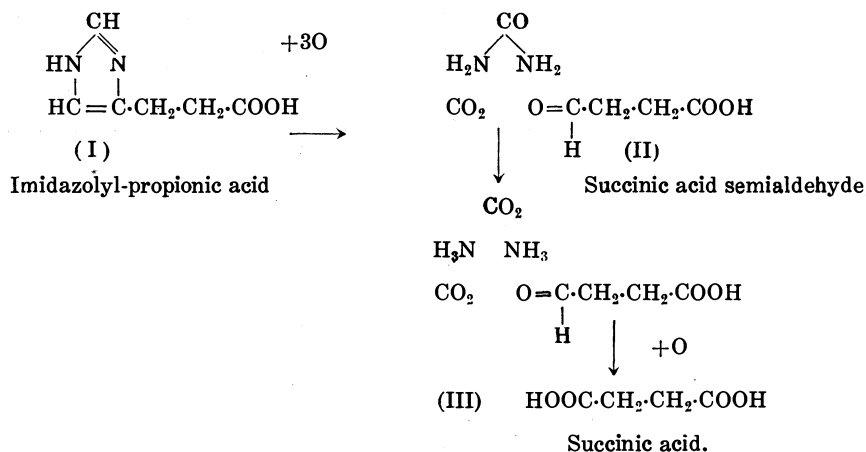
Remaining part of the solution (c) was concentrated to a syrup under reduced pressure and was extracted with hot isobutyl alcohol, and the crystals were obtained from the extract. It was found to be unchanged imidazolyl-propionic acid.

Mechanism of Oxidation of Imidazol Compounds.

As already mentioned⁽³⁾ oxamide and oxamic acid were isolated by Radziszewski by the oxidation of imidazol. In this case it must be considered that the oxidation of imidazol took place at its carbon (2).



On the contrary, in the above anodic oxidation large amount of succinic acid together with little urea was isolated. This time the oxidation proceeded through another course, imidazol nucleus being attacked at carbon(5). It may be concluded that imidazol nucleus, on oxidation, behaves differently according to the kinds of oxidising agents (and probably to the presence or absence of the side chain). The mechanism of the anodic oxidation of imidazolyl-propionic acid may be represented as follows.



Succinic acid semialdehyde might as well be considered as the product of the secondary cathodic reduction of succinic acid, but the course of formation above cited was justified by the experiments reported in the previous communication.⁽⁵⁾

Experimental Part.

Imidazolyl-propionic acid⁽⁶⁾

Anal.: Subst. = 0.2347 gr. NH_3 = 33.00 c.c. of N./10- H_2SO_4 ,

Found: H = 19.70 %.

Calc. for $\text{C}_6\text{H}_8\text{O}_2\text{N}_2$: N = 19.99 %.

4.2 Gr. of imidazolyl-propionic acid (ca. 30 millimol) were dissolved in 100 c.c. of 2N.-sulphuric acid and electrolysed under the following conditions. Cell: without diaphragm. C.D. = 2 amp/dm². Electrodes (3×7 cm.): lead peroxide—lead. Electric quantity applied: 6.58 F/mol.

Distribution of Nitrogen. The electrolysate was filtered and made up to 125 c.c. 10 c.c. of the solution were taken for the following determinations,

(1) An excess of magnesia was added and distilled under reduced pressure.

(5) Y. Takayama, this Bulletin, **8** (1933), 125: Succinic acid was electrolytically oxidised under the same conditions as above. The electrolysate did not show characteristic reaction of aldehyde.

(6) S. Akabori, *J. Chem. Soc. Japan*, **52** (1931), 849. The sample of imidazolyl-propionic acid was kindly offered by Dr. Akabori and Mr. Numano, to whom the author is very grateful.

$\text{NH}_3 = 31.68 \text{ c.c. of N./10-H}_2\text{SO}_4$	N = 44.2 mg.
total-N in 10 c.c. (calc.)	N = 67.2 mg.
$\text{NH}_3\text{-N (MgO) / total-N}$	65.8 %.

(2) 30% sodium hydroxide solution was added to the residue and distilled again.

$\text{NH}_3 = 5.82 \text{ c.c. of N./10-H}_2\text{SO}_4$	N = 8.28 mg.
total-N in 10 c.c. (calc.)	N = 67.2 mg.
$\text{NH}_3\text{-N (NaOH) / total-N}$	12.3 %.

It was previously ascertained that imidazolyl-propionic acid did not yield ammonia when it was boiled with concentrated sodium hydroxide.

Succinic Acid. The oxidised solution was thoroughly extracted with ether. The colourless crystals were obtained from the extract. (0.576 gr.). After recrystallisation from water it melted at 184°C .

Anal.: Subst. = 0.0607; $\text{CO}_2 = 0.0904$; $\text{H}_2\text{O} = 0.0275 \text{ gr.}$

Found: C = 40.61; H = 5.07 %.

Calc. for $\text{C}_4\text{H}_6\text{O}_4$ (succinic acid): C = 40.63; H = 5.12 %.

The residue of the extraction was evaporated to a syrup under reduced pressure and extracted with acetone. A crystalline residue (0.540 gr.) was obtained from the extract, it was found to be nothing else than succinic acid. The joined yield of succinic acid amounted to 1.116 gr. (9.45 millimol) representing 31.4% of imidazolyl-propionic acid used.

Succinic Acid Semialdehyde. The viscous mother liquor of succinic acid was kept over concentrated sulphuric acid under reduced pressure and crystallised succinic acid was filtered off. Following the description of Carrière,⁽⁷⁾ to the filtered solution of *p*-nitrophenylhydrazine (0.5 gr.) in acetic acid (3 gr.) the aldehyde was added. Reddish yellow precipitate formed was collected and drained on porous plate. After repeated recrystallisation from alcohol, with addition of animal charcoal, it melted at $172\text{--}174^\circ\text{C}$.

The melting points of *p*-nitrophenylhydrazone of succinic acid semialdehyde given by many authors are as follows.

Alefeld ⁽⁸⁾	175°C .	1909
Langheld ⁽⁹⁾	174°C .	1909
Harries ⁽¹⁰⁾	177°C .	1912
Dakin ⁽¹¹⁾	$185\text{--}187^\circ\text{C}$. (when rapidly heated)	1917
Carrière	$180\text{--}181^\circ\text{C}$.	1922

(7) Carrière, *Ann. chim.*, [9] **17** (1922), 75.

(8) Alefeld, *Ber.*, **42** (1909), 165, 1426.

(9) Langheld, *Ber.*, **42** (1909), 2371.

(10) Harries, *Ber.*, **45** (1912), 2585.

(11) Dakin, *Biochem. J.*, **11** (1917), 84.

The value obtained by the author (172–174°C.) was lower than any of the above. But the sample was too minute to try further recrystallisation.

Anal.:⁽¹²⁾ Subst. = 7.264 mg.; NH_3 = 6.24 c.c. of N./70- H_2SO_4 .

Found: N = 17.18%.

Calc. for $\text{C}_{10}\text{H}_{11}\text{O}_4\text{N}_3$: N = 17.7%.

Ammonia and Urea. An excess of barium hydroxide was added to the solution (b) and it was distilled under reduced pressure. The distillate was received in hydrochloric acid and the volatile base was collected as hydrochloride. It was found to be ammonia by the analysis of its platinic double chloride.

Anal.: Subst. = 0.1712; Pt = 0.0746 gr. Found: Pt = 43.6%.

Calc. for $(\text{NH}_4)_2\text{PtCl}_6$: Pt = 43.9%.

The excess of barium was removed exactly and the solution was concentrated to 50 c.c. under reduced pressure. Urea was estimated as follows.

(1) *Xanthydrol Method*.⁽¹³⁾ 5 c.c. out of 50 c.c. (corresponding to 8/100 part of the total volume) were taken and poured into three parts of acetic acid, to which 3 c.c. of 7% methyl alcoholic solution of xanthydrol (Kahlbaum) were added. After the solution was allowed to stand overnight, the flocculent precipitate was collected on a filter. The dioxanthyl urea obtained weighed 12.0 mg. corresponding to 1.71 mg. urea.

Anal.: Subst. = 8.169 mg.; NH_3 = 2.60 c.c. of N./70- H_2SO_4

Found: N = 6.36%.

Calc. for $\text{C}_{27}\text{H}_{20}\text{O}_3\text{N}_2$: N = 6.66%.

(2) *Urease Method*.⁽¹⁴⁾ The same volume as in the above method was taken and it was neutralised. A buffer solution of phosphates and 0.1 gr. of urease (Squibb) were added to it. After the solution was kept at 40–50°C. for 15 minutes, an excess of sodium carbonate was added and the rapid current of air was passed through the solution, transferring the formed ammonia into N./70- H_2SO_4 (method of Folin). The same treatment was repeated without adding urease.

(a) Urease added: N./70- H_2SO_4 6.74 c.c. N = 1.348 mg.

(b) Without urease: N./70- H_2SO_4 2.29 c.c. N = 0.458 mg.

diff. N = 0.890 mg.

calc. for urea 1.91 mg.

(12) As this compound contains nitro and hydrazo groups, it must be previously reduced. Zn and alcohol were chosen as reducing agent. See Hans Meyer's *Methodik* (1931) p. 426 and Weyl's *Methoden*, I (1921) p. 52.

(13) Fosse, *Ann. chim.*, (9), 6 (1916), 67.

(14) See Hoppe-Seyler, Thierfelder, „*Physiologisch- und pathologisch-chemische Analyse*“ (1924), p. 702.

The urease used was ascertained beforehand not to contain an appreciable amount of ammonia. Therefore, ammonia formed in (b) may have been produced by the hydrolysis of urea during the concentration of the solution.

Imidazolyl-propionic Acid. The remaining part of the solution was concentrated to a syrup under reduced pressure and was extracted with hot isobutyl alcohol. The solvent was expelled and the residue was redissolved in a small bulk of water. A large amount of acetone was added to it. Colourless crystals were deposited on the wall of the beaker, which melted at 201–202°C. It was found to be imidazolyl-propionic acid by the determination of nitrogen and mixed melting point test.

Anal.: Subst. = 7.883 mg.; NH_3 = 7.90 c.c. of N./70 H_2SO_4 .

Found: N = 20.04%.

Calc. for $\text{C}_6\text{H}_8\text{O}_2\text{N}_2$: N = 19.99%.

In conclusion, the author wishes to express his sincere thanks to Professor K. Matsubara for his kind encouragement and invaluable advices given to this study, and also to Mr. H. Ôeda for his untired assistance.

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**FREEZING POINT CURVES OF BINARY MIXTURES:
TiCl₄-SiCl₄, TiCl₄-CCl₄, TiCl₄-SnCl₄ AND TiCl₄-SbCl₅.**

By Nobuyuki NASU.

Received June 10th, 1933. Published July 28th, 1933.

Synopsis.

Freezing point curves of binary mixtures, TiCl₄-SiCl₄, TiCl₄-SnCl₄, TiCl₄-CCl₄, and TiCl₄-SbCl₅ have been determined by the methods of both total and differential thermal analyses. In the system TiCl₄-SiCl₄ an eutectic point lies on the position almost 100% of SiCl₄, and with the mixtures TiCl₄-CCl₄ and TiCl₄-SbCl₅ a simple eutectic system has been shown, while the mixture TiCl₄-SnCl₄ shows a simple solid solution.

Introduction.

Titanium tetrachloride can be prepared from titanium dioxide which is usually found in the iron sand. Consequently the investigation of

titanium tetrachloride has very profound interest with the industrial application of the iron sand. The present author has intended as a first attempt to investigate the freezing point curves of the binary mixtures of liquid chlorides containing titanium tetrachloride.

Experimental Method.

1. **Sampling of the Chlorides avoiding those from Decomposition.** It will be difficult to prepare mixtures of known composition, which is extremely smoky in the presence of wet atmosphere, such as, those chlorides (excepting carbon tetrachloride), by weighing them with a balance. There is also a method of measurement by which these can be distilled in a measuring apparatus which is kept in vacuum, but then this will be of greatly complicated in such a case as to determine the freezing point curve. Hence in the present experiment the volumes of these chlorides have been measured with burettes avoiding them contact with moisture,

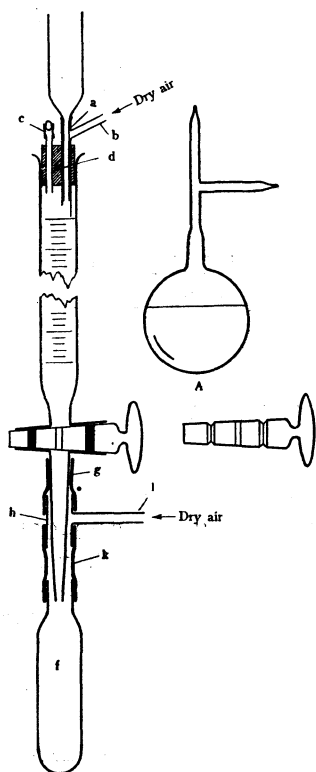


Fig. 1.

and calculated the composition of these mixtures from their density. All these chlorides were purified by the distillation before use. Stocked chlorides were kept in flasks each of which has a side tube as shown in Fig. 1 A, and when those were used, dried air were let in from the tube avoiding the contact of moisture with chlorides. When the chlorides were let into a burette from the stocked flask through a long mouthed funnel inserted into a tube *a* shown in Fig. 1, dry air was sent from the tube *b* letting it out from the funnel, avoiding the contact of moisture with the chlorides, and taking the lid *c* off to allow the chlorides into the burette. After the chlorides were let into the burette, the lid *c*, being replaced the funnel being removed and the tube *a* was closed, at the same time, sending of the dry air from *b* was ceased. *d* in Fig. 1 and *d'* in Fig. 2 are gum stoppers whose surfaces are previously attacked by the chloride vapour for a sufficiently long time to avoid chlorides from being contaminated. Two grooves are dug on the stop-cock as shown in the figure and mercury is poured in them to protect the chlorides from

the moisture and to keep it movable. Although the boundary between the mercury and the chlorides became brownish black due to the contamination of the mercury during the experiment, the phenomenon was simply confined in the boundary; hence, the chlorides in the burette were able to keep their original purity. The purity was further assured by discarding the first small quantity of chlorides into *f*, before measuring the chlorides out from the burette into the apparatus. *g* and *k* are gum tubes and *h* is made of glass. The measuring of the chlorides into the apparatus was consisted of lowering *g*, *h* and *k* downwards, passing the dry air very slowly from tube *l*, connecting the side tube *m* in Fig 2 with rubber tube *k*, at the same time *f* is removed and while opening the lid *n* allowing the air coming out, the desired quantity of the chlorides was measured into the apparatus. When the measurement was completed, *m* is removed from *k*, letting the dry air pass through from *n*, and *m* is quickly covered up, and finally the air supply from *n* was discontinued. *f* is re-set into *k*, at the same time letting the dry air cease to come from *l*. When carbon tetrachloride was used, an usual burette was employed, as it does not fume in the wet air. Since the data available in the literature relating to the density of these chlorides are very meagre, the density of these chlorides was calculated by the interpolation of several values in the literature. The references on the value adopted are as follows; the density of titanium tetrachloride from T. Sagawa,⁽¹⁾ a member of our institute, of silicon tetrachloride from T. E. Thorpe,⁽²⁾ O. Ruff, and C. Albert,⁽³⁾ of carbon tetrachloride from T. E. Thorpe⁽⁴⁾ and Joseph,⁽⁵⁾ of stannic chloride from Young and Fortey,⁽⁶⁾ of antimony tetrachloride from A. Haagen,⁽⁷⁾ O. Ruff, and W. Plato.⁽⁸⁾

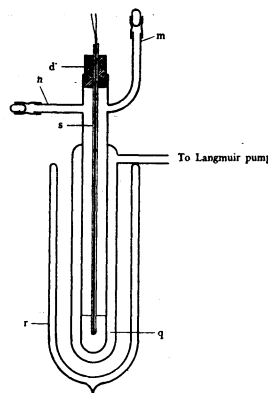


Fig. 2.

2. Thermal Analyses. The cooling velocity is regulated by the pressure at the space *q* in Fig. 2 to which Langmuir pump is connected. *r* is a Dewar vessel containing liquid nitrogen or mixture of solid carbon

- (1) T. Sagawa, *Kinzoku no Kenkyū*, **9** (1932), 189.
- (2) T. E. Thorpe, *J. Chem. Soc.*, **37** (1880), 327.
- (3) O. Ruff, C. Albert, *Ber.*, **38** (1905), 2222.
- (4) T. E. Thorpe, *Trans. Chem. Soc.*, **37** (1880), 141.
- (5) Joseph, *Trans. Chem. Soc.*, **107** (1915), 1.
- (6) Young & Fortey, *J. Chem. Soc.*, **81** (1902), 783.
- (7) A. Haagen, *Pogg. Ann.*, **131** (1867), 122.
- (8) O. Ruff & W. Plato, *Ber.*, **37** (1904), 679.

dioxide and ether. *s* is a protecting glass tube in which one junction of the copper-constantan thermocouple is inserted, and the other junction is inserted in the melting ice. The temperature was read by a pyrometer. The copper-constantan thermocouple was previously calibrated by the melting points of pure chlorobenzene, chloroform, ethyl acetate, toluene,

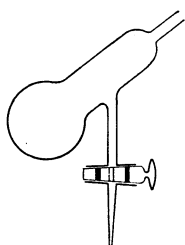


Fig. 3.

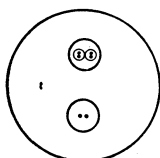


Fig. 4.

ethyl ether, and mercury, and also by the boiling point of liquid nitrogen. On the differential thermal analysis the mixture of the desired composition was prepared firstly in the flask shown in Fig. 3 with the burette shown in Fig. 1, and then about 0.05 c.c. of the mixture was introduced into the glass tube whose diameter is 3 mm. shown in Fig. 4. The purpose of using such a small quantity of chloride was to make the uniform temperature at the extremity of the thermocouple. In Fig. 4 *t* is a copper block, 3 cm. in diameter and 4 cm. in length, into which two glass tubes are inserted; the one contains chloride, and the other water. In the tube containing chloride two junctions, each end of the temperature measurement thermocouple and of the differential thermal analysis, are inserted. These two junctions are inserted respectively into two capillaries which are placed symmetrically about the inner wall of the tube containing chloride. Two wires of the junction are insulated with

the oxide coating on the copper wire made by the Bunsen burner. When the differential thermal analysis was carried on the copper block was previously dipped in liquid nitrogen, solidifying both the chloride and the neutral matter (water), and they were then taken out in the air, and finally the heating curves were drawn from the readings of a galvanometer. The velocity of the heating was about 0.4° per minute.

In the case of the total thermal analysis the solidus points on both sides of the eutectic point in the system $\text{TiCl}_4\text{-CCl}_4$ were indicated slightly lower temperature on the cooling curve and somewhat higher temperature on the heating curves. The similar phenomena were observed on the antimony pentachloride rich-side in the system $\text{TiCl}_4\text{-SbCl}_5$; consequently in both diagrams the mean values of these temperatures were adopted. Curves of the thermal analyses were shown in Figs. 9 and 10, and the results were tabulated and illustrated diagrammatically in next paragraph.

Results of Experiment.

(1) $\text{TiCl}_4\text{-SiCl}_4$. When the cooling curve of the total thermal analysis was taken in this system, the eutectic flat did not appears until the

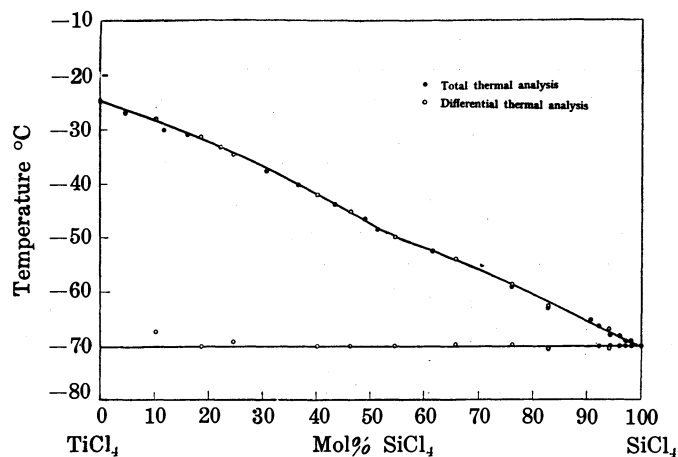
Fig. 5. Freezing point curve of the mixture: TiCl_4 - SiCl_4 .1. TiCl_4 - SiCl_4

Table 1. Total Thermal Analysis (Cooling Curves)

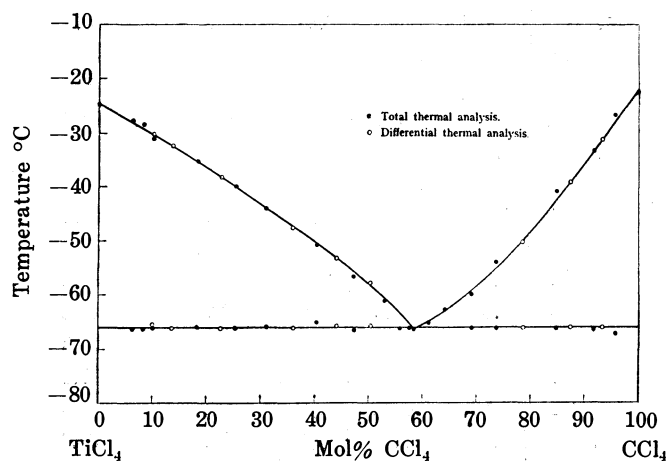
No.	Temp.	TiCl_4		SiCl_4		Mol% SiCl_4	Liquidus point —°C	Eutectic point —°C
		s.g.	c.c.	s.g.	c.c.			
1	15.4	1.7354	5.0	1.4927	0.0	0.0	24.8	—
2	15.5	1.7352	„	1.4926	0.25	4.6	27.0	—
3	15.3	1.7356	„	1.4928	0.7	11.9	30.3	—
4	15.5	1.7353	„	1.4926	1.0	16.2	31.0	—
5	15.8	1.7346	„	1.4924	1.5	22.4	33.4	—
6	14.2	1.7376	„	1.4937	2.3	30.6	37.6	—
7	14.5	1.7370	„	1.4935	3.0	36.6	40.4	—
8	15.1	1.7360	„	1.4930	4.0	43.5	43.9	—
9	13.2	1.7393	„	1.4946	5.0	49.0	46.7	—
10	12.1	1.7410	„	1.4755	5.5	51.3	48.7	—
11	12.2	1.7408	3.0	1.4954	5.0	61.5	52.6	—
12	12.5	1.7403	2.0	1.4952	„	70.6	55.2	—
13	13.5	1.7386	1.5	1.4943	„	76.2	59.3	—
14	16.5	1.7336	1.0	1.4918	„	82.8	63.3	—
15	15.4	1.7352	0.5	1.4927	„	90.6	65.3	—
16	14.8	1.7364	0.4	1.4932	„	92.3	66.8	70.3
17	15.9	1.7346	0.3	1.4923	„	94.1	68.3	70.3
18	14.1	1.7376	0.2	1.4938	„	96.0	68.3	70.3
19	13.2	1.7391	0.15	1.4946	„	97.0	69.3	70.3
20	15.1	1.7359	0.1	1.4930	„	98.0	69.3	70.3
21	15.1	1.7359	0.0	1.4930	„	100.0	70.4	—

Table 2. Differential Thermal Analysis (Heating Curves)

No.	Temp.	TiCl ₄		SiCl ₄		Mol% SiCl ₄	Liquidus point —°C	Eutectic point —°C
		s.g.	c.c.	s.g.	c.c.			
22	12.5	1.7403	5.0	1.4952	0.6	10.3	28.0	67.3
23	13.0	1.7394	„	1.4948	1.2	18.7	31.4	70.3
24	13.4	1.7388	„	1.4944	1.7	24.6	34.6	69.3
25	13.5	1.7386	„	1.4943	3.5	40.2	42.0	70.3
26	12.5	1.7303	„	1.4952	4.5	46.3	45.3	70.3
27	12.8	1.7398	4.0	1.4949	5.0	54.5	50.4	70.3
28	13.2	1.7391	2.5	1.4946	„	65.8	54.2	70.3
29	13.4	1.7388	1.5	1.4944	„	76.2	58.9	70.3
30	13.8	1.7381	1.0	1.4941	„	82.8	60.3	70.9
31	13.5	1.7386	0.3	1.4943	„	94.1	66.6	70.9

mixture contained a quite large quantity of SiCl₄, say 90.6 Mol % SiCl₄. In the case of the differential thermal analysis the eutectic points were observed until the mixtures contained as small quantity of SiCl₄ as 10.3 Mol %. In both analyses this eutectic point was perfectly equal to the freezing point of pure SiCl₄. Liquidus curve descends, as shown in Fig. 5, gradually from 100% TiCl₄ to 100% SiCl₄. In another words in this system when a mixture freezes, TiCl₄ crystallizes out firstly, and until all the TiCl₄ freezes out, the crystallization of SiCl₄ does not begin.

(2) TiCl₄-CCl₄. In this system both the liquidus and the eutectic point appeared distinctly, as shown in Fig. 6, even in the case of the

Fig. 6. Freezing point curve of the mixture: TiCl₄-CCl₄.

total thermal analysis; but the eutectic point found to be somewhat higher temperature in the heating curves than that of the cooling. This difference grew greater and greater as the composition of the mixture remote from the eutectic point, as shown in Table 3; hence in the figure mean values have been plotted. Perhaps these abnormalities can be removed if small quantity of the sample is used. In the case of the differential thermal analysis, therefore, small quantities of the samples were employed as described before, and almost definite eutectic temperature was observed.

2. $\text{TiCl}_4\text{-CCl}_4$

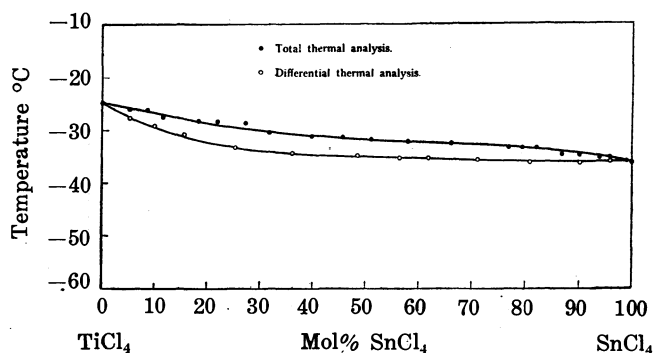
Table 3. Total Thermal Analysis (Cooling Curves)

No.	Temp.	TiCl_4		CCl_4		Mol % CCl_4	Liquidus point —°C	Eutectic point —°C		
		s.g.	c.c.	s.g.	c.c.			Cooling	Heating	Mean
1	16.0	1.7344	5.0	1.5817	0.0	0.0	24.8	—	—	—
2	16.1	1.7341	"	1.5816	0.3	6.3	27.6	75.2	57.3	66.3
3	16.5	1.7336	"	1.5813	0.4	8.3	28.5	75.2	57.3	66.3
4	16.8	1.7331	"	1.5810	0.5	10.1	31.0	74.0	58.0	66.0
5	17.9	1.7311	"	1.5801	1.0	18.4	35.4	74.0	58.0	66.0
6	18.2	1.7308	"	1.5799	1.5	25.3	40.0	73.5	59.0	66.1
7	17.6	1.7318	"	1.5804	2.0	31.0	44.3	73.0	59.3	65.8
8	18.1	1.7309	"	1.5800	3.0	40.3	50.7	70.2	59.8	65.0
9	19.0	1.7294	"	1.5793	4.0	47.4	56.7	68.8	64.3	66.6
10	20.8	1.7264	"	1.5778	5.0	53.0	61.1	66.8	—	—
11	21.3	1.7256	"	1.5774	5.6	55.8	—	66.3	—	—
12	21.8	1.7247	"	1.5770	6.5	57.5	—	66.3	—	—
13	23.9	1.7211	4.0	1.5753	5.0	58.5	—	66.5	—	—
14	22.8	1.7230	5.0	1.5762	7.0	61.2	65.3	67.8	—	—
15	23.0	1.7227	5.0	1.5960	8.0	64.4	62.8	67.8	—	—
16	24.5	1.7202	2.5	1.5748	5.0	69.3	60.3	69.3	63.2	66.3
17	24.2	1.7207	2.0	1.5750	"	73.8	54.2	70.2	62.3	66.3
18	25.9	1.7178	1.0	1.5736	"	85.0	41.3	72.0	60.6	66.3
19	25.2	1.7190	0.5	1.5742	"	91.9	33.4	73.0	60.0	66.5
20	26.5	1.7168	0.25	1.5732	"	95.8	26.9	75.2	59.3	67.3
21	26.4	1.7170	0.0	1.5733	"	100.0	22.9	—	—	—

Table 4. Differential Thermal Analysis (Heating Curves)

No.	Temp.	TiCl ₄		CCl ₄		Mol% CCl ₄	Liquidus point —°C	Eutectic point —°C
		s.g.	c.c.	s.g.	c.c.			
22	11.2	1.7424	5.0	1.5856	0.5	10.1	30.4	65.7
23	11.5	1.7420	„	1.5854	0.7	13.6	32.4	66.3
24	12.5	1.7403	„	1.5845	1.3	22.6	38.2	66.3
25	10.5	1.7436	„	1.5862	2.5	35.9	47.6	66.1
26	12.3	1.7406	„	1.5847	3.5	44.0	53.2	65.9
27	12.5	1.7403	„	1.5846	4.5	50.3	58.1	65.9
28	12.8	1.7398	1.5	1.5843	5.0	78.9	50.2	66.1
29	12.7	1.7400	0.8	1.5844	„	87.5	39.4	66.2
30	12.7	1.7400	0.4	1.5844	„	93.4	31.4	66.1

(3) $\text{TiCl}_4\text{-SnCl}_4$. In this system, as shown by the cooling curves in Fig. 12, while the primary crystallization points were observed distinctly, the eutectic flat did not appear at all. From this fact it is to be assumed that this system is to form the solid solution; but in spite of this prospect, the decision as to whether this system would form the solid solution or not seemed inadequate merely by the total thermal analysis. Only when the differential thermal analysis was taken it was able to decide that all the mixtures in this system, whatever was the composition, would form the solid solution. In Fig. 7 liquidus points from cooling curves of the total thermal analysis and the solidus points from heating curves of the differential thermal analysis were plotted.

Fig. 7. Freezing point curve of the mixture: $\text{TiCl}_4\text{-SnCl}_4$.

3. TiCl_4 - SnCl_4

Table 5. Total Thermal Analysis (Cooling Curves)

No.	Temp.	TiCl_4		SnCl_4		Mol% SnCl_4	Liquidus point —°C
		s.g.	c.c.	s.g.	c.c.		
1	26.7	1.7165	5.0	2.2088	0	0.0	24.8
2	25.8	1.7164	"	2.2085	0.3	5.3	26.0
3	26.6	1.7167	"	2.2090	0.5	8.6	27.1
4	27.1	1.7168	"	2.2078	0.7	11.6	27.5
5	26.5	1.7168	"	2.2093	1.2	18.4	28.3
6	26.4	1.7170	"	2.2096	1.5	22.0	28.4
7	26.5	1.7185	"	2.2119	2.0	27.3	28.6
8	26.4	1.7187	"	2.2121	2.5	31.9	30.5
9	25.8	1.7180	"	2.2111	3.5	39.6	31.2
10	25.7	1.7181	"	2.2114	4.5	45.8	31.3
11	25.1	1.7192	"	2.2129	5.5	50.8	31.6
12	24.2	1.7208	3.4	2.2152	5.0	58.0	32.2
13	23.8	1.7214	2.4	2.2163	"	66.1	32.5
14	22.2	1.7240	1.4	2.2224	"	77.0	33.4
15	22.4	1.7237	1.2	2.2199	"	79.6	33.4
16	22.0	1.7244	1.0	2.2210	"	82.4	34.4
17	20.0	1.7278	0.7	2.2262	"	87.0	34.7
18	18.0	1.7311	0.5	2.2315	"	90.4	34.8
19	19.5	1.7286	0.3	2.2275	"	94.0	35.2
20	19.5	1.7286	0.2	2.2275	"	95.9	35.4
21	19.3	1.7889	0.05	2.2280	"	98.9	35.8
22	19.4	1.7287	0.0	2.2278	"	100.0	36.2

Table 6. Differential Thermal Analysis (Heating Curves)

No.	Temp.	TiCl_4		SnCl_4		Mol% SnCl_4	Solidus point —°C
		s.g.	c.c.	s.g.	c.c.		
23	11.0	1.7428	5.0	2.2497	0.3	5.3	27.9
24	11.2	1.7424	"	2.2492	0.6	10.1	29.4
25	12.5	1.7403	"	2.2458	1.0	15.8	30.8
26	13.0	1.7394	"	2.2445	1.8	25.3	33.4
27	13.5	1.7386	"	2.2432	3.0	36.1	34.4
28	12.5	1.7403	"	2.2458	5.0	48.5	34.8
29	12.4	1.7404	3.65	2.2461	5.0	56.3	35.4
30	13.4	1.7388	2.9	2.2434	"	61.8	35.4
31	12.8	1.7398	1.9	2.2450	"	71.2	35.6
32	13.0	1.7394	1.1	2.2445	"	81.0	36.1
33	12.0	1.7411	0.5	2.2472	"	90.4	36.4
34	14.2	1.7374	0.2	2.2414	"	96.0	35.9

(4) $\text{TiCl}_4\text{-SbCl}_5$. From the results of the total and the differential thermal analyses, it has been found that the eutectic could be observed regularly in this system. But when cooling and heating curves of total thermal analysis were drawn the eutectic temperature varied only on the SbCl_5 rich side.

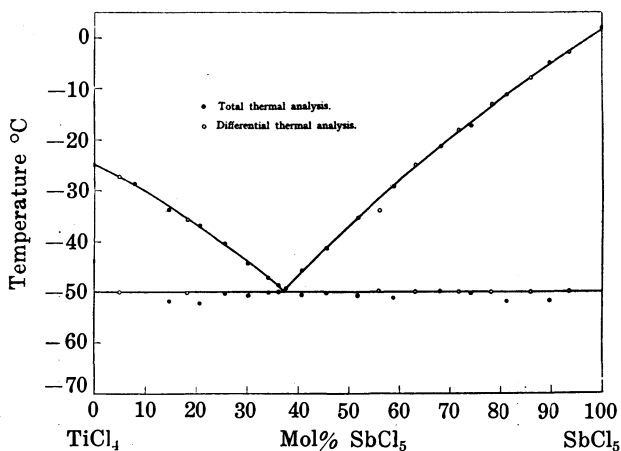


Fig. 8. Freezing point curve of the mixture: $\text{TiCl}_4\text{-SbCl}_5$.

4. $\text{TiCl}_4\text{-SbCl}_5$

Table 7. Total Thermal Analysis (Cooling Curves)

No.	Temp.	TiCl_4		SbCl_5		Mol% SbCl_5	Liquidus point —°C	Eutectic point —°C		
		s.g.	c.c.	s.g.	c.c.			Cooling	Heating	Mean
1	26.1	1.7176	5.0	2.3325	0.0	0.0	24.8	—	—	—
2	26.0	1.7177	„	2.3327	0.5	7.9	28.7	—	—	—
3	26.2	1.7174	„	2.3322	1.0	14.7	33.8	51.6	—	—
4	26.1	1.7175	„	2.3324	1.5	20.5	36.8	52.2	—	—
5	25.8	1.7180	„	2.3331	2.0	25.6	40.4	50.2	—	—
6	25.5	1.7185	„	2.3338	2.5	30.1	44.4	50.6	—	—
7	25.6	1.7184	„	2.3336	3.0	34.1	47.2	50.2	—	—
8	25.8	1.7180	„	2.3331	3.3	36.3	48.7	50.0	—	—
9	25.7	1.7182	„	2.3335	3.5	37.6	—	49.2	—	—
10	26.0	1.7177	„	2.3327	4.0	40.8	45.7	50.7	—	—
11	25.6	1.7184	„	2.3336	5.0	46.3	41.4	50.2	—	—
12	25.8	1.7180	4.0	2.3331	5.0	51.9	35.4	50.7	—	—
13	25.6	1.7184	3.0	2.3336	„	59.0	29.4	51.2	—	—
14	25.7	1.7182	2.0	2.3334	„	68.3	21.3	53.2	46.2	49.7
15	25.8	1.7180	1.5	2.3331	„	74.2	17.3	52.7	47.7	50.2
16	25.8	1.7180	1.0	2.3331	„	81.2	11.3	57.8	45.2	51.9
17	25.5	1.7185	0.5	2.3338	„	89.6	5.0	59.3	43.8	51.7
18	25.4	1.7187	0.0	2.3340	„	100.0	+ 2.0	—	—	—

Table 8. Differential Thermal Analysis (Heating Curves)

No.	Temp.	TiCl ₄		SbCl ₅		Mol% SbCl ₅	Liquidus point —°C	Eutectic point —°C
		s.g.	c.c.	s.g.	c.c.			
19	12.5	1.7403	5.0	2.3627	0.3	4.9	27.3	50.0
20	12.3	1.7406	„	2.3631	1.3	18.3	35.8	50.2
21	12.4	1.7404	3.5	2.3629	5.0	56.0	34.0	49.8
22	12.3	1.7406	2.5	2.3631	„	63.3	25.1	50.2
23	12.3	1.7406	1.7	2.3631	„	71.7	18.1	50.0
24	12.4	1.7404	1.2	2.3629	„	78.2	13.1	50.0
25	12.5	1.7403	0.7	2.3627	„	86.0	8.0	50.2
26	12.5	1.7403	0.3	2.3627	„	93.5	3.0	50.0

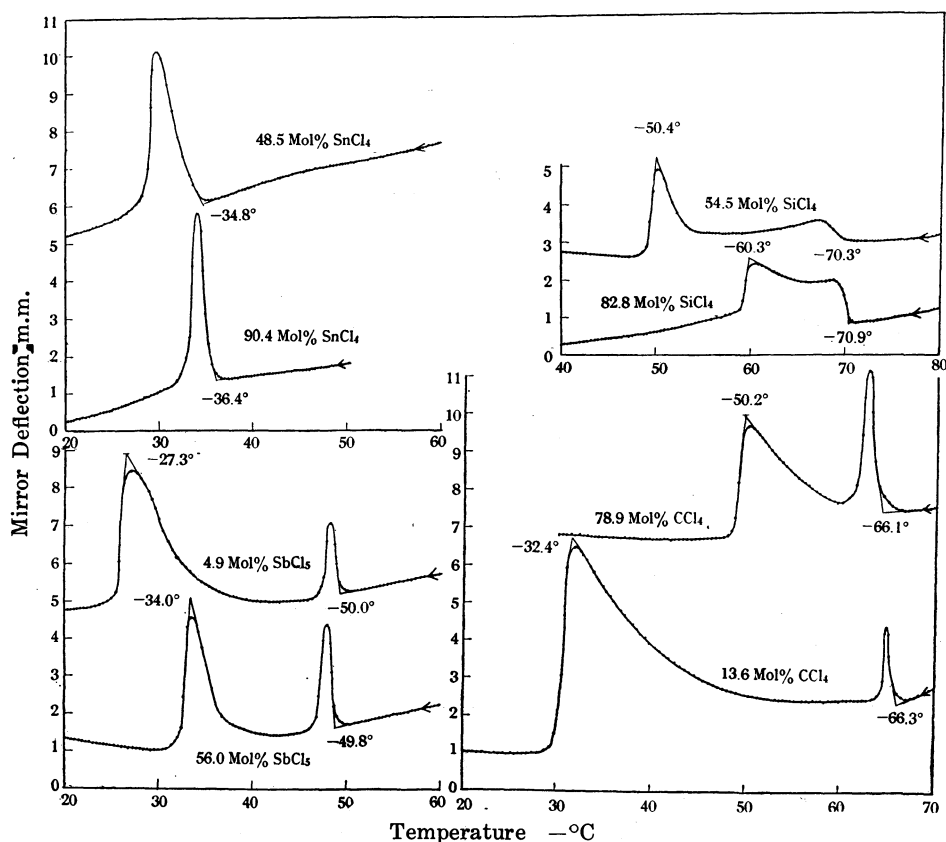


Fig. 9. Differential Thermal Analysis (Heating Curves).

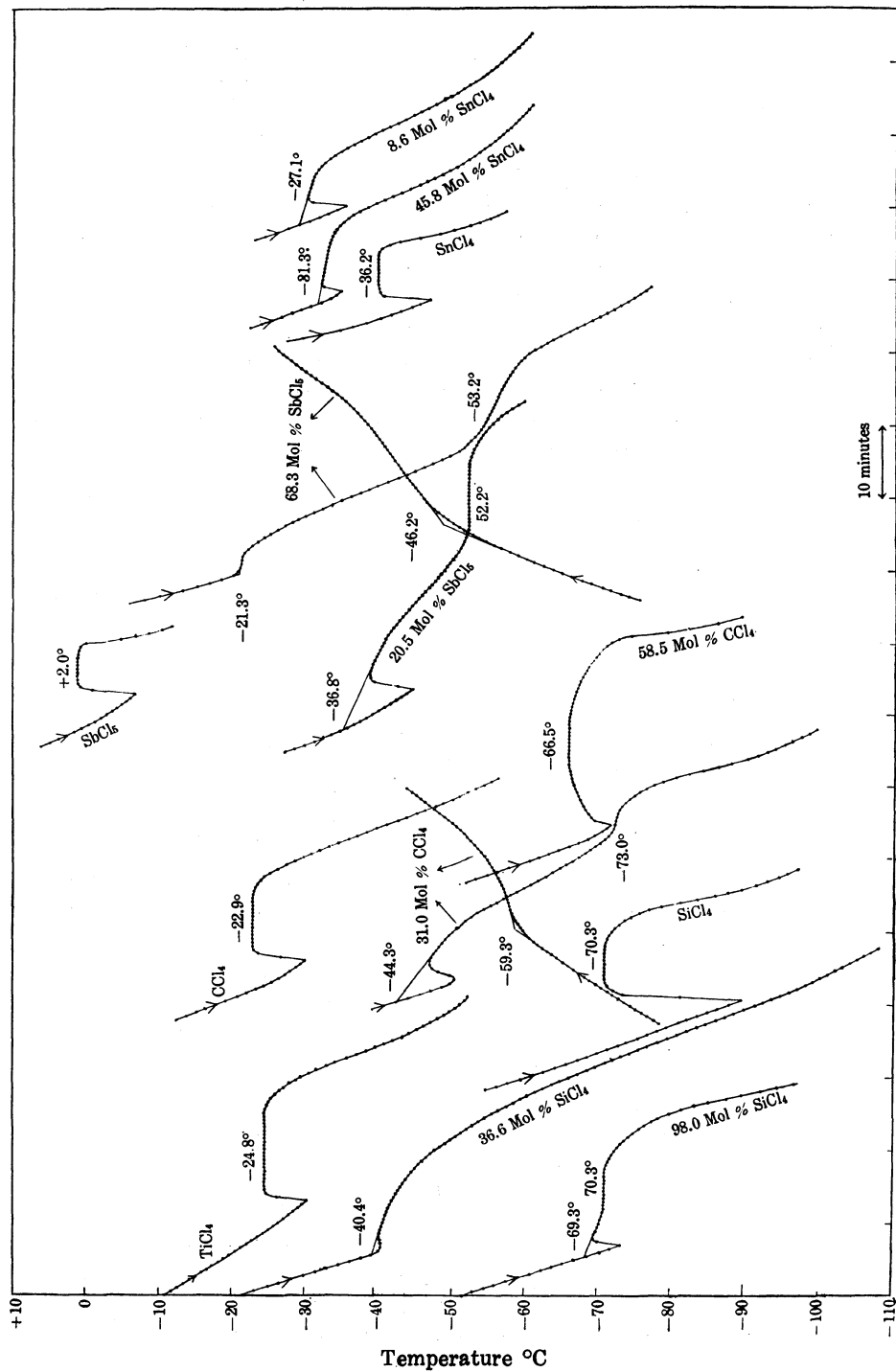


Fig. 10. Total Thermal Analysis.

As almost all of the cooling curves shows the supercooling of samples, primary crystallization points were decided by the back extrapolation method as shown in Fig. 10. In the case of the differential thermal analysis the points of intersection of the curves were taken as the required points.

In conclusion the present writer wishes to express his hearty thanks to Prof. Dr. K. Iwasé for his kind guidance, and thanks are also due to Mr. T. Okamura for his valuable advice.

Summary.

1. The apparatus was devised for the measurement of the liquids which smokes in the wet atmosphere without letting them smoke.

2. Using the apparatus described above the freezing point curves of the mixtures, $\text{TiCl}_4\text{-SiCl}_4$, $\text{TiCl}_4\text{-CCl}_4$, $\text{TiCl}_4\text{-SnCl}_4$, and $\text{TiCl}_4\text{-SbCl}_5$ were determined.

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GLUCO-SULFATASE VI.⁽¹⁾
ON NATURAL SUBSTRATES OF THE ENZYME.

By Tokuro SODA and Junzo YAMAZAKI.

Received June 14th, 1933. Published July 28th, 1933.

In the preceding papers we have chiefly dealt with the properties, the purification of the enzyme and its distribution in molluscan phylum as well as in organs of the animal. It was, however, since the beginning of our research a problem what rôle does the enzyme, glucosulfatase, play in the physiology of those animals.

It is well known that the substrates of pheno-sulfatase naturally occur in the animal body. Couldn't we expect the corresponding substrate of glucosulfatase? Glucose-mono-sulphate, so far as we know, has not yet been found in nature. We have, however, observed during our experiments that the tissues of those animals seem to contain some organic sulphate and to liberate inorganic sulphate by the enzyme. Therefore,

(1) Gluco-sulfatase. Part I; III; V; this Bulletin, **6** (1931), 258; **8** (1933), 65; **8** (1933), 148. Part II; IV; *J. Chem. Soc. Japan*, **54** (1933), 59, 377.

it would be interesting and worth while to look for such a natural substrate in the body of those animals.

Of course, the merit of the enzyme would not be restricted merely to a single physiological function. It is known that there are some organic sulphates in fronds and in animal tissues, and these might be eaten and digested by those animals which contain gluco-sulfatase. Some kinds of gastropoda, such as *Dolium galea* or *Natica ampla*, are said to excrete sulphuric acid. It is very attractive to suppose some relation between those phenomena and the physiological rôle of our enzyme, but at present, it is merely a speculation. In the present paper, as a preliminary research, we have dealt with the distribution of ethereal sulphate in some forms of gastropoda.

The estimations of organic and inorganic sulphates were made on 5 kinds of animals. On *Viviparus japonicus* Martens (mud-snail) the body parts were roughly separated and the sulphates were estimated in each part. In muscular and organ parts the contents of organic sulphate were nearly equal; in embryo the content was markedly high, being 4-5 times of the content of muscular part. (Table I).

On other 4 species of marine origin the sulphates were determined not separately in parts, but the shell contents were boiled and crushed altogether in each case and their sulphates were determined. In all cases, the contents of organic sulphate (as S) were higher than that of *Viviparus* (9.8 mg.), ranging diversely from 10.4 up to 259 mg. per 100 gr. (see Table II). From the results it would be obvious that the order of activities of enzyme is about the same as that of contents of organic sulphate. The latter, it is worthy of special mention, is just the same as that of the relative weight of the shells, thus suggesting the intimate relation between shell-formation and organic sulphate as well as gluco-sulfatase (see Table III).

The extraction by sodium chloride solution was ineffective in all cases. At the best result (*Viviparus*, muscular part) 1/2.4 of organic sulphate was extracted and at the worst one only 1/6.5 was extracted, and yet it is probable that the organic sulphate in the extract may be due to the suspending proteinous matter. Contrary to chondroitin-sulphuric acid ester, therefore, the substance seems to be difficultly soluble in sodium chloride solution. Alcohol and acetone were much more inefficient for extraction.

Some insoluble parts containing organic sulphate were subjected to peptic digestions, but in many cases they went very slowly. But the embryo of *Viviparus* was dissolved by pepsin-HCl in 2 days and the solution showed the presence of a considerable amount of organic sulphate.

The mucus secreted from fresh *Charonia* by pouring chloroform into its shell showed very interesting properties; it is coagulated by acetone or by boiling, giving gelatinous coagulum and it contains much organic sulphate together with a large quantity of inorganic sulphate. The coagulum did not dissolve in peptic and tryptic mixtures and thus we could not obtain organic sulphate in soluble form. We found, however, the existence of soluble organic sulphate in the filtrate of heat-coagulum. This filtrate, when mixed with the enzyme obtained from the liver of *Charonia*, showed some increase of inorganic sulphate, and thus we could ascertain the hydrolysis of this soluble organic sulphate by glucosulfatase. Furthermore, it is clear from our experiment that the insoluble organic sulphate was also hydrolysed by the sulfatase. (58.2% of S of insoluble organic sulphate was hydrolysed during 2 weeks' digestion by the enzyme). From the above results we are convinced of the existence of substrate of glucosulfatase probably both in soluble and insoluble form in the bodies of some shell-fishes.

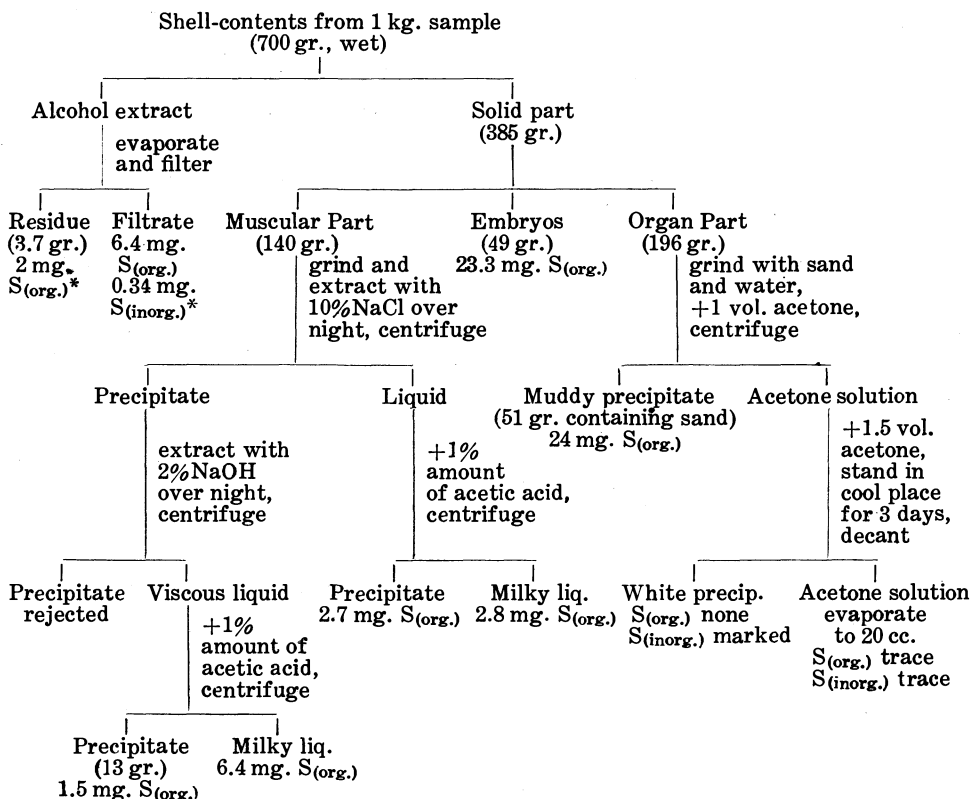
Experimental Details.

Organic and Inorganic Sulphates in *Viviparus japonicus*, Martens.
Sample: Collected in Tokyo at the beginning of July, 1932. 1 kg. of large animals was taken. After washing with running water over night, they were dipped into boiling water for 2 minutes and the shell contents were drawn out, on which the sulphates were determined separately as shown in the following scheme. On liquid parts (extracts) both organic and inorganic sulphates were determined, but on the insoluble parts the organic sulphate only was determined, as there might be no insoluble inorganic sulphate remained in the extract residue. Hydrolysis of organic sulphate was conducted by boiling 50 c.c. of extract (or the suspension of extract residue) with 14 c.c. of conc. HCl for 8-12 hrs. under a reflux condenser.

Table I.

Distribution of organic sulphate in some parts of a body of *Viviparus*.

Parts	S mg.	S mg. per 100 gr. sample
Alcohol extract	8.1	—
Muscular part	13.4	9.6
Embryos	23.3	47.6
Organ part	24	12.2
Total	68.8	(mean) 9.8

Scheme of analysis of *Viviparus japonicus*, Martens.

* S_(org.) or S_(inorg.) means sulphur of organic or inorganic sulphate.

Analyses of 4 Marine Shell-fishes.

Samples:	<i>Haliotis gigantea</i> Gmelin (Awabi)	} from market.
	<i>Turbo cornutus</i> Solander (Sazae)	
	<i>Charonia lampas</i> Linne (Bōshu-bora)	} from Misaki Marine Biological Station.
	<i>Strombus luhuanus</i> Linne (Magaki-gai)	

Their shell-contents were boiled for few minutes, ground to paste with some water and sand (free from sulphate) and extracted by 5-12 times of 10% sodium chloride solution in an ice-chamber for 2 days. The liquids were then centrifuged and the sulphates were determined on the supernatant liquid and the precipitate respectively.

Table II.

	<i>Haliotis</i>	<i>Turbo</i>	<i>Charonia</i>	<i>Strombus</i>
Weight gr.	200	131	167	88 (3 shells)
Shell-content gr. (wet)	134	39	37	24
S _(org.) mg.	in precipitate	8.5	24.0	78.4
	in extract	5.4	13.0	17.3
S _(inorg.) mg. in extract	27.4	17.4	27.0	6.7
Per 100 gr. } S _(org.) mg.	10.4	95	259	144
Shell-content } S _(inorg.) mg.	20.5	44.6	73.0	27.9

In comparing these results with the activities of enzyme reported in the previous paper,⁽¹⁾ we see the order of magnitudes of percentage of organic sulphate is in general same as that of activities of enzyme:

Table III.

	Hydrolysing power of enzyme (%)	Org. Sulphate (mg. S)	Total sulphate (mg. S)	Relative weight of shell weight of shell Total weight × 100
		Per 100 gr. shell-content		
<i>Charonia</i>	74.6	259	332	78
<i>Strombus</i>	18.3	144	171.9	73
<i>Haliotis</i>	12.5	10.4	30.9	33
<i>Turbo</i>	7.2	95	139.6	70

Digestion of the Embryos of *Viviparus* by Pepsin. Some embryos of *Viviparus*, after 1 hour's boiling with water, were digested with pancreatin and pepsin-HCl solutions. After 2 days the embryos disappeared in pepsin mixture, giving white turbid solution, which after clarification by Esbach's picric acid reagent and "Silikatzuckerkohle" showed a considerable amount of organic sulphate.

Mucus secreted from *Charonia*. Fresh *Charonia*, when treated with chloroform, secretes a large amount of mucus. The gelatinous mass, formed by the precipitation of mucus with acetone and subsequent washing with water until free from sulphate, gave on hydrolysis a marked amount of sulphate with a smaller amount of phosphate. On the other hand, soluble organic sulphate was found in the mucus, when it was heated to 100° and the heat-coagulum was filtered off. This soluble organic sulphate was precipitated incompletely by lead acetate, but completely by basic lead acetate.

Hydrolysis of Soluble and Insoluble Organic Sulphates by Gluco-sulphatase. The solution of soluble organic sulphate just above mentioned was treated with barium chloride to remove inorganic sulphate and the filtrate was mixed with enzyme obtained from the liver of *Charonia* as follows:

	A	B
Extract of enzyme	10 c.c.	10 c.c.
Filtrate (substrate)	50 c.c.	—
Water + BaCl ₂	—	50 c.c.
4/10 N-Na acetate	10 c.c.	10 c.c.
Chloroform	1 c.c.	1 c.c.

At the start there was 7.16 mg. S of organic sulphate in A. After standing for a week at 32–33°C., both were centrifuged and the precipitates of barium sulphate formed were separately collected, washed and ignited.

Found: 7.6 mg. BaSO₄ in A; 3.7 mg. BaSO₄ in B. Therefore 3.9 mg. BaSO₄ were produced from substrate by enzyme action.

The action of enzyme upon insoluble organic sulphate was examined as follows: 10 gr. of the insoluble part of *Charonia* (containing 19.1 mg. S_(org.), none of inorganic sulphate), prepared in the course of foregoing analysis, were kneaded with 20 c.c. of enzyme solution (aqueous extract of the liver of another *Charonia*, containing none of organic sulphate and 18.8 mg. S_(inorg.)) and the suspension was kept at 35–36°C. for 2 weeks with some chloroform. At the end of the experiment, there was an increase of inorganic sulphate in liquid portion (11.1 mg. S), that is to say, 58.2% of the insoluble organic sulphate were hydrolysed by the enzyme. Thus, the soluble and insoluble organic sulphates occurring naturally in the shell-fish are attacked by the enzyme.

Thanks are due to Dr. C. Hattori who kindly supplied us the sample of enzyme.

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STUDIES ON AMINO-ACIDS AND RELATED COMPOUNDS.
PART VII. ON THE OXIDATION OF VARIOUS
AMINO-ACIDS.

By Yoshitaro TAKAYAMA.

Received April 13th, 1933. Published August 28th, 1933.

Amino-acids occurring in nature can be represented by the general formula $R(NH_2) \cdot COOH$. R denotes diverse radicals of aliphatic, aromatic and heterocyclic fields, functional group of which varies from acidic, neutral to basic. In addition to these, the two compounds having imino-group, namely proline and oxyproline, are obtained from the hydrolysate of protein.

Many paper⁽¹⁾ have been published on the oxidation of amino-acids by various oxidising agents. But in almost all of these it is discussed merely on the first stage of oxidation (oxidation of α -amino-group), and the changes of the radical R are left untouched.

Recently F. Lieben and E. Molner⁽²⁾ oxidised many amino-acids with a mixture of potassium bichromate and sulphuric acid and from the results of their oxidation they classified the amino-acids into three groups as follows:

- (1) Glycine, leucine, aspartic acid, arginine, cystine, tyrosine and tryptphane.
- (2) Alanine, glutamic acid and valine.
- (3) Proline, histidine and lysine.

The author reported several studies on the electrolytic oxidation of seven kinds of amino-acids including some of their related compounds, and observed that at the equal consumption of electricity the amounts of decomposed amino-acids widely differed according to their kinds. This difference may be attributed to the relative oxidisability of the group R in the acid. Now the author intends to investigate more scrupulously the oxidation of these compounds by the following experiments.

(1) A. Strecker, *Ann.*, **123**(1862), 363; K. Langheld, *Ber.*, **42** (1909), 392, 2360; H. D. Dakin, T. B. Cohen, M. Daufresne and J. Kenoyon, *Chem. Abstract*, **10** (1916) 2912; H. Wieland und E. Bergel, *Ann.*, **439** (1924), 196; S. Goldschmidt und W. Beuschel, *Ann.*, **447** (1926), 197.

(2) F. Lieben und E. Molnar, *Monatsh.*, **53-54** (1929), 1-13.

More than ten of the amino-acids having various structure were selected and they were electrolysed under the same conditions. During the course of electrolysis the amounts of carbon dioxide and ammonia produced were measured from time to time. The experiments were carried out with following substances, those with similar structure being taken in pair in each case.

Monoamino-carboxylic acids:

Glycine, alanine, valine, leucine (aliphatic);
 Aspartic acid, glutamic acid (aliphatic dicarboxylic);
 Tyrosine, phenylalanine (aromatic);
 Proline, pyrrolidone-carboxylic acid (heterocyclic);

Diamino-carboxylic acids and others:

Lysine (aliphatic);
 Tryptophane, imidazolyl-propionic acid and histidine (heterocyclic).

Electrolytic conditions. 10 Millimols of the sample are dissolved in 30 c.c. of 2N.-sulphuric acid. C.D.: 2 amp./dm²., electrodes: lead peroxide anode and lead cathode.

Tyrosine and Phenylalanine. (Fig. I). The curves representing the course of formation of carbon dioxide and ammonia from these amino-acids nearly coincide with each other. The curves of tyrosine always lie slightly above those of phenylalanine. The same results were discussed in a previous paper.⁽³⁾

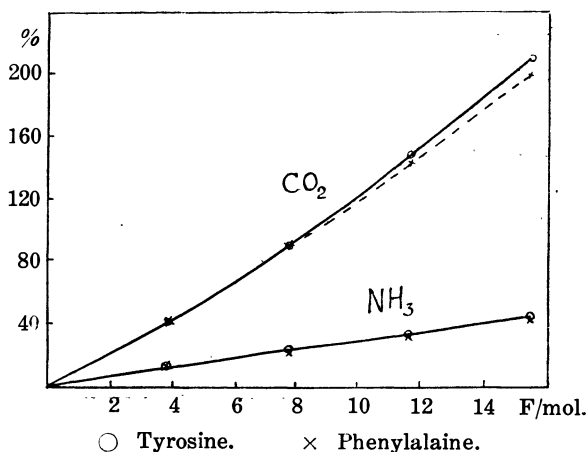


Fig. I.

(3) Part V. This Bulletin, 8 (1933), 178.

Alanine,⁽⁴⁾ Glutamic Acid⁽⁵⁾ and Aspartic Acid. (Fig. II). NH_3 -curves of the former two are in good coincidence, but some difference is observed between their CO_2 -curves. This fact may be explained as follows. α -Oxidation of the two amino-acids proceeds at equal rate, and alanine gives acetic acid while glutamic acid gives succinic acid, and the latter is less stable to oxidation than the former. CO_2 formed in excess in the case of glutamic acid is due to the more readiness to oxidation of succinic acid. NH_3 -curve of aspartic acid lies below the above two, and CO_2 -curve, on the contrary, lies far above. Aspartic acid gives the highest yield of CO_2 , which may be explained by the fact that its oxidation product (malonic acid) is markedly unstable towards oxidation.

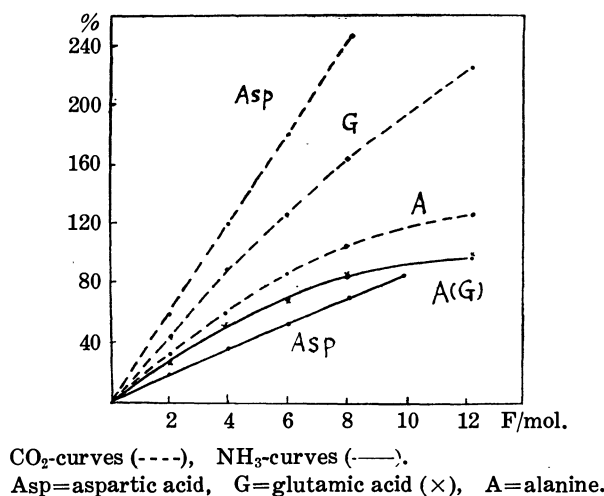
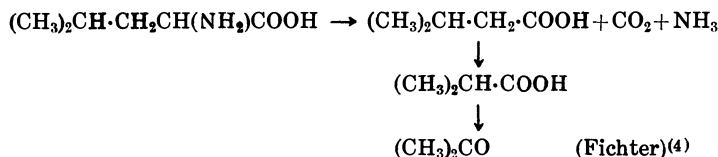


Fig. II.

Glycine, Leucine⁽⁴⁾ and Valine. (Fig III). NH_3 -curves of glycine and valine belong to the same type as that of alanine. In the case of leucine it lies considerably beneath that of alanine. CO_2 -curves of these compounds lie above that of alanine. The result shows that the radical R in leucine is less stable to anodic oxidation as Fichter has pointed out.



(4) Fr. Fichter und F. Kuhn, *Helv. chim. Acta*, **7** (1924), 167.

(5) Part. I. This Bulletin, **8**(1933), 125.

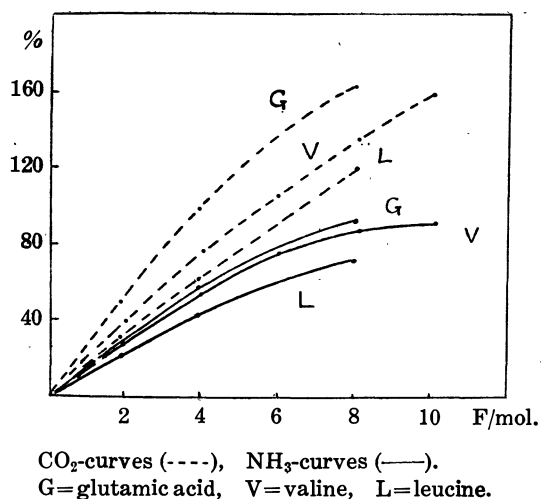


Fig. III.

Pyrrolidone-Carboxylic Acid⁽⁶⁾ and Proline. (Fig. IV). NH₃-curve of the former occupies the highest position of those of all amino-acids, and that of proline is apart from it. But the author, in fact, isolated succinimide from the oxidation products of proline—the same product as

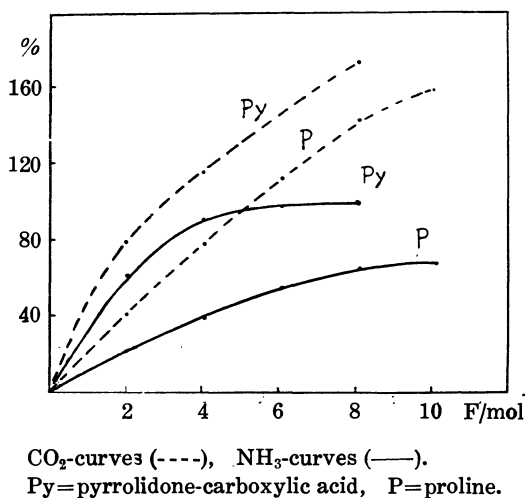
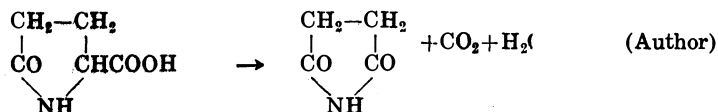


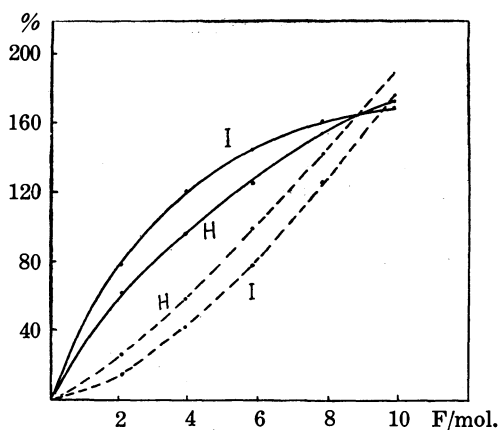
Fig. IV.

(6) Part. II. This Bulletin, 8 (1933), 137.

from pyrrolidone-carboxylic acid. The similar type of oxidation may proceed in these compounds, though somewhat different in rate.

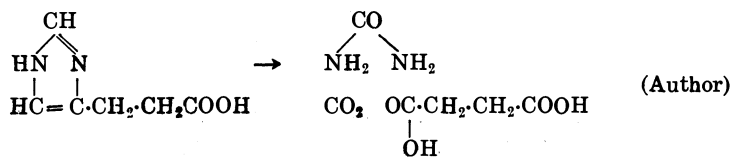


Histidine and Imidazolyl-Propionic Acid.⁽⁷⁾ (Fig. V). NH_3 -curves and CO_2 -curves of these compounds present the similar type. On oxidation, these compounds are easily attacked at their imidazol nucleus, and it is observed that a considerable amount of urea was also formed from histidine. Further works on histidine and proline are now in progress.



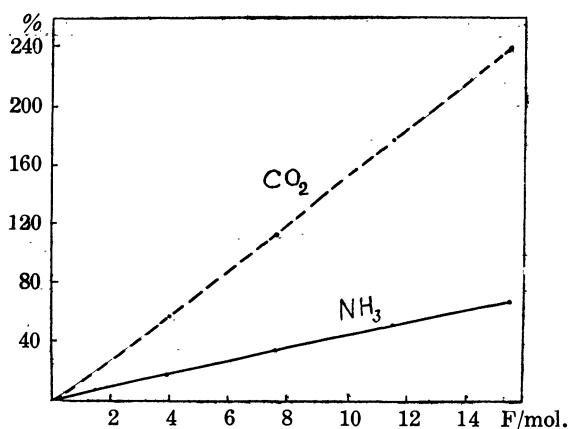
NH_3 -curves (—), CO_2 -curves (---).
I=imidazolyl-propionic acid, H=histidine.

Fig. V.



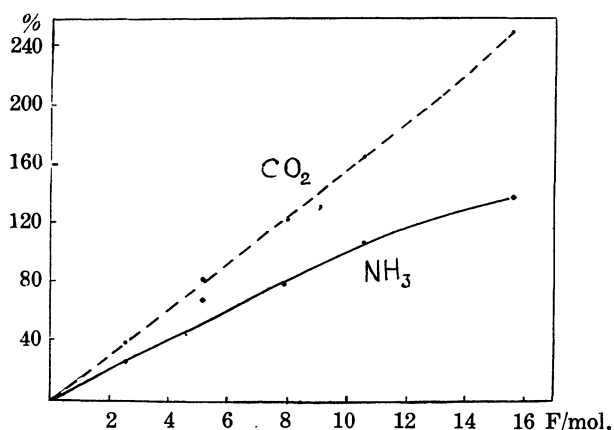
Tryptophane and Lysine. (Fig. VIa, VIb). CO_2 -curves of these compounds lie not far away from each other.

(7) Part VI. This Bulletin, 8 (1933), 189.



Tryptophane.

Fig. VIa.



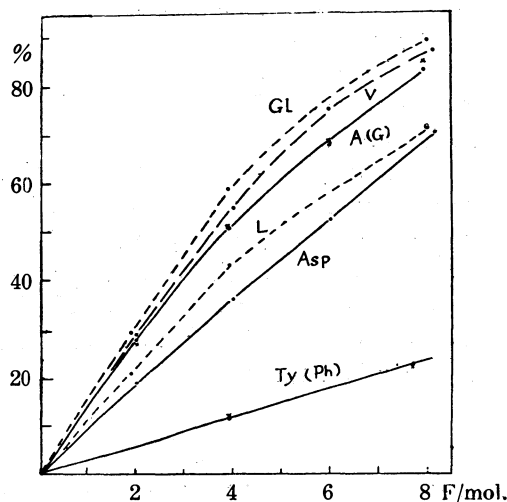
Lysine.

Fig. VIb.

Comparison of the Oxidisability of Monoaminocarboxylic Acids. (Fig. VII). By taking NH_3 -curves as a criterion of oxidisability, all amino-acids can be arranged in the following order and divided into three groups.

- I) Glycine, valine, glutamic acid and alanine.
- II) Leucine and aspartic acid.
- III) Tyrosine and phenylalanine.

The members of the first group give curves which are close together, and may be regarded as typical. Curves of the compounds of the third group are completely superposed. Those of the second group are located between the two groups.



GL=glycine, V=valine, A=alanine, G=glutamic acid (×).
L=leucine, Asp=aspartic acid, Ty=tyrosine, Ph=phenylalanine (×).

Fig. VII.

Colours of the Electrolysates. The electrolysates of some amino-acids are colourless, while those of others are coloured.

- (A) Colourless:
Glycine, alanine, valine, leucine, aspartic acid, glutamic acid and pyrrolidone-carboxylic acid.
- (B) Coloured, but formation of melanin-like substance is not observed:
Lysine (faint yellow), proline (light brown then colourless).
- (C) Dark coloured, and a black melanin (humins) is formed after a certain time:
Tyrosine, phenylalanine (red, then turning to dark brown), tryptophane (dark yellowish brown), histidine (dark purple).

It is a well known fact that during the hydrolysis of protein a black amorphous powder named humins is formed. According to Roxas⁽⁸⁾ following amino-acids have a share in humins formation during the hydrolysis of protein; namely tryptophane, tyrosine, cystine, lysine, arginine, histidine and proline (under a certain condition). Author's results fairly agree with that of Roxas, thus, substances which are classified under (B)

(8) M. L. Roxas, *J. Biol. Chem.*, **27** (1916), 71.

and (C) groups are all those mentioned by Roxas as amino-acids that form humin.

It is cited by many authors that the amino-acids, on oxidation, yield corresponding aldehydes having one atom of carbon less. But in the author's experiments carbonyl compounds are not isolated except in one case, namely imidazolyl-propionic acid. It may be considered that the carbonyl compounds perhaps once formed are soon further oxidised to acids by the vigorous action of lead peroxide anode.

The results of the communications hitherto published may be briefly summarised as follows. Aliphatic α -amino-acids first undergo α -oxidation and produce corresponding aldehydes, which are at once converted into acids. Through further oxidation various products are obtained according to the difference of R-groups. As for aromatic and heterocyclic α -amino-acids, their behaviour on electrolytic oxidation are complicated, and specific groups R are easily attacked. Moreover, these amino-acids produce melanin or humin-like substances.

Experimental Part.

Amino-acids used in this experiment were as follows:

- l*-Tyrosine, N = 7.76% (calc. for $C_9H_{11}O_3N$, N = 7.74%).
- l*-Phenylalanine, N = 8.47% (calc. for $C_9H_{11}O_2N$, N = 8.48%).
- dl*-Alanine (Kahlbaum), N = 15.75% (calc. for $C_3H_7O_2N$, N = 15.73%).
- d*-Glutamic acid, N = 9.36% (calc. for $C_5H_9O_4N$, N = 9.50%).
- Glycine (Merck), N = 18.58% (calc. for $C_2H_5O_2N$, N = 18.67%).
(Kahlbaum) N = 18.66%.
- dl*-Valine (Eastman), N = 12.27% (calc. for $C_5H_{11}O_2N$, N = 11.96%).
- l*-Leucine, N = 10.84% (calc. for $C_6H_{13}O_2N$, N = 10.69%).
- dl*-Aspartic acid (Kahlbaum), N = 10.68% (calc. for $C_4H_7O_4N$, N = 10.53%).
- d*-Lysine picrate, picric acid = 60.87% (calc. for $C_6H_{14}O_2N_2 \cdot C_6H_3O_7N_3$, picric acid = 61.06%).
- l*-Tryptophane (Th. Schuchardt), N = 13.42% (calc. for $C_{11}H_{12}O_2N_2$, N = 13.72%).
- l*-Pyrrolidone-carboxylic acid, N = 10.82% (calc. for $C_5H_7O_3N$, N = 10.85%).
- l*-Proline (Fraenkel u. Landau), N = 11.96% (calc. for $C_5H_9O_2N$, N = 12.17%).
- β -Imidazolyl-propionic acid, N = 19.80% (calc. for $C_6H_8O_2N_2$, N = 19.99%).
- l*-Histidine dihydrochloride, N = 18.43% (calc. for $C_6H_9O_2N_3 \cdot 2HCl$, N = 18.42%).

Apparatus is shown in Fig. VIII.

Cell: A cylindrical glass vessel of 60 c.c. capacity, provided with a rubber stopper which carries two electrodes and a rubber stoppered tube (C). The latter (C) is used to pass air after every interruption of electrolysis and at the same time to withdraw the solution with a pipette. To the cell was fused a spiral condenser which serves as delivery tube. It was connected to a bubbler (E) by a piece of rubber tubing.

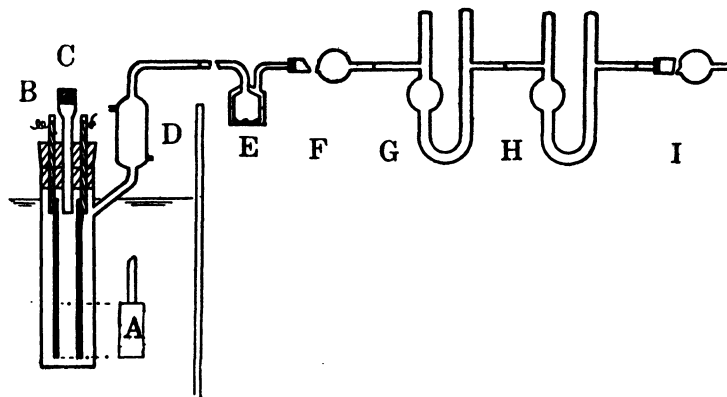


Fig. VIII.

- A: Electrodes, lead peroxide anode and lead cathode (2×4 cm.)
 B: Brass rods which support electrodes, coated with bakelite varnish.
 D: Spiral condenser.
 E: Bubbler containing concentrated sulphuric acid.
 F: Calcium chloride tube for drying gases.
 G and H: Tared absorption tubes for CO₂ containing soda-lime.
 I: Calcium chloride guard tube.

Generally ten millimols (in some cases 5 millimols) of amino-acids were dissolved in 30 c.c. of 2N.-sulphuric acid. The solution was electrolysed in the above cell which was kept at a constant temperature (30° or 35°) in a thermostat. Current density was 0.16 amp./ 2×4 cm. = 2 amp./dm². The amount of electricity was determined by copper coulometer.

After every definite consumption of electricity, i.e. 2F/mol, 4 F/mol and so on, electrolysis was interrupted. Air freed from CO₂ was passed through the apparatus from the tube (C) for about half an hour until all of the CO₂ was replaced by air. Soda-lime tubes were weighed. From the increase of weight of these tubes the amount of carbon dioxide formed was estimated and expressed in molar percentage to amino-acid used. 0.2–0.3 c.c. and 0.3–1.0 c.c. of the solution were drawn out with a pipette from the tube (C) and exactly weighed. In the former total-N and in the latter NH₃-N were determined.* After each set of determinations

* Determination of NH₃ was strictly carried out under the following conditions using micro-Kjeldahl apparatus. 5 c.c. of 30% NaOH were added and steam was passed through the solution for ten minutes.

The amount of water decomposed by electrolysis under this condition is ca. 0.09 c.c. for 1F/mol. Thus the loss of water caused by this effect is neglected.

the volume of the solution was diminished by 0.5–1.3 c.c. The current quantity applied before next determination was reduced to such an extent as 2F/mol is maintained in relation to the original volume of the solution. Correction was made to the amount of CO₂ by the same reason.

Table I. Tyrosine and Phenylalanine.

Solutions: 1.8049 gr. (10.04 millimols) of tyrosine in 30 c.c. of 2N.-H₂SO₄; 1.6498 gr. (9.99 millimols) of phenylalanine in 30 c.c. of 2N.-H₂SO₄; Temp.: 35°C.

Subst. millimols.	Faradays per mol.	CO ₂ mol %	NH ₃ -N mg.	Total-N mg.	NH ₃ -N/Total-N mol %
I Tyrosine 10.04	1.2093 gr. Cu 3.81	0.1753 gr. 39.9	0.448 mg. in 1 c.c.	1.237 mg. in 0.3 c.c.	10.85
I Phenylalanine 9.99	„	40.1	0.456 1 c.c.	1.240 0.3 c.c.	10.97
II Tyrosine $10.04 \times \frac{28.0}{30.0}$	$\frac{3.87}{\text{Total } 7.68}$	$\frac{49.2}{\text{Total } 89.1}$	0.951 1 c.c.	1.262 0.3 c.c.	22.27
II Phenylalanine $9.99 \times \frac{28.0}{30.0}$	„	$\frac{48.8}{88.9}$	0.913 1 c.c.	1.262 0.3 c.c.	21.72
III Tyrosine $10.04 \times \frac{26.7}{30.0}$	$\frac{3.95}{11.63}$	$\frac{59.2}{148.3}$	0.726 0.5 c.c.	1.257 0.3 c.c.	34.64
III Phenylalanine $9.99 \times \frac{26.7}{30.0}$	„	$\frac{53.7}{142.6}$	0.688 0.5 c.c.	1.256 0.3 c.c.	32.96
IV Tyrosine $10.04 \times \frac{25.9}{30.0}$	$\frac{3.91}{15.54}$	$\frac{60.7}{209.0}$	0.955 0.5 c.c.	1.292 0.3 c.c.	44.34
IV Phenylalanine $9.99 \times \frac{25.9}{30.0}$	„	$\frac{57.0}{199.6}$	0.896 0.5 c.c.	1.264 0.3 c.c.	42.54

Table II. Glutamic Acid and Alanine.

Solutions: 1.4765 gr. (10.04 millimols) of glutamic acid in
30 c.c. of 2N.-H₂SO₄; 0.8917 gr. (10.03 millimols) of
alanine in 30 c.c. of 2N.-H₂SO₄; Temp.: 35°C.

Subst. millimols.	Faradays per mol.	CO ₂ mol %	NH ₃ -N mg.	Total-N mg.	NH ₃ -N/Total-N mol %.
I Glutamic acid 10.04	2.010	42.5	1.111 1 c.c.	0.853 0.2 c.c.	26.0
I Alanine 10.03	„	32.95	1.231 1 c.c.	0.892 0.2 c.c.	27.6
II Glut. acid $10.04 \times \frac{28.8}{30.0}$	3.918	87.53	1.075 0.5 c.c.	0.842 0.2 c.c.	51.0
II Alanine $10.03 \times \frac{28.8}{30.0}$	„	59.91	1.129 0.5 c.c.	0.897 0.2 c.c.	50.4
III Glut. acid $10.04 \times \frac{28.1}{30.0}$	5.972	126.8	1.418 0.5 c.c.	0.832 0.2 c.c.	68.1
III Alanine $10.03 \times \frac{28.1}{30.0}$	„	86.11	1.570 0.5 c.c.	0.933 0.2 c.c.	67.3
IV Glut. acid $10.04 \times \frac{27.6}{30.0}$	7.950	163.0	1.027 0.3 c.c.	0.808 0.2 c.c.	84.7
IV Alanine $10.03 \times \frac{27.6}{30.0}$	„	104.6	1.168 0.3 c.c.	0.874 0.2 c.c.	82.9
V Glut. acid $10.04 \times \frac{27.1}{30.0}$	12.19	224.2	1.145 0.3395 gr.	1.180 0.2220 gr.	97.0
V Alanine $10.03 \times \frac{27.1}{30.0}$	„	125.8	1.348 0.3286 gr.	0.950 0.2211 gr.	95.5

Table III. Valine and Aspartic Acid.

Solutions: 1.1686 gr. (10.03 millimols) of valine in 30 c.c. of 2N.-H₂SO₄; 1.3303 gr. (9.997 millimols) of aspartic acid in 30 c.c. of 2N.-H₂SO₄; Temp.: 35°C.

Subst. millimols.	Faradays per mol.	CO ₂ mol %.	NH ₃ -N mg.	Total-N mg.	NH ₃ -N/Total-N mol %.
I Valine 10.03	2.014	38.5	1.254 1.032 gr.	1.775 0.4141 gr.	28.4
I Aspartic acid 9.997	„	59.1	0.860 1.0549 gr.	1.867 0.4296 gr.	18.8
II Valine $10.03 \times \frac{28.6}{30.0}$	4.024	75.2	1.231 0.5221 gr.	0.895 0.2067 gr.	54.4
II Aspartic acid $9.997 \times \frac{28.6}{30.0}$	„	119.9	0.831 0.5450 gr.	0.902 0.2111 gr.	35.7
III Valine $10.03 \times \frac{27.9}{30.0}$	6.031	106.6	1.632 0.5247 gr.	0.881 0.2130 gr.	75.2
III Aspartic acid $9.997 \times \frac{27.9}{30.0}$	„	179.6	1.155 0.5306 gr.	0.891 0.2128 gr.	52.1
IV Valine $10.03 \times \frac{27.2}{30.0}$	8.135	135.8	1.885 0.5135 gr.	0.938 0.2222 gr.	87.0
IV Aspartic acid $9.997 \times \frac{27.2}{30.0}$	„	243.6	1.497 0.5249 gr.	0.856 0.2112 gr.	70.3
V Valine $10.03 \times \frac{26.5}{30.0}$	10.17	156.8	2.070 0.5236 gr.	0.948 2.070 gr.	91.2
V Aspartic acid $9.997 \times \frac{26.5}{30.0}$	„	303.3	1.792 0.5210 gr.	0.838 0.2131 gr.	87.2

Table IVa. Glycine and Leucine.

Solutions: 0.7553 gr. (10.07 millimols) of glycine in 30 c.c. of 2N.-H₂SO₄; 1.3126 gr. (10.02 millimols) of leucine in 30 c.c. of 2N.-H₂SO₄; Temp.: 35°C.

Subst. millimols.	Faradays per mol.	CO ₂ mol %.	NH ₃ -N mg.	Total-N mg.	NH ₃ -N/Total-N mol %.
I Glycine 10.07	1.905	48.8	1.277 1.0497 gr.	0.880 0.2118 gr.	29.2
I Leucine 10.02	„	30.0	0.878 1.0326 gr.	0.859 0.2075 gr.	20.5
II Glycine $10.07 \times \frac{28.8}{30.0}$	3.932	98.6	1.231 0.5289 gr.	0.870 0.2199 gr.	58.9
II Leucine $10.02 \times \frac{28.8}{30.0}$	„	62.3	0.938 0.5345 gr.	0.898 0.2200 gr.	43.0
III Glycine $10.07 \times \frac{28.1}{30.0}$	8.06	161.5	1.741 0.5298 gr.	0.796 0.2152 gr.	89.1
III Leucine $10.02 \times \frac{28.1}{30.0}$	„	121.6	1.425 0.5110 gr.	0.839 0.2141 gr.	71.2

Table IVb. Glycine and Leucine.

Solutions: 0.7514 gr. (10.01 millimols) of glycine in 30 c.c. of 2N.-H₂SO₄; 1.3087 gr. (9.982 millimols) of leucine in 30 c.c. of 2N.-H₂SO₄; Temp.: 30°C.

Subst. millimols	Faradays per mol.	CO ₂ mol %.	NH ₃ -N mg.	Total-N mg.	NH ₃ -N/Total-N mol %.
I Glycine 10.01	2.056	45.25	0.568 0.5434 gr.	1.368 0.3332 gr.	25.5
I Leucine 9.982	„	24.70	0.3180 0.5315 gr.	1.310 0.3285 gr.	15.0

Table IVb.—(Concluded)

Subst. millimols	Faradays per mol	CO ₂ mol %.	NH ₃ -N mg.	Total-N mg.	NH ₃ -N/Total-N mol %
II Glycine $10.01 \times \frac{29.2}{30.0}$	4.094	85.33	1.051 0.5430 gr.	1.250 0.3297 gr.	51.1
II Leucine $9.982 \times \frac{29.2}{30.0}$	„	56.85	0.662 0.5298 gr.	1.323 0.3253 gr.	30.7
III Glycine $10.01 \times \frac{28.4}{30.0}$	6.170	120.5	1.266 0.5270 gr.	1.253 0.3257 gr.	60.5
III Leucine $9.982 \times \frac{28.4}{30.0}$	„	87.85	0.957 0.5320 gr.	1.323 0.3290 gr.	44.8
IV Glycine $10.01 \times \frac{27.6}{30.0}$	8.16	145.2	0.727 0.2199 gr.	1.296 0.3318 gr.	84.7
IV Leucine $9.982 \times \frac{27.6}{30.0}$	„	118.3	0.518 0.2259 gr.	1.294 0.3266 gr.	57.9
V Glycine $10.01 \times \frac{27.1}{30.0}$	10.12	161.1	1.215 0.3289 gr.	0.858 0.2226 gr.	95.7
V Leucine $9.982 \times \frac{27.1}{30.0}$	„	145.7	0.830 0.3210 gr.	0.848 0.2175 gr.	66.3
VI Leucine $9.982 \times \frac{26.6}{30.0}$	12.24	171.6	0.881 0.3163 gr.	0.868 0.2235 gr.	71.7

Table V. Pyrrolidone-Carboxylic Acid and Proline.

Solutions: 1.2909 gr. (10.00 millimols) of *l*-pyrrolidone-carboxylic acid in 30 c.c. of 2N.-H₂SO₄; 1.1507 gr. (10.00 millimols) of proline in 30 c.c. of 2N.-H₂SO₄; Temp.: 30°C.

Subst. millimols.	Faradays per mol.	CO ₂ mol %.	NH ₃ -N mg.	Total-N mg.	NH ₃ -N/Total-N mol %
I Pyrrolidone carb. acid 10.00	2.054	74.3	1.462 0.5568 gr.	1.393 0.3238 gr.	60.9
I Proline 10.00	„	41.3	0.494 0.5420 gr.	0.425 0.100 gr.	21.4
II Pyrrolidone carb. acid $10.00 \times \frac{29.2}{30.0}$	4.067	101.5	1.680 0.4280 gr.	1.380 0.3157 gr.	89.7
II Proline $10.00 \times \frac{29.2}{30.0}$	„	77.6	0.668 0.4341 gr.	1.356 0.3210 gr.	36.5
III Pyrrolidone carb. acid $10.00 \times \frac{28.5}{30.0}$	6.099	136.0	1.389 0.3288 gr.	0.986 0.2241 gr.	96.1
III Proline $10.00 \times \frac{28.5}{30.0}$	„	111.5	0.738 0.3256 gr.	0.943 0.2205 gr.	54.8
IV Pyrrolidone carb. acid $10.00 \times \frac{28.0}{30.0}$	8.031	173.4	1.396 0.3210 gr.	1.470 0.3296 gr.	97.4
IV Proline $10.00 \times \frac{28.0}{30.0}$	8.096	142.9	0.895 0.3266 gr.	0.944 0.2290 gr.	66.4
V Proline $10.00 \times \frac{27.5}{30.0}$	10.32	158.5	0.965 0.3321 gr.	0.927 0.2165 gr.	68.0

Table VI. β -Imidazolyl-Propionic Acid and Histidine.

Solutions: 1.4013 gr. (10.00 millimols) of imidazolyl-propionic acid in 30 c.c. of 2N.-H₂SO₄; 10 millimols of histidine in 30 c.c. of 2N.-H₂SO₄; Temp.: 30°C.

Subst. millimols.	Faradays per mol.	CO ₂ mol %	NH ₃ -N mg.	Total-N mg.	NH ₃ -N/Total-N mol %.
I Histidine 10.00	2.072	24.78	0.624 0.2298 gr.	1.446 0.1130 gr.	63.7
I Imidaz. prop. acid. 10.00	„	13.93	0.724 0.2244 gr.	0.927 0.1107 gr.	76.8
II Histidine $10.00 \times \frac{29.7}{30.0}$	3.95	59.60	0.894 0.2210 gr.	0.1610 0.1263 gr.	95.1
II Imidaz. prop. acid. $10.00 \times \frac{29.7}{30.0}$	„	42.00	1.108 0.2219 gr.	1.00 0.1204 gr.	120.5
III Histidine $10.00 \times \frac{29.4}{30.0}$	5.830	99.5	1.148 0.2230 gr.	1.436 0.1155 gr.	124.2
III Imidaz. prop. acid $10.00 \times \frac{29.4}{30.0}$	„	78.63	1.345 0.2215 gr.	0.842 0.100 gr.	144.2
IV Histidine $10.00 \times \frac{29.1}{30.0}$	7.82	143.0	1.336 0.2072 gr.	1.397 0.1120 gr.	155.4
IV Imidas. prop. acid $10.00 \times \frac{29.1}{30.0}$	„	127.9	1.512 0.2180 gr.	0.981 0.1149 gr.	162.4
V Histidine $10.00 \times \frac{28.8}{30.0}$	9.94	189.6	1.615 0.2265 gr.	1.361 0.1123 gr.	176.7
V Imidas. prop. acid $10.00 \times \frac{28.8}{30.0}$	„	175.8	1.588 0.2205 gr.	1.044 0.1230 gr.	169.4

Eleven millimols of histidine dihydrochloride were dissolved in 25 c.c. of 2N.-sulphuric acid and sufficient water was added to it. It was distilled under reduced pressure to drive off hydrochloric acid. The above treatment was repeated several times until the solution showed no trace of hydrochloric acid. The solution was made up to 25 c.c. (total-N 455.9 mg.) from which 23.08-c.c. were taken for electrolysis (corresponding to 10 millimols of histidine).

It was ascertained that imidazolyl-propionic acid did not yield ammonia when it was treated with steam in the presence of conc. sodium hydroxide.

The electrolysate of β -imidazolyl-propionic acid assumed yellowish tint as the electrolysis proceeded, it was transparent throughout the whole course. In the case of histidine, dark purple colouration was already observed after an hour and melanine-like substance began to deposit at 4F/mol and adhered to the electrodes.

Table VII. Tryptophane.

Solutions: 1.0200 gr. (5.00 millimols) of tryptophane in
30 c.c. of 2N.-H₂SO₄; Temp.: 35°C.

Subst. millimols	Faradays per mol	CO ₂ mol %.	NH -N mg.	Total-N mg.	NH ₃ -N/Total-N mol %.
Tryptophane 5	3.88	57.2	0.396 1.094 gr.	0.954 0.2241 gr.	17.0
" $5 \times \frac{28.8}{30.0}$	7.55	113.2	0.715 1.0571 gr.	0.835 0.2087 gr.	33.8
" $5 \times \frac{27.6}{30.0}$	11.45	176.8	0.556 0.5194 gr.	0.949 0.2278 gr.	51.4
" $5 \times \frac{26.9}{30.0}$	15.35	239.6	0.730 0.5244 gr.	0.897 0.2174 gr.	67.4

Table VIII. Lysine.

Solutions: 7.49 millimols of lysine* in 30 c.c. of ca. 2N.-H₂SO₄;
Temp.: 35°C.

Subst. millimols.	Faradays per mol	CO ₂ mol %.	NH ₃ -N mg.	Total-N mg.	NH ₃ -N/Total-N mol %.
Lysine 7.49	2.49	37.6	0.433 0.5 c.c.	0.700 0.1 c.c.	24.6
" $7.49 \times \frac{29.4}{30.0}$	5.16	80.1	0.495 0.2 c.c.	1.471 0.2 c.c.	67.2
" $7.49 \times \frac{28.4}{30.0}$	7.94	122.2	1.533 0.5 c.c.	1.578 0.2 c.c.	77.8
" $7.49 \times \frac{27.7}{30.0}$	10.55	165.0	1.749 0.4 c.c.	1.624 0.2 c.c.	107.8
" $7.49 \times \frac{26.7}{30.0}$	15.85	249.8	2.280 0.4 c.c.	1.651 0.2 c.c.	138.2

* 3.75 gr. (10 millimols) of lysine picrate were dissolved in 25 c.c. of 2N.-sulphuric acid. The solution was thoroughly extracted with ether to remove picric acid. By adding 2N.-sulphuric acid the solution was made up to 30 c.c. (content of lysine equals to 7.49 millimols).

In conclusion, the author wishes to express his sincere thanks to Professor K. Matsubara for his kind encouragement and invaluable advices given to these studies. At the same time, the author is also indebted to continuous suggestions of Mr. W. Nagai and untired assistance of Mr. H. Ôeda to complete these studies.

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WATER VAPOUR EQUILIBRIA ON VANADIUM AND ITS OXIDES.

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Received June 16th, 1933. Published August 28th, 1933.

Synopsis.

The oxidation-reduction equilibrium of vanadium has been investigated by the dynamical method of Wartenberg and Aoyama. By the experiment it has been suggested that the chemical changes take place in the two stages under the experimental conditions, and the reactions might be expressed by the following: $V + H_2O \rightleftharpoons VO + H_2$ and $2VO + H_2O \rightleftharpoons V_2O_3 + H_2$. Thermodynamic calculations have been made for the above reactions, and the result of the calculated heats of formation agreed fairly well with that of the determinations made by other investigators.

Introduction.

A reduction equilibrium on chromic oxide was determined by H. v. Wartenberg and S. Aoyama⁽¹⁾ in 1927. The principle applied by these investigators consisted of passing a stream of hydrogen saturated with water vapour of known partial pressure on metallic chromium and the oxidation equilibrium is measured at various temperatures by observing the change in colour which takes place on the surface of the metal due to the process of oxidation and reduction going on by the small quantity of oxygen. Later in 1932, by applying the same principle S. Aoyama and Y. Oka⁽²⁾ determined the oxidation-reduction equilibrium of manganese, in distilled state. Since vanadium is a very refractory substance, and is hardly reducible like the metals mentioned above, and its oxide is reducible by hydrogen only when the latter is carefully dried⁽³⁾, it has been attempted by the present writer to measure the oxidation equilibrium of vanadium by the principle described above.

Experimental.

Apparatus. The apparatus used was quite the same as described by Wartenberg and Aoyama in their paper, except the reaction tube and the pump for circulating gas. Instead of a silica-tube, a pyrex glass-tube,

(1) *Z. Elektrochem.*, **33** (1927), 144.

(2) *Nippon Kagaku-kaishi (J. Chem. Soc. Japan)*, **53** (1932), 417.

(3) H. v. Wartenberg, J. Broy & R. Reinicke. *Z. Elektrochem.*, **29** (1923), 214.

5 cm. in diameter and 50 cm. in length, was used as the reaction tube (Fig. 1). To the lower end of the pyrex tube was attached a glass cap with a side tube for introducing hydrogen having a rubber stopper which is overlaid with mercury, and through which two insulated copper leading rods, each 3 mm. in thickness, were thrust into the pyrex tube. The

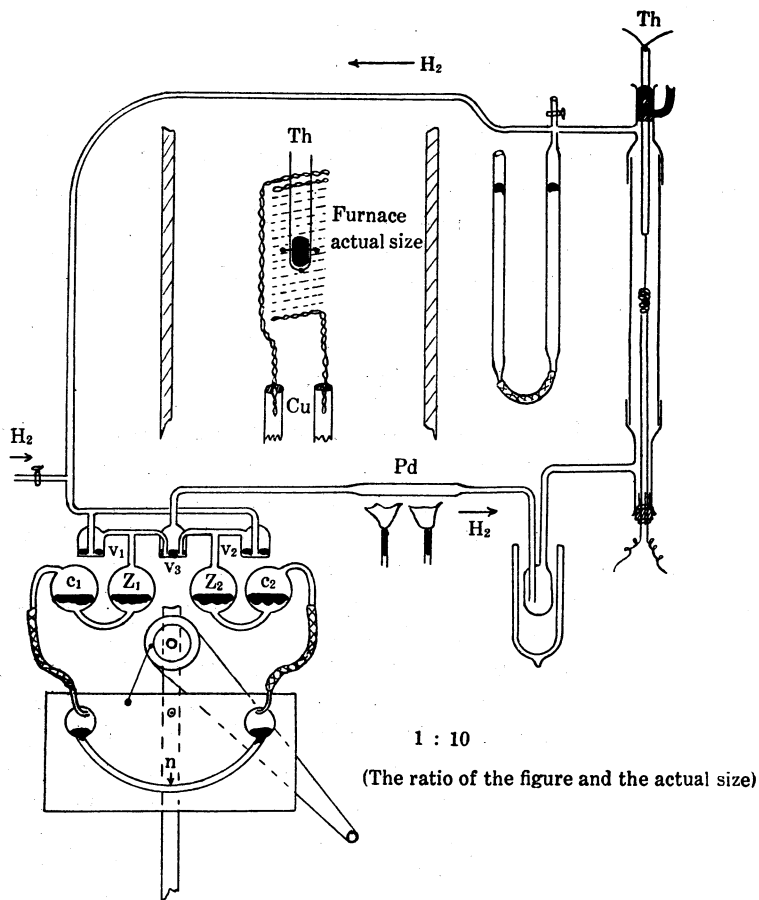


Fig. 1.

joint between the pyrex tube and the glass cap was made tight with picein. A small hole was made at the top of each copper rod to which was inserted each end of molybdenum spiral, of the furnace which is 25 mm. in length, 1 cm. in diameter and 18 turns of the spiral. (Two molybdenum wires each 0.4 mm. in diameter were twisted in making the furnace). On the top of the pyrex tube a glass cap was placed having

an exit tube for hydrogen and also a hanger for a piece of metallic vanadium ($3 \times 4 \times 5$ mm.). A thermocouple was fused in a glass tube, which is movable through two cork stoppers and is made gas tight with mercury seal. The piece of the metallic vanadium was bound with Pt-wire directly at the junction of the couple.

The pump for circulating gas used in this experiment was a modified form of mercury pump devised by K. Scheel and W. Heuse⁽⁴⁾, and had been constructed by Dr. S. Aoyama for his recent experiment on manganese. The mercury pump which has been kindly lent by Dr. Aoyama consists of two glass bulbs Z_1 and Z_2 , in which mercury is filled and emptied, alternately, by the pressure due to contraction and expansion of air of constant volume in the communicating bulbs c_1 and c_2 . The contraction and expansion of the air are caused by the alternating lateral motion (effected by a motor) of glass tube n , which is half filled with mercury and each end of which is connected to the communicating bulbs with rubber tubes; the mercury in n remains almost stationary even while n moves. If, for example, n inclines to the right, the air in c_1 expands resulting the mercury in Z_1 to be emptied and filling the mercury in c_1 . Due to the depression of mercury in Z_1 hydrogen is inhaled through mercury valve v_1 ; when n inclines to the left the hydrogen is puffed off through mercury valve v_3 . Hydrogen passes then over Pd-asbestos heated at about 200°C ., and then through the trap dipped in a Dewar's beaker into the pyrex tube and from here returns again to Pd-asbestos through the pump, with a current velocity of about 200 c.c. per minute. The communicating tube of mercury serves to keep the pressure in the closed system at one atmospheric pressure when the furnace is heated at high temperatures.

The furnace was heated by an electric current; a temperature of 1300°C . has been obtained by a current of 18 amperes at 24 volts:

Bath. The temperatures of the bath applied were:

-78.5°C. (carbon dioxide-alcohol),	
-19.5°C. (sodium chloride-ice mixtures),	
-37.0°C. (melting mercury)	} frozen by pouring liquid air drop by drop on mercury and kept it constant temperature within $\pm 0.3^\circ\text{C}$. by hand regulation,
-47.0°C. (solid mercury)	
-57.0°C. (" ")	

corresponding respectively to $p_{\text{H}_2\text{O}} = 6.65 \cdot 10^{-7}$ atm. press.⁽⁵⁾; $1.07 \cdot 10^{-3}$, $1.76 \cdot 10^{-4}$, $5.53 \cdot 10^{-5}$, $1.45 \cdot 10^{-5}$ atm. press.⁽⁶⁾

(4) *Ann. Phys.*, **40** (1913), 474.

(5) Vapour pressure of H_2O , Daut, *Z. Physik. Chem.*, **106** (1923), 263.

(6) " " " Landolt Börnstein Roth/Scheel, Hw., II, 1315.

Material. The vanadium was prepared by the Goldschmidt method, using 100 parts V_2O_5 , 40 parts Al, and 12 parts Na_2CO_3 as flux⁽⁷⁾ in an alundum crucible lined with pure magnesia, and the chemical analysis indicates:

Slag (mainly Al_2O_3)	V	Al	Fe
1.4	97.0	1.5	0.4

Results.

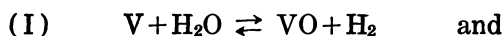
Preliminary Experiments. By the use of the apparatus described above some preliminary experiments were carried out as to see whether vanadium metal could be distinguished merely by its appearance from its oxide that has been produced when the metal was heated at various temperatures in an atmosphere of hydrogen saturated with water vapour of very small partial pressure. In the first experiment, the temperature of the bath was kept at $-19.5^\circ C$. (sodium chloride-ice mixtures), and vanadium was heated at $1000^\circ C$. for 2 hours. After cooling it was found that the silver-white metallic surface altered to black. As the temperature of the furnace was then raised to $1050^\circ C$. and maintained at this temperature for half an hour, the colour of the metallic surface became darker. After the temperature was raised to and maintained at $1150^\circ C$. for an hour, it was found that the colour faded to grey. Then, it was again heated at the same temperature for another hour, but no change in colour was noticed. In spite of the fact that the heating temperature was further raised about every $100^\circ C$. up to $1550^\circ C$., and the time for maintaining each temperature was set to about 3 hours, it still remained grey; thus an attempt to reduce the metal to its initial condition was proved unsuccessful, since it was found experimentally difficult to maintain the heating for so many hours at such an elevated temperature as above $1550^\circ C$. In the second experiment, the temperature of the bath was lowered and kept at $-78.5^\circ C$. (carbon dioxide-alcohol), and a different piece of vanadium metal was heated at $1400^\circ C$. for an hour and a half. This time no physical change has been observed upon the metal. The temperature was then lowered to $1000^\circ C$. and maintained at this temperature for a quarter of an hour. During this time the colour of the surface changed to faint grey. The temperature was, therefore, again raised to $1100^\circ C$., and after being maintained at this temperature for an hour, it was reduced to its original condition. When the metal was heated at $900^\circ C$. for half an hour, it was again tinged with grey. The colour

(7) M. Oya, *Sci. Rep., Tohoku Imp. Univ., Japan*, **19** (1930), 236.

was still unchanged after the heating had been continued for further 3 hours under the same temperature. In order to see whether it would be darkened in colour at the lower temperatures, as might have been expected from the above first preliminary experiment, the temperature was lowered about 100°C. at a time. At 600°C. it remained grey, in spite of the fact that the heating had been continued for 20 hours; while after 20 hours' heating at 500°C., it was recognized undoubtedly that the grey colour changed to black.

It will be obvious from the above experiments that there must be two different forms of vanadium oxides under the present experimental conditions. It can be stated that they are in equilibrium with each other, besides vanadium with the lower oxide. It is also found that the equilibrium temperatures of carbon dioxide-alcohol bath (-78.5°C.) are between 500 and 600°C. and also 1000 and 1100°C.

Among the following well known vanadium oxides⁽⁸⁾, VO (or V₂O₂), V₂O₃, V₂O₄ and V₂O₅, the last two are easily reduced to V₂O₃ by dry hydrogen⁽⁹⁾, and, moreover, according to H. Müller⁽¹⁰⁾ the values of $K = p_{\text{H}_2\text{O}}/p_{\text{H}_2}$ in the V₂O₄/V₂O₃-reaction, $\text{V}_2\text{O}_3 + \text{H}_2\text{O} \rightleftharpoons \text{V}_2\text{O}_4 + \text{H}_2$, are to be 2.20–5.03 over the range of temperature 493–606°C, and the values of K in the V₂O₅/V₂O₄-reaction, $\text{V}_2\text{O}_4 + \text{H}_2\text{O} \rightleftharpoons \text{V}_2\text{O}_5 + \text{H}_2$, are to be 7.6–23.3 over the range of temperature 496–600°C. In the present experiment the values of $K = p_{\text{H}_2\text{O}}/p_{\text{H}_2} = p_{\text{H}_2\text{O}}/1 = 10^{-7} \sim 10^{-3}$ as it has been described above. Therefore, under the present experimental conditions these oxides are considered to be out of question, and it is assumed that the reactions may be expressed by (I) and (II), as follows :



This must yet be confirmed by the calculation of thermal values of the reactions. This calculation will be described subsequently.

Final Experiments. Now then, the equilibrium temperatures of both reactions were measured at the bath temperatures mentioned above. Each equilibrium temperature of oxidation and reduction was obtained as the mean of adjacent temperatures within about 20°C.

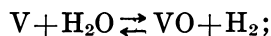
The results are shown in Tables 1 and 2. The experimental results are best detected by the fact that in each reaction the relation between

(8) J. W. Mellor, *Comp. Treat. Inorg. Chem.*, **9** (1929), 739.

(9) cf. (8) p. 741, 744.

(10) W. Biltz's *Festschrift*, Hannover (1927); cf. (8) p. 741, 744.

Table 1.

(i) Bath -78.5°C .

Thermoelec. force millivolts	Initial colour of V	Result	Concluded to be
10.7	silver-white	after 4 hrs. grey	oxidation
11.8	grey	„ 2 „ silver-white	reduction
11.0	faint grey	„ 5 „ grey	oxidation
11.2	grey	„ 3 „ silver-white	reduction

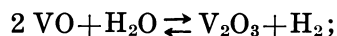
Equilibrium temperature between 11.0 and 11.2 = 11.1 millivolts = 1052°C .(ii) Bath -57.0°C .

12.8	faint grey	after 2 hrs. grey	oxidation
14.2	grey	„ 3 „ silver-white	reduction
14.0	silver-white	„ '4 „ grey	oxidation
14.9	grey	„ 1.5,, silver-white	reduction

Equilibrium temperature between 14.0 and 14.2 = 14.1 millivolts = 1268°C .(iii) Bath -47.0°C .

15.6	silver-white	after 3.5 hrs. grey	oxidation
16.7	grey	„ 1 „ silver-white	reduction
15.9	silver-white	„ 1 „ grey	oxidation
16.1	grey	„ 2 „ silver-white	reduction

Equilibrium temperature between 15.9 and 16.1 = 16.0 millivolts = 1397°C .

(i) Bath -78.5°C .

Thermoelec. force millivolts	Initial colour of V	Result	Concluded to be
4.6	faint grey	after 6 hrs. grey	oxidation reduction oxidation reduction
4.9		„ 18 „ black	
5.5	black	„ 20 „ grey	
4.4	grey	„ 20 „ black	
5.1	black	„ 24 „ grey	

Equilibrium temperature between 4.9 and 5.1 = 5.0 millivolts = 550°C .(ii) Bath -57.0°C .

6.7	grey	after 2.5 hrs. black	oxidation
7.3	black	„ 1.5 „ grey	reduction
6.5	grey	„ 3 „ black	oxidation
6.9	black	„ 2 „ grey	reduction

Equilibrium temperature between 6.7 and 6.9 = 6.8 millivolts = 710°C .(iii) Bath -37.0°C .

8.5	grey	after $1\frac{1}{4}$ hrs. black	oxidation reduction „ oxidation
8.8		„ 1 „ more black	
9.4	black	„ $\frac{1}{2}$ „ grey	
9.1	„	„ 1.5 „ grey	
8.9	grey	„ 2 „ black	

Equilibrium temperature between 8.9 and 9.1 = 9.0 millivolts = 890°C .(iv) Bath -19.5°C .

11.8	grey	after 2 hrs. black	oxidation
12.8	black	„ 1 „ grey	reduction
12.4	„	„ 2 „ grey	„
12.0	„	„ 3 „ grey	„

Equilibrium temperature between 11.8 and 12.0 = 11.9 millivolts = 1112°C .

Table 2.

a) $K_{p.1}$ -values and equilibrium temps. for V/VO.

Bath (°C)	$K_{p.1}$	$\log K_{p.1}$	Temp. C°	T	$1/T$
-78.5	$6.65 \cdot 10^{-7}$	-6.1772	1052	1325	0.0007547
-57.0	$1.45 \cdot 10^{-5}$	-4.8394	1268	1541	6489
-47.0	$5.53 \cdot 10^{-5}$	-4.2576	1397	1670	5988

b) $K_{p.2}$ -values and equilibrium temps. for VO/V₂O₃.

Bath (°C)	$K_{p.2}$	$\log K_{p.2}$	Temp. C°	T	$1/T$
-78.5	$6.65 \cdot 10^{-7}$	-6.1772	550	823	0.0012150
-57.0	$1.45 \cdot 10^{-5}$	-4.8394	710	983	10172
-37.0	$1.76 \cdot 10^{-4}$	-3.7537	890	1163	08598
-19.5	$1.07 \cdot 10^{-3}$	-2.9723	1112	1385	07220

the logarithms of equilibrium constants ($\log K_p = p_{\text{H}_2\text{O}}/p_{\text{H}_2}$) and the reciprocals of absolute temperatures ($1/T$) is indicated by a straight line (Fig. 2, they are analogous with those in W/WO₂ and WO₂/W₂O₅)⁽¹¹⁾. Consequently, they can be expressed by the general equation of first order of the reaction isochore

$$\log K_p = -\frac{Q}{4.571 T} + C.$$

Thermodynamical Calculations.

From the values given in the above Table 2 a) and b) the following empirical equations for straight lines can be derived:

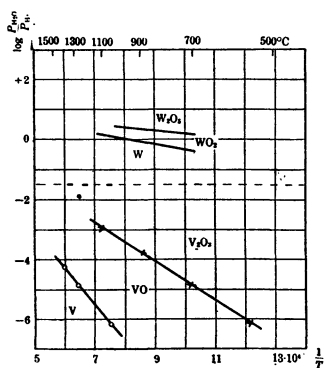


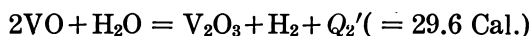
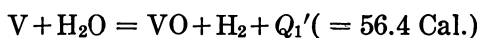
Fig. 2.

- (11) L. Wöhler & R. Günther, *Z. Elektrochem.*, **29** (1923), 276;
L. Wöhler, Z. Shibata & R. Kunst, *Z. Elektrochem.*, **38** (1932), 808.

$$\text{V/VO: } \log K_{p,1} = -\frac{12333}{T} + 3.141$$

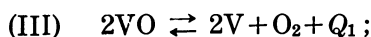
$$\text{VO/V}_2\text{O}_3: \log K_{p,2} = -\frac{6482}{T} + 1.747.$$

By the equation $\log K_p = -\frac{Q}{4.571 T} + C$, in which $-\frac{Q}{4.571} = tg \alpha$ in the equation of first order, it follows that Q'_1 and Q'_2 , the heat of the reactions (I) and (II), are obtained as the product of -4.571 with -12333 and -6482 , respectively: that is,

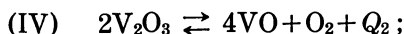


By combining the above empirical equations with the equation for dissociation of water vapour, the dissociation pressures of the vanadium oxides can be calculated;

$$K'_{p_{\text{H}_2\text{O}}} = \frac{p_{\text{H}_2}^2 \cdot p_{\text{O}_2}}{p_{\text{H}_2\text{O}}^2} = \frac{1 \cdot p_{\text{O}_2}}{K_p^2}, \quad \text{thus} \quad p_{\text{O}_2} = K'_{p_{\text{H}_2\text{O}}} \cdot K_p^2.$$



$$\text{O}_2\text{-pressure} = p_1 = K'_{p_{\text{H}_2\text{O}}} \cdot K_{p,1}^2,$$



$$\text{O}_2\text{-pressure} = p_2 = K'_{p_{\text{H}_2\text{O}}} \cdot K_{p,2}^2.$$

By applying equation for dissociation of water⁽¹¹⁾ which, although approximate, is useful, $\log K'_{p_{\text{H}_2\text{O}}} = -\frac{26000}{T} + 6.06$, we obtain

$$\begin{aligned} \log p_1 &= -\frac{26000}{T} + 6.06 + 2\left(-\frac{12333}{T} + 3.141\right) \\ &= -\frac{50666}{T} + 12.342 \quad \text{atm. press.} \end{aligned}$$

and similarly

$$\log p_2 = -\frac{38964}{T} + 9.554 \quad \text{atm. press.}$$

By the most general form of equation for vapour pressure, $\log p = -\frac{Q}{4.571T} + C$, approximate heat tonings Q_1 and Q_2 of the reactions (III) and (IV) can be calculated. That is,

$$Q_1 = -50666 \cdot -4.571 = 231.6 \text{ Cal.}$$

$$Q_2 = -38964 \cdot -4.571 = 178.1 \text{ Cal.}$$

or, the heat of the reactions:

$$2V + O_2 = V_2O_2 + Q_1 (= 231.6 \text{ Cal.})$$

$$V_2O_2 + 1/2 O_2 = V_2O_3 + 1/2 Q_2 (= 89.0 \text{ Cal.})$$

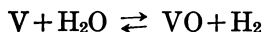
and by addition

$$2V + 3/2 O_2 = V_2O_3 + Q_3 (= Q_1 + 1/2 Q_2 = 320.6 \text{ Cal.})$$

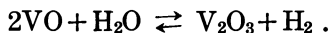
Although the approximate value of heat of oxidation Q_1 of vanadium to its dioxide is little higher than that calculated by R. E. Slade & G. I. Higson⁽¹²⁾ and that determined by W. G. Mixter, it was very close to their values. Heat of oxidation Q_3 of vanadium to its trioxide is found between those determined by Mixter and O. Ruff & L. Friedrich⁽¹³⁾; but of the two it was closer to that of Ruff & Friedrich. The values obtained by the author and the others mentioned above are given below for comparison:

	Author	Mixter	Ruff and Friedrich	Slade and Higson
Q_1	231.6	greater than 209 ⁽¹⁴⁾	—	222.0
Q_3	320.6	„ 353 ⁽¹⁵⁾	302±10	—

Since the values obtained closely agree with the others, it becomes obvious that the equilibria dealing here are correct, that is to say, the following reactions will undoubtedly take place,



and



(12) *J. Chem. Soc.*, **115** (1919), 205.

(13) *Z. anorg. Chem.*, **89** (1914), 279.

(14) and (15) Calcd. according to Mixter's data; *Sill. Journ.* **34** (1912), 148; *Z. anorg. Chem.*, **78** (1912), 221.

Further, by applying Siegel's exact equation⁽¹⁶⁾ for dissociation of water vapour, $[\log K_c = \frac{-24900}{T} + 1.335 \log T - 9.65 \cdot 10^{-5} T + 1.37 \cdot 10^{-7} T^2 - 6.65 \cdot 10^{-11} T^3 + 1.907 \cdot 10^{-18} T^5 - 1.08]$ the dissociation pressures of the two oxides at various temperatures are calculated as follows :

O₂-pressure at atmospheric.

abs. temp.	$p_1(\text{V/VO})$	$p_2(\text{VO/V}_2\text{O}_3)$
823	—	$2.47 \cdot 10^{-37}$
983	—	$1.49 \cdot 10^{-29}$
1163	—	$2.69 \cdot 10^{-23}$
1325	$2.13 \cdot 10^{-25}$	—
1385	—	$3.94 \cdot 10^{-18}$
1541	$5.97 \cdot 10^{-20}$	—
1670	$1.80 \cdot 10^{-17}$	—
3610	—	1.0
3720	1.0	—

It will be noticed from the table that the oxygen pressure of trioxide will be one atmosphere at about 3610° abs., and that of dioxide at about 3720° abs.

The Free Energy and Heat of Formation of VO. Using the following heat capacities of substances

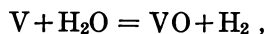
$$\text{for VO ; } C_p = 10.2^{(17)}$$

$$,, \text{ H}_2 ; C_p = 6.50 + 0.0009 T^{(18)}$$

$$,, \text{ V ; } C_p = 6.2^{(17)}$$

$$,, \text{ H}_2\text{O (g) ; } C_p = 8.81 - 0.0019 T + 0.00000222 T^{(18)}$$

being involved in the reaction,



the general equation for heat of formation and free energy equation can be given as follows :

(16) W. Siegel, *Z. Physik. Chem.*, **87** (1914), 641.

(17) Calcd. by Kopp's rule; cf. Noyes & Sherrill, "Chem. Principle," (1930), 93.

(18) Lewis & Randall, "Thermodynamics," (1923), 80.

$$(A) \quad \Delta H = \Delta H_0 + 1.69 T + 0.0014 T^2 - 0.00000074 T^3$$

$$(B) \quad \frac{\Delta F^0}{T} = \frac{\Delta H_0}{T} - 1.69 \ln T - 0.0014 T + 0.00000037 T^2 + I.$$

In the latter equation the values of ΔH_0 and I are obtained by an application of the relation

$$\Delta F^0 = -RT \ln K_p,$$

in which the values of K_p are known, as shown in Table 2 a),

$$\Delta H_0 = -59526 \text{ cal}, \quad I = 30.09$$

Substituting these values in (A) and (B),

$$\Delta H = -59526 + 1.69 T + 0.0014 T^2 - 0.00000074 T^3$$

$$\frac{\Delta F^0}{T} = \frac{-59526}{T} - 1.69 \ln T - 0.0014 T + 0.00000037 T^2 + 30.09.$$

Solving for T at 298° , we find

$$\Delta F_{298}^0 = -53543 \text{ cal}, \quad \Delta H_{298} = -58918 \text{ cal},$$

Combining the values of $\Delta F_{298}^0 = -54507 \text{ cal}^{(19)}$ and $\Delta H_{298} = -57820 \text{ cal}^{(20)}$ for the free energy and heat of formation of water vapour from its element, the free energy and heat of formation of VO from its element can be calculated as follows:

$$\text{V} + \text{H}_2\text{O} = \text{VO} + \text{H}_2 ; \quad \Delta F_{298}^0 = -53543 \text{ cal}, \quad \Delta H_{298} = -58918 \text{ cal}.$$

$$\text{H}_2 + 1/2 \text{O}_2 = \text{H}_2\text{O}(\text{g}) ; \quad \Delta F_{298}^0 = -54507 \text{ cal}, \quad \Delta H_{298} = -57820 \text{ cal}.$$

$$\text{hence } \text{V} + 1/2 \text{O}_2 = \text{VO} \quad ; \quad \Delta F_{298}^0 = -108050 \text{ cal}, \quad \Delta H_{298} = -116738 \text{ cal}.$$

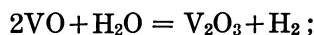
$$\text{or (i) } 2\text{V} + \text{O}_2 = \text{V}_2\text{O}_2 \quad ; \quad \Delta F_{298}^0 = -216100 \text{ cal}, \quad \Delta H_{298} = -233476 \text{ cal}.$$

The final value -233476 cal , the heat of formation of V_2O_2 from its element, is nearly equivalent to the approximate value $Q_1 = 231.6 \text{ Cal}$, for the corresponding heat of formation already obtained, in which it has been calculated by neglecting the change in heat capacities with temperature.

(19) Lewis & Randall, "Thermodynamics," (1923) p. 485.

(20) *ibid.* p. 477.

The Free Energy and Heat of Formation of V_2O_3 . In the same manner as in the preceding section the general equations for heat of formation and also for free energy are derived for the reaction



From the heat capacities of these substances:

$$V_2O_3 \quad ; \quad C_p = 24.4^{(17)}$$

$$H_2 \quad ; \quad C_p = 6.50 + 0.0009 T$$

$$2VO \quad ; \quad C_p = 20.4^{(17)}$$

$$H_2O(g) \quad ; \quad C_p = 8.81 - 0.0019 T + 0.00000222 T^2,$$

are derived

$$\Delta H = \Delta H_0 + 1.69 T + 0.0014 T^2 - 0.00000074 T^3$$

$$\frac{\Delta F^0}{T} = \frac{\Delta H_0}{T} - 1.69 \ln T - 0.0014 T + 0.00000037 T^2 + I.$$

Solving, we find

$$\Delta H_0 = -32124 \text{ cal.} \quad I = 23.22,$$

we may write,

$$\Delta H = -32124 + 1.69 T + 0.0014 T^2 - 0.00000074 T^3$$

$$\frac{\Delta F^0}{T} = \frac{-32124}{T} - 1.69 \ln T - 0.0014 T + 0.00000037 T^2 + 23.22.$$

Hence

$$2VO + H_2O = V_2O_3 + H_2; \quad \Delta F_{298}^0 = -28189 \text{ cal,} \quad \Delta H_{298} = -31516 \text{ cal.}$$

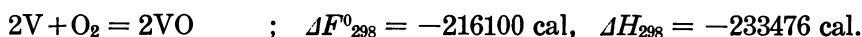
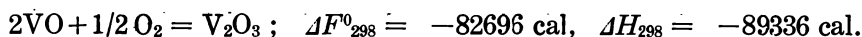
$$H_2 + 1/2 O_2 = H_2O(g) \quad ; \quad \Delta F_{298}^0 = -54507 \text{ cal,} \quad \Delta H_{298} = -57820 \text{ cal.}$$

hence

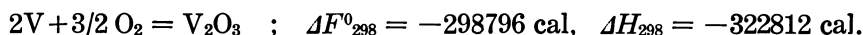
$$(ii) \quad 2VO + 1/2 O_2 = V_2O_3 \quad ; \quad \Delta F_{298}^0 = -82696 \text{ cal,} \quad \Delta H_{298} = -89336 \text{ cal.}$$

The final value -89336 cal, the heat of formation of V_2O_3 from VO and oxygen is equal to the approximate value $Q_2/2 = 89.0$ Cal, for the corresponding heat of formation already described.

Lastly, from the values (i) and (ii) are calculated the free energy and heat of formation of V_2O_3 from its element:



hence



This final value, -322812 cal , the heat of formation of V_2O_3 from its element is also nearly equal to the approximate value $Q_3 = 320.6 \text{ Cal}$, for the corresponding heat of formation already obtained.

In conclusion the writer wishes to express his sincere thanks to Prof. Dr. Keizô Iwasé, under whose guidance this work has been carried out and also to Dr. Shin-ichi Aoyama for his kind advice he has extended in carrying out this work.

Summary.

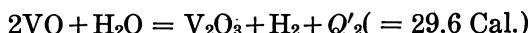
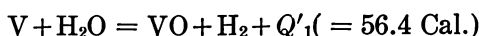
1. The vanadium-water vapour equilibria on the phase V/VO and $\text{VO}/\text{V}_2\text{O}_3$ have been determined over the range $p_{\text{H}_2\text{O}} = 1.07 \cdot 10^{-3}$ to $6.65 \cdot 10^{-7}$ atmospheric pressure by the method of H. v. Wartenberg and S. Aoyama.

2. From the measured equilibrium temperatures and the corresponding K_p -values, it has been derived the general equations of the reaction isochore $\log K_p = -\frac{Q}{4.571 T} + C$ for the two systems:

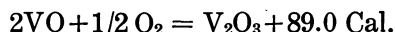
$$\text{V}/\text{VO} \quad ; \quad \log K_{p,1} = -12333 / T + 3.141$$

$$\text{VO}/\text{V}_2\text{O}_3; \quad \log K_{p,2} = -6482 / T + 1.747,$$

and from these the approximate heat of reaction have been calculated:



3. Combining the above equations with the equation for dissociation of water vapour, the general equations for dissociation of vanadium oxides have been derived, and from these it has been calculated O_2 -pressures for several temperatures and approximate values for the heat of formation of VO from V , of V_2O_3 from VO , and of V_2O_3 from V :



4. By the use of the equations for heat capacities of substances being involved in each reaction, the free energies and heats of formation have been calculated at 25°C.; that of VO from its element and that of V₂O₃ from its element and also from VO and oxygen:

$$2V + O_2 = V_2O_2 \quad ; \quad \Delta F_{298}^0 = -216100 \text{ cal}, \quad \Delta H_{298} = -233476 \text{ cal}.$$

$$2VO + 1/2 O_2 = V_2O_3; \quad \Delta F_{298}^0 = -82696 \text{ cal}, \quad \Delta H_{298} = -89336 \text{ cal}.$$

$$2V + 3/2 O_2 = V_2O_3 \quad ; \quad \Delta F_{298}^0 = -298796 \text{ cal}, \quad \Delta H_{298} = -322812 \text{ cal}.$$

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SOME APPLICATIONS IN THE POTENTIOMETRIC TITRATIONS BY USING VACUUM TUBE.

By Kosaku MASAKI and Okiro HIRABAYASHI.

Received June 2nd, 1933. Published August 28th, 1933.

Introduction.

During the process of work in analysis, it is very necessary to execute a titration securely and swiftly. The potentiometric titrations in oxidation and reduction reactions by using a vacuum tube were reported by many investigators.⁽¹⁾ In all of these investigations, a negative potential is put on the grid with respect to the filament and the indicator electrode is directly connected to the grid; for example the indicator electrode is platinum and the calomel electrode is connected to the battery impressing the negative potential to the grid. By this method it is necessary to plot $\Delta E / \Delta V$ to obtain the equivalence point, where ΔE is a small change of the e.m.f. of the cell during titration and ΔV is the volume of the titrating solution. The values of galvanometer or milliammeter deflections may be used in place of ΔE . Recently J. L. Kassner, R. B. Hunze

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- (1) Goode, *J. Amer. Chem. Soc.*, **44** (1922), 26; **47** (1925), 2483.
Calhane and Cushing, *J. Ind. Eng. Chem.*, **15** (1923), 1118.
Treadwell, *Hel. Chem. Acta.*, **8** (1925), 89.
Williams and Whitenack, *J. Physik. Chem.*, **31** (1927), 519.
Morton, *Pharm. J.*, **118** (1927), 761.
E. Beri, W. Herbert und W. Wohlig, „Die Chem. Fabrik,“ 1930, 445; 448.

and J. N. Chatfield⁽²⁾ studied the method to avoid the complication of plotting curves to obtain the equivalence point. It was reported that their method was preferable in the electrometric titrations of some oxidation-reduction reactions. The present investigation was started to find out the characteristics of the apparatus modified by the author, when it was applied on the electrometric titrations of many oxidation-reduction reactions.

Apparatus.

The circuit of the apparatus is shown in Fig. 1, in which the details of every parts are as follows. V in circle is voltmeter reading in units of 0.1 volt. D is potential divider of 10,000 ohms. C is 4-volt battery, A 6-volt storage battery and B 45-volt dry-battery. W is 30-ohm variable resistance. R is 10,000-ohm variable resistance. A in circle is milliammeter reading 500 milliamperes. T is Mazda vacuum tube, UX 201A, whose filament is operated normally with 5 volts, drawing 0.25 ampere. G is galvanometer, whose rating is as follows; made by Yokokawa, Type D₂, Class L, Sensibility 5×10^{-8} -Ampere, 6.8×10^{-5} -volt, Period 3 seconds, galvanometer resistance 300-ohm. C and c' are platinum electrodes, 0.4 mm. in diameter and 40 cm. of length. P is shunt resistance, 5,000, 10,000, 20,000 and 30,000-ohms. K shown in Fig. 1 is the reaction vessel which is a beaker or an Erlenmeyer flask of about 200 c.c. But in accurate titrations, it is necessary to use the apparatus designed by Hostetter and Roberts.⁽³⁾ Ours is shown in Fig. 2. Reaction vessel is made of glass, 6 cm. in diameter and 13 cm. in length. From G carbon dioxide is passed into the vessel. S is a stirrer driven by a motor. Additions of a solution in a small quantity were carried out by the aid of slender glass rod L.

In potentiometric titrations, up to the present, a negative potential is impressed on the grid of the vacuum tube, while the apparatus shown in Fig. 1 differs from other's in that a positive potential is placed on the grid with respect to the filament of the vacuum tube. Accordingly, the grid current, which is very small due to the construction of the vacuum tube, flows through the titrating cell and has been employed to polarize bimetallic platinum electrodes which have been substituted for the monometallic system. The theory of polarized electrodes has been studied by

(2) J. L. Kassner, R. B. Hunze and J. N. Chatfield, *J. Amer. Chem. Soc.*, **54** (1932), 2278.

(3) Hostetter and Roberts, *J. Amer. Chem. Soc.*, **41** (1919), 1337.

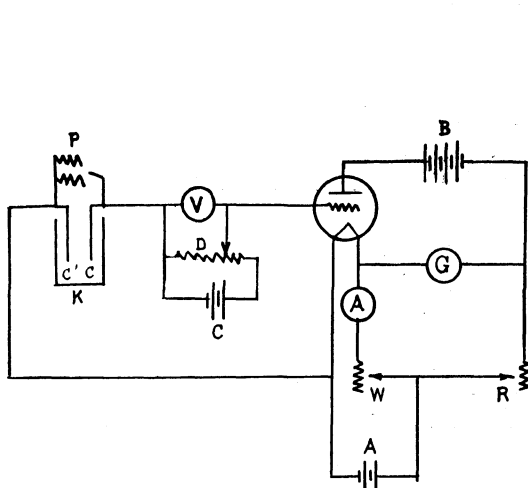


Fig. 1.

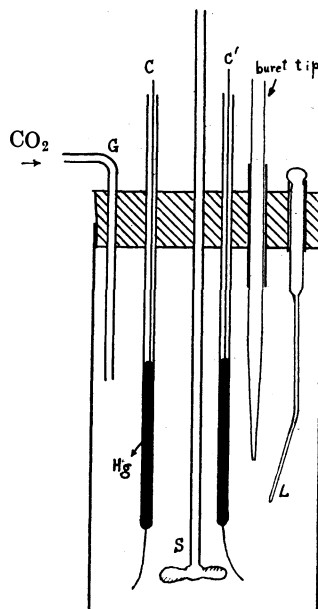


Fig. 2.

Willard and Fenwick⁽⁴⁾ and Van Name and Fenwick.⁽⁵⁾ They have shown that polarized electrodes owe their effect in electrometric titration to gas reaction taking place on the surface of the electrodes and that the potential difference between the electrodes remains practically constant up to the equivalence point. Moreover, a part of the grid current is shunted to the bimetallic electrodes with shunt resistance P as shown in Fig. 1 for the successful operation of this apparatus. It is very necessary that the potential difference between the electrodes remains constant up to the equivalence point in order to operate this apparatus, and this has been accomplished by shunting a part of the polarizing current to the electrodes. Thus shunted electrodes were first used by Foulk and Bawden.⁽⁶⁾ They stated no current flows through the solution when the drop in potential across the shunt is equal to the back e.m.f. due to polarization.

If the bimetallic platinum electrodes have been placed in the solution to be titrated and the resistance R adjusted so that the galvanometer reading is zero, then the potential at M and N would be the same. Electrons flow through the vacuum tube in three circuits; namely, filament, filament to grid, and filament to plate. The electrons picked up

(4) *J. Amer. Chem. Soc.*, **44** (1922), 2504.

(5) Van Name and Fenwick, *J. Amer. Chem. Soc.*, **47** (1925), 9; 19.

(6) Foulk and Bawden, *J. Amer. Chem. Soc.*, **48** (1926), 2045.

by the plate may be considered as flowing through the B-battery, R, and back to the A-battery. The strength of this current depends upon the temperature of the filament which is controlled by the filament current varied with W, the voltage of the B-battery, the value of R, and the potential impressed on the grid. The electrons picked up by the grid polarize the bimetallic platinum electrodes. The current in these three circuits will remain constant during the course of a titration as long as the potential difference between c and c' remains constant if the other adjustments are not changed. A slight change in the potential between c and c' will produce a corresponding change in the potential impressed on the grid, and this will produce a relatively large change in the plate current by the characteristics of the vacuum tube. Accordingly the balance at M and N is disturbed and it causes the deflection of the needle of the galvanometer.

Experimental.

The preparations of the solutions used were as follows. The reagents used were from Kahlbaum.

(1) Sodium thiosulphate is purified by recrystallization. About 26 gr. of it are weighed out and diluted to about 1 litre. The solution is standardized indirectly by titration with potassium bichromate. Dissolve 5 gr. KI and 4 gr. NaHCO_3 in 500 c.c. H_2O in an Erlenmeyer flask at room temperature and add HCl slowly, shaking the flask, until there is no more evolution of CO_2 and then add about 10 c.c. more of the acid, and 35 c.c. of 0.1 N. $\text{K}_2\text{Cr}_2\text{O}_7$. After mixing the solution, rinse the sides of the flask with a few c.c. of water, allowing it to form a layer over the solution without mixing; stopper the flask and allow to stand about 10 minutes. Then with thorough mixing run in thiosulphate until the solution is slightly yellow, add a few drops of starch solution and continue to add slowly the thiosulphate solution until the bright blue colour disappears and only the pale green colour of CrCl_3 remains.

(2) Potassium bichromate is purified by recrystallization and dried in an air oven, 4.9035 gr. of it are exactly weighed out and dissolved to 1 litre.

(3) Iodine. Dissolve about 13.5 gr. of pure iodine in a solution of 24 gr. of KI in 200 c.c. of H_2O and dilute to 1 litre. This solution is standardized by thiosulphate using starch as indicator.

(4) Ferrous sulphate. Weigh out exactly 39.214 gr. of ferrous sulphate and dissolve in dilute sulphuric acid (sp. gr. 1.2) to 1 litre.

(5) Potassium permanganate. Dissolve 3.3 gr. of KMnO_4 in 1 litre of distilled water and allow to stand a day. This is standardized by sodium oxalate extremely pure and dry.

(6) Potassium cyanide. Weigh out about 8 gr. and dissolve in 1 litre H_2O . This is standardized by 0.1 N. standard AgNO_3 .

(7) Potassium bromate. Weigh out exactly 16.701 gr. and dilute to 1 litre exactly.

(8) Potassium iodide is purified by recrystallization and dried in air oven. Weigh out exactly 16.603 gr. and dilute to 1 litre.

(9) Potassium iodate. Weigh out exactly 4.2806 gr. and dissolve to 1 litre.

It was thought at first that it would be necessary to control the shunt to obtain good results with this apparatus, but in practice it was often not necessary. The results of the titrations using different shunts are shown in Table 1. The calculated value of c.c. of 0.1 N. sodium thiosulphate is the average of five determinations using starch as the indicator.

Table 1.

Titrations of approximately 0.1 N. iodine solution with sodium thiosulphate.⁽⁷⁾

V: 1.5 volts; A: 0.25 ampere; B: 45 volts.

Run	P:ohms	Sodium thiosulphate		
		c.c. calc.	c.c. found	c.c. dif.
1	5.000	10.45	10.45	0.00
2	10.000	10.45	10.43	0.02
3	20.000	10.45	10.43	0.02
4	30.000	10.45	10.45	0.00
5	50.000	10.45	10.44	0.01

When no shunt resistance was employed the needle of the galvanometer drifted off the scale after the addition of about 1 c.c. of thiosulphate, and under certain circumstances even after one drop. It is distinct that the end-point obtained by this apparatus is slightly in advance of the end-point obtained by the starch.⁽⁸⁾ In many titrations described below, P shunt resistance was used in the range shown above.

The galvanometer deflections during titrations, for example, are shown in Table 2, but in many cases there are no great difference.

(7) A. Schlfeichen, *Z. Anal. Chem.*, **65** (1925), 406.

(8) Foulk and Bawden, *J. Amer. Chem. Soc.*, **48** (1926), 2047.

Table 2.

Titration of approximately 0.1 N. iodine with sodium thiosulphate.

c.c. of 0.1 N. $\text{Na}_2\text{S}_2\text{O}_3$	Gal. def. (zero center)	c.c. of 0.1 N. $\text{Na}_2\text{S}_2\text{O}_3$	Gal. def. (zero center)
0.00	0.0	10.35	4.7 left
5.00	1.0 left	10.40	5.3 ,,
8.00	1.7 ,,	10.42	5.5 ,,
10.00	2.9 ,,	10.43	5.6 ,,
10.20	3.6 ,,	10.44	14.0 right
10.31	4.5 ,,		

Further, in order to show that it is not necessary to control the different variables in this apparatus within narrow limits the following data are presented (Table 3).

Table 3.

Titration of approximately 0.1 N. iodine with sodium thiosulphate.

Run	Sodium thiosulphate			Filament Current ampere	V volts	P ohms
	c.c. calc.	c.c. found	c.c. dif.			
1	24.40	24.39	0.01	0.25	2.0	30.000
2	24.40	24.40	0.00	0.20	2.0	30.000
3	24.40	24.40	0.00	0.22	2.0	30.000
4	24.40	24.41	0.01	0.25	1.7	20.000
5	24.40	24.40	0.00	0.25	1.6	30.000
6	24.40	24.39	0.01	0.20	2.2	35.000
7	24.40	24.38	0.02	0.22	1.5	20.000
8	24.40	24.40	0.00	0.25	1.2	15.000
9	24.40	24.38	0.02	0.25	1.0	20.000
10	24.40	24.38	0.02	0.20	1.0	20.000
11	24.40	24.40	0.00	0.25	1.0	10.000
12	24.40	24.39	0.01	0.20	1.0	10.000

B-battery is 45 volts.

As is shown in Fig. 2, one of the platinum electrodes is placed close under the burette, so that there will be temporarily a slight difference in the composition of the solution when the drops of a titrating solution is added. And the deflection of the needle of the galvanometer will be also

temporarily unstable and great. But it again becomes stable if the addition of the titrating solution is interrupted. Thus the approach of the end-point is indicated.

Results of some applications in oxidation-reduction reactions using this apparatus are given in the following tables.

As an additional characteristic in this apparatus, there is the indication of the approach of the end point.

Table 4.

Titration of ferrous sulphate with potassium permanganate.

V: 1.5 volts; A: 0.20 ampere; P: 20.000 ohms; B: 45.0 volts.

Run	c.c. calc.	c.c. found	c.c. dif.
1	22.94	22.89	0.05
2	22.94	22.89	0.05
3	22.94	22.90	0.04
4	22.94	22.88	0.06
5	22.94	22.89	0.05

V: 1.0 volt; A: 0.25 ampere; P: 25.000 ohms; B: 45 volts.

1	22.94	22.89	0.05
2	22.94	22.88	0.06
3	22.94	22.89	0.05

The calculated values are the average of five determinations when the solution to be titrated is coloured pink.

Table 5.

Titration of iodine with potassium cyanide.

V: 0.7 volt; A: 0.21 ampere; P: 20.000 ohms; B: 45 volts.

Run	c.c. calc.	c.c. found	c.c. dif.
1	12.84	12.75	0.09
2	12.84	12.76	0.08
3	12.84	12.76	0.08
4	12.84	12.76	0.08
5	12.84	12.76	0.08

The c.c. calculated is the average of five determinations using starch as indicator.

The following experiments were carried out to test the possibility of the titrations of some oxidation-reduction reactions, though the c.c. calculated is not so accurate as the value obtained from the weight of reagents.

Table 6.

Titration of ferrous sulphate with 0.1 N. potassium bichromate.

V: 0.8 volt; A: 0.20 ampere; P: 20.000 ohms; B: 22.5 volts.

Run	c.c. calc.	c.c. found	c.c. dif.
1	23.12	23.10	0.02
2	23.12	23.11	0.01
3	23.12	23.11	0.01

Table 7.

Titration of ferrous sulphate with 0.1 N. potassium bromate.

V: 1.4 volts; A: 0.20 ampere; P: 10.000 ohms; B: 45 volts.

Run	c.c. calc.	c.c. found	c.c. dif.
1	8.17	8.18	0.01
2	8.17	8.17	0.00
3	8.17	8.18	0.01

Table 8.

Titration of potassium iodide with 0.1 N. potassium bichromate.

V: 0.8 volt; A: 0.20 ampere; P: 10.000 ohms; B: 22.5 volts.

Run	c.c. calc.	c.c. found	c.c. dif.
1	25.00	24.96	0.04
2	25.00	24.95	0.05
3	25.00	24.95	0.05

In this case, the galvanometer deflection is very unstable and the titration becomes difficult. Above data are only the most likely results selected among many titrations.

Table 9.

Titration of potassium iodide with 0.1 N. potassium bromate.

V: 1.0 volt; A: 0.25 ampere; P: 20.000 ohms; B: 45 volts.

Run	c.c. calc.	c.c. found	c.c. dif.
1	25.00	25.05	0.05
2	25.00	25.07	0.07
3	25.00	25.06	0.06

Table 10.

Titration of potassium iodide with potassium permanganate.

V: 2.0 volts; A: 0.25 ampere; P: 25.000 ohms; B: 45 volts.

Run	c.c. calc.	c.c. found	c.c. dif.
1	23.30	23.27	0.03
2	23.30	23.25	0.05
3	23.30	23.25	0.05

In this case, the galvanometer deflection is exceptional and the end-point is very apparent.

Table 11.

c.c. of KMnO_4	gal. deflection	c.c. of KMnO_4	gal. deflection
0.00	0.0	23.10	18.1 left
10.00	10.4 left	23.20	18.1 „
20.00	17.7 „	23.23	18.0 „
22.00	18.1 „	23.24	18.1 „
23.00	18.1 „	23.25	to right extremely

Table 12.

Titration of potassium iodide with 0.1 N. potassium iodate.

V: 1.5 volts; A: 0.20 ampere; P: 20.000 ohms; B: 45 volts.

Run	c.c. calc.	c.c. found	c.c. dif.
1	25.00	24.89	0.11
2	25.00	24.80	0.20
3	25.00	24.80	0.20

Table 13.

Titration of potassium permanganate with potassium ferrocyanide.

V: 0.6 volt; A: 0.20 ampere; P: 10.000 ohms; B: 45 volts.

Run	c.c. calc.	c.c. found	c.c. dif.
1	23.19	23.00	0.19
2	23.19	22.99	0.20
3	23.19	22.99	0.20

Author wishes to express his thanks to Prof. K. Kido who gave him the reagents.

Summary.

In the above investigation, the polarized platinum electrodes by means of grid current, which is obtained by impressing a positive potential on the grid, were used in the potentiometric titrations. In this apparatus, the approach of the end point is indicated, thus the neither plotting or recording nor adjustments is necessary during the titration; but it is necessary to control the positive potential impressed on the grid at the beginning of the titration lest the needle of galvanometer will kick off. The agreement between the calculated and found values is very good in each case.

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THE VISCOSITY OF VAPOURS OF ORGANIC COMPOUNDS. PART III.

By Toshizo TITANI.

Received June 26th, 1933. Published September 28th, 1933.

The determinations of the viscosity of vapours of organic compounds with the boiling points lower than ordinary room temperature were already made by the present author.⁽¹⁾ The similar experiment has been further continued for the determination of the viscosity of the vapours of other organic compounds such for an example as benzene, ethyl alcohol, carbon tetrachloride and etc., which are in a liquid state at room temperature.

Experimental Procedure.

The measurements of viscosity were made by the traspiration method according to the principle devised by M. Trautz and W. Weizel,⁽²⁾ which will be briefly explained by using the diagrammatical figure 1. Three glass bulbs A, B and C are connected to one another with glass tubes having a large bore, and measured quantities of mercury are placed in them, as is shown in the figure. The total bulb system is heated in a thermostat to a constant temperature T_0 . The lower bulb C is connected with a glass tubing to a preheating tube W and a glass capillary tube K, other end of

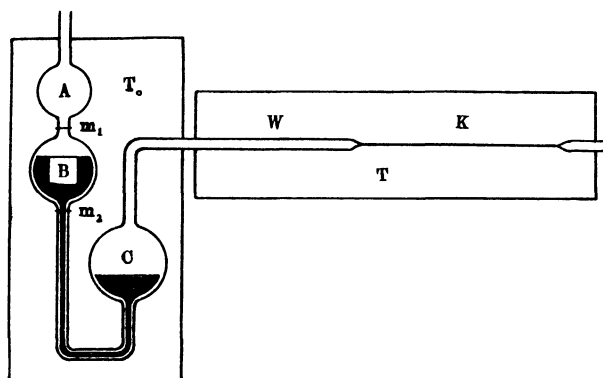


Fig. 1.

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- (1) T. Titani, this Bulletin, **4** (1929), 277; **5** (1930), 98.
(2) M. Trautz & W. Weizel, *Ann. Phys.*; (4) **78** (1925), 305.

which is opened to air, both W and K being placed in another thermostat T. The vapour of organic compound is drawn through the capillary K and the preheating tube W into a space in the bulb C partially filled with mercury, by drawing up the mercury high enough into the bulbs A and B.

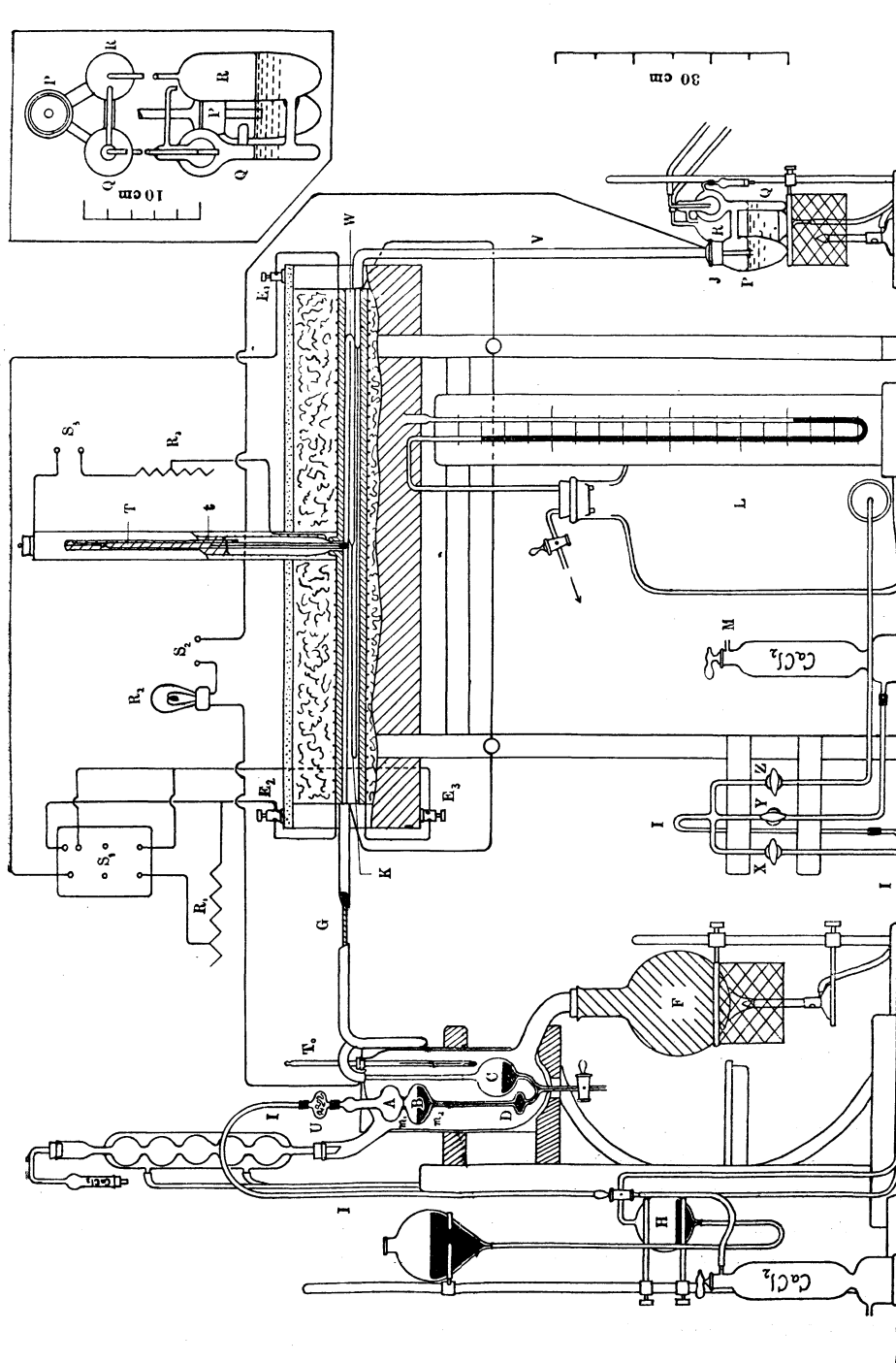
The vapour in the bulb C is driven out, when it attains the same temperature as that of the thermostat T_0 , in the reverse direction into the air, by letting the mercury flow down from the upper bulbs A and B into the lower one C. The time t required for the mercury to travel a distance between m_1 and m_2 which are marked on the neck of the both ends of the bulb B is taken, while at the same time the temperature T of the capillary tube K, measured in the absolute scale, is recorded. Then the viscosity η of the vapour at the temperature T can be calculated by the formula⁽³⁾:

$$\eta = K \frac{t}{T},$$

where K is a constant for a given apparatus so long as the temperature T_0 of the bulb system remains constant.

The total apparatus is shown in Fig. 2. The whole system is made of glass. The two bulbs A and B are of spheroidal form and the bulb C is a sphere having the dimensions: A 25×40 mm., B 30×50 mm. and C 50×50 mm. respectively. The three bulbs are connected to one another by glass tubes 6 mm. bore, which are somewhat contracted at the points of two marks m_1 and m_2 and between the bulb B and C a small spheroidal bulb D having dimensions 15×30 mm. is inserted for the reasons which will be mentioned below. Exactly weighted quantities of mercury namely 1000 grams, are placed in the bulb system which is sealed into a large glass jacket, to be heated to a constant temperature T_0 by a toluene vapour produced in a large copper flask F. The vapour jacket supported on a strong wooden stative is covered with an asbestos plate having several windows for observation. The upper opening of the bulb A can be communicated either to a high pressure H or a suction L or it can also be opened to air M through the three stoppers X, Z or Y respectively. In a small bulb U above A are placed cotton wools in order to prevent dust particles from falling into the bulb system. The lower bulb C is jointed to a preheating tube W by sealing with a glass tube G 3 mm. bore, which is bent at three points as is shown in the figure for the purpose of buffering, and is heated electrically by winding it with a nichrom wire and by wrapping it with asbestos paper.

(3) The derivation of this equation is referred to the original paper of M. Trautz and W. Weizel, loc. cit.



Both the preheating tube W 3 mm. inner diameter and 86 cm. long and the glass capillary tube K about 0.1 mm. inner diameter and 83 cm. long are bent in U-form at the points about one third the distance from the ends and sealed together at the ends of the shorter limbs. They are placed in an electrical resistance furnace, consisting of a brass pipe having a thick wall of 1 cm. and 1.5 cm. inner diameter and 68 cm. long. The outside of the pipe is wrapped with asbestos paper and then wound with a set of nichrom wires, which are parallel to each other and which have one common terminal E_1 at one end and two separated terminals E_2 and E_3 at the other end, so that they may be communicated either in series or in parallel and also may be used quite separately by using the switch board S_1 . In the latter two cases the current can be regulated by the resistance R_1 . The brass pipe is once more thickly covered with asbestos and is placed centrally in a large asbestos cylinder, the space between them being packed with asbestos wools. On the middle parts of both the outer asbestos cylinder and the inner brass tube are drilled holes to be used for inserting a thermometer T to measure the temperature of the furnace. The following device is made in order to minimize for the mercury column of the thermometer T not in direct contact with the chamber of the resistance furnace the temperature corrections which would be remarkably large at high temperatures. On the middle part of the column of the thermometer T is held another small thermometer t. These two thermometers are placed within a glass cylinder wrapped with asbestos paper over which a nichrom wire is wound for heating purpose. Another glass cylinder of larger size wrapped with asbestos is placed over them. This whole system is heated electrically by means of nichrom wire wound over the inner glass cylinder, the switch S_3 and the resistance R_3 , to a known temperature which is easily read by the second thermometer t held on to the middle part of the first larger one T as is mentioned just before. In these two respective asbestos covering the two glass cylinders are made windows through which reading on the thermometers is made possible.

The end of the capillary tube K is sealed to a long glass tube V 3 mm. inner diameter, which is bent vertically downward to be connected to a vapourising device PQR with a ground joint J. The vertical tube V wrapped with asbestos has a doubly winding of nichrom wires so as to make electrical heating connection in series with that of the glass tube G by means of the switch S_2 and the resistance R_2 . The vapourising apparatus consists of this vertical tube V together with a bulb apparatus PQR, which is separately shown in the upper corner of the right hand

side of Fig. 2. The organic liquid the vapour of which is to be investigated is placed in the bulbs PQR, which are gently warmed either with a small Bunsen burner or with an incandescent lamp. The loss of the liquid placed in the bulbs PQR through evaporation must be prevented and the entry of dust particles into it has to be also made impossible. For this purpose, over the bulb Q is fitted a water condenser whose running water is also used to cool the bulb R.

The lower end of the vertical tube V is placed few millimeter below the surface of the organic liquid in the bulb P, so that the liquid may run up into the vertical tube V, when we connect the upper opening of the bulb A to the suction L by carefully opening the stopper Z. But, as the tube V is electrically heated, the liquid is vapourised as soon as it run up into the tube V, the organic vapour thus produced being drawn through both the capillary and the preheating tube and finally collected over the mercury in the bulb C. When sufficient quantities of vapour are collected in the bulb C, this mixture of air and the organic vapour is pushed back through the capillary tube into the bulb P, by the pressure brought about by letting the mercury flow down first from the bulbs A and B to C and then by the further pressure obtained by the opening of the stopper X to the high pressure bulb H, which process results in bringing down the level of the mercury finally into the small bulb D. The organic vapour is then again drawn into the bulb C and when sufficient quantities of vapour get into it, they are pushed back by applying the pressure to the bulb C, as is mentioned above. With the repetition of this process number of times, the air in the whole system is gradually driven out by the organic vapour. As the total volume of the tube system is only one tenth as compared with the volume of the bulb C, the replacement of air with the organic vapour by means of this method is very easy. As a matter of fact, the time required for the mercury to pass a distance between the two marks m_1 and m_2 becomes practically constant only after repetition of such processes five times. The present author has repeated the process at least ten times before the beginning of the actual measurement. Therefore it may be quite justified in stating that the system is filled with pure vapour of the organic compound.

When sufficient quantities of vapour are collected over the mercury in the bulb C, after waiting for a while, about 15 minutes being found to be sufficient in addition to the time required for the collection of the vapour in the bulb C for the vapour to attain the temperature of the bath T_0 , the vapour is finally driven back through the preheating tube W, the capillary K and vertical tube V into the liquid placed in the bulb apparatus PQR, with the pressure brought about by the mercury flowing

from the bulbs A and B down to C. The time required for the mercury to pass the distance between two marks m_1 and m_2 is measured by a stop watch and this observed value is reduced to an ideal value by adding some corrections which will be discussed below. The temperature T of the electrically heated thermostat, in which the capillary is placed, is regulated and is read every three minutes during the run and the average of these readings is adopted after being corrected for the exposed column, which is greatly diminished with the devices mentioned before.

The whole apparatus is carefully cleaned before each experiment with nitric acid and chromic mixture. It is then thoroughly washed with distilled water, alcohol and benzene and finally dried by passing dry air through the whole system alternatively in opposite directions. It will also be noted here, that when the experiment is interrupted the liquid in the bulb apparatus PQR must be drawn up into the one bulb R until the lower end of the vertical tube V becomes clear off the surface of the liquid. Otherwise, the liquid gets easily up into the measuring apparatus in the liquid form, thereby giving rise to a trouble, when the total system is cooled down.

Results of Experiments.

The viscosity η of the vapour at the absolute temperature T can be computed by means of the following formula:

$$\eta = K \frac{t}{T} \dots\dots\dots (1),$$

where t is the time required for the mercury to travel a distance between the marks m_1 and m_2 , T the temperature of the capillary measured in the absolute scale and K a constant for a given apparatus. But as this formula is derived by supposing ideal conditions, some corrections have to be applied in the actual case either to the time t or the constant K . The present author has applied them to the observed value of t . The corrections to be made are as follows:

(1) The correction due to the fluctuation of the temperature T_0 of the bulb C from the mean value ($108.0 + 273.1^\circ$ abs.):

$$\Delta_1 = \pm \Delta T_0 / T_0 = \pm 0.26\% / \pm 1^\circ\text{C}.$$

(2) The correction due to the fluctuation of the barometer readings from the mean value 760 mm. was experimentally determined and found to be:

$$\Delta_2 = \pm 0.012\% / \pm 1 \text{ mm}.$$

(3) The correction due to the thermal expansion of the glass capillary tube when its temperature T is different from the standard temperature ($115.0 + 273.1^\circ$ abs.):

$$\Delta_3 = 3\alpha(T - 388.1) = \pm 0.0025\% / \pm 1^\circ\text{C.},$$

where α is a linear expansion coefficient of glass.

(4) The correction due to the kinetic energy of the vapour in the capillary tube has been calculated from the consideration that the amount of the energy lost due to the molecular friction of the vapour in the capillary being equal to the total energy of the vapour entering the capillary minus the amount of the kinetic energy possessed by the vapour at the outlet of the capillary tube, and it has been found to be:

$$\Delta_4 = \frac{1}{K} \frac{V}{8\pi l R T} \cdot \frac{T M}{t^2} = 0.00557 \frac{T M}{t^2} \dots\dots\dots (2)$$

where V is the total volume of the vapour transpired during the time t , l the length of the capillary, R the gas constant, M the molecular weight and T the temperature of the vapour.

(5) The correction due to the deviation from the ideal gas state of the organic vapour employed⁽⁵⁾:

$$\Delta_5 = \frac{1}{RT_0} \left(\frac{a}{RT_0} - b \right) \frac{a}{760} - \frac{2}{3RT} \left(\frac{a}{RT} - b \right) \frac{\beta}{760} \dots\dots\dots (3),$$

where a and b are constants in the van der Waals equation, T the temperature of the capillary, T_0 that of the bulb C, α and β being constants for a given apparatus. For the present apparatus they have been found to be: $\alpha = 880$, $\beta = 1210$.

These corrections were made to the directly observed values of the time of passage t , and the reduced values of t thus obtained were put in the formula (1) to compute the viscosity η . The constant K in eq. (1) was determined experimentally by using air as a standard substance which has given 1023 sec. at 115.0°C. to the value for reduced t . At this temperature the viscosity of air⁽⁶⁾ is known to be $\eta = 2234 \times 10^{-7}$. Therefore

$$K = \frac{\eta \times T}{t} = \frac{2234 \times 10^{-7} \times (115.0 + 273.1)}{1023} = 0.8453 \times 10^{-4}.$$

(5) The derivation of this equation is referred to the original paper of M. Trautz and W. Weizel, loc. cit.

(6) T. Titani, loc. cit.

At the same time the apparatus has been tested by making measurements at several temperatures between 115.0° and 278.9°C . using air as a specimen. And from these data together with those obtained in the preceding paper (loc cit.) for Sutherland's constant 107 and for Reinganum's constant 84 were obtained. Then the measurements were continued for the other organic compounds.

The specimen used were all obtained from reliable commercial sources and carefully purified in the ordinary way. Their purity were checked by measuring the normal boiling points: *n*-pentane, $33.5^{\circ}\pm 3.2$; *n*-hexane, $69.0^{\circ}\pm 0.3$; hexamethylene, $80.9^{\circ}\pm 0.3$; benzene, $80.1^{\circ}\pm 0.0$; methyl acetate, $57.0^{\circ}\pm 0.2$; ethyl acetate, $77.1^{\circ}\pm 0.1$; ethyl ether, $34.55^{\circ}\pm 0.05$; methyl alcohol, $64.65^{\circ}\pm 0.05$; ethyl alcohol, $78.3^{\circ}\pm 0.0$; *n*-propyl alcohol, $97.1^{\circ}\pm 0.1$; isopropyl alcohol, $82.25^{\circ}\pm 0.05$; acetone, $56.05^{\circ}\pm 0.05$; chloroform, $61.05^{\circ}\pm 0.05$; carbon tetrachloride, $76.7^{\circ}\pm 0.0$; carbon disulphide, $46.2^{\circ}\pm 0.0$.

The results of the measurements for benzene and carbon tetrachloride vapour are shown in Tables 1 and 2 as examples.

Table 1.

Benzene.

$T-273.1$	t observed	Corrections %			t reduced	$\eta \cdot 10^7$
		$\Delta_1 + \Delta_2 + \Delta_3$	Δ_4	Δ_5		
131.2°	494.3	+0.07	-0.07	+0.36	496.1	1031
161.3	569.6	+0.19	-0.05	+0.57	573.6	1110
194.6	660.6	+0.23	-0.04	+0.75	666.8	1198
221.9	737.8	+0.19	-0.04	+0.89	745.5	1266
252.5	828.6	+0.39	-0.03	+1.00	839.9	1343
279.9	909.6	+0.46	-0.03	+1.09	923.4	1404
312.8	1017.4	+0.54	-0.02	+1.18	1034.7	1484

Table 2.

Carbon tetrachloride.

$T-273.1$	t observed	Corrections %			t reduced	$\eta \cdot 10^7$
		$\Delta_1 + \Delta_2 + \Delta_3$	Δ_4	Δ_5		
127.9°	630.2	-0.02	-0.09	+0.35	631.7	1334
169.3	759.7	+0.08	-0.07	+0.65	764.7	1463
200.2	865.1	+0.17	-0.06	+0.83	873.2	1562
237.2	993.9	+0.30	-0.05	+0.99	1006.2	1669
282.2	1168.1	+0.39	-0.04	+1.17	1185.9	1808
314.9	1299.0	+0.50	-0.03	+1.24	1321.2	1902

The results of the experiments are tabulated below, together with the calculated value of viscosity either with the Sutherland's or with Reinganum's formula:

$$\eta = K \frac{\sqrt{T}}{1 + \frac{C}{T}} \quad (\text{Sutherland}) \quad \dots\dots\dots (4),$$

$$\eta = K' \frac{\sqrt{T}}{e^{\frac{C'}{T}}} \quad (\text{Reinganum}) \quad \dots\dots\dots (5).$$

The constants K , C in eq. (4) and K' , C' in eq. (5) were computed by means of the method of least square from the observed data of viscosity. The agreement with the observed values is found to be equally good in both cases.

Table 3.

Air. (Free from carbon dioxide and moisture).

$K = 144.4 \times 10^{-7}$, $C = 106.8$; $K' = 140.8 \times 10^{-7}$, $C' = 84.3$

Temperature Centigrade	$\eta \times 10^7$		
	Observed	Calculated (Sutherland)	Calculated (Reinganum)
20.0° ⁽⁷⁾	1809	1812	1809
40.0	1897	1906	1904
60.0	2007	1999	1996
80.0	2079	2084	2085
100.0	2169	2169	2171
115.0	2234	2231	2233
133.0	2302	2305	2306
135.1	2315	2313	2315
175.2	2480	2470	2471
227.1	2665	2662	2662
278.9	2835	2843	2841

(7) The data between 20.0° and 100.0°C. were taken from the preceding paper. (T. Titani, loc. cit.).

Table 4.

Normal pentane.

$$K = 90.30 \times 10^{-7}, C = 382.8; K' = 78.32 \times 10^{-7}, C' = 212.4$$

Temperature Centigrade	$\eta \times 10^7$		
	Observed	Calculated (Sutherland)	Calculated (Reinganum)
121.6°	911	911	909
158.9	995	995	996
189.6	1064	1063	1065
219.1	1126	1127	1129
249.5	1191	1192	1193
277.1	1250	1249	1249
305.9	1307	1308	1306

Table 5.

Normal hexane.

$$K = 92.16 \times 10^{-7}, C = 436.1; K' = 77.83 \times 10^{-7}, C' = 228.3$$

Temperature Centigrade	$\eta \times 10^7$		
	Observed	Calculated (Sutherland)	Calculated (Reinganum)
120.7°	866	868	865
160.8	958	957	958
188.9	1021	1019	1021
220.1	1088	1086	1088
248.0	1144	1145	1147
280.4	1213	1213	1212
306.6	1265	1266	1264

Table 6.

Hexamethylene (Cyclohexane).

$$K = 86.95 \times 10^{-7}, C = 350.9; K' = 76.56 \times 10^{-7}, C' = 201.6$$

Temperature Centigrade	$\eta \times 10^7$		
	Observed	Calculated (Sutherland)	Calculated (Reinganum)
121.7°	913	915	913
154.0	987	987	987
188.3	1064	1061	1063
218.1	1124	1124	1126
248.9	1189	1188	1189
278.5	1245	1248	1248
306.4	1305	1304	1302

Table 7.

Benzene.

$$K = 108.2 \times 10^{-7}, C = 447.5; K' = 90.81 \times 10^{-7}, C' = 231.2$$

Temperature Centigrade	$\eta \times 10^7$		
	Observed	Calculated (Sutherland)	Calculated (Reinganum)
131.2°	1031	1033	1031
161.3	1110	1111	1112
194.6	1198	1196	1198
221.9	1266	1265	1267
252.5	1343	1340	1341
279.9	1404	1407	1406
312.8	1484	1485	1482

Table 8.

Methyl acetate.

$$K = 122.9 \times 10^{-7}, C = 501.8; K' = 100.4 \times 10^{-7}, C' = 245.9$$

Temperature Centigrade	$\eta \times 10^7$		
	Observed	Calculated (Sutherland)	Calculated (Reinganum)
143.3°	1139	1137	1136
177.7	1236	1235	1236
218.5	1348	1348	1351
248.2	1429	1429	1431
277.9	1508	1509	1509
306.6	1583	1586	1582

Table 9.

Ethyl acetate.

$$K = 114.7 \times 10^{-7}, C = 504.0; K' = 93.58 \times 10^{-7}, C' = 246.1$$

Temperature Centigrade	$\eta \times 10^7$		
	Observed	Calculated (Sutherland)	Calculated (Reinganum)
128.1°	1018	1018	1015
158.6	1098	1099	1100
192.9	1195	1189	1192
218.3	1250	1255	1257
248.6	1332	1332	1334
280.1	1409	1411	1411
313.7	1497	1495	1491

Table 10.

Ethyl ether.

$$K = 100.3 \times 10^{-7}, C = 404.0; K' = 86.36 \times 10^{-7}, C' = 220.5$$

Temperature Centigrade	$\eta \times 10^7$		
	Observed	Calculated (Sutherland)	Calculated (Reinganum)
121.8°	983	985	982
159.4	1079	1079	1079
189.9	1152	1153	1154
217.7	1222	1219	1221
251.0	1300	1297	1298
277.8	1358	1358	1359
308.9	1425	1428	1427

Table 11.

Methyl alcohol.

$$K = 145.7 \times 10^{-7}, C = 486.9; K' = 119.0 \times 10^{-7}, C' = 237.8$$

Temperature Centigrade	$\eta \times 10^7$		
	Observed	Calculated (Sutherland)	Calculated (Reinganum)
111.3°	1259	1260	1257
153.9	1408	1407	1409
188.8	1527	1525	1529
217.5	1620	1620	1624
250.0	1725	1726	1728
277.6	1815	1815	1813
311.5	1921	1922	1916

Table 12.

Ethyl alcohol.

$$K = 117.6 \times 10^{-7}, C = 407.3; K' = 101.2 \times 10^{-7}, C' = 222.3$$

Temperature Centigrade	$\eta \times 10^7$		
	Observed	Calculated (Sutherland)	Calculated (Reinganum)
130.2°	1173	1175	1170
170.7	1293	1292	1293
191.8	1355	1352	1353
217.5	1421	1423	1426
251.7	1519	1517	1520
278.2	1585	1588	1588
308.7	1670	1669	1667

Table 13.

Normal propyl alcohol.

$$K = 119.1 \times 10^{-7}, C = 515.6; K' = 95.50 \times 10^{-7}, C' = 243.5$$

Temperature Centigrade	$\eta \times 10^7$		
	Observed	Calculated (Sutherland)	Calculated (Reinganum)
121.7°	1025	1026	1024
149.0	1102	1102	1102
179.8	1186	1185	1187
209.7	1267	1266	1267
243.2	1350	1354	1354
273.0	1434	1432	1429

Table 14.

Iso-propyl alcohol.

$$K = 113.2 \times 10^{-7}, C = 459.9; K' = 94.13 \times 10^{-7}, C' = 233.0$$

Temperature Centigrade	$\eta \times 10^7$		
	Observed	Calculated (Sutherland)	Calculated (Reinganum)
119.2°	1028	1032	1030
121.3	1034	1038	1036
138.4	1084	1085	1084
149.2	1112	1114	1114
169.4	1169	1168	1170
190.7	1231	1224	1227
192.9	1237	1230	1233
198.4	1248	1245	1247
218.3	1299	1297	1299
235.1	1340	1340	1342
251.1	1382	1381	1382
279.2	1450	1452	1451
293.1	1488	1487	1484
307.9	1517	1523	1519

Table 15.

Acetone.

$$K = 119.2 \times 10^{-7}, C = 541.5; K' = 95.45 \times 10^{-7}, C' = 254.7$$

Temperature Centigrade	$\eta \times 10^7$		
	Observed	Calculated (Sutherland)	Calculated (Reinganum)
119.0°	991	992	937
159.5	1101	1101	1102
190.4	1186	1184	1186
217.3	1253	1255	1258
247.7	1334	1334	1336
278.8	1416	1414	1414
306.4	1481	1484	1481

Table 16.

Chloroform.

$$K = 132.9 \times 10^{-7}, C = 373.0; K' = 115.4 \times 10^{-7}, C' = 207.6$$

Temperature Centigrade	$\eta \times 10^7$		
	Observed	Calculated (Sutherland)	Calculated (Reinganum)
121.3°	1357	1356	1354
161.3	1491	1490	1492
189.1	1579	1581	1584
218.7	1674	1676	1678
250.0	1776	1774	1775
279.4	1868	1865	1863
307.5	1947	1950	1945

Table 17.

Carbon tetrachloride.

$$K = 127.1 \times 10^{-7}, C = 365.4; K' = 110.9 \times 10^{-7}, C' = 205.6$$

Temperature Centigrade	$\eta \times 10^7$		
	Observed	Calculated (Sutherland)	Calculated (Reinganum)
127.9°	1334	1332	1331
169.3	1463	1464	1466
200.2	1562	1561	1563
237.2	1669	1673	1675
282.2	1808	1807	1805
314.9	1902	1901	1896

Table 18.

Carbon disulphide.

$$K = 151.1 \times 10^{-7}, C = 499.5; K' = 122.7 \times 10^{-7}, C' = 241.3$$

Temperature Centigrade	$\eta \times 10^7$		
	Observed	Calculated (Sutherland)	Calculated (Reinganum)
114.3°	1303	1299	1296
152.8	1434	1436	1438
190.2	1561	1565	1570
228.2	1692	1695	1698
267.3	1830	1826	1826
309.8	1966	1965	1959

Some results of the present author are compared with those of the other observers. The values of viscosity observed by the author at 100°C. are listed together with those of the other observers in Table 19.

Table 19.

Viscosity at 100°C. $\times 10^{-7}$.

Substance	Author's	Other observers'
Normal pentane	859	841 (Bleakney 1932) ⁽⁸⁾
Normal hexane	818	880 (Nasini 1929) ⁽⁹⁾
Hexamethylene	864	{ 1176 (Schumann 1884) ⁽¹⁰⁾
		{ 930 (Rappenecker 1910) ⁽¹¹⁾
Benzene	947	{ 940 (Nasini 1929)
Methyl acetate	1008	1015 (Rappenecker 1910)
Ethyl acetate	939	955 { " " }
Ethyl ether	927	{ 942 (Pedersen 1907) ⁽¹²⁾
Methyl alcohol	1218	{ 967 (Rappenecker 1910)
Ethyl alcohol	1082	{ 1088 (Pedersen 1907)
Normal propyl alcohol	964	{ 1090 (Rappenecker 1910)
Iso-propyl alcohol	977	_____
Acetone	936	943 (Rappenecker 1910)

(8) Bleakney, *Physics*, **3** (1932), 123.(9) Nasini, *Proc. Roy. Soc. London*, A **123** (1929), 692.(10) Schumann, *Wied. Ann.*, **23** (1884), 353.(11) Rappenecker, *Z. physik. Chem.*, **72** (1910), 695.(12) Pedersen, *Phys. Rev.*, **25** (1907), 225.

Table 19.—(Concluded)

Substance	Author's	Other observers'
Chloroform	1281	{ 1307 (Rappenecker 1910) { 1244 (Braune & Linke 1930) ⁽¹³⁾
Carbon tetrachloride	1238	{ 1164 () { 1203 (Sperry & Mack 1932) ⁽¹⁴⁾
Carbon disulphide	1245	1218 (Bleakney 1932)

The agreement between the values of the author and those of the other observers is generally good except few cases.

The Sutherland's and Reinganum's constants obtained by the author are listed in Tables 20 and 21 respectively, together with those reported by the other observers. Large differences between the values of the author and those of the other observers are often found. But it must be taken

Table 20.

Sutherland's constants.

Substance	Author's	Other observers' ⁽¹⁵⁾
Normal pentane	383	299 (Bleakney 1932)
Normal hexane	436	————
Hexamethylene	351	330 (Nasini 1929)
Benzene	448	{ 700 (Rappenecker 1910) { 380 (Nasini 1929)
Methyl acetate	502	660 (Rappenecker 1910)
Ethyl acetate	504	650 (,)
Ethyl ether	404	325 (,)
Methyl alcohol	487	————
Ethyl alcohol	407	525 (Rappenecker 1910)
Normal propyl alcohol	516	————
Iso-propyl alcohol	460	————
Acetone	542	670 (Rappenecker 1910)
Chloroform	373	{ 292 () { 462 (Braune & Linke 1930)
Carbon tetrachloride	365	{ 492 () { 335 (Sperry & Mack 1932)
Carbon disulphide	500	————

(13) Braune and Linke, *Z. physik. Chem.*, **A148** (1930), 195.(14) Sperry and Mack, *J. Am. Chem. Soc.*, **54** (1932), 904.

(15) loc. cit.

Table 21.
Reinganum's constants.

Substance	Author's	Other observers' ⁽¹⁶⁾
Normal pentane	212	—
Normal hexane	228	—
Hexamethylene	202	—
Benzene	231	260 (Rappenecker 1910)
Methyl acetate	246	258 („)
Ethyl acetate	246	260 („)
Ethyl ether	221	180 („)
Methyl alcohol	238	—
Ethyl alcohol	222	210 (Rappenecker 1910)
Normal propyl alcohol	244	—
Iso-propyl alcohol	233	—
Acetone	255	251 (Rappenecker 1910)
Chloroform	208	173 („)
Carbon tetrachloride	206	—
Carbon disulphide	241	—

into consideration that in determining the values for Sutherland's and Reinganum's constants, the method based on the data at few successive temperatures, as was done by Rappenecker, would be more liable to lead to great errors than the method in which a greater number of observations are made.

J. Arnold⁽¹⁷⁾ has recently pointed out that the Sutherland's constants can be calculated from the viscosity determination at a single temperature T by the use of the molecular diameter calculated from the molecular volume V_S at boiling point, according to the formula:

$$C^* = 2.70 \times 10^{-5} (M^{\frac{1}{2}} T^{\frac{3}{2}} / \eta V_S^{\frac{2}{3}}) - T \dots\dots\dots (6),$$

where M means molecular weight. The values of C^* calculated from the viscosity data at 100°C. are listed in Table 22 together with the values of C computed by the ordinary method. The agreement between C and C^* is generally good, average deviation being 5%, except few cases i.e. hexamethylene, methyl alcohol, chloroform and carbon tetrachloride.

(16) Rappenecker, loc. cit.

(17) J. H. Arnold, *J. Chem. Phys.*, **1** (1933) 170.

Table 22 contains also the values of Sutherland's constants calculated according to the rules of Rankine⁽¹⁸⁾ and Vogel⁽¹⁹⁾, the Sutherland's constant being found to be roughly proportional either to the critical temperature T_K or to the boiling point T_S , both of which are measured in the absolute scale;

$$C = T_K/1.12 \quad (\text{Rankine}) \dots\dots\dots (7),$$

$$C = 1.47 T_S \quad (\text{Vogel}) \dots\dots\dots (8).$$

Table 22.
Sutherland's constants.

Substance	C	C^*	$T_K/1.12$	$1.47 T_S$
Normal pentane	383	427	420	454
Normal hexane	436	446	454	503
Hexamethylene	351	494	494	521
Benzene	448	492	501	519
Methyl acetate	502	494	453	485
Ethyl acetate	504	495	467	515
Ethyl ether	404	432	417	453
Methyl alcohol	487	366	458	497
Ethyl alcohol	407	405	461	516
Normal propyl alcohol	516	459	479	549
Iso-propyl alcohol	460	452	461	522
Acetone	542	501	454	484
Chloroform	373	489	479	491
Carbon tetrachloride	365	510	496	515
Carbon disulphide	500	496	494	469

The agreement with the observed values seems to be better for the Rankine's formula than for that of Vogel.

Collision Diameter.

The collision diameters of the molecules were computed by using the following equations all of which are derived from the kinetic theory of gases⁽²⁰⁾:

(18) Rankine, *Proc. Roy. Soc. London*, A **84** (1910), 181.

(19) Vogel, *Ann. Phys.*, **43** (1914), 1235.

(20) Kuenen, „Die Eigenschaften der Gase“, (1919), p. 136.

$$\bar{u}^2 = \frac{8}{\pi} \frac{p}{d} = \frac{8}{\pi} \times 1013250 \times \frac{30619}{M} \dots\dots\dots (9),$$

$$l = \frac{32\eta}{5\pi d\bar{u}} = \frac{\eta \times 30619}{0.49 \times M \times \bar{u}} \dots\dots\dots (10),$$

$$\sigma^2 = \frac{1}{\sqrt{2n\pi l F(T)}}, \quad (n = 2.0 \times 10^{19}) \dots\dots\dots (11),$$

where $F(T) = 1 + \frac{C}{T}$ (Sutherland) $\dots\dots\dots (12),$

or $F(T) = e^{\frac{C'}{T}}$ (Reinganum) $\dots\dots\dots (13),$

and the symbols in the equations have the following meanings:

- $\bar{u}$: mean velocity of the molecule at 100°C.,
- p : atmospheric pressure,
- d : density of the vapour at 100°C. and under the atmospheric pressure,
- M : molecular weight,
- l : mean free path of the molecule at 100°C. and under the atmospheric pressure,
- η : viscosity of the vapour at 100°C.,
- σ : collision diameter of the molecule,
- n : number of molecules contained in 1 c.c. at 100°C. and under the atmospheric pressure.

The results of the calculation are listed in Tables 23 and 24, where σ_S means the molecular diameter calculated by the use of the Sutherland's formula (12) and σ_R that of Reinganum (13). The molecular diameter can also be computed from the constant b in the van der Waals equation⁽²¹⁾ namely:

$$\sigma_b = \frac{3}{2} \frac{b}{N_A \pi}, \quad (N_A = 6.06 \times 10^{23}) \dots\dots\dots (14),$$

where N_A means the Avogadro's constant. The values σ_b are given in the fourth column of Table 24, and it will be seen in most cases that σ_b is nearly equal to σ_S . The last column of Table 24 contains the cube root of the molecular volume V_S at boiling point, which may be proportional to σ_S , as it was already pointed out in the preceding paper⁽²²⁾. It

(21), (22) T. Titani, loc. cit.

Table 23.

Substance	M	$\bar{u}$	$\eta \cdot 10^7$	$l \cdot 10^8$	C	C'
Normal pentane	72.10	33100	859	225	383	212
Normal hexane	86.11	30290	818	196	436	228
Hexamethylene	84.10	30650	864	210	351	202
Benzene	78.05	31820	947	238	448	231
Methyl acetate	74.05	32660	1008	260	502	246
Ethyl acetate	88.06	29950	939	223	504	246
Ethyl ether	74.08	32660	927	239	404	221
Methyl alcohol	32.03	49660	1218	478	487	238
Ethyl alcohol	46.05	41420	1082	355	407	222
Normal propyl alcohol	60.06	36270	964	277	516	244
Iso-propyl alcohol	60.06	36270	977	280	460	233
Acetone	58.05	36890	936	273	542	255
Chloroform	119.39	25720	1281	261	373	208
Carbon tetrachloride	153.84	22660	1238	222	365	206
Carbon disulphide	76.12	32220	1245	317	500	241

Table 24.

Substance	$\sigma_S \times 10^8$ (Sutherland)	$\sigma_R \times 10^8$ (Reinganum)	$\sigma_b \times 10^8$ (From b)	Cube root of Mol. Vol. at B.P. $\sqrt[3]{V_S}$
Normal pentane	5.00	5.35	4.86	4.90
Normal hexane	5.18	5.61	5.18	5.19
Hexamethylene	5.19	5.63	4.83	4.88
Benzene	4.66	5.07	4.56	4.58
Methyl acetate	4.32	4.76	4.46	4.38
Ethyl acetate	4.67	5.15	4.81	4.73
Ethyl ether	4.78	5.13	4.73	4.74
Methyl alcohol	3.21	3.55	3.75	3.50
Ethyl alcohol	3.92	4.21	4.05	3.96
Normal propyl alcohol	4.16	4.63	4.42	4.34
Iso-propyl alcohol	4.27	4.66	4.26	4.33
Acetone	4.12	4.59	4.19	4.26
Chloroform	4.67	5.01	4.32	4.39
Carbon tetrachloride	5.09	5.44	4.64	4.70
Carbon disulphide	3.92	4.34	3.93	3.96

is actually the case for most compounds listed in Table 24 except few cases. The compounds whose molecules are of extremely non-polar nature, such as hexamethylene, chloroform and carbon tetrachloride seem to give σ_s too large a value as compared with σ_b or $\sqrt[3]{V_s} \cdot 10^{-8}$. However, for the compounds of strong polar nature such as methyl alcohol the reverse is the case. These differences must result either from the function $F(T)$ in eq. (11) or more directly from the Sutherland's constant C in $F(T)$, which measures the work required to separate two molecules from each other against the intermolecular attraction.

The collision diameter of benzene seems to be interesting in relation to its magnitude. It has become clear not only from the X-ray crystallographical study but also from the thermochemical investigations that the benzene nucleus is the same as the hexagonal carbon atom lattice in graphite, the length of the one side of this hexagonal model being found to be 2.45 Å. Therefore, its diameter is equal to $2 \times 2.45 = 4.9$ Å, when we assume the model to have a regular form. This value is very nearly equal to the collision diameter of benzene, $\sigma = 4.7 - 5.1$ Å deduced from the viscosity measurement in the present research.

The experimental part of the present research was carried out between April 1929 and April 1930 in the Katayama Laboratory of the Institute of Physical and Chemical Research, Hongo, Tokio. The delay of the publication is mainly due to the trip which the author made in Europe.

The author wishes to express his cordial thanks to Prof. Katayama for his interest and encouragement taken in this research.

Summary.

(1) An apparatus, based on the principle of Trautz and Weizel, was constructed for measuring the viscosity of vapours.

(2) With this apparatus the viscosity of vapours of the following substances were measured at temperatures between about 120° and 300°C.: air, *n*-pentane, *n*-hexane, hexamethylene, benzene, methyl acetate, ethyl acetate, ethyl ether, methyl alcohol, ethyl alcohol, *n*-propyl alcohol, iso-propyl alcohol, acetone, chloroform, carbon tetrachloride and carbon disulphide.

(3) From these measurements the constants of both Sutherland and Reinganum as well as collision diameters of molecules were calculated.

(4) The collision diameters calculated from viscosity data were found to be nearly equal to those computed from the constants b in the

van der Waals equation and they came out to be proportional to the cube roots of molecular volumes at boiling points, as was already pointed out in the preceding paper except few cases.

(5) Values obtained for collision diameters of non-polar compounds such as carbon tetrachloride and hexamethylene seem to be too large and those for strong polar compounds such as methyl alcohol too small as compared with the values of molecular diameters computed from b or from the molecular volumes at boiling points.

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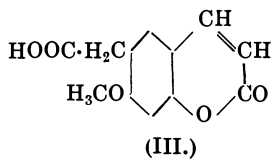
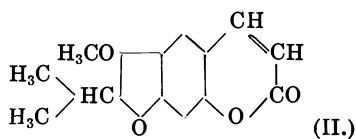
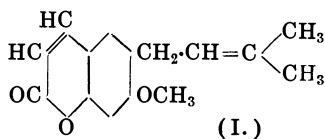
June, 1933.

A SYNTHESIS OF DIHYDROISOOSTHOL. NOTE ON THE CONSTITUTION OF OSTHOL.

By Masataro YAMASHITA.

Received July 20th, 1933. Published September 28th, 1933.

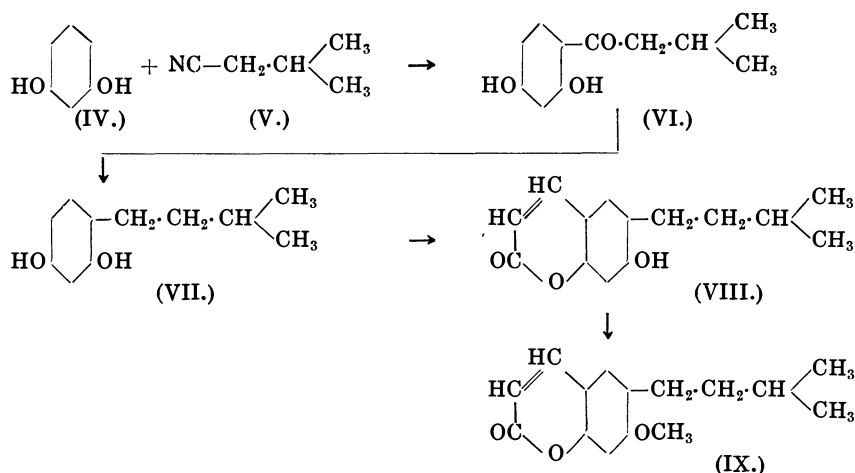
A fish-poison, Osthol, was first isolated from the root of *Imperatoria Ostruthium* by Herzog and Krohn⁽¹⁾, who, however, did not determine its constitution. This (I) was suggested last year by Butenandt and Marten⁽²⁾, from its relation to peucedanin (II) and from the formation of acetone and ostholic acid (III) by its oxidation with chromic acid.



The present work has been undertaken to synthesise dihydro-osthol in the following scheme:—

(1) *Arch. Pharm.*, **247** (1909), 553.

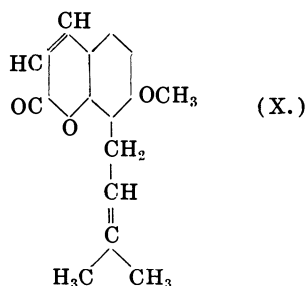
(2) *Ann.*, **495** (1932), 187.



In 1926, Dohme and his collaborators⁽³⁾ synthesised the ketone (VI) by means of a condensation of isovaleric acid with resorcinol in the presence of zinc chloride. The present author attempted to synthesise it by condensing resorcinol with isovaleronitrile by the Hoesch reaction. However, when dry hydrogen chloride gas was passed into a mixture of isovaleronitrile and resorcinol in ethereal solution in the presence of zinc chloride, neither precipitate nor oily substance was separated. This phenomenon is very different from the ordinary Hoesch reaction. After hydrolysing the reaction product, many attempts were made to obtain the desired ketone in the crystalline state, but without success. In order to prove the presence of the ketone, the crude product was converted into its oxime, m.p. 203–205°C. As Dohme and his collaborators⁽³⁾ had not synthesised this oxime, the present author synthesised ketone (VI) according to their method, and converted it into its oxime for comparison's sake. Both the oximes melted at the same temperature, and no depression of the melting point was caused on mixing them. The formation of 2:4-dihydroxyphenyl isobutyl ketone having been thus confirmed, the crude ketone was next reduced to 2:4-dihydroxyisovaleryl benzene (VII) by means of amalgamated zinc and hydrochloric acid, and the resulting compound was converted into 6-isoamyl-7-hydroxycoumarine (VIII) according to the Pechmann reaction. 6-Isoamyl-7-hydroxycoumarine was finally methylated with diazomethane or with methyl iodide and caustic alkali, when 6-isoamyl-7-methoxycoumarine, m.p. 61–62°C. was obtained. This melting point differs by about 20°C. from that of dihydro-osthol.

(3) *J. Amer. Chem. Soc.*, **48**(1926), 1690.

The constitution of dihydro-osthol appears therefore to be different from that of (IX) as suggested by Butenandt and his collaborator⁽⁴⁾. This fact receives strong support from the recent work of Späth and Peste⁽⁵⁾, who advanced the view that osthol has the structure (X) in contrary to formula (I), for they isolated 2:6-dihydroxytoluene as its decomposition product.



The present author proposes to designate the synthetical 6-isoamyl-7-methoxycoumarine as "dihydroisoosthol."

Experimental.

2:4-Dihydroxyphenyl Isobutyl Ketoxime, $C_4H_9C(=NOH)C_6H_3(OH)_2$. Isovaleronitrile (3.3 gr.) and resorcinol (3 gr.) were dissolved in 40 c.c. of absolute ether, and after adding two grams of freshly fused and powdered zinc chloride, a gentle stream of dry hydrogen chloride was passed into the mixture. The ethereal solution was first separated into two layers. The upper layer was colourless, whilst the lower one was reddish. After a short time, the former was redissolved in the latter, and the solution became viscous and reddish. After the solution has been saturated with hydrogen chloride, it was allowed to stand overnight, and the ether was then evaporated. The oily residue was warmed with 50 c.c. of water on a water-bath for half an hour, and, after cooling, the product was extracted several times with ether, and the ethereal solution was washed with water, dried, and evaporated. The oily substance (A) thus separated was dissolved in a concentrated solution of potassium hydroxide (10 gr.), mixed with a concentrated solution of hydroxylamine hydrochloride (6 gr.), and allowed to stand overnight. The mixture was acidified with dilute hydrochloric acid, when a precipitate (0.6 gr.) was deposited. It was recrystallised from dilute methyl

(4) *Ann.*, **495**(1932), 187.

(5) *Ber.*, **66**(1933), 754.

alcohol with the addition of animal charcoal, from which it separated in the form of colourless plates, m.p. 203–205°C.

Anal.: Subst. = 5.694 mg. N_2 = 0.325 c.c. at 15°C. and 757.7 mm.

Found: N = 6.80%.

Calc. for $C_{11}H_{15}O_3N$: N = 6.73%.

It is soluble in acetone and in alcohol, but only slightly so in benzene, and insoluble in chloroform, carbon tetrachloride, water and ether. Its alcoholic solution gave a violet coloration with ferric chloride.

The ketone prepared by the method of Dohme and his collaborators was converted into the oxime under the same conditions as those in the above experiment, when the oxime melted at 203–205°C., and no depression of the melting point by admixture with the above-mentioned oxime resulted.

2:4-Dihydroxy-isoamylbenzene (VII). The crude oil (A) was reduced with zinc amalgam and hydrochloric acid by the same method as that used by Dohme and his collaborators⁽⁶⁾. The purified substance melted at 61–62.5°C. Dohme and his collaborators⁽⁶⁾ gave 61–62.5°C. as its melting point.

6-Isoamyl-7-hydroxycoumarine (VIII). Seven grams of 2:4-dihydroxy-isoamylbenzene were thoroughly mixed with 5.5 gr. of malic acid, and, to this mixture, 12 c.c. of concentrated sulphuric acid (D. 1.84) were added. The whole was warmed for a short time on a sand-bath, which had been previously heated. After the reaction mixture had been cooled, it was mixed with finely crushed ice and allowed to stand overnight, when it solidified to a greyish mass. It was separated by decantation, well washed with water, and recrystallised several times from dilute methyl alcohol with the addition of animal charcoal, from which it separated in the form of colourless needles, melting at 108–110°C. The yield was 5.1 gr. after one crystallisation.

Anal.: Subst. = 3.487; CO_2 = 9.223; H_2O = 2.11 mg.

Found: C = 72.24; H = 6.80%.

Calc. for $C_{14}H_{16}O_3$: C = 72.37; H = 6.94%.

6-Isoamyl-7-methoxycoumarine (Dihydroisoosthol) (IX).

(1) An ethereal solution of diazomethane prepared from 2 c.c. of nitrosomethylurethane was added to a methyl alcoholic solution of 0.2 gr. of 6-isoamyl-7-hydroxycoumarine and allowed to stand for a short time

(6) *J. Amer. Chem. Soc.*, **48** (1926), 1691.

After the removal of the solvents from the reaction mixture, the resinous residue was digested with a dilute solution of caustic alkali, and allowed to stand for two or three hours, when the methylated product was separated as a precipitate, which was collected, washed with water, and recrystallised from dilute methyl alcohol with the addition of animal charcoal.

(2) 6-Isoamyl-7-hydroxycoumarine (0.2 gr.), methyl iodide (1 gr.), potassium hydroxide (0.05 gr.) and methyl alcohol (5 c.c.) were mixed and boiled for two hours under a reflux condenser. After the removal of the alcohol, the resinous reaction mixture was purified in the same way as (1).

The purified specimen in each experiment crystallised in the form of colourless plates, m.p. 61–62°C.

Anal.: Subst. = 3.260; CO₂ = 8.769; H₂O = 2.224 mg.

Found: C = 73.36; H = 7.63%.

Calc. for C₁₅H₁₈O₃: C = 73.12; H = 7.37%.

In conclusion, the present author wishes to express his hearty thanks to Professor Hiroshi Nomura for his kind guidance and encouragement during this investigation.

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A VISCOSITY FORMULA FOR BINARY MIXTURES, THE
ASSOCIATION DEGREES OF CONSTITUENTS BEING
TAKEN INTO CONSIDERATION. VII.

By Tetsuya ISHIKAWA.

Received June 23rd, 1933. Published September 28th, 1933.

In the earlier communication of the study on this subject⁽¹⁾ the writer has shown that the viscosity of binary mixtures showing a maximum against the concentration, such as systems $\text{CH}_3\text{COOH-H}_2\text{O}$, $\text{CH}_3\text{OH-H}_2\text{O}$, and $\text{C}_2\text{H}_5\text{OH-H}_2\text{O}$, can be explained with quite satisfaction by postulating the difference (δ) of measured viscosity (η) from that calculated from his viscosity formula for chemically indifferent mixtures (η_0) or "the solva-

(1) This Bulletin 4 (1929), 25.

tion viscosity" to be proportionate to the encounter probability of ν_1 and ν_2 molecules of the components to form a molecular compound. Thus,

$$\begin{aligned}\eta &= \eta_0 + \delta, \\ \eta_0 &= \eta_1 + (\eta_2 - \eta_1) \frac{k_2 a_2 z_m}{k_1 a_1 (1 - z_m) + k_2 a_2 z_m}, \\ \delta &= C(1 - z_m)^{\nu_1} z_m^{\nu_2},\end{aligned}$$

where η , a , k with suffixes 1 and 2 signify the viscosity coefficients, the association degrees and field constants of components 1 and 2 respectively; z_m a formal molar fraction of component 2; and C a proportional constant.

According to this theory the criterion for determining the composition of a molecular compound is not the position of the maximum often shifting with temperature which has given annoyance to many earlier investigators, but the keeping constancy of the proportional constant C which strictly holds good for viscosity isotherms so long as the molecular compound exists in the mixture.

Dependence of the Field Constant k on Temperature.

Before entering into further study on the proportional constant C , it is necessary to test the dependence of the field constant on temperature. Since association degrees of liquids are functions of temperature, the mixtures which are to be taken for test of the proposition are those which must be composed of two non-associated and chemically indifferent liquids. The following case studied by Meyer and Mylius⁽²⁾ is very favorable for this purpose.

The fact that is readily understood from Table 1 is that the field constant of any liquid is independent of temperature or otherwise it has the same temperature variation, and that the factor in $\frac{k_2 a_2}{k_1 a_1}$ which changes with temperature is the ratio of the association degree of component 2 to that of component 1. So that, for such pairs as are composed of liquids having the same temperature coefficient of the association degrees, the term $\frac{k_2 a_2}{k_1 a_1}$ is of course independent of temperature and the above equation which originally holds true for viscosity isotherms is also valid for any temperature.

(2) J. Meyer & B. Mylius, *Z. physik. Chem.* **95** (1920), 349.

Table 1.
C₆H₆-C₆H₅Br, Meyer & Mylius.

z -C ₆ H ₅ Br	0°C.	10°C.	20°C.	30°C.	40°C.	50°C.	60°C.	70°C.
0.00000 η	0.00912	0.00758	0.00652	0.00564	0.00503	0.00443	0.00392	0.00358
η	0.00976	0.00827	0.00703	0.00616	0.00546	0.00487	0.00438	0.00398
0.24746 $\left(\frac{k_2 a_2}{k_1 a_1}\right)_z$	0.37	0.46	0.38	0.43	0.39	0.44	0.50	0.39
η	0.01115	0.00926	0.00788	0.00635	0.00603	0.00567	0.00500	0.00448
0.50238 $\left(\frac{k_2 a_2}{k_1 a_1}\right)_z$	0.49	0.47	0.41	0.41	0.37	0.52	0.48	0.44
η	0.01257	0.01059	0.00915	0.00803	0.00709	0.00636	0.00579	0.00524
0.74746 $\left(\frac{k_2 a_2}{k_1 a_1}\right)_z$	0.45	0.45	0.44	0.46	0.43	0.42	0.45	0.44
1.00000 η	0.01515	0.01282	0.01117	0.00979	0.00872	0.00794	0.00719	0.00652
Mean $\left(\frac{k_2 a_2}{k_1 a_1}\right)_z$	0.44	0.46	0.41	0.43	0.40	0.46	0.48	0.42

Table 2.
CH₃OH-C₂H₅OH, Bingham, White, Thomas, & Cadwell.

z -C ₂ H ₅ OH	25°C.		35°C.		45°C.		55°C.	
	η	$\left(\frac{k_2 a_2}{k_1 a_1}\right)_z$	η	$\left(\frac{k_2 a_2}{k_1 a_1}\right)_z$	η	$\left(\frac{k_2 a_2}{k_1 a_1}\right)_z$	η	$\left(\frac{k_2 a_2}{k_1 a_1}\right)_z$
0.0000	0.00548		0.00476		0.00420		0.00371	
0.2616	0.00639	0.55	0.00552	0.59	0.00481	0.60	0.00423	0.66
0.4960	0.00737	0.53	0.00635	0.58	0.00548	0.60	0.00476	0.63
0.7385	0.00880	0.54	0.00746	0.56	0.00636	0.59	0.00546	0.62
1.0000	0.01099		0.00917		0.00766		0.00645	
	Mean	0.54		0.58		0.60		0.63

Table 3.

$$\text{H}_2\text{O}-\text{CH}_3\text{OH}, \text{ Traube.}^{(3)} \quad \eta_0 = \eta_1 + (\eta_2 - \eta_1) \frac{0.96 z_m}{(1 - z_m) + 0.96 z_m}.$$

$z-\text{CH}_3\text{OH}$	0.00	0.10	0.20	0.30	0.40	0.50	0.60	0.80	1.00
$z_m-\text{CH}_3\text{OH}$	0.0000	0.0588	0.1233	0.1943	0.2727	0.3601	0.4576	0.6925	1.0000
20°C.	η	0.01035	0.01338	0.01639	0.01829	0.01881	0.01816	0.01629	0.01142
	η_0	—	0.01011	0.00984	0.00955	0.00922	0.00885	0.00844	0.00742
	δ		0.00327	0.00655	0.00874	0.00959	0.00931	0.00785	0.00400
	δ		0.063	0.069	0.069	0.067	0.063	0.058	0.063
	$(1-z_m)^2 z_m$			Mean	0.065				
30°C.	η	0.00819	0.01056	0.01240	0.01378	0.01417	0.01378	0.01273	0.00933
	η_0	—	0.00803	0.00786	0.00767	0.00745	0.00722	0.00695	0.00629
	δ		0.00253	0.00454	0.00611	0.00672	0.00656	0.00578	0.00304
	δ		0.049	0.048	0.048	0.047	0.045	0.043	0.046
	$(1-z_m)^2 z_m$			Mean	0.047				
40°C.	η	0.00668	0.00823	0.00960	0.01064	0.01091	0.01073	0.01004	0.00769
	η_0	—	0.00656	0.00644	0.00629	0.00614	0.00596	0.00576	0.00528
	δ		0.00167	0.00316	0.00435	0.00477	0.00477	0.00428	0.00241
	δ		0.032	0.033	0.035	0.033	0.032	0.032	(0.037)
	$(1-z_m)^2 z_m$			Mean	0.033				
50°C.	η	0.00566	0.00638	0.00788	0.00867	0.00884	0.00875	0.00817	0.00650
	η_0	—	0.00557	0.00547	0.00536	0.00524	0.00510	0.00494	0.00457
	δ		0.00131	0.00241	0.00331	0.00360	0.00365	0.00323	0.00193
	δ		0.025	0.025	0.026	0.025	0.025	0.024	(0.030)
	$(1-z_m)^2 z_m$			Mean	0.025				
60°C.	η	0.00495	0.00565	0.00645	0.00699	0.00717	0.00730	0.00685	0.00569
	η_0	—	0.00487	0.00479	0.00470	0.00460	0.00448	0.00435	0.00403
	δ		0.00078	0.00166	0.00229	0.00257	0.00282	0.00250	0.00166
	δ		(0.015)	0.018	0.018	0.017	0.019	0.019	(0.025)
	$(1-z_m)^2 z_m$			Mean	0.018				

(3) J. Traube, *Ber.* **19** (1886), 871.

Table 4.

H₂O—C₂H₅OH, International Critical Tables, V, 22.

$$\eta_0 = \eta_1 + (\eta_2 - \eta_1) \frac{0.70 z_m}{(1 - z_m) + 0.70 z_m}.$$

z —C ₂ H ₅ OH	0.00	0.10	0.20	0.30	0.40	0.50	0.60	0.70	0.80	0.90	1.00
z_m —C ₂ H ₅ OH	0.0000	0.0417	0.0891	0.1435	0.2068	0.2811	0.3698	0.4773	0.6101	0.7787	1.0000
η	0.01794	0.03215	0.05275	0.06900	0.07150	0.06625	0.05715	0.04720	0.03648	0.02694	0.01776
η_0	—	0.01793	0.01793	0.01792	0.01791	0.01790	0.01789	0.01787	0.01785	0.01781	—
δ		0.01422	0.03482	0.05108	0.05359	0.04835	0.03926	0.02933	0.01863	0.00913	
0°C. δ		(0.388)	0.518	0.565	0.519	0.463	0.424	0.430	0.515	(1.08)	
$\frac{(1-z_m)^3 z_m}{\delta}$				Mean	0.491						
$\frac{\delta}{(1-z_m)^2 z_m}$							(0.267)	0.220	0.201	0.239	
							Mean	0.232			
η	0.01310	0.02162	0.03235	0.04095	0.04355	0.04174	0.03787	0.03268	0.02663	0.02048	0.01480
η_0	—	0.01315	0.01321	0.01328	0.01336	0.01346	0.01359	0.01376	0.01399	0.01431	—
δ		0.00847	0.01914	0.02767	0.03019	0.02828	0.02428	0.01892	0.01264	0.00617	
10°C. δ		(0.231)	0.284	0.307	0.292	0.271	0.262	0.278	(0.350)	(0.731)	
$\frac{(1-z_m)^3 z_m}{\delta}$				Mean	0.282						
$\frac{\delta}{(1-z_m)^2 z_m}$							(0.165)	0.145	0.136	0.161	
							Mean	0.147			
η	0.01009	0.01548	0.02168	0.02670	0.02867	0.02832	0.02642	0.02369	0.01998	0.01601	0.01221
η_0	—	0.01015	0.01023	0.01031	0.01042	0.01055	0.01071	0.01092	0.01120	0.01160	—
δ		0.00533	0.01145	0.01639	0.01825	0.01777	0.01571	0.01277	0.00878	0.00441	
20°C. δ		(0.145)	0.170	0.182	0.177	0.170	0.170	(0.187)	(0.243)	(0.522)	
$\frac{(1-z_m)^3 z_m}{\delta}$				Mean	0.174						
$\frac{\delta}{(1-z_m)^2 z_m}$							0.107	0.098	0.095	0.116	
							Mean	0.104			
η	0.00800	0.01153	0.01539	0.01849	0.01991	0.02001	0.01906	0.01744	0.01519	0.01270	0.00997
η_0	—	0.00806	0.00813	0.00821	0.00830	0.00842	0.00857	0.00877	0.00903	0.00940	—
δ		0.00347	0.00726	0.01028	0.01161	0.01159	0.01049	0.00867	0.00616	0.00330	
30°C. δ		(0.095)	0.108	0.114	0.113	0.111	0.113	(0.127)	(0.170)	(0.391)	
$\frac{(1-z_m)^3 z_m}{\delta}$				Mean	0.112						
$\frac{\delta}{(1-z_m)^2 z_m}$							0.071	0.066	0.066	(0.086)	
							Mean	0.068			

Table 4.—(Concluded)

$z-C_2H_5OH$	0.00	0.10	0.20	0.30	0.40	0.50	0.60	0.70	0.80	0.90	1.00
$z_m-C_2H_5OH$	0.0000	0.0417	0.0891	0.1435	0.2068	0.2811	0.3698	0.4773	0.6101	0.7787	1.0000
η	0.00654	0.00896	0.01144	0.01353	0.01455	0.01475	0.01426	0.01328	0.01181	0.01022	0.00824
η_0	—	0.00659	0.00665	0.00672	0.00680	0.00691	0.00704	0.00720	0.00743	0.00775	—
δ		0.00237	0.00479	0.00681	0.00775	0.00784	0.00722	0.00608	0.00438	0.00247	
40°C. $\frac{\delta}{(1-z_m)^3 z_m}$		(0.065)	0.071	0.075	0.075	0.075	(0.078)	(0.089)	(0.121)	(0.293)	
δ				Mean	0.074						
$\frac{\delta}{(1-z_m)^2 z_m}$						(0.054)	0.049	0.047	0.047	(0.065)	
							Mean	0.048			
η	0.00549	0.00725	0.00896	0.01038	0.01116	0.01136	0.01109	0.01044	0.00950	0.00835	0.00695
η_0	—	0.00553	0.00558	0.00565	0.00572	0.00580	0.00592	0.00606	0.00625	0.00653	—
δ		0.00172	0.00338	0.00473	0.00544	0.00556	0.00517	0.00438	0.00325	0.00182	
50°C. $\frac{\delta}{(1-z_m)^3 z_m}$		(0.047)	0.050	0.052	0.053	0.053	(0.056)	(0.064)	(0.090)	(0.216)	
δ				Mean	0.052						
$\frac{\delta}{(1-z_m)^2 z_m}$						(0.038)	0.035	0.034	0.035	(0.048)	
							Mean	0.035			
η	0.00470	0.00602	0.00728	0.00826	0.00887	0.00904	0.00887	0.00841	0.00778	0.00695	0.00590
η_0	—	0.00474	0.00478	0.00483	0.00489	0.00496	0.00505	0.00517	0.00533	0.00555	—
δ		0.00128	0.00250	0.00343	0.00398	0.00408	0.00382	0.00324	0.00245	0.00140	
60°C. $\frac{\delta}{(1-z_m)^3 z_m}$		(0.035)	0.037	0.038	0.039	0.039	(0.041)	(0.047)	(0.068)	(0.166)	
δ				Mean	0.038						
$\frac{\delta}{(1-z_m)^2 z_m}$						(0.028)	0.026	0.025	0.026	(0.039)	
							Mean	0.026			
η	0.00407	0.00509	0.00606	0.00677	0.00724	0.00739	0.00727	0.00696	0.00648	0.00549	0.00506
η_0	—	0.00410	0.00413	0.00417	0.00422	0.00428	0.00436	0.00446	0.00459	0.00477	—
δ		0.00099	0.00193	0.00260	0.00302	0.00311	0.00291	0.00250	0.00189	0.00072	
70°C. $\frac{\delta}{(1-z_m)^3 z_m}$		(0.027)	0.029	0.029	0.029	0.030	(0.031)	(0.037)	(0.052)	(0.085)	
δ				Mean	0.029						
$\frac{\delta}{(1-z_m)^2 z_m}$						(0.021)	0.020	0.019	0.020	0.019	
							Mean	0.020			

Table 5.

H₂O—CH₃COOH, International Critical Tables, V, 20.

$$\eta_0 = \eta_1 + (\eta_2 - \eta_1) \frac{1.29 z_m}{(1 - z_m) + 1.29 z_m}.$$

z —CH ₃ COOH	0.00	0.10	0.20	0.30	0.40	0.50	0.60	0.70	0.80	0.90	1.00
z_m —CH ₃ COOH	0.0000	0.0323	0.0698	0.1140	0.1677	0.2417	0.3104	0.4120	0.4737	0.7300	1.0000
η	0.01145	0.01360	0.01630	0.01910	0.02160	0.02475	0.02765	0.03020	0.03105	0.02680	0.01350
η_0	—	0.01153	0.01163	0.01174	0.01187	0.01205	0.01220	0.01242	0.01255	0.01304	—
15°C. δ		0.00207	0.00467	0.00736	0.00973	0.01270	0.01545	0.01778	0.01850	0.01376	
δ		(0.066)	0.072	0.073	0.070	0.069	0.072	0.073	0.074	0.070	
$(1-z_m)z_m$					Mean	0.072					
η	0.01009	0.01210	0.01415	0.01635	0.01870	0.02135	0.02390	0.02640	0.02695	0.02310	0.01265
η_0	—	0.01020	0.01032	0.01045	0.01062	0.01084	0.01103	0.01131	0.01147	0.01208	—
20°C. δ		0.00190	0.00383	0.00590	0.00808	0.01051	0.01287	0.01509	0.01548	0.01102	
δ		0.061	0.059	0.058	0.058	0.057	0.060	0.062	0.062	(0.056)	
$(1-z_m)z_m$					Mean	0.060					
η	0.00895	0.01065	0.01250	0.01450	0.01685	0.01870	0.02085	0.02290	0.02365	0.02050	0.01155
η_0	—	0.00906	0.00918	0.00932	0.00949	0.00971	0.00991	0.01019	0.01035	0.01097	—
25°C. δ		0.00159	0.00332	0.00518	0.00706	0.00899	0.01094	0.01271	0.01330	0.00953	
δ		0.051	0.051	0.051	0.051	0.049	0.051	0.053	0.053	0.048	
$(1-z_m)z_m$					Mean	0.051					
η	0.00800	0.00955	0.01110	0.01290	0.01475	0.01660	0.01850	0.02040	0.02095	0.01840	0.01065
η_0	—	0.00811	0.00823	0.00838	0.00855	0.00877	0.00897	0.00926	0.00942	0.01006	—
30°C. δ		0.00144	0.00287	0.00452	0.00620	0.00783	0.00953	0.01114	0.01153	0.00834	
δ		0.046	0.044	0.045	0.044	0.043	0.045	0.046	0.046	0.042	
$(1-z_m)z_m$					Mean	0.045					
η	0.00721	0.00855	0.01000	0.01150	0.01315	0.01480	0.01650	0.01815	0.01855	0.01655	0.00990
η_0	—	0.00732	0.00745	0.00759	0.00776	0.00799	0.00820	0.01849	0.00866	0.00930	—
35°C. δ		0.00123	0.00255	0.00391	0.00539	0.00681	0.00830	0.00966	0.00989	0.00725	
δ		0.039	0.039	0.039	0.039	0.037	0.039	0.040	0.040	0.037	
$(1-z_m)z_m$					Mean	0.039					

Table 5.—(Continued)

$z-\text{CH}_3\text{COOH}$	0.00	0.10	0.20	0.30	0.40	0.50	0.60	0.70	0.80	0.90	1.00
$z_m-\text{CH}_3\text{COOH}$	0.0000	0.0323	0.0698	0.1140	0.1677	0.2417	0.3104	0.4120	0.4737	0.7300	1.0000
η	0.00654	0.00780	0.00905	0.01040	0.01180	0.01325	0.01470	0.01620	0.01660	0.01490	0.00925
η_0	—	0.00665	0.00678	0.00692	0.00709	0.00733	0.00753	0.00782	0.00799	0.00864	—
40°C. δ		0.00115	0.00227	0.00348	0.00471	0.00592	0.00717	0.00838	0.00861	0.00626	
δ		(0.037)	0.035	0.035	0.034	0.032	0.034	0.035	0.035	0.032	
$(1-z_m)z_m$					Mean	0.034					
η	0.00597	0.00710	0.00820	0.00940	0.01060	0.01185	0.01320	0.01445	0.01485	0.01345	0.00865
η_0	—	0.00608	0.00620	0.00635	0.00652	0.00674	0.00694	0.00723	0.00739	0.00803	—
45°C. δ		0.00102	0.00200	0.00305	0.00408	0.00511	0.00626	0.00722	0.00746	0.00542	
δ		(0.033)	0.031	0.030	0.029	0.028	0.029	0.030	0.030	0.028	
$(1-z_m)z_m$					Mean	0.029					
η	0.00549	0.00650	0.00745	0.00855	0.00965	0.01080	0.01190	0.01305	0.01340	0.01225	0.00810
η_0	—	0.00650	0.00572	0.00586	0.00603	0.00625	0.00645	0.00673	0.00689	0.00752	—
50°C. δ		0.00090	0.00173	0.00269	0.00362	0.00455	0.00545	0.00632	0.00651	0.00478	
δ		(0.029)	0.027	0.027	0.026	0.025	0.026	0.026	0.026	0.024	
$(1-z_m)z_m$					Mean	0.026					
η	0.00507	0.00600	0.00680	0.00775	0.00880	0.00985	0.01080	0.01195	0.01215	0.01125	0.00760
η_0	—	0.00517	0.00529	0.00543	0.00559	0.00581	0.00600	0.00627	0.00643	0.00704	—
55°C. δ		0.00083	0.00151	0.00232	0.00321	0.00404	0.00480	0.00568	0.00572	0.00421	
δ		(0.027)	0.023	0.023	0.023	0.022	0.022	0.023	0.023	0.021	
$(1-z_m)z_m$					Mean	0.023					
η	0.00470	0.00550	0.00625	0.00710	0.00800	0.00900	0.00995	0.01090	0.01105	0.01030	0.00700
η_0	—	0.00479	0.00490	0.00503	0.00517	0.00537	0.00555	0.00579	0.00594	0.00649	—
60°C. δ		0.00071	0.00135	0.00207	0.00283	0.00363	0.00440	0.00511	0.00511	0.00381	
δ		(0.023)	0.021	0.021	0.020	0.020	0.021	0.021	0.021	0.019	
$(1-z_m)z_m$					Mean	0.020					
η	0.00437	0.00505	0.00575	0.00655	0.00735	0.00820	0.00900	—	0.01010	—	0.00675
η_0	—	0.00447	0.00458	0.00471	0.00486	0.00506	0.00524		0.00565		—
65°C. δ		0.00058	0.00117	0.00184	0.00249	0.00314	0.00376		0.00445		
δ		(0.019)	0.018	0.018	0.018	0.017	0.018		0.018		
$(1-z_m)z_m$					Mean	0.018					

Table 5.—(Concluded)

$z-\text{CH}_3\text{COOH}$	0.00	0.10	0.20	0.30	0.40	0.50	0.60	0.70	0.80	0.90	1.00
$z_m-\text{CH}_3\text{COOH}$	0.0000	0.0323	0.0698	0.1140	0.1677	0.2417	0.3104	0.4120	0.4737	0.7300	1.0000
η	0.00381	0.00440	0.00495	0.00560	0.00630	0.00700	0.00765	—	0.00855	—	0.00605
η_0	—	0.00390	0.00401	0.00413	0.00427	0.00446	0.00463	—	0.00501	—	—
75°C. δ	—	0.00050	0.00094	0.00147	0.00203	0.00254	0.00302	—	0.00354	—	—
δ	—	0.016	0.015	0.015	0.015	0.014	0.014	—	0.014	—	—
$(1-z_m)z_m$	—	—	—	—	Mean	0.015	—	—	—	—	—
η	0.00336	0.00385	0.00435	0.00490	0.00545	0.00605	0.00660	—	0.00740	—	0.00545
η_0	—	0.00345	0.00354	0.00366	0.00379	0.00397	0.00413	—	0.00448	—	—
85°C. δ	—	0.00040	0.00081	0.00124	0.00166	0.00208	0.00247	—	0.00292	—	—
δ	—	0.013	0.013	0.012	0.012	0.011	0.012	—	0.012	—	—
$(1-z_m)z_m$	—	—	—	—	Mean	0.012	—	—	—	—	—
η	0.00299	0.00340	0.00385	0.00430	0.00475	0.00530	0.00575	—	0.00640	—	0.00490
η_0	—	0.00307	0.00316	0.00326	0.00338	0.00355	0.00369	—	0.00402	—	—
95°C. δ	—	0.00033	0.00069	0.00104	0.00137	0.00175	0.00206	—	0.00238	—	—
δ	—	0.011	0.011	0.010	0.010	0.010	0.010	—	0.010	—	—
$(1-z_m)z_m$	—	—	—	—	Mean	0.010	—	—	—	—	—

Table 6.

Molecular compound $\text{CH}_3\text{OH} \cdot 2\text{H}_2\text{O}$. $\log C_{calc.} = 2.964 + \frac{2.00}{2+1} \log (\eta_1^2 \eta_2)$.

Temp. C.	η_1	η_2	$C_{obs.}$	$C_{calc.}$	r_m
20	0.01035	0.00607	0.065	0.069	6.3
30	0.00819	0.00541	0.047	0.047	4.3
40	0.00668	0.00463	0.033	0.032	3.0
50	0.00566	0.00406	0.025	0.024	2.2
60	0.00495	0.00361	0.018	0.018	1.7

Table 7.

Molecular compound $C_2H_5OH \cdot 3H_2O$. $\log C_{calc.} = 3.191 + \frac{2.00}{3+1} \log(\eta_1^3 \eta_2)$.

Temp. C.	η_1	η_2	$C_{obs.}$	$C_{calc.}$	η_m
0	0.01794	0.01776	0.491	0.498	773
10	0.01310	0.01480	0.282	0.283	439
20	0.01009	0.01221	0.174	0.174	270
30	0.00800	0.00997	0.112	0.111	172
40	0.00654	0.00824	0.074	0.074	115
50	0.00549	0.00695	0.052	0.053	82
60	0.00470	0.00590	0.038	0.038	59
70	0.00407	0.00506	0.029	0.029	45

Table 8.

Molecular compound $C_2H_5OH \cdot 2H_2O$. $\log C_{calc.} = 2.612 + \frac{1.83}{2+1} \log(\eta_1^2 \eta_2)$.

Temp. C.	η_1	η_2	$C_{obs.}$	$C_{calc.}$	η_m
0	0.01794	0.01776	0.232	0.265	108
10	0.01310	0.01480	0.147	0.145	59
20	0.01009	0.01221	0.104	0.102	42
30	0.00800	0.00997	0.068	0.068	28
40	0.00654	0.00824	0.048	0.048	20
50	0.00549	0.00695	0.035	0.035	14
60	0.00470	0.00590	0.026	0.026	11
70	0.00407	0.00506	0.020	0.020	8.2

Table 9.

$$\text{Molecular compound } \text{CH}_3\text{COOH} \cdot \text{H}_2\text{O}. \quad \log C_{calc.} = 2.065 + \frac{1.68}{1+1} \log (\eta_1 \eta_2).$$

Temp. C.	η_1	η_2	$C_{obs.}$	$C_{calc.}$	η_m
15	0.01145	0.01350	0.072	0.073	8.5
20	0.01009	0.01265	0.060	0.062	7.2
25	0.00895	0.01155	0.051	0.052	6.0
30	0.00800	0.01065	0.045	0.044	5.1
35	0.00721	0.00990	0.039	0.038	4.4
40	0.00654	0.00925	0.034	0.033	3.8
45	0.00597	0.00865	0.029	0.029	3.4
50	0.00549	0.00810	0.026	0.026	3.0
55	0.00507	0.00760	0.023	0.023	2.7
60	0.00470	0.00700	0.020	0.020	2.3
65	0.00437	0.00675	0.018	0.018	2.1
75	0.00381	0.00605	0.015	0.015	1.7
85	0.00336	0.00545	0.012	0.012	1.4
95	0.00299	0.00490	0.010	0.010	1.2

As to the temperature variation of association degrees Ramsay and Shields⁽⁴⁾ calculated those of the abnormal liquids-water, methyl alcohol, ethyl alcohol and acetic acid from the deviation of their surface tension equation. Apart from the justification of their calculation for the absolute values of association degrees, we acknowledge from their results that the decreasing rates of molecular association of these liquids with rising temperature are nearly equal, temperature coefficients being $-0.0030 \sim -0.0035$.

A further test for methyl and ethyl alcohols with the viscosity data observed by Bingham, White, Thomas and Cadwell⁽⁵⁾ affirms the fact.

Moreover as already studied, the solvation viscosities of systems $\text{CH}_3\text{COOH} \cdot \text{H}_2\text{O}$, $\text{CH}_3\text{OH} \cdot \text{H}_2\text{O}$ and $\text{C}_2\text{H}_5\text{OH} \cdot \text{H}_2\text{O}$ have high values in comparison with η_0 at moderate concentrations, it is quite sufficient to regard that in the calculation of η_0 of each system $\frac{k_2 a_2}{k_1 a_1}$ is independent of temperature. In the above calculation, therefore, $\frac{k_2 a_2}{k_1 a_1}$ in each system has been put to be the same value as obtained in the previous paper.

(4) W. Ramsay & J. Shields, *Z. physik. Chem.* **12** (1893), 468; W. Ramsay, *Z. physik. Chem.* **15** (1894), 113.

(5) E. C. Bingham, G. F. White, A. Thomas, J. L. Cadwell, *Z. physik. Chem.* **83** (1913), 652.

The Viscosity Coefficient of a Molecular Compound and its Stability Coefficient.

As the theory demands, the proportional constant C in each system has proved to keep constancy for isothermal mixtures. The next study is its temperature variation.

Since the proportional constant C must involve in it the term which corresponds to the viscosity of a molecular compound, it is expected that there may exist some relationship between C and the viscosities of components η_1 and η_2 , and if any, the component viscosities may probably take part in the form $\eta_1^{\nu_1} \eta_2^{\nu_2}$ as considered from the composition term $(1-z_m)^{\nu_1} z_m^{\nu_2}$. Then we may put C in the following form:

$$C = C_0(\eta_1^{\nu_1} \eta_2^{\nu_2})^{\frac{m}{\nu_1 + \nu_2}},$$

where C_0 and m are constants independent of temperature.

The test of the postulation with the molecular compounds in the above three pairs is extremely good. The results of the calculation are tabulated in Tables 6, 7, 8 and 9.

Transform the expression into

$$\frac{C}{C_0} = (\eta_1^{\nu_1} \eta_2^{\nu_2})^{\frac{m}{\nu_1 + \nu_2}}.$$

The left-hand side of the equation is no other than the viscosity coefficient of a molecular compound and let it be denoted by η_m , then

$$\eta_m = (\eta_1^{\nu_1} \eta_2^{\nu_2})^{\frac{m}{\nu_1 + \nu_2}},$$

or taking logarithms of both sides

$$\log \eta_m = m \left\{ \frac{\nu_1}{\nu_1 + \nu_2} \log \eta_1 + \frac{\nu_2}{\nu_1 + \nu_2} \log \eta_2 \right\} \dots \dots \dots (1)$$

Kendall⁽⁶⁾ showed, with eighty four mixtures of presumably non-associated and chemically indifferent liquids, that the deviation from the straight line is generally least when the composition in the Arrhenius

(6) J. Kendall, Medd. K. Vetenskapsakad. *Nobelinst.* **2**, No. 25 (1913), 1.

logarithmic formula is expressed as molar fraction, i.e. in the same concentration as above

$$\log \eta = \frac{\nu_1}{\nu_1 + \nu_2} \log \eta_1 + \frac{\nu_2}{\nu_1 + \nu_2} \log \eta_2 \dots\dots\dots (2)$$

The average divergence of this formula from the observed viscosity values is estimated by him to be $\pm 2.3\%$ or $m = 1 \pm 0.02$.

Comparing (1) with (2) it is understood that the greater the difference of m from unity the more stable the molecular compound may be in the mixture. The m is called hereafter "the stability coefficient" of a molecular compound. In the following table are summarized the stability coefficients of the molecular compounds above studied.

Molecular compound	m
$\text{CH}_3\text{OH} \cdot 2\text{H}_2\text{O}$	2.00
$\text{C}_2\text{H}_5\text{OH} \cdot 3\text{H}_2\text{O}$	2.00
$\text{C}_2\text{H}_5\text{OH} \cdot 2\text{H}_2\text{O}$	1.83
$\text{CH}_3\text{COOH} \cdot \text{H}_2\text{O}$	1.68

Among the four hydrates the hydrates $\text{C}_2\text{H}_5\text{OH} \cdot 3\text{H}_2\text{O}$ has η_m of the greatest value which suggests the possibility of crystallization of this hydrate at lower temperatures. In fact, Tammann and Pillsbury⁽⁷⁾ reported to yield transparent crystals of a hydrate by cooling the mixtures of 34–43 wt. % (20–30 mol %) alcohol which they attributed to a tetrahydrate, simply considering the admixing composition, but observed no separation of crystalline hydrates of methyl alcohol and acetic acid. The writer also observed transparent crystals of cubic system by cooling the mixtures of molar ratios of from 1 $\text{C}_2\text{H}_5\text{OH}$: 1 H_2O to 1 $\text{C}_2\text{H}_5\text{OH}$: 4 H_2O with solid carbon dioxide and alcohol freezer. From the writer's viewpoint of the present study, however, this hydrate of ethyl alcohol is undoubtedly a trihydrate.

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(7) G. Tammann & M. E. Pillsbury, *Z. anorg. allg. Chem.* **172** (1928), 243.

A VISCOSITY FORMULA FOR BINARY MIXTURES, THE ASSOCIATION DEGREES OF CONSTITUENTS BEING TAKEN INTO CONSIDERATION. VIII.

By Tetsuya ISHIKAWA.

Received June 23rd, 1933. Published September 28th, 1933.

If the writer's viscosity formula for chemically indifferent mixtures is assumed rigorously valid, it may be also applicable to a binary mixtures, each component of which is composed of a homogeneous mixture of two or more chemically indifferent liquids. A typical case of such mixture is a binary mixture of lubricating oils. The problem to make up a mixture having a desired viscosity from lubricating oils light and heavy is of technical importance, but few attempts have been done to find a satisfactory formula by which the viscosity of a blended lubricant may be calculated from the viscosities of its components.

Quite recently Epperson and Dunlap⁽¹⁾ studied the viscosities at 210°F. of lubricating oils prepared from the fractions of Midcontinent and Pennsylvania oils, together with the cryoscopic study of their molecular weights, and came to the conclusion that Kendall and Monroe's cube-root formula is in close agreement with observed values but gives a few per cent divergence.

The present paper is the results of the test of the writer's formula by use of Epperson and Dunlap's data. In the following table $\eta_{calc.}$ denotes the calculated values from the writer's formula, η_k those from Kendall and Monroe's formula, and m the ratios of logarithms of measured viscosities to those calculated from Kendall's logarithmic formula for reference to the preceding study on the stability coefficient.

Table 1.
Shell oil 4 (symbol D)—Shell oil 1 (symbol A).

$z_m - A$	η	$\frac{k_2 a_2}{k_1 a_1}$	$\eta_{calc.}$	$\frac{\eta - \eta_{calc.}}{\eta} \times 100$	η_k	$\frac{\eta - \eta_k}{\eta} \times 100$	m
0.000	0.3391		—		—		
0.168	0.2704	1.60	0.2706	-0.07	0.2682	-0.81	0.950
0.347	0.2134	1.39	0.2100	+1.59	0.2044	-4.22	0.909
0.614	0.1340	1.68	0.1369	-2.12	0.1293	-3.51	0.919
0.773	0.1010	1.59	0.1010	± 0.00	0.0915	-9.44	0.932
0.921	0.0707	1.69	0.0714	-0.98	0.0688	-2.13	0.974
1.000	0.0571	1.59	—		—		

(1) E. R. Epperson & H. L. Dunlap, *Ind. Eng. Chem.* **24**(1932), 1369.

Table 2.

Shell oil 3 (symbol C)—Shell oil 1 (symbol A).

$z_m - A$	η	$\frac{k_2 a_2}{k_1 a_1}$	$\eta_{calc.}$	$\frac{\eta - \eta_{calc.}}{\eta} \times 100$	η_k	$\frac{\eta - \eta_k}{\eta} \times 100$	m
0.000	0.1655		—		—		
0.216	0.1416	1.03	0.1404	+0.85	0.1355	—4.31	0.964
0.415	0.1168	1.18	0.1182	—1.18	0.1113	—4.71	0.958
0.579	0.1003	1.10	0.1005	—0.02	0.0936	—6.70	0.952
0.727	0.0853	1.07	0.0849	+0.47	0.0794	—6.92	0.957
1.000	0.0571	1.09	—		—		

Table 3.

Shell oil 4 (symbol D)—Shell oil 2 (symbol B).

$z_m - B$	η	$\frac{k_2 a_2}{k_1 a_1}$	$\eta_{calc.}$	$\frac{\eta - \eta_{calc.}}{\eta} \times 100$	η_k	$\frac{\eta - \eta_k}{\eta} \times 100$	m
0.000	0.3391		—		—		
0.208	0.2840	1.31	0.2872	—1.11	0.2823	—0.60	0.975
0.376	0.2484	1.21	0.2484	± 0.00	0.2413	—2.86	0.953
0.618	0.1973	1.19	0.1967	+0.30	0.1896	—3.90	0.952
0.690	0.1845	1.15	0.1822	+1.26	0.1755	—4.88	0.952
1.000	0.1239	1.21	—		—		

Table 4.

Standard oil 2 (symbol F)—Standard oil 1 (symbol E).

$z_m - E$	η	$\frac{k_2 a_2}{k_1 a_1}$	$\eta_{calc.}$	$\frac{\eta - \eta_{calc.}}{\eta} \times 100$	η_k	$\frac{\eta - \eta_k}{\eta} \times 100$	m
0.000	0.3659		—		—		
0.227	0.2792	1.44	0.2767	+0.90	0.2726	—2.36	0.933
0.389	0.2235	1.50	0.2235	± 0.00	0.2168	—3.00	0.923
0.573	0.1711	1.50	0.1711	± 0.00	0.1632	—4.62	0.921
0.726	0.1303	1.59	0.1331	—2.10	0.1261	—3.22	0.943
1.000	0.0745	1.50	—		—		

Table 5.

Standard oil 2 (symbol F)—Shell oil 1 (symbol A).

$z_m - A$	η	$\frac{k_2 a_2}{k_1 a_1}$	$\left(\frac{k_2 a_2}{k_1 a_1}\right)_{calc.}$	$\eta_{calc.}$	$\frac{\eta - \eta_{calc.}}{\eta} \times 100$
0.000	0.3659		(0.85)	—	
0.195	0.3094	0.92	1.05	0.3034	+1.98
0.368	0.2376	1.22	1.22	0.2376	± 0.00
0.507	0.1860	1.36	1.36	0.1860	± 0.00
0.694	0.1250	1.56	1.55	0.1255	-0.40
0.850	0.0888	1.54	1.71	0.0859	+3.38
1.000	0.0571		(1.86)	—	

Table 6.

Shell oil 4 (symbol D)—Standard oil 1 (symbol E).

$z_m - E$	η	$\frac{k_2 a_2}{k_1 a_1}$	$\left(\frac{k_2 a_2}{k_1 a_1}\right)_{calc.}$	$\eta_{calc.}$	$\frac{\eta - \eta_{calc.}}{\eta} \times 100$
0.000	0.3391		(1.30)	—	
0.210	0.2655	1.45	1.45	0.2655	± 0.00
0.380	0.2097	1.56	1.57	0.2094	+0.14
0.572	0.1544	1.73	1.71	0.1550	-0.39
0.723	0.1210	1.80	1.82	0.1205	+0.42
1.000	0.0745		(2.02)	—	

For the first four pairs the constancy of $\frac{k_2 a_2}{k_1 a_1}$ is quite satisfactory in each case and the calculated viscosity values done from the mean value of them are concordant with the observed values. As to the last two pairs i.e. the mixtures of Shell and Standard oils, the values of $\frac{k_2 a_2}{k_1 a_1}$ vary linearly with concentrations, which suggest that these mixtures are chemically reactive and either of the components may suffer molecular dissociation. As the study on the molecular dissociation has been done in part IV,⁽²⁾ it may be enough here to show that the values $\frac{k_A a_A}{k_F a_F} = 1.86$ and $\frac{k_E a_E}{k_D a_D} = 1.30$ out of the extrapolated values at $z_m = 0$ and $z_m = 1$

(2) This Bulletin, 4 (1929), 288.

of each system suffice the condition:

$$\frac{k_A a_A}{k_D a_D} = \frac{k_A a_A}{k_F a_F} \frac{k_F a_F}{k_E a_E} \frac{k_E a_E}{k_D a_D}.$$

From these and the remaining values we may acknowledge that A(Shell 1) dissociates in F(Standard 2) and D(Shell 4) dissociates in E(Standard 1), the degrees of molecular dissociation of the former at infinite dilution of the latter being 0.54 and 0.36 respectively.

Before this manuscript is sent to press, I found the unfortunate communication given by Dunlap (*Ind. Eng. Chem.* **25** (1933), 592-3) that the above viscosities were values substituted for D. sp. grs. at 60°F. instead of those at 210°F. in the Herschel equation:

$$\frac{\eta}{D} = 0.0022t - \frac{1.8}{t}.$$

As it is highly probable, however, that similar oils have almost equal values of the temperature coefficient of viscosities, no serious error may occur in the calculation of $\frac{k_2 a_2}{k_1 a_1} = \frac{(1-z_m)(\eta-\eta_1)}{z_m(\eta_2-\eta)}$, the constancy of which is the criterion of the validity of the writer's formula for physical mixtures.

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ON THE REFRACTIVE INDICES OF ETHYLENE CHLORIDE,
1, 1, 2, 2,-TETRACHLORETHANE AND OF THEIR
MIXTURE AND THE MOLAR REFRACTIONS OF THESE SUBSTANCES.

By Senzo HAMAI.

Received June 10th, 1933. Published October 28th, 1933.

In connection with our study on the chemical reactions of some of chlorine derivatives of lower hydrocarbon, we are confronted with the necessity of knowing the refractive indices of these solvents and of their binary mixture. Refractive indices have been measured with an ordinary method using Pulfrich Refractometer (Carl Zeiss). The temperature of the solvent vessel and of the prism have been kept constant by passing the water which is kept constant temperature within $\pm 0.1^\circ$ during measurements.

The materials have been purified by fractional distillation several times and only the middle portions were used.

Ethylene chloride: Takeda's product	B.P. 83.0°C .
1, 1, 2, 2,-Tetrachlorethane: Kahlbaum	B.P. 145.0°C .

For both ethylene chloride and tetrachlorethane, the refractive indices have been observed at various temperatures using H_α line ($\lambda = 656.8 \text{ m}\mu$) and the results were plotted as a function of temperature as shown in Figs. 1 and 2. For the binary mixture ($N_2 = 0.782$) also as shown in Fig. 3 the refractive indices were plotted against the reciprocals of the absolute temperatures. Variation of the refractive index of the binary mixture of ethylene chloride and 1, 1, 2, 2,-tetrachlorethane with the molal fractions has also been studied. The results are given in Fig. 4. All of the above results are also tabulated in the tables 1 to 6 respectively.

Figs. 1, 2 and 3 immediately would show that in each case the refractive index is linearly dependent on the reciprocals of the absolute temperatures within the range of temperature we have studied. The shape of the curve for the binary mixture as plotted against the molal fractions of tetrachlorethane is somewhat convex upward.

For the sake of practical convenience the refractive indices of both ethylene chloride and of tetrachlorethane at round temperature, and in the case of the binary mixture at round molal fractions are given in the table 5 for the range of 10° – 30°C . and in the table 6 respectively.

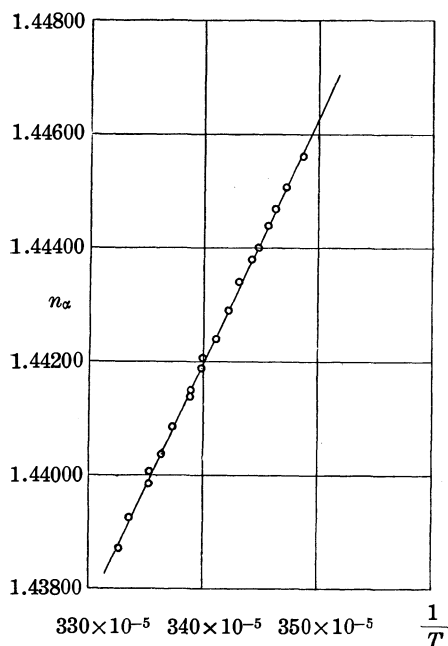


Fig. 1. Refractive indices of ethylene chloride as a function of temperature.

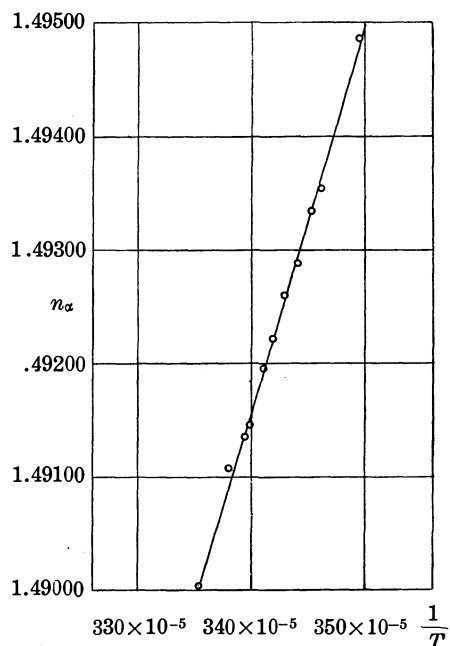


Fig. 2. Refractive indices of 1, 1, 2, 2,-tetrachlorethane as a function of temperature.

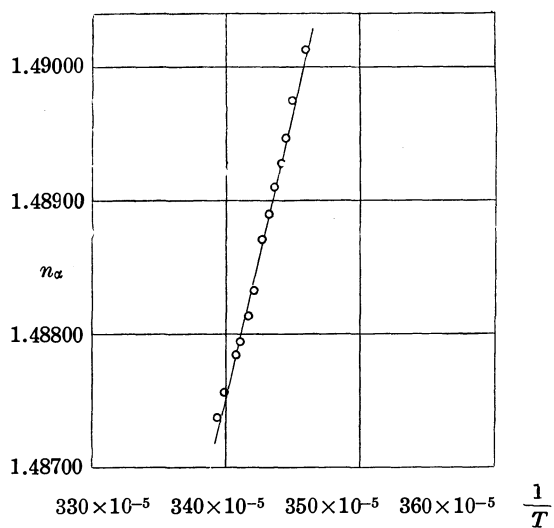


Fig. 3. Refractive indices for ethylene chloride-1, 1, 2, 2,-tetrachlorethane mixture, as a function of temperature of $N_2 = (0.782)$ (1, 1, 2, 2,-tetrachlorethane).

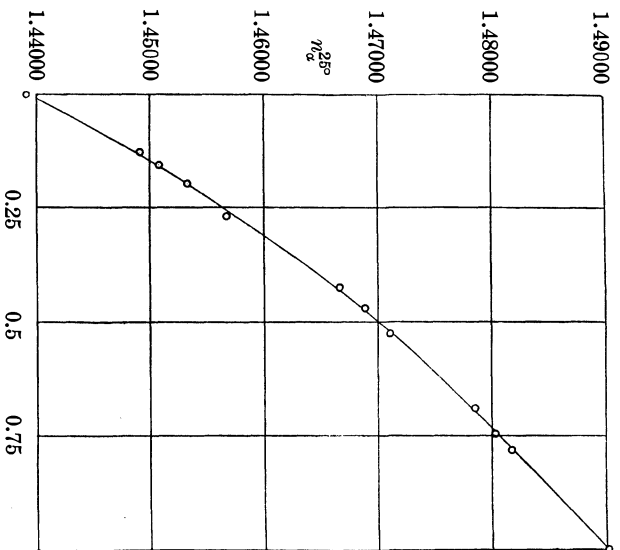


Fig. 4. Variation of index of refraction with respect to the mol. fraction of 1, 1, 2, 2-tetrachlorethane in the mixture of ethylene chloride and tetrachlorethane at 25°C.

Table 1.
(Ethylene chloride).

t° C.	T	$\frac{1}{T} 10^{-5}$	n_x	n_x
14.0	287.1	348.6	1.44561	* = different sample 1.44239* 1.44208* 1.44148*
15.0	288.1	347.1	1.44510	
15.7	288.8	346.2	1.44470	
16.2	289.3	345.6	1.44440	
17.0	290.1	344.7	1.44400	
17.5	290.6	344.1	1.44380	
18.5	291.6	342.9	1.44341	
19.1	292.2	342.2	1.44290	1.44239* 1.44208* 1.44148*
20.0	293.1	341.1	1.44240	
21.1	294.2	339.9	1.44189	
22.0	295.1	338.9	1.44138	
23.6	296.7	337.3	1.44083*	
24.1	297.2	336.4	1.44038	
25.0	298.1	335.4	1.43987	
26.8	299.9	333.4	1.43927*	1.43927 1.43866
27.0	300.1	333.2	1.43927	
27.4	300.5	332.7	1.43866	

Table 2.
(1, 1, 2, 2,-Tetrachlorethane).

$t^{\circ}\text{C.}$	T	$\frac{1}{T} \times 10^{-5}$	n_{α}
13.0	286.1	349.5	1.49486
15.7	288.8	346.2	1.49354
16.5	289.6	345.3	1.49345
17.5	290.6	344.1	1.49298
18.5	291.6	342.9	1.49260
19.3	292.4	341.9	1.49222
20.0	293.1	341.1	1.49196
21.1	294.2	339.9	1.49146
21.4	294.5	339.5	1.49136
22.0	295.1	338.9	1.49108
25.0	298.1	335.4	1.49004

$\text{C}_2\text{H}_4\text{Cl}_2$		Authors	B.P.
t°	n_{α}		
20.0	1.44189	(Brühl, <i>Ann.</i> 203 (1880) 1) (Kanonnikoff, <i>Z. prakt. Chem.</i> , 32 (1885), 497)	84.5–85° at 750.9 mm. 83.5–84°
21.2	1.44218		
21.4	1.44213		
21.8	1.44206		
22.1	1.44184		

$\text{C}_2\text{H}_2\text{Cl}_4$		Authors	B.P.
t°	n_{α}		
18.5	1.49209	(Veley, <i>Phil. Mag.</i> , 11 (1906) 73) (Kanonnikoff, <i>Z. prakt. Chem.</i> , 32 (1885), 497)	146°
21.8	1.49155		
22.0	1.49148		
22.2	1.49143		
22.4	1.49127		

Table 3.

Mixture of ethylene chloride and 1, 1, 2, 2,-tetrachlorethane
 $N_2 = 0.782$ (tetrachlorethane).

$t^{\circ}\text{C.}$	T	$\frac{1}{T} \times 10^{-5}$	n_{α}
16.0	289.1	345.9	1.49013
16.8	289.9	344.9	1.48975
17.2	290.3	344.4	1.48947
17.5	290.6	344.1	1.48928
17.9	291.0	343.6	1.48910
18.2	291.3	343.2	1.48890
18.7	291.8	342.7	1.48871
19.2	292.3	342.1	1.48853
19.5	292.6	341.7	1.48814
20.0	293.1	341.1	1.48795
20.3	293.4	340.8	1.48785
21.1	294.2	339.9	1.48757
21.6	294.7	339.3	1.48738

Table 4.

Refractive index of mixture $\text{C}_2\text{H}_4\text{Cl}_2$ and 1, 1, 2, 2,- $\text{C}_2\text{H}_2\text{Cl}_4$ at 25°C.

N_2	n_{α}	N_2	n_{α}
0.000	1.43990	0.470	1.46884
0.129	1.44903	0.525	1.47109
0.156	1.45074	0.687	1.47861
0.198	1.45324	0.748	1.48035
0.270	1.45664	0.782	1.48171
0.425	1.46617	1.000	1.49004

Table 5.

Refractive indices of ethylene chloride and 1, 1, 2, 2,-tetrachlorethane
 at various temperatures as obtained from the graphs.

$t^{\circ}\text{C.}$	$\text{C}_2\text{H}_4\text{Cl}_2$		$\text{C}_2\text{H}_2\text{Cl}_4$	
	n_g	n_{ob}	n_g	n_{ob}
10	1.44765	1.44561	1.49600	1.49486
11	1.44716		1.49563	
12	1.44673		1.49520	
13	1.44611		1.49477	
14	1.44573		1.49447	

Table 5.—(Concluded)

$t^{\circ}\text{C.}$	$\text{C}_2\text{H}_4\text{Cl}_2$		$\text{C}_2\text{H}_2\text{Cl}_4$	
	n_g	n_{ob}	n_g	n_{ob}
15	1.44510	1.44510	1.49396	
16	1.44455		1.49356	
17	1.44400	1.44400	1.49315	
18	1.44350		1.49275	
19	1.44300		1.49238	
20	1.44240	1.44240	1.49194	1.49196
21	1.44195		1.49155	
22	1.44144	1.44138	1.49120	1.49108
23	1.44095		1.49080	
24	1.44045		1.49038	
25	1.43990	1.43987	1.49003	1.49004
26	1.43946		1.48965	
27	1.43900	1.43927	1.48928	
28	1.43850		1.48890	
29	1.43800		1.48854	
30	1.43752		1.48817	

 $n_g = n$ from the graph $n_{ob} = n$ as observed

Table 6.

Refractive indices at various mol fractions of the binary mixture of ethylene chloride and 1, 1, 2, 2,-tetrachlorethane at 25°C.

Molal fractions N_2	Refractive indices n_α	Molal fractions N_2	Refractive indices n_α
0.0	1.43987	0.6	1.47460
0.1	1.44680	0.7	1.47880
0.2	1.45340	0.8	1.48260
0.3	1.45930	0.9	1.48650
0.4	1.46490	1.0	1.49004
0.5	1.47000		

Molar Refraction. Molar refraction, in general, can be computed from the formula as derived by Lorenz—Lorentz.⁽¹⁾

$$P_0 = \frac{(n^2 - 1)M}{(n^2 + 2)\rho} \quad (1)$$

Where: M = molecular weight
 ρ = density
 n = refractive index
 P_0 = molar refraction⁽²⁾.

If in the expression (1) n is replaced by n_∞ i.e. refractive index for zero frequency, then $P_0 = \frac{n_\infty^2 - 1}{n_\infty^2 + 2} \frac{M}{\rho}$ becomes the molar polarization which in general, is not very much different from a in the expression:

$$P = a + \frac{b}{T} \quad (2)$$

a , the constant is what we called P_0 .

The molar refraction P_0 calculated from n_α where H_α line = $656.3m\mu$ and the density is taken from the values computed by the expression as given in the International Critical Table namely:

Density for $C_2H_4Cl_2$:

$$d_s = 1.28248 - 1.4217(t - t_s) \times 10^{-3} - 0.933(t - t_s)^2 \times 10^{-6} + 2.29(t - t_s)^3 \times 10^{-9}$$

$$t_s = 0^\circ C.$$

and for $C_2H_2Cl_4$:

$$d_s = 1.5869 - 1.53(t - t_s) \times 10^{-3} - 0.78(t - t_s)^2 \times 10^{-6} + 2.5(t - t_s)^3 \times 10^{-9}$$

Thus the P_0 as computed gave very concordant results as are to be shown in the following tables 7 and 8.

Table 7.

The molar refraction for $C_2H_4Cl_2$ $P_0 = \frac{n_\alpha^2 - 1}{n_\alpha^2 + 2} \frac{M}{\rho}$

$t^\circ C.$	ρ	n_α	P_0
10	1.26817	1.44765	20.83
15	1.26095	1.44510	20.81
17	1.25805	1.44400	20.83
20	1.25369	1.44240	20.82
25	1.24639	1.43990	20.84
30	1.23904	1.43752	20.80
			Ave. 20.82

641. (1) L. A. Lorenz, *Wied. Ann.*, **11** (1880) 70; L. A. Lorentz, *Wied. Ann.*, **9** (1880),

(2) Debye's, "Polar Molecules" 1929.

(3) Debye's, "Polar Molecules" p. 57.

Table 8.

The molar refraction for $\text{C}_2\text{H}_2\text{Cl}_4$ $P_0 = \frac{n_\alpha^2 - 1}{n_\alpha^2 + 2} \frac{M}{\rho}$

$t^\circ \text{C.}$	ρ	n_α	P_0
10	1.57152	1.49600	31.15
15	1.56380	1.49396	31.21
17	1.56070	1.49315	31.21
18.5	1.55830	1.49260	31.21
20	1.55600	1.49194	31.21
25	1.54820	1.49004	31.32
30	1.54040	1.48817	31.31
			Ave. 31.23

For ethylene chloride, H. Jahn and G. Möller⁽⁴⁾ have given the value for $P_0 = \frac{n_\alpha^2 - 1}{n_\alpha^2 + 2} \frac{M}{\rho} = 20.81$, while Weegmann⁽⁵⁾ reported $P_0 = 20.44$ calculated from $n_\infty = 1.431367$. For tetrachlorethane, there is no reference found in connection with the molar refraction as far as the present author knows.

Calculation of Electric Moment for $\text{C}_2\text{H}_4\text{Cl}_2$. Smyth, in 1924 presented a method for calculation of electric moment by extrapolating for n_∞ ⁽⁶⁾ but since we know the value $P_0 = 20.44$ of Weegmann for $\lambda = \infty$, combining with those values of $\frac{M}{\rho} \frac{\epsilon^2 - 1}{\epsilon^2 + 2}$ as given by various authors as well as the value computed by the present author, the value μ can be calculated.

60.29 (H. Jahn and G. Möller, *Z. physik. Chem.*, **13** (1894) 385).

60.06 (19.8°C.) (Walden, *Z. physik. Chem.*, **70** (1910) 569).

60.42 (20.0°C., $\lambda = \infty$) The present author; using the value of dielectric constant $\epsilon = 10.8$.

(Joachim, *Ann. Phys.* **60** (1919), 570).

Using $P_0 = 20.44$ (Weegmann) and $\frac{M}{\rho} \frac{\epsilon^2 - 1}{\epsilon^2 + 2} = 60.42$ μ is found by:

(4) *Z. physik. Chem.*, **13** (1894), 385.

(5) *Z. physik. Chem.*, **2** (1888), 218.

(6) Smyth, *J. Amer. Chem. Soc.*, **46** (1924), 2151.

$$\mu = 0.0127\sqrt{(P-P_0)T} \times 10^{-18} \quad (2)$$

to be 1.375×10^{-18} .

The dielectric constant for tetrachlorethane, hitherto is not found in the literatures so that we were unable to calculate the value of μ , however, the molar refraction has been given in the table already mentioned.

Table 9.

For ethylene chloride.

P_0	Authors	P	Authors
20.44 ($\lambda = \infty$)	Weegmann ⁽⁷⁾	60.06	Walden ⁽⁸⁾ ($t = 19.8^\circ$)
20.81 ($\lambda = H_\alpha$)	Jahn and Möller ⁽⁹⁾	60.29 ($t = 20^\circ$)	Jahn and Möller
20.82 ($\lambda = H_\alpha$)	The present author	60.42 ($t = 20^\circ$)	The author's calculation from $\epsilon = 10.8$, ($\lambda = \infty$) of Joachin ⁽¹⁰⁾

For the sake of comparison μ 's of various authors for ethylene chloride in various states are tabulated as follows in the table 10:

Table 10.

Electric moment of ethylene chloride $\mu \times 10^{-18}$				
In benzene	In hexane	In heptane	Liquid	As vapour
1.83 ⁽¹¹⁾	1.26-1.42 ⁽¹¹⁾	1.16-1.42 ⁽¹⁴⁾	1.55 ⁽¹⁵⁾	1.56 ⁽¹⁶⁾
1.86 ⁽¹²⁾				1.01 ⁽¹⁷⁾
1.75 ⁽¹³⁾			1.375 ⁽¹⁹⁾	1.12-1.54 ⁽¹⁸⁾

- (7) Weegmann, *Z. physik. Chem.*, **2** (1888), 218.
 (8) Walden, *Z. physik. Chem.*, **70** (1910), 569.
 (9) Jahn and Möller, *Z. physik. Chem.*, **13** (1894), 385.
 (10) Joachin, *Ann. Phys.*, **60** (1919), 570.
 (11) Meyer, *Z. physik. Chem.*, B **8** (1930), 27.
 (12) Gross, *Phys. Zeit.*, **30** (1929), 504.
 (13) Williams, *Zeit. f. physik. Chem.*, **138** (1928), 75.
 (14) Smyth, *J. Am. Chem. Soc.*, **53** (1931), 4242.
 (15) Walden, *Z. physik. Chem.*, **70** (1910), 569.
 (16) Ghosh Mahanti and Sen Gupta, *Z. physik.*, **54** (1929), 711.
 (17) Sängner, *Physik. Z.*, **32** (1931), 21.
 (18) Zahn, *Phys. Rev.*, **38** (1931), 52.
 (19) The author's calculation.

In conclusion, the author wishes to express his thanks to Prof. S. Mitsukuri for his kind advices.

Summary.

(1) Refractive indices of ethylene chloride, 1, 1, 2, 2-tetrachlorethane and their binary mixture have been measured.

(2) Variation of the refractive index with respect to temperature and to the molar fractions at 25°C. have been studied.

(3) Linear dependence of the refractive index on the reciprocals of absolute temperature in each case was observed.

(4) Refractive index at room temperature for ethylene chloride and 1, 1, 2, 2-tetrachlorethane and refractive index at room molal fraction for the binary mixture at 25°C. have been tabulated.

(5) The molar refraction for both ethylene chloride and 1, 1, 2, 2-tetrachlorethane have been calculated as 20.82 and 31.23 respectively.

(6) The electric moment μ has been calculated for liquid ethylene chloride to be 1.375×10^{-18} .

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DAS VERHALTEN DES PYRIDINRINGES BEI DER ELEKTROCHEMISCHEN OXYDATION.

IV. PIPERIDIN.

Von Moriaki YOKOYAMA und Kadzuo YAMAMOTO.

Eingegangen am 5. August 1933. Ausgegeben am 28. Oktober 1933.

Das Piperidin, dessen Ring aus fünf CH_2 -Gruppen und einer NH -Gruppe besteht, lässt sich als Cyclohexan auffassen, in dessen Ring eine CH_2 -Gruppe durch die Iminogruppe ersetzt ist.

Denkt man sich analoger Weise eine Methingruppe des Benzols durch N ersetzt, so kommt man zum Pyridin, welches dem Benzol an Beständigkeit kaum nachsteht.

Das Verhalten des Pyridins⁽¹⁾ bei der elektrochemischen Oxydation ist bereits früher Gegenstand einer Untersuchung gewesen. Vor kurzem hat der eine von uns die elektrochemische Oxydation des Cyclohexans⁽²⁾ und seiner Derivate durchgeführt. Dabei wurde der Oxydationsverlauf des Cyclohexans bei der Elektrolyse mit dem des Benzols verglichen und grosse Unterschiede in Bezug auf den Reaktionsmechanismus gefunden; im grossen und ganzen wurde beobachtet, dass das Cyclohexan viel beständiger als das Benzol gegenüber anodischer Einwirkung ist. Auf Grund dieser Verhältnisse liessen sich auch für die Elektrolyse des Pyridins und Piperidins Analogien vermuten.

Denn es drängt sich auch hier die Frage auf, wie der Einfluss der Durchhydrierung des Kernes ist und ob die Verhältnisse denen der hydrierten Benzol-Körper gleichen.

Beschreibung der Versuche.

Der Anolyt wurde in Anlehnung an unsere frühere Arbeit aus 5.15 gr. Piperidin (Kahlbaum; Sdp. 108°C.; $D_4^{25} = 0.8586$.) und 100 cm³ 2-N Schwefelsäure zusammengesetzt. Die Oxydation erfolgte in einer Tonzelle; als Anode diente ein Bleiblech, als Kathode ein Pt-Blech, welches die Tonzelle umgab. Die Stromdichte betrug 0.05 Amp./cm², die Strommenge 13 Amp.-Std. (für die Umwandlung von 1 gr. Piperidin in C₅H₈O₄ sind theoretisch 2.02 Amp.-Std. erforderlich). Die Dauer eines Versuches betrug etwa 6.5 Stunden.

Während der Elektrolyse wurde der Anolyt kräftig gerührt; die Temperatur wurde bei ca. 22°C. gehalten.

A. Die gasförmigen Produkte. Zur Analyse der im Anodenraume entwickelten Gase verfahren wir möglichst sorgfältig nach der bei der elektrochemischen Oxydation von Pyridin⁽³⁾ erwähnten Methode.

In folgender Uebersicht sind nun die Ergebnisse der Gasanalyse zusammengestellt. Die Gasvolumina wurden darin auf 0°C. und 760 mm Druck reduziert.

In dieser Figur sind die Kurven eingetragen, die die Resultate der Gasanalysen wiedergeben.

Es fällt auf, dass die Stromausbeute bez. auf den in der Zelle verbrauchten Sauerstoff nach Durchsendung einer Strommenge von 2 Amp.-

(1) M. Yokoyama u. K. Yamamoto, dieses Bulletin, **7** (1932), 28.

(2) M. Yokoyama, dieses Bulletin, **8** (1933), 71.

(3) M. Yokoyama u. K. Yamamoto, dieses Bulletin, **7** (1932), 28.

Tabelle 1.

Anode: Bleidioxyd; Temperatur: 22°C.;
Stromstärke: 2 Amp.; Stromdichte: 0.05 Amp./cm²

Std.	Sauerst. Coulom. (ccm)	Menge der aufgefangene Gase				Auf- genomm. O ₂ (ccm)	Strom- ausbeute (%)
		Ges. Vol. (ccm)	CO ₂ (ccm)	O ₂ (ccm)	CO (ccm)		
0.5	73.5	26.9	5.9	21.0	—	52.5	71.5
1	73.7	31.7	13.6	17.8	0.3	55.7	75.9
2	73.5	44.7	14.62	29.8	0.3	43.7	59.5
3	73.6	45.0	14.0	30.7	0.3	42.9	58.3
4	73.3	47.0	14.4	32.2	0.4	41.1	56.8
5	73.7	46.4	14.9	31.0	0.5	42.7	58.0
6	73.3	47.9	16.5	30.8	0.6	42.5	57.9

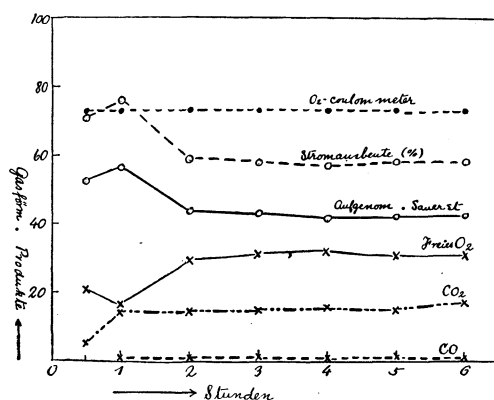


Fig. 1.

Std. (ca. 1.5 F/mol.) einen Optimalpunkt, dessen Lage bei etwa 75.9% ist, erreicht. Demgemäss fällt bei längerer Dauer der Elektrolyse die Ausbeute der Oxydation wieder und nach 2 Stunden (3 F/mol.) bleibt sie fast konstant (bei etwa 56%). Eine andere Kurve gibt den zeitlichen Verlauf der CO₂-Entwicklung wieder.

Die CO₂-Entwicklung steigt bis zu einem Maximalwert an und bleibt dann annähernd konstant. Es lässt sich also daraus schliessen, dass im Verlauf der Elektrolyse eine besonders leicht oxydable Substanz gebildet wird, deren Konzentration zunächst stark ansteigt und später wieder fällt.

B. Die sauren Elektrolysenprodukte. (1) *Ameisensäure*. Nach dem Unterbrechen der Elektrolyse wurde der fast farblose Anolyt zu-

nächst mit Aether mehrmals (etwa 10 Mal) ausgeschüttelt. Nach Verdunsten der ätherischen Lösung blieb eine stechend riechende, gelblich gefärbte Flüssigkeit zurück, die jeweils von einer Parallelversuchsreihe zusammengesammelt wurde (etwa 5 gr. aus 10 Elektrolyten). Zunächst wurde durch Destillation eine Fraktion erhalten, die gegen Lackmus sauer reagierte und deren Sdp. für 755 mm Druck bei 101.0°C. lag (Ausbeute 1.8 gr.). Das Produkt wurde mit BaCO₃ behandelt und das erhaltene Bariumsalz von überschüssigen BaCO₃ abfiltriert.

Die Analyse des Bariumsalzes lieferte folgende Zahlen:

Anal.: 0.2165 gr. gaben beim Abrauchen mit Schwefelsäure 0.2209 gr. BaSO₄.
Gef.: 60.04% .
Ber. für (CHO₂)₂Ba: 60.42 %.

(2) *Bernsteinsäure*. Der Rückstand von der Destillation erstarrte teilweise krystallinisch; die Kryställchen wurde zuerst mit Benzol behandelt. Aus der in Benzol schwer löslichen Masse (etwa 2.0 gr.) wurde nach dem Umkrystallisieren aus Aether eine Substanz vom Smp. 181°C. erhalten, die sich als Bernsteinsäure erwies (Smp. des käuflichen Präparates 183°C.).

Anal.: Subst. = 0.2265; CO₂ = 0.3359; H₂O = 0.1683 gr.
Gef.: C = 40.44; H = 5.80% .
Ber. für C₄H₆O₄: C = 40.66; H = 5.13% .

(3) *Glutarsäure*. Aus dem Benzolauszug wurde Glutarsäure (etwa 0.5 gr.) vom Schmelzpunkt 97°C. erhalten; der Mischschmelzpunkt mit einem käuflichen Präparat (von Kahlbaum) ergab keine Erniedrigung.

Anal.: Subst. = 3.053; CO₂ = 5.325; H₂O = 1.652 mg.
Gef.: C = 45.42; H = 6.01% .
Ber. für C₅H₈O₄: C = 45.43; H = 6.05% .

(4) *δ-Aminovaleriansäure*. Die mit Aether extrahierte Lösung des Anolyten wurde zunächst mit Bariumkarbonat vorsichtig neutralisiert und dadurch von Schwefelsäure vollständig befreit. Die so erhaltene filtrierte Lösung wurde im Vakuum destilliert, wobei der Aufnahmekolben mit einer geeigneten Menge von ca. 1-N HCl-Lösung beschickt wurde um flüchtige Basen abzufangen.

Der bräunlichgefärbte syrupartige Rückstand der Vakuumdestillation ergab mit Triketohydratlösung eine Blaufärbung⁽⁴⁾.

(4) Rosenthaler, „Der Nachweis organischer Verbindungen,“ II. Auflage, S. 602.

Demzufolge konnten wir auf die Entstehung einer Aminosäure schliessen. Zur Isolierung der Aminosäure trugen wir den Rückstand der Vakuumdestillation in Aether-Alkohol ein. Dabei entstand eine weisse nicht krystallinische Fällung, die mit Alkohol gewaschen und über Schwefelsäure in Vakuum getrocknet wurde.

Die erhaltenen etwas hygroskopischen Krystalle wurden aus Wasser umkrystallisiert und zeigten einen Schmelzpunkt von 157–158°C. Der Körper erwies sich als δ -Aminovaleriansäure. (Ausbeute 0.95 gr. 13.6% der Theorie.).

Anal.: Subst. = 0.3102; CO_2 = 0.5810; H_2O = 0.2699 gr.

N_2 = 59.06 cm^3 .

Gef.: C = 51.09; H = 9.67; N = 11.90%.

Ber. für $\text{C}_5\text{H}_{11}\text{O}_2\text{N}$: C = 51.24; H = 9.39; N = 11.95%.

(5) *δ -Aminovalerianaldehyd.* Schon kurz nach Stromschluss entnahmen wir mit einer Pipette 1 ccm des Elektrolyten und versetzten die nach sorgfältiger Neutralisation mit Natriumkarbonat erhaltene Lösung mit einer durch schweflige Säure entfärbten Fuchsinlösung; nach Zufügung einiger Tropfen Kali entstand eine rote Farbe. Damit sowohl, wie durch andere Reaktionen war die Gegenwart eines Aldehyds, nämlich des δ -Aminovalerianaldehyds, erwiesen, der jedoch bisher nicht isoliert werden konnte.

(6) *Ammonia.* Das Destillat der Vakuumdestillation wurde im Vakuum bis zur vollständigen Trockene zur Befreiung von der geringen Menge unveränderten Piperidinchlorhydrats⁽⁵⁾ eingedampft. Wir erhielten dabei eine kleine Menge einer weissen, nadelförmig krystallinischen Masse. Diese lieferte mit Platinchlorid eine orangegelbe Fällung, die keinen definierten Schmelzpunkt hatte und sich als aus Ammoniumchloroplatinat bestehend erwies.

Anal.: Subst. = 0.2305; Pt = 0.1004 gr.

Gef.: Pt = 43.55%.

Ber. für $(\text{NH}_4)_2\text{PtCl}_6$: Pt = 43.96%.

Die Aenderung des P_H im Verlauf der Elektrolyse. Um die Frage des Reaktionsmechanismus weiter klarzustellen, untersuchten wir nun, wie sich das P_H des Elektrolyten im Verlauf der Elektrolyse ändert.

Zu diesem Zwecke musste natürlich die Zusammensetzung des Elektrolyten geändert und genau definiert werden, um die Pufferwirkung der Reaktionsprodukte zu vermeiden.

Eine wässrige Lösung von 2.57 gr. Piperidin wurde mit verdünnter Schwefelsäure sorgfältig neutralisiert und nach Zufügung eines Tropfens Schwefelsäure mit Wasser genau auf 200 ccm verdünnt, wobei sich ein P_H von 3~4 ergab.

(5) Ausbeute: 2.1 gr.

Diese Flüssigkeit wurde als Elektrolyt direkt verwendet und ohne Diaphragma elektro-oxydiert. Die Bedingungen der Elektrolyse waren im allgemeinen dieselben wie bisher, mit Ausnahme folgender Abänderungen.

Als Kathode diente ein kurzes Platindrähtchen, damit eine Reduktion an der Kathode möglichst vermieden wurde.

Die Temperatur wurde stets bei 50°C. gehalten. Zur P_H -Messung benutzten wir eine Chinhydron-Elektrode und entnahmen dem Elektrolyten für jede Einzelmessung 1 ccm Flüssigkeit⁶⁾.

Wir haben unsere Versuche tabellarisch zusammengefasst.

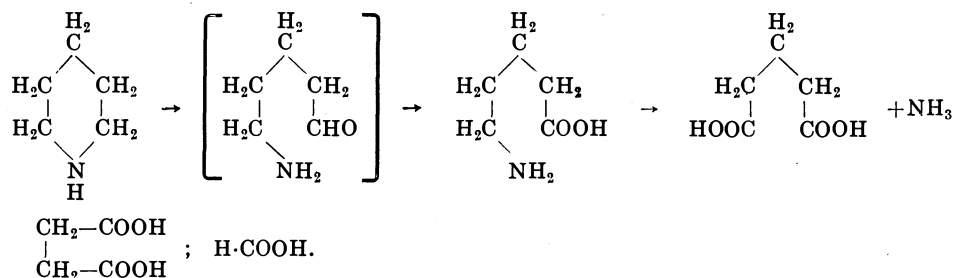
Tabelle 2.

Std.	—	0.25	0.5	1	2	3	4	5	6
P_H	3.21	3.08	2.89	2.77	2.39	2.28	2.18	2.11	2.03

Aus der Tabelle ergibt sich, dass das P_H in ersten Stadium der Elektrolyse rasch abnahm. Es zeigt sich dadurch, dass schon kurz nach Stromschluss eine Säure in ziemlich erheblicher Menge entstehen muss. Somit lässt sich die Ansicht vertreten, dass das als erstes entstehende Oxydationsprodukt (wahrscheinlich δ -Aminovalerianaldehyd) wohl nur eine sehr geringe Existenzfähigkeit hat, und sogleich weiter zu einer Säure oxydiert wird.

Der Befund, dass die Wasserstoffionen-Konzentration gleich zu Beginn der Elektrolyse stark steigt, ist somit befriedigend erklärt. [Daher ist es auch schwierig eine derartige Substanz aus dem Elektrolyten (S. 308) zu isolieren.]

Unter Zusammenfassung aller Beobachtungen lässt sich einstweilen folgendes vorläufige Schema für den Oxydationsverlauf am Piperidin aufstellen (wobei die letzten Stufen bis zum Kohlendioxyd nicht berücksichtigt sind); es lautet



(6) Durch Blindversuche untersuchten wir den Einfluss des im Elektrolyten gelösten Kohlendioxyds, das im Verlauf der Elektrolyse entstand, auf das P_H , und kamen zu dem sicheren Ergebnis, dass die Aenderung des P_H durch Auflösung von CO_2 zu vernachlässigen ist.

Bei der Oxydation des Piperidins findet eine Ringsprengung an der -NH-Gruppe statt, da die oxydative Wirkung an der schwächsten Stelle eingreift.

Diese Reaktion erinnert lebhaft an die von R. Wolffenstein⁽⁷⁾ über die Oxydation des Piperidins mit Peroxyverbindungen durchgeführten Versuche: auch von ihm wurde als eines der Ringsprengungsprodukte der δ -Aminovalerianaldehyd isoliert.

Wie wir schon eingangs erwähnt haben (S. 306), wird die Oxydationsfähigkeit des Benzols an der Anode, wenn es durch Aufnahme von Wasserstoff bis zur Sättigung in das Cyclohexan umgewandelt wird, ausserordentlich stark herabgesetzt.

Beim Vergleich des Verhaltens von Piperidin mit dem von Pyridin finden wir gerade das umgekehrte Verhältniss. Das als 6-fach hydriertes Pyridin aufzufassende Piperidin zeigt eine wesentlich geringere Stabilität als das Pyridin und lässt sich leicht in Nachbarschaft des N-Atoms aufsprengen.

Ueber den bedeutenden Unterschied, der sich hier zwischen der Beständigkeit eines gesättigten isocyclischen 6-Ringes und der eines entsprechenden, in dem ein C-Atom durch N ersetzt ist, zeigt hat, hoffen wir noch Gelegenheit zu haben an Hand weiterer Untersuchung die Diskussion fortzusetzen.

Herr Prof. Dr. Shigeru Komatsu sei an dieser Stelle für seine freundlichen Ratschläge bei dieser Arbeit herzlichst gedankt.

Zusammenfassung.

(1) Bei der elektrochemischen Oxydation von Piperidin an der Bleidioxidanode in verdünnter Schwefelsäure wurden die folgenden Oxydationsprodukte erhalten: δ -Aminovaleriansäure, Bernsteinsäure, Ammonia, Glutarsäure, Ameisensäure, Kohlendioxyd und Kohlenoxyd. Auch die Existenz des δ -Aminovalerianaldehyds konnte wahrscheinlich gemacht werden.

(2) Während der Elektrolyse wurde der kinetische Verlauf der Gasabscheidung an der Anode analytisch verfolgt.

(3) Durch Messung der während der Elektrolyse unter geeigneten Bedingungen auftretenden P_H -Änderungen konnten weitere Anhaltspunkte für den Reaktionsverlauf gewonnen werden.

Technische Hochschule zu Yokohama.

(7) Ber. 25 (1892), 2777.

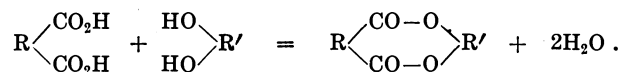
GLUTARSÄURE-AETHYLENESTER.

Von Yojiro TSUZUKI.

Eingegangen am 24. Juni, 1933. Ausgegeben am 28. Oktober, 1933.

In bezug auf die Konstitutionsfrage der hochmolekularen Substanzen bieten die Untersuchungen von W. H. Carothers über die Glykolester von Dicarbonsäuren nicht geringes Interesse. Durch Überlegungen und Experimente hat er gezeigt, dass die Polymerie dieser Ester ist der Art von intermolekularer Kondensation, und nicht von der Addition des monomeren Grundkörpers⁽¹⁾. Dies gibt eine Stütze für die Auffassung über den Bau hochmolekularer Verbindungen, die bereits von Kekulé⁽²⁾ ausgesprochen und neuerdings von Staudinger⁽³⁾ vertreten worden ist.

Bei der Reaktion der Dicarbonsäure $R(CO_2H)_2$ mit dem Glykol $R'(OH)_2$ könnte man einfach annehmen, dass ein monomerer ringförmiger Ester entstehe, nämlich:



Aber, wenn die Zahl der Atome in dem System $[-CO-R-CO-O-R'-O-]$ zu gross ist um die Schliessung des 5- oder 6-gliedrigen Ringes zu ermöglichen, so wird die Reaktion polymolekular und dann sind die Polymeride meistens von linearem Typ. Es sind Aethylen-, Trimethylen-, Hexamethylen- und Dekamethylen-Ester der Malon-, Bernstein-, Adipin- und Sebacin-Säure als kristallisierte und sämtlich hochpolymere Verbindungen erhalten worden, deren Molekulargrösse 2300-5000 beträgt⁽⁴⁾. Aethylen- und Trimethylen-Carbonat sind, wie zu erwarten war, in monomerem Form erhalten worden, aber das letztere kann durch Erhitzen mit Kaliumcarbonat in echtes Polymer verwandelt werden, aus welchem das Monomere durch Destillation in Vakuum regeneriert wird⁽⁵⁾. Monomeres Aethylenoxalat ist zu erhalten, aber es polymerisiert sich langsam bei gewöhnlicher Temperatur und rasch beim Erhitzen. Trimethylen-, Hexamethylen- und Dekamethylen-Oxalat sind Polymere von linearer Kondensation⁽⁶⁾.

(1) Allgemeine Theorie: W. H. Carothers, *J. Am. Chem. Soc.*, **51** (1929), 2548.

(2) A. W. Kekulé, Rektoratsrede Bonn 1877; R. Anschütz, A. Kekulé II, S. 912-3.

(3) H. Staudinger, *Ber.*, **59** (1926), 3019, und in zahlreichen anderen Arbeiten.

(4) W. H. Carothers und J. A. Arvin, *J. Am. Chem. Soc.*, **51** (1929), 2560.

(5) W. H. Carothers und F. J. Van Natta, *J. Am. Chem. Soc.*, **52** (1930), 314.

(6) W. H. Carothers, J. A. Arvin und G. L. Dorrough, *J. Am. Chem. Soc.*, **52** (1930), 3292.

In diesen Arbeiten ist zwar über die geraden Glieder der Oxalsäure-Reihe wohl ausführlich studiert worden, jedoch über die ungeraden Glieder, ausser Malonsäure, ist noch kein Versuch gemacht worden.

Die ungeraden Glieder der Oxalsäure-Reihe besitzen bekanntlich viel niedrigeren Schmelzpunkt sowie grössere Löslichkeit als die geraden Glieder, und auch zeigen grössere Unbeständigkeit, was nach Verbrennungswärme zu ersehen ist. Hinsichtlich der Konfiguration ist so erläutert zu werden, dass bei der ungeraden Dicarbonsäuren die beiden CO_2H -Gruppen am zickzackförmigen Molekül in cis-Stellung liegen, während sich die der geraden Dicarbonsäuren in trans-Stellung befinden;⁽⁷⁾ anderseits ist auch vermutet, dass in Lösung oder Schmelze die Spiralförmigkeit für eine lange Kohlenstoffkette bevorzugt ist.⁽⁸⁾

Wenn die ungeraden Dicarbonsäure, deren beiden CO_2H -Gruppen in cis-Lage stehen, mit Glykol reagieren, wäre es infolge der Raumverhältnisse möglich, dass sie niedriger polymerisierte Aethylenester geben als die oben erwähnten Polyester. Tatsächlich ist gefunden worden, dass bei der Reaktion mit Glykol die Maleinsäure (cis) niedriger polymerisierten Aethylenester liefert als die Fumarsäure (trans)⁽⁹⁾.

Mit dieser Erwartung ist in dieser Arbeit unternommen worden, die Aethylenester der ungeraden Säuren (Glutar-, Pimelin-, Azelainsäure usw.) zu gewinnen. Aber diese Säuren sind meist schwer zugänglich, und ich habe daher noch nicht näher über die sämtlichen Säuren untersucht. Ich möchte hier vorläufig zuerst über den Aethylenester der Glutarsäure berichten, die der bedeutende Vertreter⁽¹⁰⁾ der ungeraden Dicarbonsäuren ist.

Zur Darstellung der Polyester erhitzte Carothers⁽¹¹⁾ ein äquimolares Gemisch von Säure und Glykol (5% Überschuss) auf 175–185°C. drei Stunden und dann in Hochvakuum bei hoher Temperatur (200–250°C.) noch drei Stunden, wobei die theoretische Menge Wasser ausdestilliert wurde. Aus der schwach dunkelgefärbten Reaktionsmasse erhielt er den reinen Ester durch Umkristallisierung.

Bei der Darstellung des Glutarsäure-Aethylenesters habe ich die Reaktion bei möglichst tiefer Temperatur und durch kurzes Erhitzen mit

(7) Vergl. A. Müller, *Proc. Roy. Soc., A*, **124** (1929), 317.

(8) W. B. Lee, *Nature* **120** (1927), 48; *Chem. Zentr.* **1928**, I, 794.

(9) Y. Tsuzuki, unveröffentlicher Versuch.

(10) Malonsäure, der erste Glied der ungeraden Dicarbonsäuren, ist dem Oszillieren des Schmelzpunktes nach nicht der typische Glied der ungeraden Säuren betrachtet. Die Anomalie der Malonsäure in der homologen Reihe ist auch in dem aus der Dissoziationskonstanten berechneten interionischen Abstand zu beobachten. R. Gane und C. K. Ingold, *J. Chem. Soc.*, **1928**, 1589; **1931**, 2153; C. K. Ingold, *J. Chem. Soc.*, **1931**, 2170.

(11) W. H. Carothers und J. A. Arvin, *J. Am. Chem. Soc.*, **51** (1929), und in anderen Arbeiten.

Hilfe von Katalysator sich vollziehen lassen, um die Veränderung der Konfiguration der Säure durch thermische Agitation zu vermeiden. So ein äquimolares Gemisch von Glutarsäure und Aethylenglykol (10% Überschuss) wurde mit geschmolzenem Zinkchlorid (0.5 Mol.) als Katalysator im Ölbad bei 135–140°C. ca. 45 Minuten erhitzt. Im Laufe der Reaktion wurde die lebhaftete Wasserdampf-Entwicklung beobachtet.

Das farblose Reaktionsprodukt wurde in Wasser gegossen, die ausgeschiedene halb feste Masse einige Male mit Wasser verrieben, wobei die unveränderten Ausgangsmaterialie (Säure u. Glykol) sowie Zinkchlorid fast völlig in Wasser übergingen. Dann wurde sie mit Essigester aufgenommen, mit Wasser zweimal geschüttelt. Die Essigester-Lösung wurde mit Natriumsulfat getrocknet, filtriert und verdampft.

Der zurückgebliebene Ester (Ausbeute 45% d. Theorie) bildet ein farbloses, zähes Gummi. Es löst sich sehr leicht in Essigester und Aceton, leicht in Benzol, ziemlich schwer in Aether und Wasser.

Die ebullioskopische Messung von dem Molekulargewicht dieses Esters in Aceton gibt die Werte von 600–680 (Konzentration, 0.9–1.2%). Da die Moleküleinheit (Grundkörper) von dem Ester $[-CO-(CH_2)_3-CO-O-(CH_2)_2-O-] = C_7H_{10}O_4$ 158 ist, müsste das Molekül 4-fach polymerisiert sein. Also ist ein Ester mit kleinerem Polymerisationsgrad als Carothers's Polyester erhalten worden, was mit der Erwartung im Einklang steht. Strukturell ist aber dieser Polyester linear, und bildet eine offene Kette mit der endständigen freien OH- und CO_2H -Gruppe; denn dieser Ester reagiert sauer, und die Titriermessung der Carboxylgruppe hat deutlich gezeigt, dass dieser saure Ester einbasisch ist⁽¹²⁾. Das aus dieser Messung berechnete Molekulargewicht stimmt mit dem aus der Ebullioskopie erhaltenen völlig überein. Auch die Elementaranalyse bestätigt die Schlussfolgerung. Aus diesen Gründen wird die Struktur dieses Esters in der folgenden Formel dargestellt:



(12) Hierbei sei bemerkt, dass Carothers's experimenteller Beweisgrund für die offenen Ketten-Struktur des Moleküls ziemlich schwach ist. Seine Polyester sind so hochpolymerisiert, dass es ihm nicht gelungen ist, die endständigen freien OH- bzw. CO_2H -Gruppe deutlich nachzuweisen. Die seiner Schlussfolgerung günstigen Versuchsergebnisse sind nur die Analysenzahlen an Kohlenstoff. W. H. Carothers und J. A. Arvin, loc. cit. Aber in seiner späteren Arbeit über die neutralen und sauren Aethylenester der Bernsteinsäure konnte er die endständigen Gruppen nachweisen und bestimmen. In diesem Falle wurden zwar aus *überschüssiger Säure* und dem Glykol eine Anzahl saurer Ester mit verschiedenem Polymerisationsgrad (von 6 auf 23) erhalten, und aus *überschüssigem Glykol* und der Säure ein neutraler Ester. Diese Ester tragen an ihren Molekül-Enden zwei gleiche Gruppen (bei den sauren Estern CO_2H -Gruppe, beim neutralen Ester OH-Gruppe). Die Struktur dieser Ester ist demnach mit der des meinigen etwas verschieden. W. H. Carothers und G. L. Dorrough, *J. Am. Chem. Soc.*, **52** (1930), 314.

Titrierung: Die Substanz wurde in 20 ccm. Aceton gelöst, und mit $\frac{n}{50}$ -KOH titriert. 0.0995 gr. Subst. verbrauchten 7.78 ccm. $\frac{n}{50}$ -KOH.

Mol. Gew.	Gef. 632
$(C_7H_{10}O_4)_4H_2O = C_{28}H_{42}O_{17}$	Ber. 650.3
Anal.: Subst. = 0.0900; CO_2 = 0.1684; H_2O = 0.0536 gr.	

	Gef. C = 51.04; H = 6.67%.
$C_{28}H_{42}O_{17}$ (650.3)	Ber. C = 51.66; H = 6.51%.
$(C_7H_{10}O_4)_4$ (632.3)	Ber. C = 53.14; H = 6.38%.

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A THEORY OF THE RATE OF SOLUTION OF SOLID INTO LIQUID.

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Received July 13th, 1933. Published October 28th, 1933.

Introduction.

The rate of solution of solid into liquid⁽¹⁾ is expressed generally by

$$\frac{dc}{dt} = KS(c_{\infty} - c) \dots\dots\dots (1),$$

where c is the concentration of the dissolved substance in the liquid phase, c_{∞} the saturation concentration, S the area of the boundary surface, K a constant, and t the time.

Noyes,⁽²⁾ Whitney⁽²⁾ and Nernst,⁽³⁾ in advancing equation (1) as representing the rate of diffusion, made the assumption that a film of saturated solution is continuously present on the surface of solid phase, and that a stationary diffusion layer of adequate thickness is present at the interface. According to this theory the thickness of the diffusion

(1) Noyes and Whitney, *Z. physik. Chem.*, **23** (1897), 689; Nernst, *Z. physik. Chem.*, **47** (1904), 52; Brunner, *Z. physik. Chem.*, **47** (1904), 56.

(2) Ibid.

(3) Ibid.

layer⁽⁴⁾ is about $2 \times 10^{-3} \sim 5 \times 10^{-3}$ cm., the exact value naturally depending upon the rate of revolution of the stirrer in the main body of the liquid phase.

The rate of solution of metals or metallic oxides into acidic solution is expressed in the majority of cases by

$$\frac{dc}{dt} = -KSc \dots\dots\dots (1)'$$

where c is the concentration of the acid. This equation is similarly derived by assuming that the rate of solution is the rate of diffusion of the reacting substance through an assumed diffusion layer.

There are many experimentally obtained facts which it would be difficult to interpret by the diffusion layer theory. For example,

(a) The rate of solution of metals into acidic solution is independent of the rate of stirring when the velocity of stirring is sufficiently high⁽⁵⁾.

(b) The rate of solution differs according to the faces of the crystal concerned⁽⁶⁾.

(c) The rate of solution is dependent on the curvature of the solid surface⁽⁷⁾.

(d) Roller studied the relation between the rates of solution and the size of the solid particles, and concluded that no diffusion layer exists at the boundary surface⁽⁸⁾.

Theories of the rate of solution of solid into liquid, which do not assume the existence of a diffusion layer, have been proposed by several writers⁽⁹⁾.

The following is a new theory of the rate of solution of solid into liquid, similar to that of the rate of solution of gas into liquid proposed by the present writer,⁽¹⁰⁾ and based upon the kinetic theory of gas.

A New Theory of the Rate of Solution of Solid into Liquid.

The process of solution of solid into liquid can be divided into two processes, namely the escape of the solid molecules into the liquid phase

(4) Brunner, *Z. physik. Chem.*, **47** (1904), 56; Wagner, *Z. physik. Chem.*, **71** (1910), 401.

(5) Centnerszwer and Zablocki, *Z. physik. Chem.*, **122** (1926), 455; Centnerszwer and Straumanis, *ibid.*, **128** (1927), 369; Centnerszwer, *ibid.*, **137** (1928), 352; **141A** (1929), 297.

(6) Tammann and Sartorius, *Z. anorg. Chem.*, **175** (1929), 197; Glauner, *Z. physik. Chem.*, **142** (1929), 67.

(7) Luce, *Ann. Phys.*, **11** (1929), 167; Podszus, *Z. physik. Chem.*, **92** (1917), 227.

(8) Roller, *J. Phys. Chem.*, **35** (1931), 1133; **36** (1932), 1202.

(9) Ericson-Auren, *Z. anorg. Chem.*, **18** (1898), 83; **27** (1901), 209; Palmaer, *Z. physik. Chem.*, **56** (1906), 689; Wildermann, *Z. physik. Chem.*, **66** (1909), 445.

(10) Miyamoto, *Chem. News*, **144** (1932), 273; this Bulletin, **7** (1932) 8, 388.

and the condensation of the dissolved molecules on the solid surface. Then the rate of solution of solid into liquid is generally given by

$$\frac{N}{S} \left(\frac{dn}{dt} \right) = N_1 - N_2 \dots\dots\dots (2),$$

where N is Avogadro's constant, S the area of the boundary surface, N_1 the number of molecules of the solid which enter into the liquid phase per unit area of the interface per unit time, N_2 the number of molecules which condense per unit area of the interface per unit time, n the number of moles of the dissolved substance in the liquid phase.

According to Maxwell's distribution law, the number of molecules, whose components of energies of vibration at right angles to a fixed plane lie between ε and $\varepsilon + d\varepsilon$, among N' molecules is given by

$$dN = \frac{N'}{kT} e^{-\frac{\varepsilon}{kT}} d\varepsilon \dots\dots\dots (3),$$

where k is Boltzmann's constant.

Then the number of molecules, per unit area of the solid surface, whose energies of vibration at right angles to the interface are greater than a threshold value ε_0 , is given by

$$N_x = \frac{N_0}{kT} \int_{\varepsilon_0}^{\infty} e^{-\frac{\varepsilon}{kT}} d\varepsilon = N_0 e^{-\frac{\varepsilon_0}{kT}} = N_0 e^{-\frac{N\varepsilon_0}{RT}},$$

where N_0 is the number of molecules which make up unit area of the solid surface.

Now an assumption is proposed. Among the molecules of which the surface of the solid consists, only those, whose components of energies of vibration at right angles to the interface are greater than a threshold value ε_0 , are able to enter into the liquid phase. Then it is clear that the value N_1 is proportional to N_x and is given by

$$N_1 = \beta N_x = \beta N_0 e^{-\frac{N\varepsilon_0}{RT}} \dots\dots\dots (4),$$

where β is a constant.

On the above mentioned assumption it easily follows that the value ε_0 depends upon the characteristic qualities of solid and liquid, and also upon pressure and temperature. The packing of the molecules in the

solid surface will have a great influence on the value of ϵ_0 . When the solid surface is convex, the value ϵ_0 is of course smaller and consequently the value N_1 is greater than when the solid surface is plane.

The rate of condensation or the value N_2 is obtained in the following way. By Maxwell's distribution law of velocities the number of molecules whose components of velocities at right angles to a fixed plane lie between u and $u+du$ among N'' molecules in the liquid phase is given by

$$dN = \frac{N''}{\sqrt{\frac{2\pi RT}{M}}} e^{-\frac{Mu^2}{2RT}} du \quad \dots\dots\dots (5),$$

where M is the molecular weight of the dissolved substance, R the gas constant, and T the absolute temperature.

Now the following assumption is proposed. Among the molecules, which collide with the solid surface, only those, whose components of velocities at right angles to the interface are greater than a threshold value u_0 , can condense on the solid surface.

This assumption has great probability in view of the fact that in the majority of cases the collisions between gas molecules and surface are perfectly inelastic, that is, every gas molecule which collides with the solid surface condenses⁽¹¹⁾. The greater the component of velocity at right angles to the interface, the more inelastic will be the collision. According to this assumption the value N_2 is given by

$$N_2 = \int_{u_0}^{\infty} \frac{cN}{\sqrt{\frac{2\pi RT}{M}}} u e^{-\frac{Mu^2}{2RT}} du = cN \sqrt{\frac{RT}{2\pi M}} e^{-\frac{Mu_0^2}{2RT}} \quad \dots\dots (6),$$

where c is the concentration of the dissolved substance expressed as the number of moles per c.c.

The value u_0 depends upon the natures of solid and liquid, temperature and pressure, and the value N_2 increases or decreases as the value u_0 decreases or increases. From equations (2), (4) and (6) we have

$$\frac{dn}{dt} = S \left(\frac{\beta N_0}{N} e^{-\frac{N\epsilon_0}{RT}} - c \sqrt{\frac{RT}{2\pi M}} e^{-\frac{Mu_0^2}{2RT}} \right) \quad \dots\dots\dots (7).$$

(11) Langmuir, *J. Am. Chem. Soc.*, **38** (1916), 2257; **54** (1932), 2801; Egerton, *Phil. Mag.*, **33** (1917), 33.

In the state of saturation,

$$\frac{dn}{dt} = 0 \quad \dots\dots\dots (8).$$

From equations (7) and (8) we have

$$\frac{\beta N_0}{N} e^{-\frac{N\epsilon_0}{RT}} = c_\infty \sqrt{\frac{RT}{2\pi M}} e^{-\frac{Mu_0^2}{2RT}} \quad \dots\dots\dots (9),$$

where c_∞ is the concentration of the saturated solution. From equations (7) and (9) we have

$$\frac{dn}{dt} = S \sqrt{\frac{RT}{2\pi M}} e^{-\frac{Mu_0^2}{2RT}} (c_\infty - c) \quad \dots\dots\dots (10).$$

Now

$$c = \frac{n}{v} \quad \dots\dots\dots (11),$$

where v is the volume of the liquid phase.

Then, neglecting the change of volume of the liquid phase due to the dissolution of the solid substance; we have,

$$\frac{dc}{dt} = \frac{1}{v} \frac{dn}{dt} = \frac{S}{v} \sqrt{\frac{RT}{2\pi M}} e^{-\frac{Mu_0^2}{2RT}} (c_\infty - c) \quad \dots\dots\dots (12),$$

or

$$\frac{dc}{dt} = KS(c_\infty - c) \quad \dots\dots\dots (13),$$

where

$$K = \frac{1}{v} \sqrt{\frac{RT}{2\pi M}} e^{-\frac{Mu_0^2}{2RT}} \quad \dots\dots\dots (14).$$

Thus equation (1) has been derived from the new theory without the assumption of a diffusion layer.

Equation (1)' is similarly derived as follows:—It is assumed that, among the molecules which collide with the solid surface, only those, whose components of velocities at right angles to the interface are greater than a threshold value u_0 , can react with the solid.

Then from equation (6) the rate of solution is expressed by

$$-\frac{N}{S} \frac{dn}{dt} = cN \sqrt{\frac{RT}{2\pi M}} e^{-\frac{Mu_0^2}{2RT}} \dots\dots\dots (15),$$

where n is the number of moles of the reacting substance and c its concentration. Now

$$c = \frac{n}{v} \dots\dots\dots (16),$$

where v is the volume of the liquid phase. From equations (15) and (16) we have

$$\frac{dc}{dt} = -\frac{c}{v} S \sqrt{\frac{RT}{2\pi M}} e^{-\frac{Mu_0^2}{2RT}} \dots\dots\dots (17),$$

or

$$\frac{dc}{dt} = -KSc \dots\dots\dots (18),$$

where

$$K = \frac{1}{v} \sqrt{\frac{RT}{2\pi M}} e^{-\frac{Mu_0^2}{2RT}} \dots\dots\dots (19),$$

Thus equation (1)' has been obtained.

The Initial Rate of Solution. The initial rate of solution, or the rate of solution when the liquid is perfectly free from solid substance, is obtained from equation (7) by putting $c = 0$.

$$\left(\frac{dn}{dt}\right)_{\text{initial}} = \frac{\beta SN_0}{N} e^{-\frac{N\epsilon_0}{RT}},$$

or

$$\left(\frac{dc}{dt}\right)_{\text{initial}} = \frac{\beta SN_0}{Nv} e^{-\frac{N\epsilon_0}{RT}} \dots\dots\dots (20).$$

The initial rate of solution is a function of ϵ_0 only.

From equations (9) and (20) we may also express the initial rate of solution by the following equation.

$$\left(\frac{dc}{dt}\right)_{\text{initial}} = \frac{Sc_\infty}{v} \sqrt{\frac{RT}{2\pi M}} e^{-\frac{Mu_0^2}{2RT}} \dots\dots\dots (20)'$$

The Solubility of Solid.

From equation (9) the solubility of a solid, c_∞ moles per c.c., is given by

$$c_\infty = \frac{\beta N_0}{N} \sqrt{\frac{2\pi M}{RT}} e^{-\frac{1}{RT} \left(N\varepsilon_0 - \frac{Mu_0^2}{2} \right)} \dots\dots\dots (21).$$

The solubility of a solid is quite independent of the initial rate of solution. The solubility is expressed as a function of ε_0 and μ_0 , but the initial rate of solution as a function of ε_0 only. Now the value N_0 , the number of molecules which compose unit area of the solid surface, is generally given by

$$N_0 = \gamma \left(\frac{N}{v_m} \right)^{\frac{2}{3}} = \gamma \left(\frac{\rho N}{M} \right)^{\frac{2}{3}} \dots\dots\dots (22),$$

where N is Avogadro's constant, v_m the molar volume, ρ the density of the solid, M the molecular weight, γ a constant, the value of which depends upon the arrangement of the molecules of the solid. From equations (21) and (22) we have

$$c_\infty = \beta \gamma N^{-\frac{1}{3}} \left(\frac{2\pi}{R} \right)^{\frac{1}{2}} M^{-\frac{1}{6}} \rho^{\frac{2}{3}} T^{-\frac{1}{2}} e^{-\frac{1}{RT} \left(N\varepsilon_0 - \frac{Mu_0^2}{2} \right)} \dots (23).$$

The osmotic pressure, p_∞ , of the saturated solution is given in the ideal case by

$$p_\infty = RTc_\infty = \beta \gamma N^{-\frac{1}{3}} (2\pi R)^{\frac{1}{2}} M^{-\frac{1}{6}} \rho^{\frac{2}{3}} T^{\frac{1}{2}} e^{-\frac{1}{RT} \left(N\varepsilon_0 - \frac{Mu_0^2}{2} \right)} \dots (24).$$

From equation (21) we have

$$\ln c_\infty = \frac{-\left(N\varepsilon_0 - \frac{Mu_0^2}{2} \right)}{RT} - \frac{1}{2} \ln T + \ln \frac{\beta N_0}{N} \sqrt{\frac{2\pi M}{R}} \dots\dots (25).$$

For the temperature range within which the values ε_0 , u_0 , N_0 may be taken as constant, we have from equation (25)

$$\ln c_\infty = \frac{A}{RT} - \frac{1}{2} \ln T + B \dots\dots\dots (26),$$

where

$$\left. \begin{aligned} A &= -\left(N_{\varepsilon_0} - \frac{Mu_0^2}{2}\right) \\ B &= \ln \frac{\beta N_0}{N} \sqrt{\frac{2\pi M}{R}} \end{aligned} \right\} \dots\dots\dots (27).$$

From Clapeyron-Clausius equation we have⁽¹²⁾

$$\frac{d \ln c_{\infty}}{dT} = \frac{-Q}{RT^2} \dots\dots\dots (28).$$

By putting

$$Q = Q_0 + aT \dots\dots\dots (29),$$

in equation (28) we have

$$\frac{d \ln c_{\infty}}{dT} = \frac{-(Q_0 + aT)}{RT^2}$$

This equation represents the relation between the solubility and the temperature over the temperature range for which Q may be expressed by equation (29). By integrating this equation we have

$$\ln c_{\infty} = \frac{Q_0}{RT} - \frac{a}{R} \ln T + \beta \dots\dots\dots (30),$$

where β is the integration constant. Equation (26) derived kinetically has a form analogous to equation (30) derived thermodynamically.

Discussion.

As equations (1) and (1)' have been derived according to the new theory, it is certain that this theory can be used to interpret any experimental fact that can be interpreted by the diffusion theory. It is hardly necessary to mention that the same theory can also be applied when the bulk of the liquid phase is quiescent, in which case the existence of a diffusion layer must be taken into consideration.

From equations (7) and (17) the rate of solution is dependent upon the values ε_0 and u_0 . The fact, experimentally verified, that the rate of solution differs at different faces of the crystal,⁽¹³⁾ is thus explained:—

(12) Eucken, „Lehrbuch der chemischen Physik,“ S. 345.

(13) Loc. cit.

The values ϵ_0 and u_0 are dependent not only on the chemical natures of the solid and the liquid but also on the packing of the molecules in the solid surface. The results of Roller's investigations⁽¹⁴⁾ can be similarly interpreted by means of equation (7).

The solubility of the solid depends upon the curvature of the solid surface.

(a) Hulett⁽¹⁵⁾ found that the solubility of gypsum increases when the size of the particle is less than 2×10^{-4} cm.

(b) Dundon and Mack⁽¹⁶⁾ observed an increase in the solubility of gypsum between $0.2 \times 10^{-4} \sim 0.5 \times 10^{-4}$ cm. in size, and Dundon⁽¹⁷⁾ extended these observations to other powders.

These facts are interpreted easily from equation (21), obtained by the present theory.

Nernst⁽¹⁸⁾ had proposed that a diffusion layer of adequate thickness normally exists at the interface between different phases. But there are a number of experimentally obtained facts which contradict the existence of the Nernst diffusion layer.

(a) Langmuir⁽¹⁹⁾ has concluded from the studies on adsorption, that only a monomolecular film exists at the interface between solid and gas, and interpreted a number of phenomena according to his theory.

(b) As mentioned above, the rate of solution of metals into acidic solutions is independent of the rate of stirring when the stirring speed is sufficiently high;⁽²⁰⁾ the rates of solution at the different faces of a crystal are different;⁽⁶⁾ the rate of solution of solid depends upon the curvature of the solid surface⁽²¹⁾. These facts are difficult to interpret by the diffusion layer theory.

(c) The diffusion layer theory demands the existence of a diffusion layer whose thickness is $20 \times 10^{-4} \sim 50 \times 10^{-4}$ cm. at the interface between solid and liquid⁽²²⁾. On the contrary Spangenberg⁽²³⁾ found optically that the thickness of the stationary layer at the interface between sodium chloride crystal and its saturated solution, if it exist, must be less than 0.4×10^{-4} cm. Bulkley⁽²⁴⁾ showed from the measurements of flow through

(14) Loc. cit.

(15) *Z. physik. Chem.*, **37** (1901), 385; **47** (1904), 357.

(16) *J. Am. Chem. Soc.*, **45** (1923), 2479.

(17) *Ibid.*, **45** (1923), 2658.

(18) *Z. physik. Chem.*, **47** (1904), 52.

(19) *Trans. Farad. Soc.*, **17** (1921), 621.

(20) Loc. cit.

(21) Loc. cit.

(22) Loc. cit.

(23) *Z. Krist.*, **59** (1923), 383.

(24) *Bureau Standards, J. Res.*, **6** (1931), 89.

capillary tubes that the liquid moves at least up to 0.03×10^{-4} cm. from the solid surface.

From the study of the effect of molecular films of fatty acids on the rate of oxidation of sodium sulphite solution the present writer and his collaborators⁽²⁵⁾ have concluded that no Nernst diffusion layer exists at the interface between liquid and gas, when the bulk of liquid phase is stirred at high speed.

(d) From the study of the initial rate of solution of oxygen into alcoholic solutions of anhydrous stannous chloride the present writer and his collaborator⁽²⁶⁾ have shown that the effect of the change of concentrations of stannous chloride on the initial rate of solution does not satisfy the equation derived from the diffusion layer theory.

Roller⁽¹⁴⁾ concluded from the results of his study that no theoretical Nernst film exists at the interface between solid and liquid. The present writer is also of the opinion that no diffusion layer of such thickness as that demanded by the diffusion layer theory exists at the interface between different phases when the bulk of the phases is stirred at a sufficiently high speed.

Summary.

(1) A theory of the rate of solution of solid into liquid was proposed, which is based upon the assumptions that among the molecules, which compose the solid surface, only those, whose components of energies of vibration at right angles to the interface are greater than a threshold value ϵ_0 , can enter into the liquid phase, and that among the molecules in the liquid phase, only those, which collide with the interface with velocities, whose components at right angles to the interface are greater than a threshold value u_0 , can condense on the solid surface.

According to this theory the rate of solution is expressed by

$$\frac{dc}{dt} = \frac{S}{v} \left(\frac{\beta N_0}{N} e^{-\frac{N\epsilon_0}{RT}} - c \sqrt{\frac{RT}{2\pi M}} e^{-\frac{Mu_0^2}{2RT}} \right),$$

which can be transformed into the following equation.

$$\frac{dc}{dt} = KS(c_\infty - c).$$

(25) Miyamoto, Kaya and Nakata, this Bulletin, **6** (1931), 133.

(26) Miyamoto and Utunomiya, this Bulletin, **53** (1932), 1096; *J. Science of the Hiroshima University*, A, **3** (1933), 193.

(2) According to the present theory the solubility of solid is given by

$$c_{\infty} = \frac{\beta N_0}{N} \sqrt{\frac{2\pi M}{RT}} e^{-\frac{1}{RT} \left(N_{\epsilon_0} - \frac{Mu_0^2}{2} \right)}$$

or

$$c_{\infty} = \beta \gamma N^{-\frac{1}{3}} \left(\frac{2\pi}{R} \right)^{\frac{1}{2}} M^{-\frac{1}{3}} \rho^{\frac{2}{3}} T^{-\frac{1}{2}} e^{-\frac{1}{RT} \left(N_{\epsilon_0} - \frac{Mu_0^2}{2} \right)}$$

(3) The experimental facts obtained by a number of writers have been interpreted in the light of the present theory.

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A THEORY OF THE RATE OF SUBLIMATION.

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Received July 13th, 1933. Published October 28th, 1933.

Introduction.

Langmuir⁽¹⁾ gave the following theoretical interpretation of the rate of sublimation. The rate of sublimation is expressed as the difference of the rate of evaporation and that of condensation, that is,

$$\begin{aligned} \text{Rate of sublimation} &= \text{Rate of evaporation} \\ &\quad - \text{Rate of condensation} \dots\dots\dots (1), \end{aligned}$$

and the rate of evaporation and that of condensation were expressed by the following equations respectively.

$$\text{Rate of evaporation}^{(2)} = A\sqrt{T} e^{-\frac{\lambda}{RT}} \text{ gr./cm}^2\text{./sec.} \dots\dots\dots (2),$$

$$\text{Rate of condensation} = \alpha p \sqrt{\frac{M}{2\pi RT}} \text{ gr./cm}^2\text{./sec.} \dots\dots\dots (3),$$

(1) *J. Am. Chem. Soc.*, **38** (1916), 2221.

(2) *Ibid.*, **35** (1913), 122; **38** (1916), 2254.

where A is a constant, T the absolute temperature, γ a constant, R gas constant, α a constant, M the molecular weight, p the partial pressure of the sublimed substance in the gas phase.

In the majority of cases every incident atom or molecule condenses,⁽³⁾ so that the value α is 1.

From equations (1), (2) and (3) we have

$$\frac{1}{S} \frac{dm}{dt} = A \sqrt{T} e^{-\frac{\lambda}{RT}} - \alpha p \sqrt{\frac{M}{2\pi RT}} \dots\dots\dots (4),$$

where S is the area of the boundary surface, m the mass of the solid sublimed. In the state of equilibrium, $dm/dt = 0$. Then from equation (4) we have

$$A \sqrt{T} e^{-\frac{\lambda}{RT}} = \alpha p_{\infty} \sqrt{\frac{M}{2\pi RT}} \dots\dots\dots (5),$$

where p_{∞} is the vapour pressure of solid. From equations (4) and (5) we have

$$\frac{1}{S} \frac{dm}{dt} = \alpha \sqrt{\frac{M}{2\pi RT}} (p_{\infty} - p) \dots\dots\dots (6).$$

From equation (5) the vapour pressure of solid is given by

$$p_{\infty} = \frac{A}{\alpha} \sqrt{\frac{2\pi R}{M}} T e^{-\frac{\lambda}{RT}} \dots\dots\dots (7),$$

or

$$\log p_{\infty} = -\frac{\lambda}{2.303RT} + \log T + \log \frac{A}{\alpha} \sqrt{\frac{2\pi R}{M}} \dots\dots\dots (8).$$

Recently the following equation for the vapour pressure of a solid was derived by Langmuir⁽⁴⁾ by applying Dushman's theory⁽⁵⁾ for the rate of evaporation.

$$p_{\infty} = B \beta b p^{\frac{2}{3}} M^{-\frac{1}{6}} T^{\frac{1}{2}} e^{-\frac{b}{T}} \dots\dots\dots (9),$$

(3) Langmuir, *J. Am. Chem. Soc.*, **54** (1932), 2801; Egerton, *Phil. Mag.*, **33** (1917), 33.

(4) *J. Am. Chem. Soc.*, **54** (1932), 2802.

(5) *Ibid.*, **43** (1921), 397.

where ρ is the density of the solid, M the molecular weight, T the absolute temperature, B , β and b constants.

A New Theory.

Theories for the rate of solution of gas into liquid⁽⁶⁾ and for that of solid into liquid⁽⁷⁾ were proposed by the present writer, and the following is the application of an analogous theory to the interpretation of the mechanism of the rate of sublimation. The rate of sublimation dn/dt moles/sec. is generally expressed by

$$\frac{N}{S} \frac{dn}{dt} = N_1 - N_2 \quad \dots\dots\dots (10),$$

where N is Avogadro's constant, S the area of the boundary surface, N_1 the number of molecules of the substance which escape from the solid phase per unit area per unit time, N_2 the number of molecules which condense per unit area per unit time.

The number of molecules, whose energies of vibration at right angles to the interface lie between ϵ and $\epsilon + d\epsilon$ among N' molecules of the solid, is given by Maxwell's distribution law,

$$dN = \frac{N'}{kT} e^{-\frac{\epsilon}{kT}} d\epsilon \quad \dots\dots\dots (11),$$

where k is Boltzmann's constant. Then the number of molecules, per unit area of the solid surface, whose energies of vibration at right angles to the interface are greater than a threshold value ϵ_0 , is given by

$$N_x = \frac{N_0}{kT} \int_{\epsilon_0}^{\infty} e^{-\frac{\epsilon}{kT}} d\epsilon = N_0 e^{-\frac{\epsilon_0}{kT}} = N_0 e^{-\frac{N\epsilon_0}{RT}} \quad \dots\dots\dots (12),$$

where N_0 is the number of molecules which make up unit area of the solid surface.

Now an assumption is proposed. Among the molecules of which the surface of the solid is composed, only those, whose components of energy of vibration at right angles to the interface are greater than a threshold

(6) Miyamoto, this Bulletin, **7** (1932), 8, 388; *Chem. News*, **144** (1932), 273.

(7) Miyamoto, this Bulletin, **8** (1933), 316.

value ϵ_0 , are able to enter into the gas phase. Then the value N_1 is proportional to N_x and is given by

$$N_1 = a N_0 e^{-\frac{N\epsilon_0}{RT}} \dots\dots\dots (13),$$

where a is a constant. The values ϵ_0 and N_0 in equation (13) depend upon the specific nature of the solid and the rate of evaporation increases or decreases as the value ϵ_0 decreases or increases.

The rate of condensation is next considered, and the following assumption is proposed. Among the molecules of gas, which collide with the solid surface, only those, whose components of velocities at right angles to the interface are greater than a threshold value u_0 , are able to condense on the solid surface. Then the following equation is obtained readily according to Maxwell's distribution law, as mentioned in the previous paper⁽⁷⁾.

$$N_2 = \frac{Np}{\sqrt{2\pi MRT}} e^{-\frac{Mu_0^2}{2RT}} \dots\dots\dots (14).$$

From equation (3) and (14) it can be easily shown that

$$\alpha = e^{-\frac{Mu_0^2}{2RT}} \dots\dots\dots (15).$$

As above mentioned the value α is 1 in the majority of cases and it follows from equation (15) that the value u_0 is in such cases zero. From equations (10), (13) and (14) we have

$$\frac{dn}{dt} = S \left(a \frac{N_0}{N} e^{-\frac{N\epsilon_0}{RT}} - \frac{p}{\sqrt{2\pi MRT}} e^{-\frac{Mu_0^2}{2RT}} \right) \dots\dots\dots (16).$$

Equation (16) represents the rate of sublimation according to the present theory. In the state of equilibrium, $dn/dt = 0$, and we have from equation (16).

$$\frac{aN_0}{N} e^{-\frac{N\epsilon_0}{RT}} = \frac{p_\infty}{\sqrt{2\pi MRT}} e^{-\frac{Mu_0^2}{2RT}} \dots\dots\dots (17),$$

where p_∞ is the vapour pressure of the solid. From equations (16) and (17) we have

$$\frac{dn}{dt} = KS(p_\infty - p) \dots\dots\dots (18),$$

where

$$K = \frac{1}{\sqrt{2\pi MRT}} e^{-\frac{Mu_0^2}{2RT}} \dots\dots\dots (19).$$

Equation (18) is analogous to equation (6). It follows from equation (16) that the rate of sublimation depends upon the curvature of the solid surface, as the value ϵ_0 will be smaller when the solid surface is convex.

The Initial Rate of Sublimation.

The initial rate of sublimation or the rate of sublimation in a vacuum is expressed by putting $p = 0$ in equation (16).

$$\left(\frac{dn}{dt}\right)_{\text{initial}} = Sa \frac{N_0}{N} e^{-\frac{N\epsilon_0}{RT}} \dots\dots\dots (20),$$

or

$$\log \left(\frac{dn}{dt}\right)_{\text{initial}} = -\frac{N\epsilon_0}{2.303RT} + \log \frac{SaN_0}{N} \dots\dots\dots (20)'.$$

From equations (17) and (20) we have

$$\left(\frac{dn}{dt}\right)_{\text{initial}} = \frac{p_\infty S}{\sqrt{2\pi MRT}} e^{-\frac{Mu_0^2}{2RT}} \dots\dots\dots (21).$$

The Vapour Pressure of Solid.

From equation (17) the vapour pressure of solid is expressed by

$$p_\infty = \frac{aN_0}{N} (2\pi MR)^{\frac{1}{2}} T^{\frac{1}{2}} e^{-\frac{1}{RT} \left(N\epsilon_0 - \frac{Mu_0^2}{2} \right)} \dots\dots\dots (22),$$

or

$$\log p_\infty = -\frac{Q}{2.303RT} + \frac{1}{2} \log T + C \dots\dots\dots (22)',$$

where

$$Q = N\epsilon_0 - \frac{Mu_0^2}{2},$$

$$C = \log \frac{aN_0\sqrt{2\pi MR}}{N}.$$

From equation (22) it follows that the vapour pressure of a convex surface is greater than that of plane surface, as the value ϵ_0 will be smaller in the former case according to the present theory.

Now the value N_0 , the number of molecules which make up unit area of the solid surface, is normally given by

$$N_0 = \gamma \left(\frac{N}{v_m} \right)^{\frac{2}{3}} = \gamma \left(\frac{\rho N}{M} \right)^{\frac{2}{3}} \dots\dots\dots (23),$$

where N is Avogadro's constant, v_m the molar volume, ρ the density of the solid, M the molecular weight, γ a constant, the value of which depends upon the arrangement of the molecules of solid. From equations (22) and (23) we have

$$p_\infty = a\gamma N^{-\frac{1}{3}} (2\pi R)^{\frac{1}{2}} \rho^{\frac{2}{3}} M^{-\frac{1}{6}} T^{\frac{1}{2}} e^{-\frac{1}{RT} \left(N\epsilon_0 - \frac{Mu_0^2}{2} \right)} \dots\dots (24).$$

Thus an equation analogous to equation (9) is obtained according to the present theory.

The writer's intention is to apply this new theory to the interpretation of the mechanism of adsorption on a subsequent occasion.

Summary.

A theory of the rate of sublimation was proposed, which is based upon the assumptions, that among the molecules, which make up the solid surface, only those, whose energies of vibration at right angles to the interface are greater than a threshold value ϵ_0 can escape from the solid phase, and that among the molecules in the gas phase, only those, which collide with the interface with velocities, whose components at right angles to the interface are greater than a threshold value u_0 , can condense on the solid surface.

On the basis of this theory the following equations have been derived for the rate of sublimation and for the vapour pressure of solid.

$$\frac{dn}{dt} = S \left(\frac{aN_0}{N} e^{-\frac{N\epsilon_0}{RT}} - \frac{p}{\sqrt{2\pi MRT}} e^{-\frac{Mu_0^2}{2RT}} \right),$$

$$p_\infty = a \frac{N_0}{N} (2\pi MR)^{\frac{1}{2}} T^{\frac{1}{2}} e^{-\frac{1}{RT} \left(N\epsilon_0 - \frac{Mu_0^2}{2} \right)},$$

or

$$p_\infty = a\gamma N^{-\frac{1}{3}} (2\pi R)^{\frac{1}{2}} \rho^{\frac{2}{3}} M^{-\frac{1}{6}} T^{\frac{1}{2}} e^{-\frac{1}{RT} \left(N\epsilon_0 - \frac{Mu_0^2}{2} \right)}.$$

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STUDIES OF THE RAMAN EFFECT OF ORGANIC SUBSTANCES.
PART I. RAMAN EFFECT OF A SERIES OF ESTERS
OF BENZOIC ACID AND PHENYL
ESTERS OF FATTY ACIDS.

By Kichimatsu MATSUNO and Kwan HAN.

Introduction.

Since the Raman effect was discovered in 1928, the investigations of this line have made a rapid progress especially in the field of organic chemistry. Studies of the effect of the length of an organic molecule and of a splitting of the hydrocarbon chain upon the vibration of an atom or atom group attached at the end of the molecule have been a matter of interest. Harkins and his coworkers⁽¹⁾, Dadiou and Kohlrausch⁽²⁾ have been published several papers on this subject. Alkyl habides⁽³⁾, fatty acids⁽⁴⁾, some of esters of the fatty acids⁽⁵⁾, fatty alcohols⁽⁶⁾ have been already studied by the investigators above mentioned and others. The present authors carried out the experiment on esters of the aromatic carboxylic acid and fatty acids in view of the standpoint to ascertain the free rotation of the alkyl groups and to confirm the inner and outer vibration of the valency frequencies between the alkyl groups and other atom groups. The materials used in the present research have been synthesized carefully and purified by repeated distillations. Some of the physical constants of the samples used have also been studied.

Experimental.

The investigation was carried out by an arrangement similar to that described by Dadiou-Kohlrausch.⁽⁷⁾ A quartz mercury vapour lamp working at 100 volts, 2.7–3.2 amperes, D.C., was used as the source of illumination.

The spectrum of the scattered light was taken by means of an Adam Hilger glass prism spectrograph. The photographic plates APEM, 5000 H. and D. were used. The dispersion obtained was 15 Å. per m.m. at 4050 Å. and 40 Å. per m.m. at 5040 Å, which was the range over which the experiments were conducted. The exposure was required from four to fourteen hours for different substances. The spectra were taken several

In Fig. 1, A is a flat glass plate perpendicular to the beam of light. The part, B, of the tube is made of the brown glass to prevent the light scattered from the outside. A side tube, D, is provided for pouring the sample in and inserting the thermometer for measuring the temperature of the sample. For small quantity of sample, the tube of about 10 c.c. in capacity, made in our laboratory, was used.

The two electrodes of the quartz mercury vapour lamp are cooled by the water jackets fixed to the two sides to protect them from superheating (Fig. 2).

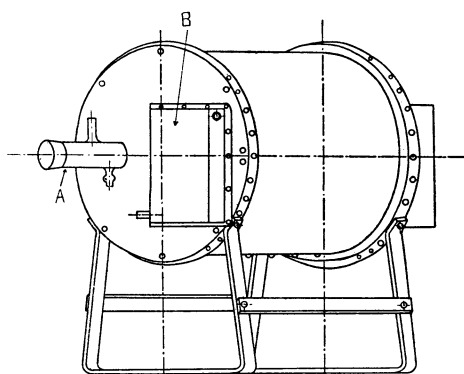


FIG.3 EXTERNAL APPEARANCE

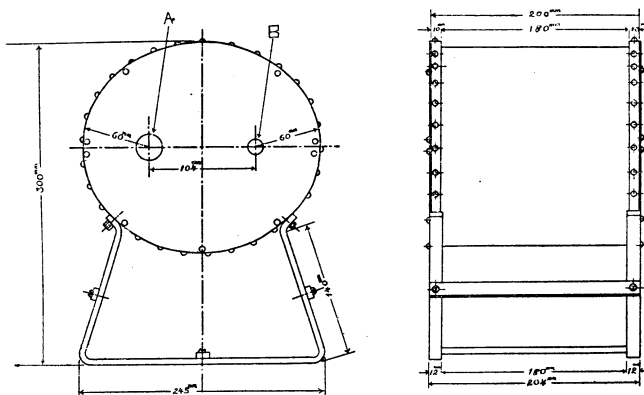


FIG.4 SECTION OF THE APPARATUS

The tube of the light-source and the Raman tube are so enclosed in an elliptical cylinder that the axes of the tube and that of the body of the light fall at the two foci. The cylinder is made of metal which has been well polished and plated with nickel. These tubes and the wall of cylinder are in parallel to each other (Fig. 3).

The quartz mercury vapour lamp and the set of the Raman tube, constructed by Prof. Asada of the Osaka Imp. Univ., were obtained from the Central Trading and M.F.G. Co. Ltd., Osaka.

Preparation and Purification of the Substances. All the alkyl esters⁽⁹⁾ of benzoic acid were made from the dehydrated alcohols and the acid by the action of conc. sulphuric acid or dry hydrochloric acid gas.

Cyclohexyl benzoate⁽⁹⁾ was prepared by warming the mixture of cyclohexanol and benzoyl chloride in presence of pyridine.

o-Kresyl benzoate⁽¹⁰⁾ was prepared from *o*-kresol and benzoyl chloride. Acetate of phenol⁽¹¹⁾ and *o*-kresol were synthesized from acetic acid anhydride and phenol and *o*-kresol respectively, in presence of anhydrous sodium acetate.

Penol ester⁽¹²⁾ of butyric acid was prepared from butyric acid chloride and phenol.

All the samples used were purified by repeated vacuum distillation (10-6 mm. Hg.), after dehydrated over calcium chloride. For testing the purities of the samples, the physical constants, namely, density (D^{15}) at 15°C., refractive index (n^{15}) at 15°C. and boiling point were measured.

The Experiment. For the sake of simplicity, the number of the substance observed (the 1st column), the name of the substances (the 2nd), the number of the table (Tb. No.) (the 3rd), the numbers of the Raman lines (n) (the 4th), the number of the plate (pl. No.) (the 5th), and the conditions under which the spectra were taken, viz., breadth of the slit (St.) (the 6th), electric current (C) working the mercury vapour lamp (the 7th), temperature (T) of the sample during the experiment (the 8th) and the time of exposure (t) (the 9th), have been tabulated in the following:

Table A.

No.	Substance	Tb. No.	n	Pl. No.	St 10^{-2}mm.	C (amp)	T° (C)	t (hours)
1	Methyl benzoate	I	40	{ 1	7	2.7	24	7
				{ 10	6	,,	23	9
				{ 14	6	,,	22	13
2	Ethyl benzoate	II	37	{ 2	6	2.7	23	8
				{ 11	6	,,	22	4
				{ 15	8	2.8	22	13
3	<i>n</i> -Propyl benzoate	III	39	{ 3	7	2.8	24	8
				{ 4	6	,,	23	12
				{ 16	5	3.0	21	13
4	<i>n</i> -Butyl benzoate	IV	42	{ 8	7	2.8	23	8
				{ 17	6	,,	21	13
5	<i>i</i> -Propyl benzoate	V	39	{ 5	7	2.7	23	9
				{ 6	7	3.2	24	10
				{ 12	6	2.8	21	10
				{ 13	5	2.8	21	14
6	<i>i</i> -Butyl benzoate	VI	44	{ 7	7	2.8	23	12
				{ 18	6	2.8	21	14
7	<i>i</i> -Amyl benzoate	VII	40	{ 9	6	3.2	23	14
				{ 19	7	2.8	21	13
8	Cyclohexyl benzoate	VIII	29	{ 20	8	2.8	20	8
				{ 21	7	3.2	20	13
				{ 22	6	2.8	20	13
9	<i>o</i> -Kresyl benzoate	IX	37	{ 76	7	3.2	19	8
				{ 77	6	3.2	19	12
10	<i>n</i> -Octyl	X	30	{ 23	6	3.2	20	10
				{ 26	6	3.2	20	14
11	Benzoyl chloride	XI	26	{ 24	6	3.2	20	4
				{ 25	6	3.2	20	3
12	Acetyl phenol	XII	29	82	6	3.2	20	9
13	Phenyl butyrate	XIII	29	91	6	3.2	20	12
14	Acetyl <i>o</i> -kresol	XIV	33	87	8	3.2	20	10

The Notations of the unmodified mercury lines are shown below:—

Table B.

Notation	Wave length (in Å)	Wave number (in cm ⁻¹)
<i>q</i>	3650	27388
<i>p</i>	3655	27353
<i>o</i>	3663	27293
<i>k</i>	4047	24705
<i>i</i>	4078	24518
<i>g</i>	4339	23039
<i>f</i>	4348	22995
<i>e</i>	4358	22938

The physical constants of the substances studied are tabulated:

Table C.

No.	Substance	b.p. (in reduced pressure mm. (Hg))	b.p. (at 1 atm.)	<i>D</i> ¹⁵	<i>n</i> ¹⁵
1	Methyl benzoate	77° / 8	199°	1.0929	1.5177
2	Ethyl benzoate	82 / 10	212	1.0510	1.5068
3	<i>n</i> -Propyl benzoate	105 / 10	231	1.0248	1.5013
4	<i>n</i> -Butyl benzoate	108 / 10	249	1.0101	1.4989
5	<i>i</i> -Propyl benzoate	92 / 10	219	1.0150	1.4962
6	<i>i</i> -Butyl benzoate	109 / 8	242	1.0026	1.4956
7	<i>i</i> -Amyl benzoate	122 / 8		0.9923	1.4950
8	Cyclo-hexyl benzoate	144 / 8		1.0567	1.5223
9	<i>o</i> -Kresyl benzoate	153 / 10		1.1170	1.5719
10	<i>n</i> -Octyl benzoate	164 / 7		0.9658	1.4913
11	Benzoyl chloride	—	197	1.2187	1.5579
12	Phenyl acetate	83 / 10		1.0831	1.5047
13	Phenyl butyrate	85 / 8		1.0382	—
14	<i>o</i> -Kresyl acetate	89 / 10		1.0533	1.5003

Ten kinds of esters of benzoic acid, benzoyl chloride, phenyl acetate, butyrate and *o*-kresyl acetate have been studied. Among them, methyl, ethyl benzoate and benzoyl chloride have been studied by Dadieu-Kohl-rauchs⁽¹³⁾. Their results are cited for comparison.

Table D.

Methyl benzoate		Ethyl benzoate		Benzoyl chloride	
D. K.	Ours	D. K.	Ours	D. K.	Ours
212(3)	211(3)	184(4)	191(4)	161(3 <i>b</i>)	158(4 <i>d</i>)
353(3)	351(3)	334(4)	333(3)	314(3)	314(3)
613(3)	612(3)	614(4)	615(5)	412(1)	414(2 <i>d</i>)
670(1 <i>d</i>)	670(1 <i>d</i>)	670(1)	668(1 <i>d</i>)	505(3)	505(4)
812(3)	814(4)	775(1)	780(¹ / ₂)	615(3)	615(4)
1000(7)	999(8)	1000(10)	1000(8)	670(3)	669(5)
1023(1)	1023(2)	1029(2)	1026(2)	771(¹ / ₂)	769(¹ / ₂ <i>b</i> , <i>d</i>)
1082(1)	1078(2)	1106(3)	1107(2)	1000(6)	998(4)
1110(2)	1114(2)	(1162)(2)	1164(4 <i>d</i>)	1028(2)	1027(4)
1160(1)	1161(2 <i>b</i>)	1276(5)	1268(8)	1168(3 <i>b</i>)	1166(6)
1278(4)	1268(4)	1310(1)	1305(¹ / ₂)	1206(3 <i>b</i>)	1200(8)
(1302)(1)	(1310)(¹ / ₂)	1368(1 <i>b</i>)	(1366)(0)		
		1394(¹ / ₂)	(1395)(¹ / ₂ <i>d</i>)		
1452(1 <i>b</i>)	1454(2 <i>d</i>)	1454(2 <i>b</i>)	1451(2 <i>d</i>)		
1602(10)	1601(10)	1602(10)	1600(10)	1592(6)	1591(10)
1723(8)	1720(8)	1720(9)	1719(8)	1774(4)	1776(6 <i>b</i> , <i>d</i>)
		2929(5 <i>b</i>)	2930(2)		
2950(4)	2948(3 <i>d</i>)	2981(3)	2980(2 <i>d</i>)		
3070(5)	3069(8)	3072(6 <i>b</i>)	3072(8)	3067(4 <i>b</i>)	3067(7 <i>b</i>)

Table I.

Methyl benzoate, C₆H₅.CO.O.CH₃.

No.	ν in cm. ⁻¹	<i>I</i>	$\nu_0 - \Delta\nu$	No.	ν in cm. ⁻¹	<i>I</i>	$\nu_0 - \Delta\nu$
1	24437	0(<i>d</i>)	<i>q</i> -2951	11	23544	2(<i>b</i>)	<i>k</i> -1161
2	24405	0(<i>d</i>)	<i>p</i> -2948	12	23517	0(<i>d</i>)	<i>i</i> - 999
3	24319	¹ / ₂ (<i>d</i>)	<i>q</i> -3069	13	23438	5	<i>k</i> -1267
4	24285	2	<i>p</i> -3068	14	23395	¹ / ₂ (<i>d</i>)	(<i>k</i> -1310)
5	24220	2(<i>b</i> , <i>d</i>)	<i>o</i> -3073	15	23254	¹ / ₂ (<i>d</i>)	<i>k</i> -1451
6	24093	3	<i>k</i> - 612	16	23148	1	<i>e</i> +210 ?
7	23891	3	<i>k</i> - 814	17	23106	6	<i>k</i> -1599
8	23705	6	<i>k</i> -1000	18	22797	1(<i>d</i>)	<i>i</i> -1719
9	23680	2	<i>k</i> -1025	19	22727	3	<i>e</i> - 211
10	23599	2(<i>d</i>)	<i>k</i> -1106	20	22587	3	<i>e</i> - 612

Table I.—(Concluded)

No.	ν in cm.^{-1}	I	$\nu_0 - \Delta\nu$	No.	ν in cm.^{-1}	I	$\nu_0 - \Delta\nu$
21	22326	3	<i>e</i> - 612	31	21669	8(<i>d</i>)	<i>e</i> -1269
22	22268	1	<i>e</i> - 670	32	21638	8(<i>d</i>)	<i>k</i> -3067
23	22124	4	<i>e</i> - 814	33	21570	0	<i>i</i> -2947
24	21971	$\frac{1}{2}$	<i>f</i> -1024	34	21489	2(<i>b</i>)	<i>e</i> -1449
25	21940	8(<i>s</i>)	<i>e</i> - 998	35	21446	2	<i>i</i> -3070
26	21917	2(<i>s</i>)	<i>e</i> -1021	36	21393	$\frac{1}{2}$	<i>f</i> -1602
27	21860	2	<i>e</i> -1078	37	21335	10(<i>s</i>)	<i>e</i> -1602
28	21825	2	<i>e</i> -1113	38	21218	8	<i>e</i> -1720
29	21777	2	<i>e</i> -1161	39	19991	3	<i>e</i> -2947
30	21757	3(<i>d</i>)	<i>k</i> -2948	40	19868	5	<i>e</i> -3070

$\Delta\nu$: 211 (3); 351 (3); 612 (3); 670 (1); 814 (4); 999 (8); 1023 (2); 1078 (2); 1108 (2); 1161 (2*b*); 1268 (8); 1310 ($\frac{1}{2}$ *d*); 1450 (2*d*); 1601 (10); 1720 (8); 2948 (3*d*); 3069 (8).

Table II.

Ethyl benzoate $\text{C}_6\text{H}_5\cdot\text{CO}\cdot\text{O}\cdot\text{C}_2\text{H}_5$.

No.	ν in cm.^{-1}	I	$\nu_0 - \Delta\nu$	No.	ν in cm.^{-1}	I	$\nu_0 - \Delta\nu$
1	24422	0	<i>p</i> -2931	16	22751	4(<i>b</i>)	<i>k</i> - 187
2	24377	0	<i>p</i> -2976	17	22605	3	<i>e</i> - 333
3	24220	$\frac{1}{2}$	<i>o</i> -3073	18	22323	5	<i>e</i> - 615(<i>f</i> - 672)
4	24090	2	<i>k</i> - 615	19	22270	1(<i>d</i>)	<i>e</i> - 668
5	23861	2	<i>k</i> - 844	20	22158	$\frac{1}{2}$ (<i>d</i>)	<i>e</i> - 780
6	23705	4	<i>k</i> -1000	21	22091	5	<i>e</i> - 847
7	23680	$\frac{1}{2}$	<i>k</i> -1025(<i>i</i> -836)	22	21999	8	<i>e</i> - 999
8	23599	1(<i>d</i>)	<i>k</i> -1106	23	21911	2	<i>e</i> -1027
9	23543	2(<i>d</i>)	<i>k</i> -1162	24	21830	3(<i>d</i>)	<i>e</i> -1108
10	23515	$\frac{1}{2}$	<i>i</i> -1001	25	21774	4(<i>d</i>)	<i>e</i> -1164(<i>k</i> -2931)
11	23438	3	<i>k</i> -1267	26	21726	2(<i>d</i>)	<i>k</i> -2979(<i>f</i> -1269)
12	23399	$\frac{1}{2}$	<i>k</i> -1305	27	21675	8	<i>e</i> -1268
13	23339	$\frac{1}{2}$	<i>k</i> -1366	28	21635	8	<i>k</i> -3070(<i>e</i> -1303)
14	23252	$\frac{1}{2}$ (<i>d</i>)	<i>k</i> -1453(<i>i</i> -1264)	29	21585	1(<i>d</i>)	<i>i</i> -2931(<i>e</i> -1353)
15	23106	5	<i>k</i> -1599	30	21538	$\frac{1}{2}$ (<i>d</i>)	<i>e</i> -1395(<i>i</i> -2978)

Table II.—(Concluded)

No.	ν in cm.^{-1}	I	$\nu_0 - \Delta\nu$	No.	ν in cm.^{-1}	I	$\nu_0 - \Delta\nu$
31	21489	2(<i>d</i>)	<i>e</i> -1449	36	19957	1	<i>e</i> -2981
32	21446	1	<i>i</i> -3070	37	19866	5	<i>e</i> -3072
33	21338	10	<i>e</i> -1600				
34	21219	8	<i>e</i> -1719				
35	20010	2	<i>e</i> -2928				

$\Delta\nu$: 187 (4); 333 (3); 615 (5); 668 (1*d*); 780 ($\frac{1}{2}$ *d*); 846 (5); 1000 (8); 1026 (2); 1107 (3*d*); 1163 (4*d*); 1268 (8); 1305 ($\frac{1}{2}$); (1366) ($\frac{1}{2}$); (1395) ($\frac{1}{2}$ *d*); 1451 (2*d*); 1600 (10); 1719 (8); 2930 (2); 2980 (2*d*); 3071 (8).

Table III.

n-Propyl benzoate $\text{C}_6\text{H}_5\cdot\text{CO}\cdot\text{O}\cdot\text{C}_3\text{H}_7$.

No.	ν in cm.^{-1}	I	$\nu_0 - \Delta\nu$	No.	ν in cm.^{-1}	I	$\nu_0 - \Delta\nu$
1	24423	$\frac{1}{2}$ (<i>b</i>)	<i>p</i> -2930	21	22127	3(<i>d</i>)	<i>e</i> - 811
2	24318	$\frac{1}{2}$ (<i>d</i>)	<i>q</i> -3070(<i>o</i> -2975)	22	22093	0	<i>e</i> - 845
3	24283	$\frac{1}{2}$ (<i>b</i>)	<i>p</i> -3070	23	22028	3(<i>d</i>)	<i>e</i> - 910
4	24221	1(<i>b</i>)	<i>o</i> -3072	24	21939	8	<i>e</i> - 999
5	24086	3	<i>k</i> - 619	25	21917	2	<i>e</i> -1021
6	24036	$\frac{1}{2}$ (<i>d</i>)	<i>k</i> - 669	26	21823	4(<i>d</i>)	<i>e</i> -1115(<i>k</i> -2882)
7	23895	2(<i>d</i>)	<i>k</i> - 810(<i>i</i> - 619)	27	21772	5(<i>d</i>)	<i>e</i> -1166
8	23707	6	<i>k</i> - 998(<i>i</i> - 809)	28	21726	3	<i>k</i> -2979(<i>f</i> -1269)
9	23684	2(<i>d</i>)	<i>k</i> -1021	29	21669	8	<i>e</i> -1269
10	23599	2(<i>b</i> , <i>d</i>)	<i>k</i> -1106(<i>i</i> - 917)	30	21637	8	<i>k</i> -3068(<i>e</i> -1301)
11	23542	2(<i>bb</i>)	<i>k</i> -1163	31	21535	2	<i>i</i> -2981
12	23435	4	<i>k</i> -1270	32	21487	3(<i>b</i>)	<i>e</i> -1451
13	23402	1(<i>d</i>)	<i>k</i> -1303(<i>i</i> -1114)	33	21441	2(<i>d</i>)	<i>i</i> -3075
14	23251	3(<i>d</i>)	<i>k</i> -1454(<i>i</i> -1265)	34	21339	10	<i>e</i> -1599
15	23103	5	<i>k</i> -1602	35	21217	8	<i>e</i> -1721
16	22749	0(<i>d</i>)	<i>e</i> - 189	36	20058	3(<i>d</i>)	<i>e</i> -2880(Hg)
17	22631	1(<i>d</i>)	<i>e</i> - 307	37	20024	3(<i>b</i>)	<i>e</i> -2914(<i>f</i> -2972)
18	22600	0(<i>d</i>)	<i>e</i> - 338	38	19959	3(<i>b</i>)	<i>e</i> -2972
19	22321	4	<i>e</i> - 617	39	19869	5	<i>e</i> -3069
20	22271	1(<i>d</i>)	<i>e</i> - 667				

$\Delta\nu$: 189 (0*d*)?; 307 (1*d*); 618 (4); 668 (1*d*); 811 (3*b*); 845 (0); 910 (1*d*); 999 (8); 1021 (2); 1110 (4*d*); 1165 (5*d*); 1270 (8); 1303 (1*d*); 1452 (3*b*); 1601 (10); 1721 (8); (2881) (3*b*); (2914) (2*b*); 2979 (3*d*); 3070 (8).

Table IV.

n-Butyl benzoate C₆H₅.CO.O.(CH₂)₃.CH₃.

No.	ν in cm. ⁻¹	<i>I</i>	$\nu_0 - \Delta\nu$	No.	ν in cm. ⁻¹	<i>I</i>	$\nu_0 - \Delta\nu$
1	24318	1/2	<i>q</i> -3070	26	21939	10	<i>e</i> - 999
2	24284	1/2 (<i>d</i>)	<i>p</i> -3069	27	21915	3	<i>e</i> -1023
3	24223	1/2	<i>o</i> -3070	28	21857 ?	0(<i>d</i>)	<i>e</i> -1081
4	24086	2(<i>b</i>)	<i>k</i> - 619	29	21817	5(<i>d</i>)	<i>e</i> -1121
5	24034	1/2(<i>b</i>)	<i>k</i> - 671	30	21779	6(<i>bb, dd</i>)	<i>e</i> -1159
6	23896	1/2	<i>k</i> - 809	31	21745	2(<i>d</i>)	<i>k</i> -2960
7	23861	1/2(<i>d</i>)	<i>k</i> - 844	32	21666	7	<i>e</i> -1272
8	23708	6	<i>k</i> - 997	33	21637	8(<i>b, d</i>)	<i>k</i> -3068(<i>e</i> -1301)
9	23679	2	<i>k</i> -1026	34	21487	5(<i>b</i>)	<i>e</i> -1451
10	23592	1	<i>k</i> -1113	35	21543	3	<i>e</i> -1395(<i>f</i> -1452)
11	23537	2(<i>bb</i>)	<i>k</i> -1168	36	21444	3(<i>d</i>)	<i>i</i> -3072
12	23436	4	<i>k</i> -1269	37	21340	10	<i>e</i> -1598
13	23399	2	<i>k</i> -1306(<i>i</i> -1117)	38	21216	8	<i>e</i> -1722
14	23314	1(<i>d</i>)	<i>k</i> -1391	39	20070	2(<i>d</i>)	<i>e</i> -2868
15	23244	3(<i>b, d</i>)	<i>k</i> -1461(<i>i</i> -1272)	40	20044	2(<i>b, d</i>)	<i>e</i> -2894(<i>f</i> -2951)
16	23105	8	<i>k</i> -1600	41	19980	2(<i>b, d</i>)	<i>e</i> -2958
17	22796	2(<i>b</i>)	<i>i</i> -1720	42	19868	5	<i>e</i> -3070
18	22736	2(<i>b, d</i>)	<i>e</i> - 202				
19	22640	2(<i>d</i>) ?	<i>e</i> - 298				
20	22600 ?	1/2(<i>b</i>)	<i>e</i> - 338				
21	22320	5	<i>e</i> - 618(<i>f</i> - 675)				
22	22268	3	<i>e</i> - 670				
23	22126	2(<i>d</i>)	<i>e</i> - 812				
24	22097	3(<i>b</i>)	<i>e</i> - 841				
25	21981	1	<i>e</i> - 957				

$\Delta\nu$: 202 (2*b, d*); 298 (2*d*); 338 (1/2*d*)?; 619 (5); 670 (3); 810 (2*d*); 843 (3*b*); 957 (1); 998 (10); 1025 (2); (1081) (0)?; 1117 (5); 1164 (6*d*); 1271 (7*d*); 1304 (1*d*); 1393 (3*b, d*); 1455 (5*d*); 1599 (10); 1722 (8); 2868 (2); 2894 (2*b, d*); 2959 (2*b, d*); 3070 (8).

Table V.
Iso-propyl benzoate $C_6H_5.CO.O.CH(CH_3)_2$.

No.	ν in $cm.^{-1}$	I	$\nu_0 - \Delta\nu$	No.	ν in $cm.^{-1}$	I	$\nu_0 - \Delta\nu$
1	24422	$\frac{1}{2}(b)$	$p-2931 \begin{pmatrix} k-283, \\ o-2871 \end{pmatrix}$	21	22270	3	$e-668$
2	24319	$\frac{1}{2}$	$q-3069 \begin{pmatrix} k-386, \\ o-2974 \end{pmatrix}$	22	22092	5	$e-846$
3	24287	1	$p-3068$	23	22021	$3(d)$	$e-917$
4	24222	$\frac{1}{2}$	$o-3071$	24	21940	10	$e-998$
5	24093	1	$k-612$	25	21916	2	$e-1022$
6	24039	0	$k-666$	26	21824	$3(b, d)$	$e-1114(f-1171)$
7	23861	2	$k-844$	27	21775	$5(b)$	$e-1163(k-2930)$
8	23792	$\frac{1}{2}(d)$	$k-913$	28	21726	4	$k-2979(f-1269)$
9	23707	6	$k-998$	29	21670	8	$e-1268$
10	23683	1	$k-1022$	30	21639	$8(d)$	$k-3066(f-1356)$
11	23598	$2(b)$	$k-1107(i-918)$	31	21588	2	$e-1350$
12	23544	$2(b)$	$k-1161$	32	21489	3	$e-1449$
13	23436	5	$k-1269$	33	21447	2	$i-3069$
14	23355	2	$k-1350(i-1161)$	34	21341	10	$e-1597$
15	23251	$3(b)$	$k-1454(i-1265)$	35	21222	8	$e-1716$
16	23106	6	$k-1599$	36	20066	1	$e-2872(f-2929)$
17	22755	5	$e-183$	37	20008	3	$e-2930(f-2987)$
18	22654	$3(b)$	$e-284$	38	19960	2	$e-2978$
19	22560	$\frac{1}{2}$	$e-378$	39	19871	4	$e-3067$
20	22325	4	$e-613(f-670)$				

$\Delta\nu$: 183 (4); 284 (3b); 378 ($\frac{1}{2}$); 613 (4); 668 (3); 846 (5); 916 (3d); 998 (8); 1022 (2); 1110 (3b); 1162 (5b); 1269 (8); 1350 (2); 1451 (4d); 1598 (10); 1716 (8); (2872) (1); 2930 (3); 2979 (2); 3068 (8).

Table VI.
Iso-butyl benzoate $C_6H_5.CO.O.CH_2.CH(CH_3)_2$.

No.	ν in $cm.^{-1}$	I	$\nu_0 - \Delta\nu$	No.	ν in $cm.^{-1}$	I	$\nu_0 - \Delta\nu$
1	24419 ?	0	$q-2969$	6	24032	$\frac{1}{2}(d)$	$k-673$
2	24319	$\frac{1}{2}$	$q-3069$	7	23902	$1(d)$	$k-803$
3	24282	$\frac{1}{2}$	$p-3071$	8	23840	$\frac{1}{2}(d)$	$k-865(i-676)$
4	24220	$\frac{1}{2}$	$o-3073$	9	23705	5	$k-1000$
5	24089	1	$k-616$	10	23679	2	$k-1026$

Table VI.—(Concluded)

No.	ν in cm. ⁻¹	<i>I</i>	$\nu_0 - \Delta\nu$	No.	ν in cm. ⁻¹	<i>I</i>	$\nu_0 - \Delta\nu$
11	23602	1(<i>d</i>)	k-1103	31	21820	5(<i>b</i>)	<i>e</i> -1116(<i>f</i> -1173, <i>k</i> -2883)
12	23537	2(<i>b</i> , <i>d</i>)	k-1168	32	21775	6(<i>b</i>)	<i>e</i> -1163
13	23436	4(<i>d</i>)	k-1269	33	21732	5(<i>b</i>)	k-2973(<i>f</i> -1263)
14	23392	¹ / ₂	k-1313	34	21670	6	<i>e</i> -1268
15	23313	¹ / ₂ (<i>d</i>)	k-1392	35	21639	8	k-3066(<i>f</i> -1356)
16	23247	3(<i>d</i>)	k-1458(<i>i</i> -1269)	36	21589	1	<i>e</i> -1349
17	23107	6	k-1598	37	21553	2(<i>b</i>)	<i>e</i> -1385(<i>i</i> -2963)
18	22797	3(<i>d</i>)	<i>i</i> -1719	38	21486	4(<i>b</i>)	<i>e</i> -1452
19	22770	2(<i>b</i> , <i>d</i>)	<i>e</i> -168	39	21445	2	<i>i</i> -3071
20	22676	2(<i>b</i>)	<i>e</i> -262	40	21333	10	<i>e</i> -1605
21	22560	1(<i>b</i>)	<i>e</i> -378	41	21220	8	<i>e</i> -1718
22	22324	4	<i>e</i> -614(<i>f</i> -671)	42	20065	3(<i>b</i>)	<i>e</i> -2373
23	22268	2(<i>d</i>)	<i>e</i> -670	43	19969	3(<i>b</i>)	<i>e</i> -2369
24	22161	¹ / ₂	<i>e</i> -777	44	19869	4	<i>e</i> -3069
25	22133	3(<i>b</i>)	<i>e</i> -805				
26	22075	3(<i>b</i>)	<i>e</i> -863				
27	22037	¹ / ₂	<i>e</i> -901				
28	21979	1(<i>d</i>)	<i>e</i> -959?				
29	21940	8	<i>e</i> -993				
30	21914	2	<i>e</i> -1024				

$\Delta\nu$: 168 (2*b*, *d*); 262 (2*b*); 378 (1*b*); 615 (4); 671 (2*d*); 804 (3*b*); 863 (3*b*); 901 (¹/₂); 959 (1*d*)?; 999 (8); 1024 (2); 1110 (1*d*); (1165) (5*b*); 1269 (8); (1313) (1*d*); 1349 (1); 1392 (¹/₂*d*); 1455 (4*b*); 1601 (10); 1718 (8); 2873 (3*b*); 2968 (3*b*); 3068 (8).

Table VII.

Iso-amyl benzoate C₆H₅.CO.O.CH₂.CH₂.CH(CH₃)₂.

No.	ν in cm. ⁻¹	<i>I</i>	$\nu_0 - \Delta\nu$	No.	ν in cm. ⁻¹	<i>I</i>	$\nu_0 - \Delta\nu$
1	24280	¹ / ₂	<i>p</i> -3073	6	23833	1(<i>b</i>)	k-862(<i>i</i> -678)
2	24222	¹ / ₂ (<i>d</i>)	<i>o</i> -3073	7	24707	5	k-938
3	24087	2	k-618	8	23677	1	k-1028(<i>i</i> -839)
4	24029	0	k-676	9	23600	1(<i>d</i>)	k-1105(<i>i</i> -916)
5	23898	1(<i>b</i>)	k-807(<i>i</i> -618)	10	23537	2(<i>b</i> , <i>d</i>)	k-1168

Table VII.—(Concluded)

No.	ν in cm.^{-1}	I	$\nu_0 - \Delta\nu$	No.	ν in cm.^{-1}	I	$\nu_0 - \Delta\nu$
11	23435	4	k -1270	26	21938	10	e -1000
12	23399	1	k -1306(i -1117)	27	21915	2(s)	e -1023
13	23246	3(d)	k -1459(i -1270)	28	21835	4(b)	e -1103(f -1160)
14	23106	5	k -1599	29	21776	5(d)	e -1162
15	22791	2(d)	i -1725	30	21734	4(d)	k -2971
16	22760 ?	0(d)	e - 178	31	21666	8	e -1272
17	22656 ?	0	e - 282	32	21632	8(d)	k -3073(e -1306)
18	22582 ?	$1/2$	e - 356	33	21541	3(d)	f -1454(i -2975)
19	22318	4	e - 620(f - 672)	34	21479	5(d)	e -1459
20	22265	2(b)	e - 673	35	21445	1(d)	i -3071
21	22157	2(b)	e - 781(f - 838)	36	21336	10	e -1602
22	22102	3(b, d)	e - 836	37	21216	8	e -1722
23	22078	3(b, d)	e - 860	38	20058	3	e -2880
24	22025	$1/2$ (d)	e - 913	39	19968	3(b)	e -2970
25	21983	1	e - 955	40	19863	4	e -3075

$\overline{\Delta\nu}$: 178 ($1/2$) ?; 282 (0) ?; 356 ($1/2$) ?; 619 (4); 673 (2 b); (781) (2 b) ?; 836 (3 b, d); 861 (3 b, d); 915 ($1/2$ d); (955) (1 d); 999 (8); 1026 (2); 1104 (4 b); 1165 (5 b); 1271 (8); 1306 (1); 1459 (5 d); 1601 (10); 1722 (8); (2880) (3); 2971 (8); 3073 (8).

Table VIII.

Cyclo-hexyl benzoate $\text{C}_6\text{H}_5\cdot\text{CO}\cdot\text{O}\cdot\text{C}_6\text{H}_{11}$.

No.	ν in cm.^{-1}	I	$\nu_0 - \Delta\nu$	No.	ν in cm.^{-1}	I	$\nu_0 - \Delta\nu$
1	24323	0	q -3065	11	22712	$1/2$ (d)	e - 226
2	23859	1	k - 846	12	22319	2(d)	e - 619
3	23701	5	k -1004	13*	22268	$1/2$	e - 670
4	23676	1	k -1029(i - 846)	14	22094	1	e - 844
5	23541	1(d)	k -1164	15	21937	7	e -1001
6	23436	3(b, d)	k -1269	16	21910	2	e -1028
7	23344	$1/2$	k -1361(i -1172)	17	21843	4	k -2862
8	23260	$1/2$ (b, d)	k -1445	18	21768	5(b, d)	e -1170(k -2937)
9	23096	5	k -1609	19	21670	5(b, d)	e -1268
10	22760	2(d)	e - 178	20	21629	5	k -3076

Table VIII.—(Concluded)

No.	ν in cm.^{-1}	I	$\nu_0 - \Delta\nu$	No.	ν in cm.^{-1}	I	$\nu_0 - \Delta\nu$
21	21585	1(<i>d</i>)	<i>e</i> -1353(<i>i</i> -2931)	26	20148	2	<i>e</i> -2790(<i>f</i> -2848)
22	21488	1	<i>e</i> -1450	27	20075	3(<i>d</i>)	<i>e</i> -2863
23	21442	$\frac{1}{2}$	<i>i</i> -3074	28	19997	3(<i>b, d</i>)	<i>e</i> -2941
24	21332	8	<i>e</i> -1606	29	19868	3	<i>e</i> -3070
25	21216	6	<i>e</i> -1722				

$\Delta\nu$: 178 (2*d*); 226 ($\frac{1}{2}$ *d*); 619 (2); 670 ($\frac{1}{2}$); 845 (1); 1003 (7); 1028 (2); 1168 (5*d*); 1269 (5*b, d*); 1357 (1*d*); 1450 (2); 1607 (8); 1722 (6); (2790) (2); 2863 (4); 2937 (5*b, d*); 3073 (5).

Table IX.

o-Kresyl benzoate $\text{C}_6\text{H}_5\cdot\text{CO}\cdot\text{O}\cdot\text{C}_6\text{H}_4\cdot\text{CH}_3$.

No.	ν in cm.^{-1}	I	$\nu_0 - \Delta\nu$	No.	ν in cm.^{-1}	I	$\nu_0 - \Delta\nu$
1	23710	1	<i>k</i> - 995	21	21942	8	<i>e</i> - 996
2	23546	$\frac{1}{2}$ (<i>d</i>)	<i>k</i> -1159	22	21920	2(<i>d</i>)	<i>e</i> -1018
3	23495	3	<i>k</i> -1210	23	21902	4	<i>e</i> -1036
4	23442	3(<i>d</i>)	<i>k</i> -1263	24	21830	$\frac{1}{2}$ (<i>d</i>)	<i>e</i> -1108
5	23257	$\frac{1}{2}$ (<i>d</i>)	<i>k</i> -1448	25	21788	6	<i>k</i> -2917
6	23107	5	<i>k</i> -1598	26	21772	5	<i>e</i> -1160
7	22776	4(<i>b, d</i>)	<i>e</i> - 162	27	21720	7	<i>e</i> -1218
8	22741	1(<i>d</i>)	<i>e</i> - 196	28	21679	6(<i>d</i>)	<i>e</i> -1259
9	22667	2(<i>d</i>)	<i>e</i> - 271	29	21641	6(<i>b, d</i>)	<i>k</i> -3064
10	22620	1(<i>b, d</i>)	<i>e</i> - 318	30	21561	2(<i>b, d</i>)	<i>e</i> -1377
11	22491	0(<i>b</i>)	<i>e</i> - 447 ?	31	21491	2	<i>k</i> -1447
12	22393	3(<i>d</i>)	<i>e</i> - 545	32	21452	4	<i>i</i> -3064
13	22352	2	<i>e</i> - 586	33	21391	$\frac{1}{2}$	<i>f</i> -1604
14	22322	5	<i>e</i> - 616	34	21343	10	<i>e</i> -1595
15	22265	3	<i>e</i> - 673	35	21208	8	<i>e</i> -1730
16	22235	4	<i>e</i> - 703	36	20022	2(<i>d</i>)	<i>e</i> -2916
17	22187	5(<i>b, d</i>)	<i>e</i> - 751	37	19874	6(<i>b</i>)	<i>e</i> -3064
18	22137	$\frac{1}{2}$	<i>f</i> - 858				
19	22095	4	<i>e</i> - 843				
20	22068	5	<i>e</i> - 870				

$\Delta\nu$: 162 (4*b, d*); 196 (1*d*); 271 (2*d*); 318 (1*b, d*); (447) (0*b*) ?; 545 (3*d*); 586 (2); 675 (3); 703 (4); 751 (5*b, d*); 843 (4); 870 (5); 996 (8); 1036 (4); 1108 ($\frac{1}{2}$ *d*); 1160 (5); 1214 (7); 1261 (6*d*); (1377) (2*b, d*); 1447 (2); 1596 (10); 1730 (8); 2917 (6); 3064 (6*b*).

Table X.

n-Octyl benzoate $C_6H_5.CO.O.C_8H_{17}$.

No.	ν in $cm.^{-1}$	<i>I</i>	$\nu_0 - \Delta\nu$	No.	ν in $cm.^{-1}$	<i>I</i>	$\nu_0 - \Delta\nu$
1	23704	4	<i>k</i> -1001	16	22090 ?	$\frac{1}{2}$	<i>e</i> - 848
2	23680	$\frac{1}{2}$	<i>k</i> -1025	17	21938	7	<i>e</i> -1000
3	23632 ?	0	<i>k</i> -1073 ?	18	21918	1	<i>e</i> -1020
4	23603	$\frac{1}{2}(d)$	<i>k</i> -1102	19	21864	5(<i>d</i>)	<i>k</i> -2841(<i>e</i> -1074)
5	23542	0(<i>d</i>)	<i>k</i> -1163	20	21774	5(<i>d</i>)	<i>k</i> -2931(<i>e</i> -1164)
6	23515	$\frac{1}{2}(d)$	<i>i</i> -1001	21	21671	5(<i>d</i>)	<i>e</i> -1267
7	23437	3	<i>k</i> -1268	22	21638	6(<i>d</i>)	<i>k</i> -3067(<i>e</i> -1300)
8	23402 ?	0(<i>d</i>)	<i>k</i> -1303	23	21555	$\frac{1}{2}(dd)$	<i>f</i> -1440
9	23255	$\frac{1}{2}(b)$	<i>k</i> -1450	24	21484	2(<i>b</i>)	<i>e</i> -1444
10	23104	5	<i>k</i> -1601	25	21391	$\frac{1}{2}$	<i>f</i> -1604
11	22753	1(<i>b, d</i>)	<i>e</i> - 185	26	21340	8	<i>e</i> -1598
12	22674	1(<i>b, d</i>)	<i>e</i> - 264	27	21221	6(<i>d</i>)	<i>e</i> -1717
13	22318	4	<i>e</i> - 620	28	20097	1	<i>e</i> -2841
14	22264	1	<i>e</i> - 674	29	20012	1	<i>e</i> -2926
15	22140 ?	0	<i>f</i> - 855 ?	30	19869	1	<i>e</i> -3069

$\Delta\nu$: 185 (1*b, d*); 264 (1*b, d*) ?; 620 (4); 674 (1); 848 ($\frac{1}{2}$) ?; 1000 (7); 1023 (1); (1074) (5*d*); 1102 ($\frac{1}{2}d$); 1164 (5*d*); 1268 (5*d*); 1303 (0*b*); 1450 (2*b*); 1600 (8); 1717 (6*d*); 2841 B(2928) (5*b*); 3068 (6*b*).

Table XI.

Benzoyl chloride $C_6H_5.CO.Cl$.

No.	ν in $cm.^{-1}$	<i>I</i>	$\nu_0 - \Delta\nu$	No.	ν in $cm.^{-1}$	<i>I</i>	$\nu_0 - \Delta\nu$
1	23937 ?	0	<i>k</i> - 768	16	21939	4	<i>e</i> - 999
2	23708	4	<i>k</i> - 997	17	21910	4	<i>e</i> -1028
3	23678	1	<i>k</i> -1027	18	21773	6	<i>e</i> -1165
4	23539	3	<i>k</i> -1166	19	21740	6	<i>e</i> -1198
5	23503	3	<i>k</i> -1202	20	21639	7(<i>b</i>)	<i>k</i> -3066
6	23113	8	<i>k</i> -1592	21	21447	1	<i>i</i> -3069
7	22780	4(<i>d</i>)	<i>e</i> - 158	22	21394	$\frac{1}{2}$	<i>f</i> -1601
8	22688	$\frac{1}{2}(d)$	<i>f</i> - 307	23	21349	10	<i>e</i> -1589
9	22624	4	<i>e</i> - 314	24	21211	4(<i>b, d</i>)	<i>f</i> -1784
10	22524	3(<i>d</i>)	<i>e</i> - 414	25	21170	6(<i>b, d</i>)	<i>e</i> -1868
11	22433	4	<i>e</i> - 505	26	19871	3	<i>e</i> -3067
12	22323	4	<i>e</i> - 615				
13	22271	5	<i>e</i> - 667				
14	22169	$\frac{1}{2}(b, d)$	<i>e</i> - 769				
15	21969	0	<i>f</i> -1026				

$\Delta\nu$: 158 (4*d*); 314 (2*d*); 414 (2*d*); 505 (4); 615 (4); 669 (5); 769 ($\frac{1}{2}b, d$); 998 (4); 1027 (4); 1166 (6); 1200 (8); 1591 (10); 1776 (6*b, d*); 3067 (7*b*).

Table XII.
Phenyl acetate $C_6H_5.O.O.C.CH_3$.

No.	ν in $cm.^{-1}$	I	$\nu_0 - \Delta\nu$	No.	ν in $cm.^{-1}$	I	$\nu_0 - \Delta\nu$
1	24053	$1/2$	$k-652$	16	22048 ?	$1/2(b, d)$	$e-890 ?$
2	23703	5	$k-1002$	17	21938	8	$e-1000$
3	23687	0 ?	$k-1018$	18	21920	$1/2$	$e-1018$
4	23511	4	$k-1194$	19	21860 ?	$1/2(b, d)$	$e-1078 ?$
5	23214	0(d)	$k-1491$	20	21779	7(b, d)	$k-2926(e-1159)$
6	23116	5	$k-1589$	21	21746	4(b, d)	$e-1192$
7	22816 ?	3(b, d)	$e-122$	22	21636	8(b)	$k-3069$
8	22676	5	$e-262$	23	21581	0(d)	$e-1358(i-1358)$
9	22602	5	$e-336$	24	21517 ?	$1/2$	$f-1488$
10	22413	4	$e-525$	25	21451	2(d)	$e-1487(i-3065)$
11	22326	4	$e-612$	26	21347	5	$e-1591$
12	22277	3	$e-661$	27	21163	2(d)	$e-1760$
13	22243	$1/2$	$f-752$	28	20008	3	$e-2930$
14	22192	5	$e-746(f-803)$	29	19872	3(b, d)	$e-3066$
15	22118	5	$e-810$				

$\Delta\nu$: (122) (3, d) ?; 262 (5); 336 (5); 525 (4); 612 (4); 661 (3); (746) (5); 810 (5); (890) ($1/2 b, d$); 1001 (8); 1018 (1); 1078 ($1/2 b, d$) ?; (1159) (7 b, d); 1193 (4 b, d): (1358) ($1/2$); 1487 (2 d) ?; 1590 (5); 1760 (2 d); 2928 (7 b, d); 3068 (8 b, d).

Table XIII.
Phenyl butyrate $C_6H_5.O.CO.C_3H_7$.

No.	ν in $cm.^{-1}$	I	$\nu_0 - \Delta\nu$	No.	ν in $cm.^{-1}$	I	$\nu_0 - \Delta\nu$
1	23705	4	$k-1000(i-811)$	16	22332	3	$e-606$
2	23608	2	$k-1097$	17	22259 ?	$1/2(d) ?$	$e-679$
3	23559 ?	$1/2 ?$	$k-1146$	18	22128	3	$e-810$
4	23513	1(d)	$k-1192$	19	22023 ?	$1/2(d) ?$	$e-915$
5	23340 ?	$1/2 ?$	$k-1365$	20	21939	6	$e-999$
6	23303	$1/2$	$i-1213$	21	21923	$1/2$	$e-1015$
7	23246	0(d)	$k-1459$	22	21847	1	$e-1091$
8	23188	4(b, d)	$e-250$	23	21774	3(d)	$e-1164(k-2931)$
9	23128	2(d)	$e-191$	24	21742	1(d)	$e-1196(k-2963)$
10	23070 ?	2(d)	$k-1635$	25	21644	6(d)	$k-3061(e-1347)$
11	22747	1	$e-191$	26	21488	$1/2$	$e-1450$
12	22698	5(d)	$e-240$	27	21345	3(d)	$e-1593$
13	22610 ?	0	$e-328$	28	21185	2(b, d)	$e-1753$
14	22544	$1/2$	$e-398$	29	19875	1	$e-3063$
15	22406	2	$e-532$				

$\Delta\nu$: 191 (1); 245 (5 d); 328 ($1/2$) ?; 394 (1 d); 532 (2); 606 (3); 679 ($1/2 d$); 810 (3); 915 ($1/2 d$?); 1000 (6); 1015 ($1/2$); 1094 (1); (1164) (3 d); 1194 (1 d); (1365) ($1/2$) ?; 1455 ($1/2$) ?; 1593 (3 d); (1632) (2 d) ?; 1753 (2 b, d); (2931) (3 d); (2963) (1 d); 3062 (6 b, d).

Table XIV.

o-Kresyl acetate $\text{CH}_3\text{CO.O.C}_6\text{H}_4\text{CH}_3$.

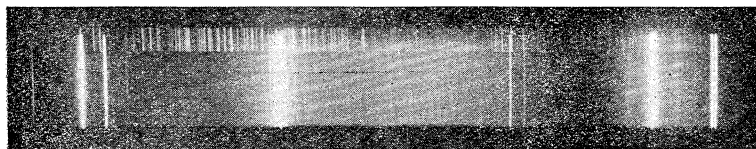
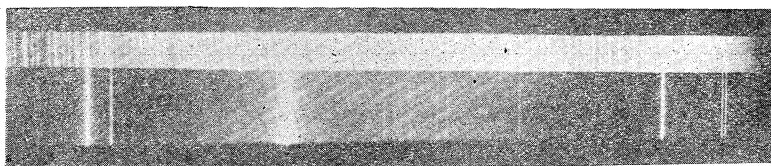
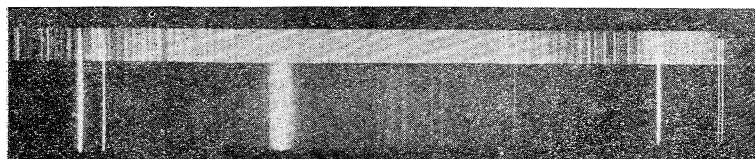
No.	ν in cm.^{-1}	I	$\nu_0 - \Delta\nu$	No.	ν in cm.^{-1}	I	$\nu_0 - \Delta\nu$
1	23948	$\frac{1}{2}$	$k-757$	21	21900	5	$e-1038$
2	23663	1(<i>b</i>)	$k-1042$	22	21814	$\frac{1}{2}(b, d)$	$e-1124$
3	23542 ?	0(<i>b, d</i>)	$k-1163 ?$	23	21773	8(<i>b, d</i>)	$e-1165(k-2932)$
4	23486	3(<i>b</i>)	$k-1219$	24	21720	7	$e-1218$
5	23133	2(<i>b</i>)	$k-1572$	25	21651	6(<i>d</i>)	$k-3054$
6	23095	1	$k-1610$	26	21562	1(<i>b, d</i>)	$e-1376$
7	23061	1	$e-123$	27	21503	1(<i>d</i>)	$e-1435$
8	22822	5(<i>b</i>)	$e-116$	28	21461	$\frac{1}{2}(d)$	$e-1477$
9	22741	4	$e-197$	29	21363	1	$e-1575$
10	22637	3	$e-301$	30	21330	4(<i>s</i>)	$e-1608$
11	22596	2(<i>d</i>)	$e-342$	31	21174	2	$e-1764$
12	22414	2	$e-524$	32	19996	2(<i>d</i>)	$e-2942$
13	22376	5	$e-562$	33	19886	1	$e-3052$
14	22282	4	$e-656(f-713)$				
15	22229	4	$e-709(f-766)$				
16	22194	4	$e-744$				
17	22166	4	$e-772$				
18	22116	$\frac{1}{2}(d)$	$e-822$				
19	22078	0(<i>d</i>)	$e-860$				
20	22024	2(<i>d</i>)	$e-914$				

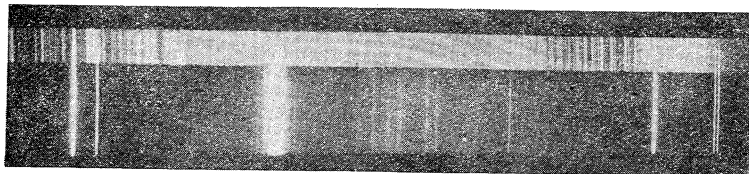
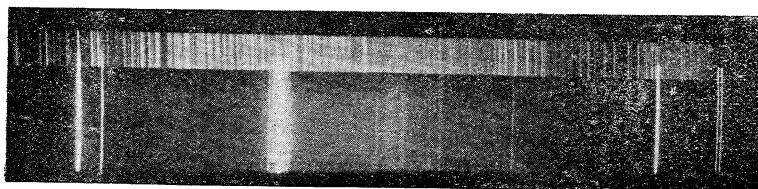
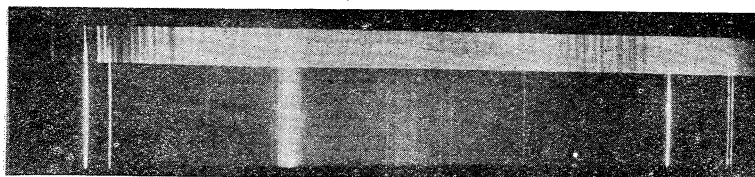
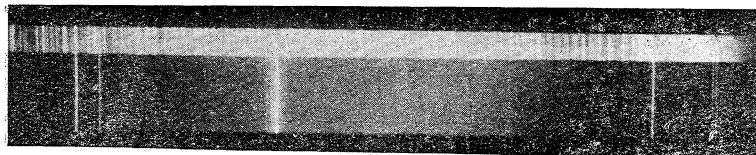
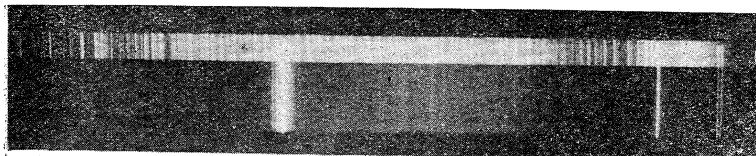
$\Delta\nu$: 120 (5*b*); 197 (4); 301 (3); 342 (2*d*); 524 (2); 562 (5); 656 (4); 709 (4); 744 (4); 772 (4); (822) ($\frac{1}{2}$)?; (860) (0)?; 914 (2*d*); 1040 (5); (1124) (1*b, d*); 1165 (8); 1218 (7); 1376 (2*b, d*); 1435 ($\frac{1}{2}d$)?; 1477 ($\frac{1}{2}d$)?; 1574 (1*b*); 1609 (4*s*); 1764 (2); 2942 (2*d*); 3053 (6*b, d*).

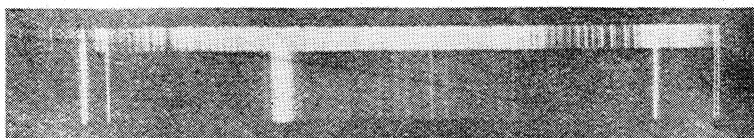
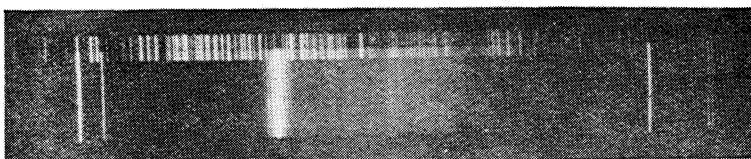
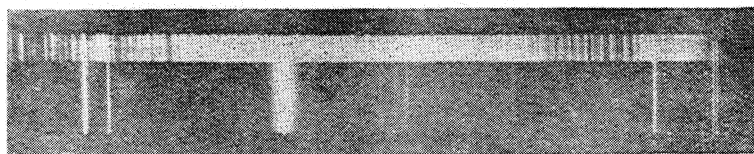
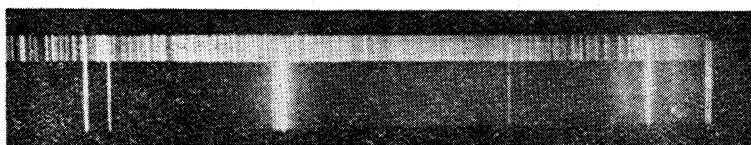
Discussion of the Results.

1. **Frequencies Associated with the Benzene Ring.** In all the benzoates studied, the frequencies of $\Delta\nu = 615, 670, 1000, 1025, 1106, 1164, 1269, (1303), 1452, 1600, 1720$ and 3070 cm.^{-1} have been observed in good constance, of which those of $\Delta\nu = 615, 1000, 1164, 1600$ and 3070 cm.^{-1} have been known to be associated with the vibrations of C-C, C:C and C-H linkage in the benzene ring. These frequencies are little

The mercury spectrum

(1) Methyl Benzoate $\text{C}_6\text{H}_5\cdot\text{CO}\cdot\text{O}\cdot\text{CH}_3$ (2) Ethyl Benzoate $\text{C}_6\text{H}_5\cdot\text{CO}\cdot\text{O}\cdot\text{CH}_2\text{CH}_3$ (3) *n*-Propyl Benzoate $\text{C}_6\text{H}_5\cdot\text{CO}\cdot\text{O}\cdot\text{CH}_2\text{CH}_2\text{CH}_3$ (4) *n*-Butyl Benzoate $\text{C}_6\text{H}_5\cdot\text{CO}\cdot\text{O}\cdot\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_3$ 

(5) *i*-Propyl Benzoate $\text{C}_6\text{H}_5\text{CO}\cdot\text{O}\cdot\text{CH}(\text{CH}_3)_2$ (6) *i*-Butyl Benzoate $\text{C}_6\text{H}_5\text{CO}\cdot\text{O}\cdot\text{CH}_2\text{CH}(\text{CH}_3)_2$ (7) *i*-Amyl Benzoate $\text{C}_6\text{H}_5\text{CO}\cdot\text{O}\cdot\text{CH}_2\text{CH}_2\text{CH}(\text{CH}_3)_2$ (8) Cyclo-hexyl Benzoate $\text{C}_6\text{H}_5\text{CO}\cdot\text{O}\cdot\text{C}_6\text{H}_{11}$ (9) *o*-Kresyl Benzoate $\text{C}_6\text{H}_5\text{CO}\cdot\text{O}\cdot\text{C}_6\text{H}_4\cdot\text{CH}_3$ 

(10) *n*-Octyl Benzoate $C_6H_5CO \cdot O \cdot C_8H_{17}$ (11) Benzoyl Chloride $C_6H_5CO \cdot Cl$ (12) Phenyl Acetate $CH_3CO \cdot O \cdot C_6H_5$ (13) Phenyl Butyrate $C_3H_7CO \cdot O \cdot C_6H_5$ (14) *o*-Kresyl Acetate $CH_3 \cdot CO \cdot O \cdot C_6H_4 \cdot CH_3$ 

influenced by increasing carbon atoms of the chain of alkyl radicals in the benzoates, and show little variation in phenyl acetate, butyrate and *o*-kresyl acetate. The absence of $\Delta\nu = 615 \text{ cm.}^{-1}$ in *o*-kresyl acetate may be considered that the shift is taken place by the appearance of $\Delta\nu = 562 \text{ cm.}^{-1}$, and that the latter shift seems to characterize the *o*-di-derivative, the former the monoderivative. The appearance of 586 and 616 cm.^{-1} in *o*-kresyl benzoate, $(\text{C}_6\text{H}_5.\text{CO.O.C}_6\text{H}_4.\text{CH}_3)$, gives the verification that the substance is a mono-derivative as well as di-derivative. This fact was confirmed by the studies of salicylates and phthalates, the report of which will be published soon.

The frequency of 1026 cm.^{-1} in the benzoates which characterizes the mono-derivates of aromatic compounds shows a little decrease in phenyl acetate (1018) and in phenyl butyrate (1015), but increase in *o*-kresyl acetate (1040). The fact that the line in question, increases the frequencies and its intensity in the di-derivatives, which has been investigated by Kohlrausch⁽¹⁴⁾ is confirmed also in this experiment. It is interesting that in the case of *o*-kresyl benzoate which is a mono-derivative as well as di-derivative, these relations appeared clearly, that is, $\Delta\nu = 1018$ and 1036 cm.^{-1} , have been observed.

2. Frequencies Associated with the C-H Linkage of Alkyl Radicals.

The frequencies between 2850 and 2980 cm.^{-1} which have been well known to be attributable to the aliphatic C-H linkage are almost in accord with those in the corresponding alkyl halides⁽¹⁵⁾ and alcohols⁽¹⁶⁾. The lines of this kind are diffuse and broad.

In the first member of the series, viz., methyl benzoate, only a well defined line of $\Delta\nu = 2950 \text{ cm.}^{-1}$ reveals in this region. In the case of ethyl benzoate the corresponding line is spalted into two lines, $\Delta\nu = 2930$ and 2980 cm.^{-1} , of the same intensity. On the other hand, in the case of *n*-propyl ester, the aggregation of many diffuse lines appears like a band. In the case of iso-propyl ester, however, three lines of $\Delta\nu = 2872$, 2930 and 2979 cm.^{-1} reveal clearly, the middle one of which is the most intense and broad. As we proceed still higher up the series, viz., iso-butyl ester, the continuous spectrum between the two lines of $\Delta\nu = 2873$ and 2968 cm.^{-1} appears like a band while in the case of iso-amyl ester the continuous part is quite homogeneous in the same position. These relations are shown in Diagram (1). In addition, it is found that iso-compounds show more intense and clear lines in this region, than those of the corresponding *n*-compounds.

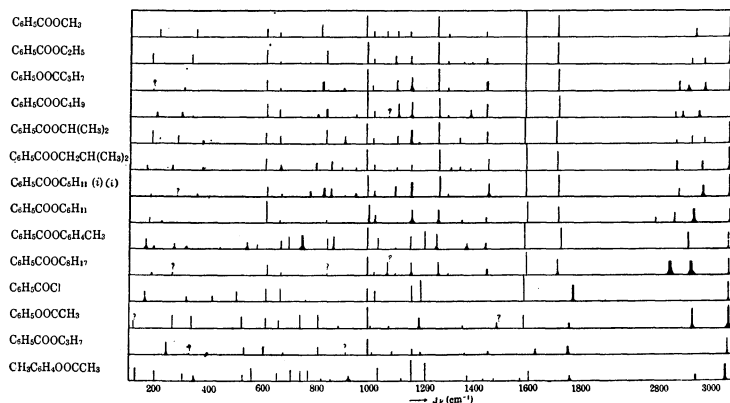
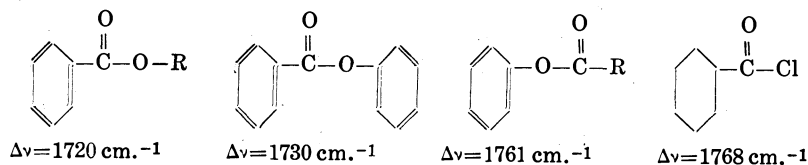


Diagram 1. Raman frequencies of esters of benzoic acid and fatty acids.

The frequency of 1452 appears in all the substances investigated except in the case of benzoyl chloride which does not contain the CH_2 -group. The frequency has been known to be due to the transverse vibration of the hydrogen atoms in CH_2 -group.

In the series of alkyl benzoates, the same line increases the intensity and its breadth as the carbon atoms increase.

3. Frequencies Possibly Associated with the $\text{-}\overset{\text{O}}{\underset{\text{||}}{\text{C}}}\text{-O-}$ Group. The well-known frequency attributed to C:O linkage was observed also in good constance, practically, in all the benzoates. The shift of $\Delta\nu = 1720 \text{ cm.}^{-1}$ in alkyl benzoates, $\Delta\nu = 1730 \text{ cm.}^{-1}$ in *o*-kresyl benzoate, $\Delta\nu = 1760 \text{ cm.}^{-1}$ in phenyl acetate and $\Delta\nu = 1768 \text{ cm.}^{-1}$ in benzoyl chloride have been measured. It is found that there is a little increase of 10 cm.^{-1} , by substituting the $\text{-C}_n\text{H}_{2n+1}$ radical with the $\text{-C}_6\text{H}_4\text{-CH}_3$ radical, and a prominent increase of 50 cm.^{-1} , by exchanging the position of the benzene ring and alkyl radical or by substituting the -O.R group with Cl . The structure and the Raman frequencies in question are compared in the following:



The frequencies of 1270 cm.^{-1} was observed in good constance and in the strong intensity in all the benzoates. Benkateswaran and Bhagavantam⁽¹⁷⁾ have explained that it is attributed to the COH group from the results of alcohols and fatty acids. Wood and George Collins⁽¹⁸⁾

have explained that the same frequency is attributable to the transversal vibration of the hydrogen atoms of the $\begin{array}{c} \text{H} \\ | \\ -\text{C}-\text{OH} \\ | \\ \text{H} \end{array}$ group, from the fact that

methyl alcohol $\text{CH}_3\text{-OH}$ and isopropyl alcohols $(\text{CH}_3)_2\text{-CHOH}$ contain no CH_2OH and do not show the 1270 cm.^{-1} frequency. The absence of the line in butyl and higher alcohols has been explained by the possibility that it exists in the higher alcohols and is simply too weak to be recorded.

Their explanations can not be applied, however, in the case of the benzoates which do not contain any COH or $\text{-CH}_2\text{OH}$ group in the molecule.

The frequency at 670 cm.^{-1} was observed also in all the benzoates independent of the numbers of the carbon atoms in the alkyl group. The fact that carbon dioxide⁽¹⁹⁾ reveals a system of valency frequencies at 2295 , 1280 , 1223 , and 673 cm.^{-1} leads us to suggest that the frequencies at 1720 , 1270 and 670 cm.^{-1} in the benzoates may be possibly attributable to the valency frequencies of the carboxyl group, -CO-O- .

It is considered that the frequency at 1270 cm.^{-1} in the benzoate corresponds to that at 1200 cm.^{-1} in phenyl acetate, butyrate and *o*-kresyl acetate ($\text{CH}_3\text{-CO.O-C}_6\text{H}_4\text{CH}_3$). And the existence of the same frequency, in benzoyl chloride may be attributed to the -CO-Cl . It is also considered that the shift of $\Delta\nu = 1720\text{ cm.}^{-1}$ in the benzoates corresponds to 1760 cm.^{-1} in phenol acetate and benzoyl chloride. And the existence of these frequencies in most of the fatty acids,⁽²⁰⁾ especially, in formic acid⁽²¹⁾ which has not any alkyl radical, seems to given an other verifications of considerations above mentioned. The results have been compared:

$\text{C}_6\text{H}_5\text{CO-O-R}$	1720	1270	670
$\text{C}_6\text{H}_5\text{COCl}$	1776	1200	669
$\text{C}_6\text{H}_5\text{-O-CO-CH}_3$	1760	1193	661
$\text{C}_6\text{H}_5\text{-O-CO-C}_3\text{H}_7$	1753	1194	679
$\text{CH}_3\text{-C}_6\text{H}_4\text{-O-CO-CH}_3$	1764	{ 1218	656
		{ 1261	
$\text{C}_6\text{H}_5\text{-CO.O-C}_6\text{H}_4\text{CH}_3$	1730	1214	675
HCOOH	{ 1724	1200	673 ⁽²²⁾
	{ 1694	1223	187
CH_3COOH	1670	1280	623 ⁽²³⁾
$\text{CH}_3\text{-COOC}_7\text{H}_7$	1740	1250	630 ⁽¹⁰⁾

Thus the consideration that the frequencies of $\Delta\nu = 1720$, 1270 and 670 cm.^{-1} are attributed to the -CO-O- group in the compound of the type of $\text{C}_6\text{H}_5\text{-CO-O-X}$ and 1776 , 1194 and 661 cm.^{-1} are attributed to that in the compound of the type of $\text{X-CO-O-C}_6\text{H}_5$ seems to be supported by the fact that in the case of *o*-kresyl benzoate, which has the both types of $\text{C}_6\text{H}_5\text{-CO-O-X}$ and $\text{X-CO-O-C}_6\text{H}_5$, the both frequencies of $\Delta\nu = 1214$ and 1261 cm.^{-1} reveal in the same intensity.

4. **Inner and Outer Frequencies between Atoms or Atom Groups.** Frequencies of the inner and outer vibration between two atoms or atom groups in a molecule are calculated by using the well-known equation⁽²⁴⁾

$$\omega = \sqrt{\frac{f}{C\mu}}$$

where μ is the reduced mass; i.e., $\frac{1}{\mu} = \frac{1}{m_1} + \frac{1}{m_2}$. The constant C is known as $C = \frac{4\pi^2 c^2}{L} = 5.863 \times 10^{-2}$, where L is the Loschmidt numbers, 6.06×10^{23} and c is the velocity of light, 3×10^{10} cm./sec. More practically, by using the thermochemical data, work of dissociation, A (in Cal./Mol.), the wave numbers may be calculated from the formula⁽²⁵⁾

$$\omega = 291.5 \sqrt{A \cdot \frac{1}{\mu}}$$

For the simplicity, the molecular formula, the bond, the force constant, f (in dynes/cm.) between the two atoms or atom groups taken from the table of Kohlrausch⁽²⁶⁾ or the „Aufspaltungsarbeit“ A (in Cal./Mol.) taken from the table of H. G. Grimm⁽²⁷⁾, the reduced mass, the wave numbers (in cm.⁻¹) calculated and that of observed have been tabulated as follows:

No.	Molecular formula	Bond	$f \times 10^{-5}$	$\frac{1}{\mu}$	$\omega_{\text{cal.}}$	$\omega_{\text{abs.}}$
1.	<chem>C6H5.CO.O.R</chem>	$\text{O} \longleftrightarrow \text{C}$	4.99 ($A=102$)	0.1458	1114 (1124)	1110
2.	„	$\text{C} \longleftrightarrow \text{C}$	4.31	0.1667	1107	1110?
3.	<chem>C6H5.CO.O.CH3</chem>	$\text{O} \longleftrightarrow \text{CH}_3$	4.99	0.1292	1088	1078
4.	<chem>C6H5.CO.Cl</chem>	$\text{C} \longleftrightarrow \text{Cl}$	3.12 ($A=70$)	0.1115	770 (814)	769
5.	<chem>C6H5.O.O.C.R</chem>	$\text{C}_6\text{H}_5 \longleftrightarrow \text{O}$	($A=101$)	0.0755	804	810
6.	<chem>C6H5.CO.O.CH3</chem>	$\text{C}_6\text{H}_5\text{COO} \longleftrightarrow \text{CH}_3$	4.99 ($A=102$)	0.0749	779 (806)	814
7.	<chem>C6H5.CO.Cl</chem>	$\text{C}_6\text{H}_5\text{CO} \longleftrightarrow \text{Cl}$	3.12	0.03969	448	414
8.	<chem>CH3.CO.O.C6H5</chem>	$\text{CH}_3\text{COO} \longleftrightarrow \text{C}_6\text{H}_5$	($A=101$)	0.02994	507	525

The line of $\Delta\nu = 1110$ cm.⁻¹ appears in all the benzoates and disappeared in benzoyl chlorides and phenyl acetate. It have been found also in alcohols and most of the esters of fatty acids observed by other authors.⁽²⁸⁾ These facts seem to make the confirmation of the estimation that it is attributed to the inner vibration of the O-C linkage.

The approximate calculation of the inner vibration of two atoms shows that the line at $\Delta\nu = 1110$ cm.⁻¹ may be possibly attributed to the

C-C as well as to the O-C bond. Accidental as it may be, it seems to be not impossible. And the fact that the line of about $\Delta\nu = 1110 \text{ cm.}^{-1}$ has been found in some of the alkyl halides, such as, $(\text{CH}_3)_2\text{CH.CH}_2\text{Cl}$, $(\text{CH}_3)_2\text{CH.CH}_2\text{Br}$, etc.,⁽²⁹⁾ which have no O-C bonds, and the line has been found in CH_3OH ⁽³⁰⁾ and $\text{C}_6\text{H}_5\text{CO.O-CH}_3$ which have no aliphatic C-C bond seems to give a verification about it. Kohlrausch and his co-worker⁽³¹⁾ have shown the fact that the OH and CH_3 groups exert the similar effect on the rest, that is, for example, the following pairs give the similar Raman lines related with the alkyl rest.



In the present case, we consider that the frequencies related with the $-\text{CH}_2\text{-O-}$ or $\text{CH}_3\text{-O-}$ may be possible similar to those related with the $-\text{CH}_2\text{-CH}_2\text{-}$ or $-\text{CH}_2\text{-CH}_3$ and that the two kinds of the frequencies are associated or united, which make an appearance of broad and diffuse line as the dispersion of the prism is not so large in our experiments. The fact seems to be more possible, especially, in the complex molecules.

The frequencies of $\Delta\nu = 810 \text{ cm.}^{-1}$ observed in phenyl acetate and butyrate are in good coincidence with the calculated value and the consideration is confirmed by the existence of the same line in phenol.

The same shift in methyl benzoate, however, is evidently different in its origin. The outer vibration or the valence frequency between the CH_3 group and the acid rest may be taken in this case, as shown in the above table.

Since the lengthening of the carbon chain exerted little effect on the benzene ring and on the $-\text{CO-O-}$ group as mentioned above, it seems right to assume that only the $-\text{CH}_2\text{-}$ group attached to the rest relates with the valency frequencies as in the cases of alkyl halides studied by Harkins.⁽³²⁾ Thus, as one of the possible ways to explain the frequencies in the range of $800\text{--}900 \text{ cm.}^{-1}$ in the present investigation we may take the frequency shift of 846 cm.^{-1} in ethyl benzoate as the valence frequency between the alkyl radical or the $-\text{CH}_2\text{-}$ group and the acid rest, corresponding to that of $\Delta\nu = 814 \text{ cm.}^{-1}$ in methyl benzoate.

It is surprising, however, that in the case of *n*-propyl benzoate a shift of $\Delta\nu = 811 \text{ cm.}^{-1}$ and a very weak line of $\Delta\nu = 845 \text{ cm.}^{-1}$ were observed. In the case of *n*-butyl benzoate two broad and diffuse lines, corresponding $\Delta\nu = 810$ and 843 cm.^{-1} were observed in the same inten-

sity. In iso-propyl benzoate only a intense line with the same frequency as that in the case of ethyl ester was observed clearly. In iso-butyl benzoate two broad lines corresponding to 804 and 863 cm^{-1} and in iso-amyl benzoate, 836 and 861 cm^{-1} of the same intensity were observed.

To explain these facts let us consider the "Free rotation" of the alkyl group, namely, that the chain and the ring form in the free space as considered by K.W.F. Kohlrausch and his co-workes in their studies of alkyl halides⁽³³⁾.

Thus in the case of *n*-propyl benzoate, the *n*-propyl radical takes two forms in the space against the rest of benzoic acid, viz.,



where: X is the rest of benzoic acid.

With these two forms we can explain the two frequencies occurred, though one of which is very weak. And with the same principle, we can also explain the two frequencies observed in the other benzoates. The fact that iso-propyl benzoate which can not take two forms, and has only the frequency of 845 cm^{-1} as that in ethyl ester, seems to give a support of the principle. The frequencies of the benzoates are tabulated as follows:

	I	II
X-CH ₃	$\omega_1 = 814$	
X-CH ₂ -	$\omega_2 = 846$	
X-CH ₂ -CH ₂ -CH ₃	$\omega_2 = 845$	$\omega_3 = 811$
X-CH ₂ -CH ₂ -CH ₂ -CH ₃	$\omega_2 = 843$	$\omega_3 = 810$
X-CH $\begin{array}{l} \nearrow \text{CH}_3 \\ \searrow \text{CH}_3 \end{array}$	$\omega_4 = 845$	
X-CH ₂ -CH $\begin{array}{l} \nearrow \text{CH}_3 \\ \searrow \text{CH}_3 \end{array}$	$\omega_2 = 863$	$\omega_3 = 804$
X-(CH ₂) ₂ -CH $\begin{array}{l} \nearrow \text{CH}_3 \\ \searrow \text{CH}_3 \end{array}$	$\omega_2 = 861$	$\omega_3 = 836 ?$

We may consider the relation between the forms and the frequencies as shown in following:

X-CH ₃	ω_1
{ X-CH ₂ -	ω_2
{ X-CH ₂ -	$\omega_2 \ \omega_3$
X-CH $\begin{array}{l} \nearrow \\ \searrow \end{array}$	ω_4

A remarkable deviation was found in iso-butyl and iso-amyl ester, which may attributable to the error of measurement, on account of the

broad lines or a possible deviation due to the influence of the $-\text{CH}(\text{CH}_3)_2$ group.

The fact that $\Delta\nu = 845 \text{ cm.}^{-1}$ in iso-propyl benzoate coincides with that of $\Delta\nu = 846$ in ethyl benzoate may be compared with the relation in iso-propyl iodide⁽³⁴⁾ ($\Delta\nu = 489 \text{ cm.}^{-1}$) and ethyl iodide ($\Delta\nu = 497 \text{ cm.}^{-1}$) and the weight of the molecular rests i.e. $\text{C}_6\text{H}_5\text{COO-} = 121$ and $J = 127$; though it is not only the weight that associated with the frequencies. And the fact that the frequency at $\Delta\nu = 814 \text{ cm.}^{-1}$, in methyl benzoate, is less than the corresponding one (at $\Delta\nu = 846 \text{ cm.}^{-1}$), in ethyl benzoate, seems to be possible when we compare it with the relation that in the case of alkyl chloride the difference between methyl ($\Delta\nu = 712 \text{ cm.}^{-1}$) and ethyl derivative ($\Delta\nu = 655 \text{ cm.}^{-1}$) is larger than that in the case of the corresponding iodide ($\Delta\nu = 522 \text{ cm.}^{-1}$ in methyl and 497 cm.^{-1} in ethyl iodide).

An Attempt of the Calculation of the Valency and Deformation Frequencies. If we make an assumption that the vibration of the system of three atoms or atom groups exerts the Raman lines, in the first order of approximation, independent of the other molecular rest, we may apply the theoretical calculations of Friedrich Lechner,⁽²⁵⁾ which are given in:

$$\begin{aligned} n_1^2 + n_2^2 + n_3^2 &= \frac{f_{12}}{\mu_{12}} + \frac{f_{23}}{\mu_{23}} + \frac{d}{\mu_4} \\ n_1^2 n_2^2 + n_2^2 n_3^2 + n_1^2 n_3^2 &= \frac{f_{12}}{\mu_{12}} \cdot \frac{f_{23}}{\mu_{23}} \left\{ 1 - \frac{\mu_{12} \cdot \mu_{23}}{m_2^2} \cos^2 \alpha \right\} \\ &+ \frac{f_{12}}{\mu_{12}} \cdot \frac{d}{\mu_4} \left\{ 1 - \frac{\mu_{12} \mu_4}{m_2^2} \left(\frac{s}{s_{23}} \right)^2 \sin^2 \alpha \right\} \\ &+ \frac{f_{23}}{\mu_{23}} \cdot \frac{d}{\mu_4} \left\{ 1 - \frac{\mu_{23} \mu_4}{m_2^2} \left(\frac{s}{s_{12}} \right)^2 \sin^2 \alpha \right\} \\ n_1^2 \cdot n_2^2 \cdot n_3^2 &= \frac{f_{12}}{\mu_{12}} \cdot \frac{f_{23}}{\mu_{23}} \cdot \frac{d}{\mu_4} \left\{ 1 - \frac{\mu_{12} \mu_{23}}{m_2^2} \right\} \end{aligned}$$

where μ_{12} , μ_{23} ; f_{12} , f_{23} ; s_{12} , s_{23} are the reduced masses, the force constants and the distance between material particles, m_1 and m_2 , m_2 and m_3 respectively, $\alpha' = (180^\circ - \alpha)$ is the valency angle and

$$\frac{1}{\mu_4} = \frac{1}{\mu_{12}} \cdot \frac{s^2}{s_{12}^2} + \frac{2}{m_2} \cdot \frac{s^2}{s_{12} s_{23}} \cos \alpha + \frac{1}{\mu_{23}} \cdot \frac{s^2}{s_{23}^2}$$

$$s_{12}^2 d_{12} = s_{23}^2 d_{23} = s^2 d$$

$$n^2 = 5.863 \times 10^{-2} \omega^2$$

When the three particles make an isosceles triangle, that is when $m_1 = m_3 = m$ and $m_2 = M$, $f_{12} = f_{23} = f$, $s_{12} = s_{23} = s$, the above equation can be simplified as following :

$$n_1^2 = \frac{f}{m} z$$

$$n_1^2 + n_2^2 + n_3^2 = \frac{f}{m} (1-p) + \frac{2d}{m} z \quad (2)$$

$$n_2^2 n_3^2 = \frac{f}{m} \cdot \frac{2d}{m} \cdot p$$

where $p = \frac{2m}{M} + 1$, $z = p + (1-p) \sin^2 \frac{\alpha}{2}$ (3)

And the equations (2) have been rewritten in:

$$z^3 - \alpha z + b = 0 \quad (4)$$

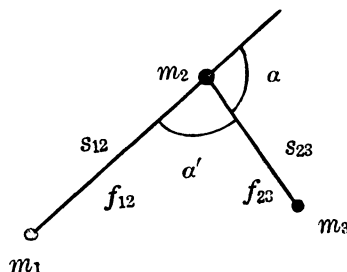
where $\alpha = \frac{n_1^2(n_1^2 + n_2^2 + n_3^2)p}{n_2^2 n_3^2}$, $b = \frac{n_1^4(p+1)p}{n_2^2 n_3^2}$ (5)

and the necessary conditions for the real solutions in the above equation are: $\frac{\alpha^2}{27} > \frac{b^2}{4}$ and $1 < z \leq p$.

Lechner has applied the above theory to the simple molecules, such as, CH_2Cl_2 , CH_2Br_2 , etc. for calculating the force constants and valency angles.

In the substances studied, the following assumptions have been made, since the molecules are very complicated. In the first, we assume that the theory can be applied to the system of three atom groups or an atom and two atom groups, and secondly, that it can be applied to a portion of the molecule, that is, the molecule is considered as some systems of three atoms or atom groups.

Under the assumptions above mentioned, we attempt to calculate the valency system by taking the part of $-\text{CH}_2-\text{CH}_2-\text{CH}_2-$ in *n*-butyl radical as an isosceles triangle model and applying the equations of the valence system, mentioned above. In this case, if we take $m = M = 14$,



$\alpha' = 110^\circ$, the tetrahedral valence angle of the carbon atom, and the force constant $f = 4.3 \times 10^5$ dyne/cm., given by Kohlrausch,⁽³⁶⁾ the following values are obtained:

$$p = 3, z = 2.342, \omega_1 = 1108 \text{ cm.}^{-1}$$

And by assuming $\omega_3 = 298 \text{ cm.}^{-1}$, the valence of $\omega_2 = 930 \text{ cm.}^{-1}$ and $d = 0.21 \times 10^5$ dyne/cm. are obtained, which may compare with the set of the observed values, in *n*-butyl benzoate: $\omega_1 = 1110$, $\omega_2 = 957$, $\omega_3 = 298 \text{ cm.}^{-1}$. And from these values, f , d and α in butyl benzoate has been calculated as shown below:

$$f = 4.28 \times 10^5, d = 0.21 \times 10^5, \alpha' = 109^\circ.40'.$$

An other calculation is carried out by taking the part of $\text{CH}_3-\overset{\text{I}}{\text{CH}}-\text{CH}_3$ as a system of an iso-sceles triangle. In this case if we take $m = 15$, $M = 13$, $\alpha' = 110$, $f = 4.3 \times 10^5$ dyne/cm. we obtain:

$$p = 3.3076, z = 2.5483, \alpha_1 = 1116.$$

Thus, when we assume $\omega_3 = 376 \text{ cm.}^{-1}$ which seems to characterize the group in question, from the fact that it reveals in iso-propyl and iso-butyl benzoates but does not reveal in the normal benzoates, the following values are obtained:

$$\omega_2 = 963, d = 0.34 \times 10^5.$$

Comparing with the set of the observed frequencies $\omega_1 = 1110$, $\omega_2 = 916$, $\omega_3 = 378 \text{ cm.}^{-1}$, the assumption seems to be possible. And if we take $m = 12$, $M = 15$ in $\text{---C} \begin{smallmatrix} \text{CH}_3 \\ \text{CH}_3 \end{smallmatrix}$ group, we obtain, under the same assumption, $\omega_1 = 1143$, $\omega_2 = 959$ and $\omega_3 = 378 \text{ cm.}^{-1}$

The facts that the frequencies of $\Delta\nu = 1110, 916, 378 \text{ cm.}^{-1}$ in iso-propyl benzoate, $1110, 901, 378 \text{ cm.}^{-1}$ in iso-butyl benzoate and $1104, 915(?)$, $356(?)$, cm.^{-1} in iso-amyl benzoate, are found, seem to confirm the above consideration, on one hand, and the facts that these frequencies have been found also in iso-propyl, iso-butyl and iso-amyl alcohols and halides, studied by other authors,⁽³⁷⁾ seem to give an other maintenance of our consideration, on the other hand.

And since the frequencies calculated for the system of $\text{---CH}_2-\overset{\text{I}}{\text{CH}_2}-\text{CH}_2\text{---}$ are closed in their values with the frequencies calculated for the system of $\text{CH}_3-\overset{\text{I}}{\text{C}}-\text{CH}_3$, we may also be permitted to assume that the group of

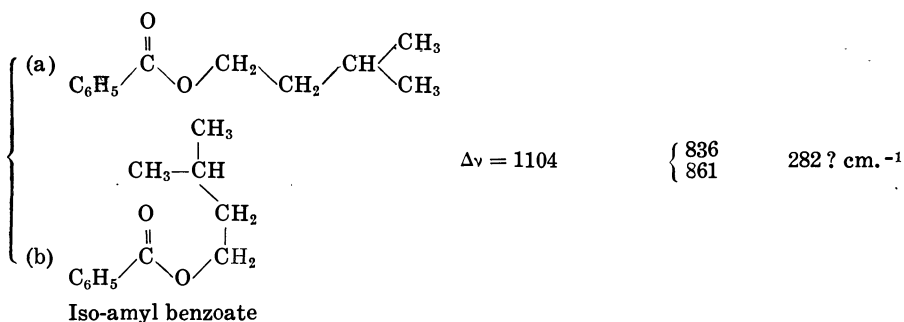
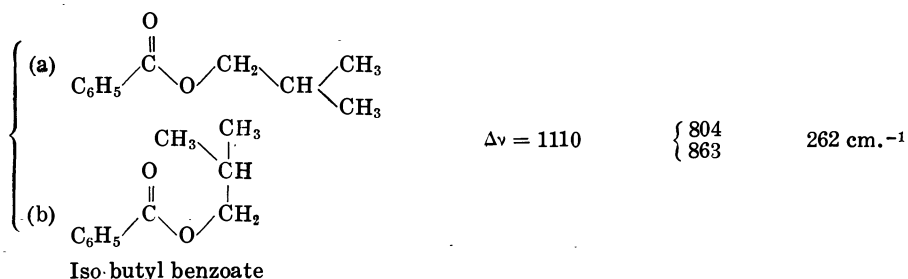
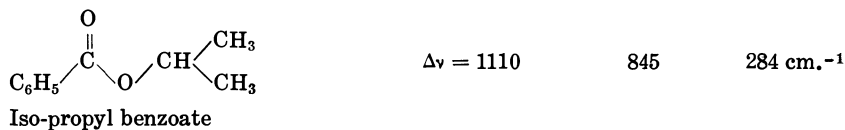
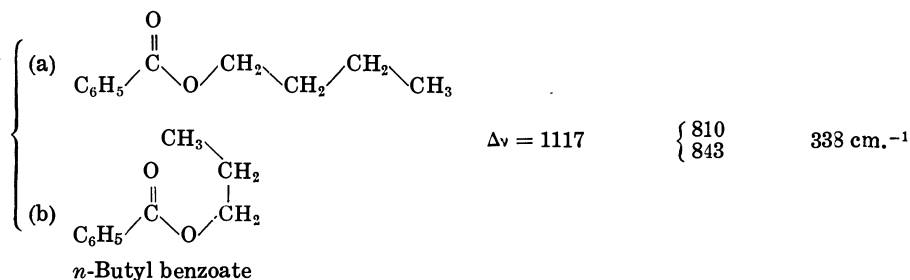
$-\text{CH}_2-\text{CH}_2-\text{CH}_3$ in *n*-butyl and *n*-propyl benzoates, or $-\text{CH}_2-\text{CH}-\text{CH}_3$ in iso-butyl and iso-amyl benzoates, have also the system of the frequencies closed with the above values, viz., $\Delta\nu = 1117, 957, 289$ in *n*-butyl and *n*-propyl benzoates and $1110, 916, 378 \text{ cm.}^{-1}$ in iso-butyl and iso-amyl benzoates are compared.

Thus, we can explain the frequencies of $\Delta\nu = 1110, 959, 910, 378 \text{ cm.}^{-1}$ in iso-butyl benzoates and $1104, 955, 915, 356 (?) \text{ cm.}$ iso-amyl benzoate, which have the system of $-\text{CH}-\begin{matrix} \text{CH}_3 \\ \diagup \\ \text{CH}_3 \end{matrix}$ as well as $-\text{CH}_2-\text{CH}_2-\text{CH}_2-$ group, that is, the combination of the two types. And since the frequencies of $\Delta\nu = 1110 \text{ cm.}^{-1}$ is so broad and diffuse that it may be suggested as the aggregation of the closed lines.

Unfortunately, these frequencies in question are so weak, especially in the case of iso-amyl benzoate, that we can not measure them exactly and the experiments are carried out by means of the spectroscope of lower dispersion, so that we have little right to advocate the consideration, but by comparing with the results of other derivatives which have the same type of alkyl groups, studied by other authors, as mentioned above, the estimation seems to be not impossible.

As regards to the vibration between alkyl radical and the complicated acid rest an other explanation has been done. Corresponding to the frequencies $\Delta\nu = 1110, 916, 378$ for the system of $-\text{CH}_2-\text{CH}_2-\text{CH}_2-$, it seems to be possible to take $\Delta\nu = 1108, 814, (845), 351 \text{ m.}^{-1}$ as the frequencies for the system of $-\text{C}(=\text{O})-\text{O}-\text{CH}_3$ or $-\text{C}(=\text{O})-\text{O}-\text{CH}_2-$ in the benzoates. Thus we can explain the following frequencies in alkyl benzoates studied :

$\begin{array}{c} \text{O} \\ \parallel \\ \text{C}_6\text{H}_5-\text{C}-\text{O}-\text{CH}_3 \\ \text{Methyl benzoate} \end{array}$		$\Delta\nu = 1108$	814	351 cm.^{-1}
$\begin{array}{c} \text{O} \\ \parallel \\ \text{C}_6\text{H}_5-\text{C}-\text{O}-\text{CH}_2-\text{CH}_3 \\ \text{Ethyl benzoate} \end{array}$		$\Delta\nu = 1107$	845	335 cm.^{-1}
$\left\{ \begin{array}{l} \text{(a)} \begin{array}{c} \text{O} \\ \parallel \\ \text{C}_6\text{H}_5-\text{C}-\text{O}-\text{CH}_2-\text{CH}_2-\text{CH}_3 \end{array} \\ \text{(b)} \begin{array}{c} \text{O} \\ \parallel \\ \text{C}_6\text{H}_5-\text{C}-\text{O}-\text{CH}_2-\text{CH}_2-\text{CH}_3 \end{array} \\ \text{\textit{n}-Propyl benzoate} \end{array} \right.$		$\Delta\nu = 1110$	$\left\{ \begin{array}{l} 811 \\ 845 \end{array} \right.$	— cm.^{-1}



With the assumption that only the CH_2 - group adjacent to the oxygen atom relates with the vibration of the system and the free rotation of the alkyl rest which has been mentioned in the foregoing article, we can explain these frequencies, as attributable to the system of $-\overset{\parallel}{\text{C}}-\text{O}-\text{CH}_2-$ in place of the frequencies between the alkyl radical and the complicated acid rest. The frequency of $\Delta\nu = 1110 \text{ cm.}^{-1}$ may be explained by the accidental accordance of lines arising from the two origins, viz., from the systems of $-\text{CH}_2-\text{CH}_2-\text{CH}_2-$ and $-\overset{\parallel}{\text{C}}-\text{O}-\text{CH}_2-$.

In conclusion, the authors wish to express their thanks to Ass. Profs. T. Nozoe and Y. Ota for their advices and help and to Messrs. Y. Ishigaki and S. Murayama for their kind help. The authors express their indebtedness to the Taihoku High School which lent us the spectroscope during the present investigation.

Summary.

(1) The Raman spectra of the following substances have been measured: methyl, ethyl, *n*-propyl, *n*-butyl, iso-propyl, iso-butyl, iso-amyl, cyclo-hexyl, *o*-kresyl and *n*-octyl benzoates, benzoyl chloride, phenol esters of acetic acid and butyric acid and *o*-kresyl acetate.

(2) The constitutive influences exerted on the well-known frequencies of the benzene ring have been observed.

(3) The relation among the frequencies in the region between $\Delta\nu = 2860$ and 2980 cm.^{-1} associated with the C-H linkage of alkyl radicals have been studied for the series of benzoates. It has been found that the intensity and the breadth of the line corresponding to the shift of $\Delta\nu = 1450 \text{ cm.}^{-1}$, considered to be attributable to the transversal vibration of hydrogen atom in the CH_2 - group, increases as the carbon atoms of the homologue are increased.

(4) The frequencies of $\Delta\nu = 1720, 1270, 670 \text{ cm.}^{-1}$ in benzoates are estimated to be possibly attributed to the frequencies of the -CO-O- group.

(5) The following shifts corresponding to the inner vibrations between atoms or atom groups shown below have been established:

Molecular formula	Bond	$\omega_{\text{Cal.}}$	$\omega_{\text{Obs.}}$
$\text{C}_6\text{H}_5\text{-CO-O-R}$	$\text{O} \leftrightarrow \text{C}$	1114	1110
$\text{C}_6\text{H}_5\text{-CO-O-R}$	$\text{C} \leftrightarrow \text{C}$	1107	1110
$\text{C}_6\text{H}_5\text{-CO-O-CH}_3$	$\text{O} \leftrightarrow \text{CH}_3$	1088	1078
$\text{C}_6\text{H}_5\text{-CO-Cl}$	$\text{C} \leftrightarrow \text{Cl}$	770	769
$\text{C}_6\text{H}_5\text{-O-CO-R}$	$(\text{C}_6\text{H}_5) \leftrightarrow \text{O}$	804	810

(6) The frequency of $\Delta\nu = 814 \text{ cm.}^{-1}$ in methyl benzoate has been estimated to be attributed to the bond between methyl group and the acid rest. The frequencies in the region between $\Delta\nu = 810$ and 863 cm.^{-1} have been explained to be attributable to the valency frequencies between the acid rest and the adjacent -CH_2 - group. The two frequencies in the region between $\Delta\nu = 810$ and 846 cm.^{-1} , in *n*-propyl, *n*-butyl, iso-butyl and iso-amyl benzoates have been explained by the consideration of the free rotation of the alkyl rest.

(7) The valency and the deformation frequencies have been thore-tically calculated, assuming that the molecule is composed of some systems of three atoms or atom groups.

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 - (33) *Z. physik. Chem.*, (B) **18** (1932), 65.
 - (34) *ibid.*
 - (35) *Monat. Chem.*, **61** (1932), 385.
 - (36) K. W. F. Kohlrausch, "Der Smekal-Raman-Effect," p. 154.
 - (37) *Monat. Chem.*, **61** (1932), 397-425.
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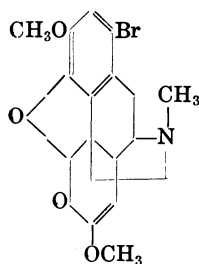
UEBER DIE ACETOLYSE VON 1-BROM-SINOMENEIN⁽¹⁾.

Von Kakuji GOTO, Kanno IIDA und Hideo SHISHIDO.

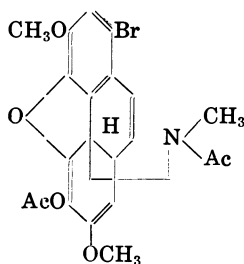
Eingegangen am 14. Oktober, 1933. Ausgegeben am 28. November, 1933.

Nach Anschauung Schöpfs⁽²⁾ und Abbauversuch Gotos⁽³⁾ ist es fast festgestellt dass 1-Brom-sinomenein (I) ein (+)-1-Brom-7-methoxy-kodeinon ist. Nun zeigt diese Substanz zwei Abweichungen von Kodeinon. Erstens, wird sein Jodmethylat nicht so leicht zu Phenanthrenkörper abgebaut durch Erhitzen mit Alkohol. Dies beruht vielleicht auf dem Vorhandensein von einem Enol-methoxyl an C(7). Zweitens gibt es bei der Acetolyse nur Spur von Phenanthrenkörper, aber als Hauptprodukt einen stickstoffhaltigen Körper von der Zusammensetzung $C_{23}H_{24}O_6NBr$. (Schöne, fade gelbe Nadeln von Schmp. 125–135°).

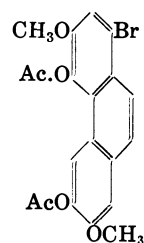
Die Konstitutionermittlung dieser Substanz bietet einige Schwierigkeiten, weil bei weiterer Behandlung diese Substanz stetz unkrystallisierbar wird. So gewinnt man daraus bei der Hydrolyse mit 10-proc. Salzsäure, bei der katalytischen Reduktion oder bei der Acetolyse in Schliessrohr bei 180° nur amorphe Masse.



I.



II.



III.

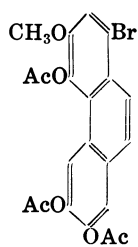
Mikro-acetyl-bestimmung zeigt dass diese Substanz zwei Acetylene enthält. Eine davon muss am Stickstoff haften, weil diese Substanz fast neutral reagiert, d.h. sie muss eine des-N-Acetyl-base sein. Die Stellung von dem anderen Acetyl lässt sich noch nicht feststellen. Die sehr naheliegende Vermutung ist dass es sich an dem enolisierbaren Keton an C(6) haftet. Wir nehmen in dieser Substanz den Oxydring nicht geöffnet an,

(1) XXXVII. Mitteilung über Sinomenin.

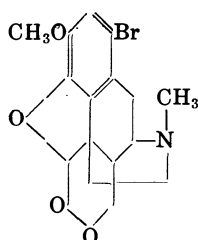
(2) *Ann.*, **483** (1930), 160.(3) *Ann.*, **489** (1931), 86.

weil sonst der dritte Ring des Phenanthrens aromatisiert werden müsste. Aber dies stösst sich auf dem Drehungsvermögen dieser Substanz, obgleich sehr gering ist. Die sehr leichte Oxydierbarkeit dieser Substanz stimmt auch mit der Annahme dass der dritten Kern teilweise hydriert ist. Ueber die Seitenkette-verschiebung lässt sich auch kein Sicheres äussern. Wir wollen in diesem Zustand diese Substanz nur 1-Brom-diacetyl-sinomenenin (II ?) nennen und die genauere Untersuchung in Zukunft ausführen.

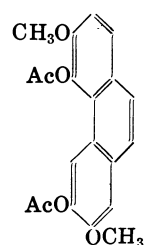
Acetolyse von 1-Brom-sinomeneninjodmethylat oder seiner des-N-Base gestaltet sich etwas anders. Hier krystallisiert ausschliesslich 1-Brom-diacetyl-sinomenol (III) aus, welcher mit dem durch Acetolyse von 1-Brom-sinomenin erhaltenen Produkt identisch ist. Es gibt sogar beim Entbromen Diacetyl-sinomenol (VI), welcher auch direkt aus Sinomenin schon lange dargestellt worden war. Vorherige Entjodieren von dem obigen Jodmethylat gibt bei der Acetolyse wieder ein anderes Produkt. Hier gewinnt man 1-Brom-3 methoxy-4, 6, 7-triacetoxy-phenanthren (IV). Dieser Körper wird auch durch die Acetolyse von 1-Brom-sinomenin-keton (V)⁽⁴⁾ erhalten. Dass in diesem Phenanthren keine Verschiebung von Hydroxyl-gruppe zustande gekommen ist, lässt sich nicht zurzeit feststellen, weil in den Versuchen, diesen Phenanthren-körper in Tetramethoxy- oder Tetraacetoxy-derivaten überzuführen, wir erhielten nur schlechte Resultate. Dies beruht vielleicht auf den Paaren von den orthoständigen Hydroxyl-gruppen.



IV.



V.



VI.

C. Schöpf⁽⁵⁾ hat bei der Acetolyse von dem entjodierten Jodmethylat von seinem wahren Thebainon bemerkt dass der C₃-ständige Phenol-methoxyl verseift wird. Er hat dabei die Vermutung geäussert dass eine etwa beigemengte Verunreinigung katalytisch diese Verseifung bewirkt hätte. Dass in unserem Fall der Eisessig die Verseifung des Enol-methoxyl nicht bewirkt, wurde dadurch bewiesen dass ein vorheriges

(4) Dieses Bulletin, 5 (1930), 168.

(5) C. Schöpf, H. Hirsch: *Ann.*, **489** (1931), 224.

Kochen des Jodmethylat es mit Eisessig allein nicht den Anstoss, diesen Triacetyl-körper zu bilden, gegeben hat.

Versuche.

1-Brom-diacetyl-sinomenol. (III). Diese Substanz wird durch die Acetolyse von den folgenden Substanzen gebildet.

	<i>Ausbeute</i>
1. 1-Brom-sinomenin-chlorhydrat	ca. 30 %
2. des-N-Methyl-1-brom-sinomenin	ca. 10 %
3. 1-Brom-sinomenin-jodmethylat	ca. 10 %
4. 1-Brom-sinomenein-jodmethylat	ca. 30 %
5. des-N-Methyl-1-brom-sinomenein	ca. 90 %
6. 1-Brom-sinomenein	Spur

Als Darstellungsmethode, gibt die Substanz 5 die beste Ausbeute.

1-Brom-diacetyl-sinomenol krystallisiert aus Eisessig in lange Prismen, die bei 187° schmelzen.

Anal.: Subst. = 0.1740; AgBr = 0.0758 gr. Subst. = 0.0456;

AgJ = 0.0458 gr.

Gef.: Br = 18.56; CH₃O- = 13.24%.

Ber. für C₂₀H₁₇Br₆ (433): Br = 18.48; CH₃O- = 14.32 %.

Durch katalytische Reducierung, gibt 1 gr. dieser Substanz 0.5 gr. reinen Diacetyl-sinomenol (Schmp. 151°; auch die Mischprobe mit der Substanz direkt aus Sinomenin).

1-Brom-diacetyl-sinomenenin (II?). 5 gr. 1-Brom-sinomenein wurden mit 30 ccm. Essigsäure-anhydrid und 0.5 Na-acetat unter Rückfluss 3.5 Stunden gekocht. Nach dem Verjagen des Anhydrides i. V., der Rückstand wird mit viel Wasser behandelt. Die getrocknete, gelbe, voluminöse Masse wird aus heissem Methanol umkrystallisiert. Es bildet lange, fade gelbe Prismen. Schmp. 135° (Sintern ab 125°). Ausbeute etwa 30 Proc.

Makro-anal.: Subst. = 0.0735; CO₂ = 0.1513; H₂O = 0.0336 gr. Subst. = 0.1820; AgBr = 0.6675 gr. Subst. = 0.0502; AgJ = 0.0450 gr.

Gef.: C = 56.14; H = 5.08; Br = 15.77, CH₃O- = 11.83 %.

Mikro-anal.: Subst. = 5.643; CO₂ = 11.699; H₂O = 2.513 mg. Subst. = 7.866 mg.; N₂ = 0.168 ccm., 16.5°C., 764 mm. Subst. = 4.744; AgBr = 1.818 mg. Subst. = 2.579, 4.037; AgJ = 2.498, 3.802 mg. Subst. = 5.853 mg.; N/100 NaOH = 2.42 ccm.

Gef.: C = 56.54; H = 4.94; N = 2.49; Br = 16.31, CH₃O- = 12.80, 12.48; CH₃CO- = 17.78%.

Ber. für C₂₅H₂₄NO₃Br (490): C = 56.33; H = 4.90; N = 2.86; Br = 16.33; CH₃O- = 12.65; CH₃CO- (2) = 17.55 %.

Ber. für C₂₅H₂₆NO₇Br (532): C = 56.39; H = 4.89; N = 2.63; Br = 15.04; CH₃O- = 11.66; CH₃CO- (3) = 24.25.

Wir ziehen hauptsächlich auf Grund des Acetyl-, Methoxyl- und Bromgehalt die erste Bruttoformel vor.

Spec. Drehung: 0.5651 gr. Subst. 25 ccm. Chloroform. 1-dm. Rohr $\alpha = +0.20^\circ$

$$[\alpha]_D^{20} = +8.84^\circ$$

Beim Aufbewahren in der Luft, nimmt 1-Brom-diacetyl-sinomenin eine fade braune Farbe an. Es zeigt eine schöne, grüne Eisenchloridreaktion, aber es rührt nicht von dem freien Phenol her, weil dieselbe Farbenreaktion mit Silbernitrat,* oder beim blossen Lösen in Eisessig hervorgerufen wird. Bei weiteren Umwandlungen, wird die Substanz unkrystallisierend, so z. B. bei der Hydrolyse mit 10-proc. Salzsäure oder Natronlauge, bei der katalytischen Reduktion, oder bei der Acetolyse im Schliessrohr bei 180° . Diese Eigenschaft verhindert zur Zeit den weiteren Abbau.

Kali-schmelze. 1-Brom-diacetyl-sinomenin wird mit viel Kaliumhydroxyd und wenig Wasser bei $180^\circ \sim 200^\circ$ erhitzt. Das entwichene Amin wird in Salzsäure gefangen. Das Goldchloridsalz krystallisiert in schlanken Prismen. Schmp. $233 \sim 235^\circ$ (Zers.).

Anal.: Subst. = 2.908; Au = 1.489 mg. Gef.: Au = 51.20%.

Ber. für $C_2H_5NH_2 \cdot HCl \cdot AuCl_3$ (385): Au = 51.17%.

Das Platinchloridsalz ist nicht wohl charakterisierend. Daher wurde das Amin-chlorhydrat an seinem Chlorgehalt analysiert.

Anal.: Subst. = 0.0088; Ag Cl = 0.0155 gr. Gef.: Cl = 43.58%.

Ber. für $C_2H_5NH_2 \cdot HCl$ (81.5): Cl = 43.56%.

Ob es hier sich mit C_2H_7N oder $(C_2H_6N)_2$ behandelt, lässt sich nicht feststellen.

1-Brom-3-methoxyl-4, 6, 7 (?) - triacetoxyl-phenanthren (IV.) 1. Aus dem Sinomeneinjodmethyolat. Sinomeneinjodmethyolat wird, durch Kochen in Eisessig mit Silberacetat entjodiert, das Filtrat wird zum Trocknen abgedampft und dann acetolysiert. Die Isolierung von Phenanthrenkörper geschieht wie gewöhnlich. Umkrystallisiert aus Eisessig, stellt er Prismen dar, die bei 216° schmelzen. Ausbeute etwa 30 Proc.

2. Aus 1-Brom-sinomenein-Keton. Dieses Keton wird in gewöhnlicher Weise neun Stunden lang acetolysiert. Nach dem Abdampfen von Essiganhydrid i.V., wird der Rückstand mit viel Wasser behandelt. Das

* Nur ist es zu bemerken dass beim Eintragen des ca. 1/5 der berechneten Menge des Silbernitrats für 2H, diese Substanz die Eigenschaft, sich damit grün zu färben, verliert.

wasserunlösliche Teil wird in Methanol gelöst und einige Tage an sich überlassen. Der auskrystallisierte Phenanthren schmilzt bei 212°, aber der Schmp. wird nach mehrmaligem Umkrystallisieren aus Eisessig zu 216° erhöht. Die Mischprobe schmilzt auch bei 216°.

Anal.: Subst. = 0.0700; CO₂ = 0.1402; H₂O = 0.0236 gr. Subst. = 0.1712;

AgBr = 0.0704 gr. Subst. = 0.0495, 0.0536; AgJ = 0.0232, 0.0250 gr.

Subst. = 4.340, 3.726 mg.; N/100 NaOH = 2.60, 2.38 ccm.

Gef.: C = 54.62; H = 3.74; Br = 17.52; CH₃O- = 6.19, 6.16;

CH₃CO- = 27.75, 27.60 %.

Ber. für C₂₁H₁₇O₇Br (461): C = 54.66; H = 3.69; Br = 17.35; CH₃O- = 6.72;

CH₃CO- (3) = 27.98 %.

3-Methoxy-4, 6, 7 (?) - triacetoxxy-phenanthren (VI). Diese Substanz wird durch katalytische Reducierung von 1-Brom-3-methoxy-4, 6, 7 (?) - triacetoxxy-phenanthren dargestellt.⁽⁵⁾ Prismen von Schmp. 168°. Beilsteinreaktion negativ.

Anal.: Subst. = 0.0752; CO₂ = 0.1804; H₂O = 0.0315 gr.

Gef.: C = 65.41; H = 4.65 %.

Ber. für C₂₁H₁₈O₇ (382): C = 65.97; H = 4.71 %.

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Shiba, Tokyo.*

(5) Die Bedingungen wie in *Ann.*, **497** (1932), 295 angegeben.

STUDIES ON THE CONSTITUENTS OF THE VOLATILE OIL FROM THE WOOD OF CHAMAECYPARIS FORMOSENSIS, MATSUM. .

By Kinzô KAFUKU and Nobutoshi ICHIKAWA.

Received September 7th, 1933. Published December 28th, 1933.

This paper is a sequel to a previous one—"Studies on the constituents of the volatile oil from the leaf of *Chamaecyparis formosensis*, Matsum..",⁽¹⁾ and deals with the chemistry of the volatile compounds contained in the wood of the same plant. The material for examination was prepared on Mt. Ari from a freshly felled tree about 250 years old. The tree was freed from its leaves, twigs, branches, and bark, and then chopped into small slices $3 \times 10 \times 15$ cm. in size. These were put into an ordinary wooden still such as is employed in the manufacture of camphor, and were distilled with steam then and there. The yield of the volatile oil amounted to 1.10% on the average, the product representing a pale red viscous fluid of the characteristic odour, which darkened and thickened on standing. As a result of the authors' experiments, there were proved the presence of a strongly dextro-rotatory α -pinene, *d*-camphene, α -terpineol, *l*-cadinol, and allyl-protocatechin together with a number of newly discovered substances as listed below :—

(1) Benihiol $C_{10}H_{18}O$. A saturated primary alcohol of dicyclic nature, oxidizable into the corresponding aldehyde "benihial" $C_{10}H_{16}O$ (Semicarbazone m.p. $169^{\circ}C$.), and further into a crystalline acid "benihic acid" melting at $110^{\circ}C$.

(2) Benihinol $C_{10}H_{16}O$. An unsaturated primary alcohol of monocyclic nature, giving the corresponding aldehyde "benihinal" $C_{10}H_{14}O$ on oxidation.

(3) Benihinal $C_{10}H_{14}O$. The oxidation product of benihinol as stated above. Its oxime and semicarbazone are crystalline and melt at $65^{\circ}C$. and $216^{\circ}C$. respectively.

(4) *d*-Sesquibenihene $C_{15}H_{24}$. A dicyclic sesquiterpene closely akin to cadinene. It gives a crystalline dihydrochloride melting at $104^{\circ}C$. which is optically inactive, while the sesquiterpene regenerated from this dihydrochloride reverses the sign of its optical rotation and becomes laevo-rotatory. This regenerated hydrocarbon, on being acted on by hydrogen chloride,

(1) K. Kafuku and N. Ichikawa, this Bulletin, **6** (1931), 1.

gives the inactive dihydrochloride perfectly identical with that from the dextro-rotatory sesquibenihene.

(5) A primary sesquiterpene alcohol. Not yet isolated in a state of sufficient purity, but probably of the composition $C_{15}H_{24}O$. No crystalline derivatives could be obtained from this substance.

(6) A crystalline phenolic body. Melting at 127° – $128^{\circ}C$.

(7) A liquid acid. Composition corresponding to $C_{10}H_{16}O_2$.

Experimental.

The Crude Oil. The crude oil used in the experiments showed the following properties :—

Colour	Dark red	—
Refractive Index	n_D^{22}	1.5020
Specific Gravity	d_4^{22}	0.9685
Rotation	α_D^{22}	+4.76°
Acid Value	A.V.	6.13
Saponification Value	S.V.	24.0
Do. after Acetylation	S.V.a.A.	196.4
Specific Viscosity	η_{22}	67.7

Acids and Phenols. 1840 Gr. of the crude oil was shaken with an excess of 5% caustic soda solution on the machine for several hours, stood still, and then the aqueous layer separated. It was observed that the dark red colour of the oil passes over to the aqueous layer during this treatment. From this alkaline extract, acids and phenols were recovered in the usual manner and finally 12 gr. of acidic and 6 gr. of phenolic oils were obtained.

The acidic oil, after two consecutive fractionations in vacuo, exhibited the following properties :—

b.p.	146°–147°/7 mm. 263°–265°/764 mm.
n_D^{25}	1.5010
d_4^{19}	1.0635
A.V.	335.8
Mol.W. from A.V.	167
Ag in Ag-salt	39.5%
Mol.W. from Ag%	165.8

$$(C_{10}H_{16}O_2 = 168, C_{10}H_{14}O_2 = 166)$$

That it does absorb but little bromine, and that it is not easily acted on by dilute permanganate in cold, show that it is a saturated compound. Its chloride, amide, and anilide are all fluid. The chloride was distillable in

vacuo, boiling approximately at about 100°C. under 10 mm. pressure. The ammonium salt showed a melting point at about 150°C. The insufficiency of the material made it impossible to carry on the experiments further.

The phenolic oil was distilled under the atmospheric pressure into two fractions, the one boiling within 235°C., whilst the other boiling between 270° and 274°C. These, on cooling, deposited crystals, those from the former melting at 47°–48°C., (after purification from petroleum ether), and those from the latter at 127°–128°C. (after recrystallization from 80% alcohol). The dilute alkaline solution of the former reddened rapidly on exposure to the air and gave on benzylation a crystalline ester melting at 71°C., which in every respect coincided with allyl-pyrocatechin dibenzoate. The other one did not give the characteristic colour reaction on addition of alcoholic ferric chloride alone, but on further addition of a drop or two of hydrochloric acid a faint colouration set in. The determination of methoxy-groups was made but to negative result, also the esterification after Schotten-Baumann by means of benzoyl chloride did not succeed.

The Neutral Oil. The crude oil after removal of acids and phenols, showed following constants :—

d_4^{22}	0.9689	S.V.	16.9
n_D^{22}	1.5020	S.V.a.A.	184.3
α_D^{22}	+4.40°	γ_{22}	67.7

The oil was dried over anhydrous sodium sulphate and then it was fractionated five times consecutively under reduced pressures using Wiedemann's column of about 30 cm. length for dephlegmation. The fractions so divided exhibited the following characteristics :—

	b.p./5 mm.	d_4^{21}	n_D^{16}	α_D^{16}	Yield (gr.)
1	Up to 30°C.	0.8603	1.4707	+40.58°	6
2	30°—70°	0.9230	1.4886	+35.20°	2
3	70°—75°	0.9761	1.4963	+5.75°	7
4	75°—80°	0.9807	1.5000	+7.00°	21
5	80°—85°	0.9786	1.4986	+14.55°	13
6	85°—90°	0.9754	1.4988	+23.92°	106
7	90°—95°	0.9700	1.4964	+30.94°	396
8	95°—100°	0.9658	1.4960	+23.75°	272
9	100°—105°	0.9512	1.5010	+21.75°	20
10	105°—110°	0.9325	1.5080	+21.50°	13

	b.p./5 mm.	d_4^{21}	n_D^{16}	α_D^{16}	Yield (gr.)
11	110°—115°	0.9307	1.5100	+22.50°	124
12	115°—120°	0.9360	1.5106	+17.14°	62
13	120°—125°	0.9690	1.5108	—29.60°	5
14	125°—130°	0.9718	1.5112	—34.14°	9
15	130°—135°	0.9825	1.5120	—41.75°	250
16	135°—140°	0.9864	1.5136	—35.75°	153
17	140°—145°	0.9912	1.5179	—13.00°	5
18	145°—150°	0.9960	1.5216	—14.00°	85
19	150°—155°	1.0030	1.5238	— 2.50°	30
20	155°—159°	1.0087	1.5242	0°	20

The Terpenes. The fraction (1) consisted chiefly of terpenes as can be seen from the physical constants, so it was boiled over metallic sodium for some hours and then carefully distilled under atmospheric pressures into two portions, the one boiling between 156° and 157°C., and the other between 157.5° and 159.5°C., the properties of which were as follows :—

	b.p.	d_4^{16}	α_D^{16}	Yield (gr.)
(a)	156°—157.3°	0.8430	+39.30°	3.1
(b)	157.5°—159.5°	0.8434	+29.30°	2.3

The former, on being treated with dry hydrogen chloride gas in cold, gave a crystalline hydrochloride melting at 127°—128°C., which, on further treatment with nitrosyl chloride was converted into an unstable nitrosochloride in form of white needles. This nitrosochloride readily decomposed on filtering. The higher boiling fraction, on hydration according to Bertram and Walbaum, gave isoborneol, which was identified as such by preparing the characteristic phenylurethane melting at 137°C.

The Terpene Alcohols. The fractions ranging from (2) to (8) consisted chiefly of terpene alcohols with a little ester, so they were separately saponified, and the liberated alcoholic portions were collected, and were fractionally distilled. After eight consecutive fractional distillations under 10 mm. using Wiedemann's column as dephlegmator, the following eleven fractions were obtained :—

	b.p./10 mm.	d_4^{20}	n_D^{20}	α_D^{20}	Yield (gr.)
1'	86°—88°C.	0.9708	1.4982	— 4.0°	16
2'	88°—90°	0.9676	1.4982	— 1.6°	7
3'	90°—92°	0.9701	1.4974	+ 1.5°	9
4'	92°—94°	0.9662	1.4960	+12.0°	7
5'	94°—96°	0.9619	1.4946	+27.5°	13
6'	96°—98°	0.9644	1.4946	+44.0°	70
7'	98°—100°	0.9675	1.4944	+44.3°	40
8'	100°—102°	0.9688	1.4938	+38.4°	53
9'	102°—104°	0.9673	1.4934	+31.7°	41
10'	104°—106°	0.9766	1.4930	+28.0°	48
11'	106°—108°	0.9655	1.4938	+23.0°	276

Benihinol and Benihinal. The fraction (1') smelled like piperitone or some such aldehyde, so it was first shaken with 30% sodium bisulphite solution to get rid of the aldehydic component. The aqueous extract was then decomposed by means of alkali in the usual manner, and finally about 2 gr. of an oil (b.p. 86°–88°C./7.5 mm.; d_4^{17} 0.9391; n_D^{17} 1.4992) was obtained, exhibiting a remarkable reducing action on Tollen's solution and giving the characteristic colour reaction with Schiff's reagent. It gave a crystalline semicarbazone melting at 214°–215°C., and also a crystalline oxime melting at 64°–65°C. 0.3 Gr. of this aldehyde was digested with an excess of hydrogen peroxide and caustic potash solution at 60°–70°C., the turbidity ensuing at first gradually cleared up in course of time with formation of the corresponding potassium salt. This aldehyde was later proved to be identical with that which is obtained by oxidizing the fraction (6'). From the residual oil no crystalline derivatives could be obtained.

Nextly, the fractions (2') to (7') were separately boiled with phthalic anhydride in benzene solution, the resulting ester acids recrystallized from a mixture of ether and petroleum ether and finally saponified and distilled with steam. The main product amounted to 60 gr., and collected between 96° and 98°C. under 10 mm. pressure on fractionation. The properties of this main fraction as well as the results of analyses are shown below :—

Characteristic Constants.

b.p.	96.3°—97.7°C./10 mm. 216°C./766 mm.
d_4^{19}	0.9790
$n_D^{18.5}$	1.4960
α_D^{19}	+46.80°

Absorption of Bromine.

Substance 0.257 absorbed 0.529 bromine.

Calculated as $C_{10}H_{16}O \mid _2$ 0.540.

Elementary Analyses.

Substance	CO ₂	H ₂ O	C%	H%
0.2298	0.6670	0.2142	79.15	10.35
0.2066	0.5975	0.1947	78.87	10.47
Calculated as $C_{10}H_{16}O$			79.0	10.4

The Ester-Phthalic Acid and Its Silver Salt.

m.p.	107°—108°C.
Acid Value	190
Do. as $C_{18}H_{20}O_4$	187
m.p. of Ag Salt	88°—90°C.
Ag % in Ag Salt	25.92%
Do. as $C_{18}H_{19}O_4Ag$	25.86%

From the forgoing, the chief constituent of the fractions seems to consist of a primary alcohol $C_{10}H_{16}O \mid _2$, so that, in order to ascertain this point, the substance was oxidized by means of chromic acid. Thus, 6 gr. of the substance was dissolved in 30 c.c. of glacial acetic acid, to which a calculated amount of chromic acid in the same solvent was slowly added, vigorously stirred keeping the reaction temperature within 15° and 20°C. Finally the whole mass was warmed to about 50°C. and then thrown into cold water. The oily substance separating out was caught by ether, the ethereal solution washed with 2% sodium bicarbonate solution and then treated with 30% sodium bisulphite solution. The bisulphite layer was then carefully separated, strong alkali added thereto, the regenerated aldehydic substance ethered out, washed, dried, evaporated, and then fractionated under reduced pressures. The main portion thus obtained exhibited the following characteristics:—

b.p.	87°C./8 mm.
$n_D^{15.5}$	1.5000
d_4^{16}	0.9893
Molecular Refraction	44.59
Do. as $C_{10}H_{14}O \mid _2$	45.23

This aldehyde was proved to be perfectly identical with that isolated from fraction (1)—Cp. benihinal—the respective semi-carbazones melting at 216°C., and showing no depression of the melting temperature on 'mischproben.'

Analyses. Substance (mg)	Nitrogen (c.c.)	t°	p (mm)	N%
3.63	0.683	27	757	20.17
4.77	0.902	28	758	20.20
$C_{10}H_{14}NNH-CO-NH_2$ requires				20.3

To the alcohol the authors propose the name 'benihinol,' and to the aldehyde 'benihinal.'

Benihiol and the Oxidation Products. The fractions (8') to (11') when treated with phthalic anhydride in benzene solution, give esterphthalic acids, and if such be recrystallized from a mixture of ether and petroleum ether, from all of them, a crystalline esterphthalic acid melting at 123°–125°C. results, whose silver salt invariably decomposing at 165°C. Thus, from these fractions the alcohol was extracted as esterphthalic acid and such was ultimately saponified. The saponified mass was then distilled with steam, and the oily distillate finally fractionated in vacuo.

	b.p./10 mm.	b.p./atm.p.	d_4^{21}	n_D^{21}	α_D^{22}	Yield (gr.)
(a)	106°–108°C.	234°–235°C.	0.9776	1.4903	+23.15°	135
(b)	108°–109°C.	234°–235°C.	0.9776	1.4910	+22.00°	85
(c)	109°–111.6°C.	235°–237°C.	0.9779	1.4910	+25.00°	45

Each one of these fractions gave the same esterphthalic acid on treatment with phthalic anhydride in benzene solution, which after purifications could be obtained in form of a compact crystalline mass. This esterphthalic acid was optically active and showed a specific rotation +4.55° (1.9 gr. in 8.6 c.c. of alcohol). Its silver salt represented a beautiful needle crystal which decomposed on heating at about 165°C. The titrimetric determination of its acid value agreed fairly well with the supposed composition $C_{18}H_{22}O_4$. Namely, for neutralizing 0.250 gr. of the acid with a decinormal caustic soda solution, 8.38 c.c. of the latter was consumed in place of 8.28 c.c., the amount theoretically required.

The absorption of bromine observed with these fractions varied considerably, but the amount was very small compared with the value as required for one double linking per molecule, so it might well be imputed to the presence of certain impurities.

	Substance	Br absorbed	Br Number
(a)	0.2230	0.0190	0.085
(b)	0.3136	0.0082	0.026
(c)	0.2024	0.0069	0.033
	Required for $C_{10}H_{18}O$ $\frac{1}{1}$		1.039

Elementary analyses.

Substance	CO ₂	H ₂ O	C%	H%
0.1272	0.3673	0.1302	78.75	11.37
0.1487	0.4283	0.1580	78.55	11.80
0.1542	0.4441	0.1616	78.54	11.64
0.1315	0.3749	0.1389	77.76	11.74
0.1542	0.4399	0.1636	77.81	11.79
0.1863	0.5317	0.1950	77.84	11.63
0.1444	0.4126	0.1528	77.92	11.76
C ₁₀ H ₁₈ O requires			77.9	11.7
C ₁₀ H ₁₆ O requires			79.0	10.4

Oxidation by KMnO₄. These fractions are but slowly oxidized by potassium permanganate in cold but in the presence of KOH somewhat more rapidly. Thus, 10 gr. of the oil was shaken on the machine with 25 gr. KMnO₄, 11 gr. KOH, 700 c.c. cold water, and 500 gr. shaved ice for four hours, then the unchanged oil and the neutral products of oxidation were driven off by steam, manganic slime was then filtered, and the filtrate was allowed to evaporate in an atmosphere of carbon dioxide. To the concentrated solution thus obtained an excess of dilute sulphuric acid was added, and the mass was ethered out, ethereal solution evaporated. The residue represented a sour-smelling viscid mass, boiling at 193°–195°C. under 7 mm. pressure. The distilled oil, on standing overnight in a cool place crystallized in needles. The crystals could be recrystallized from hot water and showed a melting point 175°–175.5°C.

Oxidation by Chromic Acid. A solution of 30 gr. of the forgoing alcohol in 100 c.c. of glacial acetic acid was prepared, into which a solution of 21 gr. of CrO₃ in the same solvent was allowed to drop down under stirring, keeping the reaction temperature below 15°C. for the whole while. After all the oxidizing agent had been added, the mass was warmed to about 50°C. and kept at that temperature for half an hour. It was then treated with sodium bicarbonate and then with sodium bisulphite in the usual manner, and thus acidic and aldehydic portions were separately obtained. The crude acid was crystalline, which after purifications—sublimation in a partial vacuum followed by recrystallization from 60% alcohol—melted at 110°C. This acid, on titration with alcoholic potash and on analyses of its silver salt as well as the elementary analyses, agreed fairly well with the composition C₁₀H₁₆O₂.

The acid value.

0.3000 gr. acid neutralized by 0.0986 gr. KOH
 Calculated value for C₁₀H₁₆O₂: 0.1000 gr. KOH

The silver salt.

Ag %	39.28	Calculated for $C_{10}H_{15}O_2Ag$	39.24
M.W. observed =	167.8	$C_{10}H_{16}O_2 =$	168.0

Elementary analyses.

Substance	CO ₂	H ₂ O	C%	H%
0.1013	0.2660	0.0887	71.61	9.72
0.1118	0.2918	0.0970	71.81	9.64
	$C_{10}H_{16}O_2$ requires :		71.48	9.52

The aldehydic portion obtained as bisulphite compound was treated with dilute caustic soda, ethered out, ether evaporated, and distilled in vacuo. It distilled over at 83°–85°C. under 9.5 mm. pressure, and represented a colourless oil lighter than water. It was very unstable and was liable to oxidize into the forgoing acid on exposure to air. It was easily soluble in sodium bisulphite solution and was very sensitive to Schiff's reagent and Tollen's solution. The semicarbazone could easily be prepared and it melted after purification at 169°C.

The analyses.

Substance	N ₂ (c.c.)	t°	p	N%
2.72 mg.	0.512	30	762.3	19.99
4.96 mg.	0.934	30	761.0	19.96
$C_{10}H_{16} = N-NH-CO-NH_2$ requires				20.10

From the forgoing, it becomes clear that the chief constituent of the fractions (a), (b) and (c) is a primary terpene alcohol, dicyclic in structure, corresponding to a composition $C_{10}H_{18}O$. The terpene alcohol, as well as the corresponding aldehyde and acid have never been mentioned in the literature, so the authors proposed the names "*benihiol*," "*benihial*," and "*benihic acid*" for them.

The Dehydration of Benihiol. (i) *Dehydration by means of 50% Sulphuric Acid.* 30 Gr. benihiol was warmed with 100 gr. of 50% sulphuric acid on the water-bath to 80°–90°C. under vigorous stirring. After two hours' treatment, the whole was diluted with water and then distilled with steam. The pale yellow oil which distilled over was separated from water, dried, and then redistilled over metallic sodium. Thus, the following two fractions were obtained which showed the constants :—

	b.p./18 mm.	n_D^{27}	d_4^{27}	rotation
(i)	56°–58°C.	1.4693	0.8524	nil.
(ii)	58°–60°C.	1.4740	0.8524	nil.

Nextly, they were rectified under the atmospheric pressure and about 5 gr. of a colourless oil was obtained which smelled decidedly like terpenes.

b.p./757 mm.	162°—163°C.	d_4^{27}	0.8530
n_D^{27}	1.4693	M.R. obs.	44.43
Rotation	nil.	Do. as $C_{10}H_{16}$ $l=1$	43.53

This terpene, on oxidation, gave no defined products so as to identify itself with any known terpenes in the literature.

(ii) *Dehydration with Phosphoric Acid.* Benihiol, 30 gr. was warmed on the water-bath with syrupy phosphoric acid, 40 gr. The product in this case was similar to those in the forgoing experiment. The hydrocarbon boiled under 50 mm. pressure at 82°–84°C., the yield amounting to only 5 gr., and the remainder mostly passing into resinous mass. Nextly it was dehydrated in the following manner: viz., benihiol, 30 gr., was kept in a dropping funnel A, which was allowed to drip down into a double-necked flask B, containing 40 gr. of syrupy phosphoric acid at 150°C. and 15 mm.

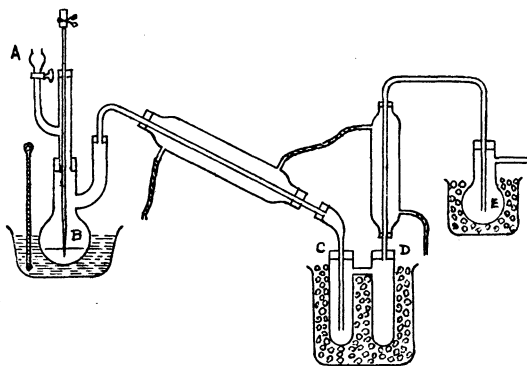


Fig. 1.

pressure. The rate of flow of benihiol was so adjusted that about 1 c.c. per minute dropped down into the acid. Thus, as soon as these drops of benihiol came in contact with the hot acid, they parted with their water to be distilled instantly over to the receivers C, D and E. After all benihiol reacted with the acid, the content of those receivers was collected, separated from water, dried over metallic sodium, and rectified in vacuo. In this way, about 20 gr. of a colourless mobile oil was obtained.

b.p./760.8 mm.	172.4—173°C.	Rotation	nil.
d_4^{23}	0.8537	Bromine value obs.	1.071
$n_D^{21.5}$	1.4730	Do. calc. as $C_{10}H_{16}$ $l=1$	1.176

This product was a little different from that obtained by dehydration with 50% sulphuric acid, however, all efforts to get crystalline derivatives therefrom were futile.

(iii) *Dehydration with Zinc Chloride.* Benihiol, 5 gr., was heated on the oil-bath to 160°–170°C. with an equal weight of anhydrous zinc chloride for an hour. After cooling, the whole mass was thrown into water, the separating oil recovered and rectified over metallic sodium. Thus, a hydrocarbon with the following characteristics was obtained :—

b.p./760 mm.	172°–173°C.
d_4^{32}	0.8493
n_D^{32}	1.4670

Esters of Benihiol. (i) *Benihyl Formate.* A mixture of an equal weight of benihiol and pure formic acid was treated with a current of dry hydrogen chloride, warmed on the water-bath for an hour, cooled, washed with water, shaken with a mixture of ether and very dilute alkali, dried over anhydrous sodium sulphate, ether evaporated, and then rectified in vacuo. Thus an ester with the following characteristics was obtained :—

b.p./10 mm.	101°–103°C.	M.R. observed	50.72
n_D^{32}	1.4720	Do. calc. as $C_{11}H_{18}O_2$	50.13
d_4^{32}	1.005	Sap. Value observed	311.3
α_D^{32}	+20.50°	Do. calc. as $C_{11}H_{18}O_2$	308
Br-Value	nil.		

(ii) *Benihyl Acetate.* Benihiol was acetylated with an excess of acetic anhydride in presence of anhydrous sodium acetate at 140°–150°C., and the product was purified in the ordinary manner :—

b.p./10 mm.	107°–108°C.	M.R. observed	53.38
n_D^{32}	1.4680	Do. calc. as $C_{12}H_{20}O_2$	54.75
d_4^{32}	0.9888	Sap. Value observed	278.8
α_D^{32}	+22.50°	Do. calc. as $C_{12}H_{20}O_2$	285
Br-Value	nil.		

(iii) *Benihyl Benzoate.* Benihiol, 10 gr., was dissolved in 80 c.c. of toluene, anhydrous potassium carbonate, 14 gr. and benzoyl chloride, 10 c.c. added, and warmed on the water-bath until evolution of CO_2 ceased, then the whole was thrown into cold water, and the oily later was separated. The ester was then distilled under reduced pressure.

b.p./5 mm.	161°–162°C.	M.R. observed	76.8
n_D^{30}	1.5233	Do. calc. as $C_{17}H_{22}O_2$ ₃	74.24
d_D^{30}	1.0289	Sap. Value, observed	204.3
α_D^{30}	+15.00°	Do. calc. as $C_{17}H_{22}O_3$	202.1

(iv) *Benihyl Propionate*. The propionic ester was prepared just as the formic ester. Its properties were as follows :—

b.p./10 mm.	117°–120°C.	α_D^{22}	+14.24°
n_D^{22}	1.4685	Sap. Value, observed	249
d_4^{22}	0.9825	Do. calc. as $C_{13}H_{22}O_2$	257

Methyl-Benihyl Ether. Benihiol 5 gr. was dissolved in 15 c.c. of toluene, and was boiled under reflux on an oil-bath with 0.7 gr. of metallic sodium. After all the sodium passed away into the alkoholate, the mass was cooled, and then 7 gr. of methyl iodide was added thereto, and was warmed under reflux for some hours. Then the mass was washed with water, ethered out, dried, ether and toluene expelled by distillation, and then the residual oil was fractionated in vacuo. The distillate, on rectification over metallic sodium, showed the following properties :

b.p./11 mm.	83°–84°C.	d_D^{20}	0.9096
n_D^{20}	1.4638	α_D^{20}	+24.00°

Halides of Benihiol. (i) *Benihyl Chloride*. Benihiol, 10 gr., dissolved in petroleum ether, was allowed to drop slowly on phosphorus pentachloride, 13 gr., kept under a layer of the same solvent. After all had been added, the whole mass was heated to 50°–70°C. until all the solid matter disappeared. Then the solvent and phosphorus oxychloride thereby produced were distilled off, the residue rectified under a pressure of 10 mm., and thus 6 gr. of a colourless liquid was obtained :—

b.p./10 mm.	94°–97°C.	α_D^{21}	+11.0°
d_4^{21}	1.007	M.R. observed	49.15
n_D^{21}	1.4860	Do. calc. as $C_{10}H_{17}Cl$	48.84

(ii) *Benihyl Iodide*. Benihiol, 20 gr., red phosphorus, 5.9 gr., and 30 gr. of 57% hydriodic acid were put into a sealed tube and was heated in a bomb furnace at 130°C. for the first two hours, and then at 150°C. for the next three hours. The product after cooling was freed from the admixing terpenes by distillation, and then was dissolved in ether, shaken with aqueous sulphurous acid in order to get rid of free iodine, washed with water, dried over anhydrous sodium sulphate, and ultimately the ether was carefully distilled off. The pale yellowish red liquid thus obtained was fairly difficultly soluble in 90% alcohol and in glacial acetic acid, also in pure methyl alcohol, but readily soluble in ether, absolute alcohol, carbon tetrachloride, benzene, etc., etc. It exhibited the following properties :—

d_4^{28}	1.2596	I-content	46.54
n_D^{28}	1.5215	Do. as $C_{10}H_{17}I$	48.11

It was likely that it contained some unchanged benihiol along with the iodide, and the authors tried to distil it in vacuo but with bad results.

Reduction of Benihiol. (i) *Catalytic Reduction of the Dehydrated Product.* The dehydrated product obtained by the action of phosphoric acid on benihiol was allowed to absorb hydrogen in presence of palladium chloride. The absorption proceeded smoothly until the absorption of hydrogen corresponded to one molecule of it against one of benihiol and the product obtained showed the following constants:—

b.p./760 mm.	162°	M.R. obs.	44.79
n_D^{28}	1.4608	Do. calc. as $C_{10}H_{18}$	43.98
d_4^{22}	0.8449		

(ii) *Catalytic Reduction of Benihyl Chloride.* Nextly benihyl chloride was catalytically reduced just as above, using about 1% its own weight of palladium chloride as catalyst. The product obtained was a little different from the hydrocarbon in the preceeding experiment, and its properties after rectification were as follows:—

b.p./760 mm.	165°–167°C.	M.R. obs.	44.31
n_D^{21}	1.4648	Do. as $C_{10}H_{18}$	43.98
d_4^{21}	0.8603		

(iii) *Catalytic Reduction of Benihyl Iodide.* The iodide above described (40 gr.) was dissolved in 250 c.c. of 10% alcoholic potash, and was shaken in an atmosphere of hydrogen with 5 gr. of $Pd-BaSO_4$ at 30°C., 758 mm. Thus it absorbed 2830 c.c. of hydrogen instead of 3400 c.c. which is the theoretical amount. It was likely that part of the iodide had been converted into the corresponding alcohol so that the product was fractionated under reduced pressure and about 8 c.c. of a fraction 54°–56°/30 mm. and 6 c.c. of another 109°–130°/10 mm. were obtained. This latter fraction, on examination, was decidedly alcoholic and obviously represented an impure benihiol, so that the former fraction was carefully boiled over metallic sodium under reflux, and then it was rectified in vacuo. The hydrocarbon thus obtained, exhibited the following constants:—

b.p./753.4 mm.	165°C.	α_D^{28}	+7.5°
Do./45 mm.	75°C.	Br. absorbed	nil.
d_4^{28}	0.846	M.R. obs.	44.25
n_D^{28}	1.4550	Do. calc. as $C_{10}H_{18}$	43.98

Analyses :

Substance	CO ₂	H ₂ O	C%	H%
0.1561	0.4966	0.1773	86.78	12.68
0.1209	0.3865	0.1398	86.47	12.69
C ₁₀ H ₁₈ requires :			86.96	13.03

This hydrocarbon, as far as its boiling point and density are concerned, seems to be related to that which had formerly been obtained by Sabatier and Sendrens⁽²⁾ by the reduction of camphene with hydrogen in presence of nickel catalyser.

Oxidation of Benihiol. (i) *Formation of Benihial.* Benihiol, as has been described, when oxidized with chromic acid, gives benihial and benihic acid but, in this case, the best part of the product is benihic acid. In order to obtain the aldehyde in a better yield, it is best to use Beckmann's solution. Thus, 20 gr. of benihiol was dissolved in 30 c.c. of glacial acetic acid, then, 100 gr. of ice-cold Beckmann's solution was added thereto, stood still for a while, then warmed at 40°–45°C. for twenty minutes, and finally the whole mass was thrown into cold water and extracted with ether. The ethereal solution was washed with water, then with dilute sodium bicarbonate solution, dried over anhydrous sodium sulphate, ether distilled away. The residual aldehydic substance amounted to about 12 gr. which could be distilled in vacuo. It represented a colourless oil after rectifications and showed the following characteristics :—

b.p./ 9.5 mm.	76°–77.8°
d_4^{20}	0.9698
n_D^{20}	1.4770
α_D^{20}	+ 15.0°
Semicarbazone m.p.	169°C.
Do. (0.0457 gr. in 3.5 cc. CHCl ₃)	+151.6°
Phenylhydrazone m.p.	122°C.
Do. (0.0498 gr. in 2.5 cc. CHCl ₃)	+167.5°
Oxime	fluid

α -Terpineol. The alcoholic fractions (2) to (7), after repeated treatment with phthalic anhydride, became practically free from all primary alcohols, and such was then fractionated under 10 mm. pressure :—

(2) *Compt. rend.* **132**, 1256; *Ann. chim. Phys.*, [8] **4**, 391.

	b.p./10 mm.	d_4^{18}	n_D^{18}	α_D^{18}	Yield (gr.)
(i)	86°—88°C.	0.9836	1.4982	—	3
(ii)	88°—90°C.	0.9633	1.4866	—	2
(iii)	90°—94°C.	—	—	—	2
(iv)	94°—98°C.	0.9395	1.4831	+35.7°	8
(v)	98°—100°C.	0.9397	1.4836	+43.6°	12
(vi)	100°—118°C.	0.9680	1.4953	+23.0°	28

On examination of these fractions the first was proved to consist chiefly of benihinal (semicarbazone m.p. 214°–216°C.), and the last one to represent benihol (benihic acid m.p. 110°C.). The fourth and the fifth exhibited constants similar to α -terpineol, so, they were oxidized with potassium permanganate to obtain 1-2-8-trioxy-menthane therefrom. The oxidation was carried out exactly as Wallach prescribed with 6 gr. of the substance, and a crystalline product with m.p. 121°C. was obtained. This substance, on mixing with 1-2-8-trioxy-menthane showed no depression of the melting point. Furthermore, on preparing the nitrosochloride directly from the fractions, α -terpineol nitrosochloride m.p. 112°C. was obtained.

The Sesquiterpenes. The fractions (10) to (13) in the foregoing table (p. 373-374) namely, those fractions boiling between 105° and 125°C. under 5 mm. pressure seemed likely to represent sesquiterpenes as their saponification number as well as that after acetylation were very small, so they were boiled with metallic sodium for several days under reflux, and then they were rectified. The greater part of the distillate, on such treatment, collected between 127° and 131°C., and showed the following properties:—

b.p./10 mm.	127°—131°C.	α_D^{24}	+35.7°
d_4^{24}	0.9162	M.R. obs.	66.45
n_D^{24}	1.5088	M.R. as $C_{15}H_{24} F_2$	66.15

This was then repeatedly fractionated with Widmer's dephlegmator on, under 10 mm. pressure, and thus it was divided into the following five fractions:—

	b.p./10 mm.	d_4^{21}	n_D^{21}	α_D^{21}	M.R.	gr.
(l)	128.5°—130°C.	0.9176	1.5081	+22.0°	66.26	25
(m)	130°C.	0.9177	1.5088	+31.6°	66.23	30
(n)	130°C.	0.9182	1.5093	+37.0°	66.35	35
(o)	130°C.	0.9194	1.5095	+38.0°	66.30°	35
(p)	130°—131°C.	0.9232	1.5097	+40.2°	66.05	38

On testing Liebermann's reaction with each of these fractions, each showed yellowish green colour at first which passed gradually into purple-violet.

If acetic anhydride be used as solvent, the initial colouration was bright green and changed gradually into blue. With chloroform as solvent the colouration at first was yellow green which passed to orange yellow with lapse of time.

(i) *Action of Hydrogen Halides.* (a) *Action of Hydrogen Chloride.* These fractions, dissolved in absolute ether, were exposed to the action of dry hydrogen chloride in cold. From all of the fractions crystalline hydrochloride m.p. 103° – 104°C . deposited which after purification if mixed half in half with cadinene hydrochloride, m.p. 117°C ., showed a considerable depression of the melting point, viz. the mixture melting around 110°C .

(b) *Action of Hydrogen Bromide.* All fractions, if dissolved in glacial acetic acid, and a proper quantity of hydrogen bromide in form of 48% aqueous acid gradually added thereto, and shaken vigorously, solidified into a crystalline mass. The crystalline mass was stood still overnight in an ice chamber, filtered while cold, washed with cold alcohol, and was recrystallized from acetone. Alcohol and ethyl acetate were not suitable solvents for the recrystallization, as the crystals were liable to decompose on dissolution in these solvents. The melting point of the pure recrystallized product was 112° – 114°C ., which if mixed with pure cadinene dihydrobromide, m.p. 125°C ., showed a remarkable depression of the melting point, viz., the mixture melting around 98° – 106°C . It was optically inactive.

(c) *Action of Hydrogen Iodide.* Glacial acetic acid solutions of the fractions, on treatment with hydriodic acid s.g. 1.56 in cold, deposited a large amount of crystalline hydriodide,—a remarkable absorption of heat was experienced during the reaction. This hydriodide, after filtration, was washed with cold alcohol, dried, and then recrystallized from acetone. The pure product melted at 117° – 118°C ., but seemed likely to be rather unstable, and was apt to decompose, even if kept dry in vacuo. It was also optically inactive. The pure crystal mixed with pure cadinene dihydriodide, melted around 96° – 103°C .

(ii) *The Nitrosite, the Nitrosate, and the Nitrosochloride.* Preparations of nitrosite, nitrosate, and nitrosochloride were tried with each of the fractions, but with no fruitful results.

(iii) *The Regeneration of the Sesquiterpene from the Hydrochloride.* The hydrochloride, m.p. 103° – 104°C ., 7 gr., was dissolved in 30 c.c. of glacial acetic acid, 7 gr. of anhydrous sodium acetate added, boiled under reflux for some hours and the regenerated hydrocarbon was rectified by distillation under reduced pressures. The sesquiterpene showed the following characteristics :—

b.p./10 mm.	129°—130°C.	α_D^{21}	—10.32°
d_4^{21}	0.9191	M.R. obs.	66.10
n_D^{21}	1.5074	Do. as $C_{15}H_{24} =2$	66.15

On treating this sesquiterpene with hydrogen chloride, the selfsame hydrochloride melting at 103°–104°C. resulted, and on observing the mixed melting point with the original hydrochloride, no lowering of the melting point was to be found. It was optically inactive.

On experimenting with hydrogen bromide or hydrogen iodide, the identical hydrobromide or hydriodide resulted, and these also, on isolating the sesquiterpene as above, equally gave rise to laevo-rotatory sesquiterpene. The purest sample of the regenerated sesquiterpene obtained from the dihydrochloride from the fraction (p) exhibited the following constants:—

b.p./10 mm.	130°—131°C.	α_D^{21}	—40.34°
d_4^{21}	0.9189	M.R. obs.	66.17
n_D^{21}	1.5080	Do. as $C_{15}H_{24} =2$	66.15

That this sesquiterpene reverses its sign of optical rotation through a transformation into an inactive hydrochloride, is most remarkable, and it reminds us of the behaviour of *d*-cadinene, which transforms into the *l*-modification through formation of laevo-rotatory hydrochloride.

(iv) *Catalytic Reduction*. The fraction (p), 2.707 gr., was dissolved in 50 c.c. of glacial acetic acid, 0.03 gr. of freshly prepared platinum black added thereto, was shaken in an atmosphere of pure hydrogen at 25°C., 762.3 mm. pressure. In about three hours it absorbed 679 c.c. of the gas, which amount is a little too high—by about 5%—but practically corresponds with the calculated quantity for saturating the two ethylene linkages. The reduced product, after rectifications, showed the following constants:—

b.p./10 mm.	123°—124.2°C.	α_D^{21}	—9.52°
$n_D^{20.5}$	1.4820	M.R. obs.	66.92
d_4^{21}	0.8860	Do. as $C_{15}H_{28}$	67.07

(v) *Reduction by Sodium and Alcohol*. 4 Gr. of the fraction (p) was treated with 10 gr. of metallic sodium and hot amyl alcohol and heated under reflux for many hours, but no perceptible change took place. The substance recovered from the reaction mixture proved to be quite identical with the starting material.

(vi) *Bromine Number*. The fraction (p) 0.2207 gr. was treated with an excess of a standardized solution of bromine in carbon tetrachloride and then was titrated back with thiosulphate. The consumed bromine in this

case, amounted to 0.3459 gr., while that calculated for the same weight as $C_{15}H_{24}|_2$ is 0.3458 gr.

(vii) *Racemization by Sulphuric Acid.* The fraction (p), on being shaken with 50% sulphuric acid, loses its optical activity with lapse of time. The features of such racemization with respect to time and temperature are as follows :—

Hours	0	2	4	6	8	10	12	14	28
Temp.	20°	20°	20°	80°	80°	80°	80°	80°	80°
α_D^{20}	+40°	+36°	+30°	+25°	+18°	+14°	+7°	+1.4°	+0.35°

(viii) *Dehydrogenation.* The sesquiterpene was treated, exactly as Ruzicka had done in the case of dehydrogenating cadinene, with sulphur, and the product of reaction distilled. It came over at 287° to 291°C., with a refractive index n_D^{20} 1.5820, the melting points of the picrate and styphnate being 115°C. and 138°–139°C. respectively. They did not show any depression of melting points if mixed with cadalin picrate or cadalin styphnate.

Thus, it becomes obvious, that the sesquiterpene is one which contains a cadalin nucleus and two double bonds that are not conjugated, but different from ordinary cadinene. To this sesquiterpene the authors propose the name “*sesquibenihene*,” whose chemical constitution will be discussed on another occasion.

The Sesquiterpene Alcohols. The fractions (15), (16), (17) and (18) look likely to consist of sesquiterpene alcohols from their constants. On observing their saponification numbers before and after acetylation, they gave the following values :—

	Sapo. V.	Sapo. V. after Acetylation
(15)	17.3	143.8
(16)	17.2	143.6
(17)	—	—
(18)	11.7	200.7

(i) *The Tertiary Alcohol.* The fractions (15) and (16) were separately saponified by means of alcoholic potash, the saponified product after due treatment was rectified in vacuo. Thus, from both of these, the same product resulted, the physical properties of which are given below :—

b.p./10 mm.	149°–152°C.	Br. Value obs.	0.737
d_4^{18}	0.9818	Do. calc. as $C_{15}H_{26}O _1$	0.720
n_D^{16}	1.5122	M.R. obs.	67.87
α_D^{18}	–33.00°	Do. as $C_{15}H_{26}O _1$	68.03

The substance, on Liebermann's test, with chloroform, glacial acetic acid, and acetic anhydride as solvents, showed respectively bordeaux, violet, and blue colours.

(a) Action of Hydrogen Chloride. The substance was dissolved in ether (1/1) and exposed to the action of dry hydrogen chloride under cooling. Thus, after a while, beautiful needle crystals separated out in abundance, which after recrystallizations from alcohol showed a melting point 117°C . These crystals were proved to be identical with cadinene dihydrochloride, as they showed no depression of the melting temperature if mixed with a pure specimen of cadinene dihydrochloride.

(b) Dehydration by Formic Acid. The substance 8 gr. was boiled under reflux with 25 gr. of pure formic acid for two hours. Then the mass was thrown into cold water and the oil separating out was collected and rectified. The product represented a sesquiterpene with the following properties :

b.p./10 mm.	$126^{\circ}\text{--}127^{\circ}\text{C}$.	m.p. of Dihydrochloride	117°C .
d_4^{17}	0.9181	M.R. obs.	66.48
n_D^{17}	1.5103	Do. as $\text{C}_{15}\text{H}_{24} _{=2}$	66.15
α_D^{17}	$+5.6^{\circ}$		

The dihydrochloride mentioned above also proved to be identical with cadinene dihydrochloride.

(c) Action of Phthalic Anhydride. The substance, on treatment with phthalic anhydride either in benzene solution or directly at $120^{\circ}\text{--}130^{\circ}\text{C}$., no ester formation was observable. Thus, it seems likely that this alcohol is tertiary in structure, and closely related to cadinol of Semmler and Jonas⁽³⁾ as well as to taiwanol which one of the present authors⁽⁴⁾ (K) had isolated from the volatile principle of Formosa cedar or *Taiwania Cryptomerioides* Hay.

	The Substance in question	Cadinol (Semmler)	Taiwanol (Kafuku)
b.p.	$149^{\circ}\text{--}152^{\circ}/_{10}$	$155^{\circ}\text{--}165^{\circ}/_{15}$	$141^{\circ}\text{--}143^{\circ}/_6$
d_4^{20}	0.9802	0.9720	0.9772
n_D	1.5122 (₁₆)	1.50702 (₂₀)	1.5045 (₃₀)
α_D^{20}	-33.00°	$+22^{\circ}$	-42.56°
M.R. obs.	67.87	67.97	67.88
m.p. of phenyl urethane	—	—	$134^{\circ}\text{--}135^{\circ}\text{C}$.

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

(4) This Bulletin, **6** (1931), 7.

(ii) *The Primary Alcohol.* The fraction (18), after saponification by an excess of alcoholic potash, was rectified in vacuo. The main portion exhibited the following properties :—

b.p./10 mm.	162°—164°C.	Br. V.	1.19
b.p./758 mm.	294°—296°C.	Do. calc. as $C_{15}H_{26}O \equiv$	0.721
d_4^{15}	0.9896	M.R. obs.	68.18
n_D^{15}	1.5200	M.R. calc. as above	68.13
α_D^{16}	—13.00°		

On being acted on by hydrogen in presence of platinum black, 0.4720 gr. of the substance absorbed 537.6 c.c. of the gas under 758.3 mm. at 18°C. The calculated quantity for the above amount being about 4% lower than this value.

(a) *Colour Reaction.* The dilute chloroformic solution of the sesquiterpene, on addition of a drop of concentrated sulphuric acid, assumes beautiful crimson colour which passes with time to reddish brown. The glacial acetic acid solution under the same conditions is coloured purple red at first and passes into blue, while the solution in acetic anhydride takes the green colour which changes into blue.

(b) *Action of Hydrogen Chloride.* On passing dry hydrogen chloride gas into the ethereal solution (1/1), no dehydrating action is perceptible, and no separation of crystalline substance takes place.

(c) *Action of Formic Acid.* On boiling the sesquiterpene alcohol with pure formic acid under reflux, no dehydrating action took place, but formation of the formic ester was observed.

(d) *Action of 50% Sulphuric Acid.* On stirring the substance vigorously with 50% sulphuric acid, some sesquiterpene is formed but the yield is very poor, most part of the substance remaining unchanged. A small portion passes at the same time into a resinous mass.

(e) *Action of Phthalic Anhydride.* On boiling it with a calculated amount of phthalic anhydride in benzene solution on the water-bath for 2 hours, it is converted almost quantitatively into the acidic phthalate. Thus, after eliminating the unchanged portion by ethering out, the semi-ester was saponified with alcoholic potash, and about 86% of the pure sesquiterpene alcohol was obtained, which after rectifications exhibited the following constants :—

b.p./10 mm.	163°C.	α_4^{22}	-12.00°	
b.p./760 mm.	294°C.	M.R. obs.	68.16	
d_4^{22}	0.9890	Do. calc. as C ₁₅ H ₂₆ O ₁	68.13	
n_D^{22}	1.5192			
Analyses.				
Substance	CO ₂	H ₂ O	C%	H%
0.2154	0.6384	0.2059	80.83	10.58
0.2237	0.6737	0.2214	80.34	10.76
	C ₁₅ H ₂₄ O requires :		81.82	10.91
	C ₁₅ H ₂₆ O requires :		81.08	11.71

These data show that the substance under investigation may not be a simple alcohol but a mixture of alcohols, so various attempts were made in order to carry out their separation but without result.

Summary.

(i) The volatile oil from the wood of *Chamaecyparis formosensis*, Matsum., or Formosa cypress (benihi), contains much less terpenes and much more terpene alcohols as compared with the volatile oil from the leaf of the same plant.

(ii) The predominant terpenes in the oil are *d*- α -pinene and *d*-camphene, and they are optically strongly active.

(iii) Among the terpenic alcoholic components there have been proved two new substances 'benihol' C₁₀H₁₈O, and 'benihinol' C₁₀H₁₆O.

(iv) In the sesquiterpene fraction, a new sesquiterpene whose hydrochloride has the melting point 103°-104°C. was isolated, and it was named sesquibenihene.

(v) Among the sesquiterpene alcohol fraction, there are, along with a tertiary alcohol of cadinol type, at least one more primary alcohol the exact nature of which is not yet definitely known.

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BOILING POINT CURVES OF THE BINARY SYSTEMS, $\text{TiCl}_4\text{-CCl}_4$, $\text{TiCl}_4\text{-SiCl}_4$ and $\text{TiCl}_4\text{-SnCl}_4$.

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Received September 4th, 1933. Published December 28th, 1933.

Synopsis.

Boiling point curves of these binary mixtures have been determined by a newly designed apparatus which serves well in the treatment of such fuming liquids as these chlorides. The analytical method of these mixtures have also been contrived in such a manner that it can be prevented decomposition of titanium tetrachloride by the use of ethyl ether as a defending material from fuming.

Introduction.

In previous to this work the author has determined the freezing point curves of these binary mixtures for the study of the nature of titanium tetrachloride⁽¹⁾; this paper being the continuation of that work. Among the systems previously studied $\text{TiCl}_4\text{-SbCl}_5$ has been purposely omitted, due to the fact that the antimony pentachloride decomposes into trichloride and chlorine under the pressure of one atmosphere before it reaches to the boiling point.

Experimental.

1. **Apparatus and Procedure.** Samples used in this experiment were the same as that has been used in the investigation of the freezing point curve. The apparatus used for the measurement of the boiling points of fuming chlorides is shown in Fig 1. In Fig. 1, B is a boiling vessel connected with an equilibrium chamber E. At the base of E capillary tube P is equipped. T is a normal thermometer inserted into the mixture which is boiling and C is a cooler at which the vapour condenses and fills E, overflowing and returning the liquid into the boiling liquid. V is a tube through which vapour passes to the condenser. Boiling tube B is well wrapped with cloths to avoid the vapour from condensing. Short capillaries whose one end is sealed by fusing are inserted into the boiling chamber B, and by these capillaries the constant boiling is assumed. F is an electric furnace, and D is a Dewar vessel whose inner side is not silvered. The upper end of C is connected to a chamber containing P_2O_5 . The extremity of capillary P is introduced into a drying chamber G, in which a

(1) This Bulletin, 8 (1933), 195.

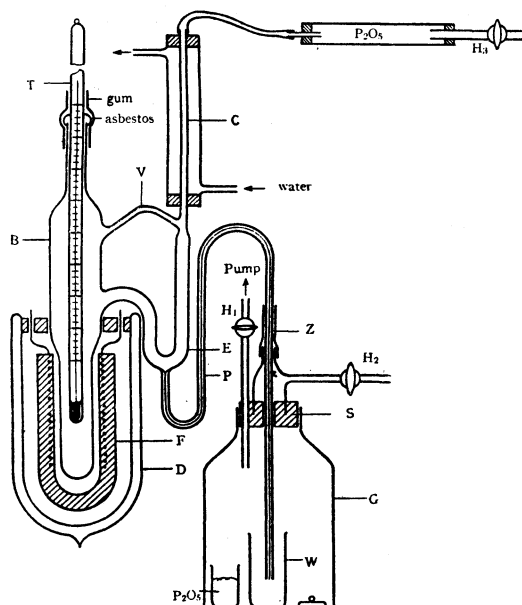


Fig. 1. Apparatus for Boiling Point Curve Measurement.

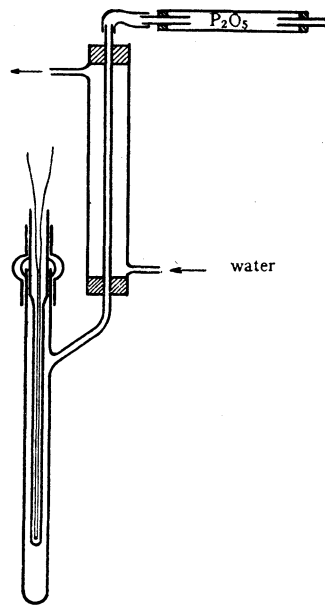


Fig. 2. Boiling Point Apparatus for the Liquid Condensed from Vapour.

weighing bottle W, its lid, and a vessel containing P_2O_5 are placed. Tubes provided with cocks H_1 and H_2 are tightly fit into the gum stopper S. G and S are movable up and down by sliding a gum tube Z along the capillary tube P. H_1 is connected to a cenco-pump and H_2 to air drying tube.

Before starting the experiment the whole apparatus is evacuated through H_1 by the cenco-pump and then filled with the dried air. By repeating this procedure the moisture in the whole apparatus is expelled, then the known quantities of chlorides are introduced into the boiling vessel from the upper end of C by the same method⁽²⁾ as used in determining the freezing point curve. When these preparations were completed the chlorides are heated by a furnace F, and after the reading of thermometer T becomes constant by boiling for long time, F with D are quickly removed for the purpose of stopping the boiling of the liquid. After the liquid in E was cooled, the air is introduced into this chamber through the air-hole H_3 and this liquid is siphoned out into the vessel W, which is quickly covered with the lid at the removal of S from G; then this condensed chloride is weighed. The atmospheric pressure is always read when the boiling temperature becomes constant.

(2) loc. cit.

2. **Determination of the Compositions of Boiling Liquid and of Vapour which are in Equilibrium with Each Other.** For the determination of the composition of vapour which is in equilibrium with boiling liquid, it is sufficient to know the composition of the liquid condensed in the equilibrium chamber E.

(a). $\text{TiCl}_4\text{-CCl}_4$. The composition of the condensed liquid was determined by the direct chemical analysis. To the chloride in the vessel W ethyl ether was introduced little by little through a capillary. After the chloride became dark yellow and not fuming, it was introduced, a small amount at a time, into a beaker containing water; the surface of the water being covered with small quantity of ether. In so doing every portion of the titanium tetrachloride in this dark yellow solution of chlorides with ether was dissolved into water, making a pale yellow solution, while on the other hand a little portion of the titanium tetrachloride was decomposed into smoke by hydrolysis, but since it was held in the layer between water and ether, no smoke was come out into the air from the solution. The smoke was soon dissolved into the solution by stirring. Carbon tetrachloride in the dark yellow solution remained undissolved at the bottom of the beaker, containing a small portion of titanium tetrachloride. A very small part of titanium tetrachloride, which was seemed to be remained in ether over the solution and in carbon tetrachloride, were washed by large quantity of water, and this water was added to the solution. Finally, carbon tetrachloride and ether were expelled by warming this solution, from which titanium hydroxide was precipitated by the addition of ammonia to the solution. The precipitate thus obtained was filtered, ignited in a porcelain crucible, and then weighed in terms of dioxide. From the weight of this titanium dioxide the compositions of the condensed liquid and of the boiling liquid were calculated.

(b). $\text{TiCl}_4\text{-SiCl}_4$. The chemical analysis was carried out as in the preceding experiment in determining the composition of condensed liquid in this system. Ethyl ether was also used as a defending material from fuming produced from titanium tetrachloride. In this case a large part of silicon tetrachloride was decomposed into meta-silicic acid, titanium tetrachloride with the remaining portion of silicon tetrachloride dissolving into water under the cover of ether. After diluting this solution with a large quantity of water, these chlorides were decomposed and were precipitated by the addition of ammonia. All the precipitate was placed in a platinum crucible, added sufficient quantities of concentrated sulphuric acid and hydrofluoric acid solution, and by warming this mixture of precipitate and the acids all the silicon was driven away as fluoride. Lastly, titanium hydroxide was

precipitated with ammonia from this solution, and it was then ignited in porcelain crucible and weighed in terms of dioxide. Compositions of both condensed and boiling liquid were calculated as before.

(c). $\text{TiCl}_4\text{-SnCl}_4$. If an ordinary chemical analysis were carried on in this system it should be obtained a mixture of oxides of both titanium and tin. According to the literature⁽³⁾ the separation of tin from titanium could be made by heating this mixture of oxides in the atmosphere of hydrogen, reducing the oxide of tin to metallic state, and treating it with hydrochloric acid. But according to the author's point of view this method is far from application, because, firstly, it is very difficult to grind this ignited mixture of oxides to the extent of such powder as the oxide of tin can be reduced merely with hydrogen, and secondly it is doubtful that only the oxide of tin is reduced to the metallic state, and not the oxide of titanium even to its some oxide of lower grade, though not to metallic titanium. If this lower oxide of titanium is soluble in hydrochloric acid the above referred method of analysis will be evidently in error. On account of these reasons the direct chemical analysis was not carried on, but the following method was adopted.

With a boiling vessel, unconnecting equilibrium chamber E, the boiling points of the mixed chlorides of this system were determined. In this case correction for small quantity of vapour and condensed liquid was neglected owing to the smallness of their value. The results obtained were shown as the lower part of the curve in Fig. 5. The boiling points of this system were determined in the usual manner as before with an apparatus shown in Fig. 1 and the boiling point of liquid condensed in the equilibrium chamber E was measured by a small boiling vessel shown in Fig. 2, then from the boiling point-composition curve stated above the composition of the condensed liquid was determined. In this case corrections were neglected as before.

Results.

Values obtained from the above experiment were corrected for atmospheric pressure at which the mixtures of chlorides were boiling. Results obtained are tabulated in Tables 1, 2 and 3 and illustrated diagrammatically in Figs. 3, 4 and 5. In all these three systems there appears neither maxima nor minima in their boiling point curve. The distances between the liquid curve and the vapour curve are the widest in the system of $\text{TiCl}_4\text{-SiCl}_4$ and are the narrowest in the system of $\text{TiCl}_4\text{-SnCl}_4$.

(3) A. Hilger and H. Haas, *Ber.*, **23** (1890), 458.

In conclusion the writer wishes to express his hearty thanks to Prof. K. Iwasé for his direction and encouragement throughout this work.

Table 1. $\text{TiCl}_4\text{-CCl}_4$

No.	TiCl_4 gr.	CCl_4 gr.	Bar. press. mm.	Boiling point $^{\circ}\text{C}$		Condens- ed liq. Mol % CCl_4	Boiling liq. Mol % CCl_4
				Reading of thermometer	Corrected for bar. press.		
1	0.0000	39.4625	761.6	76.6	76.6	100.00	100.00
2	5.2032	47.4510	762.6	79.3	79.2	99.33	90.24
3	13.8888	50.6400	762.7	84.2	84.1	98.68	78.84
4	17.2610	39.4625	748.0	89.0	89.4	97.50	68.73
5	32.8169	41.5104	765.3	93.8	93.6	95.16	55.73
6	40.9935	32.9508	763.9	100.5	100.3	91.60	43.00
7	43.4450	26.9161	764.4	106.2	106.0	88.51	36.56
8	43.5075	15.8450	758.8	116.6	116.7	78.65	24.19
9	50.5261	10.8182	748.6	124.5	124.0	54.40	15.11
10	60.5059	6.6747	763.3	129.6	129.5	29.17	8.36
11	61.2737	1.5823	764.4	134.3	134.1	10.03	1.97
12	32.4380	0.0000	765.1	135.3	135.7	0.00	0.00

Table 2. $\text{TiCl}_4\text{-SiCl}_4$

No.	TiCl_4 gr.	SiCl_4 gr.	Bar. press. mm.	Boiling point $^{\circ}\text{C}$		Condens- ed liq. Mol % SiCl_4	Boiling liq. Mol % SiCl_4
				Reading of thermometer	Corrected for bar. press.		
1	0.0000	63.4568	746.0	56.6	57.1	100.00	100.00
2	17.3610	63.4568	753.3	63.2	63.5	98.21	77.66
3	34.4798	53.4016	753.1	75.1	75.4	96.96	59.18
4	51.4768	44.3443	758.5	81.2	81.3	95.62	43.55
5	51.8970	29.7980	760.5	90.5	90.5	86.98	32.14
6	67.7980	21.4148	760.3	106.5	106.5	74.51	19.62
7	51.9060	9.3876	758.6	118.0	118.1	58.91	8.23
8	51.8820	6.7036	757.8	124.8	124.9	45.12	5.45
9	51.8820	2.9049	759.3	130.1	130.1	20.92	2.15
10	34.4380	0.0000	765.1	135.5	135.7	0.00	0.00

Table 3. $\text{TiCl}_4\text{-SnCl}_4$

a. Liquid

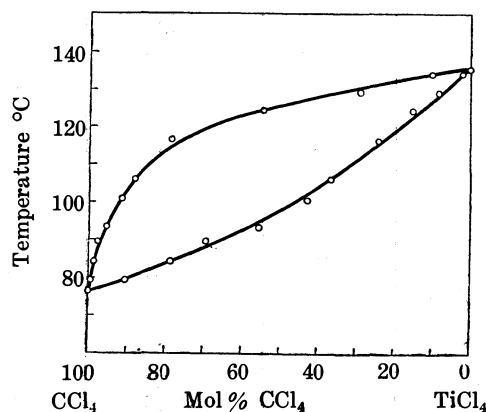
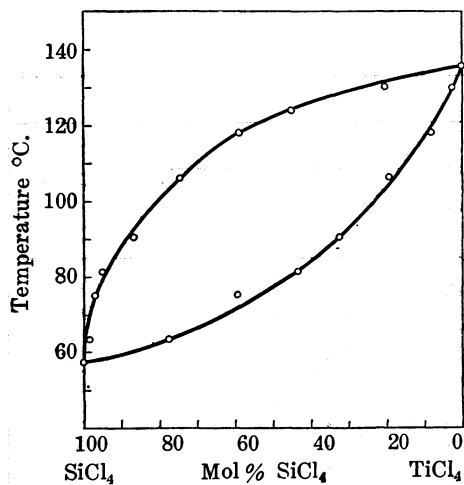
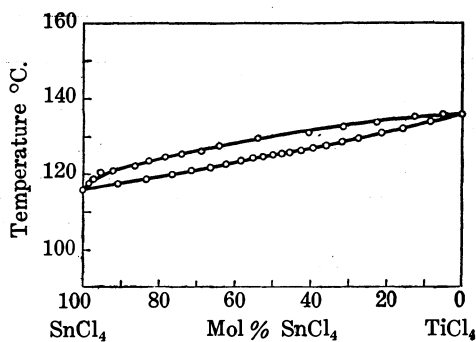
No.	TiCl_4 gr.	SnCl_4 gr.	Bar. press. mm.	Boiling point $^{\circ}\text{C}$		Mol % SnCl_4
				Reading of thermometer	Corrected for bar. press.	
1	0.0000	47.3456	749.1	115.3	115.8	100.00
2	3.4462	"	748.8	116.7	117.2	90.91
3	6.8900	"	748.8	118.0	118.6	83.35
4	10.3338	"	748.6	119.4	119.9	76.94
5	13.7746	"	748.6	120.4	120.9	71.45
6	17.2150	"	748.7	121.4	121.9	66.70
7	20.6548	"	748.7	122.3	122.8	62.54
8	24.0946	"	748.7	123.0	123.5	58.87
9	27.5344	"	748.7	123.6	124.1	55.60
10	30.9742	"	748.7	123.9	124.4	52.68
11	34.4164	"	749.2	124.6	125.1	50.05
12	34.4380	44.3056	752.3	125.1	125.4	48.37
13	"	39.8766	"	125.5	125.8	45.75
14	"	35.4476	"	126.1	126.4	42.84
15	"	31.0168	"	126.8	127.1	39.61
16	"	26.5896	"	127.6	127.9	36.02
17	"	22.1606	"	128.6	128.9	31.94
18	"	17.7290	"	129.4	129.7	27.29
19	"	13.2974	"	130.7	131.0	21.97
20	"	8.8658	"	131.9	132.2	15.79
21	"	4.4342	"	133.7	134.0	8.57
22	"	0.0000	756.1	135.5	135.7	0.00

b. Vapour

No.	Boiling liquid			Condensed liquid			
	Bar. press. mm.	Boiling point $^{\circ}\text{C}$		Bar. press. mm.	Boiling point $^{\circ}\text{C}$		Mol % SnCl_4
		Reading of thermo- meter	Corrected for bar. press.		Reading of pyrometer	Corrected for bar. press.	
1	753.2	117.2	117.5	753.2	115.4	116.1	98.5
2	751.0	118.5	118.9	751.0	115.8	116.2	97.5
3	752.2	120.1	120.4	752.2	116.2	116.5	95.5
4	752.3	120.3	120.6	752.3	116.7	117.1	92.0
5	751.3	121.6	122.0	751.3	117.6	118.0	86.5
6	751.0	123.2	123.6	751.0	118.4	118.8	82.8
7	751.5	124.2	124.6	751.5	119.1	119.5	78.5
8	756.5	125.2	125.4	756.5	120.1	120.4	74.0
9	754.0	125.7	126.0	754.0	120.9	121.2	69.0
10	753.3	127.2	127.5	753.3	122.0	122.3	64.0

b. Vapour—(Concluded)

No.	Boiling liquid			Condensed liquid			
	Bar. press. mm.	Boiling point °C		Bar. press. mm.	Boiling point °C		Mol % SnCl ₄
		Reading of thermometer	Corrected for bar. press.		Reading for pyrometer	Corrected for bar. press.	
11	753.3	129.2	129.5	753.3	124.0	124.3	54.0
12	753.8	130.7	131.0	753.8	126.6	126.9	40.5
13	754.0	132.5	132.8	754.0	128.6	128.9	31.5
14	754.0	133.6	133.9	754.0	130.5	130.8	22.5
15	752.3	134.8	135.2	752.3	132.6	132.9	12.5
16	752.3	135.1	135.5	752.3	134.3	134.6	5.0

Fig. 3. Boiling Point Curve of the System TiCl₄-CCl₄.Fig. 4. Boiling Point Curve of the System TiCl₄-SiCl₄.Fig. 5. Boiling Point Curve of the System TiCl₄-SnCl₄.

Summary.

1. An apparatus has been devised in which a capillary is introduced into a drying chamber at which the condensed liquid is siphoned out into a weighing bottle.
2. Analytical methods of the mixtures have also been contrived in which ethyl ether is used to prevent titanium tetrachloride from fuming out.
3. By using this apparatus and applying this analytical method, boiling point curves of the mixtures have been determined.

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