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Title	90. The Exchange Reaction of Cl36 between Chloroform and Aqueous Hydrochloric Acid. : The Decomposition Mechanism of Chloroform. (From the Proceedings of the Japan Academy, Vol. 27 (1951), No. 8)
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Citation	JOURNAL OF THE RESEARCH INSTITUTE FOR CATALYSIS HOKKAIDO UNIVERSITY, 2(3), 404-409
Issue Date	1953-03
Doc URL	https://hdl.handle.net/2115/24615
Type	departmental bulletin paper
File Information	2(3)_P404-409.pdf

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[From the Proceedings of the Japan Academy, Vol. 27 (1951), No. 8]

90. *The Exchange Reaction of Cl^{36} between Chloroform and Aqueous Hydrochloric Acid. —The Decomposition Mechanism of Chloroform.*

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(Comm. by M. KATAYAMA, M.J.A., Oct. 12, 1951.)

Introduction.

The present paper is concerned with the verification of the theoretical conclusion derived from the decomposition mechanism put forward by Sakamoto in conjunction with one of the authors by means of the exchange reaction of the project.[1] We might give below a brief account of the mechanism and the underlying theory.[2]

It was assumed that the acid-base catalysis including the decomposition of chloroform in aqueous solution was consisted of elementary reactions of the three types i.e. the proton transfer from a Brönsted's acid AH to the substrate SH,

$$AH + SH \longrightarrow A^- + H^+SH \qquad (I)$$

that from SH to a Brönsted's base B,

$$SH + B \longrightarrow S^- + H^+B \qquad (II)$$

and finally the simultaneous proton acceptance from the acid and donation to the base of the substrate,

$$AH + SH + B \longrightarrow A^- + HS + H^+B \qquad (III)$$

Assuming further the validity of the mass action law and that acid or base consists in H_3O^+ and H_2O or OH^- and H_2O respectively, the rate v(I) of type (I) is given as the sum of the two rates $k_A^W[SH]$ and $k^{H^+}[H^+][SH]$ as that,

$$\frac{v(I)}{[SH]} = k_A^W + k^{H^+}[H^+] = k(I) \qquad (I\cdot I)$$

where $[H^+]$ etc. are concentrations of H_3O^+ etc. and k_A^W and k^{H^+} constants. The rate v(II) and v(III) respectively of types (II) and

1) Horiuti and Sakamoto: Bull. Chem. Soc. Japan, **11** (1936), 627. Sakamoto: "Catalyst" **5** (1949), 1 (in Japanese).

2) Horiuti: Collection of Discourses of 13th Committee of Japanese Society for the Promotion of Scientific Research, **1** (1943), 15 (in Japanese).

(III) are similarly expressed in accordance with the relation $[H^+][OH^-] = \text{constant}$, as that,

$$\frac{v(\text{II})}{[\text{SH}]} = k_B^W + \frac{k^{OH^-}}{[H^+]} = k(\text{II}) \qquad (\text{I}\cdot\text{II})$$

$$\frac{v(\text{III})}{[\text{SH}]} = k^{AB} + k^{H^+}[H^+] + \frac{k^{OH^-}}{[H^+]} = k(\text{III}) \qquad (\text{I}\cdot\text{III})$$

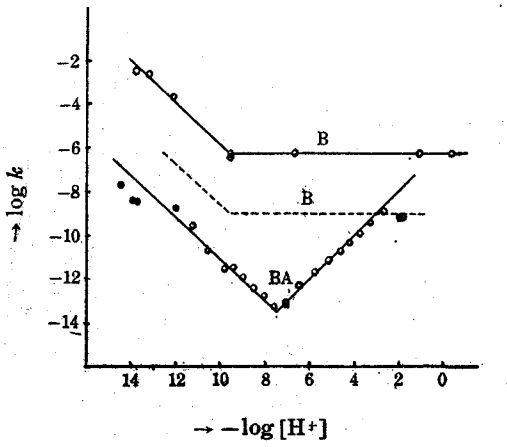

Fig. 1.

By plotting $\log k(\text{II})$ against $-\log[H^+] = \text{pH}$, the curve of the form B in Fig. 1 is obtained, whereas that BA for $k(\text{III})$, the inclination of the individual parts of the curve being ± 1 or 0.

The rate of the acid-base catalysis was now constructed from these patterns of the consecutive elementary reaction simply by reserving the lowest curve, the corresponding elementary reaction being the governing step at the appropriate condition.

Sakamoto[1] has previously determined in conjunction with one of the present authors the rate of the exchange reaction of deuterium between chloroform and water as well as the decomposition rate of chloroform in contact with water at precisely controlled temperature and pH. Circlets on curve B in Fig. 1 show the exchange rate at 50°C and those on BA the decomposition rate at 0°C. Broken line B′ shows the horizontal part of the curve B extrapolated to 0°C from the result at 50°C as well as that at 100°C not indicated in the figure.

1) Horiuti and Sakamoto: Bull. Chem. Soc. Japan, **11** (1936), 627. Sakamoto: "Catalyst" **5** (1949), 1 (in Japanese).

Since B and BA cut each other at pH = 3, the decomposition rate would run horizontally along B′ over the region pH < 3, according to the above composition principle of the resultant rate, provided that the elementary reaction responsible for the deuterium exchange reaction is itself the constituent one of the decomposition.

This being in agreement with experiment as shown in the figure, the following decomposition mechanism was proposed:

$$B + HCCl_3 \longrightarrow BH^+ + CCl_3^- \qquad (2, a)$$

$$CCl_3^- \longrightarrow CCl_2 + Cl^- \qquad (2, b)$$

$$B + \begin{matrix} H \\ \diagdown \\ O \\ \diagup \\ H \end{matrix} \cdot\cdot CCl_2 + HA \longrightarrow BH^+ + HOCCl + ClH + A^- \qquad (2, c)$$

$$B + HOCCl + HA \longrightarrow BH^+ + CO + ClH + A^- \qquad (2, d)$$

The deuterium exchange reaction was attributed to (2, a) and its reverse process because of experimental results in accordance with curve B, whereas the governing step of the decomposition either to (2, c) or to (2, d), because of those in accordance with BA. It follows then that the deuterium exchange reaction proceeds only at pH > 3, where (2, c) or (2, d) governs the rate of the decomposition allowing (2, a) to proceed back and forth, but not at pH < 3 where (2, a) itself governs the rate, H of chloroform going into solution one-sidedly.

It may further be inferred now that chloroform exchanges chlorine atom with the solution or not according as pH > 3 or pH < 3, inasmuch as in the former region (2, b) proceeds back and forth introducing chlorine ion in the solution into the chloroform molecule, whereas in the latter case where (2, a) governs the rate, CCl_3^- once formed decomposes one-sidedly never returning to chloroform.

It is the purpose of the present research to submit the above theoretical prediction to the experimental test.

Experimental.

One c.c. aqueous solution of radioactive hydrogen chloride was shaken in the presence or absence of air with 1.5 c.c. chloroform at room temperature for a recorded time in a glass tube of 6~12 c.c. capacity covered by black paper to protect from light and then the glass tube was opened, 1 c.c. chloroform carefully pippeted out and determined for its radioactivity by means of Geiger-Müller counter Modell 16 supplied by Research Institute of Science, Ltd. Tokio.

The aqueous solution of radioactive chlorine ion was prepared by diluting properly hydrochloric acid solution containing Cl^{36} supplied by U.S. Atomic Energy Commission, its pH being adjusted before use by adding a proper quantity of H_2SO_4 or NaOHaq. Sample I was prepared by diluting 0.023 c.c., 1.03 N-HCl containing 0.2 μc Cl^{36} directly supplied by U.S. A.E.C. to 10 c.c. and sample II by diluting HCl sample received through the courtesy of Dr. Kakei of Tokio University which, according to him, contained 0.25 μc Cl^{36} to 12 c.c. Sample I has given 1352 ct./min. c.c. whereas II 736 ct./min. c.c. inclusive of the background, the both being used for the experiment.

Purchased chloroform of reagent grade, was washed with conc. H_2SO_4, by distilled water, dried over calcium chloride and then distilled, the centre cut at constant boiling point being used.

The experiment in the absence of air was carried out by freezing preliminarily the content of the reaction tube by liquid air, evacuating the latter to $10^{-5}\sim10^{-6}$ mmHg, allowing it to melt giving off the occuluded air, the tube being shut off from the vacuum line in the mean time, and then by repeating the above process several times.

The sample for the Geiger-Müller counter was put in a round basin of stainless steel of 25 mm diameter and 6 mm height, covered by circular aluminum-leaf of 2.2 mg/cm^2 thickness and sealed by pasting the margin on the outer side of the basin to protect the counter from contamination.

Results.

The result is shown in the table below.
"Date" is that of radioactivity measurement of chloroform. "Run" numbers the experiment or experiments simultaneously conducted. "Temp." is the mean temperature at the shaking and "Air" shows the presence or absence of air in the reaction tube. "Solution" shows the number I or II of the sample of aqueous radioactive hydrochloric acid solution described above and its pH adjusted at the outset as well as final one measured after the experiment, the decrease being due to the decomposition of chloroform as previously observed by Sakamoto.[1] The pH was determined by pH testpaper set either directly or by properly diluting the solution. Only with run 4 the pH was fixed at 13.4 by adding solid barium hydroxide to the solution. "Activity of Chloroform" is that directly observed with 1 c.c. chloroform as described above, the data in parentheses for sample II being that derived from the direct observation by multiplying its excess part of the count by the ratio of the excess count of sample I to that of II.

1) Sakamoto: "Catalyst" **5** (1949), 1 (in Japanese).

Experimental Results.

Date	Run	Temp. °C	Time hr.	Air	Back-ground ct./min.	Solution sample	Solution pH	Activity of Chloroform ct./min.c.c.	Back-ground ct./min.
June 13	1	19	1.75	present	31	I	0.0~0.0	37	25
						I	13.5~ >9.6*)	58	
June 18	2	19	76	present	35	I	0.0~0.0	36	28
						I	13.6~ >9.6*)	53	
June 22	3	20	73	present	31	I	9.6~4.6	32	30
June 26	4	20	73	present	37	I	13.4~13.4	36	30
June 30	5	20	73	absent	34	I	13.5~ >9.6*)	79	29
July 7	6	20	73	absent	30	I	0.0~0.0	28	27
July 16	7	20	146	absent	30	I	13.5~ >9.6*)	91	30
July 29	8	26	73	absent	32	II	0.0~0.0	29	25
						II	13.5~ >9.6*)	62 (89)	
August 4	9	26	70	absent	29	II	7.2~5.3	50 (67)	28
						II	9.5~6.6	49 (65)	

*) The upper limit of the sensitive range of pH test paper.

We might proceed further commenting on the table. With the run 1 it was found that the excess of count over the background is practically none at pH = 0.0 whereas small but surely perceptible at pH = 13.5~9.6 in favour of the theoretical conclusion. With the purpose to amplify the contrast the time of shaking of run 2 was several tenfolded the result being however rather disappointing. The excess was, however, ascertained in this case not due to the contamination of solution caused by the incomplete separation, by washing the chloroform by a small quantity of water, and determining the water for its radioactivity. Further evidence for this point was afforded by the inperceptible excess of the chloroform treated at pH $<$ 3. Another similar run, No. 3 of nearly the same time of shaking but shifted toward smaller pH was found altogether negative. Run 4 was conducted keeping pH, on the contrary to the foregoing run, constantly at high value the result being however again negative. Apparently quite inconsistent result so far obtained at pH $>$ 3 seemed now a natural consequence of the fact that the decomposition was, as observed by Sakamoto, appreci-

ably accelerated by the presence of air and hence the latter must have somehow disturbed the mechanism.

Run 5, 6, 7, 8 and 9 were now conducted by carefully excluding air from the reaction tube. The results are as shown in the table rather conclusive and consistent in verifying our theoretical prediction. The run over the range $pH > 3$ seems to show that the rate of exchange somewhat increases with pH although not very conclusive.

It is desirable for establishing the mechanism to determine the chlorine exchange rate quantitatively tracing out the rate of, say, (2, b), which is concealed above curve BA otherwise and to investigate the effect of air; these are the project of our further research.

We are indebted to grants in aid for fundamental scientific research of the Ministry of Education by which help the present research has been carried out.