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31. *The Exchange Reaction of Cl^{36} between Carbon Tetrachloride and Aqueous Chloride Solution.*

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Introduction.

Our previous work[1] has confirmed the theoretical conclusion that chloroform and aqueous chloride solution exchanges chlorine atom at pH above 3 but not below which was derived from the decomposition mechanism put forward by J. Horiuti and Y. Sakamoto[2,3].

This does not however exclude the possibility that the observed exchange reaction were due partly or exclusively to the elementary reaction that,

$$Cl^- + \begin{matrix} H \\ C\ Cl \\ Cl_2 \end{matrix} \longrightarrow \begin{matrix} H \\ Cl\ C \\ Cl_2 \end{matrix} + Cl^- \qquad (I)$$

even though the previous result was, as observed, sufficiently in concordance with the theoretical requirement. If at all and moreover its occurence is not particularly favored by the hydrogen atom in chloroform, the similar exchange reaction may well be observed with carbon tetrachloride under the same condition.

In the present work this point was appealed to experiment by observing similarly the exchange reaction of carbon tetrachloride with aqueous chloride solution side by side with that of chloroform under the same condition for comparison.

The experimental procedure and the results are described below.

Experimental procedure.

Purchased carbon tetrachloride of reagent grade was washed with conc. H_2SO_4, aqueous NaOH solution and distilled water and then distilled, the centre cut at constant boiling point being used.

Radioactive hydrogen chloride was prepared from solid calcium chloride kindly offered by Prof. S. Sakamoto and Dr. K. Uchizono of Tokio University, to whom our best thanks are due. The latter sample, a few mgr. radioactive solid calcium chloride was cooled

1) J. Horiuti and K. Tanabe: Proc. Japan Acad., **27**, 494 (1951).
2) J. Horiuti and Y. Sakamoto: Bull. Chem. Soc. Japan **11** 627 (1936).
3) Y. Sakamoto: "Catalyst" **5** (1949) 1. (in Japanese).

by liquid air, added with a few drops of concentrated sulphuric acid, evacuated, then warmed to 50~60°C, the evolving hydrogen chloride collected in a vessel cooled in liquid air through the vacuum line, detached from the line and finally diluted with 23 c.c. water. One c.c. of the aqueous solution thus obtained has given 1384 ct/min. inclusive of the background count. The solution was adjusted to the desired pH value before use by adding to the latter a proper quantity of H_2SO_{4aq} or $NaOH_{aq}$.

The experiment of the exchange reaction proceeded as follows: One c.c. aqueous chloride solution thus prepared was sealed in a glass tube of 6~12 c.c. capacity together with 1.5 c.c. carbon tetrachloride after careful evacuation as in the previous experiment[1], kept at 100°C for a recorded time, being shaken from time to time. The glass tube was then opened, 1 c.c. carbon tetrachloride carefully pipetted out and determined for its radioactivity just as described in the previous paper[1].

Results.

The results are shown in Table 1 below. "pH of Solution" shows that adjusted at the outset as well as the final one measured after the experiment. The pH was directly determined by pH test paper set whose sensitive range is from 1.2 to 9.6. The value of pH adjusted at the outset in Run 1, 4, 5, 8 and 10 was calculated from the normality of NaOH solution assuming the complete dissociation of the latter and the dissociation constant of water 14. "Activity of CCl_4" is that directly observed with 1 c.c. carbon tetrachloride as described above. "Background count (I) and (II)" are respectively those measured before and after the determination of activity of carbon tetrachloride. "Activity of washed CCl_4" was that of carbon tetrachloride sample washed with distilled water after the measurement of "Activity of CCl_4". This was done to ascertain whether the slight excess of activity in Run 4 and 6 were due to the incomplete separation from the solution. The result shows the excess is only apparent as questioned while the complete separation inevitably follows with other runs from the observed absence of the excess.

The data of Table 1 show now apparently that the chlorine exchange between carbon tetrachloride and aqueous chloride does not occur over the whole range of pH observed.

It is remarkable however that carbon tetrachloride is nevertheless not altogether inactive as shown by the decrease of pH in the cases of Run 6 and 7, although the extent is less compared

1) J. Horiuti and K. Tanabe: Proc. Japan Acad. 27, 404 (1951).

with the case of chloroform. This shows that carbon tetrachloride is giving off acid, as chloroform does in contact with solution, in spite of the absence of the exchange.

Table 1

The Exchange Reaction of Cl^{36} between CCl_4 and Cl^-_{aq}.

Run	Temp. °C	Time hr.	Background count (I) ct/min.	pH of Solution	Activity of CCl_4 ct/min. c.c.	Background count (II) ct/min.	Activity of washed CCl_4 ct/min. c.c.
1	96.5	8	31	14.0~>9.6	31	31	
2	97.0	8	31	0.0~ 0.0	29	30	
3	97.0	7	31	1.2~<1.2	28	28	
4	97.0	7	31	14.0~>9.6	35	31	32
5	98.0	7	32	14.0~>9.6	32	31	
6	98.0	7	32	9.2~ 6.5	35	30	30
7	97.0	7	30	9.5~ 7.4	29	30	

The results of the exchange reaction of Cl^{36} between chloroform and aqueous chloride solution carried out under the same condition with that of carbon tetrachloride and aqueous chloride solution are shown in Table 2. "Activity of distilled water shaken with active $CHCl_3$" shows that the definite excess of activity of chloroform over the background count is not due to the incomplete separation but to the genuine exchange reaction on the contrary to the case of carbon tetrachloride.

Table 2

The Exchange Reaction of Cl^{36} between $CHCl_3$ and Cl^-_{aq}.

Run	Temp. °C	Time hr.	Background count (I) ct/min.	pH of Solution	Activity of $CHCl_3$ ct/min. c.c.	Background count (II) ct/min.	Activity of distilled water shaken with active $CHCl_3$ ct/min. c.c.
8	98.0	7	32	14.0~6.9	80	28	30
9	98.0	7	32	9.2~6.5	39	31	31
10	97.0	7	30	14.3~8.2	126	28	28

The conclusion is that the exchange reaction of chloroform is not due to the mechanism (I), provided that the hydrogen atom in the chloroform molecule does not particularly favor the latter.