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32. *The Effect of Oxygen in the Exchange Reaction of Cl^{36} between Chloroform and Aqueous Chloride Solution.*

By Juro HORIUTI and Kozo TANABE.
The Research Institute for Catalysis, Hokkaido University.
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Introduction.

It has been previously found that the chlorine exchange of chloroform with aqueous chloride solution is considerably reduced by the presence of air and moreover quite irregularly[1].

In the present paper the exchange reaction was further investigated with special reference to the influence of oxygen at its different partial pressure with chloroform as well as with carbon tetrachloride for comparison.

Experimental.

One c.c. of radioactive aqueous chloride solution was put together with 1.5 c.c. chloroform or carbon tetrachloride in a glass tube of 6~12 c.c. capacity, the air inside removed as in the previous work by alternative repitition of the evacuation with the content frozen by liquid air and the subsequent thawing at discommunication from the vacuum line until the vacuum inside the tube attains 10^{-5}~10^{-6} mmHg, oxygen admitted at measured pressure, the tube sealed off, kept at 100°C for a recorded time, the content being shaken from time to time. The tube was now opened, 1 c.c. chloroform or carbon tetrachloride carefully pipetted out and determined for its radioactivity just as in the previous work[1].

The oxygen pressure admitted in the tube at room temperature was measured by a mercury manometer attached to the vacuum line with the contents either frozen with liquid air (Run 1, 2, 9 and 10 for chloroform and 12, 13 and 14 for carbon tetrachloride) or molten at room temperature (Run 3, 4, 5 and 6 for chloroform).

Some experiments were carried out in the presence of air (Run 11) without evacuation and subsequent processes or only with evacuation (Run 7 and 8) without admission of oxygen.

Radioactive aqueous chloride solution of 1384 ct/min. c.c. inclusive of the background count, chloroform and carbon tetrachloride used in the present experiment are the same preparations respec-

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

tively as those for the previous work[1)2)]. Oxygen was evolved by heating the potassium permanganate in the vacuum line, condensed by liquid air and then evaporated, the centre cut being used.

Results.

The results obtained are shown in Table 1.

The second and third column give the temperature and the recorded time of the experiments. The fourth one shows the oxygen pressure measured as described above. "pH of Solution" shows that adjusted at the outset as well as the final one measured after the experiment, as determined by pH test paper set with sensitive range from 1.2 to 9.6. "Background count (I) and (II)" are respectively those measured before and after the determination of "Activity of Chloroform" described above. The last column, "Activity of distilled water shaken with active $CHCl_3$" shows now that the observed excess of activity of chloroform over the background count is not due to the incomplete separation but to the genuine exchange reaction.

Table 1

Run	Temp. °C	Time hr.	Pressure of Oxygen mmHg	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.
1	97	7	720	30	14.0~7.7	65	28	28
2	〃	〃	720	29	14.0~6.9	73	32	32
3	〃	〃	655	30	14.0~7.2	68	28	29
4	〃	〃	432	28	14.0~7.2	72	29	29
5	〃	〃	225	29	14.0~7.2	71	29	30
6	〃	〃	75	29	14.0~7.2	76	29	30
7	〃	〃	10^{-5}~10^{-6}	29	14.0~6.7	80	29	29
8	〃	〃	10^{-5}~10^{-6}	32	14.0~6.9	80	28	30
9	〃	〃	720	29	9.2~7.8	35	29	30
10	〃	〃	720	33	0.0~0.0	34	30	33
11	〃	〃	air	29	14.0~7.5	67	29	30

Table 1 shows that the presence of oxygen reduces the exchange at 100°C, although not so appreciably as at room temperature[2)].

The results of the exchange reaction with carbon tetrachloride in the presence of oxygen are shown in Table 2, which shows, in conjunction with the result of the previous work[1)], that carbon

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

tetrachloride does not exchange in any way, in the presence or absence of oxygen.

Table 2

Run	Temp. °C	Time hr.	Pressure of Oxygen mmHg	Background count (I) ct/min.	pH of Solution	Activity of CCl_4 ct/min. c.c.	Background count (II) ct/min.
12	97		720	29	0.0～ 0.0	29	31
13	〃	〃	720	31	14.0～>9.6	30	0
14	〃	〃	720	29	9.2～ 7.8	29	30