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Title	THE MECHANISM OF THE EXCHANGE REACTION OF CHLORINE BETWEEN BENZOTRICHLORIDE AND AQUEOUS CHLORIDE SOLUTION
Author(s)	TANABE, Kozo; SAN0, Tomoko
Citation	JOURNAL OF THE RESEARCH INSTITUTE FOR CATALYSIS HOKKAIDO UNIVERSITY, 13(2), 102-109
Issue Date	1966-01
Doc URL	<a href="https://hdl.handle.net/2115/24796">https://hdl.handle.net/2115/24796</a>
Type	departmental bulletin paper
File Information	13(2)_P102-109.pdf



## THE MECHANISM OF THE EXCHANGE REACTION OF CHLORINE BETWEEN BENZOTRICHLORIDE AND AQUEOUS CHLORIDE SOLUTION

By

Kozo TANABE\*<sup>1)</sup> and Tomoko SANO\*<sup>1)</sup>

(Received September 30, 1965)

### Abstract

The rate of the chlorine exchange of benzotrichloride with chloride ion in aqueous solution was measured by using radioactive  $^{36}\text{Cl}$  at  $5^\circ\text{C}$  over a pH range from 0 to 14. The exchange rate was found to be dependent on chloride ion concentration in solution, but not of the first order with respect to the concentration. It is concluded from the observed results incorporated with those of the hydrolysis that the chlorine exchange proceeds by a reversal of the rate-determining step of the hydrolysis, *i.e.*, recombination of chloride ion with the carbonium ion intermediate.

### Introduction

We have hitherto investigated the acid-base catalysis in the chlorine exchanges and the hydrolyses of chloroform<sup>1)</sup>, carbon tetrachloride<sup>2)</sup>, methylene chloride<sup>3)</sup>, benzyl chloride<sup>4)</sup> and benzal chloride<sup>5)</sup> and proposed the mechanisms of these reactions. The purpose of a series of these studies is to establish a relative reactivity-structure relation among the chloromethane derivatives. In the present work the chlorine exchange of benzotrichloride has been studied and its mechanism discussed.

### § 1. Experimental

**Reagents:** Benzotrichloride (guaranteed reagent, Kanto Chemical Co.) was purified by washing with conductivity water and by distilling under reduced pressure. The radioactive chloride solution of desired pH was prepared by adding dropwise about 4.5 N radioactive hydrochloric acid\*\*<sup>1)</sup> into conductivity water, sulfuric acid, sodium hydroxide solution or phosphate buffer solution (2/15 mol/l  $\text{Na}_2\text{HPO}_4$  + 2/15 mol/l  $\text{KH}_2\text{PO}_4$ ) as described previously<sup>1)</sup>. Sodium chloride used in experiments for the mass effect of chloride ion concentration on the exchange rate was a guaranteed reagent of Kanto Chemical Co. Tokyo.

\* ) The Research Institute for Catalysis, Hokkaido Univ. Sapporo, Japan.

\*\* ) Hydrochloric acid containing  $^{36}\text{Cl}$  imported from Atomic Energy Commission, U.S.A.

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**Kinetic Runs:** Each 2.5 ml of benzotrichloride and aqueous radioactive chloride solution of known concentration and pH which attained thermal equilibrium in a water-bath maintained at 5°C were pipetted into a 30 ml Erlenmeyer flask placed in the same bath and the mixture was stirred vigorously by a magnetic stirrer. At a recorded time, the flask was taken out and about 2.0 ml of benzotrichloride was pipetted out and washed with conductivity water more than seven times until no radioactivity was found in the washings, and the radioactivity of 1 ml of benzotrichloride determined by a G-M counter as in the previous work<sup>1)</sup>. The radioactivity of the aqueous chloride solution before reaction was determined similarly. The specific radioactivity  $C^s$  (radioactivity in the absence of self-absorption) of the solution and that  $C^c$  of benzotrichloride were obtained by multiplying the apparent radioactivity  $C^s$  or  $C^c$  by the respective conversion factors. The factor  $a^s = C^s/C^s$  for aqueous solution was determined to be 3.72 in the previous work<sup>1)</sup>. The factor  $a^c = C^c/C^c$  for benzotrichloride is estimated to be 4.24 from the factor  $a^{CHCl_3}$  for chloroform determined previously<sup>1)</sup> by assuming that the factor is proportional to specific weight of a material.

The pH of solution before reaction was measured at room temperature by means of a pH-meter or calculated from the concentration of hydroxide ion titrated with standard acid in the case of extremely strong alkaline solution as in the previous work<sup>1)</sup>. The pH after reaction was calculated from the rate of hydrolysis given in the subsequent paper<sup>6)</sup>.

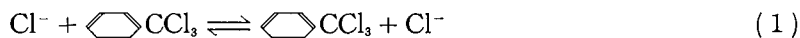
In order to see the effect of oxygen on the chlorine exchange, an experiment was carried out by degassing the reaction mixture by three cycles of freezing, evacuation ( $10^{-4}$  mmHg) and thawing as described previously<sup>1)</sup>.

As shown in the subsequent paper<sup>6)</sup>, the hydrolysis rate of benzotrichloride which is higher than the exchange rate is independent of shaking rates and the volume of aqueous phase. It may, therefore, be admitted that the exchange proceeds homogeneously in aqueous layer and that the dissolution of benzotrichloride into solution and its reversal are not controlling.

## § 2. Exchange Rate Expression

The following three elementary reactions controlling the chlorine exchange are kinetically distinguishable.

i) An elementary reaction whose rate of chlorine exchange is of the first order with respect to the chloride ion concentration in solution; for instance, the following reaction in equilibrium,

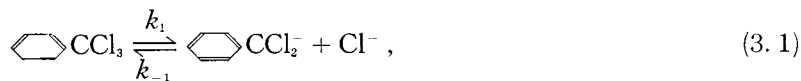


ii) An elementary reaction whose rate of chlorine exchange is constant independently of the chloride ion concentration in solution; for instance, the reaction in equilibrium such as,



iii) An elementary reaction whose rate of chlorine exchange is dependent on chloride ion concentration in solution, but is not of the first order with

respect to the concentration. Namely, the case where the reactive transient species which give rise to the chlorine exchange participate in any reaction, other than the chlorine exchange. Such an elementary reaction is a reversal of the rate-determining step (3.1) of the hydrolysis, whose mechanism will be determined in the subsequent paper<sup>6)</sup>.



where A denotes all species other than chloride ion which reacts with the carbonium ion.

In the case of i) and ii), the exchange rate<sup>\*)</sup>  $r$  is expressed respectively by the following two equations derived previously<sup>1,2)</sup>, where  $r$  must be proportional to  $[\text{Cl}^-]$ <sup>\*\*)</sup> or constant independently of  $[\text{Cl}^-]$  according as i) or ii) operates, since the equations were integrated assuming  $U_D \equiv r$  or  $U_s \equiv r/[\text{Cl}^-]$  alternatively constant independently of  $[\text{Cl}^-]$ .

$$U_s \equiv r/[\text{Cl}^-] = - \frac{\dot{n}^c}{n \ln \left( 1 + \frac{\dot{n}^c}{n_0^c} t \right)} \ln \left( 1 - \frac{a^c C_i^c v^c n}{a^c C_0^c v^c n^c} \right), \quad (4)$$

$$U_D \equiv r = - \frac{\dot{n}^c}{1 + \frac{\dot{n}^c t}{n_0^c} \ln \left( 1 - \frac{a^c C_i^c v^c n}{a^c C_0^c v^c n^c} \right)}, \quad (5)$$

where  $C_i^c$  or  $C_0^c$  is the apparent radioactivity of 1 ml benzotrichloride at time  $t$  or that of 1 ml solution at  $t=0$  respectively and  $a^c$  or  $a^s$  the appropriate conversion factor described in § 1, hence  $a^c C_i^c v^c$  or  $a^s C_0^s v^s$  is proportional to the number of radioactive chlorine atoms present in benzotrichloride at time  $t$  or the total number present in the reaction vessel respectively. The  $n$  in the equations is the sum of  $n_0^s$  and  $n_0^c$ , which are given in Table 1 and  $n^c$  is the rate of decrease of chlorine in benzotrichloride. Both  $U_s$  and  $U_D$  are calculated according to Eqs. (4) and (5) from the observed values  $C_i^c$ ,  $C_0^c$  etc. given in Table 1.

In the case of iii), we have the following well-known equation.

\*) The exchange rate  $r$  is defined as forward rate of chlorine transfer from solution to benzotrichloride for unit volume of solution. (See ref. 1)

\*\*\*) Activity of chloride ion was identified with the concentration  $[\text{Cl}^-]$ .

TABLE 1. Exchange of Chlorine Labeled by  $^{36}\text{Cl}$  between Benzotrichloride and Aqueous Chloride at  $5^\circ\text{C}$ .

Runs	Time of Reaction min	Aqueous Chloride Solution								Benzotrichloride					Rates	
		Radioactivity before Reaction		pH		Qt. $\text{Cl}^-$ ion		Volume $v^s$ ml	Added Reagents	Radioactivity after Reaction		Volume $v^c$ ml	Qt. $\text{Cl}^-$ atom		$\log_{10} U_D$ mol/l min	$\log_{10} U_s$ min $^{-1}$
		Counts/min	Back-ground Counts/min	Before	After	$n_0^s$ m mol	$n^s$ m mol			Counts/min	Back-ground Counts/min		$n_0^c$ m mol	Rate of Decrease $-i^c/v^s \times 10^5$ mol/l, min		
		min, ml	min													
1	422	16,040	45	1.80	0.95	0.0551	0.1285	2.5	none	416	43	2.5	52.95	6.3	-8.28	-4.19
2	365	11,420	40	-0.58	-0.63	0.0237	0.0872	2.5	$\text{H}_2\text{SO}_4$	167	42	2.5	52.95	6.3	-8.73	-4.46
3	300	14,910	42	1.80	1.08	2.351	2.403	2.5	NaCl	125	38	2.5	52.95	6.3	-7.15	-4.65
4	302	10,660	42	13.27	5.40	0.0370	0.0895	2.5	NaOH	143	39	2.5	52.95	6.3	-8.53	-4.43
5	362	10,190	38	13.27	5.50	2.226	2.289	2.5	NaOH+NaCl	89	41	2.5	52.95	6.3	-7.43	-4.83
6	361	13,370	38	14.01	13.84	0.0514	0.1140	2.5	NaOH	84	39	2.5	52.95	6.3	-9.03	-4.97
7	420	13,310	41	14.01	13.85	2.047	2.120	2.5	NaOH+NaCl	63	39	2.5	52.95	6.3	-8.02	-5.31
8	365	16,310	41	7.91	1.30	0.0522	0.1160	5.5	Buffer	351	42	2.5	52.95	6.3	-8.28	-4.22
9	368	15,090	40	7.91	1.40	2.034	2.098	2.5	Buffer+NaCl	166	38	2.5	52.95	6.3	-7.23	-4.58
10	360	15,200	39	8.70	1.60	0.2016	0.2640	2.5	Buffer	308	41	2.5	52.95	6.3	-7.84	-4.25
11*	375	15,200	39	8.70	1.40	0.2016	0.2670	2.5	Buffer	314	41	2.5	52.95	6.3	-7.86	-4.26
12	354	13,730	49	2.0	—	1.557	1.618	2.5	NaCl	167	49	2.5	52.95	6.3	-7.30	-4.55

\*) Conducted in vacuum ( $10^{-4}$  mmHg)

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$$r = \frac{\alpha k_1 [\text{Bz}][\text{Cl}^-]}{1 + \alpha [\text{Cl}^-]}, \quad (6)$$

$$\alpha = \frac{k_{-1}}{k_2 [\text{A}]}, \quad (7)$$

where  $[\text{Bz}]$  is the concentration of benzotrichloride and  $[\text{Cl}^-]$  that of chloride ion in solution.

### § 3. Results and Discussion

The experimental results of chlorine exchange are shown in Table 1. "Radioactivity before reaction" gives the radioactivity of 1 ml aqueous solution before reaction measured as described in § 1 inclusive of a background count. Quantity  $n_0^*$  of chloride ion before reaction was determined by modified VOLHARD'S method or calculated from the known amount of added chloride. Quantity  $n^*$  after reaction was the sum of  $n_0^*$  and the increment  $\Delta n$  of chloride ion formed during the reaction. The increment was the rate  $-\dot{n}^c/v^s$  of increase of chloride ion, given in the subsequent column, multiplied by the time  $t$  of the reaction and the volume  $v^s$  of solution. "Radioactivity after reaction" gives the observed radioactivity of 1 ml benzo trichloride after reaction inclusive of background count.  $-\dot{n}^c/v^s$  is the rate of the decrease of chlorine in benzotrichloride per unit volume of solution which was quoted from the results of the hydrolysis reported in the subsequent paper<sup>6)</sup>. The last column "Rates" shows  $\log_{10}U_D$  and  $\log_{10}U_s$  calculated according to Eqs. (5) and (6) from the data given in the foregoing columns.

In runs conducted in strong acidic or alkaline solution, the exchange was investigated confining the pH-shift due to hydrogen chloride formed by the hydrolysis within possibly narrow range. In runs in mediate pH region, however, it was impossible to observe the exchange in narrow range of pH-shift. Nevertheless, these runs are enough to show the exchange in the mediate pH range. Run 11 was conducted in the absence of air. A comparison with run 10 conducted in the presence of air shows that oxygen has a negligible effect on the exchange. The effect of chloride ion concentration on the exchange rate was investigated in runs 3, 5, 7, 9 and 12.

The  $\log_{10}U_D$  and  $\log_{10}U_s$  are plotted respectively in Figs. 1 and 2 against pH, each at the median of pH, if varied appreciably. The pH-variation is shown by a horizontal dotted line. The figures clearly indicate that both  $U_D$  and  $U_s$  vary with  $[\text{Cl}^-]$ . However,  $U_s$  derived from mechanism i) and  $U_D$  from mechanism ii) must be constant independently of  $[\text{Cl}^-]$  as described in § 2, this being incompatible with the experimental facts. Therefore, mechanism

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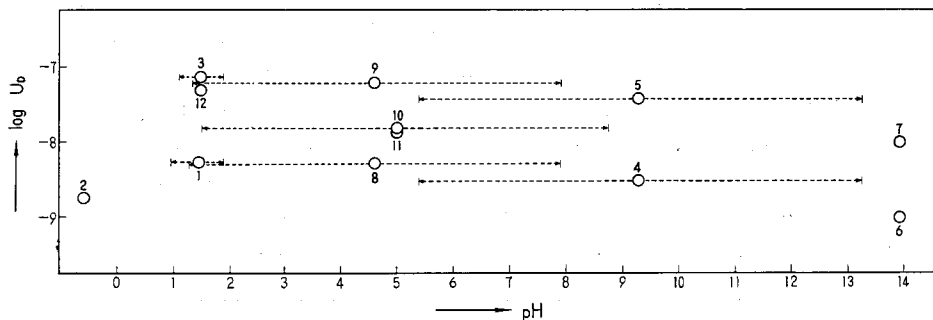


Fig. 1. Rate  $U_D \equiv r$  mole of  $\text{Cl}/\ell$ , min. of chlorine transfer from solution to benzotrichloride at  $5^\circ\text{C}$ .  
 $\leftarrow \cdots \cdots \rightarrow$ : Range of pH-variation.

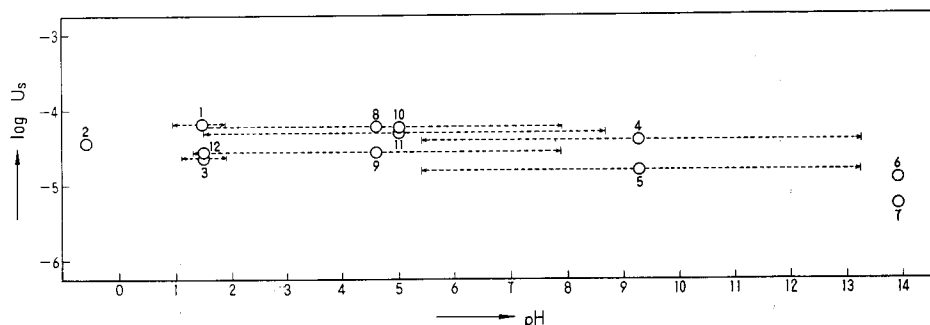


Fig. 2. Specific rate  $r/[\text{Cl}^-]$   $\text{min}^{-1}$  of chlorine transfer from solution to benzotrichloride at  $5^\circ\text{C}$ .  
 $\leftarrow \cdots \cdots \rightarrow$ : Range of pH-variation.

i) and ii) are ruled out. Mechanism iii) now remains where the chlorine exchange proceeds by the reversal of the rate-determining step of the hydrolysis. The validity of this mechanism is confirmed as described below.

If  $r^*$  is defined as the forward rate of the transfer of radioactive chlorine  $\text{Cl}^*$  from solution to benzotrichloride for unit volume of solution, Eq. (6) derived in the case of mechanism iii) is expressed as,

$$r^* = \frac{\alpha k_1 [\text{Bz}] [\text{Cl}^{*-}]}{1 + \alpha [\text{Cl}^-]}, \quad (7)$$

where  $[\text{Cl}^{*-}]$  denotes the concentration of  $\text{Cl}^*$  ion in solution.

Transforming Eq. (7), we have

$$\frac{[\text{Cl}^{*-}]}{r^*} = \frac{[\text{Cl}^-]}{k_1 [\text{Bz}]} + \frac{1}{k_1 \alpha [\text{Bz}]}. \quad (8)$$

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The hydrolysis rate  $k_1[\text{Bz}]$  is kept constant under the present experimental condition by the presence of pure benzotrichloride phase and  $\alpha$  is also kept constant in neutral and acidic solution where  $[\text{A}]$  is constant. Thus, a plot of  $[\text{Cl}^{*-}]/r^*$  vs.  $[\text{Cl}^-]$  should give a straight line, as far as the exchange proceeds by mechanism iii). Fig. 3 shows that the plot<sup>\*)</sup> gives a straight line,  $\alpha$  being calculated to be 2.1 from the intercept of the straight line, taking  $3.15 \times 10^{-5}$  as the value of  $k_1[\text{Bz}]^{**})$ . This value of  $\alpha$  coincides with that obtained from the data on the hydrolysis reported in subsequent paper<sup>5)</sup>.

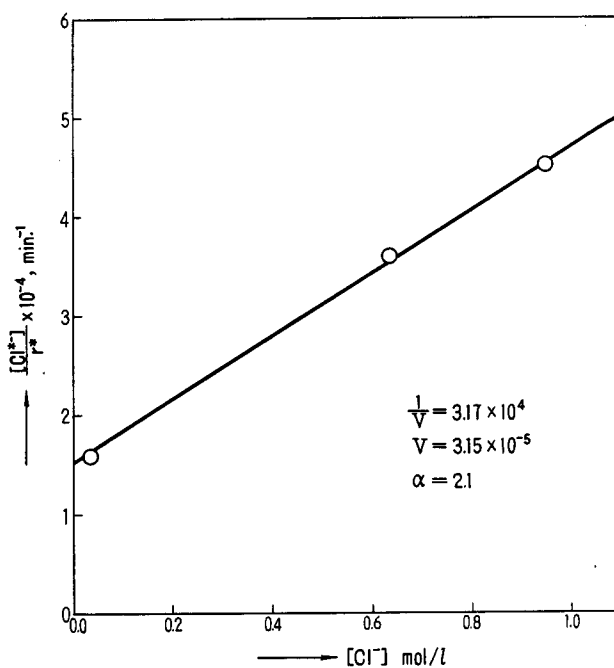


Fig. 3. Plot of  $[\text{Cl}^{*-}]/r^*$  vs.  $[\text{Cl}^-]$

It is clearly seen according to mechanism iii) that the chlorine exchange rate is dependent on the chloride ion concentration and slower than the hydrolysis rate as long as the chloride ion concentration is not too large.

#### Acknowledgment

We wish to thank Professor Emeritus J. HORIUTI for his support of this investigation and Dr. T. TAKESHITA for helpful discussion.

\*)  $[\text{Cl}^{*-}]/r^*$  was calculated from the relationship  $[\text{Cl}^{*-}]/r^* = \alpha^2 c_1^2 t / \alpha^2 c_1^2$ .

\*\*\*) Obtained from the slope of the straight line in Fig. 3.

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