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THE MECHANISM OF THE CHLORINE EXCHANGE REACTION OF METHYLENE CHLORIDE WITH AQUEOUS CHLORIDE SOLUTION

By

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Since no kinetic study has been made of the chlorine exchange of methylene chloride, we have investigated the exchange reaction at 100°C over the whole pH range from 0 to 14, with special reference to the effect of chloride ion concentration. The exchange rate was found to be constant independently of hydrogen ion concentration and proportional to chloride ion concentration in solution. It was concluded that the controlling step of the chlorine exchange is a $S_N 2$ type in character.

Introduction

In order to investigate the mechanism of the chlorine exchange between methylene chloride and aqueous chloride solution and the relative reactivities of the chlorides of methane, the exchange reaction has been carried out under the same experimental conditions as those of chloroform[1] and carbon tetrachloride[2] reported previously. In the present paper, the mechanism of the chlorine exchange is discussed on the basis of the observed kinetic data incorporated with those of the hydrolysis of methylene chloride under the similar conditions reported in the subsequent paper[3].

§ 1. Experimental

Reagents: Methylene chloride (Kanto Chemical Co., guaranteed reagent) was further purified by washing with conc. sulfuric acid and conductivity water and then by fractional distillation under nitrogen. The radioactive aqueous chloride solution of desired pH was prepared by adding dropwise 1.76 N radioactive hydrochloric acid[**] into conductivity water, sulfuric acid, sodium hydroxide solution or phosphate buffer solution (2/15 mol/ℓ Na$_2$HPO$_4$ + 2/15 mol/ℓ KH$_2$PO$_4$). Sodium chloride (guaranteed reagent) was used in experiments for the mass effect of chloride ion concentration on the exchange rate.

Kinetic Runs : Two ml of methylene chloride was sealed air-free*⁾ together with 1.5 or 2.0 ml aqueous radioactive chloride solution of known concentration and of known pH, in a quartz tube of 15~20 ml capacity similarly as in the previous works⁴⁾⁵⁾ and shaken vigorously at 100°C for a recorded time. The tube was then opened, about 1.5 ml of methylene chloride carefully pipetted out and washed with conductivity water several times**⁾ and then its radioactivity determined by putting 1 ml of the sample in a definite stainless steel tray fitted to a definite G–M counter as described previously¹⁾⁴⁾.

The radioactivity of the initial solution before the reaction was determined just similarly as that of methylene chloride after the reaction using the above definite apparatusses. The specific radioactivity C^S (radioactivity in the absence of self-absorption) of the solution and that C^C of methylene chloride were obtained by multiplying the apparent radioactivity C^S or C^C, *i. e.*, the excess count over the background count observed directly by the respective conversion factors particular to the above procedure of measurment. The factor $a^S = \dfrac{C^S}{C^S}$ for aqueous solution was determined to be 3.72 in the previous work¹⁾. The factor $a^{CH_2Cl_2}$ for methylene chloride has been estimated to be 4.18 from the factor a^{CHCl_3} for chloroform determined previously¹⁾, assuming that the factor is proportional to specific weight of a meterial.

The pH of solution was measured at room temperature before the reaction by means of pH-meter or calculated from the concentration of hydroxide ion titrated with standard oxalic acid solution in the case of extremely strong alkaline solution. The pH after the reaction was calculated from the hydrolysis rate given in the subsequent paper³⁾, except in Run 1 where the pH was directly measured by pH-meter.

§ 2. Exchange Rate Expression

If the chlorine exchange be controlled for instance by the step,

$$CH_2Cl^+ + Cl^- \longrightarrow CH_2Cl_2 \tag{1. D}$$

at equilibrium, the exchange rate***⁾ r is constant independently of the activity of chloride ion at constant pH, since the rate of the reversal of Eq. (1. D) which equals r because of the equilibrium is unaffected by the activity of chloride ion.

If on the other hand the exchange be controlled by the step,

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*) For the procedure of evacuating the tube, see p. 407 of Ref. 4 and p. 84 of Ref. 5.

**) The contamination due to the radioactive solution was completely eliminated by washing three times.

***) The exchange rate r is defined as forward rate of chlorine transfer from solution to methylene chloride for unit volume of solution.

$$Cl^- + CH_2Cl_2 \longrightarrow ClCH_2Cl + Cl^- \tag{1. S}$$

at equilibrium, r must be proportional to the activity of chloride ion or $r/[Cl^-]^{*)}$ must be constant.

Assuming

$$U_D \equiv r \quad \text{or} \quad U_S \equiv r/[Cl^-] , \tag{2. D) (2. S}$$

namely that r is either constant independently of $[Cl^-]$ or proportional to $[Cl^-]$, we have the following two equations for U_D and U_S similarly as in the cases of chloroform[1] and carbon tetrachloride[2].

$$U_D \equiv r = - \cfrac{\dot{n}^C}{v^S \ln \cfrac{1 + \cfrac{\dot{n}^C t}{n_0^C}}{1 - \cfrac{\dot{n}^C t}{n_0^S}}} \ln \left(1 - \frac{a^C C_t^C v^C n}{a^S C_0^S v^S n^C} \right)^{**)}, \tag{3. D}$$

$$U_S = r/[Cl^-] = - \frac{\dot{n}^C}{n \ln \left(1 + \cfrac{\dot{n}^C}{n_0^C} t \right)} \ln \left(1 - \frac{a^C C_t^C v^C n}{a^S C_0^S v^S n^C} \right), \tag{3. S}$$

where C_t^C or C_0^S is the apparent radioactivity of 1 ml methylene chloride 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 $a^C C_t^C v^C$ or $a^C C_0^S v^S$ is proportional to the number of radioactive chlorine atoms present in methylene chloride at time t or the total number present in the reaction vessel respectively.

Both U_D and U_S are calculated according to Eq. (3. D) and (3. S) from the observed values C_t^C, C_0^S etc. given in Table 1.

§3. Results of Experiment

In Table 1 are shown the experimental results. The third column "Aqueous Chloride Solution" gives the radioactivity of 1 ml sample before the reaction directly measured as described in §1 inclusive of background count, pH before or after the reaction, the total quantity of chloride ion before or after the reaction, the volume v^S of solution and the various reagents added. Quantity n_0^S of chloride ion before the reaction was determined by MOHR's titration method or calculated from the specific concentration and the known dilution of radioactive

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

**) The hydrolysis of methylene chloride which takes place simultaneously with the chlorine exchange was taken into consideration. *Cf.* p. 123 of Ref. 1 and p. 189 of Ref. 2. The n in the equation is the sum of n_0^S and n_0^C, which are given in Table 1.

TABLE 1. Exchange of Chlorine Labelled by ^{36}Cl between

Runs	Reaction Time min.	Aqueous Chloride Solution							
		Radioactivity before Reaction		pH		Qt. Cl$^-$ ion		Volume	Added Reagents
		Counts /min. ml	Background Counts/min	Before	After	n_0^S m mol	n^S m mol	v^S ml	
1	6,000	20,052	52	13.67	2.22	0.170	0.46 (9.60)	1.5	NaOH
2	6,000	20,736	52	0.31	0.17	0.194	0.48	1.5	H$_2$SO$_4$
3	244	16,243	55	13.65	12.9	6.26	6.77	2.0	NaOH+NaCl
4	244	22,572	56	13.65	12.9	0.26	0.77	2.0	NaOH
5	244	17,127	56	6.8	6.8	6.26	6.28	2.0	Buffer+NaCl
6	244	21,110	56	6.8	6.8	0.26	0.28	2.0	Buffer
7	29	19,934	55	11.50	11.27	0.179	0.18	2.0	NaOH
8	29	19,584	55	11.50	11.27	3.60	3.60	2.0	NaOH+NaCl
9	79.5	17,344	55	2.60	2.3	0.179	0.23	2.0	H$_2$SO$_4$
10	79.5	16,030	55	2.60	2.3	3.60	3.65	2.0	H$_2$SO$_4$+NaCl
11	79.5	15,868	55	1.20	1.18	4.63	4.68	2.0	H$_2$SO$_4$+NaCl

hydrogen chloride sample mentioned in §1 and from the known amount of added chloride, if any. Quantity n^S after the reaction was the sum of n_0^S and the increment Δn of chloride ion formed during the reaction. The increment was the rate $-\dot{n}^C$ of increase of chloride ion, given in the subsequent column, multiplied by the time t of the reaction.

The next column "Methylene Chloride" shows the directly observed radio-activity of methylene chloride after the reaction, the volume v^C of methylene chloride before the reaction at room temperature and the rate $-\dot{n}^C/v^S$ of the decrease of chlorine in methylene chloride per unit volume of solution which was quoted from the results of the hydrolysis in the subsequent paper[3].

The last column "Rates" shows $\log_{10} U_D$ and $\log_{10} U_S$ calculated according to Eqs. (3. D) and (3. S) from the data given in the foregoing columns.

Run 1 was conducted with strong alkaline solution, a pronounced exchange being observed as seen in the Table. Since, however, the pH shifted greatly due to the hydrogen chloride formed by the decomposition of methylene chloride, two different values of $-\dot{n}^C/v^S$ at different pH's were taken for the calculation of the rate. The rates calculated by taking the higher hydrolysis rate in alkaline solution are shown in parenthesis. In Runs 3 to Run 11, the exchange rate was quantitatively investigated, confining the associated pH-shift possibly narrow range, either by shortening the reaction time or by employing a buffer solution.

Methylene Chloride and Aqueous Chloride at 100°C.

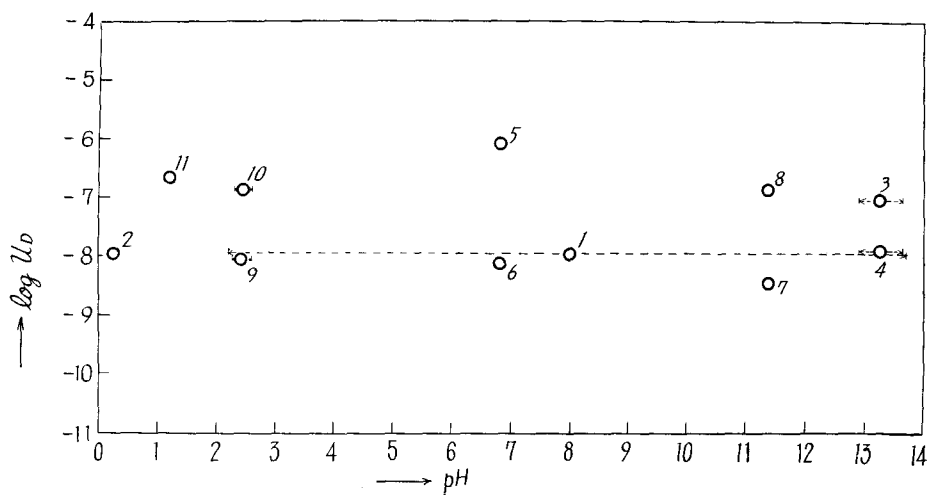| Methylene Chloride					Rates	
Radioactivity after Reaction		Volume	Qt. Cl-atom		$\log_{10} U_D$	$\log_{10} U_S$
Counts	Background	v^C	n_0^C	Rate of Decrease $-\dot{n}^C/v^S$	mol/l.	
/min. ml	Counts/min	ml	m mol	mol/ml. min	min	min^{-1}
4,620	52	2.0	62.92	3.17×10^{-8} (1.05×10^{-6})	-7.97 (-6.92)	-4.20 (-4.13)
4,505	52	2.0	62.92	3.17×10^{-8}	-7.96	-4.23
160	55	2.0	62.92	1.05×10^{-6}	-7.04	-4.56
331	56	2.0	62.92	1.05×10^{-6}	-7.91	-4.28
178	56	2.0	62.92	3.17×10^{-8}	-6.06	-4.36
343	56	2.0	62.92	3.17×10^{-8}	-8.12	-4.19
98	57	2.0	62.92	3.17×10^{-8}	-8.45	-4.37
92	48	2.0	62.92	3.17×10^{-8}	-6.84	-4.09
189	53	2.0	62.92	3.17×10^{-8}	-8.03	-3.95
146	57	2.0	62.92	3.17×10^{-8}	-6.88	-4.12
146	52	2.0	62.92	3.17×10^{-8}	-6.66	-4.08

Fig. 1. Rate $U_D \equiv r$ mol Cl/ℓ min of chlorine transfer from solution to methylene chloride in one direction at 100°C.

|←‑‑‑‑‑‑‑‑→|: Range of pH-variation.

The effect of chloride ion concentration on the exchange rate was investigated by adding sodium chloride in Runs 3, 5, 8, 10 and 11.

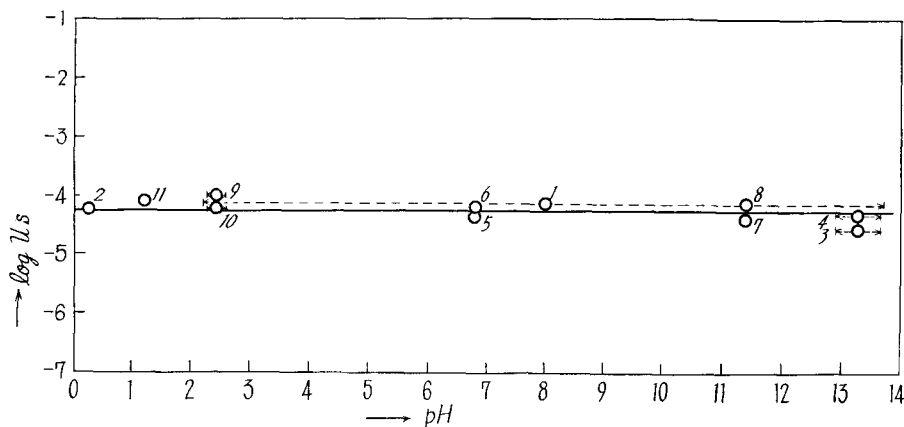The $\log_{10} U_D$ and $\log_{10} U_S$ are plotted respectively in Figs. 1 and 2 against

Fig. 2. Specific rate $r/[Cl^-]$ min^{-1} of chlorine transfer from solution
to methylene chloride in one direction at 100°C.
$|{\rightarrow} {-------} {\rightarrow}|$: Range of pH-variation.

pH, each at the median of pH, if varied. The pH-variation is shown by
a horizontal dotted line. It is seen from Fig. 1 that U_D varies with $[Cl^-]$ by
a factor of ten to a hundred, whereas from Fig. 2 U_S is independent of $[Cl^-]$.
It is also seen that pH has no appreciable effect on the rate constant U_S. A
straight line is drawn through the observed points in Fig. 2.

It is now concluded from the above results that the exchange rate is
proportional to $[Cl^-]$, the appropriate proportionality factor U_S being inde-
pendent of $[Cl^-]$ and pH.

Since the reaction rate was found independent of shaking rates, it may
be admitted that the reaction takes place in the aqueous phase and that the
rates of diffusion of methylene chloride in and out of the aqueous phase are
fast compared to the exchange rate.

§ 4. Discussion

On the basis of the results in the foregoing section, we shall discuss the
mechanism of the chlorine exchange of methylene chloride in a similar manner
as in the case of carbon tetrachloride reported previously[2]. On the ground of
the experimental result that the exchange rate is constant independently of pH,
we consider the two steps, which are assumed to govern the rate of the chlorine
exchange,

(I) $Cl^- + CH_2Cl^+ \longrightarrow CH_2Cl_2$,

(II) $Cl^- + CH_2Cl_2 \longrightarrow ClCH_2Cl + Cl^-$,
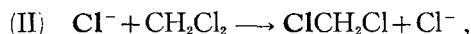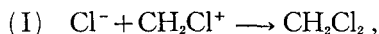
where Cl denotes chlorine atom originating from chloride ion in solution. The

rate-determining step of the hydrolysis of methylene chloride depends on the concentration of hydroxide ion as shown in the subsequent paper[3]. It follows that either step (I) or (II) which is different from the rate-determining step of the hydrolysis is practically in equilibrium[*] or that its rates in both directions are ballanced with each other, since the hydrolysis of methylene chloride is only the process proceeding irreversibly in our assembly.

The exchange rate r must now be constant independently of $[Cl^-]$[**] or proportional to $[Cl^-]$ according as (I) or (II) operates. The experimental results in the foregoing section show that r is proportional to $[Cl^-]$. Therefore, the step (II) fits the observed results but the step (I) is ruled out.

It is now concluded that the chlorine exchange proceeds by the step (II) which is in equilibrium.

References

1) J. HORIUTI, K. TANABE and K. TANAKA, This Journal, **3**, 119 (1955).

2) K. TANABE and A. ARAMATA, ibid., **8**, 188 (1961).

3) K. TANABE and M. MATSUDA, ibid., **9**, 246 (1961).

4) J. HORIUTI and K. TANABE, Proc. Japan Acad., **27**, 404 (1951).

5) K. TANABE and Y. WATANABE, J. Chim. Physique, **57**, 486 (1960); This Journal, **7**, 79 (1959).

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*) It can be also shown by applying the same argument as that described in the case of chloroform that no chlorine exchange of methylene chloride takes place through the rate-detemining step of the hydrolysis in either direction. See pp. 133~135 of Ref. 1.

**) The activity of chloride ion was identified with the concentration.