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THE MECHANISM OF THE EXCHANGE REACTION OF CHLORINE BETWEEN BENZYL CHLORIDE AND AQUEOUS CHLORIDE SOLUTION

By

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Abstract

The exchange rate of the chlorine of benzyl chloride with chloride ion in aqueous solution has been determined at 30°C over the whole pH range from 0 to 14, the hydrolysis of benzyl chloride which takes place simultaneously with the chlorine exchange being taken into consideration. It has been found that the exchange rate is constant independently of pH and proportional to chloride ion concentration in solution. On the basis of the observed results, it was concluded that the chlorine exchange proceeds by a bimolecular mechanism of nucleophilic substitution.

Introduction

We have previously investigated the chlorine exchange of chloroform¹⁾, carbon tetrachloride²⁾ or methylene chloride³⁾ with aqueous chloride solution and proposed each exchange mechanism. The present work was initiated with the purpose of learning the mechanism of chlorine exchange of more complicated organic chloride in aqueous solution as well as its hydrolysis mechanism. De La MARE and HUGHES have studied the chlorine exchange of benzyl chloride with lithium chloride in anhydrous acetone. Since in aqueous solution, however, the hydrolysis takes place appreciably during the exchange, we have studied the exchange together with the hydrolysis under the same experimental condition.

§ 1. Experimental

Reagents: Benzyl chloride (KANTO Chemical Co., guaranteed reagent) was purified by distillation after washing with distilled water. The fraction boiling at 52--52.5°C at 8 mmHg was used. The radioactive aqueous chloride solution of desired pH was prepared by adding dropwise about 4.5 N radioactive hydrochloric acid**) into conductivity water***), sulfuric acid, sodium hydroxide solu-

*) The Research Institute for Catalysis, Hokkaido University.

**) Hydrochloric acid containing ³⁶Cl imported from the Atomic Energy Commission, U. S. A.

***) Conductivity water from Amberlite resin column.

tion or phosphate buffer solution (2/15 mol/l $\text{Na}_2\text{HPO}_4 + 2/15 \text{ mol/l } \text{KH}_2\text{PO}_4$) as described previously^{1,2,3)}. Sodium chloride (KANTO Chemical Co., guaranteed reagent) was used in experiments for the mass effect of chloride ion concentration on the exchange rate.

Kinetic Runs: In a typical run, 2.5 ml of benzyl chloride was pipetted into a 30 ml Erlenmeyer flask placed in a thermostat maintained at 30°C and 2.5 ml of aqueous radioactive chloride solution of known concentration and known pH was added and the mixture was stirred vigorously by a magnetic stirrer. At a recorded time, the flask was taken out and cooled in cold water and about 1.8 ml of benzyl chloride was pipetted out and washed with conductivity water more than ten times until no radioactivity was found in the washing and then its radioactivity determined by putting 1 ml sample in a definite stainless steel tray fitted to a definite G-M counter as in the previous works^{1,5)}. The radioactivity of the initial solution before reaction was determined by the same method as that of benzyl chloride after reaction using the above definite apparatuses. The specific radioactivity C^S (radioactivity in the absence of self-absorption) of the solution and that C^C of benzyl chloride were obtained by multiplying the apparent radioactivity C^S or C^C by the respective conversion factors particular to the above procedure of measurement. The factor $a^S = C^S/C^S$ for aqueous solution was determined to be 3.72 in the previous work¹⁾. The factor a^C for benzyl chloride has been estimated to be 3.85 from the factor a^{CHCl_3} for chloroform determined previously¹⁾ 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 pH-meter^{*)} or calculated from the concentration of hydroxide ion titrated with a standard oxalic acid solution in the case of extremely strong alkaline solution (runs 4 and 7) as in the previous work^{1)**)} or from the concentration of hydroxide ion titrated with standard sodium hydroxide solution in some cases (runs 1 and 5). The pH after reaction was calculated from the rate of hydrolysis given in the subsequent column.

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} – 10^{-5} mmHg) and thawing as described previously^{5,7)}.

As shown in the subsequent paper⁶⁾, the hydrolysis rate which is larger than the exchange rate is independent of shaking rates and the volume of aqueous phase. It may therefore be admitted that the exchange reaction proceeds

*) HORIBA glass electrode pH meter, HORIBA Mfg. Co., Tokyo.

***) In the present work, the value 1.52×10^{-14} was taken as the dissociation constant of water at 30°C in the calculation of the concentration of hydrogen ion from that of hydroxide ion.

homogeneously in the aqueous phase and that the rates of diffusion of benzyl chloride in and out of the aqueous phase are fast compared to the exchange rate.

§ 2. Exchange Rate Expression

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



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,



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

Assuming

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

namely that r is either constant independently of $[\text{Cl}^-]$ or proportional to $[\text{Cl}^-]$, we have the following two equations for U_D and U_S similarly as in the cases of chloroform¹⁾ and carbon tetrachloride²⁾.

$$U_D \equiv r = \frac{\dot{n}^c}{v^s \ln \left(\frac{1 + \frac{\dot{n}^c t}{n_0^c}}{1 - \frac{\dot{n}^c t}{n_0^s}} \right)} \ln \left(1 - \frac{a^c C_t^c v^c n}{a^s C_0^s v^s n^c} \right), \quad (3. D)$$

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

where C_t^c or C_0^s is the apparent radioactivity of 1 ml benzyl 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 $a^s C_0^s v^s$ is proportional to the number of radioactive chlorine atoms present in benzyl chloride 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 \dot{n}^c is the

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

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

TABLE 1 Exchange of Chlorine Labeled by ^{36}Cl

Runs	Time of Reaction min	Aqueous Chloride Solution						
		Radioactivity before Reaction		pH		Qt. Cl^- ion		Volume v^s mℓ
		Counts/min, mℓ	Background Counts/min	Before	After	n_0^s mmol	n^s mmol	
1	562	4834	21	0.77	0.77	0.443	0.456	2.5
2	420	9692	21	5.20	2.42	0.957	0.967	2.5
3 ^{*)}	360	9692	21	5.20	2.49	0.957	0.965	2.5
4	300	8080	21	14.0	13.8	0.801	0.842	2.5
5	420	9828	22	0.42	0.42	5.160	5.170	2.5
6	455	8000	22	8.00	2.39	5.458	5.468	2.5
7	420	7308	22	14.0	13.8	3.934	3.992	2.5
8	423	9878	18	11.41	9.92	1.187	1.197	2.5
9	425	9031	18	6.32	2.42	5.719	5.729	2.5
10	421	13351	18	6.81	2.42	1.180	1.190	2.5
11	402	12311	18	6.81	2.44	4.732	4.741	2.5
12	425	9227	18	12.05	11.94	5.826	5.836	2.5
13	2162	4710	16	8.50	1.71	0.406	0.455	2.5
14	1659	4427	16	12.60	12.35	0.391	0.458	2.5
15	2045	3343	16	12.60	12.26	0.275	0.357	2.5

* This run was conducted in vacuum.

rate of decrease of chlorine in benzyl chloride.

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

§ 3. Results of Experiment

Table 1 shows the experimental results. The third column "Aqueous Chloride Solution" gives the radioactivity of 1 mℓ sample before reaction directly measured as described in § 1 inclusive of background count, pH before or after reaction, the total quantity of chloride ion before or after reaction, the volume v^s of solution and the various reagents added. Quantity n_0^s of chloride ion before reaction was determined by a modification of VOLHARD's method or calculated from the known amount of added chloride, if any. Quantity n^s after reaction was the sum of n_0^s and the increment Δn of chloride ion formed during the reaction. The increment was the rate $-\dot{n}^c/v^s$ of increase of chloride ion, given in the subsequent column, multiplied by the time t of the reaction and

The Mechanism of the Exchange Reaction of Chlorine Between Benzyl Chloride

between Benzyl Chloride and Aqueous Chloride at 30°C

Added Reagents	Benzyl Chloride					Rates	
	Radioactivity after Reaction		Volume v^c ml	Qt. Cl-atom		$\log_{10} U_D$ mol/l, min	$\log_{10} U_S$ min ⁻¹
	Counts/min ml	Background Counts/min		n_0^c mmol	Rate of Decrease $-\dot{n}^c/v^s \times 10^5$ mol/l.min		
none	61	21	2.5	21.73	0.9	- 5.56	- 4.81
NaOH	97	21	2.5	21.73	0.9	- 5.13	- 4.72
NaOH	73	21	2.5	21.73	0.9	- 5.23	- 4.81
NaOH	44	21	2.5	21.73	5.5	- 5.49	- 5.00
NaCl	61	22	2.5	21.73	0.9	- 4.69	- 5.01
NaOH+NaCl	49	22	2.5	21.73	0.9	- 4.78	- 5.12
NaOH+NaCl	39	22	2.5	21.73	5.5	- 5.14	- 5.24
NaOH	80	18	2.5	21.73	0.9	- 5.56	- 4.81
NaOH+NaCl	52	18	2.5	21.73	0.9	- 4.78	- 5.04
Buffer	104	18	2.5	21.73	0.9	- 5.24	- 4.80
Buffer+NaCl	66	18	2.5	21.73	0.9	- 4.72	- 5.00
NaOH+NaCl	41	18	2.5	21.73	0.9	- 4.95	- 5.22
NaOH	193	16	2.5	27.73	0.9	- 5.50	- 4.74
NaOH	136	16	2.5	21.73	1.6~1.0	- 5.55	- 4.76
NaOH	114	16	2.5	21.73	1.6~1.0	- 5.74	- 4.82

the volume v^s of solution. The next column "Benzyl Chloride" shows the directly observed radioactivity of benzyl chloride after reaction, the volume v^c of benzyl chloride before reaction at room temperature and the rate $-\dot{n}^c/v^s$ of the decrease of chlorine in benzyl chloride per unit volume of solution which was quoted from the results of the hydrolysis reported in the subsequent paper⁶⁾. 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.

In runs conducted in strong acidic or alkaline solution, the exchange was investigated confining the pH-shift due to the hydrogen chloride formed by the hydrolysis within possibly narrow range. In runs in the mediate pH region and in buffer solution (runs 10 and 11), 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 3 was conducted in the absence of air. A comparison with this run with run 2 conducted in the presence of air shows that oxygen has negligible effect on the exchange. The effect of chloride ion concentration on the exchange rate was investigated by adding sodium chloride in runs 5, 6, 7, 9, 11 and 12. In runs 14 and 15, the

hydrolysis rate changes from 1.6×10^{-5} to 1.0×10^{-5} as pH changes from 12.60 to 12.35 or 12.26. Therefore, the exchange rate was calculated taking two different values of $-\dot{n}^c/v^s$ at different pH's, but no appreciable difference was found.

The $\log U_D$ and $\log U_S$ 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. It is seen from Fig. 1 that U_D varies with $[Cl^-]$ by a factor of ten, whereas from Fig. 2 U_S is almost 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

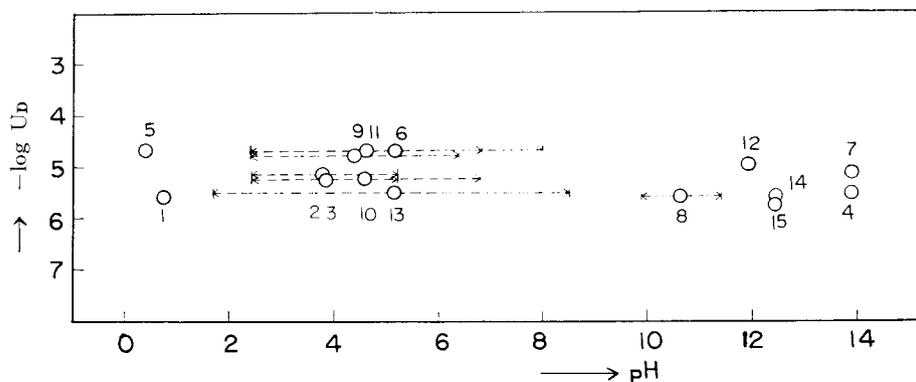


Fig. 1. Rate $U_D \equiv r$ mol of Cl/ℓ , min. of chlorine transfer from solution to benzyl chloride at $30^\circ C$. $\left\langle \leftarrow \text{-----} \rightarrow \right\rangle$: Range of pH-variation.

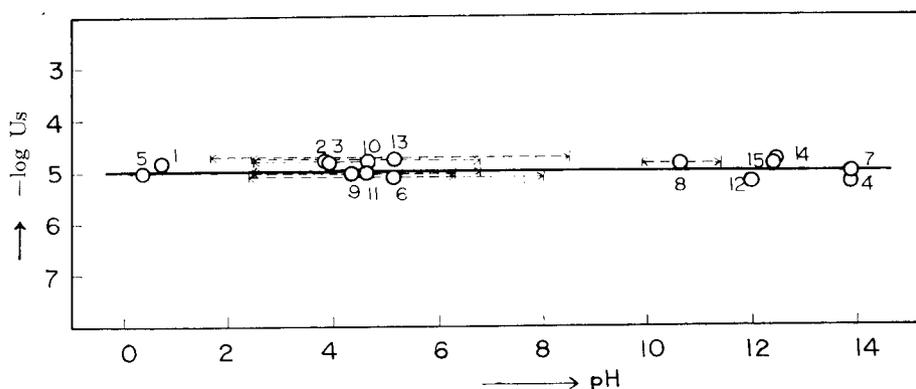
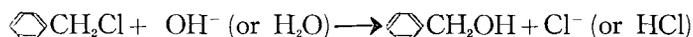


Fig. 2. Specific rate $r/[Cl^-]$ min^{-1} of chlorine transfer from solution to benzyl chloride at $30^\circ C$. $\left\langle \leftarrow \text{-----} \rightarrow \right\rangle$: Range of pH-variation.

proportional to $[\text{Cl}^-]$, the appropriate proportionality factor U_s being independent of $[\text{Cl}^-]$ and pH.

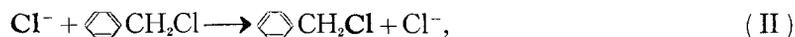
§ 4. Discussion

Let us first consider the case where chlorine exchange takes place through any of the elementary steps of the hydrolysis of benzyl chloride. If so, it must occur through the reversal of the rate-determining step of the hydrolysis, since the observed exchange rate r is small compared to the hydrolysis rate under the same experimental conditions^{*)}. The rate-determining step of the hydrolysis was assigned to a bimolecular nucleophilic substitution shown below as discussed in the subsequent paper⁶⁾.



If the chlorine exchange occurs through the reversal of this step, the rate of the exchange is proportional to $[\text{Cl}^-]$ in accordance with the experimental results, but must increase with increase of pH in contradiction with the observed results that the exchange rate is independent of pH, since under the present experimental condition where the concentration of benzyl chloride is kept constant the exchange rate is also proportional to the concentration of benzyl alcohol which increases as pH does. It can be also shown by applying the same argument as that described in the case of chloroform^{**)} that no chlorine exchange of benzyl chloride takes place through the reversal of the rate-determining step of the hydrolysis. Therefore, the chlorine exchange must be attributed to any step which is different from any elementary steps of the hydrolysis and is practically in equilibrium, since the hydrolysis of benzyl chloride is only the process proceeding irreversibly in our assembly.

On the ground of the experimental results that the exchange rate is constant independently of pH, we shall consider the following two steps in equilibrium,



which are assumed to govern the rate of the chlorine exchange, where Cl denotes chlorine atom originating from chloride ion in solution.

The exchange rate r must now be constant independently of $[\text{Cl}^-]$ or proportional to $[\text{Cl}^-]$ according as (I) or (II) operates. The experimental results

^{*)} See foot-note of page 179 of Ref. 6.

^{***)} See pp. 133-135 of Ref. 1.

in the foregoing section show that r is proportional to $[\text{Cl}^-]$. Therefore, the step (II) fits the observed results but step (I) does not. The latter step is thus ruled out. It is now concluded that the chlorine exchange proceeds by step (II) which is in equilibrium.

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