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# THE EXCHANGE REACTIONS OF CHLORINE AND HYDROGEN BETWEEN BENZAL CHLORIDE AND AQUEOUS CHLORIDE SOLUTION

By

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## Abstract

The exchange rates of chlorine and hydrogen of benzal chloride were measured by using radioactive  $^{36}\text{Cl}$  and  $^3\text{H}$  at  $12^\circ\text{C}$  in aqueous acidic or basic solution. The findings that the rate of the chlorine exchange is neither of the first order with respect to the chloride ion concentration in solution nor constant independently of the concentration led us to conclude that the chlorine exchange proceeds by the reversal of the rate-determining step of the hydrolysis. The hydrogen exchange was found to be catalyzed by BRÖNSTED base and slower than the hydrolysis rate. The observed hydrogen exchange was suggested to proceed by the proton transfer between benzal chloride and BRÖNSTED base which is in equilibrium.

## Introduction

We have previously investigated the chlorine exchange<sup>1)</sup> of benzyl chloride together with its hydrolysis.<sup>2)</sup> Since no kinetic study has been made of the chlorine and the hydrogen exchange of benzal chloride, the present work was initiated. The mechanisms of the both exchange reactions are discussed on the basis of the observed kinetic data incorporated with those of the hydrolysis of benzal chloride under the similar conditions reported in the subsequent paper.<sup>3)</sup>

## § 1. Experimental

**Reagents:** Benzal chloride (Kanto Chemical Co., guaranteed reagent) was purified by distillation after washing with distilled water. The radioactive aqueous chloride solution of desired pH was prepared by adding dropwise about 4.5 N radioactive hydrochloric acid<sup>\*\*)</sup> into conductivity water<sup>\*\*\*)</sup>, sulfuric acid or

\*) The Research Institute for Catalysis, Hokkaido University.

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

\*\*\*) Conductivity water from Amberlite resin column.

sodium hydroxide solution as described previously.<sup>4)</sup> Sodium chloride (**Kanto** Chemical Co., guaranteed reagent) was used in experiments for the effect of chloride ion concentration on the chlorine exchange rate. The radioactive water containing tritium imported from Atomic Energy Commission, U. S. A. was used for the hydrogen exchange by diluting with conductivity water or sodium hydroxide solution.

**Chlorine exchange reaction:** 2.5 ml of benzal chloride was pipetted into a 30 ml Erlenmeyer flask placed in a water-bath maintained at 12°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 about 2.2 ml of benzal chloride was pipetted out and washed with conductivity water more than seven times until no radioactivity was found in the washings and then the radioactivity of 1 ml sample determined by a G-M counter as in the previous works.<sup>1,5)</sup> The radioactivity of the initial solution before reaction was determined just similarly as that of benzal chloride after reaction. The specific radioactivity  $C^s$  (radioactivity in the absence of self-absorption) of the solution and that  $C^c$  of benzal chloride were obtained by multiplying the apparent radioactivity  $C^a$  or  $C^r$  by the respective conversion factors particular to the above procedure of measurement. The factor  $\alpha^s = C^a/C^s$  for aqueous solution was determined to be 3.72 in the previous work.<sup>4)</sup> The factor  $\alpha^c$  for benzal chloride has been estimated to be 4.12 from the factor  $\alpha^{CHCl_3}$  for chloroform determined previously<sup>4)</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 pH-meter<sup>\*)</sup> 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>3)</sup>

As shown in the subsequent paper<sup>3)</sup>, the hydrolysis rate 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 reaction proceeds homogeneously in the aqueous phase and that the rates of diffusion of benzal chloride in and out of the aqueous phase are fast compared to the exchange rate.

**Hydrogen exchange reaction:** The experiment of hydrogen exchange was

\*) Horiba glass electrode pH meter, **Horiba** Mfg. Co., Tokyo.

\*\*\*) In the present work, the value  $0.35 \times 10^{-14}$  was taken as the dissociation constant of water at 12°C in the calculation of the concentration of hydrogen ion from that of hydroxide ion.

carried out similarly as in the case of chlorine exchange except that the measurement of radioactivity is different. The radioactivity of the solution before reaction or benzal chloride after reaction was determined as described below. 0.5 ml of the radioactive initial solution was dissolved in 15 ml of ethanol-toluene mixture containing scintillator<sup>\*)</sup> and 0.5 ml non-radioactive benzal chloride was added to make the quenching and the self-absorption of radioactivity due to the sample before reaction the same as those after reaction. 15 ml of the resulted 16 ml mixture was put in a quartz sample tube and its radioactivity determined by a liquid scintillation counter.<sup>\*\*)</sup> The radioactive benzal chloride after reaction was washed at least seven times with conductivity water until no radioactivity was found in the washings. 0.5 ml of the benzal chloride was dissolved together with 0.5 ml of non-radioactive water in ethanol-toluene-scintillator mixture and its radioactivity of the mixture was determined similarly as above. The background count was taken as the count of 15 ml of ethanol-toluene-scintillator mixture in which both non-radioactive water (0.5 ml) and benzal chloride (0.5 ml) are dissolved.

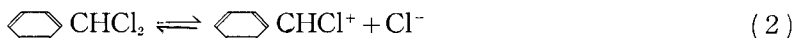
## § 2. Exchange Rate Expression

**Chlorine exchange:** The following three kinds of 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,

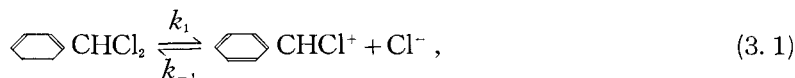


- iii) An elementary reaction whose rate of chlorine exchange is dependent on chloride ion concentration in solution, but is not of the first order with respect to the concentration. Namely, the case where the reactive transient species which give rise to the chlorine exchange participate in any reaction, which is not in equilibrium, other than the chlorine exchange.

\*) The mixture of 30 ml-ethanol and 60 ml-toluene in which 0.4805 g of PPO (2,5-diphenyl-oxazole) and 0.01202 g of POPOP (2,2'-p-phenylene-bis-(5-phenyloxazole)) are dissolved. The scintillators are reagents of Packard Instrument Co.

\*\* ) Model NE 8301 of Nuclear Enterprise Ltd.

Such an elementary reaction is reversal of the rate-determining step (3.1) of the hydrolysis, of which mechanism will be determined in the subsequent paper.<sup>3)</sup>



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

In the cases of i) and ii), the exchange rate<sup>\*)</sup>  $r$  is expressed respectively by the following two equations derived previously<sup>4,6)</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  $[\text{Cl}^-]$ .

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

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

where  $C_i^c$  or  $C_0^s$  is the apparent radioactivity of 1 ml benzal 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  $a^c C_i^c v^c$  or  $a^s C_0^s v^s$  is proportional to the number of radioactive chlorine atoms present in benzal 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 rate of decrease of chlorine in benzal chloride. Both  $U_s$  and  $U_D$  are calculated according to Eqs. (4) and (5) from the observed values  $C_i^c$ ,  $C_0^s$  etc. given in Table 1.

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

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

\*) The exchange rate  $r$  is defined as forward rate of chlorine transfer from solution to benzal chloride for unit volume of solution. (See ref. 4).

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

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

where [Bz] is the concentration of benzal chloride and [Cl<sup>-</sup>] that of chloride ion in solution.

**Hydrogen exchange:** If  $q$  is taken as the rate of hydrogen transfer from solution to benzal chloride for unit volume of solution, the rate of transfer of radioactive hydrogen is  $qv^s(x^s - x^c)$ , where  $x^s$  or  $x^c$  is the atomic fraction of radioactive hydrogen in solution or in benzal chloride respectively and  $v^s$  the volume of solution.

Since the rate of isotopic transfer  $qv^s(x^s - x^c)$  can be expressed by an alternative form  $-n^s dx^s/dt$ , where  $n^s$  is the amount of hydrogen in solution which is practically kept constant during the reaction under the present experimental condition and  $t$  the time of reaction, we have,

$$-n^s \frac{dx^s}{dt} = qv^s(x^s - x^c)^* \quad (8)$$

The total amount of hydrogen in the reaction vessel is kept constant during the reaction. Thus, we have the relation,

$$n^s x^s + n^c x^c = n^s x_0^s, \quad (9)$$

where  $n^c$  is the quantity of hydrogen of side chain<sup>\*\*</sup>) in benzal chloride and  $x_0^s$  the atomic fraction of radioactive hydrogen in solution at  $t=0$ . Substitution of Eq. (9) to (8) yields,

$$qv^s \left( \frac{n^s x_0^s - n^c x^c - n^s x^c}{n^s} \right) = n^c \frac{dx^c}{dt}. \quad (10)$$

This equation may be integrated after rearrangement as,

$$\frac{qv^s}{n^c n^s} t = \frac{\ln \frac{n^s x_0^s - n^c x^c - n^s x^c}{-n^c - n^s}}{-n^c - n^s} + \text{const.}$$

Since  $x^c=0$  at  $t=0$ , the constant is obtained as,

$$\text{const.} = \ln \frac{\ln n^s x_0^s}{n^c + n^s}. \quad (11)$$

Thus, we have,

\*) The amount of benzal chloride which decomposed during the exchange reaction was found so small compared to the total amount present in reaction vessel that it was neglected in this equation.

\*\*\*) Only the hydrogen of the side chain which is known much more reactive than the ring hydrogens was assumed to undergo the exchange reaction.

$$\frac{qv^s}{n^c n^s} t = \frac{1}{n^c + n^s} \ln \frac{n^s x_0^s}{n^s x_0^s - n^c x^c - n^s x^c}, \quad (12)$$

or,

$$q = -\frac{1}{tv^s} \cdot \frac{n^c}{1 + \frac{n^c}{n^s}} \ln \left\{ 1 - \left( \frac{n^c}{n^s} + 1 \right) \frac{x^c}{x_0^s} \right\}. \quad (13)$$

The  $x^c/x_0^s$  in Eq. (13) may be expressed as,

$$x^c/x_0^s = \frac{C_i^c v^c n^s}{C_0^s v^s n^c}, \quad (14)$$

where  $C_i^c$  or  $C_0^s$  is the radioactivity of benzal chloride per unit volume at time  $t$  or that of solution per unit volume at  $t=0$  respectively, and  $v^c$  is the volume of benzal chloride.

### § 3. Results and Discussion

Table 1 shows the experimental results of the chlorine exchange. The third column "Aqueous Chloride Solution" gives the radioactivity of 1 ml sample before reaction measured as described in §1 exclusive 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  $\Delta n$  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. The next column "Benzal Chloride" shows the observed radioactivity of benzal chloride after reaction, the quantity of chlorine atom  $n_0^c$  and the volume  $v^c$  of benzal chloride before reaction at room temperature and the rate  $-\dot{n}^c/v^s$  of the decrease of chlorine in benzal chloride per unit volume of solution which was quoted from the results of the hydrolysis reported in the subsequent paper.<sup>3)</sup> The last column "Rates" shows  $\log_{10} U_D$  and  $\log_{10} U_s$  calculated according to Eqs. (5) and (4) 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 8, 9 and 10 in the 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. The effect of chloride ion concentration on the

TABLE 1. Exchange of Chlorine Labeled by  $^{36}\text{Cl}$  between Benzal Chloride and Aqueous Chloride at  $12^\circ\text{C}$ .

Runs	Time of Reactions min.	Aqueous chloride solution							Benzal chloride				Rates	
		Radioactivity before reaction cpm	pH		Qt. $\text{Cl}^-$ ion		Volume $v^s$ ml	Added reagents	Radioactivity after reaction cpm	Volume $v^s$ ml	Qt. Cl atom		$\log_{10} U_D$ mol/l min.	$\log_{10} U_s$ min $^{-1}$
			Before	After	$n_0^s$ mol	$n^s$ mol					$n_0^c$ mol	Rate of decrease $-\dot{n}^c/v^s$ mol/l min.		
1	360	17730	1.60	1.20	$6.28 \times 10^{-5}$	$2.10 \times 10^{-4}$	2.5	none	327	2.5	$4.02 \times 10^{-2}$	$7.62 \times 10^{-5}$	-8.57	-4.24
2	400	10160	2.07	1.17	$1.72 \times 10^{-5}$	$1.39 \times 10^{-4}$	2.0	none	124	3.0	$4.83 \times 10^{-2}$	$7.62 \times 10^{-5}$	-8.83	-4.29
3	360	17730	1.60	1.20	$6.28 \times 10^{-5}$	$2.00 \times 10^{-4}$	2.5	none	270	2.5	$4.02 \times 10^{-2}$	$7.62 \times 10^{-2}$	-8.52	-4.33
4	360	5330	2.07	1.17	$1.01 \times 10^{-3}$	$1.12 \times 10^{-3}$	2.0	NaCl	31	3.0	$4.83 \times 10^{-2}$	$7.68 \times 10^{-5}$	-7.84	-4.57
5	360	17480	1.60	1.21	$1.44 \times 10^{-3}$	$1.58 \times 10^{-3}$	2.5	NaCl	114	2.5	$4.02 \times 10^{-2}$	$7.68 \times 10^{-5}$	-7.92	-4.70
6	360	17300	1.60	1.22	$2.68 \times 10^{-3}$	$2.78 \times 10^{-3}$	2.5	NaCl	89	2.5	$4.02 \times 10^{-2}$	$5.82 \times 10^{-5}$	-7.76	-4.80
7	300	9260	2.07	1.17	$5.02 \times 10^{-3}$	$5.09 \times 10^{-3}$	2.0	NaCl	18	3.0	$4.83 \times 10^{-2}$	$5.82 \times 10^{-5}$	-7.56	-4.97
8	360	9300	11.08	1.50	$2.76 \times 10^{-4}$	$4.15 \times 10^{-4}$	2.5	NaCl+NaOH	107	2.5	$4.02 \times 10^{-2}$	$7.68 \times 10^{-5}$	-8.34	-4.36
9	440	9670	11.08	1.40	$1.38 \times 10^{-3}$	$1.50 \times 10^{-3}$	2.5	NaCl+NaOH	68	2.5	$4.02 \times 10^{-2}$	$7.68 \times 10^{-5}$	-8.22	-4.75
10	540	8440	11.08	1.50	$2.70 \times 10^{-3}$	$2.96 \times 10^{-3}$	2.5	NaOH+NaCl	58	2.5	$4.02 \times 10^{-2}$	$5.82 \times 10^{-5}$	-7.80	-4.85
11	240	18330	12.88	12.60	$6.86 \times 10^{-5}$	$1.59 \times 10^{-4}$	2.5	NaOH	145	2.5	$4.02 \times 10^{-2}$	$7.50 \times 10^{-5}$	-8.80	-4.44
12	540	17660	12.88	12.00	$1.42 \times 10^{-3}$	$1.63 \times 10^{-3}$	2.5	NaCl+NaOH	137	2.5	$4.02 \times 10^{-2}$	$7.68 \times 10^{-5}$	-8.01	-4.80
13	480	16890	12.88	12.32	$2.94 \times 10^{-3}$	$3.03 \times 10^{-3}$	2.5	NaOH+NaCl	68	2.5	$4.02 \times 10^{-2}$	$5.82 \times 10^{-5}$	-7.95	-5.03
14	420	7330	13.59	13.51	$1.72 \times 10^{-5}$	$1.43 \times 10^{-4}$	2.0	NaOH	22	3.0	$4.83 \times 10^{-2}$	$7.50 \times 10^{-5}$	-9.45	-4.92

exchange rate was investigated in runs 4, 5, 6, 7, 8, 9, 10, 12 and 13.

The  $\log_{10} U_s$  and  $\log_{10} U_D$  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 the figures that both  $U_s$  and  $U_D$  varies with  $[Cl^-]$ . However,  $U_s$  derived from mechanism i) and  $U_D$  from mechanism ii) must be constant independently of  $[Cl^-]$  as described in §2, this being incompatible with the experimental facts. Therefore, mechanism 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 by the fact that the plot of the reciprocal of the hydrolysis rate *vs.* the chloride ion concentration gives a straight line as discussed in detail in the subsequent paper.<sup>3)</sup> It is clearly seen according to this mechanism that the chlorine exchange rate is dependent on the chloride ion concentration and is slower than the hydrolysis rate as long as the chloride ion concentration is not too large. The exchange rates  $r$  at various concentrations of chloride ion, calculated according to Eq. (6)<sup>\*</sup>, are shown in Table 2, where, for a comparison, the hydrolysis rates<sup>\*\*</sup>) observed

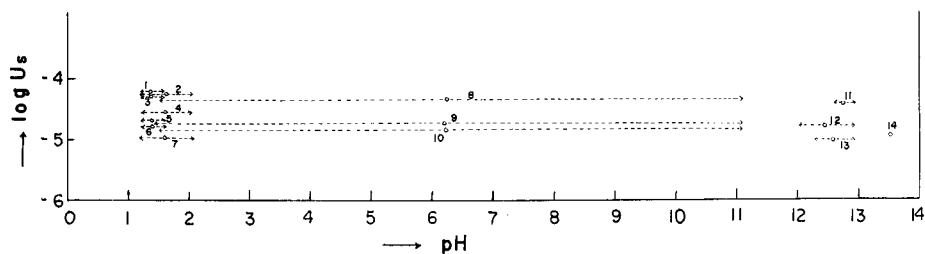


Fig. 1. Specific rate  $r/[Cl^-]$  min<sup>-1</sup> of chlorine transfer from solution to benzal chloride at 12°C.  $\longleftrightarrow$ : Range of pH-variation.

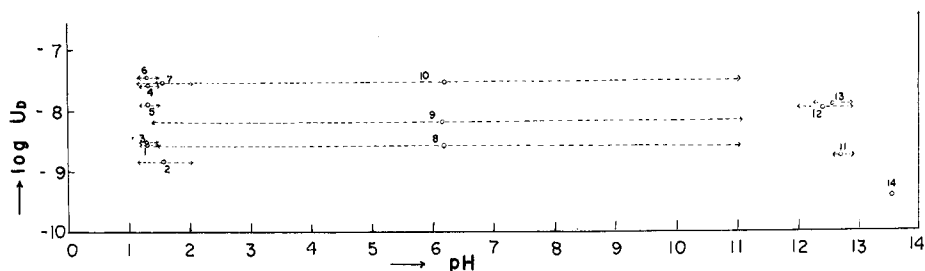


Fig. 2. Rate  $U_D \equiv r$  mole of Cl/l, min. of chlorine transfer from solution to benzal chloride at 12°C.  $\longleftrightarrow$ : Range of pH-variation.

\*) The value of  $\alpha$  in the equation is obtained to be 1.7 from the work in the subsequent paper.<sup>3)</sup>

\*\*\*) Taken from Table in the subsequent paper.<sup>3)</sup>

TABLE 2. The Rate of Chlorine Exchange at Various Chloride Ion Concentrations at 12°C.

[Cl <sup>-</sup> ] mol/l	Rate of Chlorine Exchange <i>r</i> mol/l min. × 10 <sup>-5</sup>	Rate of Hydrolysis <i>V<sub>d</sub></i> mol/l min. × 10 <sup>-5</sup>
very small	—	7.86
0.1	0.18	7.68
0.5	2.04	5.82
1.0	4.86	3.00
3.0	6.42	1.44
5.0	7.08	0.78

at the corresponding conditions are also given.

The experimental results of the hydrogen exchange are shown in Table 3. Fig. 3 shows a part of the results of radioactivity measurement at various pulse heights. Radioactivity before or after reaction given respectively in the second or eighth column of Table 3 is the radioactivity integrated over the pulse height range appropriate to initial solution or benzal chloride after reaction, each being reduced by the integrated value of blank material.

The rates of the hydrogen exchange conducted in alkaline solution (runs 3 and 4) were found to be faster than those in neutral or acidic solution (runs 1 and 2).

That the rate of the base-catalyzed hydrogen exchange is slower than that

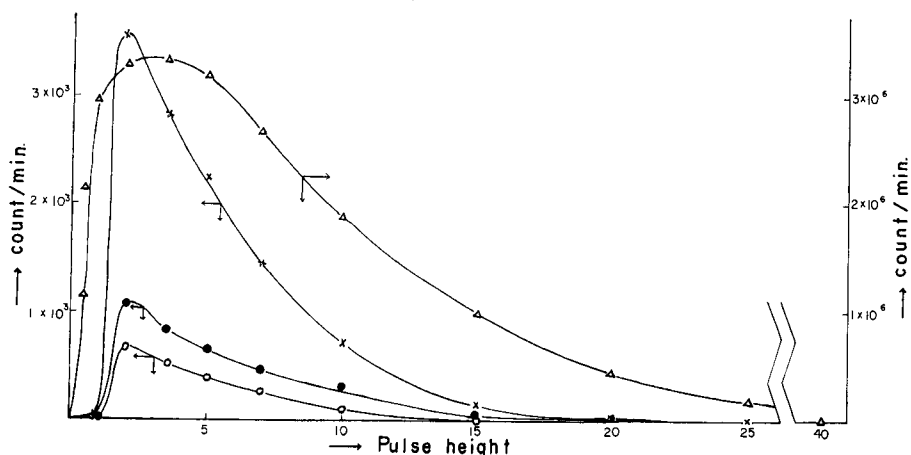


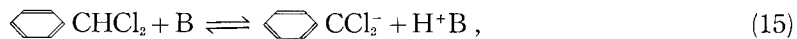
Fig. 3. The observed radioactivity at various pulse heights.

○ : Blank material, ● : Benzal chloride after reaction at pH=6~1.15, (run 1),  
 × : Benzal chloride after reaction at pH=14, (run 3), △ : Initial solution (pH=6).

TABLE 3. Exchange of Hydrogen Labeled by  $^3\text{H}$  between Benzal Chloride and Water at  $12^\circ\text{C}$ .

Runs	Time of reaction min.	Aqueous solution						Benzal chloride			Rate $q$ mole/ $\ell$ min.
		Radioactivity before reaction $C_1^3$ : cpm	pH		Volume $v_1^s$ m $\ell$	$n^s$ moles	Added reagent	Radioactivity after reaction $C_2^3$ : cpm	Volume $v_2^c$ m $\ell$	$n^c$ moles	
			Before	After							
1	1235	$4.11 \times 10^7$	6.00	1.15	3.0	$3.34 \times 10^{-1}$	none	$3.09 \times 10^3$	3.0	$2.41 \times 10^{-2}$	$0.225 \times 10^{-5}$
2	540	$5.72 \times 10^6$	6.00	1.49	2.5	$2.78 \times 10^{-1}$	none	$1.97 \times 10^2$	2.5	$2.01 \times 10^{-2}$	$0.230 \times 10^{-5}$
3	1200	$4.11 \times 10^7$	14.13	14.11	3.0	$3.34 \times 10^{-1}$	NaOH	$1.74 \times 10^4$	3.0	$2.01 \times 10^{-2}$	$1.32 \times 10^{-5}$
4	540	$5.72 \times 10^6$	13.93	13.91	2.5	$2.78 \times 10^{-1}$	NaOH	$7.32 \times 10^2$	2.5	$2.41 \times 10^{-2}$	$0.852 \times 10^{-5}$

of the hydrolysis ( $5 \times 10^{-5}$  mol/ $\ell$  min.) reported in the subsequent paper suggests that the hydrogen exchange proceeds by the following step in equilibrium, which is not included in the reaction path leading to the hydrolysis,



where B is BRÖNSTED base.

### Acknowledgment

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