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Author(s)	TANABE, Kozo; IDO, Tadaatsu
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THE MECHANISM OF THE HYDROLYSIS
OF BENZAL CHLORIDE

By

Kozo Tanabe and Tadaatsu Ido[*]
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Abstract

The hydrolysis rate of benzal chloride was determined at 12°C over the pH range from 0 to 14. It was found that the rate is constant independently of pH, that the nucleophilic reagents such as piperidine, thiophenol and sodium azide have no appreciable effect on the hydrolysis rate and that the hydrolysis rate decreases with increase of the chloride ion concentration in solution. On the basis of these results together with those on the chlorine and hydrogen exchange reported in the foregoing paper, the mechanism of the hydrlysis is discussed.

Introduction

We have previously investigated the hydrolysis of chlorofrom[1], carbon tetrachloride[2], methylene chloride[3] or benzyl chloride[4] and proposed each mechanism. In the foregoing paper, the chlorine and hydrogen exchange of benzal chloride has been studied.[5] The hydrolysis of benzal chloride is now investigated at 12°C under the same experimental condition as those in the exchange reactions to elucidate the mechanism.

§ 1. Experimental

Reagents: The purification of benzal chloride has been described in the foregoing paper.[5] All other chemicals were guaranteed reagents of Kanto Chemical Co. Solution of different pH used is simply conductivity water, aqueous sodium hydroxide, sulfuric acid or buffer solutions (0.0350 mol/ℓ KH$_2$PO$_4$ + 0.0225 mol/ℓ Na$_2$B$_4$O$_7 \cdot$ 10H$_2$O; 0.0125 mol/ℓ Na$_2$B$_4$O$_7 \cdot$ 10H$_2$O + 0.0375 mol/ℓ Na$_2$CO$_3$).

Kinetic Runs: In a typical experiment, a 50 mℓ Erlenmeyer flask with ground glass-stopper containing 20 mℓ of aqueous solution of known pH with or without added reagents was allowed to reach thermal equilibrium in a water-

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bath maintained at 12°C and then 1 mℓ of benzal chloride was added and stirred vigorously by a magnetic stirrer. At a recorded time, the flask was taken out and cooled in ice-water and then 5 mℓ of the solution was pipetted out and the amount of chloride ion was determined by a modification of VOLHARD's method. The pH of the sample before or after reaction was determined by means of a glass-electrode pH-meter or by titrating the hydrogen ion or hydroxide ion concentration respectively with a standard alkali or acid.

Some experiments were carried out in dark or in the absence of air as described previouly.[1)6)]

Preliminary experiments showed that the hydrolysis rate is independent of shaking rates and the variation of the ratio of the amount of solution to that of benzal chloride. It may, therefore, be admitted that the hydrolysis proceeds homogeneously in the interior of aqueous solution and that the dissolution of benzal chloride into solution and its reversal are not controlling.

Calculation of Hydrolysis Rate: Since a benzal chloride molecule yields, as it decomposes, two chloride ions and two protons, the hydrolysis rate Vd for unit volume of solution may be expressed by the equation under the present experimental condition that the concentration of benzal chloride in solution is kept constant.

$$Vd = \frac{d\Delta[\text{Cl}^-]}{2dt} = \frac{d\Delta[\text{H}^+]}{2dt} , \qquad (1)$$

where $\Delta[\text{Cl}^-]$ or $\Delta[\text{H}^+]$ is the increment of chloride ion or proton in solution formed by the hydrolysis and t the time of the reaction.

§ 2. Results

Table 1 shows the results of the experiment which was carried out in acidic or alkaline solution without addition of nucleophilic reagents. The hydrolysis rates Vd calculated from $\Delta[\text{Cl}^-]$ given in Table 1 were in agreement with those calculated from the pH-measurement within the limit of experimental error. Runs 2 and 3 were conducted in vacuum and runs 28 and 29 in dark. The $\log_{10} Vd$ of Table 1 was plotted against pH in Fig. 1, each at the median of pH, if varied appreciably. The runs without any added salts are shown by open circles and those conducted in the presence of sodium sulfate, in buffer solutions, in vacuum or in dark by triangles, double circles, circles with cross or solid circles, respectively. A straight line may be drawn through the circles as shown in the figure. The Vd is almost constant independently of pH and light and oxygen have no effect on the hydrolysis rate.

TABLE 1. Hydrolysis of Benzal Chloride in Aqueous Solution at 12°C.

Runs	Time of Reaction min.	Quantity of Benzal Chloride mℓ	Quantity of Aqueous Solution mℓ	pH Before	pH After	Added Reagents	$\Delta[Cl^-]$ mol/$\ell \times 10^{-2}$	$Vd = \frac{1}{2} \cdot \frac{d\Delta[Cl^-]}{dt}$ mol/ℓ, min. $\times 10^{-5}$	$\log_{10} Vd$ mol/ℓ, min.
1	120	1	20	3.95	1.95	none	1.88	7.83	−4.11
2*	120	0.5	10			none	1.40	5.83	−4.23
3*	120	0.5	10			none	1.41	5.83	−4.23
4	120	1	20	13.38	13.35	NaOH	1.81	7.54	−4.12
5	120	1	20	13.38	13.30	NaOH	2.00	8.33	−4.08
6	120	1	20	13.38	13.30	NaOH	1.56	6.50	−4.19
7	120	1	20	12.79	11.70	NaOH	1.94	8.08	−4.09
8	120	1	20	12.79		NaOH	1.93	8.04	−4.10
9	120	1	20	12.79	11.80	NaOH	1.87	7.79	−4.11
10	120	1	20	12.04	2.70	NaOH	1.77	7.38	−4.13
11	120	1	20	12.04	2.70	NaOH	2.08	8.67	−4.06
12	120	1	20	12.38	3.05	NaOH	1.84	7.67	−4.11
13	60	1	20	12.04	3.38	NaOH	0.98	8.17	−4.09
14	120	1	20	12.46	4.03	NaOH	1.47	6.13	−4.21
15	60	1	20	12.46	6.10	NaOH	1.00	8.33	−4.08
16	120	1	20	12.46	4.12	NaOH	1.61	6.71	−4.17
17	120	1	20	12.60	4.80	NaOH	1.42	5.91	−4.23
18	120	1	20	12.60	4.18	NaOH	1.60	6.67	−4.18
19	120	1	20	12.60	4.40	NaOH	1.53	6.38	−4.20
20	120	1	20	4.43	3.01	0.5 M, Na_2SO_4	1.65	6.88	−4.16
21	120	1	20	4.06	2.64	0.1 M, Na_2SO_4	1.54	6.42	−4.19
22	120	1	20			1.1 M, NaOH	1.06	4.42	−4.35
23	120	1	20			0.5 M, NaOH	1.40	5.83	−4.23
24	120	1	20			1.0 M, H_2SO_4	1.40	5.83	−4.23
25	120	1	20			0.5 M, H_2SO_4	1.64	6.83	−4.17
26	120	1	20	7.05	6.54	Buffer**	1.50	6.25	−4.20
27	120	1	20	9.90	9.40	Buffer***	1.99	8.29	−4.08
28****	120	1	20	3.75	2.09	none	1.68	7.00	−4.16
29****	120	1	20	3.80	2.02	none	1.60	6.67	−4.18

*) Runs conducted in vacuum (10^{-3} mmHg).
**) $KH_2PO_4 + Na_2B_4O_7 \cdot 10H_2O$.
***) $Na_2B_4O \cdot 10H_2O + Na_2CO_3$.
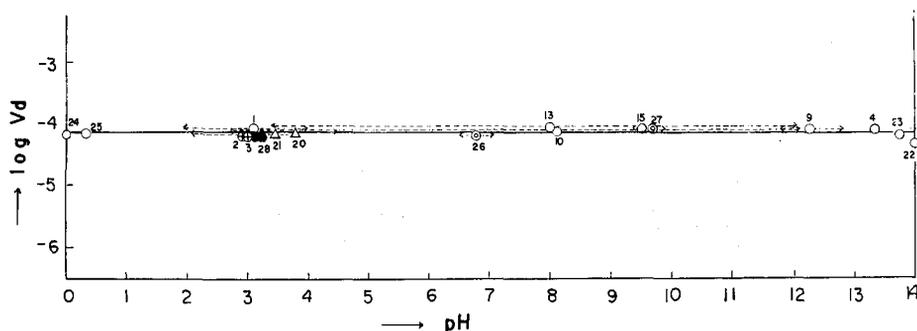****) Runs conducted in dark.

Fig. 1. Hydrolysis rate of benzal chloride in aqueous solution at 12°C.
○ : no salt added, △ : sodium sulfate added, ◎ : in buffer solution, ⊕ : in vacuum, ● : in dark, ←---→ : range of pH-variation.

TABLE 2. The Effect of the Additon of Nucleophilic Reagents on Hydrolysis.

Added Reagents	Amount of Added Reagents mol/ℓ	Hydrolysis Rate mol/ℓ min.$\times 10^{-5}$
none	none	5.9–7.9
Piperidine	0.08	8.4
Piperidine	0.25	11.6
Piperidine	0.51	11.8
Piperidine	0.86	12.5
NaN$_3$	0.50	8.8
p-Nitro Thiophenol	Saturated Solution	5.3

In Table 2 is shown the effect of the addition of piperidine, sodium azide or *p*-nitrothiophenol on the *Vd*. Those runs were conducted under the same experimental conditions as in the runs of Table 1 except that the amounts of the reagents shown in the second column are added. As shown in the Table, the addition of nucleophilic reagents have little effect on the rate, although larger amount of piperidine accelerate the rate somewhat.

Since it is reported that the hydrolysis rate of benzyl chloride[4] and methylene chloride[3] is increased about one hundred times by the addition of 0.2 mol/ℓ piperidine, piperidine does not seem to act as a nucleophile in this case. The small acceleration is considered due to the increase of the solubility of benzal chloride by the addition of piperidine.

The effect of the addition of chloride ion on the *Vd* is shown in Table 3. The third column gives the concentration of sodium chloride added which is practically total concentration of chloride ion in solution, since the amount
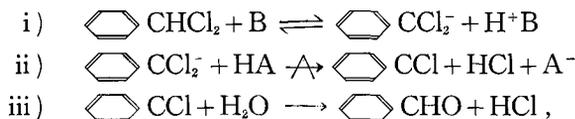
TABLE 3: The Effect of Chloride Ion on Vd.

Time of Reaction	Quantity of		Concentration of Sodium Chloride Added	Rate of Hydrolysis $Vd = \dfrac{1}{2} \cdot \dfrac{d\varDelta[H^+]}{dt}$
	Benzal Chloride	Aqueous Solution		
min.	mℓ	mℓ	mol/ℓ	mol/ℓ min. $\times 10^{-5}$
120	1	20	none	7.86
120	1	20	0.1	7.68
120	1	20	0.5	5.82
120	1	20	1.0	3.00
120	1	20	3.0	1.44
120	1	20	5.0	0.78

of chloride ion formed by hydrolysis is negligibly small. As shown in the Table, the rate of the hydrolysis decreases as the concentration of chloride ion increases.
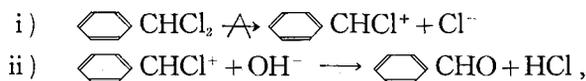
§ 3. Discussion

It is known that benzal chloride decomposes in aqueous solution to form benzaldehyde and hydrogen chloride under the present experimental conditions.[7] The possible mechanisms for the hydrolysis of benzal chloride which satisfy the observed independence of Vd on pH and the fact that the rate of hydrolysis is faster than that of chlorine exchange as reported in the foregoing paper[5], are only the following three.
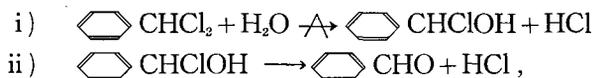
Mechanism A)

i) ⬡CHCl$_2$ + B ⇌ ⬡CCl$_2^-$ + H$^+$B

ii) ⬡CCl$_2^-$ + HA ⇢ ⬡CCl + HCl + A$^-$

iii) ⬡CCl + H$_2$O ⟶ ⬡CHO + HCl ,

Mechanism B)

i) ⬡CHCl$_2$ ⇢ ⬡CHCl$^+$ + Cl$^-$

ii) ⬡CHCl$^+$ + OH$^-$ ⟶ ⬡CHO + HCl ,

Mechanism C)

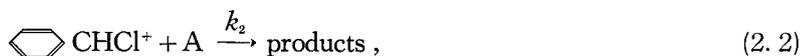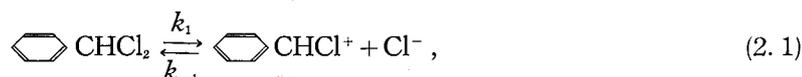i) ⬡CHCl$_2$ + H$_2$O ⇢ ⬡CHClOH + HCl

ii) ⬡CHClOH ⟶ ⬡CHO + HCl ,

where B and HA denote BRÖNSTD base and acid respectively and step ii) in mechanism A) or step i) in mechanisms B) and C) is the rate-determining step of the hydrolysis.

If the hydrolysis proceeds by mechanism A), a hydrogen exchange must occur by step A) i) and its rate must be fast compared to the rate of the hydrolysis. It was found, however, that the rate of hydrogen exchange is slower than that of hydrolysis reported in the foregoing paper. Therefore, mechanism A) is excluded.

If, on the other hand, the hydrolysis occurs by a bimolecular mechanism of nucleophilic substitution as in mechanism C), then highly nucleophilic reagents such as thiophenol, piperidine *etc.* would accelerate the reaction. The experimental results of Table 2, however, show that the nucleophilic reagents have little effect on the hydrolysis rate, as discussed in §2.

On the grounds described above, the hydrolysis is considered to proceed by mechanism B).

This conclusion is further confirmed as discribed below. Let us write mechanism B) more in detail.

$$\bigcirc CHCl_2 \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} \bigcirc CHCl^+ + Cl^- , \tag{2.1}$$

$$\bigcirc CHCl^+ + A \xrightarrow{k_2} products , \tag{2.2}$$

where A denotes all chemical species other than Cl^- which react with the carbonium ion. In this case, Vd is expressed as,

$$Vd = \frac{k_1[Bz]}{1 + \alpha[Cl^-]} , \tag{3}$$

$$\alpha = \frac{k_{-1}}{k_2[A]} , \tag{4}$$

where [Bz] is the concentration of benzal chloride in solution and $[Cl^-]$ that of chloride ion in solution.

Transformation of Eq. (2) yield,

$$\frac{1}{V} = \frac{\alpha[Cl^-]}{k_1[Bz]} + \frac{1}{k_1[Bz]} , \tag{5}$$

Since $k_1[Bz]$ is kept constant under the present experimental condition by the presence of practically pure benzal chloride phase and α is also kept constant under the pxperimental condition that [A] is constant in neutral or acidic range of pH, the plot of $1/V$ *vs.* $[Cl^-]$ must give a straight line, provided that the hydrolysis proceeds by the mechanism as shown in Eq. (2).

Table 3 shows the hydrolysis rate in the presence of various concentrations of chloride ion. In Fig. 2 is plotted the $1/V$ against $[Cl^-]$, a good straight line being obtained. It is, therefore, confirmed that the hydrolysis
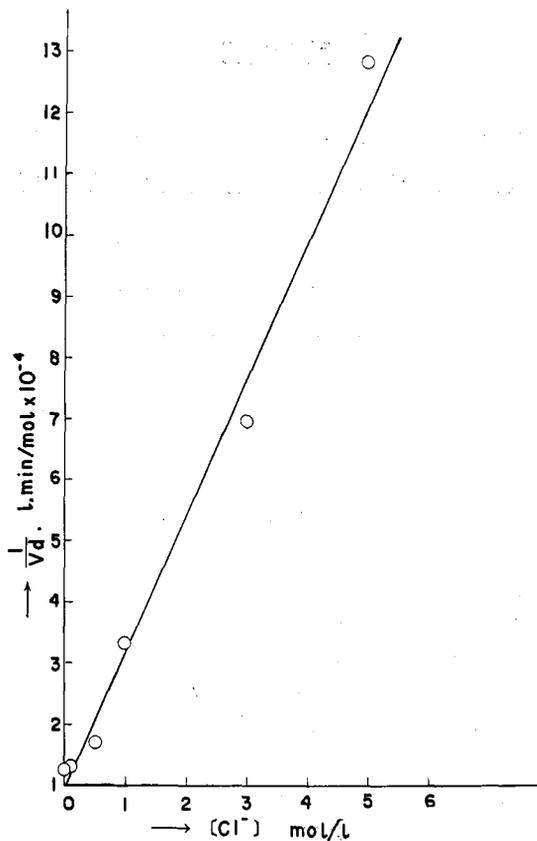
Fig. 2. Plot of $1/Vd$ *vs.* $[Cl^-]$.

proceeds by the mechanism shown by Eq. (2).

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