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THE MECHANISM OF THE HYDROLYSIS OF BENZOTRICHLORIDE

By

Kozo TANABE*) and Tomoko SANO*)

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Abstract

The rate of the hydrolysis of benzotrichloride was determined at 5, 20 and 30°C over a pH range from 0 to 14. The rate was found to be constant independently of pH. It was also found that the nucleophilic reagents such as piperidine and thiophenol have no appreciable effect on the hydrolysis rate and that the rate decreases with increase of chloride ion concentration in solution. On the basis of these results together with those on the chlorine exchange reported in the foregoing paper, the mechanism of the hydrolysis is discussed.

Introduction

In the foregoing paper, the chlorine exchange of benzotrichloride with aqueous chloride solution was studied[1]. The hydrolysis of benzotrichloride is now investigated under the same experimental condition as those in the exchange reaction to elucidate the mechanism.

§ 1. Experimental

The reaction was carried out in the same way as in the case of benzal chloride[2]. The purification of benzotrichloride has been described in the foregoing paper[1]. All other chemicals used were guaranteed reagents of Kanto Chemical Co.

Since a benzotrichloride molecule hydrolyzes to yield a benzoic acid molecule and three hydrogen chloride molecules, the hydrololysis rate Vd for unit volume of solution may be expressed by the following equation under the present experimental condition that the concentration of benzotrichloride in solution is kept constant.

$$Vd = \frac{1}{3} \cdot \frac{\Delta [Cl^-]}{t} = \frac{1}{(3+f)} \cdot \frac{\Delta [H^+]}{t}, \qquad (1)$$

where $\Delta [Cl^-]$ or $\Delta [H^+]$ is the increment of chloride ion or proton in solution formed by the hydrolysis and t the time of reaction. When $\Delta [H^+]$ was determined by pH-measurement, the value of f was neglected in the case of neutral or acidic solution, since pK_a of benzoic acid is 4.201 ± 0.005 at 25°C[3], though it becomes 1 in alkaline solution.

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

§ 2. Results

Table 1 shows the results of the experiment which was carried out at 5°C in acidic or alkaline solution without addition of chlorides or nucleophilic reagents. Those at 20 and 30°C are given in Table 2. The hydrolysis rates *Vd* calculated from $\Delta[Cl^-]$ were in good agreement with those calculated from $\Delta[H^+]$, as shown in Table 1. Since the hydrolysis rate is independent of shaking rates (see runs 7, 14 and 16), it may be admitted that the hydrolysis proceeds homogeneously in aqueous solution and that the dissolution of benzotrichloride into solution and its reversal are not controlling. Runs 20, 21 and 22 were conducted in vacuum and runs 18, 19 and 23 in dark. Some of $\log_{10} Vd$ in Table 1 were plotted against pH in Fig. 1, each at the median

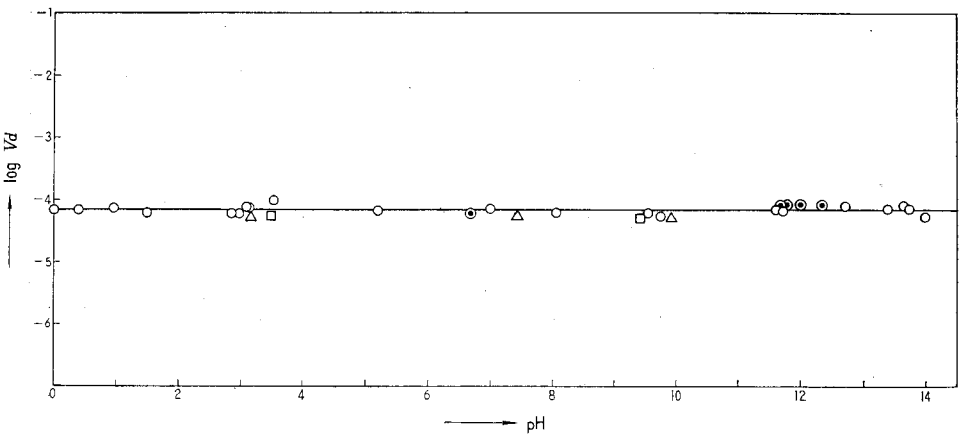


Fig. 1. Hydrolysis Rate of Benzotrichloride in Aqueous Solution at 5°C.
△: in dark, □: in vacuum, ◉: piperidine added.

of pH, if varied appreciably. The runs conducted in vacuum or in dark are shown by triangles or squares respectively and other runs by open circles. A straight line may be drawn through the circles as shown in the figure. The *Vd* is almost constant independently of pH, light and oxygen.

Table 3 and 4 show the effect of the addition of piperidine and thiophenol on the hydrolysis rate. As shown in the Tables, these nucleophilic reagents have little effect on the rate, although a small acceleration due to increased solubility by solvent (aqueous acetone) is observed. Since the hydrolysis rate of benzyl chloride[4] and methylene chloride[5] 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.

TABLE 1. Hydrolysis of Benzotrichloride in Aqueous Solution at 5°C.

Runs	Time of Reaction	Quantity of Benzotrichloride	Quantity of Aqueous Solution	Added Reagents	pH Before	pH After	$\Delta[Cl^-]$	Hydrolysis Rate $Vd=\frac{1}{3}\frac{\Delta[Cl^-]}{t}$	Hydrolysis Rate $Vd'=\frac{1}{(3+f)}\frac{\Delta[H^+]}{t}$	Hydrolysis Rate $-\log_{10}Vd$	Hydrolysis Rate $-\log_{10}Vd'$
	min	mℓ	mℓ				mol/ℓ×10²	mol/ℓ, min×10⁵	mol/ℓ, min×10⁵	mol/ℓ, min	min⁻¹
1	66	1	20	H_2SO_4	(−0.12)	(−0.12)	1.30	6.59	—	4.18	—
2	55	1	20	H_2SO_4	(0.38)	(0.38)	1.16	7.08	—	4.15	—
3	78	1	20	H_2SO_4	1.00	0.93	1.71	7.32	7.37	4.14	4.13
4	88	1	20	H_2SO_4	1.60	1.39	1.59	6.01	5.56	4.22	4.25
5	60	1	20	none	4.23	2.00	1.43	7.92	5.52	4.10	4.26
6	120	1	20	none	4.27	1.65	2.10	5.83	6.21	4.24	4.21
*) 7	60	1	20	none	4.30	1.99	1.33	7.44	5.71	4.13	4.24
8	79	1	20	none	5.01	(1.63)	2.34	9.85	—	4.01	—
9	61	1	20	NaOH	12.77	6.70	0.99	5.39	6.13	4.27	4.21
10	70	1	20	NaOH	12.81	10.40	1.45	6.96	5.81	4.16	4.24
11	90	1	20	NaOH	12.89	6.31	1.67	6.19	5.41	4.21	4.27
12	60	1	20	NaOH	13.00	12.43	1.50	8.32	7.71	4.08	4.11
13	78	1	20	NaOH	13.42	13.29	1.80	7.72	5.56	4.11	4.26
*)14	55	1	20	NaOH	(13.72)	(13.71)	1.26	7.58	—	4.12	—
15	68	1	20	NaOH	(13.72)	(13.65)	1.74	8.52	7.51	4.07	4.12
*)16	90	1	20	NaOH	(14.03)	(14.02)	1.45	5.38	—	4.27	—
17	75	1	20	NaOH	(14.06)	(14.06)	1.12	4.97	—	4.30	—
**)18	120	1	20	none	4.57	1.76	2.05	5.67	4.79	4.25	4.32

**)19	122	1	20	NaOH	12.96	6.70	1.75	4.77	4.77	4.32	4.32
***)20	71	0.5	10	none	4.35	1.98	1.09	5.12	4.90	4.29	4.31
***)21	131	0.5	10	none	4.35	1.65	2.31	5.86	5.69	4.23	4.25
***)22	95	0.5	10	NaOH	12.90	5.40	1.52	5.35	5.32	4.27	4.27
**)23	90	1	20	NaOH	12.63	2.22	1.36	5.05	5.26	4.10	4.28
24	90	1	20	NaOH	(14.04)	(14.03)	1.11	4.11	—	4.39	—
25	121	1	20	B.S.	7.56	6.51	2.61	7.19	—	4.14	—
26	125	1	20	B.S.	11.87	11.50	2.53	6.73	—	4.17	—
27	118	1	20	B.S.	8.45	7.68	2.14	6.05	—	4.22	—
28	128	1	20	B.S.	9.93	9.28	2.41	6.30	—	4.20	—
29	122	1	20	B.S.	3.40	2.30	2.14	5.86	—	4.23	—
30	92	1	20	B.S.	5.80	4.56	1.80	6.52	—	4.19	—
31	38	1	20	0.231 M Na_2SO_4	2.00	1.78	0.69	5.89	5.90	4.23	4.23
32	67	1	20	0.528 M Na_2SO_4	6.05	2.00	0.98	4.88	4.99	4.31	4.30
33	93	1	20	0.470 M Na_2SO_4	12.93	11.02	1.19	4.25	—	4.37	—
34	89	1	20	0.462 M Na_2SO_4	(14.04)	(14.04)	0.98	3.65	—	4.44	—

*) Shaking rate was changed.
**) Conducted in dark.
***) Conducted in vacuum ($10^{-4} \sim 10^{-5}$ mmHg).
B.S.: Buffer solution.

TABLE 2. Hydrolysis of Benzotrichloride in Aqueous Solution at 20°C.

Runs	Time of Reaction min	Quantity of Benzo-trichloride mℓ	Quantity of Aqueous Solution mℓ	Added Reagent	pH Before	pH After	$\Delta[Cl^-]$ mol/ℓ×10²	Hydrosis Rate $Vd=\frac{1}{3}\frac{\Delta[Cl^-]}{t}$	Hydrosis Rate $-\log Vd$ mol/ℓ, min
1	121	1	20	none	4.40	1.20	9.24	25.4×10^{-5}	3.59
2	123	1	20	none	4.40	1.22	9.13	24.8×10^{-5}	3.61
3	104	1	20	NaOH	12.60	4.17	8.76	28.0×10^{-5}	3.55
4	122	1	20	H_2SO_4	1.00	—	9.13	25.0×10^{-5}	3.60
5	111	1	20	NaOH	14.04	14.02	4.93	14.8×10^{-5}	3.83

Hydrolysis of Benzotrichloride in Aqueous Solution at 30°C

6	120	1	20		3.60	0.80	25.2	6.99×10^{-4}	3.16
7	120	1	20	H_2SO_4	1.25	0.80	25.6	7.10×10^{-4}	3.15
8	105	1	20		3.67	0.79	22.8	7.24×10^{-4}	3.14
9	122	1	20	H_2SO_4	1.25	0.59	25.3	6.92×10^{-4}	3.16
10	108	1	20	NaOH	12.60	1.00	22.4	6.93×10^{-4}	3.16
11	122	1	20	NaOH	(13.68)	(13.62)	15.2	4.16×10^{-4}	3.38
12	120	1	20	NaOH	(13.68)	(13.61)	15.6	4.34×10^{-4}	3.36
13	123	1	20	B.S.	10.00	1.04	27.5	7.44×10^{-4}	3.13
14	68	1	20	B.S.	6.00	1.29	13.3	6.51×10^{-4}	3.19

TABLE 3. The Effect of the Addition of Piperidine on Vd in Aqueous Solution at 5°C.

Runs	Time of Reaction	Quantity of		pH		Concentration of Piperidine	$\Delta[Cl^-]$	Hydrolysis Rate	
		Benzo-trichloride	Aqueous Solution	Before	After			$Vd = \frac{1}{3}\frac{\Delta[Cl^-]}{t}$	$-\log_{10} Vd$
	min	mℓ	mℓ			mol/ℓ	mol/ℓ × 10^2	mol/ℓ, min × 10^5	mol/ℓ, min
1	90	1	20	12.05	11.95	0.2	2.24	8.19	4.09
2	60	1	20	11.91	11.73	0.1	1.65	8.45	4.07
3	90	1	20	12.00	11.43	0.1	2.31	8.54	4.07
4	62	1	20	10.68	3.30	0.01	1.06	5.72	4.24
5	120	1	20	12.35	12.37	0.4	2.97	8.26	4.08
						0			4.20*)

*) Average value of $-\log_{10} V_d$ in Table 1.

TABLE 4. The Effect of the Addition of Thiophenol on Vd in 30 Vol.% Aqueous Acetone at 5°C.

Runs	Time of Reaction	Quantity of		pH		Concentration of Thiophenol	$\Delta[Cl^-]$	Hydrolysis Rate	
		Benzo-trichloride	30 Vol.% Aqueous Acetone	Before	After			$Vd = \frac{\Delta[Cl^-]}{3t}$	$-\log_{10} Vd$
	min	mℓ	mℓ			mℓ/ℓ	mol/ℓ × 10^2	mol/ℓ, min^{-1} × 10^5	mol/ℓ, min^{-1}
1	60	1	20	12.30	12.12	0	1.994	11.08	3.96
2	53	1	20	12.30	—	0.016	2.072	13.03	3.89
3	74	1	20	12.97	12.70	0	2.027	9.13	4.04
4	63	1	20	12.97	12.70	0.016	2.200	11.64	3.94
5	60	1	20	13.31	12.85	0	1.819	10.11	4.00
6	72	1	20	13.31	12.85	0.016	2.861	13.24	3.88

TABLE 5. Hydrolysis of Benzotrichloride in Aqueous Solution at 5°C. Sodium Chloride Present.

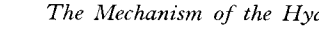
Runs	Time of Reaction	Quantity of		Concentration of Sodium Chloride	Rate of Hydrolysis $Vd = \frac{\Delta[H^+]}{3t}$
		Benzo-trichloride	Aqueous Solution		
	min	mℓ	mℓ	mol/ℓ	mol/ℓ, min×10^5
1	120	1	20	0.100	3.14
2	128	1	20	0.200	2.37
3	131	1	20	0.200	2.31
4	140	1	20	0.513	1.83
5	115	1	20	0.513	1.91
6	122	1	20	1.00	1.41
7	121	1	20	1.00	1.37
8	120	1	20	2.00	0.742
9	131	1	20	2.00	0.739
10	122	1	20	3.00	0.438
11	185	1	20	3.00	0.418
12	113	1	20	0.100	3.34
13	121	1	20	0.100	3.27
14	115	1	20	0	3.83
15	115	1	20	0	3.89

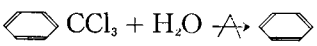
The effect of the addition of chloride ion on the Vd is shown in Table 5. The third column gives the concentration of sodium chloride added which is practically equal to total concentration of chloride ion in solution, since the amount of chloride ion formed by hydrolysis is negligibly small. As shown in the Table, the rate of the hydrolysis decreases as the concentration of chloride ion increases. This is due to the mass effect of chloride ion, but not due to the effect of increase of ionic strength in aqueous solution, since it was found that the hydrolysis rate was not much changed by the addition of sodium perchlorate up to 3.00 mol/ℓ within the limit of experimental error.

§ 3. Discussion

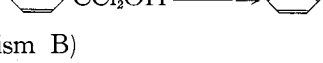
It is known that benzotrichloride decomposes in aqueous solution to benzoic acid and hydrogen chloride under the present experimental conditions[6]. The following two mechanisms for the hydrolysis of benzotrichloride fit the observed pH dependence and the fact that the hydrolysis rate is faster than that of chlorine exchange as reported in the foregoing paper[1].

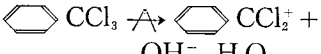
Mechanism A)

i) 

ii) 

Mechanism B)

i) 

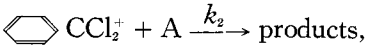
ii) 

where step i) of both mechanisms is the rate-determining step of the hydrolysis.

If the hydrolysis of benzotrichloride proceeds by a bimolecular mechanism of nucleophilic substitution as in mechanism A), it might be expected that the highly nucleophilic thiophenolate ion or piperidine would react more rapidly than water. The experimental results of Table 3 and 4 show that the nucleophilic reagents have little effect on the hydrolysis rate. Thus, mechanism A) being excluded, the hydrolysis is considered to proceed by mechanism B).

Validity of mechanism B) is discussed below. Let us write mechanism B) more in detail.

(2. 1)



(2. 2)

where A denotes all chemical species other than Cl^- which react with the carbonium ion. In this case, Vd may be expressed as[2],

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

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

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

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

In Fig. 2 is plotted $1/Vd$ against $[Cl^-]$, a straight line being obtained. It is, therefore, confirmed that the hydrolysis proceeds by mechanism B).

The value of α (2.1) for benzotrichloride obtained in this paper is greater

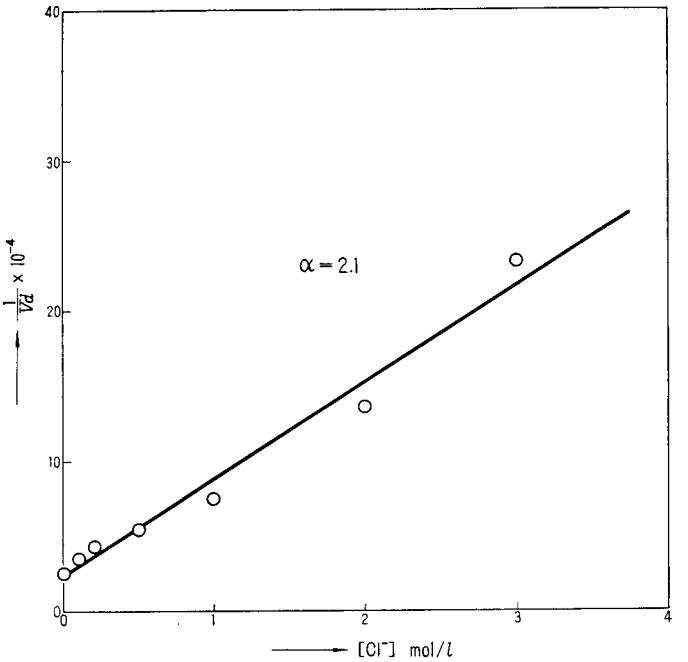


Fig. 2. Plot of $1/Vd$ *vs.* $[Cl^-]$

than that of benzal chloride[2], $\alpha = 1.5$. This indicates that the intermediate carbonium ion, $C_6H_5C^+Cl_2$ is more stable than $C_6H_5C^+HCl$, which is in agreement with the observed faster rate of hydrolysis of benzotrichloride than that of benzal chloride.

Acknowledgment

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