



Title	THE MECHANISM OF THE HYDROLYSIS OF BENZOTRICHLORIDE
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Citation	JOURNAL OF THE RESEARCH INSTITUTE FOR CATALYSIS HOKKAIDO UNIVERSITY, 13(2), 110-118
Issue Date	1966-01
Doc URL	http://hdl.handle.net/2115/24797
Type	bulletin (article)
File Information	13(2)_P110-118.pdf



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THE MECHANISM OF THE HYDROLYSIS OF BENZOTRICHLORIDE

By

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(Received September 30, 1965)

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 studied¹⁾. 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 chloride²⁾. The purification of benzotrichloride has been described in the foregoing paper¹⁾. 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 hydrolysis 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.

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

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 reaction. When $\Delta [\text{H}^+]$ 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°C³⁾, though it becomes 1 in alkaline solution.

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§ 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 V_d calculated from $\Delta[\text{Cl}^-]$ were in good agreement with those calculated from $\Delta[\text{H}^+]$, 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 $\log_{10} V_d$ in Table 1 were plotted against pH in Fig. 1, each at the median

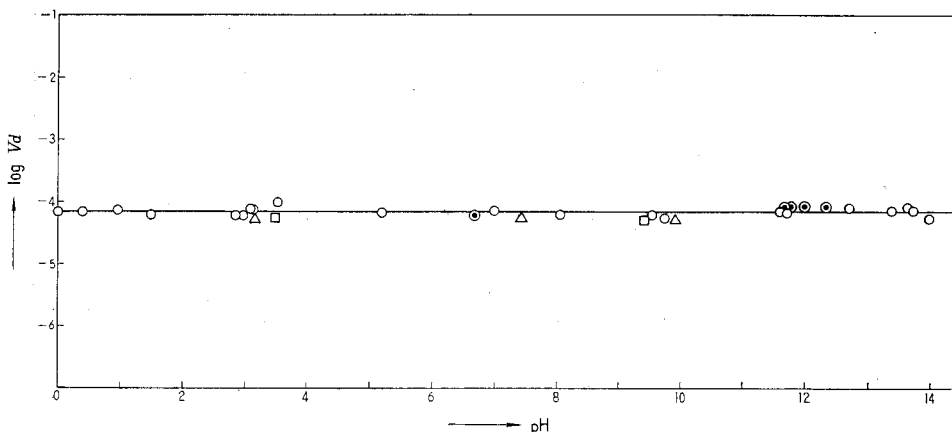


Fig. 1. Hydrolysis Rate of Benzotrichloride in Aqueous Solution at 5°C.

△: 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 V_d 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 chloride⁴⁾ and methylene chloride⁵⁾ 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		Added Reagents	pH		$\Delta[\text{Cl}^-]$ mol/ℓ × 10 ²	Hydrolysis Rate				
		Benzo- trichlo- ride mℓ	Aqueous Solution mℓ		Before	After		$Vd = \frac{1}{3} \frac{\Delta[\text{Cl}^-]}{t}$ mol/ℓ, min × 10 ⁵	$Vd' = \frac{1}{(3+f)} \frac{\Delta[\text{H}^+]}{t}$ mol/ℓ, min × 10 ⁵	$-\log_{10} Vd$ mol/ℓ, min	$-\log_{10} Vd'$ min ⁻¹	
	min											
1	66	1	20	H ₂ SO ₄	(−0.12)	(−0.12)	1.30	6.59	—	4.18	—	
2	55	1	20	H ₂ SO ₄	(0.38)	(0.38)	1.16	7.08	—	4.15	—	
3	78	1	20	H ₂ SO ₄	1.00	0.93	1.71	7.32	7.37	4.14	4.13	
4	88	1	20	H ₂ SO 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	

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**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	NaOH	(14.04)	(14.03)	1.11	4.11	—	4.39	—
	25	121	1	B.S.	7.56	6.51	2.61	7.19	—	4.14	—
	26	125	1	B.S.	11.87	11.50	2.53	6.73	—	4.17	—
	27	118	1	B.S.	8.45	7.68	2.14	6.05	—	4.22	—
	28	128	1	B.S.	9.93	9.28	2.41	6.30	—	4.20	—
	29	122	1	B.S.	3.40	2.30	2.14	5.86	—	4.23	—
	30	92	1	B.S.	5.80	4.56	1.80	6.52	—	4.19	—
	31	38	1	0.231 M Na ₂ SO ₄	2.00	1.78	0.69	5.89	5.90	4.23	4.23
	32	67	1	0.528 M Na ₂ SO ₄	6.05	2.00	0.98	4.88	4.99	4.31	4.30
	33	93	1	0.470 M Na ₂ SO ₄	12.93	11.02	1.19	4.25	—	4.37	—
	34	89	1	0.462 M Na ₂ SO 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		Added Reagent	pH		$\Delta[\text{Cl}^-]$ mol/l $\times 10^2$	Hydrolysis Rate	
		Benzotrichloride mℓ	Aqueous Solution mℓ		Before	After		$Vd = \frac{1}{3} \frac{\Delta[\text{Cl}^-]}{t}$	$-\log Vd$ 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 ₂ SO 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 ₂ SO 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 ₂ SO 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 V_d in Aqueous Solution at 5°C.

Runs	Time of Reaction min	Quantity of		pH		Concentration of Piperidine mol/l	$\Delta[\text{Cl}^-]$ mol/l $\times 10^2$	Hydrolysis Rate	
		Benzo-trichloride ml	Aqueous Solution ml	Before	After			$V_d = \frac{1}{3} \frac{\Delta[\text{Cl}^-]}{t}$ mol/l, min $\times 10^5$	$-\log_{10} V_d$ 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 V_d in 30 Vol.% Aqueous Acetone at 5°C.

Runs	Time of Reaction min	Quantity of		pH		Concentration of Thiophenol ml/l	$\Delta[\text{Cl}^-]$ mol/l $\times 10^2$	Hydrolysis Rate	
		Benzo-trichloride ml	30 Vol.% Aqueous Acetone ml	Before	After			$V_d = \frac{\Delta[\text{Cl}^-]}{3t}$ mol/l, min ⁻¹ $\times 10^5$	$-\log_{10} V_d$ 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 min	Quantity of		Concentration of Sodium Chloride mol/ℓ	Rate of Hydrolysis $Vd = \frac{\Delta[H^+]}{3t}$ mol/ℓ, min $\times 10^5$
		Benzotrichloride mℓ	Aqueous Solution mℓ		
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

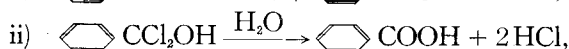
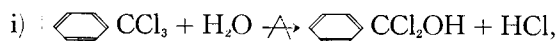
The effect of the addition of chloride ion on the Vd is shown in Table 5. The third column gives the concentration of sodium chloride added which is practically equal to total concentration of chloride ion in solution, since the amount of chloride ion formed by hydrolysis is negligibly small. As shown 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

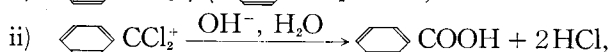
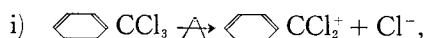
It is known that benzotrichloride decomposes in aqueous solution to benzoic acid and hydrogen chloride under the present experimental conditions⁶. The following two mechanisms for the hydrolysis of benzotrichloride fit the observed pH dependence and the fact that the hydrolysis rate is faster than that of chlorine exchange as reported in the foregoing paper¹.

The Mechanism of the Hydrolysis of Benzotrichloride

Mechanism A)



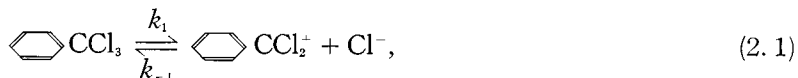
Mechanism B)



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.



where A denotes all chemical species other than Cl^- which react with the carbonium ion. In this case, Vd may be expressed as²⁾,

$$\frac{1}{Vd} = \frac{\alpha[\text{Cl}^-]}{k_1[\text{Bz}]} + \frac{1}{k_1[\text{Bz}]}, \quad (3)$$

$$\alpha = \frac{k_{-1}}{k_2[\text{A}]}, \quad (4)$$

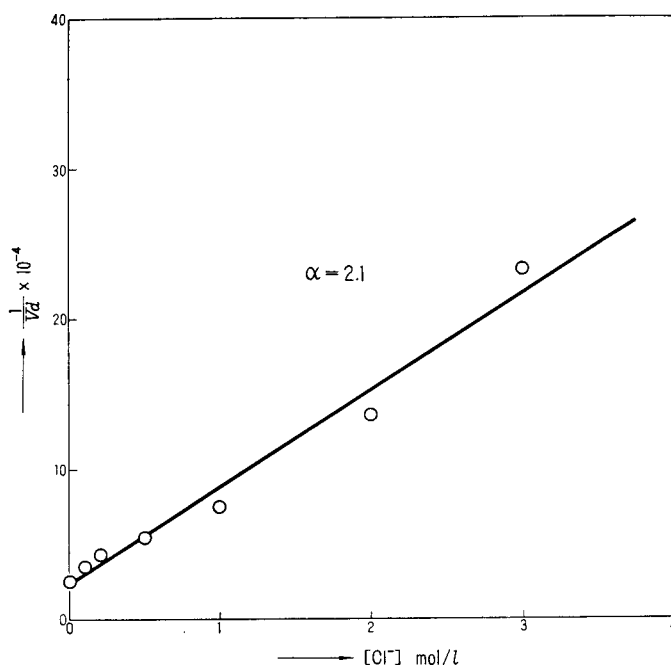
where $[\text{Bz}]$ is the concentration of benzotrichloride and $[\text{Cl}^-]$ that of chloride ion in solution.

Since $k_1[\text{Bz}]$ 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 $[\text{A}]$ is constant in neutral or acidic range of pH, the plot of $1/Vd$ vs. $[\text{Cl}^-]$ 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 $[\text{Cl}^-]$, 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

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

than that of benzal chloride²⁾, $\alpha=1.5$. 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

We wish to thank Professor Emeritus J. HORIUTI for his support of this investigation and Dr. T. TAKESHITA for his helpful discussion.

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