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THE MECHANISM OF THE HYDROLYSIS
OF BENZYL CHLORIDE

By

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Introduction

A number of kinetic studies have been reported on the hydrolysis of benzyl chloride. They were carried out in aqueous acetone, alcohol and dioxane etc[1]., but not in pure water. We have studied the chlorine exchange reaction of benzyl chloride with chloride ion in aqueous solution and proposed the mechanism of the reaction[2]. The kinetics of the hydrolysis of benzyl chloride in pure water has been now investigated at 30°C over the pH range from 0 to 14 under the same experimental conditions as those in the chlorine exchange reaction reported in the foregoing paper[2]. It has been found that the rate of the hydrolysis is constant independently of pH up to pH 13.0, whence it increases inversely proportional to the activity of hydrogen ion and that the hydrolysis rate is faster than the rate of the chlorine exchange. There were also found no appreciable neutral salt effect and no mass effect of chloride ion on the rate, but the increase in the rate on the addition of piperidine or thiophenol. The analysis of the observed kinetic data leads us to conclude that benzyl chloride hydrolyzes by a S_N2 mechanism.

§ 1. Experimental

Reagents: The purification of benzyl chloride has been described in the foregoing paper[2]. All other chemicals were guaranteed reagent-grade of KANTO Chemical Co. Solution of different pH used is simply conductivity water, aqueous sodium hydroxide, sulfuric acid or phosphate buffer solution as in the previous works[2,3].

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 were allowed to reach thermal equilibrium in a thermostat maintained at 30°C and then 1 mℓ of benzyl chloride was added and stirred vigorously by a magnetic stirrer. At a recorded time, the flask was taken

TABLE 1. Hydrolysis of Benzyl Chloride in Aqueous Solution at 30°C.

Runs	Time of Reaction min	Quantity of		pH		Added Reagents	Δ [Cl$^-$] mol/ℓ $\times$ 10^{-3}	Hydroysis Rate	
		Benzyl Chloride mℓ	Agueous Solution mℓ	Before	After			$Vd = \dfrac{d\Delta [Cl^-]}{dt}$ mol/ℓ, min $\times$ 10^{-5}	$\log_{10} Vd$ mol/ℓ, min
1	180	1	20	0.98	0.97	H$_2$SO$_4$	1.41	0.783	-5.11
2	180	1	20	1.85	(1.77) [1.81]	H$_2$SO$_4$	1.62	0.900	-5.05
3	180	1	20	1.85	(1.77)	H$_2$SO$_4$	1.62	0.900	-5.05
4	180	1	20	2.30	2.19	H$_2$SO$_4$	1.45	0.830	-5.08
5	180	1	20	3.83	2.82	H$_2$SO$_4$	1.36	0.757	-5.12
6	180	1	20	3.83	2.81	H$_2$SO$_4$	1.40	0.777	-5.11
7	180	1	20	5.60	2.76	none	1.72	0.953	-5.02
8*)	180	1	20	5.61	2.73	none	1.86	1.03	-4.99
9*)	180	1	20	5.61	2.81	none	1.55	0.861	-5.07
10	180	1	20	5.60	(3.01) [2.84]	none	1.14	0.634	-5.19
11	180	1	20	5.60	(2.98) [2.85]	none	1.35	0.751	-5.12
12	180	1	20	5.64	2.77	none	1.71	0.952	-5.02
13	180	1	20	4.63	2.77	none	1.66	0.923	-5.03
14	60	1	20	7.72	3.18	NaOH	0.667	1.11	-4.95
15	60	1	20	7.72	3.28	NaOH	0.523	0.872	-5.06
16	60	1	20	10.85	10.38	NaOH	0.716	1.19	-4.92
17	120	1	20	11.60	(11.20) [11.47]	NaOH	1.30	1.08	-4.99
18	60	1	20	11.91	11.88	NaOH	1.704	1.17	-4.93
19	60	1	20	11.91	11.88	NaOH	0.758	1.26	-4.90
20	120	1	20	12.65	12.64	NaOH	1.58	1.32	-4.88

21*)	60	1	20	12.97	12.97	NaOH	1.14	1.90	−4.72
22*)	60	1	20	12.97	12.97	NaOH	1.25	2.08	−4.68
23*)	60	1	20	12.97	12.97	NaOH	1.45	2.42	−4.62
24*)	60	1	20	12.97	12.97	NaOH	1.31	2.15	−4.67
25*)	60	1	20	12.97	12.96	NaOH	1.98	1.63	−4.79
26**)	60	0.35	7	12.97	12.97	NaOH	1.41	2.35	−4.63
27**)	60	0.35	7	12.97	12.97	NaOH	1.25	2.08	−4.68
28	60	1	20	13.91	13.91	NaOH	2.56	4.27	−4.37
29	61	1	20	13.92	13.91	NaOH	3.01	4.92	−4.31
30	60	1	20	12.97	12.97	NaOH	1.15	1.91	−4.72
31	60	1	20	13.93	13.93	NaOH	3.28	5.47	−4.26
32	62	1	20	12.09	12.07	NaOH	1.02	1.64	−4.79
33	63	1	20	12.27	12.25	NaOH	1.01	1.60	−4.80
34	64	1	20	12.50	12.49	NaOH	1.02	1.59	−4.80
35	61	1	20	6.55	3.27	none	0.54	0.886	−5.05
36	107	1	20	5.64	3.08	none	0.83	0.774	−5.11
37	95	1	20	13.82	13.82	NaOH	4.32	4.53	−4.34
38	62	1	20	13.50	13.50	NaOH	2.03	3.28	−4.48
39	66	1	20	13.50	13.50	NaOH	2.09	3.17	−4.50
40	90	1	20	13.02	13.02	NaOH	1.54	1.72	−4.77
41	136	1	20	13.02	13.01	NaOH	2.51	1.99	−4.70
42	120	1	20	13.65	13.65	NaOH	4.13	3.44	−4.46
43	120	1	20	13.65	13.65	NaOH	4.44	3.70	−4.43

*) Shaking rate was changed.

**) Conducted in vacuum ($10^{-4} - 10^{-5}$ mmHg).

out and cooled in cold 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. In some cases, the concentration of hydrogen ion 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 sodium hydroxide solution or oxalic acid solution.

Some experiments were carried out in aqueous acetone or in the absence of air by the method described previously[2,4,5].

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

$$Vd = \frac{d\varDelta[Cl^-]}{dt},\tag{1}$$

where $\varDelta[Cl^-]$ is the increment of chloride ion concentration $[Cl^-]$ in solution formed by the hydrolysis and t the time of reaction. In the case where $[Cl^-]$ was directly observed, $d\varDelta[Cl^-]/dt$ was determined simply as the quotient of $\varDelta[Cl^-]$ over t. In some cases where hydrogen ion concentration was also measured, the hydrolysis rate was obtained by equating the increment $\varDelta[H^+]$ to $\varDelta[Cl^-]$ in Eq. (1).

§ 2. Results

Table 1 shows the results of the experiment which was carried out without addition of neutral salts, piperidine or thiophenol. In the second to the fourth column of the Table are shown respectively the time of reaction, the quantities of benzyl chloride and aqueous solution, pH before and after reaction and the added reagents. The pH of solution before reaction was measured by the pH-meter in most cases except in the runs conducted in strong alkaline solution above pH = 13 where pH was calculated from the concentration of hydroxide ion titrated with oxalic acid solution as described in § 1. The pH after reaction measured directly by the pH-meter or calculated from the hydrogen ion or hydroxide ion concentration is shown in round or square brackets respectively. The pH's after reaction in the other runs were calculated from the observed $\varDelta[Cl^-]$, equating it to $\varDelta[H^+]$. The sixth column gives the increment $\varDelta[Cl^-]$ of the chloride ion concentration $[Cl^-]$ in aqueous solution determined as described in § 1. The hydrolysis rate Vd and $\log_{10} Vd$ calculated from the increment of chloride ion concentration according to Eq. (1) are shown in the last column. The hydrolysis rate calculated from pH measured by pH-meter or from the

TABLE 2.   Hydrolysis of Benzyl Chloride in Aqueous Solution at 30°C. Neutral Salt Present.

Runs	Time of Reaction min	Quantity of		pH		Concentration of Added Salts mol/ℓ	$\Delta[Cl^-]$ mol/$\ell \times 10^{-3}$	Hydrolysis Rate	
		Benzyl Chloride mℓ	Agueous Solution mℓ	Before	After			$Vd = \dfrac{d\Delta[Cl^-]}{dt}$ mol/ℓ, min $\times 10^{-5}$	$\log_{10} Vd$ mol/ℓ, min
44	136	1	20	6.50	2.94	0.0794 NaCl	1.16	0.858	−5.07
45	103	1	20	13.88	13.88	0.0781 NaCl	3.52	3.402	−4.47
46	137	1	20	13.88	13.88	0.0781 NaCl	5.33	3.894	−4.41
47	212	1	20	0.99	0.98	0.0788 NaCl	1.52	0.714	−5.15
48	128	1	20	0.99	0.99	0.0788 NaCl	1.17	0.912	−5.04
49	60	1	20	2.90	2.74	0.25 Na$_2$SO$_4$	0.55	0.919	−5.04
50	120	1	20	5.20	[3.07]	0.5 Na$_2$SO$_4$	0.61	0.511	−5.15
51	60	1	20	6.80	3.28	0.5 Na$_2$SO$_4$	0.53	0.883	−5.05
52	60	1	20	6.62	3.26	0.25 Na$_2$SO$_4$	0.55	0.889	−5.05
53	60	1	20	12.97	12.97	0.5 Na$_2$SO$_4$	0.78	1.305	−4.88
54	60	1	20	12.97	12.97	0.25 Na$_2$SO$_4$	0.93	1.552	−4.81
55	60	1	20	13.97	13.97	0.5 Na$_2$SO$_4$	0.33	5.475	−4.26

titers of standard acid or alkaline solution is in agreement with those calculated from $\Delta[Cl^-]$ within the limit of the experimental error in the present work.

In runs 8, 9, 21, 22 ond 23, stirring rate was changed by switching the dial of magnetic stirrer and in runs 24 and 25, the flask was shaken vigorously up and down by a shaking machine (*ca.* 600 times/min). It can be said from these results that the hydrolysis rate is independent of shaking rates or methods. It may therefore be admitted that the hydrolysis proceeds homogeneously in the interior of aqueous solution and that the dissolution of benzyl chloride into solution and its reversal are not controlling. Runs 26 and 27 were conducted in vacuum. It is shown by comparing these runs with those conducted in the solution of the same initial pH that oxygen has no appreciable effect on the rate of the hydrolysis.

In Table 2 is shown the effect of the addition of neutral salts. The concentration of sodium chloride or sodium sulfate is given in the fifth column of the Table. The pH after reaction was calculated from $\Delta[Cl^-]$ as above except in run 50 where pH was calculated from the titers of sodium hydroxide solution.

The $\log_{10} Vd$ of Tables 1 and 2 were 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 with added sodium chloride or sodium sulfate by circles with cross or solid circles. A straight line with a break may be drawn through the circles as shown in the figure. The Vd is almost constant independently of pH up to 13.0, whence it increases inversely proportional to the activity of hydrogen ion. The rate at the region below
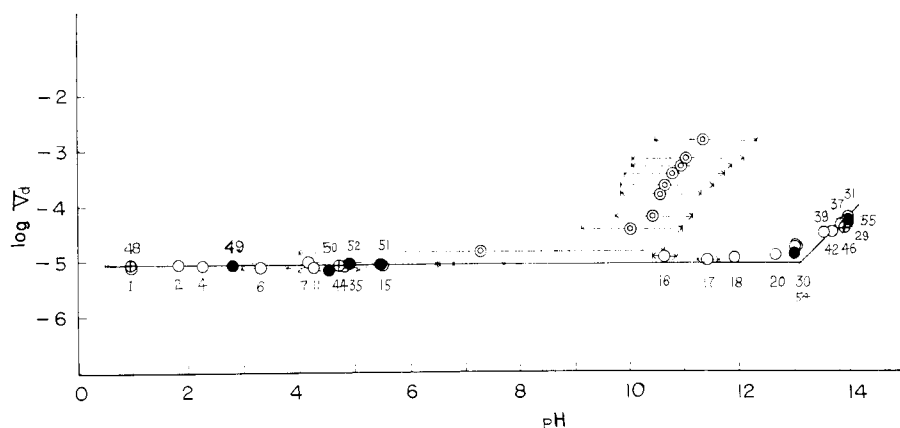

Fig. 1. Hydrolysis rate of benzyl chloride in aqueous solution at 30°C.
○ : no salt adedd, ● : sodium sulfate added, ⊕ : sodium chloride added, ◉ : piperidine added, ◀······▶ : Range of pH-variation.

pH = 13.0 was found to be about one hundred times larger than that of the chlorine exchange at 0.01 N chloride ion concentration[*]. The pH-dependence of Vd in alkaline region is more clearly shown in Fig. 2 by plotting Vd instead of $\log_{10} Vd$.
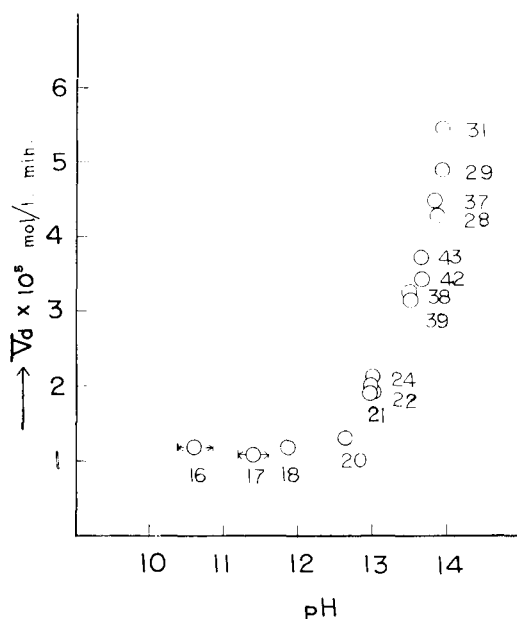

Fig. 2. pH-dependence of Vd in strong alkaline region.

The effect of the addition of piperidine or thiophenol on the Vd is shown in Tables 3 or 4. Runs in Table 3 were conducted under the same experimental conditions as in the runs of Table 1 except that $0.005 \sim 0.2$ mol/ℓ of piperidine was added, where the solution becomes alkaline due to the basicity of piperidine as shown in the fourth column. The pH before or after reaction was measured by pH-meter. The Vd plotted against pH is shown by double circles in Fig. 1. It is seen from these data that the Vd increases with increase of the concentration of piperidine at the range of pH $10 \sim 12$. The runs in Table 4 were conducted with or without addition of 0.045 mℓ thiophenol in 30% aqueous acetone (30 volume % of acetone), since thiophenol is hard to

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[*] Exchange rate r observed in the foregoing paper[2] was averaged at 1×10^{-5} [Cl$^-$] (mol of Cl$^-$/ℓ, min). Since [Cl$^-$] formed by the hydrolysis under the experimental condition of Table 1 is less than 0.01 mol/ℓ, r is 1×10^{-7} mol/ℓ at most under the condition of the hydrolysis.

TABLE 3.   The Effect of the Addition of Piperidine on Vd in Aqueous Solution at 30°C.

| Runs | Time of Reaction min | Quantity of | | pH | | Concentration of Piperidine mol/ℓ | Δ[Cl$^-$] mol/$\ell \times 10^{-2}$ | Hydrolysis Rate | |
		Benzyl Chloride mℓ	Aqueous Solution mℓ	Before	After			$Vd = \dfrac{d\Delta[\text{Cl}^-]}{dt}$ mol/ℓ, min$\times 10^{-4}$	$\log_{10} Vd$ mol/ℓ, min
56	60	1	20	10.57	3.97	0	0.088	0.148	−4.83
57	67	1	20	10.89	9.10	0.005	0.26	0.383	−4.42
58	54	1	20	11.10	9.70	0.01	0.35	0.653	−4.19
59	65	1	20	11.26	9.79	0.03	1.03	1.589	−3.80
60	64	1	20	11.47	9.78	0.04	1.46	2.301	−3.64
61	62	1	20	11.65	9.85	0.05	2.35	3.804	−3.42
62	62	1	20	11.80	9.98	0.075	3.03	4.899	−3.31
63	63	1	20	11.98	10.00	0.1	4.58	7.327	−3.14
64	61	1	20	12.18	10.40	0.2	8.91	14.71	−2.83

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

| Runs | Time of Reaction min | Quantity of | | pH | | Amount of Added Thiophenol mℓ | Δ[Cl$^-$] mol/$\ell \times 10^{-3}$ | Hydrolysis Rate | |
		Benzyl Chloride mℓ	30 vol. % Aqueous Acetone mℓ	Before	After			$Vd = \dfrac{d\Delta[\text{Cl}^-]}{dt}$ mol/ℓ, min$\times 10^{-5}$	$\log_{10} Vd$ mol/ℓ, min
65	146	1	20	11.00	9.94	—	1.387	0.950	−5.02
66	94	1	20	11.00	2.95	0.045	2.648	2.817	−4.58
67	81	1	20	11.92	11.89	—	0.894	1.104	−4.96
68	63	1	20	11.92	11.78	0.045	3.497	5.551	−4.26
69	103	1	20	12.50	12.49	—	0.892	0.866	−5.06
70	90	1	20	12.50	12.39	0.045	10.62	11.80	−3.93
71	133	1	20	12.80	12.76	—	1.125	0.846	−5.07
72	117	1	20	12.80	12.70	0.045	19.29	16.49	−3.78
73	60	1	20	13.08	13.08	—	1.401	2.336	−4.63
74	105	1	20	13.08	13.02	0.045	22.71	21.63	−3.66
75	180	1	20	5.90	2.93	—	1.167	0.649	−5.19
76	66	1	20	5.10	2.61	0.045	2.465	3.734	−4.43

dissolve in water. The rate Vd without the addition of thiophenol is almost the same as those in aqueous solution. The hydrolysis rate decreases with increasing the acetone percentage in aqueous solution, but the increase of the solubility of benzyl chloride compensates the solvent effect in this case. Results of Table 4 are shown in Fig. 3, where double or open circles show Vd with
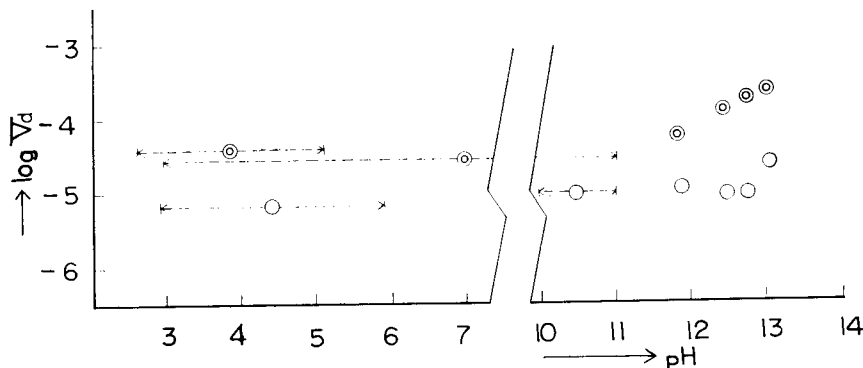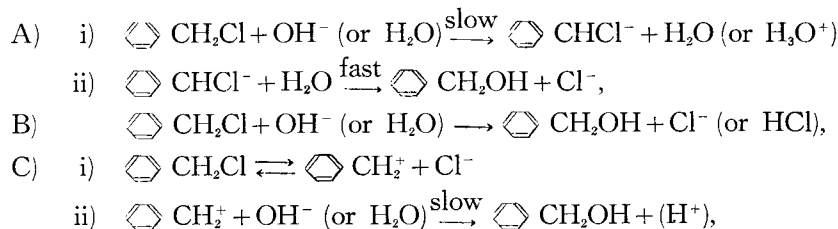

Fig. 3. Effect of the addition of thiophenol on log Vd in 30% aqueous acetone.

○ : thiophenol absent, ◎ : thiophenol present, ◄······► : Range of pH-variation.

or without the addition of thiophenol respectively. It is seen that the Vd is increased by the addition of thiophenol. The increase in Vd with increasing pH in runs with the same amount of added thiophenol is considered due to the increase in the concentration of thiophenolate ion with increase of pH.

§ 3. Discussion

Benzyl chloride decomposes in aqueous solution to form benzyl alcohol and hydrogen chloride under the present experimental conditions[*]. As the mechanism of the hydrolysis of benzyl chloride giving these final products, the possible ones which fit the observed pH dependence of Vd are only the following three.

A) i) $\langle\!\!\!\rangle CH_2Cl + OH^-$ (or H_2O) $\xrightarrow{\text{slow}}$ $\langle\!\!\!\rangle CHCl^- + H_2O$ (or H_3O^+)

   ii) $\langle\!\!\!\rangle CHCl^- + H_2O \xrightarrow{\text{fast}} \langle\!\!\!\rangle CH_2OH + Cl^-$,

B) $\langle\!\!\!\rangle CH_2Cl + OH^-$ (or H_2O) $\longrightarrow \langle\!\!\!\rangle CH_2OH + Cl^-$ (or HCl),

C) i) $\langle\!\!\!\rangle CH_2Cl \rightleftarrows \langle\!\!\!\rangle CH_2^+ + Cl^-$

   ii) $\langle\!\!\!\rangle CH_2^+ + OH^-$ (or H_2O) $\xrightarrow{\text{slow}} \langle\!\!\!\rangle CH_2OH + (H^+)$,

*) See Ref. 1, a).

where step i) in mechanism A) or step ii) in mechanism C) is the rate-determining step of the hydrolysis respectively. Hydroxide ion or water molecule acts as Brönsted base in mechanism A), but as nucleophilic reagent in mechanism B).

If the hydrolysis proceeds by mechanism C), a chlorine exchange must occur by step C) i) and its rate must be fast compared to the rate of the hydrolysis. It was found, however, that the exchange rate is slower than the hydrolysis rate*). Therefore, mechanism C) is excluded.

If the hydrolysis occurs by a base catalyzed reaction as in mechanism A), then thiophenolate ion or piperidine should be less reactive than hydroxide ion, since it is less basic. If on the other hand the reaction is nucleophilic displacement as in mechanism B), highly nucleophilic reagents would react more rapidly than hydroxide. The experimental results show that the rate of the hydrolysis is increased by the addition of piperidine or thiophenol. It is thus concluded that benzyl chloride hydrolyzes by mechanism B).

Acknowledgments

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*) See foot-note of page 179.