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# THE MECHANISM OF THE HYDROLYSIS OF METHYLENE CHLORIDE

By

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## Introduction

We have studied the kinetics of the chlorine exchange reaction of methylene chloride with aqueous chloride solution and proposed the mechanism of the reaction<sup>1)</sup>. The kinetics of the hydrolysis of methylene chloride has now been investigated over the pH range from 0 to 12 under the same experimental conditions as those in the exchange reaction reported in the foregoing paper<sup>1)</sup>. It has been found that the rate of the hydrolysis is approximately constant independently of pH up to pH 10, 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 was found no mass effect of chloride ion on the rate, but the great increase of the rate by the addition of thiophenol or piperidine. The analysis of the observed kinetic data leads us to conclude that methylene chloride hydrolyzes by a S<sub>N</sub>2 mechanism, which was recently discussed in a different way of kinetic presentation by MOELWYN-HUGHES *et al*<sup>2)</sup>.

## § 1. Experimental

**Reagents:** The purification of methylene chloride has been described previously<sup>1)</sup>. All other chemicals were guaranteed reagent-grade. Solution of different pH used was simply conductivity water<sup>\*\*\*)</sup>, aqueous sodium hydroxide, sulfuric acid or phosphate buffer solution<sup>\*\*\*\*)</sup>.

**Kinetic Runs:** In a typical run, 1 ml of methylene chloride and 5 ml of aqueous solution of known pH with or without addition of neutral salt were sealed air-free<sup>\*\*\*\*\*)</sup> in a quartz tube of 15~20 ml capacity and shaken vigorously in a boiling water bath as described previously<sup>5)6)</sup>. At a recorded time, the tube

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

\*\*\*\*) 2/15 mol/l Na<sub>2</sub>HPO<sub>4</sub> + 2/15 mol/l KH<sub>2</sub>PO<sub>4</sub>.

\*\*\*\*\*) The tube was evacuated to 10<sup>-4</sup>~10<sup>-5</sup> mmHg. For the procedure of evacuating tube, see p. 407 of Ref. 3 or p. 84 of Ref. 4.

was removed, opened, about 4 ml solution pipetted out and analyzed for the hydrolysis rate in several different ways as below.

i) The amount of chloride ion formed due to the decomposition of methylene chloride was measured by MOHR's titration method or UTSUMI's colorimetric method<sup>7)</sup> (colorimetry of ferric thiocyanate liberated by chloride ion in the presence of mercury thiocyanate and iron alum). The rate was determined from the amount of liberated chloride ion as described below. The associated pH-change at 100°C was calculated according to Eq. (6) from the observed pH values at room temperature.

ii) The pH of the sample was determined at room temperature before and after the reaction by means of a glass electrode pH meter or by titrating hydroxide ion concentration with standard oxalic acid solution in the case of extremely strong alkaline solution (Runs 3 and 6 in Table 1). The rate of the hydrolysis was determined from the pH-change at 100°C which was calculated from the observed pH values at room temperature as below.

**Calculation of Hydrolysis Rate:** Admitting that a methylene chloride molecule yields, as it decomposes, two chloride ions, the hydrolysis rate  $V_a$  for unit volume of solution may be expressed by the equation,

$$V_a = \frac{1}{2} \frac{d\Delta[\text{Cl}^-]}{dt}, \quad (1)$$

where  $\Delta[\text{Cl}^-]$  is the increment of chloride ion concentration  $[\text{Cl}^-]$  in solution due to the decomposition and  $t$  the time of reaction.

In the case of i) where  $[\text{Cl}^-]$  was directly observed,  $d\Delta[\text{Cl}^-]/dt$  was determined simply as the quotient of  $\Delta[\text{Cl}^-]$  over  $t$ . In the other case ii) where pH alone was measured, the hydrolysis rate was obtained by equating the increment  $\Delta[\text{H}^+]$  of hydrogen ion concentration  $[\text{H}^+]$  in solution to  $\Delta[\text{Cl}^-]$  in Eq. (1). The latter cases were Runs 12 and 13 conducted in acidic solution or Run 11 in weak alkaline solution<sup>\*)</sup>.

**Calculation of pH at 100°C:** The pH's at 100°C were calculated as below<sup>\*\*)</sup>. We have the equation because of electric neutrality of the solution,

$$\Delta[\text{Cl}^-] + [\text{OH}^-] = [\text{H}^+] + I, \quad (2)$$

where  $[\text{OH}^-]$  or  $[\text{H}^+]$  is normal concentration of hydroxide or hydrogen ion respectively and  $I$  the excess of total concentration of cation over that of

\*) It must be noted that under the strong alkaline solution the reaction of formed formaldehyde with the sodium hydroxide to give methyl alcohol and formic acid (the Cannizzaro reaction) may occur and therefore the rate calculated from  $\Delta[\text{H}^+]$  may differ from that from  $\Delta[\text{Cl}^-]$ . Cf. p. 1330 of Ref. 2.

\*\*\*) Cf. p. 149 of Ref. 5.

anion, exclusive of  $[H^+]$ ,  $[OH^-]$  and  $\Delta[Cl^-]$ . Rewriting  $[OH^-]$  or  $[H^+]$  in Eq. (2) into respective ratio of activity  $a^{OH^-}$  or  $a^{H^+}$  to activity coefficient  $f^{OH^-}$  or  $f^{H^+}$  and introducing the thermodynamical dissociation constant,  $K_r = a^{H^+} a^{OH^-}$ , we have,

$$\frac{K_r}{a^{H^+} f^{OH^-}} - \frac{a^{H^+}}{f^{H^+}} = I - \Delta[Cl^-] \quad (3)$$

or before reaction in particular,

$$\frac{K_r}{a^{H^+} f^{OH^-}} - \frac{a^{H^+}}{f^{H^+}} = I \quad (4)$$

The  $I$  was first calculated according Eq. (4) from the observed pH or  $a^{H^+}$  by putting  $f^{H^+} = f^{OH^-} = 1$  and  $K_r$  value\*) at 20°C (the temperature at which pH was measured). The appropriate ionic strength was then worked out from the  $I$  value incorporated with known concentration of neutral salt, if added, equating  $a^{H^+}$  or  $K_r/a^{H^+}$  respectively to  $[H^+]$  or  $[OH^-]$ . The  $f^{H^+}$  and  $f^{OH^-}$  were now calculated by the limiting law,

$$-\log_{10} f^{H^+} = -\log_{10} f^{OH^-} = \frac{1.8148 \times 10^{-6}}{(DT)^{\frac{3}{2}}} \sqrt{\mu}, \quad (5)$$

where  $T$  is absolute temperature,  $D$  the dielectric constant\*\*).

Using the obtained values of  $f^{H^+}$  and  $f^{OH^-}$ ,  $I$  and henceforth  $\mu$  were computed again according to Eq. (4), equating now  $a^{H^+}/f^{H^+}$  or  $K_r/f^{H^+} f^{OH^-}$  to  $[H^+]$  or  $[OH^-]$  respectively. This procedure of successive approximation was repeated until  $I$ -value remained practically unvaried by repetition. In the case of the solution of extremely high ionic strength,  $f^{H^+}$  and  $f^{OH^-}$  were quoted from the values obtained by HÜCKEL<sup>7)</sup>. The  $I - \Delta[Cl^-]$  after the reaction was calculated similarly as above, letting  $\Delta[Cl^-]$  include in the calculation of  $\mu$ . The  $I - \Delta[Cl]$  at 100°C was obtained by multiplying that at room temperature by the ratio  $\alpha = 0.96$  of the specific volume of water at room temperature to that at 100°C.

Now solving the quadratic equation (3) with respect to  $a^{H^+}$ , we have

$$a^{H^+} = \frac{-B \pm \sqrt{B^2 + 4K_r/f^{H^+} f^{OH^-}}}{2}, \quad (6)$$

where  $B = I - \Delta[Cl^-]$ .

The pH of solution at 100°C was now determined according to Eq. (6),

\*)  $0.7 \times 10^{-14}$ , which was interpolated from the values observed by Heydweiller, Landolt-Börnstein Tabellen II. p. 1164.

\*\*\*) Drude, Ann. Phys., (3) 59, 49 (1896).

TABLE 1. Hydrolysis of Methylene Chloride at 100 °C

Runs	Quantity of		Added Reagents	Reaction Time min	pH		Cl <sup>-</sup> ion Concentration in Aqueous Solution after Reaction, Δ[Cl <sup>-</sup> ]		Hydrolysis Rate	
	Methylene Chloride ml	Aqueous Solution ml			Before	After	mol/l	Method	$V_a = \frac{1}{2} \cdot \frac{\Delta[\text{Cl}^-]}{t}$ mol/l, min	log V <sub>a</sub> mol/l, min
1	1	5	none	300	5.75 (5.31)	2.30 (2.32)	6.37 × 10 <sup>-3</sup>	Colorimetry	1.06 × 10 <sup>-5</sup>	- 4.98
2	1	5	Buffer	300	6.72 (6.16)	6.80 (6.16)	1.27 × 10 <sup>-2</sup>	Colorimetry	2.12 × 10 <sup>-5</sup>	- 4.67
3	1	5	NaOH	300	13.65 (11.77)	12.60 (10.79)	0.314	Colorimetry	5.23 × 10 <sup>-4</sup>	- 3.28
4	1	5	NaOH	300	12.25 (10.40)	11.20 (9.35)	1.34 × 10 <sup>-2</sup>	Colorimetry	2.24 × 10 <sup>-5</sup>	- 4.65
5	1	5	H <sub>2</sub> SO <sub>4</sub>	300	0.61 (0.83)	0.60 (0.82)	6.04 × 10 <sup>-3</sup>	Colorimetry	1.01 × 10 <sup>-5</sup>	- 5.00
6	1	5	NaOH	80	13.90 (12.02)	13.65 (11.75)	0.236	Mohr	1.47 × 10 <sup>-3</sup>	- 2.83
7	1	5	NaOH	80	12.98 (11.13)	12.60 (10.76)	0.0315	Mohr	1.97 × 10 <sup>-4</sup>	- 3.70
8	1	5	NaOH	10	11.08 (9.13)	7.95 (6.30)	5.33 × 10 <sup>-4</sup>	Colorimetry	2.62 × 10 <sup>-5</sup>	- 4.57
9	1	5	NaOH	10	9.59 (7.73)	3.38 (3.40)	4.52 × 10 <sup>-4</sup>	Colorimetry	2.26 × 10 <sup>-5</sup>	- 4.65
10	1	5	H <sub>2</sub> SO <sub>4</sub>	80	2.98 (3.00)	2.97 (2.99)	2.34 × 10 <sup>-3</sup>	Colorimetry	1.46 × 10 <sup>-5</sup>	- 4.83
11	1	5	NaOH + 1.43N-NaCl	10	9.59 (7.58)	3.76 (3.80)	2.5 × 10 <sup>-4*</sup>	pH	1.3 × 10 <sup>-5</sup>	- 4.9
12	1	5	1.24N-NaCl	15	5.82 (5.78)	3.45 (3.49)	5.2 × 10 <sup>-4*</sup>	pH	1.7 × 10 <sup>-5</sup>	- 4.8
13	1	5	H <sub>2</sub> SO <sub>4</sub> + 1.24N-NaCl	80	2.32 (2.36)	2.16 (2.20)	3.1 × 10 <sup>-3*</sup>	pH	1.9 × 10 <sup>-5</sup>	- 4.7

\*) Increment of hydrogen ion concentration Δ[H<sup>+</sup>].

putting into it  $K_{100}=48 \times 10^{-14}$ \*) and  $I-\Delta[\text{Cl}^-]$  obtained above at 100°C and  $f^{\text{H}^+}=f^{\text{OH}^-}$  at 100°C calculated by Eq. (5) on the basis of  $\mu$  obtained above multiplied by  $\alpha$ .

## § 2. Results

Results of the experiment are shown in Tables 1 and 3. In the second to the fourth column in Table 1 are shown respectively the quantities of methylene chloride and aqueous solution, the added reagents and the time of reaction. The fifth column gives pH before and after the reaction measured directly by pH meter at room temperature and pH at 100°C (shown in parentheses) calculated by Eq. (6) in the foregoing section. The chloride ion concentration in aqueous solution after the reaction is given in the next column, together with the methods of its determination. The last column shows the hydrolysis rate  $V_a$  calculated by Eq. (1) and  $\log V_a$ . Table 2 shows that in acidic or neutral

TABLE 2.

	Hydrolysis Rate		
	No. of Run in Table 1	$V_a = \frac{1}{2} \cdot \frac{d\Delta[\text{H}^+]}{dt}$ Calculated from pH- change in Table 1 mol/l, min	$V_a = \frac{1}{2} \cdot \frac{d\Delta[\text{Cl}^-]}{dt}$ Taken from Table 1 mol/l, min
Acidic Region	1	$0.8 \times 10^{-5}$	$1.06 \times 10^{-5}$
Neutral Region	9	$2.1 \times 10^{-5}$	$2.26 \times 10^{-5}$
Alkaline Region	8	$3.3 \times 10^{-5}$	$2.62 \times 10^{-5}$
	4	$2.1 \times 10^{-5}$	$2.24 \times 10^{-5}$
	7	$3.1 \times 10^{-4}$	$1.97 \times 10^{-4}$
	3	$6.8 \times 10^{-4}$	$5.23 \times 10^{-4}$
	6	$2.7 \times 10^{-3}$	$1.47 \times 10^{-3}$

solution the hydrolysis rate  $V_a$  calculated from  $\Delta[\text{Cl}^-]$  given in Table 1 are in agreement with those calculated from the pH-measurement within the limit of the experimental error, whereas in alkaline solution the latter rate is certainly a little larger than the former, although the  $V_a$  calculated from pH-change contains considerable error because of inaccuracy of activity coefficient  $f^{\text{H}^+}$  or  $f^{\text{OH}^-}$ . This seems to indicate that the formed formaldehyde reacts further with hydroxide ion in alkaline region to give formic acid and methanol, as observed

\*) NOYES and KATO, Landolt-Börnstein Tabellen II. p. 1164.

TABLE 3. The Effect of the Addition of Piperidine or Thiophenol on  $V_d$

Runs	Solution		Concentration of Methylene Chloride mol/l	Added Reagents mol/l	Reaction Time min	pH		Cl <sup>-</sup> ion Concentration in Solution after Reaction		Hydrolysis Rate	
	Volume ml	Nature				Before	After	mol/l	Method	$V_d = \frac{1}{2} \cdot \frac{4[Cl^-]}{t}$ mol/l, min	$\log_{10} V_d$ mol/l, min
14	5	Water	Saturated*) Solubility	0.200- Piperidine	20	10.95 (9.10)	9.45 (7.60)	$8.88 \times 10^{-2}$	Colorimetry	$2.22 \times 10^{-3}$	- 2.65
15	5	Water	Saturated*) Solubility	0.200- Piperidine	20	10.95 (9.10)	9.45 (7.60)	$8.88 \times 10^{-2}$	Colorimetry	$2.22 \times 10^{-3}$	- 2.65
16	5	60 Vol. % Dioxane	0.315~0.272	0.200- Thiophenol	20	5.70 (5.28)	4.50 (4.50)	$1.29 \times 10^{-1}$	Colorimetry	$3.23 \times 10^{-3}$ ( $2.58 \times 10^{-3}$ )	- 2.49 (- 2.58)
17	5	60 Vol. % Ethanol	0.315~0.273	0.200- Thiophenol	20	5.70 (5.28)	4.20 (4.20)	$1.26 \times 10^{-1}$	Colorimetry	$3.15 \times 10^{-3}$ ( $2.52 \times 10^{-3}$ )	- 2.50 (- 2.60)
18	5	80 Vol. % Ethanol	0.315~0.273	0.200- Thiophenol	20	5.70 (5.28)	4.20 (4.20)	$1.26 \times 10^{-1}$	Colorimetry	$3.15 \times 10^{-3}$ ( $2.52 \times 10^{-3}$ )	- 2.50 (- 2.60)

\*) Cf. foot-note of p. 252.

by MOELWYN-HUGHES *et al.*<sup>2)</sup> In Table 3 is shown the effect of the addition of piperidine or thiophenol on the  $V_d$ . Runs 14 and 15 were conducted under the same experimental conditions as in Run 1 of Table 1 except that 0.200 mol/l of piperidine was added, where the solution became alkaline due to the basicity of piperidine as shown in the sixth column. In Runs 16 to 18 where 0.200 mol/l of thiophenol was added, aqueous dioxane or ethanol was used as solvent because of the low solubility of thiophenol into water. In these runs, the concentrations of methylene chloride before and after the reaction are given in the third column of the Table. Since the averaged concentration (0.294 mol/l) of methylene chloride is 1.25 times as large as that\*) in other runs (Runs 1~13 of Table 1) and Runs 14~15 of Table 3), the hydrolysis rate corrected for the difference is given in parentheses in the last column of the Table.

The  $\log V_d$  of Tables 1 and 3 were plotted against pH in Fig. 1 each at the median of pH, if varied. The circles show the rates without added salt, through which a straight line with a break may be drawn as shown in the Figure. The  $V_d$  is almost constant independently of pH up to pH 10, whence

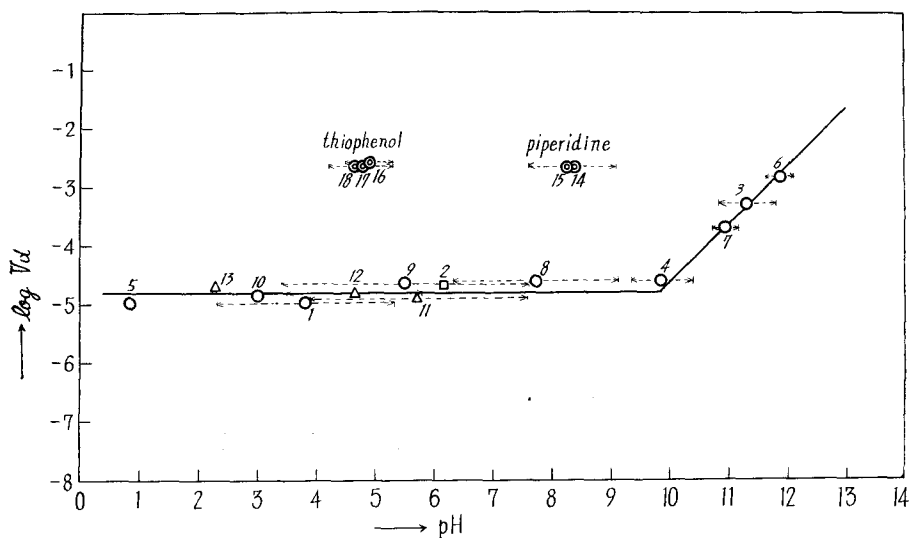


Fig. 1. Hydrolysis rate of methylene chloride at 100°C.

○: no salt added, △: salt added, □: buffer solution, ⊙: piperidine or thiophenol added, |←-----→|: Range of pH-variation.

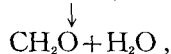
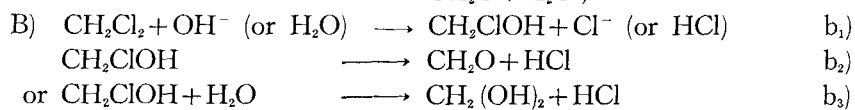
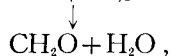
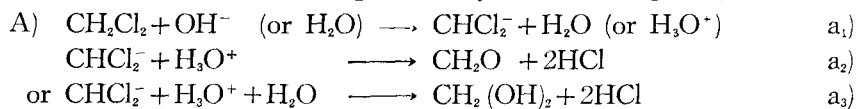
\*) 0.2355 mol/l, which was calculated from the solubility of methylene chloride into water at 20°C. It is anticipated from the observed solubilities of chloroform and carbon tetrachloride at various temperatures that the solubility of methylene chloride at 100°C does not differ much from that at 20°C.

it increases proportional to the activity of hydrogen ion. The rate at the region below pH 10 was found to be about twenty eight times larger than that of the chlorine exchange<sup>1)</sup>, at 0.01 *N* chloride ion concentration. The effects of neutral salt and buffer solution are shown respectively by triangles and a square in the same figure: the hydrolysis rate was not perceptibly affected by phosphate buffer solution or by the addition of about 1.3 *N* sodium chloride. The rate  $V_d$  with the addition of piperidine or thiophenol is shown by double cricles in the same figure. It is seen that the nucleophilic reagents caused the  $V_d$  to increase by about one hundred times, although the solvent effect is also included in the case of thiophenol.

It will be admitted similarly as in the case of the chlorine exchange<sup>1)</sup> that the hydrolysis proceeds homogeneously in the interior of aqueous solution and that the dissolution of methylene chloride into solution and its reversal are not controlling.

### § 3. Discussion

It is known that methylene chloride decomposes in water to give formaldehyde and hydrogen chloride and in alkaline solution the formaldehyde formed further reacts with hydroxide ion to give methyl alcohol and formic acid<sup>2)\*</sup>. For the mechanism of the hydrolysis of methylene chloride giving these final products, we have first considered more than one hundred kinds in terms of elementary steps. Of these mechanisms, however, the possible ones which fit the observed pH dependence of  $V_d$  and the fact that the hydrolysis rate is rapid compared to the chlorine exchange are only the following two,



in alkaline solution in particular,



\*) The reaction of formaldehyde with the formed methyl alcohol and the polymerization of formaldehyde to sugars do not occur under the conditions of our experiments, where the concentration of formaldehyde is generally small and at 100°C the formaldehyde is removed as quickly as it is formed. See pp. 1330~1332 of Ref. 2.

where step a<sub>1</sub>) in mechanism A) or step b<sub>1</sub>) in B) 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 of methylene chloride proceeds by a base catalyzed reaction as in mechanism A), then the thiophenolate ion should be much less reactive than hydroxide ion, since it is much less basic. However, if the reaction is a direct nucleophilic displacement as in mechanism B), it might be expected that the highly nucleophilic thiophenolate ion would react rapidly than hydroxide<sup>9)</sup>. The experimental results show that the rate of the hydrolysis was greatly increased by the addition of thiophenol over the range of pH 4~5. Under almost the same conditions\*<sup>9)</sup> where the concentration of thiophenol is about the same as that of sodium hydroxide, the reaction with thiophenolate ion is about five times as large as the reaction with hydroxide ion (see Run 3 of Table 1 and Runs 16~18 of Table 3). It is also shown in Fig. 1 that the addition of 0.200 mol/l of piperidine which is less basic than hydroxide caused the hydrolysis rate to increase by about one hundred times over the range of pH 9.1~7.6. With the equal concentrations of piperidine and hydroxide (see Run 3 of Table 1 and Runs 14~15 of Table 3), the reaction with piperidine is four times fast compared to that with hydroxide ion. This seems to indicate that piperidine is more nucleophilic than hydroxide in this reaction probably because the former reagent is more polarizable than the latter\*\*).

From the above arguments it can be concluded that methylene chloride hydrolyzes by mechanism B).

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\*<sup>9)</sup> The effect of solvent polarity is comparatively small in S<sub>N</sub>2 type, although aqueous dioxane or ethanol is used as solvent in the experiments with thiophenol. Cf. sec. 25a of Ref. 10.

\*\*<sup>9)</sup> For a relation of the nucleophilic strengths to the corresponding polarizabilities and basicities, see Ref. 11.

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