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Instructions for use

THE KINETICS OF THE HYDROLYSIS OF
CARBON TETRACHLORIDE

By

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Introduction

We have investigated the kinetics of the chlorine exchange reaction be-
tween carbon tetrachloride and aqueous chloride solution and proposed the
mechanism of the reaction[1]. The kinetics of the hydrolysis of carbon tetra-
chloride has now been investigated over the whole pH range from 0–14 under
the same experimental conditions as those in the exchange reaction reported
in the foregoing paper[1]. It has been found that the rate of hydrolysis is
approximately constant independently of pH and about eight hundreds times
larger than that of the chlorine exchange and that there was no mass effect
of chloride ion on the rate. The experimental results are discussed in connec-
tion with those recently obtained by FELLS and MOELWYN-HUGHES[2].

Experimental

Reagents: The preparation of carbon tetrachloride has been described in the
foregoing paper[1]. Solution of different pH used was simply water[**], aqueous
sodium hydroxide, sulfuric acid or phosphate buffer solution[***]. Neutral salt
added was sodium chloride or sodium sulfate.

Kinetic runs: One mℓ of carbon tetrachloride was sealed air-free[****]
together with 5 or 7 mℓ aqueous solution of known pH with or without ad-
dition of neutral salt in a quartz tube of 25–30 mℓ capacity and the tube was
placed in a constant temperature bath[*****] similarly as described in the pre-
vious works[1,3,4,5]. At a recorded time, the tube was removed, opened, about

5 mℓ solution pipetted out and then analyzed for the decomposition rate at different pH in a few different ways as shown below.

(i) The amount of chloride ion formed due to the decomposition was measured by MOHR's titration method or by UTSUMI's colorimetric method[5] (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 in the next section. The associated pH-change was determined by pH measurement at room temperature by means of a glass electrode pH meter.

(ii) The pH of the sample was determined at room temperature by means of pH meter. The rate of decomposition was calculated from the observed pH value as described in the next section.

Calculation of Decomposition Rates : The decomposition rate V_d for unit volume may be represented by the equation, since a carbon tetrachloride molecule yields four chloride ions[2], as it decomposes,

$$V_d = \frac{1}{4} \frac{d\Delta[\text{Cl}^-]}{dt} , \qquad (1)$$

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

In the case of (i) in the foregoing section where $[\text{Cl}^-]$ was directly observed, $d\Delta[\text{Cl}^-]/dt$ was determined simply as the quotient of $\Delta[\text{Cl}^-]$ over t. The associated pH range was determined by pH measurement. In the other case (ii) where pH alone was measured, the decomposition 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) in the acidic solution, since, according to MOELWYN-HUGHES *et al.*[2], the final products of carbon tetrachloride were found to be only hydrochloric acid and carbon dioxide, the acidity of the latter being neglected.

Results and Discussion

Table 1 shows the results of decomposition. In the second to the fourth column are shown respectively the quantities of carbon tetrachloride and aqueous solution, the added reagents and the time of reaction. The fifth colum gives pH before and after reaction measured by pH meter at room temperature. The chloride ion concentrations in aqueous solution after the reaction is given in the sixth column, together with the methods of its determination. The last column shows the decomposition rate V_d calculated by Eq. (1) and $\log_{10} V_d$. The reaction tubes were shaken by a shaking machine in runs 1 and 3, but

TABLE 1. Decomposition of Carbon Tetrachloride in
Aqueous Solution at 100°C.

| Run | Quantity of | | | Time of Reaction | pH | | Cl⁻ ion Concentration in Aqueous Solution after Reaction | | Decomposition Rate | |
| | Carbon Tetra-chloride | Aqueous Solution | Added Reagent | | Before | After | | | $V_d = \dfrac{1}{4}\dfrac{\Delta[Cl^-]}{t}$ | $\log_{10} V_d$ |
	mℓ	mℓ		min			m mol/ℓ	Method	mol/ℓ, min	mol/ℓ, min
1*)	1	5	None	242	5.76	2.54	4.36	Colorimetry	4.51×10^{-6}	-5.35
2	”	”	”	”	5.76	2.53	4.36	”	4.51×10^{-6}	-5.35
3*)	”	”	NaOH	”	13.50	13.37	7.05	”	7.28×10^{-6}	-5.14
4	”	”	”	”	13.50	13.41	7.85	”	8.12×10^{-6}	-5.09
5	”	”	None	”	5.76	2.34	5.03	”	5.20×10^{-6}	-5.29
6	”	7	0.1 N NaCl	131	5.79	2.48	3.31**)	pH	3.58×10^{-6}	-5.45
7	”	”	1 N NaCl	”	5.96	2.27	5.37**)	”	5.82×10^{-6}	-5.24
8	”	”	0.2 N Na₂SO₄	”	6.19	2.94	2.55	Colorimetry	2.76×10^{-6}	-5.56
9	”	”	Buffer	”	6.73	6.55	1.71	”	1.85×10^{-6}	-5.73
10	”	”	NaOH	”	11.43	8.87	6.04	”	6.53×10^{-6}	-5.19
11	”	”	”	”	12.15	9.27	6.38	”	6.91×10^{-6}	-5.16
12	”	5	H₂SO₄	2300	0.75	0.25	45.0	Mohr's Method	4.89×10^{-6}	-5.31

*) The reaction tube was shaken briskly.

**) The increment Δ[Cl⁻] of chloride ion concentration.

not in runs 2 and 4, no appreciable effect of shaking upon the decomposition rate V_d being observed as seen in the Table.

It is shown in Table 2 that the decomposition rates V_d obtained in the present work are in agreement with those calculated from the pH-measurement in the experiment of the chlorine exchange[1] within the experimental error.

TABLE 2.

		Decomposition rate		
	No. of run in Table 1 of Ref. 1	$V_d = \dfrac{1}{4} \cdot \dfrac{d\Delta[H^+]}{dt}$ Calculated from pH-change in Table 1 of Ref. 1. 10^{-6} mol/ℓ min	No. of run in Table 1 of this paper	$V_d = \dfrac{1}{4} \cdot \dfrac{d\Delta[Cl^-]}{dt}$ Taken from Table 1 of this paper 10^{-6} mol/ℓ min
Acidic region	1	6.6	1, 2	4.5
	3, 4, 7	7.7	5	5.2
	9	6.3	12	4.9
Buffer solution	10	1.3	9	1.8
Alkaline region	2	6.5	3	7.3
	5	7.5	4	8.1
	8	6.9	10	6.5
			11	6.9

The $\log_{10} V_d$ was plotted against pH in Fig. 1 by circles, triangles or a square, each at the median of pH, if varied. The circles show the rates without added salt, through which a straight horizontal line may be drawn as shown in the Figure. The effects of neutral salt and buffer solution are shown respectively by triangles and a square in the same Figure ; the decomposition rate was not perceptively affected by the addition of 0.1 N or 1 N sodium chloride but decreased slightly by 0.2 N sodium sulfate and considerably decreased in buffer solution.

Fig. 1 shows that the mass effect of chloride ion is imperceptible and that log V_d is almost constant independently of pH over the whole range.

The rate V_d of the hydrolysis was found to be about eight hundreds times larger than that r of the chlorine exchange[1] at 0.01 N chloride ion concentration.

MOELWYN-HUGHES *et al.*[2] have recently shown that the decomposition of carbon tetrachloride in aqueous solution can be represented by the equation, $CCl_4 + 2H_2O = CO_2 + 4HCl$ and the rate of the reaction is of the second order
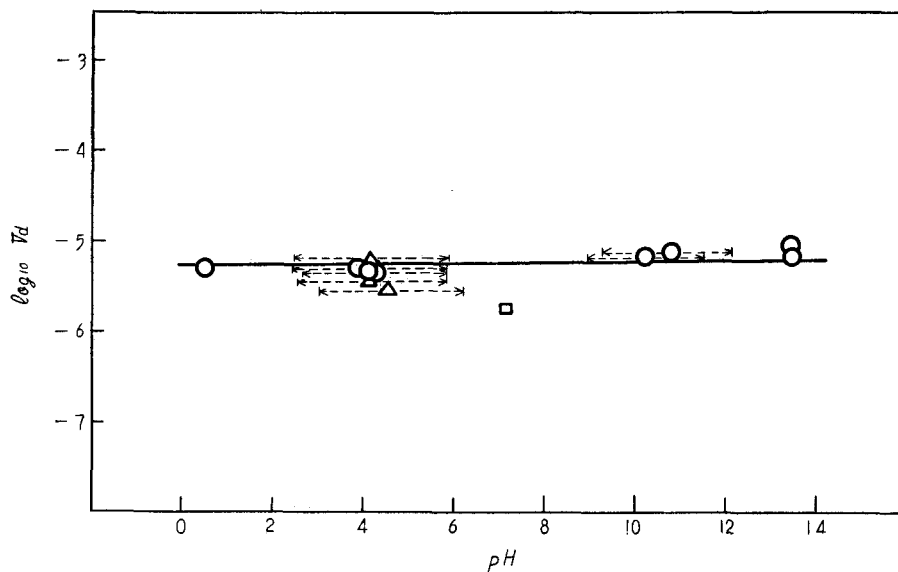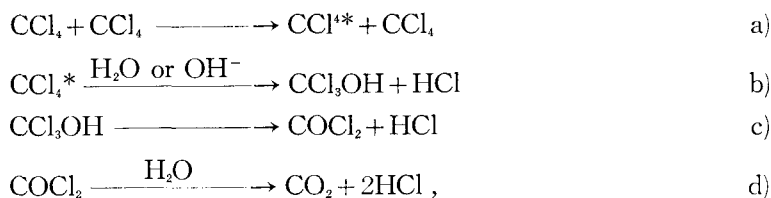
Fig. 1. Decomposition Rate of Carbon Tetrachloride (100°C).

◯ : No salt added,   △ : Salt added,   ☐ : Buffer solution.

with respect to carbon tetrachloride.   The mechanism of the decomposition suggested by them may be represented by the scheme.

$$CCl_4 + CCl_4 \xrightarrow{\hspace{2cm}} CCl^{4*} + CCl_4 \qquad\qquad a)$$

$$CCl_4* \xrightarrow{H_2O \text{ or } OH^-} CCl_3OH + HCl \qquad\qquad b)$$

$$CCl_3OH \xrightarrow{\hspace{2cm}} COCl_2 + HCl \qquad\qquad c)$$

$$COCl_2 \xrightarrow{H_2O} CO_2 + 2HCl, \qquad\qquad d)$$

where CCl_4* denotes an activated molecule of carbon tetrachloride formed by step a), which determines the rate of the decomposition.

It is seen that the following three facts obtained in the present work fits in sufficiently with the mechanism.

 i) No mass effect of chloride ion upon the decomposition rate.

ii) Much smaller rate of chlorine exchange than that of decomposition.

iii) No pH effect on the decomposition rate over the whole range of pH.

Acknowledgment

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