

## 72. The Kinetics of the Hydrolysis of the Chlorinated Methanes.

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The kinetics of the hydrolysis of chloroform and carbon tetrachloride have been investigated over a range of temperature in acidic and alkaline aqueous solution. The results, combined with earlier work on methyl chloride and methylene dichloride, give an account of the differing stability towards hydrolysis of the chlorinated methanes.

For chloroform the changes resolve themselves into a very slow first-order reaction with the solvent and a rapid second-order reaction between chloroform and the hydroxyl ion, probably involving the carbon dichloride radical as an intermediate and giving both carbon monoxide and formate ion as products.

Carbon tetrachloride reacts with water more rapidly than methylene dichloride or chloroform. The reaction appears to be of the second order with respect to carbon tetrachloride. The rate of hydrolysis is unaffected by hydrogen ion, hydroxyl ion, or chloride ion.

The effect of temperature on the rates of the acid hydrolysis of the first three members of the series and of the alkaline hydrolysis of chloroform cannot be represented by an equation having only two constants. The variation of the apparent energy of activation with respect to temperature is discussed in terms of the number of solvating water molecules. The data for the remaining reactions can be summarised in equations containing two constants only.

The positions of relevant equilibria have been computed thermodynamically by using spectroscopic data supplemented by static measurements.

A general mechanism of hydrolysis for all the methyl halides and methylene dichloride is discussed in terms of the solvation numbers of the reactants.

It is suggested that the unusual kinetic behaviour of carbon tetrachloride in water may be due to the absence of a carbon-hydrogen bond and thus of a vibration frequency in the solute molecule lying near to one of the three vibration frequencies in the solvent molecule.

THIS work completes an investigation of the acid and alkaline hydrolysis of the chlorinated methanes. Data on methyl chloride are given by Moelwyn-Hughes,<sup>1</sup> and for methylene dichloride by Fells and Moelwyn-Hughes.<sup>2</sup> The present account concerns the behaviour of chloroform and carbon tetrachloride in water under acid and basic conditions.

### KINETICS OF THE HYDROLYSIS OF CHLOROFORM.

(a) *Hydrolysis of Chloroform in Water.*—The hydrolysis of chloroform in water proceeds extremely slowly even at the b. p. of the solvent. The reaction has been investigated over the temperature range 370—423° K. (In this range the reaction is slow and the solubility low but both are measurable. At higher temperatures the solubility is too low to allow the use of the techniques adopted here.)

*Experimental.* The sealed-ampoule technique previously described was used to follow the reaction over the temperature range indicated.

*Reagents.* Chloroform (Harrington Bros. Ltd.) was treated in the same way as methylene dichloride.<sup>2</sup> On distillation the fraction of b. p. 61.15—61.25° (corr.) was collected (lit.,<sup>3</sup> b. p. 61.20°). Vapour-phase chromatography showed that less than 0.01% of other chlorinated methanes were present.

<sup>1</sup> Moelwyn-Hughes, *Proc. Roy. Soc.*, 1949, *A*, **196**, 540; 1953, *A*, **220**, 386.

<sup>2</sup> Fells and Moelwyn-Hughes, *J.*, 1958, **268**, 1326.

<sup>3</sup> Timmermans, "Physico-Chemical Constants," Elsevier, Amsterdam, 1950.

Conductivity water from an Amberlite resin column was used for making up all solutions for kinetic runs.

*Analysis.* The products of the hydrolysis of chloroform in water are carbon monoxide, formic acid, and hydrochloric acid:



In general, considerably more carbon monoxide is formed than formic acid. Each sample was analysed for chloride ion and for strong and weak acids. Chloride ion and total hydrogen ion were estimated by the techniques described previously.<sup>2</sup> The indicator used in the determination of total hydrogen ion was phenolphthalein. In addition to obtaining the hydrochloric and formic acid concentrations from the difference between the chloride ion and total hydrogen ion, values were also obtained by conductometric analysis, which confirmed the values obtained by the difference method.

*Kinetic analysis and results.* The acid hydrolysis of chloroform follows a first-order law; the constants are calculated from the slopes of the plots of the logarithm of the concentration of chloroform against time, using the equation  $k_1 = (1/t) \log a/(a - x)$ , where  $a$  is the initial concentration of chloroform and  $a - x$  its concentration after time  $t$ . The extent to which the

TABLE 1. *Acid hydrolysis of chloroform at 373.16° K.*

Time (min.)	[Cl <sup>-</sup> ] (mmoles/l.)	[H <sup>+</sup> ] (mmoles/l.)	$x$ mmoles/l.	
			Obs. from Cl <sup>-</sup>	Calc. as $a[1 - \exp(-k_1 t)]$
0	0	0	0	0
22,893	2.70	2.90	0.90	0.90
32,688	4.01	4.34	1.34	1.25
44,173	4.70	5.39	1.57	1.64
55,993	5.92	6.44	1.97	2.05
63,043	6.26	6.66	2.09	2.27
70,215	7.68	8.03	2.56	2.46
80,591	7.82	8.40	2.61	2.80
$\infty$	28.32	—	9.43	9.43

hydrolysis gives carbon monoxide or formic acid as product does not affect this kinetic analysis. The results of a specimen run, for which the quarter life was 69,000 min., are given in Table 1. The values of  $k_1$  found at different temperatures do not conform with the integrated two-constant Arrhenius equation but can be represented by the equation:

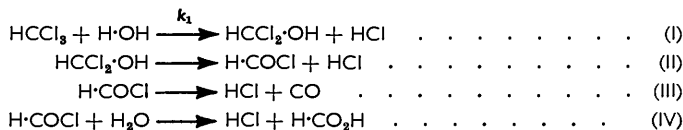
$$\log_{10} k_1 = 149.6905 - 46.28 \log_{10} T - 14,108/T \quad . \quad . \quad . \quad (1)$$

according to which the apparent energy of activation ( $E_A$ ) decreases with increase in temperature. In this respect chloroform quantitatively resembles methylene dichloride and methyl chloride, but the value of  $-\partial E_A/\partial T$  ( $92 \pm 30$  cal./deg.) is greater. A comparison of the observed values of  $k_1$  and those reproduced by equation (1) is given in Table 2. The observed values of  $k_1$  are correct to  $\pm 2\%$ . The fraction of chloroform molecules reacting to give formic acid is 18%.

TABLE 2.

$T$ (K)	373.16°	404.05°	413.01°	422.94°
$10^6 k_1$ (sec. <sup>-1</sup> ), calc.	7.099	139.0	288.2	608.3
$10^6 k_1$ (sec. <sup>-1</sup> ), obs.	7.119	138.8	287.8	609.8

*Discussion.*—It has been quantitatively established that the chemical changes in the hydrolysis of chloroform by water are as given above. Both reactions can proceed by a common rate-determining mechanism which is of first order with respect to the solute, the reactive intermediate formed breaking down rapidly in part to carbon monoxide and in part to formic acid by some such mechanism as the following:



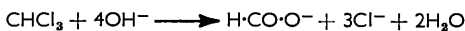
The rate-determining step (I) is slower than that of the corresponding step in the hydrolysis of methylene dichloride. The first-order rate constant is one-ninth of that for methylene dichloride at 373° K. The subsequent steps involving the breakdown of the unstable intermediate  $\text{HCCl}_2\text{-OH}$  into formyl chloride, and the breakdown and hydrolysis of formyl chloride to give carbon monoxide and formic acid, are probably very rapid. Formyl chloride has not been isolated, but a mixture of carbon monoxide and hydrochloric acid in the presence of a catalyst can be made to behave as though formyl chloride were present (Gatterman-Koch synthesis, 1897). Formyl chloride at 100° would certainly be hydrolysed very rapidly.

Since chloroform reacts with water to give two products other than hydrochloric acid, the changes in the standard free energies for the two reactions in aqueous solution have been calculated in the hope of discovering which reaction is thermodynamically more probable. The thermodynamic treatment is described in detail in our previous paper.<sup>2</sup> The standard free energies have been obtained from the National Bureau of Standards publications, and Henry's constants from International Critical Tables.

For the reaction  $\text{CHCl}_3 + 2\text{H}_2\text{O} \longrightarrow \text{H}\cdot\text{CO}_2\text{H} + 3\text{HCl}$  in aqueous solution at 25° with the products and reactants in their standard states,  $\Delta G^\circ(\text{aq.}) = -51,280$  cal. For the reaction  $\text{CHCl}_3 + \text{H}_2\text{O} \longrightarrow \text{CO} + 3\text{HCl}$ ,  $\Delta G^\circ(\text{aq.}) = -47,751$  cal.

These calculations make it clear that, as far as free-energy considerations go, both reactions are equally probable within the limits of accuracy of the data. On the basis of the suggested mechanism, therefore, it appears that formyl chloride is more likely to break down to carbon monoxide than to hydrolyse to formic acid although the free-energy change is the same. This view is strengthened by the observation that formic acid does not break down to carbon monoxide and water in dilute aqueous solution even at high temperatures.<sup>4</sup>

(b) *Reaction between Chloroform and Aqueous Potassium Hydroxide.*—The kinetics of this reaction have been examined. The concurrent reactions:



have been investigated over the temperature range 288—334° K. It is found that reaction between chloroform and the hydroxide ion takes place so rapidly compared with the solvolysis that the reaction with the solvent can be ignored.

*Experimental.* The reactions were carried out in the presence of a small volume of vapour (less than 0.5%) in a Pyrex reaction vessel similar in design to the nickel vessel used for the alkaline hydrolysis of methylene dichloride. Samples were removed through a mercury-sealed, grease-free tap. The apparatus was immersed in a water thermostat accurate to  $\pm 0.01^\circ$  over a period of several days.

*Analysis.* As the alkaline hydrolysis of chloroform proceeds at a measurable rate at room temperature, the reaction cannot be stopped effectively by chilling the sample. Samples removed from the reaction vessel were, therefore, immediately run into excess of nitric acid. Chloride ion, total hydrogen ion, and strong and weak acids were estimated as before.

*Kinetic analysis and results.* The reaction between chloroform and hydroxide ion is of the second kinetic order, but is complicated by an unusual mechanism (to be discussed later) and the fact that there are two products of hydrolysis other than hydrochloric acid, namely, carbon monoxide and potassium formate. The fraction ( $g$ ) of chloroform reacting to give formate is found, from the analytical results, to fall from 0.24 at 288° K to 0.10 at 307° K and then to rise to 0.18 at 334° K. A bimolecular constant involving  $g$  has been calculated. If  $a$  is the initial concentration of chloroform,  $b$  that of hydroxide, and  $a - x$  that of chloroform after time  $t$ , then

$$k_2 = \frac{2.303}{t[a(3+g) - b]} \log_{10} \frac{b(a-x)}{a[b - (3+g)x]}$$

<sup>4</sup> Barnham and Clark, *J. Amer. Chem. Soc.*, 1951, **73**, 4638.

Hine<sup>5</sup> has used a similar expression for a bimolecular constant in his work on the alkaline hydrolysis of haloforms in mixed solvents.

The results of a specimen run are given in Table 3. The calculated values of chloroform concentrations are obtained by substituting  $b$ ,  $g$ ,  $t$ , and the adopted value of  $k_2$  into this rate-constant equation. The bimolecular rate constants governing the reaction of chloroform with

TABLE 3. *Alkaline hydrolysis of chloroform at 307.96° K.* (Concentrations in mmoles/l.):  $10^4 k_2 = 3.082 \pm 0.093$  l. mole<sup>-1</sup> sec.<sup>-1</sup>.

Time (min.)	[KOH]	[Cl <sup>-</sup> ]	[CHCl <sub>3</sub> ], obs.	[CHCl <sub>3</sub> ], calc.	Time (min.)	[KOH]	[Cl <sup>-</sup> ]	[CHCl <sub>3</sub> ], obs.	[CHCl <sub>3</sub> ], calc.
0	68.86	0	18.00	18.00	560	46.96	22.08	10.64	10.73
30	66.71	2.09	17.31	17.31	660	44.46	24.59	9.81	9.91
50	66.22	2.73	17.09	17.00	1019	37.15	31.16	7.61	7.59
140	61.70	7.64	15.45	15.59	2622	24.32	42.78	3.74	3.38
270	55.90	13.08	13.64	13.69	∞	—	54.00	0	0
410	50.67	17.91	12.03	11.99					

the hydroxyl ion cannot be fitted to the integrated form of the Arrhenius equation and are best represented by the three-constant equation:

$$\log_{10} k_2 = 212.80249 - 67.18 \log_{10} T - 15,132/T \quad . \quad . \quad . \quad (2)$$

TABLE 4.

$T$ (K) .....	288.19°	298.06°	307.96°	317.90°	334.41°
$10^5 k_2$ (l. mole <sup>-1</sup> sec. <sup>-1</sup> ), obs. ....	1.140	6.527	30.82	111.2	925.5
$10^5 k_2$ (l. mole <sup>-1</sup> sec. <sup>-1</sup> ), calc. ....	1.133	6.465	30.85	125.5	936.6

The observed values of  $k_2$  are compared with those reproduced by equation (2) in Table 4. The change of the apparent activation energy with temperature is:

$$\partial E_A / \partial T = -133.5 \pm 35 \text{ cal./deg.}$$

The observed values of  $k_2$  are correct to  $\pm 2\%$ . A forced fit to an equation of the Arrhenius type is:

$$\log_{10} k_2 = 16.0141 - 27,582/2.303RT$$

The effect of added salts on  $k_2$  is shown in Table 5. In the absence of hydroxide, chloroform showed no chlorine-iodide exchange with iodide ion after 10,000 min. at 307.96° K.

TABLE 5.

Added salt	Concn. (mmoles/l.)	$10^4 k_2$ at 307.96° K (l. mole <sup>-1</sup> sec. <sup>-1</sup> )
None .....	—	$3.08 \pm 0.09$
KNO <sub>3</sub> .....	100	$3.02 \pm 0.06$
KCl .....	90	$2.66 \pm 0.05$
KI .....	85	$1.99 \pm 0.10$

gradually increasing with time

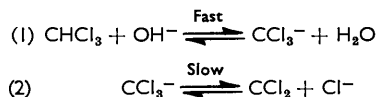
*Discussion.*—The hydrolysis of chloroform in neutral or acidic aqueous solution resembles, in many ways, that of methyl chloride and methylene dichloride, but is about nine times slower than that of the latter and 1800 times slower than that of the former at 373° K. Kinetically the reaction is of the first order with respect to the solute. The energy of activation and the rate of decrease of the energy of activation with respect to the temperature are both higher for chloroform than for methyl chloride and methylene dichloride. The mechanism and general characteristics of the reaction appear to be the same as for the first two members of the series.

It was expected by analogy with the solvent reaction of methyl chloride and methylene dichloride that the second-order constant for the reaction between chloroform and hydroxide ion would be lower than that for methylene dichloride. The experimentally

<sup>5</sup> Hine, *J. Amer. Chem. Soc.*, 1950, **72**, 2438.

determined ratios for  $\text{CH}_3\text{Cl} : \text{CH}_2\text{Cl}_2 : \text{CHCl}_3$  at  $373^\circ \text{K}$  are 830 : 5.5 : 10,000. The three unusual features in the alkaline hydrolysis of chloroform are its unexpectedly high rate, the effect of added salts, and the decrease of the activation energy with increase in temperature.

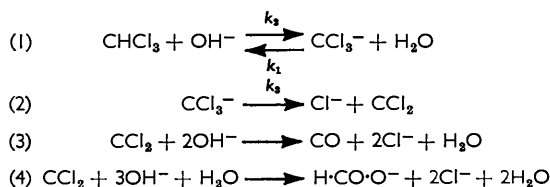
The kinetics of the alkaline hydrolysis of the trihalogenated methanes have been investigated in detail by Hine *et al.*<sup>5-8</sup> whose conclusions are qualitatively confirmed by the present work: their rate constants are about 25% lower than the values obtained in this work. The discrepancy in experimental results may well be due to differences in techniques. The type of reaction vessels used by Hine *et al.* allowed a relatively large vapour phase (3-4% of the liquid phase) and the reactions were carried out in excess of chloroform, so that the reaction stopped as soon as the hydroxide ion had been consumed. They discussed several reaction mechanisms. On the basis of the experimental evidence then available the most likely mechanism appeared to be a rapidly established equilibrium giving  $\text{CCl}_3^-$  ions, followed by a rate-determining unimolecular breakdown of  $\text{CCl}_3^-$ :



The initial equilibrium has been investigated<sup>9,10</sup> and shown, by isotopic analysis, to be reached very rapidly compared with the hydrolysis—an essential factor in the proposed mechanism. The breakdown of  $\text{CCl}_3^-$  to  $\text{CCl}_2$  appears, in the light of available evidence, to be the most probable second step. Carbon dichloride can then react rapidly to give carbon monoxide or formate ion. The specific salt effects obtained by adding chloride ion and iodide ion to the reactants are readily explained in terms of this mechanism. The reversal of stage (2) would result in a slowing down of the reaction, and in the case of iodide ion the formation of some trichloriodomethane would account for the gradual increase of the rate constant with time, for this is hydrolysed more rapidly than chloroform.

Further evidence that carbon dichloride is an active intermediate has been obtained by Hine *et al.*<sup>5-7</sup> who have shown that several reactions of chloroform are strongly base-catalysed. In this work iodide-chlorine exchange into chloroform is shown to be strongly base-catalysed. Woodworth and Skell<sup>11</sup> have added carbon dichloride and carbon dibromide to buta-1 : 3-diene, showing that addition is of a three-centre type thus emphasising the electron-deficient character of the species. Wynberg<sup>12</sup> has also discussed carbon dichloride in the Reimer-Tiemann reaction.

If the mechanism for the alkaline hydrolysis of chloroform is as follows:



where reaction (2) is the rate-determining step, and reactions (3) and (4) are rapid, the rate of production of chloride ion is:

$$d[\text{Cl}^-]/dt = [k_2k_3/(k_1 + k_3)][\text{CHCl}_3][\text{OH}^-]$$

<sup>6</sup> Hine and Dowell, *J. Amer. Chem. Soc.*, 1954, **76**, 2688.

<sup>7</sup> Hine, Dowell, and Singley, *ibid.*, 1956, **78**, 479.

<sup>8</sup> Hine, Burske, Hine, and Langford, *ibid.*, 1957, **79**, 1406.

<sup>9</sup> Horiuti and Tanabe, *Proc. Japan Acad.*, 1951, **27**, 404; 1952, **28**, 127.

<sup>10</sup> Hine and Oaks, *J. Amer. Chem. Soc.*, 1954, **76**, 827.

<sup>11</sup> Woodworth and Skell, *ibid.*, 1957, **79**, 2542.

<sup>12</sup> Wynberg, *ibid.*, 1954, **76**, 4998.

The observed bimolecular constant is thus, not a unitary constant, but a unimolecular constant multiplied by what approximates to an equilibrium constant. This can account for the very high pre-exponential term ( $10^{16}$ ) obtained in the Arrhenius equation. The decrease in the activation energy with increase in temperature, a most unusual feature for a reaction between an ion and a polar molecule,<sup>13</sup> can also be accounted for if the rate-determining step is a unimolecular reaction. The value for  $\delta E_A/\delta T$  obtained in the alkaline hydrolysis of chloroform is higher even than that obtained in the acid hydrolysis ( $-133$  and  $-92$  cal./deg., respectively). This suggests that, in classical terms, the number of simple harmonic oscillators contributing to the decrease in activation energy with temperature of the first-order breakdown of the solvated  $\text{CCl}_3^-$  ion is higher than the number operating in the first-order breakdown of the solvated chloroform molecule. This could be explained in terms of the effect of the charge on solvation, but the increased value of  $\delta E_A/\delta T$  may be complicated by a temperature effect on the equilibrium constant  $K$ .

#### KINETICS OF THE HYDROLYSIS OF CARBON TETRACHLORIDE

(a) *Hydrolysis of Carbon Tetrachloride in Water.*—This hydrolysis has been investigated in the temperature range  $343$ — $373^\circ \text{K}$ , which is determined by the low solubility of carbon tetrachloride at the upper limit and the slowness of its reaction at the lower limit.

*Experimental.* Solutions for kinetic runs were prepared by injecting a measured volume of pure carbon tetrachloride from a 1 ml. glass syringe into a known volume of outgassed conductivity water. The concentration of carbon tetrachloride used was  $\sim 2$  mmoles (max. 2.5). The reactions were carried out in the vapour-free, thermostat-controlled, Pyrex reaction vessel described on p. 400.

*Reagents.* Carbon tetrachloride ("AnalaR," Harrington Bros.) was treated in the same way as methylene dichloride.<sup>2</sup> On distillation the fraction of b. p.  $76.70$ — $76.80^\circ$  (corr.) was collected (lit.,<sup>3</sup> b. p.  $76.75^\circ$ ). Analysis by vapour-phase chromatography showed that less than 0.01% of other chlorinated methanes were present.

All solutions for kinetic runs were made up with conductivity water as above.

*Analysis.* The products of the hydrolysis are carbon dioxide and hydrogen chloride. The suggestion that hypochlorous acid is one of the products has been disproved, since no trace of the acid could be detected. Hydrogen ion and chloride ion were estimated by the methods previously described. Since the solutions used in the investigation were very dilute, uniformly illuminated backgrounds, carefully standardised techniques, and accurately calibrated, grade A, microburettes and pipettes were essential. The initial concentrations of solutions were checked by complete hydrolysis and chloride-ion analysis, using the sealed ampoule technique. The hydrolysing solution used was 4N-KOH in methanol-water (1:9 v/v).<sup>14</sup> The reaction has been established as  $\text{CCl}_4 + 2\text{H}_2\text{O} \rightarrow \text{CO}_2 + 4\text{HCl}$ .

*Kinetic analysis and results.* The hydrolysis of carbon tetrachloride in water does not follow a first-order law. As this result was unexpected, some effort was made to reconcile the results with a first-order law. Careful examination of a series of runs at the same temperature with different concentrations of carbon tetrachloride showed that the reaction was of second order with respect to carbon tetrachloride. The results have therefore been calculated by using the equation  $k_2 = (1/t)x/(a-x)$ , where  $a$  is the concentration of carbon tetrachloride initially and  $a-x$  that after time  $t$ . Values of  $k_2$  are obtained graphically. Since the concentrations of hydrogen ion and chloride ion follow each other precisely within the limits of accuracy of the methods employed, the chloride-ion values are used in calculating  $k_2$  as they are the more accurate. The results for a specimen run are given in Table 6. The ratio  $t_{1/2} : t_{1/4} : t_{3/4}$  was found to be  $1 : \frac{1}{3} : \frac{2}{3}$  in all cases, emphasising the second-order character of the kinetics. Table 7 gives the variation of the half-life with concentration for three runs at  $373.16^\circ \text{K}$ . Again the reaction is shown to be of second order with respect to carbon tetrachloride.

<sup>13</sup> Hurst, Thesis, Cambridge, 1948.

<sup>14</sup> Matchett, *J. Assoc. Off. Agric. Chem.*, 1929, 12, 264.

TABLE 6. *Acid hydrolysis of carbon tetrachloride at 373·16° K.*

$$10^3 k_2 = 1.208 \pm 0.027 \text{ l. mole}^{-1} \text{ sec.}^{-1}.$$

Time (min.)	[Cl <sup>-</sup> ] (mmoles/l.)	$x$ , obs.	$x$ , calc.	Time (min.)	[Cl <sup>-</sup> ] (mmoles/l.)	$x$ , obs.	$x$ , calc.
0	0	0	0	11,447	1.512	0.378	0.377
2,840	0.626	0.156	0.136	13,002	1.667	0.417	0.405
5,788	0.890	0.220	0.240	15,770	1.808	0.452	0.448
8,565	1.342	0.336	0.315	$\infty$	3.612	0.903	0.903

$$t_{1/2} = 15,870 \text{ min.}; t_{1/4} = 5200 \text{ min.}; t_{1/8} = 2150 \text{ min.}; t_{1/2} : t_{1/4} : t_{1/8} = 1 : 1/3 : 1/7.3$$

TABLE 7.

[CCl <sub>4</sub> ] (mmoles/l.)	$t_{1/2}$ (min.)	$10^3 k_2$ (l./mole <sup>-1</sup> sec. <sup>-1</sup> )	[CCl <sub>4</sub> ] (mmoles/l.)	$t_{1/2}$ (min.)	$10^3 k_2$ (l./mole <sup>-1</sup> sec. <sup>-1</sup> )
0.903	15,870	$1.208 \pm 0.027$	2.261	4,850	$1.592 \pm 0.045$
1.465	8,870	$1.258 \pm 0.031$			

The results obtained experimentally conform, within the limits of the experimental accuracy, to the equation:

$$\log_{10} k_2 = 11.0189 - 23,646/2.303RT \quad . \quad . \quad . \quad - \quad (3)$$

The apparent energy of activation is probably correct to  $\pm 1.0$  kcal. The rate constants obtained experimentally show a slight decrease with decrease in initial concentration of carbon tetrachloride. Equation (3) refers to an initial concentration of 2.00 mmoles/l. of carbon tetrachloride. A comparison of the observed values of  $k_2$  and those reproduced by equation (3) is given in Table 8. The observed values of  $k_2$  are correct to  $\pm 5\%$ .

TABLE 8.

$T$ (K)	$10^5 k_2$ , obs. (l./mole <sup>-1</sup> sec. <sup>-1</sup> )	[CCl <sub>4</sub> ] <sub>0</sub> (mmoles/l.)	$10^5 k_2$ corr.	$10^5 k_2$ calc.
343.14°	8.416	2.00	8.416	8.415
353.38	32.83	2.52	30.11	24.90
363.28	55.40	2.07	54.65	62.38
373.16	159.2	2.261	151.8	148.4
373.16	125.8	1.465	151.8	148.4
373.16	120.8	0.903	151.8	148.4

(b) *Kinetics of the Reaction between Carbon Tetrachloride and Dilute Aqueous Potassium Hydroxide.*—The kinetics of the hydrolysis of carbon tetrachloride in alkaline solution have been examined, different concentrations of potassium hydroxide being used, at 363° and 373° K, but, up to 0.08N, it has no effect on the rate of hydrolysis of the carbon tetrachloride, the rate being the same as that in pure water.

*Experimental.* The apparatus and techniques used to follow the reaction were the same as those described in part (a) of this section.

*Analysis.* Chloride ion was estimated by the modified Mohr's method; hydroxide ion was estimated by using standard nitric acid with Bromothymol Blue as indicator and nitrogen bubbling through the solution.

*Kinetic analysis and results.* As potassium hydroxide appears to have no effect on the rate of hydrolysis of carbon tetrachloride in aqueous solution, the kinetic analysis used is the same as that used in the acid hydrolysis of carbon tetrachloride; the bimolecular rate constants so obtained can then be compared with those obtained in pure water. The results of a specimen run are given in Table 9.

Similar runs were carried out at 363° and 373° K in solutions up to 0.08N in potassium hydroxide. The bimolecular rate constants obtained were identical with those obtained for the hydrolysis in pure water. 0.008N-Potassium chloride also had no effect on the rate of hydrolysis of carbon tetrachloride.

TABLE 9. *Alkaline hydrolysis of carbon tetrachloride at 373.16° K. (Concentrations in mmoles/l.)*

$$10^3 k_2 = 1.515 \pm 0.030 \text{ l. mole}^{-1} \text{ sec.}^{-1}.$$

Time (min.)	[Cl <sup>-</sup> ]	[KOH]	$x$ , obs.	$x$ , calc.
0	0	27.06	0	0
213	0.735	26.17	0.184	0.107
1429	2.20	24.90	0.550	0.570
2958	3.84	23.48	0.960	0.942
4278	4.34	22.50	1.085	1.158
5695	5.74	21.45	1.435	1.329
7129	5.82	21.16	1.455	1.461
$\infty$	9.60	—	2.40	2.40

$$t_{1/2} = 4400 \text{ min.}; t_{1/4} = 1500 \text{ min.}; t_{1/8} = 600 \text{ min.}; t_{1/2} : t_{1/4} : t_{1/8} = 1 : 1/2.95 : 1/7.3$$

*Discussion.*—The hydrolysis of carbon tetrachloride in neutral and acidic solutions does not conform to the general pattern displayed by the other members of the chlorinated methane series. The reaction appears to be bimolecular with respect to carbon tetrachloride and the values of  $k_2$  obtained experimentally at different temperatures can be represented by an Arrhenius equation. If the rate of hydrolysis of carbon tetrachloride is compared with that for methylene dichloride on the basis of the half-lives of the reactions, using a concentration of 2 mmoles/l. for carbon tetrachloride, the rate for carbon tetrachloride is four times that for methylene dichloride.

The presence of potassium hydroxide in concentrations up to 0.08N has no detectable effect upon the rate of hydrolysis of carbon tetrachloride, the rate being the same as in pure solvent. If the reaction is carried out in 10% methyl alcohol the rate is increased fourfold. The rate of hydrolysis of carbon tetrachloride in water appears to be unaffected by the presence of potassium chloride in a concentration four times that of carbon tetrachloride.

A survey of the literature reveals conflicting results for the rate and mechanism of the hydrolysis of carbon tetrachloride. The confusion results from the comparison of work using different solvents and the neglect of the reaction between carbon tetrachloride and the solvent.

The following reactions have been reported. Hydrolysis in alcoholic potassium hydroxide gives carbon monoxide, ethyl orthoformate, and, under more dilute conditions, chloroform.<sup>15</sup> In water, carbon dioxide and hydrochloric acid are formed.<sup>16</sup> With excess of carbon tetrachloride it is claimed that carbonyl chloride is formed.<sup>17</sup> Qualitatively inexplicable results have been reported by Hine *et al.*<sup>8</sup> Anomalous isotopic-exchange reactions of carbon tetrachloride have also been reported.<sup>18</sup> It is thus clear that, when carbon tetrachloride is subjected to hydrolysis, the mechanism and products depend on the solvent.

Under the conditions of the present experiments, the products of hydrolysis are carbon dioxide and hydrochloric acid with no trace of hypochlorous acid, formic acid, or carbon monoxide. The reaction in pure water can be represented by the equation  $\text{CCl}_4 + 2\text{H}_2\text{O} \rightarrow \text{CO}_2 + 4\text{HCl}$ , and the rate of the reaction is of the second order with respect to carbon tetrachloride. The reaction is found to go to completion in aqueous solution: the change in standard free energy is  $-90,000$  cal. The reaction may proceed *via* an intermediate  $\text{CCl}_3\text{OH}$  which breaks down rapidly to carbonyl chloride and then to carbon dioxide and hydrochloric acid. Like the reaction intermediates postulated in the acid hydrolysis of the other chlorinated methane,  $\text{CCl}_3\text{OH}$  is probably unstable. Carbonyl chloride is known to react very rapidly with water,<sup>19</sup> the reaction being complete in less

<sup>15</sup> Turner and Harris, "Organic Chemistry," Longmans, Green and Co., London, 1952, p. 162.

<sup>16</sup> Benrath, *Annalen*, 1911, **382**, 223.

<sup>17</sup> Goldschmidt, *Ber.*, 1881, **14**, 928.

<sup>18</sup> Neyman, Miller, and Shapavalov, *J. Phys. Chem. U.S.S.R.*, 1955, **29**, 1042.

<sup>19</sup> Vles, *Rev. Trav. chim.*, 1934, **53**, 962.



than 60 sec. at 0°. Further evidence for the production of carbonyl chloride as an intermediate in this reaction is furnished by Goldschmidt, who obtained it when hydrolysing excess of carbon tetrachloride in water.

The bimolecular nature of the reaction with respect to carbon tetrachloride seems to indicate that the carbon tetrachloride molecule cannot directly interact with, or acquire energy from, water molecules. If the solvent is inert in this respect the bimolecular nature of the reaction can be explained by using Christiansen and Kramer's<sup>20</sup> formulation of the so-called Lindemann<sup>21</sup> effect in gaseous reactions at fairly low pressures. It is only necessary to postulate that a molecule of carbon tetrachloride can only be activated or deactivated by collision with another molecule of its own kind. The concentrations of carbon tetrachloride used in this investigation correspond to pressures in the range 20—50 mm. Hg, which is the range in which first-order characteristics of certain gas reactions give place to those of the second order.

The numerical value of the pre-exponential term in the Arrhenius equation supports inert-solvent interpretation, and is consistent with a simple collision process between solute molecules having an effective collision diameter of 3.72 Å. It is conceivable that the inert behaviour of water molecules towards carbon tetrachloride is connected with the absence of the C-H bond. The first three members of the chlorinated methane series have a common vibration frequency of about 3040 cm.<sup>-1</sup>, which is attributable to C-H bonds. The fundamental vibration frequencies of water are 3652, 1595, and 3756 cm.<sup>-1</sup> and lie sufficiently close to the C-H value to make interaction likely. The carbon tetrachloride molecule has no vibration frequency which can be compared with those of the water molecule. The importance of the C-H group and its position in an ester molecule undergoing hydrogen-ion catalysed hydrolysis has been discussed by Moelwyn-Hughes.<sup>22</sup>

The very different hydrolysis rates found when organic molecules such as methyl alcohol are introduced into the carbon tetrachloride-water system may well be due to the presence of C-H bonds in the mixed solvents. The pollution of aqueous solutions by methanol or ethanol certainly simplifies manipulation by ensuring a much higher solubility, but it does not simplify the chemistry of the reactions.

Carbon tetrachloride, as the last member of the chlorinated methane series, probably reacts by a rate-determining ionic mechanism rather than the "bimolecular" mechanism of the other three members of the series. The absence of any difference in rate of hydrolysis in water or 0.08N-potassium hydroxide shows clearly that the rate-determining step is a breakdown of the carbon tetrachloride molecule followed by reaction with either water or hydroxide ion.

The alternative mechanism leading to products of hydrolysis such as chloroform, carbon monoxide, formate, etc., is presumably the result of performing the reaction in a solvent which is less ionising than water. Under these conditions attack by hydroxide ion on the non-polar, heavily chlorinated carbon tetrachloride molecule could give hypochlorous acid and the CCl<sub>3</sub><sup>-</sup> ion, resulting in a rapid reaction with hydroxide ion giving products similar to those obtained in the alkaline hydrolysis of chloroform.

#### GENERAL DISCUSSION

The experimental study of the hydrolysis and substitution reactions of the halogenomethanes was undertaken in the hope that the effect of substitution on their rates could be interpreted theoretically. There are many theories on the kinetics and mechanisms of such reactions. The theories of organic chemistry, such as those developed by Ingold<sup>23</sup> and his collaborators, interpret the effect of substituting one atom for another in terms of the drift of electrons towards or away from the seat of attack. The theories of physical

<sup>20</sup> Christiansen and Kramer, *Z. phys. Chem.*, 1923, **103**, 91.

<sup>21</sup> Lindemann, *Trans. Faraday Soc.*, 1922, **17**, 599.

<sup>22</sup> Moelwyn-Hughes, "Kinetics of Reactions in Solution," 2nd Ed., Oxford, 1947, p. 336.

<sup>23</sup> Ingold, "Structure and Mechanism in Organic Chemistry," Bell and Sons Ltd., London, 1953.

chemistry include an attempt to interpret rates of reactions in terms of intermolecular forces,<sup>1</sup> particularly those of electrostatic origin, and to evaluate the absolute limiting heat content of reactive solutes.<sup>2</sup> Such theories, though naturally differing in approach and emphasis, are complementary rather than contradictory. Moreover, they have at least one feature in common; while each is capable of providing a logical basis for discussing the effects of substitution in a series of reactions proceeding by a common mechanism, neither is capable of predicting at what stage in any series a postulated mechanism breaks down, to be replaced by one that is quite different. In this respect they resemble the most advanced theories of simple gas reactions. While Heitler and London's theory of the mutual conversion of covalent bonds allows an evaluation of the energy of activation, as Eyring and Polanyi in particular have shown, it can interpret but not predict the fact that hydrogen and iodine react by a molecular mechanism while hydrogen and bromine react by an atomic mechanism. The completely unexpected change of mechanism evinced by the molecules  $\text{CH}_3\text{Cl}$ ,  $\text{CH}_2\text{Cl}_2$ ,  $\text{CHCl}_3$ , and  $\text{CCl}_4$  in simple reactions in solution exposes the inadequacy of all theories hitherto advanced on the kinetics of reactions in solution.

Methyl chloride, the first member of the series, is hydrolysed in pure water at a constant pressure, and in the absence of the vapour phase, by a reaction which is of the first order with respect to the solute, and of a high but undetermined order with respect to the solvent. The energy of activation decreases as the temperature is raised, until it reaches either a limiting or a minimum value. No equation has been found to represent the variation of the velocity constant with respect to temperature. The reaction between methyl chloride and the hydroxyl ion is ostensibly simpler, being of second order, and not unlike substitution reactions of the same class in various solvents. The second member of the series, methylene dichloride, kinetically resembles the first member in many respects. The pseudo-unimolecular constant governing its reaction with the solvent increases with temperature in such a way as to indicate a decrease in the value of the activation energy as the temperature is raised. In alkaline solution, each molecule of methylene dichloride reacts with two hydroxyl ions, yielding formaldehyde, but the reaction is of the second and not the third order. The mechanism of the substitution seems not to have changed, except that the first substitution is followed by a further and relatively rapid one. The numerical value of the second-order constant is only 1/150 of the value for methyl chloride, the reduction in rate being attributable in nearly equal measure to a lowering in the  $A$  term and an increase in the  $E_A$  term of the Arrhenius equation  $k_2 = A \exp(-E_A/RT)$ . There are also subsequent chemical changes, including the Cannizzaro reaction, which can be allowed for or eliminated. As far as its reaction with the pure solvent is concerned, the third member, chloroform, does not differ markedly from the first two members, except that the rate is slower and the energy of activation, as well as its rate of decrease with temperature, is higher. It is in its reaction with the hydroxyl ion that anomalies appear. The second-order velocity constant is found to be 10 times as great as for methyl chloride and nearly 2000 times as great as for methylene dichloride. Moreover,  $\log k_2$  does not vary linearly with respect to  $1/T$  but changes in a manner resembling that in pure hydrolysis. Some of these effects were not unexpected. On electrostatic grounds, one would expect the hydroxyl ion to approach the methyl chloride molecule from the carbon end of the C-Cl bond, and the chloroform molecule from the hydrogen end of the C-H bond. Collateral work by Hine *et al.*<sup>5,6,7,8</sup> suggests that the reaction involves the formation of labile intermediaries, such as the  $\text{CCl}_3^-$  ion and the  $\text{CCl}_2$  radical, for the existence of which there is circumstantial evidence. The widest departure from a consistent behaviour is shown by the fourth member of the series, carbon tetrachloride, the rate of hydrolysis of which (to carbon dioxide and hydrochloric acid) is unaffected by hydroxyl ions, and is, as far as can be judged, a reaction of the second order, *i.e.*, the instantaneous rate of hydrolysis is proportional to the square of the concentration of carbon tetrachloride.

While no known theory can at present accommodate such a diversity of phenomena, the data for methyl chloride and methylene dichloride may profitably be compared with

one another and with those relating to other methyl halides in aqueous solution. It is clear from the data in Tables 10 and 11 that, although the rates of the various hydrolyses and of the substitution of the hydroxyl group into the various molecules differ by factors of several thousands, the constitutive effect on the velocity, whatever may be its origin, is similar in the hydrolytic and the substitutive reactions. Allowing for the extrapolation necessary to compare the first-order coefficients obtained at high temperatures with the second-order coefficients obtained at lower temperatures, we may regard the ratio  $k_2/k_1$  as constant. Its average value from these data is 216, to within  $\pm 27\%$ . A rough value previously accepted<sup>24</sup> was 250. The constancy of this ratio indicates the similarity in the

TABLE 10. *Hydrolysis of halogenomethanes.*

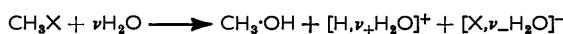
Solute	$k_1$ at 373.16° K (sec. <sup>-1</sup> )	Relative $k_1$	$E_A$ at 373.16° K (kcal./mole)	$k_2/k_1$ (l. mole <sup>-1</sup> )
CH <sub>2</sub> Cl <sub>2</sub> .....	$5.77 \times 10^{-7}$	1	26.5	279
CH <sub>3</sub> F .....	$4.35 \times 10^{-6}$	7.5	22.9	206
CH <sub>2</sub> Cl .....	$1.49 \times 10^{-4}$	260	26.3	162
CH <sub>3</sub> Br .....	$1.71 \times 10^{-3}$	3000	25.3	206
CH <sub>3</sub> I .....	$5.44 \times 10^{-4}$	940	26.3	228
CH <sub>3</sub> NO <sub>2</sub> .....	$2.98 \times 10^{-5}$	52	26.3	—

TABLE 11. *Reactions of halogenomethanes with hydroxyl ion in water.*

Reaction	$k_2$ at 373.16° K (l. mole <sup>-1</sup> sec. <sup>-1</sup> )	Relative $k_2$	$E_A$ at 373.16° K (kcal./mole)	$A \times 10^{10}$ (l. mole <sup>-1</sup> sec. <sup>-1</sup> )
CH <sub>2</sub> Cl <sub>2</sub> + OH <sup>-</sup> .....	$1.61 \times 10^{-4}$	1	26.2	36.9
CH <sub>3</sub> F + OH <sup>-</sup> .....	$8.98 \times 10^{-4}$	5.6	21.6	0.405
CH <sub>2</sub> Cl + OH <sup>-</sup> .....	$2.42 \times 10^{-2}$	150	24.3	411
CH <sub>3</sub> Br + OH <sup>-</sup> .....	$3.52 \times 10^{-1}$	2200	23.0	1040
CH <sub>3</sub> I + OH <sup>-</sup> .....	$1.24 \times 10^{-1}$	770	22.2	124

reactions (1)  $RX + H_2O \rightarrow ROH + HX$  and (2)  $RX + OH^- \rightarrow ROH + X^-$ . It is conceivable that reaction (2), like (1), is in fact a hydrolysis, differing from reaction (1) only in that the water molecule reacting is brought to the sphere of action attached to a hydroxyl ion. Alternatively, reaction (1) may be an ionic substitution, differing from reaction (2) only in that the hydroxyl ion is generated from one of the water molecules surrounding RX.

The chemical change during hydrolysis of the methyl halides may be represented as:



where  $\nu$  stands for the order of reaction with respect to water, and  $\nu_+$  and  $\nu_-$  are the respective co-ordination numbers of the cation and anion formed.

The rate-determining step is thought to be the simultaneous attack of the solute molecule by a number,  $\nu$ , of the solvent molecules which surround it. The evidence for accepting this view is that substituted methyl halides do not react with steam at temperatures where hydrolysis in water is extremely rapid, and that the rate of fall of the activation energy with respect to temperature is greater than can be accounted for unless a number of water molecules participate in the activation.<sup>25</sup> Indirect evidence is the similarity between the values of  $\delta E_A/\delta T$  for the first three members of the series and the values of  $\Delta C_p$  given by Glew and Moelwyn-Hughes<sup>26</sup> for the process of escape of these chloromethane vapours from water. If it is assumed that only two of the three vibration frequencies of water are active in both dissolution and hydrolysis, it appears that most of the water molecules in the solvating shell take part in the hydrolysis.

The rate of hydrolysis may then be written as  $-dn/dt = k_w \cdot n \cdot n_w^\nu$ , where  $n$  is the

<sup>24</sup> Moelwyn-Hughes, *op. cit.*, ref. 22, p. 80.

<sup>25</sup> *Idem*, *Proc. Roy. Soc.*, 1938, *A*, 164, 295.

<sup>26</sup> Glew and Moelwyn-Hughes, *Discuss. Faraday Soc.*, 1953, 15, 150.

concentration of methyl halide and  $n_w$  is that of water;  $\nu$  is the number of water molecules taking part in the activation process.

In the reactions of the methyl halides with the hydroxide ion a similar mechanism may well prevail, the solvating water molecules again playing a significant rôle in the reaction. The rate of reaction would then be

$$-dn/dt = k_2 \cdot n[n_w - \sum n_i \nu_i]^p n_{OH^-} [n_w - \sum n_i \nu_i]^q$$

The term in square brackets denotes the concentration of free water molecules in terms of the total, formal concentration of water,  $n_w$ , and the concentrations of the ions. Effectively the term is  $n_w$  so that:

$$k_1 = k_w n_w^\nu \text{ and } k_2 = k_g n_w^{p+q}$$

where  $p + q$  is the number of water molecules taking part in the reaction between hydroxyl ion and methyl halide. The ratio  $k_1/k_2$  thus depends on  $k_g/k_w$  and on the numbers  $\nu$ ,  $p$ , and  $q$ . As the numbers of oscillators contributing to the activation energy in the systems are not known accurately, a more precise formulation is not possible. The fact that the variation of  $k_2$  with respect to temperature conforms to the simple equation of Arrhenius suggests that the reaction with hydroxide ion is in some way simpler than the solvolysis. It is possible that the hydroxide-ion attack on the halide molecule is brought about by a proton-transfer mechanism through the solvating shells of the reactants, causing ionisation of one of the solvating water molecules adjacent to the halide molecule. Such a mechanism can account for the simplification in the energetics of the system, and is, of course, restricted to reactions between un-ionised solutes and one of the ions into which the solvent can ionise.

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