268. The Kinetics of the Hydrolysis of Methylene Dichloride.

By I. Fells and E. A. Moelwyn-Hughes.

The kinetics of the hydrolysis of methylene dichloride have been investigated at various temperatures in acidic and alkaline aqueous solutions. The changes concerned resolve themselves into (1) a pseudo-unimolecular reaction between methylene dichloride and the solvent, (2) a bimolecular substitution reaction between methylene dichloride and the hydroxyl ion, and (3) an apparent third-order Cannizzaro reaction between formaldehyde and the hydroxide ion. The constants obtained for reactions (1) and (2) have been compared with the corresponding constants for methyl chloride. Those obtained for reaction (3) agree with the results obtained under different conditions by Pajunen.

The effect on the rate of hydrolysis of the C–Cl group produced by successive substitution of chlorine for hydrogen atoms in methyl chloride is unpredictable from current theories of reaction kinetics. Data for methyl chloride over a range of temperature are given by Moelwyn-Hughes,[1] and work at one temperature on the alkaline hydrolysis of chloroform has been carried out by Hine [2] and his co-workers. A semi-quantitative investigation by Petrenko-Kritshenko and Opotsky [3] in 1926 showed that methylene dichloride appeared more resistant to hydrolytic attack than other members of the chlorinated methane series, but accurate data are not available. This work gives an account of an experimental investigation of the behaviour of methylene dichloride when hydrolysed in water under acidic and basic conditions in the temperature range 353—423° K.

The Hydrolysis of Methylene Dichloride in Water.

Experimental.—A solution of pure methylene dichloride (less than 0·01% of other chlorinated methanes were present according to our analysis by vapour-phase chromatography) in conductivity water was prepared, the water having previously been freed from dissolved gases as well as electrolytes. The concentration of methylene dichloride was considerably less than the saturated value at the temperature and pressure of the kinetic run. A sample was first taken for complete hydrolysis. A series of carefully annealed Pyrex ampoules were then filled and sealed off immediately, and a final sample taken for complete hydrolysis as a check on any possible loss of vapour during filling operations. The Pyrex ampoules were placed in concentric brass safety cylinders and kept at the temperature of the run in an oil thermostat. The ampoules were removed at intervals from the thermostat and immediately chilled in iced water, and their contents analysed for products.

Thermostat. This was a well-lagged, five-gallon, cylindrical metal tank filled with Shell Tellus 74 Oil. The tank was heated by two electrical heaters, one being switched in and out by an ethylene glycol–mercury filled spiral thermoregulator activating (through a spark-eliminating device) a Sunvic relay. The temperature control was accurate to ±0·05° over a period of 10 days.

Purity of reagents. (*a*) Methylene dichloride (Harrington Bros. Ltd.) was purified by shaking it with concentrated sulphuric acid, aqueous sodium hydrogen carbonate, and distilled water, dried (P_2O_5) for 72 hr., and twice distilled in a three-foot fractionating column packed with glass helices. The fraction of b. p. 39·85—39·95° (corr.) was collected (lit.,[4] b. p. 39·89°).

(*b*) Distilled water which had been passed through an Amberlite resin ion-exchange column was used for making up all solutions for kinetic runs.

Analysis. Each sample was analysed for chloride ion, hydrogen ion, and formaldehyde.

(*a*) Hydrogen ion. Hydrogen ion was estimated by using standard sodium hydroxide with bromothymol-blue as indicator, nitrogen being bubbled through the solution for 10 min. before the final adjustment to remove all traces of carbon dioxide.

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[1] Moelwyn-Hughes, *Proc. Roy. Soc.*, 1949, *A*, **196**, 540; 1953, *A*, **220**, 386.
[2] Hine *et al.*, *J. Amer. Chem. Soc.*, 1950, **72**, 2438; 1954, **76**, 827, 2688.
[3] Petrenko-Kritshenko and Opotsky, *Ber.*, 1926, **59**, 2131.
[4] Missen, Thesis, Cambridge.

(*b*) Chloride ion. Chloride ion was estimated by a modification of Mohr's method. Solutions were neutralised with calcium carbonate, titrated to the red-brown silver chromate end-point, and then back-titrated to a lime-green colour by standard potassium chloride solution. Each end-point was repeated five times.

(*c*) Formaldehyde. The conventional sodium sulphite method of estimating formaldehyde is not suitable for the very dilute solutions (about 4 mmoles per l.) involved in this reaction, so a colorimetric method was adopted. Formaldehyde develops a violet colour when heated with chromotropic acid in the presence of concentrated sulphuric acid. A standard technique [5] was employed. Calibration curves based on standard formaldehyde solutions were prepared, and the optical density of the " unknown " solution compared with them. A Unicam quartz spectrophotometer operating with light of 570 mμ wavelength was used to measure optical density.

A polarographic method, due to Boyd and Bambach,[6] was also used to determine the concentration of formaldehyde. A Cambridge Instrument Company recording polarograph with a thermostat added was used to obtain the polarograms of carefully standardised samples. A carrier of potassium hydroxide and potassium chloride was used, the polarograms were recorded photographically, and the concentration of formaldehyde deduced by comparing wave heights with those obtained by using standard samples. By this method the concentrations of formaldehyde (in moles/l.) was found to be one half of that of hydrochloric acid up to the half-life of the reaction. When the reaction had proceeded further this method proved unreliable without a more accurate stabilisation of pH, but by the colorimetric method this ratio was obtained at all stages of the reaction.

The net chemical change taking place during the acid hydrolysis of methylene dichloride is its quantitative conversion into formaldehyde:

$$CH_2Cl_2 + H_2O \xrightarrow{k_1} CH_2O + 2HCl$$

Kinetic Analysis.—The hydrolysis of methylene dichloride in acidic solution follows a simple, first-order law. The hydrogen ion, chloride ion, and formaldehyde concentrations keep abreast with one another precisely. The only deviation is a slight falling off in the velocity constant after the three-quarter life period.

The first-order constant k_1 is calculated from the slopes of plots of the logarithm of the concentration of methylene dichloride against time by using the equation $k_1 = (1/t) \ln a/(a - x)$, where a is the initial concentration of methylene dichloride and $a - x$ its concentration at time t. The results of a specimen run are given in Table 1. Since the concentrations of hydrogen ion, chloride ion, and formaldehyde agree with one another precisely within the limits of accuracy of the methods employed, the chloride-ion values are chiefly used in calculating k_1 as they are the most accurate.

TABLE 1. *Acid hydrolysis of methylene dichloride at* 373·16° K.

$10^7 \times k_1 = 5·77 \pm 0·05$ sec.$^{-1}$

	x (mmoles/l.)				x (mmoles/l.)		
Time (min.)	Obs. from Cl^- estn.	Obs. from H·CHO estn.	Calc. as $a[1 - \exp(k_1t)]$	Time (min.)	Obs. from Cl^- estn.	Obs. from H·CHO estn.	Calc. as $a[1 - \exp(k_1t)]$
0	0	0	0	22,589	14·56	14·4	14·99
3,872	3·59	3·3	3·46	28,349	16·63	16·2	17·28
8,192	6·72	7·0	7·10	70,286	24·09	—	25·18
12,509	9·62	9·6	9·72	∞	27·63	—	27·63
18,269	12·96	12·5	12·95				

Measured half-life period = 19,800 min.

The values of k_1 found at different temperatures do not conform with the integrated form of the Arrhenius equation but can be represented by the equation

$$\log_{10} k_1 = 98·4408 - 29·66 \log_{10} T - 10,597·3/T \quad . \quad . \quad . \quad . \quad . \quad (1)$$

Values for E_A (the Arrhenius activation energy) are 25,590 ± 350 cal. at 388° K and 24,080 ± 350 cal. at 414° K. The change of E_A with temperature is given by $dE_A/dT = -59 \pm 26$ cal./deg.

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[5] Bricker and Johnson, *Ind. Eng. Chem. Anal.*, 1945, **17**, 400—402.

[6] Boyd and Bambach, *ibid.*, 1943, **15**, 314—315.

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 ±1%. A four-fold change in the initial concentration of methylene dichloride does not change the value of k_1 by more than 2%: at 373·16° K, $k_1 = 5{\cdot}77$ sec.$^{-1}$ for $a = 27{\cdot}63$ mmole/l. and $k_1 = 5{\cdot}93$ sec.$^{-1}$ for $a = 105{\cdot}25$ mmole/l. Thus the change of k_1 with change in initial concentration of methylene dichloride is small.

TABLE 2.

T (°K)	373·16	392·96	403·31	415·20	424·41
10^7k_1 (sec.$^{-1}$), calc.	5·75	33·4	77·4	184	339
10^7k_1 (sec.$^{-1}$), obs.	5·76	30·3	77·3	187	339

Discussion.—The net reaction is quantitatively established as being that given on p. 1327. It is possible, or even probable, that the reaction takes place in two stages of which the first is

$$CH_2Cl_2 + HOH \longrightarrow CH_2Cl{\cdot}OH + HCl \quad . \quad . \quad . \quad . \quad . \quad . \quad (I)$$

followed by one of the two conceivable subsequent reactions

$$CH_2Cl{\cdot}OH \longrightarrow CH_2O + HCl \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (IIa)$$

or

$$CH_2Cl{\cdot}OH + HOH \longrightarrow CH_2(OH)_2 + HCl \longrightarrow CH_2O + H_2O + HCl \quad . \quad (IIb)$$

In these equations formaldehyde in aqueous solution has been given the formula CH_2O although some, or most of it, is probably[6a] present as methylene glycol $CH_2(OH)_2$. Reaction (II*a*) is more likely to occur than (II*b*). The second reaction must be rapid compared with the first, which consequently determines the net rate. If the reaction intermediate postulated were present in analytically detectable amounts its effect would be detected in the kinetic measurements, and in the earlier stages of the reaction more hydrochloric acid would be formed than formaldehyde. Experimentally it is found that hydrochloric acid and formaldehyde are produced in equivalent concentrations from the beginning of the reaction. The polarographic analysis is the significant result here, as the colorimetric analysis involves treatment of the sample with concentrated sulphuric acid at 100°, which would certainly convert any unstable intermediate into formaldehyde. The simple first-order nature of the kinetic runs proves that the reaction intermediate postulated is always present in subanalytical concentrations.

The only deviation from straightforward first-order behaviour shown by the experimental results is a slight falling off in reaction rate after the three-quarter life period. Litterscheid and Thimme[7] have studied the action of excess of hydrogen chloride on formaldehyde in the presence of cold concentrated sulphuric acid, finding that dichlorodimethyl ether is formed in 85% yield. The reaction mechanism suggested by them involves the same reaction intermediate as is postulated in the hydrolysis mechanism. When the reaction mixture is warmed, however, some methylene dichloride is formed, according to Schneider.[8]

In order to test this idea of a reversibility of reaction, equilibrium constants have been calculated, first for the system

$$CH_2Cl_2 + H_2O \rightleftharpoons CH_2O + 2HCl$$

in the ideal vapour phase at 25° C and secondly in aqueous solution at the same temperature by allowing for the free-energy changes attending the dissolution of each component.

Thermodynamic Calculations.—(a) *Equilibrium in the vapour phase.* From the heats of formation, which are −21,700 cal. (CH_2Cl_2), −57,800 cal. (H_2O), −28,700 cal. (H·CHO),

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[6a] See Walker, " Formaldehyde," Rheinhold, New York, 1953.

[7] Litterscheid and Thimme, *Annalen*, 1904, **334**, 1.

[8] Schneider, *Angew. Chem.*, 1938, **51**, 274.

and −22,060 cal. (HCl), the gain in heat content obtained in the vapour-phase hydrolysis is $\Delta H^\circ = 6680$ cal. The molar entropies in the standard states are 64·65 (CH_2Cl_2), 45·106 (H_2O), 52·23 (H·CHO), and 44·62 cal. (HCl). ΔS° is therefore 31·71 cal. Thus $\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ = -2775$ cal. Then, substituting in $\Delta G^\circ = -\boldsymbol{R}T \ln K_p$, we find that $K_p = 108$. In the equilibrium

$$\begin{array}{ccccc} CH_2Cl_2 & + \; H_2O & \rightleftharpoons & CH_2O & + \; 2HCl \\ (a - x) & (a - x) & & x & 2x \end{array}$$

the concentrations given are equilibrium concentrations, so that $2x^2/(a - x)^2 = 108$, and, therefore $x/a = 0{\cdot}87$. This is approximately the yield reported by Michael[9] for the vapour-phase hydrolysis of methylene dichloride by steam over a catalyst at 285° C. He reports yields of 85—90%. Raising the temperature does not seem seriously to affect the equilibrium position.

(b) *Equilibrium in aqueous solution.* For the equilibrium in solution the free-energy change on dissolving each component in water must be added to the free-energy terms already calculated in the gas phase; *i.e.*,

$$\Delta G^\circ(\text{aq}) = \Delta G^\circ(\text{g}) + \sum \Delta G^\circ(\text{diss.})$$

$$\sum \Delta G^\circ(\text{diss.}) = 2\Delta G^\circ(\text{diss.})\ \text{HCl} + \Delta G^\circ(\text{diss.})\ \text{H·CHO}\Delta G^\circ(\text{diss.})\ CH_2Cl_2 - \Delta G^\circ(\text{diss.})\ H_2O$$

Now $\Delta G^\circ(\text{aq}) = \Delta G^\circ(\text{g}) + \sum \boldsymbol{R}T \ln r_i$, where r = Henry's constant, except in the case of water, for which $\Delta G^\circ(\text{diss.}) = \boldsymbol{R}T \ln (p^\circ/760)$, where p° = vapour pressure of water (in mm. Hg) at temperature T. Hence, we have

	ΔG°(diss.) (cal./mole)		ΔG°(diss.) (cal./mole)
CH_2Cl_2	570	CH_2O	−5000
H_2O	−2194	HCl	−8890

$\sum \Delta G^\circ(\text{diss.}) = -21{,}156$; $\Delta G^\circ\ (\text{aq.}) = -2{,}775 - 21{,}156 = -23{,}931$ cal.; $K = 3{\cdot}63 \times 10^{17}$.

Data for these calculations have been obtained from a variety of sources. Heats of formation are from Bichowski and Rossini.[10] Absolute entropies for water and hydrogen chloride were obtained from the National Bureau of Standards[11] publications. The values for formaldehyde and methylene dichloride have been calculated by evaluating the molecular partition function (f), using Herzberg's data,[12] and substituting in the relation $S = N_0k[\ln f + T(\text{d} \ln f/\text{d}T)_v]$.

The free-energy change on dissolution for formaldehyde was obtained from Parkes and Huffman,[13] for hydrogen chloride from Ellis's vapour-pressure data,[14] for water by using tabulated vapour pressures given by Kaye and Laby,[15] and for methylene dichloride the solubility–vapour pressure data were obtained experimentally.

The reaction clearly goes effectively to completion in aqueous solution, and the falling off in the velocity constant cannot therefore be accounted for by supposing the products are recombining to form the reactants.

Another suggestion is the effect of increasing ionic strength on the reaction intermediate as the reaction proceeds, since the rearrangement of charge distribution in the transition complex may be considerably affected by the increased concentration of ions in its vicinity.

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[9] Michael, G.P. 382,391; *Chem. Zentr.*, 1924, I, 1710.

[10] Bichowski and Rossini, " Thermochemistry of Chemical Substances," Rheinhold, New York, 1936.

[11] National Bureau of Standards, Series III, Vol. 1.

[12] Herzberg, " Infra-Red and Raman Spectra," D. Van Nostrand Co. Inc., New York, 1945.

[13] Parkes and Huffman, " Free Energies of Some Organic Compounds," Reinhold, New York, 1932.

[14] Ellis, *J. Amer. Chem. Soc.*, 1916, **38**, 737.

[15] Kaye and Laby, " Physical and Chemical Constants," Longmans, Green, London, 1948.

Hydrolysis of Methylene Dichloride in Aqueous Potassium Hydroxide

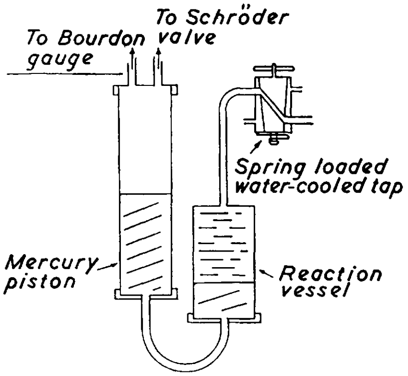
The kinetics of the hydrolysis of methylene dichloride in alkaline solution has been examined by using potassium hydroxide as hydrolysing agent. The concurrent reactions

$$CH_2Cl_2 + HOH \xrightarrow{k_1} CH_2O + 2HCl \text{ and } CH_2Cl_2 + 2OH^- \xrightarrow{k_2} CH_2O + 2Cl^-$$

have been investigated over the temperature range 350—404° K.

Experimental.—The reactions were carried out in the absence of the vapour phase in a nickel reaction vessel of 300 ml. capacity, closed by a mercury piston which could be pumped to 4 atm. pressure. Samples were removed through a heavy, steel, water-cooled, spring-loaded tap. The reaction vessel was completely immersed in the oil thermostat previously described. A diagram of the apparatus is shown in Fig. 1.

FIG. 1.



Analysis. (a) Hydroxide ion. This was estimated by using standard nitric acid with bromothymol-blue as indicator, nitrogen being bubbled through the solution for 10 min. as before.

(b) Chloride ion. This was estimated as before.

(c) Formaldehyde. This was estimated polarographically. Since the reaction proceeds in a solution of potassium hydroxide and potassium chloride, comparisons with polarograms of standard solutions of formaldehyde are easily made, as the carrying solution consists of potassium hydroxide and potassium chloride. The wave height varies with KOH : KCl ratio; standard solutions having carrying solutions of different KOH : KCl ratios were therefore prepared, and the requisite standard for comparison selected. Unchanged methylene dichloride does not intefere in the estimation as the half wave for formaldehyde occurs at $-1{\cdot}63$ v (S.C.E.) and for methylene dichloride at $-2{\cdot}33$ v.

Kinetic Analysis and Results.—Reaction between between methylene dichloride and potassium hydroxide in aqueous solution is not a simple second-order reaction. Reaction with the solvent occurs, and in addition the formaldehyde formed reacts with the potassium hydroxide, giving methyl alcohol and formic acid (Cannizzaro's reaction, 3 below). The methyl alcohol can in turn react with the formaldehyde to give methylal. Under the alkaline conditions prevailing it is also possible for the formaldehyde formed to polymerise to sugars:

$$\begin{array}{ll} (1) & CH_2Cl_2 + HOH \xrightarrow{k_1} CH_2O + 2H^+ + 2Cl^- \\ (2) & CH_2Cl_2 + 2OH^- \xrightarrow{k_2} CH_2O + 2Cl^- + H_2O \\ (3) & 2CH_2O + OH^- \longrightarrow H{\cdot}CO_2^- + CH_3{\cdot}OH \\ (4) & 2CH_3{\cdot}OH + CH_2O \longrightarrow CH_2(OCH_3)_2 + H_2O \\ (5) & nCH_2O \longrightarrow (CH_2O)_n \end{array}$$

Under the conditions of our experiments, reactions (4) and (5) do not occur.

The bimolecular velocity constants for the reaction between methylene dichloride and hydroxide ion have been found by using the equation

$$-\mathrm{d}[\mathrm{CH_2Cl_2}]_t/\mathrm{d}t = k_1[\mathrm{CH_2Cl_2}]_t + k_2[\mathrm{CH_2Cl_2}]_t[\mathrm{OH^-}]_t$$

The values of $-\mathrm{d}[\mathrm{CH_2Cl_2}]_t/\mathrm{d}t$ are obtained by drawing tangents to the progress curve at equally spaced intervals from zero time to the three-quarter life period. The values accepted as the most reliable are those obtained when the reaction is between 25% and 70% complete. When it is less than 10% complete bimolecular constants can be obtained by using the integrated equation

$$t = \frac{1}{k_1 + k_2(b - 2a)}\left\{\ln \frac{a}{(a - x)} \frac{[k_1 + k_2(b - 2x)]}{(k_1 + k_2b)}\right\}$$

where $a = [\mathrm{CH_2Cl_2}]_0$, $b = [\mathrm{OH^-}]_0$, and $(a - x) = [\mathrm{CH_2Cl_2}]_t$. This equation ignores the Cannizzaro reaction, which does not proceed to any appreciable extent at the beginning of the reaction.

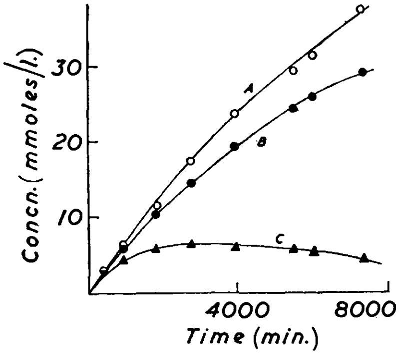


FIG. 2. *A, rate of removal of* $\mathrm{OH^-}$; *B, rate of formation of* $\mathrm{Cl^-}$; *C, rate of formation of* H·CHO.

$[\mathrm{CH_2Cl_2}]_0 = 25{\cdot}15$ mmoles/l., $[\mathrm{KOH}]_0 = 109{\cdot}0$ mmoles/l., $T = 352{\cdot}96°$ K, $10^5k_2 = 2{\cdot}07$ l./mole^{-1} sec.$^{-1}$, $k_3 = 0{\cdot}0146$ l.^{2} mole^{-2} sec.$^{-1}$.

A set of data from a typical kinetic run is shown in Fig. 2; the rise and fall of the formaldehyde concentration and the divergence of the hydroxide-ion and chloride-ion progress curves are clearly shown. The values for k_2 are obtained by drawing tangents to the progress curve; k_1 values are obtained from equation (1).

Analysis of all the results obtained in this way shows that the reaction between methylene dichloride and hydroxide ion is definitely of the second order although stoicheiometrically one molecule of methylene dichloride reacts with two molecules of hydroxide ion.

TABLE 3.

T (°K)	352·96	376·18	385·42	395·22	404·26
10^5k_2 (l. moles^{-1} sec.$^{-1}$), calc.	2·03	21·7	50·3	117	249
10^5k_2 (l. moles^{-1} sec.$^{-1}$), obs.	2·09	22·0	48·6	114	244

The values obtained for k_2 conform to the Arrhenius equation $\log_{10} k_2 = 11{\cdot}5669 - 5730{\cdot}2/T$, with $E_{\mathrm{A}} = 26{,}221 \pm 450$ cal. Table 3 shows the calculated and observed values of k_2. The observed values of k_2 have been corrected for the expansion of the solvent and resultant concentration change over the temperature range used, and are correct to ±4%. An increase in hydroxide-ion concentration of 100% raises the value of k_2 by less than 1%. The concentration of hydroxide ion used is just sufficient to react with all the methylene dichloride present.

The Cannizzaro Reaction between Formaldehyde and Potassium Hydroxide as a Consecutive Reaction in the Alkaline Hydrolysis of Methylene Dichloride.—The reaction between formaldehyde and hydroxide ion has been investigated by a variety of workers. Pajunen [16] gives third-order constants which, over a range of temperature, conform to the Arrhenius equation. More recent papers by Abel [17] and Martin [18] show that the reaction is not of third order but consists of two reactions, one of the third and one of the fourth order, proceeding simultaneously. Consistent

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[16] Pajunen, *Suomen Kem.*, 1948, **21**, *B*, 21—24; *Ann. Acad. Sci. Fenn.*, Ser. *A*, II, Chemica, 1950, **37**, 7—60.

[17] Abel, *Z. phys. Chem.* (*Frankfurt*), 1954, **1**, 201.

[18] Martin, *Australian J. Chem.*, 1954, **7**, 335—347.

third-order constants can be obtained during any one run, but variation of the initial formaldehyde and hydroxide-ion concentrations results in a variation of the constant. All previous work has been carried out in the temperature range 40—60° with relatively concentrated solutions (0·1M-formaldehyde and 0·05M-potassium hydroxide). Above 70°, aldol condensation to sugars is said to take place. Loew [19] has obtained hexose sugars in 75% yield, and Katzschmann [20] has suggested an autocatalytic mechanism for sugar formation involving bishydroxymethylacetol as catalyst. This he isolated and identified.

In this work the concentration of potassium hydroxide is approximately the same as that used by Pajunen.[16] The formaldehyde concentration, however, never rises above 5 mmoles/l. and is generally less. The reaction has been followed from 80° to 120°; in this range and under the conditions specified, the formaldehyde is removed almost as quickly as it is formed. Third-order constants in good agreement with values obtained by extrapolating Pajunen's values [16] have been obtained.

The third-order constants have been obtained in two ways. In those reactions in which a maximum appears in the formaldehyde progress curve the rates of its appearance and disappearance have been equated. Thus

$$k_3 = \frac{k_1[\mathrm{CH_2Cl_2}]_t + k_2[\mathrm{CH_2Cl_2}]_t[\mathrm{OH^-}]_t}{[\mathrm{H{\cdot}CHO}]_t^2[\mathrm{OH^-}]_t}$$

For reactions in which no maximum appears, tangents have been drawn to the hydroxide-ion progress curve and the k_3 values obtained from the following differential equation

$$k_3 = \frac{1}{[\mathrm{H{\cdot}CHO}]_t^2[\mathrm{OH^-}]_t}\left\{-\frac{\mathrm{d}[\mathrm{OH^-}]_t}{\mathrm{d}t} - 2[\mathrm{CH_2Cl_2}]_t(k_2[\mathrm{OH^-}]_t + k_1)\right\}$$

The series of k_3 values obtained conform to the Arrhenius equation

$$\log_{10} k_3 = 11{\cdot}7669 - 4{,}819{\cdot}8/T \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad \text{(III)}$$

This is in remarkably close agreement with the equation given by Pajunen based on work done in the temperature range 40—70°, *viz.*,

$$\log_{10} k_3 = 11{\cdot}9042 - 4{,}877{\cdot}5/T \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad \text{(IV)}$$

Table 4 shows the observed and calculated values of k_3 obtained in this work and those obtained by Pajunen; k_3 values from equations (III) and (IV) are quoted over the total temperature range. The accuracy of the experimental values of k_3 obtained by the two methods described is ±10%. As the concentration of formaldehyde is never greater than 5 mmoles/l. the accuracy of the rate constants is limited by the accuracy with which dilute formaldehyde solutions can be analysed.

TABLE 4.

Temp. (°K)	k_3 (l.^{2} mole^{-2} sec.$^{-1}$) This work Obs.	This work Calc.	Pajunen's work Calc.	Pajunen's work Obs.
313·16	—	0·000243	0·000209	0·000212
323·16	—	0·000727	0·000636	0·000624
333·16	—	0·00203	0·00180	0·00175
343·16	—	0·00537	0·00422	0·00491
353·04	0·0136	0·0133	0·0123	—
363·55	0·0316	0·0329	0·0308	—
376·16	0·087	0·0916	0·0867	—
385·42	0·206	0·186	0·178	—
395·22	0·366	0·379	0·366	—

[H·CHO] varies from 0 to 5 mmoles/l.; [KOH] varies from 30 to 80 mmoles/l.

Both Abel [17] and Martin [18] have suggested mechanisms for the Cannizzaro reaction involving ionisation of a formaldehyde molecule to $\mathrm{CH_2(OH){\cdot}O^-}$ and $\mathrm{CH_2O_2^{2-}}$ ions. A rigorous examination of a series of runs at one temperature with different formaldehyde and hydroxyl-ion concentrations shows both third- and fourth-order kinetics. Martin has suggested that third-order constants together with reactant concentrations be quoted, and this suggestion has been followed here. Rate constants based on a simple third-order mechanism are pH dependent. The hydroxide-ion concentrations used in this work are the same as those used by Pajunen [16] and it is for this reason that a comparison of the results is possible.

These results show that under conditions of constant pH and in a system in which the

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[19] Loew, *Ber.*, 1887, **20**, 144.

[20] Katzschmann, *Ber.*, 1944, **77**, 579—585.

formaldehyde concentration is low during the entire course of the run the Cannizzaro reaction occurs up to 120°, with negligible condensation of the formaldehyde to sugars. At 130° the kinetic runs indicate that some sugar formation occurs although the Cannizzaro reaction still proceeds.

DISCUSSION

The hydrolysis of methylene dichloride in neutral or acidic aqueous solution closely resembles that of methyl chloride but is about 200 times slower. Kinetically, the reaction is of the pseudo-first order, the rate at any instant being proportional to the concentration of solute. The rate-determining step may be simply

$$CH_2Cl_2 + nH_2O \longrightarrow CH_2O + 2[H,mH_2O]^+ + 2[Cl,\{\tfrac{1}{2}(n-1) - m\}H_2O]^-$$

where m and n are solvation numbers, or it may be

$$CH_2Cl_2 + nH_2O \longrightarrow CH_2Cl(OH) + [H,mH_2O]^+ + [Cl,(n-1-m)H_2O]^-$$

followed by a relatively rapid second reaction. The apparent energies of activation for the hydrolyses of methyl chloride and methylene dichloride are equal, within the accuracy of the work, being, *e.g.*, 25,200 and 25,600 cal. at the b. p. of the solvent. The temperature variations of the apparent energies of activation are also approximately the same.

In alkaline solution, the pseudo-first-order reaction with the solvent takes place simultaneously with several other reactions, of which the first to be considered is the bimolecular substitution reaction $CH_2Cl_2 + 2OH^- \longrightarrow CH_2O + 2Cl^-$, which is found to be of the first kinetic order with respect to each reactant and therefore to be a reaction of the second order. As in the hydrolytic change, the second substitution must be relatively rapid and may, in fact, be an elimination rather than a substitution. As is usual with bimolecular reactions between ions and polar molecules, no variation of the apparent energy of activation of this reaction with respect to temperature could be detected. The bimolecular velocity constant at 373·16° K is lower than that for the reaction between methyl chloride and the hydroxide ion by a factor of 154, and the energy of activation is higher by 1940 cal. Thus the relative slowness is due only in part to an increase in the activation energy. It is noteworthy that the effect of substituting a chlorine atom for one of the hydrogen atoms in methyl chloride should reduce the rate more effectively than does the substitution of a charged carboxyl group, as shown here:

Reaction	k_2 at 373·16° K (l. mole^{-1} sec.$^{-1}$)	A (l. mole^{-1} sec.$^{-1}$)	E_A (cal./mole)
$CH_3Cl + OH^-$	$2{\cdot}48 \times 10^{-2}$	$4{\cdot}11 \times 10^{12}$	24,280
$CH_2Cl_2 + OH^-$	$1{\cdot}61 \times 10^{-4}$	$3{\cdot}69 \times 10^{11}$	26,220
$CH_2Cl{\cdot}CO{\cdot}O^- + OH^-$	$3{\cdot}22 \times 10^{-4}$	$4{\cdot}55 \times 10^{11}$	25,850

Finally, the instantaneous rate of production of formate ions and methanol according to the Cannizzaro reaction

$$2CH_2O + OH^- \longrightarrow H{\cdot}CO{\cdot}O^- + CH_3{\cdot}OH$$

is found to be proportional to the concentration of hydroxyl ion and to the square of the concentration of formaldehyde under the conditions of the experiments. The reaction is therefore effectively a reaction of the third kinetic order. The magnitude of the pre-exponential term in the Arrhenius equation, however, is somewhat greater than that expected from the frequency of ternary collisions, but is not inconsistant with the mechanism suggested by Abel,[17] according to which the rate-determining step is that between molecules of formaldehyde and the charged complexes $[HO{\cdot}CH_2{\cdot}O]^-$ and $[CH_2O_2]^{--}$, the equilibrium concentrations of which are proportional to $[H{\cdot}CHO][OH^-]$ and $[H{\cdot}CHO][OH^-]^2$, respectively.

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DEPARTMENT OF PHYSICAL CHEMISTRY,
FREE SCHOOL LANE, CAMBRIDGE.

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