528. *The Kinetics of the Reaction between Methyl Chloride and Lithium Iodide in Acetone.*

By Farhat-Aziz and E. A. Moelwyn-Hughes.

The rate of chemical reaction between methyl chloride and the iodide ion in acetone has been measured at various temperatures and concentrations in a newly designed reaction vessel which allows the system to be studied in the absence of the vapour. The rate of the reverse reaction is greater than that of the direct reaction by a factor of about 4000, and greater than that found by other workers by a factor of more than 1000.

ACCURATE information has long been available on the kinetics of chemical reactions between polar molecules and ions in solution. New data, of unascertainable accuracy, continue to appear. Many of the reactions studied are of the type $RX + Y^- \longrightarrow RY + X^-$, where R is an alkyl radical, X a halogen atom, and Y^- an anion. They are bimolecular. From the second-order velocity coefficients and the derivatives obtained therefrom, when R is variable while X and Y are constant, several organic theories of chemical " reactivity " have been built. When these reactions take place in water, RX reacts with it, giving an alcohol. When they take place in an alcohol, RX reacts with it to give an ether. Such side reactions with the solvent can be evaded, as Conant and Kirner[1] realised, by using acetone as solvent. If, however, R is any alkyl radical other than methyl, RX in any medium breaks down into HX and an olefin, as Brusoff[2] observed. To avoid both solvolysis and the formation of olefins, one must therefore work with methyl derivatives in a non-hydroxylic medium like acetone.

For these reasons, an attempt was made[3] to study the kinetics of the reaction between methyl bromide and the iodide ion in acetone ($CH_3Br + I^- \longrightarrow CH_3I + Br^-$). According to current standards, the technique then adopted was crude, but it sufficed to show that the reaction proceeds bimolecularly to an equilibrium at a rate which is about 1000 times faster than in water. The velocity constant decreased as the initial concentration of salt was increased. The gradient of the plot of the logarithm of the velocity constant against ionic strength was shown to be greater than could be accounted for by simple electrostatic theory, and the effect was thought to be due to incomplete ionisation or dissociation of the potassium salts in acetone, but quantitative allowance was not then attempted. The standard kinetic law for opposing second-order reactions was adapted to the case where one of the products was only slightly soluble and its concentration was taken as constant, which cannot be strictly true. In the present extension of this work to the system $CH_3Cl + I^- \rightleftharpoons CH_3I + Cl^-$, heterogeneity has been avoided by the use of lithium instead of potassium salts.

Experimental Materials.—Acetone, of analytical standard, was kept for several days over anhydrous calcium sulphate, and then distilled in an all-glass apparatus with a fractionating column (2·5 cm. diam. × 45 cm. long) filled with glass helices. The b. p. was 56·1°. Values reported by other workers[4] range from 56·1° to 56·3°.

Lithium iodide and chloride were twice crystallised from distilled water and then dried by the technique of Turner and Bissett,[5] which consists of the combined effects of a vacuum, a high temperature and desiccation with phosphoric oxide. Solutions of the salts were made by dissolving them, with agitation, in acetone in conical flasks with male joints fitted with ground glass caps the lower parts of whose joints were greased.

[1] Conant and Kirner, *J. Amer. Chem. Soc.*, 1924, **46**, 232.
[2] Brusoff, *Z. phys. Chem.*, 1900, **34**, 129.
[3] Moelwyn-Hughes, *Trans. Faraday Soc.*, 1949, **45**, 167.
[4] Timmermans, " Physicochemical Constants of Pure Organic Compounds," Elsevier, Amsterdam, 1950.
[5] Turner and Bissett, *Proc. Chem. Soc.*, 1913, **29**, 233.

4 R

The commercial sample of methyl chloride used was pure by spectroscopic and gas-chromatographic standards. A concentrated solution of methyl chloride in acetone was prepared in an absorption pipette and sufficed for the whole investigation.

Commercial methyl iodide was purified by the method of Brown and Acree.[6] The distillate was collected from 42·41° to 42·45°. The boiling points reported by other workers are 42·30—42·36° (Brown and Acree [6]) and 42·50° (Timmermans [4]).

Experimental Method.—A special vessel was designed to permit the reaction to be studied in the absence of the vapour phase and out of contact with mercury (Figure). It consists of a Pyrex glass cylinder (*A*) of 45 mm. bore and 30 cm. length, ground inside, and a ground-glass piston (*B*) with a capillary (2 mm. diam.) outlet (*C*) at the top. Mercury (*D*) poured on the top of the piston acts as a seal, and assists in driving it down. A head of mercury of 7—8 cm. was found suitable.
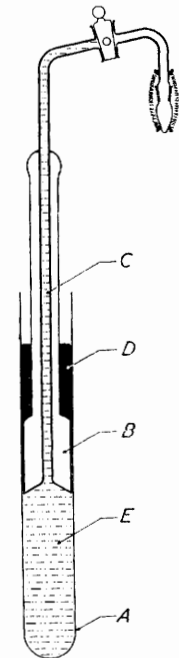
Approximately 300 ml. of lithium iodide solution of known strength were brought up to the working temperature, and then 5 ml. of a strong solution of methyl chloride in acetone were added. The mixture was thoroughly shaken and then poured into the reaction vessel.

The reaction was followed by expressing samples at measured time intervals, chilling them in ice, pipetting 5 ml. into 10 ml. of distilled water and 5 ml. of acetone, adding 5 ml. of 50% sulphuric acid and then titrating the mixture for inorganic iodide against approximately 0·02 molar ceric sulphate solution, ferroin being used as indicator (Lewis [7]).

The initial concentration of lithium iodide was obtained by titration with ceric sulphate at zero time, and (after the removal of organic compounds by evacuation) by titration with silver nitrate with dichlorofluorescein as adsorption indicator at zero time. The latter method is more accurate as it gives the total salt concentration, which is independent of the time of removal of the sample. The initial concentration of inorganic iodide was generally checked twice during the reaction by the silver nitrate method. The latter titrations were performed in the presence of 5 ml. of 2% dextrin solution, as otherwise the end point with a mixture of iodide and chloride is not detectable. Dextrin shifts the end point by a small amount, which can be determined in blank experiments.

The initial concentration of methyl halide was determined by heating known volumes of the reaction mixture with excess of N-sodium hydroxide solution in sealed glass tubes at 100° for 24 hr., and titrating the hydrolysed sample for total halide by the silver nitrate method after neutralising it with acetic acid and boiling it under vacuum, which helps in the detection of the end point.

Vapour-free reaction vessel.

Kinetic Formulation.—The general evidence on the kinetics of reactions between salts and alkyl halides in hydroxylic media [8] is that the reactions take place entirely between the anions and the organic compounds. The rate of reaction, if there is any, between the undissociated or un-ionised salt and the alkyl halide has been found to be so small as to be insignificant. The same conclusion has later been drawn for these reactions in acetone. Evans and Sugden,[9] for example, find that, though the salt concentration is altered by a factor of 400 in the reaction n-C_4H_9Br + LiBr* $\longrightarrow$ n-C_4H_9Br* + LiBr, the second-order constant for the reaction between the organic compound and the ion does not vary, provided allowance is made for the incomplete dissociation of the salt. For these reasons, and because we have otherwise found it difficult to interpret our results, we have assumed that the reactions taking place are the ionic replacements

$$CH_3Cl + I^- \underset{k_4}{\overset{k_2}{\rightleftharpoons}} CH_3I + Cl^-$$
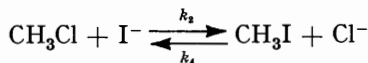
[6] Brown and Acree, *J. Amer. Chem. Soc.*, 1916, **38**, 2145.
[7] Lewis, *Ind. Eng. Chem. Analyt.*, 1936, **8**, 199.
[8] Moelwyn-Hughes, "The Kinetics of Reactions in Solution," 2nd Edn., Oxford, 1947, pp. 128—130.
[9] Evans and Sugden, *J.*, 1949, 270.

The instantaneous velocity of reaction is consequently

$$-d[CH_3Cl]_t/dt = k_2[CH_3Cl_t][I^-]_t - k_4[CH_3I]_t[Cl^-]_t$$

Denoting by a the initial concentration of methyl chloride, by b the initial concentration of lithium iodide (ionised and un-ionised), by x the concentration of methyl iodide at time t, and by α the degree of ionisation of lithium iodide at time t, we see that

$$[CH_3Cl]_t = a - x$$

$$[I^-]_t = (b - x)\alpha$$

and
$$[CH_3I]_t = x = [LiCl]_t + [Cl^-]_t \quad \ldots \ldots \ldots \quad (1)$$

The rate law now becomes

$$dx/dt = k_2(a - x)(b - x)\alpha - k_4 x[Cl^-]_t \quad \ldots \ldots \quad (2)$$

Because lithium chloride in acetone is much less ionised than lithium iodide, we can express its ionisation constant as follows:

$$K_1 = [Li^+]_t[Cl^-]_t/[LiCl]_t = [I^-]_t[Cl^-]_t/[LiCl]_t \quad \ldots \ldots \quad (3)$$

For the same reason, $[LiCl]_t$, according to eqn. (1), is very nearly x. Then $[Cl^-]_t = K_1 x(b - x)\alpha$, and eqn. (2) reduces to

$$\frac{dx}{dt} = k_2(a - x)(b - x)\alpha - \frac{k_4 K_1}{\alpha} \cdot \frac{x^2}{b - x} \quad \ldots \ldots \quad (4)$$

The equilibrium conditions are governed by the equation

$$K = \frac{k_2}{k_4} = \frac{K_1}{\alpha_\infty^2} \frac{x_\infty}{(a - x_\infty)(b - x_\infty)^2} \cdot \quad \ldots \ldots \quad (5)$$

where x_∞ is the final concentration of methyl iodide. On combining eqns. (4) and (5), we have

$$\frac{dx}{dt} = k_2\alpha \left[(a - x)(b - x) - \frac{K_1}{K\alpha^2} \frac{x^2}{(b - x)} \right] \quad \ldots \ldots \quad (6)$$

Because α is a function of the concentration, this equation is not integrable. When α is treated as a constant, there results a highly complicated integrated form, which is not here reproduced. During the course of a run, α varies little from the arithmetic mean of its initial and final values, and the term $K_1/K\alpha^2(b - x)$ has the approximately constant value of $2K_1/K\alpha^2(2b - x_\infty) = W$. These facts allow eqn. (6) to be integrated, giving

$$k_2 = \frac{1}{2\alpha\beta(1 - W)t} \ln \left[\frac{1 - x/(\gamma + \beta)}{1 - x/(\gamma - \beta)} \right] \quad \ldots \ldots \quad (7)$$

where $\gamma = \dfrac{a + b}{2(1 - W)}$ and $\beta = [(a - b)^2 + 4Wab]^{\frac{1}{2}}/2(1 - W)$.

Experimental Results.—In the equilibrium data summarised in Table 1, values marked with an asterisk refer to results obtained from the reverse direction, *e.g.*, the figure 39·41 at 20° stands for the initial concentration of methyl iodide and 43·12 for the total initial concentration of inorganic chloride. The reactions were followed until no further change in the composition of the solution could be detected. About 3 days at 20° and about 1 day at 40° sufficed. Those entries in Table 1 which refer to solutions containing the same initial concentrations of reactants were obtained in purely equilibrium experiments, carried out without studying the kinetics. One and the same solution, kept in the same vessel, was examined for equilibrium concentrations at different temperatures. The ionisation constants are derived from the equation $\ln K_1 = -(31\cdot28/R) + (2908/RT)$, which was constructed from Serkov's data [10] at 25°, the limiting conductances of Ross Kane,[11] and the temperature coefficients of Blokker.[12] The degrees of

[10] Serkov, *J. Russ. Phys. Chem. Soc.*, 1908, **40**, 413.
[11] Ross Kane, *Ann. Reports*, 1930, **27**, 351.
[12] Blokker, *Rec. Trav. chim.*, 1935, **54**, 975.

ionisation of lithium iodide have been interpolated or extrapolated from Blokker's figures. The slight increase of K with respect to temperature is adequately summarised by the equation $\ln K = -(11\cdot71/R) - (1440/RT)$.

TABLE 1. *Equilibrium constants for the reaction* $CH_3Cl + I^- \rightleftharpoons CH_3I + Cl^-$ *in acetone solution*: $K = [CH_3I]_\infty[Cl^-]_\infty/[CH_3Cl]_\infty[I^-]_\infty$.

t°(c)	10^5K_1 (moles/l.)	$[CH_3Cl]_0$	$[LiI]_0 + [I^-]_0$	$[LiI]_\infty + [I^-]_\infty$	α_∞	10^4K
			(millimoles/l.)			
20·00	2·15	44·25	52·26	44·71	0·284	2·08
,,		39·41 *	43·12	34·26	0·305	2·63
,,		16·18	35·39	31·66	0·312	2·47
					Average =	2·37
30·00	1·93	44·25	52·26	43·99	0·280	2·29
,,		39·41 *	43·12	33·62	0·299	2·96
,,		16·67	33·35	29·46	0·309	2·62
,,		44·31	10·64	8·23	0·417	2·16
					Average =	2·47
40·00	1·57	16·43	62·17	55·86	0·255	3·04
,,		44·25	52·26	43·01	0·276	2·72
,,		16·74	30·04	26·04	0·316	2·91
,,		17·75	14·50	12·12	0·381	2·71
,,		44·31	10·64	7·92	0·422	2·50
					Average =	2·76
50·00	1·36	44·25	52·26	42·14	0·273	3·08
,,		17·61	30·96	26·68	0·308	2·76
,,		15·82	31·65	27·57	0·305	2·72
,,		44·31	10·64	7·58	0·408	3·22
					Average =	2·93

TABLE 2. *Bimolecular velocity constants for the reaction* $CH_3Cl + I^- \longrightarrow CH_3I + Cl^-$ *in acetone at* 40·0°; $[CH_3Cl]_0 = 17\cdot75$, $[CH_3Cl]_\infty = 15\cdot37$ *mmoles/l.*

t (sec.)	$[LiI]_t + [I^-]_t$ (mmoles/l.)	10^3k_2 (l. mole^{-1} sec.$^{-1}$) Completely integrated form of eqn. 6	Eqn. 7	t (sec.)	$[LiI]_t + [I^-]_t$ (mmoles/l.)	10^3k_2 (l. mole^{-1} sec.$^{-1}$) Completely integrated form of eqn. 6	Eqn. 7
0	14·50	—	—	7152	12·43	5·07	4·93
552	14·16	6·58	6·60	1284($t_{\frac{1}{4}}$)	13·91	5·08	5·09
1152	13·95	5·21	5·22	2832($t_{\frac{1}{2}}$)	13·31	5·08	5·09
1752	13·74	4·86	4·87	5136($t_{\frac{3}{4}}$)	12·72	5·07	5·04
2652	13·37	5·08	5·10	∞	12·12	—	—
4152	12·89	5·26	5·26				

Velocity coefficients calculated from the completely integrated form of eqn. 6 are shown in column 3 of Table 2. The calculations are extremely laborious, and, as the figures in column 4 show, lead to values of k_2 which are not significantly different from those obtained by means of the simpler eqn. 7. Both equations have been applied to directly observed points and to values interpolated graphically for times corresponding to 25, 50, and 75% completion.

Velocity coefficients have also been obtained by using eqn. 6 in the incremental form. This method, though mathematically not so exact, is physically superior, because no assumption is necessary concerning α, and its exact value can be used for each composition. Values of k_2 obtained in this way are approximately 10% higher than those obtained by the other two methods, and are accepted as being the most reliable.

Runs have been repeated with various initial concentrations of methyl and lithium halides and, although they give slightly different values, there is no discernible trend. Within the limit of accuracy attained, there is no evidence that k_2 or k_4 is affected by initial concentration of electrolyte or of methyl halide (see Table 3). No general answer can be given to the question of whether un-ionised molecules of the alkali halides react with methyl halides in acetone solution. In the present system, however, such a supposition is not necessary, although it cannot, without further study, be ruled out.

A summary of the mean values of k_2 obtained from all the runs is given in Table 4. The k_4 values were derived from them by means of eqn. (5), and are to some extent dependent on the adopted values of K_1. Had we accepted the K_1 values of Blokker [12] rather than those of Serkov,[10] the absolute values of k_4 would be lower by a factor of about 2.

TABLE 3. *The influence of initial concentrations (in mmoles/l.) on the bimolecular velocity constant (k_2 in l. mole^{-1} sec.$^{-1}$) at 40·0°.*

$a = [CH_3Cl]_0$	$b = [LiI]_0 + [I^-]_0$	$10^3 k_2$	$a = [CH_3Cl]_0$	$b = [LiI]_0 + [I^-]_0$	$10^3 k_2$
17·8	14·5	6·25	30·4	31·0	6·80
16·7	30·1	6·11	16·4	62·2	6·74

TABLE 4. *Bimolecular velocity constants (in l. mole^{-1} sec.$^{-1}$) for the reactions $CH_3Cl + I^- \longrightarrow CH_3I + Cl^-$ (k_2) and $CH_3I + Cl^- \longrightarrow CH_3Cl + I^-$ (k_4) in acetone solution.*

	$10^4 k_2$				$10^4 k_2$		
$t°$	obs.	calc.	k_4	$t°$	obs.	calc.	k_4
20·0	8·08	8·96	3·85	40·0	65·2	63·7	23·3
30·0	24·8	24·8	9·82	50·0	157	157	53·5

Temperatures were maintained constant to with $\pm 0·03°$. The Arrhenius equations are

$$k_2 = 2·14 \times 10^{10} \exp(-17,950/RT) \text{ and } k_4 = 7·78 \times 10^{12} \exp(-16,510/RT)$$

It will be observed that k_4 is about 4000 as great as k_2, and that the difference in rates is reflected chiefly in the pre-exponential constants.

Comparison with Other Work.—The kinetic results of Hughes, Ingold, and Mackie [13] on the reaction $CH_3I + Cl^- \longrightarrow CH_3Cl + I^-$ in acetone are not directly comparable with ours. They used sealed ampoules with an unspecified volume of vapour; our system was studied in the absence of the vapour phase. This difference in technique, however, is not comparable with the difference in interpretations or capable of explaining the difference in the quantitative conclusions. (1) They make no allowance for the reverse reaction, and state that a decrease observed by them in their bimolecular constant as the reaction proceeds is " of the wrong form to be ascribed to reversibility." The reverse reaction is therefore dismissed. We, on the other hand, not only find that the facts are readily explained in terms of the standard kinetic treatment of opposing bimolecular reactions but have shown, by adding lithium iodide to methyl chloride, that the reverse reaction does, in fact, take place. The treatment for opposing bimolecular reactions satisfactorily fits the facts, and no drift can be detected in either velocity coefficient. (2) They claim that the reaction is subject to a salt effect, which is said to be generic to Finkelstein substitutions, negative in sign, and specific with respect to the cation. We, on the other hand, find that the bimolecular constant, computed with allowance for the reverse reaction, is unaffected, within the regions examined, by the concentration of electrolyte or methyl halide. (3) They treat lithium chloride in acetone solution as completely ionised (or dissociated) whereas, in the instance cited by them, 98% of the salt is un-ionised (or undissociated). (4) Their runs, with one exception, have been carried out in the presence of approximately 0·1N-lithium perchlorate. That the presence of this salt should decrease the apparent second-order constants can be explained in terms of its suppression of the ionisation of lithium chloride; that it should cause the drift in their constant to disappear is a result which is difficult to interpret.

Owing to their permitting the escape of the vapours of methyl iodide and methyl chloride into the free gas space in contact with their solutions, not allowing for the kinetic consequences of the reverse reaction, and neglecting the association of lithium and chloride ions, the bimolecular constants given by Ingold, Hughes, and Mackie for the reaction $CH_3I + Cl^- \longrightarrow CH_3Cl + I^-$ are more than 1000 times smaller than ours.

DEPARTMENT OF PHYSICAL CHEMISTRY, CAMBRIDGE.

[13] Hughes, Ingold, and Mackie, *J.*, 1955, 3177.