488. *The Kinetics of the Reaction of Methyl Iodide with Silver Nitrate and Silver Perchlorate in Aqueous Solution.*

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The kinetics of the reaction between methyl iodide and soluble silver salts ($AgNO_3$ and $AgClO_4$) have been investigated in vapour-free reaction vessels by titrimetric and conductometric methods at temperatures between 15 and 45°, at various concentrations of reactants, and at constant ionic strength. The course of each run is bimolecular, but the value of the constant k_2 depends on the initial concentration of the soluble silver salt, as found by earlier workers using ethanol and various organic solvents. These effects can be explained in terms of two complexes, $(MeI,Ag)^+$ and $(NO_3^-MeI,Ag^+)^0$, which are assumed to exist in thermodynamic equilibrium with their progenitors, and to decompose at rates proportional to their concentrations. The nitrate ion takes no part in the chemical reaction, but catalyses the rate at which the silver ion attacks the molecule. At 25° the observed bimolecular constant is given by the equation $k_2 = k_2^0 + k_3[NO_3^-]\gamma^2$, where γ is the mean ionic activity coefficient. There is nothing in the numerical constants of the Arrhenius equation, $k_2 = 4.3_3 \times 10^{11}$ exp $(-19,400/RT)$, to distinguish it from equations giving the rate at which anions effect substitution in methyl halides.
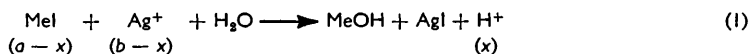
Most kinetic data on reactions between ions and polar molecules relate to those with anions; there are relatively few data on reactions of cations with polar molecules. The present Paper describes experiments on the rate of the reaction between methyl iodide and the silver ion in water.

Experimental

Silver nitrate was purified by crystallisation from ethanol, and methyl iodide by a method described previously.[1] Rates of reaction were measured by chemical analysis of samples expressed at known times from a vapour-free piston reactor,[2] and by electrical conductivity measurements [3] in a blackened cell. Both methods gave the same results, which agreed, in the one instance where comparison was possible, with the findings of Burke and Donnan.[4] The initial concentrations, b, of silver salt used generally exceeded the initial concentrations, a, of methyl iodide.

Discussion

Stoicheiometry.—The chemical change is represented quantitatively by reaction (1).

$$\text{MeI} + \text{Ag}^+ + \text{H}_2\text{O} \longrightarrow \text{MeOH} + \text{AgI} + \text{H}^+ \qquad (1)$$
$$(a-x) \quad (b-x) \qquad\qquad\qquad\qquad (x)$$

The concentration of hydrogen ion at any time, measured by titration with alkali and by the electrometric method, was identical with the decrease in concentration of silver salt, as determined by titration against potassium thiocyanate. Such would not have been the case if reaction (2) occurred, for then the decrease in the concentration of silver nitrate

$$\text{MeI} + \text{Ag}^+ + \text{NO}_3^- \longrightarrow \text{MeNO}_3 + \text{AgI} \qquad (2)$$
$$(a-y) \quad (b-y) \qquad\qquad (y)$$
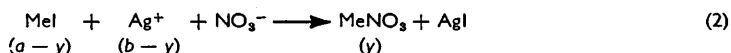
would exceed the concentration of hydrogen ions produced. If, however, any methyl nitrate formed were to react rapidly with water, equivalence between $[H^+]_t$ and $([AgNO_3]_0 - [AgNO_3]_t)$ would again be found. Earlier work proves that this does not

[1] Fahim and Moelwyn-Hughes, *J.*, 1956, 1035.
[2] Farhat-Aziz and Moelwyn-Hughes, *J.*, 1959, 2635.
[3] Biordi and Moelwyn-Hughes, *J.*, 1962, 4291.
[4] Burke and Donnan, *J.*, 1904, **85**, 555; *Z. phys. Chem.*, 1909, **69**, 148.

happen.   The rate of hydrolysis of methyl nitrate [5] in water at 25° is 2.2×10^{-9} sec.$^{-1}$, corresponding to a half-life of 3650 days.   This stable ester, if formed, would remain unhydrolysed.   It follows that the nitrate ion takes no chemical part in the reaction, although, as is shown later, it increases the rate of reaction between the silver ion and methyl iodide.   The part played by the hydrolysis of methyl iodide is negligible;   the velocity constant [6] for its hydrolysis at 25° is $(7.56 \pm 0.14) \times 10^{-8}$ sec.$^{-1}$ ($t_{\frac{1}{2}} = 106$ days).

Bimolecular Constants.—Velocity constants have been calculated from the ordinary equation for an irreversible bimolecular process:

$$k_2 = \frac{1}{(a-x)(b-x)} \cdot \frac{dx}{dt} = \frac{2.303}{t(b-a)} \log_{10} \frac{a(b-x)}{b(a-x)},$$ (3)

which, in terms of specific conductivities, κ, takes the form:

$$k_2 = \frac{2.303}{t(b-a)} \left[\log_{10} \left(\frac{\kappa_\infty - \kappa_0}{\kappa_0(s-1)} \right) + \log_{10} \left(\frac{\kappa_0 s - \kappa_t}{\kappa_\infty - \kappa_t} \right) \right],$$ (4)

where

$$s = \Lambda_{HNO_3} / \Lambda_{AgNO_3}$$ (5)

The equivalent conductivities of silver nitrate were taken directly, or computed from the data of McInnes,[7] and Jones.[8]   With given initial concentrations a and b, the reaction is bimolecular throughout the course of the run, as the specimen logarithmic plot (Fig. 1) shows.   During the last stages of reaction, there were, in certain runs, deviations from

TABLE 1.

Variation of rate constant (k_2, l. mole^{-1} sec.$^{-1}$) with silver nitrate and methyl iodide concentration at 298·25°K.

$b = [AgNO_3]_0$ and $a = [MeI]_0$ (mmoles/l.).

b	9·12	9·36	19·15	27·53	29·55	48·09	48·85	58·81	61·05	68·67	74·34
a	1·91	4·06	6·47	19·34	2·95	12·47	6·13	6·01	7·46	6·90	9·52
$10^3 k_2$	3·66	3·69	5·03	5·91	6·13	7·85	7·82	8·85	8·86	9·95	10·03

the initial gradient.   These were generally in the direction of higher values of k_2, did not exceed 9%, and were not reproducible.   Values of k_2 determined from the initial gradients are reproducible to within 1% of the mean.   When, therefore, slight deviations attended the last stages, we accepted the initial value of k_2.

Although the reaction during a given run is bimolecular, the value of k_2 depends on the initial concentration, b, of the inorganic silver salt.   At a given salt concentration, k_2 is independent of a.   Results with silver nitrate at 25·09°c are summarised in Table 1, and shown, with those using silver perchlorate, in Fig. 2.   The increase in k_2 as b is increased is greater with silver nitrate than with the perchlorate.   Changes in the initial concentration of silver ion from zero to 0·0491M, at a constant ionic strength of 0·0491M (by addition of potassium nitrate), caused k_2 to decrease from 8.1×10^{-3} to 7.4×10^{-3}.   The order of reaction, as determined by conventional methods, is 1 with respect to methyl iodide, and between 1 and 2 with respect to silver nitrate.   These facts relate to aqueous solutions, and resemble those already established in ethanol [4] and other solvents.[9]

The Mechanism of the Reaction.—The problem is to explain the bimolecular course of the reaction during a given run and the positive catalytic effect of the anions NO_3^- and ClO_4^-.   We agree with Hammond [9] and his collaborators that the kinetic facts can be rationalised only by a mechanism wherein the silver ion and the anions take part in the rate-determining step.   We have been unable to do this without assuming the existence

[5] McKinley-McKee and Moelwyn-Hughes, *Trans. Faraday Soc.*, 1952, **48**, 247.

[6] Heppolette and Robertson, *Proc. Roy. Soc.*, 1959, A, **253**, 273;   Moelwyn-Hughes, *ibid.*, 1953, A, **220**, 386.

[7] McInnes, " The Principles of Electrochemistry," Reinhold, New York, 1939.

[8] Jones, *J. Amer. Chem. Soc.*, 1945, **67**, 855.

[9] Hammond, Hawthorne, Waters, and Graybill, *J. Amer. Chem. Soc.*, 1960, **82**, 704.

of two complexes, for which there is no independent evidence. They are $(MeI,Ag)^+$ and $(NO_3^-,MeI,Ag^+)^0$. It is assumed that the binary and ternary complexes exist in thermodynamic equilibrium with their progenitors, and that the rate of chemical change is proportional to their concentrations. According to the method of Davies and his co-workers,[10] the observed bimolecular constant is then given by equation (6), where

$$k_2 = k_2^° + k_3[NO_3^-]\gamma^2 \tag{6}$$

γ is the mean activity coefficient of the ions. That $[NO_3^-]\gamma^2$ is constant throughout a given run explains why k_2 does not vary during its course. That γ^2 decreases as the
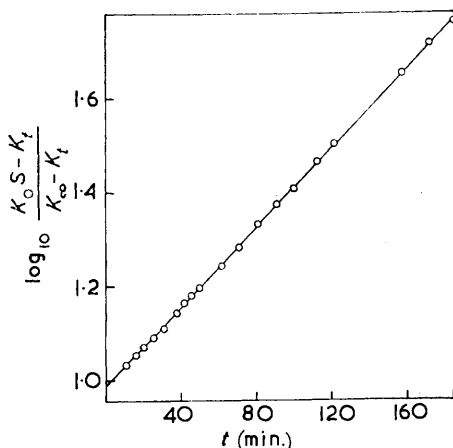

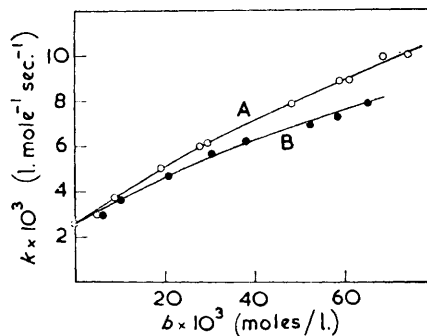FIG. 1.   Specimen logarithmic plot for the reaction of methyl iodide with silver salts.

FIG. 2.   Variation of rate constant with initial silver salt concentration.

O $AgNO_3$, $\bullet$ $AgClO_4$.

ionic strength increases explains the non-linearity of k_2 against $[NO_3^-]$. Accepting the activity coefficients of McInnes [7] at 25°, we find equation (6) to hold (Table 2), with the following numerical terms:

$$k_2 = 2.61 \times 10^{-3} + 1.72 \times 10^{-1}[NO_3^-]\gamma^2.$$

It follows that, at ionic strengths exceeding 0.021, the number of molecules reacting per second by the termolecular mechanism exceeds the number reacting by the bimolecular mechanism. This can come about only if the energy of activation of the termolecular

TABLE 2.

Comparison of observed and calculated rate constants.

[AgNO₃] (mmoles/l.)	20	40	60	80
γ	0.858	0.813	0.778	0.752
10^3k_2 (obs.) (l. mole⁻¹ sec.⁻¹)..............	5.15	7.17	8.85	10.40
10^3k_2 (calc.) (l. mole⁻¹ sec.⁻¹)	5.15	7.16	8.86	10.40

reaction is much lower than that of the bimolecular reaction. Such a lowering is to be expected if the anion, approaching the methyl end of the molecule (though not reacting with it), gives coulombic assistance in drawing the silver ion, approaching the halide end of the molecule, to within a critical distance of the iodine atom.

The Influence of Temperature on $k_2^°$.—Similar features were revealed by experiments performed at 15, 35, and 45°. In the absence of activity coefficients, however, empirical

[10] Wyatt and Davies, *Trans. Faraday Soc.*, 1949, **45**, 774; Davies and Williams, *ibid.*, 1958, **54**, 1547.

methods were used to determine $k_2°$, yielding less reliable results than would have been found by means of equation (6). Chiefly for this reason, the apparent energy of activation could be found only within the limits $E_A = 19,400 \pm 800$ cal./mole. Approximately, therefore,

$$k_2° = 4.3_3 \times 10^{11} \exp(-19,400/RT). \tag{7}$$

The numerical constants of this equation resemble closely the values found for many reactions between methyl halides and anions in water.