

**392.** *The Kinetics of the Reaction between Methyl Iodide and the Thiocyanate Ion in Aqueous Solution*

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A conductometric investigation of the reaction between methyl iodide and the thiocyanate ion in aqueous solution shows it to be bimolecular, though attended by the pseudo-unimolecular reaction of methyl iodide with water. The constants of the Arrhenius equation  $k_2 = A \exp(-E_A/RT)$  are  $1.49 \times 10^{11}$  l. mole<sup>-1</sup> sec.<sup>-1</sup> and 19.95 kcal. mole<sup>-1</sup>, respectively. These have been compared with the constants for the reactions of methyl iodide with seven other ions in an attempt to understand an apparent parallelism between  $\ln A$  and  $E_A$ .

KINETIC data are available on the reactions of methyl iodide in aqueous solution with numerous anions and with the silver cation.<sup>1</sup> The present Paper deals with the kinetics of the reaction between methyl iodide and the thiocyanate ion in aqueous solution.

EXPERIMENTAL

Methyl iodide was purified as described in earlier Papers of this series. Commercial potassium thiocyanate, used without purification, was 99.8% pure (Volhard's method). The chemical reaction proceeds slowly enough at ordinary temperatures and concentrations to allow its rate to be measured, in principle, by chemical analysis. Though two volumetric and two gravimetric methods were used to estimate the concentration of the iodide or the thiocyanate ion in

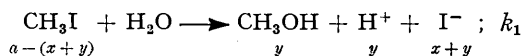
<sup>1</sup> D. W. Colclough and E. A. Moelwyn-Hughes, *J.*, 1964, 2542.

each other's presence, none was satisfactory, and the method of electrical conductivity was finally adopted. Its applicability to the system considered is, unfortunately, restricted, because unless conditions are carefully chosen the increase in conductivity attending the slight hydrolysis of methyl iodide can be a significant fraction of the increase due to the ionic exchange reaction, which depends on the relatively small difference between the ionic mobilities of the thiocyanate and iodide ions. Solutions of potassium thiocyanate were made by weight in conductivity water. The reaction was started either by injecting about 0.05 ml. of liquid methyl iodide into the pre-heated salt solution, or by mixing known volumes of the salt solution with the methyl iodide solution. The initial concentration of methyl iodide was determined by treating a sample of the reaction mixture with excess of standard silver nitrate, with which both thiocyanate ion and methyl iodide react, and back-titrating the remaining silver nitrate with standard potassium thiocyanate. When an aqueous solution of methyl iodide had been prepared, its concentration was determined after digestion with excess of potassium hydroxide, and its initial concentration in the reaction solution was determined by dilution. The reaction was followed by measuring the electrical resistance of the solution at various times until the resistance became constant. The cell-constants ranged from 0.2 to 5 cm.<sup>-1</sup>. At the end of the reaction, the contents of the cell were analysed for total [SCN<sup>-</sup>] + [I<sup>-</sup>] titrimetrically and for [H<sup>+</sup>] potentiometrically.

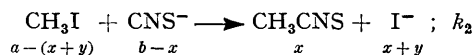
*Kinetic Formulation.*—Let  $a$  and  $b$ , respectively, denote the initial concentrations of methyl iodide and the thiocyanate ion. If, at time  $t$ , a concentration  $y$  of hydrogen ion has been produced, and the concentration of thiocyanate ion has been reduced by an amount  $x$ , we have the following expressions for the various concentrations at any time,  $t$ :

$$[\text{H}^+]_t = y; [\text{I}^-]_t = x + y; [\text{CH}_3\text{I}]_t = a - (x + y); [\text{CNS}^-]_t = b - x.$$

It has been firmly established in most reactions of this type that the pseudo-unimolecular hydrolysis,



and the bimolecular substitution



proceed independently, so that the rate equations are:

$$dx/dt = k_2\{a - (x + y)\}(b - x) \quad (1)$$

and

$$dy/dt = k_1\{a - (x + y)\}. \quad (2)$$

It follows that

$$dx/dy = (k_2/k_1)(b - x) \quad (3)$$

which, on integration, becomes

$$y = (k_1/k_2) \ln \{b/(b - x)\}. \quad (4)$$

In this work,  $x$  is always very small compared with  $b$ . Hence, throughout the course of the reaction, approximately,

$$y = (k_1/k_2)(x/b). \quad (5)$$

On elimination of  $y$  from equations (1) and (5), we have

$$dx/dt = (k_2 + k_1/b)(a - x)(b - x),$$

or

$$k_2 + k_1/b = 1/t(b - a) \ln \{\alpha(b - x)/b(\alpha - x)\} \quad (6)$$

where

$$\alpha = a/\{1 + (k_1/k_2)b\}. \quad (7)$$

From equation (5) we have

$$y_\infty = (k_1/k_2)(x_\infty/b). \quad (8)$$

Since

$$x_\infty + y_\infty = a, \quad (9)$$

it follows that

$$y_{\infty} = (k_1/k_2b)\alpha \quad (10)$$

and

$$x_{\infty} = \alpha. \quad (11)$$

Equation (6) can thus be written as follows:

$$k_2 + (k_1/b) = 1/t(b - a) \ln \{x_{\infty}(b - x)/b(x_{\infty} - x)\}. \quad (12)$$

In terms of the specific conductivity,  $\kappa$ , of the solution and the equivalent conductivities,  $\Lambda$ , of the electrolytes, we have

$$10^3\kappa = (b - x)\Lambda_{\text{KSCN}} + x\Lambda_{\text{KI}} + y\Lambda_{\text{HI}}. \quad (13)$$

Elimination of  $y$  by means of equation (5), and rearrangement, gives

$$10^3\kappa = b\Lambda_{\text{KSCN}} + x\Lambda, \quad (14)$$

where

$$\Lambda = (\Lambda_{\text{KI}} - \Lambda_{\text{KSCN}}) + (k_1/k_2b)\Lambda_{\text{HI}}. \quad (15)$$

Hence,

$$\Lambda/\Lambda_{\text{KSCN}} = s - 1,$$

where

$$s = \{\Lambda_{\text{KI}} + (k_1/k_2b)\Lambda_{\text{HI}}\}/\Lambda_{\text{KSCN}}. \quad (16)$$

From equation (13) it follows that

$$b = 10^3\kappa_0/\Lambda_{\text{KSCN}}, \quad (17)$$

$$x = 10^3(\kappa - \kappa_0)/\Lambda, \quad (18)$$

and

$$x_{\infty} = 10^3(\kappa_{\infty} - \kappa_0)/\Lambda. \quad (19)$$

Substitution in equation (12) leads to the expression

$$k_2 + (k_1/b) = \frac{1}{t(b - a)} \ln \left\{ \frac{(\kappa_{\infty} - \kappa_0)}{\kappa_0(s - 1)} \frac{s\kappa_0 - \kappa}{(\kappa_{\infty} - \kappa)} \right\} \quad (20)$$

In the experiment to which the data of Table 1 refer, the term  $(k_1/b)$  of equation (20) is less than 0.2% of  $k_2$ , and has been ignored. Omission of the ratio  $(k_1/k_2b)$  of equation (15), however, is not justified, and yields misleading results. The physical explanation is that the presence of a small concentration of hydrogen ions has a negligible effect on the net rate of chemical change, but a significant effect on the conductivity, by means of which it is measured.

Values of  $\Lambda_{\text{KSCN}}$  were determined experimentally at various concentrations and temperature. At a concentration of 20 mmoles/l., for example, it is found that

$$\log_{10} \Lambda_{\text{KSCN}} = 1.92356 + 7.683 \times 10^{-3} \theta \quad (21)$$

where  $\theta$  is the temperature ( $^{\circ}\text{C}$ ). Values of  $\Lambda_{\text{KI}}$  at  $25^{\circ}$  were taken from McInnes's monograph<sup>2</sup> and values of  $\Lambda_{\text{HI}}$  at the same temperature were constructed from his Table. We find, for example,  $d \log_{10} \Lambda_{\text{KI}}/d\theta = 6.834 \times 10^{-3}$  and  $d \log_{10} \Lambda_{\text{HI}}/d\theta = 3.684 \times 10^{-3}$  at a concentration of 20 mmoles/l. Values of  $k_1$  are known at all relevant temperatures.<sup>3</sup> An approximate estimate of  $k_2$ , such as that found from the initial concentrations and the half-life, suffices for an evaluation of the last term in equation (15).

## RESULTS

Table 1 contains one in every three of the observations in a specimen run characterised by the conditions given in its heading. From  $\kappa_0$  and equation (17),  $\Lambda_{\text{KSCN}}$  becomes 119.3. The established value of  $\Lambda_{\text{KI}}$  is 130.38, and the second term in the curly brackets of equation (16) is estimated as 0.071, taking  $k_1$  as  $6.9 \times 10^{-8} \text{ sec}^{-1}$  and the approximate value of  $3.66 \times 10^{-4} \text{ l. mole}^{-1} \text{ sec}^{-1}$  obtained for  $k_2$  from the half-life. With  $\Lambda_{\text{HI}}$  as 408.35,  $s$  becomes

<sup>2</sup> D. A. McInnes, "The Principles of Electrochemistry," Reinhold, New York, 1939.

<sup>3</sup> E. A. Moelwyn-Hughes, *Proc. Roy. Soc.*, 1938, *A*, **164**, 295; 1953, *A*, **220**, 386; R. N. Heppollette and R. E. Robertson, *ibid.*, 1959, *A*, **252**, 273.

TABLE 1

25.0°;  $a = 33.2$  mmoles.;  $b = 108.0$  mmoles.;  $s = 1.0934$

$(t + 2)$ (min.)	0	37	70	116	160	230	300	404	563	1203	$\infty$
$10^4\kappa$ (ohm <sup>-1</sup> cm. <sup>-1</sup> )	1.2884	1.2923	1.2954	1.2994	1.3026	1.3067	1.3101	1.3143	1.3190	1.3283	1.3324
$10^4k_2$ (l. mole <sup>-1</sup> sec. <sup>-1</sup> )	—	3.53	3.60	3.66	3.66	3.59	3.56	3.55	3.53	3.64	—

Average  $k_2 = 3.59$

1.0934. Bimolecular constants calculated by means of equation (20) are shown in the last column of Table 1. The mean value is the same as the mean of all the observations, and is equal to that obtained by plotting the logarithmic term in equation (20) against the time. The method of least-squares gives  $k_2 \times 10^4 = 3.59 \pm 0.05$ . Table 2 shows that  $k_2$  is unaffected by changes in the initial concentration of either reactant. The effect of temperature is summarised in Table 3. At temperatures higher than 308.16°K precise values of  $k_2$  could not

TABLE 2

The effect of varying initial concentrations at 25°

$a$ (mmole/l.)	$b$	$k_2 \times 10^4$ (l. mole <sup>-1</sup> sec. <sup>-1</sup> )
10.2	20.1	3.57
27.7	51.4	3.58
33.2	108.0	3.59

TABLE 3

The influence of temperature on  $k_2$  (l. mole<sup>-1</sup> sec.<sup>-1</sup>)  $k_2$  (calc.) =  $1.49 \times 10^{11} \exp(-19,950/RT)$

$T$ (°K)	$10^4k_2$ (obs.)	$10^4k_2$ (calc.)
298.16	3.58	3.58
302.85	6.01	5.93
306.71	9.05	8.98
308.16	10.49	10.54

be obtained because, in the first place, accurate values of  $\Lambda$  are not available, and, in the second place, no sharp end-point could be observed. After an ostensible end of reaction, the conductivity increased slowly, at a rate comparable with that of the increase found in blank experiments with aqueous solutions of methyl thiocyanate.

## DISCUSSION

The relationship between the constants  $A$  and  $E_A$  of the Arrhenius equation  $k_2 = A \exp(-E_A/kT)$  has been frequently discussed.<sup>4</sup> Let us suppose, in the first place, that the theoretical expression for  $k_2$  is  $Z_0 \exp(-E/RT)(E/RT)^{s-1}/(s-1)!$ , where  $s$  is the number of classical oscillators among which the real energy of activation is shared, and  $Z_0$ , the standard collision frequency, is independent of temperature. It follows that  $E_A = E - (s-1)RT$ , and that, for a series of reactions conforming to these conditions,  $g = (d \ln A/d \ln E_A)_T$  is approximately  $(s-1)[1 + (s-1)(RT/E_A)]^{-1}$ . From the data relating to reactions of the halide ions with methyl iodide in water (Table 4),  $g$  appears to be about 11, and  $s$  about 18. Substitution of the latter value in the theoretical expression

TABLE 4

Kinetic constants for the reactions  $\text{CH}_3\text{I} + \text{X}^- \longrightarrow \text{CH}_3\text{X} + \text{I}^-$  in aqueous solution

$\text{X}^-$	$k_2$ at 298.16°K (l. mole <sup>-1</sup> sec. <sup>-1</sup> )	$E_A$ (cal./mole)	$\log_{10} A$	Ref.
F <sup>-</sup>	$7.08 \times 10^{-8}$	$25,200 \pm 500$	11.320	<i>a</i>
Cl <sup>-</sup>	$3.30 \times 10^{-6}$	$21,970 \pm 340$	10.620	<i>a</i>
Br <sup>-</sup>	$4.16 \times 10^{-5}$	$19,310 \pm 500$	9.780	<i>b</i>
OH <sup>-</sup>	$6.36 \times 10^{-5}$	$22,220 \pm 230$	12.093	<i>c</i>
SCN <sup>-</sup>	$3.58 \times 10^{-4}$	$19,950 \pm 400$	11.173	This work
I <sup>-</sup>	$4.71 \times 10^{-4}$	$17,580 \pm 200$	9.566	<i>d</i>
CN <sup>-</sup>	$5.76 \times 10^{-4}$	$20,470 \pm 120$	11.780	<i>e</i>
S <sub>2</sub> O <sub>3</sub> <sup>2-</sup>	$2.84 \times 10^{-2}$	18,880	12.202	<i>c</i>

*a*, R. Bathgate and E. A. Moelwyn-Hughes, *J.*, 1959, 2642. *b*, E. A. Moelwyn-Hughes, *J.*, 1938, 779. *c*, E. A. Moelwyn-Hughes, *Proc. Roy. Soc.*, 1949, *A*, 196, 541. *d*, E. R. Swart and L. J. LeRoux, *J.*, 1956, 2110. *e*, B. Marshall and E. A. Moelwyn-Hughes, *J.*, 1959, 2640.

for  $k_2$  leads to an abnormally low value of  $Z_0$ . Even with  $s$  as low as 12,  $Z_0$  is too low by a factor of  $10^7$ . It is clear that this formulation alone is incapable of explaining the trend

<sup>4</sup> Early references in E. A. Moelwyn-Hughes, "Kinetics of Reactions in Solution," 2nd edn., Oxford University Press, London, 1947.

of  $\ln A$  with  $\ln E_A$ . Let us next suppose that  $Z_0$  is dependent on temperature, as would be the case, for example, if the chemical reaction were controlled by diffusion. We would then have  $Z_0 = (\kappa T/3\eta)\{(r_A + r_B)^2/r_A r_B\}(N_0/1000)$  l. mole<sup>-1</sup> sec.<sup>-1</sup> where  $\eta$  is the viscosity of the solvent and  $r_A$  and  $r_B$  are the radii of the reactants. The observed energy of activation,  $E_A$ , would then contain the term  $-RT^2(d \ln \eta/dT)_P = B$  (say). In water,  $(dB/dT)_P$  at 37.5°C is roughly  $-22$  cal. mole<sup>-1</sup> degree<sup>-1</sup>. If, in addition, the energy of activation is distributed among a number of oscillators, whether classical or quantal,  $(dE_A/dT)$  also becomes negative. Now, although the bimolecular velocity constants,  $k_2$ , for these substitution reactions are not known as accurately as the unimolecular solvolysis constants,  $k_1$ , there is as yet no evidence that  $E_A$  for the bimolecular reactions decreases with a rise in temperature. It thus appears that a diffusion-controlled mechanism is improbable. Another possibility exists. It has been argued that  $Z_0$  for collisions involving solvent molecules is directly proportional to the viscosity, being approximately

$$(3\pi\eta/4n_s)(r_A + r_B)(1/m_A + 1/m_B)(N_0/1000)$$

is the concentration of solvent molecules. The negative term  $(dE_A/dT)_P$  anticipated from the distribution of energy can then be off-set by the positive term  $-(dB/dT)_P$ , leaving  $E_A$  independent of temperature. Moreover, the factor  $A$  of the Arrhenius equation is now proportional to the factor  $a$  in the viscosity equation  $\eta = a(T) \exp(B/\kappa T)$ . In water,  $a$  increases by a factor of 16 when the temperature is raised from 0 to 50°C. Because comparable experimental methods have been used in determining the data of Table 4, it is inevitable that reactions with high values of  $E_A$  were measured at the higher temperatures. The trend in the  $A$  factors can thus be understood. It remains to point out that the trends which we are seeking to understand are not found to a comparable extent in other solvents, for which the viscosity parameters  $a$  and  $B$  are constants. Although chemical effects, specific to the solutes, must appear in the complete picture, purely physical effects due to the abnormal properties of water may yet prove to be a contributing, if not the determining, factor.

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[Received, August 7th, 1964.]