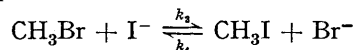


**152.** *The Kinetics of Two Ionic Exchange Reactions of the Methyl Halides in Ethylene Glycol Solution.*

By J. S. MCKINLEY-MCKEE and E. A. MOELWYN-HUGHES.

The reaction between methyl bromide and the iodide ion in ethylene glycol solution has been investigated kinetically, and the results have been compared with those previously obtained for the same reactions in other solvents.

IN this investigation the displacement reactions



have been studied in ethylene glycol as solvent in order to compare the results with those previously determined in water (Moelwyn-Hughes, *J.*, 1938, 779), methyl alcohol (*idem*,

*Trans. Faraday Soc.*, 1939, **35**, 368), and acetone (*idem, ibid.*, 1949, **45**, 167). As in other hydroxylic solvents, the displacement reactions are complicated at higher temperatures by simultaneous reaction with the solvent. The investigation has been here confined to temperatures where the solvolytic changes are negligible.

## EXPERIMENTAL

*Purification and Some Physicochemical Properties of Ethylene Glycol.*—The commercial sample of ethylene glycol used required only one distillation to be of satisfactory purity. The vacuum-distillation unit used for the purification was a Ramsay-Young apparatus, modified by the inclusion of an electrically heated 22" Fenske column packed with single-turn glass helices and equivalent to about 15 theoretical plates. The column head (Human, *J. Soc. Chem. Ind.*, 1949, **68**, 188) had a small hold-up and allowed a reflux ratio of 1 : 10 to be easily set and maintained. The pressure was regulated to  $\pm 0.1$  mm. and measured on a wide-bore manometer by means of a cathetometer. Two litres were distilled at a time at a pressure of 7–8 mm. of mercury and at a temperature of *ca.* 87.5°. A single controlled distillation gave a liquid of constant refractive index ( $n_D^{25}$  1.4304). Over the range 10–35°, the refractive index of pure ethylene glycol is given by the equation  $n_D = 1.5131 - 2.77 \times 10^{-4}T$ , where  $T$  is the absolute temperature, according to which  $n_D^{20} = 1.4318$  (Pukrev, *Trans. Inst. Pure Chem. Reagents*, 1937, **15**, 45, gives 1.4321; Landolt, *Ann. Physik*, 1864, **122**, 547, gives 1.42743).

Densities ( $d_4^t$ , g./ml.) and viscosities ( $\eta$ , g. cm.<sup>-1</sup> sec.<sup>-1</sup>) were determined at 20°, 30°, and 40°, the former being corrected for buoyancy, and the latter for kinetic energy effects according to British Standard Specification 188 (1937). The densities are given by the equation  $d_4^t = 1.31843 - 0.00070t$ , which agrees with the results of Riiber, Sorensen, and Thorkelsen (*Ber.*, 1925, **58**, 964) and of Pukrev (*loc. cit.*). The viscosities are reproduced by the equation  $\eta = 1.500 \times 10^{-4}e^{6885/RT}$  which gives values higher than those of Bingham and Fornwalt (*J. Rheology*, 1930, **1**, 373), but in agreement with those of Fordham (*Research*, 1948, **1**, 336). For the vapour-pressure measurements several temperature readings were taken when equilibrium was established at each pressure. The results are compared in the table with those given by

*Vapour pressure of ethylene glycol.*

$T$ , °K .....	358.8	373.9	379.8	386.1	392.6	397.7	406.1
$P$ , mm. { obs. ....	6.8	16.3	22.4	30.6	41.2	54.7	76.9
{ calc. ....	6.8	16.1	22.1	30.4	41.7	53.0	77.2
$T$ , °K .....	412.0	418.9	429.5	435.6	450.6	461.7	470.9
$P$ , mm. { obs. ....	98.0	132.0	202.6	244.2	400.7	592.4	773.2
{ calc. ....	99.4	132.1	198.8	249.0	416.0	590.6	776.7

the equation  $\log_{10} P$  (mm.) = 47.5695 - 12.485  $\log_{10} T$  - 5325.28/ $T$ . The boiling point is found to be 197.43° (Stull, *Ind. Eng. Chem.*, 1947, **39**, 517, gives 197.32°; Gallagher and Hibbert, *J. Amer. Chem. Soc.*, 1937, **59**, 2521, give 197.4°). The molar heat of evaporation ( $L$ ) varies with temperature according to the equation  $L$  (cal./mole) = 24 357 - 12.48 $RT$ , being 14 069 cal./mole at the b. p. (Stull, *loc. cit.*, gives 14 013; Gallagher and Hibbert, *loc. cit.*, give 13 633).

*Purification of Methyl Bromide.*—After a trap-to-trap distillation from solid carbon dioxide to liquid air, a commercial sample of methyl bromide was distilled through a low-temperature fractionating column which was equivalent to about 15 theoretical plates. The column was packed with Fenske helices and surrounded by a vacuum jacket to prevent heat interchange. A still head with a gaseous take-off was employed, a mixture of solid carbon dioxide and alcohol (–78°) being used to condense the methyl bromide. The take-off ratio was 1 : 10, an auxiliary condenser and tap enabling this to be controlled. The distillation was carried out smoothly at 40 mm. pressure, and the middle third was collected in a liquid-air condenser. The distillate was stored in a blackened glass receiver connected to the rest of the apparatus through a vacuum-tight bellows needle valve. Bubbling methyl bromide through silver nitrate solution showed that it contained no free acid or halogen, and passage over magnesium perchlorate did not affect its vapour pressure, which at the temperature of melting ice was 662.5  $\pm$  0.5 mm., in good agreement with the result of Egan and Kemp (*J. Amer. Chem. Soc.*, 1938, **60**, 2097), *viz.*, 662.61 mm. Digestion of a weighed amount with excess of potassium hydroxide also showed that the preparation was pure. The solubility of methyl bromide ( $c$ ) at various partial pressures ( $p$ ) was obtained by analysing saturated solutions prepared by shaking the vapour with ethylene glycol in a bulb attached to the vacuum-distillation apparatus. The results are shown in the following table.

*Solubility of methyl bromide in ethylene glycol at 20°.*

<i>p</i> (mm.) .....	49	105	190	293	492	758
<i>c</i> (moles/l.) .....	0.050	0.110	0.204	0.326	0.578	0.910
<i>p/c</i> × 10 <sup>-2</sup> .....	9.80	9.56	9.30	8.98	8.51	8.33

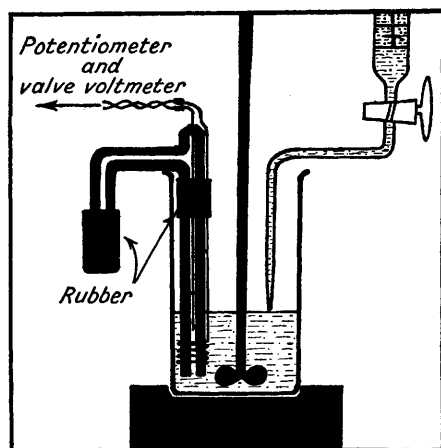
*The Solubility of Potassium Iodide and Bromide in Ethylene Glycol.*—"AnalaR" Potassium bromide and iodide were recrystallised from water, dried in a vacuum-desiccator, and kept in the dark. For the solubility measurements, saturated solutions were prepared by shaking the dry salts and ethylene glycol in stoppered tubes in a thermostat. From the accompanying

*Solubilities (g./l.) of potassium iodide and bromide in ethylene glycol.*

<i>T</i> , °K	KI		KBr		<i>T</i> , °K	KI		KBr	
	(obs.)	(calc.)	(obs.)	(calc.)		(obs.)	(calc.)	(obs.)	(calc.)
298.18	467.3	467.4	164.6	164.2	348.18	510.0	510.5	193.2	193.8
320.33	489.8	487.3	176.7	177.4	373.18	527.8	527.8	206.7	206.4

results, it is found that the solubility of the iodide is given by the equation  $S = 856.3e^{-358.7/RT}$ , the value at 298.18° K (467.3 g./l.) being lower than Walden's value of 472.3 g./l. (*Z. physikal. Chem.*, 1906, 55, 683). The solubility of the bromide is given by the equation  $S = 511.5e^{-672.8/RT}$  and is 167.2 g./l. at 303.18° K, which is slightly higher than Trimble's value of 165.9 g./l. (*J. Ind. Eng. Chem.*, 1931, 23, 165).

*Method of Analysis.*—Two methods were satisfactory for the analysis of mixtures of bromides and iodides. In the first the sample was split; the iodide was determined by Andrews's method (Moelwyn-Hughes, 1949, *loc. cit.*), and the total halide argentometrically, eosin being used as an adsorption indicator, in the presence of dilute acetic acid, which prevented the precipitation of mixed halide (Kolthoff and van Berk, *Z. anal. Chem.*, 1927, 70, 396). In the second and more convenient method, the iodide- and bromide-ion concentrations were obtained by a single potentiometric titration with 0.02M-silver nitrate. The electrode system (see Fig.) was a modification of Müller's capillary electrode (Müller, *Z. physikal. Chem.*, 1928, 135, 102; Stokes, Thesis, Cambridge, 1949), which has the advantages that there is no salt bridge, and that the titrations commence at zero e.m.f. The silver wire electrodes, when prepared by Clark's method (*J.*, 1926, 749), were quite stable, and reached equilibrium rapidly. The e.m.f. was measured on a Cambridge potentiometer, with a valve voltmeter (Garman and Drotz, *Ind. Eng. Chem. Anal.*, 1939, 11, 398) as a null indicator. From about 2 c.c. before the end-point

*Capillary electrode system.*

(indicated by the e.m.f.) to about 2 c.c. after, the silver nitrate solution was added in 0.02-c.c. increments, and the e.m.f. was recorded when steady. The first differences of the e.m.f. were plotted against the titre, symmetrical curves resulting, the mid-point of which gave the end-point of the titration. Following Leibich ("Die potentiometrische Bestimmung von Chlor, Brom und Iod," Diss., Dresden, 1920), 5% of barium nitrate was used in these titrations. Tests with prepared mixtures showed that the method was satisfactory even when the iodide : bromide ratio varied widely (1 : 8 to 8 : 1 by weight).

*Kinetic Procedure.*—Solutions of methyl bromide (0.08—0.10M) were prepared in the apparatus previously used to measure its solubility in ethylene glycol. The potassium iodide solutions (0.06—0.20M) were prepared by weight, and dissolved air was pumped out. In carrying out a run, 100 c.c. of iodide solution and 100 c.c. of methyl bromide solution were preheated in the thermostat, mixed, and sucked into a reaction vessel designed so that there was no vapour phase (Moelwyn-Hughes, *Trans. Faraday Soc.*, 1941, 37, 279). Blank experiments showed that the reactants were unaffected by mercury. As pure ethylene glycol is very hygroscopic, the solutions were protected from the atmosphere at all stages by magnesium perchlorate tubes. After being freed from air they were kept under an atmosphere of nitrogen. There was no evidence of oxidation during a run. Time was reckoned from the moment of

mixing. 10-C.c. samples, removed and analysed at convenient intervals, gave the rate of disappearance of iodide ion and the rate of appearance of bromide ion. For each run three or four samples were sealed off in Pyrex tubes with excess of potassium hydroxide solution, and after overnight digestion at 100°, analysed for inorganic iodide and bromide. The analytical values obtained for the various tubes agreed to within  $\pm 0.5\%$ .

*Stationary-state Constants.*—Runs at temperatures above 50° showed that there was reaction with the solvent, as in water (Moelwyn-Hughes, 1938, *loc. cit.*). However, at the temperatures

TABLE 1. *Observed and calculated stationary-state concentrations (m-mole/l).*

<i>T</i> , °κ	[I <sup>-</sup> ] <sub>0</sub>	[CH <sub>3</sub> Br] <sub>0</sub>	[Br <sup>-</sup> ] <sub>s</sub>	[CH <sub>3</sub> I] <sub>s</sub>	[I <sup>-</sup> ] <sub>s</sub>	[CH <sub>3</sub> Br] <sub>s</sub>	<i>K<sub>s</sub></i>
288.18	31.28	40.34	27.96 (27.96)	27.96 (27.96)	3.32 (3.32)	12.38 (12.38)	19.02 (19.0)
288.18	102.50	52.50	50.24 49.99	47.24 (49.99)	55.26 (52.51)	2.26 (2.51)	19.00 (19.00)
298.18	30.18	40.77	27.25 26.81	26.73 (26.81)	3.45 (3.37)	13.52 (13.96)	15.65 (15.4)
298.18	30.08	39.78	27.72 (26.60)	26.70 (26.60)	4.15 (3.50)	12.06 (13.18)	14.8 (15.4)
298.18	49.02	36.80	32.95 (32.58)	31.97 (32.58)	18.05 (16.44)	3.13 (4.22)	15.30 (15.40)
298.18	49.85	38.50	34.30 (33.83)	33.88 (33.83)	18.20 (16.02)	4.00 (4.67)	16.0 (15.4)
298.18	101.32	37.72	36.43 (36.39)	35.71 (36.39)	65.61 (64.93)	1.32 (1.33)	15.0 (15.4)
298.18	104.50	35.40	34.40 (34.30)	32.90 (34.30)	71.60 (70.20)	1.00 (1.09)	15.8 (15.4)
308.18	33.60	37.31	29.10 (27.50)	26.50 (27.50)	7.10 (6.10)	8.21 (9.81)	13.2 (12.7)
308.18	28.80	41.40	26.70 (25.54)	25.10 (25.54)	3.70 (3.26)	14.70 (15.86)	12.2 (12.7)
318.18	30.18	48.76	28.02 (27.02)	26.76 (27.02)	3.42 (3.16)	20.74 (21.74)	10.6 (10.6)
318.18	29.43	41.91	27.37 (25.63)	25.00 (25.63)	4.43 (3.80)	14.54 (16.28)	10.6 (10.6)

at which the exchange reactions were studied (288.18—318.18° κ) the amounts of organic halide that had reacted with the solvent were negligible, as can be seen from the very slight increase in the [I<sup>-</sup> + Br<sup>-</sup>] concentration (Table 3). The stationary state constant

$$K_s = [\text{Br}^-]_s[\text{CH}_3\text{I}]_s / [\text{I}^-]_s[\text{CH}_3\text{Br}]_s \simeq k_2/k_4$$

resembles an equilibrium constant, but changes slowly with time. Experimentally, it was obtained by analysis at the end of a run. Table 1 shows the observed and calculated stationary state concentrations obtained for the kinetic runs at the various temperatures. The observed concentration of organic halide is, as expected, generally slightly less than the calculated value.

TABLE 2. *Variation of the stationary-state constant K<sub>s</sub> with temperature.*

<i>T</i> , °κ	288.18	298.18	308.18	318.18
<i>K<sub>s</sub></i> { obs.	19.0	15.6	12.7	10.6
calc.	19.0	15.4	12.7	10.6

The equation

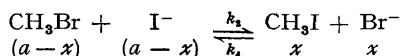
$$\log K_s = \bar{2}.5931 + 773.5/T \text{ or } K_s = 3.92 \times 10^{-2} e^{+3559/RT}$$

accounts for the change in *K<sub>s</sub>*. If *K<sub>s</sub>* is treated as an equilibrium constant, then at 298.18° κ,

$$\Delta G_s = -RT \ln K_s = -1620 \text{ cal. and } \Delta S_s = (\Delta H_s - \Delta G_s)/T = 17.3 \text{ cal./mole-degree}$$

These values are very similar to those obtained for these reactions in methyl alcohol (Moelwyn-Hughes, *loc. cit.*, 1939).

*Velocity Coefficients.*—As the concentrations used in these experiments did not exceed 0.1M, the limit of solubility of the potassium halides was not approached. The bimolecular constants for the opposing reactions



were calculated from the relation

$$dx/dt = k_2(a-x)(b-x) - k_4x^2$$

which on integration gives (see Moelwyn-Hughes, *loc. cit.*, 1938; "Physical Chemistry," Cambridge, 1950, p. 523)

$$k_2 = \frac{1}{2(1-K)Bt} \cdot \ln \left\{ \frac{1-x/(A+B)}{1-x/(A-B)} \right\}$$

$$x = \frac{ab}{1-K} \left\{ A+B \coth [(k_2 - k_4)Bt] \right\}^{-1}$$

where  $K = 1/K_s = k_4/k_2$ ,  $A = (a+b)/2(1-K)$ ,  $B = [(a-b)^2 + 4Kab]^{1/2}(1-K)$

Table 3 gives the results of a typical experiment. In all experiments  $k_2$  was calculated for each individual reading and obtained graphically by plotting  $\log \left\{ \frac{1-x/(A+B)}{1-x/(A-B)} \right\}$  against  $t$ . The latter method afforded a check on the zero of time.  $k_4$  was calculated from the relation  $k_4 = k_2/K_s$ . A three-fold increase in the concentration of potassium iodide at 298.18° K (Table 4) results in a decrease in the velocity coefficient, as found in acetone (Moelwyn-Hughes, *loc. cit.*, 1949).

TABLE 3.  $[\text{CH}_3\text{Br}]_0 = 0.04034\text{M}$ ;  $[\text{I}^-]_0 = 0.03128\text{M}$ ;  $T = 288.18^\circ \text{K}$ .

$t$ , min.	$[\text{I}^-]$	$[\text{I}^- + \text{Br}^-]$ (m-mole/l.)	$[\text{Br}^-]$		$10^3 k_2$ (l./mole- sec.)	$t$ , min.	$[\text{I}^-]$	$[\text{I}^- + \text{Br}^-]$ (m-mole/l.)	$[\text{Br}^-]$		$10^3 k_2$ (l./mole- sec.)
			(obs.)	(calc.)					(obs.)	(calc.)	
0	31.28	—	0	0	—	180	20.58	31.26	10.68	10.69	1.13
15	30.04	31.25	1.22	1.23	1.12	240	18.35	31.26	12.91	12.91	1.13
40	28.02	31.22	3.20	3.21	1.13	320	15.90	—	15.36	15.28	1.14
82	25.40	31.24	5.84	5.82	1.13	501	12.08	31.27	19.19	19.40	1.15
120	23.37	—	7.87	7.93	1.12	$\infty$	3.32	31.28	27.96	27.96	—

$K_s = 19.0$ ;  $k_2 = 1.13 \times 10^{-3}$  l./mole-sec.;  $k_4 = 0.60 \times 10^{-4}$  l./mole-sec.

TABLE 4. *Influence of concentration and temperature on the velocity coefficients.*

$T$ , °K	$[\text{I}^-]_0$ (m.-moles/l.)	$[\text{CH}_3\text{Br}]_0$ (m.-moles/l.)	$k_2 \times 10^3$ (l./mole-sec.)	$k_4 \times 10^4$ (l./mole-sec.)	$T$ , °K	$[\text{I}^-]_0$ (m.-moles/l.)	$[\text{CH}_3\text{Br}]_0$ (m.-moles/l.)	$k_2 \times 10^3$ (l./mole-sec.)	$k_4 \times 10^4$ (l./mole-sec.)
288.18	31.28	40.34	1.13	0.60	298.18	101.32	37.72	2.90	1.88
"	102.50	52.50	1.12	0.59	"	104.50	35.40	2.91	1.89
298.18	30.18	40.77	3.10	2.01	308.18	33.60	37.31	8.80	6.93
"	30.08	39.78	3.45	2.24	"	28.80	41.40	8.71	6.86
"	49.02	36.80	3.30	2.14	318.18	30.18	48.76	20.98	19.80
"	49.85	38.50	3.35	2.18	"	29.43	41.91	21.70	20.47

TABLE 5. *Influence of temperature on the velocity coefficients.*

$T$ , °K.	$k_2 \times 10^3$		$k_4 \times 10^4$		$T$ , °K.	$k_2 \times 10^3$		$k_4 \times 10^4$	
	(obs.)	(calc.)	(obs.)	(calc.)		(obs.)	(calc.)	(obs.)	(calc.)
288.18	1.13	1.14	0.60	0.60	308.18	8.76	8.70	6.90	6.85
298.18	3.28	3.26	2.13	2.12	318.18	21.70	21.84	20.47	20.58

Table 5 shows the effect of temperature on the velocity coefficients when constant concentrations of methyl bromide and potassium iodide are used. The equations

$$k_2 = 4.56 \times 10^{10} e^{-17927 \pm 260/RT} \quad \text{and} \quad k_4 = 1.08 \times 10^{12} e^{-21417 \pm 220/RT}$$

obtained by the method of least squares reproduce the experimental velocity coefficients. Owing to the nature of the reactions the results are neither extensive nor accurate enough to show whether the activation energy changes with temperature.

## DISCUSSION

In the following table the velocity constants and Arrhenius constants,  $A$  and  $E_A$ , obtained in this work are compared with those found in acetone, methyl alcohol, and water

(Moelwyn-Hughes, *loc. cit.*, 1949). The rates in ethylene glycol solution are seen to be about three times as fast as in methyl alcohol and about four times as fast as in water. A similarity between alcohols and glycols has also been found in the decarboxylation of

*Influence of the solvent on the kinetics of reactions between halogen ions and methyl halides.*

$\text{CH}_3\text{Br} + \text{I}^- \longrightarrow \text{CH}_3\text{I} + \text{Br}^-$			$\text{CH}_3\text{I} + \text{Br}^- \longrightarrow \text{CH}_3\text{Br} + \text{I}^-$				
Solvent	$10^4 k_{298.1}$ (l./mole-sec.)	$10^{10} A$	$E_A$ (cal./mole)	Solvent	$10^4 k_{298.1}$ (l./mole-sec.)	$10^{10} A$	$E_A$ (cal./mole)
Acetone ...	3550	1.15	14 340 ± 1200	Acetone...	4090	28.3	16 150 ± 1500
Glycol ...	32.6	4.56	17 927 ± 258	Glycol ...	2.12	108.0	21 417 ± 220
Methanol	9.42	2.26	18 250 ± 250	Methanol	0.798	39.1	21 400 ± 400
Water ...	6.84	1.68	18 250 ± 130	Water ...	0.461	1.08	19 620 ± 440

sodium trichloroacetate (Auerbach, Verhoek, and Henne, *J. Amer. Chem. Soc.*, 1950, **72**, 299) which proceeds at almost equal rates in ethylene glycol ( $E_A = 31\,600$  cal./mole) and in ethyl alcohol ( $E_A = 31\,800$  cal./mole).

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[Received, September 17th, 1951.]