298. *The Kinetics of the Reaction between Methyl Fluoride and Lithium Iodide in Acetone Solution.*

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The reaction between methyl fluoride and lithium iodide has been investigated in acetone solution in the absence of the vapour phase. The reversible reactions $MeCl + I^- \rightleftarrows MeI + Cl^-$ have been studied in the same solvent, by using lithium and potassium iodide. Complications arise owing to the low degree of ionisation of lithium chloride and the low solubility of potassium chloride. As far as quantitative allowance can be made for these effects, there appears to be no appreciable cationic effect on the velocity of reaction. A comparison of the rates of reaction of the iodide ion with methyl fluoride, chloride, and bromide shows that the entire effect of substitution is to alter the energy of activation E_A in the equation $k_2 = A \exp(-E_A/\mathbf{R}T)$. A has the normal value of about 2×10^{11} l. mole^{-1} sec.$^{-1}$. E_A changes by 7000 cal., and the rates of reaction at 25°c by a factor of about 77,000.

The object of this work was to obtain further experimental information on reactions of the type $MeX + Y^- \longrightarrow MeY + X^-$ in acetone solution, and in particular to examine a reaction where X is F.

Experimental

Materials.—Acetone, methyl chloride, and lithium iodide were of the purity described earlier.[1] Potassium iodide was recrystallised from distilled water and dried at 120° for several hours. Methyl fluoride was prepared by Lawson and Collie's method.[2] A 25% solution of tetramethylammonium hydroxide was neutralised with hydrogen fluoride, and the solution was evaporated at a low heat to the point of crystallisation. After cooling, the crystals were separated. It was not found possible to separate the crystals completely from the mother-liquor; they were dried in a vacuum at 160° for several hours. The dried salt was then decomposed into trimethylamine and methyl fluoride by raising the temperature to 180—210°. The issuing gases were passed through a trap cooled by solid carbon dioxide and acetone, and condensed in a receiver cooled by liquid air. The collected sample was passed through four evacuated bubblers containing concentrated sulphuric acid except that the second contained 33% potassium hydroxide solution, then over soda-lime, anhydrous calcium chloride, and phosphoric oxide, and was finally collected in a receiver cooled in liquid air. The purification was repeated and the material thrice fractionally distilled, the middle portion being retained in each operation. The final sample of methyl fluoride was pure by gas-chromatographic and spectrographic standards. The vapour pressures measured at three temperatures are shown in Table 1, along with the vapour pressure given by other investigators. Temperatures were measured with a platinum resistance thermometer calibrated by the National Physical Laboratory.

Table 1. *The vapour pressure of methyl fluoride.*

	Vapour pressure (mm. of mercury)		
Temperature	Moles and Batuecas [3]	Michels and Wassenaar [4]	This work
−82·053°	608·0	615·1	610·9
−78·321	750·8	759·4	755·2
−78·274	752·6	761·3	756·8

Solutions of the methyl halides and the alkali-metal salts in acetone were prepared as previously described.[1]

Reaction between Methyl Fluoride and Lithium Iodide in Acetone.—This reaction was studied in the absence of a vapour phase in a reaction previously described.[1] Solutions of methyl

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[1] Farhat-Aziz and Moelwyn-Hughes, *J.*, 1959, 2635.

[2] Lawson and Collie, *J.*, 1888, **53**, 624.

[3] Moles and Batuecas, *J. Chim. phys.*, 1919, **17**, 537.

[4] Michels and Wassenaar, *Physica*, 1948, **14**, 104.

fluoride in acetone (~70 mmoles/l.) and of lithium iodide of known strengths were brought to the working temperature, mixed, and poured into the reaction vessel. The reaction was followed by removing samples through a cotton-wool filter at measured time intervals, chilling to 0°, pipetting 5 c.c. into 10 c.c. of distilled water, adding 5 c.c. of 50% w/v sulphuric acid and 15 c.c. of acetone, and then titrating the mixture for inorganic iodide against standard ceric sulphate solution with ferroin as indicator.[5] The initial concentration of inorganic iodide was estimated by the same method at zero time.

The initial reaction mixture and the products were also analysed by gas-chromatography. The column contained 16% polyethylene glycol (*M* 400) on 60—80 mesh Silocel C.22. The column was 8 feet long. Hydrogen was used as carrier gas. The analysis showed that reaction goes to completion (Figs. 1 and 2). The distinctive peak of methyl fluoride in Fig. 1 has completely disappeared in Fig. 2. The peak for oxygen in both figures is attributable to oxygen absorbed in the acetone. The peaks of diethyl ether are internal standards.

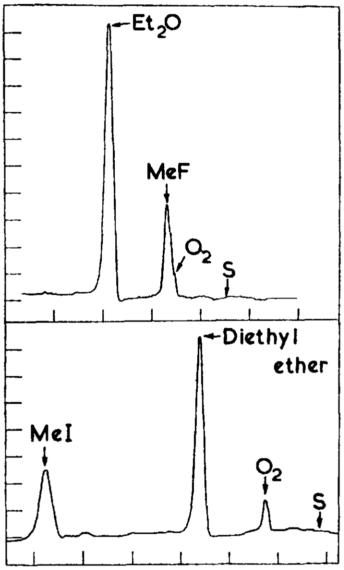

FIG. 1.

FIG. 2.

Gas-chromatograms of (FIG. 1) *methyl fluoride in ether and* (FIG. 2) *reaction product in ether.*

S = *sample injected.*

Runs carried out at 50° were followed to completion and the difference between the initial and the final concentrations of inorganic iodide gave the initial concentration of methyl fluoride. Runs at lower temperatures were too slow to be carried to their ends. In these cases, a sample of the mixture was sealed in a glass tube previously filled with nitrogen and heated for about two weeks at 50° to complete the reaction. The inorganic iodide was estimated and the initial concentration of methyl fluoride was then calculated. Incubation of the reaction mixture at 100° proved to be analytically unsuitable.

The reaction mixture stays clear to the naked eye, though lithium fluoride crystallises during the initial stages of the reaction. Temperatures were kept constant to within ±0·03°. The medical absorbent cotton wool used for filtration was washed with boiling distilled water and with acetone before being dried in an oven at low temperatures.

Kinetic Results.—As the reaction appears to be free from complications the usual second-order equation

$$k_2 = \frac{1}{t(b-a)} \ln \frac{a(b-x)}{b(a-x)}$$

can be used, where a and b are the initial concentrations of methyl halide and inorganic iodide, and x is the concentration of soluble product at time t. On the assumption that the rate-measuring step in the reaction between methyl fluoride and the iodide ion is $\text{MeF} + \text{I}^- \longrightarrow \text{MeI} + \text{F}^-$, we must modify this equation to allow for incomplete ionisation of lithium iodide, by replacing $(b - a)$ with $(b - a)\alpha_\infty$, b with $b\alpha_0$, and $(b - x)$ with $(b - x)\alpha$, where α_0, α_∞, and α

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[5] Lewis, *Ind. Eng. Chem. Analyt.*, 1936, **8**, 199.

are the degrees of ionisation of lithium iodide in acetone initially, finally, and at time t respectively. The modified equation is:

$$k_2 = \frac{1}{t(b-a)\alpha_\infty} \ln \frac{a(b-x)\alpha}{b(a-x)\alpha_0} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (1)$$

This equation is not rigorous.

Degrees of ionisation of lithium iodide in acetone solution have been derived from Blokker's data.[6] The results of a typical run are given in Table 2. The most reliable values of the second-order velocity constant k_2 are those calculated for points corresponding to 1/4, 1/2, and 3/4 of the complete reaction.

TABLE 2. *Bimolecular velocity constant k_2 for the reaction* $MeF + I^- \longrightarrow MeI + F^-$ *in acetone.*

Temp. = 50·00°; $[MeF]_0$ = 33·4 mmoles/l.

Time (hr.)	$[LiI]_t + [I^-]_t$ (mmoles/l.)	α	$10^4k_2 \times 10^4$ (l. mole^{-1} sec.$^{-1}$)	Time (hr.)	$[LiI]_t + [I^-]_t$ (mmoles/l.)	α	$10^4k_2 \times 10^4$ (l. mole^{-1} sec.$^{-1}$)
0·00	212·4	0·162	—	143·00	180·4	0·173	1·93
1·008	211·4	0·162	2·28	∞	179·0	0·173	—
3·004	209·6	0·163	2·41				Mean = 2·04
10·007	206·0	0·164	1·74	$t_{\frac{1}{4}}$ = 10·50	204·1	0·164	2·22
22·00	197·4	0·167	2·26	$t_{\frac{1}{2}}$ = 26·75	195·7	0·167	2·15
46·50	190·7	0·169	1·90	$t_{\frac{3}{4}}$ = 66·40	187·4	0·170	1·77
79·50	185·4	0·171	1·77				Mean = 2·05

Accepted value of $k_2 = 2{\cdot}05 \times 10^{-4}$ l./mole^{-1} sec.$^{-1}$.

The values of k_2 similarly obtained at different temperatures are summarised in Table 3. A systematic study of the effect of a change in the concentration of either reactant was not attempted. The Arrhenius equation obtained by the method of least squares is:

$$k_2 = 2{\cdot}01 \times 10^{11} \exp(-22{,}190/\boldsymbol{RT})$$

Values of k_2 reproduced by this equation are given in the fifth column of Table 3.

TABLE 3. *Bimolecular velocity constant k_2 in l. mole^{-1} sec.$^{-1}$ for the reaction* $MeF + I^- \longrightarrow MeI + F^-$ *in acetone.*

Temperature	$[MeF]_0$ (mmole/l.)	$[LiI]_0 + [I^-]_0$ (mmole/l.)	10^4k_2 Obs.	Calc.
25·00°	51·2	211·9	0·110	0·108
40·06	40·9	209·9	0·631	0·660
50·00	33·4	212·4	2·05	1·99

Cationic Effect in the Reaction between Methyl Chloride and Iodide Ion in Acetone.—The kinetics of the reaction between these materials in acetone have been studied before with lithium iodide as a source of I^-. To explore any possible specific effect due to a change in the cation, the same reaction has been investigated with potassium iodide as a source of I^-. The experimental conditions, unfortunately, are not quite comparable, because potassium chloride is only slightly soluble in acetone (1×10^{-5} mole/l.) [7] and the reaction from its initial stages becomes heterogeneous.

Procedure.—Kinetic and static aspects of the reaction between methyl chloride and potassium iodide in acetone have been studied by using an earlier type of vessel where mercury is used to exclude the vapour phase.[8] A vessel of the latest type [1] was used for a few equilibrium runs. Solutions of the reactants in acetone were separately prepared for each run, and samples were expressed through cotton-wool plugs as used in the methyl fluoride–lithium iodide reaction. Chilled samples were analysed for inorganic iodide by two methods. First, 5 c.c. of 50% w/v sulphuric acid and 5 c.c. of acetone were added, and the whole mixture was titrated against ceric sulphate solution for inorganic iodide with ferroin as indicator. Secondly, 5 c.c. of the same sample were evaporated under a vacuum, the residue was dissolved in 15—20 c.c. of water, and the solution was titrated against silver nitrate for total inorganic halides with dichlorofluorescein as indicator. The two titrations always agreed within the experimental error, showing the precipitation of potassium chloride to be quantitative.

The initial concentration of inorganic iodide was determined by both methods.

[6] Blokker, *Rec. Trav. chim.*, 1935, **54**, 975.
[7] Lannung, *Z. phys. Chem.*, 1932, *A*, **161**, 255.
[8] Moelwyn-Hughes, *Trans. Faraday Soc.*, 1941, **37**, 279.

To determine the initial concentration of methyl chloride, 5 c.c. of the reaction mixture were sealed with excess of N-sodium hydroxide in a glass tube and heated at 100°, for about 24 hr. to ensure complete hydrolysis. The hydrolysed sample was estimated for total halide by the silver nitrate method (with dichlorofluorescein in the presence of dextrin as a protective colloid). In some of the equilibrium runs, the concentrations of methyl chloride and iodide were estimated at equilibrium positions. The hydrolysed sample was neutralised with 33% acetic acid and then evaporated to dryness at a low heat. The residue was extracted with hot distilled water and washed. The filtrate was made up to 100 c.c. Portions (20 c.c.) were titrated against silver nitrate in the presence of 1 c.c. of N-ammonium carbonate and 4—6 drops of eosin adsorption indicator for iodide. Other parts (20 c.c.) were titrated for total inorganic halide by the silver nitrate method described above. The concentrations of total methyl halides, methyl chloride, and methyl iodide were thus obtained. The concentration of methyl iodide estimated at the equilibrium position was always in very good agreement with the decrease in the initial concentration of inorganic iodide. This fact again shows that potassium chloride is quantitatively precipitated.

Temperatures were kept constant to within ±0·03°. The reaction mixture became turbid during its initial stages but cleared within 0·5 hr., though the precipitation of potassium chloride continued. The time taken to reach transparency increased as the temperature was lowered.

Static Results.—Constancy of the expression, $K = [\text{MeI}][\text{Cl}^-]/[\text{MeCl}][\text{I}^-]$, can reasonably be expected, and, if the solubility product L of potassium chloride is constant, we have $L = [\text{K}^+][\text{Cl}^-]$, which in the present system is effectively $L = [\text{I}^-][\text{Cl}^-]$. Hence $K = [\text{MeI}]L/[\text{MeCl}][\text{I}^-]^2$. It was found, however, that $K'' = K/L$ was variable, but that the expression $K' = [\text{MeI}]/[\text{MeCl}][\text{I}^-]$ was constant. This suggests that the concentration of Cl^- in contact with crystalline potassium chloride under our experimental conditions remains constant throughout the reaction. The values of $1/K'$ at different temperatures and concentrations of the reactants have been summarised in Table 4. The iodide-ion concentration was obtained by using the degree of ionisation of potassium iodide in acetone derived from the data of Walden,[9] Fischler,[10] Walden, Ulich, and Busch,[11] Lannung,[7] Blokker,[6] and Dippy and Hughes.[12] A critical survey is given elsewhere.[13] For comparison, the value of $1/K''$ are also summarised in Table 4. The experimental values of K' are reproduced by the equation

$$\ln K' = (31{\cdot}03/\boldsymbol{R}) - (5565/\boldsymbol{RT})$$

With the concentrations shown in Table 4 it takes 5—6 weeks to reach equilibrium at 20°.

TABLE 4. *Equilibrium constants for the reaction* $\text{MeCl} + \text{I}^- \rightleftharpoons \text{MeI} + \text{Cl}^-$ *in acetone solution:* $K' = [\text{MeI}]_\infty/[\text{MeCl}]_\infty[\text{I}^-]_\infty$, $K'' = [\text{MeI}]_\infty/[\text{MeCl}]_\infty[\text{I}^-]_\infty{}^2$.

Temp.	$[\text{MeCl}]_0$	$[\text{KI}]_0 + [\text{I}^-]_0$ (mmoles/l.)	$[\text{KI}]_\infty + [\text{I}^-]_\infty$	α_∞	$10^6/K''$ (moles/l.^{2})	$10^3/K'$ (moles/l.^{2}) obs.
20·00°	35·55	29·65	6·56	0·659	10·1	2·33
20·00	53·16	15 33	$1{\cdot}00_6$	0·850	1·98	2·32
					Accepted =	2·33
25·00	—	—	—	—	—	(2·00)
30·00	18·02	30·35	15·61	0·513	14·3	1·78
30·00	52·91	30·33	$1{\cdot}66_3$	0·790	1·46	1·11
30·00	35·55	29·65	5·59	0·657	6·44	1·75
30·00	53·16	15·33	$0{\cdot}946_4$	0·850	1·74	2·17
					Mean =	1·70
40·00	18·02	30·35	15·25	0·496	11·1	1·46
40·00	52·91	30·33	$1{\cdot}49_3$	0·792	1·17	0·987
40·00	35·55	29·65	4·56	0·664	3·82	1·26
					Mean =	1·24
50·00	52·91	30·33	$1{\cdot}46_3$	0·783	1·09	0·954
50·00	34·81	29·14	3·84	0·668	2·47	0·964
50·00	53·16	15·33	0·404	0·920	0·354	0·952
					Mean =	0·957

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[9] Walden, *Z. phys. Chem.*, 1907, **59**, 196, 207.

[10] Fischler, *Z. Elektrochem.*, 1913, **19**, 131.

[11] Walden, Ulich, and Busch, *Z. phys. Chem.*, 1926, **123**, 429.

[12] Dippy and Hughes, *J.*, 1954, 953.

[13] Farhat-Aziz, Thesis, Cambridge, 1959.

Kinetic Results.—If the reactions occur exclusively between the polar molecules and the halide ions we have:

$$\mathrm{MeCl} + \mathrm{I}^- \underset{k_4}{\overset{k_2}{\rightleftharpoons}} \mathrm{MeI} + \mathrm{Cl}^-$$

With the earlier notation and the constant concentration of Cl^- denoted by s, the rate equation becomes:

$$\mathrm{d}x/\mathrm{d}t = k_2(a - x)\,(b - x)\alpha - k_4xs \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (2)$$

This equation cannot be integrated because α is a function of $(b - x)$, but if α is regarded as constant during a run and given the mean of its initial and final values then the equation can be integrated to give:[14]

$$k_2\alpha = \frac{1}{2\beta bt}\ln\left[\frac{a-(\gamma-\beta)x}{a-(\gamma+\beta)x}\right] \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (3)$$

where

$$\gamma = \tfrac{1}{2}\left[1 + \frac{a}{b} + \frac{1}{K'b\alpha}\right] \text{ and } \beta^2 = \gamma^2 - \frac{a}{b}$$

The α of ref. 14 is γ in our case.

Only the velocity constant k_2 for the direct reaction $\mathrm{MeCl} + \mathrm{I}^- \longrightarrow \mathrm{MeI} + \mathrm{Cl}^-$ can be found, because s is not known. Values of k_2 have been calculated by two methods. First, equation (2) has been used in its incremental form, by drawing tangents to the progress curve. Secondly, equation (3) has been used directly. The first method is physically superior because it involves no assumption concerning α. The values of k_2 obtained from it are the accepted values. Some of the kinetic runs were not followed to completion. Values of k_2 obtained by both methods for a specimen run are compared in Table 5. They sometimes show a falling trend with the progress of reaction but this is not general.

TABLE 5. *Bimolecular velocity constant* k_2 *for the reaction* $\mathrm{MeCl} + \mathrm{I}^- \longrightarrow \mathrm{MeI} + \mathrm{Cl}^-$ *in acetone.*

Temp. = 30·00°. $[\mathrm{MeCl}]_0$ = 24·15 mmoles/l.

Time (min.)	$[\mathrm{KI}]_t + [\mathrm{I}^-]_t$ (mmoles/l.)	α	10^4k_2 (l. mole^{-1} sec.$^{-1}$) by eqn. (3)	by eqn. (2)
0	42·28	0·408	—	—
—	38·99	0·418	—	16·8
—	37·01	0·421	—	18·8
150	36·39	—	17·9	—
—	33·19	0·431	—	17·4
—	30·98	0·438	—	18·2
—	29·41	0·441	—	16·7
570	28·47	—	17·6	—
1230	25·39	—	13·2	—
1890	22·97	—	15·5	—
3061	21·99	—	15·7	—
—	18·13	0·493	—	—
				Mean = 17·6

Values of k_2 obtained by the incremental method for runs with different initial concentrations at different temperatures are summarised in Table 6. They show that k_2 is not sensibly affected by changes in the initial concentrations. The calculated values are those reproduced by the Arrhenius equation:

$$k_2 = 6{\cdot}98 \times 10^{11} \exp\left(-20{,}250/\boldsymbol{R}T\right)$$

Comparison of the Velocity Constants k_2 *for the reaction* $\mathrm{MeCl} + \mathrm{I}^- \longrightarrow \mathrm{MeI} + \mathrm{Cl}^-$ *obtained with Lithium and Potassium Salts.*—A comparison of the experimental values of k_2 in the two systems (Table 7) shows that the reaction is somewhat faster with lithium than with potassium iodide. The apparent difference in the values of k_2 decreases with a rise in temperature and their ratio approximates to unity at the highest temperature examined. The absolute values

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[14] Moelwyn-Hughes, *Trans. Faraday Soc.*, 1949, **45**, 167.

of k_2 depend to some extent on the degrees of ionisation adopted. These, in turn, have been derived from the conductivity data of many investigators.

TABLE 6. *Accepted bimolecular velocity constant k_2 for the reaction* $MeCl + I^- \longrightarrow MeI + Cl^-$ *in acetone.*

Temp.	$[MeCl]_0$	$[KI]_0 + [I^-]_0$ (mmoles/l.)	10^4k_2 (l. mole^{-1} sec.$^{-1}$) obs.	calc.
20·00°	15·97	30·56	5·56	5·54
25·00	—	—	—	9·86
30·00	28·14	42·95	16·8	—
30·00	24·15	42·28	17·6	—
30·00	16·06	30·52	17·3	—
30·00	35·85	30·48	16·9	—
30·00	15·74	30·36	18·0	—
			Mean = 17·3	17·5
40·00	17·61	31·66	50·6	—
40·00	16·00	30·18	50·1	—
			Mean = 50·4	50·6
50·00	15·43	29·86	147	—
50·00	35·56	29·67	136	—
			Mean = 142	139

TABLE 7. 10^4k_2 (l. mole^{-1} sec.$^{-1}$) *for the reactions* $MeCl + I^- \longrightarrow MeI + Cl^-$ *in acetone.*

Temp.	With LiI	With KI	Ratio
20°	8·08	5·56	1·45
30	24·8	17·3	1·43
40	65·2	50·4	1·30
50	157	142	1·11

The uncertainty thus introduced makes it impossible to distinguish between the two sets of constants. The experimental evidence is clearly insufficient to establish any real specific effect of the cation on the rate of reaction. With either salt at 50°, $k_2 = 1{\cdot}5 \times 10^{-2}$ l. mole^{-1} sec.$^{-1}$, with a possible error of 5%. E_A for the reaction with LiI is 18,610 cal./mole, and with KI is 20,250. If we accept the mean value of $E_A = 19{,}430 \pm 820$, we obtain the equation

$$k_2 = 2{\cdot}07 \times 10^{11} \exp(-19{,}430/\boldsymbol{R}T)$$

DISCUSSION

Comparison of the Kinetics of the Reactions of the Iodide Ion with Three Methyl Halides in Acetone Solution.—Table 8 summarises what it known on the kinetics of the reactions between the iodide ion and methyl halides in acetone solution.

TABLE 8.

Reaction	10^5k_2 at 298·16°K (l. mole^{-1} sec.$^{-1}$)	$10^{-11}A$ (l. mole^{-1} sec.$^{-1}$)	E_A (cal./mole)
$MeF + I^- \longrightarrow MeI + F^-$	1·08	2·01	22,190
$MeCl + I^- \longrightarrow MeI + Cl^-$ ...	119	2·07	19,430 ± 820
$MeBr + I^- \longrightarrow MeI + Br^-$ ...	82,700	1·04	15,140 ± 1200

The last entry is based on earlier data [14] which have been corrected for the ionisation of potassium iodide at the various concentrations and temperatures employed. Unlike the other entries, the last one refers to systems containing the vapour phase. The same drawback attaches to later work on this reaction (Evans and Hamann; [15] Fowden, Hughes, and Ingold [16]). Despite this uncertainty there seems little doubt that, in this sort of reaction, changes in the velocity constants are due to changes in the activation energy, E_A.

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[15] Evans and Hamann, *Trans. Faraday Soc.*, 1951, **47**, 30.

[16] Fowden, Hughes, and Ingold, *J.*, 1955, 3187.

The term A of the Arrhenius equation $k_2 = A \exp(-E_A/\boldsymbol{R}T)$ is sensibly constant, though the absolute rates of reaction differ by a factor of 77,000. It happens, also, that E_A is a fairly constant fraction of the dissociation energy D_e of the carbon–halogen bond in the gas phase ($E_A/D_e = 0{\cdot}24$), as expected by Ogg and Polanyi.[17] In acetone solution there is thus no evidence that the energy required partially to desolvate the anion contributes significantly to the energy of activation, as it may well do in aqueous solution.[18]

[*Added in proof.*] Since this paper was communicated, Winstein, Savedoff, Smith, Stevens, and Gall (*Tetrahedron Letters*, 1960, No. 9, 24) have published kinetic results on the reaction of n-butyl *p*-bromobenzenesulphonate with lithium chloride, bromide, and iodide and with tetra-n-butylammonium chloride, bromide, and iodide in acetone solution. They confirm our conclusions that the rate-determining step is the bimolecular reaction between the organic molecule and the halogen ion, and that there is no specific effect due to the cation.

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[17] Ogg and Polanyi, *Trans. Faraday Soc.*, 1935, **31**, 615.
[18] Bathgate and Moelwyn-Hughes, *J.*, 1959, 2642.