149. *The Kinetics of Two Ionic Exchange Reactions of the Methyl Halides in Water.*

By E. A. Moelwyn-Hughes.

The replacement of bromine in methyl bromide by the iodide ion in aqueous solution is a bimolecular reaction which is opposed by the interaction of methyl iodide and the bromide ion, and complicated by the simultaneous hydrolysis of both methyl halides. The velocity constants for the two bimolecular reactions have been determined over a range of temperatures, and yield energies of activation, which, although possibly in error by a few hundred calories, are of sufficient accuracy for the purpose of comparison with similar figures for the reactions of the same halides with other ions.

The kinetics of the reactions of the methyl halides with other molecules, atoms, or ions, which we are now systematically investigating, are somewhat less complicated than those of the other *n*-alkyl halides, owing to the impossibility of olefin formation. In hydroxylic media, however, even the methyl halides react with solvent molecules, and quantitative allowance for this simultaneous reaction must be made in any careful study of such systems. The present paper describes the results of experiments on the replacement of the halogen atom in methyl bromide and methyl iodide by another halogen atom. Concurrent with the opposing bimolecular changes are the two unimolecular hydrolytic reactions, so that the kinetic scheme is as follows :

$$\begin{tikzcd}
CH_3Br + I^- \arrow[r, shift left, "k_2"] \arrow[d, "k_1"] & CH_3I + Br^- \arrow[l, shift left, "k_4"] \arrow[d, "k_3"] \\
CH_3{\cdot}OH + H^+ + Br^- & CH_3{\cdot}OH + H^+ + I^-
\end{tikzcd}$$

The magnitudes of the hydrolysis constants, k_1 and k_3, are known (Moelwyn-Hughes, *Proc. Roy. Soc.*, 1938, *A*, **164**, 295) ; and by means of chemical analysis and the velocity equations

$$+\,d[I^-]/dt = k_3[CH_3I] + k_4[CH_3I][Br^-] - k_2[CH_3Br][I^-] \quad . \quad . \quad (1)$$

$$+\,d[Br^-]/dt = k_1[CH_3Br] + k_2[CH_3Br][I^-] - k_4[CH_3I][Br^-] \quad . \quad . \quad (2)$$

the constants k_2 and k_4 have been evaluated over the workable ranges of temperature and concentration.

EXPERIMENTAL.

Solutions of the methyl halides in water were prepared in the apparatus previously described. By means of the distribution coefficients given in the previous paper, it was possible, by adjustment of the vapour pressure, to prepare solutions of the desired concentration. In order to avoid a measurable extent of hydrolysis during dissolution, the solutions were sometimes removed before they had reached the saturation point. Solutions of potassium bromide and iodide were made by weight. The two reactants were mixed after short storage in ice, and sealed off in glass tubes of about 20 c.c. capacity. Check experiments are required to obtain accurate zero-time corrections—a factor of some importance for bimolecular mechanisms. After immersion for a measured time in the thermostat, the tubes were cooled in ice, and the contents analysed for total halide by Volhard's method, for inorganic iodide by the iodate method, and for hydrogen ion. The standard solutions were about N/100. Attention to the details of the volumetric analyses (for which I am much indebted to Mr. A. J. Berry) enables the concentrations of solutes to be estimated to a fraction of a millimole per litre. This is the unit of concentration used in this work.

The simple kinetic scheme outlined above must satisfy two requirements: (1) The final concentration of that inorganic ion which is present at the start must equal its initial concentration: this condition is demanded by the effective irreversibility of the hydrolyses. (2) Over the whole range of reaction the following equation must hold:

$$[\mathrm{Br}^- + \mathrm{I}^-]_t - [\mathrm{I}^-]_0 = [\mathrm{H}^+]_t \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (3)$$

The initial and final concentrations of inorganic halides for a few experiments are shown in Table I, from which it is seen that equation (3) is more closely followed when bromide ion is present initially than when iodide ion is present initially. The figures in cols. 3 and 6 show that the apparent concentration of bromide ions and the actual concentration of iodide ions are, respectively, greater and less at the end of the reaction than at the beginning. Both discrepancies have a common origin in the oxidation of the iodide ion, chiefly, if not entirely, to molecular iodine. Titration with thiosulphate after chloroform extraction, gave, *e.g.*, the values 2·0 and 5·7 for $[\mathrm{I}_2]$, corresponding to the first and the last entry in col. 6. The present technique for working with the solutions of volatile vapours does not allow of the complete elimination of atmospheric oxygen. The effect of this side reaction on the course and velocity of the ionic exchange reaction is, however, slight, for, as seen in Table II, the oxidation reaction is relatively slow, and plays no appreciable part during such times as are required for substitution.

TABLE I.

$[\mathrm{Br}^-]_0$.	$[\mathrm{Br}^-]$.	Diff.	$[\mathrm{I}^-]_0$.	$[\mathrm{I}^-]$.	Diff.
26·3	26·3	0	49·6	47·5	−2·1
50·6	50·8	+0·2	50·0	49·1	−0·9
52·1	52·4	+0·3	50·2	48·2	−2·0
99·6	100·2	+0·6	50·5	49·7	−0·8
99·8	100·3	+0·5	50·8	49·1	−1·7
99·9	100·7	+0·8	99·5	99·2	−0·3
103·0	104·2	+1·2	151·0	144·6	−6·4

TABLE II.

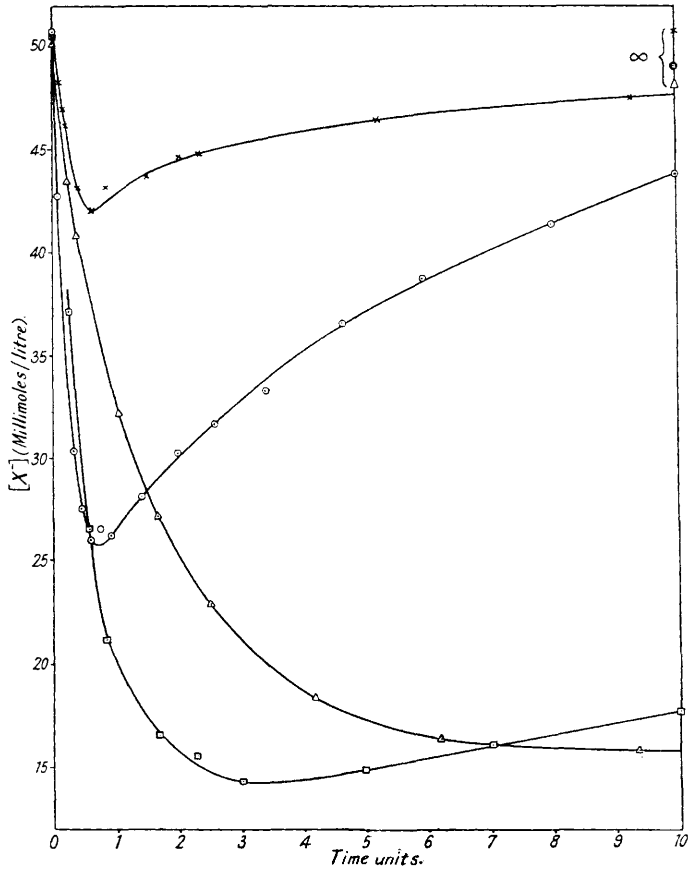
$T = 323{\cdot}37°$ K. $[\mathrm{I}^-]_0 = 50{\cdot}5$.
$[\mathrm{CH_3Br}]_0 = 52{\cdot}7$.

t, mins.	$[\mathrm{I}^-]$.	$[\mathrm{I}^- + \mathrm{Br}^-]$.	$[\mathrm{H}^+]$.	$[\mathrm{I}^- + \mathrm{Br}^-] - [\mathrm{I}^-]_0$.
0	50·4	50·6	0·2	0·1
7	43·8	50·9	0·5	0·4
10	40·3	51·7	0·6	1·2
13	38·3	51·1	0·4	0·6
23	33·4	51·0	0·6	0·5
33	28·3	51·3	1·4	0·8
43	—	51·8	1·4	1·3
63	19·3	52·3	1·8	1·8
83	14·7	52·6	2·3	2·1
153	13·9	53·8	3·1	3·3
233	12·8	55·5	4·5	5·0
393	12·2	56·8	5·8	6·3
1333	19·0	65·5	17·6	15·0
∞	49·7	103·2	49·0	52·7

$T = 362{\cdot}46°$ K. $[\mathrm{I}^-]_0 = 50{\cdot}8$.
$[\mathrm{CH_3Br}]_0 = 35{\cdot}6$.

t, mins.	$[\mathrm{I}^-]$.	$[\mathrm{I}^- + \mathrm{Br}^-]$.	$[\mathrm{H}^+]$.	$[\mathrm{I}^- + \mathrm{Br}^-] - [\mathrm{I}^-]_0$.
0	50·8	50·8	0	0
1	42·8	52·8	2·2	2·0
4	30·4	53·5	3·6	2·7
5·5	27·6	54·8	3·8	4·0
7	26·0	55·4	4·6	4·6
9	26·6	56·4	5·5	5·6
11	26·3	57·9	5·8	7·1
17	28·2	59·4	8·4	8·6
24	30·3	61·4	10·6	10·6
31	31·7	63·3	12·5	12·5
41	33·3	66·4	15·1	15·6
56	36·6	68·8	18·4	18·0
71	38·8	72·4	21·0	21·6
96	41·4	75·8	25·1	25·0
121	44·1	78·4	26·1	27·6
∞	49·1	86·4	—	35·6

The results of a few typical experiments are shown graphically in the figure, where the concentration of that halide ion which was present initially is shown as a function of the time. The plots of the concentrations of organic halide against time, would, of course, be nearly the mirror images of these curves. From the analytical data it is possible, but unnecessary, to reproduce for any given experiment graphs showing the variation in the concentrations of all six solutes with time. The course of the curve formed by the time-variation of the concentration of the liberated ion, is, however, of interest; it rises rapidly to a stationary value, after which it rises with the slower velocity that is quantitatively in agreement with that of the hydrolysis of the organic halide.



× T = 324·52° K. *Time unit* = 300 *mins.* $[CH_3I]_0$ = 39·6. $[Br^-]_0$ = 50·7.
⊙ T = 362·46° K. *Time unit* = 12 ,, $[CH_3Br]_0$ = 35·6. $[I^-]_0$ = 50·8.
⊡ T = 340·01° K. *Time unit* = 12 ,, $[CH_3Br]_0$ = 48·4. $[I^-]_0$ = 50·0.
△ T = 308·61° K. *Time unit* = 120 ,, $[CH_3Br]_0$ = 41·1. $[I^-]_0$ = 50·2.

TABLE III.

T = 308·61° K.				*T* = 298·03° K.			
t, mins.	$[I^-]$.	$[I^- + Br^-]$.	$[Br^-]$.	*t*, mins.	$[I^-]$.	$[I^- + Br^-]$.	$[Br^-]$.
0	0	99·6	99·6	0	0	99·6	99·6
25	1·3		98·3	30	0·8	99·7	98·9
35	2·0		97·6	67	1·2	99·9	98·7
105	4·7		94·9	233	2·4	99·8	97·4
165	6·8	99·6	92·8	1165	8·3	100·0	91·7
415	11·8	100·2	88·4	1680	10·0	100·5	90·5
852	14·0	101·0	87·0	4020	12·9	101·3	88·4
1313	15·1	102·0	86·9	∞	55·1	155·4	100·3
∞	58·4	158·6	100·2				

With solutions containing initially no iodide ion, the oxidation process is entirely negligible at low temperatures, and direct estimation of hydrogen ion for each sample is unnecessary. Some typical figures are shown in Table III, from which it is clear that under these conditions the exchange reaction passes its half-life without interference by the hydrolysis.

Determination of the Ratio, k_2/k_4.—In a study of opposing reactions, the determination of the ratio of the two velocity constants conveniently precedes the absolute evaluation of either. Numerous methods are available; the first one to be employed is as follows.

Two complementary experiments were carried out at 308·61° K., the reaction being allowed to start from opposite ends. In both cases the concentration of the inorganic halide decreased to a stationary value. With $[I^-]_0 = 50{\cdot}2$ and $[CH_3Br]_0 = 40{\cdot}1$, the stationary-state concentrations are reached after 1150 minutes, and yield the ratio

$$\{[Br^-][CH_3I]/[I^-][CH_3Br]\}_{I^-} = 36{\cdot}1 \times 34{\cdot}7/15{\cdot}5 \times 4{\cdot}1 = 19{\cdot}7$$

For the other experiment, with $[Br^-]_0 = 99{\cdot}6$ and $[CH_3I]_0 = 58{\cdot}4$, the values are

$$\{[Br^-][CH_3I]/[I^-][CH_3Br]\}_{Br^-} = 87{\cdot}0 \times 43{\cdot}8/14{\cdot}9 \times 12{\cdot}6 = 20{\cdot}3$$

To conclude from these figures that $k_2/k_4 = 20{\cdot}0 \pm 0{\cdot}3$ is, however, fallacious, for the figures show the incidence of hydrolysis to the extents 1·4 and 2·3 millimoles per litre respectively. The inequality of the two ratios is genuine, and, provided it can be magnified, may be used to determine the ratio of the bimolecular constants.

Let the ratio of the concentrations (as written above) which correspond to the minimal concentration of iodide ion be denoted by R_{I^-}, and the same ratio corresponding to the minimal concentration of bromide ion by R_{Br^-}; then, by equations (1) and (2) we have

$$k_2/k_4 = R_{I^-}\{1 + k_3/k_4[Br^-]_{I^-}\} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (4)$$

and

$$k_2/k_4 = R_{Br^-} - k_1/k_4[I^-]_{Br^-} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (5)$$

For a pair of experiments at 340·01° K., it was found that $[I^-]_0 = 50{\cdot}0$; $[CH_3Br]_0 = 48{\cdot}4$; $R_{I^-} = 10{\cdot}9$; $[Br^-]_0 = 99{\cdot}9$; $[CH_3I]_0 = 52{\cdot}5$; $R_{Br^-} = 14{\cdot}6$. Full allowance being made for the experimental error, these figures suffice to fix the ratio k_2/k_4 as $13{\cdot}3 \pm 0{\cdot}3$ at this temperature. At lower temperatures, fairly reliable values of the ratio may be found from experiments on the initial rates with halide ions in excess. The best values found by both methods are summarised in Table IV, along with those given by the empirical relation

$$k_2/k_4 = 2{\cdot}79 \times e^{-1,050/RT} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (6)$$

TABLE IV.

T	....	293·53°	298·19°	308·61°	323·95°	340·01°
k_2/k_4	Obs.	16·9	16·5	15·4	14·3	13·3
	By formula ...	16·9	16·4	15·5	14·3	13·2

The energy term in the formula is to be regarded as the minimum value, and may be as much as 630 cals. low. Uncertainties in the energy amounting to this are unavoidable when the ratio of the constants differs widely from unity, as is seen from the figures in Table V, where stationary concentrations (denoted by subscript S) found experimentally at some of the lower temperatures are compared with the values (shown in parentheses) calculated from the approximate relation

$$[Br^-]_s[CH_3I]_s/[I^-]_s[CH_3Br]_s \approx k_2/k_4 \quad . \quad . \quad . \quad . \quad . \quad . \quad (7)$$

In the majority of cases, the stationary concentration of the alkyl halide is less than that calculated from the approximate formula (7), as is to be expected.

Determination of the Constants k_2.—The two methods found most suitable for the evaluation of the bimolecular constant, k_2, are : (i) The determination of the position of minima for solutions with different initial concentrations at the same temperature; equations (4) and (5) are directly applicable, irrespective of the extent of hydrolysis, and yield reliable absolute values of the constants at the higher temperatures. (ii) The determination of the bimolecular constant for a system of opposing reactions, only those

TABLE V.

T.	$[Br^-]_0$.	$[CH_3I]_0$.	$[I^-]_0$.	$[CH_3Br]_0$.	$[Br^-]_e$.	$[CH_3I]_e$.	$[I^-]_e$.	$[CH_3Br]_e$.
293·21°	0	0	150·7	59·6	57·3	57·2	93·5	2·3
					(57·5)	(57·5)	(93·2)	(2·1)
	2·0	0	49·5	47·2	41·2	37·2	12·3	8·0
					(40·6)	(38·6)	(10·9)	(8·6)
	26·3	27·3	0	0	21·9	22·9	4·4	4·4
					(21·1)	(22·1)	(5·2)	(5·2)
	52·1	52·1	0	0	41·2	40·5	11·6	10·9
					(41·9)	(41·9)	(10·2)	(10·2)
	100·3	51·7	0	0	89·1	37·8	13·9	13·9
					(88·9)	(37·7)	(14·1)	(14·1)
298·11	0	0	100·8	50·4	47·7	46·7	54·1	2·7
					(47·8)	(47·8)	(53·1)	(2·7)
	99·7	56·0	0	0	88·2	42·4	13·6	11·5
					(85·0)	(41·3)	(14·7)	(14·7)
308·61	0	0	50·2	40·1	36·1	34·7	15·5	4·0
					(35·5)	(35·5)	(14·7)	(4·6)
	99·6	58·7	0	0	87·0	43·8	14·9	12·6
					(84·2)	(43·3)	(15·4)	(15·4)

values being accepted which refer to stages where hydrolysis can legitimately be ignored. Denoting by a and b the initial concentrations of methyl bromide and iodide ion respectively, and by x the amount of bromide ion at time, t, we have

$$\underset{(a-x)}{CH_3Br} + \underset{(b-x)}{I^-} \underset{k_4}{\overset{k_2}{\rightleftarrows}} \underset{x}{CH_3I} + \underset{x}{Br^-}$$

$$+\ dx/dt = k_2(a-x)(b-x) - k_4x^2 \ . \ . \ . \ . \ . \ . \ . \quad (8)$$

which gives on integration

$$x = ab/\{A + B \coth [tB(k_2 - k_4)]\}(1 - K) \ . \ . \ . \ . \ . \ . \quad (9)$$

where $K = k_4/k_2$, $A = (a + b)/2(1 - K)$, and $B = \{(a - b)^2 + 4Kab\}^{\frac{1}{2}}/2(1 - K)$.

Two examples of the applicability of this equation for the early stages of experiment are illustrated in Table VI, from which average values of $3{\cdot}71 \times 10^{-4}$ and $7{\cdot}02 \times 10^{-4}$ have been obtained for k_2, expressed in l./mole-sec.

TABLE VI.

$T = 292{\cdot}3°$ K. $a = 47{\cdot}2$. $b = 49{\cdot}6$. $k_2/k_4 = 17{\cdot}0$.

t (mins.).	x.	10^4k_2 (l./mole-sec.).
0	0	—
40	1·9	3·62
80	3·8	3·73
115	5·4	3·78
140	6·3	3·70
370	14·3	3·92
460	15·7	3·53
1580	27·2	2·91
2880	31·0	2·30
4380	35·2	2·51

$T = 298{\cdot}19°$ K. $a = 50{\cdot}4$. $b = 100{\cdot}8$. $k_2/k_4 = 16{\cdot}4$.

t (mins.).	x.	10^4k_2 (l./mole-sec.).
0	0	—
20	4·1	7·18
38	7·2	6·95
136	20·5	7·04
306	32·5	7·11
435	37·0	6·81
845	43·8	6·40

The data in Table VII show the extent to which the constants k_2 may be reproduced by the equation

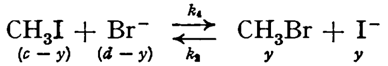
$$k_2 = 1{\cdot}68 \times 10^{10} \times e^{-18{,}260/RT} \ . \ . \ . \ . \ . \ . \ . \quad (10)$$

TABLE VII.

T	273·6°	292·30°	293·53°	298·19°	308·61°	323·37°	340·01°
$k_2 \times 10^4$ Obs.	0·453	3·71	4·26	7·02	20·0	77·6	312
$k_2 \times 10^4$ By formula ...	0·442	3·68	4·31	7·00	20·2	76·8	313

The apparent energy of activation, E_2, is accurate to within ± 130 cals., and $(\delta E_2/\delta T)_P$ must lie within the rather wide limits ± 6·9 cals./mole-degree.

Determination of the Constants k_4.—Measurements of the constants k_4 present greater difficulties because (i) the extent of chemical change is less, and (ii) on account of the low value of k_4, the hydrolytic complication is relatively greater. For the simple kinetic system



$$\underset{(c-y)}{CH_3I} + \underset{(d-y)}{Br^-} \underset{k_2}{\overset{k_4}{\rightleftharpoons}} \underset{y}{CH_3Br} + \underset{y}{I^-}$$

we have

$$+\,dy/dt = k_4(c-y)(d-y) - k_2y^2$$

which gives on integration

$$y = cd/\{C + D \coth [tD(k_2 - k_4)]\}(L - 1) \quad . \quad . \quad . \quad . \quad . \quad (11)$$

where $L = k_2/k_4$, $C = (c + d)/2(L - 1)$, and $D = \{(c - d)^2 + 4Lcd\}^{\frac{1}{2}}/2(L - 1)$.

The use of this formula, with the values of L given by equation (6), leads to initial values of k_4 which, though falling with time as required, show no regular decline from which a reliable initial figure can be obtained. With the experimental ratio of the stationary concentrations, however, the method gives moderately good results. Examples of both types of figures are shown in Table VIII, where interpolated values of y are used. In view of the inherent difficulties, the final values of k_4 (Table IX) are in satisfactory agreement with those anticipated by combining equations (6) and (10), *viz.*,

$$k_4 = 6{\cdot}02 \times 10^9 \times e^{-19{,}310/RT} \quad . \quad . \quad . \quad . \quad . \quad . \quad (12)$$

The apparent energy of activation, E_4, lies near the lower of the two limits, which are 19,170 and 20,060 cals./mole. The uncertainty in the true value of the energy of activation is thus of the same order of magnitude as the correction which appears necessary for the electrostatic contribution, which amounts to $N_0 z_B \varepsilon \mu_A \cos \theta (LT - 1)(1 - \frac{1}{2}\kappa r)e^{-\kappa r}/Dr$ (Moelwyn-Hughes, *Proc. Roy. Soc.*, 1936, *A*, **157**, 667).

TABLE VIII.

$T = 298{\cdot}03°$ K. $c = 56{\cdot}0$. $d = 99{\cdot}7$. $k_2/k_4 = 16{\cdot}4$.

t (mins.).	y.	10^5k_4 (l./mole-sec.).
0	0	—
260	2·7	3·25
560	4·7	2·75
960	6·7	2·44
1560	8·7	2·12
2800	10·7	1·64

$T = 308{\cdot}61°$ K. $c = 58{\cdot}7$. $d = 99{\cdot}6$. $k_2/k_4 = 20{\cdot}0$.

t (mins.).	y.	10^4k_4 (l./mole-sec.).
0	0	—
76	3·6	1·44
130	5·6	1·39
199	7·6	1·33
280	9·6	1·34
404	11·6	1·35

TABLE IX.

T	293·53°	308·61°	324·52°	340·01°
$k_4 \times 10^4$ Obs.	0·269	1·35	6·70	24·1
$k_4 \times 10^4$ By formula	0·257	1·29	6·02	23·4

THE DEPARTMENT OF PHYSICAL CHEMISTRY,
THE UNIVERSITY, CAMBRIDGE.

[*Received, March* 10*th*, 1938.]