Mechanism of Substitution at a Saturated Carbon Atom. Part XLVI. Kinetics of the Interaction of Iodide Ions with Simple Alkyl Bromides in Acetone.*

By L. Fowden, E. D. Hughes, and C. K. Ingold.

[Reprint Order No. 6210.]

Kinetic experiments on the second-order reactions of halogen substitution by potassium, sodium, and lithium iodides with seven simple alkyl bromides in acetone are reported. Reactions with the first two salts become heterogeneous, and, in the faster initial parts of the intrinsically faster reactions, errors arise from the relatively slow establishment of equilibrium in composition between the phases, a disturbance which a reduced temperature does not cure, since it lowers the rate of the surface transfers even more than the reaction rate. Reactions with lithium iodide remain homogeneous, and the main disturbance now is the negative salt effect, which, however, is not large enough in these reactions to interfere with the determination of good initial rates. The reactions are successively more reversible along the series, methyl, primary, secondary, and tertiary alkyl. The precipitations which occur with potassium and sodium salts as reagent limit the reversals, and, although the assistance of such limitation is not necessary for the kinetic study of the forward reaction in general, it had to be employed in the reaction of *tert.*-butyl bromide, which, fortunately, is not one of the faster reactions. With precautions against the errors diagnosed, rate constants and parameters of the Arrhenius equation were determined.

The early work of Conant, Kirner, and Hussey (*J. Amer. Chem. Soc.*, 1924, **46**, 232; 1925, **47**, 476, 488) on the kinetics of Finkelstein substitutions dealt specially with the reactions of potassium, sodium, and lithium iodides with a series of alkyl chlorides in acetone.

---

* Part XLV, preceding paper.

With potassium and sodium iodides as reagent, the alkali-metal chlorides became precipitated, with strong suppression of the back-reaction, though the substitutions are markedly reversible in homogeneous media. With lithium iodide as reagent, the solutions remained homogeneous, and the substitutions proceeded to their natural equilibria. However, it was found that, for a given alkyl chloride at a given temperature, the rate-constant of the forward reaction was substantially independent of the nature of the cation of the metal iodide, and the conclusion was drawn that the substituting agent is the iodide ion.

This was the starting point of the work now described, chronologically the first of the studies here reported together. The reactions examined were those of potassium, sodium, and lithium iodides with a series of alkyl bromides in acetone. With potassium and sodium iodides, the alkali-metal bromides became precipitated, with marked suppression of the retrograde substitutions, whilst with lithium iodide the solutions remained homogeneous, and the reactions ran to equilibrium. We went over to alkyl bromides with the idea that bromine and iodine would probably have more nearly similar properties in Finkelstein substitutions than any other pair of chemically different halogens, and that with them we might be able, with similar ease and accuracy, to examine the kinetics of substitution in both directions, and thus to pass on to a study of the thermodynamics of the reaction, as has proved to be the case.* Our main concern being with the kinetic and thermodynamic effects of simple alkyl groups in substitution, we have concentrated upon the seven groups which compose the α- and the β-methylated branching-homologous series, Me, Et, Pr^i, Bu^t, and Et, Pr^n, Bu^n, *neo*Pe (*i.e.*, *neo*pentyl). Interested as we are in the derivation of energy quantities, we have paid particular attention to effects of temperature.

As to previous work on the kinetics of reactions of alkali-metal iodides on alkyl bromides in acetone, A. G. Evans and Hamann (*Trans. Faraday Soc.*, 1951, **47**, 30) have recorded some rate constants for the reactions of potassium iodide with methyl and *iso*propyl bromide: their values are some 50% larger than ours. We think that the large discrepancy is due to their method: they tried to measure the disappearance of dissolved potassium iodide by the fall of electrical conductance, but in conditions in which a precipitate of potassium bromide was being formed between and round the electrodes, thereby contributing, by mechanical obstruction, to the fall of electrical conductance. Skolink, Day, and Miller (*J. Amer. Chem. Soc.*, 1943, **65**, 1858) had previously declared such a method to be unsuitable, and the trials of it which have been made in these laboratories support their opinion.

We followed the disappearance of iodide ions by chemical analysis. The errors involved in our work are discussed below. We used the sealed-tube technique, which permits more accurate timing than when samples have to be taken, and avoids the difficulty of sampling those reactions mixtures in which a precipitate is formed.

Anticipating part of the following discussion and record, we find that, except for disturbances which we think can be explained and are appreciable only in a few cases, the rate-constants for a given alkyl bromide at a given temperature are independent of the nature of the cation of the saline reagent. This confirms the similar finding of Conant and his co-workers for the corresponding reactions of alkyl chlorides. We conclude, as they did, that the effective substituting agent is the halide ion, our reaction being expressible by the scheme,

$$I^- + RBr \longrightarrow RI + Br^-$$

Turning now to errors, a special group of kinetic disturbances applies to the reactions with potassium and sodium iodides. The attraction of using these reagents is that the precipitation of potassium or sodium bromide suppresses the retrograde substitution, with the result that rate constants can be calculated in the simple way applicable to an

---

* Some support for this idea was subsequently found in the comparison, for lithium and methyl halides in acetone, of the equilibrium constant of the chlorine–bromine Finkelstein exchange, and of the bromine–iodine exchange: the former constant is much further from unity than is the latter. For the system, $LiCl + MeBr \rightleftharpoons LiBr + MeCl$, the equilibrium constant $K = [LiBr][MeCl]/[LiCl][MeBr]$ is 17·5 ± 1·3 in acetone at 40° (personally communicated by Dr. P. B. D. de la Mare). For the system, $LiBr + MeI \rightleftharpoons LiI + MeBr$, the constant $K = [LiI][MeBr]/[LiBr][MeI]$ is only 1·7 at 16°, and, being nearly independent of temperature, must be about 1·6 at 40° (following paper).

irreversible reaction of the second order. Actually, owing to the finite solubilities of the metal bromides, especially of the more soluble of them, sodium bromide, the retrograde substitutions are not completely suppressed; but still, in our conditions, the reactions with potassium iodide could be carried forward to over 90% of the stoicheiometric maximum, and most of the reactions with sodium iodide could be carried to more than 75%; and thus it was easily possible to apply the equation for an irreversible reaction of the second order to the first 30—50% of reaction, thereby obtaining good rate constants appropriate to the initial conditions. The reaction of *tert.*-butyl bromide formed a partial exception. Here, the natural reversibility of the substitution is so strong that, although the reaction with potassium iodide went sufficiently far forward to allow the above procedure, the reaction with sodium iodide did not go beyond about 40% of the stoicheiometric maximum, and we could find no satisfactory way, in this case, of calculating rate constants for the forward reaction with proper allowance for such a strong, yet partly restricted, retrograde reaction.

The main kinetic disturbances to be expected from the precipitation are those due to temporary supersaturation with respect to the alkali-metal bromide, and to initial co-precipitation of some of the alkali-metal iodide with the consequent possibility of a surface reaction of the alkyl bromide. It is probable that both effects have been observed, the first leading to occasional low readings of reaction progress in the earlier part of reaction, and the second to a more regular disturbance applying mainly to the more rapid early parts of the faster reactions. Both effects were most noticeable with the most reactive alkyl bromides; and it can be understood that in rapid reactions there may not be time for the continuous maintenance of equilibrium between the phases. If we compare, for the different alkyl bromides, the initial rate constants of the heterogeneous reactions of potassium and sodium iodides with the rate constants of the completely homogeneous reactions with lithium iodide, we find that the sets of values converge to coincidence as the reactivity of the alkyl halide diminishes. For methyl bromide, the most reactive, the heterogeneous rates are on the average 19% higher than the homogeneous, for ethyl bromide they are 14% higher, and for *n*-propyl bromide 6% higher; while for the remaining, still more slowly reacting, alkyl bromides, the deviations, averaging ±2%, are not larger than the casual kinetic error. Another regularity, applying to the reactions of methyl, ethyl, and *n*-propyl bromide, is that, for the same alkyl halide, the proportional difference between the heterogeneous and the homogeneous rates is larger at the lower temperatures. In order to account for this, we must assume that, whilst a reduced temperature retards the reaction, it retards still more the establishment of equilibrium in composition between the phases.

In the homogeneous reactions of lithium iodide with the alkyl bromides, the retrograde reactions are unimpeded. All the equilibria lie on the side of the factors, only slightly so in the methyl halide reaction, but successively more strongly so for the group of primary alkyl halides, for the *iso*propyl halide system, and for the *tert.*-butyl system. But still, by using a two-fold excess of the alkyl bromide, it was possible, for all reactions except those of the *tert.*-butyl group, to convert a sufficient proportion of the lithium iodide to enable the rates of the forward reactions to be measured. The proportions of salt converted were about 45% in the methyl case, about 30—35% in the various primary alkyl systems, and about 20% in the *iso*propyl example. In these rate measurements, we make use of the determined equilibrium compositions, and calculate with the aid of the equation for a reversible reaction of the second order in both directions.

The main rate disturbance noticed in these experiments arose from the negative salt effect characteristic of Finkelstein substitutions, in particular from its specific nature (already illustrated in Part XLIV), lithium iodide having a stronger retarding action than its equivalent of lithium bromide. (No doubt, this effect is present in the heterogeneous reactions also, though it is there masked by the disturbance due to the heterogeneity.) In the homogeneous reactions of lithium iodide with the alkyl bromides, the observation is that the second-order rate constants rise with progress of the reaction. At first the increase is so slow as to be almost lost amid the casual errors, with the result that rate-constants averaged over a considerable initial proportion of the followed reaction are indistinguishable from rate constants extrapolated to the initial conditions; but near equilibrium the rate constants rise very appreciably. Qualitatively, this is to be expected, since lithium iodide is the more active salt, and the kinetic effect of any salt should vary more steeply with its concentration at lower than at higher concentrations. We should have liked to be able to quote the limiting rate of each forward reaction both initially and at equilibrium. But owing to the increasing drift in the rate constants near equilibrium, we could not safely make the extrapolation necessary to give rates in the neighbourhood of equilibrium compositions. We therefore cite only initial rates, which can be evaluated easily, and with the normal degree of accuracy.

The observed second-order rate constants, k_2, are given in Table 1. All these rate

TABLE 1. *Second-order rate constants (k_2 in sec.$^{-1}$ mole^{-1} l.) for the reactions of potassium, sodium, and lithium iodides with alkyl bromides in acetone.*

[Initial concn. *a* of alkyl bromide about 0·04M throughout.]

	KI		NaI		LiI		
Temp. (c)	*b*	10^5k_2	*b*	10^5k_2	*b*	*K*	10^5k_2
			Methyl bromide				
10·0°	0·0235	6850	0·0232	6910	0·0246	0·461	6150
4·9	0·0233	4250	0·0236	4200	0·0245	0·446	3640
0·0	0·0240	2660	0·0238	2650	0·0250	0·459	2190
− 7·4	0·0241	1110	0·0238	1080	0·0231	0·433	895
−11·0	0·0238	740	0·0240	727	0·0232	0·391	582
			Ethyl bromide				
50·3	—	—	—	—	0·0229	0·159	2070
40·3	—	—	—	—	0·0232	0·138	794
40·0	0·0223	892	0·0220	889	—	—	—
35·0	0·0224	548	0·0223	544	—	—	—
32·2	—	—	—	—	0·0234	0·127	352
30·0	0·0223	330	0·0222	327	—	—	—
25·0	0·0224	197	0·0230	195	0·0237	0·119	166
20·0	0·0228	120	0·0232	117	—	—	—
17·4	—	—	—	—	0·0239	0·107	71·4
			n-*Propyl bromide*				
45·0	0·0221	1120	0·0219	1160	0·0226	0·179	1080
40·0	0·0222	731	0·0220	741	0·0197	0·156	696
35·0	0·0223	450	0·0223	424	0·0221	0·157	409
30·0	0·0223	259	0·0223	248	0·0206	0·152	238
25·0	0·0222	149	0·0230	145	0·0125	0·139	137
			iso*Propyl bromide*				
60·0	0·0217	51·0	0·0215	49·4	0·0243	0·056	48·8
55·0	0·0218	31·3	0·0216	30·6	0·0240	0·053	30·6
50·0	0·0219	19·3	0·0216	19·2	0·0242	0·050	18·7
45·0	0·0220	11·8	0·0218	11·4	0·0239	0·048	11·2
40·0	0·0223	6·97	0·0216	6·68	0·0251	0·044	6·70
			iso*Butyl bromide*				
60·0	0·0219	213	0·0216	218	0·0228	0·221	216
55·0	0·0221	134	0·0218	137	0·0229	0·193	136
50·0	0·0221	83·5	0·0218	86·4	0·0228	0·187	83·4
45·0	0·0223	52·1	0·0220	52·3	0·0239	0·173	50·8
40·0	0·0222	31·9	0·0223	31·9	0·0241	0·169	30·6
			tert.-*Butyl bromide*				
61·1	0·0214	5·63	—	—	—	—	—
52·5	0·0216	2·26	—	—	—	—	—
45·0	0·0219	1·06	—	—	—	—	—
35·4	0·0222	0·36	—	—	—	—	—
			neo*Pentyl bromide*				
98·0	—	—	—	—	0·0193	0·287	11·4
89·6	—	—	—	—	0·0195	0·287	5·31
80·6	0·0207	2·18	0·0206	2·26	0·0200	0·275	2·29
72·8	0·0209	1·01	0·0208	1·00	0·0219	0·267	1·05
64·7	0·0192	0·44	0·0194	0·45	0·0204	0·256	0·445

constants, whether calculated with the equation of an irreversible reaction, as they are for the reactions with potassium and sodium iodides, or with that of a reversible reaction, as they are for the reactions with lithium iodide, are computed from the earlier parts of the measured reactions, and thus correspond to the initial salt composition and concentration. For the reactions with lithium iodide, equilibrium constants K are given as an expression of the final compositions attained. The formula used for the reactions wth potassium and sodium iodides is

$$k_2 = [1/t(a - b)] \ln [b(a - x)/a(b - x)]$$

and the formulæ employed for the reactions with lithium iodide are

$$x = [ab/(1 - K^{-1})]\{\alpha + \beta \coth [\beta(1 - K^{-1})k_2t]\}^{-1}$$

$$\alpha = (a + b)/2(1 - K^{-1}); \ \beta = [1/2(1 - K^{-1})][(a - b)^2 + 4ab/K]^{1/2}$$

$$K = x_\infty^2/(a - x_\infty)(b - x_\infty)$$

where x is the concentration converted at time t, and $a = [\text{RBr}]_0$, and $b = [\text{KI}]_0$ or $[\text{NaI}]_0$ or $[\text{LiI}]_0$. The rate constants are corrected for thermal expansion of the solvent.

These data give good Arrhenius plots, for which the Arrhenius activation energies and frequency factors have been derived, which are contained in Table 2. The temperature range of the reactions of potassium and sodium iodides with *neo*pentyl bromide was inevitably somewhat small, being limited on the one side by the slowness of the reactions, and on the other by the reduced solubilities of potassium and sodium iodides in acetone at higher temperatures.

Generally, we place most reliance on the values obtained for the homogeneous reactions, though for nearly all the halides the difference between the homogeneous and the heterogeneous values are scarcely appreciable. Table 3 summarises our adopted values of the Arrhenius parameters, and contains also the absolute and relative rates at 25° for comparison with such values for other Finkelstein reactions, as given in the accompanying papers.

TABLE 2. *Parameters of the equation* $k_2 = B_2 \exp(-E_A/\boldsymbol{R}T)$ (*with* B_2 *in sec.*$^{-1}$ *mole*$^{-1}$ *l. and* E_A *in kcal. mole*$^{-1}$) *for the reactions of potassium, sodium, and lithium iodides with alkyl bromides in acetone.*

	KI		NaI		LiI	
Bromide	E_A	$\log_{10} B_2$	E_A	$\log_{10} B_2$	E_A	$\log_{10} B_2$
Methyl	15·1	10·5	15·9	11·1	16·3	11·4
Ethyl	19·0	11·2	19·0	11·2	18·8	11·0
n-Propyl	19·5	11·5	19·6	11·6	19·0	11·1
*iso*Propyl	20·5	10·2	20·5	10·15	20·5	10·15
*iso*Butyl	19·8	10·3	19·9	10·2	19·9	10·3
tert.-Butyl	22·0	10·2	—	—	—	—
*neo*Pentyl	24·1	10·3	24·1	10·3	24·0	10·2

TABLE 3. *Rate constants* (k_2 *in sec.*$^{-1}$ *mole*$^{-1}$ *l.*), *relative rates at common temperatures, and adopted values of the Arrhenius parameters* (B_2 *in sec.*$^{-1}$ *mole*$^{-1}$ *l. and* E_A *in kcal. mole*$^{-1}$), *for the reactions of iodide ions with alkyl bromides in acetone* (*salt,* 0·022M-*iodide*).

Bromide	Me	Et	Pr^i	Bu^t	Pr^n	Bu^i	*neo*Pe
10^5k_2 (25°) ...	25,000	166	1·3	0·10 *	137	6·0	0·0020
Rel. k_2 (25°) ...	145	1	0·0078	0·00051 *	0·82	0·036	0·000012
$\log_{10} B_2$	11·4	11·0	10·2	10·2 *	10·8	10·3	10·2
E_A	16·3	18·8	20·5	22·0 *	18·7	19·9	24·0

* Values when using potassium iodide.

EXPERIMENTAL

The alkyl bromides were prepared or purified as described in Part XLIII, and acetone was purified as noted in Part XLII. Potassium and sodium iodides were crystallised from water, and lithium iodide from acetone; and all these iodides were dried in a vacuum at 110° over phosphoric oxide.

Kinetics.—(a) *Methods.* Each sealed tube contained 10 c.c. of solution and enclosed an air-space of 5 c.c. Each was charged, first with 5 c.c. of a solution in dry acetone of the metal iodide, and after this had been cooled to −80°, with 5 c.c. of a solution of the alkyl bromide, jacketed automatic pipettes being used. The solutions were made up by weighing, excepting that of methyl bromide, which was made up in an approximate way first, and was then standardised by quantitative hydrolysis with potassium hydroxide. The reaction mixtures involving *neo*pentyl bromide were prepared with omission of the precaution, unnecessary in this case, of cooling to −80°.

For the reactions which were to be calculated with the formula from irreversible reactions of the second order, the tubes were shaken for 30 sec. after immersion in the thermostat. The end of this period was taken as the time-zero, and the analytical result obtained from a tube withdrawn at that moment was used in order to deduce the initial concentrations a and b of the reactants, as well as the concentration x_0 converted during warming, a quantity by which all the conversions x, as measured at later times, had to be corrected.

For reactions which were to be calculated with the formulæ of reversible reactions of the second order, a different principle was employed in order to establish kinetically initial conditions. Identical tubes, originally at a temperature so low that no reaction proceeded, were placed in the thermostat at a time t_a. Suppose that their contents are sensibly at thermostat temperature at a time t_c. At two successively later times t_1 and t_2, so chosen that the reaction–time curve can be treated as linear from t_c to t_2, tubes were withdrawn and analysed, the concentrations converted being x_1 and x_2, respectively. There exists a time t_b, between t_a and t_c, such that, if the tubes had, at t_b, been raised instantaneously to thermostat temperature, then, at all times after t_c, the amount of conversion would have been what it is actually found to be. This time t_b is the kinetic time-zero, and it is found by extrapolating the straight line through the points (x_1, t_1) and (x_2, t_2) back to the axis $x = 0$. At this time-zero, the initial concentrations a and b of the reactants are to be taken as the concentrations originally introduced, and the concentration converted is to be taken as zero.

The analyses were made by Lang's iodine cyanide method. A withdrawn tube was chilled to −80°, and broken under 30—40 c.c. of an aqueous solution 2N in sulphuric acid and 0·5N in hydrochloric acid. After the addition of 5 c.c. of 15% potassium cyanide solution, the mixture was titrated with 0·005N-potassium iodate, starch being the indicator.

(b) *Results.* These are summarised in Table 1. An example of a kinetic run is given in Table 4.

TABLE 4. *Rate of reaction of alkali-metal iodides with alkyl bromides in acetone: example* $\mathrm{LiI + MeBr \longrightarrow LiBr + MeI}$.

(Temp. − 7·39°. Initially, [MeBr] = 0·04350M; [LiI] = 0·02311M.)

t (sec.)	x (M)	10^3k_2 (sec.$^{-1}$ mole^{-1} l.)	t (sec.)	x (M)	10^3k_2 (sec.$^{-1}$ mole^{-1} l.)
88	0·00080	—	1018	0·00669	8·92
358	0·00289	8·94	1198	0·00742	8·88
508	0·00391	8·92	1558	0·00874	8·98
658	0·00479	8·84	2098	0·01009	9·12
838	0·00580	8·90	∞	0·01232	—

(In this Table, t and x are corrected throughout as explained in the preceding section.)

William Ramsay and Ralph Forster Laboratories,
University College, Gower St., London, W.C.1.

[*Received, March 8th,* 1955.]