Mechanism of Substitution at a Saturated Carbon Atom. Part XLVII. Kinetics of the Interaction of Bromide Ions with Simple Alkyl Iodides in Acetone.*

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Kinetic experiments on the second-order reactions of halogen substitution by lithium bromide with five simple alkyl iodides in acetone are reported. The reaction of methyl iodide is moderately reversible, but those of the other alkyl iodides comparatively slightly so. In accordance with the general rules governing salt effects in Finkelstein substitutions, the salt effect in this substitution so operates tha tthe rate constants fall at first with reaction progress, but attain relatively steady values near equilibrium. Here the salt present is mainly lithium iodide, and it is for such salt conditions that the determined rate constants have been evaluated. From them, parameters of the Arrhenius equation are derived for the reactions of the five alkyl groups directly studied; and approximate parameters have been deduced by an indirect method for a sixth alkyl group.

The particular Finkelstein reaction, the kinetics of which are here to be described, is that between an ionic bromide as substituting agent and a series of simple alkyl iodides in anhydrous acetone as solvent. We know of no previous kinetic investigation of this substitution.

The reaction is the reverse of that, considered in the preceding paper, between potassium, sodium, or lithium iodide and alkyl bromides; but in the present work we were restricted to the use of lithium bromide as reagent, since potassium and sodium bromides are insufficiently soluble in dry acetone to be thus employed. However, because of the principle of microscopic reversibility, consistency with the conclusion, reached in the preceding paper on the basis of a comparison of the kinetics of the reactions of the three alkali-metal iodides on alkyl bromides, requires the assumption that, in the reaction between lithium bromide and alkyl iodides, the bromide ion is the essential substituting agent:

$$\mathrm{Br^- + RI \longrightarrow RBr + I^-}$$

We have examined this reaction for the following five alkyl groups: Me, Et, $\mathrm{Pr^n}$, $\mathrm{Pr^i}$, and $\mathrm{Bu^i}$. In each case, rates have been measured over a temperature range, and the parameters of the Arrhenius equation have been computed. An attempt to complete our examination of the α-methylated branching homologous series by including the *tert.*-butyl group was frustrated by the instability of *tert.*-butyl iodide in the solvent at the temperatures required for the substitution. Although we did not directly complete the study of the β-methylated series by investigating the kinetics of the reaction of lithium bromide with *neo*pentyl iodide, we are able to complete it indirectly to the extent of deriving an approximate Arrhenius equation for the rate of this reaction by combining the kinetic data given in the preceding paper for the reaction between lithium iodide and *neo*pentyl bromide with the thermodynamic constants of the balanced bromine–iodine exchange reaction of the *neo*pentyl group.

The reactions between lithium bromide and the five alkyl iodides for which we report rate constants all ran to equilibria which were well towards the right-hand side of the above chemical equation. With the alkyl iodides initially present in two-fold excess, the conversion of salt by methyl iodide went forward to the extent of about 75%, its conversion by ethyl, *n*-propyl, and *iso*butyl iodide to the extent of approximately 90%, and by *iso*propyl iodide to more than 95%, of the stoicheiometric maximum. Had it not been for the kinetic disturbance next to be mentioned, it should have been possible to calculate rate constants for considerable portions of all these reactions by the formula for an

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* Part XLVI, preceding paper.

irreversible reaction of the second order. In fact, however, we always used the equations for a reversible reaction in computing rate constants for these reactions.

The reason for this was that the salt effect, particularly its specific nature with respect to the individual salts, so operates in this reaction as to produce a drift in the rate constants, which is somewhat sharp near the commencement of reaction, but relatively slight near equilibrium. As a result, we found it unsatisfactory in most cases to attempt the extrapolations necessary for the determination of initial rate constants, and were able to assign reasonably good limiting rate constants only at the other limit, that is, for salt compositions in the neighbourhood of those at equilibrium. Having therefore decided on the extraction only of final rate constants from the kinetic measurements, the rate constants had to be calculated with the equation for a reversible reaction of the second order.

The salt effect described is consistent with the observations on salt effects noted in the preceding papers, and with some direct investigations on salt effects which are to be reported later. The qualitative rules appear to be as follows. All alkali-metal salts of strong acids depress the rate of Finkelstein substitutions in acetone. Lithium iodide has a considerably greater specific retarding effect than lithium bromide; and indeed the order of intensity of the salt effect among the four lithium halides is probably LiI > LiBr > LiCl > LiF, though the only evidence that we could offer at present for the inclusion of lithium fluoride in this series applies, not to solvent acetone, but to nitromethane as solvent. For any one salt, the kinetic effect of a given increment of concentration is very much greater at low than at high concentration. From these rules it follows that, in a reaction between lithium bromide and an alkyl iodide, the reaction rate will fall as the original salt becomes progressively replaced by the kinetically more effective lithium iodide; and also that the fall will be sharp at first, when the more effective salt is in very low concentration, but relatively slight later, when this salt has attained a considerable concentration. Similarly, we can understand how, in the reaction, described in the preceding paper, between lithium iodide and an alkyl bromide, the rate constants rise, as the original salt becomes gradually replaced by the kinetically less effective lithium bromide, but rise scarcely perceptibly at first, and then more markedly, although still not steeply, near equilibrium. Near the beginning of this reaction, the salt effect is due almost entirely to the lithium iodide in relatively high concentrations, and, near the end, most of the salt effect will still be due to lithium iodide, which remains in considerable concentration as it is the preponderating salt at equilibrium.

TABLE 1. *Second-order rate constants (k_2 in sec.$^{-1}$ mole^{-1} l.) of the reaction between lithium bromide and* iso*propyl iodide in acetone at* 69·84°.

(Initially, $[\mathrm{Pr^iI}] = 0{\cdot}04010\text{M} = a$, $[\mathrm{LiBr}] = 0{\cdot}02183\text{M} = b$, $x = 0$, and $t = 0$, this time-zero being 6 sec. later than the moment of insertion of the reaction tubes, with shaking, into the thermostat. From the value of x noted below, the following are calculated : $K = 25{\cdot}4$; $\alpha = 0{\cdot}0322\text{M}$; $\beta = 0{\cdot}0113\text{M}$.)

t (corr.) (sec.)	x (mole l.$^{-1}$)	Salt converted (%)	10^2k_2	t (corr.) (sec.)	x (mole l.$^{-1}$)	Salt converted (%)	10^2k_2
150	0·00367	16·8	3·22	870	0·01150	51·6	2·53
240	0·00522	23·9	3·05	1170	0·01350	61·8	2·45
340	0·00656	30·1	2·88	1560	0·01471	67·5	2·38
460	0·00805	36·9	2·81	2100	0·01642	75·3	2·32
630	0·00967	44·3	2·70	∞	0·02093	95·9	—

(The value of k_2 extrapolated to equilibrium is $2{\cdot}23 \times 10^{-2}$ sec.$^{-1}$ mole^{-1} l.)

In illustration of the foregoing description of the marked effect of the changing composition of lithium salts on the kinetics of the reaction between lithium bromide and alkyl iodides, the details of a run with *iso*propyl iodide are recorded in Table 1. Here a and b are the initial concentrations $[\mathrm{RI}]_0$ and $[\mathrm{LiBr}]_0$, respectively, and x is the concentration converted at time t, the times being corrected to correspond to a time-zero determined by the method described in the preceding paper as appropriate for reversible reactions. From the final value x_∞ of x, an equilibrium constant is calculated :

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

and from this the concentrations α and β, defined below, are derived :

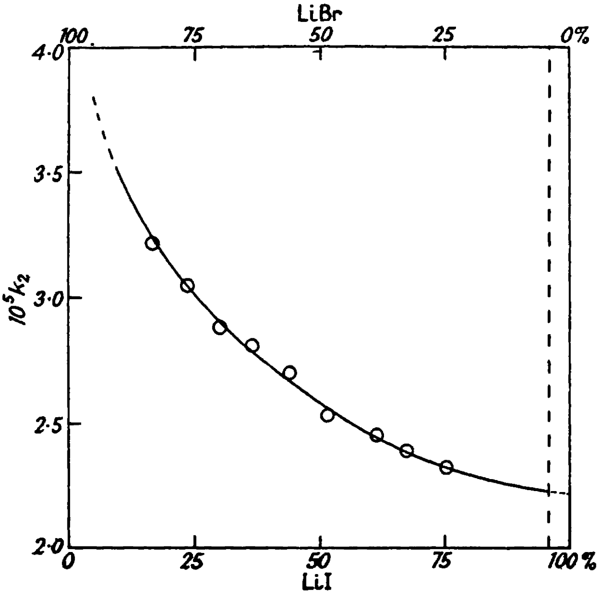
$$\alpha = (a + b)/2(1 - K^{-1})\,; \quad \beta = [1/2(1 - K)^{-1}][(a - b)^2 + 4ab/K]^{1/2}$$

The second-order rate constants k_2 are now computed from the equation

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

All concentrations are corrected for thermal expansion of the solvent.

The nature of the extrapolations involved in the deduction of limiting rate constants is illustrated in the Figure, which refers to the same kinetic run. The plot is of the calculated second-order rate constant against the percentage of salt converted. On its left, the curve is expected to take a sharper turn upwards near the axis of ordinates, where the concentrations of the kinetically more effective salt vanish; and for this reason the extrapolation required to give an initial rate for reaction is considered impracticable. On its right, the curve should become more nearly horizontal as it approaches the salt-composition corresponding to equilibrium; and it is by extrapolation in this direction that the cited value of the final rate constant is obtained.



Effect of changing composition of lithium halides of total concentration 0·0218M *on the second-order rate constant of the reaction of lithium bromide with* iso*propyl iodide in acetone at* 69·8°.

The vertical broken line represents equilibrium concentration.

The complete series of final second-order rate constants, derived in this way, is given

TABLE 2. *Final second-order rate constants (k_2 in sec.$^{-1}$ mole^{-1} l.) for the reactions of lithium bromide with alkyl iodides in acetone.*

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

RI	Temp. (° c.)	*b*	*K*	10^5k_2	RI	Temp. (° c.)	*b*	*K*	10^5k_2
MeI	16·5	0·0235	1·74	21,900	Pr^iI ...	69·8	0·0218	25·4	2230
	8·0	0·0238	1·81	9600		60·3	0·0221	27·9	1030
	0·0	0·0241	1·86	3940		50·3	0·0224	31·6	438
	−11·0	0·0205	1·87	1160		39·9	0·0227	35·5	171
EtI	39·9	0·0227	7·58	5980	Bu^iI ...	75·0	0·0217	4·44	2720
	32·2	0·0230	7·87	3020		59·8	0·0225	4·83	962
	25·0	0·0232	8·70	1490		49·0	0·0229	5·18	380
	16·5	0·0235	9·01	615		37·2	0·0229	5·71	119
Pr^nI ...	37·2	0·0252	6·17	3440					
	26·3	0·0252	6·90	1180					
	8·4	0·0259	8·62	170					
	−5·8	0·0264	11·24	30·7					

in Table 2. They refer throughout to salt conditions which, though not strictly standardised, involved salt consisting predominantly of lithium iodide, the total salt concentration being always close to 0·023M.

These rate constants give satisfactory Arrhenius plots, from which the energies of activation and frequency factors shown in Table 3 have been derived. The same Table contains the absolute and the relative rates of the reactions at 25°. For greater completeness, we have added to the Table, in the column headed "*neo*Pe" the Arrhenius energy of activation and frequency factor for the reaction of lithium bromide with *neo*pentyl iodide, even though these quantities have not been directly measured, but, as already mentioned, were obtained by an indirect method.

TABLE 3. *Rate constants (k_2 in sec.$^{-1}$ mole^{-1} l.), and relative rates at 25°, and parameters of the equation $k_2 = B_2 \exp(-E_A/RT)$ (with B_2 in sec.$^{-1}$ mole^{-1} l., and E_A in kcal. mole^{-1}) for the reactions of lithium bromide with alkyl iodides in acetone (salt* 0·023M, *mainly lithium iodide).*

R in RI	Me	Et	Pr^i	Pr^n	Bu^n	*neo*Pe
10^5k_2 (25°)	27,000	1490	37	1050	32	—
Rel. k_2 (25°)	18	1	0·025	0·71	0·021	—
$\log_{10} B_2$	11·4	11·1	10·2	10·8	10·3	10·1
E_A	16·3	17·7	18·5	17·5	18·8	23·1

Experimental.—The alkyl iodides were purified as indicated in Part XLIV. Acetone was purified as noted in Part XLII. Lithium bromide was crystallised from the concentrated solution in water, and was dried in a vacuum at 110° over phosphoric oxide.

The kinetics were followed by the sealed-tube method, with the procedure for starting and stopping runs, and the analytical technique, described in the preceding paper for the reactions of lithium iodide with alkyl bromides.

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