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

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Kinetic experiments on the second-order reactions of halogen substitution by lithium iodide with six simple alkyl bromides in acetone are reported. The reactions are only slightly reversible; but, owing to the use of non-neighbouring halogens, and the circumstance that the salt effect is more negative with higher halide ions, they are subject to a considerable salt disturbance, which was buffered with added lithium perchlorate. In these conditions, rate-constants and the parameters of the Arrhenius equation were determined.

The pioneer work of Conant and his collaborators on the kinetics of Finkelstein substitutions was concerned with the reaction of iodide ions with alkyl chlorides (Conant and Kirner, *J. Amer. Chem. Soc.*, 1924, **46**, 232; Conant and Hussey, *ibid.*, 1925, **47**, 476; Conant, Kirner, and Hussey, *ibid.*, p. 488). However, we can recall no previous account of a kinetic investigation of the reverse process, *viz.*, the reaction of chloride ions with alkyl iodides. The present paper describes a systematic study of the kinetics of this reaction.

In particular, the reactions of substitution between lithium chloride and six simple alkyl iodides in dry acetone as solvent have been investigated. The alkyl groups comprise the α- and β-methylated series of branching homologues to the following extent (*neo*Pe = *neo*pentyl):

(α-Series) Me, Et, Pr^i. (β-Series) Et, Pr^n, Bu^i, *neo*Pe. We tried to cover the α-series completely by including the *tert.*-butyl group, but failed because of the complicated and extensive nature of the side reactions.

The forward reaction, $Cl^- + RI \rightleftharpoons RCl + I^-$, was followed by titration of the iodide ion with ceric sulphate, in the presence of acetone which removed the iodine formed, so that the colour could be seen of the indicator, which was added to show the state of oxidation of the cerium ions. The reactions of which the kinetics are here described were found to be pure substitutions: no acid was formed, and the total halide ion in the solution remained constant. However, in the attempt which was made to study the reaction of lithium chloride with *tert.*-butyl iodide, acid and iodine were liberated, as well as iodide ion.

The kinetic forms of the reactions showed that a disturbance was present. As is illustrated in Table 1, rate constants, calculated for the first 30—70% of the reaction from the formula for an irreversible reaction of the second order, fall with the progress of reaction. We thought it unlikely that the fall could be due to the incursion of a reaction of higher order than two, and the fall was of the wrong form to be ascribed to reversibility.

Our explanation of the drift of the rate constants is that it is a salt effect, despite the constancy of the total concentration. We assume that, like other Finkelstein substitutions, the reactions now studied are subject to a negative salt effect. In solvent acetone, such effects will always be more or less specific to the salts, at the concentrations at which we employ them, and, for lithium chloride and lithium iodide, may be assumed to be different enough to cause a notable disturbance to the rate, as one salt becomes replaced by the

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* Part XLIII, preceding paper.

other in the course of reaction. The general correctness of this explanation is made very probable by the observation that the addition of lithium perchlorate, which takes no part in the stoicheiometric reaction, causes a marked general lowering of the rate, and also a disappearance of the drift.

TABLE 1. *Illustration of kinetic forms of reactions of lithium chloride with alkyl iodides in dry acetone.*

{Reaction progress is given in two forms, *viz.*, as the lithium chloride equivalent of the liberated iodide ion, expressed (A) as a percentage of the lithium chloride present initially, and (B) as a percentage of that present at the time zero. Measure (A) gives the composition of the salts present, while measure (B) is more closely related to the rate constants k_2, in sec.$^{-1}$ mole^{-1} l., which are computed from the formula

$$k_2 = [2{\cdot}303/t(a - b)] \log_{10} [b(a - x)/a(b - x)]$$

and are corrected for thermal expansion of the solvent.}

Methyl Iodide at 24·83°.—Initially, [MeI] = 0·06267, [LiCl] = 0·03646; at t = 0, [MeI] = 0·05721, [LiCl] = 0·03100M. Titres in c.c. of ceric sulphate of 0·00519N-iodide equivalent per 4·236-c.c. sample.

t (min.)	Titre	Reaction (%) (A)	Reaction (%) (B)	10^5k_2 (corr.)	t (min.)	Titre	Reaction (%) (A)	Reaction (%) (B)	10^5k_2 (corr.)
0·0	4·46	15·0	0·0	—	5·0	10·46	35·2	23·7	1710
1·0	6·08	20·4	6·4	1970	7·0	12·96	43·8	33·6	1670
2·0	7·47	25·1	11·9	1900	8·0	13·31	44·8	35·0	1650
3·0	8·55	28·8	16·15	1860	10·0	14·26	48·0	38·7	1480
4·0	9·57	32·0	20·2	1750					

TABLE 2. *Kinetic forms of reactions of lithium chloride with alkyl iodides in dry acetone containing lithium perchlorate.*

(See note at the head of Table 1.)

n-*Propyl Iodide at* 25·00°.—Initially, [Pr^{n}I] = 0·06019, [LiCl] = 0·03170, [LiClO$_4$] = 0·1090M; at t = 0, [Pr^{n}I] = 0·05997, [LiCl] = 0·03148M. Titre in c.c. of ceric sulphate of 0·000781N-iodide equivalent per 4·236-c.c. sample.

t (min.)	Titre	Reaction (%) (A)	Reaction (%) (B)	10^5k_2 (corr.)	t (min.)	Titre	Reaction (%) (A)	Reaction (%) (B)	10^5k_2 (corr.)
0·0	1·19	0·70	0·00	—	200	27·74	16·3	16·1	24·5
40·0	7·33	4·30	3·60	25·1	255	33·91	19·8	19·75	24·5
65·0	11·18	6·55	5·85	24·6	310	40·02	23·5	22·75	24·8
110	16·43	9·65	8·85	26·2	495	57·84	34·0	33·3	25·1
150	21·78	12·75	12·65	24·1				Mean:	24·6

TABLE 3. *Second-order rate constants for reactions of substitution between lithium chloride and alkyl iodides in dry acetone.*

(Initially, [RI] ~ 0·060—0·065, [LiCl] ~ 0·032, [LiClO$_4$] ~ 0·110M. Rate constants, k_2 in sec.$^{-1}$ mole^{-1} l., expressed as 10^5k_2. *neo*Pe = *neo*pentyl.)

Temp. (c)	R in RI: Me	Et	Pr^n	Pr^i	Bu^i	*neo*Pe
+120·06°	—	—	—	—	—	4·57
109·97	—	—	—	—	—	2·17
100·54	—	—	—	—	—	1·02
80·04	—	—	—	—	—	0·188
63·98	—	—	—	42·3	56·7	—
55·12	—	—	347	20·3	25·8	—
54·04	—	526	—	—	—	—
45·92	—	—	164	9·69	—	—
45·72	—	275	—	—	—	—
45·32	—	—	—	—	10·4	—
35·36	—	113	—	—	—	—
34·74	—	—	61·1	3·48	—	—
34·59	—	—	—	—	4·16	—
34·21	964	—	—	—	—	—
25·64	—	—	—	—	1·71	—
25·23	—	43·0	—	—	—	—
25·00	—	—	24·6	—	—	—
24·83	460	—	—	1·26	—	—
14·45	180	—	—	—	—	—
+14·08	—	14·0	7·83	—	—	—
0·00	37·9	—	—	—	—	—
−9·96	12·9	—	—	—	—	—

We found that by adding a quantity of lithium perchlorate 3—4 times greater than that of the initially present lithium chloride, good rate constants could be calculated by means of the usual equation for an irreversible reaction of the second order, thus confirming that the substitution is indeed of second-order type, and showing incidentally that its reversibility is not sufficiently marked to interfere seriously with the use in this manner of a formula which neglects the retrograde process. These points are illustrated by the examples given in Table 2.

The second-order rate-constants obtained in this way, in the presence of the same constant excess of lithium perchlorate (0·110M), are assembled in Table 3. These rate-constants give satisfactory Arrhenius plots, which lead to the energies of activation and frequency factors shown in Table 4. These figures will be discussed in Part XLIX. Table 4 also contains the absolute and relative rates at a commom temperature for the reactions.

TABLE 4. *Rate constants (k_2 in sec.$^{-1}$ mole^{-1} l.), relative rates at a common temperature, and parameters of the equation $k_2 = B_2 \exp(-E_A/\mathbf{R}T)$ (with B_2 in sec.$^{-1}$ mole^{-1} l., and E_A in kcal. mole^{-1}) for reactions of lithium chloride with alkyl iodides in acetone containing lithium perchlorate.*

R in RI	Me	Et	Pr^i	Pr^n	Bu^i	*neo*Pe
10^5k_2 (25°)	468	42·0	1·33	24·6	1·62	0·00058
Rel. k_2 (25°)	11·1	1	0·032	0·58	0·038	0·000014
$\log_{10} B_2$	9·4	9·1	8·3	8·8	8·3	7·9
E	16·0	17·0	18·0	17·0	17·8	22·0

EXPERIMENTAL

*neo*Pentyl iodide was prepared by Whitmore and Fleming's method, via *neo*pentane, *neo*pentyl chloride, and *neo*pentyl mercurichloride (*J. Amer. Chem. Soc.*, 1933, **55**, 4161). *iso*Butyl iodide was shaken with aqueous thiosulphate. The other iodides were decoloured with mercury. All the alkyl iodides were finally dried (K_2CO_3) and fractionated : MeI, b. p. 42·4—42·7°/758 mm.; EtI, b. p. 72·2—72·4°/758 mm.; Pr^{n}I, b. p. 101·7—102·1°/760 mm.; Pr^{i}I, b. p. 88·8—89·1°/761 mm.; Bu^{i}I, b. p. 120·0—120·5°/759 mm.; *neo*PeI, b. p. 76—78°/120 mm.

As the analytical method to be used in the kinetic experiments depended on the complete absence of oxidisable impurities in the acetone, this was boiled with permanganate until the colour of the latter persisted, before being distilled with quinol, and dried. Just before use it was redistilled from magnesium perchlorate.

Lithium chloride was purified as indicated in the preceding paper. Lithium perchlorate was prepared by exactly neutralising aqueous lithium hydroxide with perchloric acid, the residue left on subsequent evaporation being dried in a vacuum at 110° over phosphoric oxide.

The sealed-tube method was used for the kinetic runs. The tubes were filled with solutions which were prepared and standardised as described in the preceding paper. Lithium perchlorate, when used, was directly weighed into the acetone, and this solution was employed, instead of the pure solvent, for making up the solutions of lithium chloride and of the alkyl iodide.

Each tube withdrawn from the thermostat, whether at the time-zero or at later times, was broken under 30 c.c. of 2N-aqueous sulphuric acid. The tube contained about 4 c.c. of acetone, but a further 5 c.c. was added, to facilitate rapid absorption of the iodine which was to be produced. Some *o*-phenanthroline–iron(II) indicator was also added. The ceric sulphate titrant, made up in 4N-aqueous sulphuric acid, was standardised with potassium iodide using a like method. With the concentrations of acid and of acetone here given, the end-points were sharp and stable. Control experiments showed that chloride did not appreciably affect the determination of iodide ions by this method. It was also shown, by means of other control experiments, in which the alkyl halides were pumped off before the determination of iodide ions, that the presence of the organic halides does not disturb this determination.

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