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

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[Reprint Order No. 6207.]

Kinetic experiments on the second-order reactions of halogen substitution by lithium chloride with seven simple alkyl bromides in acetone are reported. The reactions are only mildly reversible. The second-order substitution with *tert.*-butyl bromide is accompanied by a minor amount of an elimination of lower reaction order, probably first. Rate constants and the parameters of the Arrhenius equation were determined for all the substitutions.

Olson and his co-workers studied the concurrent reactions which occur in solvent water between chloride ion and bromosuccinic acid, and between chloride ion and α-bromophenylacetic acid (Olson and Long, *J. Amer. Chem. Soc.*, 1934, **56**, 1294; 1936, **58**, 393; Young and Olson, *ibid.*, p. 1157). Solomon and Thomas examined the reactions in aqueous acetone of lithium chloride with two alkyl bromides and with three bromides of the *cyclo*hexane series (*ibid.*, 1950, **72**, 2028). We cannot recall a previous investigation of the kinetics of displacement of bromine from alkyl bromides by substituting chloride ion in dry acetone as solvent.

In this paper an investigation is described of the kinetics of the reaction in dry acetone between lithium chloride and seven alkyl bromides. The alkyl groups were the simplest of those calculated to bring out the more general polar and steric effects of alkyl structure on bimolecular nucleophilic substitution: they comprise the two branching-homologous series, which we call the α- and β-methylated alkyl series (*neo*Pe = *neo*pentyl):

Me, Et, Pr^i, Bu^t	Et, Pr^n, Bu^i, *neo*Pe
α-Methylated series	β-Methylated series

The progress of the forward reaction, $Cl^- + RBr \rightleftharpoons RCl + Br^-$, was followed by electrometric titration of the inorganic salts with silver nitrate, after removal of the organic material. Under conditions which minimise coprecipitation of the silver halides, two equivalence points are found, one for bromide ion, which measures the progress of reaction, and the second for total halide ion. The constancy in the latter establishes that the reaction consists wholly of substitution. Six of the seven reactions examined were in fact pure substitutions, while the remaining one was shown to be predominantly a substitution.

The reactions run to equilibrium. However, in our conditions, the equilibria lay so far towards the right-hand side of the above equation, that 70% or more of the forward process could be followed without sensible disturbance from reversibility. We could

* Part XLII, preceding paper.

therefore simplify the work by omitting the determination of equilibrium constants, and computing second-order rate constants from the kinetic equation for an irreversible reaction.*

With reservations applying to one case, the reactions were kinetically of second order, and showed negative salt effects. We did not make any detailed study of salt effects, but secured comparable rate constants for the evaluation of their temperature coefficient by using standardised salt concentrations. These were 0·05M for the reaction of methyl bromide, and 0·07M for the reactions of its homologues. It has been shown for related Finkelstein reactions that kinetic salt effects do not perceptibly influence the Arrhenius activation energies.

The case which called for special treatment was that of *tert.*-butyl bromide. Its reaction with chloride ion, as measured by the development of bromide ion, was found to be only roughly of second order. Moreover, the criterion for a pure substitution by constancy of total inorganic halide was not fulfilled: the amount of total halide ion rose as reaction progressed, indicating that some elimination was taking place; and this interpretation was confirmed by following the concurrent development of acid. Now it has been shown (de la Mare, Hughes, Ingold, and Pocker, *J.*, 1954, 2930) that, in solvent nitromethane, the reaction between chloride ion and *tert.*-butyl bromide is entirely unimolecular, and consists wholly, or almost wholly, of elimination. Therefore we conclude that, even in dry acetone, *tert.*-butyl bromide undergoes some ionisation, with the result that a predominating bimolecular substitution is accompanied by a side reaction consisting mainly at least of elimination:

$$\mathrm{Cl^- + Bu^tBr} \begin{array}{l} \longrightarrow \mathrm{Bu^tCl + Br^-} \quad . \; . \; . \; . \; . \; . \; . \; . \quad (S_N2) \\ \longrightarrow \mathrm{C_4H_8 + H^+ + Br^- + Cl^-} \quad . \; . \; . \; . \quad (E1) \end{array}$$

We have followed the progress of both these reactions by measurement of both bromide ion and hydrogen ion. Complications due to the reversibility of both processes affect mainly the later part of the total change, and have been studied qualitatively. The bimolecular substitution is reversible, but so slightly so that, if it were alone, one could neglect reversibility. However, as we know from the cited investigation of the unimolecular elimination in nitromethane, this reaction also is reversible, and will become more strongly reversed, as, on account of both the concurrent processes, a concentration of bromide ions is built up, so that the acid formed by elimination becomes progressively poorer in hydrogen chloride and richer in the better additive reagent, hydrogen bromide. In our acetone solvent, the effect of this growing reversibility of the elimination is to produce a progressive diversion of the total reaction from elimination towards substitution. Meanwhile, the elimination becomes retarded by its increasing reversibility, until eventually it begins to go backward, thus allowing the concurrent substitution to go further forward. Interested as we were in the rate of the forward process of substitution, we noted these points qualitatively, and then confined our quantitative treatment of the measurements to the first 30—40% of reaction, a range over which the specific rate of development of bromide ion $(\mathrm{d}x/\mathrm{d}t)/(a - x)$, falls linearly with the decreasing concentration of chloride ion $(b - x)$, thus showing that reversibility has not yet become important. Over this range, the specific rate is simply the sum of a constant part, k_1, the rate constant of reaction $E1$, and a variable part $k_2(b - x)$, which contains the rate-constant k_2 of reaction S_N2.

Tables 1—3 record specimen runs. They illustrate the extent to which the reactions are substitutions, and the applicability to these substitutions of the second-order rate law. Table 4 summarises the second-order rate-constants for the substitutions.

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* It is shown in Part XLVII, that for bromine–iodine exchange by Finkelstein substitution, $\mathrm{LiBr + RI \rightleftharpoons LiI + RBr}$, the equilibrium constant $k = [\mathrm{LiI}][\mathrm{RBr}]/[\mathrm{LiBr}][\mathrm{RI}]$ in acetone when R is a methyl group is only 1·7, but that for ethyl and higher primary alkyl groups the constants are in the neighbourhood of 7, whilst for the *iso*propyl group the constant is about 30, and for the *tert.*-butyl it is of the order of 100. In the corresponding chlorine–bromine system, $\mathrm{LiCl + RBr \rightleftharpoons LiBr + RCl}$, the equilibrium constants are probably all higher, though the only figure available to illustrate this suggestion is one determined by Dr. P. B. D. de la Mare for the methyl group: for $K = [\mathrm{LiBr}][\mathrm{MeCl}]/[\mathrm{LiCl}][\mathrm{MeBr}]$ in acetone at 40°, he found the value 17·5 ± 1·3. In this work, we did not determine them, but ascertained that all are high.

TABLE 1. *Reaction of lithium chloride with methyl bromide in acetone at* 34·04°.

(Initially, [MeBr] = 0·1343, [LiCl] = 0·0503M. Concns. in c.c. of 0·0550N-$AgNO_3$ for 7·55-c.c. sample. Rate constants k_2 in sec.$^{-1}$ mole^{-1} l. The correction to [Br⁻] is for mechanical loss, as estimated from the defect of [Cl⁻ + Br⁻] below the theoretical value, 6·90 c.c.—see Experimental section.)

t (sec.)	[Br⁻]	[Br⁻] (corr.)	[Br⁻ + Cl⁻]	10^2k_2 (uncorr.)	*t* (sec.)	[Br⁻]	[Br⁻] (corr.)	[Br⁻ + Cl⁻]	10^2k_2 (uncorr.)
0	0·38	0·39	6·82	—	255	2·25	2·26	6·86	1·30
65	0·59	0·60	6·82	1·26	315	2·54	2·57	6·82	1·23
90	0·83	0·84	6·80	1·22	375	2·86	2·89	6·83	1·21
100	1·95	0·95	6·88	1·26	420	3·03	3·11	6·72	1·20
135	1·16	1·18	6·76	1·26	660	4·05	4·09	6·83	1·18
195	1·72	1·76	6·76	1·25					

(Adopted 10^2k_2, uncorr. = 1·26. Corr. for thermal expansion of the solvent, 10^2k_2 = 1·29.)

TABLE 2. *Reaction of lithium chloride with* iso*propyl bromide in acetone at* 79·63°.

(Initially, [Pr^iBr] = 0·1217; [LiCl] = 0·0721M. Units as in Table 1 unless otherwise noted. Theoretical value of [Br⁻ + Cl⁻] = 9·91 c.c.).

t (min.)	[Br⁻]	[Br⁻] (corr.)	[Br⁻ + Cl⁻]	10^4k_2	*t* (min.)	[Br⁻]	[Br⁻] (corr.)	[Br⁻ + Cl⁻]	10^4k_2
0	1·03	1·06	9·62	—	360	4·00	4·03	9·84	2·23
125	1·92	1·92	9·91	(2·35)	410	4·35	4·35	9·92	2·20
180	2·40	2·47	9·65	2·21	480	4·59	4·71	9·66	2·23
225	2·81	2·85	9·77	2·13	515	4·93	4·99	9·80	2·20
250	3·09	3·13	9·79	2·20	600	5·32	5·43	9·71	2·20
290	3·40	3·46	9·74	2·19	1050	6·65	6·78	9·64	(1·97)

(Adopted 10^4k_2: uncorr., 2·20; corr. for thermal expansion, 2·42.)

TABLE 3. *Reaction of lithium chloride with* tert.*-butyl bromide in acetone at* 55·20°.

(Initially, [Bu^tBr] = 0·1191; [LiCl] 0·0634M. $AgNO_3$, 0·0632N; NaOEt, 0·0222N. Units as in Table 1, unless otherwise stated. Acid concentrations are converted into units used for halide ions.)

t (hr.)	[H⁺]	[Br⁻] (corr.)	[Br⁻ + Cl⁻ − H⁺]	$\{(dx/dt)/(a-x)\}$(hr.$^{-1}$)	$(b-x)$ (M)
3·25	0·67	1·20	7·40	0·0232	0·0583
7·0	1·53	2·21	7·59	0·0204	0·0499
11·0	2·07	3·37	7·34	0·0192	0·0402
14·5	2·47	3·98	7·51	0·0168	0·0351
21·75	3·09	5·20	7·53	0·0143	0·0249
24·0	3·14	5·44	7·38	0·0131	0·0231
28·0	3·39	5·89	7·33	0·0119	0·0191
38·75	3·17	6·70	7·33	0·0066	0·0123

(From graph of $(dx/dt)/(a-x)$ against $(b-x)$, 10^5k_2, uncorr. = 0·72, and, corr. for thermal expansion, = 0·76.)

TABLE 4. *Second-order rate constants for reactions of substitution between lithium chloride and alkyl bromides in dry acetone.*

(Initially, [RBr] ~ 0·12M throughout, [LiCl] ~ 0·05M for the reactions of methyl bromide, and ~0·07M for the reactions of the other alkyl bromides. Rate constants, k_2, in sec.$^{-1}$ mole^{-1} l., are tabulated as 10^5k_2. *neo*Pe = *neo*pentyl.)

Temp. (c) R in RBr :	Me	Et	Pr^n	Pr^i	Bu^i	Bu^t	*neo*Pe
129·82°	—	—	—	—	—	—	3·47
120·04	—	—	—	—	—	—	1·74
109·82	—	—	—	—	—	—	0·851
100·54	—	—	—	—	—	—	0·425
79·63	—	—	—	24·2	—	—	—
64·83	—	314	215	7·96	—	1·94	—
55·20	—	150	106	3·49	28·7	0·76	—
45·19	—	61·7	—	1·42	—	—	—
44·50	—	—	41·0	—	10·4	0·27	—
34·62	—	24·3	16·4	0·522	4·08	—	—
34·04	1290	—	—	—	—	—	—
25·00	—	9·88	6·45	—	1·53	—	—
24·85	592	—	—	—	—	—	—
11·98	175	—	—	—	—	—	—
0·00	52·0	—	—	—	—	—	—

In Table 5, the absolute and the relative rates of the various substitutions at a common temperature are given: the rates are either as measured, or as computed from results for other temperatures. The data give good Arrhenius plots, from which frequency factors and activation energies have been derived, which are included in Table 5. Discussion of the figures is reserved for Part XLIX.

TABLE 5. *Rate constants (k_2 in sec.$^{-1}$ mole^{-1} l.), relative rates at common temperatures, 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 the reactions of lithium chloride with alkyl bromides in acetone.*

R in RBr:	Me	Et	Pr^i	Bu^t	Pr^n	Bu^i	*neo*Pe
$10^5 k_2$ (25°)	600	9·88	0·13	0·029	6·45	1·53	0·00026
Rel. k_2 (25°)	61	1	0·013	0·0029	0·65	0·15	0·000026
$\log_{10} B_2$	9·3	8·9	7·9	8·9	8·6	8·4	7·4
E_A	15·7	17·6	18·8	21·0	17·5	18·1	21·7

EXPERIMENTAL

*neo*Pentyl bromide was prepared as described by Sommer, Blankman, and Miller (*J. Amer. Chem. Soc.*, 1951, **73**, 3542). *iso*Butyl bromide was freed from traces of *tert.*-butyl bromide by shaking it with water until the latter remained neutral to litmus, and was then dried with phosphoric oxide. These and all the other dried alkyl bromides were finally fractionated with a high reflux ratio through a metal-gauze-packed column. The physical constants were as follows: MeBr, b. p. 3·5°/760 mm.; EtBr, b. p. 38·1—38·4°/763 mm.; Pr^nBr, b. p. 71·7—72·1°/760 mm.; 72·1—72·4°/765 mm.; Pr^iBr, b. p. 59·1—59·5°/760 mm.; Bu^iBr, b. p. 90·0—91·0°/763 mm.; Bu^tBr, b. p. 72·8—73·0°/758 mm.; *neo*PeBr, b. p. 105·8—106·0°/767 mm.; n_D^{20} 1·4365, n_D^{25} 1·4339. Acetone was purified as described in the preceding paper. Lithium chloride was purified, and reduced to a finely divided form, by filtering its solution in acetone into benzene, and drying the precipitated material in a vacuum at 110° over phosphoric oxide.

Because of the wide range of temperature used, the sealed-tube method was found most convenient for the kinetic work. The tubes were filled with the aid of two automatic pipettes, one delivering an acetone solution of the alkyl bromide, and the other one of lithium chloride. The alkyl bromide solutions were prepared by weighing: for volatile halides, sealed ampoules of them, weighed before and after filling, were broken under the cooled solvent. The lithium chloride solution was also prepared by weighing; and its composition was checked by determination of chloride ion by electrometric titration with silver nitrate. The bulbs of the automatic pipettes were jacketed, so that after they had been charged, their contents could be cooled, before delivery into the reaction tube, if the rate of the reaction studied rendered this precaution necessary. After being charged with both reactants, the tubes were sealed, in such a way as to include as little free space as was safe, and were then kept at $-80°$, until the whole set, needed for a run, was ready. In order to start a run, the tubes were simultaneously put into the thermostat, and shaken for 1—2 min. Then two or three tubes were withdrawn, at what was to be the time-zero, for the analysis which was to give the composition at zero time; and at later times other tubes were withdrawn and their contents were analysed.

For analysis, a tube was cooled, and its contents were evaporated by rapid pumping. The residual salt was dissolved in water, and analysed for bromide ion, and for total halide ion, by electrometric titration with silver nitrate, in the presence of 5% of barium nitrate, which was added to reduce co-precipitation of the silver halides. The use of the determination of total halide ions is not only that it gave warning of any reaction other than the replacement of one halogen by another in the alkyl halide, but also that it controlled any mechanical loss of salt by the pumping. Such loss showed as a defect in the measured total halide below the halide initially introduced as lithium chloride. Mechanical losses were often in the neighbourhood of 1—2%. For each tube analysed, the estimate thus obtained of the mechanical loss was used to correct the measured content of bromide ion.

Acid was developed in the reactions of *tert.*-butyl bromide, and it was neutralised by titration with ethyl alcoholic sodium ethoxide, with the use of lacmoid as indicator, before the sample was evaporated in preparation for the halide ion analysis.

For all reactions except those of *tert.*-butyl bromide, rate constants were calculated from the equation $k_2 = [2{\cdot}303/t(a-b)] \log_{10} [b(a-x)/a(b-x)]$. The presence of concurrent processes of different order in the reactions of *tert.*-butyl bromide necessitated a graphical method. In these cases, values of dx/dt were read from the graph of x against t, and then a graph of $(dx/dt)/(a-x)$ against $(b-x)$ was plotted, from the initial steady slope of which k_2 was obtained. All second-order rate-constants were corrected for thermal expansion of the solvent.

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