

Mechanism of Substitution at a Saturated Carbon Atom. Part XXXVII.
Halide-ion Exchange with a Simple Alkyl Halide in Sulphur Dioxide
Solution.*

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Of the halides, methyl iodide, ethyl bromide, *isopropyl* bromide, and *tert.*-butyl bromide, only the last exchanged its halogen with tetramethylammonium fluoride in sulphur dioxide sufficiently rapidly for observation in the conditions used, and this reaction had the kinetic characteristics of a unimolecular substitution. Its specific rate depended on the concentration of the reagent only to such an extent as could be quantitatively understood as the expected salt effect in a unimolecular substitution with an ionic substituting agent. The common-ion retardation of the unimolecular mechanism, was considerably smaller than in non-solvolytic benzhydryl substitutions, but was quite large enough to be measured, in contrast to solvolysis in which such retardation, although large enough for measurement in the benzhydryl series, is too small for observation with *tert.*-butyl bromide.

OUR early investigation (cf. preceding paper) of substitution of benzhydryl halides in solvent sulphur dioxide was unsystematic in that we had not previously examined reactions of the simplest alkyl halides, an omission to some extent repaired by the work recorded in this and the following paper. Here we deal with the reaction of halide-ion exchange, using as before electrical conductance as a method of following the progress of reaction.

* Part XXXVI, preceding paper.

First, a qualitative survey was made of the behaviour of fluoride ion, supplied as tetramethylammonium fluoride in sulphur dioxide, towards methyl iodide, ethyl bromide, *isopropyl* bromide, and *tert.*-butyl bromide in the temperature range -20° to $+15^{\circ}$, the lower limit being determined by the performance of our thermostat, and the upper by the safety of our conductivity cells under the vapour pressure developed by the solvent. It was found that the reaction between fluoride ion and the methyl, ethyl, or *isopropyl* halide was too slow to be measured in these conditions, but that a reaction occurred with *tert.*-butyl bromide, which was conveniently measurable near the lower end of the temperature range, but somewhat fast near the upper end.

These facts alone have significance for the mechanism of the reaction of fluoride ion with the *tert.*-butyl halide. In the next paper we shall report a bimolecular reaction between pyridine and methyl iodide, which is measurable at similar temperatures, and we can feel sure that a bimolecular reaction between fluoride ion and methyl iodide would be much slower, and hence too slow for measurement at such temperatures. The bimolecular reactions of fluoride ion with ethyl, *isopropyl*, and *tert.*-butyl bromide are likely, if the usual rules are followed, to be slower still in successive degrees, and so they also will be too slow to be measured. If a unimolecular reaction of any of the same four halides is fast enough to be measured, the reaction of *tert.*-butyl bromide will surely be that one. The unimolecular reactions of the *isopropyl*, ethyl, and methyl halides will be very much slower in successive degrees, and therefore they will all be too slow to be measured in similar conditions. One sees that it is hardly possible to rationalise the few qualitative observations mentioned, unless we may assume that the reaction of fluoride ion with *tert.*-butyl bromide is unimolecular.

This conclusion is supported by the study we have made of the kinetics of this *tert.*-butyl halide-ion exchange at -15.03° . Generally, the reaction exhibits kinetic features qualitatively similar to, though quantitatively different from, those shown by the reaction between fluoride ion and *m*-chlorobenzhydryl chloride (Bateman, Hughes, and Ingold, *J.*, 1940, 1017).

The first notable point is that, although the initial specific rate of conversion of *tert.*-butyl bromide rises with increasing initial concentration of fluoride ion, this effect is altogether smaller than would correspond to a unit of kinetic order in the substituting agent. For example, a doubled concentration of the tetramethylammonium fluoride added less than 10% to the rate, and a nearly 7-fold increase in the concentration of the substituting agent did not quite double the rate. The figures are in Table 1.

TABLE 1. *Initial specific rates (k_0 in sec.⁻¹) of reaction of tert.-butyl bromide with tetramethylammonium fluoride in solvent sulphur dioxide at -15.03° .*

No.	RBr	NMe ₄ F	10 ⁵ k ₀	No.	RBr	NMe ₄ F	10 ⁵ k ₀
62	0.0281	0.0112	5.92	69	0.0830	0.0486	9.26
65	0.0278	0.0155	6.37	66	0.0253	0.0543	9.52
61	0.0280	0.0214	6.49	68	0.0805	0.0602	10.60
51	0.0304	0.0215	6.36	58	0.0305	0.0702	10.68
63	0.0255	0.0266	6.83	59	0.0280	0.0742	11.50
64	0.0257	0.0397	7.52				

This slow rise in the specific rate of conversion of the alkyl halide with increasing concentration of the reagent can very plausibly be ascribed to the positive salt effect expected in unimolecular substitution with an ionic reagent. The effect has a functional form which agrees with this interpretation, and a magnitude close to what could be calculated, with the aid of electrostatic theory, from known salt effects in the solvolytic unimolecular reactions of *tert.*-butyl bromide. The theory of the matter has been already given (Bateman, Church, Hughes, Ingold, and Taher, *J.*, 1940, 979), and need not be summarised, except with respect to the conclusions, which are as follows. The proportional rate change for a given change in the ionic strength μ depends on the solvent essentially through its macroscopic dielectric constant D , and otherwise on the conditions of reaction exclusively through the absolute temperature T . It depends on the substance undergoing the unimolecular reaction only through a molecular constant of the dimensions of length, which measures in

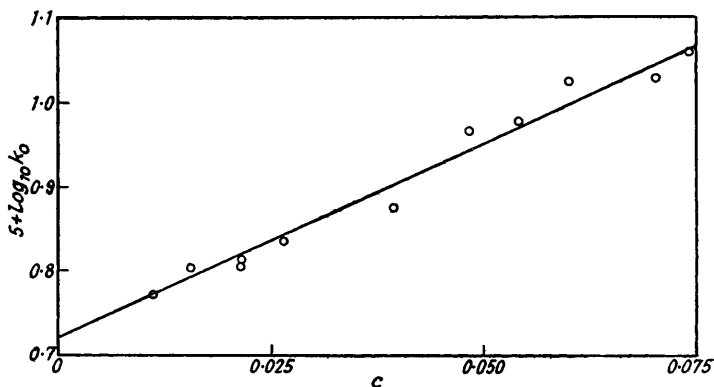
a special way the amount of electron displacement in the transition state of the rate-controlling ionisation. This quantity σ is essentially a constant of the ionising molecule, and, as an approximation, may be carried over unchanged from one solvent to another; but, in closer approximation, it is expected also to be somewhat dependent on the solvent, because the weaker the solvation of the partly formed ions of the transition state, the larger the internal transfer of electrons has to be in order to determine the breakage of the bond. A quantitative expression of the electrostatic theory is contained in the equation,

$$k_1^\mu = k_1^0 \text{antilog}_{10} (0.912 \times 10^{16} \mu \sigma / D^2 T^2)$$

where k_1^μ is the unimolecular rate constant at ionic strength μ , and k_1^0 is the limit to which it goes at zero ionic strength. This shows that the plot of $\log_{10} k_1^\mu$ against μ should be a straight line, its axial intercept being $\log_{10} k_1^0$, and its slope $0.912 \times 10^{16} \sigma / D^2 T^2$.

We can identify k_1^μ with the values of $k_0 = (dx/dt)_{t=0}/a$ in Table 1, and the relevant ionic strength μ as the introduced concentration c of tetramethylammonium fluoride. Calling k_0^0 the limit into which k_0 goes when c tends to zero, substituting $D = 16.7$ and

Logarithm of the initial specific rate of reaction of tert.-butyl bromide with tetramethylammonium fluoride in sulphur dioxide at -15.03° , plotted against the initial salt concentration.



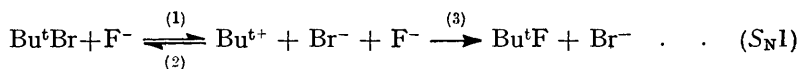
$T = 258^\circ$, and expressing σ for convenience in Ångstrom units, our theoretical equation takes the form,

$$\log_{10} k_0 = \log_{10} k_0^0 + 4.92\sigma c$$

For aqueous reactions the constant σ of *tert.*-butyl bromide has been found to be about 0.80 \AA . For reactions in sulphur dioxide we might, for the reason given above, expect a slightly larger value.

The plot of $\log_{10} k_0$ against c is shown in the Figure. It is linear to within the experimental error. The slope of the line gives the reasonable σ value, 0.93 \AA . The axial intercept gives the rate constant k_0^0 at infinite dilution as $5.2 \times 10^{-5} \text{ sec.}^{-1}$.

On the evidence so far given, the conclusion would be justified that a unimolecular substitution is under observation; but that conclusion can be confirmed. For, in principle, such a reaction, independently of its possible overall reversibility, admits of retardation of its overall forward process, through retrogression of the rate-determining step of the latter, as influenced by the anions formed in the reaction, or by added anions of the same kind:



In this reaction bromide ions are formed: when bromide ions are added as tetramethylammonium bromide, the reaction rate is reduced below that appropriate to the ionic strength; and this is true from the commencement of reaction, when there can be no disturbance from the overall retrograde substitution. Obviously this is the expected mass-law retardation of the forward process by added anions of the same kind as those

formed. As noted in the preceding paper, we can calculate the retardation constant α , that is, the ratio of the specific rate of step (2) to that of step (3) of the unimolecular substitution as written above, from the factor f by which the initial specific rate is reduced, when bromide ion is added initially in a concentration ρ times that of the fluoride ion: the formula is $\alpha = (f^{-1} - 1)/\rho$. Data relating to some experiments, which allow α to be thus calculated, are given in Table 2. The retardations f are not as large as we have observed in some other unimolecular reactions, and this is expressed in the comparatively small value of α .

TABLE 2 *Initial specific rates ($k_0^{(b)}$ in sec.⁻¹) of the reaction of tert.-butyl bromide with tetramethylammonium fluoride in the presence of initially added tetramethylammonium bromide in solvent sulphur dioxide at -15.03° .*

No.	[RBr]	[NMe ₄ F]	[NMe ₄ Br]	ρ	$10^5 k_0^{(b)}$	f	α
71	0.0304	0.0124	0.0139	1.12	4.84	0.717	0.35
72	0.0286	0.0209	0.0118	0.565	6.28	0.859	0.29
74	0.0291	0.0169	0.0305	1.81	5.66	0.651	0.30
76	0.0297	0.0083	0.0119	1.43	4.60	0.719	0.27
						Mean	0.30

In unimolecular hydrolysis in aqueous solvents, common-ion retardations are generally small, doubtless because here the ion, in low concentration, is in competition with water, present in quantity as a part of the solvent, in the common attack upon the carbonium ion. In the earlier study of aqueous reactions, it was indeed found that common-ion retardation in the hydrolysis of *tert.*-butyl bromide was too small to be observed, although common-ion retardations were readily observable in the hydrolysis of various simple and substituted benzhydryl halides (Bateman, Church, Hughes, Ingold, and Taher, *loc cit.*). In non-solvolytic substitutions in sulphur dioxide, the retardations are generally much larger; and this can be understood, because now the common ion is under competition only from a substituting agent in a comparably low concentration. However, within this raised scale of retarding effects, the difference between *tert.*-butyl bromide and the benzhydryl halides appears again, when we compare the present retardation constant of 0.30 for substitution by fluoride ion in *tert.*-butyl bromide, with the previously recorded constant of 20 for substitution by fluoride ion in *m*-chlorobenzhydryl chloride (Bateman, Hughes, and Ingold, *loc cit.*). The slower combination of bromide ion than of fluoride ion with the *tert.*-butyl cation, despite the faster combination of chloride ion than of fluoride ion with a benzhydryl cation, may be disclosing a steric effect in the union of large anions with tertiary carbonium ions.

The general kinetic course of the reactions of fluoride ion with *tert.*-butyl bromide in sulphur dioxide has been studied, and the details of an illustrative run are given in the Experimental section. However, owing to the smallness of the common-ion retardation, and the strong reversibility of the overall substitution, the kinetic form does not in this case provide a particularly distinctive test of mechanism. These substitutions, as we conducted them, came to approximate equilibrium in the broad neighbourhood of 50% conversion; but we could neither measure these equilibria accurately nor make a separate kinetic study of the retrograde substitution, for the reason that *tert.*-butyl fluoride decomposes in sulphur dioxide—somewhat slowly, but fast enough to spoil such measurements. Thus only the early part, certainly not more than 10%, of the forward substitution was suitable for a kinetic analysis which necessarily neglected disturbance by the retrograde reaction; and, within this limited range of progress of reaction, neither the kinetic order, nor the common-ion retardation, makes any striking difference to the reaction-time curve.

EXPERIMENTAL

On account of the hygroscopic nature of tetramethylammonium fluoride it was put into the conductivity cell first by transference, in a current of dry nitrogen, from a weighing-tube taken directly from the Abderhalden drier into the cell taken directly from its drying oven. Tetramethylammonium bromide, when used, was handled similarly. Dry sulphur dioxide was passed through the cell as gas for some time, before the temperature was reduced, and it was

collected as liquid. The purified *tert.*-butyl bromide, taken from a freshly opened ampoule, was added finally from a weight-pipette.

Calibration.—It was shown by experiments with synthetic mixtures of tetramethylammonium fluoride and bromide, that the replacement of a proportion of one of these salts by its equivalent of the other produced, for any fixed total salt concentration, a conductance change proportional to the amount so replaced, although the proportionality constant varied with the total salt concentration. Hence, for calibration, it was sufficient to determine the conductances of the two salts separately, over the relevant concentration range. These data are in Table 3.

TABLE 3. *Electrical conductance (κ in ohm⁻¹ cm.⁻¹) of tetramethylammonium fluoride and of tetramethylammonium bromide in sulphur dioxide at -15.03°*

NMe ₄ F				NMe ₄ Br			
Concn. (M)	10 ³ κ	Concn. (M)	10 ³ κ	Concn. (M)	10 ³ κ	Concn. (M)	10 ³ κ
0.00311	0.336	0.0540	2.77	0.00330	0.428	0.0235	2.16
0.00341	0.356	0.0573	2.97	0.0071	0.774	0.0333	2.87
0.0244	1.47	0.0752	3.87	0.0090	0.948	0.0522	4.22
0.0252	1.55	0.109	5.83	0.0146	1.42	0.0579	4.76
0.0340	1.96	0.115	6.05	0.0152	1.46	0.0868	6.48

From these figures curves were drawn, one for the electrical conductance of each salt *versus* its concentration. Then a curve was drawn for the difference in the conductances of the two salts at different common concentrations. The ratios of the ordinates to the abscissæ of this third curve, when plotted against the abscissæ, gave the rate of change of conductance with the concentration in which one salt was replaced by its equivalent of the other $d\kappa/dx$, as a function of the total salt concentration μ . Actually it was more convenient to make this fourth plot one of the reciprocal of the above derivative, namely, $dx/d\kappa$, against μ , since the ordinates were then the factors by which each measured conductance change, at a known total salt concentration, had to be multiplied in order to give the corresponding concentration of material converted.

Results.—As usual, both methods of getting initial specific rates, *viz.*, direct reading, with a reflecting straight edge, from the conductance-time curves, and extrapolation from calculated, slowly drifting "constants," were tried; but in these experiments the direct method was preferred, as the initial curvatures were not excessive, whereas random scatter among the first few calculated constants often left a doubt about how the extrapolation should be made. The results of the measurements are in Tables 1 and 2.

An illustration is given in Table 4 of the kinetic form of a run. It will be noted that the unimolecular rate constants k_1 , calculated with due allowance for the common-ion effect, by the equation given in the preceding paper, show fair constancy over the first 8% of reaction, but after that fall. This fall is due essentially to the overall reversibility of the substitution

TABLE 4. *Illustrating the kinetic course of the reaction between tert.-butyl bromide and tetramethylammonium fluoride in sulphur dioxide at -15.03° . (Run 68.)*

{Initially, $a = [\text{RBr}] = 0.0805\text{M}$, and $c = [\text{NMe}_4\text{F}] = 0.0602\text{M}$. The product concentration is x (M) at time t (sec.). The unimolecular rate constants (k_1 in sec.⁻¹) are calculated with $\alpha = 0.30$ from the equation in the preceding paper (p. 635).}

t	10 ³ x	10 ² x/c	10 ⁵ k_1	t	10 ³ x	10 ² x/c	10 ⁵ k_1
120	1.15	1.91	11.1	1260	9.38	15.6	10.1
240	2.05	3.41	10.7	1800	12.37	20.6	9.6
360	2.92	4.85	10.6	3600	19.6	32.6	8.3
480	3.96	6.58	10.5	4800	22.6	37.6	7.5
600	4.81	8.00	10.5	6000	25.6	42.5	7.0

10⁵ k_1 from mean of first five readings = 10.6
10⁵ k_0 from reaction-time graph = 10.6