375. *The Kinetics of Exchange Reactions. Part II.* n-*Propyl,*
iso*Propyl, and* iso*Butyl Bromides.*

By G. A. Elliott and S. Sugden

By the aid of radioactive bromine as an indicator the kinetics of three more exchange reactions of alkyl bromides with bromide ion have been studied in aqueous acetone containing 90% of acetone by volume. The activation energies found are : *n*-propyl, 18·12; *iso*butyl, 20·21; *iso*propyl, 22·94 kg.-cals. *iso*Propyl bromide not only shows a high activation energy but also gives an unusually high value of the effective collision diameter for the reaction.

IN Part I (this vol., p. 1279) the kinetics of the exchange reaction between *n*-butyl bromide and bromine ion were studied in some detail, radioactive bromine being used as an indicator. We have now extended this work to three more alkyl bromides; the solvent used was a mixture of 90 vols. of acetone with 10 vols. of water so that the results can be compared with those found in this solvent for *n*-butyl bromide.

The data obtained are summarised in Table I. Since the reaction with *n*-butyl bromide

has already been shown to follow a bimolecular law, we have not made a detailed study of the effect of change of concentration. A consideration of experiments 7 and 8 and 19—23 provides, however, further supporting evidence for the bimolecular character of these reactions.

TABLE I.

Velocity Coefficients.

No.	T, °K.	Time (hrs.).	a.	b.	x/c.	$10^5 k_2$, obs.	$10^5 k_2$, calc.
			n-Propyl bromide.				
1	273·1	42·92	0·2503	0·0526	0·060	1·6	2·0
2	298·2	5·08	0·1244	0·0375	0·082	38	35
3	298·2	21·8	0·1244	0·0375	0·280	36	35
4	307·6	5·2	0·2455	0·0424	0·334	92	89
5	307·6	8·4	0·2455	0·0424	0·526	110	89
6	307·6	23·2	0·2455	0·0424	0·789	108	89
7	338·9	1·16	0·2345	0·0360	0·678	1350	1480
8	338·9	2·55	0·1173	0·0349	0·632	1230	1480
			*iso*Propyl bromide.				
9	298·2	64·9	0·1504	0·0433	0·042	1·2	1·2
10	307·7	45·17	0·1484	0·0718	0·089	3·9	4·0
11	317·6	22·03	0·1463	0·0391	0·144	13·7	13·2
12	332·9	23·00	0·1430	0·0557	0·465	63	71
13	343·3	13·93	0·1409	0·0275	0·713	227	209
			*iso*Butyl bromide.				
14	298·0	67·0	0·1163	0·0501	0·038	1·4	1·8
15	298·7	44·87	0·2320	0·0845	0·054	1·5	1·8
16	307·7	43·72	0·1590	0·0287	0·154	6·8	5·1
17	309·1	41·4	0·1145	0·0405	0·119	7·6	6·5
18	309·7	40·0	0·1144	0·0541	0·123	8·3	6·6
19	322·2	24·33	0·2250	0·0425	0·360	23·9	23·4
20	322·2	45·7	0·2250	0·0350	0·499	20·1	23·4
21	322·2	23·62	0·2250	0·0426	0·337	22·5	23·4
22	322·2	24·33	0·1125	0·0373	0·205	24·3	23·4
23	322·2	22·50	0·1125	0·0386	0·188	23·9	23·4
24	342·9	14·67	0·1089	0·0508	0·491	151	166
25	343·0	15·25	0·1509	0·0357	0·664	168	166

In this table, a and b are the molar concentrations of alkyl bromide and bromide ion respectively. The radio-bromine was initially present as ion, and x/c is the fraction of the total radioactivity found in the alkyl bromide at the end of the experiment; k_2, obs. was calculated from these data by the formula recorded in Part I.

The velocity coefficients were then used to compute by the method of least squares the parameters of the modified Arrhenius equation $\log k_2/T^{\frac{1}{2}} = A - E/4\cdot57T$; these constants are collected in Table II. The values of k_2, calc. given in the last column of Table I were calculated by using these constants, and a comparison with the figures in the penultimate column shows that these reactions obey this law within the limits of the experimental error.

TABLE II.

Activation Energies and Effective Collision Diameters.

Bromide.	E, kg.-cals.	A.	$\sigma_{\text{eff.}}$, A.	Bromide.	E, kg.-cals.	A.	$\sigma_{\text{eff.}}$, A.
n-Propyl	18·12 ± 0·36	8·60 ± 0·26	1·0 ± 0·3	*iso*Butyl	20·21 ± 0·41	8·85 ± 0·23	1·3 ± 0·4
n-Butyl	18·87 ± 0·14	8·13 ± 0·10	0·6 ± 0·1	*iso*Propyl	22·94 ± 0·34	10·67 ± 0·23	11 ± 3

The activation energy increases a little on passing from *n*-propyl to *n*-butyl bromide whilst the effective collision diameter falls. The introduction of a branched chain in *iso*butyl bromide gives an increase both in activation energy and in collision diameter, although the exchangeable bromine is linked as a primary bromide, $CHMe_2\cdot CH_2Br$. With the secondary bromide, *iso*propyl bromide, there is a large increase in activation energy and an unusually high value for the effective collision diameter.

It is not easy to account for these results by the usual picture involving the cumulative

repulsion of electrons by the methyl groups. Since the reaction consists in the replacement of one isotope by another, the transition state must be symmetrical, with the attacking bromine atom and that which is expelled separated by equal distances from the carbon atom. Hence, although an accumulation of electrons on the carbon atom would hinder the approach of the incoming bromine, yet it would equally favour the expulsion as an ion of the other bromine atom, and should have little effect upon the activation energy.

EXPERIMENTAL.

n- and *iso*-Propyl bromides were purified by repeated fractionation until the boiling range was less than 0·5°. Tests for hydrolysis were made with these bromides as described in Part I, and none could be detected under the experimental conditions used in the exchange measurements.

*iso*Butyl bromide was more troublesome to purify. A specimen prepared by drying over potassium carbonate and distilling over fresh potassium carbonate was used for most of the experiments. This product when tested for hydrolysis by heating in 90% acetone at 60° rapidly produced bromine ion from $4\frac{1}{2}$% of *tert.*-butyl bromide which was present as an impurity. The reaction was complete in one hour at 60°, and no further reaction occurred when the time of heating was extended to 15 hours. In the reaction-velocity measurements the amount of bromide ion was always determined directly after separating the alkyl bromide and therefore included that set free by hydrolysis. Since the reaction of *tert.*-butyl bromide with aqueous acetone is very much faster than the exchange reaction, the total bromide ion found at the end of the experiment is effective throughout practically the whole time interval. It is only necessary to correct the concentration of *iso*butyl bromide by a factor of 0·955, and these corrected figures are quoted in Table I.

To test this conclusion, a pure specimen was prepared by heating the less pure product with aqueous acetone until hydrolysis of the tertiary bromide was complete. The residual *iso*butyl bromide was well washed with cold water, dried over potassium carbonate, and distilled. It gave no detectable hydrolysis under the conditions of the exchange reactions and was used in experiments 16 and 25. The velocity coefficients found with the pure specimen confirm those obtained by correcting the data for the less pure bromide.

The separation of the alkyl bromide and bromide ion and the measurement of the radio-activities of the samples were carried out as described in Part I.

THE SIR WILLIAM RAMSAY AND RALPH FORSTER LABORATORIES,
UNIVERSITY COLLEGE, LONDON, W.C. 1.