155. *The Kinetics of Exchange Reactions. Part III. Influence of Solvent and Molecular Structure.*

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This paper completes an account of work done in 1939 on exchange reactions of alkyl bromides with radioactive bromine ion. The reactions have been followed over a wide enough temperature range to permit the calculation of the activation energy and the effective mean collision area. Both are found to be materially influenced by the solvent and by the structure of the alkyl bromide studied. One aromatic bromide has been found to undergo measurable exchange.

A KINETIC study of exchange reactions of the type $RBr + Br^{*\prime} = RBr^{*} + Br^{\prime}$ (where $Br^{*\prime}$ represents radioactive bromine ion) has been commenced in these laboratories and some of the results have already been published (Part I, J., 1939, 1279; Part II, *ibid.*, p. 1836). This work has had to be discontinued, but we record some further observations directed mainly towards a study of the effect of changes in solvent and in structure of the alkyl bromide which undergoes exchange with radioactive bromide ion.

The significant data are collected in Table I, together with the results of the investigations described in Parts I and II. (Details of the reaction-velocity measurements are given in the experimental section.) In this table, E is the activation energy (in kg.-cals./mol.) and A the " non-exponential " term of the modified Arrhenius equation (2); $\sigma_{\text{eff.}}$ is the effective collision area calculated from A by means of equation (3).

n-Butyl bromide has been examined in three solvents. The activation energy for the exchange reaction in anhydrous acetone (No. v) is considerably lowered by the addition of 10% of water (No. iii) and in ethylene glycol diacetate E is still lower. This lowering of the activation energy is more than compensated for by a large change in $\sigma_{\text{eff.}}$ which decreases more than 50-fold in the range of solvents used. It was hoped to examine *tert.*-butyl bromide in anhydrous acetone as solvent. This substance gives a high value of $\sigma_{\text{eff.}}$ in ethylene

TABLE I.

Activation Energies and Effective Collision Areas.

	Bromide.	Solvent.	E.	A.	$\sigma_{\text{eff.}}$, A.
(i)	*n*-Propyl	90% $COMe_2$	18·12 ± 0·36	8·60 ± 0·26	1·0 ± 0·3
(ii)	*iso*Propyl	,,	22·94 ± 0·34	10·67 ± 0·23	11·0 ± 3·0
(iii)	*n*-Butyl	,,	18·87 ± 0·14	8·13 ± 0·10	0·6 ± 0·1
(iv)	*iso*Butyl	,,	20·21 ± 0·41	8·85 ± 0·23	1·3 ± 0·4
(v)	*n*-Butyl	Anhyd. $COMe_2$	19·81 ± 0·25	10·28 ± 0·18	7·0 ± 1·0
(vi)	*n*-Butyl	E.G.D.A.*	17·76 ± 0·06	6·84 ± 0·04	0·13 ± 0·01
(vii)	*iso*Propyl	,,	19·75 ± 0·15	6·71 ± 0·09	0·11 ± 0·02
(viii)	*tert.*-Butyl	,,	22·60 ± 0·80	9·33 ± 0·49	2·4 ± 1·4
(ix)	2 : 4-Dinitrophenyl	,,	19·34 ± 0·23	6·42 ± 0·13	0·09 ± 0·01

* E.G.D.A. = Ethylene glycol diacetate.

glycol diacetate: if the effect of solvent is in the same ratio as that found for the normal bromide, then $\sigma_{\text{eff.}}$ in anhydrous acetone would be much larger than is expected on the basis of current theory.

Two influences of the structure of the alkyl radical can be traced in these results. It is evident that chain branching increases E with an accompanying increase in $\sigma_{\text{eff.}}$. This is found in solutions in 90% acetone and ethylene glycol diacetate; it occurs when the branching of the carbon chain is separated by a carbon atom from the C–Br link but is particularly evident with the secondary and tertiary bromides. The second effect is seen by comparing reactions (i) and (iii). Here increase in chain length gives a small rise in E accompanied by a fall in $\sigma_{\text{eff.}}$. This result, however, needs to be tested over a wider range of homologues. Finally, the exchange studied in (ix) of bromine substituted in the benzene nucleus has some points of interest. The slowness of this reaction is due, not to a high activation energy, but to a small value of $\sigma_{\text{eff.}}$, *i.e.*, to a small probability of reaction even when the colliding molecules possess sufficient energy.

EXPERIMENTAL.

(*a*) (With L. J. LE ROUX.) The exchange of radio-bromine ion with *n*-butyl bromide has been studied in two more solvents, *viz.*, anhydrous acetone and ethylene glycol diacetate. The former was chosen since preliminary observations (Part I) had shown a marked negative catalysis by water. "AnalaR" Acetone was dried over anhydrous magnesium perchlorate and then fractionated. The constant-boiling fraction was stored over magnesium perchlorate and redistilled immediately before use. Reaction vessels and pipettes were heated to 110° and dry air blown through them. Otherwise the experimental method was that described in Part I, lithium bromide containing radioactive bromine ion being used.

In Table II, a is the concentration of alkyl bromide and b that of the bromide ion, both expressed in g.-mols./l.; x/c is the ratio of the radio-bromine found in the alkyl bromide to the total amount of radio-bromine present; k_2 is the constant for the bimolecular exchange reaction given by

$$k_2 = \frac{1}{t(a+b)} \log_e \frac{1}{1 - x(1 + b/a)/c} \qquad \text{(1)}$$

and is expressed in sec.$^{-1}$, moles^{-1}, l. The activation energy, E, was calculated by the method of least squares from the modified Arrhenius equation

$$(\log_{10} k_2)/\sqrt{T} = A - E/4{\cdot}57T \qquad \text{(2)}$$

Writing

$$A = \log_{10} \{6{\cdot}06 \times 10^{20} \sigma_{\text{eff.}}^2 (8\pi \mathbf{R}/M)^{1/2}\} \qquad \text{(3)}$$

where M is the reduced mass of the reactants, we can readily calculate the collision radius $\sigma_{\text{eff.}}$.

TABLE II.

n-*Butyl bromide in anhydrous acetone.**

					$10^5 k_2$.	
T (° K.).	Time (hours).	a.	b.	x/c.	Obs.	Calc.
262·6	52	0·1040	0·1248	0·170	0·89	0·96
,,	90	,,	0·1396	0·216	0·90	,,
273·1	49·5	0·1027	0·0557	0·478	4·6	4·3
298·1	1·25	0·0993	0·0119	0·374	108	93
,,	1·50	,,	0·0191	0·406	104	,,
313·1	0·50	0·0974	0·0222	0·500	443	480
,,	0·67	,,	0·0284	0·535	390	,,
,,	,,	,,	0·0565	0·528	486	,,
,,	,,	,,	0·0501	0·562	539	,,

* k_2 calculated from $(\log_{10} k_2)/\sqrt{T} = 10{\cdot}28 \pm 0{\cdot}18 - (19{,}810 \pm 250)/4{\cdot}57T$.

n-*Butyl bromide in ethylene glycol diacetate.*†

298·1	42	0·100	0·0550	0·148	1·10	1·07
,,	24·5	,,	0·0514	0·086	1·05	,,
323·1	22·0	0·0970	0·0566	0·481	11·8	11·5
,,	20·0	,,	0·0502	0·460	11·3	,,
353·1	2·00	0·0940	0·0568	0·470	129	126
373·1	0·50	0·0922	0·0494	0·486	537	513
,,	0·33	,,	0·0512	0·371	501	,,

† k_2 calculated from $(\log_{10} k_2)/\sqrt{T} = 6{\cdot}84 \pm 0{\cdot}04 - (17{,}760 \pm 60)/4{\cdot}57T$.

(*b*) (With C. S. LU.) Preliminary experiments with *p*-nitrobromobenzene and 2 : 4-dinitrobromobenzene with acetone as solvent gave no detectable exchange, but with the latter substance dissolved in ethylene glycol diacetate the reaction could be followed over a sufficient range of temperatures. The variations in a and b in the experiments at 363·1° and 373·0° were made to test the bimolecular mechanism for this reaction, which is assumed in the formula for k_2.

2 : 4-*Dinitrobromobenzene in ethylene glycol diacetate.*‡

343·3	42·0	0·1187	0·0628	0·283	2·1	2·3
363·1	5·5	0·1163	0·0311	0·233	12·0	11·0
,,	4·0	0·1163	0·0562	0·157	10·6	,,
373·0	4·0	0·1150	0·0434	0·319	25·4	22·9
,,	4·0	0·0766	0·0577	0·210	23·8	,,
,,	5·0	0·0575	0·0766	0·185	23·4	,,
393·1	3·0	0·1125	0·0351	0·566	85·1	89·1
,,	1·5	0·1125	0·0427	0·391	92·5	,,
403·1	3·0	0·1113	0·0502	0·642	153	166
,,	2·0	0·1113	0·0389	0·620	167	,,

‡ k_2 is calculated from $(\log_{10} k_2)/\sqrt{T} = 6{\cdot}42 \pm 0{\cdot}13 - (19{,}340 \pm 230)/4{\cdot}57T$.

In this and the following tables in this paper a and b are concentrations measured at 18°, but the values of k_2 have been corrected for solvent expansion.

(*c*) (With R. H. K. Thomson.) In order to study the effect of the accumulation of methyl groups it was intended to examine the series of ethyl, *iso*propyl, and *tert.*-butyl bromides in a number of solvents. Only the last two had been measured in ethylene glycol diacetate when the work had to be discontinued.

iso*Propyl bromide in ethylene glycol diacetate.*§

					$10^5 k_2$.	
T (° K.).	Time (hours).	a.	b.	x/c.	Obs.	Calc.
313	20	0·093	0·052	0·0092	0·14	0·14
,,	22	0·123	0·029	0·0154	0·16	,,
333	91·5	0·093	0·022	0·273	1·14	0·98
,,	93	0·062	0·037	0·151	0·87	,,
353	10	0·089	0·0132	0·212	5·11	5·5
,,	16·2	0·089	0·0288	0·197	4·71	,,
,,	16·2	0·089	0·0288	0·189	4·55	,,
,,	17	0·060	0·0223	0·166	5·54	,,
	17	0·120	0·0223	0·319	5·81	5·5
,,	17	0·180	0·0223	0·395	5·09	,,
373	15·75	0·093	0·0164	0·682	27·5	2·57
,,	4·0	0·062	0·018	0·185	25·9	,,
393	2·0	0·062	0·027	0·295	96·5	102
,,	1·0	0·062	0·028	0·172	96·0	,,
413	0·33	0·110	0·099	0·288	361	355
,,	0·20	0·119	0·052	0·248	411	..

§ k_2 calculated from $(\log_{10} k_2)/\sqrt{T} = 6{\cdot}71 \pm 0{\cdot}09 - (19{,}750 \pm 150)/4{\cdot}57T$.

tert.*-Butyl bromide in ethylene glycol diacetate.*||

313	42·33	0·063	0·046	0·042	0·49	0·61
,,	44·0	0·053	0·039	0·037	0·49	,,
333	17·0	0·063	0·042	0·286	10·6	5·5
,,	20·5	0·053	0·035	0·272	9·7	,,
353	17·3	0·053	0·022	0·425	21·0	39·0
373	1·0	0·079	0·032	0·436	257	229
,,	1·0	0·079	0·033	0·398	227	,,
393	0·22	0·105	0·032	0·449	993	1120
,,	0·33	0·079	0·024	0·513	1000	

|| k_2 calculated from $(\log_{10} k_2)/\sqrt{T} = 9{\cdot}33 \pm 0{\cdot}49 - (22{,}600 \pm 800)/4{\cdot}57T$.

Ethylene glycol diacetate was also used, since it seemed promising as a general solvent for use in a wide range of reactions. It is readily obtained in a sufficient state of purity, and its good solvent power and high b. p. allow reactions to be followed in it which proceed at a measurable rate only at temperatures in the neighbourhood of 200°. The commercial product on distillation gave a main fraction, b. p. 186—187°, which was used as a solvent.

With *tert.*-butyl bromide some hydrolysis took place during the washing of the benzene solution with water to separate the lithium bromide. This was measured, and a correction applied on the assumption that all the hydrolysis occurred during washing and that none of it took place during the reaction. Because of the uncertainty thus introduced, the observations on this substance are of a rather lower degree of accuracy and can only be regarded as giving approximate values for E and $\sigma_{\text{eff.}}$.

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