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

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Kinetic experiments on the second-order reaction of bromine exchange between lithium radio-bromide and seven simple alkyl bromides in acetone are reported. In the one case of *tert.*-butyl bromide, the bimolecular substitution is accompanied by a probably unimolecular side reaction, in an amount which is too small to show in the kinetics, but is revealed by its component elimination, which produces a trace of acid. All the reactions are subject to a negative salt effect of approximately uniform character. These disturbances being dealt with, rate constants and parameters of the Arrhenius equation are evaluated.

THEORETICAL discussions of the transition states of Finkelstein substitutions are so much simplified when the forward and retrograde processes become identical, that special interest attaches to the experimental examination of exchange reactions, such as that between lithium radio-bromide and alkyl bromides, in a solvent, such as dry acetone, in which the bimolecular mechanism of substitution prevails over a wide range of alkyl structures :

$$*Br^- + RBr \rightleftharpoons RBr^* + Br^-$$

For a few alkyl bromides rates of this exchange have been measured in the less generally applicable solvents, aqueous acetone, ethylene diacetate, and ethyl alcohol (le Roux, Lu, Sugden, and Thomson, *J.*, 1945, 586; Miller, Neimen, and Protsenko, *Doklady Akad. Nauk S.S.S.R.*, 1950, **75**, 403; 1951, **77**, 423). The exchange of α-bromopropionic acid has been examined in water, but the results are complicated by hydrolysis (Koskoski, Dodson, and Fowler, *J. Amer. Chem. Soc.*, 1941, **63**, 2149). Rates of the exchange in dry acetone have been measured hitherto only for individual alkyl bromides, each for some special purpose, *i.e.*, 1-phenylethyl bromide and α-bromopropionic acid for the proof of inversion in S_N2 substitutions (Hughes, Juliusberger, Scott, Topley, and Weiss, *J.*, 1936, 1173; Cowdrey, Hughes, Nevell, and Wilson, *J.*, 1938, 209), 1-methylallyl and crotyl bromide, for the establishment of bimolecular (S_N2') anionotropy (England and Hughes, *Nature*, 1951, **168**, 1002), and *n*-butyl and 1-methylheptyl bromide in a study of the kinetic effects of salt concentration on the substitution (Evans and Sugden, *J.*, 1949, 270).

We now record measurements of the rate, in solvent acetone, and in standardised conditions of salt-concentration, of the exchange reaction of lithium radio-bromide with a number of alkyl bromides, chosen to furnish material for a study of the simplest elements of the effect of alkyl structure on the kinetics of this substitution. The alkyl groups were those needed to form the two branching-homologous series, which we call the α- and β-methylated series (see p. 3173). Each substitution has been studied over a range of temperature, and the Arrhenius parameters have been evaluated. The effect of varying the concentrations of the reactants has been examined, with results which will be illustrated; but in the main series of experiments now reported, these concentrations were standardised.

All the substitutions are kinetically of second order, subject to the following qualifications. The first is that the exchange of *tert.*-butyl bromide only is accompanied by a minor side reaction. The second is that all the exchanges are subject to a negative salt effect of an approximately uniform nature. A third kinetic deviation, which can be described as a negative co-solvent effect of the alkyl halides, becomes appreciable only at higher concentrations of alkyl halide than were employed in the measurements now recorded (usually below 0·2M). We discuss the first two of these disturbances before reporting the main results.

The side reaction undergone by *tert.*-butyl bromide could hardly have been detected

simply from the kinetics of the halogen exchange; but it was revealed by the production of a small amount of free acid in the solution. The nature of this side reaction may be inferred from parallel work on the kinetics of halide-ion substitutions of *tert.*-butyl bromide in nitromethane : in this solvent unimolecular reactions are prominent and include elimination (de la Mare, Hughes, Ingold, and Pocker, *J.*, 1954, 2930). We know also that 1-mesitylethyl chloride, in which bimolecular substitution is subject to steric hindrance (forthcoming paper), undergoes unimolecular substitution, as measured by the accompanying racemisation, even in dry acetone (Charlton and Hughes, *J.*, 1954, 2939). We conclude that, in dry acetone, *tert.*-butyl bromide, uniquely among the alkyl halides studied, associates with its main reaction of bimolecular substitution, a small amount of unimolecular side-reaction, which we are able to detect by the distinctive stoicheiometry of its component elimination. In order to ascertain to what extent the occurrence of this unimolecular reaction could affect the determined values of the second-order rate constant of substitution, the first main series of experiments on *tert.*-butyl bromide, *i.e.*, the series corresponding exactly to those conducted on all the other alkyl bromides, was paralleled by several other series in which the concentrations of the reactants were so changed as to alter the relative importance of concurrent unimolecular and bimolecular reactions, and thus to alter the magnitude of a disturbance due to the former. Thus in the fourth series (Table 2) the concentration of *tert.*-butyl bromide was approximately halved and that of the lithium bromide doubled, changes that should reduce the disturbance. In the fifth series the concentration of lithium bromide was approximately quadrupled. However, as can be seen from Tables 1 and 2, these changes do not appreciably affect the second-order rate constants, except in the way which is described below as a salt effect and is not peculiar to *tert.*-butyl bromide.

Negative kinetic effects in Finkelstein substitutions have been observed in several solvents and for several salts, including non-interacting salts, as is illustrated in several of the present and forthcoming papers : the physical mechanism of the effect will be discussed in a later paper. Here we are concerned with the problem of so treating the effect of an increased concentration of lithium bromide in reducing the second-order rate constants of its reactions with alkyl bromides, that it will not interfere with the intended kinetic comparison of the alkyl bromides. An illustration of the salt effect, referring to the reactions of *iso*propyl and *tert.*-butyl bromide, is given in Table 1.

TABLE 1. *Relation between second-order rate constants* $(k_2^{(b)}$ *in* sec.$^{-1}$ *mole*$^{-1}$ *l.) of reactions between lithium bromide and alkyl bromides in acetone and the concentration* $(b$ *in moles per l.) of the lithium bromide.*

The rate values $k_2^{(0.024)}$, corresponding to the " standard " salt concentration 0·024M, are calculated from the equation of the straight line in the Figure, *viz.*, $\log_{10} (k_2^{(b)}/k_2^{(0.024)}) = - 0.37 \log_{10} (b/0.024)$.

	LiBr + Pr^{i}Br in Me$_2$CO at 57·8°			LiBr + Bu^{t}Br in Me$_2$CO at 44·4°.		
b	0·0172	0·0231	0·0597	0·0238	0·0474	0·0918
$10^5 k_2^{(b)}$ (obs.)	53·0	47·3	36·0	5·20	4·06	3·15
$10^5 k_2^{(0.024)}$ (calc.)	47·0	46·8	50·5	5·20	5·22	5·19

Evans and Sugden (*loc. cit.*) examined the salt effect for the corresponding reactions of *n*-butyl and 1-methylheptyl bromide. We have noticed that if for each of their halides and ours, we plot the logarithm of the rate constant against that of the salt concentration, straight lines are obtained of similar slope within the concentration range of 0·001M and 0·1M; and that, therefore, if we re-express the rates for each alkyl halide in terms of the rate for that alkyl halide at a standard salt concentration, a logarithmic plot results in which, as shown in the Figure, all the points lie close to a single straight line. It cannot, of course, have any deep significance that points applying to different alkyl halides reacting at different temperatures should fit the same line; but the observation of such an approximate fit does provide a convenient basis for standardising salt effects in the different reactions to be compared. It also confirms, what we knew on other grounds, *viz.*, that salt effects, when standardised, do not significantly disturb activation energies determined by the Arrhenius equation.

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TABLE 2. *Second-order rate constants (k_2 in sec.$^{-1}$ mole^{-1} l.) of bromine exchange between lithium radio-bromide and alkyl bromides in acetone.*

Temp. (c)	$a =$ [AlkBr]	$b =$ [LiBr]	$t_2 - t_1$ (min.)	Counting rates C	$C - X_1$	$C - X_2$	$10^5 k_2^{(b)}$	$10^5 k_2^{(0.024)}$	Mean
				Methyl bromide.					
−11·0°	0·1614	0·0268	18·4	466·7	469·3	263·1	344 ± 5	354	
,,	0·1667	0·0268	26·1	466·7	469·3	214·8	326 ± 4	336	
,,	0·1716	0·0240	27·5	447·7	432·4	180·4	341 ± 4	341	
,,	0·1714	0·0240	29·9	447·7	432·4	173·6	330 ± 3	330	
,,	0·1763	0·0242	23·7	365·6	344·3	159·7	335 ± 5	336	
,,	0·1517	0·0242	30·2	365·6	344·3	148·9	343 ± 6	344	340
−17·8	0·1644	0·0254	40·0	220·6	197·8	119·5	138 ± 4	140	
,,	0·1843	0·0254	33·7	220·6	197·8	121·4	140 ± 4	142	
,,	0·1637	0·0241	41·8	322·8	305·6	181·9	134 ± 3	134	
,,	0·1710	0·0241	43·7	322·8	305·6	173·4	134 ± 3	135	
,,	0·1715	0·0232	41·1	225·9	220·3	119·1	154 ± 4	153	
,,	0·1662	0·0232	52·3	225·9	220·3	102·0	160 ± 3	159	
,,	0·1668	0·0238	40·1	396·3	384·1	215·8	152 ± 3	152	
,,	0·1753	0·0238	53·3	396·3	384·1	172·0	156 ± 2	156	146
−24·6	0·1650	0·0231	104·4	216·8	207·3	112·7	62·2 ± 1·4	61·6	
,,	0·1575	0·0231	126·5	216·8	207·3	99·4	62·9 ± 1·3	62·3	
,,	0·1827	0·0244	118·5	526·0	533·7	238·9	66·2 ± 0·7	66·4	
,,	0·1713	0·0244	86·8	526·0	533·7	305·8	64·7 ± 0·9	65·0	
,,	0·1669	0·0228	89·0	223·4	231·8	138·7	58·0 ± 1·1	57·2	
,,	0·1836	0·0228	116·3	223·4	231·8	103·0	66·3 ± 0·9	65·5	63·0
−31·0	0·1691	0·0233	135·8	236·0	229·2	160·9	26·6 ± 1·1	25·3	
,,	0·1682	0·0233	158·9	236·0	229·2	156·6	24·6 ± 1·0	24·4	
,,	0·1530	0·0244	140·0	152·8	156·3	109·1	28·0 ± 0·8	28·1	
,,	0·1596	0·0244	172·3	152·8	156·3	98·5	28·5 ± 0·7	28·6	
,,	0·1501	0·0249	121·0	239·3	236·0	176·8	27·3 ± 1·3	27·6	
,,	0·1645	0·0249	127·4	239·3	236·0	170·1	26·8 ± 1·3	27·1	26·8

Temp. (c)	$a =$ [AlkBr]	$b =$ [LiBr]	$10^5 k_2^{(b)}$	$10^5 k_2^{(0.024)}$	Temp. (c)	$a =$ [AlkBr]	$b =$ [LiBr]	$10^5 k_2^{(b)}$	$10^5 k_2^{(0.024)}$
		Ethyl bromide					*Ethyl bromide*		
25·1°	0·1640	0·0242	171 ± 2	171	−10·9°	0·1719	0·0253	3·11 ± 0·11	3·15
,,	0·1640	0·0242	163 ± 2	163	,,	0·1719	0·0253	3·02 ± 0·12	3·06
,,	0·1639	0·0229	155 ± 3	153	,,	0·1708	0·0245	2·80 ± 0·11	2·81
,,	0·1639	0·0229	183 ± 2	181	,,	0·1708	0·0245	2·89 ± 0·11	2·91
,,	0·1639	0·0243	178 ± 4	179	,,	0·1681	0·0200	2·79 ± 0·13	2·67
,,	0·1639	0·0243	172 ± 3	173	,,	0·1681	0·0200	2·89 ± 0·14	2·76
,,	0·1639	0·0243	169 ± 3	169				Mean 2·89	
			Mean 170						
							n-*Propyl bromide*		
16·4	0·1614	0·0240	68·8 ± 1·0	66·8	30·8	0·1607	0·0242	207 ± 4	208
,,	0·1614	0·0240	66·6 ± 0·8	66·6	,,	0·1607	0·0242	160 ± 2	160
,,	0·1614	0·0240	67·8 ± 0·7	67·8	,,	0·1607	0·0242	203 ± 4	204
,,	0·1610	0·0242	64·7 ± 1·1	64·9	,,	0·1614	0·0246	164 ± 3	165
,,	0·1610	0·0242	64·9 ± 0·9	65·0	,,	0·1614	0·0246	210 ± 3	211
			Mean 66·2		,,	0·1614	0·0246	204 ± 3	206
7·9	0·1643	0·0247	24·1 ± 0·3	24·3	,,	0·1616	0·0227	201 ± 4	198
,,	0·1643	0·0247	25·8 ± 0·3	26·0	,,	0·1616	0·0227	208 ± 4	205
,,	0·1660	0·0249	29·5 ± 0·4	29·8	,,	0·1616	0·0227	167 ± 4	165
,,	0·1660	0·0249	28·9 ± 0·4	29·1				Mean 191	
,,	0·1660	0·0249	28·9 ± 0·4	29·2					
,,	0·1663	0·0242	26·8 ± 0·5	26·9	14·9	0·1679	0·0247	42·6 ± 0·6	42·9
			Mean 27·6		,,	0·1679	0·0247	39·0 ± 0·5	39·3
					,,	0·1679	0·0247	40·6 ± 0·6	40·9
0·0	0·1667	0·0251	11·0 ± 0·1	11·2	,,	0·1675	0·0227	40·8 ± 0·9	40·3
,,	0·1667	0·0251	11·2 ± 0·1	11·4	,,	0·1675	0·0227	41·3 ± 0·5	40·7
,,	0·1665	0·0249	9·2 ± 0·24	9·3	,,	0·1675	0·0227	42·3 ± 0·5	41·7
,,	0·1665	0·0249	8·5 ± 0·23	8·6				Mean 41·0	
,,	0·1629	0·0193	12·3 ± 0·2	11·7					
,,	0·1629	0·0193	12·2 ± 0·2	11·6					
			Mean 10·6						

TABLE 2. *(Continued.)*

n-Propyl bromide

Temp. (c)	a = [AlkBr]	b = [LiBr]	$10^5 k_2^{(b)}$	$10^5 k_2^{(0.024)}$
−6.6°	0.1627	0.0283	2.91 ± 0.06	3.04
,,	0.1627	0.0283	3.16 ± 0.06	3.30
,,	0.1644	0.0258	3.42 ± 0.10	3.48
,,	0.1644	0.0258	3.23 ± 0.10	3.29
,,	0.1644	0.0258	3.31 ± 0.10	3.37
			Mean	3.30

isoPropyl bromide

Temp. (c)	a = [AlkBr]	b = [LiBr]	$10^5 k_2^{(b)}$	$10^5 k_2^{(0.024)}$
65.3	0.1549	0.0226	83.6 ± 2.8	82.4
,,	0.1549	0.0226	98.5 ± 2.1	97.0
,,	0.1552	0.0222	99.2 ± 2.0	97.3
,,	0.1552	0.0212	98.4 ± 1.5	96.5
,,	0.1573	0.0227	102.0 ± 2.4	100
,,	0.1573	0.0227	99.8 ± 1.0	97.4
			Mean	95.1
57.8	0.1588	0.0222	50.0 ± 0.9	49.0
,,	0.1588	0.0222	46.9 ± 0.7	46.0
,,	0.1587	0.0207	49.5 ± 1.2	47.5
,,	0.1587	0.0207	49.0 ± 0.9	47.3
,,	0.1565	0.0263	44.9 ± 1.4	46.0
,,	0.1565	0.0263	43.6 ± 1.1	44.7
			Mean	46.7
50.0	0.1490	0.0235	27.1 ± 0.6	26.9
,,	0.1490	0.0235	23.8 ± 0.5	23.6
,,	0.1562	0.0235	24.4 ± 0.7	24.3
,,	0.1562	0.0235	24.3 ± 0.6	24.2
,,	0.1565	0.0238	24.6 ± 0.4	24.6
,,	0.1565	0.0238	24.1 ± 0.3	24.1
			Mean	24.6
42.0	0.1555	0.0242	11.3 ± 0.2	11.3
,,	0.1555	0.0242	10.1 ± 0.2	10.1
,,	0.1608	0.0231	9.7 ± 0.2	9.8
,,	0.1608	0.0231	10.5 ± 0.2	10.4
,,	0.1630	0.0244	10.8 ± 0.3	10.8
,,	0.1630	0.0244	10.9 ± 0.3	10.9
			Mean	10.5
34.9	0.1594	0.0232	5.05 ± 0.14	5.00
,,	0.1594	0.0232	5.21 ± 0.12	5.17
,,	0.1655	0.0257	5.33 ± 0.18	5.43
,,	0.1655	0.0257	5.01 ± 0.17	5.10
,,	0.1622	0.0245	4.98 ± 0.23	5.01
,,	0.1622	0.0245	4.70 ± 0.22	4.73
			Mean	5.07

isoPropyl bromide (2nd series)

Temp. (c)	a = [AlkBr]	b = [LiBr]	$10^5 k_2^{(b)}$	$10^5 k_2^{(0.024)}$
57.8	0.1597	0.0172	53.0 ± 0.3	—
,,	0.1597	0.0172	53.1 ± 1.2	—

isoPropyl bromide (3rd Series)

Temp. (c)	a = [AlkBr]	b = [LiBr]	$10^5 k_2^{(b)}$	$10^5 k_2^{(0.024)}$
57.8	0.1650	0.0597	34.7 ± 1.3	—
,,	0.1650	0.0597	37.2 ± 1.0	—

isoButyl bromide

Temp. (c)	a = [AlkBr]	b = [LiBr]	$10^5 k_2^{(b)}$	$10^5 k_2^{(0.024)}$
57.8	0.1564	0.0237	149 ± 7	149
,,	0.1564	0.0237	155 ± 6	155
,,	0.1564	0.0237	160 ± 6	159
,,	0.1605	0.0243	141 ± 6	141
,,	0.1605	0.0243	128 ± 5	128
,,	0.1605	0.0243	134 ± 5	134
			Mean	144
50.0	0.1600	0.0194	79.6 ± 2.2	75.7
,,	0.1600	0.0194	78.1 ± 2.1	74.2
,,	0.1600	0.0194	74.6 ± 1.7	70.9
,,	0.1608	0.0264	68.6 ± 3.0	70.3
,,	0.1608	0.0264	65.3 ± 2.2	67.0
,,	0.1608	0.0264	60.9 ± 1.8	64.2
			Mean	70.4

isoButyl bromide

Temp. (c)	a = [AlkBr]	b = [LiBr]	$10^5 k_2^{(b)}$	$10^5 k_2^{(0.024)}$
41.8°	0.1637	0.0242	35.7 ± 0.6	35.8
,,	0.1637	0.0242	35.7 ± 0.7	35.8
,,	0.1637	0.0242	36.2 ± 0.7	36.3
,,	0.1641	0.0214	35.9 ± 1.2	34.9
,,	0.1641	0.0214	34.1 ± 0.9	33.1
,,	0.1641	0.0214	30.5 ± 0.8	29.7
			Mean	34.3
32.8	0.1651	0.0261	13.6 ± 0.6	13.9
,,	0.1651	0.0261	13.3 ± 0.5	13.6
,,	0.1651	0.0261	13.4 ± 0.4	13.7
,,	0.1435	0.0236	14.6 ± 0.3	14.5
,,	0.1435	0.0236	14.7 ± 0.2	14.6
,,	0.1435	0.0236	13.5 ± 0.2	13.5
			Mean	14.0
25.1	0.1670	0.0229	6.20 ± 0.20	6.12
,,	0.1670	0.0229	6.67 ± 0.20	6.59
,,	0.1670	0.0229	6.28 ± 0.16	6.20
,,	0.1693	0.0232	6.46 ± 0.10	5.41
,,	0.1693	0.0232	6.62 ± 0.11	6.56
,,	0.1693	0.0232	4.90 ± 0.08	4.86
,,	0.1652	0.0237	5.82 ± 0.10	5.80
,,	0.1652	0.0237	5.92 ± 0.09	5.90
,,	0.1652	0.0237	5.50 ± 0.09	4.98
			Mean	5.82

tert.-Butyl bromide

Temp. (c)	a = [AlkBr]	b = [LiBr]	$10^5 k_2^{(b)}$	$10^5 k_2^{(0.024)}$
79.1	0.1619	0.0238	121 ± 11	121
,,	0.1619	0.0238	151 ± 14	150
,,	0.1598	0.0236	160 ± 7	159
,,	0.1598	0.0236	152 ± 4	151
,,	0.1584	0.0228	145 ± 5	143
,,	0.1584	0.0228	154 ± 3	152
			Mean	146
70.6	0.1645	0.0260	71.3 ± 0.7	72.8
,,	0.1645	0.0260	73.0 ± 2.1	74.5
,,	0.1614	0.0234	71.3 ± 3.6	70.8
,,	0.1614	0.0224	76.5 ± 2.2	75.2
,,	0.1614	0.0224	75.6 ± 1.9	74.2
			Mean	73.5
60.2	0.1680	0.0225	22.3 ± 0.5	21.9
,,	0.1644	0.0220	28.0 ± 0.9	27.4
,,	0.1644	0.0220	27.4 ± 1.9	26.8
,,	0.1637	0.0216	27.3 ± 0.7	26.6
,,	0.1637	0.0216	26.9 ± 0.6	26.2
			Mean	25.8
49.4	0.1666	0.0236	8.55 ± 0.15	8.51
,,	0.1666	0.0236	8.33 ± 0.17	8.29
,,	0.1655	0.0232	8.38 ± 0.19	8.30
,,	0.1655	0.0232	8.48 ± 0.18	8.41
,,	0.1655	0.0232	8.57 ± 0.18	8.50
,,	0.1655	0.0232	8.83 ± 0.18	8.76
			Mean	8.46
40.0	0.1697	0.0335	2.79 ± 0.19	3.06
,,	0.1697	0.0335	2.59 ± 0.18	2.84
,,	0.1689	0.0191	3.48 ± 0.44	3.29
,,	0.1689	0.0191	3.28 ± 0.22	3.11
,,	0.1689	0.0191	3.00 ± 0.24	2.84
			Mean	3.03
25.1	0.1657	0.0258	0.543 ± 0.016	0.544
,,	0.1657	0.0258	0.485 ± 0.016	0.494
,,	0.1657	0.0258	0.508 ± 0.015	0.518
,,	0.1655	0.0229	0.553 ± 0.013	0.546
,,	0.1655	0.0229	0.535 ± 0.014	0.529
			Mean	0.526

de la Mare : Mechanism of

TABLE 2. (Continued.)

Left column:

Temp. (c)	a = [AlkBr]	b = [LiBr]	$10^5 k_2^{(b)}$	$10^5 k_2^{(0.024)}$
	tert.-*Butyl bromide* (2nd series)			
44.4°	0.0720	0.0238	5.33 ± 0.024	5.32
,,	0.0720	0.0238	5.39 ± 0.026	5.37
,,	0.0720	0.0238	4.90 ± 0.027	4.89
			Mean 5.19	
	tert.-*Butyl bromide* (3rd series)		$10^5 k_2^{(0.050)}$	
44.4	0.1440	0.0477	3.94 ± 0.09	3.88
,,	0.1440	0.0477	3.97 ± 0.09	3.90
,,	0.1440	0.0477	4.08 ± 0.09	4.01
			Mean 3.93	
	tert.-*Butyl bromide* (4th series)			
59.8	0.0700	0.0477	16.1 ± 0.8	15.8
,,	0.0700	0.0477	20.9 ± 0.6	20.6
,,	0.0714	0.0441	20.3 ± 0.5	19.4
,,	0.0714	0.0441	20.6 ± 0.5	19.7
,,	0.0686	0.0479	21.1 ± 0.9	20.8
,,	0.0686	0.0479	17.7 ± 0.8	17.5
,,	0.0686	0.0479	20.4 ± 0.8	20.1
			Mean 19.1	
44.4	0.0751	0.0474	4.25 ± 0.13	4.17
,,	0.0751	0.0474	3.97 ± 0.10	3.89
,,	0.0751	0.0474	3.97 ± 0.12	3.90
			Mean 3.99	
35.0	0.0834	0.0534	1.40 ± 0.05	1.43
,,	0.0834	0.0534	1.52 ± 0.05	1.55
,,	0.0834	0.0534	1.49 ± 0.05	1.52
			Mean 1.50	
25.1	0.0738	0.0567	0.409 ± 0.020	0.429
,,	0.0738	0.0567	0.400 ± 0.021	0.420
,,	0.0738	0.0567	0.354 ± 0.020	0.371
,,	0.0822	0.0493	0.416 ± 0.021	0.413
,,	0.0822	0.0493	0.457 ± 0.022	0.455
,,	0.0724	0.0472	0.334 ± 0.016	0.328
,,	0.0724	0.0472	0.433 ± 0.019	0.424
			Mean 0.406	

Right column:

Temp. (c)	a = [AlkBr]	b = [LiBr]	$10^5 k_2^{(b)}$	$10^5 k_2^{(0.024)}$
	tert.-*Butyl bromide* (5th series)			
44.4°	0.0759	0.0918	3.50 ± 0.20	—
,,	0.0759	0.0918	2.98 ± 0.21	—
,,	0.0759	0.0918	2.97 ± 0.20	—
	neo*Pentyl bromide*			
135.2	0.1534	0.0274	55.7 ± 1.1	57.7
,,	0.1534	0.0274	55.4 ± 1.4	57.4
,,	0.1552	0.0225	58.9 ± 1.5	57.9
,,	0.1552	0.0225	63.4 ± 1.2	62.4
,,	0.1553	0.0230	56.8 ± 2.1	56.2
,,	0.1553	0.0230	62.5 ± 1.6	61.8
			Mean 58.9	
123.7	0.1662	0.0184	29.7 ± 0.8	27.9
,,	0.1662	0.0184	31.7 ± 1.0	29.8
,,	0.1601	0.0235	30.0 ± 0.8	29.8
,,	0.1601	0.0235	30.2 ± 0.6	30.0
,,	0.1570	0.0241	25.6 ± 0.8	25.6
,,	0.1570	0.0241	24.8 ± 0.5	24.9
			Mean 28.0	
116.1	0.1624	0.0236	16.0 ± 0.6	16.0
,,	0.1624	0.0236	17.2 ± 0.6	17.1
,,	0.1678	0.0244	15.4 ± 0.5	15.5
,,	0.1678	0.0244	15.4 ± 0.5	15.4
,,	0.1583	0.0239	16.8 ± 0.6	16.8
,,	0.1583	0.0239	15.9 ± 0.6	15.8
			Mean 16.1	
105.3	0.1652	0.0237	6.40 ± 0.50	6.38
,,	0.1652	0.0237	7.24 ± 0.51	7.21
,,	0.1633	0.0239	6.49 ± 0.51	6.48
,,	0.1633	0.0239	7.27 ± 0.45	7.27
,,	0.1615	0.0244	7.23 ± 0.48	7.26
,,	0.1615	0.0244	7.94 ± 0.39	7.97
			Mean 7.10	
88.6	0.1669	0.0236	1.86 ± 0.04	1.85
,,	0.1669	0.0236	2.10 ± 0.05	2.10
,,	0.1669	0.0236	1.80 ± 0.03	1.79
,,	0.1669	0.0236	1.80 ± 0.03	1.79
,,	0.1650	0.0267	1.78 ± 0.08	1.83
,,	0.1650	0.0267	1.80 ± 0.07	1.84
,,	0.1650	0.0267	1.93 ± 0.07	1.99
			Mean 1.88	

Our procedure has been to correct, to a standard salt concentration, rates measured at concentrations not far from the standard. If the relation, illustrated in the Figure, were absolute, we could, for any alkyl halide, compute the rate of its reaction at the standard concentration from measurements made at any concentration : the degree of success of such calculations, when considerable concentration differences are involved, can be judged from the degree of constancy of the values in the last line in Table 1. However, we have used the relation for computing only those small corrections to the rate which arise from the small deviations of experimental concentrations from a standard value.

The main groups of experiments are recorded in Table 2. The measurements refer to the losses of radioactivity of lithium bromide after periods of time in which it exchanges its active halogen for inactive halogen from the alkyl bromides. The counting rates C, $C - X_1$, and $C - X_2$ mean respectively specific activities of inorganic halide initially, on separation at a time t_1 soon after the reaction solution has attained thermostat temperature, and on separation at some later time t_2. But, because the radioactivity, which in general depended on the presence of both [80]Br and [82]Br, was short-lived, the figures given had to be derived in a slightly more involved way than applies to those of the chlorine exchange studied in Part XLII. When a sample taken at t_2 was to be counted, a sample taken at t_1, and an initial sample, were also counted, and these counts were repeated, more

than once if necessary, so that curves could be drawn which overlapped in time, showing, for each sample, the logarithmic fall in the counting rate with time. From the curves, counts at a common time could be read, which were then converted into specific counting rates, after determining, by Volhard's method, the bromide-ion contents of the solutions counted. Comparison of the counts C and $C - X_1$ indicates the amounts of reaction, in many cases negligible, which take place during the period of warming to thermostat temperature. The second-order rate constants, $k_2^{(b)}$, computed from the counting rates, are corrected for thermal expansion of the solvent. The main error in these values is due to the random fluctuations of finite counts. This error is measured statistically by probable errors computed from the magnitudes of the individual counts, and is expressed in Table 2

Representation of kinetic salt effects in reactions of lithium bromide with four alkyl bromides in acetone.
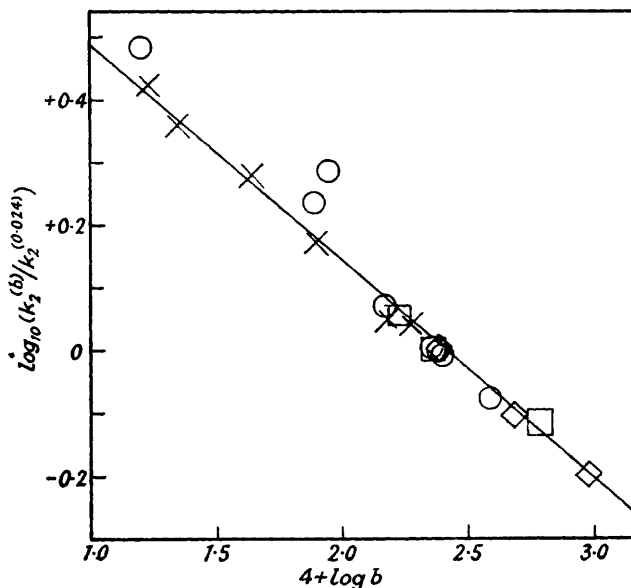
× *n*-Butyl bromide at 26·2° ....}Evans and Sugden (*loc. cit.*).
○ 1-Methylheptyl bromide at 65·3° ....}

□ *iso*-Propyl bromide at 57·6° ....}Table 1
◊ *tert.*-Butyl bromide at 44·4° ....}

The equation of the straight line is

$$\log_{10} (k_2^{(b)}/k_2^{(0·024)}) = - 0·37 \log_{10} (b/0·024).$$

in the form of probable errors in the derived individual rate constants. In the last two columns of Table 2, the individual and averaged rate constants are corrected, as already described, to the standard salt concentration, which was 0·024M, except in some of the supplementary series of runs carried out with *tert.*-butyl bromide.

In these supplementary series, the main purpose of which was to check, by varying the concentrations of the reactants, the possibility of measurable error through the incursion of unimolecular reactions, the opportunity was taken to examine whether the radioactivity in the lithium bromide, separated after a period of reaction, is noticeably disturbed by the very small amount of hydrogen bromide formed. To this end, the initial count C of the lithium bromide was remeasured, in association with counts on samples of the reaction solution after various periods of reaction, in a modified form, C', which involved, first, mixing the original lithium bromide solution with a sample of a *tert.*-butyl bromide solution which had been heated in the thermostat for the same length of time as the reaction solution, then separating the lithium bromide by the procedure used for the reaction solution, and

then carrying through the count. In fact, the counts C, C', and $C - X_1$, were all substantially identical, as is illustrated in Table 2 with respect to the counts C' and $C - X_1$ in the runs in which this modified procedure was adopted.

The mean rate constants at standard salt concentration give good Arrhenius plots, from which frequency factors and energies of activation have been derived, as entered in Table 3, which also contains the absolute and relative rates interpolated or extrapolated to 25°. Discussion of the figures is reserved for Part XLIX.

TABLE 3. *Rate constants* (k_2 *in sec.*$^{-1}$ *mole*$^{-1}$ *l.*), *relative rates at common temperatures, and parameters of the equation* $k_2 = B_2 \exp(-E_A/RT)$ *(with* B_2 *in sec.*$^{-1}$ *mole*$^{-1}$ *l. and* E_A *in kcal. mole*$^{-1}$*) for the reactions of lithium radio-bromide with alkyl bromides in acetone.*

R in RBr	Me	Et	Pr^i	Bu^t		Pr^n	Bu^i	*neo*Pe
b	0·024	0·024	0·024	0·024	0·050	0·024	0·024	0·024
$10^5 k_2$ (25°)	13,000	170	1·8	0·51	0·38	110	5·7	0·0026
Rel. k_2 (25°)	76	1	0·011	0·0030	—	0·65	0·033	0·000015
$\log_{10} B_2$	10·7	10·1	9·7	10·7	10·5	9·8	9·6	8·6
E_A	15·8	17·5	19·7	21·8	21·7	17·5	18·9	22·0

EXPERIMENTAL

*neo*Pentyl bromide was prepared by Whitmore, Wittle, and Harriman's method (*J. Amer. Chem. Soc.*, 1939, **61**, 1585); other alkyl bromides were prepared or purified as described in Part XLIII; acetone was purified as noted in Part XLII.

Lithium Radio-bromide.—The radio-bromine used in most of this work, which was done before supplies of ^{82}Br of high specific activity were obtainable from Harwell, was made in the laboratory by neutron-irradiation of ethylene dibromide containing a little aniline, the neutrons being obtained either from a radium-beryllium source, or from an ion-accelerator in which deuterons bombarded a deuterium target. The aqueous extract of the irradiated material was neutralised with lithium hydroxide and rapidly evaporated, the residual lithium bromide being fused. Its filtered aqueous solution was again evaporated, and the residue was heated until melting began, and then dissolved in acetone. The residue obtained on evaporation of the filtered acetone solution, was strongly heated in a current of dry air, and dissolved in acetone previously dried with magnesium perchlorate. The bromide content of this solution was determined by Volhard's method. For some of the later experiments, strongly radioactive ammonium bromide, prepared in the pile at Harwell, was the basic material. It was converted, by evaporation with lithium hydroxide, into lithium bromide, the acetone solution of which was suitably diluted with one of ordinary lithium bromide.

Kinetics.—For the four less reactive alkyl bromides, *iso*propyl, *iso*butyl, *tert.*-butyl, and *neo*pentyl bromide, the sealed-tube method was employed; the tubes were charged and the runs started as described in Part XLIII. In the cases of the more reactive ethyl and *n*-propyl bromide, the solutions of alkyl halide and of lithium bromide were placed in the limbs of inverted Y-tubes, which were sealed, and allowed to reach thermostat temperature; then the solutions were mixed by tilting. The volatility and high reactivity of methyl bromide necessitated enclosing it in small sealed ampoules within the reaction tubes, which contained acetone solutions of lithium bromide, the inner ampoules being broken by shaking after the tube and all its contents had been cooled to −80°.

The runs with ethyl, *n*-propyl, *iso*propyl, *iso*butyl, and *neo*pentyl bromides were stopped by cooling a tube, transferring its contents to a flask, and evaporating the volatile material by pumping. The residue, after re-evaporation with fresh acetone, was dissolved in water for counting. That no appreciable reaction accompanies this procedure, is shown by comparison of the counts C and $C - X_1$, which would include any such reaction in the estimate which it gives of the reaction accompanying warming to thermostat temperature, with the result that, if reaction during working-up were appreciable, the difference between C and $C - X_1$ would not become negligible, as in fact it does, at the lower temperatures used with each alkyl bromide. Methyl bromide reacted too rapidly to allow the use of this technique : runs with this halide were stopped by pouring the reaction solution into a mixture of benzene and water, washing the benzene extract with water, and extracting the combined aqueous solutions with benzene, and evaporating the aqueous solutions to dryness, the residue being dissolved in water for counting. For *neo*pentyl bromide a similar method was used, but with ether instead of benzene

as the organic solvent, the main reason in this case being that it was desired to recover the alkyl halide.

Counting.—All counts were made with aqueous solutions in the same counting tube. Among the checks applied was one for the proportionality of the counting rate to the concentration of radioactive material, by the counting of a solution of lithium radio-bromide in which the ^{80}Br had decayed and only the ^{82}Br was active, in five successive degrees of two-fold dilution. In general the logarithmic decay curve of the lithium radio-bromide employed was not linear owing to the simultaneous presence of both radio-isotopes; but it became linear as the shorter-lived ^{80}Br decayed. The principle of taking counts comparatively on two or more solutions during overlapping time-intervals, and of thus allowing for radioactive decay, has been explained, as well as the method of converting such counts to the specific counting rates, C, C', $C - X_1$, and $C - X_2$ (p. 3171). The other quantities required for the calculation of rate constants are a, based on direct weighing of the alkyl bromide, b, based on Volhard's determination of bromide ion, and the time-interval $t_2 - t_1$. The formula is given in Part XLII.

Note Added, August 9th, 1955.—Le Roux and Swart (*J.*, 1955, 1475) have given results for the exchange of *iso*propyl bromide and of *tert.*-butyl bromide with bromide ions in acetone. Their rates, activation energies for the second-order processes, and qualitative conclusions are in essential accordance with our results.

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