271. *The Kinetics of Exchange Reactions. Part I.* n-*Butyl Bromide.*

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The velocity of the exchange reaction $RBr + Br^{*\prime} \rightleftarrows RBr^{*} + Br^{\prime}$ has been measured in aqueous acetone (containing 90% of acetone by volume) over a range of temperatures from 0° to 65°.

The reaction is found to be bimolecular and is not catalysed by acids or bases. The activation energy is 18·87 ± 0·14 kg.-cals., and the speed of the reaction is of the same order of magnitude as that predicted for a gaseous system on the collision hypothesis.

Exchange reactions of the type $RBr + Br^{*\prime} \rightleftarrows RBr^{*} + Br^{\prime}$ present many points of interest from the standpoint of the kinetics of chemical change. They do not involve net emission or absorption of energy and the symmetry of the reaction permits many simplifications to be made in theoretical discussions of the factors which determine the velocity of the exchange (cf. Bergmann, Polanyi, and Szabo, *Z. physikal. Chem.*, 1933, *B*, **20**, 161; *Trans. Faraday Soc.*, 1936, **32**, 834; Ogg and Polanyi, *ibid.*, 1935, **31**, 604). Until recently it has only been possible to study these reactions when the halogen atom is attached to a centre of optical activity, but now that adequate sources of artificially radioactive elements are available, an extended kinetic study of such changes can be made with a sufficient degree of accuracy to give significant results. Radioactive iodine and bromine have already been used to demonstrate the mechanism of the Walden inversion (Hughes, Juliusberger, Masterman, Topley, and Weiss, J., 1935, 1525; Hughes, Juliusberger, Scott, Topley, and Weiss, J., **1936**, 1173), and some kinetic studies with radio-iodine have been published by Tuck (*Trans. Faraday Soc.*, 1938, **34**, 222).

We have chosen radio-bromine for our work (*a*) since it gives radioactivities with half-lives of 4·2 hrs. and 36 hrs., so that slow reactions can be studied, and (*b*) because a high concentration of radio-bromine in the form of lithium bromide can readily be obtained (Lu and Sugden, preceding paper). As solvent we have chosen aqueous acetone containing 10% of water by volume. In the present paper we report a study of the exchange of radio-bromine ion (Br*–) with *n*-butyl bromide. In the reaction

$$\underset{a}{\mathrm{RBr}} + \underset{c-x}{\mathrm{Br}^{*-}} \underset{k_2}{\overset{k_1}{\rightleftarrows}} \underset{x}{\mathrm{RBr}^{*}} + \underset{b}{\mathrm{Br}^{-}}$$

where a is the concentration of alkyl bromide, b that of bromide ion, c the total concentration of radio-bromine at time t, and x the concentration of RBr* at the same time, it is readily shown (since $x \ll a$ and $c \ll b$) that

$$k_2 = \frac{2{\cdot}303}{t(a+b)} \log \frac{1}{1 - x(1 + b/a)/c} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (1)$$

Since the reaction involves exchange of isotopic bromine atoms, it is evident that $k_1 = k_2$.

Course and Reversibility of the Reaction.—Experiments were made first to determine whether k_2 showed any drift with time when samples were taken from a given solution at suitable intervals. The data in Table I show that the course of the reaction is adequately represented by equation (1).

TABLE I.

Course of Reaction.

T = 297·5° K. a = 0·25 b = 0·02—0·1	t, hrs.	2	4	6	24
	$k_2^* \times 10^5$	2·4	2·5	1·9	2·3
T = 332·7° K. a = 0·9052 b = 0·0369	t, hrs.	2	4	6	Equilibrium reached in 7—8 hours.
	$k_2 \times 10^5$	106	99	101	

* All velocity constants are expressed in l, g.-mol.$^{-1}$, sec.$^{-1}$.

As McKay has pointed out (*Nature*, 1938, **142**, 997), this does not test the order of the reaction but does serve as a check on the adequacy of the experimental methods.

To test the reversibility of the reaction one experiment was made at 307·5° K. in which *n*-butyl bromide containing radio-bromine was allowed to exchange with inactive lithium bromide. This gave $k_2 = 9{\cdot}6 \times 10^{-5}$, in good agreement with the values found for the reaction between inactive alkyl bromide and active bromine ion (cf. Table II).

Order of the Reaction.—To test the order of the reaction the concentration of alkyl bromide was varied five-fold (Table II) and that of the lithium bromide eight-fold (Table III). It will be seen that there is no significant change in the value of k_2 as long as a and b are less than 0·15 M. At higher concentrations the value of k_2 falls. This, however, is to be expected, since the reaction involves ions, and deviations from ideal solution will become marked as the concentration of ions increases and as more of the less ionising alkyl bromide is present in the solvent mixture.

TABLE II.

T = 307·5° K.

a.	*b*.	10^5k_2.	*a*.	*b*.	10^5k_2.
0·049	0·0400	9·8	0·172	0·0220	9·6
0·098	0·782	10·1	0·245	0·0412	8·8
0·172	0·0220	10·8	0·245	0·0415	9·5

TABLE III.

T = 317·5° K.

a.	*b*.	10^5k_2.	*a*.	*b*.	10^5k_2.
0·0969	0·0301	23·0	0·0969	0·0924	23·0
,,	0·0560	22·6	,,	0·2443	15·7
,,	0·0811	21·6			

In sufficiently dilute solutions the reaction is therefore bimolecular.

Acid and Base Catalysis.—To test whether any appreciable effect was produced by acids or bases, the experiments summarised in Table IV were performed.

TABLE IV.

Absence of Acid and Base Catalysis.

Values of $10^5 k_2$.

$T = 303°$	No acid :	7·3	$T = 317·5°$	No base :	21·6	$T = 307·5°$	No base :	9·8
	+ 0·05N-HBr :	7·5		+ 0·05M-LiOH :	22·6		+ 0·05M-NH_4OH :	11·1

It is clear that there is no catalysis by acids and very slight catalysis by bases. The increase in k_2 observed with the bases is, however, of the order of magnitude of the experimental error.

Activation Energy and Effective Collision Diameter.—Experiments were made over a range of temperatures in 90% acetone, values of a and b less than 0·15M being used. These observations are collected in Table V.

TABLE V.

Activation Energy.

T, ° K.	$10^6 k_2$, obs.	Mean.	$10^6 k_2$, calc.	T, ° K.	$10^6 k_2$, obs.	Mean.	$10^6 k_2$, calc.
273·1°	1·7, 1·7	1·7	1·7	317·6°	216, 230, 230	225	240
298·1	33, 33	33	33	332·8	1070, 1020, 1070	1050	950
307·6	96, 108, 96, 101	100	89	338·1	1410, 1510	1460	1510

From these 16 observations, by the method of least squares the following equation was found :

$$\log k_2/\sqrt{T} = (8·13 \pm 0·10) - (18{,}870 \pm 140)/4·57T \quad . \quad . \quad . \quad . \quad (2)$$

The values of k_2 calculated by this equation are given in the last column of Table V. It will be seen that this reaction follows the Arrhenius equation within the limits of the experimental accuracy. The activation energy is 18·87 ± 0·14 kg.-cals.

For a gaseous system statistical theory gives the relation

$$\log k_2/\sqrt{T} = \log\{6·06 \times 10^{20}\sigma^2(8\pi R/M)^{\frac{1}{2}}\} - E/4·57T \quad . \quad . \quad . \quad (3)$$

Here k_2 is expressed in the usual units (l., g.-mol.$^{-1}$, sec.$^{-1}$), σ is the sum of the effective diameters of the colliding molecules, and the reduced mass $M = m_1m_2/(m_1 + m_2)$, where m_1 and m_2 are the molecular weights of the two molecules.

A comparison of equations (2) and (3) with $m_1 = 80$, $m_2 = 137$ (*i.e.*, neglecting solvation of the bromine ion which would however have a very small effect) gives

$$\log \sigma^2 = 17·54 \pm 0·10 \text{ or } \sigma = 0·60 \pm 0·07 \text{ A}.$$

This is about the order of magnitude which would be expected for a reaction in solution. If, following Hinshelwood, one writes $k_2 = PZe^{-E/RT}$, and it is assumed that $\sigma = 3$ A, then the P factor is approximately 0·04. This exchange reaction in solution therefore proceeds at a velocity which is not far from that predicted by the collision theory for a gaseous system.

EXPERIMENTAL.

(1) *Materials.*—The solvent used for kinetic studies was 9 volumes of " AnalaR " acetone mixed with 1 volume of water. This " 90% " acetone was chosen since preliminary experiments showed that small amounts of water had a large effect on the velocity when nearly anhydrous acetone was used, thus :

Acetone, % by vol. .... *ca.*	100	95	90	80
Relative velocity	100	11	5	3

A commercial specimen of *n*-butyl bromide was distilled twice and the middle fraction, b. p. 101°, retained. A stock solution of 0·5M-butyl bromide in " AnalaR " acetone was prepared, and stored in a stoppered, mercury-sealed flask.

Highly radioactive specimens of lithium bromide were prepared by the method of Lu and Sugden (preceding paper). The reduction of the silver bromide in hydrogen was carried out in a silica tube furnace at 400—500° ; test experiments showed that 98% of the hydrogen bromide was evolved in 20 mins. The gas was absorbed in a suitable quantity of 0·2N-lithium hydroxide, excess of base was then exactly neutralised with hydrogen bromide, and the solution rapidly evaporated to dryness in a silica dish.

(2) *Measurement of Reaction Velocity.*—The reactions were carried out in sealed glass vessels of inverted **Y** shape with lower arms of a capacity of about 50 c.c. The dry lithium bromide was dissolved in about 36 c.c. of dry acetone, and 35 c.c. of this solution were placed in one side arm together with 5 c.c. of water. 10 C.c. of the 0·5M-butyl bromide were placed in the other side arm, and the top of the connecting tube sealed off. The apparatus was then placed in the thermostat, and after time had been allowed for the liquids to reach the bath temperature, the contents were mixed by shaking and the time noted. On removal from the thermostat the vessel was rapidly cooled to 20° and opened. 25 C.c. of the contents were then transferred to one of the annular glass vessels used for the measurement of radioactivity.

The separation of alkyl bromide and lithium bromide was effected by dropping 25 c.c. of the reaction mixture into a separating funnel containing 200 c.c. of water and 25 c.c. of benzene. After shaking, the benzene layer was separated and washed twice with 100 c.c. of water. 25 C.c. of the benzene solution were then placed in a second annular vessel for measurement of the radioactivity transferred to the butyl bromide. The bromide-ion content of the aqueous washings was later determined by the Volhard method, and the concentration of the lithium bromide used was thus determined.

To test the efficiency of this method of separation, a solution of radioactive butyl bromide in acetone was prepared; 25 c.c. were then treated as described above, and the radioactivity transferred to the benzene layer was then compared with that of 25 c.c. of the original acetone solution. After application of the corrections described below the two activities agreed within 1%; hence there is no significant loss of butyl bromide during the transference. As a further check, a solution of butyl bromide in benzene was extracted with water, and the aqueous solution refluxed with a known amount of silver nitrate for two hours; no change in titre could be detected although a faint opalescence was produced in the solution.

The radioactivities of the two solutions were then compared by placing them in turn around a Geiger–Müller counter connected to a suitable amplifier and a Wynne-Williams scale-of-eight recording circuit. For reactions requiring less than 15 hours to give a suitable amount of exchange, an aluminium tube counter with thin walls was used which recorded chiefly β-rays from the ^{80}Br isotope. When longer reaction times were necessary, the activity measured was almost entirely due to ^{82}Br with a half-life of 36 hours. This isotope gives much softer β-rays but in addition gives relatively intense γ-rays. A γ-ray counter tube was therefore constructed consisting of an aluminium tube and tungsten filament sealed inside a hard-glass tube. This had a much larger active volume than the β-ray counter and by its aid the γ-ray activity could be followed with sufficient accuracy for 4—5 days if necessary.

The ratio of the activities, benzene solution/acetone solution, gives approximately the x/c in equation (1), but a number of corrections have to be applied to this ratio. These are due (*a*) to different thickness of the walls of the measuring vessels, (*b*) to the different effect of benzene and acetone in absorbing β-rays, and (*c*) to differences in the thickness of the layer emitting γ-rays when the γ-ray counter was used. The mean free path of β-rays is small compared with the thickness of the liquid, so that (*c*) can be neglected when these rays are measured; on the other hand (*a*) and (*b*) are unimportant when γ-rays are measured. To determine these corrections a specimen of radioactive butyl bromide was prepared by refluxing a few grams of the inactive bromide with active lithium bromide in acetone. The butyl bromide was isolated and used to prepare solutions of equal concentration in acetone and in benzene. The activity of these solutions in their appropriate vessels was then followed for two days, and the appropriate correction factors tabulated. These varied with time owing to the increasing proportion of γ-ray activity from the 36-hr. product.

It was soon observed that the activity of the benzene solution *increased* by 20—30% for the first hour after separation from the aqueous layer, whilst the acetone solution decayed normally. This curious effect has recently been explained by the discoverey by Segré, Halford, and Seaborg (*Physical Rev.*, 1939, **55**, 321) and de Vault and Libby (*ibid.*, p. 322) that the ^{80}Br isotope with a half-life of 4·5 hrs. decays with the emission of a soft γ-ray to give the isomeric ^{80}Br nucleus which emits β- and γ-rays. The recoil from the soft γ-ray is sufficient to activate the C–Br bond and cause hydrolysis in the presence of water so that the benzene solution immediately after washing contains less than the equilibrium amount of 18-min. product which produces the β-rays. To avoid errors caused by this displacement of radioactive equilibrium, the measurements of the activities of the benzene and acetone solutions were commenced 90 mins. after the last washing of the benzene solution with water.

To test whether any measurable hydrolysis of butyl bromide occurs during the reaction, a solution of *n*-butyl bromide and lithium bromide in 90% acetone was heated to 60° for 24 hrs. The bromide ion was then separated and determined as described above, and a similar test made on an unheated specimen of the solution. No increase in bromide ion was found, hence there is no hydrolysis.

The concentrations of alkyl bromide and lithium bromide were measured at room temperature, and in calculating the velocity constants these were corrected for solvent expansion. In this correction the volume coefficient of expansion of 90% acetone was taken to be 0·0014 per degree. A further small correction is needed since a quantity of butyl bromide contained in 25 c.c. of the solution is added to 25 c.c. of benzene. If there is no change of volume on mixing then the correction for a 0·1M-solution is 0·27 c.c. to be added to the volume of benzene solution.

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