

Ion-Pair Reactivity in Isotopic Exchange Reactions

II. Lithium Bromide in Acetone as Solvent

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To establish whether ion-pairs of lithium bromide in acetone are kinetically active species, the exchange of ^{82}Br between this salt and butyl bromide has been studied. Kinetic data have been applied to the Acree equation for different values of the distance of closest approach of Li^+ and Br^- in the ion-pair. The results indicate that the ion-pairs are unreactive species. On the assumption that they consist of lithium and bromide ions in contact, the kinetic data yield an ion-pair dissociation constant of 2.33×10^{-4} at 25° in close agreement with the value 2.14×10^{-4} according to conductivity data obtained in the present investigation.

Evans and Sugden¹ investigated the exchange of bromine between butyl bromide (BuBr) and lithium radiobromide in anhydrous acetone and observed decreasing values for the second-order rate constant with increasing salt concentration. In accord with the Acree hypothesis,² they assumed this effect to be due to different reactivities of free bromide ions and lithium bromide ion-pairs and calculated the values 4.41×10^{-3} and $0.12 \times 10^{-3} \text{ M}^{-1} \text{ s}^{-1}$ for k_i and k_m , the rate constants for the reaction of free ions and ion-pairs, respectively. However, the uncertainty in the calculated value of k_m was of the same order as this constant itself and it was concluded that more accurate data were required if more certain conclusions were to be reached as to the reactivity of the ion-pairs.

The purpose of the present investigation was to make a new attempt to establish whether or not the ion-pairs significantly contribute to the reaction rate. A reinvestigation of the reaction, $\text{BuBr} + \text{Li}^{82}\text{Br} \rightleftharpoons \text{Bu}^{82}\text{Br} + \text{LiBr}$, in anhydrous acetone over a broad range of concentration of the ionic reactant at 25° has therefore been undertaken. There is no evidence of any contribution of the ion-pairs to the total reaction rate.

EXPERIMENTAL

Reagents. The acetone used in kinetic measurements was purified as previously described.³ Acetone for conductivity measurements was purified according to Smith, Fainberg, and Winstein.⁴ Its specific conductivity was less than $2.5 \times 10^{-8} \Omega^{-1} \text{ cm}^{-1}$. Calculations below involve the dielectric constant and the viscosity of the solvent. The values 20.7 and 0.00316 poise, respectively, were used.

Butyl bromide (Fluka, *puriss.*) was dried over phosphorus pentoxide and fractionally distilled. Its density at 25°, corrected to vacuum, 1.2687 g ml⁻¹, is to be compared with the literature value⁵ 1.2689 g ml⁻¹.

Lithium bromide (Fluka, *suprapur*) was dried for 6 h at 200° and stored in a vacuum desiccator.

Lithium radiobromide (Li⁸²Br) was prepared from the corresponding sodium salt obtained from the Atomic Energy Institute, Kjeller, Norway. A neutral aqueous solution containing 5 mCi Na⁸²Br of specific activity 150 mCi ⁸²Br/g Br was passed through a lithium saturated Dowex 50W-X8 ion exchanger and the eluate evaporated to dryness. The solid residue was dried for 2 h at 200°, allowed to cool in a vacuum desiccator, and dissolved in 100 ml anhydrous acetone. The bromide concentration of this solution was established by potentiometrically titrating two 5 ml aliquots with silver nitrate. The radiochemical purity of the lithium radiobromide sample was tested by half-life determination as previously described.⁶ No significant amounts of radiochemical impurities could be detected by this means.

Preparation of solutions. A 0.02 M stock solution of inactive lithium bromide in acetone was prepared by weight and its concentration checked by argentimetric analysis. Lithium radiobromide solutions for kinetic measurements were prepared from this solution and the radioactive stock. Solutions of lithium bromide for conductivity measurements were prepared by diluting samples from a 0.01 M stock.

Kinetic procedure. The rate of exchange was determined electroanalytically as described in Ref. 6. The performance of the electrolytic cell was the same as in Ref. 7 with the exception that the vertical 0.126 cm² area silver anode was placed 9 mm from the centrum line of the cell.

A lithium bromide solution (50 ml), containing between 5 and 20 $\mu\text{Ci } ^{82}\text{Br}^-$, was transferred to the cell and 0.3 ml butyl bromide added by means of a micro syringe. The amount added was determined to within ± 0.1 mg by differential weighing of the syringe. The solution was agitated at 100 rpm. The temperature of the reaction mixture was $25.03 \pm 0.02^\circ$. The specific activity of the inorganic bromide was usually determined at six different reaction times.

The electrode reaction, $\text{Ag} + \text{Br}^- \rightarrow \text{AgBr} + \text{e}^-$, was investigated at several current densities and it was established that the current densities used in the analyses, 3.8 and 7.5 mA cm⁻² mM⁻¹ LiBr in expts. 1 and 2–10, respectively, were within the optimum current density range. The electrolysis times varied from 9 to 27 s. Between 0.1 and 0.5 % of the ionic bromide in the reaction mixture was deposited on each electrode.

Radioactivity measurements. The count-rate of the silver bromide samples was measured and corrected as described in Ref. 6. Its standard deviation was reduced to below ± 0.3 %.

Conductivity measurements. The conductivities of solutions of lithium bromide in acetone were determined for several concentrations in the range 1×10^{-5} M to 2.6×10^{-3} M by means of a Leeds and Northrup 4666 conductivity bridge. The cell, immersed in an oil bath at $25.00 \pm 0.01^\circ$, was fitted with bright platinum electrodes. Measurements were performed at 2000, 2500, 3300, and 5000 Hz and extrapolation made to infinite frequency to reduce polarization errors.

KINETIC RESULTS

A compilation of kinetic data for the reaction studied is given in Table 1. The rate of exchange, R , was calculated from the McKay equation⁸ by application of the method of least squares. The second-order rate constant, k , in the last column was obtained from the expression, $k = R/bc$, where $b = [\text{BuBr}]$ and $c = [\text{LiBr}]$.

Table 1. Kinetic data for the exchange of ^{82}Br between BuBr and LiBr in dry acetone at 25°.

| Expt. No. | [BuBr] $\times 10^3$ M | [LiBr] $\times 10^4$ M | $R \times 10^6$ M min $^{-1}$ | k M $^{-1}$ min $^{-1}$ |
|-----------|---------------------------|---------------------------|----------------------------------|------------------------------|
| 1 | 5.471 | 97.3 | 49.61 | 0.0932 |
| 2 | 5.101 | 48.00 | 29.23 | 0.1194 |
| 3 | 5.107 | 32.14 | 22.69 | 0.1382 |
| 4 | 5.098 | 25.74 | 19.47 | 0.1484 |
| 5 | 5.116 | 15.54 | 14.23 | 0.1790 |
| 6 | 5.140 | 11.79 | 11.91 | 0.1965 |
| 7 | 5.164 | 7.92 | 9.073 | 0.2218 |
| 8 | 5.007 | 4.978 | 6.284 | 0.2521 |
| 9 | 5.183 | 2.940 | 4.416 | 0.2898 |
| 10 | 4.924 | 1.676 | 2.753 | 0.3336 |

DISSOCIATION OF LITHIUM BROMIDE

Interpretation of the kinetic data requires knowledge of the dissociation constant, K , of lithium bromide in acetone. Values of K based on conductance data for this system, reported by several authors,⁹⁻¹² were calculated, but the values obtained were in disagreement. Further conductivity measurements were therefore undertaken as outlined in the experimental section. From the data obtained, dissociation constants were evaluated for several different choices of the ion-size parameter, a , in the Debye-Hückel equation using a computer program described in Part I, Ref. 13. The results are quoted in Table 2, in which the equivalent conductance of the salt at infinite dilution has also been included.

The degree of dissociation, α , of the salt was calculated as described in Part I.

Table 2. Dissociation constant and limiting equivalent conductance of LiBr in dry acetone at 25°.

| $a \times 10^8$ cm | $K \times 10^4$ M | Λ_0 cm 2 Ω^{-1} equiv. $^{-1}$ |
|-----------------------|----------------------|---|
| 0.00 | 2.07 | 200.1 |
| 2.55 ^a | 2.14 | 198.9 |
| 5.48 ^b | 2.21 | 197.7 |
| 8.00 | 2.27 | 196.7 |
| 10.00 | 2.32 | 196.0 |

^a Sum of crystallographic radii. ^b Sum of Stokes' radii.¹³

DISCUSSION

If the bromide exchange proceeds *via* S_N1 as well as S_N2 mechanisms and if free bromide ions and lithium bromide ion-pairs are both involved in the exchange with the organic bromide, the total rate of exchange may be represented by the equation

$$R = k_1b + k_1bca + k_mbc(1-\alpha) \quad (1)$$

where k_1 is a rate constant for S_N1 reaction and k_i and k_m rate constants for S_N2 exchange of ions and ion-pairs, respectively.

For low lithium bromide concentrations, when α is nearly equal to unity, the term $k_mbc(1-\alpha)$ in eqn. (1) may be neglected in comparison with k_1bca . In this case eqn. (1) may be rearranged to give

$$R/b = k_1 + k_1c\alpha \quad (2)$$

which is represented graphically in Fig. 1 for a equal to the sum of the crystallographic radii of Li^+ and Br^- (2.55×10^{-8} cm). The line passes through the origin indicating that $k_1=0$, *i.e.* there is no S_N1 contribution to the reaction rate.

Upon omitting k_1b in eqn. (1) and rearranging this expression we obtain

$$R/bc = k = k_i\alpha + k_m(1-\alpha) \quad (3)$$

which for evaluation of k_i and k_m may conveniently be rewritten as

$$k/\alpha = k_i + k_m(1-\alpha)/\alpha \quad (4)$$

Using the method of least squares, the rate constants k_i and k_m in eqn. (4) were evaluated for the different ion-pair dissociation constants quoted in Table 2, *i.e.* for different a values in the Debye-Hückel equation. The results

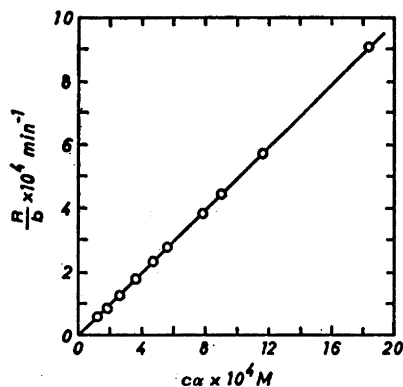


Fig. 1. Dependence of R/b on $c\alpha$ for the exchange of bromine between BuBr and $Li^{82}Br$ in acetone at 25° .

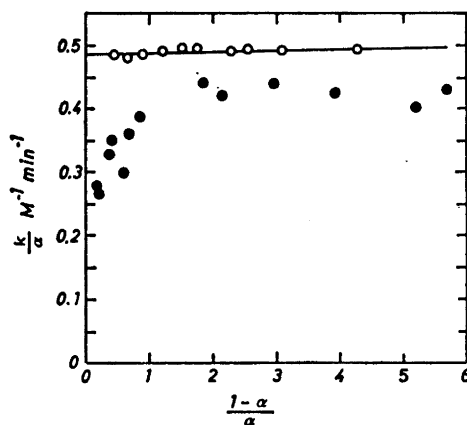


Fig. 2. Graph of k/α vs. $(1-\alpha)/\alpha$ according to eqn. (4) for the same reaction as in Fig. 1. Open circles: this investigation, 25.0° . Full circles: Ref. 1, 26.2° .

of these calculations are summarized in Table 3. The errors attached to k_i and k_m are given on a 99 % confidence level. It can be seen that k_i is little sensitive to the choice of a , whereas k_m significantly increases with increasing values of this parameter. For a values below appr. 5×10^{-8} cm, which is of the same order as the sum of Stokes' radii according to Savedoff,¹² within experimental errors, k_m is zero indicating unreactive ion-pairs. Evaluation of k_i and k_m employing conductivity data of Savedoff¹² yields insignificantly different results.

Table 3. Dependence of k_i and k_m for the reaction studied on the distance of closest approach of the ions in the ion-pair at 25°.

| $a \times 10^8$ cm | k_i $M^{-1} \text{ min}^{-1}$ | k_m $M^{-1} \text{ min}^{-1}$ |
|-----------------------|------------------------------------|------------------------------------|
| 0.00 | 0.491 ± 0.011 | 0.001 ± 0.005 |
| 2.55 | 0.485 ± 0.009 | 0.002 ± 0.004 |
| 5.48 | 0.479 ± 0.007 | 0.004 ± 0.003 |
| 8.00 | 0.475 ± 0.007 | 0.006 ± 0.003 |
| 10.00 | 0.472 ± 0.006 | 0.006 ± 0.003 |

A graph of k/α vs. $(1-\alpha)/\alpha$ according to eqn. (4) for the actual reaction at 25.0° is shown in Fig. 2 (open circles). Data according to an earlier investigation¹ for a slightly different temperature (26.2°) have also been included in the graph (full circles). The α values for all points in this graph were obtained from the ion-pair dissociation constant 2.14×10^{-4} in Table 2.

On the assumption that the ion-pairs are unreactive, it was shown in Part I that the dependence of the rate constant, k , on the salt concentration,

Table 4. Dissociation constant for LiBr in acetone at 25° from kinetic data.

| $a \times 10^8$ cm | $K \times 10^4$ M |
|-----------------------|----------------------|
| 0.00 | 2.16 |
| 2.55 | 2.33 |
| 5.48 | 2.52 |
| 8.00 | 2.68 |
| 10.00 | 2.80 |

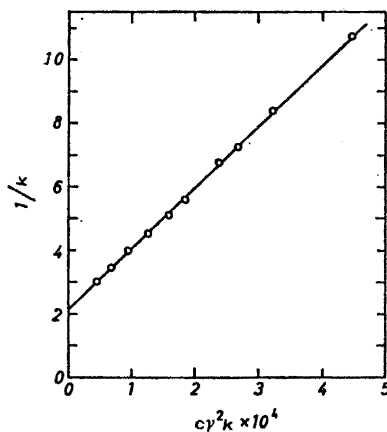


Fig. 3. Graph of $1/k$ vs. $c\gamma^2k$ according to eqn. (5) for the reaction studied.

c , may be employed to calculate the ion-pair dissociation constant, K , using the expression

$$1/k = 1/k_1 + c\gamma^2k/Kk_1^2 \quad (5)$$

in which γ is the mean molar activity coefficient and k_1 the rate constant at infinite dilution. The method of successive approximations described in Part I was used to calculate K from this equation. The results of the calculations are given in Table 4 for a number of different a values. A graphical representation of $1/k$ vs. $c\gamma^2k$ according to eqn. (5) for the final values of K and k_1 in the iteration procedure is shown in Fig. 3 for $a = 2.55 \times 10^{-8}$ cm.

Comparison of Tables 2 and 4 reveals that the dissociation constant evaluated from kinetic data is considerably more sensitive to the choice of the ion size parameter, a , than the dissociation constant calculated from conductivity data. This is due to the fact that the rate data were determined at comparatively high lithium bromide concentrations, where the term κa in the denominator of the Debye-Hückel equation¹⁴ is of greater importance than at the more dilute solutions employed in determining conductivity data.

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