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Ion-pair Reactivity in Isotopic Exchange Reactions

III. Ion-pairs of Tetraalkyl Ammonium Halides

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Ion-pairs of tetrabutyl ammonium chloride ($Bu_4N^+Cl^-$) and bromide ($Bu_4N^+Br^-$) in acetone appear to be reactive species in nucleophilic substitution reactions as indicated by the results of the present investigation in which the exchange reactions, $Bu_4N^{36}Cl + p\text{-}NO_2BzCl \rightleftharpoons Bu_4NCl + p\text{-}NO_2Bz^{36}Cl$ and $Bu_4N^{82}Br + BuBr \rightleftharpoons Bu_4NBr + Bu^{82}Br$, where "Bz" stands for "benzyl", have been studied for various concentrations of the ionic halides at 25°. Analysis of the data by means of the Acree equation indicates that the reactivity of tetrabutyl ammonium chloride ion-pairs is about 10 % of the reactivity of free chloride ions. The reactivity of ion-pairs of tetrabutyl ammonium bromide is approximately 20 % of the reactivity of free bromide ions.

Association constants of the salts in the actual solvent, which were used in the analyses of the kinetic data, were determined by conductance measurements and application of the data obtained to the Fuoss-Onsager 1957 and Shedlovsky conductance equations.

Halogen atoms in ion-pairs of lithium chloride [1] and lithium bromide [2] in acetone as solvent do not undergo any observable exchange with aliphatically bound chlorine and bromine, respectively, as was demonstrated in Parts I and II, respectively, in the present series.[1,2] In both cases unpaired halide ions were found to be solely responsible for the exchanges observed.

The purpose of the present investigation was to examine whether halogen atoms in the more loosely bound ion-pairs of tetrabutyl ammonium chloride and tetrabutyl ammonium bromide exhibit any reactivity in displacement reactions involving aliphatic halides. To that end the exchange of ^{36}Cl between tetrabutyl ammonium chloride and *p*-nitrobenzyl chloride and of ^{82}Br between tetrabutyl ammonium bromide and butyl bromide in anhydrous acetone at 25° have been studied and kinetic data analyzed according to the Acree hypothesis.[3] For both reactions free as well as paired halide ions appear to contribute to the reaction rate.

EXPERIMENTAL

Preparation of reactants. Tetrabutyl ammonium chloride was prepared from the corresponding bromide (Fluka, *purum* grade). The latter was converted to hydroxide by means of suspended silver oxide [4] in methanol. Excess silver oxide and silver bromide formed were removed by filtration and centrifugation. The hydroxide was exactly neutralized with hydrochloric acid, the solution evaporated to dryness, and the salt recrystallized eight times from ethyl acetate. The product was dried *in vacuo* at 55° for 2 days and at 110° for 2 h at normal pressure. (Found: Cl 12.74. Calc. Cl 12.76). Melting point 69.2—69.6°.

Tetrabutyl ammonium chloride labelled with ^{36}Cl was prepared by exactly neutralizing 20 μCi of $H^{36}Cl$ (The Radiochemical Centre, Amersham) of specific activity 10 mCi ^{36}Cl/g Cl with tetrabutyl ammonium hydroxide prepared as above. The solution was evaporated to dryness and the residue dried *in vacuo* at 60° for 24 h, allowed to cool, and dissolved in 100 ml anhydrous acetone. Isotopic dilution analysis [5] was used to determine the chloride concentration of this solution. Between 1 and 3 ml of the latter were used in each kinetic run (50 ml total sample volume).

Tetrabutyl ammonium bromide (see above) was recrystallized eight times from ethyl acetate and dried *in vacuo* at 55° for 3 days and at 110° for 2 h at normal pressure. (Found: Br 24.95. Calc. 24.79). Melting point 117.0—117.6°.

The following procedure was employed to label tetrabutyl ammonium bromide with radiobromide. An aqueous solution of 5 mCi $NH_4{}^{82}Br$ (The Radiochemical Centre, Amersham) of specific activity 150 mCi ^{82}Br/g Br was passed through a potassium saturated Dowex 50W-X8 ion exchanger and 0.3 g inactive tetrabutyl ammonium bromide dissolved in the eluate. The latter was evaporated to dryness and the solid residue of $K^{82}Br$ and $Bu_4N^{82}Br$ dried at 100° for 2 h, cooled *in vacuo*, and leached with 25 ml anhydrous acetone in which potassium bromide is only sparingly soluble. The solution obtained was filtered and anhydrous acetone added to give a radioactive stock of 50 ml volume. The bromide concentration was determined by argentimetric analysis. By analyzing this solution for potassium (from dissolved potassium bromide) by atomic absorption spectrophotometry it was established that the concentration of potassium bromide in the reaction mixture was less than 9×10^{-8} M, which is of no importance for the results. In each kinetic run (50 ml sample volume) 0.5 ml of the radioactive stock was used.

The organic halides, *p*-nitrobenzyl chloride and butyl bromide were purified as described in Refs. 6 and 2, respectively.

Solvent. Acetone (*pro analysi* grade) for conductance measurements was purified according to Ref. 7. The purified solvent had a specific conductivity of less than 2.5×10^{-8} Ω^{-1} cm^{-1}. The acetone used in the kinetic experiments had been dried over anhydrous calcium sulphate and fractionally distilled. The same constants as in Ref. 1 for physical properties of the solvent were used in calculations below.

Conductance measurements. Equivalent conductances of solutions of tetrabutyl ammonium chloride and bromide in anhydrous acetone at $25.00 \pm 0.01°$ were determined according to a procedure and using the equipment described in Ref. 7.

Kinetic procedure. The rates of the chlorine and bromine exchange reactions at $25.00 \pm 0.02°$ were measured as outlined in Refs. 6 and 2, respectively.

RESULTS

Equivalent conductances (in cm^2 Ω^{-1} equiv.$^{-1}$) for the two salts studied are quoted in Table 1 for various molar concentrations, *c*.

Summaries of kinetic data for the chloride and bromide exchange reactions are given in Tables 2 and 3, respectively, in which *b* represents the concentrations of *p*-nitrobenzyl chloride and butyl bromide, respectively, and *c* the concentrations of tetrabutyl ammonium chloride and bromide, respectively. The second-order rate constant, *k*, is defined by the expression, $k = R/bc$, in which *R* is the rate of exchange according to McKay.[8]

Table 1. Equivalent conductances in acetone at 25°.

Bu_4NCl					
Run A		Run B		Run C	
$c \times 10^4$ M	Λ	$c \times 10^4$ M	Λ	$c \times 10^4$ M	Λ
24.100	112.69	26.050	110.85	12.143	130.46
18.171	120.23	13.174	128.63	4.805	151.90
8.700	138.69	8.007	141.08	2.502	163.37
1.862	167.17	4.076	155.36	1.124	173.20
0.9187	174.94	1.638	169.08	0.3403	181.35
		0.5125	179.14		

Bu_4NBr					
Run A		Run B		Run C	
$c \times 10^4$ M	Λ	$c \times 10^4$ M	Λ	$c \times 10^4$ M	Λ
40.842	108.75	26.558	119.60	24.905	121.16
30.410	116.01	20.228	126.39	18.486	128.31
19.849	127.09	13.464	136.33	12.696	137.33
9.441	143.70	6.458	151.56	6.428	151.60
4.823	156.27	3.286	162.45	3.119	163.09
0.9580	175.75	0.6489	178.64	0.6657	178.10

Table 2. Rate data for the exchange of ^{36}Cl between Bu_4NCl and p-NO_2BzCl in acetone at 25°.

$b \times 10^2$ M	$c \times 10^4$ M	k M^{-1} min^{-1}
1.920	79.3	1.184
1.947	58.4	1.284
1.898	39.78	1.373
1.866	28.42	1.453
1.845	19.10	1.551
1.941	18.80	1.551
1.862	11.51	1.653
2.898	8.64	1.701
1.837	8.22	1.709
2.824	4.651	1.801
1.876	4.292	1.826
1.940	2.188	1.946
2.002	1.293	1.974

Table 3. Rate data for the exchange of ^{82}Br between Bu_4NBr and BuBr in acetone at 25°.

$b \times 10^2$ M	$c \times 10^4$ M	k M^{-1} min^{-1}
5.06	101.3	0.2797
5.05	75.0	0.2901
5.06	51.5	0.3116
5.05	41.58	0.3205
5.05	31.56	0.3265
4.984	21.71	0.3436
4.880	14.80	0.3600
4.872	8.08	0.3759
4.987	4.114	0.3935

DISCUSSION OF CONDUCTANCE DATA

Analysis by means of the Fuoss-Onsager theory. The conductance data in Table 1 were analyzed by means of the Fuoss-Onsager conductance equation [9] of 1957,

$$\Lambda = \Lambda_0 - S\sqrt{c\alpha} + Ec\alpha^{10} \log c\alpha + Jc\alpha - K_A c\alpha f^2 \Lambda \qquad (1)$$

in which Λ and Λ_0 have their usual meanings, c is the electrolyte concentration (M), α the degree of dissociation, and K_A the ion-pair association constant. The mean activity coefficient, f, and the parameters S (Onsager limiting slope), E and J are defined by the equations,

$$^{10}\log f = -\frac{A\sqrt{c\alpha}}{1 + B\mathring{a}\sqrt{c\alpha}} \qquad \text{(1:1-electrolyte)} \qquad (2)$$

$$A = 1.8246 \times 10^6/(\varepsilon T)^{3/2}$$

$$B = 50.29 \times 10^8/\sqrt{\varepsilon T}$$

where ε is the dielectric constant of the solvent, T the absolute temperature ($t + 273.15$), and $\mathring{a}$ the ion-size parameter;

$$S = \frac{0.8204 \times 10^6 \Lambda_0}{(\varepsilon T)^{3/2}} + \frac{82.501}{\eta\sqrt{\varepsilon T}} \qquad (3)$$

in which η is the viscosity of the solvent;

$$E = \frac{6.7747 \times 10^{12} \Lambda_0}{(\varepsilon T)^3} - \frac{0.9977 \times 10^8}{\eta(\varepsilon T)^2} \qquad (4)$$

$$J = \sigma_1 \Lambda_0 + \sigma_2 \qquad (5)$$

where

$$\sigma_1 = \frac{5.8844 \times 10^{12}}{(\varepsilon T)^3}\left[\frac{2b^2 + 2b - 1}{b^3} + 0.9074 + \ln \frac{0.50294 \times 10^{10}\mathring{a}}{\sqrt{\varepsilon T}}\right] \qquad (6)$$

$$b = \frac{16.708 \times 10^{-4}}{\mathring{a}\varepsilon T} \tag{7}$$

and

$$\sigma_2 = \frac{0.67683 \times 10^8}{\eta(\varepsilon T)^2} + \frac{0.38035 \times 10^{12}\mathring{a}}{\eta\varepsilon T} - \frac{0.8666 \times 10^8}{\eta(\varepsilon T)^2} \times \left[1.0170 + \ln \frac{0.50294 \times 10^{10}\mathring{a}}{\sqrt{\varepsilon T}}\right] \tag{8}$$

By using the Fuoss "$y-x$" method,[10] K_A, Λ_0, and $\mathring{a}$ were evaluated by means of CDC 3200 computer. In this method eqn. (1) is written in the form,

$$y = J - K_A x \tag{9}$$

in which

$$y = [\Lambda + S\sqrt{c\alpha} - Ec\alpha^{10} \log c\alpha - \Lambda_0]/c\alpha \tag{10}$$

and

$$x = f^2\Lambda \tag{11}$$

Starting with a Λ_0 obtained by using the Shedlovsky method,[11] approximate α's for the N pairs of values c/Λ were calculated from the expression,

$$\alpha_1 = \Lambda/[\Lambda_0 - S\sqrt{c\Lambda/\Lambda_0}] \tag{12}$$

and used to determine preliminary y/x-values for all concentrations according to eqns. (10) and (11), respectively. The activity coefficients involved in x (eqn. (11)) in this first round of computation, were calculated according to eqn. (2) using the sum of the crystallographic radii of the ions in the ion-pair as a first estimate of $\mathring{a}$. A straight line was fitted according to eqn. (9) to the y/x-points using the method of least squares giving preliminary values of J and K_A.

Better α's were then obtained by repeating the calculations above replacing eqn. (12) by the set of equations,

$$\alpha_2 = \Lambda/[\Lambda_0 - S\sqrt{c\alpha_1} + Ec\alpha_1{}^{10} \log c\alpha_1 + Jc\alpha_1] \tag{13a}$$

$$\alpha_3 = \Lambda/[\Lambda_0 - S\sqrt{c\alpha_2} + Ec\alpha_2{}^{10} \log c\alpha_2 + Jc\alpha_2] \tag{13b}$$

$$\vdots$$

and the calculations stopped when $|\alpha_{i+1} - \alpha_i|$ was less than 1×10^{-6} for all points.

The calculations above were repeated for several values of Λ_0 differing from the starting Λ_0 by $+1$, $+2$, ... $+10$ % and -1, -2, ... -10 %. The computer selected the Λ_0 making eqn. (9) the best straight line ($\sum(\Delta y_i)^2 =$ minimum). Further improvement of the linearity of eqn. (9) was obtained by repeating the last procedure for additional values of Λ_0, first with 0.1 % increments in Λ_0 and then with 0.01 % increments. After selecting the "best" Λ_0 (and J), the computer then calculated a better value of $\mathring{a}$ than the starting

value from eqns. (5) to (8). This $\mathring{a}$ was employed to start a second cycle of computations as above, and so on. The computer terminated the calculations when the difference between successive values of $\mathring{a}$ was less than 0.01 %, *i.e.* less than about 1×10^{-3} Å for ordinary values of $\mathring{a}$.

The standard deviation in K_A (Table 4) was calculated in the ordinary way [12] from the slope of eqn. (9). To obtain a measure of the uncertainty in Λ_0 (Table 4) the following procedure was adopted. For each point c/Λ, the corresponding Λ_0 was calculated from eqn. (1) using the final values of K_A and $\mathring{a}$. By this means a set of Λ_0's was obtained and the standard deviation in the average of this set calculated in the usual manner.

Table 4. Conductance parameters of tetraalkyl ammonium halides in acetone at 25° according to the Fuoss-Onsager equation of 1957.

Salt	K_A M^{-1}	Λ_0 $cm^2\ \Omega^{-1}$ equiv.$^{-1}$	$\mathring{a} \times 10^8$ cm
Bu_4NCl	481 ± 7	188.0 ± 0.2	6.3
Bu_4NBr	349 ± 10	187.4 ± 0.3	7.2

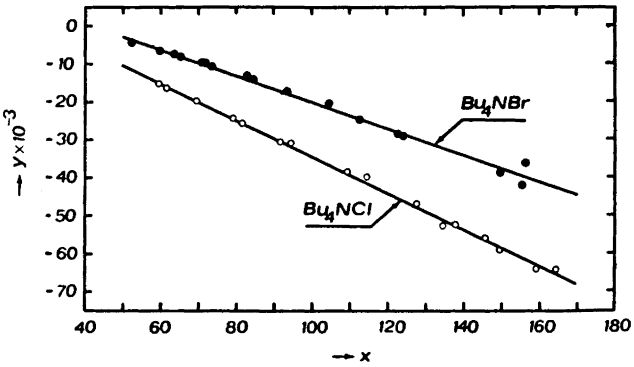

Fig. 1. Fuoss "$y-x$" plots for electrolytes in acetone at 25°.

The results of these calculations using the data in Table 1 for tetrabutyl ammonium chloride and bromide, respectively, are quoted in Table 4. Graphs of y *vs.* x according to eqn. (9) for the final conductance parameters derived are shown in Fig. 1. As can be seen from the values in the second column of Table 4, the chloride is more associated than the bromide. This may be attributed to stronger attractive coulomb forces between the ions in $Bu_4N^+Cl^-$ than in $Bu_4N^+Br^-$ because of the larger surface charge density of the chloride ion as compared with the bromide ion.

It may be of interest to compare values of $\mathring{a}$ derived from the Fuoss-Onsager equation with the sum of the crystallographic radii of unsolvated ions in the ion-pair. Robinson and Stokes [13] have estimated a radius of 4.94 Å for the tetrabutyl ammonium ion. If 1.81 Å for the crystal radius of the chloride ion [14] is added, we arrive at 6.8 Å to be compared with 6.3 Å according to Table 4. Similarly we arrive at 6.9 Å for the crystal radii sum of tetrabutyl ammonium bromide [13,14] to be compared with 7.2 Å in Table 4.

Analysis by means of the Shedlovsky equation. For comparison with the conductance parameters derived from the Fuoss-Onsager equation, the conductance data in Table 1 were analyzed by means of the semiempirical Shedlovsky conductance equation,[11]

$$\frac{1}{\Lambda S} = \frac{1}{\Lambda_0} + \frac{K_A c \Lambda S f^2}{\Lambda_0^2} \tag{14}$$

using the computer programme described in Ref. 1. (Note that S in eqn. (14) has not the same meaning as S in eqn. (1)).

Table 5. Conductance parameters of tetraalkyl ammonium halides in acetone at 25° according to the Shedlovsky equation.

$\mathring{a} \times 10^8$ cm	Bu_4NCl		Bu_4NBr	
	K_A M^{-1}	Λ_0 cm² Ω^{-1} equiv.$^{-1}$	K_A M^{-1}	Λ_0 cm² Ω^{-1} equiv.$^{-1}$
0.0	570±4.2	188.9±0.35	401±3.9	188.0±0.45
1.0	559±3.3	188.6±0.28	389±2.9	187.6±0.35
2.0	548±2.5	188.4±0.21	378±2.1	187.3±0.26
3.0	538±1.9	188.2±0.17	368±1.7	186.9±0.20
3.9 [a]	—	—	359±1.5	186.7±0.19
4.0	528±1.5	188.0±0.13	358±1.5	186.6±0.19
4.8 [a]	521±1.4	187.8±0.13	—	—
5.0	519±1.4	187.8±0.13	349±1.6	186.4±0.20
6.0	511±1.6	187.6±0.14	341±1.9	186.1±0.24
6.8 [b]	505±1.8	187.5±0.16	—	—
6.9 [b]	—	—	334±2.2	185.9±0.28
7.0	503±1.8	187.5±0.17	334±2.2	185.8±0.29
8.0	495±2.2	187.3±0.20	327±2.5	185.6±0.34
9.0	488±2.5	187.1±0.23	320±2.8	185.4±0.38
10.0	482±2.9	187.0±0.27	314±3.1	185.2±0.43

[a] Values of $\mathring{a}$ giving the best fit of the conductance data to the Shedlovsky equation.
[b] Sum of crystallographic radii.[13,14]

To establish which value of the ion-size parameter would give the best fit of eqn. (14) to the experimental points, calculations were first performed for several round values of $\mathring{a}$ (Table 5) and the standard deviation in the single $1/\Lambda S$-value, $\sigma_{1/\Lambda S}$, plotted in Fig. 2 as a function of $\mathring{a}$, *cf.* Ref. 7. The calculations were then continued for several $\mathring{a}$-values near the minima of the

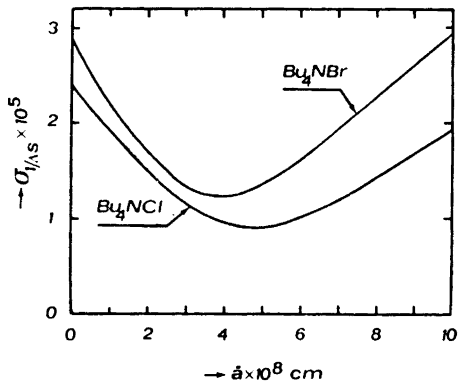

Fig. 2. Standard deviation in the single $1/\Delta S$-value (Shedlovsky equation) as a function of the ion-size parameter for electrolytes in acetone at 25°.

two curves in this graph using 0.1 Å increments for this parameter. By this means $\mathring{a}=4.8$ and 3.9 Å were found to give the best linearity of eqn. (14) for the chloride and bromide, respectively. Graphs of $1/\Delta S$ *vs.* $c\Lambda Sf^2$ according to eqn. (14) for these $\mathring{a}$-values are shown in Fig. 3.

As can be seen from the compilation in Table 6, values of K_A and Λ_0 for the two different conductance equations do not differ greatly.

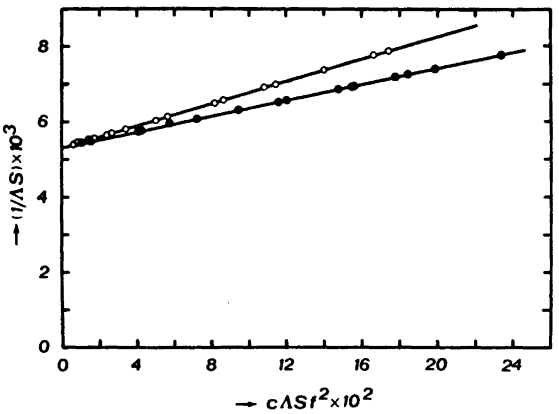

Fig. 3. Shedlovsky plots for Bu_4NCl (open circles; $\mathring{a}=4.8$ Å) and Bu_4NBr (full circles; $\mathring{a}=3.9$ Å) in acetone at 25°.

DISCUSSION OF KINETIC DATA

Analysis of the reaction rate data in Tables 2 and 3 for the presence of S_N1 exchange using a method described in Part II in this series [2] does not indicate any exchange of this kind for either the chlorine or bromine displacement reaction. Most probably the displacements occur *via* S_N2 mechanisms, and the rate of exchange may be expressed by the equation,

$$R = k_i bc\alpha + k_m bc(1-\alpha) \qquad (15)$$

Table 6. Comparison of conductance parameters.

$d \times 10^8$ cm	K_A M^{-1}	Λ_0 $cm^2\ \Omega^{-1}$ equiv.$^{-1}$	Conductance equation
Bu_4NCl			
6.3	481	188.0	Fuoss-Onsager
4.8 [a]	521	187.8	Shedlovsky
6.8 [b]	505	187.5	Shedlovsky
Bu_4NBr			
7.2	349	187.4	Fuoss-Onsager
3.9 [a]	359	186.7	Shedlovsky
6.9 [b]	334	185.9	Shedlovsky

[a], [b] See footnote to Table 5.

in which k_i and k_m are second-order specific rates of reactions of unpaired and paired halide ions, Cl^- or Br^- and $Bu_4N^+Cl^-$ or $Bu_4N^+Br^-$, respectively.

For low concentrations of the ionic halides, when $\alpha \simeq 1$, the last term in eqn. (15) may be neglected. Accordingly, at high dilutions a graph of R/b *vs.* $c\alpha$ should yield a straight line of slope equal to k_i. For higher electrolyte concentrations, when α deviates significantly from unity, the last term in eqn. (15) will make a non-negligible contribution to R, provided that $k_m \neq 0$ (reactive ion-pairs). In that case the graph of R/b *vs.* $c\alpha$ should be non-linear (upwards concavity). As a matter of fact this is so as can be seen in Fig. 4, in which the experimental points increasingly deviate from the limiting tangent

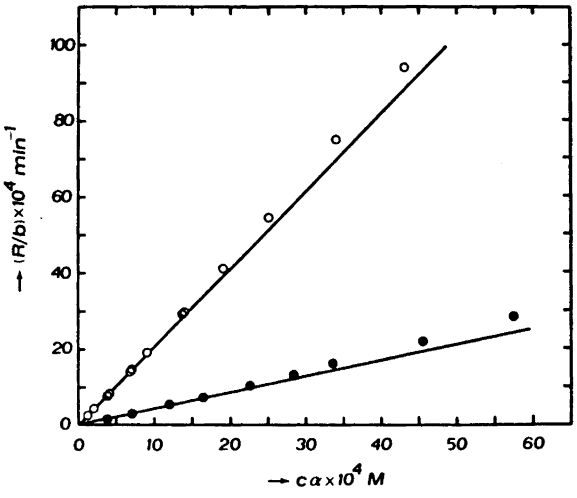

Fig. 4. Graphs of R/b *vs.* $c\alpha$ for the exchange of ^{36}Cl between Bu_4NCl and p-NO_2BzCl (open circles) and of ^{82}Br between Bu_4NBr and BuBr (full circles) in acetone at 25° using values of α calculated from the data in Table 4.

with increasing concentrations of tetrabutyl ammonium chloride and bromide, respectively.

The values of α used in determining the points in the latter graph were calculated from K_A and $\mathring{a}$ according to the Fuoss-Onsager conductance equation (Table 4).

Quantitative information about the reactivity of free and paired halide ions was obtained by fitting the data in Tables 2 and 3 to the Acree equation,

$$k = R/bc = k_i\alpha + k_m(1-\alpha) \qquad (16)$$

Graphs of k/α *vs.* $(1-\alpha)/\alpha$ according to values of K_A and $\mathring{a}$ derived from the Fuoss-Onsager equation (Table 4) are shown in Fig. 5 for the two different reactions studied. The rate constants, k_i and k_m, were evaluated by applica-

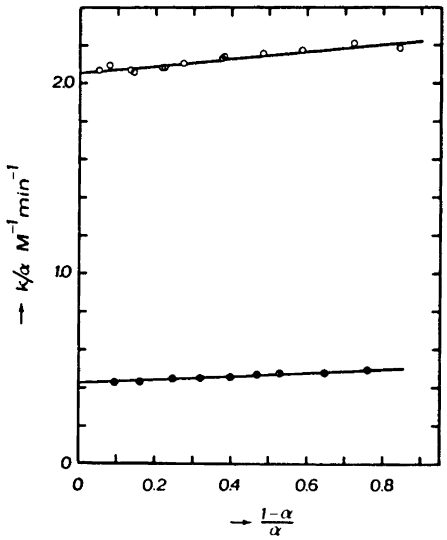

Fig. 5. Graphs of k/α *vs.* $(1-\alpha)/\alpha$ for the same reactions as in Fig. 4. Open and full circles: chlorine and bromine exchange reactions, respectively.

tion of the method of least squares to the points on this graph. The results for the chlorine and bromine exchange reactions are quoted in Tables 7 and 8, respectively, in which k_i and k_m for different K_A-values according to the Shedlovsky equation are also included. The $\pm$ errors given are standard deviations. It can be seen that the rate constants, especially k_i, are not very sensitive to the choice of conductance equation. Quoted in the last columns are k_m in per cent of k_i. The latter data indicate that the reactivity of paired chloride ions is about 10 % of the reactivity of free chloride ions. For the bromide exchange reaction, the corresponding figure is some 20 %. See also Fig. 6, in which k_m, in per cent of k_i, has been plotted as a function of the distance of closest approach of the ions in the ion-pair. The curves shown were derived by application of the Shedlovsky equation, whereas the single points (triangles) were calculated on the basis of the Fuoss-Onsager equation.

Table 7. Second-order specific rates, k_i and k_m, for reaction of Cl^- ions and $Bu_4N^+Cl^-$ ion-pairs, respectively.

$\mathring{a} \times 10^8$ cm	K_A M^{-1}	k_i M^{-1} min^{-1}	k_m M^{-1} min^{-1}	$(k_m/k_i) \times 100$ %
6.3 [a]	481	2.055 ± 0.009	0.186 ± 0.022	9.1
4.8 [b]	521	2.069 ± 0.010	0.206 ± 0.023	10.0
6.8 [c]	505	2.060 ± 0.009	0.231 ± 0.021	11.2

[a] Fuoss-Onsager conductance equation.
[b] Ion-size parameter giving the best fit of conductance data to the Shedlovsky equation.
[c] Sum of crystallographic radii of Bu_4N^+ and Cl^-.

Table 8. Second-order specific rates, k_i and k_m, for reaction of Br^- ions and $Bu_4N^+Br^-$ ion-pairs, respectively.

$\mathring{a} \times 10^8$ cm	K_A M^{-1}	k_i M^{-1} min^{-1}	k_m M^{-1} min^{-1}	$(k_m/k_i) \times 100$ %
7.2 [a]	349	0.4240 ± 0.0026	0.091 ± 0.006	21.5
3.9 [b]	359	0.4279 ± 0.0031	0.071 ± 0.007	16.6
6.9 [c]	334	0.4232 ± 0.0025	0.084 ± 0.006	19.8

[a] Fuoss-Onsager conductance equation.
[b] Ion-size parameter giving the best fit of conductance data to the Shedlovsky equation.
[c] Sum of crystallographic radii of Bu_4N^+ and Br^-.

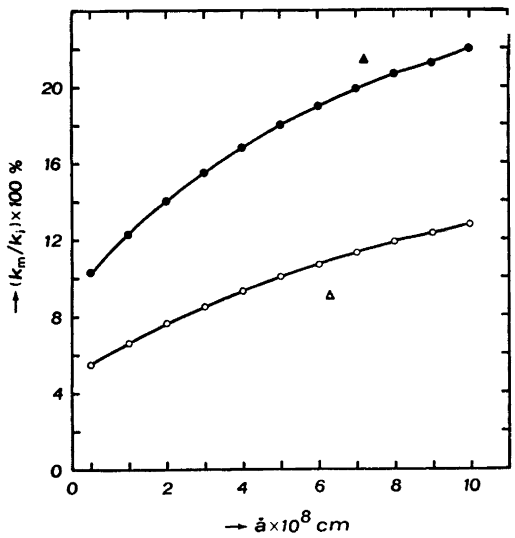

Fig. 6. Dependence of k_m, in per cent of k_i, on the ion-size parameter for the same reactions as in Fig. 4. Open and full circles: data for chlorine and bromine exchange reactions, respectively, derived using the Shedlovsky equation. Open and full triangles: points for chlorine and bromine exchanges, respectively, calculated on basis of K_A and $\mathring{a}$ in Table 4 according to the Fuoss-Onsager equation.

Kinetic and thermodynamic data for chloride ions paired with lithium ions and tetrabutyl ammonium ions, respectively, are compared in Table 9, in which the Gibbs' free energy of dissociation of the ion-pairs is given in the last column. Different kinds of bromide ion-pairs are compared in Table 10. The errors in these tables are standard deviations. All values of k_i and k_m in these two tables are based on the Shedlovsky equation because conductance data [15] for lithium chloride in the actual solvent could not be fitted to the Fuoss-Onsager equation. It is evident from these data that the ion-pair reactivity increases with decreasing free energy of dissociation of the ion-pairs. Ion-pairs involving tetrabutyl ammonium ions are more reactive than ion-pairs involving lithium ions. Apparently the tetrabutyl ammonium ion does not constitute a steric hindrance for the displacement of halogen atoms between the organic and inorganic halides. The larger reactivity of tetrabutyl ammonium ion-pairs might be explained by a smaller electrostatic interaction between the ions in ion-pairs of this sort as compared with ion-pairs in which lithium ions are involved.

Table 9. Comparison of kinetic and thermodynamic data for different kinds of chloride ion-pairs in acetone at 25° using values of K_A evaluated by the Shedlovsky method.

Salt	$K_A \times 10^{-3}$ M^{-1}	k_i M^{-1} min^{-1}	k_m M^{-1} min^{-1}	ΔG_D° kcal $mole^{-1}$
LiCl	295 [a]	2.40 ±0.06 [a]	−0.002 ±0.007 [a]	7.5
Bu_4NCl	0.505 [b]	2.060 ±0.009	0.231 ±0.021	3.7

[a] Ref. 1; $\mathring{a}$=2.41 Å. [b] See Table 5; $\mathring{a}$=6.8 Å.

Table 10. Comparison of kinetic and thermodynamic data for different kinds of bromide ion-pairs in acetone at 25° using values of K_A evaluated by the Shedlovsky method.

Salt	$K_A \times 10^{-3}$ M^{-1}	k_i M^{-1} min^{-1}	k_m M^{-1} min^{-1}	ΔG_D° kcal $mole^{-1}$
LiBr	4.68 [a]	0.485 ±0.003 [c]	0.002 ±0.001 [c]	5.0
Bu_4NBr	0.334 [b]	0.423 ±0.003	0.084 ±0.006	3.4

[a] Ref. 7; $\mathring{a}$=2.55 Å. [b] See Table 5 for $\mathring{a}$=6.9 Å. [c] Ref. 2.

The postulated reaction mechanism according to Acree implies that k_i should be independent of the nature of the cation. This appears not to be exactly so, as can be seen from the values of k_i in Tables 9 and 10. In the chloride exchange reactions, k_i for tetrabutyl ammonium chloride as a source of free chloride ions is some 15 % lower than for lithium chloride as a source of free ions. A similar situation occurs in the bromide exchange reactions.

These observations are in accord with data reported by Lichtin and Rao[16] for the exchange of ^{82}Br between various ionic bromides and *p*-nitrobenzyl bromide in liquid sulphur dioxide. Values of k_i for tetraalkyl ammonium bromides are generally lower than for potassium bromide. The reason for these differences is not apparent and demands further studies.

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