of equation 6 is greater than the right by a factor of about eight under the worst conditions encountered in this paper.

Assumption (b) (equation 7) is clearly satisfied by the fact that chain lengths were of the order of a hundred for the highest concentrations of benzyl iodide, and lower concentrations would reduce both sides of the equation proportionately.

Assumption (c) (equation 8) must be satisfied if chain lengths are long. Even at low benzyl iodide concentrations where chain lengths can be less than unity, assumption (c) must hold if $k_6[B][I_2] >> k_8[B][I]$ as implied in assumption (b).

Competition of Iodine and Oxygen for Benzyl Radicals.—The argument of equation 29 can be applied to the highest concentration of unsubstituted benzyl iodide at 30°. If $y = 0.38$, then $x = 0.53$. Thus in an air saturated solution containing 1.4×10^{-4} *M* iodine, $k_6[I_2]/k_{10}[O_2] = 0.89$ and iodine and oxygen compete with about equal effectiveness. The data of Sibbett and Noyes[22] indicate that in air saturated hexane 4×10^{-4} *M* iodine competes for allyl radicals with about the same efficiency as oxygen. The similarity of the results helps to support the rather complex interpretations that have been developed.

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[CONTRIBUTION FROM THE CHEMISTRY DEPARTMENTS, BROOKHAVEN NATIONAL LABORATORY, UPTON, NEW YORK, AND BOSTON UNIVERSITY, BOSTON, MASSACHUSETTS]

The Effect of Ion Pairing on the Reactivity of Anionic Nucleophiles. I. The Exchange Reaction of *p*-Nitrobenzyl Bromide with Bromide Ion in Liquid Sulfur Dioxide Solution[1]

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The kinetics of exchange of *p*-nitrobenzyl bromide with Br^{82} provided in the form of LiBr, KBr, $(CH_3)_4NBr$ and $(C_2H_5)_4NBr$ has been investigated over a wide range of ionophore concentrations at 0° and, with KBr, at −10.2° and +10.75° as well. Neither of the rate expressions, $R_e = k_2\,(RBr)(MBr)_s$, where (RBr) and $(MBr)_s$ are stoichiometric concentrations of aralkyl bromide and ionophore, respectively, or $R_e = k_1\,(RBr)$ correlates the data satisfactorily; k_2 decreases with increasing $(MBr)_s$ while k_1 increases to a much greater degree. The data establish that the variation of k_2 with $(MBr)_s$ is *not* a salt effect. The rate data have been analyzed with the aid of the thermodynamic dissociation constants of the ionophores evaluated from conductance data by Shedlovsky's procedure and of activity coefficients calculated by means of the Debye–Hückel equation and are consistent with the rate law $R_e = k_f(RBr)(Br^-) + k_p(RBr)(\overbrace{M^+Br^-})$ which ascribes different reactivities to free and paired ions. The magnitudes of k_p, but not of k_f, depend to a substantial degree on the values assigned to a_{DH}, the Debye–Hückel "distance of closest approach." Calculations carried out with an IBM 650 computer show that no value of the Debye–Hückel *a*-parameter in the range from 0 to 30 Å. provides a uniquely superior correlation of the data. The validity of the analysis in terms of k_f and k_p is supported by the fact that k_f is independent of the nature of the cation. In contrast, k_p varies with the nature of the cation in the same sense as does K_d: more tightly bound ion pairs are less reactive. These results support the view that the discrimination between free and paired ions provided by conductivity measurements serves to identify species which differ in their kinetic reactivity but they yield no critical information concerning the precise nature of the paired species. The data are equally consistent with Fuoss' "ions in contact" model or with Bjerrum's original statistical model. The data indicate that SN-1 contribution to the reaction is negligible or, at most, minor. The data are not capable of discriminating between the analysis in terms of k_f and k_p and a treatment based on catalysis by free cation of displacement by free anion.

Introduction

It has been known for a long time that, particularly in smenogenic[3] solvents, reactions of ionic reagents display dependence of specific rate on concentration of the ionophore.[3] The increase in second order specific rate with decrease in concentration of ionophore which is observed in many reactions between neutral molecules and ionic reagents was reported[4] as early as 1890 and was explored extensively by Acree and his students during the first two decades of this century.[5] Acree[5-7] employed his "dual hypothesis," represented essentially by equation 1, where α is the degree of dissociation, to account for these results by assigning different specific rates to free ion (k_f) and associated species (k_p). Although Brönsted

$$k_2^{\text{obsd.}} = \alpha k_f + (1 - \alpha)k_p \qquad (1)$$

rejected[8] Acree's analysis and regarded it as based on "a misunderstanding of salt effect," it has been subsequently accepted by a number of workers.

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[1] Research carried out under the auspices of the U. S. Atomic Energy Commission.

[2] Based on a dissertation submitted by K. N. Rao in fulfillment of a requirement for the Ph.D. degree granted by Boston University in June, 1960. *Cf.* N. N. Lichtin and K. N. Rao, Abstracts of the 134th meeting of the American Chemical Society, Chicago, Ill., Sept. 1958, p. 12-S for a preliminary communication.

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Moelwyn-Hughes[9] has summarized several examples and has concluded[9b] from the success of Acree's analysis that salt effects are absent or small in reactions between ions and polar molecules. Brändstrom[10] has recalculated Acree's data with the aid of revised estimates of degrees of dissociation and has found that the kinetic data are still consistent with equation 1, although the values of k_f and k_p differ from those calculated by Acree. Similar treatments have been employed in several more recent investigations.[11–17] In general, it has been found that k_f is greater than k_p, but it is not possible as yet to generalize about the dependence of the magnitude of the ratio k_f/k_p on reaction variables.

Olson and Simonson[18] have shown that an analysis like that of equation 1 rationalizes the effect of neutral salts on the kinetics of several reactions between ions of like charge in aqueous solution more successfully than does the treatment of Brönsted and Livingston.[19] Davies and his coworkers have reported[20,21] similar results but point out that they are consistent with Brönsted's theory of salt effects provided that ion pairs are treated as kinetically distinct species in considering salt effects. Very recently, Winstein and his coworkers[22] have reported a study which demonstrates the necessity of discriminating between the reactions of free and paired ions in determining relative nucleophilicities of anions.

The objective of the work reported herein was to test equation 1 critically by investigating the isotopic exchange reaction in SO_2 solution of *p*-nitrobenzyl bromide with several ionophoric bromides for which thermodynamic dissociation constants based on conductance measurements vary over a wide range. The effect of *strictly electrostatic association* has thereby been evaluated over a wide range of radii of singly charged cations. The possibility that the salt effect on activities of reactants and transition state can, by itself, account for data which adhere to equation 1 has been tested. The relationship between ionic association defined by electrical conductance and that which is kinetically significant has been considered. The sensitivity of adherence of the data to equation 1 to the choice of Debye–Hückel a parameter employed in calculating mean ionic activity coefficients has been studied. Two explanations alternative to the Acree mechanism have been considered.

Experimental

Preparation of Solutions for Reaction at 0° and −10.2°.—Reaction solutions were prepared on the vacuum line under an atmosphere of SO_2. The SO_2 was passed through anhydrous $Mg(ClO_4)_2$ before being condensed at −78° and degassed. The desired amount of solvent was then distilled into a graduated tube where its volume was measured at 0°. The entire volume of solvent was next distilled into an inverted 100 ml. U-tube, each arm of which bore a side tube containing a weighed portion of one of the reactants. The U-tube was also sealed to a crude automatic pipet capable of delivering a standard aliquot to the quenching flask. After the U-tube was sealed off from the vacuum line, the solutes were dissolved separately, the resulting solutions were brought to the desired temperature (±0.05°) in a liquid thermostat and were then mixed to start the reaction.

Sampling and Quenching Procedure for Reaction at 0° and −10.2°.—Aliquots of reaction mixture were quenched by fivefold dilution with toluene at −30° under autogenous pressure of SO_2, a procedure which precipitates the ionophore. The validity of this quenching procedure is substantiated by the fact that it was possible to obtain initial exchange values approaching very close to zero and differing from zero by an amount that depended only on the purity of *p*-nitrobenzyl bromide (*cf.* below).

Preparation of Solutions, Sampling and Quenching Procedure for Reaction at +10.75°.—At 10.75° SO_2 has a vapor pressure of more than two atmospheres and special procedures were necessary. Separate solutions of reactants were prepared in the inverted U-tube and were brought to a temperature of −10° before being mixed, all as described above. Aliquots of solution were then transferred to evacuated heavy-walled glass tubes maintained at −40°. Before sealing off these tubes, traces of reactants were rinsed from the walls of the tubes by cooling their upper portions with liquid nitrogen so that the solvent condensed there. Decomposition of traces of reactants during sealing was thus minimized, a step necessitated by the sensitivity of initial exchange to traces of impurity (*cf.* below). The heavy-walled tubes were maintained at −40° until all those necessary for a run were filled and were then immersed simultaneously in the thermostat at +10.75°. Initial time was taken as 5 minutes after their transfer to the thermostat. The time required for filling all the tubes for a run was about 0.5 hr. Since the half lives for exchange at + 10.75° were 63 hr. or greater, time uncertainty introduced by this filling procedure was negligible.

Reaction was stopped by freezing the solution in liquid nitrogen, opening the tube and pouring the solution into 5 volumes of cold toluene as soon as it had melted, *i.e.*, at approximately −75°. The reaction tube then was rinsed with toluene and water which were added to the quenched solution.

Initial exchange at this temperature was 0.5% or less.

Separation of Products and Counting.—Most of the SO_2 was removed from each aliquot of quenched reaction mixture by bubbling with nitrogen for about fifteen minutes. The ionophore was then extracted by four or five 20 ml. aliquots of water. The combined aqueous extract was extracted with 20 ml. of toluene which was added to the original toluene layer and extracted with four more 20 ml. portions of water. The toluene and water solutions were each made up to 200.0 ml.

The completeness of extraction of the ionophores into the water layer was tested by blank runs with radioactive ionophores in which *p*-nitrobenzyl bromide was omitted. No more than 0.01% of the ionophores KBr, Me_4NBr and Et_4NBr remained in the toluene layer after this procedure. This separation was not adequate for complete transfer of *n*-Pr_4NBr or *n*-Bu_4NBr to aqueous solution, however. It was found that residual SO_2 was responsible for the solubility of these compounds in toluene since, when SO_2 was excluded from blank runs, complete separation could be effected.

The radioactivity of the ionophore and *p*-nitrobenzyl bromide were determined by means of an immersion type Geiger–Muller counter employed in conjunction with an Atomic Instrument Co. Model 1050A scaler with 98.7%

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helium, 1.3% butane as counter gas. Counting was performed on 25.0 ml. aliquots of the 200.0 ml. toluene and water solutions or on diluted aliquots. The same Geiger-Muller tube and jacket were employed in counting aqueous and toluene solutions prepared from a given aliquot of SO_2 solution so as to render the resulting counts directly comparable. The necessary small corrections were made for decay during the time elapsing between counting the toluene and aqueous solutions. Radioactive background was determined before and after counting groups of reaction solutions by counting 25.0 ml. of distilled water and the appropriate corrections were applied. In all cases counting rates were sufficiently low to render dead time losses negligible. In order to establish the validity of treating the ratio of counts per unit time in the toluene and water solutions as equal to the ratio of concentrations of radioactive Br^{82} atoms in the two solutions, counting was carried out with solutions of $Br^{82}CH_2CO_2H$ in the two solvents. The ratio of counts per unit time per g. of solute in 25.0 ml. aliquots of the two solutions was indistinguishable from unity.

The data of a typical kinetic run are presented in Table I.

TABLE I

COUNTING DATA FOR A TYPICAL RUN[a]

Time,[b] min.	No. of counts[c] Aqueous	Toluene	Per cent.[d] exchange
10	131,890	470	0.36
10	129,980	550	0.42
1100	83,850	7,120	7.83
1100	86,190	7,745	8.24
2545	42,600	12,300	22.41
2545	42,100	12,140	22.37
3975	20,390	11,890	36.8
3975	22,800	13,810	37.8
5715	12,930	10,050	43.7
5715	13,020	10,070	43.6
6915	5,900	5,650	48.9
8603	3,330	4,300	56.3

[a] For the reaction at 0° of 2.108×10^{-3} *M* KBr with 5.136×10^{-2} *M* $p\text{-}NO_2C_6H_4CH_2Br$. [b] Duplicate points represent data obtained from separate aliquots of SO_2 solution withdrawn in rapid succession and worked up separately. [c] Number of counts per 5 min. per 200.0 ml. of solution, corrected for background and decay. [d] Per cent. exchange = 100 *F* $= \frac{100 \times \text{aqueous counts}}{\text{aqueous counts} + \text{toluene counts}}$.

Preparation and Purity of Reactants.—KBr: Radioactive KBr was prepared in two ways. In method I, about 0.5 g. of Baker and Adamson Reagent Grade NH_4Br, sealed in a polyethylene container, was subjected in the Brookhaven reactor to a neutron flux of about 5×10^{12} sec.$^{-1}$ for 3–6 minutes. About 48 hr. was allowed for decay of Br^{80} (half lives 18 min. and 4.5 hr.). The NH_4Br was then dissolved in 25 ml. of water, titrated with 8 *N* KOH (J. T. Baker "Analyzed Reagent") and a drop of the latter added in excess, after which the solution was boiled. Concd. aq. HBr (Baker "Analyzed Reagent") was then added to bring the *p*H to 2 and the solution was boiled to expel excess HBr. Crystals of KBr which formed when the resulting solution cooled were collected on a sintered glass funnel and dried at 125° for 2 hr. In method II, about 0.1 g. of Baker and Adamson Reagent Grade KBr, sealed in an aluminum vial, was irradiated in the reactor for 8 to 24 hr. At least 6 days were allowed for decay of Br^{80} and K^{42} (half life 12.47 hr.). It readily can be calculated that, after this interval, at least 99.93% of the remaining activity is due to $Br.^{82}$ The KBr then was recrystallized from water and dried at 125° for 2 hr.

$LiBr^{82}$.—This was prepared by method I. Fisher "anhydrous powder, purified" LiOH was employed. The solution resulting from treatment with HBr was evaporated to dryness in a platinum crucible which then was heated until the LiBr melted. A drop of concd. HBr was added and the evaporation and fusion repeated. The crucible then was allowed to cool in a vacuum desiccator.

$(CH_3)_4NBr^{82}$.—About 0.2 g. of Eastman "White Label" $(CH_3)_4NBr$ sealed in a polyethylene vial was irradiated in the reactor for 15–30 min. About 48 hr. were allowed for decay of Br^{80}, after which the product was recrystallized from 95% ethanol and dried for 1 hr. at 125°.

$(C_2H_5)_4NBr^{82}$.—Eastman "White Label" $(C_2H_5)_4NBr$ was activated by the procedure employed for the methyl compound. The product was dissolved in 95% ethanol and the solution boiled. It was precipitated by the addition of ether, collected on a sintered glass funnel and dried at 125° for 1 hr.

Radiochemical Purity of Br^{82}.—This was established by the linearity of semilogarithmic plots of activity *vs.* time yielded by data from aqueous solutions of each preparation of each ionophore over three to four half lives. From these data a half life for Br^{82} of 35.9 ± 0.3 hr. was calculated, in agreement with the accepted value.[23]

Test for Szilard–Chalmers Products.—It was established that activated $(C_2H_5)_4NBr$ was not contaminated with radioactivity other than that of the bromide ion. After an aliquot of an aqueous solution of active $(C_2H_5)_4NBr$, prepared and purified as described above, had been passed through a cation exchange resin and the column eluted with water, the eluate contained all the radioactivity initially present in the aliquot and the ion exchange resin was devoid of activity. One drop aliquots of 0.1 *M* aqueous radioactive $(C_2H_5)_4NBr$ were subjected to electrophoresis on 24″ strips of Whatman No. 1 paper saturated with 0.05 *M* sodium citrate. A current of 1 to 2 amp. was passed at 700 volts for periods of 2 hr., 1 hr. and 0.5 hr., respectively. The air-dried papers were scanned for radioactivity. Each displayed activity only at the locus of the bromide ion. The 0.5 hr. paper was cut into 2.5 cm. strips, each of which was counted on the top shelf of a beta counter. About 91% of the activity of the paper (corrected for background) resided in one strip at the expected locus of bromide ion. Five per cent. was in the two adjacent strips and the remaining 4% was randomly distributed over the other strips. Neither active cations nor active uncharged molecules could have been present in the active $(C_2H_5)_4NBr$. These tests were not applied to active $(CH_3)_4NBr$ because the procedure used in purifying it was superior to that employed with the ethyl compound.

***p*-Nitrobenzyl Bromide.**—Initial exchange experiments employed Eastman "White Label" material recrystallized once from absolute ethanol and then from 80–100° ligroin: m.p. 99–99.5°. The compound was recovered unchanged after being held in solution in SO_2 at 0° for 72 hr.

With this material at a concn. around 0.015 *M* the extent of initial exchange increased with decreasing KBr concentration over the range 0.03 to 0.0003 *M*, increasing from less than 1% to 20%. Initial exchange varied linearly with $(KBr)^{-1}$. With 0.0003 *M* KBr, F *decreased* by about one third during the first 15 or 20 hr., passed through a shallow minimum and then increased. These data suggest a toluene-soluble impurity in *p*-nitrobenzyl bromide which exchanges virtually instantaneously with bromide and which is slowly converted, at least in part, into a species which is extracted by water. Attempts to isolate the impurity were not successful. The data are consistent with the hypothesis that the impurity is Br_2 since molecular bromine exchanges practically instantaneously with radiobromide in aqueous solution[24] and would be half converted to highly water soluble HBr by slow substitutive attack on the organic substrate. If this hypothesis is correct, the concentration of Br_2 was about 3×10^{-5} *M* in the experiments described above and the *p*-nitrobenzyl bromide was contaminated with about 0.2 mole per cent. of it. Purification of *p*-nitrobenzyl bromide by four recrystallizations from absolute ethanol followed by recrystallization from 1:1:1 cyclohexene, hexane and benzene, vacuum sublimation at 0.1 mm. and a final recrystallization from the same solvent mixture provided material for which initial exchange was 0.9% with 0.0005 *M* radioactive KBr and 0.015 *M* aralkyl bromide. The purified substrate was stored at room temperature in a desiccator in the dark. Nevertheless it decomposed slowly; after six weeks, initial exchange with 0.0002 *M* active KBr and 0.014 *M* aralkyl bromide was 8%. No sample of *p*-nitrobenzyl bromide was subsequently used for more than four weeks after being subjected to the purification sequence described above. Initial

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(23) *Cf.* W. H. Sullivan, "Trilinear Chart of Nuclides," U. S. Atomic Energy Commission publication, 1957.

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exchange in 27 of the 36 runs which are subjected to kinetic analysis in this paper was less than 1%. It was more than 2% in only 3 runs and no more than 3.9% in any run.

Sulfur Dioxide.—Matheson "anhydrous grade" SO_2 was employed.

Conductance Measurements.—No attempt was made to measure the conductance of KBr in SO_2 at +10.75° for fear that the glass conductivity cell might not withstand the pressure. In order to reduce the extrapolation required to calculate the value of K_d at +10.75°, its magnitude was determined at + 6.23° where the vapor pressure of SO_2 is 1487 mm.[25]. The solvent,[26] bridge assembly,[26] procedures,[26] vacuum line,[27] thermostat[28] and conductivity cell[29] are described elsewhere.

Data

The exchange kinetics were analyzed by means of equation 2, the well known[30] McKay law for simple exchange reactions involving one atom of each reactant and a negligible kinetic isotope effect. In this equation, (RBr) and

$$\frac{R_e t\,[(\mathrm{RBr}) + (\mathrm{MBr})_s]}{2.303\,(\mathrm{RBr})(\mathrm{MBr})_s} = -\log\left[1 - \frac{(\mathrm{RBr}) + (\mathrm{MBr})_s}{(\mathrm{RBr})} F\right] \qquad (2)$$

$(MBr)_s$ represent the stoichiometric molar concentrations of *p*-nitrobenzyl bromide and ionophore, respectively, *F* is the fractional exchange at time *t* (*cf.* Experimental section) and R_e is the rate of the reaction between aralkyl bromide and ionophore. Plots of the logarithmic term of equation 2 *vs.* *t* were linear for all runs employed in the kinetic analysis. Most of the experimental points were obtained in duplicate. The average of the mean deviations of per cent. exchange (100F) for these points is 0.14. The method of least squares was used to evaluate the slopes of the McKay plots and from these the values of R_e which are presented in Table II along with the corresponding values of the specific rates for first and second order reactions calculated according to equations 3 and 4.

$$k_1 = \frac{R_e}{(\mathrm{RBr})} \qquad (3)$$

$$k_2 = \frac{R_e}{(\mathrm{RBr})(\mathrm{MBr})_s} \qquad (4)$$

The dissociation constant, K_d, and limiting conductance, Λ_0, of KBr at 6.23° were evaluated from conductance data by Shedlovsky's procedure[31] and are presented in Table III along with other K_d values which were employed in analyzing the kinetics. The values of K_d for KBr at + 10.75° and − 10.2° were calculated with equation 5, the constants of which were evaluated from experimental values of K_d at + 6.23, + 0.12,[27] − 5.25,[32] − 15.56,[32] − 20.58[32] and −24.99[32] by the method of least squares. The (correlation coefficient)^2 for these data and equation 5 is 0.988.

$$\log K_d = -8.060 + 1.147 \times 10^3/T \qquad (5)$$

Analysis of the Data

Significance of Salt Effects.—The data which are presented in Table II exclude the rate law of equation 3 since k_1 is sharply dependent on the concentration of the ionophore and even depends on its nature at fixed concentration and temperature. The major significance of the variation of k_2 of equation 4 with nature and concentration of the ionophore is emphasized by Fig. 1.

TABLE II

EXCHANGE KINETICS

$(MBr)_s$, mole l.$^{-1}$ × 10^4	(RBr), mole l.$^{-1}$ × 10^4	R_e, mole l.$^{-1}$ sec.$^{-1}$ × 10^9	k_1, sec.$^{-1}$ × 10^7	k_2, l. mole^{-1} sec.$^{-1}$ × 10^5
KBr^{82} at 0°				
499.1	518.3	38.0	7.33	1.47
313.7	168.6	8.33	4.93	1.57
203.0	103.0	3.66	3.55	1.75
176.5	158.3	4.33	2.74	1.55
168.8	443.4	14.26	3.22	1.91
53.65	141.4	1.524	1.08	2.01
34.86	153.1	1.225	0.800	2.29
21.08	513.6	3.61	.703	3.33
19.46	51.43	0.258	.502	2.58
18.93	138.1	.733	.531	2.81
15.76	154.7	.693	.447	2.83
5.293	148.5	.319	.214	4.05
1.301	61.20	.0489	.080	6.11
0.970	145.5	.0749	.052	5.33
KBr^{82} at −10.2°				
97.75	408.8	22.2	5.44	0.556
51.09	451.8	16.13	3.57	.698
13.39	324.6	4.32	1.33	.994
2.917	347.8	1.586	0.456	1.56
1.849	296.1	0.933	0.315	1.70
KBr^{82} at +10.75°				
146.5	325.4	23.9	7.34	5.01
67.42	335.1	13.67	4.08	6.05
39.46	334.4	8.75	2.62	6.63
14.55	288.2	3.57	1.24	8.51
5.022	279.7	1.508	0.54	10.74
$(CH_3)_4NBr^{82}$ at 0°				
212.5	305.7	27.8	9.07	4.27
92.17	315.3	12.99	4.12	4.47
47.17	395.0	9.70	2.46	5.20
17.72	314.1	3.09	0.97	5.57
5.643	285.1	0.973	0.34	6.05
$(C_2H_5)_4NBr^{82}$ at 0°				
199.4	282.3	30.1	10.7	5.35
99.08	315.0	17.54	5.57	5.62
45.62	300.5	8.42	2.80	6.15
12.99	388.0	3.67	0.95	7.28
4.063	412.1	1.051	0.26	6.29
1.045	357.1	0.245	0.069	6.57
$LiBr^{82}$ at 0°				
2.34	405.4	0.220	0.054	2.32

TABLE III

DISSOCIATION CONSTANTS OF IONOPHORES

Ionophore	Temp., °C.	K_d, l. mole^{-1} × 10^4	ΔF_d^0, kcal. mole
KBr	+10.75	0.96[a]	5.22
KBr	+ 6.23	1.04 ± 0.04[b]	5.09
KBr	0	1.43	4.81
KBr	−10.20	2.09[a]	4.43
$(CH_3)_4NBr$	0	11.8[c]	3.66
$(C_2H_5)_4NBr$	0	21.4[d]	3.31
LiBr	0	0.27[e]	5.71

[a] By extrapolation or interpolation, see text. [b] (Variance)$^{1/2}$ with 95% confidence limits; Λ_0 = 273.7 ± 4.2. [c] *Cf.* ref. 27. [d] *Cf.* ref. 32. [e] *Cf.* N. N. Lichtin and K. N. Rao, *J. Phys. Chem.*, **64**, 945 (1960).

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(25) "International Critical Tables," Vol. III, McGraw-Hill Book Co., Inc., New York, N. Y., 1928, p. 236.

(26) N. N. Lichtin and H. Glazer, *J. Am. Chem. Soc.*, **73**, 5537 (1951).

(27) N. N. Lichtin and H. P. Leftin, *J. Phys. Chem.*, **60**, 160 (1956).

(28) N. N. Lichtin and M. J. Vignale, *J. Am. Chem. Soc.*, **79**, 579 (1957).

(29) N. N. Lichtin, E. S. Lewis, E. Price and R. R. Johnson, *ibid.*, **81**, 4520 (1959).

(30) *Cf.* G. Friedlander and J. Kennedy, "Nuclear and Radiochemistry," John Wiley and Sons, Inc., New York, N. Y., 1955, p. 315.

(31) T. Shedlovsky, *J. Franklin Inst.*, **225**, 739 (1938).

(32) N. N. Lichtin and P. Pappas, *Trans. N. Y. Acad. of Sciences*, **20**, 143 (1957).

Equation 4 represents the rate law for an SN-2 displacement in which there is no discrimination between the reactivity of free and paired ions. *A priori*, the possibility exists that the increase in k_2 with decreasing ionic strength, characteristic of the present work and earlier studies referred to in the introduction, is a consequence of salt effects. A qualitative argument which recognizes that charge is dispersed in the transition state of the SN-2 reaction is in agreement with the direction of variation of k_2 with ionic strength. Neither quantitative theories[33] nor observed salt effects in solvents of sufficiently high dielectric constant to minimize complication by pairing[34] permit an unequivocal prediction of the sign of the salt effect for the present case, however. It has been noted above that Moelwyn-Hughes[9b] has concluded from the success of the Acree analysis that salt effects generally are absent in the reactions of ions with neutral molecules. This conclusion appears to beg the question. It is clear from Fig. 1, however, that the present data cannot be explained by a salt effect regardless of its sign. For each of three ionophores k_2 *decreases* with *increasing* concentration of the ionophore but the curves do not coincide. At fixed stoichiometric concentration of ionophore, k_2 increases with increase in K_d and consequently with increase in α, the degree of dissociation. Since paired ions do not contribute to the ionic atmosphere,[35] this is equivalent to *increase* in k_2 with *increasing* ionic strength. The salt effect cannot be simultaneously positive and negative. Accordingly, the variation of k_2 with concentration and nature of the ionophore cannot be explained in terms of the effect of ionic strength on the activity coefficients of reactants and transition states.

Quantitative Application of the Acree Analysis.—The data of Fig. 1 are qualitatively in accord with the Acree mechanism symbolized by equation 1a, provided that different ion pairs have different reactivities. Quantitative comparison requires a

$$R_e = k_f\,(\mathrm{RBr})(\mathrm{Br}^{-82}) + k_p\,(\mathrm{RBr})(\overbrace{\mathrm{M}^{+}\mathrm{Br}^{-82}}) \quad (1a)$$

knowledge of the value of α corresponding to each concentration of each ionophore. The mass action law, equation 6, where $f_\pm$ is the mean molar ionic activity coefficient and the activity coefficient of

$$K_d = \frac{\alpha^2 f_\pm^{\,2}(\mathrm{MBr})_s}{1 - \alpha} \quad (6)$$

the ion pair is assumed to be unity, yields this information provided that values of $f_\pm$ are available. Because measurements of activities of electrolytes in SO_2 solution have not been reported, these values must be calculated from theory. The Debye–Hückel equation, equation 7, where $\mathring{a}_{DH}$ is a

$$-\log f = \frac{1.814 \times 10^6\,(DT)^{-3/2}\,[\alpha(\mathrm{MBr})_s]^{1/2}}{1 + 50.30\mathring{a}_{DH}\,(DT)^{-1/2}\,[\alpha(\mathrm{MBr})_s]^{1/2}} \quad (7)$$

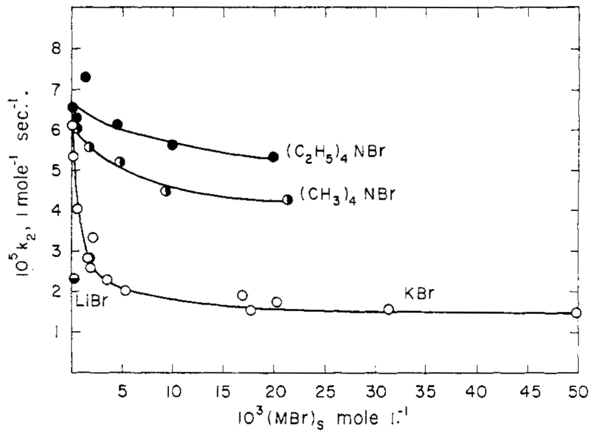

Fig. 1.—Rate constants at 0° for $v = k_2(\mathrm{RBr})(\mathrm{MBr})_s$.

distance of closest approach parameter in ångström units, can be used for this purpose. The values of K_d of Table III were calculated with the aid of the limiting form of equation 7 since only data at concentrations of $5 \times 10^{-4}M$ or less were employed in the Shedlovsky treatment. The exchange data, however, extend to $5 \times 10^{-2}M$ ionophore, a concentration range for which use of the limiting law is questionable. The choice of $\mathring{a}_{DH}$ for each electrolyte is not straightforward, however. If paired ions do not contribute to the ionic atmosphere,[35] then $\mathring{a}_{DH}$ should refer to the minimum distance of approach at which pairs are not formed. According to Bjerrum's treatment,[36] this is the quantity $\mathring{q}$, defined (in units of Å.) for singly charged ions by equation 8, where ϵ is the electronic charge and k_b is the Boltzmann constant. Substitution of $\mathring{q}$

$$\mathring{q} = \frac{10^8\,\epsilon^2}{2Dk_bT} \quad (8)$$

for $\mathring{a}_{DH}$ in equation 7 yields equation 9,[37] where S is the limiting slope of the Debye–Hückel equation

$$-\log f_\pm = \frac{S\mu^{1/2}}{1 + 2.303\,S\mu^{1/2}} \quad (9)$$

(*i.e.*, the terms preceding the bracket in the numerator of equation 7) and μ is the ionic strength. Marshall and Grunwald have found[38] that activity coefficients of hydrochloric acid in aqueous dioxane, which they determined by an e.m.f. method, are in better agreement with equation 10 than with equation 9. Brändström[10] used equation 10 to

$$-\log f_\pm = \frac{S\mu^{1/2}}{[1 + 2.303\,S\mu^{1/2}]^{2/3}} \quad (10)$$

estimate activity coefficients in his recalculation of Acree's data. Equation 10 is equivalent to $0 < \mathring{a} < \mathring{q}$.

In his recent work, Fuoss[39] has preferred a model which defines ion pairs as ions in contact, with no intervening solvent. This suggests that $\mathring{a}_{DH}$ should be approximated by the sum of ionic radii.

In the present work, the degree to which adherence of the kinetic data to equation 1 depends

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[33] *Cf.* E. S. Amis, "Kinetics of Chemical Change in Solution," Macmillan, New York, N. Y., 1949, Chap. VIII, particularly Table VII, p. 174.

[34] (a) F. A. Long, F. B. Dunkle and W. F. McDevitt, *J. Phys. and Colloid Chem.*, **55**, 829 (1951); (b) G. Åkerlof, *J. Am. Chem. Soc.*, **49**, 2968 (1927); (c) E. M. Terry, *ibid.*, **50**, 1239 (1928).

[35] *Cf.* R. A. Robinson and R. H. Stokes, "Electrolyte Solutions," 2nd Ed., Academic Press, Inc., New York, N. Y., 1959, p. 84.

[37] *Ibid.*, p. 230.

[36] Ref. 35, pp. 392–396.

[38] H. P. Marshall and E. Grunwald, *J. Chem. Phys.*, **21**, 2143 (1953).

[39] *Cf.* R. M. Fuoss and F. Accascina, "Electrolytic Conductance," Interscience Publishers, Inc., New York, N. Y., 1959, Chap. XVI.

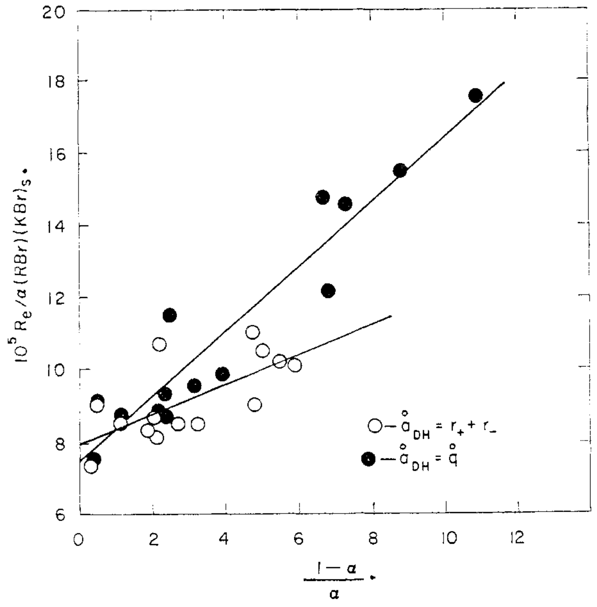

Fig. 2.—Plots of equation 11 for KBr at 0°.

on the choice of $\mathring{a}$ has been scrutinized in some detail. Iterative calculations employing equations 6 and 7 and chosen values of $\mathring{a}_{DH}$ together with the K_d values of Table III yield α values which were used in conjunction with equation 11 to determine k_f and k_p. This solution was obtained analytically

$$\frac{R_e}{(RBr)(MBr)_s\,\alpha} = k_f + k_p(1 - \alpha)/\alpha \qquad (11)$$

by the method of least squares. The use of an IBM 650 digital computer made possible rapid examination of a large number of choices of $\mathring{a}_{DH}$. The data of Table IV illustrate the extent to which the choice of $\mathring{a}_{DH}$ influences $f_\pm$ and α values. The effect of choice of $\mathring{a}_{DH}$ on k_f and k_p for KBr at 0° is shown in Table V. Analogous trends obtain for $(CH_3)_4NBr$ and $(C_2H_5)_4NBr$. Values of k_f and k_p for these two ionophores at 0° and for KBr at − 10.2° and + 10.75° calculated with $\mathring{a}_{DH}$ taken as zero, the sum of crystallographic or Van der Waals radii and as $\mathring{q}$, respectively, are assembled in Table VI.

TABLE IV

EFFECT OF CHOICE OF $\mathring{a}_{DH}$ ON $f_\pm$ AND α FOR KBr AT 0°

$(KBr)_s$, mole l.$^{-1}$ × 10^4	$f_\pm$ $\mathring{a}$ = 3.28 Å.[a]	 $\mathring{a}$ = 19.92 Å.[b]	α $\mathring{a}$ = 3.28 Å.[a]	 $\mathring{a}$ = 19.92 Å.[b]
499.1	0.341	0.609	0.145	0.084
203.0	.458	.650	.167	.121
53.65	.605	.715	.236	.204
19.46	.697	.764	.321	.298
5.293	.791	.824	.476	.463
0.970	.881	.892	.724	.720

[a] $\mathring{a}_{DH}$ = sum of crystallographic radii. [b] $\mathring{a}_{DH} = \mathring{q}$.

TABLE V

EFFECT OF CHOICE OF $\mathring{a}_{DH}$ ON k_f AND k_p FOR KBr AT 0°

$\mathring{a}_{DH}$, Å.	k_f,[a] l. mole^{-1} sec.$^{-1}$ × 10^5	k_p,[a] l. mole^{-1} sec.$^{-1}$ × 10^5	r^2 [b]
0.00	8.19	−152	
3.28	7.93 ± 0.30	0.409 ± 0.087	0.473
4.00	7.85 ± .30	.472 ± .082	.569
6.00	7.70 ± .30	.600 ± .075	.716
8.00	7.60 ± .30	.685 ± .071	.790
10.00	7.54 ± .30	.746 ± .067	.835
12.00	7.50 ± .30	.791 ± .064	.852
14.00	7.48 ± .30	.826 ± .062	.874
16.00	7.46 ± .30	.855 ± .061	.889
18.00	7.45 ± .30	.878 ± .060	.899
19.92	7.45 ± .30	.898 ± .058	.912
25.00	7.45 ± .31	.935 ± .055	.920
30.00	7.47 ± .31	.961 ± .054	.927

[a] Uncertainties are (variances)$^{1/2}$ for 50% confidence limits corrected for the number of data by Fisher's t. [b] r = correlation coefficient.

TABLE VI

k_f[a,b] AND k_p[a,b] FOR SELECTED VALUES OF $\mathring{a}_{DH}$

$\mathring{a}_{DH}$	0	$r_+ + r_-$ [c]	$\mathring{q}$ [d]
		KBr at 0°	
10^5k_f	8.19	7.93 ± 0.30	7.45 ± 0.30
10^5k_p	−152	0.409 ± 0.087	0.898 ± 0.058
r^2		0.473	0.912
		$(CH_3)_4NBr$ at 0°	
10^5k_f	6.00 ± 1.23	7.25 ± 0.28	6.88 ± 0.22
10^5k_p	2.53 ± 3.33	1.27 ± 0.42	2.89 ± 0.19
r^2		0.674	0.980
		$(C_2H_5)_4NBr$ at 0°	
10^5k_f	6.48 ± 0.60	7.09 ± 0.34	7.06 ± 0.29
10^5k_p	4.47 ± 3.67	3.13 ± 0.87	4.11 ± 0.43
r^2		0.642	0.913
		KBr at −10.2°	
10^5k_f		2.47 ± 0.17	2.42 ± 0.18
10^5k_p		−0.019 ± 0.086	0.114 ± 0.070
		KBr at +10.75°	
10^5k_f		23.5 ± 0.8	22.9 ± 0.6
10^5k_p		2.04 ± 0.19	2.80 ± 0.10

[a] In units of l. mole^{-1} sec.$^{-1}$. [b] Uncertainties are (variances)$^{1/2}$ for 50% confidence limits corrected for the number of data by Fisher's t; r^2 = (correlation coefficient)^2. [c] $r_+ + r_-$ = 3.28 Å. for KBr, 5.25 Å. for $(CH_3)_4NBr$ and 6.80 Å. for $(C_2H_5)_4NBr$. [d] $\mathring{q}$ = 19.92 Å. at 0°, 19.23 Å. at −10.2° and 20.59 Å. at + 10.75°.

The data of Tables V and VI and of Fig. 2 reveal the degree of dependence on $\mathring{a}_{DH}$ of correlation of the data by equation 11. The limiting form of equation 7 ($\mathring{a}_{DH}$ = 0) yields physically meaningless results for KBr. It also provides a distinctly inferior correlation of the data for $(CH_3)_4NBr$ and $(C_2H_5)_4NBr$.[40] The value of k_f varies little with variation of $\mathring{a}_{DH}$ from the approximate contact distance of the ions to 30 Å. nor is the precision with which k_f is defined significantly sensitive to choice of $\mathring{a}_{DH}$ in this range.

The most significant conclusion with respect to k_f that can be drawn from Tables V and VI is that the same value, within the precision of the analysis, is obtained for the three ionophores. That k_f should be independent of the nature of the cation is a necessary corollary of the postulated mechanism and the constancy of k_f thus stands in its support.

The values of k_p increase substantially and the precision with which k_p is defined improves with increasing $\mathring{a}_{DH}$ over the same range. Values of r^2, the square of the correlation coefficient,[41] given in

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(40) The very poor correlation of the KBr data probably is due to the extension of these data to higher concentrations than were employed with the other two ionophores.

(41) C. A. Bennett and N. L. Franklin, "Statistical Analysis in Chemistry and the Chemical Industry," John Wiley and Sons, Inc., New York, N. Y., 1954, p. 37.

Tables V and VI also measure the dependence on $\mathring{a}_{\mathrm{DH}}$ of the extent to which equation 11 correlates the data.

Table V and analogous data for $(CH_3)_4NBr$ and $(C_2H_5)_4NBr$ do not reveal any choices of $\mathring{a}_{\mathrm{DH}}$ capable of providing best correlations of the data. Nevertheless, certain relationships among the values of k_p and k_f are apparent. First, k_p is not the same for the different ion pairs: k_p increases in the same order as does K_d, namely $\overbrace{K^+Br^-} < \overbrace{(CH_3)_4N^+Br^-} < \overbrace{(C_2H_5)_4N^+Br^-}$. Secondly, k_f is greater than k_p. The magnitudes of the differences, however, depend on the choice of $\mathring{a}_{\mathrm{DH}}$.

Since only one value of R_e was determined with LiBr, it is not possible to determine k_f and k_p independently for this substrate. The consistency of this single datum with the other results can be demonstrated, however, by using an average value of k_f and calculating k_p from equation 11 with the aid of the appropriate α. For $\mathring{a}_{\mathrm{DH}}$ = contact distance, the average value of k_f is 7.36×10^{-5} l. mole^{-1} sec.$^{-1}$ whereas with $\mathring{a}_{\mathrm{DH}} = \mathring{q}$ it is 7.13×10^{-5} l. mole^{-1} sec.$^{-1}$. The former value of k_f yields $k_p = 0.0 \times 10^{-5}$ l. mole^{-1} sec.$^{-1}$ while the latter yields $k_p = 0.28 \times 10^{-5}$ l. mole^{-1} sec.$^{-1}$. These values are less than the corresponding ones for KBr and are therefore consistent with the relationship between the k_p and K_d values noted above.

Alternatives to the Acree Analysis.—The possibility that the observed kinetics can be correlated more precisely by equation 12, which assumes mixed SN-1 and SN-2 mechanisms, than by equation 11, which assumes only the latter, was investigated by analyzing the data for KBr at 0° in terms of equation 12. The method of least squares

$$\frac{R_e}{(\mathrm{MBr})} = k_1 + k_f\,\alpha(\mathrm{RBr}) + k_p\,(1 - \alpha)(\mathrm{RBr}) \quad (12)$$

was employed to evaluate the constants. With $\mathring{a}_{\mathrm{DH}} = 3.28$ Å. and $\mathring{q}$, respectively, $k_1 = -4 \times 10^{-9}$ and 1.1×10^{-9} sec.$^{-1}$, $k_f = 9.3 \times 10^{-5}$ and 6.8×10^{-5} l. mole^{-1} sec.$^{-1}$ and $k_p = 0.16 \times 10^{-5}$ and 0.98×10^{-5} l. mole^{-1} sec.$^{-1}$. The unimolecular mechanism apparently does not contribute significantly to the exchange reaction.

An interesting alternative to the Acree mechanism assumes that that term of equation 11 which is ascribed to reaction of the ion pair actually represents a termolecular contribution to the reaction: nucleophilic attack by free bromide ion aided by electrophilic attack by the free cation. This mechanism, which corresponds to equations 13 and

$$R_e = k_f'\,(\mathrm{Br}^{-82})\,(\mathrm{RBr}) + k_t\,(\mathrm{Br}^{-82})(\mathrm{M}^+)(\mathrm{RBr}) \quad (13)$$

$$\frac{R_e}{(\mathrm{RBr})(\mathrm{MBr})_s\,\alpha} = k_f' + k_tK_d\,\frac{(1 - \alpha)}{\alpha f_{\pm}^2} \quad (14)$$

14, differs from 1a in the location of the cation in the transition state. The variable factors of the second terms on the right sides of equations 11 and 14 appear to differ by $f_{\pm}^2$. This difference disappears, however, when transition state theory[42] is applied, yielding equations 15 and 16 for the

$$v_p = \frac{v^*K_p^*}{2K_d}\,(\mathrm{RBr})(\mathrm{M}^+)(\mathrm{Br}^-)f_{\pm}^2 f_{\mathrm{RBr}}/f_{x_p}^* \quad (15)$$

$$v_t = \frac{v^*K_t^*}{2}\,(\mathrm{RBr})(\mathrm{M}^+)(\mathrm{Br}^-)f_{\pm}^2 f_{\mathrm{RBr}}/f_{x_t}^* \quad (16)$$

"ion-pair" and "cation catalysis" mechanisms, respectively. The values of k_t calculated by means of equation 14 are consistent with the model. With $\mathring{a}_{\mathrm{DH}} = \mathring{q}$, $10^8 k_t$ at 0° is 23.3 ± 2.1, 7.40 ± 0.56 and 5.65 ± 0.76 l.^{2} mole^{-2} sec.$^{-1}$ for KBr, $(CH_3)_4NBr$ and $(C_2H_5)_4NBr$, respectively. Thus "catalytic effectiveness" diminishes as r_+ increases and electrostatic interaction with the cation diminishes.

Many years ago Acree[43] had recognized that kinetic equations analogous to equations 1a and 13 would become identical if the ionic reagent "obeyed Ostwald's dilution law," *i.e.*, if $f_{\pm}^2 = 1$. He employed an expression equivalent to equation 17, where $(\mathrm{MY})_t$ and $(\mathrm{MY})_0$ are, respectively, the concentrations of ionic reagent at time t and initially, in analyzing data for reactions such as $CH_3I + NaOC_6H_5 \rightarrow NaI + CH_3OC_6H_5$. Acree recognized that, with $\alpha = \Lambda_c/\Lambda_0$, his ionic reagents did not yield constant values of $K_{\mathrm{Ostwald}} = \alpha^2c/(1 - \alpha)$ and employed his experimental values of α. On the basis of the failure of this equation to correlate kinetic data for all but two of his reactions, Acree excluded the termolecular mechanism as the source of the second term of the two term equation.

$$v = k_f\alpha(\mathrm{RX})_t(\mathrm{MY})_t + k_t\alpha^2(\mathrm{RX})_t(\mathrm{MY})_t(\mathrm{MY})_0 \quad (17)$$

Quantities of Activation for KBr.—Values of ΔH_f^* and ΔS_f^* (equations 18–20 where k_r is the rate constant, k_b is the Boltzmann constant, h is Planck's constant, C is a constant of integration and R is the gas constant) can be calculated for the free ion reaction from the data at −10.2°, 0° and +10.75° without difficulty because k_f varies little with choice of $\mathring{a}_{\mathrm{DH}}$.[44] As shown in Table VII, ΔH_f^* and ΔS_f^* are also insensitive to the choice of $\mathring{a}_{\mathrm{DH}}$. The values of k_p are, however, sensitive to the choice of $\mathring{a}_{\mathrm{DH}}$. In addition, k_p is indistinguishable from zero at −10.2° with $\mathring{a}_{\mathrm{DH}} = 3.28$ Å. and is also subject to a large uncertainty with $\mathring{a}_{\mathrm{DH}} = \mathring{q}$. Thus interpretation of the relative magnitudes of the quantities of activation for the ion pair and free ion reactions is not warranted.

TABLE VII

QUANTITIES OF ACTIVATION FOR REACTION OF KBr AT 0°

$\mathring{a}$,	ΔF_f^*	ΔF_p^*	ΔH_f^{*a}	ΔH_p^{*a}	ΔS_f^*	ΔS_p^*
Å.	kcal. mole^{-1}		kcal. mole^{-1}		cal. mole^{-1} deg.$^{-1}$	
3.28	11.52	13.1	15.27	23^b	13.6	36
19.92	11.56	12.7	15.23	22^c	13.4	34^c

[a] Calculated from the data by the method of least squares. [b] Based on data at +10.75° and 0° only. [c] The corresponding values based on k_p at + 10.75° and 0° only are $\Delta H_p^* = 16$ kcal./mole and $\Delta S_p^* = 12$ e.u.

$$\Delta H^*/T = -2.303R\log(k_r/T) + C \quad (18)$$

$$\Delta S^* = \frac{\Delta H^* - \Delta F^*}{T} \quad (19)$$

$$\Delta F^* = 2.303\,RT\log\frac{k_bT}{k_rh} \quad (20)$$

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(42) *Cf.* L. P. Hammett, "Physical Organic Chemistry," McGraw-Hill Book Co., New York, N. Y., 1940, pp. 127–129.

(43) S. F. Acree, *Am. Chem. J.*, **48**, 372–377 (1912); *ibid.*, **49**, 478–480 (1913).

(44) Even the choice of fundamental mechanism, *i.e.*, equation 11 *vs.* equation 14, has little effect on the free ion rate constants.

Discussion

Comparison of Ion Pair and Cation Catalysis Mechanisms.—An experiment designed to discriminate between these alternatives is, in principle, difficult to design. If, in order to isolate the cation catalysis mechanism, electrostatic ion pairing is eliminated by employing a smenocolytic[3] solvent or a very large cation, electrostatic[45] association, in the transition state, of the cation with the departing anion should also be eliminated. A potential test of the reality of electrostatic cation catalysis appears if this concept is applied to nucleophilic attack by paired ions as well as by free ions. Equation 21, where k_{tp} is the specific rate of the cation catalyzed ion pair reaction, is the rate expression resulting when both reaction by paired ions and cation catalysis is assumed. If the last

$$\frac{R_{\mathrm{e}}}{\mathrm{RBr})(\mathrm{MBr})_{\mathrm{s}}\,\alpha} = k_{\mathrm{f}} + k_{\mathrm{p}}\frac{1-\alpha}{\alpha} + k_{\mathrm{t}}\,K_{\mathrm{d}}\frac{1-\alpha}{\alpha f_{\pm}{}^{2}} + k_{\mathrm{tp}}\,K_{\mathrm{d}}\left[\frac{1-\alpha}{\alpha f_{\pm}{}^{2}}\right]^{2} \quad (21)$$

term of equation 21 were important, upward concavity would be apparent in Fig. 2. This figure does not, however, provide any evidence for such a term. An experiment which, in principle, might reveal electrostatic cation catalysis involves the kinetics of exchange with a fairly tightly associated ionophore (*e.g.*, KBr) in the presence of various concentrations of an ionophore (*e.g.*, KX) with a common cation and an anion which has a negligible nucleophilic reactivity and which is less tightly associated, *i.e.*, $K_{\mathrm{d}}{}^{\mathrm{KX}} > K_{\mathrm{d}}{}^{\mathrm{KBr}}$. It might be possible thereby to suppress reaction by free anionic nucleophile, isolate the reaction of the ion pair and evaluate the significance of cation catalysis of this process.

In the absence of information capable of discriminating between reactions 1a and 13, the choice appears to be a matter of taste. Simplicity suggests utilization, for the time being, of 1a in the analysis of these data.

Salt Effects.—Although it is a major conclusion of this work that salt effects cannot by themselves account for the variation of gross second order rate constants for the exchange reaction (equation 4) with concentration and nature of the ionophore, the data do not provide a quantitative measure of salt effects in the separate reactions of free and paired ions. Equation 11 assumes that these are negligible. This assumption is supported by the ability of equation 11 to correlate the data but the possibility exists that a better correlation might result if salt effects were assumed to be significant. It would be necessary to know activity coefficients precisely and to have very precise values of R_{e} before the magnitudes of these effects could be measured.

Definition of "Ion Pair."—Ion pairs have, in effect, been defined operationally in this work as those species present in a solution of ionophore which do not conduct the electric current, since K_{d} values of the ionophores are based on conductance measurements. The possibility cannot be ruled out *a priori*, however, that the correspondence between ions which are paired with respect to conductance behavior and ions which are paired with respect to chemical reactivity, *i.e.*, which differ in reactivity from free ions, is not exact. Correlation of the data by equation 11 places limits on this potential difference: either there is a 1:1 correspondence or the concentrations of ions which are paired with respect to chemical reactivity differ from the concentrations of those which are paired with respect to electrical conductance by a factor which does not vary with stoichiometric concentration of a given ionophore. The former possibility corresponds to Fuoss' ions in contact models.[39] The latter corresponds to Bjerrum's statistical model which defines ions as paired so long as centers of charge lie no farther apart than the characteristic distance ° (equation 8), since, according to Bjerrum's theory, the relative distribution of counter ions as a function of distance, r, from a central ion of opposite charge is independent of concentration. Thus, although each characteristic value of r should be expected to correspond to a different ion pair reactivity, and for some values of $r \leq \mathring{q}$, this may be the same as for free ions, the average reactivity per n ion pairs would not vary with concentration.

The Ion Pair Transition State.—The fact that k_{p} increases in the sequence $\overbrace{\mathrm{K^{+}Br^{-}}} < \overbrace{\mathrm{(CH_3)_4N^{+}Br^{-}}} < \overbrace{\mathrm{(C_2H_5)_4N^{+}Br^{-}}}$ indicates that the cation does not interfere sterically with interaction of bromide ion and benzylic carbon in the transition state. Rather, the reactivity of the paired ion differs from that of the free ion to an extent which depends on the electrostatic interaction of the paired ions, *i.e.*, the larger $\Delta F_{\mathrm{d}}{}^{0}$ (Table III) the larger is $\Delta F_{\mathrm{p}}{}^{*}$. In no case is $\Delta\Delta F^{*}$, *i.e.*, $\Delta F_{\mathrm{p}}{}^{*} - \Delta F_{\mathrm{f}}{}^{*}$, equal to $\Delta F_{\mathrm{d}}{}^{0}$, however. The values of $\Delta\Delta F^{*}$ depend on the values of $\mathring{a}_{\mathrm{DH}}$ employed so that no precise relationships can be obtained. With $\mathring{a}_{\mathrm{DH}} = \mathring{q}$, $\Delta\Delta F^{*}$ varies from 24 to 9% of $\Delta F_{\mathrm{d}}{}^{0}$ for the above sequence. The interaction of substrate and nucleophile apparently is perturbed relatively little by the electrostriction of the latter by its associated cation.

Entropy of Activation.—It is seen in Table VII that $\Delta S_{\mathrm{f}}{}^{*}$, the magnitude of which is subject to considerable uncertainty, is positive. It is difficult to see how an increase in entropy could arise solely from the association of reactants to form the transition state; it must be caused by desolvation of the nucleophile as its charge becomes delocalized. $\Delta S_{\mathrm{a}}{}^{0}$ for association of $\mathrm{K^{+}}$ and $\mathrm{Br^{-}}$ ions at 0° is + 36.8 e.u.,[46] a value which is a consequence of the even greater diminution of interaction with the solvent accompanying ionic association. Unfortunately, the data of Table VII do not warrant interpretation of $\Delta S_{\mathrm{p}}{}^{*}$.

Acknowledgment.—Preparation of this paper was facilitated by support provided by NSF G 11315.

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(45) It must be emphasized that this work is restricted to the consequences of electrostatic association.

(46) $\Delta S_{\mathrm{a}}{}^{0} = -\Delta S_{\mathrm{d}}{}^{0}$. $\Delta H_{\mathrm{d}}{}^{0}$ from equation 5 is -5.25 kcal./mole.