ion solutions were poured into cold methanol, rather than ice. The methyl ethers were recovered in 80, 89, and 76% yields, respectively.

Solutions of **11–14** in sulfuric acid were hydrolyzed using the "rapid dispersal" technique.[16] In no case was the starting carbinol recovered; the products from these experiments have not been characterized.

Spectra and pK_{R^+} Measurement. Spectra were measured at 25° using a Beckman DB spectrophotometer equipped with a Sargent recorder. Stock solutions in anhydrous methanol were prepared of such concentration that 0.100-ml aliquots in 10.00 ml of sulfuric acid gave measurable spectra. The sulfuric acid concentrations were determined by titration of weighed samples with standard base.

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The Effect of Ion Pairing on the Nucleophilic Reactivity of Anionic Nucleophiles. II. The Reaction of *p*-Nitrobenzyl Bromide with Chloride Ion in Liquid Sulfur Dioxide Solution at 0.00°[1]

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Abstract: Reaction kinetics were studied with the aid of ^{36}Cl. Relevant ion-pair dissociation constants, K_d, were determined by application of Shedlovsky's computational procedure to electrical conductance data. Gross second-order specific rates determined over a more than tenfold range of initial ionophore concentration were correlated by means of Acree's equation: $k_2 = \alpha k_f + (1 - \alpha)k_p$, where k_f and k_p respectively represent the specific rates of the free ion and paired ion and α is the degree of dissociation of the ionophoric nucleophile. Values of K_d and α were obtained for each ionophore using several values of the Debye–Hückel distance parameter, a_{DH}, to calculate mean ionic activity coefficients. It was found that, although k_p values are sensitive to the choice of a_{DH}, the major conclusions of this work do not depend on this choice so long as a_{DH} is not taken as zero. Values of k_f and k_p (in units of $10^{-5}\ M^{-1}\ \text{sec}^{-1}$) obtained with a_{DH} taken equal to the sum of ionic radii are, respectively, for RbCl, 2.69 ± 0.14 and 0.076 ± 0.042; for $(CH_3)_4NCl$, 2.92 ± 0.25 and 0.47 ± 0.38; for $(C_2H_5)_4NCl$, 3.17 ± 0.01 and 1.61 ± 0.04. The value of k_p for KCl estimated from a single experiment with the aid of the average of k_f for the other three ionophores is $0.03 \times 10^{-5}\ \text{sec}^{-1}$. The present results and previous data[3] for bromide ion together show a regular increase of k_f/k_p with increase in $1/K_d$ and a regular increase of $(\Delta F_p^* - \Delta F_f^*)/\Delta F_d^\circ$ with increase in ΔF_d°. The mean value of $k_f^{Br^-}/k_f^{Cl^-}$ is 2.52 for $a_{DH} = r_+ + r_-$. This sequence is the same as that observed in water and other protic solvents and opposite to that observed in acetone and dimethylformamide.

The background of this contribution is presented[3] in the first paper of this series. The objective of the second paper is to compare critically the effect of ion pairing on the nucleophilic reactivity of chloride ion in liquid SO_2 solution with the analogous effect for bromide ion and to compare the nucleophilicities of the two halide ions when unencumbered by counterions. These comparisons are based on the reactions of both nucleophiles with the same substrate, *p*-nitrobenzyl bromide, PNBB. Thus, eq 1 represents the reaction investigated in this research.

$$p\text{-}NO_2C_6H_4CH_2Br + M^{36}Cl \longrightarrow p\text{-}NO_2C_6H_4CH_2{}^{36}Cl + MBr \quad (1)$$

Experimental Section

Preparation of Solutions, Sampling, Quenching, and Separation of Products. These were performed as described previously[3] for reaction of ionophoric bromides at 0°. Sulfur dioxide was Virginia Smelting Co., Extra Dry grade. The completeness of separation was judged to be satisfactory for RbCl and $(CH_3)_4NCl$ on the basis of values of initial exchange which fell below 2% in almost all cases. Initial exchange was 20.7% in the single run carried out with KCl (concentration, $8.25 \times 10^{-4}\ M$). The reason for this is not apparent. A single blank separation carried out with $10^{-3}\ M\ (C_2H_5)_4NCl$ in the absence of *p*-nitrobenzyl bromide indicated that its concentration in toluene was about 9% of its concentration in water at room temperature. Initial exchange values confirmed this assessment. Because reactions were carried to relatively low conversions, 16% (in addition to initial exchange) or less in the case of $(C_2H_5)_4NCl$, no significant error was introduced by imperfect separation.

Counting. Proportional counting of solid mercurous chloride-36[4] was used to monitor the progress of the reaction. A thin (<125 μg cm^{-2}) window flow counter, operated at a flow rate of 105 cc/min of P-10 gas, was used in conjunction with a Model SC-101 manual sample changer, a Model P-30 proportional preamplifier, and a Model SC-72 scaler, all Tracerlab products. The counter was operated at 2300 v, and the scaler at a sensitivity of 0.05 v. Sample dimensions, mounting technique, and counting geometry were constant throughout. Dead time error was negligible and statistical error in counts after correction for background less than 1.5%. Sample thicknesses were ~10 mg/cm^2.

The total aqueous extract[3] was evaporated to about 20 ml under reduced pressure and an amount of aqueous inactive KBr added sufficient to provide, *in toto*, the same mass of mercurous halide as that provided by the aliquots of the toluene extract employed for radioassay. (Throughout this work, *p*-nitrobenzyl bromide was

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(1) Research supported by the National Science Foundation under Grants G 11315 and GP 4023.

(2) Based in part on a dissertation submitted by M. S. P. in partial fulfillment of the requirements for the Ph.D. degree granted by Boston University in June 1966. *Cf.*, N. N. Lichtin and M. S. Puar, Abstracts, 151st National Meeting of the American Chemical Society, Pittsburgh, Pa., April 1966, p 87K, for a preliminary communication.

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(4) M. Kahn, A. J. Freedman, R. D. Feltham, and N. L. Lark, *Nucleonics*, 13 (5), 58 (1955).

in excess over ionophoric chloride.) The solution was then treated with five to ten drops of a 5% alcoholic solution of Aerosol OT (Cyanamid) and precipitated by addition of a 40% excess of a solution 0.03 *F* in mercurous nitrate (Allied Chemicals, Reagent Grade) and 0.1 *F* in nitric acid (Baker Analyzed Reagent). After 10 min at room temperature the precipitate was filtered in a Tracerlab E-29 stainless steel unit on 24-mm Whatman No. 50 paper which had been washed with distilled water and ethanol and dried *in vacuo* to constant weight. The precipitate was washed on the filter with 5 ml of distilled water followed by 10 ml of absolute ethanol, dried at 60° for 10 min, weighed, and paper plus precipitate mounted with the aid of Scotch tape on a 37.5 × 1 mm aluminum counting disk. The use of varying amounts of carrier salt was validated by determining that the apparent specific activity of the mercurous chloride in 35-mg samples with composition varying from 4 to 77% active mercurous chloride was constant.

The toluene extract[3] was evaporated to 50.0 ml and an appropriate aliquot transferred by pipet to a 50-ml, graduated, stoppered, centrifuge tube where it was made up to 10.0 ml. The covalent organic halides were then decomposed by allowing them to react with 1.5 ml of sodium dispersed in mineral oil (Action Associates) and ten drops of isopropyl alcohol for 5 min at room temperature.[5] Excess sodium was treated with methyl alcohol and 10 ml of distilled water added and the solution neutralized with 10% aqueous nitric acid. After addition of 2 ml of the acid in excess, the solution was centrifuged for 15 min and the aqueous layer removed by means of a syringe and filtered through Whatman No. 40H paper. Mercurous halide was then precipitated as described above. Data of a typical run are presented in Table I.

Table I. Counting Data for a Typical Run[a]

Time, sec	Counts, min^{-1} [b] Aqueous	Toluene	% reaction[c]
660	437,440	6,810	1.53
37,920	488,790	39,280	7.44
104,040	423,090	62,460	12.90
170,460	419,390	86,490	17.10
215,940	413,160	116,400	22.00

[a] 7.83 × 10^{-3} *M* $(CH_3)_4NCl$ and 6.52 × 10^{-2} *M* *p*-nitrobenzyl bromide. [b] Per aliquot of SO_2 solution taken, corrected for background. [c] 100 (aqueous counts)/(aqueous counts + toluene counts).

Preparation of Reactants. Eastman White Label ***p*-nitrobenzyl bromide**[3] was recrystallized four times from absolute ethanol, dried *in vacuo* for 2–3 hr, recrystallized twice from 1:1:1 benzene–cyclohexane–*n*-heptane, sublimed at 50° ($P < 5 \times 10^{-2}$ torr), and recrystallized once more from the three-component solvent. It was protected from light throughout purification operations and stored in the dark in a desiccator for no more than 3 weeks between completion of purification and use. Ionophoric chlorides were prepared by neutralizing the appropriate carbonate or hydroxide with $H^{36}Cl$ in aqueous solution. Radioactive hydrochloric acid used in the preparation of KCl, and RbCl was obtained from Atomic Energy of Canada, Ltd., as a 2 *M* solution with a specific activity of 0.2 mcurie/g of chlorine. The reagent used to prepare the tetraalkylammonium chlorides was obtained from Oak Ridge National Laboratory as a 2.65 *M* solution with a specific activity of 0.5 mcurie/g of chlorine. **$K^{36}Cl$** was prepared[6] by neutralizing 1.5 *M* aqueous KOH (Merck reagent grade) to pH 6 with radioactive hydrochloric acid and evaporating to dryness. It was then treated with 2 drops of the aqueous $H^{36}Cl$ and evaporated to dryness twice after which it was dried in an Abderhalden apparatus for 19 hr with benzene as the refluxing liquid and stored in a desiccator. **$Rb^{36}Cl$** was prepared from rubidium carbonate (Fluka A.G. "purum") by the same procedure. It was washed three times with cold methanol, dried, and stored as described for $K^{36}Cl$. *Anal.* Calcd: Cl, 29.31. Found (by micro Volhard): Cl, 29.14. **$(CH_3)_4N^{36}Cl$** was prepared from the corresponding hydroxide (Eastman, White Label, 10% aqueous solution) as described for $K^{36}Cl$, recrystallized twice from acetone–ethanol (90:10) under an atmosphere of dry nitrogen, dried, and stored as described for $K^{36}Cl$. **$(C_2H_5)_4N^{36}Cl$** was prepared[7] from the hydroxide (Eastman, White Label, 10% aqueous solution) as described above, recrystallized once from ethylene dichloride and once from a mixture of acetone and acetonitrile, dried, and stored as described for $K^{36}Cl$. All operations were performed under dry nitrogen.

Solvents. Reagent grade solvents were used in this work.

Data

The second-order expression corresponding to eq 1 can be expressed in the form given by eq 2, where *F*

$$k_2t[(\mathrm{PNBB})_0 - (\mathrm{MCl})_0] = 2.303 \times \log \frac{[(\mathrm{PNBB})_0 - (\mathrm{MCl})_0F]}{[(\mathrm{PNBB})_0(1 - F)]} \qquad (2)$$

is the fraction of the chlorine substituted into the benzyl compound, *i.e.*, $[(\mathrm{MCl})_0 - (\mathrm{MCl})_t]/(\mathrm{MCl})_0$ and the terms in parentheses are stoichiometric concentrations. For excess PNBB and small values of *F*, as employed in this work, eq 2 reduces to eq 3. Values

$$k_2t[(\mathrm{PNBB})_0 - (\mathrm{MCl})_0] = -2.303 \log (1 - F) \qquad (3)$$

of *F* were determined from counting data by means of eq 4 where C_{tol} and C_{aq} are, respectively, the number

$$F = C_{\mathrm{tol}}/(C_{\mathrm{aq}} + C_{\mathrm{tol}}) \qquad (4)$$

of counts per unit time for the total toluene and total aqueous layers derived from a given aliquot of the reaction mixture. The tedious nature of the counting procedure limited the number of data which could be collected in a reasonable length of time. Thus, in almost all experiments, k_2 was evaluated (by least-squares calculation) from the data for five aliquots. Values of k_2 are presented in Table II. It is assumed

Table II. Kinetics of Substitution

$10^4(\mathrm{MCl})_0$, *M*	α[a]	$10^4(\mathrm{PNBB})_0$, *M*	10^6k_2, M^{-1} sec^{-1}	Std dev of 10^6k_2, M^{-1} sec^{-1}	Max.[b] % *F*
		KCl			
8.294	0.303	997.4	9.26	0.22	16.1
		RbCl			
65.28	0.172	300.1	5.37	0.41	2.69
62.44	0.175	356.6	5.31	0.44	4.79
23.57	0.241	362.2	7.61	0.62	3.99
10.76	0.315	331.1	8.54	0.89	3.82
6.075	0.380	398.0	11.08	1.47	4.87
		$(CH_3)_4NCl$			
101.1	0.526	502.3	17.70	0.98	14.6
78.29	0.545	651.8	17.06	0.94	20.5
77.72	0.545	938.9	19.06	1.43	11.7
76.82	0.546	333.0	20.24	1.95	5.43
25.22	0.648	870.9	16.73	0.96	29.5
22.72	0.659	510.7	19.70	1.07	18.9
10.59	0.740	504.6	23.20	1.24	17.4
5.926	0.801	510.7	27.21	2.44	13.0
		$(C_2H_5)_4NCl$			
104.0	0.685	479.4	27.03	1.61	15.7
56.15	0.730	544.6	27.56	1.67	11.2
21.53	0.805	479.5	28.78	3.42	9.7
7.338	0.884	544.8	30.06	2.39	10.8

[a] Calculated with a_{DH} taken as the sum of ionic radii using K_{d} calculated by normal Shedlovsky method: 3.14 A for KCl, 3.29 A for RbCl, 5.11 A for $(CH_3)_4NCl$, 6.66 A for $(C_2H_5)_4NCl$. [b] Maximum per cent conversion during a given kinetic experiment, corrected for initial exchange.

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Table III. Ion-Pair Dissociation Constants at 0°

	$10^4 K_d$[a]		
	a_{DH}		
Ionophore	0	$r_+ + r_-$	q[b]
$LiBr$[11]	0.249 ± 0.032	0.252 ± 0.032[c]	0.272 ± 0.034
KCl[12]	0.679 ± 0.023	0.694 ± 0.025[d]	0.763 ± 0.038
$RbCl$[12]	0.909 ± 0.067	0.933 ± 0.069[e]	1.041 ± 0.083
KBr[13]	1.430 ± 0.050	1.467 ± 0.05[f]	1.628 ± 0.065
$(CH_3)_4NCl$[14]	10.05 ± 0.44	10.42 ± 0.46[g]	11.33 ± 0.56
$(CH_3)_4NBr$[13]	11.45 ± 0.87	12.54 ± 0.56[h]	14.12 ± 0.54
$(C_2H_5)_4NBr$[15]	22.8 ± 1.7	22.9 ± 2.1[i]	26.5 ± 2.6
$(C_2H_5)_4NCl$[12]	24.7 ± 1.3	26.0 ± 1.45[j]	29.2 ± 1.2

[a] Reference state, 1 *M*. Uncertainties are (variances)$^{1/2}$ with 95% confidence limits. [b] $q = 10^8E^2/2Dk_bT$, where E is the electronic charge, D is the dielectric constant, k_b is Boltzmann's constant, and T is the absolute temperature. q = 19.92 A in liquid SO_2 at 0.00°. [c] $r_+ + r_- =$ 2.55 A. [d] $r_+ + r_- =$ 3.14 A. [e] $r_+ + r_- =$ 3.29 A. [f] $r_+ + r_- =$ 3.28 A. [g] $r_+ + r_- =$ 5.11 A. [h] $r_+ + r_- =$ 5.25 A. [i] $r_+ + r_- =$ 6.80 A. [j] $r_+ + r_- =$ 6.66 A.

here that "unimolecular" (S_N1) substitution plays a negligible role as was shown[3] to be the case in the reaction of PNBB with bromide in liquid SO_2 solution.

Analysis of Data

The concentration dependence of k_2 which is apparent from the data of Table II parallels that which we observed[3] for ionophoric bromides: k_2 decreases with increasing concentration of a given ionophore but, at a fixed stoichiometric concentration of ionophore, k_2 increases with increase in the degree of dissociation of the ionophores, *i.e.*, with increasing concentration of free ions. Thus, the variation in k_2 with nature and concentration of the ionophore cannot be ascribed to salt effects. As with the bromides,[3] the data follow a pattern characteristic of reduction in reactivity of paired ions as compared to free ions, *i.e.*, $k_p < k_f$ in

$$v = (\mathrm{PNBB})[k_f(\mathrm{Cl}^-) + k_p(\mathrm{M}^+\mathrm{Cl}^-)] = k_2(\mathrm{PNBB})(\mathrm{MCl})_s \quad (5)$$

$$k_2 = k_f\alpha + k_p(1 - \alpha) \quad (6)$$

eq 5 and 6 where $(MCl)_s$ is the stoichiometric concentration of ionophoric chloride and other symbols have their usual meanings. Least-squares analysis of (6), suitably rearranged, can accordingly provide values of k_f as intercept and k_p as slope provided that values of α are available. In principle, these are available from thermodynamic dissociation constants, K_d, *via* the Ostwald dilution law, eq 7, provided that values of

$$K_d = \frac{(\mathrm{MCl})_s\,\alpha^2 f_\pm{}^2}{1 - \alpha} \quad (7)$$

$f_\pm$ are known. Since there are no measured values of mean ionic activities for solutions in liquid SO_2, these quantities must be estimated from theory. We have previously explored[3] the consequences of employing different values of the distance parameter, a_{DH}, of the Debye–Hückel theory, expressed in eq 8 in the form appropriate to liquid SO_2 at 0° (with

$$-\log f_\pm = 6.7146[\alpha(\mathrm{MX})_s]^{1/2}/(1 + 0.77645a_{DH}[\alpha(\mathrm{MX})_s]^{1/2}) \quad (8)$$

a_{DH} expressed in A), with respect to evaluating α, k_p, and k_f. No particular choice of a_{DH} was found to correlate the data in a uniquely superior fashion. It was found, however, that use of the limiting law, *i.e.*, taking a_{DH} as zero, gives unsatisfactory results. In the present work, this arithmetic exploration has been extended to determine whether the form of the Debye–Hückel expression used in the evaluation of K_d from conductance data is significant. Shedlovsky's treatment,[8] which was employed to calculate K_d values used to analyze[3] kinetic data for ionophoric bromides (as well as for all our other measurements of ionic equilibria in liquid SO_2[9]), evaluates $f_\pm$ by means of the limiting law. The data of Table III present values of K_d calculated by Shedlovsky's method taking a_{DH} alternatively as 0, equal to the sum of ionic radii, and equal to Bjerrum's q for the nucleophiles employed in the present and initial[3] study of this series. All values of K_d were calculated[10] from the original data.[11–15] These values of K_d have been used consistently in calculation of values of α employed to determine the values of k_f and k_p which are summarized in Table IV. The calculation of k_f and k_p was explored further for the case of KBr[3] (for which the largest number of rate data are available) by employing values of K_d and α, each consistently calculated with the same value of a_{DH} with systematic variation of a_{DH} over the range 0–30 A by the same increments reported in Table V of our first study.[3] The data of Table IV show that employment of values of K_d and α which are internally consistent in terms of a_{DH} has no significant effect on either the values of k_f and k_p or on their precision. The same conclusion is provided by the more extensive calculations for KBr. Thus, no "best" procedure for calculating, for both chlorides and bromides, k_f and k_p emerges. It is, however, apparent that values of k_f and k_p vary in the same way with their method of calculation. Values calculated with $a_{DH} = 0$ diverge most drastically and are considerably less precise. Otherwise, values of k_f are relatively insensitive, diminishing slightly with increase in a_{DH} while their precision changes little and values of k_p increase rather

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(9) N. N. Lichtin, *Progr. Phys. Org. Chem.*, 1, 75 (1963).

(10) Computations were performed with an IBM 1620 digital computer. See N. N. Lichtin, P. Pappas, M. S. Puar, J. Reardon, and B. Wasserman, submitted for publication.

(11) Conductance data taken from the Ph.D. dissertation of K. N. Rao, Boston University, 1960: T = 0.22°.

(12) Conductance data taken from the Ph.D. dissertation of M. S. P., Boston University, 1966: T = 0.00°.

(13) Conductance data taken from the Ph.D. dissertation of H. P. Leftin, Boston University, 1955: T = 0.12°.

(14) Conductance data taken from the Ph.D. dissertation of E. V. Clougherty, Boston University, 1966: T = 0.23°.

(15) Conductance data taken from the Ph.D. dissertation of P. Pappas, Boston University, 1960: T = 0.16°.

Table IV. Values of $k_f{}^a$ and $k_p{}^a$ Based on Calculation of K_d and α with Different Choices of $a_{DH}{}^b$

	K_d calculated with $a_{DH} = 0$; α calculated with a_{DH} =			K_d and α both calculated with a_{DH} =	
	0	$r_+ + r_-$	q	$r_+ + r_-$	q
			KBr[3]		
10^5k_f	8.17 ± 0.52	7.93 ± 0.30	7.45 ± 0.30	7.89 ± 0.30	7.17 ± 0.29
10^5k_p	0.008 ± 0.196	0.409 ± 0.087	0.898 ± 0.058	0.380 ± 0.088	0.872 ± 0.060
k_f/k_p	1000	19	8.3	21	8.2
			$(CH_3)_4NBr$[3]		
10^5k_f	6.02 ± 1.24	7.25 ± 0.28	6.88 ± 0.22	7.24 ± 0.26	6.77 ± 0.19
10^5k_p	2.52 ± 3.28	1.27 ± 0.42	2.89 ± 0.19	1.07 ± 0.42	2.77 ± 0.19
k_f/k_p	2.4	5.7	2.4	6.8	2.4
			$(C_2H_5)_4NBr$[3]		
10^5k_f	6.45 ± 0.60	7.09 ± 0.34	7.06 ± 0.29	7.07 ± 0.33	7.02 ± 0.27
10^5k_p	4.55 ± 3.60	3.13 ± 0.87	4.11 ± 0.43	2.86 ± 0.95	3.91 ± 0.47
k_f/k_p	1.4	2.3	1.7	2.5	1.8
			RbCl		
10^5k_f	2.76 ± 0.15	2.72 ± 0.15	2.67 ± 0.14	2.69 ± 0.14	2.53 ± 0.13
10^5k_p	0.042 ± 0.045	0.081 ± 0.042	0.158 ± 0.035	0.076 ± 0.042	0.150 ± 0.035
k_f/k_p	67	34	17	35	17
			$(CH_3)_4NCl$		
10^5k_f	3.57 ± 0.29	2.92 ± 0.26	2.71 ± 0.24	2.92 ± 0.25	2.69 ± 0.23
10^5k_p	−1.41 ± 0.60	0.48 ± 0.38	1.14 ± 0.24	0.47 ± 0.38	1.10 ± 0.25
k_f/k_p	−2.5	6.1	2.4	6.2	2.4
			$(C_2H_5)_4NCl$		
10^5k_f	3.35 ± 0.21	3.18 ± 0.01	3.11 ± 0.02	3.17 ± 0.01	3.10 ± 0.03
10^5k_p	0.019 ± 1.09	1.65 ± 0.04	2.17 ± 0.05	1.61 ± 0.04	2.11 ± 0.06
k_f/k_p	200	1.93	1.43	1.97	1.47

[a] Units: M^{-1} sec^{-1}; quoted uncertainties are (variances)$^{1/2}$ with 50% confidence limits. [b] For values of $r_+ + r_-$ and q see Table III.

steeply with increase in a_{DH} while their precision improves. As the model requires, the value of k_f for a given nucleophile does not depend significantly on the ionophore employed in its determination while values of k_p for both nucleophiles show the same trend with variation of the cation. In order to discuss relative reactivity of free *vs.* paired ions or to compare different ion pairs, it is, however, necessary to make an arbitrary choice as to the method of calculation. Caution must then be employed in any interpretations to avoid lending significance to relationships which are sensitive to this choice. In the balance of this paper, discussion is based on values of k_f and k_p obtained with consistent use of $a_{DH} = r_+ + r_-$ in calculation of both K_d and α. On this basis, values of k_p can be estimated for LiBr[3] and KCl, for each of which only one kinetic experiment was performed, by averaging k_f values for each halide determined with other ionophores and substituting these in eq 6. This procedure gives k_p equal to 0.045×10^{-5} M^{-1} sec^{-1} ($k_f = 7.40 \times 10^{-5}$ M^{-1} sec^{-1}, $k_f/k_p = 160$) for Li^+Br^- and 0.030×10^{-5} M^{-1} sec^{-1} for K^+Cl^- ($k_f = 2.93 \times 10^{-5}$ M^{-1} sec^{-1}, $k_f/k_p = 100$).

It is also necessary to inquire, in the present case, into two questions which were not relevant to our study of the reaction of bromide since this involved only isotopic exchange. One of these involves the role played by reversal of the reaction. The other involves the degree of variation of α during a kinetic experiment due to reduction in the concentration of the ionophoric chloride. Experiments employing *p*-nitrobenzyl chloride (PNBC) as a substrate for attack by ionic chloride, *e.g.*, $(CH_3)_4NCl$, showed that this reaction is too slow to study during convenient reaction periods (up to 5 days) and with the concentration of PNBC, about 10^{-3} M, employed in these experiments. It is apparent from Table IV that bromide ion, when free or paired with $(CH_3)_4N^+$ ion, is somewhat more than twice as reactive as chloride ion. No quantitative conclusion is possible, but it appears that the reactivity of PNBB exceeds that of PNBC by at least as large a factor. When this analysis is considered in the light of the fact that the ratio of concentrations (PNBC)(MBr)/(PNBB)(MCl) was less than 0.01 throughout the experiments summarized in Table II, it can be concluded that reversal of the substitution reaction was negligible in every case. Straightforward stoichiometric calculations show that the maximum change in α during the course of a kinetic experiment was less than 2% of its initial value for all experiments with RbCl, $(CH_3)_4NCl$, and $(C_2H_5)_4NCl$ and about 4% for the single experiment with KCl, variations which can be neglected safely.

Discussion

A major consequence of this work becomes apparent upon comparing the values of k_f/k_p presented in Table IV. Aside from values based on a_{DH} taken consistently as 0, the sequence of these ratios is essentially the same regardless of choice of a_{DH} and falls in the order LiBr > KCl > RbCl > KBr > $(CH_3)_4NCl \cong (CH_3)_4NBr > (C_2H_5)_4NBr > (C_2H_5)_4NCl$. This sequence does not differ significantly from the order of values of $1/K_d$. *Thus, our prior observation*[3] *that the reactivity of the paired nucleophilic ion is reduced in proportion to its electrostatic interaction with its counterion is generalized.* The data of Table V indicate an additional regularity: *the more tightly bound the nucleophilic anion is in the pair, the greater is the fraction of that binding energy which is lost in the transition state.*

(This generalization also does not depend on the choice of a_{DH}.) Pairing reduces the reactivity of an ion to a disproportionately enhanced degree the greater the pairing energy. This relationship is of obvious potential value. As yet, it is supported by only limited data in a single solvent. Further work is clearly justified.

Table V. Relationship between Free Energy of Dissociation[a] and Differential Free Energy of Activation[b]

Ionophore	$\Delta F_d°$, kcal/mole	$\Delta F_p^* - \Delta F_f^*$,[c] kcal/mole	$(\Delta F_p^* - \Delta F_f^*)/\Delta F_d°$
LiBr	5.75	(2.76)	(0.48)
KCl	5.21	(2.50)	(0.48)
RbCl	5.05	1.94	0.38
KBr	4.80	1.65	0.33
$(CH_3)_4NCl$	3.73	0.99	0.27
$(CH_3)_4NBr$	3.63	1.04	0.29
$(C_2H_5)_4NBr$	3.30	0.49	0.15
$(C_2H_5)_4NCl$	3.24	0.37	0.11

[a] For $a_{DH} = r_+ + r_-$. [b] Reference state, 1 mole l.$^{-1}$; $T = 273°$ A. [c] $\Delta F^* = 2.303RT \log (k_bT/k_rh)$, where k_b, T, k_r, and h are, respectively, Boltzmann's constant, absolute temperature, specific rate, and Planck's constant.

Another potentially important message emerges less clearly[16] from the data of Table V. It is seen that for potassium salts both $\Delta F_d°$ and $\Delta F_p^* - \Delta F_f^*$ are larger for chloride than for bromide. For tetraethylammonium salts the sequence of both quantities is reversed. The behavior of the tetramethylammonium salts appears to be intermediate.[17] A plausible explanation of this behavior lies in the view that chloride ion is more firmly solvated than bromide so that large ions are less able to penetrate its solvation shell than that of bromide. Tetraethylammonium ion is apparently large enough that both the equilibrium and kinetic aspects of pairing are dominated by solvation effects. The equilibrium aspects of this problem are discussed at length elsewhere[10].

The data of Table IV establish that, for the system studied, the nucleophilic reactivity of free bromide is greater than that of free chloride. With $a_{DH} = r_+ + r_-$ the average value of $k_f^{Br^-}/k_f^{Cl^-}$ is 2.52. The difference is relatively small but it is unequivocally in the sequence usually found for nucleophilic attack on sp^3 carbon in protic solvents[18] and opposite to that observed in acetone[19] and in dimethylformamide.[20] It is apparent that the reactivity sequence of unpaired halide ions does not fall into a single general order for aprotic solvents. Interpretation of the sequence observed in liquid SO_2 must await information on the behavior of fluoride and iodide. The reactivity sequence of chloride and bromide is, however, also consistent with dominant influence of solvation of the nucleophilic anions.

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(16) Less clearly because of the fragmentary nature of the kinetic data for KCl.

(17) Precision is low and the relationship depends on choice of a_{DH} for these ionophores.

(18) *Cf., e.g.*, C. G. Swain and C. B. Scott, *J. Am. Chem. Soc.*, **75**, 141 (1953).

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The Induced Decomposition of Acetyl Benzoyl Peroxides[1]

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Abstract: Acetyl benzoyl peroxide decomposes unimolecularly in chlorobenzene at 70°, $k = 2 \times 10^{-5}$ sec^{-1}, but a faster induced process occurs in the pure liquid peroxide. Major products of the induced process (up to 20% each) are *o*- and *p*-toluic acids (absent in the unimolecular reaction), but no *m*-toluic acid. Acetyl 4-chlorobenzoyl peroxide and acetyl 2,6-dichlorobenzoyl peroxide similarly yield 4-chloro-*o*-toluic acid and 2,6-dichloro-*p*-toluic acids, respectively. These results are taken as evidence that the induced reaction involves methyl radical attack on the aromatic ring with concerted cleavage of the peroxide linkage and formation of an α-lactone ring, giving lactones of 1-hydroxy-6- (or -4-) methylcyclohexa-2,4- (or -5-) dienecarboxylic acids, which subsequently rearrange to the toluic acids. Toluene is also a significant product (20%), while the substituted peroxides give *m*-chlorotoluene and 3,5-dichlorotoluene, respectively. It is suggested that these arise from the α-lactones by CO_2 elimination. *The explosive properties of these peroxides are pointed out.*

Experiments reported many years ago by Cass[2] and by Bartlett and Nozaki,[3] together with O^{18} distribution studies by Denney,[4] have shown that the fast induced decomposition of diacyl peroxides in solvents such as ethers involves attack upon peroxide oxygen by α-alkoxyalkyl radicals. In contrast, the slower induced decomposition of benzoyl peroxide in aliphatic hydrocarbon solvents and in carbon tetrachloride (and the induced decomposition at high concentrations in benzene) give significant yields of *ortho*- and *para*-substituted benzoic acids and has led to the proposal by Walling and Savas[5] that here at least one path for the induced chain is radical addition to the aromatic system with concerted cleavage

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(2) W. E. Cass, *J. Am. Chem. Soc.*, **69**, 500 (1947).

(3) P. D. Bartlett and K. Nozaki, *ibid.*, **69**, 2299 (1947).

(4) D. B. Denney and G. Feig, *ibid.*, **81**, 5322 (1959).

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