Structure and Reactivity of Ion Pairs

PER BERONIUS and LASZLO PATAKI

Department of Physical Chemistry, University of Umeå, S-901 87 Umeå, Sweden and Department of Inorganic and Analytical Chemistry, L. Eötvös University of Budapest, H-1443 Budapest, Hungary

A correlation between the structure of ion pairs of alkali iodides and their reactivities as nucleophilic reagents in ethanol, 1-propanol, 1-butanol, and 1-pentanol at 25 °C has been established. Information about the structure was derived from Bjerrum's theory, which reveals that the tightness of the ion pair increases with increasing radius of the naked cation in a given solvent, and with decreasing permittivity of the solvent for a given salt. The ion pair reactivity relative that of the unpaired iodide ion was derived from rate data for the radioiodide exchange between alkali iodides and methyl iodide. The reactivity was found to increase with increasing solvent separation of the ions in the ion pair. Using a recently developed theory, which relates the ion pair reactivity to molecular parameters, the minimum distance between centers of charge in the ion pair was calculated. The resulting values for the different systems studied are slightly less than those derived from Bjerrum's theory.

Investigations of the rates of nucleophilic displacement reactions are of interest not only from purely kinetic points of view but also because the kinetic data may be used to advance our understanding of the interaction of ions with one another and with solvent molecules. Examples of such studies may be found among the isotopic exchange reactions.[1-6]

A systematic investigation of the effect of ion pairing on the rate of the radioiodide exchange between alkali iodides and methyl iodide in n-alcohols at 25 °C has been undertaken.[7-11] The deactivating effect[12] of ion association on the nucleophile showed a marked dependence on cation and solvent properties. The objective of the present paper is to discuss these observations in terms of a theory[13] which relates the ion pair reactivity to the structure of these species.

ION ASSOCIATION

Calculation of the fractions of the nucleophile which are present as free and paired ions requires access to ion pair association constants, K_A. These constants were evaluated from conductance data for the salts under investigation in ethanol,[14] 1-propanol,[15] 1-butanol,[16,17] and in 1-pentanol,[16] using the Fuoss' 1975 conductance equation[18] for associated symmetrical electrolytes,

$$\Lambda = \alpha[\Lambda_\infty(1 - \Delta X/X) - \Delta\Lambda_e] \qquad (1)$$

in combination with the law of mass action for the equilibrium between free and paired ions and the Debye-Hückel equation[19] for the mean activity coefficient of free ions.

In eqn. (1) Λ is the molar conductivity at analytical concentration, c, of the salt, Λ_∞ is that at infinite dilution, and α is the fraction of the salt which is present as free ions. Expressions for the relaxation and hydrodynamic terms, $\Delta X/X$ and $\Delta\Lambda_e$, have been derived by Fuoss[18] using a model in which an anion, i, at distance, r, from a reference cation, j, is defined as paired in the interval, $a \le r \le R$, where a is the minimum distance between centers of charge in the ion pair and R is the distance from reference ion beyond which continuum theory may be applied.

The following values at 25 °C, $\varepsilon = 24.55$, 20.33, 17.51, and 13.9 for the relative permittivity,[20] and $\eta = 1.078$, 1.952, 2.46, and 3.347 cP for the viscosity of ethanol,[20] 1-propanol,[21] 1-butanol,[22] and 1-pentanol,[20] respectively, were adopted in the calculations.

The method used to evaluate the values of K_A and Λ_∞ which minimize $\sigma(\Lambda)$, i.e. the standard deviation between experimental and computed
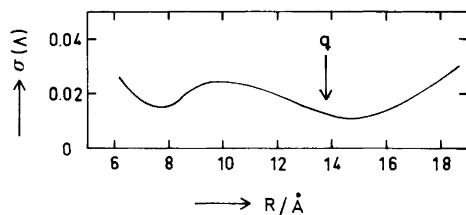
Fig. 1. Dependence of $\sigma(\Lambda)$ on distance parameter, R, for potassium iodide in 1-propanol at 25 °C. The arrow indicates the Bjerrum radius.
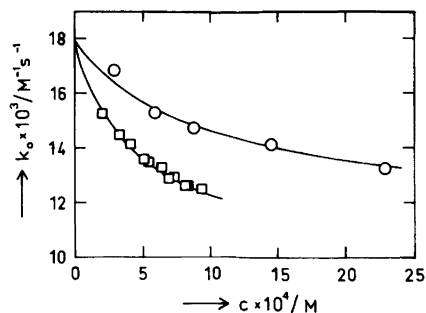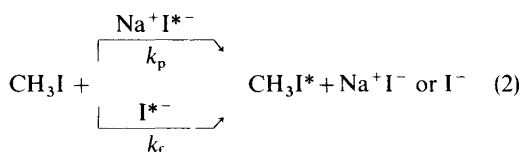

Fig. 2. Dependence of overall second-order rate constant on concentration of ionic reactant for the isotopic exchange between methyl iodide and sodium iodide (circles) and rubidium iodide (squares), respectively, in 1-butanol at 25 °C.

Λ-values, for a given value of the distance parameter, R, has been outlined.[23]

Frequently $\sigma(\Lambda)$ was found to be quite insensitive to the value of the distance parameter, cf. Fig. 1 which refers to potassium iodide in 1-propanol. The $\sigma(\Lambda)$-R curve shown exhibits two minima, one of which appears close to the Bjerrum radius, q, while the other one appears at about $q/2$. Such a behaviour has been observed for other conductance equations.[24,25] Because $\sigma(\Lambda) =$ minimum is not useful as a criterion of "best set" conductance parameters we have chosen to set $R = q$, which for univalent electrolytes in ethanol, 1-propanol, 1-butanol, and 1-pentanol at 25 °C is equal to 11.41, 13.78, 16.00, and 20.16 Å, respectively.

The values of K_A derived and their standard deviations are summarized in Table 1.

REACTION RATES

The kinetics of the radioiodide exchange between alkali iodides and methyl iodide in ethanol,[7] 1-propanol,[8] 1-butanol,[9,10] and 1-pentanol,[10,11] as solvent media at 25 °C have been investigated over a range of concentrations of the ionic iodide. Sufficiently low concentrations for triple ion formation to be negligible were used. The reactions studied are of S_N2 type.

Table 1. Values of K_A at 25 °C according to Fuoss' 1975 conductance equation.[18] Distance parameter, $R = q$.

$K_A(M^{-1})$	EtOH	1-PrOH	1-BuOH	1-PeOH
NaI	46.4(10)	168(2)	573(5)	1952(12)
KI	68.4(8)	311(1)	1159(12)	4150(18)
RbI	90.7(7)	424(2)	1593(6)	
CsI	123(1)	592(2)		

The observed second-order rate constant, k_o, decreases with increasing concentration of the ionic reactant. Examples to illustrate this statement are shown in Fig. 2 in which k_o has been plotted vs. concentration of the ionic iodide for the two exchange reactions between methyl iodide and sodium and rubidium iodides, respectively, in 1-butanol as solvent medium. This concentration effect may be ascribed to ion pair formation, which reduces the reactivity of the nucleophilic reagent, i.e. the iodide ion.

Quantitatively this effect may be treated by splitting the observed rate constant, k_o, into the rate constants, k_p and k_f, referring to the two different exchange reactions,

$$CH_3I + \begin{array}{c} \overset{Na^+I^{*-}}{\overbrace{}} \\ k_p \\ \underset{k_f}{\underbrace{}} \\ I^{*-} \end{array} \quad CH_3I^* + Na^+I^- \text{ or } I^- \quad (2)$$

involving paired and free ions, respectively. This splitting may be accomplished by means of the equation,

$$k_o = k_f\alpha + k_p(1 - \alpha) \quad (3)$$

in which α and $(1 - \alpha)$ are the fractions of the nucleophile, which are present as free and paired ions, respectively.

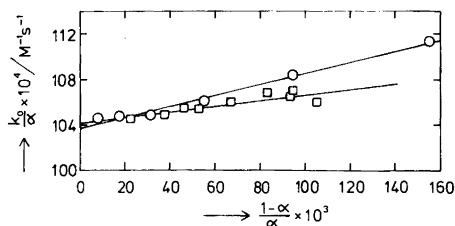To evaluate k_f and k_p it is convenient to rewrite eqn. (3) in the form,

Fig. 3. Graphs according to eqn. (4) for the isotopic exchange between methyl iodide and sodium iodide (circles) and cesium iodide (squares), respectively, in ethanol at 25 °C.

$$k_o/\alpha = k_f + k_p(1-\alpha)/\alpha \qquad (4)$$

which was applied to the experimental points of k_o/α *vs.* $(1-\alpha)/\alpha$ according to the method of least squares. Values of α were evaluated using the K_A's quoted in Table 1. Typical graphs according to eqn. (4) for the exchange reactions involving sodium and cesium iodides as nucleophilic reagents are shown in Fig. 3.

The rate constants, k_p and k_f, derived and their standard deviations are given in Table 2.

DISCUSSION

Effect of cation on ion pair reactivity. The values of K_A in Table 1 indicate that ion pairing of alkali

Table 2. Rate constants, k_p and k_f, referring to paired and free iodide ions as nucleophilic reagents in the isotopic exchange reactions between alkali iodides and methyl iodide at 25 °C.

Solvent	Salt	$k_p \times 10^4$ $M^{-1} s^{-1}$	$k_f \times 10^4$ $M^{-1} s^{-1}$	k_p/k_f
EtOH	NaI	48(3)	103.8(2)	0.46
	KI	44(2)	103.5(2)	0.43
	RbI	35(2)	103.5(2)	0.34
	CsI	25(5)	104.2(4)	0.24
1-PrOH	NaI	46(4)	136.4(8)	0.34
	KI	37(2)	139.1(6)	0.27
	RbI	34(3)	138.2(11)	0.25
	CsI	4(20)	139.7(22)	0.03
1-BuOH	NaI	34(12)	179.2(38)	0.19
	KI	33(10)	179.7(50)	0.18
	RbI	36(3)	177.2(14)	0.20
1-PeOH	NaI	44(7)	197.4(58)	0.22
	KI	34(5)	221.9(53)	0.15

Table 3. Minimum center-to-center distance between the ions in the ion pair at 25 °C according to eqn. (5).

$a/\text{Å}$	EtOH	1-PrOH	1-BuOH	1-PeOH
NaI	5.94	4.55	3.81	4.17
KI	4.61	3.47	3.19	3.61
RbI	3.87	3.15	3.00	
CsI	3.31	2.89		

iodides in a given solvent increases with increasing radius of the naked cation. Qualitatively, this effect may be explained by decreasing solvent separation[26] of the ions in the pair, which determines the minimum anion-cation distance, *a*, because of decreasing solvation of the cation with decreasing surface charge density. Hence, the character of solvent separated ion pairs increases in the order, $Cs^+I^- < Rb^+I^- < K^+I^- < Na^+I^-$.

Quantitatively, this effect may be treated by means of Bjerrum's theory[27] of ion pair formation according to which the association constant on the molarity scale may be expressed,

$$K_A = (4\pi L/1000) \int_a^q r^2 \exp(\beta/r)\, dr \qquad (5)$$

where *L* is the Avogadro constant, $\beta = e^2/\varepsilon k T$, where *e* is the protonic charge, ε is the relative permittivity of the solvent, *k* is Boltzmann's constant, and *T* is the temperature. For different 1:1-electrolytes in a given solvent at constant temperature (q = constant) increasing K_A implies decreasing value of the minimum anion-cation distance, *a*, in the ion pairs, compare the values in Table 3 evaluated by means of eqn. (5) from the association constants in Table 1.

An iodide ion in a loose pair would be more efficient as a nucleophilic reagent than an iodide ion in a tight pair. In other words we may expect the reactivity of the paired iodide ion to increase with increasing solvent separation. Of the alkali iodides investigated sodium iodide ought to exhibit the highest reactivity, while cesium iodide should exhibit the lowest one. This expectation is verified experimentally; see Fig. 4 in which the measured reactivity of the paired iodide ion relative to that of the free one in ethanol as solvent has been plotted *vs.* the alkali metal counter ion. Similar effects were observed for the other solvents investigated.
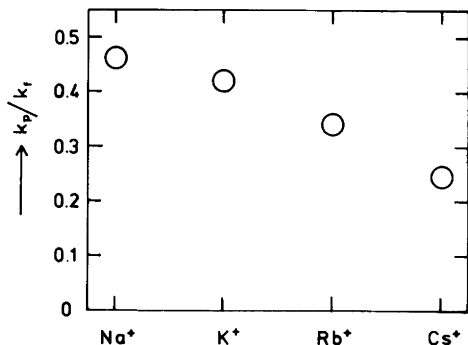
Fig. 4. Effect of cation on ion pair reactivity in the isotopic exchange reactions between alkali iodides and methyl iodide in ethanol at 25 °C.

It may be noted that the measured relative ion pair reactivity (k_p/k_f) represents an average of the different reactivities of all more or less tight ion pairs present, the anion-cation center-to-center distances of which are in the interval, $a \leq r \leq q$, as discussed above. Let us, in addition, recall that the fraction of more tight ion pairs in a given system dominates over the loose pairs. According to the Bjerrum formalism the number, dn_i, of anions, i, in a shell of thickness, dr, at distance, r, from a central cation, j, may be expressed,

$$dn_i = 4\pi n_i \exp(\beta/r)r^2 dr \qquad (6)$$

where n_i is the number of anions per unit volume (bulk concentration). Using eqn. (6) we find, e.g., for sodium iodide in 1-propanol at 25 °C, that the number of (paired) iodide ions which on a time average find themselves in a shell of 0.1 Å thickness at 5 Å distance from a central cation is equal to $8 \times 10^{-21}n_i$ while the corresponding number at 10 Å distance is only $2 \times 10^{-21}n_i$.

Effect of solvent on ion pair reactivity. For a given alkali iodide in different n-alcohols a number of factors would act together to reduce the measured relative ion pair reactivity with decreasing permittivity of the solvent.

(i) The energy required to dissociate an ion pair at given anion-cation distance, r, into free ions increases.

(ii) The minimum center-to-center distance, a, between the ions in the ion pair decreases, cf. Table 3.

(iii) The fraction of (paired) iodide ions at given

distance from a central alkali metal cation increases.

As an example, to illustrate the statement (iii) the number of iodide ions in a shell of 0.1 Å thickness at 6 Å distance from a central alkali metal ion in ethanol, 1-propanol, 1-butanol, and 1-pentanol at 25 °C amounts according to eqn. (6) to $2 \times 10^{-21}n_i$, $4 \times 10^{-21}n_i$, $9 \times 10^{-21}n_i$, and $37 \times 10^{-21}n_i$, respectively.

Hence, for a given salt in the different alcohols concerned the fraction of more tight and less reactive ion pairs would increase with decreasing permittivity of the solvent. Accordingly, we may expect the measured relative ion pair reactivity, k_p/k_f, to decrease in the order, EtOH > 1-PrOH > 1-BuOH > 1-PeOH, in these alcohols. Experimentally, it is verified that this is so; see Fig. 5 in which the effect of the solvent on k_p/k_f for the exchange reaction involving potassium iodide as nucleophilic reagent is shown. Similar effects were observed for the other alkali iodides investigated.

Association constant and reactivity. The population of more tight ion pairs increases with increasing value of the ion pair association constant. Hence, there might exist a correlation between the observed ion pair reactivity and the association constant. According to the graph of k_p/k_f vs. ln K_A in Fig. 6 a linear relationship between these quantities cannot be excluded. Extrapolation of the least squares fitted straight line in this graph,

$$k_p/k_f = 0.636 - 0.0642 \ln K_A \qquad (7)$$

to $k_p/k_f = 0$ suggests that ion pairs of alkali iodides in n-alcohols might be practically unreactive for
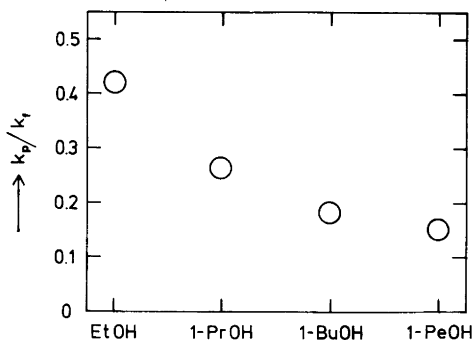

Fig. 5. Effect of solvent on ion pair reactivity in the isotopic exchange reactions between potassium iodide and methyl iodide in n-alcohols at 25 °C.
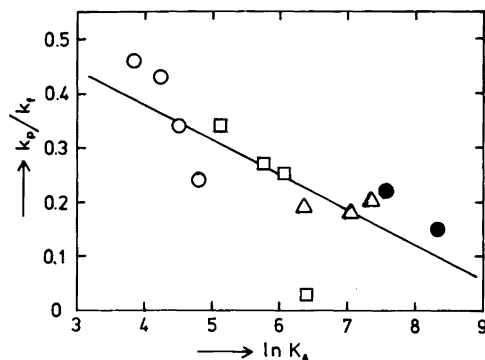
Fig. 6. Dependence of relative ion pair reactivity (k_p/k_f) on ion pair association constant for the isotopic exchange reactions between alkali iodides and methyl iodide in ethanol (open circles), 1-propanol (squares), 1-butanol (triangles), and 1-pentanol (full circles) at 25 °C.

values of K_A exceeding approximately 2×10^4 (M^{-1}). Further studies to verify this conclusion are, however, needed.

Minimum anion-cation distance from kinetic data. Regarding the solvent as a continuum of relative permittivity, ε, the dissociation energy of a univalent ion pair is equal to $D_e = \beta kT/r$. On the assumption that the reactivity of the paired iodide ion varies inversely with the dissociation energy, D_e, and that the distribution of iodide ions around a central alkali metal ion follows eqn. (6) it can be shown[13] that the observed ion pair reactivity (k_p/k_f) and the minimum and maximum distance parameters, a and q, are related to each other through the equation,

$$(k_p/k_f) \int_a^q e^{\beta/r} r^2 \, dr = (1/q) \int_a^q e^{\beta/r} r^3 \, dr \qquad (8)$$

which may be used to calculate the minimum center-to-center distance of the ions in the ion pair from the kinetic data.

By this means the values of a in Table 4 were derived from the experimental rate constant ratios, k_p/k_f, in Table 2. Comparison of the data in Tables 3 and 4 reveals that the a values derived from the kinetic data using eqn. (8) are less, in most instances by $1-2$ Å, than those derived from Bjerrum's theory using eqn. (5). Anyhow, the kinetic data yield values of a which appear to be of quite reasonable order of magnitude. They show the

Table 4. Minimum center-to-center distance between the ions in the ion pair at 25 °C according to eqn. (8).

a/Å	EtOH	1-PrOH	1-BuOH	1-PeOH
NaI	3.0	2.9	2.4	3.3
KI	2.8	2.5	2.4	2.7
RbI	2.4	2.4	2.5	
CsI	2.0	<1		

same dependence on solvent properties and characteristics of the naked cations as do the corresponding distances obtained from Bjerrum's equation.

REFERENCES

1. Beronius, P. *Acta Chem. Scand. 23* (1969) 1175.
2. Beronius, P. *Acta Chem. Scand. 23* (1969) 3120.
3. Beronius, P., Isacsson, U. and Nilsson, A.-M. *Acta Chem. Scand. 24* (1970) 189.
4. Beronius, P., Nilsson, A.-M. and Wikander, G. *Acta Chem. Scand. 24* (1970) 2826.
5. Holmgren, A. and Beronius, P. *Acta Chem. Scand. 26* (1972) 3881.
6. Holmgren, A. *Acta Chem. Scand. A 31* (1977) 539.
7. Beronius, P., Pataki, L., Nilsson, A.-M. and Wikander, G. *Radiochem. Radioanal. Lett. 6* (1971) 333.
8. Holmgren, A., Nilsson, A.-M. and Beronius, P. *Radiochem. Radioanal. Lett. 6* (1971) 339.
9. Pataki, L., Kocsis, E. and Beronius, P. *Radiochem. Radioanal. Lett. 32* (1978) 293.
10. Pataki, L., Kocsis, E. and Beronius, P. *Radiochem. Radioanal. Lett. 34* (1978) 105.
11. Pataki, L., Kocsis, E. and Beronius, P. *Radiochem. Radioanal. Lett. 33* (1978) 121.
12. Gordon, J. E. *The Organic Chemistry of Electrolyte Solutions,* Wiley, New York 1975, Chapter 3.
13. Beronius, P. *Acta Chem. Scand. A 33* (1979) 101.
14. Beronius, P., Wikander, G. and Nilsson, A.-M. *Z. Phys. Chem. (Frankfurt am Main) 70* (1970) 52.
15. Wikander, G. and Isacsson, U. *Z. Phys. Chem. (Frankfurt am Main) 81* (1972) 57.
16. Beronius, P. and Wikander, G. *Unpublished.*
17. Beronius, P. *Acta Chem. Scand. A 32* (1978) 467.
18. Fuoss, R. M. *J. Phys. Chem. 79* (1975) 525 and 1983.

19. Robinson, R. A. and Stokes, R. H. *Electrolyte Solutions*, Butterworths, London 1965, p. 229.
20. Riddick, J. A. and Bunger, W. B. *Techniques of Chemistry*, Vol. II, *Organic Solvents*, 3rd Ed., Wiley-Interscience, New York 1970.
21. Evans, D. F. and Gardam, P. *J. Phys. Chem. 72* (1968) 3281.
22. Janz, G. J. and Tomkins, R. P. T. *Nonaqueous Electrolytes Handbook*, Vol. I, Academic, New York 1972.
23. Beronius, P. *Acta Chem. Scand. A 33* (1979) 79.
24. Beronius, P. *Acta Chem. Scand. A 29* (1975) 289.
25. Beronius, P. *Acta Chem. Scand. A 30* (1976) 115.
26. Winstein, S., Clippinger, E., Fainberg, A. H. and Robinson, G. C. *J. Am. Chem. Soc. 76* (1954) 2597.
27. Bjerrum, N. *K. Dan. Vidensk. Selsk., Mat.-Fys. Medd. 7* (1926) No. 9.