# A Theory of Ion Pair Reactivity

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According to the Bjerrum concept of ion association two ions, $i$ and $j$, of opposite signs constitute an ion pair if the center-to-center distance is less than a critical distance, where the mutual electrical potential energy is equal to $2kT$. On the assumptions that the ion pair reactivity varies inversely with the energy of dissociation and that the distribution of $i$-ions around a selected $j$-ion follows the Boltzmann distribution adopted by Bjerrum, an equation is derived which relates the experimental ion pair reactivity, which represents an average of all more or less tight ion pairs present, to the minimum and maximum distances between centers of charge, $a$ and $q$, in the ion pairs. Experimentally determined reactivities of sodium, potassium, rubidium, and cesium iodides in anhydrous ethanol at 15 °C are correctly described by the equation derived for values of $a$ which are close to the crystal radii sum of the anion and cation.

Several examples illustrating the fact that ion pair formation deactivates nucleophilic reagents may be found in the literature, see, for instance, Refs. 1—6. This effect has been found for many isotopic exchange reactions, *e.g.* that between lithium radiobromide and n-butyl bromide,
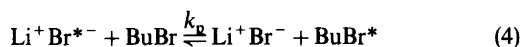
$$\text{LiBr*} + \text{BuBr} \overset{k_0}{\rightleftharpoons} \text{LiBr} + \text{BuBr*} \tag{1}$$

in acetone as solvent.[1]

In this solvent the salt is present as free ions in equilibrium with ion pairs,

$$\text{Li}^+ + \text{Br}^- \rightleftharpoons \text{Li}^+\text{Br}^- \tag{2}$$

and the rate constant, $k_0$, of the overall reaction (1) may be split into the different rate constants, $k_f$ and $k_p$, of two parallel reactions involving free ions,

$$\text{Br*}^- + \text{BuBr} \overset{k_f}{\rightleftharpoons} \text{Br}^- + \text{BuBr*} \tag{3}$$

and paired ions,

$$\text{Li}^+\text{Br*}^- + \text{BuBr} \overset{k_p}{\rightleftharpoons} \text{Li}^+\text{Br}^- + \text{BuBr*} \tag{4}$$

as nucleophilic reagents.

Provided that the reactions (3) and (4) are first order in each reactant the measured rate constant, $k_o$, may be written,

$$k_o = k_f \alpha + k_p(1 - \alpha) \tag{5}$$

where $\alpha$ and $(1 - \alpha)$ are the fractions of the ionic reactant present as free and paired ions, respectively; *cf. e.g.* Ref. 7.

The ions in the ion pair may be in contact and also more or less separated by solvent molecules.[8] Hence, we may expect to be concerned with ion pairs of different reactivities. It follows that the ion pair rate constant, $k_p$, derived from the experimental data would be an average of all more or less tight ion pairs present.

The objective of this paper is to give an account of a method to describe the observed rate constant of the paired nucleophile in terms of molecular parameters.

## DERIVATION

Consider a symmetrical electrolyte. Let $z_i$ be the algebraic valency of the anion and $z_j$ that of the cation. The number of $i$-ions per unit volume is $n_i$ (bulk concentration).

A selected $j$-ion will be used as center of a moving Cartesian coordinate system. The electrical potential energy of an $i$-ion at a given distance, $r$, from the $j$-ion is $z_i e \psi_j$, where $e$ is the protonic charge and $\psi$ is the potential.

Let us, in accord with Bjerrum's treatment of ion pair formation, assume that the average local concentration, $n_i'$, of $i$-ions at that distance from the central ion is given by Boltzmann's distribution law,

$$n_i' = n_i \exp(- \frac{z_i e \psi_j}{kT}) \qquad (6)$$

It follows that the number, $dn_i$, of $i$-ions in a shell of thickness, $dr$, at distance, $r$, from the $j$-ion is,

$$dn_i = 4\pi r^2 n_i \exp(- \frac{z_i e \psi_j}{kT}) \, dr \qquad (7)$$

For small values of $r$ Bjerrum neglects the effect of interionic forces as the potential of the central ion will be dominant. Under such conditions,

$$\psi_j = \frac{z_j e}{\varepsilon r} \qquad (8)$$

where $\varepsilon$ is the relative permittivity of the solvent medium.

According to eqns. (7) and (8) we obtain,

$$dn_i = 4\pi n_i e^{\beta/r} r^2 dr \qquad (9)$$

where,

$$\beta = - \frac{z_i z_j e^2}{\varepsilon kT} \qquad (10)$$

It will be assumed that an $i$-ion forms an ion pair with the $j$-ion provided that the interionic distance is within the Bjerrum radius,

$$q = \beta/2 \qquad (11)$$

The potential energy of the ion pair due to the Coulombic attraction is,

$$U = \frac{z_i z_j e^2}{\varepsilon r} \qquad (12)$$

It follows that the energy of dissociation, which varies with the tightness of the ion pair is,

$$D_e = \beta kT/r \qquad (13)$$

Let us now make the assumption that the reactivity of the ion pair as a nucleophilic reagent varies inversely with the energy of dissociation. On this assumption the rate constant, $k_p(r)$, referring to the ion pair is,

$$k_p(r) = p/D_e \qquad (14)$$

where $p$ is a constant of proportionality, which may be evaluated from the boundary conditions, $k_p(r) = k_f$ for $r = q$, where the dissociation energy $D_e = 2kT$. These conditions yield $p = 2kTk_f$ and hence,

$$k_p(r) = 2kTk_f/D_e \qquad (15)$$

which in view of eqns. (11) and (13) may be rewritten,

$$k_p(r) = k_f r/q \qquad (16)$$

This expression, which refers to the interval $a < r < q$, where $a$ is the minimum distance between centers of charge in the ion pair, indicates that on the assumptions made $k_p(r)$ increases linearly with the distance from the central $j$-ion. For distances, $r > q$, the $i$-ion is no longer paired to the $j$-ion and the rate constant will be equal to that of the free ion, $k_f$.

For distances, $r \leq q$, the number of $i$-ions in a shell of thickness, $dr$, is given by eqn. (9). The corresponding reaction rate referring to $i$-ions is,

$$k_p(r) n_s dn_i = (4\pi n_s n_i k_f/q) e^{\beta/r} r^3 dr \qquad (17)$$

where $n_s$ is the number of unionizable substrate molecules per unit volume. The total reaction rate, $R$, referring to all paired $i$-ions is obtained by integration from the distance of closest approach, $a$, up to the critical Bjerrum distance,

$$R = \int_a^q (4\pi n_s n_i k_f/q) e^{\beta/r} r^3 \, dr \qquad (18)$$

In terms of the experimentally observed rate constant, $k_p$, the reaction rate may be expressed,

$$R = \int_a^q 4\pi n_s n_i k_p e^{\beta/r} r^2 dr \qquad (19)$$

According to eqns. (18) and (19) the experimental ion pair rate constant may be expressed as follows in terms of molecular parameters,
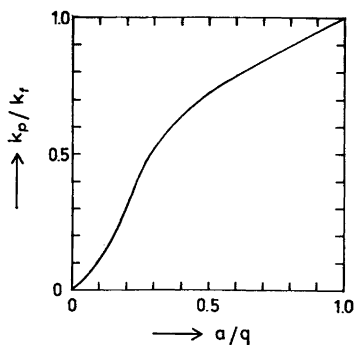
*Fig. 1.* Graphic representation of eqn. (20).

$$k_{\mathrm{p}} = \frac{k_{\mathrm{f}}}{q} \frac{\int\limits_{a}^{q} e^{\beta/r} r^3 \mathrm{d}r}{\int\limits_{a}^{q} e^{\beta/r} r^2 \mathrm{d}r} \qquad (20)$$

A graphic representation of this equation is shown in Fig. 1, where the theoretical rate constant ratio, $k_{\mathrm{p}}/k_{\mathrm{f}}$, has been plotted as a function of the minimum distance, $a$, in units of the Bjerrum radius, between the charges in the ion pair.

## APPLICATION TO EXPERIMENTAL DATA

Eqn. (20) was tested by application to kinetic data for the isotopic exchange reactions between methyl iodide and alkali iodides, *e.g.* that involving sodium iodide,

$$Na^{131}I + CH_3I \rightleftharpoons NaI + CH_3{}^{131}I \qquad (21)$$
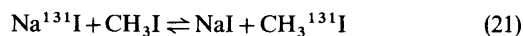
in anhydrous ethanol as solvent at 15 °C.

*Ion pair association constants.* Electrical conductance measurements, *cf.* Ref. 9, were performed to determine the ion pair association constants, $K_{\mathrm{A}}$, of sodium, potassium, rubidium, and cesium iodides in ethanol at $15.00 \pm 0.02$ °C.

The alcohols were dried using a molecular sieve and fractionally distilled. The following properties of the solvent at $15.00 \pm 0.02$ °C were established:[9] electrolytic conductivity, $\varkappa = 3.0 \times 10^{-8}$ S cm$^{-1}$; density, $d = 0.7938$ g cm$^{-3}$; viscosity, $\eta = 1.313$ cP; relative permittivity, $\varepsilon = 25.9$.

The alkali iodides (Merck, *suprapur* or *pro analysi*) were dried for 2 h at 110 °C and again dried under these conditions immediately before use.

*Table 1.* Electrical conductance data of alkali iodides in ethanol at 15 °C.

| Run A $c \times 10^4$ M | $\Lambda$ S cm$^2$ mol$^{-1}$ | Run B $c \times 10^4$ M | $\Lambda$ S cm$^2$ mol$^{-1}$ |
|---|---|---|---|
| **NaI** | | | |
| 44.911 | 30.670 | 46.352 | 30.559 |
| 38.726 | 31.145 | 36.430 | 31.332 |
| 30.358 | 31.921 | 28.643 | 32.088 |
| 25.559 | 32.404 | 24.975 | 32.481 |
| 14.989 | 33.838 | 16.041 | 33.675 |
| 7.8270 | 35.234 | 8.0520 | 35.196 |
| 5.5160 | 35.921 | 5.9870 | 35.741 |
| 2.6010 | 36.910 | 3.0510 | 36.722 |
| | | | |
| **KI** | | | |
| 41.882 | 32.023 | 51.400 | 31.195 |
| 35.038 | 32.712 | 34.151 | 32.802 |
| 27.815 | 33.571 | 29.425 | 33.376 |
| 23.474 | 34.149 | 24.503 | 34.021 |
| 11.315 | 36.406 | 16.845 | 35.269 |
| 5.2470 | 38.154 | 8.1950 | 37.208 |
| 3.0952 | 39.079 | 5.8460 | 37.955 |
| 1.6377 | 39.857 | 2.8733 | 39.178 |
| | | | |
| **RbI** | | | |
| 52.620 | 30.985 | 36.963 | 32.553 |
| 32.503 | 33.117 | 30.958 | 33.311 |
| 24.889 | 34.218 | 34.606 | 32.871 |
| 26.766 | 33.916 | 20.214 | 35.016 |
| 16.192 | 35.826 | 13.984 | 36.326 |
| 8.1830 | 37.906 | 6.2790 | 38.569 |
| 5.6290 | 38.877 | 4.7955 | 39.204 |
| 2.8002 | 40.188 | 2.7467 | 40.194 |
| | | | |
| **CsI** | | | |
| 46.705 | 31.049 | 42.100 | 31.583 |
| 36.895 | 32.253 | 32.941 | 32.820 |
| 28.843 | 33.468 | 26.063 | 33.951 |
| 23.743 | 34.354 | 20.285 | 35.075 |
| 15.727 | 36.153 | 13.868 | 36.664 |
| 8.8790 | 38.250 | 6.9100 | 39.046 |
| 6.2170 | 39.350 | 4.6829 | 40.112 |
| 2.8449 | 41.104 | 2.0311 | 41.704 |

The results of the conductance measurements are given in Table 1, in which the molar conductivity, $\Lambda$, is given at several different concentrations, $c$, of the salt.

The value of $K_{\mathrm{A}}$ was evaluated using two different conductance equations, *viz.* the Fuoss equation from 1975 ("F75" equation)[10,11] and the Fuoss-Hsia equation in the form of Fernández-Prini

*Table 2.* Ion pair association constants of alkali iodides in ethanol at 15 °C according to the F75 and FHFP conductance equations. Distance parameter, $q = 11.19$ Å.

| Salt | $K_A$ (F75) $M^{-1}$ | $K_A$ (FHFP) $M^{-1}$ |
|------|------|------|
| NaI | $39.8 \pm 0.7$ | $49.6 \pm 0.4$ |
| KI  | $58.6 \pm 0.7$ | $71.4 \pm 0.5$ |
| RbI | $77.2 \pm 0.6$ | $91.6 \pm 0.7$ |
| CsI | $107.7 \pm 0.5$ | $125.0 \pm 0.5$ |

("FHFP" equation).[12,13] The distance parameter in the conductance equations and in the Debye-Hückel equation[14] for the mean activity coefficient of free ions was set equal to $q$. The calculations were performed by means of a Cyber 172 computer using previously outlined computer programmes.[15,16]

The association constants computed and their standard deviations are given in Table 2.

*Rate constants.* Bimolecular rate constants for the isotopic exchange reactions between alkali radioiodides ($^{131}$I) and methyl iodide in ethanol at $15.00 \pm 0.03$ °C were determined by means of the electrodeposition method.[17] Details about the measurements can be found in Ref. 6 and references

*Table 3.* Dependence of overall second-order rate constant, $k_o$, on concentration of the ionic reactant for the exchange of $^{131}$I$^-$ between methyl iodide and alkali iodides in ethanol at 15 °C.

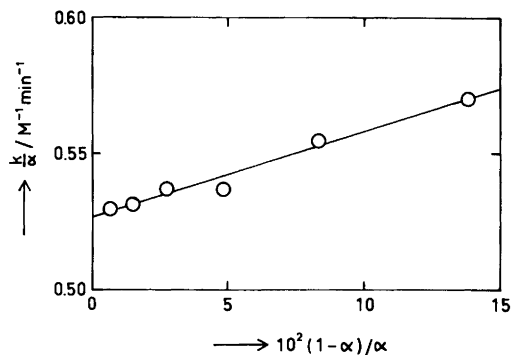| $c \times 10^4$ M | $k_o$ $M^{-1}$ min$^{-1}$ | $c \times 10^4$ M | $k_o$ $M^{-1}$ min$^{-1}$ |
|------|------|------|------|
| **NaI** | | **RbI** | |
| 2.003 | 0.5258 | 1.990 | 0.5238 |
| 5.000 | 0.5231 | 4.989 | 0.5259 |
| 10.01 | 0.5224 | 9.968 | 0.5151 |
| 19.95 | 0.5120 | 19.95 | 0.4990 |
| 39.85 | 0.5121 | 39.81 | 0.4830 |
| 80.10 | 0.5006 | 59.72 | 0.4754 |
|       |        | 79.64 | 0.4596 |
| **KI** | | **CsI** | |
| 1.997 | 0.5285 | 2.012 | 0.5222 |
| 4.991 | 0.5230 | 4.014 | 0.5222 |
| 10.04 | 0.5168 | 6.032 | 0.5155 |
| 20.13 | 0.5162 | 8.004 | 0.5086 |
| 40.11 | 0.5028 | 10.08 | 0.5073 |
| 79.94 | 0.4772 | | |



*Fig. 2.* Graph according to eqn. (22) for the exchange of $^{131}$I between sodium iodide and methyl iodide in ethanol at 15 °C. Values of $\alpha$ according to F75 equation.

therein. The results of the kinetic measurements are given in Table 3, in which the overall rate constant, $k_o$, is given at different concentrations of the ionic reactant.

The observed rate constant was separated into the ion pair and free ion rate constants, $k_p$ and $k_f$, by means of eqn. (5) rewritten in the form,

$$k_o/\alpha = k_f + k_p(1 - \alpha)/\alpha \qquad (22)$$

A graph according to this equation referring to the exchange reaction involving sodium iodide as nucleophilic reagent is shown in Fig. 2.

*Table 4.* Rate constants, $k_p$ and $k_f$, referring to paired and free iodide ions in ethanol at 15 °C. The values were calculated by means of eqn. (22) from the values of $K_A$ in Table 2 and the kinetic data in Table 3. Distance parameter, $q = 11.19$ Å.

| Ionic reactant | $k_p$ $M^{-1}$ min$^{-1}$ | $k_f$ $M^{-1}$ min$^{-1}$ | $k_p/k_f$ |
|------|------|------|------|
| $K_A$ (F75) | | | |
| NaI | $0.315 \pm 0.025$ | $0.5263 \pm 0.0018$ | 0.60 |
| KI  | $0.216 \pm 0.029$ | $0.5322 \pm 0.0029$ | 0.41 |
| RbI | $0.178 \pm 0.017$ | $0.5315 \pm 0.0024$ | 0.34 |
| CsI | $0.183 \pm 0.060$ | $0.5304 \pm 0.0030$ | 0.35 |
| $K_A$ (FHFP) | | | |
| NaI | $0.348 \pm 0.021$ | $0.5265 \pm 0.0018$ | 0.66 |
| KI  | $0.258 \pm 0.026$ | $0.5327 \pm 0.0031$ | 0.48 |
| RbI | $0.216 \pm 0.015$ | $0.5321 \pm 0.0024$ | 0.41 |
| CsI | $0.224 \pm 0.053$ | $0.5305 \pm 0.0031$ | 0.42 |

Values of $k_p$ and $k_f$ calculated from the kinetic data in combination with $\alpha$ values derived from the F75 and FHFP conductance equations, respectively, are given in Table 4 in which the errors quoted are standard deviations. It can be seen that the use of $\alpha$ values according to the FHFP equation results in $10-20\%$ higher values of $k_p$ as compared with the F75 equation, while the rate constant, $k_f$, is practically independent of conductance equation used.

*The minimum distance parameter, a.* The expression derived, eqn. (20), and the experimental rate constant ratios, $k_p/k_f$, in Table 4 were used to calculate the minimum distance, $a$, between the charges in the alkali iodide ion pairs studied using $q = 11.19$ Å for the maximum center-to-center distance according to eqns. (10) and (11).

The results of these calculations are given in Table 5 according to which $a$ decreases from 4.0 Å for sodium iodide to 2.4 Å for cesium iodide if $\alpha$ values based on the F75 equation are used. Slightly higher values, decreasing from 4.7 Å for sodium iodide to 2.7 Å for cesium iodide are obtained upon combining the kinetic data with $\alpha$ values derived from the FHFP equation.

The values of $a$ obtained on basis of eqn. (20) are close to the crystal radii sum, $(r_+ + r_-$ in Table 5), of the cation and anion. The $a$ values increase in the order, $CsI < RbI < KI < NaI$, *i.e.* with decreasing radius of the naked cation. This finding is consistent with the expectation that the radius of the solvated cation would increase with decreasing radius, and hence with increasing surface charge density, of the naked ion.

For potassium, rubidium, and cesium iodides the values of $a$ derived on the basis of ion pair reactivity are, in fact, slightly less than the crystal radii sum of the alkali metal and iodide ions. It should be remembered, however, that the derivation is

based on the hypothesis that the ion pair reactivity varies inversely with the energy of dissociation, which may be regarded as a first approximation to the solution of the problem concerned. Furthermore, the mutual potential energy of the ions in the ion pair has been calculated on the basis of Coulombic attraction neglecting repulsive forces. In addition, the macroscopic permittivity of the solvent has been used as an approximation of the microscopic permittvity. It is a matter of further research to investigate modified versions of eqn. (20) based on more complete potential-energy functions and, perhaps, alternative forms of eqn. (14).

In conclusion it may be noted that the present method of studying ion pairing requires very precise kinetic data as the effects studied are frequently quite small implying that the term, $k_p(1-\alpha)/\alpha$ in eqn. (22) referring to the reaction of ion pairs is much less than $k_f$. For the sodium iodide and methyl iodide exchange reaction this ion pair reactivity term amounts to less than $10\%$ of $k_f$.

*Table 5.* Comparison between minimum distance, $a$, between centers of charge of alkali iodide ion pairs in ethanol at 15 °C derived from kinetic data by means of eqn. (20) and crystal radii sum, $r_+ + r_-$.

| Salt | $a$ (F75) Å | $a$ (FHFP) Å | $r_+ + r_-$ Å |
| --- | --- | --- | --- |
| NaI | 4.0 | 4.7 | 3.1 |
| KI | 2.7 | 3.1 | 3.5 |
| RbI | 2.4 | 2.7 | 3.6 |
| CsI | 2.4 | 2.7 | 3.9 |

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