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Ion Pairing and Electron Transfer

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Several scenarios are considered for the effect of electrolytes, specifically for ion pairing, on the rates of electron transfer reactions: (i) electron transfer followed by ion transfer, (ii) ion-pair dissociation followed by electron transfer, or (iii) ion transfer accompanying the electron transfer. The latter may involve fast or slow (diffusive) ionic motion. A distinction is made between ion reorganization (case (iii)) and the formation of real chemical intermediates. The ion pairs themselves may be tight (contact) or loose (solvent separated). The discussion is illustrated with an example in the literature. Differences in degree in behavior of intramolecular and intermolecular electron transfer, due to differences in extent of ionic motion, are noted.

Introduction

There are now many studies of the effects of added electrolytes on electron transfer rates and on charge transfer spectra. Some of the studies have established that ion pairing can strongly influence these properties, e.g., refs 1−27. The investigations themselves have been quite varied:

In a system such as $A_1^{3-}BA_2^{2-} \rightarrow A_1^{2-}BA_2^{3-}$, where the A_i's are the charged groups, it was found[15b] that the addition of cations first shifted the charge transfer absorption spectral maximum $h\nu_{max}$ in one direction, corresponding to the absorption by $M^{n+}A_1^{3-}BA_2^{2-}$. At higher M^{n+} concentrations the $h\nu_{max}$ reverted more or less to its original value, presumably due to the absorption by the symmetrical ion pair, $M^{n+}A_1^{3-}BA_2^{2-}M^{n+}$. These changes were increasingly dramatic with increasing cationic charge $n+$. The reversal in $h\nu_{max}$ was observed for $n+ = 2+$ and $3+$, but not for $1+$. A similar reversal effect was noted[15b] for a system $M^{2-}A_1^{3+}BA_2^{2+}$.

In a study of another system, $A_1^{-}BA_2$, the effects of small alkali metal cations as well as of large tetraalkylammonium cations were investigated.[19] A striking difference was observed in the behavior of $h\nu_{max}$ and k_{et}: A large cation (e.g., tetraalkylammonium, R_4N^+) had a small effect on $h\nu_{max}$ but a large effect on k_{et}, whereas a small alkali metal cation had a large effect on $h\nu_{max}$, but surprisingly an effect on k_{et} smaller than that of R_4N^+ . Some of these effects on k_{et} differ from those expected from a simple ion atmosphere continuum expression. Indeed, a continuum description has been found to be inadequate in some other studies, such as in a ferrocenium−ferrocene self-exchange.[16]

The techniques used to study the electrolyte effect have themselves been varied, including kinetic, optical, and hyperfine coupling studies. The changes in the latter, for example, reflect the electron exchange between different parts of the molecule in large organic ions, e.g., refs 12 and 24. Significant effects of the counterion were found in reducing the rate of electron exchange.

The ion atmosphere or ion-pair effect is sometimes described in the literature as a reorganization, by analogy with the usual solvational and vibrational reorganization in ET reactions. It is presumed to contribute thereby to the reorganization parameter λ. The actual situation can be more complex, because of the large ionic motion which must occur in some cases, particularly in intramolecular electron transfer between well-separated donor/acceptor sites.

In the present article, several scenarios are considered for the effect of ion pairing, reorganization being one and actual chemical intermediates being another, to see whether any of these alternatives can be excluded on the basis of approximate quantitative estimates. The discussion is illustrated with an example. We first recall two types of ion pairs, loose and tight, which have been studied with thermodynamic measurements, optical absorption, ultrasonic absorption, NMR and other spectroscopic methods.[25−33]

Theory

1. Tight versus Loose Ion Pairs. Previous spectroscopic, conductance, and other experiments have revealed several types of ion pairs. In one of these, the tight or contact pair, the cation and anion are in close contact, and the ion pairing may have a major effect on the optical absorption spectrum, e.g., refs 26−28 and 31−32. In the loose or solvent-separated pair, on the other hand, the effect of ion pairing on the spectrum is typically much less. Again, in the tight pair, when some solvent molecules are originally in the coordination shell of one of the ions, some are liberated in forming the pair, resulting in an increase in entropy.[26,27,31] Any such decrease in ion solvation then results in an increase in energy, an enhanced direct ion−ion Coulombic attraction notwithstanding. Thus, an increase in temperature T actually increases the tight contribution at the expense of the loose in such a case.[26,27,31] This shift in equilibrium with temperature causes a curvature in plots of ln K_p, the total ion-pair dissociation constant, versus $1/T$. The tight pair is then associated with the larger temperature coefficient, while for the loose ion pair, the energy of solvation is similar to that of the free ions and so the temperature coefficient of its ln K_p is typically small. Inasmuch as both types of ion pairs sometimes coexist, they do not necessarily have very different dissociation constants at any given temperature. Any equilibrium between tight and loose ion pairs is also reflected in ultrasonic absorption[31,33] and in a temperature-dependent optical absorption spectrum.[26,27,31]

2. Effect of Ion Pairing on k_{et}. Several schemes may be proposed for the effect of ion pairing on k_{et}: (I) an electron

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may transfer first, followed by an ion transfer, or (II) an ion-paired reactant may dissociate first, followed by electron transfer, or (III) the electron and ion transfer may occur simultaneously, more specifically an ion atmosphere or ion-pair "reorganization" may accompany the electron transfer. In some cases this reorganization may occur via an intramolecular diffusion.[20b] We consider these three cases and note that in each case the ion pairs could be tight, loose, or both. In cases I and II, actual chemical intermediates are formed.

I. Electron Transfer First. In one scheme for an ion-pair effect on k_{et}, the electron transfer occurs first, followed by an intramolecular ion transfer. In such a scheme the intermediate, $\mathrm{M^+A_1BA_2{}^-}$, is sufficiently long-lived that the $\mathrm{M^+}$ can subsequently migrate in reaction 2 under the influence of the charge distribution in $\mathrm{A_1BA_2{}^-}$. When the ion transfer is intramolecular, we have

$$\mathrm{M^+A_1{}^-BA_2} \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} \mathrm{M^+A_1BA_2{}^-} \tag{1}$$

$$\mathrm{M^+A_1BA_2{}^-} \xrightarrow{k_2} \mathrm{A_1BA_2{}^-M^+} \tag{2}$$

The steady-state rate constant $k_{\mathrm{et}}^{\mathrm{I}}$ is given by

$$\frac{1}{k_{\mathrm{et}}^{\mathrm{I}}} = \frac{1}{k_1} + \frac{k_{-1}}{k_2 k_1} \tag{3}$$

When, instead of being intramolecular, the ion transfer in reaction 2 proceeds by dissociation of the ion pair, followed by re-formation of a new pair, we have

$$\mathrm{M^+A_1BA_2{}^-} \underset{k_{-4}}{\overset{k_4}{\rightleftharpoons}} \mathrm{M^+} + \mathrm{A_1BA_2{}^-} \tag{4}$$

$$\mathrm{A_1BA_2{}^-} + \mathrm{M^+} \xrightarrow{k_5} \mathrm{A_1BA_2{}^-M^+} \tag{5}$$

and the k_2 in eq 3 is then replaced by

$$k_2 \rightarrow k_5 k_4/(k_{-4} + k_5) \tag{6}$$

This factor clearly cannot exceed k_5K_4, where K_4 is the ion-pair dissociation constant of reaction 4. In any case the maximum value of $k_{\mathrm{et}}^{\mathrm{I}}$ in eq 3 or eqs 3 and 6 is k_1.

II. Ion-Pair Dissociation First. When the ion-pair dissociation precedes the electron transfer, we have instead of reaction 1

$$\mathrm{M^+A_1{}^-BA_2} \underset{k_{-7}}{\overset{k_7}{\rightleftharpoons}} \mathrm{M^+} + \mathrm{A_1{}^-BA_2} \tag{7}$$

followed by

$$\mathrm{A_1{}^-BA_2} \underset{k_{-8}}{\overset{k_8}{\rightleftharpoons}} \mathrm{A_1BA_2{}^-} \tag{8}$$

and the stabilization reaction

$$\mathrm{A_1BA_2{}^-} + \mathrm{M^+} \xrightarrow{k_9} \mathrm{A_1BA_2{}^-M^+} \tag{9}$$

The steady-state rate constant, $k_{\mathrm{et}}^{\mathrm{II}}$, is now given by

$$k_{\mathrm{et}}^{\mathrm{II}} = \frac{k_9 k_7}{k_{-7} + \dfrac{k_8 k_9}{k_{-8} + k_9}} \tag{10}$$

This rate clearly cannot exceed k_9K_7, where K_7 is the ion-pair dissociation constant for reaction 7. At sufficiently high concentrations of suitable ion pairs from the electrolyte, reaction 7 could be catalyzed by those pairs,[34] making that reaction bimolecular. However, such catalysis would not affect K_7, and hence would not affect the maximum value of $k_{\mathrm{et}}^{\mathrm{II}}$ from this mechanism.

III. Fluctuational Ionic Motion and Electron Transfer. In a third scheme for the electron/ion transfer, the ion transfer occurs as a reorganization, rather than via the actual chemical intermediates in I and II. In the transition state there is now not only the usual reorganization of the bond lengths (and/or angles) of the reactants and of orientations of individual polar solvent molecules but also, in addition, of the position of the transferring ion. When a large displacement of the ion is needed, it is useful to introduce the notion of precursor and successor complexes, indicated by the parentheses in eq 11.

$$\mathrm{M^+A_1{}^-BA_2} \rightleftarrows \left(\begin{array}{ccc} \mathrm{A_1{}^-BA_2} & \rightleftarrows & \mathrm{A_1BA_2{}^-} \\ \mathrm{M^+} & & \mathrm{M^+} \end{array}\right) \rightarrow \mathrm{A_1BA_2{}^-M^+} \tag{11}$$

The $\mathrm{M^+}$ transfer coordinate, which may be "slow",[20b] leads in eq 11 to the formation of a precursor complex from the reactant and to the disappearance of a successor complex to form products. The following equation is derived in the Appendix for this case by solving diffusion-reaction equations using several simplifying approximations, one of which is that the reaction occurs largely near some value $x^\dagger$ of the $\mathrm{M^+}$ transfer coordinate x, rather than over a broad interval of x:

$$\frac{1}{k_{\mathrm{et}}^{\mathrm{III}}} = \frac{1}{k_{\mathrm{diff}}^{\mathrm{r}}} + \frac{1}{k_{\mathrm{act}}} + \frac{1}{K_{\mathrm{eq}} k_{\mathrm{diff}}^{\mathrm{p}}} \tag{12}$$

Here, the $k_{\mathrm{diff}}^{\mathrm{r}}$ and k_{act} are respectively the rate constants for the diffusion of $\mathrm{M^+}$ along reactant's free energy curve to reach a point $x^\dagger$ of the $\mathrm{M^+}$ transfer coordinate x, and for the (activation) formation of the successor complex in parentheses in reaction 11. K_{eq} is the equilibrium constant for forming this successor, and $k_{\mathrm{diff}}^{\mathrm{p}}$ is the diffusion rate constant for forming the product, $\mathrm{A_1BA_2{}^-M^+}$, from it. Expressions for these terms are derived in the Appendix. A subtlety regarding the x-dependent rate constants, used to obtain eq 12, and the nature of the reaction coordinate is discussed in the Appendix.

The value of $x^\dagger$ can be obtained by maximizing the expression for $k_{\mathrm{et}}^{\mathrm{III}}$ with respect to $x^\dagger$. The result in eq 12 can be understood also by a simple steady-state kinetic argument for forming each of the species in reaction 11, upon introducing specific expressions for each k that appears there. When necessary, an additional aspect, in which solvent dynamics can affect the term labeled k_{act} in eq 12, is readily incorporated. When the diffusion rate constants in eq 12 are large, it becomes $k_{\mathrm{et}}^{\mathrm{III}} \cong k_{\mathrm{act}}$.

When the electron transfer is intermolecular, the reactants and counterion can readily choose their positions and orientations and so the diffusive terms for the $\mathrm{M^+}$ coordinate in eq 12 can be so fast that only the second term on the right, the term labeled k_{act}, remains. For *intramolecular* electron transfers, when donor and acceptor are distant, the x-diffusion terms may contribute significantly in this mechanism. Using the approximation of the electron transfer being concentrated near a particular value of x, $x^{\dagger}$, namely using eq 12, case I becomes the special case of case III, one where $x^{\dagger}$ has the initial value of x, $x = 0$. In that case $k^{\mathrm{r}}_{\mathrm{diff}}$ in eq 12 is absent, and k_1 and k_2k_1/k_{-1} in eq 3 correspond to k_{act} and $k^{\mathrm{p}}_{\mathrm{diff}}K_{\mathrm{eq}}$ in eq 12, respectively.

We consider next the effect of ion pairing on $h\nu_{\max}$.

3. Effect of Ion Pairing on Charge Transfer Spectral Maximum, $h\nu_{\max}$. For a photoinduced charge transfer

$$\mathrm{DA} + h\nu \rightarrow \mathrm{D}^{+}\mathrm{A}^{-} \tag{13}$$

where D and/or A may also bear a charge, we have[35]

$$h\nu_{\max} = \lambda + \Delta G^{\circ} \tag{14}$$

where λ is the reorganization energy for solvent molecules and reactant's bond lengths (and/or angles) and ΔG° is the standard free energy change in reaction 13; i.e., ΔG° is the free energy of the product of the reaction minus that of the reactant prior to any subsequent reaction of the product. At a fixed position of M^{+}, λ is expected to be approximately the same for $\mathrm{M}^{+}\mathrm{A}_1{}^{-}\mathrm{BA}_2$ as for $\mathrm{A}_1{}^{-}\mathrm{BA}_2$, if one judges from the evidence mentioned earlier,[15b] where the symmetrical pair $\mathrm{M}^{n+}\mathrm{A}_1{}^{2-}\mathrm{BA}_2{}^{3-}\mathrm{M}^{n+}$ has approximately the same $h\nu_{\max}$ as $\mathrm{A}_1{}^{2-}\mathrm{BA}_2{}^{3-}$. This approximate equality indicates that, at least for this system, these two λ's are similar. The symmetry itself does not require equality of these λ's, but only that $\Delta G^{\circ} = 0$ in each case.

The ΔG° in eq 14 for $\mathrm{M}^{+}\mathrm{A}_1{}^{-}\mathrm{BA}_2$ arises from the free energy change due to the interaction of M^{+} with $\mathrm{A}_1{}^{-}$ being replaced by the weaker interaction of the M^{+} with the more distant $\mathrm{A}_2{}^{-}$. When this attractive interaction in the ion pair $\mathrm{M}^{+}\mathrm{A}_1{}^{-}\mathrm{BA}_2$ is large, this ΔG° is expected to be large.

Approximate Equations

The various parameters in theoretical expression for k_{et} used in refs 19 and 36 were obtained using eq 15 below, where any high-frequency modes are treated as having a single frequency ν and contributing λ_{v} to the reorganization parameter λ. The solvent (and low-frequency modes) reorganization contribution is denoted by λ_{S}. The rate constant k_{et} for a nonadiabatic reaction is then given by[35,37]

$$k_{\mathrm{et}} = \frac{2\pi}{\hbar}\frac{|V|^2}{(4\pi\lambda_{\mathrm{s}}k_{\mathrm{B}}T)^{1/2}}\sum_{w=0}^{\infty}\frac{\mathrm{e}^{-S}S^{w}}{w!}\mathrm{e}^{-(\Delta G^{\circ}+\lambda_{\mathrm{s}}+wh\nu)^2/4\lambda_{\mathrm{s}}k_{\mathrm{B}}T} \tag{15a}$$

where

$$S = \lambda_{\mathrm{V}}/h\nu \tag{15b}$$

Equation 15a presumes that the reactant is vibrationally unexcited, a good assumption in the inverted region and frequently in other regions, but not when ΔG° is significantly positive. This limitation of eq 15 is immediately apparent on noting that the formula is unsymmetric with respect to the vibrational quantum state w of the product and that of the reactant, zero. So, to treat reactions where ΔG° is positive, eq 15 can be used for the reverse reaction and k_{et} is then obtained from the equilibrium constant. One obtains thereby

$$k_{\mathrm{et}} = \frac{2\pi}{\hbar}\frac{|V|^2}{(4\pi\lambda_{\mathrm{s}}k_{\mathrm{B}}T)^{1/2}}\sum_{w=0}^{\infty}\frac{\mathrm{e}^{-S}S^{w}}{w!}\mathrm{e}^{-\Delta G^{\circ}/k_{\mathrm{B}}T}\mathrm{e}^{-(\Delta G^{\circ}+\lambda_{\mathrm{s}}+wh\nu)^2/4\lambda_{\mathrm{s}}k_{\mathrm{B}}T} \tag{16}$$

where ΔG° is now the value in the presence of this cation and is positive. The ΔG° in eq 15 is negative.

For our purposes it will normally suffice to use the largest term in the sum, for any approximate estimate in the regime $\Delta G^{\circ} + \lambda_{\mathrm{S}} \geq 0$ for eq 15 and $-\Delta G^{\circ} + \lambda_{\mathrm{S}} \geq 0$ for eq 16. One then finds for both equations the simple and convenient result

$$k_{\mathrm{et}} \cong \frac{2\pi}{\hbar}\frac{|V|^2}{(4\pi\lambda_{\mathrm{s}}k_{\mathrm{B}}T)^{1/2}}\mathrm{e}^{-(\Delta G^{\circ}+\lambda_{\mathrm{s}})^2/4\lambda_{\mathrm{s}}k_{\mathrm{B}}T}\mathrm{e}^{-S} \qquad (-\lambda_{\mathrm{s}} \leq \Delta G^{\circ} \leq \lambda_{\mathrm{s}}) \tag{17}$$

The same equation arises from both eqs 15 and 16, since in this regime the reactant and product are both in their lowest vibrational states. The $\exp(-S)$ factor in eq 17 is due to the overlap of the lowest vibrational state wave functions of reactant and of product and agrees with physical intuition.[38] It is substantially less than unity when $\lambda_{\mathrm{v}}/h\nu$ is large.

In the case of the ΔG° which maximizes k_{et}, a number of terms in eq 15 typically contribute. Although the summation in eq 15 is easily made, it is useful to see at what ΔG° the maximum occurs, $\Delta G^{\circ}_{\max}$, and to have a simple approximate and immediately visualizable expression for k_{et} at $\Delta G^{\circ}_{\max}$, k^{max}_{et}. The maximum term at any ΔG° is obtained by maximizing the summand with respect to w, treating w as a continuous variable, and using Stirling's approximation for w! One finds

$$-\Delta G^{\circ}_{\max} = \lambda \equiv \lambda_{\mathrm{V}} + \lambda_{\mathrm{S}} \tag{18}$$

One further obtains, on treating the sum as an integral and using the method of steepest descent,

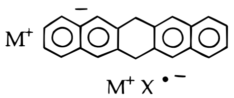
$$k^{max}_{\mathrm{et}} \cong \frac{|V|^2}{\hbar}\left[\frac{2\pi}{\lambda_{\mathrm{v}}h\nu + 2\lambda_{\mathrm{s}}k_{\mathrm{B}}T}\right]^{1/2} \tag{19}$$

The right side of eq 19 reduces to the usual classical value $(|V|^2/\pi)(\pi/\lambda k_{\mathrm{B}}T)^{1/2}$ when the reorganization is only of solvent and low-frequency modes, i.e., when $\lambda = \lambda_{\mathrm{s}}$. When λ_{S} vanishes, i.e., when $\lambda = \lambda_{\mathrm{v}}$, the right side reduces instead to $(|V|^2/\hbar)(\pi/\lambda(h\nu/2))^{1/2}$.

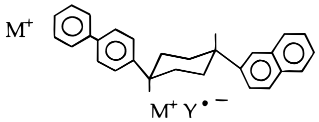
We next apply the results to an example in the literature.

Illustration with A Particular System

Dihydropentacene ($\mathrm{X}^{\bullet-}$) and Biphenylylnaphthylcyclohexane ($\mathrm{Y}^{\bullet-}$) Radical Anions. When $\mathrm{A}_1{}^{-}\mathrm{BA}_2$ is the dihydropentacene radical anion, $\mathrm{X}^{\bullet-}$, the charge is presumed to be initially localized on the naphthyl group near the M^{+} and optical absorption then results in a charge transfer to the far naphthyl.



$\mathrm{M}^{+}\,\mathrm{X}^{\bullet-}$



$\mathrm{M}^{+}\,\mathrm{Y}^{\bullet-}$

In the following we note that the low-frequency (torsional) contribution to λ_{S} of $\mathrm{Y}^{\bullet-}$ is about 0.15 eV,[39] a term not present in $\mathrm{X}^{\bullet-}$. As noted earlier, we suppose that λ is largely unaffected by M^{+} in mechanisms I and II. Optical charge transfer data are presently absent for $\mathrm{Y}^{\bullet-}$ and $\mathrm{M}^{+}\mathrm{Y}^{\bullet-}$, because their charge transfer transition is weak. From the effect of M^{+} on $h\nu_{\max}$ for $\mathrm{X}^{\bullet-}$, assuming λ to be largely unchanged, the ΔG° for reaction 1 is shifted by ca. 0.52 eV for $\mathrm{M} = \mathrm{Na}^{+}$ and only by ca. 0.14 eV for a large tetraalkylammonium cation, $\mathrm{R}_4\mathrm{N}^{+}$, for the $\mathrm{M}^{+}\mathrm{X}^{\bullet-}$ system. Presumably the Na^{+} salt forms a tight ion pair, which causes the pronounced shift in $h\nu_{\max}$.

When M^{+} is Na^{+}, a detailed estimate then indicates that the first mechanism (ET first) is inapplicable: One sees from eq 3 that the rate cannot exceed k_1. Using eq 17, one finds that in the $\Delta G°$ region specified there (valid here) the M^+ reduces the value of k_1 in eq 1 for the $A_1{}^-BA_2$ by a factor of $\exp[(\Delta G° + \lambda_S)^2 - (\Delta G°_0 + \lambda_S)^2]/4\lambda_S k_B T$, where $\Delta G°$ is -0.05 eV (i.e., $\Delta G°_0$) plus the increase, 0.52 eV, found from the shift in $h\nu_{\max}$ for $X^{\bullet-}$ for $M^+ = Na^+$. This shift is assumed here to be approximately the same for $Y^{\bullet-}$. Since λ_S is 0.75 eV,[19,38] one thereby concludes that the Na^+ would lower k_1 by a factor of $\sim 6 \times 10^5$. This factor is considerably larger than the observed reduction in k_{et} of a factor of 130, and so this mechanism is excluded for this reaction, if the assumptions made above are reasonably correct.

To consider mechanism I for $M^+ = TBA^+$ we shall need in eq 3, k_1, k_{-1}, and k_2. For $M^+ = TBA^+$ k_1 is lowered from its value in the absence of M^+, 1.6×10^9 s^{-1}, by a factor of about 15, due to an increase in $\Delta G°$ of 0.14 eV inferred from the $h\nu_{\max}$ shift. The new expected value of k_1 is thereby $\sim 10^8$ s^{-1}. The k_{-1} equals this value multiplied by $\exp[(0.14 - 0.05)/0.025]$, i.e. , $\sim 10^{10}$ s^{-1}. The k_2 is the rate constant for the motion of M^+ from the now neutral biphenyl to the anionic naphthyl. If this motion is intramolecular, as in eq 2, and for the moment we neglect the attractive term due to the attraction of M^+ to $A_2{}^-$, we estimate k_2 as the reciprocal of a mean first-passage time in the Appendix. It equals $D(\pi/2a)^2$, where D is the diffusion constant of M^+ along the molecule.

If the rate constant k_d for a bimolecular diffusion controlled process is $k_d = 4\pi DR$, where R is a reaction radius, and typically $k_d \sim 10^{10}$ M^{-1} s^{-1} for $R \sim 5$ Å, then $k_2 \cong k_d\pi/(4a)^2R$, i.e., 5×10^9 s^{-1}. The rate constant in eq 3 is $k_1k_2/(k_{-1} + k_2)$. This yield factor $k_2/(k_{-1} + k_2)$ is seen to be ~ 0.3, so the calculated $k_{et} \sim 3 \times 10^7$s^{-1}. The observed value is 1.2×10^6s^{-1}. The discrepancy may be due to the diffusion of TBA^+ from one group to the other being more hindered, among other possibilities, even though diffusion of M^+ is enhanced by its electrostatic attraction to $A_2{}^-$. Thus, this mechanism I cannot be eliminated for TBA^+ and could be the mechanism of choice for this cation. Since mechanism III contains mechanism I as a special case, it too cannot be eliminated for TBA^+.

For the mechanism II, where a dissociation of the ion pair occurs first, the k_{et} cannot exceed, as noted earlier, k_9K_7, where K_7 is the ion-pair dissociation constant for reaction 7. Since[27] K_7 is 10^{-6} M for $M^+ = Na^+$ and k_9 is of the order of a diffusion-controlled rate constant, $\sim 10^{10}$ M^{-1} s^{-1}, the calculated k_{et} cannot exceed $\sim 10^4$ s^{-1}, a maximal value. The observed k_{et} is 1.2×10^7s^{-1}. Thereby, it appears that mechanism II can be safely excluded for $M^+ = Na^+$.

For $M^+ = TBA^+$ the K_p for the ion pair $TBA^+Y^{\bullet-}$ does not appear to have been determined. For the tetraphenylborate salts of Na^+, Li^+, and TBA^+ in THF the K_p's are comparable.[40] At the moment if we take K_p for the $TBA^+Y^{\bullet-}$ to be similar to that of the $Na^+Y^{\bullet-}$ salt, then with $k_9 \sim 10^{10}$ M^{-1} s^{-1} we have $k_{et} \sim 10^4$ s^{-1} and so this mechanism II could then be excluded for the $TBA^+Y^{\bullet-}$ system also.

Discussion

The $X^{\bullet-}$ and $Y^{\bullet-}$ *appear* to show quite different λ_s's, and we expand on this aspect first. For $X^{\bullet-}$ the $h\nu_{\max}$ was reported as ≤ 0.51 eV.[19] But if the λ_v for $X^{\bullet-}$ were approximately the same as the value assigned in a parametrization for $Y^{\bullet-}$, namely 0.45 eV, then the λ_s for $X^{\bullet-}$ would have to be ≤ 0.06 eV. This value is unreasonably low unless the odd electron in $X^{\bullet-}$ in neat THF is delocalized over the two naphthyls.

One expects the λ_s for $X^{\bullet-}$ (when the electron is localized) to be at least less than that value (0.75 eV) for $Y^{\bullet-}$ by 0.15 eV. (The latter is the contribution from the torsional motion, present in $Y^{\bullet-}$ but not in $X^{\bullet-}$.)[39] Since the charge centers in $X^{\bullet-}$ are separated by a smaller distance (7.3 Å) than in $Y^{\bullet-}$ (11.8 Å) one expects the λ_s in $X^{\bullet-}$ also to be smaller than that in $Y^{\bullet-}$ on this account: Using the parametrization given in ref 41 for the solvent contribution to λ_s, which contains the continuum factor $(2a)^{-1} + (2a_2)^{-1} - R^{-1}$, and recalling that $a_1 = a_2 = 5.07$ Å in that parametrization, one finds that the expected λ_s is $(0.75 - 0.15)[(5.07)^{-1} - (7.3)^{-1}]/[(5.07)^{-1} - (11.8)^{-1}]$, i.e., about 0.32 eV. This value is substantially larger than the ≤ 0.06 eV noted above. Perhaps the spectrum of the M^+-free $X^{\bullet-}$ needs reexamination in at least two respects: there is a suggestion of a shoulder in region of ~ 0.65 eV, where TBA^+ $X^{\bullet-}$ has a maximum in $h\nu$. If TBA^+ has, in fact, a negligible effect on the $h\nu_{\max}$ of $X^{\bullet-}$ and if the spectrum in neat THF were in part due to the solvated electron used to form the radical anion, then the λ_s for $X^{\bullet-}$ becomes 0.20 eV. This value is at least closer to the ca. 0.32 eV estimated above.

Again, λ_v was estimated originally in the literature by fitting the ln k_{et} vs $-\Delta G°$ curve. The authors, in one of their landmark papers,[37] recognized that the λ_v in the normal region, involving mainly aromatic electron acceptors, could differ from λ_v in the inverted region, where the acceptors were aromatics quinones. The quantum effects are largest in the inverted region, and so this λ_v is most sensitive to data in that region. If the share of λ for λ_v were smaller for the aromatic acceptors and hence the λ_s would have a larger share, (the CO group in the quinones may make a significant contribution to λ_v), then the calculated λ_s contribution for $X^{\bullet-}$ would be larger, substantially larger than the ≤ 0.06 eV inferred from the data with the existing parametrization. There are, of course, other questions mentioned above, such as aspects of the spectrum $X^{\bullet-}$ itself. There may also be a question of how localized the electron is in $X^{\bullet-}$ in neat THF. Hyperfine coupling studies might provide some answer to this latter question, including perhaps direct measurements using spin resonance techniques for the intramolecular k_{et} in $X^{\bullet-}$.

There is another argument suggesting that λ_v for aromatics may be smaller than the 0.45 eV. The bimolecular k_{et} for the reaction of neat biphenylyl radical anion with the naphthyl group is[19] $\sim 1/20$ of the adiabatic value, $\sim 10^{11}$ M^{-1} s^{-1} (and one-half the diffusion–controlled value, $\sim 10^{10}$ M^{-1} s^{-1}). We can estimate a λ_s, assuming $\lambda_v = 0.45$ eV and $h\nu = 1500$ cm^{-1}, using eq 16: We first replace the factor outside the sum (which can be shown to be[42] a nonadiabatic Landau–Zener factor with the solvation as the slow coordinate) by the adiabatic value for a bimolecular k_{et}, namely $\sim 10^{11}$ M^{-1} s^{-1}. Equating the subsequent rate constant to the k_{et} in neat THF, 5.7 10^9M^{-1}s^{-1}, one finds $\lambda_s \sim 0.15$ eV if $\lambda_v = 0.45$ eV. Since 0.15 eV of λ_s arises from the torsional motion of the biphenyl,[39] one concludes that the solvation part of λ_s is then zero! This clearly incorrect result, even for reactants in contact, again suggests that a smaller λ_v (smaller $\lambda_v/h\nu$) be used for aromatics in the normal region, or that some other effect is occurring.

In the models I to III for the electron/ion transfer we have considered cases where some of the transient dynamics of formation of the initial ion-paired reactant does not affect the observations. For example, in the experiments in which the two radical anions $X^{\bullet-}$ and $Y^{\bullet-}$ were studied,[19] the system was prepared by having a solvated electron, accompanied by its cation, first react with the relevant aromatic group and thereby forming a cation–anion pair before the desired reaction occurs. In this way, it was pointed out, any slow transient dynamics involving the formation of the subsequent $M^+X^{\bullet-}$ or $M^+Y^{\bullet-}$ ion pair was avoided.[19] In another experiment the transient complicating effect of ion pairing on shifting the maximum of the usual fluorescence (1−5 ns) of a charge transfer singlet state was avoided by observing, instead, the absorption by a long-lived (several microseconds) charge transfer *triplet* state.[20] In this way, the complications due to the relative slowness of ion-pair formation could again be avoided: With an electrolyte concentration of 0.01 M and a diffusion-controlled ion pair formation rate of 10^{10} M^{-1} s^{-1}, a time of 10 ns is needed, by which time most of any singlet state fluorescence would have disappeared, but the spectrum and hence the $h\nu_{max}$ of the newly equilibrated ion-paired CT triplet state could be observed.

As noted above, the description in the preceding section focuses on systems where the ion-paired reactant in reaction 1, 7, or 11 is already prepared. For systems when a charge transfer charge-separated pair is formed, e.g., intramolecularly, by the absorption of light, ion dynamics is involved in forming the ion pairs.[17,20,21] A detailed analysis of some experimental data in terms of formation and dissociation rates of solvent-separated and contact ion pairs is given in ref 21. The kinetics of ion-pair formation in the CT triplet state system was studied in ref 20. The ion-pairing occurred, in the system studied, by rearrangement with the existing ion pairs in the electrolyte and the rate constant of the rearrangement was largely diffusion-controlled.

It is interesting to compare the effect of the ions M^+ on the intramolecular k_{et} with that on the intermolecular one. For $M^+ = Li^+$, Na^+, TBA^+, $CTMA^+$ (cetyltrimethylammonium), and TOA^+ (tetraoctylammonium) the intramolecular k_{et} was reduced by factors of 90, 130, 1300, 850, and 2000, respectively, while for the intermolecular k_{et} the corresponding reductions were only factors of 9, 30, 11, 9, and 16.[19] (See also ref 7.) The effect of M^+ in the intermolecular case is seen to be relatively little, presumably because the counter ion no longer has to move far and, further, the reactants can orient themselves so as to avoid a large uphill $\Delta G°$ for any ET reaction that occurs when the transition is vertical (fixed ions).

The large spectral effect when M^+ is Na^+ may be attributed to the ion-pair being tight, since solvent separated pairs usually involve only a small spectral effect.[26,27,31,32] On the other hand, when M^+ is a large tetraalkylammonium ion, such as TBA^+, the spectral shift is small, and may correspond either to that ion pair being loose or to the ion centers being too far apart to have a spectral effect. As noted earlier, the ion-pair dissociation constants K_p of the Li^+, Na^+, and TBA^+ salts of tetraphenylborate have been measured in tetrahydrofuran (THF) and are quite comparable.[40] Presumably the hydrophobic interaction plays a substantial role in making the K_p for the large TBA^+ ion comparable with that for the smaller cations.

Mechanism II appears to be ruled out for the systems studied in ref 19. Mechanism I, which is a special case of III, was seen to be a possible mechanism for $M^+ = TBA^+$ but not for $M^+ = Na^+$. For $M^+ = Na^+$ mechanism III is preferred and may also occur for $M^+ = TBA^+$. However, any conclusions rest on approximations, such as the interpretation of the effect of M^+ on $h\nu_{max}$ (namely, that it affects $\Delta G°$ rather than λ).

It was also noted that there is a considerable difference between the intermolecular results, where little diffusion of M^+ is needed, and the intramolecular results. A better estimate of the intramolecular diffusion constant D for M^+ is needed. Studies where reaction 11 is more downhill, so enhancing the possibility of intramolecular diffusion control, may provide additional information on D. A comparison of results for pyrene and naphthalene as acceptors in the intermolecular electron transfer[19] was revealing, and reflected the fact that the former was a more downhill reaction and so was diffusion controlled.

The present article began as an exercise in exploring briefly different possible mechanisms for ion-pairing effects on electron transfer rates and charge transfer spectra. We have delineated their relationships and raised several questions which can be addressed in future experiments. Some recent work cited above on the dynamics of the transient systems can also be expected to define more precisely some of the rate constants involved.

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Appendix. Intramolecular Diffusion−Reaction of M^+

We consider the diffusion of M^+ along a coordinate x, where $x = 0$ and $x = a$ denote the equilibrium positions of M^+ in reaction 11 when the anionic charge is localized on A_1 and A_2, respectively. We denote by $P_r(x)$ and $P_p(x)$ the probability density of finding M^+ at any x, for these two respective systems.

The diffusion coefficient of M^+ is denoted by D . The local reaction rate constant for forming the $A_1^- \rightarrow A_2^-$ transfer at x is denoted by $k_{et}^r(x)$ and for the reverse transfer at x by $k_{et}^p(x)$. The diffusion−reaction equations for P_r and P_p are given by

$$\frac{\partial P_r}{\partial t} = -\frac{\partial J_r}{\partial x} - k_{et}^r P_r + k_{et}^p P_p \tag{A.1}$$

$$\frac{\partial P_p}{\partial t} = -\frac{\partial J_p}{\partial x} - k_{et}^p P_p + k_{et}^r P_r \tag{A.2}$$

where the forced diffusive fluxes are

$$J_r(x) = -D\frac{\partial P_r}{\partial x} - DP_r\frac{dg_r}{dx} \tag{A.3a}$$

$$J_p(x) = -D\frac{\partial P_p}{\partial x} - DP_p\frac{dg_p}{dx} \tag{A.3b}$$

Here

$$g_r = G_r/k_BT, \quad g_p = G_p/k_BT \tag{A.4}$$

and $G_r(x)$ and $G_p(x)$ are the corresponding free energies of the systems when the electron resides on A_1 and on A_2, respectively, and M^+ is at x. The survival probability of the reactant at time t, $Q_r(t)$, is $\int_{-\infty}^{\infty} P_r(x,t)\, dx$ and provides a description of the course of the reaction. By using individual rate constants in eqs A.1 and A.2, the P_r and P_p are treated as being associated with precursor and successor complexes, respectively.

By way of illustration for the present discussion we introduce two simplifying approximations: (i) the steady-state approximation, $\partial P_r/\partial t = \partial P_p/\partial t = 0$, and (ii) the dominant reaction occurs in some x-interval $\Delta^\dagger$ centered at $x^\dagger$. In this case the net reactant flow $J_r(x)$ must vanish for $x > x^\dagger$, and similarly $J_p(x)$ is zero for $x < x^\dagger$.

We can implement (ii) by setting

$$\begin{aligned} k_{et}^r(x) &= k_{et}^r(x^\dagger)\Delta^\dagger\delta(x - x^\dagger) \\ k_{et}^p(x) &= k_{et}^p(x^\dagger)\Delta^\dagger\delta(x - x^\dagger) \end{aligned} \tag{A.5}$$

where $\delta(x - x^\dagger)$ is the Dirac delta function. Integration of eqs A.3−A.5 yields

$$J_r(x<x^\dagger) = J_p(x>x^\dagger) \equiv J = k_{et}^{r}(x^\dagger)\Delta^\dagger P_r^{\ \dagger} - k_{et}^{p}(x^\dagger)\Delta^\dagger P_p^{\ \dagger} \tag{A.6}$$

Integration of eqs A.1 and A.2 using eq A.6 then yields for the rate constant k_{et}^{III} of reaction 11, after some manipulation

$$\frac{1}{k_{et}^{III}} = \frac{1}{k_{diff}^{r}} + \frac{1}{k_{act}} + \frac{1}{K_{eq}k_{diff}^{p}} \tag{A.7}$$

where

$$k_{diff}^{r} \equiv k_{diff}^{r}(x^\dagger) = D/\Delta_r \int_0^{x^\dagger} \exp[g_r(x) - g_r(0)]\, dx \tag{A.8a}$$

$$k_{act} \equiv k_{act}(x^\dagger) = k_{et}^{r}(x^\dagger)(\Delta^\dagger/\Delta_r) \exp(-[g_r(x^\dagger) - g_r(0)]) \tag{A.8b}$$

$$k_{diff}^{p} \equiv k_{diff}^{p}(x^\dagger) = D/\Delta^\dagger \int_{x^\dagger}^{a} \exp[g_p(x) - g_p(x^\dagger)]\, dx \tag{A.8c}$$

$$K_{eq} \equiv K_{eq}(x^\dagger) = (\Delta^\dagger/\Delta_r) \exp(-[g_p(x^\dagger) - g_r(0)]) \tag{A.8d}$$

Here, Δ_r and the Δ_p used later denote

$$\Delta_r = \int_{-\infty}^{\infty} \exp(-[g_r(x) - g_r(0)])\, dx$$

$$\Delta_p = \int_{-\infty}^{\infty} \exp(-[g_p(x) - g_p(a)])\, dx \tag{A.8e}$$

Δ_r and Δ_p represent the size of dominant x-intervals occupied by M^+ along x, and are centered in the reactant and in the product regions in reaction 11, i.e., $x = 0$ and $x = a$, respectively. The units of all three rate constants in eq A.8 are reciprocal time. In obtaining eq A.7 we also used

$$k_{et}^{r}(x^\dagger)/k_{et}^{p}(x^\dagger) = \exp(-[g_p(x^\dagger) - g_r(x^\dagger)]) \tag{A.8f}$$

Any theory for $k_{et}^{r}(x)$ automatically contains how sharply behaved it is as a function of x and so yields a value for $\Delta^\dagger$.

The combination of symbols in eqs A.8 arose from those in eqs A.1−A.4. To justify the labeling of the k's and K in eqs A.8a−A.8d, we consider the individual steps in reaction 11. We denote the four successive species in that reaction by **A**, **B**, **C**, and **D**, respectively. If we use a steady-state treatment of a diffusion-controlled formation of **B** in reaction 11 from **A**, namely for $P_r^\dagger$ from $x = 0$ to $x^\dagger$, with an absorbing boundary condition at $x = x^\dagger$, one obtains the right-hand side of eq A.8a for the rate constant, and so we have denoted it by k_{diff}^{r}. For the result in eq A.8b, denoted by k_{act}, we first note that when **C** is formed from **A** in reaction 11 by an activation-controlled process, the rate constant equals the equilibrium probability of forming **B** from **A**, $(\Delta^\dagger/\Delta_r) \exp(-[g_r(x^\dagger) - g_r(0)])$, multiplied by the rate constant k_{et}^{r} for **B** → **C** and thence to products, so obtaining eq A.8b. The equilibrium constants are discussed below.

To consider eq A.8c we first calculate a diffusion-controlled rate constant from **C** to **D**, by considering the reverse step: Solving the steady-state equation for diffusion of P_p from $x = a$ to $x = x^\dagger$, with an absorbing boundary condition at $x = x^\dagger$ one obtains $D/\Delta_p \int_{x^\dagger}^{a} \exp[g_p(x) - g_p(a)]\, dx$ for the rate constant for the diffusion from **D** to **C**. The equilibrium constant for forming **D** from **C** is $(\Delta_p/\Delta^\dagger) \exp(-[g_p(a) - g_p(x^\dagger)])$, so the rate constant for diffusion from **C** to **D**, obtained by multiplying these two expressions, is given by the right-hand side of eq A.8c. To understand eq A.8d, we note that the equilibrium constant for forming **C** from **A** is seen below to be $(\Delta^\dagger/\Delta_r)$ exp$(-[g_p(x^\dagger) - g_r(0)])$, which is the right-hand side of eq A.8d. Although we have labeled a rate constant in eq A.7 by k_{act}, and written it in terms of eq A.8b, the reaction step can itself be subject to slow solvent dynamics, and eq A.8b would then be modified.[43]

We comment further on equilibrium constants, such as eq A.8d for the formation of **C** from **A**. The free energy for **A** is $G_r(0) - k_BT \ln q_{trans}^{\mathbf{A}}$, where $q_{trans}^{\mathbf{A}}$ is the translational partition function of M^+ in species **A,** and equals $(2\pi m k_BT)^{1/2}\Delta_r$, m being the mass of M^+. $G_r(0)$ refers only to the free energy of **A** when x is fixed at $x = 0$. Similarly, the free energy for **C** is $G_p(x^\dagger) - k_BT \ln q_{trans}^{\mathbf{C}}$, where $q_{trans}^{\mathbf{C}} = (2\pi m k_BT)^{1/2}\Delta^\dagger$. K_{eq} is obtained from this free energy difference, and so is given by eq A.8d.

We also use in the text a mean-first-passage time for diffusion of M^+ from $x = 0$ to $x = a$. This time is obtained by writing the solution of eqs A.1−A.2 in the form of an eigenvalue expansion and equating the mean first passage time to the reciprocal of the lowest eigenvalue.[44] We illustrate the result here for a particular case of eq A.1, neglecting any back reaction of the product. The mean first-passage time is obtained by setting $P_r(x)$ equal to $p(x) \exp(-k_2t)$, where k_2 is the lowest eigenvalue.[44] One solves thereby the equation obtained from eq A.1

$$D\frac{d^2p}{dx^2} + D\frac{d}{dx}\left(p\frac{dg_r}{dx}\right) + k_2p = 0 \tag{A.9}$$

We use as boundary conditions $p = 0$ at $x = a$ (i.e., the reactant does not return after reaching $x = a$) and $dp/dx = 0$ at $x = 0$ (no net diffusive flux into $x < 0$). If the forcing term dg/dx is neglected, one finds that the unnormalized eigenfunction p is $\cos (k_2/D)^{1/2}x$ and that the eigenvalue k_2 is given by

$$k_2 = D(\pi/2a)^2 \tag{A.10}$$

Equation A.10 is used in the text. Equation A.9 can be solved more generally, for example by converting the equation to a Schrodinger-like equation[43] and solving the latter for the eigenvalue k_2.

The formulation of k_{et} as a function of x, as in eqs A.1−A.2, tacitly implies that x is at most only a minor contributor to the reaction coordinate: When it *is* the reaction coordinate the transition state occurs by definition only at a particular x and not over a range of x. In that case one replaces the pair of equations eqs A.1−A.2 by a single equation, the Kramers−Klein equation for the population.[44,45]

In some cases there may be two $x^\dagger$'s.[46]

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