Specific ion-pairing effects in weakly exoergic intramolecular electron transfer

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Abstract

A simple theoretical model of the effect of specific ion-pairing with a chemically inert counterion on the rate of intramolecular charge transfer reactions is presented. The counterion motion is treated as corresponding to a separate reaction coordinate on the two-dimensional free energy surface. For the limiting case of strong ion-pairing and low driving force, i.e. $|E_{pair}| > |\Delta G^0| > k_B T$, the dependence of the effect on the donor–acceptor separation, r_{DA}, and on the ΔG^0 of reaction are discussed in detail. In this limit the counterion dynamics effectively controls the rate of the intramolecular electron transfer over a broad range of donor–acceptor distances. For the limiting case of fast counterion motion the analytical relationship between the reorganization energy and activation energy along the Coulomb coordinate of the free energy surface has been derived.

Keywords: Intramolecular electron transfer; Ion-pairing effect

1. Introduction

Among other areas of this intensely active field, two aspects of electron transfer (ET) processes have been receiving a substantial amount of attention in recent years: one of them is the question of the non-equilibrium medium dynamics [1] and the non-adiabatic to adiabatic transition in ultrafast ET reactions; the other one is the influence of electrolytes on the rates of intramolecular charge transfer reactions [2]. Even though the dynamic solvation effects are the domain of ultra-fast femtosecond spectroscopists [3,4], while on the other hand the electrolyte effects can be studied on nanosecond, even microsecond, time scales [5,6], these two phenomena are very closely related. Indeed, the most clear examples of the transition from a non-adiabatic intramolecular ET to an adiabatic, medium controlled ET process originate from the salt effect studies rather than from the ultra-fast measurements on polar solvation [7].

Specific ion-pairing effects are of particular, if not necessarily fully appreciated, importance for intramolecular electron transfer reactions studied in inorganic or organometallic donor–acceptor model compounds. Most of these systems are prepared as salts and as such they come with their counterions inseparably 'built in'. Electrostatic interactions with these coun-terions will influence, and in some instances even control, the overall behavior of the models.

While the Debye–Hückel theory and its variations have been applied with variable success to both intermolecular electron transfer [8], as well as to intramolecular ET reactions [5] in solutions of electrolytes in the absence of ion-pairing, we feel that there is a need for a simple explicit model which would account for, and help to predict, the trends of strong specific ion-pairing effects in intramolecular electron transfer. The outline of the proposed model, as well as more detailed discussion of two limiting cases, is given below.

2. The theoretical model

The general approach presented in this paper is based on the concept of a two-dimensional reaction coordinate advanced by van der Zwan and Hynes [9], Agmon and Hopfield [10], and perhaps best known in the form presented by Sumi and Marcus [11]. In these works one coordinate corresponds to the 'fast reorganization mode', usually associated with the internal vibrations, and the 'slow reorganization mode' associated with the solvent relaxation (Fig. 1(a)). The reaction along the fast mode coordinate is treated as non-adiabatic, while the evolution along the slow mode coordinate can lead to the onset of adiabatic behavior.
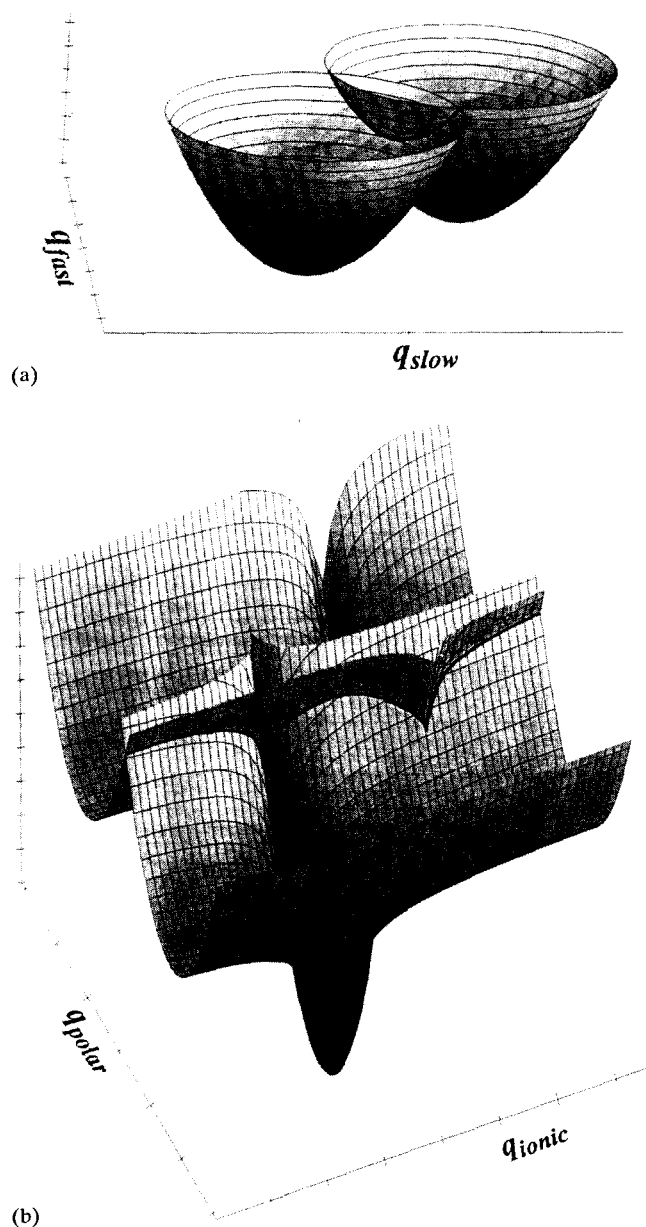
Fig. 1. Two-dimensional free energy surfaces: (a) the original Sumi–Marcus model, parabolic along both fast and slow reaction coordinates; (b) the model advanced in this paper with parabolic free energy profile along the fast solvent reorganization coordinate, q_{polar}, and Coulombic profile along the slow counterion dissociation-association coordinate, q_{ionic} (the scaling corresponds to $\lambda_{ionic} \approx \frac{1}{2}\lambda_{polar}$).

In our picture the internal vibrations and the polar solvation are combined together into one fast mode along q_{polar}, while the significantly slower and physically distinct diffusive dynamics of the chemically inert counterion is described by the slow mode along q_{ionic} (Fig. 1(b)). The difference between the original two-dimensional free energy surface theory and this work is made apparent in Fig. 1. In the first case both orthogonal modes give rise to approximately harmonic potentials (Fig. 1(a)). In the second one the potential along the

fast mode coordinate, $V(q_{polar})$, remains parabolic, however, the potential along the slow mode coordinate, $V(q_{ionic})$, corresponding to ion diffusion, is Coulombic. This difference has significant consequences. Firstly, it leads to a different Boltzman distribution and different time evolution along this coordinate. Secondly, it complicates the formal treatment by making certain crucial equations of the Sumi–Marcus theory not solvable analytically, thus forcing one to evaluate the survival probability numerically [11]. However, the objective of this paper is not the formal detail of the model, which will be discussed elsewhere, but rather the derivation of simple approximations useful for an experimentalist.

For the sake of simplicity we will focus on a system consisting of a univalent counterion associated with a univalent charge-shift model compound of an opposite charge in a linear arrangement (Fig. 2). Naturally, the approach applies to all similar systems, as long as the donor–acceptor assembly carries a net charge. However, in the present form it does not directly apply to charge-separation reactions in neutral molecules. For the same reason of simplicity we will ignore ionic atmosphere effects and treat the potential along the slow coordinate as purely Coulombic. Corrections for these contributions can certainly be added to the potential, however, it is highly questionable how realistic they would be, since the expression for the ionic atmosphere term is obtained on the basis of an expansion which is valid only if the ion–ion interaction, $z_1 z_2 e^2/\epsilon r_{12}$, is significantly lower than the thermal energy $k_B T$ [12], while in this paper we are specifically addressing the case of strong specific ion-paring with the model compound, i.e. $|E_{pair}| \gg k_B T$.

To begin with, it is important to note that the Onsager radius, $d_O = e^2/\epsilon k_B T$, for univalent ions in moderately polar solvents is usually larger than the donor–acceptor distance in typical electron transfer model compounds. For example, in CH_2Cl_2 d_O is equal to 55 Å, and even in acetonitrile it is 15 Å, while the R_{DA} of only relatively few models which have been investigated exceeds 15 Å. Indeed, since the exchange dynamics in tight ion-pairs in moderately polar solvents can be as slow as 1×10^6 s^{-1} [13], it is appropriate to treat the counterion/ model compound complex as a closely correlated ion-pair, whose average lifetime is in most of cases significantly longer than the duration of the electron transfer event (Fig. 2). In this instance the counterion diffusion has to be treated explicitly, and an onset of adiabatic behavior, as well as multiexponential ET kinetics, are expected. This special regime corresponding to $|E_{pair}| > |\Delta G^0|$ is discussed as 'limiting case A'.

Fig. 2. Schematic representation of an intramolecular charge shift reaction in the presence of an associated counterion.

In the relatively rare cases for which $|E_{pair}| \gg k_B T$, yet $k_{ion} \gg k_{ET}$, the intramolecular ET process is non-adiabatic and it is sufficient to include the ionic effects in the description of the energetics of the system. This means calculating the λ_{ionic}, i.e. the ionic contribution to the overall reorganization energy λ, as well as the free energy of activation $\Delta G^{\neq}_{ionic}$ which is not linked with λ_{ionic} by the usual linear relationship [7,14]. The behavior in this regime is discussed as 'limiting case B'.

3. Two limiting cases

3.1. Case A. The limit of slow counterion motion, $k_{ion} \ll k_{ET}$

This case is similar to the 'narrow reaction window limit' of the Sumi–Marcus theory. In accordance with their work, it will generally lead to a multiexponential behavior described by a convolution of the time dependence of the diffusive motion along the slow coordinate and electron transfer rate from a given point along this coordinate [11], i.e. if the system evolves along the slow coordinate as $q_{ionic} = f(t)$, and the electron transfer rate depends on this coordinate as $k_{ET} = f(q_{ionic})$, then the overall rate is characterized by a rate function, $k_{overall} = f(t)$, rather than a proper rate constant. Nevertheless, in certain special situations a simple single exponential approximation is expected to be adequate. Such an approximation can be very useful and, indeed, desirable, since most likely the majority of experimental data will not be complete enough to warrant the full multiexponential analysis.

In particular, in the case of a weakly exoergic intramolecular ET reaction and strong pairing with a counterion, such that $|E_{pair}| > |\Delta G^0|$, the reaction is effectively endoergic by as much as $(E_{pair} - \Delta G^0)$, as long as the counterion remains in the vicinity of the donor–acceptor system, and, therefore, it will not proceed at any appreciable rate. The reaction will take place only if the counterion diffuses sufficiently far away from the donor site. It is true that the barrier crossing can occur due to evolution exclusively along the fast coordinate, q_{polar}, (Fig. 1(b)), and, indeed, this will be the major channel in a highly exoergic ET in the presence of electrolytes. However, in the case of weakly exoergic ET, if the system remains in a fixed position along the q_{ionic} coordinate, a rapid back transfer will be always preferred over the slow evolution towards the product equilibrium and no net reaction will be observed. Therefore, the counterion motion becomes the rate determining step, and effectively it is gating the electron transfer process [15]. The adiabaticity of an intramolecular ET process in the presence of an associated counterion can be demonstrated by com-

paring the rate of the electron exchange at the crossing point with the velocity of the counterion in the attractive electrostatic field. At the crossing point the electron oscillates between the two non-adiabatic surfaces with the full frequency $f_0 = 2\pi \times 2V$, where V is the electronic coupling between the donor and the acceptor. Even for electronic coupling as small as, e.g. 30 cm^{-1}, this frequency will be as high as 1.2×10^{13} s^{-1}. On the other hand, the upper limit of the velocity of a counterion in the crossing region can be estimated from the corresponding ion mobility, μ, and the magnitude of the electrostatic field, $\bar{E}$, acting upon it. For example, for the Na$^+$ ion the terminal velocity in a field generated by a point charge located at 5 Å is estimated to be approximately 4×10^{11} Å s^{-1}, i.e., in the crossing region the ion moves at least thirty times slower than the intrinsic electron exchange rate.

In this limit a simple stepwise kinetic model, in which the ET is preceded by ion-pair separation, is applicable. Therefore, the overall ET rate, $k_{overall}$, is given by

$$k_{overall} = \frac{k_{ion} k_{ET}}{k_{ion} + k_{ET}} \tag{1}$$

where k_{ion} describes the diffusion of the counterion with respect to the donor–acceptor system, and k_{ET} is the corresponding intramolecular electron transfer rate in the absence of ion-pairing.

Kuznetsov et al. proposed that, in order for the electron transfer to take place, the system has to find itself in a transition state in which the counterion has diffused to the mid-point between the donor and the acceptor [14], and, therefore, the k_{ion} from the above equation would be defined as the rate of formation of such a transition state. We offer a more general picture which includes the above suggestion as a special case: the ET reaction can proceed with an appreciable rate only if the counterion diffuses to a point d, which renders the donor and acceptor isoenergetic. For an electron exchange reaction in a degenerate system this point corresponds to half of the donor–acceptor distance, R_{DA} (Fig. 3(a)). Naturally, for non-zero driving forces this point will lie closer to the donor than to the acceptor (Fig. 3(b)), and in general its position can be found by solving Eq. (2)
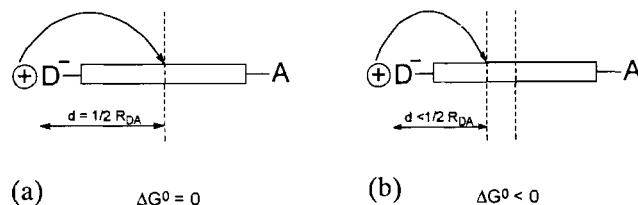

(a) $\Delta G^0 = 0$ (b) $\Delta G^0 < 0$

Fig. 3. Schematic representation of the optimum position of the counterion, d: (a) in the case of degenerate electron exchange; (b) in the case of weakly exoergic ET.

$$\Delta G^0 + \frac{e^2}{4\pi\epsilon d} - \frac{e^2}{4\pi\epsilon(R_{DA}-d)} = 0 \qquad (2)$$

where the second term corresponds to the stabilization of the donor site due to ion-pairing, and the third term to the stabilization of the acceptor by the counterion at distance d from the donor. The solution is given by

$$d = \frac{1}{2}R_{DA} - \frac{e^2}{\Delta G^0 4\pi\epsilon} + \frac{\sqrt{4(\Delta G^0)^2\pi^2\epsilon^2 \cdot R_{DA}^2 + e^4}}{4\pi\epsilon \cdot \Delta G^0} \qquad (3)$$

Eq. (3) and resulting dependence of d on the free energy of reaction and on the donor–acceptor distance is plotted in Fig. 4. The corresponding rates of electron transfer, k_{ET} at point d, correspond to degenerate electron exchange and will be denoted as k^0_{ET}.

Once d has been established, the rate of ion separation to this distance, k_{ion}, can be calculated from the Boltzman distribution as

$$k_{ion}(R_0 \longrightarrow d) = \text{const. } \exp(-[E_{pair} - e^2/\epsilon d]/k_B T)$$

$$= \text{const. } \exp(-E_{pair}/k_B T) \times \exp(e^2/\epsilon dk_B T) \qquad (4)$$

where

$$E_{pair} = \frac{e^2}{4\pi\epsilon(r_{av}+r_{ion})} \qquad (5)$$

is the Coulombic interaction in a contact ion-pair consisting of the counterion and the donor–acceptor system ion, where r_{av} is the average donor and acceptor radius and r_{ion} is the radius of the counterion, and $R_0 = r_{av} + r_{ion}$. The pre-exponential factor can be either calculated on the basis of existing theories [12] or, perhaps not as elegantly but much more reliably, an experimental value
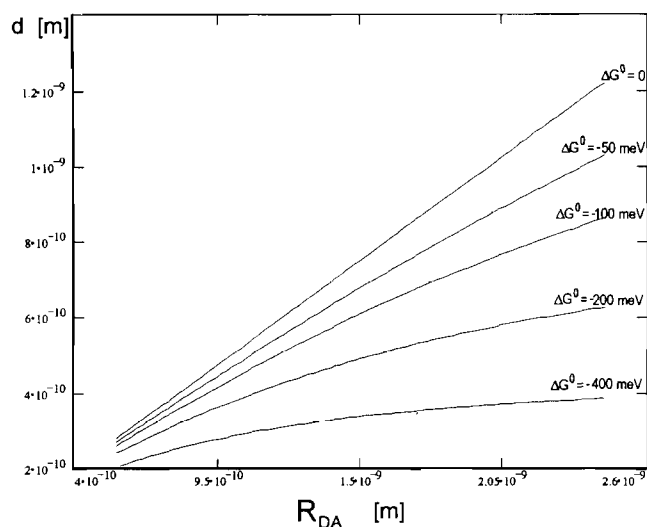
for the dissociation rate of the appropriate contact ion-pair consisting of the counterion and the donor ion into free ions can be inserted in place of the const. $\times \exp(E_{pair}/kT)$ term. This single-point scaling procedure is sufficient for an entire family of donor–acceptor compounds since both the distance and the free energy dependence of k_{ion} are fully described by the $\exp(e^2/\epsilon dk_B T)$ term.

There are some interesting consequences of this model: since k_{ion} decreases with distance approximately as $\exp(1/r)$, while k_{ET} decreases as $\exp(-\beta r)$ (where β is the characteristic attenuation of the electron transfer rate with distance), the ion-pairing control of electron transfer peaks at a certain donor–acceptor separation and subsequently weakens with increasing R_{DA}, as shown qualitatively in Fig. 5. This effect has been confirmed by the recent experimental work [16].

The quantitative dependence of the overall rate on the driving force, ΔG^0, and on the donor–acceptor distance, is obtained by substituting Eq. (4) into Eq. (1). The results are presented in Fig. 6. The values of k_{ET} used in generating these plots are the values for the rate of isoenergetic, $\Delta G^0 = 0$, intramolecular electron exchange at distance R_{DA}, in a medium of dielectric constant ϵ, and, as mentioned above, should be denoted as k^0_{ET}. They were calculated using the slope and pre-exponential factor from the work by Closs et al. [17].

It is also of interest to compare the rates in the presence of the counterion, $k_{overall}$, to the original rates k_{ET} in the neat solvent as a function of the driving force, ΔG^0. Such a comparison reveals more strikingly the strong dependence counterion effects on R_{DA}, and the existence of a pronounced maximum of the rate depression (Fig. 7). The most important feature of Figs. 6 and 7 is the prediction of effective counterion dynamics control, and the resulting adiabaticity of intramolecular electron transfer, over a broad range of donor–acceptor distances which practically encompasses all model compounds which have been prepared and investigated by researchers.

As expected, as the driving force increases, the magnitude of the rate reduction due to ion-pairing decreases.
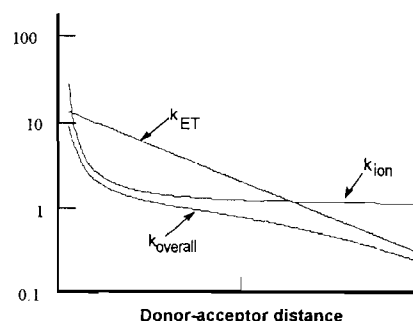

Fig. 4. Dependence of the optimum counterion distance d on the donor–acceptor separation, R_{DA}, and the driving force, ΔG^0, for a solvent with dielectric constant of 7.6 (tetrahydrofuran). The rates of an isoenergetic electron exchange, $\Delta G^0 = 0$, and of a weakly exothermic reaction, $\Delta G^0 = -150$ meV, are included for comparison.

Fig. 5. Qualitative dependence of the overall reaction rate on the relative magnitude of k_{ET} and k_{ion}, as a function of the donor–acceptor separation.
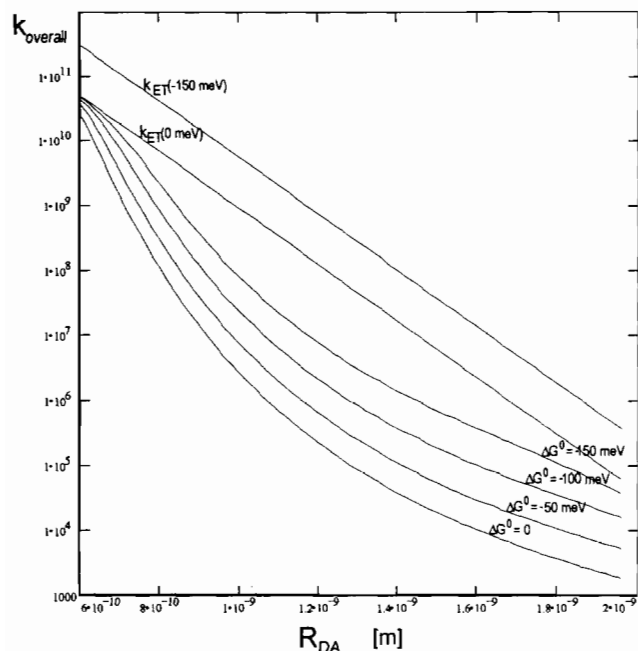
Fig. 6. Dependence of the overall electron transfer reaction rate in the presence of a counterion, $k_{overall}$, on the donor–acceptor separation R_{DA} and ΔG^0. Parametrized on the basis of Refs. [7,16,17], for an Na^+ counterion paired with a naphthalene radical anion donor, in tetrahydrofuran, $\beta = 1.0$.
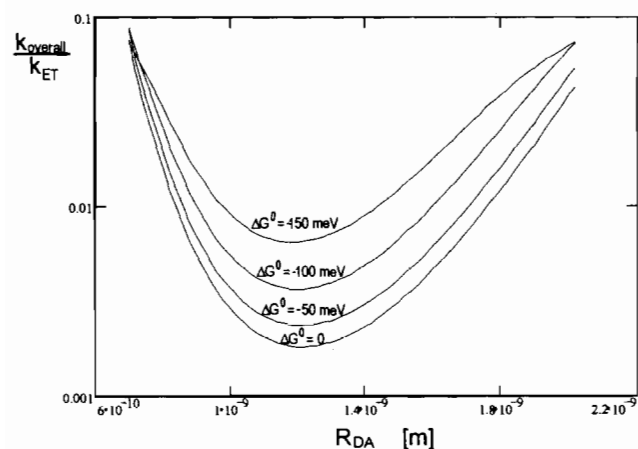

Fig. 7. Ratio of the overall charge transfer rate, $k_{overall}$, in the presence of strong ion-pairing to the rate k_{ET} in neat solvent, plotted as a function of the donor–acceptor distance R_{DA} and ΔG^0; the same parameters as in Fig. 6.

A somewhat less intuitive result is that the predicted dependence of the effect on the donor–acceptor distance becomes more shallow with increasing ΔG^0 (Fig. 7). This prediction awaits experimental confirmation.

It is useful to observe that in the above limit the intramolecular ET rates will exhibit strong dependence on the mobility of the counterion, and hence on its radius, and on the solvent viscosity, through the normal Stokes–Einstein expression $k_B T / 6\pi\eta r_{ion}$. Since the radius of the counterion affects also the E_{pair}, the overall

dependence of the ET rate on r_{ion} will be more complex, and it will be similar to the Eigen equation [18].

It should be noted, that as $|\Delta G^0|$ approaches $|E_{pair}|$ the gating effect of the counterion motion diminishes and the electron transfer reaction can proceed with a significant rate from an increasing range of positions along the q_{ionic} coordinate. This will lead to an increasingly multiexponential character of the kinetics of the reaction, until the limiting case B is achieved, when the reaction will again exhibit a single exponential behavior.

3.2. Case B. The limit of fast counterion motion, $k_{ion} \gg k_{ET}$

This is the 'slow reaction limit' of the Sumi–Marcus model [11]. When the relative motion of the ions, k_{ion}, is much faster than the intrinsic rate of electron transfer in a given solvent in the absence of an electrolyte, k_{ET}, the system returns to the normal non-adiabatic behavior, and the influence of the counterion can be fully described by the additional reorganization energy λ_{ionic}, along the q_{ionic} coordinate of the free energy surface (see Fig. 1(b)). The nature of the ion motion is now irrelevant, since the ET reaction always takes place from fully thermally equilibrated distribution along both coordinates. The experimentally observed ET reactions corresponding to this limit will exhibit a single exponential behavior. It should be pointed out that this limit is not likely to be of importance in solvents of moderate polarity, or in general, when the condition $|E_{pair}| > k_B T$, is satisfied. Nevertheless, it is worthwhile providing the explicit expression for the ionic contribution to the reorganization energy, λ_{ionic}. From simple electrostatic considerations (Fig. 8) one obtains

$$\lambda_{ionic} = -E_{pair} - \frac{e^2}{4\pi\epsilon R_{DA}}$$

$$= \frac{e^2}{4\pi\epsilon(r_{av} + r_{ion})} - \frac{e^2}{4\pi\epsilon R_{DA}} \tag{6}$$

where all symbols have been defined previously. The reorganization energy, λ_{ionic}, is equal to the work nec-
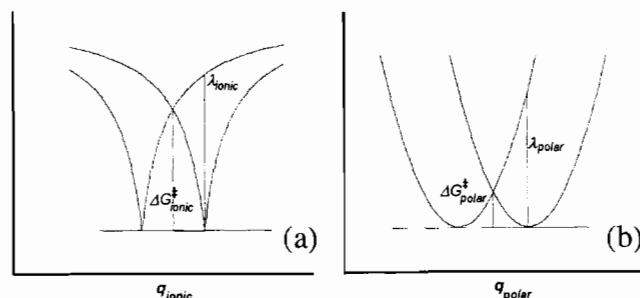

Fig. 8. The relationship between the reorganization energy and free energy of activation: (a) for the Coulombic free energy profile corresponding to ion-pairing; (b) for the standard parabolic free energy curves. Both diagrams correspond to the isoenergetic case.

essary to separate the donor$^-$/counterion pair to a distance equal to R_{DA}. In the limiting case of $R_{DA} \to \infty$, this work, and the ionic reorganization energy, are equal to the total ion-pairing energy, E_{pair}.

Since, as mentioned previously, the convenient linear relationship between the reorganization energy and the activation free energy ($\Delta G^{\neq} = \frac{1}{4}\lambda_s$ for an iso-energetic exchange) does not exist in the case of Coulombic potentials [14], it is necessary to establish the dependence of $\Delta G^{\neq}_{ionic}$, the free energy of activation along the q_{ionic} coordinate, on the corresponding λ_{ionic}. Again, a simple expression is obtained

$$\Delta G^{\neq}_{ionic} = \lambda_{ionic} - \frac{e^2}{4\pi\epsilon R_{DA}} - \Delta G^0$$

$$= -E_{pair} - 2\frac{e^2}{4\pi\epsilon R_{DA}} - \Delta G^0 \qquad (7)$$

$$= \frac{e^2}{4\pi\epsilon}\left[\frac{1}{(r_{av}+r_{ion})} - \frac{2}{R_{DA}}\right] - \Delta G^0$$

In the limit of $R_{DA} \to \infty$, the activation energy converges to the difference between ion-pairing energy, E_{pair}, and the free energy of reaction, ΔG^0.

The size of the counterion will continue to influence the intramolecular ET rate, however, it will be only through the dependence of $\Delta G^{\neq}_{ionic}$ and λ_{ionic} on the contact ion-pair stabilization, E_{pair}. Naturally, the ionic component of activation energy is diminished in highly polar solvents, in contrast with the activation barrier associated with normal, polar solvation, which in the weakly exergic region increases with increasing solvent polarity.

4. Conclusions

We have presented an approximate theoretical model of the influence of specific ion-pairing with chemically inert ions on the rates of weakly exergic intramolecular electron transfer. The model is based on the concept of two-dimensional free energy surface where the mutual diffusion of ions corresponds to the slow, adiabatic mode. The dependence of the overall transfer rate on the interplay between the donor–acceptor electronic coupling, counterion diffusion and the driving force has been discussed.

The model treats the counterion/donor–acceptor ion complex as an isolated, strongly correlated ion-pair, a picture quite appropriate for weakly dissociated so-

lutions in solvents of low polarity [13]. In the above considerations we have consciously omitted all second-order phenomena, such as the ionic atmosphere or the reduction of the dielectric constant of the solvent in the presence of an electrolyte (dielectric saturation).

In addition, expressions for the ionic contribution to the reorganization energy and the free energy of activation have been derived for the $k_{ion} \gg k_{ET}$ limit. The behavior in this regime is currently being studied experimentally in this laboratory.

The work to extend the model beyond the single exponential rate approximation and to cover the entire ΔG^0 range is in progress.

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