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Time-Resolved Resonance Raman Study of the Rate of Separation of a Geminate Ion Pair into Free Ions in a Medium Polarity Solvent

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Abstract: The rate of separation into free ions of a geminate ion pair generated by photoinduced electron transfer between 9,10-anthraquinone excited to the lowest triplet state and 1,2,4-trimethoxybenzene in 1,1,2,2-tetrachloroethane has been measured at different temperatures by nanosecond time-resolved resonance Raman spectroscopy (TR^3). The intrinsic activation energy for the separation amounts to 0.04 eV, suggesting that the center-to-center interionic distance in the geminate ion pair is about 7.5 Å. The activation barrier is due to a loss of electrostatic stabilization upon separation to a distance of about 9.5 Å, where a solvent molecule or part of it can interpenetrate to increase the solvation energy. This suggests that the geminate ion pair is a loose ion pair but is not truly solvent separated.

Introduction

Over the past years, a great theoretical as well as experimental effort has been devoted to the understanding of the dynamics of photoinduced electron transfer (ET) reactions.[1] While the general scheme for this process is now well accepted, the structure of the intermediates and their kinetics have not been totally elucidated. One of these intermediates is the geminate ion pair generated after the forward ET. In order to explain the dynamics of the geminate ion pair, Mataga and co-workers[2] as well as Gould, Farid, and their co-workers[3] and Peters and co-workers[4] have proposed the existence of two types of geminate ion pairs: a contact or compact ion pair with a center-to-center interionic distance, *d*, of about 3.5 Å generated by direct excitation of the charge transfer complex in the ground state, and a loose or solvent-separated ion pair with a distance *d* of about 7.5 Å formed by diffusional ET quenching of the electronically excited partner. Interconversion between these two types of ion pairs can also take place. Most of the information on these intermediates has been obtained from transient absorption spectroscopy. It is well-known that the electronic absorption spectra of radical ions within a geminate ion pair are not distinguishable from those of the solvated free ions. This explains why the actual structure of these transients is unknown and why the interconversion kinetics between these different intermediates has not been completely solved. An important step is the separation of the geminate ion pair into free ions. Until recently, the only values for the rate constant of this process, k_{sep}, have been obtained from fitting transient absorption kinetics to a complex kinetic scheme,[5] from photoconductivity measurements,[6] and from magnetic field effects.[7] A precise knowledge of this rate constant of separation is important since the rate constant for back-ET within the geminate ion pair has often been calculated from the measured free ion yield and by using an assumed value for k_{sep} in acetonitrile of 5×10^8 s^{-1}.[3,8] As long as it does not depend too much on the nature of the radical ions, an imprecise value of k_{sep} has no influence on the relative magnitude of the rate constants of back-ET. However, in order to obtain the parameters used in ET theories such as the electronic coupling constant, *V*, the absolute values of the back ET rate constants are required, hence k_{sep} must be known precisely.

Recently, we reported the application of time-resolved resonance Raman (TR^3) spectroscopy to the investigation of the ET reaction between anthraquinone (AQ) in the lowest triplet state and 1,2,4-trimethoxybenzene (TMB) in solvents of different polarity.[9] It was shown that the frequency of the aromatic C–C stretch of $TMB^{\bullet+}$ was environment dependent. In a solvent of medium polarity like 1,1,2,2-tetrachloroethane (TCE), where k_{sep} is expected to be within the time resolution of the ns-TR^3 setup, a frequency shift from 1607 cm^{-1} at short time delay to 1590 cm^{-1} after 1 μs was observed. The 1607 and 1590 cm^{-1} bands were assigned to the aromatic C–C stretch of $TMB^{\bullet+}$ within the geminate ion pair and of the free solvated $TMB^{\bullet+}$, respectively. With this system, it is therefore possible to measure the kinetics of the geminate ion pair and of the free ions **directly** and **independently**.

We now report measurements of the rate constant of the separation of the geminate ion pair generated via ET quenching of ^3AQ by TMB in TCE as a function of temperature. Knowing the activation energy for the separation, it is possible to get an insight into the structure of the ion pair.

Experimental Section

All chemicals were of the highest commercially available purity and were used without further purification with the exception of AQ which was recrystalized twice from chloroform and sublimed under vacuum. The concentrations of AQ and TMB were 1×10^{-3} and 0.1 M, respectively. The TR^3 equipment is as described in ref 9 with the exception of the Raman detector which has been replaced by a back illuminated liquid nitrogen cooled CCD detector from Princeton Instruments (CSMA LN/CCD-1024/TKB/I CCD system). Samples were bubbled for 20 min with solvent-saturated argon prior to irradiation to remove oxygen. The

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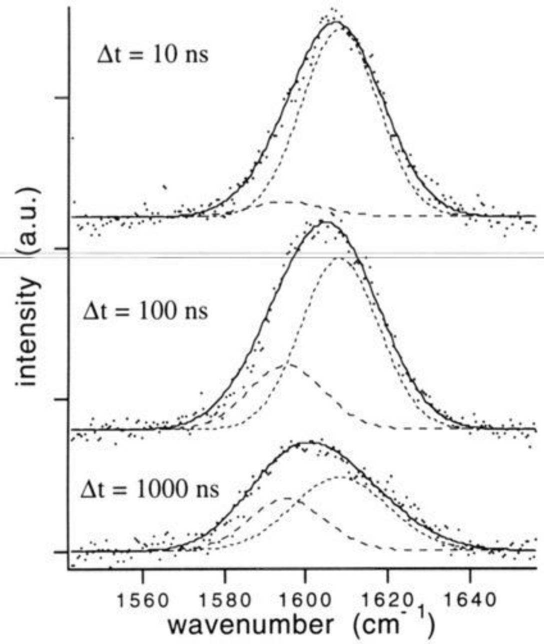


Figure 1. Time evolution of the shape of the resonance Raman band situated around 1600 cm^{-1} obtained by pumping at 351 nm and probing at 460 nm a solution of AQ and TMB in TCE at −5 °C. The dotted and the dashed Gaussians correspond to the C–C stretching of TMB$^{\bullet+}$ within the geminate ion pair and free in the solvent, respectively. The solid curve is the convolution of the two Gaussians.

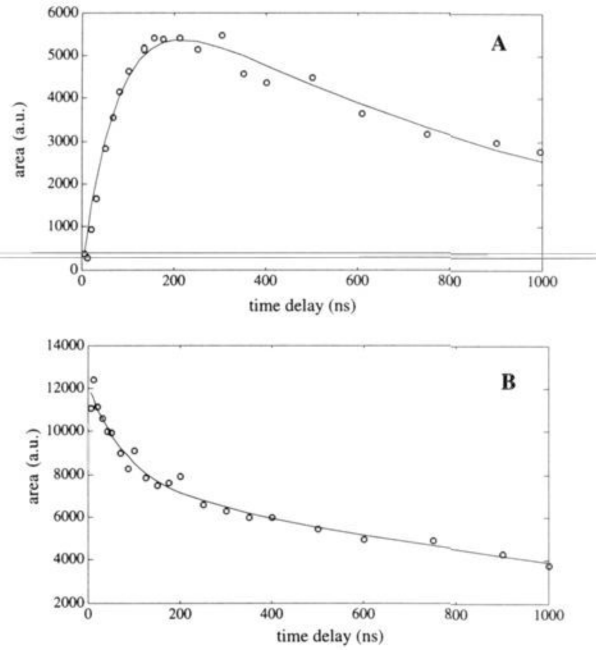


Figure 2. Time evolution of the area of the high wavenumber Gaussian, corresponding to the geminate ion pair (A), and of the low wavenumber Gaussian, corresponding to free ions (B). The continuous lines are the best fits of eq 1 and eq 2, respectively.

samples were flowed through a Spectrosil B quartz silica tube (*ca.* 2 mm i.d.) placed perpendicular to the laser beams and the Spex Triplemate 1400 spectrograph. Raman scatter was collected using right angle geometry. Both pump and probe energies were between 0.2 and 1 mJ per pulse at the sample. Spectra were collected at 10–20 Hz over 2–3 min at each time delay; jitter between pump and probe lasers was *ca.* 4 ns. Raman spectra were calibrated with solvents such as toluene, recorded under identical condition as the samples with wavenumber values taken from ref 10. Frequencies quoted are expected to be accurate to within ±2 cm^{-1}. Raman intensities for each spectrum were determined using a purpose developed software based on the Levenberg–Marquardt method which fits the spectrum to a series of Gaussian and/or Lorentzian line shapes. The program allows spectrally unresolved bands to be separated into their individual components. Once fitting has been achieved, resultant net integrals of the Raman bands can be calculated and used for kinetic analysis.

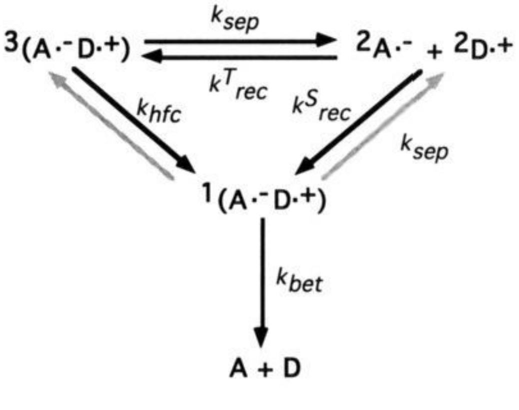
Results and Discussion

Figure 1 shows the resonance Raman band located around 1600 cm^{-1} after subtraction of the spectrum obtained with the probe beam only. This band can be fitted by the convolution of two Gaussians, whose heights vary with the time delay between the pump and probe pulses. At short time, the high wavenumber Gaussian located around 1608 cm^{-1} is much more intense than the low wavenumber one situated around 1595 cm^{-1}. At longer time delay, the 1608 cm^{-1} band decreases while the low wavenumber one increases to a maximum and then decreases as well. The width and center of the Gaussians are time independent. The time behavior of the integral of each Gaussian is plotted on Figure 2.

The low wavenumber band is ascribed to a vibration of the free TMB$^{\bullet+}$. The intensity rise corresponds to the formation the free TMB$^{\bullet+}$ by separation of the geminate ion pair and the decay to the diffusional recombination.

The high wavenumber band is assigned to a vibration of TMB$^{\bullet+}$ of the geminate ion pair. The fast initial decay corresponds to the separation into free ions. The slow decay can be understood by considering that the geminate ion pair is in a triplet state and the back-ET to the initial neutral state is spin forbidden.[11] Therefore, apart from spin inversion through hyperfine coupling, the only decay channel for the geminate ion pair is separation into free ions. According to spin statistics, only one-fourth of the recombination of the free ions can lead to the formation of a geminate ion pair in the singlet state, which can undergo a fast back-ET to the ground state. The remaining three-quarters form a triplet geminate ion pair which will separate again. This process will repeat until the complete depletion of the population of both intermediates. This explains why the ion pair kinetics follows the free ion kinetics. This can be modeled with the following scheme:

Scheme 1



In this scheme, the back reactions depicted with light arrows can be neglected as their efficiency must be very small because the fast back-ET is no longer spin forbidden. This is a typical coupled system, as used for example to describe delayed fluorescence, with the following solutions:[12]

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$$[\mathrm{FI}] = [\mathrm{IP}]_0\{k_{\mathrm{sep}}/(\gamma_1 - \gamma_2)\}\{\exp(-\gamma_2 t) - \exp(-\gamma_1 t)\} \quad (1)$$

$$[\mathrm{IP}] = [\mathrm{IP}]_0\{g_1 \exp(-\gamma_1 t) - g_2 \exp(-\gamma_2 tO)\} \quad (2)$$

with:

$$g_{1,2} = (X - \gamma_{2,1})/(\gamma_1 - \gamma_2) \quad (3)$$

$$\gamma_{1,2} = \{(X + Y) \pm [(X - Y)^2 + 4k_{\mathrm{sep}}\,k_{\mathrm{rec}}]^{1/2}\}/2 \quad (4)$$

$$X = k_{\mathrm{hfc}} + k_{\mathrm{sep}}; \qquad Y = k^{\mathrm{T}}_{\mathrm{rec}} + k^{\mathrm{S}}_{\mathrm{rec}} \quad (5)$$

$$k^{\mathrm{T}}_{\mathrm{rec}} = 3k^{\mathrm{S}}_{\mathrm{rec}} \quad (6)$$

where FI and IP stand for free ion and geminate ion pair, respectively.

In order to simplify the analysis, the hyperfine coupling constant, k_{hfc}, has been neglected as it has been measured to be around 10^6 s^{-1},[13] i.e. about 10 times slower than the expected value of k_{sep},[9] and as it is known to be temperature independent.[14] Moreover, k_{rec} was approximated to a first-order rate constant. This is of course not strictly correct as the recombination is a second-order process.[15] However, as the concentration of free ions is not known and could vary from one experiment to another due to different excitation energy, a precise determination of k_{rec} was not possible and was not the aim of this work.

The rate constants of separation, k_{sep}, obtained from fitting eq 1 to the time variation of the low wavenumber band area are listed in Table 1 as a function of temperature. The validity of the analysis is supported by the fact that if the values of $k^{\mathrm{T}}_{\mathrm{rec}}$ and $k^{\mathrm{S}}_{\mathrm{rec}}$ were allowed to vary independently, the $k^{\mathrm{T}}_{\mathrm{rec}}/k^{\mathrm{S}}_{\mathrm{rec}}$ ratio obtained from the fit was always close to 3. The fit of eq 2 to the kinetics of the high wavenumber band gave similar values but was more delicate because of the complexity of the equation.

The temperature dependence of k_{sep} follows an Arrhenius behavior as illustrated in Figure 3. From the slope of this plot, the activation barrier amounts to 0.16 eV (3.7 kcal/mol). As the separation into free ions is in essence a diffusional process, one part of this activation energy is associated with the temperature dependence of the solvent viscosity.[16] The temperature dependence of k_{sep} can be expressed as:

$$k_{\mathrm{sep}}(T) = F(\eta)\exp\left(-\frac{\Delta E^{\ddagger}_{\mathrm{sep}}}{k_{\mathrm{B}}T}\right) = A\exp\left(-\frac{(E_\eta + \Delta E^{\ddagger}_{\mathrm{sep}})}{k_{\mathrm{B}}T}\right) \quad (7)$$

where $\Delta E^{\ddagger}{}_{\mathrm{sep}}$ is the intrinsic activation energy for the separation and E_η the activation energy associated with the temperature dependence of the solvent viscosity. The latter can be generally expressed as:[17]

$$\eta(T) = \eta_0 \exp\left(\frac{E_\eta}{kT}\right) \quad (8)$$

From the fit of this equation to the value of the viscosity of TCE at different temperatures,[18] E_η amounts to 0.12 eV (2.7 kcal/mol). The remaining 0.04 eV corresponds to the intrinsic activation energy associated with the separation of the geminate ion pair into free ions, $\Delta E^{\ddagger}_{\mathrm{sep}}$.

Table 1. Temperature Dependence of the Rate Constant of Separation of the Geminate Ion Pair into Free Ions

temp (°C)	k_{sep} (10^7 s^{-1})	temp (°C)	k_{sep} (10^7 s^{-1})
−4.5	1.10	21	1.98
5	1.22	28.5	2.20
12.5	1.66	36	2.46

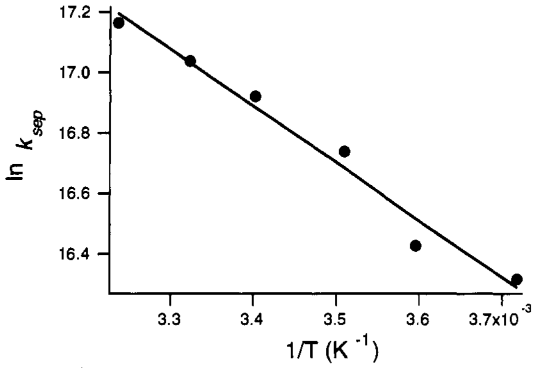

Figure 3. Temperature dependence of the rate constant of separation of the geminate ion pair into free ions.

From the point of view of thermodynamics, the energy of the geminate ion pair state and of the free ions state can differ through the electrostatic energy between the two ions and the solvation energy.[19] The solvation energy of the geminate ion pair can be estimated from the solvation energy of a dipole in a spherical cavity with two opposite charges separated by the ionic radii, r:[20]

$$E^{\mathrm{IP}}_{\mathrm{solv}} = -\frac{(2re)^2}{2a^3}\frac{2(\epsilon - 1)}{2\epsilon + 1} = -\frac{e^2}{r}\frac{2(\epsilon - 1)}{2\epsilon + 1} \quad (9)$$

where ϵ is the dielectric constant of the solvent, and a is the cavity radius. The right-hand side of eq 9 is obtained by calculating the radius a of a sphere having the volume of the two ions of radius r, $a^3 = 2r^3$.

On the other hand, the solvation of the free ions can be calculated from the Born equation:[21]

$$E^{\mathrm{FI}}_{\mathrm{solv}} = -\frac{e^2}{r}\left(1 - \frac{1}{\epsilon}\right) \quad (10)$$

These two equations predict that in very polar solvents the solvation energy of a geminate ion pair is the same as that of two free ions.[19] In a medium polarity solvent like TCE ($\epsilon = 8.2$ at 20 °C), the solvation energy is slightly larger for the free ions than for the geminate ion pair, $E^{\mathrm{FI}}_{\mathrm{solv}}/E^{\mathrm{IP}}_{\mathrm{solv}} = 1.06$. Taking the ions as spheres having the average molecular volumes of AQ and TMB results in ionic radii of 3.6 Å. The solvation energy difference between the free ions and the geminate ion pair is then about −0.19 eV. This value is of course only a rough estimate considering our approximations for the shape of the ions.

The Coulomb term accounting for the electrostatic interaction within a geminate ion pair is very often described by the following equation:[22]

$$C = \frac{e^2}{\epsilon d} \quad (11)$$

For a loose ion pair with d = 7.5 Å,[16] the electrostatic stabilization amounts to −0.23 eV in TCE. If one considers the geminate ion pair as a tight ion pair with a typical interionic

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distance of 3.5 Å,[16] the Coulomb stabilization increases to −0.52 eV. For free ions there is of course no electrostatic interaction.

From these considerations, the energy difference between the free ions and the geminate ion pair, ΔE_{sep}, is about 0.04 eV in the case of a geminate ion pair with an interionic distance of 7.5 Å whereas it is 0.33 eV for a tight ion pair. In the latter case, the separation is very endothermic. Although entropy must favor separation,[19] the equilibrium between geminate ion pair and free ions should be mostly on the geminate ion pair side, which is contrary to our experimental observations. A geminate ion pair with an interionic distance of about 7.5 Å seems therefore more realistic at least for the present system. Although the reaction seems to be still slightly endothermic, the contribution of entropy must render the process substantially exergonic.

In the case of a tight ion pair formed by direct excitation of a ground state charge transfer complex, the ions must retain the coplanar geometry of the ground state complex.[23] This results in an interionic distance of 3.5 Å, the Van der Waals "thickness" of an aromatic ring. The relative orientation of two ions formed by diffusional ET quenching is not known. Contrary to the previous case, the excited molecule and the quencher seem not to need a very precise geometry for the ET. Indeed, when the free energy for the forward ET is sufficiently large, the quenching rate constant is equal to the diffusion rate constant, indicating that ET takes place at each encounter of the two partners. If a preferential orientation was required, the quenching rate constant would be substantially smaller than the diffusion rate constant. Moreover, the back-ET within a short-lived exciplex has been observed to be influenced by solvent friction, indicating that some rearrangement has to take place prior to the back-ET.[24] Therefore, one has to consider an average interionic distance which takes into account all the possible relative orientations of the ions. Consequently, 7.5 Å is close to the sum of the two ions' Onsager radii and seems therefore to be a reasonable interionic distance.

The separation of the geminate ion pair involves two opposite contributions. As it separates, the ion pair loses electrostatic stabilization, therefore the energy of the system increases. As separation goes on, some solvent molecules can penetrate between the two ions and the solvation energy stabilizes the system and compensates partially for the loss of electrostatic stabilization. The activation energy, $\Delta E^{\ddagger}_{sep}$, must be the energy which has to be given to the ion pair to separate enough to allow solvent to penetrate:

$$\Delta E^{\ddagger}_{sep} = \frac{e^2}{\epsilon}\left(\frac{1}{d} - \frac{1}{d^{\ddagger}}\right) \qquad (12)$$

where $d^{\ddagger}$ is the interionic distance in the transition state, and where the temperature dependence of ϵ can be neglected. Indeed, if the temperature dependence of ϵ is taken into account, the intrinsic activation energy for the separation increases by less than 8%.

Taking for $\Delta E^{\ddagger}_{sep}$ the measured value 0.04 eV and a value for d of 7.5 Å, the interionic distance at the transition state is 9.5 Å. The molecular shape of TCE can be approximated to an ellipsoid with an average axis of 6 Å.[25] The interionic distance at the transition state seems to be large enough for a solvent molecule to fit between the ions, if one considers that the ions are disk-shaped molecules with a thickness of about 3.4 Å. In this state, the solvation energy is larger and attenuates the loss of Coulomb energy. If the ion pair does not have this sandwich geometry, the interionic distance at the transition state is at least large enough to allow part of a solvent molecule to interpenetrate.

If the ion pair was a tight geminate ion pair, the interionic distance at the transition state would be about 3.7 Å, which is only 0.2 Å larger than in the ion pair. A third possibility is that the ion pair is really solvent separated. To allow a solvent molecule to fit between the ions, the interionic distance has to be at least 9.5 Å. Applying eq 12 results in a value for $d^{\ddagger}$ of 12 Å, which is too small for the insertion of a second solvent molecule.

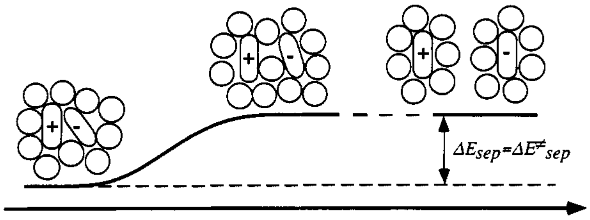

Figure 4. Schematic representation of the ion pair at the different stages of separation into free ions, with the corresponding energy.

Therefore, the geminate ion pair seems not to be truly solvent separated. If this was the case, firstly its solvation energy would be almost as large as for the free ions, hence the energy difference between the free ions and the geminate ion pair would be almost equal to $-C$, the Coulomb energy, i.e. $\Delta E_{sep} \approx 0.21$ eV. The separation into free ions would then be strongly endothermic. Secondly, if the geminate ion pair was really solvent separated, the environment of $TMB^{\bullet+}$ within the ion pair would be almost the same as in the solvent. In that case, the measured frequency shift of the $TMB^{\bullet+}$ C–C stretching upon separation should not be observed.

However, the structure of the ion pair could be loose enough to allow some part of the solvent molecules to interpenetrate. Indeed, if the interionic space was completely unaffected by the solvent field, the dielectric constant of the solvent should be removed from the equation describing the Coulomb stabilization and replaced by the polarisability of the ions.[26] In such a case, C would be about 4 times larger and the activation energy should be much larger as well.

Figure 4 shows a schematic diagram of the energy levels involved in the separation. Considering the size of the activation energy, $\Delta E^{\ddagger}_{sep}$, and of the energy difference ΔE_{sep}, it appears that there is, if any, only a very small intrinsic activation barrier for the back-reaction, i.e. for the recombination of the free ions to the geminate ion pair. This is in good agreement with the equation developed by Debye[27] and Eigen[28] to describe the diffusion rate constant of two charged species, k_{dif}. For two ions of opposite charge and of the same size, k_{dif} is:

$$k_{dif} = \frac{8RT}{3000\eta}\frac{b}{\exp(b) - 1} \qquad (13)$$

where

$$b = -\frac{e^2}{\epsilon 2 r k_B T}$$

Apart from the activation energy associated with the temperature dependence of the viscosity, the second term of the right-hand side of eq 13 has a temperature dependence that is very small and is negligible considering the variation of ϵ with temperature .

This result implies that there is no proper transition state but rather a state from which the separation process can freely proceed, the solvation energy compensating for the loss of electrostatic stabilization. For the recombination process, the "desolvation" of the free ions is compensated by a gain of Coulomb energy.

The above results are in fair agreement with a recent study of the separation of a tight radical ion pair (*trans*-stilbene/

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fumaronitrile) in alkylnitriles reported by Li and Peters.[5] They fitted a complex reaction scheme, involving tight ion pair, loose ion pair, ground state charge transfer complex, and free ions, to the observed dynamics of the *trans*-stilbene radical cation, and they found a solvent polarity dependent intrinsic separation barrier which would be of the order of 0.16 eV in a solvent having the same polarity as TCE. This is about four times larger than the value reported here for a loose ion pair.

These two different values support the existence of two types of geminate ion pairs: a tight geminate ion pair with a high activation barrier for separation as measured by Li and Peters[5] and a loose ion pair with a lower barrier for separation as reported here. The structure of this loose ion pair must depend strongly on the geometry of the encounter complex formed by the neutral molecules during the ET quenching. This implies that one should only speak of an average interionic distance and about a distribution of ion pair structures. It also implies that some ion pairs may be solvent separated, although our results indicate that the majority are not. The designation *loose* ion pair seems therefore to corresponds better to reality than solvent-separated ion pair. By contrast, the structure of the *tight* ion pair is much better defined as the precursor, the ground state electron donor/acceptor complex having a very precise structure that can be measured for example by X-ray diffraction.[29]

In the present study, the geminate ion pair is formed as a loose ion pair in accordance with the ps transient absorption study of a similar system, benzophenone/DABCO in acetonitrile.[30] There is no spectroscopic or kinetic evidence of the formation of a tight ion pair upon collapse of the loose ion pair. If a tight ion pair was formed, it would live long enough to be observable within the time scale of the experiment, due to the spin forbidden back-ET. Even if its TR^3 spectrum was the same as that of the loose ion pair, the temperature dependence of the separation into free ions would be much larger than that observed. This absence of tight ion pair after diffusional ET quenching is also in accordance with kinetic studies performed with singlet excited states.[3]

Conclusions

Owing to the properties of time-resolved resonance Raman spectroscopy, the dynamics of separation of a loose ion pair into free ions has been measured by observing separately the kinetics of formation of the free ions and that of decay of the ion pair. As the ion pair is formed in the triplet state, its main deactivation pathway to the neutral ground state is the separation into free ions until spin correlation is lost. If this is not the case, triplet ion pairs are regenerated. The dynamics of the ion pair and of the free ions can be modeled by a scheme used to describe delayed fluorescence.

According to the intrinsic activation barrier for the separation of the ion pair into free ions, the center-to-center interionic distance within the ion pair is of the order of 7–8 Å. This value means that the ion pair is not separated by solvent molecules and therefore should not be called a solvent separated ion pair but rather a loose ion pair. The intrinsic activation barrier is due to a loss of electrostatic stabilization upon separation of the ions to a distance of 9.5–10 Å. At this distance, the separation must be large enough to let a solvent molecule or part of it penetrate between the ions and increase its solvation energy. At this stage the association energy of the complex is close to that of the free ions. According to a simple electrostatic model, the energy difference between the free ions and the loose ion pair is slightly endothermic, around 0.04 eV. However, entropy must strongly favor the separation, making the overall process exergonic.

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