Competitive Energy and Electron-Transfer Reactions of the Triplet State of 1-Nitronaphthalene: A Laser Flash Photolysis and Time-Resolved Resonance Raman Study

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A laser flash photolysis and time-resolved resonance Raman study of 1-nitronaphthalene (1NN) in sodium nitrite and *trans*-stilbene (tS) solution, in both polar and nonpolar solvents, is reported. The transient absorption data suggest that 1NN acts as an electron acceptor with nitrite ions and tS in polar solvents but undergoes energy transfer to tS in nonpolar solutions. At high concentrations of tS the electron-transfer reaction leads ultimately to the formation of a dimer radical cation $(tS_2)^{\bullet+}$. We report here the Raman spectrum of the radical anion of 1-nitronaphthalene and the differences in the Raman spectra of the monomeric and dimeric radical cation of *trans*-stilbene in the 1500−1650 cm^{-1} region. The switch from energy to electron transfer when going from nonpolar to polar solutions is discussed in terms of the electronic and nuclear factors that govern these reactions.

1. Introduction

Two predominant mechanisms for the bimolecular quenching of electronically excited molecules are through energy and electron transfer. Models for these reaction processes were developed through the pioneering studies of Weller and co-workers,[1] and most of the emphasis in this field has been placed upon the free energy dependence of the kinetics of the reactions.[2−5] However, owing to the complexity of these intermolecular reactions, many aspects remain unsolved.

The rates of both electron- and energy-transfer reactions, in the weak coupling limit, may be described by a Fermi Golden Rule formalism, which involves an electronic and a nuclear term.[5,6] The former dictates the mechanism of the interaction; the latter incorporates temperature, isotope, and activation energy effects and imposes fundamental differences between the reactions. These are highlighted in the present study, where it is shown that the dielectric constant of the solvent medium determines whether electron or energy transfer will occur.

Most aromatic nitro molecules are known to be nonfluorescent, and their excited states have been the subject of study for many years.[7−9] The quantum yield of triplet formation of 1-nitronaphthalene is high (0.63 in EPA at 77 K[10]) and the buildup time constant of the $T_n \leftarrow T_1$ absorption is fast (<25 ps in polar and nonpolar solvents[11]). While the luminescent properties and the transient absorption of the triplet have been intensively studied,[10−15] much less is known about the radical anion of this molecule.[16,17] On the other hand *trans*-stilbene has been widely used as a model in studies of *cis*−*trans* C═C double-bond isomerization[18−20] and the structure and dynamics of its S_1 and T_1 states, and its radical ions have been the object of a multitude of papers.[21−29]

This work examines the quenching reactions of triplet 1-nitronaphthalene by nitrite ions in acetonitrile/water (sections 3A and 4A) and by *trans*-stilbene in solvents of varying polarities (sections 3B and 4B). We present the resonance Raman spectrum of the 1-nitronaphthalene radical anion and show some of the differences in the resonance Raman spectra of the monomeric and dimeric radical cations of *trans*-stilbene in solution. Finally, in section 5, we discuss the switch from energy to electron transfer when the polarity of the solutions is increased in terms of the electronic and nuclear factors governing these reactions.

2. Experimental Section

(A) Materials. All solvents—carbon tetrachloride [CCl_4] (HPLC grade, Aldrich Chemical Co, Ltd); acetonitrile [MeCN] and 1,2-dichloromethane [DCM] (spectrophotometric grade, Aldrich Chemical Co, Ltd); water (AnalaR, BDH Laboratory Supplies)—were used as received. 1-Nitronaphthalene (1NN, 99% purity), *trans*-stilbene (tS, 96% purity) and sodium nitrite ($NaNO_2$, 97% purity) (all Aldrich Chemical Co, Ltd) were used without further purification.

(B) Methods. The laser flash photolysis setup has been described in detail elsewhere.[30] Briefly, the third harmonic at 355 nm of a Nd:YAG laser (Continuum 8000) was used to excite the sample while the light from a xenon lamp (Applied Photophysics 250 W Xe arc lamp) provided the probing continuum; the transmitted light was dispersed by a Bentham TM300 monochromator on a Hamamatsu IP28 photomultiplier tube. The signal was collected by a digital oscilloscope and transmitted and treated on a PC. The kinetics at the different wavelengths were accumulated over only four laser pulses, so that no detectable degradation was observed for the samples (regularly refreshed) over the recording of the spectra in the ca. 400−650 nm region at 10 nm intervals. The concentrations in the various experiments were as follow: [1NN] = 1 mM, $[NaNO_2]$ = 10 mM, 0 mM ≤ [tS] ≤ 10 mM. All solutions were degassed with solvent-saturated argon (99.998%, Air Products).

The time-resolved resonance Raman (TR^3) spectra of T_1 1NN were obtained using a 90° collection configuration as described previously.[31] The triplet state of 1NN was produced by pumping

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into the S_0-S_1 with 360 nm laser pulses band from an excimer-pumped dye laser (XeCl excimer: Lumonics HX460 or PM840; dye laser: Lambda Physik FL3002, DMQ dye); the S_1 state then undergoes a rapid (<15 ps[11]) and efficient (0.63 triplet yield[10]) intersystem conversion to the first triplet excited state. Diffusion-controlled reactions with NO_2^- lead to electron transfer, and with tS to energy or electron transfer. The samples were then probed at 440 nm by a second excimer-pumped dye laser (XeCl excimer: Lumonics HX460; dye laser: Lambda Physik FL3002, coumarin 120 dye) for the reaction with the nitrite ions or at 480 nm by an optical parametric oscillator/amplifier system pumped by the third harmonic of a Nd:YAG laser (Nd:YAG: Continuum 8000; OPO: Continuum Sunlite) for the reaction with tS. The pump energy was between 0.5 and 1.5 mJ at the sample, and the probe between 0.3 and 1 mJ. Both lasers were pulsed at 10 Hz with pulse lengths 10−15 ns for the dye lasers and 5 ns for the OPO system; the pump−probe time delays were varied between 0−5 ns and 1 μs. Individual spectra were accumulated over 24 000 or 18 000 pulses respectively for the reaction with nitrite and *trans*-stilbene. The TR^3 spectra were obtained by spectral subtraction procedures described in more detail in the Results. For the various experiments the concentration of 1NN varied between 1 and 5 mM, that of $NaNO_2$ was at 10 mM, and that of tS was varied from 0 to 50 mM. All solutions were degassed with solvent saturated argon (99.998%, Air Products), and all samples were flowed to waste.

3. Results

(A) 1-Nitronaphthalene and Sodium Nitrite. Laser flash photolysis and Raman experiments are reported for the reaction of triplet 1NN with sodium nitrite in Ar-saturated solutions at room temperature (293 K). ^{3}1NN was produced by rapid intersystem crossing from the first singlet excited state produced by laser excitation and then diffused to react with the NO_2^- ion in a 95/5 v/v MeCN/water mixture.

Figure 1 shows the transient differential absorption spectra obtained at various time delays after the 355 nm excitation laser pulse. The spectrum obtained just after the excitation pulse is characterized by two absorption bands peaking at ca. 410 and ca. 580 nm and is characteristic of the $T_n \leftarrow T_1$ transitions in polar solvents as reported by Capellos and Porter.[12] This absorption decays on a submicrosecond time scale and its disappearance is accompanied by the formation of new bands peaking at ≤390 nm, ca. 600 nm, and ≥650 nm.

The resonance Raman spectra of the transients formed by the reaction between ^{3}1NN and NO_2^- were recorded by pumping at 360 nm and probing at 440 nm (in the red tail of the highest energy absorption bands of the transients (Figure 1)). The following Raman spectra were recorded: Pump and probe (pump−probe delays: 0−2 μs) irradiated samples of (a) 1NN only, (b) $NaNO_2$ only, and (c) both 1NN and $NaNO_2$ solutions; and probed only samples of (d) only the solvent, (e) 1NN only, (f) $NaNO_2$ only, and (g) both 1NN and $NaNO_2$ solutions.

No bands were visible originating from ground-state 1NN or $NaNO_2$; no effect of the pump beam on $NaNO_2$ could be detected. By normalizing the solvent bands in the spectra of type (a) and (c) to that in spectra (d) and then subtracting (d) from them, we were able to remove the solvent bands (spectra type (a′) and (c′)). There was no observable reabsorption of the Raman-scattered light since the MeCN solvent bands at 917 and 1372 cm^{-1} could be subtracted by the same operation.

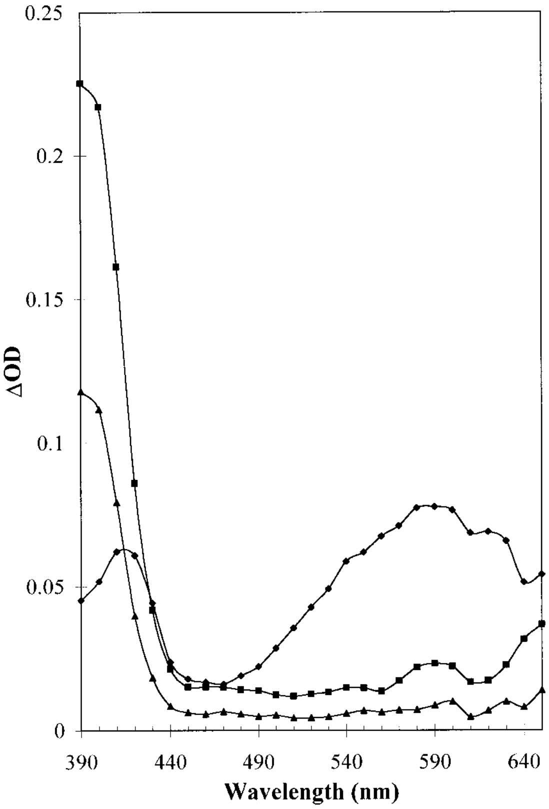

Figure 1. Differential absorption spectra of 1NN (1 mM) + $NaNO_2$ (10 mM) in MeCN.

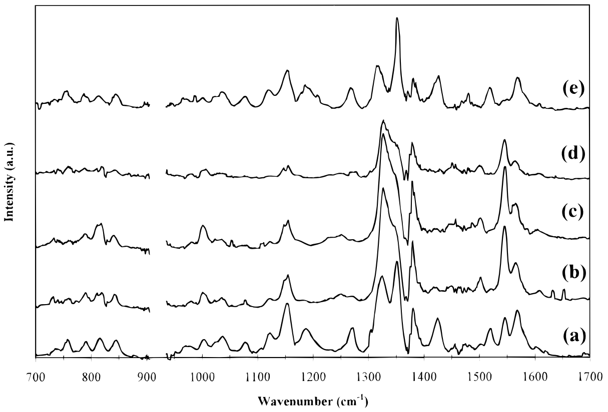

Figure 2. TR^3 spectra of 1NN (3 mM) + $NaNO_2$ (5 mM) at time delays (a) 10 ns, (b) 100 ns, (c) 200 ns, (d) 1 μs, and (e) of 1NN (3 mM). All solutions in MeCN/H_2O (v/v 95/5). Pump 360 nm, probe 440 nm.

The resulting spectra are presented Figure 2, and the vibrational frequencies summarized in Table 1. In sample (c), the evolution of the spectrum at short delay times (<200 ns) is mainly characterized by an increase in the intensities of the bands at 1326, 1502, and 1547 cm^{-1}, the disappearance of the bands at 1272, 1424, and 1518 cm^{-1}, and the transformation of the separate band at 1350 cm^{-1} into a shoulder; at longer delay times we observe only the decay of the spectrum present after 200 ns. In 1NN only solution, we solely observe the decay of the initial spectrum (Figure 2e).

(B) 1-Nitronaphthalene and *trans*-Stilbene. Laser flash photolysis experiments were performed in CCl_4 (nonpolar, $\epsilon = 2.2$), in DCM (medium−low polarity, $\epsilon = 9.0$) and MeCN (polar, $\epsilon = 36$) solutions containing 1 mM 1NN and varying concentrations of tS. The spectra obtained at various time delays are shown in Figure 3a (nonpolar solution) and Figure 3b (polar solution) while typical kinetics are presented in Figure 4.

In nonpolar solution (Figure 3a) the spectrum formed within the laser pulse has maxima at ca. 400 and 540 nm which disappear to give rise to a spectrum whose sole intense

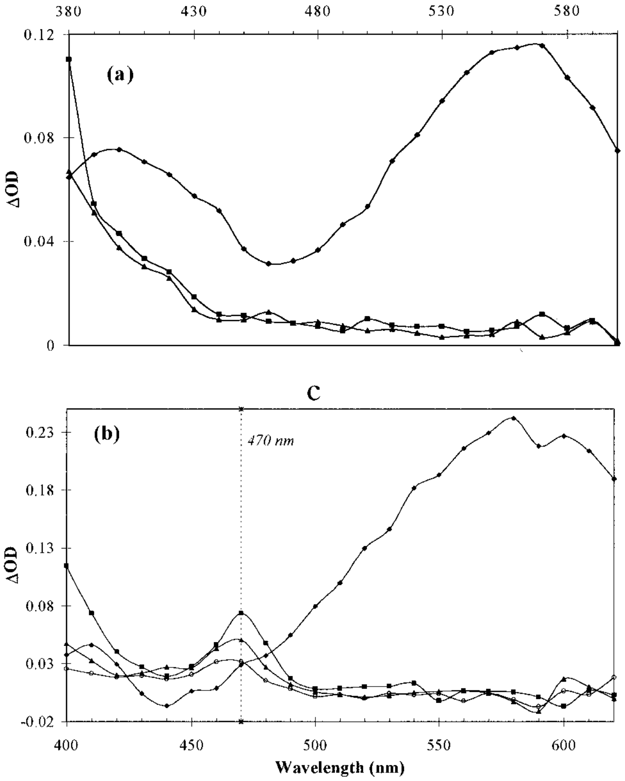

Figure 3. (a) Differential absorption spectra of 1NN (1 mM) + tS (10 mM) in CCl_4 at time delays (◆) 200 ns, (■) 540 ns, and (▲) 2 μs. (b) Differential absorption spectra of 1NN (1mM) + tS (10 mM) in MeCN at time delays (◆) 180 ns, (■) 380 ns, (▲) 1.18 μs and (○) 2.58 μs. Pump 355 nm.

TABLE 1: Raman Frequencies of the Triplet and Radical Anion of 1NN in MeCN/Water (v/v 95/5) between 700 and 1650 cm^{-1}. sh = Shoulder

$\nu(^{3}1NN^{\bullet-})$ (cm^{-1})	$\nu(1NN^{\bullet-})$ (cm^{-1})	$\nu(^{3}1NN^{\bullet-})$ (cm^{-1})	$\nu(1NN^{\bullet-})$ (cm^{-1})
754		1272	1253
790	790	1323	1326
846	845	1350	1351(sh)
972	1002	1383	1382
1022	1030 (br, probably 2 bands)	1424	
1040		1454	
1077			1502
1120	1122 (sh)	1518	
1144	1156		1547
1184	1176 (sh)	1567	1564
	1229 (sh)		1605

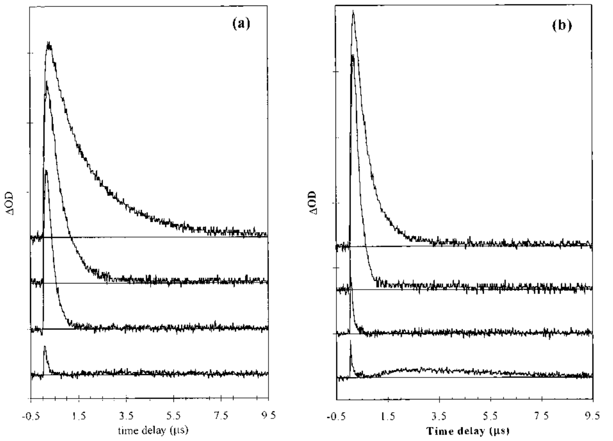

Figure 4. (a) Kinetics at 580 nm of 1NN (1mM) + tS in CCl_4 (from top to bottom 0, 0.33, 1, and 10 mM). (b) Kinetics at 580 nm of 1NN (1mM) + tS in MeCN (from top to bottom 0.33, 1, 4, 10 mM). Pump 355 nm.

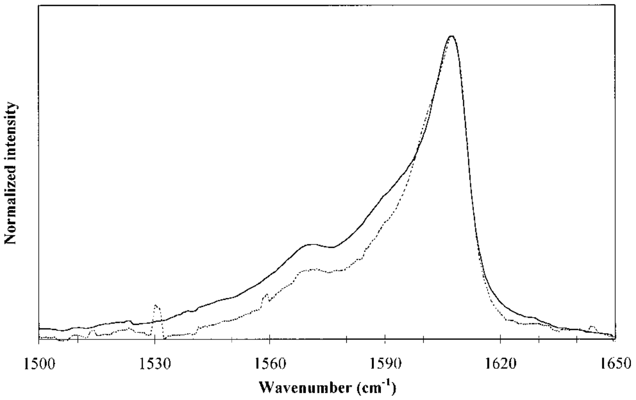

Figure 5. Normalized TR^3 spectra of 1NN (2 mM) + tS (3 mM) in MeCN solution at time delays 50 ns (—) and 1 μs (···). Pump 360 nm, probe 480 nm.

absorption peaks below 380 nm. The kinetics (e.g., Figure 4a) for all wavelengths above 450 nm can be fitted to a monoexponential decay for all concentrations of tS and the lifetime of ^{3}1NN follows eq 1:

$$1/\tau = 1/\tau_T + k_Q[tS] \qquad (1)$$

with $\tau_T = 2.1$ μs and $k_Q = 3.2\ 10^9\ M^{-1}\ s^{-1}$.

In polar solution (Figure 3b) the initial spectrum is similar although the maxima are red-shifted with respect to the corresponding bands in nonpolar solvent. However, its disappearance is now concomitant with the formation of absorption bands at 470 nm and below 400 nm. Furthermore, for higher concentrations of tS the 470 nm band shifts with time toward 465 nm. This is reflected in the kinetic data (Figure 4b), where three consecutive reactions can be detected: first a quenching, followed by the formation of a second transient, and finally the decay of the latter. For some wavelengths the three reactions are easily distinguished and the initial quenching can be reasonably well fitted to eq 1 with $\tau_T = 0.8$ μs and $k_Q = 2.3 \times 10^9\ M^{-1}\ s^{-1}$.

The resonance Raman spectra of the transients formed by the reaction between ^{3}1NN and tS were recorded by pumping at 360 nm and probing at 480 nm. A procedure similar as that described for 1NN and $NaNO_2$ was used to subtract the solvent bands, giving spectra for tS only (f′) and 1NN/tS (c′). Where appropriate, the ground-state bands of tS were removed by subtracting the (f′) spectra from the (c′) one by adjusting the (f′) spectra with a scaling factor. Once again, no effect of different reabsorption with wavelength could be detected.

At short delay times (<50 ns) three bands at ca. 1518, 1570, and 1607 cm^{-1} as well as a shoulder at ca. 1590 cm^{-1} are observed. The intensity of the 1518 cm^{-1} band decreases with time, while the intensities of the others increase; only at longer delays are these other bands seen to decay. However, a close inspection of the shape of the latter bands by normalizing the intensity at 1607 cm^{-1} (Figure 5) reveals that the shoulder at 1590 cm^{-1} disappears, and the ratio of the intensity at 1607 cm^{-1} to that at 1570 cm^{-1} increases with increasing time delays. At high concentration of tS (50 mM) very little change in this ratio could be detected, and the shape of the band was similar to that obtained at long delay times for the solution containing only 3 mM tS.

In CCl_4 and DCM no difference was observed between the probed-only sample and the pumped and probed one: only ground-state tS bands were detected.

4. Discussion

(A) 1-Nitronaphthalene and Sodium Nitrite. 1NN is a nonfluorescent molecule whose first singlet excited state undergoes a rapid intersystem crossing to the triplet excited state.[8] At 77 K in EPA the triplet yield was measured by Hurley and Testa[10] to be 0.63, and the molecule was found to be phosphorescent.[13] Triplet 1NN is a well-known electron acceptor[32,33] and energy donor,[34] and its properties have been extensively studied by laser flash photolysis.[11-15] The UV-visible transient absorption spectrum obtained immediately after the laser pulse (Figure 1) is easily identified as that of the triplet 1NN by comparison with the results of Capellos and Porter.[12] In the presence of nitrite ions this species reacts by electron transfer and forms the radical anion of 1NN ($1NN^{\bullet-}$), as can be seen from the spectrum obtained at longer time delays which is comparable to that obtained electrolytically[16] or by triplet electron transfer from 1,2,4-trimethoxybenzene in acetonitrile.[17]

The Raman spectrum of the triplet 1NN (Figure 2e) in the mixture MeCN/water is similar to that obtained in MeCN only.[35] The Raman spectrum obtained just after the excitation pulse for the solution containing both 1NN and sodium nitrite (Figure 2a) is assigned to a mixture of the triplet and the radical anion; it can be reconstructed by adding the spectrum of the triplet (Figure 2e) to the spectrum obtained at longer pump-probe delays (multiplied by a coefficient less than 1), which is ascribed to the radical anion (Figure 2b-d). The spectrum of the anion is characterized by intense bands at 1326 (with a strong shoulder at ca. 1350 cm^{-1}), 1382 and 1547 cm^{-1}, medium intensity bands at 815, 1002, 1156, and 1564 cm^{-1}, as well as various low-intensity bands (see summary in Table 1). This spectrum is reasonably similar to that obtained for the triplet, which suggests that its structure is not too different from that of the triplet.

(B) 1-Nitronaphthalene and *trans*-Stilbene. By pumping solutions containing both 1NN and tS at 355 or 360 nm, we mainly excite the 1NN $S_1 \leftarrow S_0$ electronic absorption band owing to the small extinction coefficient of tS (at 350 nm $\epsilon < 250\ M^{-1}\ cm^{-1}$). Despite this low absorption, some fluorescence from tS is observed in the laser flash photolysis experiment at very short delays.

Low-Polarity Solvents. The transient differential absorption experiment in CCl_4 shows only two regimes, whatever the concentration of tS used (Figures 3a and 4a): (i) The decay of the initial excited species, identified as the triplet of 1NN by its absorption peaks at 400 and 540 nm,[12] together with the appearance of a new species possessing an absorption maximum below 380 nm (decreasing monotonically up to 430 nm). (ii) The decay of this second transient on a microsecond time scale. Such an absorption has been observed previously by Görner and Schulte-Frohlinde,[28] who studied the T_1 state of tS by optical absorption methods. Furthermore, the lifetime of ^{3}tS has been reported as 14 μs in nonpolar solvents.[36] We therefore attribute the second transient observed in our experiment to the first triplet excited state of tS, formed by diffusion-controlled energy transfer from the T_1 state of 1NN.

The quenching rate of ^{3}1NN is estimated from the pseudo-first-order decays at 580 nm (Figure 5a) to be $3.2 \times 10^9\ M^{-1}\ s^{-1}$, which is close to the diffusion limit. No transients were observed in the TR^3 experiment, which is expected considering that a high concentration of tS was used (which means a very rapid quenching of the triplet 1NN), and that the triplet tS does not absorb at all at the probe wavelength of 480 nm (and the Raman signal of such a species is therefore not enhanced).

The laser flash photolysis and TR^3 experiments performed on solutions in DCM solvent yielded similar results to those presented in detail above. Hence in low-polarity solvents, the primary process observed is triplet-triplet energy transfer:

$$^{3}1NN + tS \rightarrow 1NN + {}^{3}tS \qquad (R1)$$

Polar Solvents. In contrast to the results in the nonpolar solvents, the laser flash photolysis experiment for MeCN solutions shows that although the triplet 1NN initially formed is still quenched by tS, the new species formed are now characterized by two absorption bands peaking at 470 nm and below 400 nm (Figure 3b). Furthermore, a second reaction follows the quenching of the triplet 1NN at high concentrations of tS (Figure 4b, bottom) and leads to a small hypsochromic shift in the differential absorption spectrum. A similar behavior was observed by Akaba et al.[37] in the electron-transfer reaction between tS and 2,4,6-triphenylpyrilium salts. These authors attributed the second reaction to the formation of a dimer radical cation consisting of the monomer radical and a ground-state molecule. Such an assignment is supported by a more recent study by Kuriyama et al.,[38] who showed by pulse radiolysis on highly concentrated solutions that $tS^{\bullet+}$ reacts with tS to form a dimer radical cation. They observed an associated shift of the visible absorption from 490 to 480 nm in DCM solvent during the dimerization process.

In the absence of solvent, a dimer radical cation species is expected to be significantly stabilized with respect to a monomeric species owing to charge delocalization effects.[39] The origin of such a stabilization derives from long-range charge polarization interactions as well as the key, short-range charge-transfer interactions. In the presence of polar solvent there will be competition between this stabilization (i.e., purely electronic) and the difference between dielectric stabilization of the monomer compared to the dimer (which, in the Onsager treatment[40] amounts to the difference in cavity radii and should be less significant for large molecules).

We therefore attribute the absorption at 470 nm to the monomer radical cation $tS^{\bullet+}$ and the 465 nm absorption to the dimeric form $(tS_2)^{\bullet+}$. The absorption in the UV part of our spectrum could arise either from the presence of the 1NN radical anion or from some triplet tS. Our failure to distinguish the bands in the 600-700 nm range of $1NN^{\bullet-}$ could be due to the low absorption of the radical anion in this region and the lesser amount of $1NN^{\bullet-}$ produced by tS compared to NO_2^- in section 4A. The quenching rate constant of the triplet 1NN in MeCN, obtained from the kinetics at 580 nm (Figure 4b), was determined to be $2.3 \times 10^9\ M^{-1}\ s^{-1}$, slightly less than that obtained previously for the energy-transfer reaction in nonpolar solution but similar to that measured by Martins et al.[17] for the electron-transfer reaction of ^{3}1NN from halide and pseudohalide ions in water.

In a recent publication,[41] Kuriyama and Oishi were able to present Raman spectra for the monomer and dimer radical cation of tS produced by continuous UV irradiation in boric acid glasses. They observed a change in the ratio of the intensities of the 1604 and 1564 cm^{-1} bands—the former intensity increasing more quickly than the latter's—upon formation of the dimeric species when they used high concentration of tS but not when they used low concentration. In this matrix, at low concentration of tS they obtained a similar spectrum when the monomer radical cation was formed by electron transfer to dicyanoanthracene. They consequently argued that the spectra reported earlier by Hub et al. for $tS^{\bullet+}$ in solution[29] may well be in fact that of the dimeric species, since these authors were using high concentrations of tS (50 mM) in their experiments. To investigate this hypothesis, we performed TR^3 experiments on solutions containing 2 mM 1NN and 3 or 50 mM tS in MeCN.

As expected from the transient absorption experiments, bands in the 1500−1650 cm^{-1} region different from those of the ground state were observed for a 2 mM 1NN, 3 mM tS solution. At very short pump−probe time delays, bands originating from both 1NN triplet (e.g., 1520 cm^{-1})[35] and the tS radical cation species are evident. The former bands disappear within 50 ns, and only bands at 1570 and 1607 cm^{-1} as well as a shoulder at ca. 1590 cm^{-1} remain. Furthermore, the relative intensities of these bands were found to change with time (Figure 5): the band at 1607 cm^{-1} became more intense relative to the band at 1570 cm^{-1}, while the shoulder at ca. 1590 cm^{-1} disappeared. On the other hand, for the solution containing 50 mM tS very little change could be distinguished and the shape of the band was similar to that oberved for the previous solution at long time delays.

This behavior is similar to that observed by Kuriyama and Oishi in boric acid matrixes.[41] Moreover, Schneider et al.,[42] when calculating force field constants and vibrational frequencies for the radical ions of various stilbenes, calculated a frequency at 1598 cm^{-1} for the radical cation of tS, which was not observed by Hub et al.,[29] but can be assigned to the shoulder we observed at ca. 1590 cm^{-1} at short delay times for the solution containing a medium concentration of tS. Kuriyama and Oishi did not observe any band near 1590 cm^{-1}, probably owing to an overestimation of the intensity of the ground-state bands (which can be seen as troughs in the published spectrum[41]). We therefore assign the spectrum containing the bands at 1570 and 1607 cm^{-1} and the shoulder at 1590 cm^{-1} to the monomer radical cation $tS^{\bullet +}$ (or at least a mixture of monomer and dimer) and the spectrum containing only the bands at 1570 and 1607 cm^{-1} to the dimeric radical cation $(tS_2)^{\bullet +}$. The multiple overlapping bands structure required to fit the spectral profile did not allow the results to be quantified.

Hence in polar solvents the above results suggest that the most important reactions are (R2) and (R3), as well as (R1):

$$^{3}1NN + tS \rightarrow 1NN^{\bullet -} + tS^{\bullet +} \tag{R2}$$

$$tS^{\bullet +} + tS \rightarrow (tS_2)^{\bullet +} \tag{R3}$$

5. Competitive Energy- and Electron-Transfer Reactions

(A) Theory. The competition between energy[43,44] and electron transfer[45,46] reactions observed in the present work is examined further in this section. We establish here a nexus as well as a key difference between the phenomena, enabling a more detailed interpretation of the results. A competition between intramolecular photoinduced electron-transfer and singlet−singlet energy-transfer reactions by solvent "tuning" has been reported recently.[47]

It is known that the mechanism for triplet−triplet energy transfer differs from that for singlet−singlet energy transfer.[48,49] The difference lies in the form of the electronic coupling between donor and acceptor, which has been investigated in detail recently.[50−53] The most significant conclusions for the purposes of the present work is that the form of the electronic couplings that promote singlet−singlet and triplet−triplet energy transfer and that are dependent upon orbital overlap between donor and acceptor are isomorphic. Moreover, the most significant contribution to these interactions is not from the Dexter exchange integral but arises from the *through-configuration interaction*. The form of this interaction enables us to make a formal connection between energy-transfer and electron-transfer couplings and distance dependences. Such a relationship was first suggested by Closs et al.[54,55] and was firmly demonstrated recently.[56]

The relationship between the primary couplings which promote photoinduced (triplet state) electron transfer (V) and triplet−triplet energy transfer (T) between chromophores A and B is summarized in eq 2 (strictly valid for $V << A$):

$$^{3}T(A^{*}B \rightarrow AB^{*}) \approx [V(A^{*}B \rightarrow A^{+}B^{-})V(A^{*}B \rightarrow A^{-}B^{+})]/A \tag{2}$$

where A is the energy difference between locally excited and charge-transfer states. Hence a correlation is expected between the rates of energy and electron transfer as a function of separation, orientation, and electronic state.

The rate of energy transfer in the weak coupling limit may be expressed as in eq 3:

$$w = \frac{1}{ch^2}|T|^2 \int_0^\infty d\nu\, f_D(\nu)\, a_A(\nu) \tag{3}$$

where T is the electronic coupling and the latter term is the spectral overlap integral between donor emission and acceptor absorption (on a wavenumber scale).

Similarly, according to Marcus−Hush theory,[57−59] the rate of electron transfer in this limit is written as in eq 4:

$$k_{ET} \approx \frac{2\pi}{h}|V|^2(\mathrm{FCWD}) \tag{4}$$

with

$$(\mathrm{FCWD}) \approx (4\pi\lambda_s k_B T)^{-1/2} \exp(-\Delta G^{\ddagger}/k_B T) \tag{5}$$

where

$$\Delta G^{\ddagger} \approx (\Delta G + \lambda_s)^2/4\lambda_s - V \tag{6}$$

with V on the order of 0.02 eV is generally negligible.

The free energy of the electron-transfer reaction may be estimated using the theory of Rehm and Weller[60] by eq 7, and

$$\Delta\Gamma \approx E_{1/2}^{ox}(\Delta) - E_{1/2}^{rod}(A) - E_T + \frac{e^2}{4\pi\epsilon_0}\left\{\frac{1}{2r_+}\left(\frac{1}{\epsilon} - \frac{1}{\epsilon'}\right) + \frac{1}{2r_-}\left(\frac{1}{\epsilon} - \frac{1}{\epsilon'}\right)\right\} - \frac{e^2}{4\pi\epsilon R} \tag{7}$$

$$\lambda_s \approx \frac{e^2}{4\pi\epsilon_0}\left(\frac{1}{2r_+} + \frac{1}{2r_-} - \frac{1}{R}\right)\left(\frac{1}{n^2} - \frac{1}{\epsilon}\right) \tag{8}$$

the solvent reorganization energy may be approximated by eq 8, where $E_{1/2}^{red}(A)$ is the halfwave potential for reduction of the electron accceptor (measured in solvent with dielectric constant ϵ'), $E_{1/2}^{ox}(D)$ the half-wave potential for oxidation of the donor (measured in solvent with dielectric constant ϵ''), E_T is the energy of the triplet. The solvent has refractive index n and dielectric constant ϵ, r_+ and r_- denote the radii of cation and anion respectively and R is their separation.

We emphasize that the above equations are very approximate but can serve as a useful guide to the relative probabilities of electron-transfer reactions. In the present work we use them as follows: If the free energy of the reaction from eq 7 is positive, then the electron-transfer reaction will probably not occur. If it is found to be negative, then we examine the activation barrier for the reaction via eq 6.

(B) Application to ^{3}1NN Reactions. The present study suggests that in nonpolar (CCl_4) or slightly polar (DCM) solvents the triplet 1NN reacts with tS by energy transfer, whereas in polar solution (MeCN) electron transfer is the dominant reaction. Tinkler et al.[33] have reported a similar observation for the reaction of ^{31}NN with various carotenoids (septapreno-β-carotene and 7,7′-dihydro-β-carotene).

By inspection of eq 3, it is clear that triplet−triplet energy transfer from 1NN to tS is possible in both polar and nonpolar solvents. The energies of the triplet states of 1NN and tS, relative to the ground states have been measured as respectively 2.39 eV[13] (in a polar medium) and 2.14 eV[61] (both polar and nonpolar media), and ^{31}NN is polar (ca. 5 D[12,35]). Hence we infer that the spectral overlap integral is different from zero and may exhibit a small solvent dependence owing to solvatochromism. It seems reasonable therefore to attribute the observed solvent dependence of the competition between energy and electron transfer to the free energy and activation barrier dependences of the electron-transfer reaction only. We discuss this further below.

No evidence was found that the energy transfer was the result of an electron transfer followed by a very fast recombination of the geminate ion pair in nonpolar solvents; indeed no absorption bands and none of the vibrational bands characteristic of $tS^{\bullet+}$ were detected in nonpolar solvents as would be expected[62,63] if an exciplex with some charge-transfer character was formed. The radical ions are observable only in polar solutions where the free ions are more stabilized. Kuzmin et al.[62] showed that even in nonpolar solvents, if the encounter complex has some charge-transfer character, the UV−visible spectra of the radical ion species can be detected, while Tahara and Hamaguchi[63] were able to observe the increasing charge-transfer character in the TR^3 spectra of chloranil/alkylbenzene exciplexes when the donor strength of the alkylbenzenes increased.

Differences in the reactions in solvents of variable polarity may be governed by the thermodynamics of the reactions or by the nature of the triplet state of 1NN. The nature of the latter species has been the object of many hypotheses: while some authors[13−15] propose a $\pi-\pi^*$ state, sometimes with a low-lying n−π^* inducing vibronic coupling,[45] others suggest that it is $\pi-\pi^*$ with some measure of intramolecular charge-transfer character[46,47] or even that the lowest triplet is n−π^* in non polar solvents and $\pi-\pi^*$ with a charge-transfer character in polar solvents.[9,11] We have recently performed[35] a TR^3 study of the triplet state of 1NN in various solvents as well as detailed ab initio calculations which showed that although the lowest triplet state is of $\pi-\pi^*$ nature, the second triplet is of n−π^* type and the latter is estimated to lie less than 0.1 eV above the former in the gas phase but has a much lower dipole moment. So we may expect either some mixing between the two states or vibronic coupling in nonpolar solvents but less so in polar solvents where the $\pi-\pi^*$ polar triplet would be much more stabilized due to its dipolar nature. By inspection of the form of eq 2, however, it is not expected that such factors could differentially influence the rates of electron and energy transfer.

To examine the thermodynamic factors for the electron-transfer reaction between 1NN and tS, we use the following values for the parameters in eqs 5−7: $E_{1/2}^{\text{red}}(1\text{NN}) = -0.97$ V (vs SCE in dimethylformamide[64]), $E_{1/2}^{\text{ox}}(\text{tS}) = +1.43$ V (vs SCE in MeCN[64]), $E_\text{T}(1\text{NN}) = 2.39$ eV, $r_+(\text{tS}) = 4$ Å, $r_-(1\text{NN}) = 3$ Å, and $R = 5$ Å for 1NN and tS, and $\epsilon = 36$, $n = 1.36$ for MeCN, $\epsilon = 2.2$, $n = 1.46$ for CCl$_4$, $\epsilon = 9.0$, $n = 1.42$ for DCM, and $\epsilon = 37$ for DMF. Consequently it is found that approximate free energies for the reaction in various solvents are 0.50 eV (CCl$_4$), 0.04 eV (DCM), and −0.07 eV (MeCN). Thus it is expected that the electron-transfer reaction is possible only in quite polar solvent (MeCN), with an activation barrier determined by $\Delta G^\ddagger = 0.14 - V$ eV. This is consistent with our experimental observations.

A very different situation occurs with the carotenoids: if we consider the triplet energies and the oxidation potentials of the molecules used by Tinkler et al.[33] to be similar to that of β-carotene (both will probably be 0.1−0.2 eV higher), we can see that the lowest carotenoid triplet state should lie ca. −1.49 eV below that of 1NN ($E_\text{T}(^3\beta\text{-carotene}) = 0.91$ eV in a nonpolar solvent[65] and 0.88 eV in a polar solvent[66]). If we take $E_{1/2}^{\text{ox}}(\beta\text{-carotene}) = +0.76$ V (vs SCE in THF[83]) and $r_+(\text{carotenoid}) = 6$ Å, $\epsilon = 33$, $n = 1.33$ (methanol), $\epsilon = 2.02$, $n = 1.42$ (cyclohexane), and $\epsilon = 7.6$ (THF), we obtain the following free energies and reorganization energies for the solvents used by Tinkler et al.:[33]

$$\text{cyclohexane:}\quad \Delta G = -0.53\ \text{eV},\qquad \lambda_\text{s} = 0.001\ \text{eV},\quad \Delta G^\ddagger = 117 - V\ \text{eV}$$

$$\text{methanol:}\quad \Delta G = -0.86\ \text{eV},\qquad \lambda_\text{s} = 0.39\ \text{eV},\quad \Delta G^\ddagger = 0.14 - V\ \text{eV}$$

In this example the energy transfer was observed in both polar and nonpolar solvents, with yields of 1 and 0.65 in cyclohexane (nonpolar) and methanol (polar), respectively.[33] However, although the electron transfer is predicted to be exothermic ($\Delta G < 0$), radical ions were only detected in methanol, not in cyclohexane. The reason becomes evident upon inspection of the predicted barriers for the reaction (see values of $\Delta G^\ddagger$ above).

6. Conclusion

We have shown that in MeCN/water mixture the triplet state of 1NN undergoes an electron-transfer reaction with nitrite ions resulting in the formation of the radical anion $1\text{NN}^{\bullet-}$ and we have presented the resonance Raman spectrum of this species in the 700−1700 cm^{-1} range. We have also studied the quenching of ^{31}NN by tS in various solvents. By recording the resonance Raman spectra of solutions containing various amount of tS we have been able to demonstrate some subtle differences in the vibrational spectra of the monomeric and dimeric radical cation species of tS in solution. Moreover, by comparing the reactions occurring in solvents of different polarities, it was found that energy- and electron-transfer reactions compete, with their relative probabilities determined primarily by the thermodynamics of the electron transfer, in accord with Marcus−Hush theory. A related example observed between 1NN and carotenoids[33] was discussed also in this framework. A thorough study of the triplet 1NN is the subject of further work.[35]

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