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Specific solvent effects on the charge separation efficiency in photoinduced electron transfer processes

Graciela P. Zanini, Hernán A. Montejano, Carlos M. Previtali*

Departamento de Química y Física, Universidad Nacional de Río Cuarto, 5800 Río Cuarto, Argentina

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Abstract

The photoinduced electron transfer (PET) quenching of singlet excited pyrene and 1,2,5,6-dibenzanthracene (DBA) by 3-cyanopyridine and *o*-dicyanobenzene, respectively, was investigated in several protic and aprotic solvents. The triplet quenching of DBA by *p*-nitrobenzaldehyde was also studied in the same solvents. In all cases free radical ions yield were measured by laser flash photolysis. In the case of the triplet reaction, forward electron transfer quenching rate constants were also measured. Charge separation efficiencies, φ_{cs} were determined from the free radical ions yields. The solvent effect on φ_{cs} in singlet state PET may be explained in aprotic solvents by a model based on the macroscopic properties of the solvent. For alcohols the efficiencies are lower than the corresponding quantities for aprotic solvents of similar viscosities and dielectric constant. For triplet mediated PET reactions, the forward rate constants are scarcely sensitive to the solvent, while strong specific solvent effects are important in determining the back-electron-transfer to ground state.

Keywords: Photoinduced electron transfer; Charge separation efficiency; Solvent effects

1. Introduction

An important issue in bimolecular photoinduced electron transfer (PET) reactions is the efficiency of the charge separation, that is the yield of free radical ions (FI). The quantum yield of FI formation results from a competition between the several decay processes of the radical ion pair (RIP) that is formed in the initial electron transfer step [1,2]. The dynamics of these processes in turn depends upon the nature of the RIP and the medium in which it is generated [3,4]. According to the molecular structure of the reactants and the solvent, the RIP may be a contact ion pair (CRIP) where the partners are at molecular contact, or a solvent separated ion pair (SSRIP). For a given system both CRIP and SSRIP may be formed and interconvert [5]. They may lead to FI by an escape process that depends mainly on the viscosity and dielectric properties of the solvent. This competes with the back-electron-transfer reaction to produce the reactants in the ground state or one of them in an excited state lower in energy than the starting state.

When the precursor is the excited singlet, it is commonly observed that the triplet state is formed in high yield in the back-electron-transfer process [5–7]. On the other hand, when the precursor state is the lower triplet, only FI are observed after the decay of the RIP. It is commonly accepted that, due to the spin forbiddeness of the back-electron-transfer to ground state, high yields of free ions would be observed in this case [8]. However, in some cases low quantum yields of FI has been observed in PET reactions originated in the triplet state [9]. Conversely, although a large back recombination rate is expected for singlet state originated RIPs, high quantum yields were found for FI in some excited singlet PET reactions [10].

Several papers have dealt with the medium and structural effects on the charge separation yield in PET reactions. The energy gap law was used to explain the structural effects, which result in changes in the driving force for both the forward and back-electron-transfer processes [11]. However, some specific structural effects, such as the nature of the MO, whether n or π, involved in the electron transfer [12,13] or symmetry factors [14] may influence the kinetics of the processes from the RIP. The medium effects, specially those related to reactions carried out in organized molecular assemblies, was also extensively investigated [15]. In homogeneous solvents it was found that the efficiency of charge separation strongly increases with an augment of the dielectric constant, while the forward rate constant for the electron transfer quenching reaction was scarcely affected [6].

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* Corresponding author.

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However, less attention was paid to the effect of solvent in reactions performed in media of similar polarity but with distinct molecular structure. We have found [9] widely different charge separation yields in the quenching of 1,2,5,6-dibenzanthracene (DBA) triplet state by nitrobenzenes for methanol and acetonitrile, two solvents of very similar macroscopic dielectric constant and viscosity. The FI yield was >5 times larger in methanol than in acetonitrile. Later, we carried out a study in these two solvents of the charge separation efficiency in the singlet quenching of polycyclic aromatic hydrocarbons by several electron acceptors [16]. In this case we found the same trend for the quenching by nitrobenzenes, but the opposite was the case when the acceptors were cyanobenzenes. So, it seems that specific solvent effects are important in controlling the yield of free ions, and in turn, these specific effects depend upon the structure of the reaction partners. In order to obtain a better understanding of the solvent dependence of the charge separation efficiency in PET reactions, we undertook a study of the effect of a series of protic and aprotic solvents of amply varying dielectric properties on the FI yield of singlet and triplet state processes. In this paper we present results for the singlet quenching of pyrene (Py) by 3-cyanopyridine (3CNP) and of DBA by *o*-dicyanobenzene (*o*-DCNB). For these two systems we have previously investigated the solvent effect on the forward electron transfer rate constant [17] and found that the observed dependence can be explained by the classical or semi-classical theories for electron transfer reactions with a dielectric continuum model for the solvent. However, most of the research on the solvent effect on PET reactions was carried out on singlet processes and much less attention was paid to the triplet reactions. Here, we also studied the triplet quenching of DBA by *p*-nitrobenzaldehyde (*p*-NBz). Both the forward electron transfer quenching and the FI yield were measured in several solvents.

2. Experimental details

Propionitrile (PrCN) from Fluka AG, was distilled and passed trough a silica gel column before use. Ethanol (EtOH), from Merck was purified by distillation. The other solvents: acetone, ethyl acetate (EtAc), 2-propanol (2-PrOH), acetonitrile (MeCN), dimethylsulfoxide (DMSO) and methanol (MeOH) were HPLC grade and were used without further purification. Pyrene (Py) from Merck was purified by recrystallization from methanol. DBA was Fluka puriss. *o*-DCNB, 3CNP and *p*-NBz were from Aldrich. All of them were used as received. Fluorescence spectra were determined with a Spex Fluoromax spectrofluorometer. Transient absorption experiments were performed with a nitrogen laser as previously described [9]. The samples were deoxygenated prior to use by bubbling with high purity argon. Quantum yields of transient species were determined by actinometry with zinc tetraphenyl porphyrin (ZnTPP) in benzene. The triplet yield of ZnTPP was measured at 470 nm immediately after the laser pulse. Values of $7.3\times10^4\,\mathrm{M^{-1}\,cm^{-1}}$ and 0.83 were used for ε_T and ϕ_T of ZnTPP, respectively [18]. All the solutions were matched in absorbances at 337 nm. For the triplet of Py the absorption coefficient was taken as $30\,000\,\mathrm{M^{-1}\,cm^{-1}}$ at the maximum [19] and $48\,000\,\mathrm{M^{-1}\,cm^{-1}}$ was used for the pyrene radical cation [10]. The DBA radical cation was measured at 510 nm with absorption coefficients of $10\,000\,\mathrm{M^{-1}\,cm^{-1}}$ [9]. In the singlet quenching of DBA by *o*-DCNB the determination of the radical ions' absorbance was complicated by the simultaneous absorption of DBA triplet state in the same region of the radical cation. Therefore, the absorbance at 380 nm was used with absorption coefficients of 11 000 and $6000\,\mathrm{M^{-1}\,cm^{-1}}$ for the radical cation of DBA and the radical anion of *o*-DCNB, respectively [20]. The absorption coefficients were assumed to be the same in all the solvents. Although there are few reliable reports on absorption coefficients of radical ions in different solvents, the few existing data [21–24][1] confirm that the error that may be introduced in this way is in any case of the same order that the experimental uncertainty in the measurements of the relative transient absorptions.

3. Results and discussion

3.1. Singlet state processes

The quenching of excited singlet of Py by 3CNP and of DBA by *o*-DCNB are well-known electron transfer processes. In polar solvents free radical ions are observed by laser flash photolysis for both systems. Even in the less polar solvent investigated, ethyl acetate, exciplex emission was not detected. In this solvent the total electron transfer nature of the quenching process is evidenced by the effect of adding tetrabutylammonium perchlorate. In the presence of this salt the radical cation of Py is formed in high yield, confirming the total charge transfer mechanism in this low polarity solvent [17]. Moreover, the plots of τ_0/τ remain linear in all cases, without indication of downward curvature that could be taken as an evidence of exciplex formation in the absence of its emission [25–27]. Therefore, the quenching processes may be summarized by Eqs. (1) and (2)

$$^1\mathrm{Py}^* + \mathrm{3CNP} \rightarrow \mathrm{Py}^{\bullet +} + \mathrm{3CNP}^{\bullet -} \tag{1}$$

$$^1\mathrm{DBA}^* + o\text{-}\mathrm{DCNB} \rightarrow \mathrm{DBA}^{\bullet +} + o\text{-}\mathrm{DCNB}^{\bullet -} \tag{2}$$

The free radical ions yield is strongly dependent on the solvent properties. In Fig. 1 the transient absorption spectra for the system Py-3CNP are shown in acetone and ethyl acetate. In the absence of the quencher the only absorbing

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[1] Rodgers [22] gives ε=11 900 (±20%) $\mathrm{M^{-1}\,cm^{-1}}$ for biphenyl radical cation at 680 nm in acetone to be compared with $14\,500\,\mathrm{M^{-1}\,cm^{-1}}$in acetonitrile at 670 nm, informed by Gould et al. [23]. Iwamura and Eaton [24] also report 12 000 (±1000) $\mathrm{M^{-1}\,cm^{-1}}$for biphenyl radical cation in Ar/$\mathrm{CH_2Cl_2}$ at 20 K.

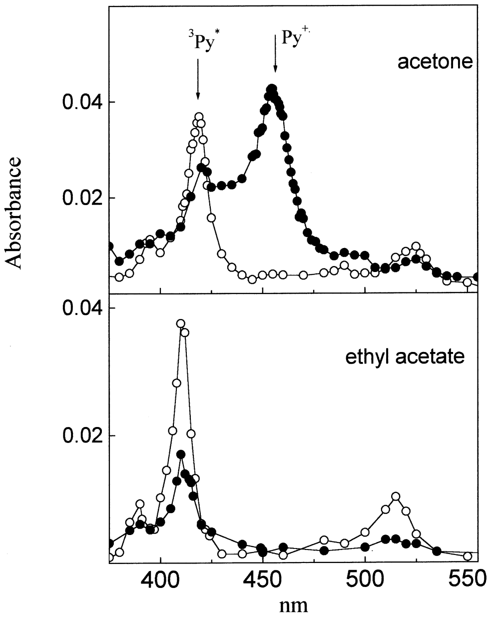


Fig. 1. Transient absorption spectra for the system Py-3CNP in acetone and ethyl acetate, taken 4 μs after the laser pulse in the absence (○) and in the presence (●) of the quencher. The concentration of 3CNP was 0.4 M in acetone and 0.6 M in ethyl acetate.

species in both solvent, after the singlet decay, is the triplet state with λ_{max}~420 nm in acetone and 414 nm in EtAc. In acetone, in the presence of the quencher at a concentration that more than 95% of the excited singlets are intercepted, a new transient absorption with λ_{max}=455 nm is present. This new band may be assigned to the pyrene radical cation. On the other side, in ethyl acetate the triplet remains as the only transient species after the quenching. In spite of the high fraction of singlets quenched in acetone, the triplet absorption remaining after the quenching event is clearly noticeable. Therefore, an important fraction of the quenching events must lead to the triplet state. This is not unexpected, since the energy level of Py triplet (2.10 eV) lies below the energy level of the RIP (3.23 eV).

Similar results were obtained for the system DBA–*o*-DCNB. In Fig. 2 the transient absorption spectra in three solvents are presented for this system. In the presence of the quencher the bands of DBA radical cation at 380 and 510 nm can be clearly identified. However, even when the quencher concentration is such that more than 95% of the singlets are quenched, it can be seen that the triplet state, absorbing at ca. 540 and 570 nm is still present in all cases. Therefore, in addition to Reactions (1) and (2) the following quenching process must be taken into consideration

$$^1\mathrm{Py}^* + 3\mathrm{CNP} \rightarrow {}^3\,\mathrm{Py}^* + 3\mathrm{CNP} \qquad (3)$$

$$^1\mathrm{DBA}^* + o\text{-}\mathrm{DCNB} \rightarrow {}^3\,\mathrm{DBA}^* + o\text{-}\mathrm{DCNB} \qquad (4)$$

From the laser photolysis experiments, free radical ions quantum yields, Φ_{ion} were obtained as described in the experimental section. The corresponding charge separation efficiency, φ_{cs} were derived from the following equation

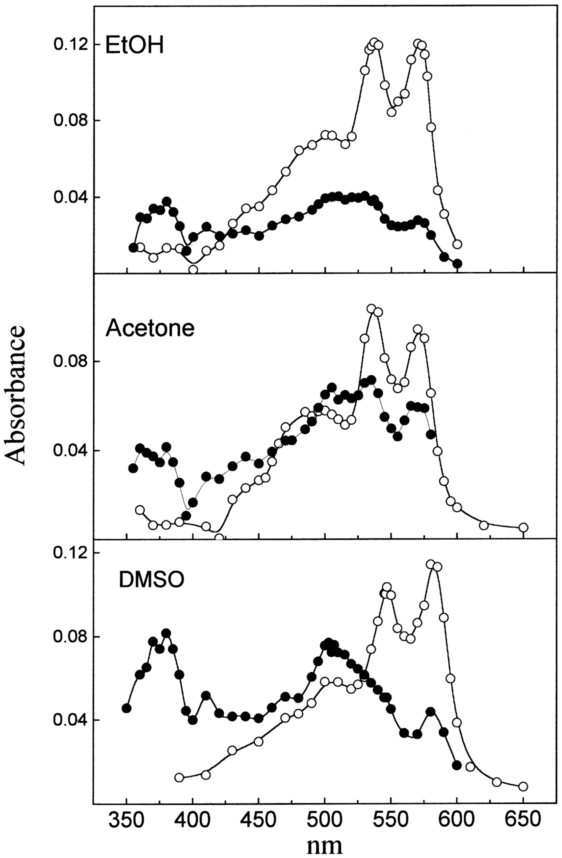


Fig. 2. Transient absorption spectra for the system DBA–*o*-DCNB at 2 μs after the laser pulse in the absence (○) and in the presence (●) of the quencher. The concentration of *o*-DCNB was 0.066 M in EtOH, 0.15 M in acetone and 0.1 M in DMSO.

$$\varphi_{cs} = \Phi_{ion}\left(\frac{1 + k_q\tau_0[Q]}{k_q\tau_0[Q]}\right) \qquad (5)$$

where k_q and τ_0 are the singlet quenching rate constant and the singlet lifetime in the absence of quencher, respectively. The results are collected in Table 1. The solvents in the table are grouped according to its hydrogen bonding capability. It can be seen that for aprotic solvents the efficiencies increase with the solvent polarity, while for hydrogen bonding solvents the values are lower than those in aprotic solvents of similar dielectric constants.

The experimental results are better discussed in terms of the Gibbs energy changes for the various electron transfer processes depicted in the Scheme 1, where k_{et} stands for the forward electron transfer rate constant, $k_b(G)$ and $k_b(T)$ are rate constants for back-electron-transfer reactions to ground and triplet states, respectively, and k_{esc} is the diffusive rate constant for the charge separation process. In the scheme ($\mathrm{D}^{\bullet+}\ldots\mathrm{A}^{\bullet-}$) represents the RIP formed in the initial electron transfer step.

Table 1
Charge separation efficiencies and back-electron-transfer rate constants

Solvent	Py-3CNP		^{1}DBA*–*o*-DCNB		^{3}DBA*–*p*-NBz		
	φ_{cs}	k_b (s^{-1})	φ_{cs}	k_b (s^{-1})	k_q ($M^{-1}s^{-1}$)	φ_{cs}	k_b (s^{-1})
EtAc (6.02)[a]	0.0		0.0		1.8×10^9	0.0	
EtAc-MeCN (9:1) (11.7)	0.0		0.0		2.0×10^9	0.0	
EtAc-MeCN (7:3) (19.05)	0.17	1.1×10^9	0.58	1.7×10^8			
Acetone (20.70)	0.25	1.1×10^9	0.80	8.7×10^7	3.1×10^9	0.11	2.7×10^9
PrCN (28.86)					5.9×10^9	0.063	8.2×10^9
MeCN (35.94)	0.49	1.0×10^9	1.0		5.7×10^9	0.10	8.6×10^9
DMSO (46.45)	0.41	3.4×10^9	1.0				
2-PrOH (19.92)	0.14	3.0×10^8	0.38	7.6×10^7	1.7×10^9	0.44	8.9×10^8
EtOH (24.55)	0.072	1.9×10^9	0.49	1.6×10^8	4.1×10^9	0.38	2.4×10^8
MeOH (32.66)	0.040	1.3×10^{10}	0.69	2.5×10^8	3.9×10^9	0.48	7.0×10^8

[a] Dielectric constant at 20°C.

In aprotic solvents the variation of k_{et} with the driving force calculated with the Weller equation [28] could be explained by the Marcus classical or semi-classical electron transfer theories [17]. A satisfactory correlation of $\log k_{et}$ with ΔG_f could be established using a distance of 0.7 nm in the RIP [28].

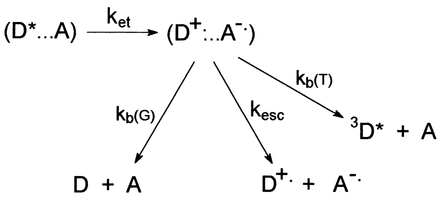
From the reaction scheme the charge separation efficiency is given by

$$\varphi_{cs} = \frac{k_{esc}}{k_b(G) + k_b(T) + k_{esc}} \tag{6}$$

According to Eq. (6) φ_{cs} is affected by a series of factors that in one way or another affect k_{esc}, $k_b(G)$ and $k_b(T)$. A theoretical expression for k_{esc} is given by the Eigen [29] equation

$$k_{esc} = \left(\frac{2kT}{\pi r^3 \eta}\right)\left(\frac{z_A z_B e^2}{\varepsilon rRT}\right)\left(1 - \exp\left(-\frac{z_A z_B e^2}{\varepsilon rRT}\right)\right)^{-1} \tag{7}$$

Here η and ε are the solvent viscosity and dielectric constant, respectively. z_A and z_B are the charges of the separating ions initially at a distance r. With the aid of Eq. (7) k_{esc} was estimated for each solvent as previously discussed [16,30], using 0.7 nm for the distance in the RIP. With these values and the experimentally determined φ_{cs} the total back-electron-transfer rate constant $k_b = k_b(G) + k_b(T)$ can be determined. The values of k_b are also reported in Table 1. The two rate constants could be separate if the intersystem crossing efficiencies were reliable determined. However, in the present case they are difficult to estimate due to the superposition of T–T and radical ions absorption spectra.



Scheme 1.

At this point it is important to consider the experimental uncertainties in the rate constants determined in this way. The difficulty in obtaining reliable quantum yields for charge separation by the technique of laser flash photolysis was discussed by Vauthey et al. [31]. Small errors in the charge separation efficiency may translate in large ones in the back rate constants. Nevertheless, the relative values of charge separation efficiencies and the back recombination rate constants from them derived in the different solvents here investigated, are more reliable than the absolute values based on absorption coefficients of radical ions, since the latter can be affected by large errors.

The overall Gibbs energy changes for the forward and back-electron-transfer reactions obtained through Eqs. (8)–(10) are reported in Table 2, together with the experimental data employed in the calculations.

$$\Delta G_f = E_{1/2}\left(\frac{D}{D^{\bullet+}}\right) - {}^*E_0(D) + E_{1/2}\left(\frac{A}{A^{\bullet-}}\right) \tag{8}$$

$$\Delta G_b(G) = -E_{1/2}\left(\frac{D}{D^{\bullet+}}\right) - E_{1/2}\left(\frac{A}{A^{\bullet-}}\right) \tag{9}$$

$$\Delta G_b(T) = -E_{1/2}\left(\frac{D}{D^{\bullet+}}\right) + {}^3E_0(D) - E_{1/2}\left(\frac{A}{A^{\bullet-}}\right) \tag{10}$$

$E_{1/2}(D/D^{\bullet+})$ and $E_{1/2}(A/A^{\bullet-})$ are the one electron redox potentials of D and A, respectively and ${}^*E_0$ is the excited singlet or triplet state energy level. The coulombic term usually included in the expressions above have been omitted, since it depends upon the specific value of the solvent dielectric constant. For the more polar solvents it amounts to less than 0.1 eV, while for the less polar ones there is not general agreement with regard to the effective dielectric constant to be used in the coulombic term [32,33]. Therefore, since we are going to discuss the experimental results using Gibbs energy in a semi-quantitative way we do not include the coulombic term in Eqs. (8)–(10).

The results are better discussed considering separately protic and aprotic solvents. The two singlet reactions have nearly equal ΔG_f , hence the geminate ion pair is most

Table 2
Free energy quantities^a

System	$^1E_0(\mathrm{D})^b$	$^3E_0(\mathrm{D})^b$	$E_{1/2}(\mathrm{D/D^{\bullet+}})^c$	$E_{1/2}(\mathrm{A/A^{\bullet+}})^c$	ΔG_f	$\Delta G_b(G)$	$\Delta G_b(T)$
^{1}Py*-3CNP	3.34	2.10	1.20	2.03	−0.11	−3.23	−1.13
^{1}DBA*–*o*-DCNB	3.15	2.25	1.19	1.82	−0.14	−3.01	−0.76
^{3}DBA*–*p*-NBz	3.15	2.25	1.19	0.86	−0.20	−2.05	–

[a] All quantities in eV.
[b] From [36].
[c] From [37].

likely to be of similar characteristics, although it may change from a SSIP in the most polar solvents to CRIP in the less polar ones. In the first case, for the system Py-3CNP a nearly solvent independent value of k_b close to $1\times10^9\,\mathrm{s}^{-1}$ results. Therefore, for this system the observed trend of the charge separation efficiency may be explained by the effect on k_{esc} of the macroscopic dielectric constant and viscosity of the different solvents. The same is valid for the system DBA–*o*-DCNB, with $k_b\cong1\times10^8\,\mathrm{s}^{-1}$, although in this case a larger uncertainty results because of the values close to 1 of φ_{cs}. The differences in k_b between the two systems may be understood if the reaction competing with the cage escape process is the back-electron-transfer to the excited triplet of the donor. The in-cage back recombination to ground state rate constant $k_b(G)$ corresponds to an electron transfer process with a driving force $\Delta G_b(G)<3$ eV (Table 2) and therefore lies in the inverted region. On the other hand the rate constant for the back recombination to the triplet state $k_b(T)$ is more likely to be in the normal region, since $\Delta G_b(T)$ is much less exergonic. Now, the Gibbs energy $\Delta G_b(T)$ for the system Py-3CNP in polar solvents, is more exergonic by 0.37 eV than the corresponding quantity for DBA–*o*-DCNB. Therefore, considering that $k_b(T)$ is in the normal region, a higher value for the system Py-3CNP may be foreseen.

For the alcoholic solvents in all cases k_b is higher for the system Py-3CNP. The same argument than before may be used to explain this difference. However, while for the system DBA–*o*-DCNB k_b show a low dependence on the solvent, being very similar to the values in aprotic solvents, for the other system a more erratic behavior is observed. This may be the result either of specific solvent effect or an effect of the uncertainty of the experimental measurements added to the assumption made to obtain k_b. Nevertheless, for several other systems previously investigated, it was consistently found that k_b is higher in MeOH than in MeCN [16]. Therefore, we think that the differences obey to specific solvent effects and that it is not possible to explain the results in terms of the macroscopic solvent properties.

3.2. Triplet state processes

The quenching of the triplet state of DBA by *p*-NBz was investigated in several protic and aprotic solvents. Quenching rate constants were determined from the decay of DBA triplet state as a function of *p*-NBz concentration. The results are reported as k_q in Table 1. Transient absorption spectra taken after the quenching event are shown in Fig. 3. In all cases the spectrum can be reproduced by the addition of the absorptions of the radical ions DBA$^{\bullet+}$ and *p*-NBZ$^{\bullet-}$ [34]. The bands with λ_{max} 370–380 nm corresponds to the absorption of DBA$^{\bullet+}$ and *p*-NBZ$^{\bullet-}$, while at 510 nm only DBA$^{\bullet+}$ absorbs. Therefore, the quenching reaction may be written as

$$^3\mathrm{DBA}^* + p\text{-NBz} \rightarrow \mathrm{DBA}^{\bullet+} + p\text{-NBz}^{\bullet-} \qquad (11)$$

Charge separation efficiencies were obtained from the free ions quantum yield as explained before and are also collected in Table 1.

The rate constants for the quenching of DBA triplet by *p*-NBz present a very low sensitivity to changes in solvent dielectric constant. For the more polar solvents the order of magnitude of the rate constants is compatible with a driving force of −0.2 eV (Table 2) for the electron transfer process. The lack of solvent effect is not uncommon for electron transfer reactions. Ghoneim et al. [35] found that in the quenching of excited singlet 9,10-dicyanoanthracene the rate constants do not differ by more than one order of mag-

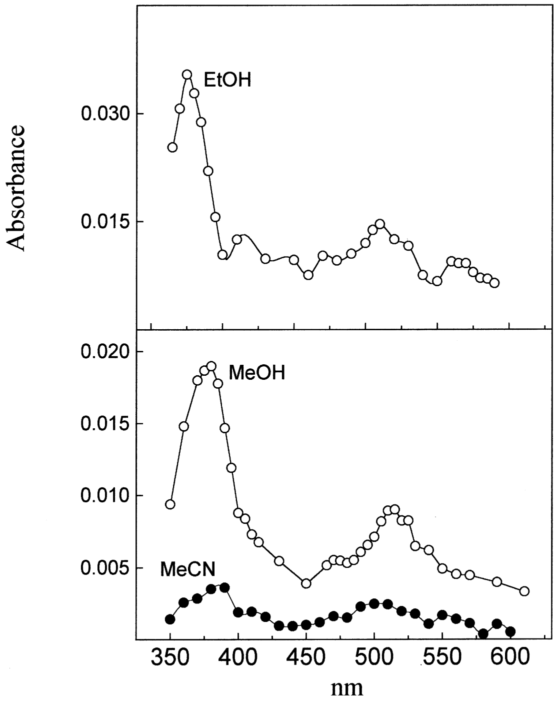


Fig. 3. Transient absorption spectra of DBA in the presence of *p*-NBz 2×10^{-4} M taken at 20 μs after the laser pulse.

nitude on going from hexane to acetonitrile. Nevertheless in this case two different Rehm–Weller plots are obtained for π or n-donors. More recently Schael and Löhmannsröben did not find differences in the electron transfer quenching of excited singlet of diphenyl-hexatriene in acetonitrile and toluene [6]. Conversely, for the two singlet quenching processes presented in this paper, the forward rate constants increase by more than one order of magnitude on going form ethyl acetate to MeCN [17].

The low variation in the forward rate constants is contrasting with the solvent effect on the charge separation efficiency. From them, the rate constants for back-electron-transfer to ground state were obtained in the same way than for the singlet reactions, with the exception that in this case the only back-electron-transfer to be considered is $k_b(G)$. The values are collected in Table 1. It can be seen that $k_b(G)$ changes drastically on going from aprotic to protic solvents, in a way not clearly predictable from the macroscopic properties of the medium. In the hydrogen bonding solvents they are of the same order of magnitude than those for the singlet processes, while they are higher in the aprotic solvents. These differences must be traced to specific solvent effects. The alcohols, hydrogen bonding donors, may interact with the quencher, either changing its effective reduction potential, or affecting the properties of the RIP, in a way that favors the charge recombination process.

In summary, the effect of aprotic solvents on the charge separation efficiencies in singlet state PET reactions may be explained by a model based on the macroscopic properties of the solvent. For alcohols the efficiencies are lower than the corresponding quantities for the other solvents of similar viscosities and dielectric constant, and this may be due to specific solvent effects. For triplet mediated reaction, the forward rate constants are scarcely sensitive to the solvent, while the back-electron-transfer to ground state are of the same order of magnitude that those for the back-electron-transfer to triplet in the case of the singlet reactions. Again in the triplet state processes, specific solvent effects are important in determining the back-electron-transfer rate to ground state.

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