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Solvent effects on intermolecular photoinduced electron transfer reactions of aromatic molecules

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Abstract

The electron transfer quenching of excited singlet of pyrene by indole and 3-cyanopyridine, and a,h-dibenzanthracene by o-dicyanobenzene was investigated in solvents of different polarity. The electron transfer nature of the quenching reaction in all the solvents was confirmed by the transient absorption spectra of the radical ions formed. Quenching rate constants were determined and their variation with the solvent was compared with the prediction of the current electron transfer theories. It was found that for aprotic solvents the trend may be explained by the semiclassical theory for non-adiabatic electron transfer if a dielectric continuum model is used for the solvent. In hydroxylic solvents the rate constants do not fall on the same correlation, probably due to specific effects not taken into account by the model. © 1997 Elsevier Science S.A.

Keywords: Photoinduced electron transfer; Solvent effects; Aromatic hydrocarbons; Singlet quenching; Rate constants

1. Introduction

The solvent effect on photoinduced electron transfer (PET) reactions has been widely investigated [1]. However the majority of the work has focused on intramolecular processes. For this case, several experimental [2,3] and theoretical [4] papers have dealt with the effects of solvent reorganization and dynamics. On the other hand, for intermolecular processes the amount of work is considerably less. In part, this may be due to the difficulty in interpreting the experimental results. This difficulty resides in part in the problem of separating the diffusional contribution to the rate constant from the electron transfer constant. Establishing the distance between donor and acceptor in the precursor complex at which the actual electron transfer takes place, occasions a second difficulty in the theoretical interpretation of the results [5,6].

In many cases of previous work on intermolecular PET reaction, it was assumed, without clear confirmation, that the reactions under consideration involve full charge transfer. However, in some cases the quenching of an excited state by an electron donor or acceptor may take place through an exciplex, with partial charge transfer character. This may explain some of the apparently contradictory effects on the rate constants reported in the literature. Chen et al. [7] investigated the reductive quenching of phenanthrene derivatives and naphthalene by a series of electron donors and acceptors in acetonitrile (MeCN), dimethylformamide (DMF) and cyclohexane. They found that in the two polar solvents, bimolecular rate constants are very similar while they decrease markedly in the non-polar medium. However, in the latter case there is no direct evidence for a total charge transfer process. On the other hand, other workers [8] found that in the quenching of the excited singlet of 9,10-dicyanoanthracene, the rate constants do not differ by more than one order of magnitude on going from hexane to acetonitrile. Nevertheless, in this case two different Rehm–Weller plots are obtained for π- or n-donors.

This apparent contradictory effect of solvent polarity may be due to several causes. One of the forms in which the solvent may alter the kinetics of a PET reaction is by changing the nature of the intermediary state, from a solvent separated ion pair in a high polarity solvent, to a contact ion-pair or exciplex in a low polarity one. In the first case the solute–solvent interaction is treated by the Born model of ion solvation, while in the second situation the model has to be changed to that of a dipole–solvent interaction. The difficulty resides on deciding when one or the other has to be applied, especially when the exciplex emission is not observed. One way to overcome this difficulty is to assess the nature of the reaction by investigating the apparition of radical ions by laser flash photolysis.

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For a PET reaction with total charge transfer, the solvent may influence the rate by affecting several of the parameters that control the process. The macroscopic dielectric properties may change the driving force and the intrinsic barrier in a way that is amenable to treatment with the current theories [3,9,10]. On the other hand, in many cases the presence of specific effects may produce large changes in the rate, even in cases where the dielectric properties are practically unchanged [11].

In order to obtain a further insight on the solvent effect on intermolecular PET processes we present in this paper results on three well-characterized reactions. These reactions were selected for this study because of their rate constants in polar solvents being at least one order of magnitude lower than the diffusional limit. In this way the effect of the solvent dielectric properties may be easily separated from the diffusive contributions. One system is the reductive quenching of excited singlet pyrene by indole. It is a well known electron transfer process and the medium effect on this reaction has been studied [12,13]. We extend the investigation here to a series of non-protic solvents. The other two PET reactions are the oxidative quenching of pyrene by 3-cyanopyridine and of 1,2,5,6,-dibenzanthracene by o-dicyanobenzene. These two reactions have been previously studied in methanol and acetonitrile [14], and here we expand the study to a series of protic and aprotic solvents of amply varying dielectric properties. For the three systems, and in all the solvents employed, the processes were identified as a PET reaction by direct observation of the radical ions formed.

2. Experimental details

Propionitrile from Fluka AG, was distilled and passed trough a silica gel column before use. Ethanol from Merck was purified by distillation. The other solvents were HPLC grade and were used without further purification. Pyrene (Py) from Merck was purified by recrystallization from methanol. 1,2,5,6-Dibenzanthracene (DBA) was Fluka puriss. Indole (In) was from Sigma (crystalline) and was used without further purification. o-Dicyanobenzene (o-DCNB) and 3-cyanopyridine (3-CNP) were from Aldrich. Tetra-n-butylammonium perchlorate (TBAP) was from Sigma. All of them were used as received.

Stationary fluorescence quenching experiments were carried out with a Spex Fluoromax spectrofluorometer. Transient absorption and fluorescence lifetime determinations were performed with a nitrogen laser as previously described [12]. The samples were deoxygenated prior to use by nitrogen bubbling.

3. Results and discussion

The quenching of pyrene excited singlet by indole was previously studied in solvents of high and medium polarity [12,13]. Laser flash photolysis experiments showed that radical ions are formed in the quenching process. The oxidative quenching of Py by 3-CNP was also previously investigated in methanol and acetonitrile [14]. Transient absorption spectra demonstrate the electron transfer nature of the quenching process. In Figs. 1 and 2 typical absorption spectra are shown for this system in two solvents of different polarity. In both cases in the absence of quenchers, the absorption bands correspond to those of the Py triplet state, λ_{max} 419 and 525 nm [15]. The addition of the quencher in acetone produces the appearance of the typical absorption of the radical cations of Py [16]. However when the solvent is ethyl acetate free ions are not observed even at a high fraction of singlet quenching. This may be explained by the very low value of the cage escape rate constant in this low polarity solvent. In order to confirm for this particular case the electron transfer character of the quenching processes, the effect of added salt on the transient absorption spectrum after the quenching, was investigated. It is well known that PET reactions are susceptible to salt effects because of the increase of the ionic strength (the normal salt effect) and/or specific interactions of the salt with the geminate ion pairs and the free radical ions (the special or specific salt effect). It is well documented that the presence of salts, especially those of tetralkylammonium cations, increases the charge separation yield [17]. In Fig. 2 it is shown the effect of adding tetrabutylammonium perchlorate (TBAP) to the Py–3-CNP system. It can be seen that Py radical cation is present in high yield confirming that in the

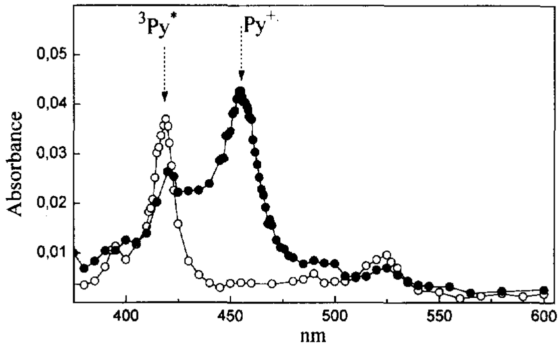

Fig. 1. Transient absorption spectrum for the system Py-3-CNP in acetone 4 μs after the laser pulse. (○) Py; (●) Py + 3-CNP, 0.4 M.

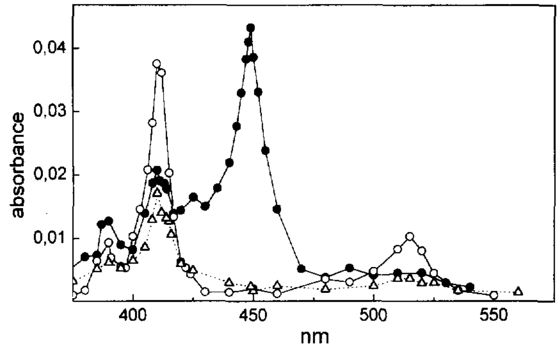

Fig. 2. Transient absorption spectrum for the system Py-3-CNP in ethyl acetate 4 μs after the laser pulse. (○) Py; (△) Py-3-CNP, 0.6 M; (●) Py-3-CNP, 0.6 M–TBAP, 0.08 M.

low polarity solvent the reaction proceeds by a total charge transfer mechanism.

For the system DBA–o-DCNB the laser flash photolysis results in acetonitrile and ethyl acetate are presented in Figs. 3 and 4 respectively. In the absence of quencher the only transient is the triple state of DBA absorbing at 570 and 535 nm [15]. In acetonitrile DBA radical cation is identified by its absorption bands at 380 and 510 nm [16]. While the yield of radical ions in ethyl acetate is very much less than for the other system, the presence of DBA radical cation is evident in the inset of Fig. 4. In all the experiments in the presence of the salt it was checked that TBAP affects neither the hydrocarbon lifetime nor the quenching rate constant.

Bimolecular quenching rate constants k_q, were determined experimentally by measuring the fluorescence lifetime τ of Py or DBA as a function of quencher concentration. In all cases the plots of τ^{-1} vs. $[Q]$ were linear, and the values of k_q in Tables 1–3 were calculated from the slopes.

Having confirmed that the reactions under consideration are PET processes with total charge transfer, the well-established Rehm–Weller [18] mechanism may be used to discuss the observed trend in rate constants. This mechanism is most frequently written as

$$M^* + Q \underset{k_{-d}}{\overset{k_d}{\rightleftharpoons}} (M^* \ldots Q) \underset{k_{-et}}{\overset{k_{et}}{\rightleftharpoons}} (M^{+\cdot} \ldots Q^{-\cdot}) \xrightarrow{k_r}$$

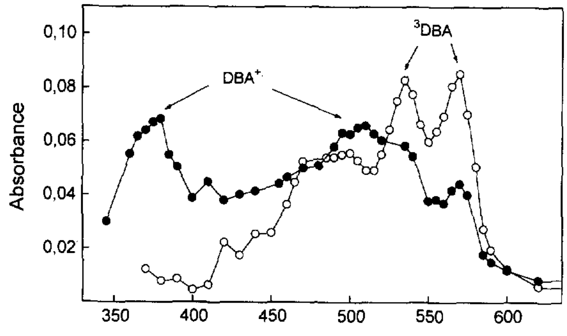

Fig. 3. Transient absorption spectrum for the system DBA–o-DCNB in acetonitrile 2 μs after the laser pulse. (○) DBA; (●) DBA + o-DCNB, 0.081 M.

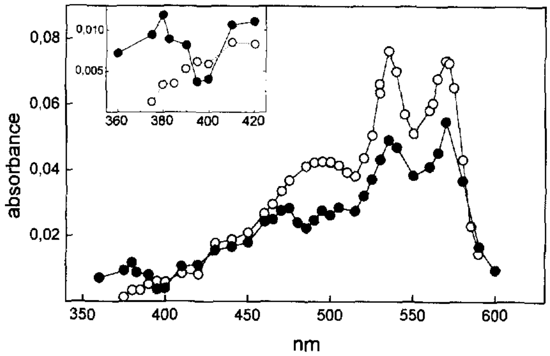

Fig. 4. Transient absorption spectrum for the system DBA–o-DCNB in ethyl acetate 2 μs after the laser pulse. (○) DBA; (●) DBA + o-DCNB, 0.14 M + TBAP, 0.06 M. Inset graph is an expansion of the region where the absorption assigned to DBA radical cation is more clearly separated from the T–T absorption.

Table 1
Quenching rate constant for excited singlet pyrene by indole

Solvent (dielectric constant)	ΔG^0 (eV)	λ_O (eV)	k_q ($M^{-1}\,s^{-1}$)
Ethyl acetate (6.02)	+0.30	0.781	1.5×10^7
Acetone (20.70)	0.0	1.056	4.8×10^7
Ethanol (24.55)	−0.02	1.068	6.4×10^7
Propionitrile (28.90)	−0.04	1.074	1.1×10^8
Methanol (32.66)	−0.05	1.148	1.5×10^8
Acetonitrile (35.94)	−0.058	1.126	2.4×10^8
Dimethyl sulfoxide (46.45)	−0.074	0.932	8.9×10^8
Water–ethanol (1:1 v/v) (54.40)	−0.082	1.154	1.8×10^9
Water–ethanol (7:3 v/v) (65.6)	−0.090	1.167	3.1×10^9

where the rate constant k_r includes all processes competing with the electron back-transfer to the precursor complex: cage escape, electron back-transfer to the ground state, etc. The experimental steady state quenching rate constant, k_q can be expressed as:

$$k_q = \frac{k_d}{1 + \frac{k_{-d}}{k_{et}}\left(1 + \frac{k_{-et}}{k_r}\right)} \tag{1}$$

According to the reaction scheme, in the presence of quencher M^* a bi-exponential decay should be observed. However, in our experiments the decay remained monoexponential. This may be explained if k_r is assumed to be much larger than k_{-et}. In this case the rate constant becomes,

$$k_q = \frac{k_d k_{et}}{k_{-d} + k_{et}} \tag{2}$$

Eq. (2) may be reordered to

$$\frac{1}{k_q} = \frac{1}{k_d} + \frac{1}{K_D k_{et}} \tag{3}$$

where k_d is the diffusional rate constant and $K_D = k_d / k_{-d}$ is the equilibrium constant for the formation of the precursor complex. Since k_d may be estimated with a high degree of confidence, the product $K_d k_{et}$ may be obtained from the experimental k_q using Eq. (3). For uncharged reactants, K_D depends only on r_{12}, the donor–acceptor distance in the precursor complex. Usually K_D is in the range 0.5–0.8 M^{-1} [19].

The electron transfer rate constant k_{et} may be written as [20]

$$k_{et} = \kappa \nu_n \exp(-\Delta G^* / RT) \tag{4}$$

where κ is the transmission coefficient (unity for an adiabatic reaction) and ν_n is a nuclear frequency factor (usually between 10^{11} and 10^{12} s^{-1}). The activation Gibbs energy derived from the Marcus classical theory for electron transfer [20], is given by

Table 2
Quenching rate constant for excited singlet a,h-dibenzanthracene by o-dicyanobenzene

Solvent (dielectric constant)	ΔG^0 (eV)	λ_O (eV)	k_q ($M^{-1}\,s^{-1}$)
Ethyl acetate (6.02)	+0.160	0.781	1.6×10^8
Ethyl acetate–acetonitrile (9:1 v/v) (11.17)	−0.037	0.953	2.2×10^8
2-Methyl-1-butanol, (16.56)	−0.113	0.968	1.8×10^9
Ethyl acetate–acetonitrile (7:3 v/v) (19.05)	−0.134	1.046	2.4×10^8
2-Propanol (19.92)	−0.139	1.021	1.7×10^9
Acetone (20.70)	−0.144	1.056	7.3×10^8
Ethanol (24.55)	−0.164	1.068	4.5×10^9
Propionitrile (28.90)	−0.180	1.074	6.4×10^8
Methanol (32.66)	−0.190	1.148	8.0×10^9
Acetonitrile (35.94)	−0.197	1.126	2.9×10^9
Water–methanol (9:1v/v) (41.46)	−0.207	1.160	7.1×10^9
Dimethyl sulfoxide (46.45)	−0.214	0.932	2.3×10^9

Table 3
Quenching rate constant for excited singlet pyrene by 3-cyanopyridine

Solvent (dielectric constant)	ΔG^0 (eV)	λ_O (eV)	k_q ($M^{-1}\,s^{-1}$)
Ethyl acetate (6.02)	+0.192	0.781	5.7×10^6
Ethyl acetate–acetonitrile (9:1 v/v) (11.17)	−0.007	0.953	1.5×10^7
Ethyl acetate–acetonitrile (7:3 v/v) (19.05)	−0.104	1.046	4.3×10^7
2-Propanol (19.92)	−0.110	1.021	7.2×10^8
Acetone (20.70)	−0.114	1.056	6.7×10^7
Ethanol (24.55)	−0.134	1.068	3.0×10^9
Propionitrile (28.90)	−0.150	1.074	1.3×10^8
Methanol (32.66)	−0.160	1.148	6.4×10^9
Acetonitrile (35.94)	−0.168	1.126	2.9×10^8
Dimethyl sulfoxide (46.45)	−0.184	0.932	3.1×10^8

$$\Delta G^* = \frac{\lambda}{4}\left[1+\frac{\Delta G^0}{\lambda}\right]^2 \tag{5}$$

The reorganization energy λ, has two contributions:

$$\lambda = \lambda_{in} + \lambda_{out} \tag{6}$$

The inner term, λ_{in} arises in structural changes on going from the equilibrium configuration of the reactants to that of the products. The second term, λ_{out} is called the solvent reorganization energy and is the major contribution to the total reorganisation energy for electron transfer reactions involving rigid organic molecules. When a dielectric continuum model is applied, the solvent contribution, assuming spherical shape for the reactants, λ_{out} can be written as [20]

$$\lambda_{out} = e^2\left(\frac{1}{2r_1}+\frac{1}{2r_2}-\frac{1}{r_{12}}\right)\left[\frac{1}{\epsilon_{op}}-\frac{1}{\epsilon_s}\right] \tag{7}$$

where ϵ_{op} and ϵ_s are the optical and static dielectric constants respectively, and $r_{12} = r_1 + r_2$ is the sum of the molecular radii of the reactants. The theoretical estimation of the solvent reorganization energy using Eq. (7) with radii $r_1 = 0.4$ nm for the PAHs and $r_2 = 0.3$ nm for the quenchers results in $\lambda_{out} = 1.13$ eV in MeCN. Assuming that the radii are the same in the different solvents, the reorganization energy may be obtained as a function of the dielectric properties of the solvent from Eq. (7). In the following the inner term in Eq. (6) is disregarded.

According to Rehm and Weller [18] the Gibbs energy change in the electron transfer process can be calculated from the redox potentials of the donor $E_{(D/D^-)}$ and acceptor $E(_{A/A^-})$, and the energy of the excited state involved

$$\Delta G^0 = E_{(D/D^+)} - E_{(A/A^-)} - E^* + \frac{Z_1Z_2}{\epsilon_s r_{12}} \tag{8}$$

where E^* is the energy of the excited state and the last term represents the coulombic energy necessary to form an ion pair with charges Z_1 and Z_2 in a medium of dielectric constant ϵ_s at a distance r_{12}.

On the basis of this model, the solvent may influence k_{et} by changing several of the parameters involved. First, the driving force ΔG^0 may be altered by different stabilization of the product ion pair. This may be taken into account by the equation proposed by Weller [9]

$$\Delta G^0(\epsilon_s) = E^{MeCN}_{(D/D^-)} - E^{MeCN}_{(A/A^-)} - E^* + \frac{2.6\ \text{eV}}{\epsilon_s} - 0.13\ \text{eV} \tag{9}$$

where $E^{MeCN}_{(D/D^+)}$ and $E^{MeCN}_{(A/A^-)}$ are the redox potentials measured in acetonitrile and $\Delta G^0(\epsilon_s)$ is the free energy change in a solvent of dielectric constant ϵ_s. This equation is based on the Born model of solvation energy and it is valid only for the here assumed radii of quencher and quenchee.

Second, the solvent contribution to the reorganization energy λ_{out} is modified through changes in the static and optical dielectric constants through Eq. (7). Finally, the nuclear frequency may be expected to be solvent dependent if it is predominantly a solvent mode.

In the second term of Eq. (3) K_D is at a first approximation solvent independent. If it is further assumed that the nuclear frequency factor is a constant for all the solvents investigated, we may write for the product $K_d k_{et}$

$$K_D k_{et} = Z \exp(-\Delta G^*/RT) \qquad (10)$$

with Z as a solvent-independent frequency factor.

If the semiclassical version of electron transfer theories is employed, Z becomes solvent dependent and is given by [21]

$$Z = \frac{K_D 2\pi}{\hbar} H_{AB}^2 (4\pi\lambda k_B T)^{-1/2} \qquad (11)$$

By taking logarithms and reordering Eqs. (10) and (11) we may write

$$\ln (K_D k_{et} \lambda^{1/2}) = C - \frac{\Delta G^*}{RT} \qquad (12)$$

In Tables 1–3 the quantities ΔG^0 and λ, calculated with Eqs. (9) and (7) are also collected for all the solvents. With these parameters and Eqs. (5)–(9), ΔG^* may be obtained in each solvent under the assumption of constant radii. The product $K_d k_{et}$ was calculated from the experimental k_q and the literature value of k_d [22] by means of Eq. (3). In most cases the contribution of the diffusive term was very small. The data was plotted according to Eq. (12) for the aprotic solvents in Figs. 5–7. The solid lines were drawn with the theoretical slope of -1. It may be seen that considering all the approximations involved, the experimental data conform very satisfactorily to the model. From the ordinates at the origin the value of the electronic coupling matrix element, H_{AB} was evaluated, assuming $K_D = 0.8$, and it is collected in Table 4 for the three systems. The low values of H_{AB} are in line with the expectation for a non-adiabatic process [20].

If instead the classical model is used, i.e. Z solvent independent, Eq. (12) simplifies to

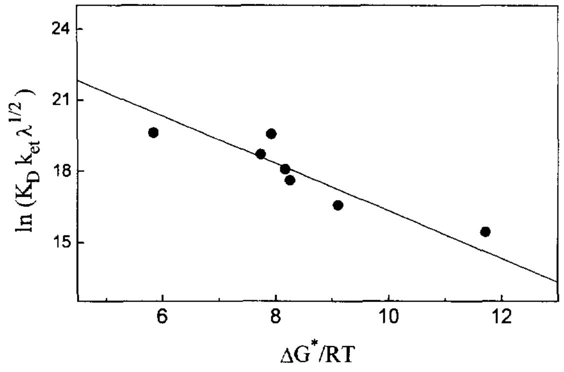

Fig. 5. Plot of $\ln(K_D k_{et} \lambda^{1/2})$ vs. $\Delta G^*/RT$ for the system Py–3-CNP in aprotic solvents at 298 K. The line is a least-square fit with the slope fixed at the theoretical value of -1.0.

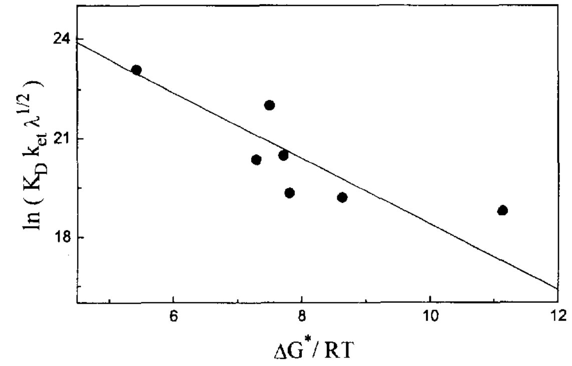

Fig. 6. Plot of $\ln(K_D k_{et} \lambda^{1/2})$ vs. $\Delta G^*/RT$ for the system DBA–o-DCNB in aprotic solvents at 298 K. The line is a least-square fit with the slope fixed at the theoretical value of -1.0.

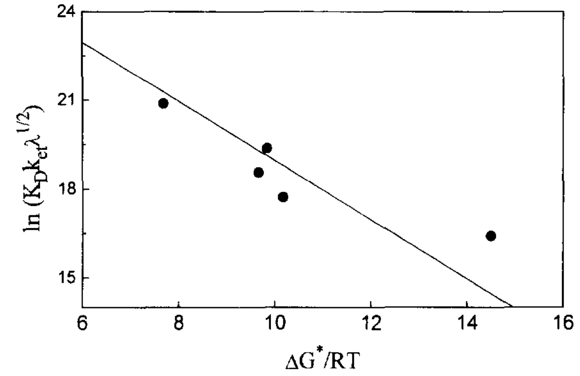

Fig. 7. Plot of $\ln(K_D k_{et} \lambda^{1/2})$ vs. $\Delta G^*/RT$ for the system Py–indole in aprotic solvents at 298 K. The line is a least-square fit with the slope fixed at the theoretical value of -1.0.

$$\ln(K_D k_{et}) = \ln Z - \frac{\Delta G^*}{RT} \qquad (13)$$

The plot of Eq. (13) for the three systems is given in Fig. 8. It can be seen that nearly parallel lines are obtained. The slopes and Z values are also given in Table 4. The slopes values are less than unity and Z is of the order of magnitude expected for the frequency collision in solution, i.e. 10^{11} dm^3 mol^{-1} s^{-1}. Considering the dispersion of the experimental data and all the approximations and assumptions involved in the model we think that there is no reason to prefer the classical model over the semiclassical version as given by Eq. (11).

On the other hand, if the data for protic solvents are treated in the same way, there is no agreement with the theory. In Fig. 9 the rate constants are plotted for the system Py–3-CNP in protic and aprotic solvents. It can be seen that the data conform two separate sets of values.

Table 4
Electronic coupling, slope (Eq. (13)) and frequency factor

System	H_{AB} (eV)	slope (Eq. (13))	Z (dm^3 mol^{-1} s^{-1})
Py–Ind	0.020	−0.59	5.6×10^{10}
Py–3-CNP	0.005	−0.77	3.8×10^{10}
DBA–o-DCNB	0.014	−0.73	2.6×10^{11}

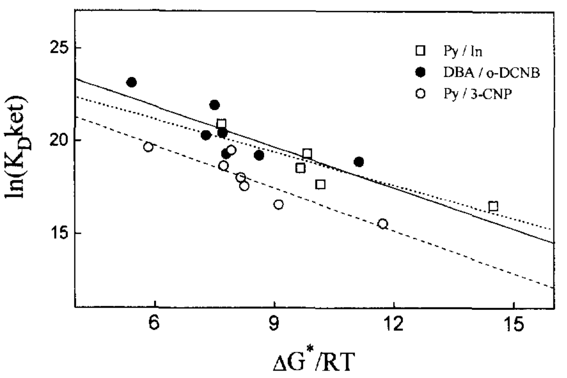

Fig. 8. Plot of Eq. (13) for the three systems, aprotic solvents.

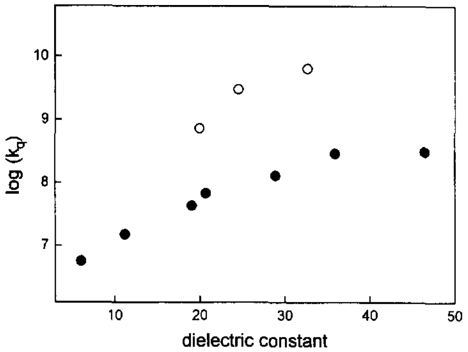

Fig. 9. Quenching rate constant as a function of the dielectric constant in protic (○) and aprotic (●) solvents for the system Py–3-CNP.

In conclusion, the solvent effect on PET rate constant may be reasonably explained by a continuum dielectric model for aprotic solvents. The data do not allow a clear distinction between the classical adiabatic and the semiclassical non-adiabatic models for PET reactions. Specific effects must be considered in the case of hydroxylic media. As previously proposed, these effects may be related to the contribution of the solvent structure to the reorganization energy [11] and also to hydrogen bonding interactions with the quencher [14].

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