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Solvent effects on the photoinduced electron transfer reaction between excited singlet pyrene and indole

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Abstract

The quenching of the excited singlet of pyrene was studied in acetonitrile (MeCN), propionitrile (PrCN), methanol (MeOH) and ethanol (EtOH). Rate constants for the quenching processes and their activation parameters were determined. The activation enthalpies are -2.9 kcal mol^{-1} (MeCN), -1.4 kcal mol^{-1} (PrCN), -0.2 kcal mol^{-1} (MeOH) and 0.0 kcal mol^{-1} (EtOH). The activation entropies are -30.0 cal K^{-1} mol^{-1} (MeCN), -26.4 cal K^{-1} mol^{-1} (PrCN), -21.8 cal K^{-1} mol^{-1} (MeOH) and -22.8 cal K^{-1} mol^{-1} (EtOH). The electron transfer nature of the quenching was confirmed by laser flash photolysis. The radical anion and triplet state of pyrene are both produced in the quenching process. The quantum yields of these species were determined in the four solvents. The quantum yield of radical ions follows a good correlation with the cage escape rate constants calculated with the Eigen equation. The rate constants for back electron transfer to the triplet and ground state were estimated from the quantum yields and the cage escape rate constants. They are independent of the solvent.

Keywords: Photoinduced Electron Transfer; Excited Singlet Pyrene; Indole

1. Introduction

In spite of the large amount of work carried out on photoinduced intermolecular electron transfer reactions, a systematic study of the temperature and solvent effects on the rate constants has not been usual practice. Of the few examples of such investigations, the reductive and oxidative quenching of $Ru(bpy)_3^{2+}$ (bpy, bipyridyl) by small aromatic molecules has been the most thoroughly examined [1-3]. It was found that, when two polar solvents with similar macroscopic dielectric constants, methanol (MeOH) and acetonitrile (MeCN) were compared, the activation enthalpies were generally zero or negative for the aprotic solvent [3] while small positive values were found in the alcohol. In all cases, the activation entropies were more negative in MeCN than in MeOH [3]. The quenching of the excited singlet state of polycyclic aromatic hydrocarbons (PAHs) by electron acceptors or donors has also been studied as a function of temperature [4]. Very low or even negative activation energies were also determined for these systems. In previous work [5], we have extended these studies to the electron transfer reactions between the triplet states of anthracene and 1,2,5,6-dibenzanthracene as electron donors and nitrobenzenes as acceptors. We found that the quenching rate constants in MeOH are generally higher than those in MeCN. The activation enthalpies and entropies were also measured for these systems in both solvents. Here again the activation entropies are more negative in MeCN and, in some cases, negative values are observed for the activation enthalpies in MeCN. We also found that, for the quenching of 1,2,5,6-dibenzanthracene, the charge separation efficiency, i.e. the radical ion yield, depends strongly on the nature of the solvent, being much higher for MeOH than MeCN. These results pertain to electron transfer quenching involving the triplet state of PAHs acting as electron donors. In the present paper, we report a similar investigation but with the excited singlet of the aromatic hydrocarbon acting as an electron acceptor. The pyrene–indole system was chosen for two reasons: firstly, because the photochemical processes involving the indole ring are of great biological interest, and secondly, for practical reasons, since the radical ions of pyrene formed in the electron transfer reaction are readily observed by laser flash photolysis.

The quenching of the excited singlet of pyrene by indole compounds has been the subject of several papers [6–9]. The rate constant depends strongly on the solvent polarity [7]; it increases with increasing dielectric con-

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stant to near the diffusion-controlled limit in water [8]. The reaction has also been employed by Encinas and Lissi in micellar systems to determine the partition coefficient of indole and tryptophan [7,8]. In non-polar solvents, indole derivatives have been shown to form emissive exciplexes with pyrene and 1-cyanopyrene [9]. However, although the quenching reaction has been ascribed to a charge transfer mechanism, a detailed study of the charge separation mechanism has not been reported for this system. In this paper, we present results on the effect of temperature on the quenching rate constant and the effect of the solvent on the quantum yields of the charge separation process. Four different polar solvents were investigated: two aprotic, MeCN and propionitrile (PrCN), and two hydrogen bonded, MeOH and ethanol (EtOH).

2. Experimental details

The solvents MeCN and MeOH were Sintorgan, high performance liquid chromatography (HPLC) grade and were used without further purification. EtOH was distilled twice before use. PrCN was from Fluka AG; it was distilled and passed through a silica gel column before use. Pyrene (Py) from Merck was purified by recrystallization from MeOH. Indole (In) was from Sigma (crystalline) and was used without further purification.

Stationary fluorescence quenching experiments were carried out with an Aminco Bowman spectrofluorometer. For transient absorption and fluorescence lifetime determinations, a nitrogen laser (Laseroptics; 5 ns full width at half-maximum (FWHM) and 5 mJ per pulse) was employed. The laser flash photolysis set-up has been described previously [10]. For fluorescence measurements, the laser beam was highly attenuated. The sample was placed in a TRW 75A filter fluorometer with appropriate filters. The signal was acquired by a digitizing scope where it was averaged and then transferred to a computer. The samples were deoxygenated by nitrogen bubbling for at least 15 min. Rate constants were determined in the temperature range 10–55 °C.

Quantum yields of the Py triplet state and radical anions were determined by the laser flash photolysis technique. Since photoexcited Py readily reacts with In, especially in MeCN, the solutions were changed after exposure to a few laser pulses. The quantum yields were determined by actinometry with zinc tetraphenylporphyrin (ZnTPP) in benzene. The triplet yield of ZnTPP was measured at 470 nm immediately after the laser pulse. Values of 7.3×10^4 M^{-1} cm^{-1} and 0.83 were used for ϵ_T and Φ_T of ZnTPP respectively [11]. For the triplet of Py, ϵ_T was taken as 30000 M^{-1} cm^{-1} at the maximum [12] and 49200 M^{-1} cm^{-1} was used for the extinction coefficient of the Py radical anion [13]. The extinction coefficients were assumed to be the same in the four solvents.

3. Results

The rate constants k_q for the quenching of $^1Py^*$ by In were obtained by measuring the fluorescence lifetime τ as a function of the In concentration at several temperatures. For some systems, the results were checked by stationary fluorescence quenching experiments. The decay of Py in the presence of In was monoexponential in all cases. The results were plotted according to

$$\tau^{-1}=\tau_0^{-1}+k_q[\mathrm{In}] \qquad (1)$$

where τ_0 is the fluorescence lifetime in the absence of In. Linear plots were obtained in all cases and the results are collected in Table 1. Exciplex emission was not observed in any case, even at the higher quencher concentrations. The effect of temperature on the rate constants was examined in terms of transition state theory

$$k_q=\frac{k_BT}{h}\exp\left(\frac{\Delta S^\ddagger}{R}\right)\exp\left(\frac{-\Delta H^\ddagger}{RT}\right) \qquad (2)$$

Corrections for diffusional effects were not applied since the rate constants are approximately two orders of magnitude lower than the diffusional limit for each solvent. Activation enthalpies and entropies were determined from Eyring plots of $\ln(k_q/T)$ vs. $1/T$ according to

$$\ln\left(\frac{k_q}{T}\right)=\ln\left(\frac{k_B}{h}\right)+\frac{\Delta S^\ddagger}{R}-\frac{\Delta H^\ddagger}{RT} \qquad (3)$$

The plots according to Eq. (3) are shown in Fig. 1 for all the solvents employed. The error bars are related to the statistical deviation of the slope of the plots of τ^{-1} vs. [In] in Eq. (1). The enthalpies and entropies are collected in Table 1. The errors quoted were estimated from the linear regression analysis of the plots according to Eq. (3). The activation parameters follow the general trend previously observed for this type of reaction [3,5]. Very low or negative activation

Table 1

Rate constants and activation parameters for the electron transfer quenching of the excited singlet of Py by In

Solvent	τ_0 (ns)	k_q (M^{-1} s^{-1})	$\Delta H^\ddagger$ (kcal mol^{-1})	$\Delta S^\ddagger$ (cal K^{-1} mol^{-1})
MeCN	338	2.4×10^8	-2.9 ± 0.2	-30.0 ± 0.5
PrCN	368	1.1×10^8	-1.4 ± 0.2	-26.4 ± 0.5
MeOH	320	1.5×10^8	-0.2 ± 0.1	-21.8 ± 0.4
EtOH	384	6.4×10^7	0.0 ± 0.1	-22.8 ± 0.3

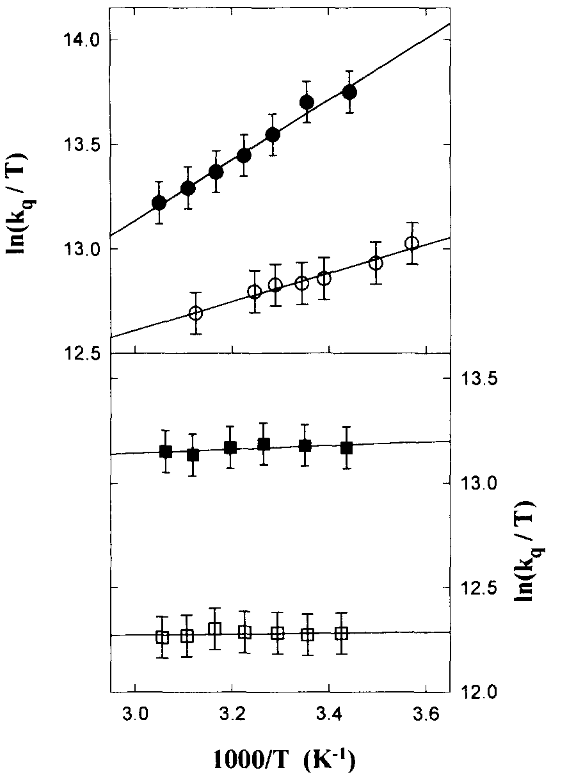


Fig. 1. Eyring plot for the bimolecular quenching rate constant of excited singlet Py by In in MeCN (●), PrCN (○), MeOH (■) and EtOH (□).

enthalpies are observed, with the lower values found for the aprotic solvents.

In order to understand the nature of the quenching process, laser flash photolysis experiments were performed. The transient absorption spectra immediately after the laser pulse are shown in Fig. 2. In the absence of In the typical triplet absorption of Py is observed. In the presence of In, at a concentration such that nearly 90% of the excited singlets are intercepted, two species are predominant in the spectrum in all cases: the triplet state (λ_{max} = 414 nm [12]) and the Py radical anion (λ_{max} = 490 nm [13,14]). Quantum yield measurements were carried out for the triplet and radical anion of Py and the results are reported in Table 2. They were measured relative to the triplet state of ZnTPP as described in Section 2. The experimental errors quoted reflect the uncertainty in the absorbance measurements of our experiments. The absorption coefficients of $^3Py^*$ and $Py^{\cdot -}$ and the triplet absorption coefficient and quantum yield of ZnTPP were taken as error-free reference values. If the uncertainties in these quantities are considered, especially when several different sources are consulted, the actual uncertainty of the quantum yields may be much higher. The triplet quantum yields were determined in the absence and presence of In. The yields in the absence of In are in good agreement with those given in the literature [15]. In the presence of In the yields are very much higher than those expected according to the fraction of excited singlet states quenched. Therefore it can be concluded that the quenching process leads in part to the triplet state of Py.

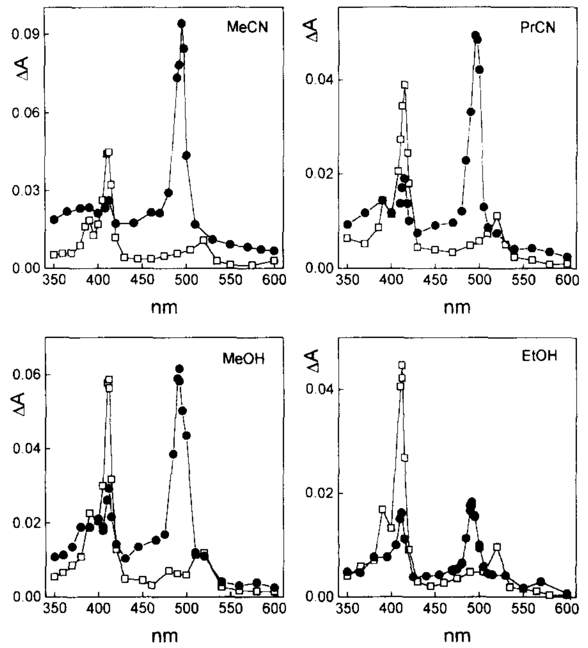


Fig. 2. Transient absorption spectra of Py in the absence (□) and presence (●) of In taken immediately after the laser pulse. The In concentration is such that the fraction of excited singlets quenched is 0.93 in MeCN, 0.90 in PrCN, 0.88 in MeOH and 0.87 in EtOH.

4. Discussion

The overall Gibbs energy change for the electron transfer process

$$^1Py^* + In \longrightarrow Py^{\cdot -} + In^{\cdot +} \tag{4}$$

can be calculated by [16]

$$\Delta G^\circ = E_{1/2}(Py) - E_{1/2}(In) - E_0(^1Py^*) + W \tag{5}$$

where $E_{1/2}(Py)$ is the reduction potential of Py (2.10 V in MeCN vs. a saturated calomel electrode (SCE) [17]) and $E_{1/2}(In)$ is the reduction potential of In. $E_0(^1Py^*)$ is the energy of the excited singlet state of Py (3.34 eV [18]) and W is the electrostatic work term taken as −0.06 eV which is an average value in MeCN [19]. The redox potential of In is not reported in the literature for MeCN solutions. However, a value of 1.52 V was assigned to this quantity in water vs. SCE [20]; using this value, ΔG° for reaction (4) can be estimated as +0.22 eV. According to the Rehm–Weller correlation [16] of k_q with the overall Gibbs free energy change for the electron transfer quenching of aromatic hydrocarbons, a value of 10^7–10^8 M^{-1} s^{-1} can be expected for k_q at this ΔG° value. The values of the quenching rate constants in Table 1 are in agreement with this expectation.

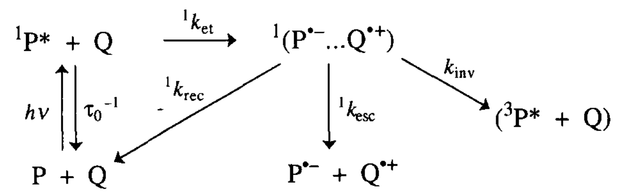
Table 2
Triplet and free radical ion quantum yields during the quenching of the Py excited singlet by In

Solvent	[In] (M)	f^a	Φ_T^0	Φ_T	α	Φ_{ion}
MeCN	0.14	0.93	0.28 ± 0.01	0.09 ± 0.01	0.073	0.37 ± 0.02
PrCN	0.25	0.90	0.29 ± 0.01	0.09 ± 0.01	0.065	0.24 ± 0.04
MeOH	0.15	0.88	0.36 ± 0.03	0.12 ± 0.02	0.081	0.22 ± 0.02
EtOH	0.29	0.87	0.43 ± 0.05	0.13 ± 0.03	0.090	0.11 ± 0.03

[a] Fraction of singlets quenched.

The activation parameters in Table 1 follow a similar trend as those determined for the triplet quenching of aromatic hydrocarbons by electron acceptors [5]. Activation entropies are more negative in this case and zero or negative values result for the activation enthalpy. The highly negative $\Delta S^\ddagger$ value can be explained by considering the solvent reorganization on formation of the transition state. When the electron transfer takes place, a new charge asymmetry develops. The polar solvent molecules must adopt specific orientations for charge stabilization. This may be considered as the "freezing" of the solvent molecules in the transition state and results in a negative activation entropy. In a solvent such as MeOH, the molecules are in a more ordered structure in the initial state due to hydrogen bonding; therefore the entropy change for reaching the transition state will be less than in an aprotic solvent such as MeCN. The negative values of $\Delta H^\ddagger$ in these types of reactions have been discussed previously [5].

The electron transfer nature of the quenching reaction is confirmed by the observation of the Py radical anion in the laser photolysis experiments. From these results a simple reaction scheme can be written as



This scheme is a simplified version of the general reaction scheme for electron transfer quenching in polar solvents proposed by Weller [21]. Accordingly, quantum yields for the production of the triplet state can be written as

$$\Phi_T=\frac{k_{isc}}{\tau_0^{-1}+k_q[\text{In}]}+\frac{k_q[\text{In}]}{\tau_0^{-1}+k_q[\text{In}]}\times\alpha \tag{6}$$

where k_{isc} is the intersystem crossing rate constant in the absence of In and α is the efficiency of triplet state formation during the decay of the radical ion pair, given by

$$\alpha=\frac{k_{inv}}{^1k_{rec}+{}^1k_{esc}+k_{inv}} \tag{7}$$

Eq. (6) can be rearranged to give

$$\Phi_T=\frac{\Phi_T^0+k_q\tau_0[\text{In}]\alpha}{1+k_q\tau_0[\text{In}]} \tag{8}$$

where Φ_T and $\Phi_T^0=\text{k}_{isc}\tau_0$ are the triplet yields in the presence and absence of In respectively. From the experimentally determined Φ_T, Φ_T^0 and $k_q\tau_0$ values, the values of α in Table 2 were obtained. The estimated experimental error of α is between 10% and 20%. Within these limits it can be seen that the efficiency of triplet state formation is approximately independent of the solvent.

On the time scale of our laser photolysis experiments, the Py radical anions observed are those that escape the cage recombination processes. According to the scheme, the free ion quantum yield can be written as

$$\Phi_{ion}=f\times\frac{^1k_{esc}}{^1k_{esc}+k_{inv}+{}^1k_{rec}} \tag{9}$$

where f is the fraction of singlets quenched. Eq. (9) can be rewritten as

$$\frac{\Phi_{ion}}{f-\Phi_{ion}}=\frac{^1k_{esc}}{^1k_{rec}+k_{inv}} \tag{10}$$

According to Eq. (10), a plot of the left-hand side vs. $^1k_{esc}$ should result in a straight line to the origin, provided that $^1k_{rec}+k_{inv}$ remains solvent independent. The difficulty of treating the data in this way is the lack of experimental data for $^1k_{esc}$ in solvents other than MeCN. Therefore, in order to estimate $^1k_{esc}$, we used the Eigen equation [22] modified by the Stokes–Einstein relation

$$^1k_{esc}=\left(\frac{2k_BT}{\pi\eta r^2}\right)\left(\frac{z_Az_Be^2}{\epsilon rk_BT}\right)\left[1-\exp\left(-\frac{z_Az_Be^2}{\epsilon rk_BT}\right)\right]^{-1} \tag{11}$$

where 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. Assuming a value of 0.7 nm for r, Eq. (11) gives 6×10^9 s^{-1} for $^1k_{esc}$ in MeCN. Mataga et al. [23] measured $^1k_{esc}$ in MeCN by picosecond laser spectroscopy for several systems. They found values in the range $(0.5\text{–}2.3)\times10^9$ s^{-1} with a mean value of 1.0×10^9 s^{-1}. Similarly, Gould and Farid [24] obtained 8×10^8 s^{-1} for $^1k_{esc}$ in MeCN for the system tetracyanoanthracene–alkylbenzenes.

Hence it may be concluded that Eq. (11) overestimates $^1k_{esc}$ by a factor of six. In order to proceed with the analysis of the data according to Eq. (10), we assume that the same correction factor can be applied for the other solvents under consideration, and rescale the calculated values accordingly. The resulting values for $^1k_{esc}$ are collected in Table 3. With these values the results for Φ_{ion} were plotted in the form of Eq. (10) in Fig. 3. Within the experimental error of the data, a linear plot with zero intercept is obtained. The linearity of the plot implies a constant value of $^1k_{rec}+k_{inv}$, and from the slope $^1k_{rec}+k_{inv}=1.5\times10^9$ s^{-1} results. Using this value for the sum, together with Eq. (7) and the calculated values of $^1k_{esc}$, all the rate constants for the decay of the geminate ion pair in the reaction scheme can be evaluated. They are collected in Table 3, together with the physical properties for each solvent. Considering the assumptions made about $^1k_{esc}$ and the uncertainties of the experimental values, it can be concluded that the back recombination to either the triplet or ground state is approximately solvent independent. The values for the decay to the ground state ($^1k_{rec}$) are of the same order as those reported by Mataga [25] for the excited tetracyanobenzene–toluene system. For this system, $^1k_{rec}$ is independent of the solvent properties. Since these reactions are most probable in the inverted region regime, the actual value will depend on the free energy gap between the radical ion pair and the ground state. It will also depend on the electronic coupling between these states. Thus Mataga [26] for the systems Py–dimethylaniline, Py-*p*-dicyanobenzene and Py–triethylamine reports rate constants much lower than those found for Py–In in this work, although the Gibbs energy change for the back recombination in these systems is very much less exergonic than for the system Py–In.

Table 3
Rate constants for the decay of the geminate radical ion pair

Solvent	η[a] (cP)	ϵ[b]	$^1k_{esc}$ (s^{-1})	k_{inv} (s^{-1})	$^1k_{rec}$ (s^{-1})
MeCN	0.34	35.9	1.0×10^9	1.8×10^8	1.3×10^9
PrCN	0.43	28.9	5.5×10^8	1.3×10^8	1.4×10^9
MeOH	0.54	32.7	5.3×10^8	1.5×10^8	1.4×10^9
EtOH	1.09	24.6	1.5×10^8	1.4×10^8	1.4×10^9

[a] Viscosity at 298 K; [b]dielectric constant at 298 K.

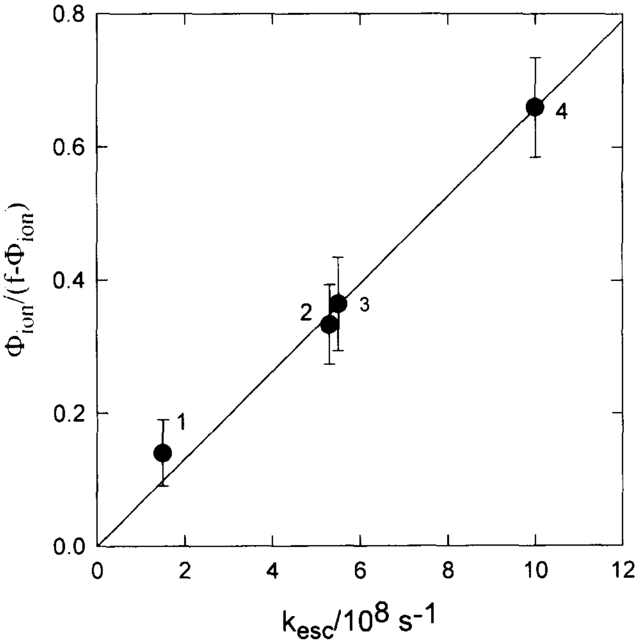


Fig. 3. Plot of the left-hand side of Eq. (10) vs. the cage escape rate constant k_{esc} calculated by the Eigen model (Eq. (11)). Solvent key: 1, EtOH; 2, MeOH; 3, PrCN; 4, MeCN. The error bars result from the experimental errors of Φ_{ion} in Table 2.

We also found that the rate constant for back recombination to the triplet state is much lower than to the ground state. While the lower energy gap is more favourable, the spin inversion required is probably the cause of the low value.

In summary, the geminate ion pairs formed during the excited singlet quenching of Py by In decay to the ground state or triplet state with a solvent-independent rate constant. This result is remarkable since it is independent of the protic or aprotic nature of the solvent.

Acknowledgments

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