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Medium effects on the photochemical reaction between pyrene and indole. A laser flash photolysis study

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Abstract

A laser flash photolysis study of the photoinduced electron-transfer reaction between pyrene and indole is reported. The pyrene radical anion and the hydropyrenil radical were confirmed as reaction intermediates from their transient absorption spectra. The photobleaching of pyrene was observed in the presence of indole but not in the presence of 1-methylindole. The quantum yields of the reaction and of the transient species are highly dependent on the solvent. The reaction was also carried out in the presence of tetrabutylammonium perchlorate, and an inhibitory effect by the salt was observed. At the same time, the quantum yield of the free ions increased. The results were interpreted by a mechanism that involves a proton transfer following the initial electron transfer. The effect of micelles on the reaction was also investigated.

Keywords: Pyrene; Indole; Laser flash photolysis; Electron transfer

1. Introduction

The quenching of the excited singlet state of pyrene by indolic compounds has been the subject of several studies both in homogeneous [1,2] and microheterogeneous [3–5] solution. In non-polar solvents, indole derivatives have been shown to form emissive exciplexes with pyrene and 1-cyanopyrene [1]. In polar solvents, the bimolecular quenching rate constant increases with increasing solvent polarity [4], becoming near diffusion controlled in water. In micellar solutions, the quenching of pyrene by indole and tryptophan was employed by Encinas and Lissi [4,5] for the determination of the partition coefficient of the indolic compounds. The electron-transfer nature of the quenching process has been confirmed by laser flash photolysis experiments [2] and the solvent effect on the quantum yield of charge separation was measured. It was also observed [2] that a photochemical reaction that leads to the consumption of pyrene takes place in homogeneous solvents with fair efficiency. The reaction presents several aspects of interest from the point of view of the medium effects on electron-transfer reactions.

The photoaddition of aromatic amines to polycyclic aromatic hydrocarbons is a well known reaction [6]. The particular case of the reaction of aniline with anthracene has been the subject of a kinetic study [7] with special emphasis on the solvent effect on the quantum yield. The reaction proceeds from the excited singlet of anthracene and it is thought that an exciplex is the intermediate. We also observed that indole reacts in a similar way with anthracene [8]. During our investigation of the solvent effects on the quenching of the excited singlet of pyrene (Py) by indole (In) [2], we noticed that also in this case the efficiency of the photobleaching of pyrene was highly dependent upon the solvent. However, several aspects of the mechanism of these reactions are still obscure. In this paper, we present a study by laser flash photolysis of mechanistic aspects of the reaction between photoexcited pyrene and indole. In particular, solvent effects on the quantum yield and the transient absorption spectra are analysed.

Electron-transfer reactions are susceptible to salt effects because of the increase in 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). The role of contact and solvent-separated ion pairs in the presence of salts in organic photochemistry has been reviewed recently [9]. A study of how the Py–In photoreaction is affected when it is carried out in micelles and in the presence of tetrabutylammonium perchlorate (TBAP) is also presented here.

2. Experimental details

The solvents acetone, acetonitrile (MeCN) and methanol (MeOH) of Sintorgan HPLC grade and ethanol (EtOH)

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from Merck were used without further purification. Propionitrile (PrCN) was obtained from Fluka, it was distilled and passed through a silica gel column before use. Pyrene from Merck was purified by recrystallization from methanol. Indole was purchased from Sigma (crystalline) and was used without further purification. 1-Methylindole (MeIn) from Aldrich was vacuum distilled and stored under nitrogen. TBAP was obtained from Sigma and used as received. The surfactants sodium dodecyl sulphate (SDS) and cetyltrimethylammonium chloride (CTAC) were recrystallized prior to use. Brij 35 from Koch-Light was used without further purification. It was verified that the absorption and emission intensities of the detergents were negligible at the wavelength ranges of interest.

Stationary fluorescence quenching experiments were carried out with a Spex Fluoromax spectrofluorimeter. For transient absorption and fluorescence lifetime determinations, a nitrogen laser (Laseroptics), 5 ns FWHM and 5 mJ per pulse, was employed. The laser flash photolysis set-up was described previously [10]. For fluorescence measurements, the laser beam was highly attenuated. The sample was placed in a TRW 75A filter fluorimeter 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 prior to use by nitrogen bubbling.

Quantum yields of pyrene triplet state and radical anions were determined by the laser flash photolysis technique. To avoid photolysis effects the solutions were changed after exposure to a few laser pulses. The quantum yields were determined by actinometry with ZnTPP (zinc tetraphenylporphyrin) 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 for ZnTPP, respectively [11]. For the triplet of pyrene ϵ_T was taken as 30 000 M^{-1} cm^{-1} at the absorption maximum [12] and 49 200 M^{-1} cm^{-1} was used for the extinction coefficient of the pyrene radical anion [13]. The extinction coefficients were assumed to be the same in all the solvents.

Continuous photolysis experiments were performed with a monochromatic illumination system (Photon Technology International) equipped with a 150 W xenon lamp. Actinometry was effected with Aberchrome 540 (Aberchromics) according to the experimental procedure described in the literature [14].

3. Results

3.1. Photoreaction in homogeneous solution

When pyrene is irradiated continuously at one of its absorption peaks in the near-UV region in the presence of indole, bleaching of the former is apparent, concomitantly with the appearance of a new broad band shifted to the red (Fig. 1). An isosbestic point can be observed, which may be taken as an indication of a clean photochemical reaction. This effect is observed at high indole concentration and it is solvent dependent. In Fig. 2 the bleaching of the Py band at 334 nm is plotted as a function of time under different conditions for

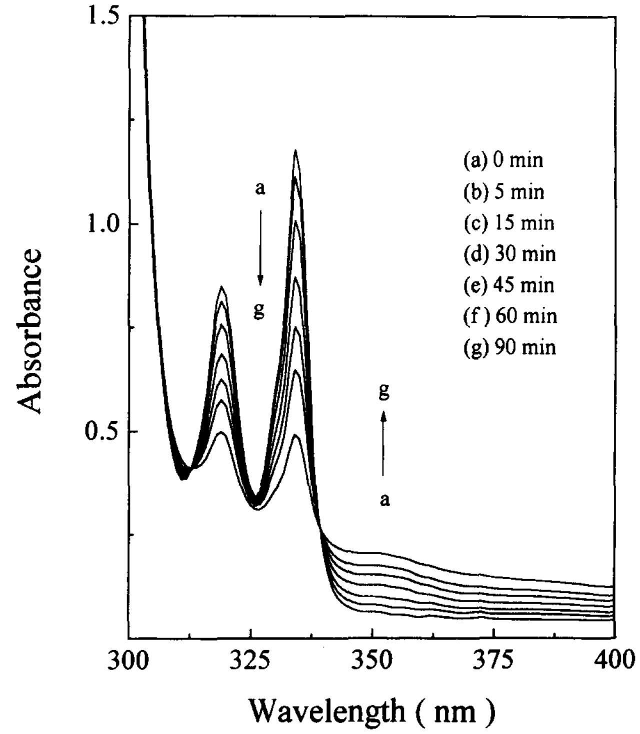


Fig. 1. Absorption spectra of an ethanolic solution of pyrene in the presence of indole as a function of the photolysis time. Indole concentration, 0.3 M; irradiation, 334 nm.

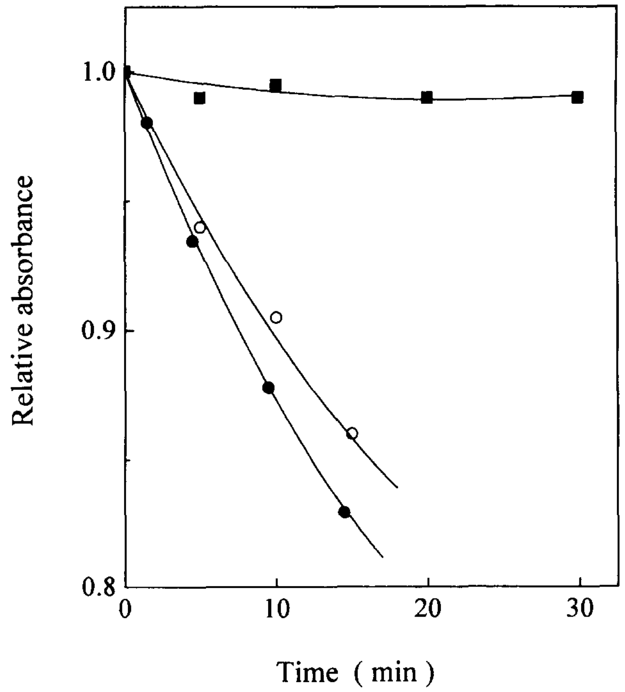


Fig. 2. Continuous photolysis at 334 nm of pyrene in the presence of indoles in acetone and ethanol. Relative absorbance of the pyrene longest wavelength band vs. time. Concentration of indoles, 0.3 M. (■) 1-Methylindole in ethanol; (○) indole in ethanol; (●) indole in acetone.

Table 1
Photobleaching quantum yields, rate constants and free ion quantum yields for the electron-transfer quenching of pyrene excited singlet by indole

Solvent	ϵ [a]	Φ_r	k_q ($M^{-1} s^{-1}$)	Φ_{ion}
MeCN	35.9	0.022	2.4×10^8	0.37 ± 0.02
PrCN	28.9	0.018	1.1×10^8	0.24 ± 0.04
Acetone	20.6	0.013	4.8×10^7	0.16 ± 0.02
MeOH	32.7	0.0012	1.5×10^8	0.22 ± 0.02
EtOH	24.6	0.0083	6.4×10^7	0.04 ± 0.01
EtOH	24.6	<0.0005 [b]	5.5×10^7 [b]	0.04 ± 0.01 [b]

[a] Dielectric constant.
[b] For 1-methylindole.

In itself and the *N*-methylated derivative (MeIn). It can be seen that when the H atom on the N heteroatom is replaced by a methyl group the system is very much less reactive. From the absorbance changes as a function of time, quantum yields for pyrene photobleaching were determined. The data were plotted according to Eq. (1) and the quantum yields were evaluated from the initial slope of the plots.

$$\ln\left(\frac{10^{A}-1}{10^{A_0}-1}\right)=(2.303I_0\epsilon_G\Phi_r)t \qquad (1)$$

where A_0 and A are the absorbance of pyrene at the irradiation wavelength when $t=0$ and after time t, respectively, ϵ_G is the extinction coefficient at the same wavelength, I_0 is the incident light intensity and Φ_r is the reaction quantum yield. The quantum yields in the different solvents are collected in Table 1.

It is known that indole quenches the singlet state of pyrene with rate constants that are dependent on the dielectric constant of the solvent [2,4]. For the solvents studied here, the quenching rate constants as determined from fluorescence lifetime measurements are also shown in Table 1. It can be seen that they decrease with a decrease in the dielectric constant irrespective of the nature of the solvent, protic or aprotic. It is also apparent from Table 1 that there is not a simple correlation between photobleaching quantum yields and the quenching rate constants. This is not unexpected since the quantum yields were determined under experimental conditions such that more than 90% of the excited singlets were quenched by indole. Therefore, the variation in quantum yields must reflect differences in the processes following the initial quenching step.

In order to obtain further insight into the photoreaction, laser flash photolysis experiments were carried out on the system. When transient absorption spectra are taken in a homogeneous solvent, it is observed that at 2 μs after the laser pulse the typical absorption peaks of the triplet (415 nm) and the radical anion (495 nm) of pyrene are present (Fig. 3). After 200 μs, the bands of the radical anion and the triplet have been replaced by a new band centred near 400 nm. This new band can be ascribed to the hydropyrenyl radical [13]. The results are qualitatively similar in all the solvents, with varying proportions of the transient products. The quantum yields of ion radicals in ethanol were approximately the same for both MeIn and In. However, the absorption band of the hydropyrenyl radical was not observed at 200 μs after the flash when pyrene was quenched by MeIn.

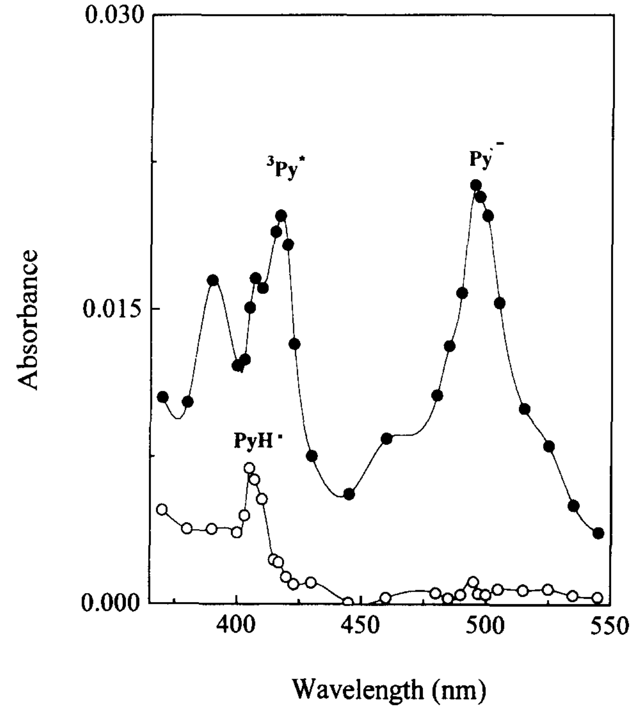


Fig. 3. Transient absorption spectra of pyrene–indole 0.3 M in acetone. (●) 2 μs after the laser pulse; (○) 200 μs after the laser pulse.

3.2. *Effect of added salt*

It is well known that the presence of salts affects the rate and yield of photoinduced electron-transfer reactions [9]. When the irradiation of Py–In solutions is carried out in the presence of TBAP, inhibition of the photobleaching of pyrene is observed. Fig. 4 shows a plot of absorbance versus time in acetone in the absence and presence of TBAP at two different concentrations. No complexation of TBAP with Py or In was observed by optical absorption measurements in the concentration range employed. Together with a reduction in the photobleaching quantum yield, the addition of TBAP to the system produces an increment in the quantum yield of pyrene radical anion. In Table 2 the photobleaching and the radical anion quantum yields are given as a function of the salt concentration. When the photobleaching quantum yields in acetone are plotted in the form of a Stern–Volmer relationship as a function of TBAP concentration, a straight line is obtained as shown in Fig. 5.

3.3. *Micellar effect on the photoreaction*

The effect of surfactants on the photoreaction can be seen in Fig. 6. Both cationic (CTAC) and anionic (SDS) micelles greatly reduce the photobleaching of Py, whereas for the neutral Brij 35 micelles the inhibitory effect is much less. In

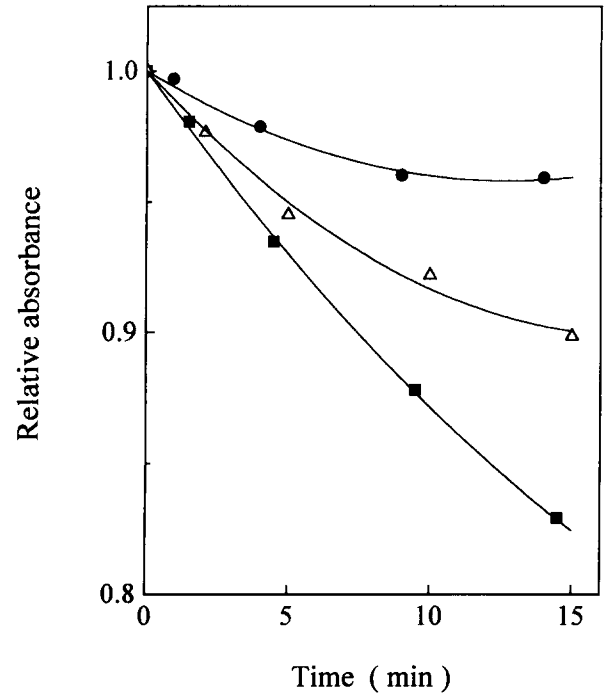


Fig. 4. Effect of TBAP on the photobleaching of pyrene by indole in acetone. [TBAP]: (■) 0; (△) 0.018; (●) 0.017 M.

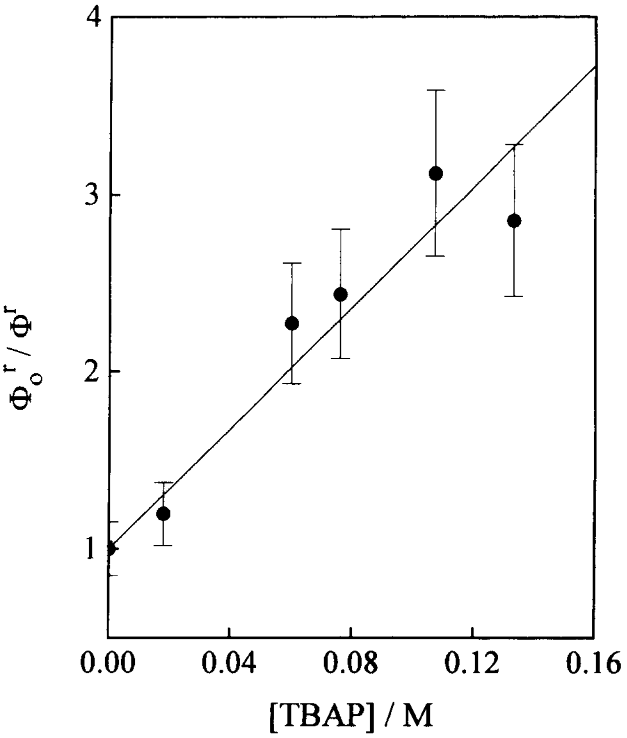


Fig. 5. Stern–Volmer plot for the photobleaching of pyrene in the presence of TBAP in acetone. The error bars were estimated from the experimental uncertainty in the actinometry and the reproducibility of the photobleaching curves.

Table 2
Salt and micellar effects on the photoreaction and quantum yields of free ions

Solvent	[TBAP] (M)	Φ_r	Φ_{ion}
MeCN	0	0.022	0.37
	0.089	0.016	0.56
EtOH	0	0.0083	0.037
	0.098	0.0023	0.162
Acetone	0	0.013	0.16
	0.018	0.011	–
	0.043	–	0.32
	0.060	0.0059	0.36
	0.076	0.0055	0.39
	0.107	0.0043	–
	0.133	0.0047	0.46
CTAC		0.0004	0.32
SDS		0.0005	0.11
Brij 35		0.0014	0.12

Fig. 7 the effect of the three surfactants on the radical ion yield is shown. For CTAC micelles, at the same time that inhibition of the reaction is observed, an enhancement in the yield of free ions is apparent. On the other hand, in SDS the yield of radical ions is very low. The photobleaching and quantum yields of radical ions in the micellar solutions are also presented in Table 2.

4. Discussion

The experimental results show that the photobleaching of pyrene by indole derivatives is much more important for

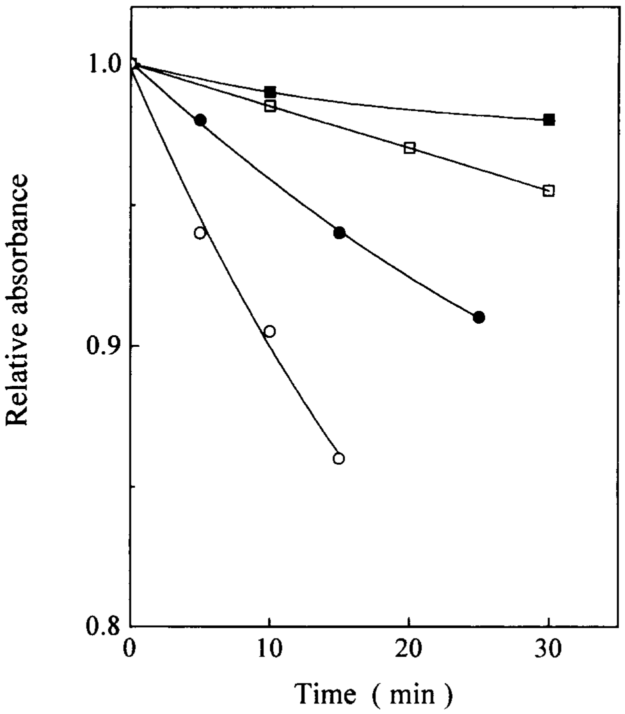


Fig. 6. Micellar effect on the photolysis of pyrene–indole. The surfactant concentration was 0.08 M in all cases and the indole concentration was such that more than 90% of the excited singlets were intercepted. The curve in ethanol is included for the sake of comparison. (○) Ethanol; (●) Brij 35; (□) SDS; (■) CTAC.

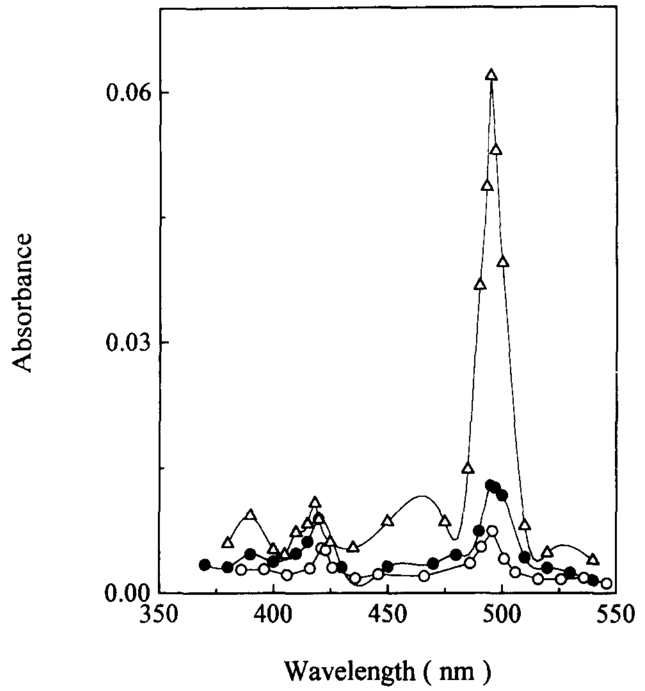
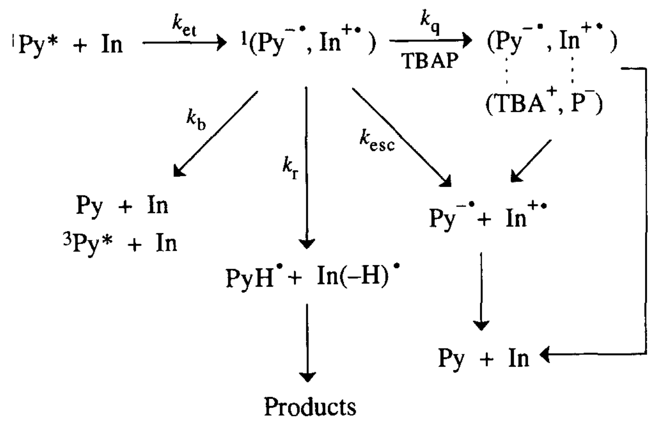


Fig. 7. Transient absorption spectrum 1 μs after the laser pulse for the system pyrene–indole in micellar solutions. Experimental conditions as in Fig. 6. (○) SDS; (●) Brij 35; (△) CTAC.



Scheme 1.

indole itself than for 1-methylindole. Another important result is that we were unable to observe the hydropyrenyl radical by laser photolysis when it was carried out in the presence of MeIn. The above results suggest that the hydrogen atom on the nitrogen of the indole ring is taking part in the reaction. Furthermore, the addition of TBAP to the system produces an increment in the quantum yield of pyrene radical anion and a reduction in the pyrene photobleaching quantum yield. These results suggest that both the hydropyrenyl radical and the pyrene radical anion have a common precursor. In this way, the photoreaction may be explained if it is assumed that the mechanism involves a proton-transfer step after the initial electron transfer and parallel to the separation into free ions (Scheme 1). Hydropyrenyl and indolyl radical are produced, which by reaction with the solvent or geminate recombination give rise to the stable photoproducts.

In Scheme 1, ${}^1(Py^{-\bullet}, In^{+\bullet})$ represents the geminate ion pair formed in the electron-transfer process. Two extreme cases for the structure of this ion pair are commonly distinguished: one is the contact ion pair, similar in many aspects to the exciplex, and the other is the solvent separated ion pair [9]. That one or the other is formed depends on, among other factors, the solvent polarity and the nature of the donor and acceptor. Of course, both types may be present simultaneously for a given reacting pair, and the interconversion between them may be a very fast process. In this case they will be in a pseudo-equilibrium and the distinction, based only on kinetic evidence, will be very difficult. In the case of proton-transfer reactions of the radical ion pair, the intermediate is better characterized as a contact ion pair [15]. In the photoreaction between anthracene and aniline [7], it was observed that the quantum yield was higher in the low-polarity solvents. The higher yield in low-polarity solvents may be rationalized by a stabilization of the contact ion pair with respect to the solvent-separated ion pair, which will be the preferred species in the more polar solvents. When our results in MeCN and the two alcohols are compared with those in Ref. [7], it is observed that the trends are very similar. However, these solvents are of similar macroscopic polarity and the reaction quantum yields differ widely. Therefore, the trend is not easily explained by changes in the solvent polarity, but specific effects are also playing an important role.

Moreover, that this is the case is confirmed by laser photolysis results. In acetonitrile the radical anion of pyrene decays faster than the rate expected for a second-order recombination reaction. It was previously observed for the quenching of pyrene by aliphatic amines that also in this case the radical anion decays faster in acetonitrile and it does not follow a simple kinetic law [16]. Therefore, the higher quantum yield in acetonitrile may be due to a different reactive route. In fact, in the continuous photolysis experiments it was observed that the spectrum remaining after a high extent of bleaching is totally different in acetonitrile than in acetone.

The effect of TBAP on the reaction quantum yield and the photoreaction can be analysed quantitatively with the aid of Scheme 1. The quenching of exciplexes by salts is a well known effect. In most cases it is due to the participation of a quadrupolar intermediate formed between a contact ion pair (exciplex) or a solvent-separated ion pair and the undissociated salt [17–20]. In our case, the linearity of the Stern–Volmer plot of the photobleaching quantum yields in acetone as a function of TBAP concentration is an indication that the addition of the salt introduces a new channel for the decay of the contact ion pair. For a solvent of medium polarity such as acetone, the quadrupolar mechanism could explain the experimental results, although the participation of dissociated ions of TBAP and the counterion exchange with the contact ion pair cannot be ruled out in the solvent employed.

According to the mechanism, the Stern–Volmer relation can be written as

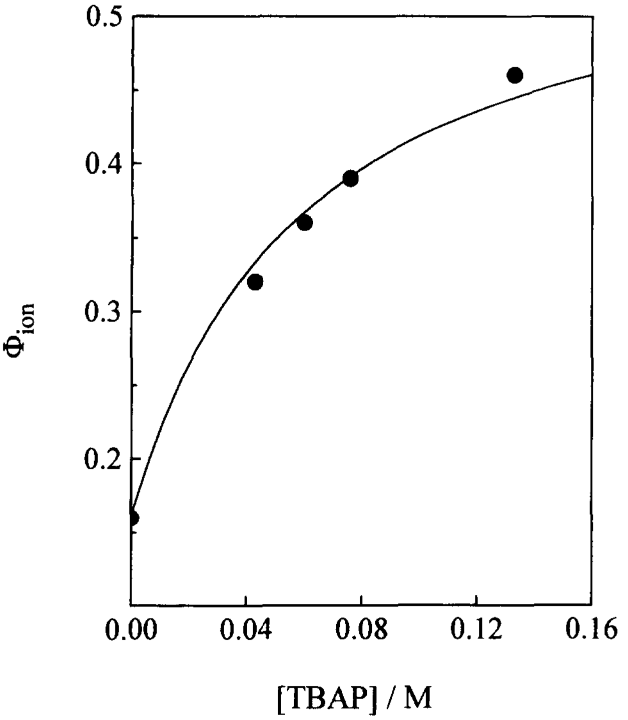


Fig. 8. Quantum yield of pyrene anion radical in the presence of tetrabutylammonium perchlorate in acetone. The solid line was calculated with Eq. (5) as discussed in the text.

$$\frac{\Phi_r^0}{\Phi_r} = 1 + k_q\tau_{ip}[\mathrm{TBAP}] \qquad (2)$$

where

$$\tau_{ip} = \frac{1}{k_b + k_r + k_{esc}} \qquad (3)$$

is the lifetime of the contact ion pair in the absence of the salt. From the slope in Fig. 5, a Stern–Volmer constant ($k_q\tau$) value of $17.0 \pm 1.3\ \mathrm{M}^{-1}$ was obtained.

According to the scheme, the quenching of the ion pair by the salt may also produce free pyrene radical anions. Therefore, the radical anion quantum yield must be written as the sum of two processes:

$$\Phi_{ion} = \Phi_{ip}\left(\frac{k_{esc}}{\tau_{ip}^{-1} + k_q[\mathrm{TBA}]} + \frac{Pk_q[\mathrm{TBA}]}{\tau_{ip}^{-1} + k_q[\mathrm{TBA}]}\right) \qquad (4)$$

where Φ_{ip} is the quantum yield of formation of the geminate ion pair and P is the probability that the quadrupolar complex produces a free pyrene radical anion. After reorganization, Eq. (4) results in

$$\Phi_{ion} = \Phi_{ip}\,\frac{\Phi_{ion}^0 + Pk_q\tau_{ip}[\mathrm{TBA}]}{1 + k_q\tau_{ip}[\mathrm{TBA}]} \qquad (5)$$

where $\Phi_{ion}^0 = k_{esc}\tau_{ip}$. Φ_{ip} was taken as equal to the fraction of pyrene quenched by indole.

The experimental data for Φ_{ion} vs. [TBAP] in Fig. 8 were fitted by a non-linear least-squares method to Eq. (5). The product $k_q\tau_{ip}$ is known from the Stern–Volmer plot for the photobleaching and Φ_{ion}^0 is the radical ion quantum yield in the absence of TBAP. Therefore, the fitting was performed with only one adjustable parameter, P. A value of 0.57 ± 0.01 was obtained for P, which confirms the likelihood of the model.

From the results in Table 2, it can be seen that ionic micelles greatly reduce the photoreaction quantum yield compared with those in polar solvents. Nevertheless, the quantum yields of the free ions remain low in these media. The micellar interface of CTAC may preclude the proton-transfer step by expelling the indole radical cation from the interface [21] or, more probably, by establishing a longer distance for the electron-transfer step, such that the proton transfer is very much less probable. On the other hand, the inhibitory effect of SDS and the very low yield of radical ions can be explained by the negative interface which retains the radical ion of the indole, while the more hydrophobic pyrene radical anion remains more deeply located in the micellar core, at such a distance that proton transfer is inhibited, and the ions decay to the ground state by a long-distance back electron-transfer process. That the inhibitory effect of CTAC and SDS is due to the charged interface is confirmed by the smaller inhibitory effect for the neutral Brij 35 micelles.

In conclusion, the reaction between Py and In proceeds by an electron-transfer mechanism that involves the participation of a contact ion pair (exciplex) initially formed in the quenching of the excited singlet state. The photoreaction quantum yield is reduced by the presence of salt or surfactant molecules. This effect may be rationalized by the interaction of the salt with the exciplex, or by the presence of the charged interface in the case of micelles.

Acknowledgements

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