

Salt Effects on Photoinduced Electron Transfer Reactions. The Role of Quadrupolar Intermediates in the Quenching of Exciplexes by Quaternary Ammonium Salts

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São apresentados vários exemplos de efeito salino na transferência fotoinduzida de elétrons. São discutidas as interações específicas de sais de amônio quaternários com exciplexos e/ou pares iônicos geminados, e o papel de intermediários quadrupolares na supressão de exciplexos. O efeito salino na eficiência da separação de carga para reações de fototransferência de elétrons também foi estudada para a supressão do singlete de pireno por doadores e aceptores de elétrons.

Several examples of salt effects on photoinduced electron transfer reactions are presented. The specific interactions of quaternary ammonium salts with exciplexes and/or geminate ion pairs and the role of quadrupolar intermediates in the quenching of exciplexes are discussed. The salt effect on the charge separation efficiency of photoelectron transfer reactions was also studied for the singlet quenching of pyrene by electron donors and acceptors.

Keywords: *electron transfer, quadrupolar intermediates*

Introduction

The electron transfer mediated photoreactions are an extensively studied domain in chemistry. Starting with two neutral molecules, a donor (D) and an acceptor (A), an electron transfer reaction between these entities produces charged species. The photoinduced electron transfer and charge separation processes may be classified^{1,2} according to Scheme 1.

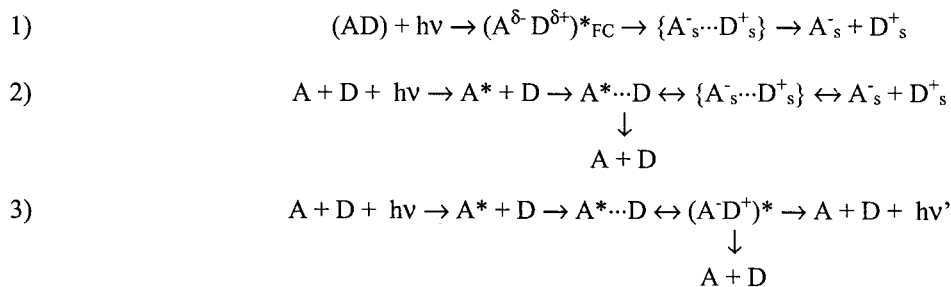
In the Scheme 1, path 1 represents the excitation and production of ions from an EDA (electron donor acceptor) complex in polar solvents. $(A^{\delta-} D^{\delta+})^*_{FC}$ is the excited Franck-Condon state that undergoes geometrical rearrangements and solvent reorganisation to form solvent shared ions pairs and/or dissociated ions. Path 2 represents the interaction in polar solvents between electron donor and electronically excited acceptor molecules. $\{A_s^- \cdots D_s^+\}$ is a geminate pair of solvated ion radicals or a solvent shared ion pair. Path 3 represents the exciplex type interaction, in nonpolar solvents the exciplex is the predominant species. $(A \cdot D)^*$ is a contact ion-pair or exciplex. In solvents of intermediate polarity, both the $(A \cdot D)^*$ type exciplex and

$\{A_s^- \cdots D_s^+\}$ geminate ion-pairs can be produced during the photoinduced electron transfer reaction.

Processes 1 and 2 may occur simultaneously for the same donor-acceptor pair, and process 1 may be important at high concentrations of one of the reaction partners. In some cases they can be studied selectively because of the red shifted absorption band of the EDA complex.

In these reactions, the separation of the initially formed radical ion pair into free ions A_s^- and D_s^+ competes with the occurrence of the back electron transfer. Normally the back reaction is a very important process and, as a consequence the yield of dissociated ions is small. Therefore, a target of the research on photoredox systems is to suppress or diminish the back electron transfer. The use of coulombic effects to favour the separation of charged species is an effective approach, as shown by the studies of photoinduced electron transfer in micellar and/or polyelectrolyte solutions³.

These reactions should be also susceptible to salt effects because of the increase of the ionic strength (the normal salt effect) and/or specific interactions of the salt with $(A \cdot D)^*$, $\{A_s^- \cdots D_s^+\}$ and the free radical ions A_s^- and D_s^+ (the special or specific salt effect). The salt effects on electron transfer



Scheme 1.

reactions has been reviewed recently by Pac and Ishitani⁴ and the role of contact and geminated ion pairs in the presence of salts in organic photochemistry by Mattay and Vondenhof⁵.

Exciplex intermediates play an important role in electron transfer reactions. However, only recently coulombic effects have been employed in investigations on exciplexes. The quenching of exciplex emission by quaternary ammonium salts has been investigated by several groups^{6,7,8,9,10}. The quenching of exciplexes by salts is a case of the special salt effect where the participation of a quadrupolar intermediate formed between a contact ion pair (exciplex) or a geminate ion pair and the salt was proposed^{7,8,9}. Some attempts to understand the nature of the quenching species and the quenching dynamic were made^{7,8,9,10}, but not conclusive evidence of the presence of a quadrupolar intermediate was given. In low and intermediate polarity solvents the salts are partially or not dissociated at all^{11,12} and, furthermore, the formation of aggregates of two or more nondissociated molecules has been also reported¹⁰. The participation of the ions as quenchers, in solvents like pyridine and dichloromethane where the occurrence of free ions is important, could not be conclusively disregarded⁸.

Here we wish to present a series of results on the specific interactions of quaternary-ammonium salts with exciplexes and/or geminate ion pairs, observed in several photoinduced electron transfer reactions studied in our laboratory. Results are given on the fluorescence quenching of exciplexes by tetrabutylammonium salts and by a quaternary ammonium surfactant able to form reverse micelles. The salt effect upon the charge separation efficiency of photoelectron transfer reactions was also studied for the singlet quenching of pyrene by electron acceptors.

Experimental

The solvents used were Sintorgan or Aldrich HPLC grade and used without further purification. Tetrabutylammonium perchlorate was Fluka electrochemical grade and was dried before using. The amine, 1N2NE, was prepared by reduction with LiAlH₄ of the corresponding amide, which was obtained from the acid chloride and the amine^{13,14}. The compound gave satisfactory spectral and

elemental analysis¹⁵. All other chemicals were from Aldrich or Sigma and purified by standard procedures.

Chloride ion produced by photolysis was measured with an Orion specific ion electrode.

Fluorescence spectra and fluorescence quenching experiments were carried out with an Fluoromax spectrofluorimeter. Absorption spectra were obtained with a Hewlett Packard 8452A diode array spectrophotometer.

The set-up for transient absorption experiments consisted of a nitrogen laser (Laser Optics, 7 ns FWHM, 5 mJ per pulse) as the excitation source. The laser beam was directed at right angles to the analysing beam from a Xenon arc lamp. The detection system comprises a *f*/4 monochromator and a red extended photomultiplier (Hamamatsu R666 or RCA 4840). The signal of the photomultiplier was displayed, averaged and digitized by a Hewlett-Packard 54504A oscilloscope. It was then transferred via an IEEE interface to a PC computer, where it was processed.

Picosecond time resolved fluorescence spectroscopy was performed by the technique of time correlated single photon counting¹⁶ using a cavity-dumped, synchronously pumped, mode-locked dye laser (Coherent Antares/701-3CD/7220). The dye laser used Rhodamine 6G as the gain medium. This produces a pulse train of 3.8 MHz of less than 15 ps at 610 nm. This was frequency doubled and used as the excitation source ($\lambda_{ex} = 305$ nm). The fluorescence was collected at 90° and passed through a polarising filter set at the magic angle. The emission wavelength was selected with a Spex double monochromator in subtractive dispersion mode. A Hamamatsu R1564-U07 microchannel plate was used to detect the fluorescence, which together with Tennelec discriminators, an Ortec time to amplitude converter and a Canberra 35 multichannel analyser, give typical instrument response of 50 ps FWHM.

Results and Discussion

The effect of added salts on exciplex mediated photosensitised dechlorination reactions

The dimethylaniline sensitised dechlorination of 4-chlorobiphenyl

In previous work¹⁷ we showed that electronically excited dimethylaniline (DMA) sensitises the dehalogenation

of dichlorobenzenes by a mechanism that involves electron transfer from both the excited singlet and triplet state of DMA. In a study of the photodechlorination of 4-chlorobiphenyl (CIBi) sensitised by DMA, we found that the quenching of the singlet excited state of the DMA by CIBi in ethyl acetate solutions, is accompanied by the appearance of a fluorescence band ascribed to the formation of an exciplex⁹. In this medium polarity solvent we have shown that this exciplex is an intermediate in the dechlorination of CIBi. The quenching of the exciplex by lithium perchlorate and tetrabutylammonium perchlorate (TBAP) leads to an enhancement of the dechlorination quantum yield, Fig. 1. The results were interpreted by a specific electrostatic interaction between ion pairs of the salts and the exciplex. These ion pairs are believed to be the quenching species, probably an ion pair associates with the dipolar exciplex state to form an intermediate complex with the characteristics of a quadrupole^{7,9}. The formation of the quadrupole should reduce the back electron transfer reaction, increasing the decomposition probability of the radical anion of chlorobiphenyl, Scheme 2.

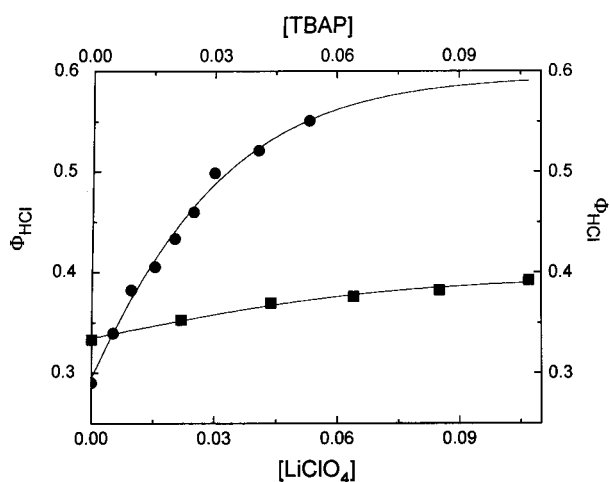
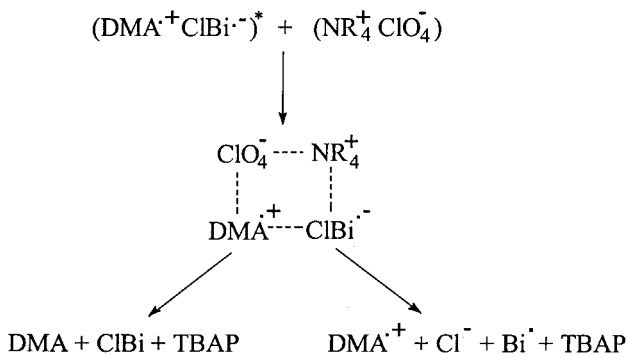


Figure 1. Plots of the hydrogen chloride quantum yield vs. the concentration of added salts: (●), TBAP (initial chlorobiphenyl concentration 0.084 M); (■), lithium perchlorate (initial chlorobiphenyl concentration 0.167 M).



Scheme 2.

The dechlorination of chlorobenzenes sensitised by the naphthalene-triethylamine exciplex

Exciplex fluorescence quenching is a powerful tool for examining the intermediacy of exciplexes in bimolecular photoreactions. The participation of an exciplex can be demonstrated if the exciplex fluorescence and the photo-product are reduced to the same degree when a quencher is added to a reaction system.

In the presence of triethylamine (TEA), the fluorescence of naphthalene (N) is quenched and the band of the exciplex is observed in low and medium polarity solvents. The exciplex fluorescence is quenched by the addition of chlorobenzenes. In ethyl acetate the quenching is accompanied by the dechlorination of the chlorobenzene together with the production of hydrogen chloride. An electron transfer mechanism from the exciplex to the chlorobenzene was postulated to explain the experimental results¹⁸.

To test the proposed mechanism, we studied the effect of TBAP on the N-TEA exciplex emission, and the hydrogen chloride quantum yield at a given chlorobenzene concentration. TBAP is stable to oxidation and reduction and has no low lying excited states, therefore quenching of the exciplex by electron transfer or energy transfer can be disregarded. The above properties, and because it does not quench the fluorescence of naphthalene, make these salts ideal to introduce a competitive pathway in a reaction scheme involving exciplexes. Stern-Volmer analysis of the exciplex quenching shows linear behaviour in a reduced concentration range of TBAP with a slight downward curvature at higher concentrations, Fig. 2. From the initial slope of the Stern-Volmer plot and the fluorescence lifetime of the exciplex, a rate constant of $2.8 \pm 0.3 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$ was obtained for the quenching. The production of hydrogen chloride was also measured in the presence of

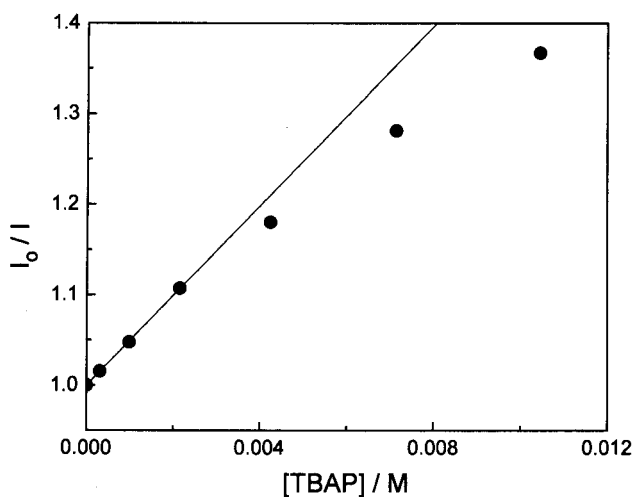


Figure 2. Quenching of the naphthalene-triethylamine exciplex by tetrabutylammonium perchlorate in ethyl acetate.

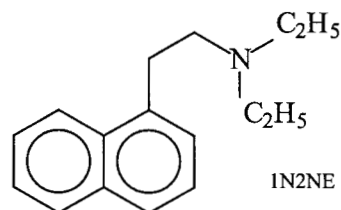
TBAP. As a result of the quenching of the exciplex by TBAP, a decrease in the production of hydrogen chloride is expected. A Stern-Volmer plot for the hydrogen chloride quantum yield is shown in Fig. 3. Scheme 3 shows the reactions involved, and the following Stern-Volmer equation applies:

$$\Phi_{\text{ClH}}^0 / \Phi_{\text{ClH}} = 1 + k_q \tau_{\text{exc}} [\text{TBAP}] \quad (1)$$

where τ_{exc} is the fluorescence decay time of the exciplex in the presence of the chlorobenzene. From Fig. 3, a value of $2.3 \pm 0.4 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$ was obtained for k_q in good agreement with the rate constant obtained from fluorescence quenching. The quenching of the N-TEA exciplex by the salt can be explained by the same mechanism used for the chlorobiphenyl-DMA exciplex.

The salt effect on the emission properties of the naphthalene-TEA intramolecular exciplex

Another system on which we investigated the salt effects is the intramolecular exciplex of 1-(1-naphthyl)-2-N,N-diethylaminoethane (1N2NE), Scheme 4. When naphthalene and triethylamine are linked by a methylene chain, it has been reported that after excitation of the naphthalene moiety it is possible to observe intramolecular exciplex formation^{19,20,21,22}. In contrast to intermolecular exciplexes of aromatic hydrocarbons and amines, the intramolecular exciplex of 1N2NE fluoresces in polar solvents like acetonitrile, with high quantum yield (approximately



Scheme 4.

0.04)^{20,21,22}. The unusual fluorescence properties of 1N2NE suggested its use to probe the quenching mechanism of exciplexes by quaternary ammonium salts.

The fluorescence intensity of the intramolecular exciplex formed by 1N2NE is clearly quenched by TBAP in tetrahydrofuran (THF), as shown in Fig. 4. It can be seen

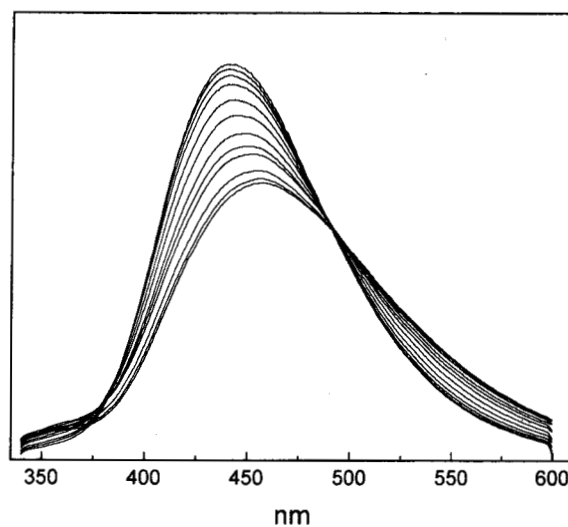


Figure 4. Fluorescence spectra of 1N2NE in tetrahydrofuran with increasing concentrations of TBAP $0 \leq [\text{TBAP}] \leq 0.021 \text{ M}$

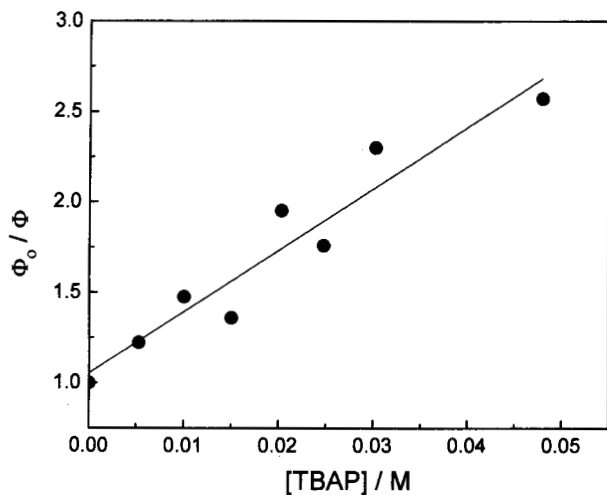
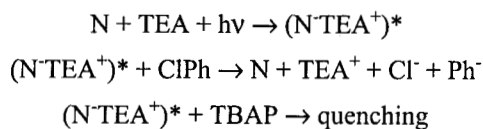


Figure 3. Stern-Volmer plot for the production of hydrogen chloride in the presence of tetrabutylammonium perchlorate.



Scheme 3.

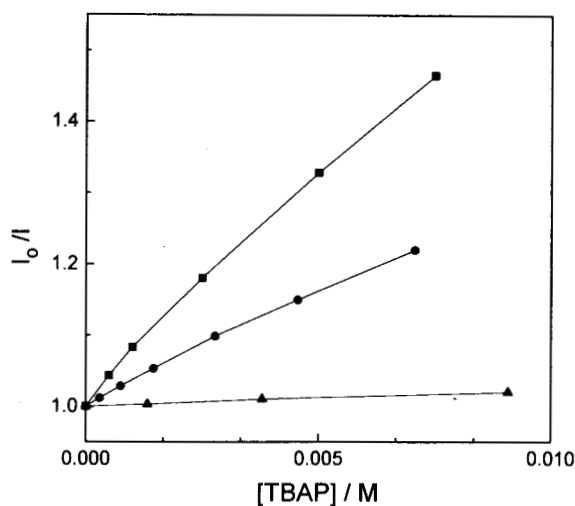


Figure 5. Stern-Volmer plots for the quenching of 1N2NE by TBAP in 1,4-dioxane (■), tetrahydrofuran (●) and acetonitrile (Δ).

that the fluorescence quenching is accompanied by a red shift of the emission maximum and the appearance of an isoemissive point.

In Fig. 5 the Stern-Volmer plots for the quenching of 1N2NE by TBAP in three solvents are shown. The results indicate that the quenching is strongly dependent on the polarity of the medium, it increases when the dielectric constant of the solvent decreases. In a polar solvent like acetonitrile, there is almost no quenching of the exciplex by the salt. It can be observed in Table 1 that there is a qualitative relationship between the extent of quenching and the fraction of salt associated, which was calculated by means of the Fuoss equation^{11,12}. As this fraction is reduced the quenching becomes less, indicating that the free ions do not contribute significantly to the quenching of the exciplex.

To understand the red shift of the fluorescence band of the exciplex with the addition of TBAP, picosecond time resolved fluorescence spectroscopy was performed. The fluorescence of 1N2NE decays exponentially in acetonitrile and THF with decay times of 12.18 and 14.17 ns, respectively. In 1,4-dioxane the decay is complex and more than one exponential is necessary to fit it.

In Fig. 6 are shown the time resolved spectra of 1N2NE in THF solution. They were obtained in the presence of 0.028 M TBAP at different times after the excitation of 1N2NE. The fluorescence decay is complex, and depends

Table 1. Estimated association percentage calculated by means of the Fuoss equation at 5 and 50 μ M concentration of the salt in different solvents.

Solvent	ϵ	K	% association at 5 mM	% association at 50 mM
1,4-dioxane	2.23	8.04×10^{16}	100	100
THF	7.8	2.76×10^4	92	97
Acetonitrile	37.5	3.21	1.6	12

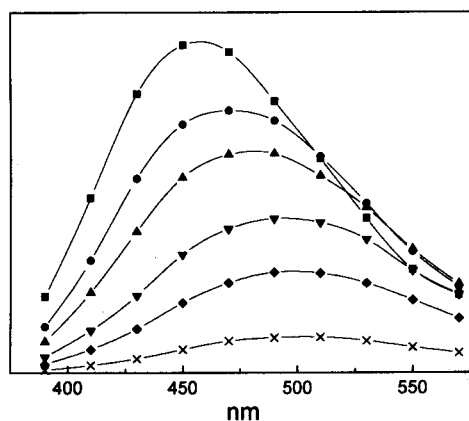


Figure 6. Fluorescence spectra of 1N2NE in tetrahydrofuran in the presence of 0.028 M TBAP obtained at different times after the excitation of 1N2NE. ■ = 0.3 ns; ● = 1.5 ns; Δ = 3.0 ns; ▽ = 7.0 ns; ◆ = 12.0 ns; × = 24.0 ns

on the emission wavelength at which it is analysed. It can be seen that the emission maximum progressively shifts to the red as time increases, indicating the presence of a new emitting species. The fluorescent spectrum observed 24 ns after the excitation is principally due to this new species²³.

The system was modelled as a typical one for two coupled fluorescent species, as shown in Scheme 5.

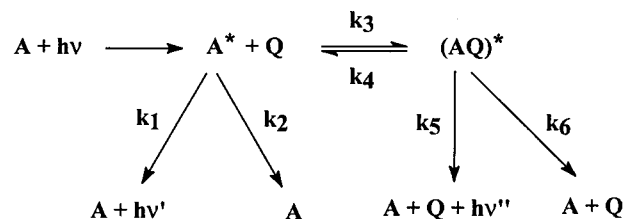
In the above scheme, A and (AQ)* represent 1N2NE and the quadrupolar complex, respectively. This complex probably has a structure as that proposed for the chlorobiphenyl-DMA exciplex^{7,9} (Scheme 6):

In conclusion, the quenching efficiency of the 1N2NE intramolecular exciplex by TBAP depends on the polarity of the solvent used. In polar solvents like acetonitrile, where the largest dissociation into free ions can be assumed, the quenching constant is small. This result indicates that free ions interact poorly with the exciplex, or that such interactions do not contribute to the deactivation of the fluorescent species. On the other hand, in solvents of intermediate polarity, like THF, the quenching of the exciplex leads to the reversible formation of a new fluorescent intermediate, with a quadrupole structure. This new species is stabilised by coulombic interactions and as a consequence, its fluorescence band is red-shifted relatively to that of the exciplex.

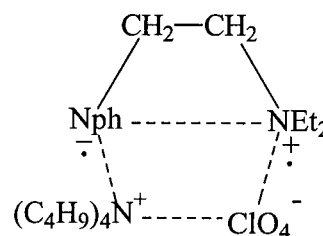
Fluorescence behaviour of exciplexes in BhdC reverse micelles

The addition of DMA to a solution of 1-methylpyrene (MP) in benzene results in the quenching of the MP fluorescence. This quenching is accompanied by the characteristic exciplex emission. Table 2 shows the fluorescence decay times, the emission maxima and fluorescence quantum yields of the exciplex.

The addition of benzylhexadecyldimethylammonium chloride (BHDC) to the exciplex solution quenches the



Scheme 5.



Scheme 6.

exciplex fluorescence. In Fig. 7 the Stern Volmer plot for the quenching of the MP-DMA exciplex by BHDC is shown. Here, evidently the quenching by BHDC is very efficient. This large quenching may be explained with the quadrupole model proposed for the quenching of several exciplexes by quaternary ammonium salts^{7,9}. In benzene the detergent will be mainly as ion pairs¹² or aggregates of ion pairs. Probably an ion pair associates with the exciplex to form an intermediate complex with the characteristics of a quadrupole, which favours non radiative transitions to the ground state.

It can be seen in Figs. 2, 5 and 7 that the Stern-Volmer plots for the fluorescence quenching of the exciplexes by the quaternary ammonium salts deviate from the linearity. In all cases the plots show a downward curvature indicating that the quenching efficiency decreases systematically with

Table 2. Fluorescence parameters of the MP-DMA exciplex in BHDC-benzene solutions at 30 °C.

Solvent	ϕ_f^a	λ_{\max} (nm)	$\tau_{(ns)}^b$
BHDC 0.05M			
R = 0	0.042	475	26
10	0.143	475	55
20	0.163	475	74
BHDC 0.2 M			
R = 0	0.023	475	13
10	0.047	475	23
20	0.061	475	31
Benzene	0.266	475	112

a) estimated error 10% b) estimated error 5%

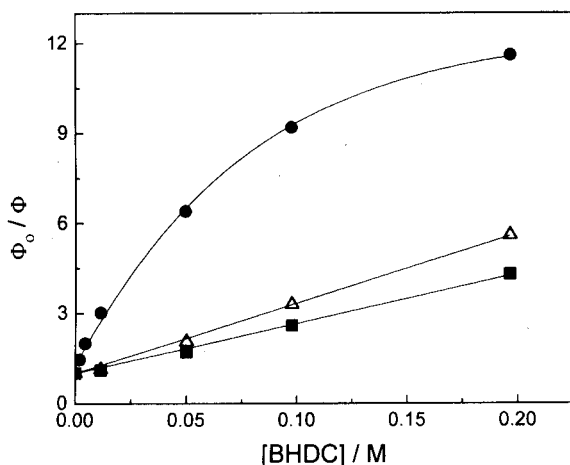


Figure 7. Stern-Volmer plots for the quenching of MP-DMA exciplexes by BHDC in benzene solutions at 30 °C. (●) R = 0; (Δ) R = 10; (■) R = 20.

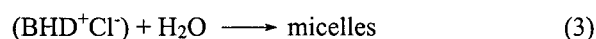
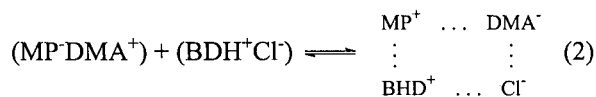
the increase of the quencher concentration. In the case of Fig. 7, the quencher is an amphiphilic compound (BHDC) that aggregates in solution, and this may be the reason of the observed curvature. When the quencher is TBAP dissolved in medium polarity solvents such as THF and ethyl acetate, the curvature in the Stern-Volmer plots can not be assigned conclusively to aggregation of the salt (see Table 1). Probably the downward curvature is the result of the emission of a fluorescent complex formed between the exciplex and the salt, in the same spectral region as the exciplex, as shown for the case of 1N2NE in Fig. 6. This new species is stabilised by coulombic interactions and as a consequence, its fluorescence band is red-shifted relatively to that of the exciplex.

The addition of water to a solution of BHDC in benzene results in the formation of reverse micelles. Reverse micelles in organic solvents are droplets of water surrounded by a layer of an amphiphilic compound. In these systems there are three compartments in which small probe molecules can be solubilized: the internal water pool, the interface formed by a monolayer of the surfactants' molecules and the external organic phase^{24,25}. In benzene solutions, BHDC is able to form microemulsions that are optically transparent and stable upon the addition of water until a molar water to BHDC ratio $R = [\text{water}]/[\text{BHDC}]$ of 25.

The addition of water to the solution of the MP-DMA exciplex in the presence of BHDC, produces incremental changes in the fluorescence quantum yield and fluorescence decay time of the exciplex. In Fig. 7 the Stern-Volmer plots for the quenching of the MP-DMA exciplex by BHDC at different values of R are shown. It is observed that the quenching decreases when R increases at a given BHDC concentration. The fluorescence quantum yield and the fluorescence decay time behaviour of the exciplex with the water content of the microemulsion are opposite to those observed in AOT/heptane solutions²⁶ and AOT/benzene solutions²⁷.

A quenching mechanism that can explain the experimental results is given by equations 1- 3 (Scheme 7).

In Scheme 7, BHD^+ stands for the benzylhexadecyldimethylammonium cation. This quenching mechanism may explain the observed increase in emission quantum yields and lifetimes with R. When water is added, the reverse micelles begin to form and less detergent ionic pairs are left free for quenching the exciplex. The emission maximum of the exciplex in BHDC solutions is at the same wavelength as in benzene (Table 2), indicating that the exciplex is formed in the organic phase. When all the polar groups of BHDC are hydrated and the reverse micelles are formed with their water pools, there is still a BHDC concentration quenching effect. This quenching may be explained with the model proposed by Kikuchi and Thomas²⁸. In this case



Scheme 7.

the quenching is due to the reverse micelle as a whole, and not to the ion pairs.

Salt effects on radical ion pairs and the charge separation efficiency of photoelectron transfer reactions

The pyrene-indole system

When a solution of pyrene in acetone is irradiated at 334 nm in the presence of indole, a bleaching of the absorption of pyrene is observed. Together with the bleaching, the

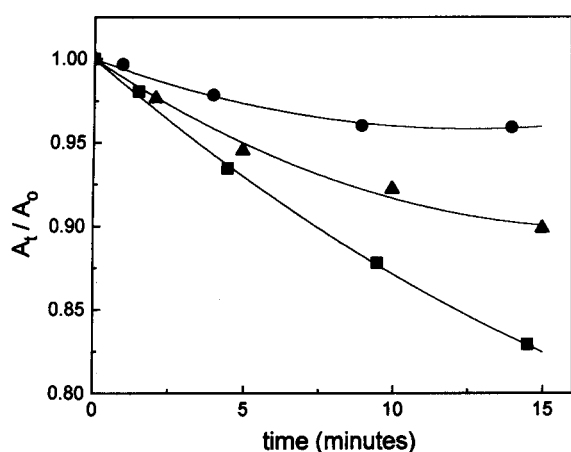


Figure 8. Photobleaching of pyrene by indole in acetone. (●) [TBAP] = 0 mM; (▲) [TBAP] = 18 mM; (■) [TBAP] = 107 mM.

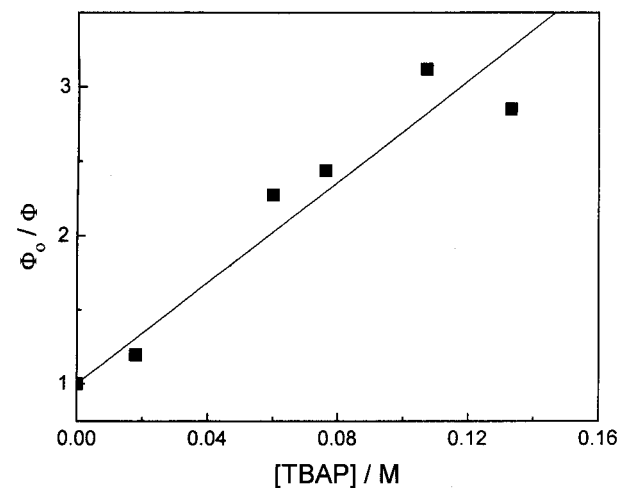


Figure 9. Stern-Volmer plot for the photobleaching of pyrene in the presence of tetrabutylammonium perchlorate.

appearance of new red shifted broad absorption band is observed. The electron transfer nature of the reaction has been confirmed by laser flash photolysis²⁹. The transient absorption spectra show that after the decay of the radical anion and triplet of pyrene a band centred at 400 nm still remains. This band can be ascribed to the hydroxyphenyl radical^{30,31}. The system was studied at a concentration of indole high enough to ensure that more than 95% of pyrene singlet was quenched. A reaction scheme with a geminate ion pair as a common precursor for the hydroxyphenyl radical, triplet and radical anion of pyrene was postulated^{29,32}.

No complexation of TBAP with pyrene or indole was observed by optical absorption measurements. Thus TBAP was chosen to study the salt effect on the photochemistry. The addition of TBAP to the reaction mixture inhibits the photobleaching of pyrene, Fig. 8. The reaction quantum yields were determined at different TBAP concentrations. A Stern-Volmer plot of the quantum yields is shown in Fig. 9, and a fairly good linear plot was obtained. This is an indication that the addition of TBAP introduces a new channel for the decay of the geminate ion pair. In Scheme 8 the set of reactions that can explain the experimental results is given.

From the Stern-Volmer expression for the photobleaching is:

$$\Phi_r^0/\Phi_r = 1 + k_q \tau [\text{TBAP}] \quad (2)$$

where

$$\tau = 1/(k_b + k_r + k_{\text{esc}}) \quad (3)$$

a Stern Volmer constant ($k_q\tau$) value of $17.0 \pm 1.3 \text{ M}^{-1}$ was obtained.

Together with a reduction in the pyrene photobleaching quantum yield, the addition of TBAP to the system produces an increment in the quantum yield of the pyrene

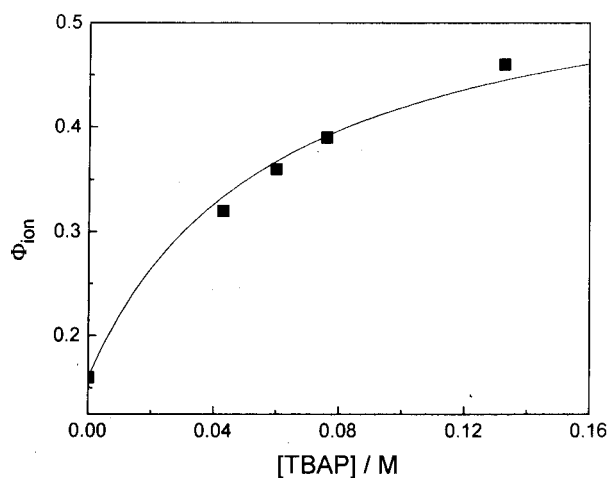
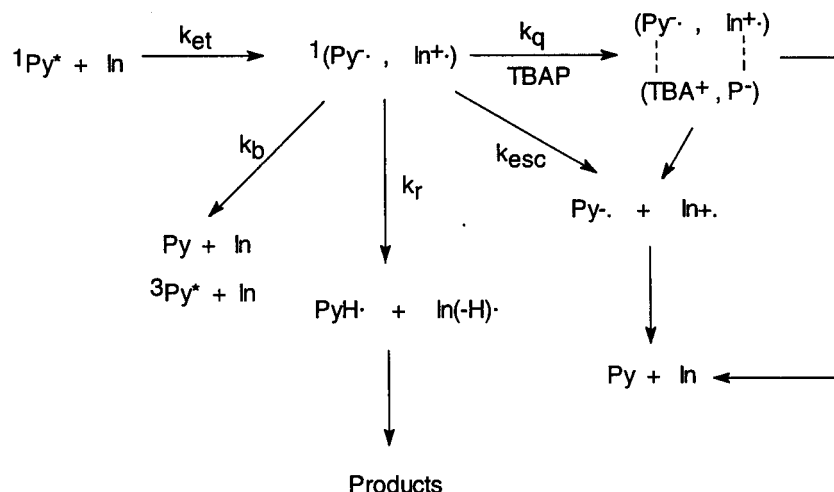


Figure 10. Quantum yield of pyrene anion radical in the presence of tetrabutylammonium perchlorate.



Scheme 8.

radical anion, as shown in Fig. 10. An increase of the quantum yield of radical ions has been also observed when a quaternary ammonium salt is added to the systems pyrene-1,4-dicyanobenzene in dimethoxyethane¹⁰ and zinc tetraphenylporphyrin-1,4-benzoquinone in 4-methylpentan-2-one³³. According to Scheme 8 there are two routes for the production of the pyrene radical anion. A unimolecular one that it is quenched by TBAP, and a bimolecular one that is more important when the TBAP concentration is increased. Therefore the radical anion quantum yield can be written as the sum of both processes:

$$\Phi_{\text{ion}} = \Phi_{\text{ip}} \left[\frac{k_{\text{esc}}}{((1/\tau) + k_{\text{q}}[\text{TBAP}])} + \left[\frac{Pk_{\text{q}}[\text{TBAP}]}{((1/\tau) + k_{\text{q}}[\text{TBAP}])} \right] \right] \quad (4)$$

which after reorganization results in

$$\Phi_{\text{ion}} = \Phi_{\text{ip}} \left[\frac{(\Phi_{\text{ion}}^{\circ} + P k_{\text{q}} \tau [\text{TBAP}])}{1 + k_{\text{q}} \tau [\text{TBAP}]} \right] \quad (5)$$

where $\Phi_{\text{ion}}^{\circ} = k_{\text{esc}}\tau$, Φ_{ip} is the quantum yield of formation of the geminate ion pair and P is the probability that the quadrupolar complex produces pyrene radical anion. Φ_{ip} was taken as equal to the fraction of pyrene quenched by indole, in this case approximately equal to one, because the experiments were performed at a quenching fraction larger than 0.95.

The experimental data of Fig. 10 were fitted by a non-linear minimum square method to Eq. 5. The fitting was performed with only one adjustable parameter, P , because $k_{\text{q}}\tau$ and $\Phi_{\text{ion}}^{\circ}$ are known from the photobleaching Stern-Volmer plot and the radical ion quantum yield without TBAP, respectively. From the fitting a value of 0.57 ± 0.01 was obtained for P . In conclusion, the addition of TBAP to the reaction system results in a large increase in the charge separation efficiency. The reaction mechanism probably involves a quadrupolar intermediate, al-

though the participation of dissociated ions of TBAP can not be ruled out in the solvent employed.

The Pyrene-Methylviologen and Pyrene-1,4-dicyanobenzene systems

Both, methylviologen (MV^{++}) and 1,4-dicyanobenzene (DCB) quench the fluorescence of pyrene behaving as electron acceptors. The systems were studied in a solvent mixture of acetonitrile-10% water, to dissolve a large amount of methylviologen to ensure that at least 90% of pyrene singlet state was quenched.

Transient absorption spectra of the system methylviologen-pyrene, obtained by laser flash photolysis, show two absorption maxima. One of them around 400 nm is assigned to the methylviologen cation radical ($\text{MV}^{+\cdot}$)^{34,35}, the other one centred at 452 nm is attributed to the cation radical of pyrene ($\text{Py}^{+\cdot}$)³⁶, Fig. 11. The addition of TBAP to the system reduces slightly the amount of radical cations.

Transient absorption spectra of the system Pyrene-1,4-dicyanobenzene are shown in Fig. 12. In this spectrum, the

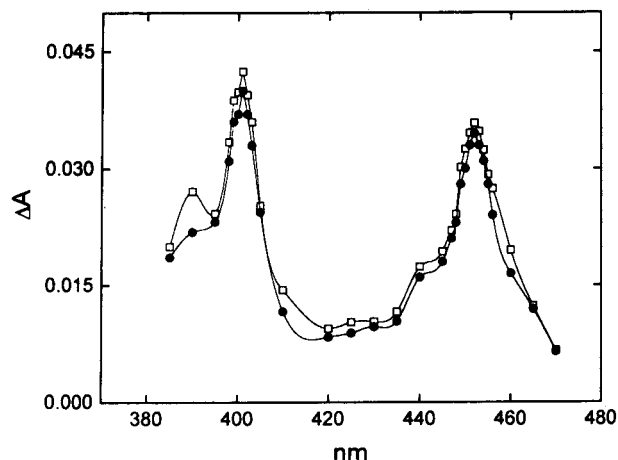


Figure 11. Transient absorption spectra of the pyrene-methyl viologen system in acetonitrile-water 9:1. (□) TBAP = 0 M; (●) TBAP = 0.052 M.

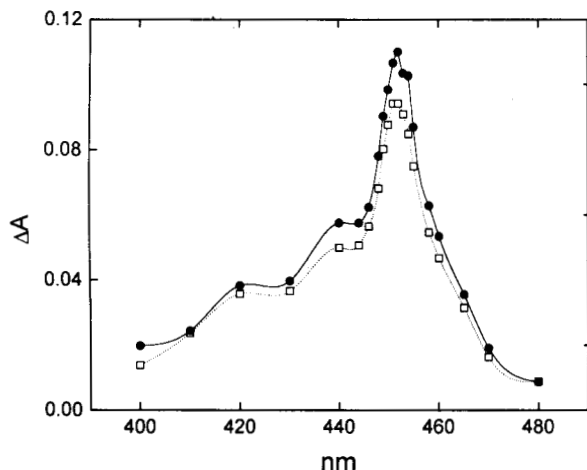


Figure 12. Transient absorption spectra of the pyrene-1,4-dicyanobenzene system in acetonitrile-water 9:1. (□) TBAP = 0 M; (●) TBAP = 0.052 M.

characteristic absorption of the pyrene cation radical are observed again. In this system, the addition of TBAP produces an increase of the pyrene cation radical.

A tentative explanation of the results must take into account that in the solvent employed the degree of association of the salt as a contact ion pair is probably less than 10% (Table 1). Primary salt effects, based on the Debye-Hückel theory, can be disregarded in both systems because the rate constants for the decay of the pyrene radical cation are the same in the presence and absence of TBAP.

Probably the effect of added TBAP is to exchange the counterions in the geminate radical ion pair ($\text{Py}^+\cdots\text{DCB}^-$) giving rise to the ion pairs ($\text{Py}^+\cdots\text{ClO}_4^-$) and ($\text{Bu}_4\text{N}^+\cdots\text{DCB}^-$). This type of association was observed by picosecond laser flash photolysis^{37,38,39}. This may be the cause of the increase of the radical ion quantum yield in the system Py-DCN. In the system Py-MV⁺⁺ the counterions exchange is not as effective as in the above example, because in the geminate radical ion pair both components have positive charge. Therefore, Bu_4N^+ will not be able to interact with the ion pair, and the ClO_4^- anion is probably not able to produce a specific interaction with the pyrene radical cation. Therefore, the system shows only minor changes in the absorption bands of the radical ions.

Conclusions

In low and medium polarity solvents, tetrabutylammonium salts are forming contact ion pairs. These ion pairs are believed to be the quenching species because free ions do not contribute much to the deactivation of the fluorescence of exciplexes. Since an exciplex can be considered in a restricted way⁴⁰ also a contact ion pair, the quadrupolar or distorted quadrupolar structure formed by the association of this ion pair with the one from the salt may be, plausibly claimed to be responsible for the quenching.

In the case of the DMA sensitised dechlorination of chlorobiphenyl, the addition of the salts probably changes the geometry of the exciplex enlarging the separation of the exciplex components. This will increase the decomposition probability of the chlorobiphenyl anion radical moiety of the exciplex. The quadrupolar intermediate can be considered also a precursor to counterion exchange in medium polarity solvents. This process results in an increase of the quantum yield of formation of radical ions as observed for the pyrene-indole system.

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