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Photodehalogenation of 9,10-Dichloroanthracene Induced by Electron Transfer Fluorescence Quenching with Primary and Tertiary Amines in Acetonitrile and *n*-Hexane. Salt Effect on Photodechlorination Process

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Quenching of 9,10-dichloroanthracene (DCA) fluorescence by primary or tertiary amines in acetonitrile solution results in formation of DCA radical anions, amine radical cations and triplet DCA, which were observed by nanosecond flash photolysis. In *n*-hexane, only the triplet-triplet absorption of DCA is observed. Rate constants of back electron transfer from the solvent separated radical ion pair (SSRIP), k_{bet}, were calculated from the quantum yields of charge separation and triplet state formation by assuming a rate of $5 \cdot 10^8$ s^{-1} for ion separation from the SSRIP. The rate constants k_{bet} follow the trends expected from the electron transfer theory (inverted Marcus region). Proton transfer from radical cation of primary amine to the radical anion of DCA, occurring in the contact radical ion pair (CRIP) has been found to be the decisive step for photodehalogenation in *n*-hexane. Importance of the heavy atom effect has been discussed on the basis of photophysical scheme, describing the processes occurring in the CRIP (SSRIP). It has been found, that lithium perchlorate catalyses the photodechlorination of DCA in acetonitrile solution, due to acceleration of the charge separation and retardation of the recombination of formed radical ion pair.

Key words: electron transfer fluorescence quenching, heavy atom effect, photodehalogenation, salt effect

The photodehalogenation of haloanthracenes with tertiary amines in acetonitrile has been thoroughly investigated [1–6]. The authors have identified the excited singlet state of the anthracene derivatives as the photoreactive state and have shown that the chemical process is initiated by charge transfer.

Previously [7] we found that the quenching rates of anthracene and bianthryl fluorescence by primary amines were consistent with classical electron transfer theories, but that the quantum yields of both triplet formation and charge separation, yielding radical ions, were low. We concluded that the contact radical ion pair (CRIP) decays by processes other than intersystem crossing and radiationless back electron transfer. Fast proton transfer from the radical cation of a primary amine to the radical anion of anthracene or bianthryl may be responsible for the unusually low yields of free radicals and triplet states in these systems, as proposed by Mataga [8,9] and Lewis [10,11] and their coworkers for related aryl–amine systems. In the systems containing 9,10-dichloroanthracene with aromatic amines, the possibility of the formation of contact radical ion pair (CRIP) should be lowered, due to lower reduction potential of DCA compared to anthracene and bianthryl, therefore, primary electron transfer step will lead to the solvent separated radical ion pair without the CRIP intermediacy.

The aim of this work was to determine the photophysical and photochemical processes, following the electron transfer quenching of excited 9,10-dichloroanthracene (DCA) by primary and tertiary amines in polar and nonpolar solvents, and to elucidate the role of proton transfer and of the heavy atom effect on the photodehalogenation of DCA. The influence of the so called inert salt (lithium perchlorate) on quantum yield of photochemical decomposition will also be discussed.

EXPERIMENTAL

DCA (Fluka) was recrystallized from ethanol. Aniline (A) and *N,N*-dimethylaniline (DMA) were distilled under vacuum prior to use. *p-N,N*-Dimethylaminobenzonitrile (DMABN) was sublimed twice under vacuum. The remaining amines and the solvents (spectroscopic grade, Fluka) were used as received. Freshly opened lithium perchlorate (Aldrich) was used as received. Fluorescence was measured on a Spex Fluorolog spectrofluorimeter equipped with an EMI R928 photomultiplier. 2-Naphthol, quinine sulfate, and *m*-dimethylaminonitrobenzene were used as fluorescence standards [12] to correct the fluorescence spectra for the spectral response of the instrument. A solution of DCA in MeCN was taken as a reference, $\phi_{\mathrm{MeCN}} = 0.64$ [4], to determine the quantum yields of exciplex fluorescence in *n*-hexane according to [13]:

$$\Phi_x = \Phi_{MeCN} \frac{(\int I(\nu)d\nu)_x}{(\int I(\nu)d\nu)_{MeCN}} \frac{D_{MeCN}}{D_x} \frac{n_{hex}^2}{n_{MeCN}^2} \tag{1}$$

where Φ_{MeCN} is the absolute fluorescence quantum yield of DCA in acetonitrile, the integrals with subscripts MeCN and x denote the integrated fluorescence spectrum of unperturbed DCA in acetonitrile and spectrum of exciplex fluorescence in the systems DCA + amine in *n*-hexane, respectively, $D_{\mathrm{x(MeCN)}}$ are the optical densities of DCA + amines mixtures and unperturbed DCA at the excitation wavelength (400 nm) and $n_{\mathrm{MeCN(hex)}}$ indicate the refraction indexes of MeCN and hexane, respectively. It should be noted that addition of the quencher does not influence the absorption densities (*ca.* 0.1–0.2) at excitation wavelength, which excludes the formation of the ground-state complexes between DCA and amines. Concentrations of the amines were sufficiently high to make the quenching efficiency more than 95%. The low absorbances at the excitation wavelength allow to apply (1) for estimations of the exciplex fluorescence quantum yields.

Steady state irradiations were done with the 405-nm line of a medium-pressure mercury lamp, which was isolated using a band-pass filter. The reaction progress was monitored by UV absorption spectroscopy. Quantum yields of photodehalogenation, ϕ_{r}, were determined spectrophotometrically by the disappearance of the first absorption band of DCA at 400 nm; a solution of *ca.* 10^{-5} M DCA and 0.08 M DMA in MeCN was used as an actinometer ($\phi_{\mathrm{r}} = 0.117$ [4]).

An excimer laser operated on XeF (25 ns, 351 nm) was used for flash photolysis. The kinetic and spectrographic transient absorption instrumentation has been described previously [13]. Relative quantum yields of triplet formation (determined from the initial transient absorbances at 420 nm) were converted to absolute values by reference to the intersystem quantum yield of DCA in MeCN in the absence of quenchers, $\phi_{\mathrm{T}} = 0.36$, which was reported in [4]. The quantum yields of charge separation, ϕ_{cs}, were determined from the initial absorbances of the DCA radical anion at 675 nm, making use of Hamanoue's extinction coefficients for the radical anion, ε_{DCA^-} (675 nm) = 28′000 $\mathrm{M^{-1}\ cm^{-1}}$, and for triplet DCA, ε_{T} (420 nm) = 42′000 $\mathrm{M^{-1}\ cm^{-1}}$ [4].

Cyclic voltammetry was done at 21 C with a Metrohm Polarecord E 506 with VA Scanner 612/VA (scan rates 100 mV/s) at Pt electrode in degassed acetonitrile solutions.

Photoproduct analysis was done with gas chromatograph apparatus HP 5890 with mass selection spectrograph HP 5971.

RESULTS AND DISCUSSION

The fluorescence of DCA is quenched by amines in both acetonitrile and *n*-hexane solutions. Stern-Volmer plots of the fluorescence intensity against amine concentrations exhibited upward curvature at quencher concentrations exceeding 0.06 M; the nonlinearity is attributed to nonequilibrium distributions of the quencher molecules around the excited fluorophores [7]. The Stern-Volmer quenching constants, K_{SV}, determined from the initial slopes of the quenching plots ([Q] < 0.05 M), are given in Table 1 for acetonitrile and in Table 2 for *n*-hexane solutions.

Table 1. Quantum yields of triplet formation (ϕ_T), free radical formation (ϕ_{cs}), and reaction (ϕ_r) produced by fluorescence quenching of DCA by amines in acetonitrile solution.

amine[a]	$-\Delta G_{et}$[b] (eV)	K_{SV} (M^{-1})	$-\Delta G_{bet}$[b] (eV)	ϕ_T	ϕ_{cs}	ϕ_r	k_{bet} ($10^9\ s^{-1}$)	k_{isc} ($10^9\ s^{-1}$)
DMA	0.71		2.36	0.23	0.153	0.117	1.75	0.75
4BrDMA	0.66		2.41	0.76	0.115	0.065	0.195	3.30
DMABN	0.30	127.1	2.77	0.62	0.284	0.156	0.028	1.1
A	0.65	154.1	2.42	0.066	0.132	~ 0.0	2.89	0.25
2BrA	0.42	127.8	2.65	0.60	0.123	~ 0.0	0.72	2.4
4BrA	0.63	157.4	2.44	0.53	~ 0.0	~ 0.0	> 19.0	> 26.5
DTBuA	0.58	138.0	2.49	0.105	0.086	~ 0.0	4.2	0.61
DABCO	0.95		2.12	0.033	~ 0.0	~ 0.0	> 36.0	> 4.3

[a] Abbreviations: DMA – *N,N*-dimethylaniline, 4BrDMA – 4-bromo-*N,N*-dimethylaniline, DMABN – *p-N,N*-dimethylaminobenzonitrile, A – aniline, 2BrA – 2-bromoaniline, 4BrA – 4-bromoaniline, DTBuA – 2,5-di-tertbutyl-aniline, DABCO – 1,4-diazabicyclo[2.2.2] octane.

[b] Calculated as E_{ox}(donor) – E_{red}(DCA) – E_S(DCA) or – E_{ox}(donor) + E_{red}(DCA), as appropriate. Electrochemical and spectral properties: DCA: $E_S = 3.07$ eV [4], $E_T = 1.76$ eV [14], $E_{red} = -1.55$ V (this work), $\tau_{fl} = 8.6$ ns [4]. E_{ox}(amines): A (0.87 V) [15], 2BrA (1.1 V) [7], 4BrA (0.89 V) [15], DTBuA (0.94 V, this work), DMA (0.81 V) [15], 4BrDMA (0.86 V) [15], DMABN (1.22 V, this work), DABCO (0.57 V) [7]. All values refer to acetonitrile solutions and were measured *vs.* SCE.

Table 2. Triplet and exciplex fluorescence quantum yields in *n*-hexane solution.

amine	K_{SV} (M^{-1})	ϕ_T	ϕ_{exc}	reaction
DMA	131.4	0.81	0.018	no
DMABN	97.8	0.73	0.067	no
4BrDMA	136.4	0.93		no
A	112.1	0.07	no	yes
DTBuA	117.1	0.10	no	yes
2BrA	20.3	0.39	no	yes
4BrA	127.0	0.24	no	yes
DABCO	142.1	0.2	no	no

Quenching of DCA in hexane is accompanied by the appearance of a broad, structureless emission at longer wavelengths, which is attributed to exciplex fluorescence. In acetonitrile, exciplex fluorescence was observed only with DMABN ($\phi_{\mathrm{exc}} = 0.01$) and its spectrum did not significantly depend on the concentration of amine. This indicates that ternary exciplexes, which were observed in some related olefin-amine exciplexes [16], are unimportant. In less polar solvents, such as acetone, THF, and *n*-hexane, the intensity of the exciplex emission increases and is blue-shifted compared to that in MeCN. The dependence of the exciplex fluorescence maximum on the solvent polarity parameter $\Delta f(2)$ [17] is shown in Figure 1 for the systems containing anthracene and DCA.

$$\tilde{\nu}_{max}(\Delta f) - \tilde{\nu}_{max}(\Delta f = 0) = -\frac{2\mu_e^2}{hca^3}\Delta f, \text{ where } \Delta f = \frac{\varepsilon - 1}{2\varepsilon + 1} - \frac{n^2 - 1}{2(2n^2 + 1)} \qquad (2)$$

The parameters ε and n are the dielectric constant and index of refraction of the solvent [18], $\tilde{\nu}_{max}(\Delta f = 0)$ represents the position of the maximum of the exciplex emission in the vacuum, a is the Onsager radius, and μ_e is the dipole moment of the exciplex. With *n*-hexane solutions, the exciplex emission was detected only in systems containing tertiary amines (Table 2). The transient absorption spectra of DCA in the presence of DMA in acetonitrile are shown in Figure 2. The transient absorption spectra of this system, but with addition of 0.66 M lithium perchlorate or tetrabutylammonium perchlorate, are also plotted.

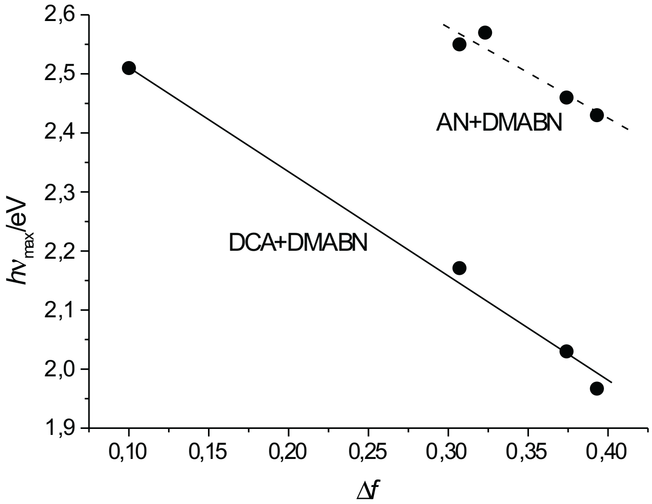

Figure 1. Dependence of the maxima of exciplex emission in the systems anthracene + DMABN (AN) and DCA + DMABN (DCA) on the solvent polarity parameter Δf (eq 1). Solvents: acetonitrile, acetone, dichloromethane, THF, hexane. Static dielectric constants ε and refraction indexes n for the calculation of the Lippert-Mataga parameter Δf were taken from [18].

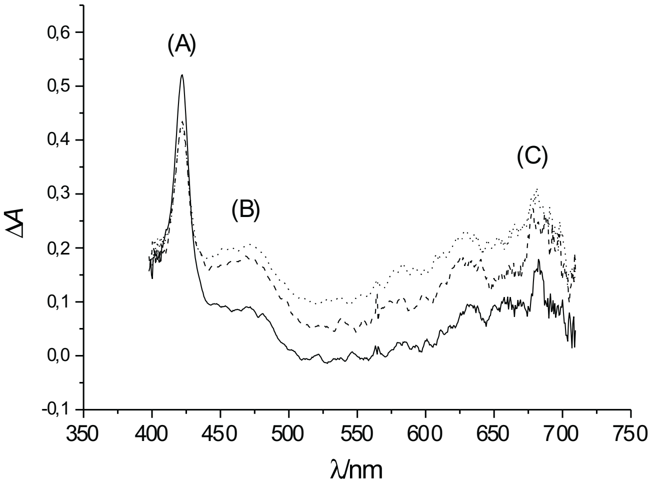

Figure 2. Transient absorption spectra of DCA and 0.1 M DMA in acetonitrile, taken within 20 ns at a time delay of *ca.* 190 ns after flash without (solid), with 0.066 M $LiClO_4$ (dashed) and with 0.066 M tetrabutylammonium perchlorate (dotted). The absorption bands are attributed to ^{3}DCA (A), the radical cation of DMA (B), and the radical anion of DCA (C).

At 420 nm one observes the absorption band characteristic of triplet DCA (band A). At longer wavelengths the absorptions of the radical cation of DMA (band B) and of the radical anion of DCA (band C) are present. With *n*-hexane as a solvent only band A is observed. Quantum yields for triplet formation, ϕ_T, charge separation, ϕ_{cs}, and photodechlorination, ϕ_r, in the presence of various amines in acetonitrile and *n*-hexane are collected in Tables 1 and 2. The concentration of amines was chosen sufficiently high (up to 0.25 M) to quench > 97% of the excited states. Analysis of the GC spectra shows that 9-chloroanthracene is the major photoproduct in all investigated systems in both solvents. In acetonitrile the photodechlorination is completely quenched by the presence of molecular oxygen. Additionally, it has been found that the photodehalogenation quantum yields are strongly dependent on the ground state concentration of the tertiary amines, indicating that the singlet state of DCA is engaged in the photodechlorination process*. Photoreaction quantum yields were not determined for *n*-hexane solutions, however, it has been found that the reaction is not retarded by the presence of oxygen, indicating a different mechanism of the photodechlorination. To explain the role of primary amines in the process, the following experiment was performed: the mixture of the primary (DTBuA) and tertiary (DMA) amines (4:1 molar ratio) was used. We expected that the reaction quantum yield will be lowered to one half of the value with DMA, as it emerges from

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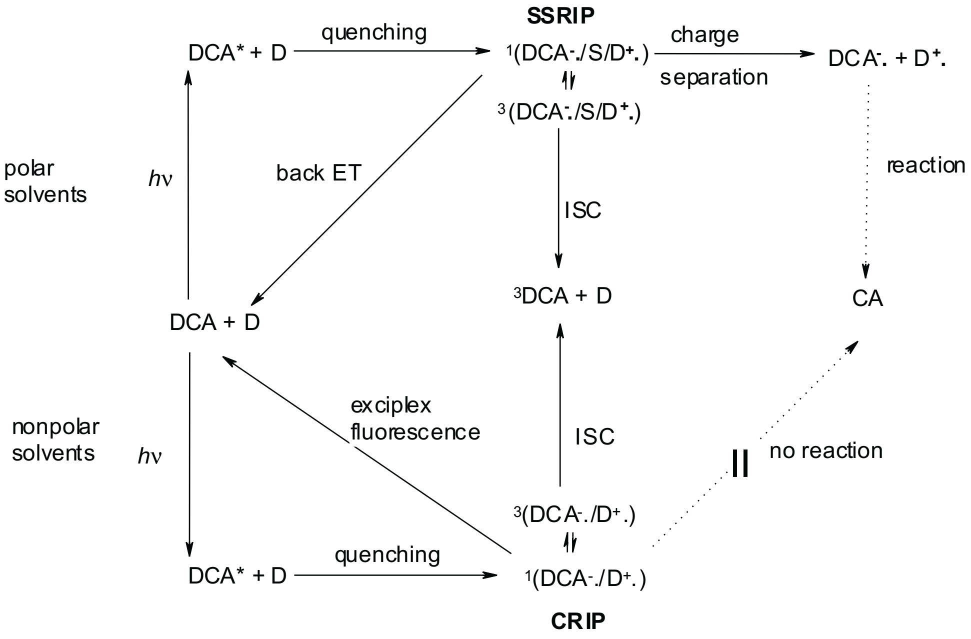
*For example, quantum yields of photodechlorination in the presence of 0.08 and 0.16 M DMA are 0.117 and 0.15 respectively. In the presence of mixture of DMA and DTBA (1:4 molar ratio) the photodechlorination quantum yield was 0.005.

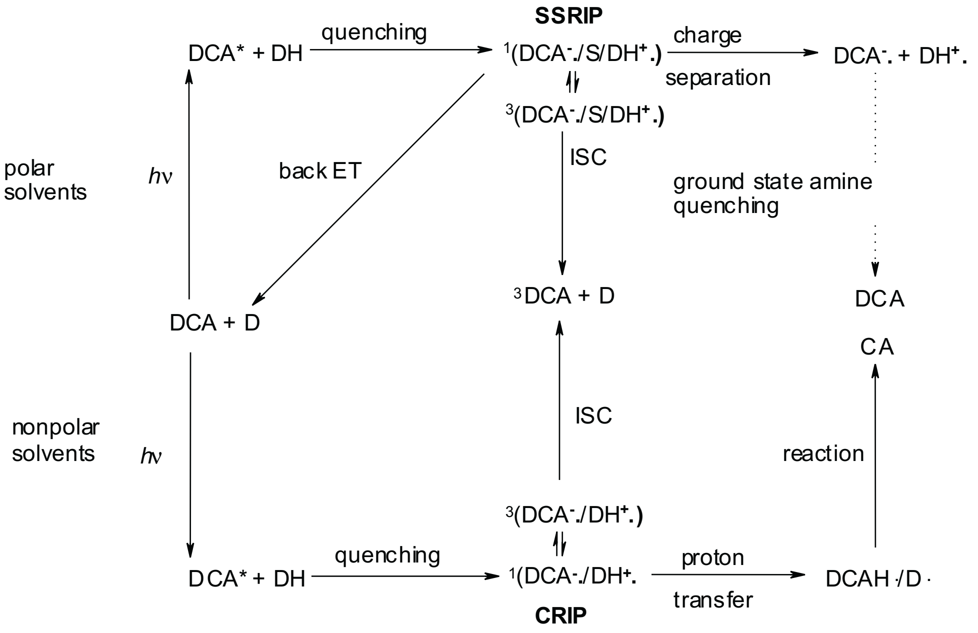
radical escape quantum yields in the presence of DTBA and DMA. However, the photodechlorination was almost completely quenched. This indicates that free radicals of DCA, which are initially formed in the primary electron transfer step, undergo a reaction with the ground state primary amine without chemical dehalogenation.

Electron and proton transfer processes: Electron transfer quenching of the excited singlet state of DCA by primary and tertiary aromatic amines leads to the formation of DCA radical anion, amine radical cation and triplet DCA in acetonitrile, but only to ^{3}DCA in *n*-hexane. With primary amines the charge separation quantum yields are slightly smaller than with tertiary amines, although the oxidation potentials of the primary and tertiary anilines are similar (*cf.* footnotes of Table 1). The photodehalogenation quantum yield of DCA is also much higher with tertiary amines than with primary amines in acetonitrile (Table 1). The opposite holds for *n*-hexane solutions (Table 2). These results can be qualitatively explained on the basis of the reaction mechanisms presented in Schemes 1 and 2, which show all of the proposed intermediate states after excitation of DCA in the presence of amines.

As can be seen from Table 1, the free energy changes of the electron transfer fluorescence quenching are in all cases strongly negative, suggesting that the quenching process leads directly to the solvent separated radical ion pair in the singlet state (^{1}SSRIP) without intermediacy of contact radical ion pair (CRIP). Thus, the exciplex emission is in majority of the cases not observed and the proton transfer between cation radicals of primary amines and anion radicals of DCA seems to be not



Scheme 1. Photophysical processes occurring after exclusive excitation of DCA in the presence of tertiary amines in MeCN and *n*-hexane.



Scheme 2. Photophysical processes occurring after exclusive excitation of DCA in the presence of primary amines in MeCN and *n*-hexane.

important. A weak exciplex fluorescence is observed only when DMABN is used as a quencher in acetonitrile, but the origin of the production of CRIP is not clear. The fluorescence quenching may lead to the CRIP, but also this state may be produced from the SSRIP *via* desolvation process [19]. Possible deactivation pathways of the ^{1}SSRIP are: (1) spin inversion, leading to the SSRIP in the triplet state (^{3}SSRIP), k_{st}; (2) cage escape leading to charge separation, *i.e.*, free radical ions, k_{cs}; (3) nonradiative or radiative back electron transfer leading to the ground states of fluorescer and quencher, $^1k_{bet}$. With primary amines in acetonitrile solution, we observe a substantial formation of the free radical ions, but practically no photodechlorination, *e.g.*, similar yields of free ions are formed in the presence of DMA and A, but dehalogenation is observed only with DMA (Table 1). Moreover, it has been found that the quantum yield of chemical reaction depends strongly on the concentration of the tertiary amines, but the lifetimes of anion radicals of DCA do not change upon addition of the ground state amines. Opposite situation holds when primary amines are used as quenchers: we observe no reaction and the lifetimes of DCA anion radicals depend on the ground state amine concentrations (Fig. 3).

Fast back electron transfer in the system containing DABCO is responsible for the absence of free radicals and for the low triplet quantum yield in agreement with Marcus theory: the low oxidation potential of DABCO locates this system near the maximum of the Marcus curve, making back electron transfer to the ground state much faster than the other deactivation processes.

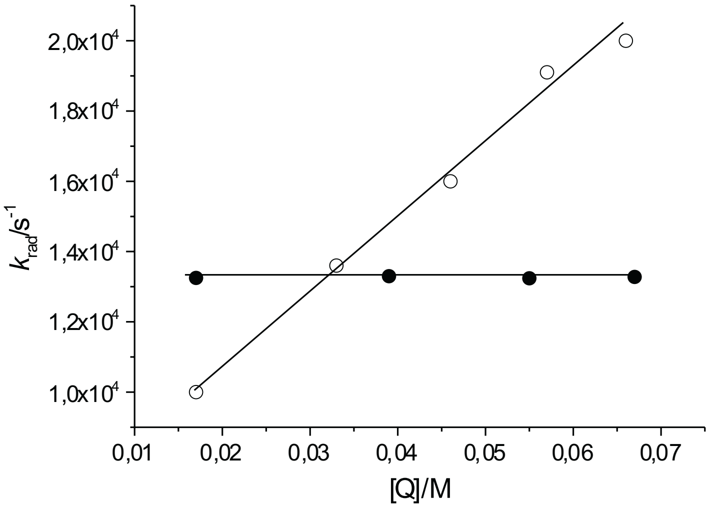


Figure 3. Dependence of DCA radical anion decay rate constant on ground state amine concentration in acetonitrile (open circles – DTBA, black circles 4BrDMA).

The situation is different for nonpolar solvents. Now the quenching process leads to the contact radical ion pair (^{1}CRIP), due to lower electron transfer reaction exothermicity [20]. The CRIP will be strongly stabilized by Coulombic attraction and we observe no cage escape. Moreover, the distance between radicals is now smaller than that in the SSRIP [21]. When primary amines are used as quenchers, the proton transfer from the N-H group of the amine radical cation to the DCA radical anion competes with other deactivation processes, therefore, no exciplex emission can be detected in such systems. In the systems containing tertiary amines such proton transfer reaction is not possible and the radiative electron transfer processes compete with nonradiative ones, leading to the ground state recovery and to the triplet state. The latter process is additionally enhanced by the presence of heavy atom (chlorine or bromine). The triplet yield is almost independent of the presence of a heavy-atom perturber and nonradiative back electron transfer competes with intersystem crossing only in the case of DABCO. In the presence of primary amines no exciplex emission is observed and a heavy-atom effect is clearly present (*cf.* Table 2).

In acetonitrile active species are the free anion radicals of DCA. They undergo slower dissociation into 9-chloroanthracenyl radicals and chloride anions. Hydrogen transfer from CH_3 group produces 9-chloroanthracene molecules, when tertiary amines are present. Such process from the N-H group of the ground state primary amine seems to be thermodynamically impossible, because dissociation energy in the later case is 9 kcal/mole higher than in the case of tertiary amines [10] and probably second electron transfer step leads to the DCA in the ground state.

In *n*-hexane the charge-transfer pair formed from DCA and tertiary amines undergoes radiative (exciplex fluorescence) or nonradiative processes, leading to the triplet and ground states. The charge escape to form the free radicals is not possible. Most probably in the presence of primary amines fast NH proton transfer from the radical cation to the radical anion of DCA competes with other deactivation processes within ^{1}CRIP and forms the 9-hydro, 9,10-dichloroanthracene radicals. The lifetime of this species seems to be very short (shorter than laser pulse duration – *ca*. 20 ns), because no transient absorption band corresponding to this intermediate can be detected in nanosecond flash photolysis experiments.

Heavy atom effect: Comparison of the DCA triplet quantum yields, obtained upon quenching with amines and with their bromo-substituted analogues, shows that intersystem crossing is accelerated in the presence of a heavy-atom substituent. The magnitude of this effect, measured as the ratio of the yields of ^{3}DCA in the presence of bromo-substituted and of parent amine, is different in the case of primary and tertiary amines and depends on solvent polarity. The triplet quantum yield is given by $\phi_{\mathrm{T}} = k_{\mathrm{isc}}/\sum k_d$, where $\sum k_d$ denotes the sum of the rate constants of all processes, which deactivate the ^{1}CRIP (or ^{1}SSRIP) , *i.e.*, intersystem crossing, k_{isc}, proton transfer, k_{pt}, charge separation, k_{cs} (or solvation of the CRIP) and back electron transfer to the ground state, $^1k_{\mathrm{bet}}$. When the quencher molecule contains bromine, then $k_{isc}^{Br} = \alpha\, k_{isc}^{H}$ where the factor $\alpha >> 1$ expresses the heavy atom effect [7,15]. Let us define k_Σ as the sum of all decay rate constants except k_{isc} k_{isc}, *i.e.*, $k_\Sigma = \sum k_{\mathrm{d}} - k_{\mathrm{isc}} = k_{\mathrm{pt}} + k_{\mathrm{cs}} + {}^1k_{\mathrm{bet}}$. We assume that k_Σ is not affected by the presence of bromo substituents, because A, 4BrA, DMA, and 4BrDMA posses similar oxidation potentials. The ratio of the triplet quantum yields with and without heavy-atom perturbers will then be given by (3).

$$\frac{\Phi_T^{Br}}{\Phi_T^{H}} = \frac{\alpha(k_{isc}^{H} + k_\Sigma)}{\alpha k_{isc}^{H} + k_\Sigma} = \frac{\alpha(1+\gamma)}{\alpha\gamma + 1} \tag{3}$$

where $\gamma = k_{isc}^{H} / k_\Sigma$. Three limiting cases may be defined:

1) In the case $\gamma << 1$, which holds for primary amines in both solvents, (3) may be simplified as follows and a significant heavy-atom effect will be observed:

$$\frac{\Phi_T^{Br}}{\Phi_T^{H}} = \frac{\alpha(1+\gamma)}{\alpha\gamma + 1} = \frac{\alpha(1+\gamma)}{\alpha(1+\gamma) + 1 - \alpha} = \frac{1}{1 + \dfrac{1-\alpha}{\alpha(1+\gamma)}} \cong \alpha \tag{3a}$$

2) When γ approaches unity, as is the case with tertiary amines in acetonitrile, (2) simplifies to

$$\frac{\Phi_T^{Br}}{\Phi_T^{H}} = \frac{2\alpha}{\alpha + 1} \cong 2 \tag{3b}$$

and the heavy-atom effect will be small.

3) If $\gamma >> 1$, as in the case of tertiary amines in n-hexane,

$$\frac{\Phi_{isc}^{Br}}{\Phi_{isc}^{H}} \cong 1 \tag{3c}$$

the heavy-atom effect is no longer observed.

Influence of lithium perchlorate on photodechlorination quantum yield of 9,10-dichloroanthracence: The photochemical investigations were also performed in the presence of lithium perchlorate in acetonitrile. This salt is known as an inert salt, *i.e.* it is not influencing on photophysical properties of DCA alone, such as the fluorescence lifetime and the fluorescence quantum yield. However, the situation is changed in the systems having a charge transfer character, *i.e.* in exciplexes, radical pairs, *etc.* [22–24]. It has been previously shown, that lithium perchlorate quenches the fluorescence of the exciplexes formed between excited aromatic electron acceptors (9,10-dicyanoanthracene and 9-cyanoanthracene) and some organic electron donors, such as biphenyl, durene, and naphthalene [22,23]. In some cases formation of the complex between the radical anion of electron acceptor and the lithium cation has been experimentally confirmed, using the time-resolved infrared technique [24] or optical laser flash photolysis measurements [25]. In this paper the influence of the inert salts on charge separation process has been also investigated in the systems containing 9,10-dichloroanthracene and aromatic amines in acetone [26]. It has been found, that the inert salt causes an acceleration of the charge escape rate constant. This behaviour is valid also in presently investigated systems as it is shown in Fig. 2.

It was undoubtedly confirmed, that the salt accelerates the charge separation process making formation of free radical ions more effective and reducing the formation of the triplet state of DCA. The last process is a kind of the back electron transfer, occurring from the solvent separated radical ion pair. These results may be at least qualitatively described in terms of Eigen equation for charge separation rate constant [27]:

$$k_{sep} = \frac{kT}{2\pi\eta a^2}\left(\frac{1}{r_A}+\frac{1}{r_B}\right)\frac{\exp[w(a,\mu)/kT]}{a\int\limits_a^\infty r^{-2}\exp[w(r,\mu)/kT]dr} \tag{4}$$

where

$$w(r,\mu) = \frac{z_A z_B e^2}{2\varepsilon r}\left(\frac{\exp(\beta\sigma_A\sqrt{\mu})}{1+\beta\sigma_A\sqrt{\mu}}+\frac{\exp(\beta\sigma_B\sqrt{\mu})}{1+\beta\sigma_B\sqrt{\mu}}\right)\exp(-\beta r\sqrt{\mu}) \tag{4a}$$

and

$$\beta = \left(\frac{8\pi N e^2}{1000 \varepsilon k T} \right)^{1/2} \tag{4b}$$

where k is the Boltzmann constant, η is the viscosity coefficient, r_A, r_B, and $a = (r_A + r_B)$ are radii of the radicals A and B and the distance of closest approach, respectively. The terms of $w(r,\mu)$ and b are given by (4a) and (4b), where z_A and z_B are the charges of the ions A and B, e is the electron charge, ε is the dielectric permittivity of the solvent and μ is the ionic strength of the solution. Finally, σ_A and σ_B are the radii of the reactants A and B plus that of dominant counterion. Note that the solvated radii should be used instead of those of the bare ions. (4) predicts an increase of charge separation rate constant as ionic strength increases. This behaviour is depicted in Fig. 4. Consequently, the charge separation quantum yield should be also dependent of salt concentration, because:

$$\Phi_{cs} = \frac{k_{cs}([S])}{\sum k_d}$$

where $\sum k_d$ (including the salt concentration-dependent term k_{cs}, too) was defined previously.

This is a simple way to understand the behaviour illustrated in Fig. 5. In the presence of lithium perchlorate the quantum yield of photodechlorination of DCA, catalysed by the presence of DMA, increases and achieves a saturation at higher salt concentration.

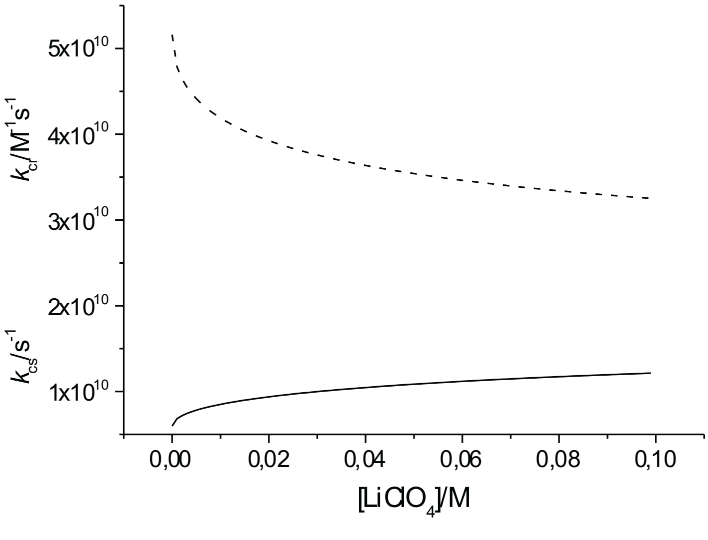


Figure 4. Salt concentration dependence of the charge escape (lower) and charge recombination (upper) rate constants. Note that the charge recombination is a second-order process.

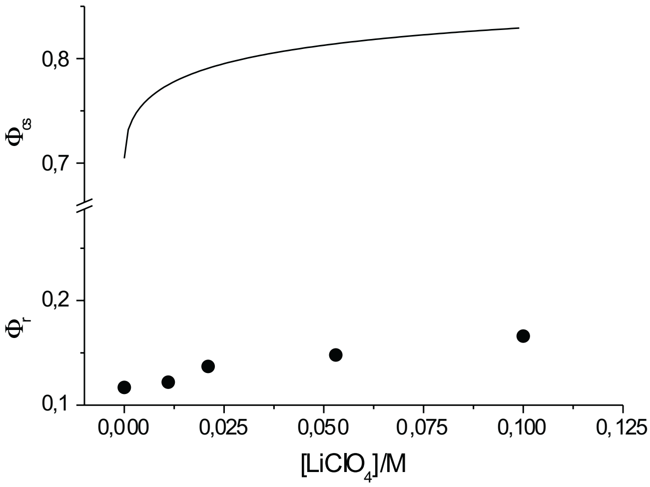


Figure 5. Predicted salt concentration dependence of the charge separation quantum yield (top) and measured photodechlorination quantum yield of DCA in the presence of DMA (bottom).

CONCLUSIONS

Our results reveal the importance of an intermediate radical pair, which is formed by N-H proton transfer from the primary amine radical cation to the DCA radical anion within the solvent cage. Similar observations were reported by Lewis *et al.* [11]: in their investigations of the photoaddition between 9-cyanophenanthrene and diethylamine in non-polar solvents, they observed only transfer of N-H protons, leading to the exclusive formation of *N,N*-diethyl-9-phenanthrenamine within the CRIP.

The heavy-atom effect of bromo substituents of the aniline donors, which was measured as an enhancement of the triplet quantum yields upon fluorescence quenching, depends on the lifetime of the CRIP. The heavy-atom effect is more important with primary amines in nonpolar solvents, where proton transfer strongly decreases the lifetime of the CRIP.

Lithium perchlorate causes an increase of the photochemical decomposition of DCA in acetonitrile, at least at small concentration of the salt. This effect seems to be different for two used donors, *N,N′*-dimethylaniline (DMA) and *p*-cyano, *N,N′*-dimethylaniline (DMABN). In the second case even a decrease of the photodecomposition quantum yield has been observed when the salt concentration exceeds 0.04 M. This effect is not fully clear. Probably, at higher salt concentration a complex between the salt and amine is formed and, thus, the fluorescence quenching ability of amine is lowered. Much more surprising was the effect of the addition of tetrabutylammonium perchlorate as an inert salt. Figure 2 shows a significant increase of the charge separation quantum yield, due to added salt, even larger than in the presence of lithium perchlorate. However, a small amount of tetrabutylammonium perchlorate causes a significant inhibition of the photodecomposition of DCA. This effect needs more detailed investigations.

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REFERENCES

1. Davidson R.S., Goodwin J.W. and Kemp G., *Adv. Phys. Org. Chem.*, **20**, 191 (1984).
2. Fulara J. and Latowski T., *Polish J. Chem.*, **64**, 369 (1990).
3. Nagamura T., Nakayama T. and Hamanoue K., *Chem. Phys. Lett.*, **193,** 30 (1992).
4. Hamanoue K., Nakayama T., Ikenaga K. and Ibuki K., *J. Phys. Chem*., **96**, 10297 (1992).
5. Hamanoue K., Nakayama T., Ikenaga K., Ibuki K. and Otani A., *J. Photochem. Photobiol.*, **69**, 305 (1993).
6. Nakayama T., Hanada T., Ibuki K. and Hamanoue K., *Chem. Phys. Lett.*, **209**, 367 (1993).
7. Mac M., Najbar J. and Wirz J., *Chem. Phys. Lett.*, **35**, 187 (1995).
8. Okada T., Mori T. and Mataga N., *Bull. Chem. Soc. Jpn.*, **49**, 3398 (1976).
9. Okada T., Karaki I. and Mataga N., *J. Am. Chem. Soc.*, **104**, 7191 (1982).
10. Lewis F.D., *Acc. Chem. Res.*, **19**, 401 (1986).
11. Lewis F.D., Zebrowski B.E. and Correa P.E., *J. Am. Chem. Soc.*, **106**, 187 (1984).
12. Lippert E., Nägele W., Seibold-Blankenstein I., Steiger U. and Voss W., *Z. Anal. Chem.*, **170**, 1 (1964).
13. Hasler E., Hörmann A., Persy G., Platsch H. and Wirz J., *J. Am. Chem. Soc.*, **115**, 5400 (1993).
14. Scaiano J., Handbook of Organic Photochemistry, Boca Raton, 1989, CRC Press, Chapter 18.
15. Kikuchi K., Hoshi H., Niwa T., Takahashi Y. and Miyashi T., *J. Phys. Chem.*, **95,** 38 (1991).
16. Lewis F.D., Reddy G.D., Bassani D., Schneider S. and Gahr M., *J. Photochem. Photobiol. A: Chem.*, **65**, 205 (1992).
17. Lippert E., *Z. Naturforsch.*, **109,** 541 (1955); Mataga N., Kaifu Y. and Koizumi M., *Bull. Chem. Soc. Jpn.*, **29,** 465 (1956).
18. Landolt-Börnstein, Zahlenwerte und Funktionen aus Physik, Chemie, Astronomie, Geophysik und Technik, Berlin, 1959, Vol. 6 and 8, Springer Verlag.
19. Gould I.R., Young R.H., Mueller L.J. and Farid S., *J. Am. Chem. Soc.,* **116,** 8176 (1994) .
20. Kikuchi K., Niwa T., Takahashi Y., Ikeda H., Miyashi T. and Hoshi M., *Chem. Phys. Lett.*, **173**, 421 (1990).
21. Gould I.R., Young R.H. and Farid S., Photochemical Processes in Organized Molecular Systems, BV, 1991, p. 19–40, K. Honda editor, Elsevier Science Publishers.
22. Mac M., Kwiatkowski P. and Turek A.M.*, J. Luminesc*., **65,** 341 (1996).
23. Mac M., Kwiatkowski P. and Turek A.M., *Chem. Phys. Lett.*, **250**, 104 (1996).
24. Mac M. and Wirz J., *Photochem. Photobiol. Sci.*, **1,** 27 (2002).
25. Matay J. and Vandenhof A.M., *Top. Curr. Chem.*, **159,** 220 (1991).
26. Mac M., *J. Luminesc*., **81,** 33 (1999).
27. Ciorboli C., Indelli M.T.,. Scandola M.A.R. and Scandola F., *J. Phys. Chem.*, **92,** 156 (1988).