

Deuterium isotope effect on the charge recombination dynamics of contact ion pairs formed by electron-transfer quenching in acetonitrile

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Abstract

The deuterium isotope effect on the fluorescence lifetime of contact ions pairs (CIP) composed of 9,10-dicyanoanthracene and weak aromatic electron donors in acetonitrile has been investigated. For all pairs studied, an increase of the emission lifetime with increasing deuterium substitution on both the electron acceptor and the electron donor was observed. The free ion yield shows the same variation upon deuteration. It is concluded that the efficiency of free ions formation is essentially determined by the competition, within the CIP, between charge recombination and dissociation into free ions and that loose ion pairs do not play a significant role. © 2000 Elsevier Science B.V. All rights reserved.

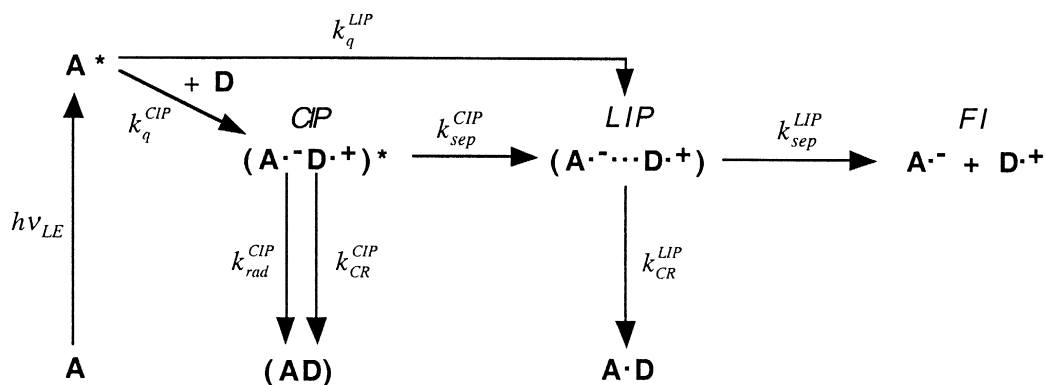
1. Introduction

Since the pioneering work of Weller and co-workers, bimolecular electron-transfer (ET) quenching in polar solvents is known to result into the formation of geminate ion pairs (GIP) [1]. The GIP dynamics is often discussed in terms of contact or compact ion pairs (CIP) and solvent separated or loose ion pairs (LIP) as shown in Scheme 1 [2–5]. CIPs are generally formed upon direct excitation in the charge-transfer (CT) band of ground state complexes. This species is characterised by a weak fluorescence in polar solvents [5]. CIPs can also be

generated by diffusional ET quenching (k_q^{CIP} in Scheme 1), when the free energy of this process is small ($\Delta G_{\text{ET}} > \sim -0.4$ eV) [6,7]. As in the latter case, the CT character of the resulting intermediate is not really unity, the appellation exciplex is probably more appropriate. However, to avoid confusion the name CIP will be used throughout this Letter even if the CT character is not full. More exergonic diffusional ET quenching reactions seem to lead directly to the formation of the LIP (k_q^{LIP} in Scheme 1) [8].

In principle, charge recombination (CR) can take place in both CIP and LIP. The relative magnitude of CR in CIP and LIP is a subject of controversy. Investigations by Mataga and co-workers on CIPs formed by direct excitation of the ground state complex have shown that, in most cases, CR was taking place within the CIP only and that the LIP was not

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involved, i.e. $k_{\text{sep}}^{\text{LIP}} \gg k_{\text{CR}}^{\text{LIP}}$ [3,9]. CR within LIP was observed in a few cases only, and was substantially slower than in the corresponding CIP [10–12]. Gould, Farid and co-workers have intensively investigated the CR dynamics of ion pairs composed of 9,10-dicyanoanthracene (DCA) or 2,6,9,10-tetracyanoanthracene and methylbenzene derivatives [5,13]. These authors have observed that the decrease of the CIP fluorescence lifetime with decreasing the oxidation potential of the donor was weaker than that predicted for CR in the Marcus inverted region. From this, they have concluded that dissociation to the LIP is the main deactivation pathway of the CIP ($k_{\text{sep}}^{\text{CIP}} \gg k_{\text{CR}}^{\text{CIP}}$) and that CR essentially takes place in the LIP [5,14].

We have recently reported an investigation of the CR dynamics following the ET quenching of $^1\text{DCA}^*$ by various weak aromatic donors in ACN, where we showed that the decay of the ion pair population was identical to that of the CIP fluorescence [15]. This observation can be interpreted in two different ways:

Model 1: CR predominantly takes place in the CIP and the LIP does not play any significant role in the reaction ($k_{\text{sep}}^{\text{CIP}} \approx k_{\text{CR}}^{\text{CIP}}$ and $k_{\text{sep}}^{\text{LIP}} \gg k_{\text{CR}}^{\text{LIP}}$).

Model 2: CR in the CIP is much slower than dissociation to the LIP, which is itself substantially slower than CR in the LIP ($k_{\text{CR}}^{\text{LIP}} \gg k_{\text{sep}}^{\text{CIP}} \gg k_{\text{CR}}^{\text{CIP}}$). In other words, $k_{\text{sep}}^{\text{CIP}}$ is the rate determining step for CR in the LIP.

Although model 1 was more consistent with other direct investigations of the CR dynamics of CIPs, model 2 could not be unambiguously discarded [15].

We present here our investigation of the deuterium isotope effect on the CR dynamics of CIPs formed by diffusional ET quenching of $^1\text{DCA}^*$ by durene (DUR) and hexamethylbenzene (HMB) in ACN. These are weak donors, thus the free energy of ET is small ($\Delta G_{\text{ET}} = -0.12$ eV with DUR and -0.31 eV with HMB) and the quenching of $^1\text{DCA}^*$ results to the formation of a CIP. By comparing the effect of deuterium substitution on the CIP fluorescence lifetime and on the free ion yield, we will be able to clearly distinguish model 1 from model 2.

2. Experimental

2.1. Fluorescence lifetime measurements

Fluorescence lifetimes were measured using the time correlated single photon counting (TCSPC) technique. The frequency doubled output of a Kerr mode-locked Ti:Sapphire oscillator (Spectra-Physics Tsunami) pumped by a Nd:YVO₄ laser (Spectra-Physics, Millennia) was used for excitation. The pulses at 400 nm had duration of about 80 fs and energy of 0.1 nJ at 82 MHz. The fluorescence was collected at 90° and filtered through narrow bandpass filters, centred at 450 and 633 nm and located in front of the photomultiplier tube (Hamamatsu, H5783-P-01). The detector output was connected to the input of a TCSPC computer board module (Becker and Hickl, SPC-300-12). The full width at half maximum of the response was less than 200 ps.

The fluorescence time profiles were analysed by iterative reconvolution with the response function, assuming a two exponential kinetics corresponding to CIP formation and deactivation.

2.2. Free ion yield measurements

The free ion yields have been determined using photoconductivity [16]. The photocurrent cell has been described in detail previously [17]. The samples were excited at 355 nm using the frequency-tripled output of a Q-switched Nd:YAG laser (Continuum, Surelite II-10). The pulse had duration of 6 ns and energy of 7 mJ. The system benzophenone with 0.02 M 1,4-diazabicyclo [2.2.2]octane in ACN, which has a free ion yield of unity [18], was used as a standard.

2.3. Samples

9,10-dicyanoanthracene- d_8 (DCA $_d$) was synthesised according to the literature [19,20] using anthracene- d_{10} (Cambridge Isotopes) as starting material. 9,10-dicyanoanthracene (DCA, Kodak), durene (DUR, Fluka), durene- d_{14} (DUR $_d$, Cambridge Isotopes), hexamethylbenzene (HMB, Fluka) and hexamethylbenzene- d_{18} (HMB $_d$, Cambridge Isotopes) were recrystallised. Acetonitrile (ACN, Fluka UV grade) was used without further purification.

For fluorescence measurements, the absorbance of the sample solutions at 400 nm was around 0.2 on 1 cm, whereas the absorbance at 355 nm was 0.5 on 1 cm for photoconductivity. In both cases, the solutions were deoxygenated by Ar bubbling. No sample degradation was observed after the measurements. All experiments were performed at $20 \pm 1^\circ\text{C}$.

3. Results and discussion

Fig. 1 shows the exciplex fluorescence spectra measured with the DCA/DUR and DCA $_d$ /DUR $_d$ pairs in ACN. Fig. 2 shows the time profile of the fluorescence intensity at 450 nm with DCA/DUR and at 633 nm with DCA/DUR and DCA $_d$ /DUR $_d$. The decay at 450 nm is biexponential: the fastest component, with a relative amplitude of 0.91, is due to the diffusional ET quenching of $^1\text{DCA}^*$, while the slowest component with a relative amplitude of 0.09,

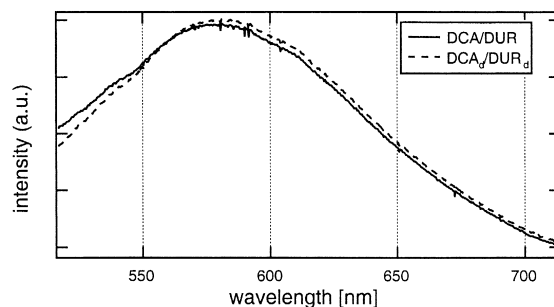


Fig. 1. Uncorrected exciplex fluorescence spectra measured with DCA/DUR and DCA $_d$ /DUR $_d$ in ACN.

is due to the emission of the CIP, which is also present at this wavelength. The time profile at 633 nm is also biexponential: the initial rise corresponds to the formation of the CIP upon ET quenching of the excited precursor and its time constant is the same as that of the fast 450 nm component, whereas the decay reflects the deactivation of the CIP. No CT band due to the formation of a ground state complex was observed in the absorption spectra of the various A/D pairs. This confirms that the CIP is truly formed upon diffusional ET quenching (k_q^{CIP} in Scheme 1) and not by direct excitation of a ground state complex. Similar fluorescence time profiles have been measured with the other acceptor/donor (A/D) pairs. The decay times of the CIP emission are independent on the donor concentration ($[\text{DUR}] = 0.05 \text{ M}$, 0.1 M and 0.2 M ; $[\text{HMB}] = 0.03 \text{ M}$ and 0.05 M). This indicates that there is no significant equilibrium between the CIP and the locally excited state, $^1\text{DCA}^* + \text{D}$. This also eliminates the occurrence of self-quenching. The fluorescence lifetimes, τ_{fl} , are listed in Table 1.

The lifetimes of the undeuterated CIPs are in good agreement with those already reported in the literature [8,15]. Table 1 and Fig. 2 show that the lifetime of the CIP increases noticeably with deuterium isotope substitution, the strongest effect occurring when both A and D are deuterated. As the fluorescence quantum yields of these CIPs are very small (< 0.05), the measured fluorescence decay constant, k_{fl} , is given by:

$$k_{\text{fl}} = \tau_{\text{fl}}^{-1} \cong k_{\text{sep}}^{\text{CIP}} + k_{\text{CR}}^{\text{CIP}} \quad (1)$$

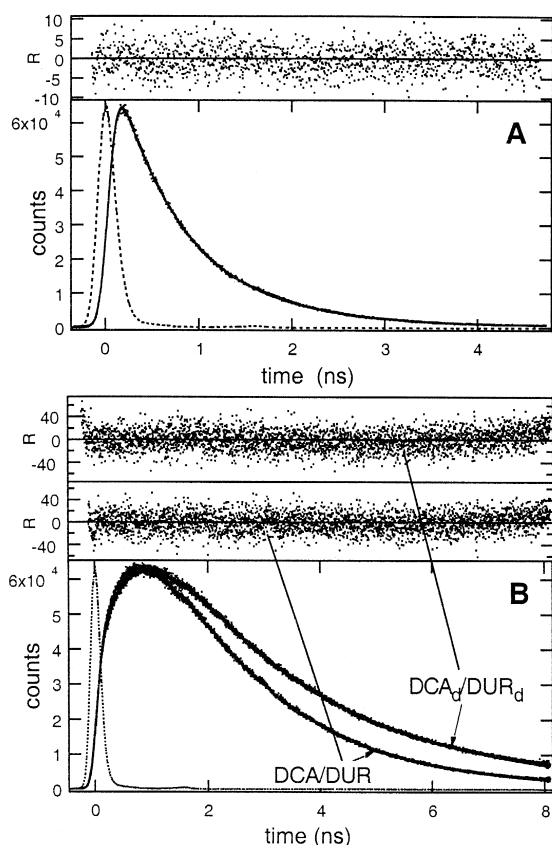


Fig. 2. (A) Fluorescence time profile at 450 nm measured with DCA/DUR; (B) Fluorescence time profiles at 633 nm measured with DCA/DUR and DCA_d/DUR_d (dots: experimental data; solid line: best double exponential fit; dotted line: response function; top graph: weighted residuals).

where $k_{\text{sep}}^{\text{CIP}}$ is the rate constant of separation of the CIP to LIP or to free ions and $k_{\text{CR}}^{\text{CIP}}$ the rate constant of CR to the neutral ground state.

The exciplex emission spectrum is independent of the deuteration of A and D as shown in Fig. 1. This suggests that the energy gap between the CIP and the neutral ground state, hence the free energy for CR, ΔG_{CR} , is not affected by isotopic substitution. This is in agreement with the observation that the variation of the oxidation potential of methylbenzene derivatives upon deuteration is of the order of 5 mV [21]. Similarly, the absorption spectra of the ground state complexes as well the emission spectra of the CIPs composed of tetracyanobenzene and HMB, DUR and xylene have been reported to be unaffected by the

perdeuteration of the electron donors [22]. Moreover, the variation upon deuterium substitution of the CT absorption band maximum of complexes composed of tetracyanoethylene and methylbenzene derivatives is smaller than 150 cm^{-1} [23].

The free ion yields, Φ_{ion} , measured with these A/D pairs are also listed in Table 1. The Φ_{ion} measurements were performed with the highest donor concentration used for the determination of the fluorescence lifetime. Except for HMB and HMB_d, which are poorly soluble in ACN, the donor concentration was enough to ensure a quenching efficiency of the excited precursor of more than 95%. Nevertheless, the listed Φ_{ion} values have been normalised to 100% quenching efficiency ($\Phi_q = 1$).

Table 1 shows that the isotope effect observed on the free ion yield is the same, within the experimental error, as that observed on the CIP decay constant. An increase of Φ_{ion} upon deuteration of the donor has already been reported for DCA/DUR and DCA/HMB is close to that listed in Table 1. We will now reconsider models 1 and 2 described in Section 1 in the light of these new results.

Model 1: The LIP does not play any significant role in the CR process. In this case, the free ion yield is given by:

$$\Phi_{\text{ion}} = \Phi_q \cdot \frac{k_{\text{sep}}^{\text{CIP}}}{k_{\text{fl}}} \cong \Phi_q \cdot \frac{k_{\text{sep}}^{\text{CIP}}}{k_{\text{sep}}^{\text{CIP}} + k_{\text{CR}}^{\text{CIP}}} \quad (2)$$

where Φ_q is the quenching efficiency, which can be calculated from the Stern–Volmer constant of fluo-

Table 1

CIP fluorescence lifetimes and free ion yields of A/D pairs with various degrees of deuterium substitution and corresponding deuterium isotope effects (relative error on $\tau_{\text{fl}} = \pm 2.5\%$, absolute error on $\Phi_{\text{ion}} = \pm 0.005$)

A/D	τ_{fl} (ns)	$\tau_{\text{fl,d}}/\tau_{\text{fl,h}}$	Φ_{ion}	$\Phi_{\text{ion,d}}/\Phi_{\text{ion,h}}$
DCA/DUR	2.04		0.22	
DCA/DUR _d	2.54	1.24	0.28	1.27
DCA _d /DUR	2.70	1.32	0.30	1.36
DCA _d /DUR _d	2.88	1.41	0.33	1.5
DCA/HMB	1.60		0.09	
DCA/HMB _d	2.0	1.25	0.12	1.33
DCA _d /HMB	1.80	1.12	0.10	1.11
DCA _d /HMB _d	2.20	1.37	0.135	1.5

rescence quenching, K_{SV} , $\Phi_q = 1 - (K_{SV}[Q] + 1)^{-1}$.

According to this model, it is possible to determine both k_{sep}^{CIP} and k_{CR}^{CIP} using the CIP fluorescence decay constant and the free ion yield. The resulting rate constants are listed in Table 2. This table shows that, for a given A/D pair, the separation rate constant, k_{sep}^{CIP} , is not influenced by deuterium substitution and that the isotope effect observed on Φ_{ion} is only due to changes in k_{CR}^{CIP} . The dissociation of the CIP into free ions is essentially a diffusional process. We have recently shown that k_{sep}^{CIP} becomes larger with growing CT character of the CIP, which itself increases with the exergonicity of the primary ET quenching process, ΔG_{ET} [15]. The free energy of ET quenching can be calculated as $\Delta G_{ET} = E_{ox}(D) - E_{red}(A) - E(S_1)$, $E_{ox}(D)$ and $E_{red}(A)$ being the oxidation and reduction potentials of D and A, respectively, and $E(S_1)$ being the energy of the excited precursor. As discussed above, the redox potentials of A and D are almost unaffected by deuterium substitution. The reduction potential of DCA amounts to -0.98 V versus SCE and the oxidation potentials of DUR and HMB are 1.78 and 1.59 V versus SCE, respectively [24]. Moreover, the absorption and fluorescence spectra of both DCA and DCA_d are identical, and thus $E(S_1)$ is the same for both acceptors and amounts to 2.88 eV [24]. Consequently, ΔG_{ET} , hence the CT character of the CIP, and k_{sep}^{CIP} can be expected to be independent of deuterium substitution. According to the Stokes–Einstein equation, the diffusion coefficient of a spherical particle is proportional to its radius. The average length of a C–D

bond in methane has been determined to be smaller than a C–H bond by less than 0.006 Å, due to the smaller vibrational amplitude of the C–D bond [25]. Therefore, the molecular volume should in principle decrease slightly upon deuterium substitution. However, the difference in molecular volume between HMB and HMB_d can be estimated to be smaller than 1% and thus the diffusion coefficients of HMB and HMB_d should be identical. Consequently, the absence of an isotope effect on k_{sep}^{CIP} is physically reasonable.

Turning now to the rate constant of CR, k_{CR}^{CIP} , it appears that the deuterium isotope effect depends on the extent of deuteration. When both A and D are deuterated, the isotope effect is of the order of 1.5 – 1.6 . However, with A_d/D and A/D_d pairs, the effect is weaker and varies substantially from one D to another. However, the number of A/D pairs studied here is too small to attempt to find a correlation between the isotope effect and the nature of D. The magnitude of the isotope effect on k_{CR}^{CIP} is in agreement with those reported in the literature [22,26]. For example, k_H/k_D ratios of 1.6 , 1.8 and 1.9 have been reported for the CR of CIPs formed by direct excitation in the CT band of ground state complexes composed of tetracyanobenzene with HMB, DUR and xylene, respectively, in non-polar solvents [22]. Such an effect on the ET dynamics is generally discussed within the framework of the semi-classical non-adiabatic ET theory [27]. In this model, the ET rate constant is proportional to the Franck–Condon weighted density of states, whose magnitude depends on the frequency of the modes coupled to the ET.

According to Gould et al. [8], the efficiency of CIP formation upon ET quenching of DCA by HMB is not unity, a parallel direct formation of the LIP being also operative. From indirect considerations, they have estimated the efficiency of CIP formation to be around 0.7 . If this is really the case, the free ion yield might also be influenced by the competition, within the LIP, between CR and separation. Unfortunately, the decay of the ion pair population could not be determined due to the poor solubility of HMB in ACN. If CR also take place in the LIP, k_{sep}^{CIP} and k_{CR}^{CIP} can no longer be calculated using Eq. (2). However, the isotope effect observed on k_{fl} shows that CR in the CIP is still operative. Moreover, the

Table 2

Rate constants of CR and separation of the CIPs determined from Eq. (2) using the data listed in Table 1 and corresponding deuterium isotope effects

A/D	k_{CR}^{CIP} (10^8 s $^{-1}$)	$k_{CR,h}^{CIP} / k_{CR,d}^{CIP}$	k_{sep}^{CIP} (10^8 s $^{-1}$)	$k_{sep,h}^{CIP} / k_{sep,d}^{CIP}$
DCA/DUR	3.8		1.1	
DCA/DUR _d	2.8	1.36	1.1	1
DCA _d /DUR	2.6	1.46	1.1	1
DCA _d /DUR _d	2.3	1.65	1.1	1
DCA/HMB	5.7		0.6	
DCA/HMB _d	4.4	1.30	0.6	1
DCA _d /HMB	5.0	1.14	0.6	1
DCA _d /HMB _d	3.95	1.45	0.6	1

similarity of the isotope effects on k_{fl} and on Φ_{ion} , indicates either that CR in the LIP is not significant or that the isotope effects on $k_{\text{BET}}^{\text{CIP}}$ and $k_{\text{CR}}^{\text{LIP}}$ are similar, which is physically reasonable.

Model 2: The CIP decays essentially via dissociation to the LIP, i.e. $k_{\text{fl}} \cong k_{\text{sep}}^{\text{CIP}}$. Consequently, the free ion yield depends on the competition, within the LIP, between BET and further separation to free ions:

$$\Phi_{\text{ion}} = \Phi_{\text{q}} \cdot \frac{k_{\text{sep}}^{\text{LIP}}}{k_{\text{sep}}^{\text{LIP}} + k_{\text{CR}}^{\text{LIP}}} \quad (3)$$

It is important to note that, Φ_{ion} is, in this case, independent of the decay time of the CIP, i.e. of k_{fl} . Moreover, it is not possible to have access to the values of $k_{\text{sep}}^{\text{LIP}}$ and $k_{\text{CR}}^{\text{LIP}}$. In some investigations, $k_{\text{CR}}^{\text{LIP}}$ has been determined by assuming a constant value of $k_{\text{sep}}^{\text{LIP}}$ of $5 \times 10^8 \text{ s}^{-1}$ in ACN [13,28,29]. However, direct investigations of the dynamics of LIPs formed with other A/D pairs have shown that $k_{\text{sep}}^{\text{LIP}}$ in ACN is not constant and can range from about 10^8 s^{-1} to more than 10^9 s^{-1} , depending on the A/D pair [30,31].

If this model is correct, the deuterium isotope effect observed on k_{fl} is due to $k_{\text{sep}}^{\text{CIP}}$, i.e. the dissociation of the CIP becomes slower upon deuterium substitution. For the reasons discussed above (same CT characters, same molecular volumes, same free energies of formation), there is no physical explanation to justify such an effect. Deuterium effects similar to those reported here have been observed for the decay of CIPs in non-polar solvents [22] as well as in rigid matrices at 77 K [26], where dissociation into a LIP is not possible.

In this model, the isotope effect measured on Φ_{ion} would due to $k_{\text{sep}}^{\text{LIP}}$ and $k_{\text{CR}}^{\text{LIP}}$. If deuterium substitution influences $k_{\text{sep}}^{\text{CIP}}$, it should affect almost similarly $k_{\text{sep}}^{\text{LIP}}$, which is also a diffusive process. This effect alone should make Φ_{ion} smaller upon deuteration, contrarily to the observation. Thus, one has to invoke a strong isotope effect on $k_{\text{CR}}^{\text{LIP}}$ in order to account for the increase of Φ_{ion} with deuterium substitution. This isotope effect for $k_{\text{CR}}^{\text{LIP}}$ should amount to 2.5 for DCA/DUR and to 2.3 for DCA/HMB. This is considerably stronger than the effect reported so far for ET reactions.

Consequently, the difficulties to justify a substantial isotope effect for the diffusive processes and an

exceptionally large isotope effect for ET strongly suggest that the CR dynamics within the ion pairs investigated here cannot be explained with model 2. If this model is correct, the fact that the isotope effects observed on k_{fl} and Φ_{ion} are the same is purely fortuitous. This similarity has been observed with eight A/D pairs, and thus such a large number of coincidences is highly improbable.

4. Conclusion

The data presented here show clearly that the contact ion pairs formed upon ET quenching of $^1\text{DCA}^*$ by weak electron donors in acetonitrile do not only decay by dissociation but also by charge recombination to the ground state. The very close similarity between the deuterium isotope effect on the decay time of the contact ion pair and on the free ion yield indicates that most of the charge recombination takes place in the contact ion pair and that the loose ion pair is essentially not involved. However, the latter intermediate might play a more important role in the subsequent homogeneous recombination of the free ions.

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