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Exciplex and Radical Ion Intermediates in Electron-transfer Reactions: Solvent Effect on the Photo-oxygenation of 1,4-Dimethylnaphthalene sensitized by 9,10-Dicyanoanthracene

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The 9,10-dicyanoanthracene-sensitized photo-oxygenation of 1,4-dimethylnaphthalene is shown to depend on solvent polarity. Radical ion pair and singlet exciplex are suggested to be intermediates in this photochemical reaction. Mechanisms consistent with the effects of solvent polarity are proposed.

Light-induced intermolecular electron-transfer reactions are important steps in many chemical processes.[1] The interaction between an electron donor and an excited electron acceptor can result either in the formation of an exciplex or in a radical ion pair. Strongly polar solvents favour the formation of radical ions and exciplex fluorescence is usually not observed.[2]

A species suitable for accepting electrons is 9,10-dicyanoanthracene (DCA) which sensitizes the photo-oxygenation of a wide variety of compounds.[3] Here, the photochemical reaction of DCA and the aromatic hydrocarbon donor, 1,4-dimethylnaphthalene (**1**), is investigated. The role of solvent polarity on the photochemical behaviour is discussed and some fluorescence properties of the DCA–(**1**) system are reported.

Results and Discussion

As is seen in Scheme 1, the products obtained upon irradiation for 1 h under oxygen of DCA (10^{-5}M) and (**1**) (6.4×10^{-2}M) depend on solvent polarity (ε = dielectric constant). The formation of the *endo*-peroxide (**4**) is the exclusive reaction in the non-polar solvents benzene and methylene dichloride. A similar result is obtained upon irradiation for 5 h of (**1**) sensitized by dyes such as Rose Bengal or Methylene Blue.

The essential difference in the fluorescence spectra comes from the observation of an exciplex emission in non-polar solvents such as benzene and methylene dichloride. The fluorescence of this DCA–(**1**) exciplex in these media illustrates the solvent dependence of frequency and intensity already observed for example in the anthracene–diethylaniline exciplex.[4] As the polarity of the solvent increases, the fluorescence intensity and the frequency of the maximum emission of the exciplex decrease (Figure 1). In strongly polar solvents like acetonitrile, the electron-transfer reaction leads to a radical ion pair and the new structureless emission band can no longer be detected. Exciplex properties as well as Stern–Volmer fluorescence quenching constants K_{SV} are reported in the Table. As an example, the temperature dependence of the emission spectra of the DCA–(**1**) system is given in Figure 2.

The presence of an isoemissive point in the range of temperature studied indicates that quenching processes and back reaction to excited monomer (M*) are not competing with exciplex fluorescence. A logarithmic plot of the ratio of exciplex to monomer intensity I_E/I_M as a function of temperature is shown in Figure 3. The apparent activation energies E_a for exciplex formation evaluated from the slope of the lowest part of the temperature plot are given in the Table.

In connection with the fluorescence data, the exclusive product of irradiation of the DCA–(**1**) system in non-polar solvent is attributed to reaction *via* a singlet exciplex. The formation of (**2**) and (**3**) (Scheme 1) is attributed to reaction *via* a radical ion pair.

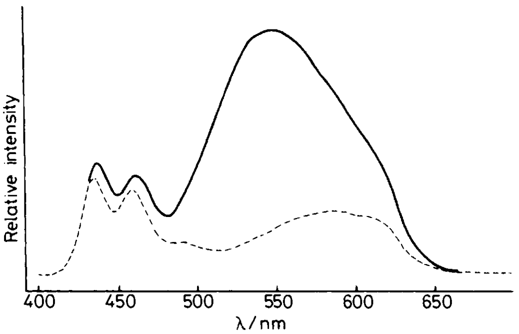
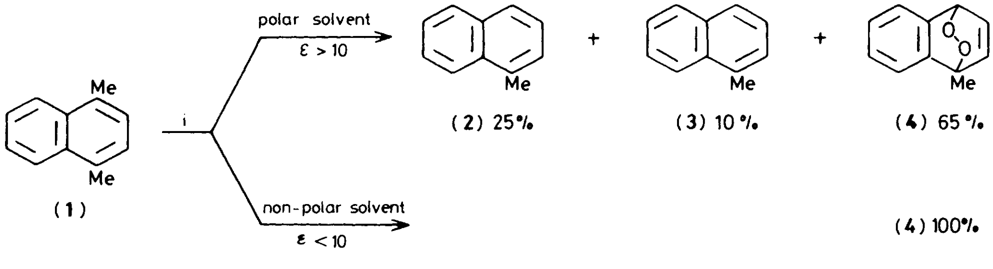


Figure 1. Corrected fluorescence spectra at 25 °C of degassed solutions of the DCA–(**1**): ——, in benzene; – – – –, in methylene dichloride. [DCA] 1.1×10^{-5}M; [(**1**)] 6.4×10^{-2}M



Scheme 1. *Reagents:* i, *hν*, DCA, O_2, $\lambda \geqslant$ 420nm, 60—90 min

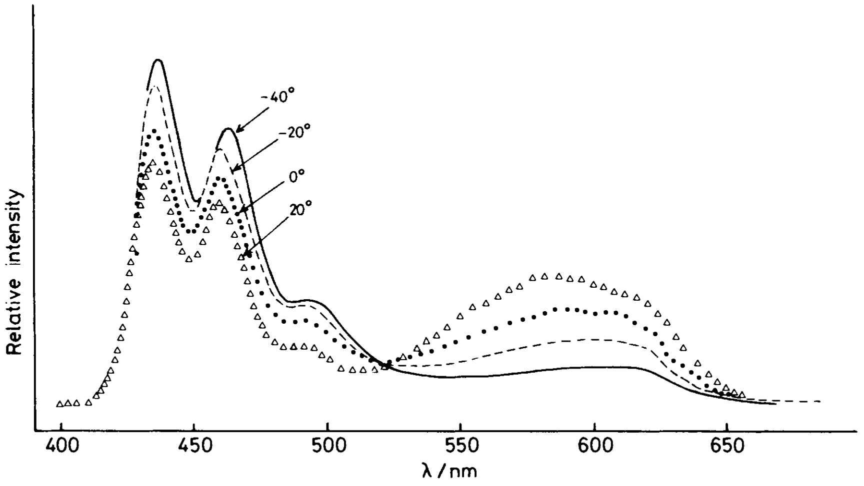


Figure 2. Temperature dependence of the emission spectrum of DCA–(1) in methylene dichloride

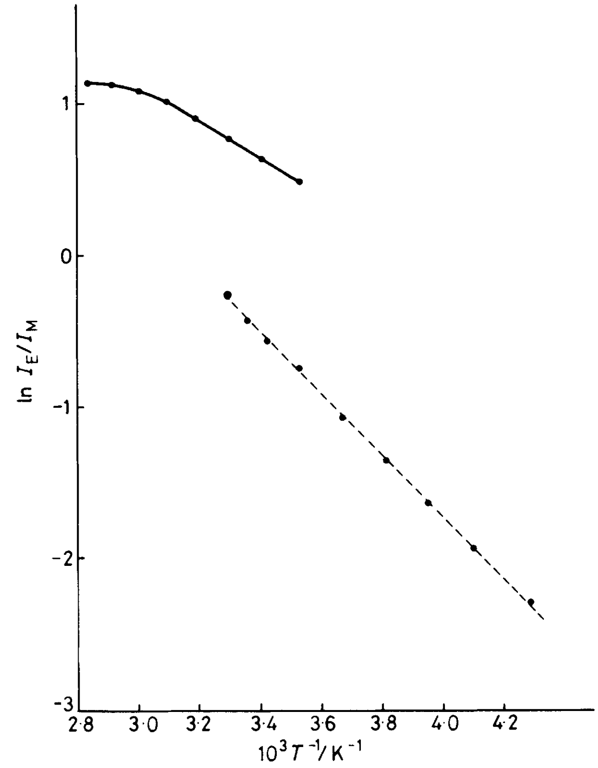


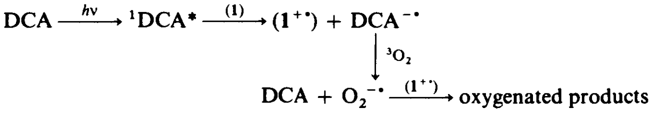
Figure 3. Temperature dependence of the ratio of exciplex to monomer fluorescence intensities: ——, in benzene; – – – –, in methylene dichloride. I_E and I_M are respectively measured at the maximum of the exciplex emission and at the (0,0) band of the monomer component

The similar photochemical behaviour obtained in non-polar solvents and upon irradiation of (**1**) sensitized by dyes well known to produce singlet oxygen gives evidence of the intermediacy of $^1O_2$ in the DCA-sensitized photo-oxygenation of (**1**). We suggest that the singlet DCA–(**1**) exciplex gives rise by an intersystem crossing process to a triplet exciplex which dissociates to yield the triplet state of DCA.[5] Singlet oxygen could then be generated by action of ^{3}DCA with ground-state oxygen. Support for our assertions can be found in the recent work of Davidson and Pratt[6] showing evidence of the ability of excimers and exciplexes to sensitize the photo-oxidation of di-t-butyl sulphide and citronellol which are known to be reactive towards singlet oxygen.

Table. Fluorescence quenching of 9,10-dicyanoanthracene by 1,4-dimethylnaphthalene

Solvent	$K_{SV}{}^a$/ l mol^{-1}	Exciplex properties $\lambda_{max.}{}^a$/nm	$\tau_E{}^a$/ns	E_a/kJ mol^{-1}
Benzene	124	545	93	10.05
Methylene dichloride	194	585	39	17.17
Acetonitrile	304			
Acetone	326			

[a] At 25 °C.



$$\begin{tikzcd}
\mathrm{DCA} \arrow[r, "h\nu"] & {}^1\mathrm{DCA}^* \arrow[r, "(1)"] & (1^{+\cdot}) + \mathrm{DCA}^{-\cdot} \arrow[d, "^3O_2"] \\
 & & \mathrm{DCA} + O_2^{-\cdot} \xrightarrow{(1^{+\cdot})} \text{oxygenated products}
\end{tikzcd}$$

Scheme 2.

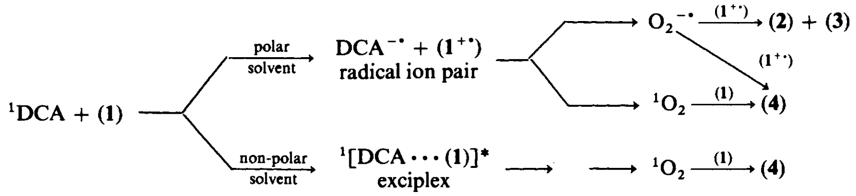
The occurrence of (**2**) and (**3**) only in polar solvents, where no exciplex emission is observed, suggests that radical ions are intermediate in the reaction. The mechanism previously proposed by Foote *et al.*[7] involving a sensitizer radical anion which subsequently reduced oxygen to superoxide (Scheme 2) can explain the results obtained upon irradiation of the DCA–(**1**) system in acetonitrile or acetone.

In addition to the above mechanism, another process involving singlet oxygen can account for the formation of the endoperoxide (**4**) in polar solvents. Singlet oxygen formation was effectively characterized by its emission at 1 270 nm in some DCA-sensitized photo-oxygenations by Foote *et al.*[7]

These authors suggested that the major source of $^1O_2$ is charge-transfer-promoted intersystem crossing of ^{1}DCA to ^{3}DCA with subsequent energy transfer from ^{3}DCA to $^3O_2$ [equations (1) and (2)]. We have carried out irradiations of the DCA–(**1**) system in the presence of reductants like Ph_3P or

$$^1\mathrm{DCA} + {}^3O_2 \longrightarrow {}^3\mathrm{DCA} + ({}^1O_2 \text{ or } {}^3O_2) \quad (1)$$

$$^3\mathrm{DCA} + {}^3O_2 \longrightarrow \mathrm{DCA} + {}^1O_2 \quad (2)$$



Scheme 3.

$NaBH_4$. In polar solvents, no oxygenated product is obtained while in non-polar solvents the reductants do not affect the photochemical reaction. The lack of reactivity in polar solvents leads us to assume that the triplet state of ^{3}DCA is formed from the radical ion pair and not from ^{1}DCA as proposed by Foote *et al.*[8,9] The work of Weller *et al.*[2,10] giving evidence that triplet formation arises from the radical ions further supports our conclusion.

These results indicate that the photo-oxygenation of (1) sensitized by DCA proceeds in a polar solvent by a dual mechanism involving superoxide ion ($O_2^{-\bullet}$) as well as singlet oxygen ($^1O_2$) (Scheme 3). The photochemical reaction in a non-polar solvent proceeding *via* an exciplex involves exclusively singlet oxygen.

Experimental

Corrected fluorescence spectra were recorded on a Fica Model 55 MK II spectrofluorometer and fluorescence lifetimes were measured on a single-photon counting apparatus. The excitation wavelength was 420 nm and measurements were made on solutions carefully degassed by a repetitive freeze–pump–thaw cycle. High-pressure liquid chromatography was carried out on a Gilson 303 instrument equipped with a reverse-phase column of μ Bondapack C-18. ^{1}H N.m.r. spectra were obtained on a Varian EM 390 spectrometer (90 MHz), using Me_4Si as the internal standard. 9,19-Dicyanoanthracene (DCA) (Eastman Kodak) was recrystallized from boiling acetonitrile; 1,4-dimethylnaphthalene (1) (reagent grade; Schuchardt) was purified by silica gel column chromatography.

DCA-sensitized Photo-oxidation of 1,4-*Dimethylnaphthalene* (1).—A solution of (1) (6.4×10^{-2}M) and DCA (10^{-5}M) in polar or non-polar solvents placed in a Pyrex tube was irradiated for 60—90 min with a 500 W high-pressure mercury lamp through a u.v.-cut-off glass filter ($\lambda \geqslant 420$ nm) in a thermostat at 15 °C. Dry oxygen was bubbled through the solution during the irradiation. The final mixture was analysed by h.p.l.c. with authentic samples and after removal of the solvent of 0 °C under vacuum was analysed by ^{1}H n.m.r. in $CDCl_3$.

Singlet Oxygenation of (1).—A CH_2Cl_2 or ether solution of (1) (0.2 g) also containing 10^{-4}M-Rose Bengal, Methylene Blue, or tetraphenylporphin was irradiated for 5—6 h. Upon completion of the reaction, the solvent was removed *in vacuo* at 0 °C. For isolation of the *endo*-peroxide (4) the solid residue was chromatographed over Merck Kieselgel 60 PF_{254} by column chromatography with ether as eluant (m.p. 84 °C).[11]

DCA-sensitized Photo-oxidation of (1) *in the Presence of Reductants*.—Irradiation of (1) carried out in polar solvents (MeCN or Me_2CO) in the presence of Ph_3P or $NaBH_4$ (in excess) produces no reaction after 2 h. In non-polar solvents (PhH or CH_2Cl_2), irradiation is not affected by addition of the reductant. The *endo*-peroxide (4) is obtained quantitatively.

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