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Mechanisms of Photooxygenation. 2. Formation of 1,2-Dioxetanes via 9,10-Dicyanoanthracene-Sensitized Electron-Transfer Processes

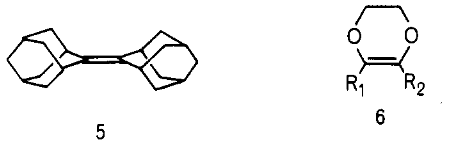
Sir:

Electron-transfer quenching of singlet excited sensitizers by olefins has recently received considerable attention.[1] Radical-ion intermediates have been characterized by transient absorption spectroscopy[2] and CIDNP methods.[3] 9,10-Dicyanoanthracene (DCA) is a typical sensitizer for photogeneration of radical ions. Electron-transfer quenching of the fluorescence of DCA by a variety of substrates has been postulated from correlations of quenching rate constants and free energies of electron transfer,[4] from solvent dependent exciplex emissions,[4a] and on the basis of distinctive photochemistry.[5]

We now provide direct evidence for the photochemical formation of the DCA radical anion ($DCA^{-}\cdot$) with the observation of the ESR spectrum of this species upon irradiation of solutions of DCA and various quenchers in deoxygenated acetonitrile.[6] Figure 1 shows an ESR spectrum obtained with 1,1-diphenylethylene (**1**). The spectrum is identical with that reported by Brunner and Dörr for $DCA^{-}\cdot$ prepared by metal/ammonia reduction.[7] Under conditions of high modulation, the spectrum becomes similar to that obtained by Happ and Janzen following addition of cyanide ion to an air-saturated solution of 9-cyanoanthracene.[8] The ESR spectrum of $DCA^{-}\cdot$ was also obtained upon electrochemical reduction of DCA[9,10] or on irradiation of DCA in the presence of quenchers **2–6a–d** (Chart I), all of which can reduce singlet excited DCA exothermically.[11] Additionally, $DCA^{-}\cdot$ could be photogenerated in dichloromethane and acetone in the presence of **6a**.

Chart I

(p-$MeOC_6H_4)_2C{=}CH_2$ **2**
Ph_2S **3**
$Ph_2C{=}CPh_2$ **4**



5
6

a, $R_1{=}R_2{=}$p-$MeOC_6H_4$
b, $R_1{=}R_2{=}$2-naphthyl
c, $R_1{=}H$; $R_2{=}C_6H_5$
d, $R_1{=}C_6H_5$; $R_2{=}$2-(6-dimethylaminonaphthyl)
e, $R_1{=}R_2{=}$m-$MeOC_6H_4$
f, $R_1{=}R_2{=}$p-MeC_6H_4

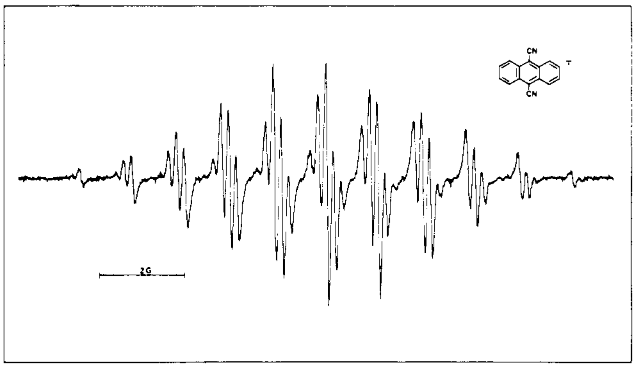
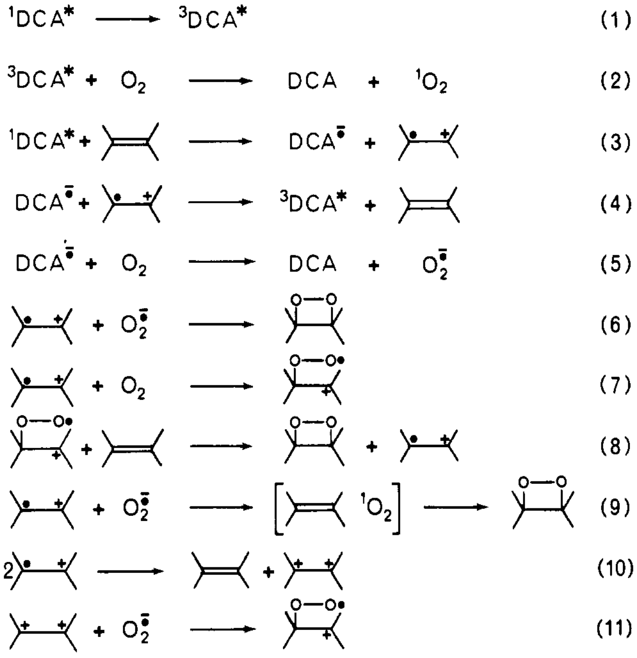


Figure 1. ESR spectrum of $DCA^{-}\cdot$ obtained by photolysis of a solution of DCA (5×10^{-4} M) and 1,1-diphenylethylene (10^{-2} M) in dry acetonitrile under Ar.[6]

Scheme I



The radical cation of the quencher should also be a primary product of electron transfer to singlet excited DCA (Scheme I, eq 3). We have characterized by ESR spectroscopy a variety of radical cations of the general structure **6** produced by electrochemical oxidation[12] or by chemical oxidation with tris(*p*-bromophenyl)ammoniumyl tetrafluoroborate (**7**).[13] Although ESR signals due to **6**$^{+}\cdot$ are readily detected, we have so far been unable to observe them upon irradiation of mixtures of DCA and **6**.[14] Flash experiments with 1,1-diphenylethylene (**1**) and the related sensitizer methyl *p*-cyanobenzoate[2] are, however, reported to result in a transient absorption ascribable to **1**$^{+}\cdot$.

While the photochemical generation of $DCA^{-}\cdot$ is of general significance to electron-transfer quenching, it is particularly relevant to the mechanism of DCA-sensitized photooxygenation recently proposed by Foote.[5a] A related reaction had been described earlier by Farid.[5b,15] Foote observed carbonyl products suggestive of 1,2-dioxetane intermediates when olefins were photooxygenated under these conditions. We find that oxygenation of olefins of structure **6** using DCA or 9,10-dicyano-2-methylanthracene (MeDCA) as sensitizers leads to substantial yields of 1,2-dioxetanes.[16] Figure 2 shows the time evolution of the photooxygenation of **6a** using MeDCA in acetone. It is evident that, unless the MeDCA is efficiently quenched by the olefin, it sensitizes the cleavage of the 1,2-dioxetane[17] which can therefore escape observation. In another experiment **6a** yielded 45% dioxetane (characterized by ^{1}H NMR spectroscopy and chemiluminescence[18]), whereas the yields were 53% with **6e** and 61% with **6f**. Pho-

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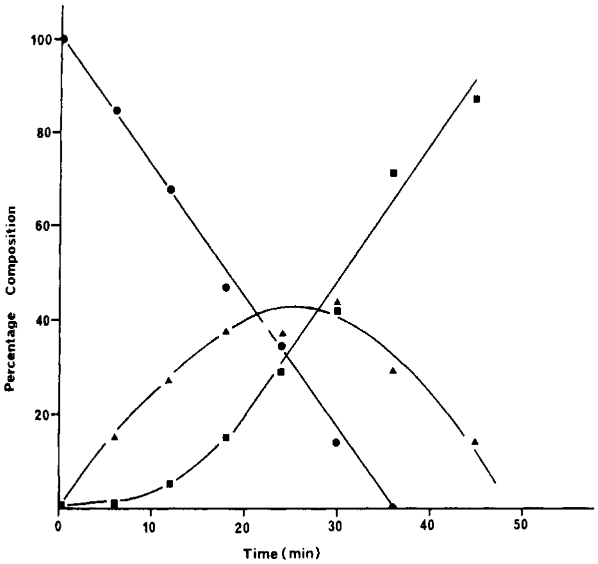

Figure 2. Time evolution of the MeDCA-sensitized photooxygenation of 2,3-di(*p*-methoxyphenyl)-1,4-dioxene (**6a**) at 0 °C in acetone-d_6.[16] ^1H NMR spectroscopy was used to determine the concentration of **6a** (●), the corresponding 1,2-dioxetane (▲), and the resultant cleavage product (■).

tooxygenation of adamantylideneadamantane (**5**) in dichloromethane led to isolation of the stable dioxetane[19] in 88% yield. Similar treatment of olefins **1** and **2** gave the corresponding benzophenones in 30[20] and 37% isolated yield.

Competition kinetics between olefins of structure **6** suggest singlet oxygen ($^1O_2$), derived from triplet DCA, is not involved.[21] Relative rates are distinct from singlet oxygen rates and are, moreover, a function of photooxygenation time. For instance, the relative rate for **6a**/**6f** is 1.64 for reaction with $^1O_2$ but ranges from 6.7 (16% **6a** reacted) to 2.4 (94% **6a** reacted) in the DCA system.[24] Reaction of **6** with $^1O_2$ produced by eq 1 and 2 (intersystem crossing)[25] or by eq 3, 4, and 2 (annihilation)[26] appears therefore to be excluded. Since $DCA^{-}\cdot$ is efficiently quenched by oxygen under our conditions (eq 5), as evidenced by ESR spectroscopy and cyclic voltammetry, we focused attention on eq 6, the final step of the Foote mechanism (eq 3, 5, and 6).

Treatment of **6a** with 1 equiv of tris(*p*-bromophenyl)-ammoniumyl tetrafluoroborate (**7**) in dichloromethane at −78 °C under argon generated a deeply violet solution of $\mathbf{6a}^{+}\cdot$. Following addition at −78 °C of 1 equiv of potassium superoxide dissolved in dichloromethane using 18-crown-6, the color was discharged within 5 min upon warming to −20 °C.[27] Chemiluminescence resulted when the reaction mixture was heated after dilution with a solution of 9,10-dibromoanthracene in *o*-xylene. The luminescence decayed at a rate identical with that from the 1,2-dioxetane formed from **6a** and singlet oxygen,[18] at several temperatures spanning a 20 °C range. Addition of authentic dioxetane to the spent chemiluminescence solutions at known concentration and integration of the emitted light showed that this dioxetane was formed in 0.4% yield from $\mathbf{6a}^{+}\cdot$ and $O_2^{-}\cdot$. Analysis of the reaction mixture revealed tris(*p*-bromophenyl)amine, recovered **6a** (42%), the diester cleavage product of the dioxetane, ethylene glycol di(*p*-methoxybenzoate) (**8**, 5%), and three other products derived from **6a** which are as yet not fully characterized. Recovery of substantial amounts of **6a** suggests that electron transfer from $O_2^{-}\cdot$ to $\mathbf{6a}^{+}\cdot$ is a competitive reaction. In a control experiment, where oxygen was bubbled into the solution at −20 °C in place of addition of superoxide, 60 min were required for complete decolorization of the solution.[28] The yield of dioxetane was diminished 4.5-fold; 35% **6a** was recovered while 2% **8** was found along with the other products. In a similar experiment with **6a** and **7** at −20 °C with acetonitrile as solvent, the solution decolorized as soon as superoxide was added. Dioxetane was again found in 0.4% yield, together with **6a** (14%), **8** (19%), and the other products. Admission of oxygen without addition of superoxide[29] using either 0.5 or 1 equiv of **7** reduced the yield of dioxetane 18-fold. Dioxetane yields have not been optimized.

The longer reaction times and reduced yields of dioxetane in the absence of superoxide make it unlikely that the bulk of the dioxetane can arise by a chain mechanism (eq 7 and 8) similar to that proposed[30] for an oxygenation first described by Barton et al.[13c,31] In the case of **6a**, formation of $^1O_2$ and olefin by electron transfer within the solvent cage is a possibility[32] (eq 9). Cycloaddition would then be competitive with diffusion into the bulk solution where quenching by superoxide would predominate.[33] Based on the known rate constants and on production of $^1O_2$ with unit efficiency, the maximum yield of dioxetane is predicted to be 2.1%.[35] However, $^1O_2$ is formed with an efficiency much less than 1 in analogous reactions[32] and **4** will undergo DCA-sensitized photooxygenation, even though it is unreactive toward $^1O_2$.[5a] Equation 9 is, therefore, a poor contender for the major pathway of dioxetane formation in this instance. However, some contribution from $^1O_2$ cannot be excluded at present.

Another mechanism, additional to that of Foote, which could account for formation of dioxetane from chemically or photochemically generated $\mathbf{6a}^{+}\cdot$ is the sequence described by eq 10, 11, and 8. Disproportionation of ions $\mathbf{6}^{+}\cdot$ appears to be thermodynamically, but not necessarily kinetically, favored.[36] This possibility is under investigation. Work is in progress to further define the scope and mechanistic basis of the experiments reported here. Nevertheless, the results presently available show clearly that oxygenation mediated by electron transfer can be a viable mechanism for a variety of olefinic substrates.

Acknowledgments. Support of this research by the U.S. Army Research Office and the National Science Foundation is gratefully acknowledged. We also thank Professor John F. Endicott for helpful discussions.

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(20) Isolated as the 2,4-dinitrophenylhydrazone.

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(27) No apparent color change occurred over a period of 1.7 h at −78 °C.

(28) No apparent color change occurred over a period of 1.3 h at −78 °C.

(29) In this case the solution decolorized within 3 min.

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(33) $O_2^{-}\cdot$ quenches[34] $^{1}O_2$ with $k_q = 7 \pm 6 \times 10^{9}\ M^{-1}\ s^{-1}$, whereas k_q for **6a** is $6.6 \times 10^{7}\ M^{-1}\ s^{-1}$. The triarylamine and 18-crown-6 are expected to quench less efficiently still than **6a.**[22]

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(35) Calculated for **6a** using a reaction rate with $^{1}O_2$ of $12.6 \times 10^{7}\ M^{-1}\ s^{-1}$ (see ref 12b) and a diffusion rate constant of $12.6 \times 10^{10}\ M^{-1}\ s^{-1}$ for acetonitrile at −20 °C.

(36) Compounds **6** show a second oxidation wave with a peak potential 0.2–0.5 V more positive than the half-wave potential for one-electron oxidation (see ref 12b).

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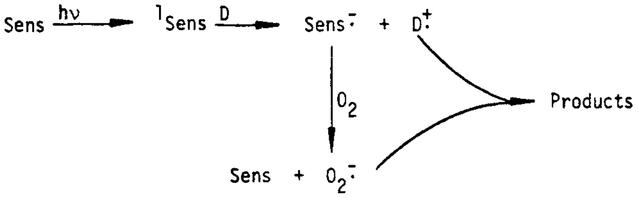
Electron-Transfer Photooxidation. 3. Detection of Radical-Ion Intermediates in the Cyanoaromatic-Sensitized Photooxidation of *trans*- and *cis*-Stilbene[1]

Sir:

Radical ions have been proposed as intermediates in a number of photochemical systems,[2] including photooxidation reactions involving cyanoaromatic sensitizers and electron-rich substrates.[3,4] The proposed mechanism for these photooxidation reactions (Scheme I) involves electron transfer from the substrate to the excited singlet sensitizer; the radical anion of the sensitizer then reacts with oxygen to produce superoxide ion, which reacts with the substrate radical cation to produce the oxidation products.[5]

Scheme I



We now report the direct observation of the radical-ion intermediates in the photooxidation of *trans*-stilbene (TS) and *cis*-stilbene (CS) using 9,10-dicyanoanthracene (DCA) and 9-cyanoanthracene (CA) as sensitizers. The absorption spectra were obtained by laser flash photolysis[8] using a Nd-YAG laser as the excitation source at 355 nm and monitoring with a xenon flash lamp. Figure 1 shows the absorption spectrum (1 μs after laser pulse) produced from 2.0×10^{-4} M CA and 0.05 M TS in N_2-saturated dry CH_3CN. The absorption (λ_{max} 470 nm) is very similar to that of $TS^{+}\cdot$ previously published.[9-11] The spectrum also shows an absorption at λ_{max} 587 nm that corresponds well to the absorption spectra of $CA^{-}\cdot$.[12] The transient decay rate at 587 nm increases on going from N_2- to air- to oxygen-saturated solution. In N_2, the decay appears to be second order, while, in air and O_2, there is an initial fast component and a slower decay at longer times. In contrast, the decay rate at 470 nm shows mixed first- and second-order kinetics. The decay rate under air is equal to or only slightly faster than that under N_2 and is larger under O_2 (Figure 2).

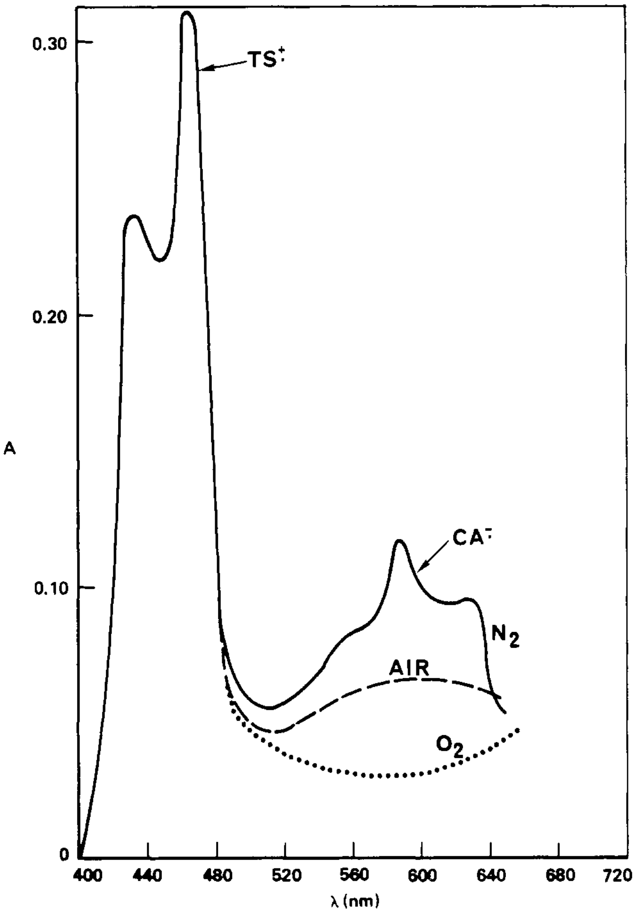


Figure 1. Absorption spectrum of 0.05 M TS + 2.0×10^{-4} M CA in CH_3CN, 1.0 μs after flash.

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