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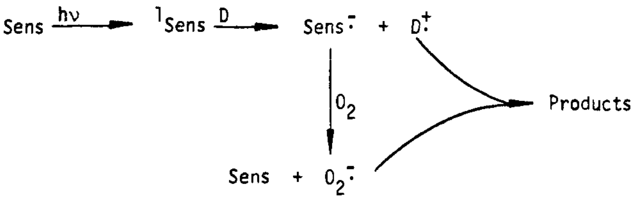
Electron-Transfer Photooxidation. 3. Detection of Radical-Ion Intermediates in the Cyanoaromatic-Sensitized Photooxidation of *trans*- and *cis*-Stilbene[1]

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).

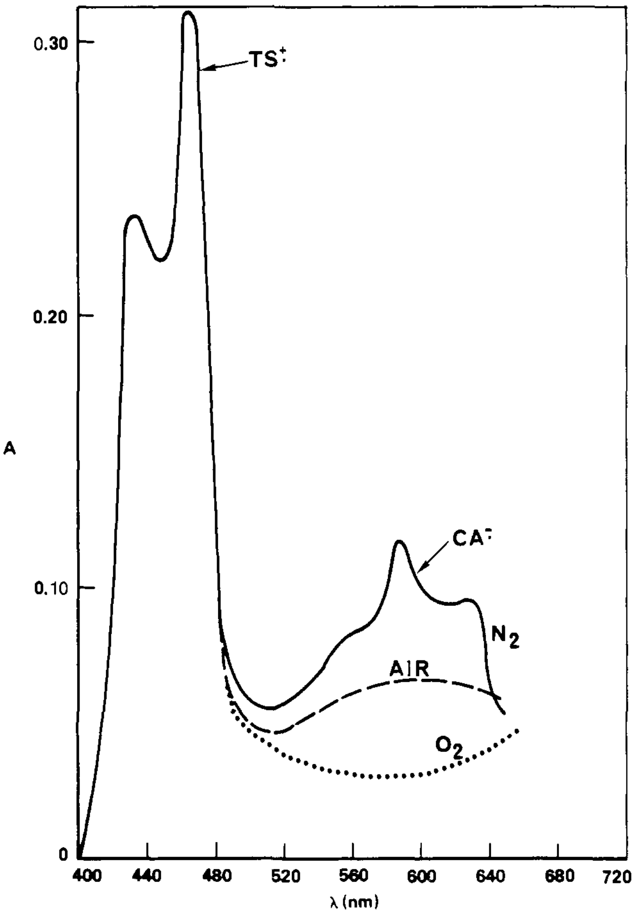


Figure 1. Absorption spectrum of 0.05 M TS + 2.0 × 10^{-4} M CA in CH_3CN, 1.0 μs after flash.

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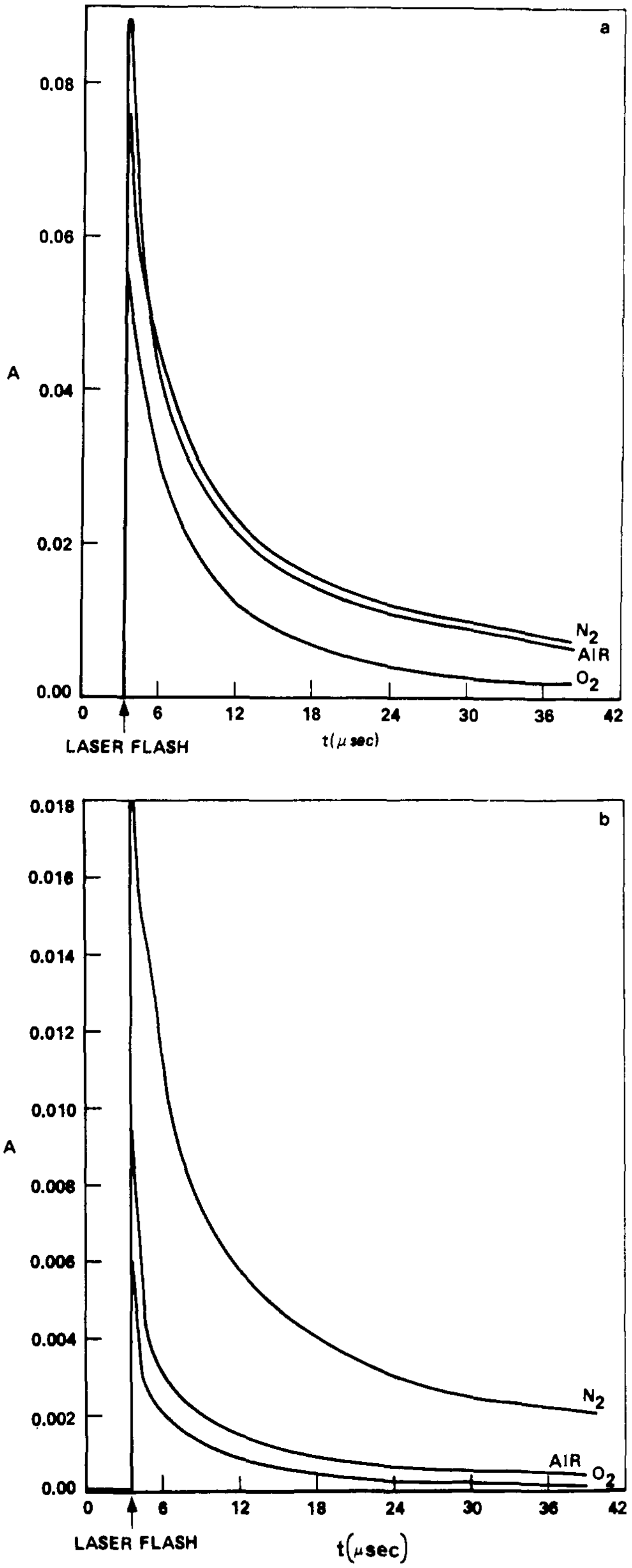

Figure 2. (a) Transient decay of TS$^{+}\cdot$ at 470 nm. (b) Transient decay of CA$^{-}\cdot$ at 587 nm.

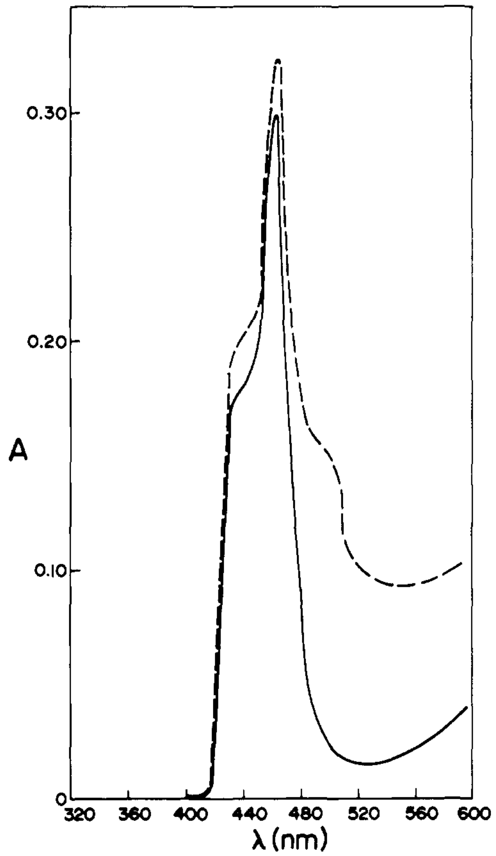

Figure 3. TS$^{+}\cdot$ absorption spectrum from 2.0×10^{-5} M DCA + 0.05 M TS, 1 μs after laser pulse, under N$_2$ (- - -) and air (—).

The same spectrum for TS$^{+}\cdot$ is observed with DCA as sensitizer. However, the spectrum is broadened because it is superimposed on the broad absorption of DCA$^{-}\cdot$ (λ_{max} 480 nm).[12] Oxygen saturation of the sample removes DCA$^{-}\cdot$ and reveals the true TS$^{+}\cdot$ spectrum (Figure 3). Continuous irradiation (400–450 nm) of the same solution in an ESR cavity[13] produces an ESR signal ($g = 2.0170$) with a hyperfine pattern that corresponds well to that of the DCA$^{-}\cdot$ ESR spectrum reported by Happ and Janzen.[14] The same ESR spectrum has been observed by Schaap et al.[15] using DCA-sensitized photooxidation of a variety of electron-rich substrates. However, in neither our experiments nor Schaap's[15] has an ESR spectrum of the radical cation been observed.

To further substantiate the assumption that the absorption at 470 nm is caused by TS$^{+}\cdot$, 1,2,4-trimethoxybenzene (TMB) and tetraphenylethylene (TPE) were used to trap it. Based on their half-wave potentials[16] (TMB, 1.12;[17] TPE, 1.33;[4b] TS, 1.51 V[4b]), electron transfer from these compounds to TS$^{+}\cdot$ should be diffusion controlled.[18] Farid et al.[3] and Foote and Eriksen[6] have shown that compounds with lower oxidation potential than the substrate quench the formation of electron-transfer oxidation products, presumably by reducing the radical cation of the substrate. In our experiment, the absorption at 470 nm decreased and the transient decay rate increased linearly with the concentration of TMB. A rate constant of $1.2 \pm 0.1 \times 10^{10}$ M^{-1} s^{-1} for the electron transfer was derived, consistent with the rate expected for an exothermic electron transfer.[4b,18]

The spectrum obtained by adding 1.0×10^{-3} M TPE to the DCA–TS solution in air-saturated MeCN (Figure 4) shows a decrease in the 470-nm band and a new peak at 500 nm that corresponds to TPE$^{+}\cdot$.[9] In the absence of TS, no TPE$^{+}\cdot$ absorption is observed because the TPE concentration is too low to trap the short-lived (15 ns)[4b,19] ^{1}DCA*, although it is high enough to trap the longer-lived TS$^{+}\cdot$.

The DCA-sensitized oxidation of CS shows absorption maxima at 475 and 515 nm. The 515-nm absorption corresponds to CS$^{+}\cdot$,[9,10] while that at 475 nm is probably that of TS$^{+}\cdot$. It has been reported[10] that CS$^{+}\cdot$ photoisomerizes to TS$^{+}\cdot$.[20] When CA is the sensitizer for CS, no absorption is observed. A reasonable explanation is that electron transfer from CS ($E_{1/2}$ = 1.63 V)[16] to ^{1}CA ($E_{1/2}$ = 1.46 V.)[4b,16] is energetically unfavorable.

The spectral evidence above provides strong confirmation

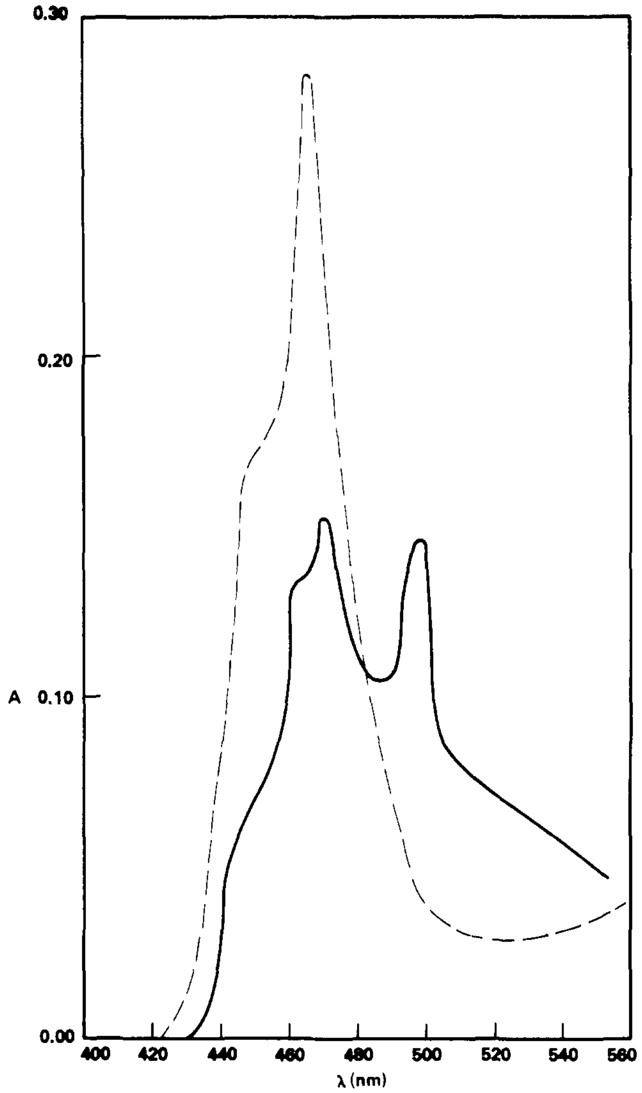

Figure 4. Absorption spectrum from 3.0 × 10^{-4} M DCA + 0.05 M TS + 1.0 × 10^{-3} M TPE, 1 μs after laser pulse, in air-saturated CH_3CN (—). - - - is the same as in Figure 3 under air, no TPE.

for the suggestion that radical ions are intermediate in the cyanoaromatic-sensitized photooxidation. It also suggests that oxygen reacts very rapidly with the sensitizer radical anion, most likely forming $O_2^{-}\cdot$. The small change in the lifetime of the radical cation in going from N_2- to air-saturated solution implies that direct reaction of oxygen with the radical cation (Barton mechanism)[21,22] is comparatively slow under air. However, it may be somewhat more important under O_2, where there is a considerable decrease in the lifetime of the radical cation. Thus, although other mechanisms for the formation of oxidation products are not ruled out, the mechanism suggested[4] is consistent with the observed facts.

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Phenyl Participation in the Cleavage of β-Phenethyl–Palladium Bonds by Cupric Chloride

Sir:

Although oxidative cleavage of transition metal–carbon bonds has been studied extensively,[1-8] the detailed mechanism of such reactions is still unclear. Stereochemical studies on oxidative cleavage processes have shown both inversion[3-6] and retention[6,7] of configuration at carbon as well as lack of stereospecificity.[1,8]

One oxidative cleavage reaction that has been a matter of much speculation is the cupric halide cleavage of palladium–carbon bonds, in which palladium is replaced by halide.[5,8,9] This cleavage reaction has been proposed to proceed either by reductive elimination,[10] a radical mechanism,[1,8] or an ionic mechanism involving nucleophilic displacement at carbon.[5,9e] Budnik and Kochi observed loss of stereochemistry in the cu-