

**PHOTOCHEMISTRY OF KETONES IN SOLUTION
LXXVIII: KINETICS OF FLUORESCENCE QUENCHING OF
9,10-DICYANOANTHRACENE AND 9,10-DIMETHOXYANTHRACENE
BY ACYCLIC AND CYCLIC UNSATURATED KETONES AND THE
BEHAVIOR OF THE RESULTING RADICAL ION PAIRS[†]**

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(Received June 4, 1986)

Summary

The rates of quenching of the fluorescence of 9,10-dicyanoanthracene (DCA) and 9,10-dimethoxyanthracene by a series of cyclic conjugated ketones, acyclic homoconjugated ketones, 3,5-cycloheptadienones and 3,5-cycloheptadienols have been determined in several solvents. In general, these rates are consistent with the ability of the quenchers to act as either electron donors or acceptors toward the electronically excited anthracenes. The cycloheptadienones are unique in showing both donor and acceptor reactivity. For some of these systems, no reactions are seen under these photosensitization conditions, while in other cases typical triplet state products are observed, which can be attributed to the generation of substrate triplets from the initial radical ion pair produced in the reaction. Novel products formed on DCA-sensitized photo-oxygenation of 2,2,7,7-tetramethyl-3,5-cycloheptadienone and the corresponding alcohol in acetonitrile appear to be formed via intermediate radical cations in processes which do not involve singlet oxygen.

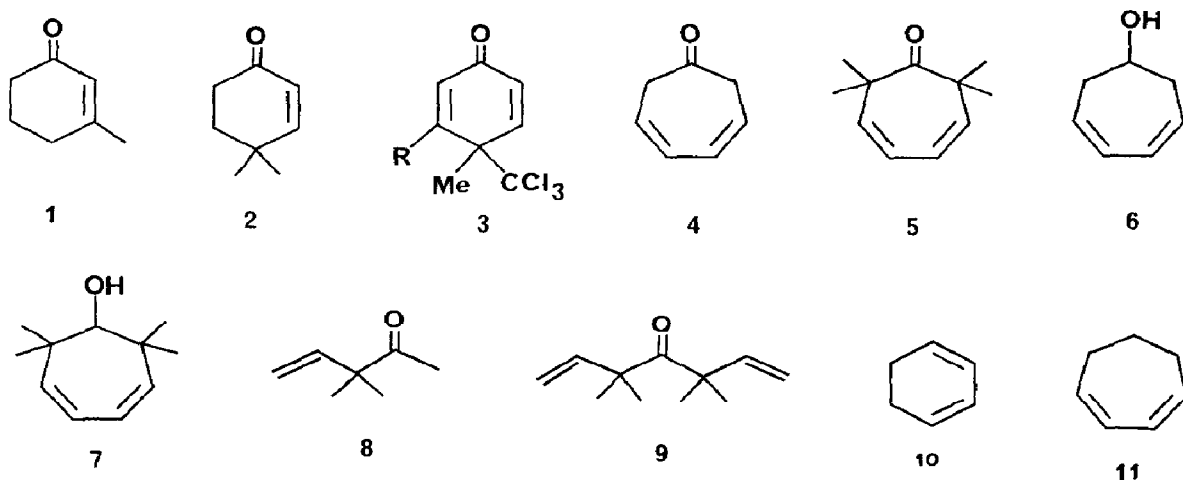
1. Introduction

The generation of radical ions on electron-transfer quenching of photo-excited anthracenes or other aromatic compounds by a variety of organic substrates is a well-known process. Reviews and leading references are given in ref. 1. Prominent examples of this type of photosensitization involve formation of olefinic radical cations and anions, which undergo a variety of

[†]Photochemistry of Ketones in Solution, Part LXXVII, is W. A. Wilczak and D. I. Schuster, *Tetrahedron Lett.*, 27 (1986) 5331.

reactions including nucleophilic and electrophilic addition reactions, cycloadditions, dimerizations and oxygenations (see ref. 2 for an extensive recent review). In some cases, singlet exciplexes have been detected in systems in non-polar media by a broad red-shifted fluorescence which grows in intensity linearly with quencher concentration as the monomer fluorescence is quenched (for representative examples, see refs. 3 - 6). In only a few cases has the exciplex been actually demonstrated to be a reaction intermediate [7].

For some years, we have studied the photochemistry of a large variety of cyclic unsaturated ketones with an emphasis on the determination of the mechanisms of the observed phototransformations [8 - 10]. It was therefore of some interest to determine the chemistry of radical anions and radical cations derived from these systems. The lowest singlet and triplet electronic excited states of these systems contain one electron in the lowest unoccupied molecular orbital (LUMO) and one in the highest occupied molecular orbital (HOMO), with paired and unpaired spins respectively. From the most simplistic point of view, the observed photochemical behavior is a consequence of the vacancy in the HOMO and the extra electron in the LUMO. Therefore, determination of the chemistry of the radical cation (which has a vacancy in the HOMO) and the radical anion (which has an extra electron in the LUMO) of the same systems may shed light on the origins of their photochemical behavior. Accordingly, we set out to generate such species using the following ketones: 3-methylcyclohexenone (1), 4,4-dimethylcyclohexenone (2), 3,4-dimethyl-4-trichloromethyl-2,5-cyclohexadienone (3), 3,5-cycloheptadienone (4) and the corresponding 2,2,7,7-tetramethyl analogue (5), and the acyclic β,γ -unsaturated ketones 8 and 9. For comparison, we have also studied the behavior of some analogous dienes, including dienols 6 and 7 corresponding to 4 and 5, 1,3-cyclohexadiene 10 and 1,3-cycloheptadiene 11. We have used 9,10-dicyanoanthracene (DCA) as the photoexcited electron acceptor and 9,10-dimethoxyanthracene (DMA) as the photoexcited electron donor. From rate constants for the quenching of the fluorescence



of DCA and DMA by this series of compounds, we wished to define those structural features which affect the ability of these ketones to act as electron acceptors and donors toward DMA* and DCA* respectively, and to determine if compounds containing both donor (1,3-diene) and acceptor (carbonyl) functionalities, as in 4 and 5, could act in both capacities. Finally, we have briefly surveyed the chemistry resulting from photoinduced electron transfer in these systems.

2. Results and discussion

2.1. Quenching kinetics

Figure 1 shows the results of a typical fluorescence quenching experiment, involving DCA and the cycloheptadienone 5. The excitation wavelength on the Spex Fluorolog instrument was varied from 395 - 405 nm using DCA and DMA concentrations from 1×10^{-3} to 5×10^{-5} M, depending on the quencher under study. In general, light absorption by the quencher was shown to be insignificant according to fluorescence excitation spectra. However, in the cases of enones 1 and 2, the intensity of the short-wavelength bands in the excitation spectra were affected at high quencher concentrations, indicating that some competitive light absorption occurred under these conditions. In no cases were new bands indicative of the formation of ground state complexes observed in the excitation spectra. Stern-

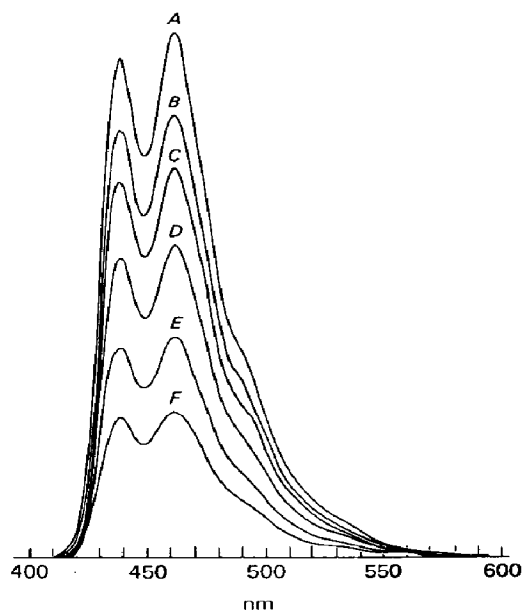


Fig. 1. Quenching of fluorescence of DCA by 2,2,7,7-tetramethyl-3,5-cycloheptadienone (TMCH) (5) in acetonitrile at various concentrations of TMCH: curve A, 0; curve B, 5.45×10^{-3} M; curve C, 1.09×10^{-2} M; curve D, 2.18×10^{-2} M; curve E, 4.36×10^{-2} M; curve F, 8.72×10^{-2} M.

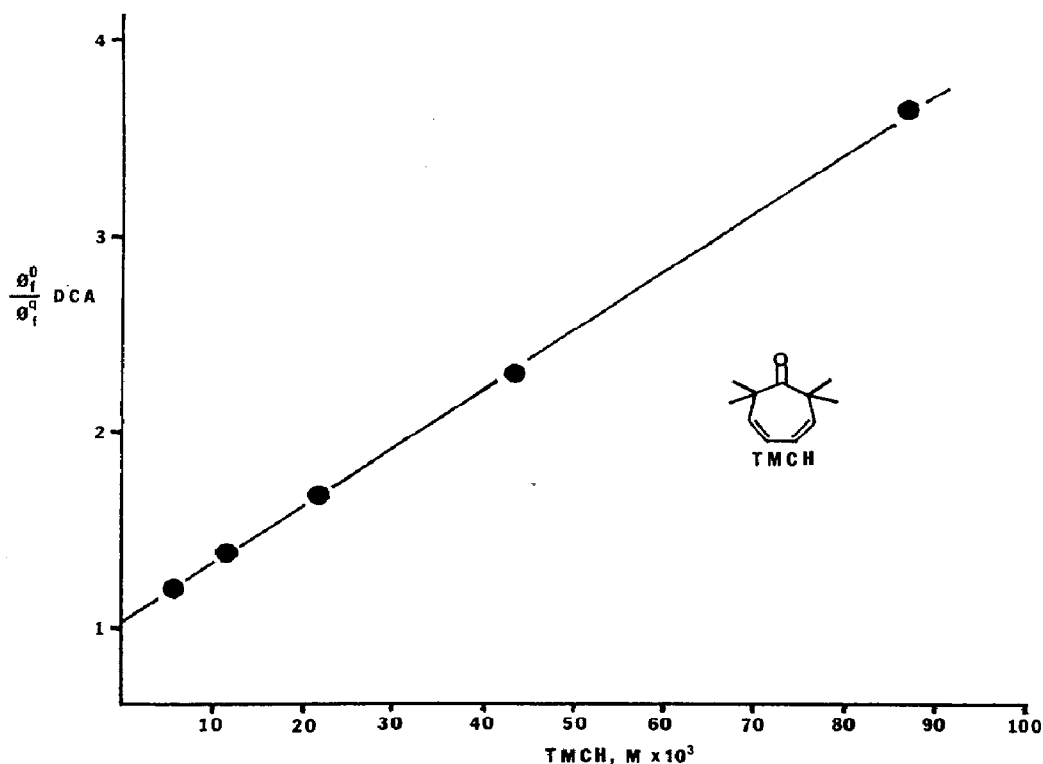


Fig. 2. Stern-Volmer plot for quenching of DCA fluorescence by TMCH (5) in acetonitrile.

Volmer quenching plots were constructed from the variation in intensity of the emission of the anthracene derivative at one or more wavelengths corresponding to fluorescence maxima. In most cases, the short wavelength maximum at 430 - 440 nm was utilized. Typical quenching plots are shown in Figs. 2 and 3. Excitation and fluorescence showed the expected sensitivity to solvent polarity, being red shifted in polar media. In the case of enone 1 in cyclohexane, a red shift in both the excitation and fluorescence spectra was observed as the enone concentration was increased, which is attributed to a change in the overall polarity of the medium. No spectral evidence of exciplex formation was obtained for the interaction of compounds 1 - 9 with either DCA or DMA, although solubility limitations prevented experiments at high quencher concentrations in some cases. Broad weak exciplex fluorescence, accompanied by the presence of an isosbestic point, was clearly discernible using dienes 10 and 11; a full description of our findings using these dienes will appear elsewhere [11].

Our quenching data are summarized in Table 1, which presents Stern-Volmer slopes $k_q\tau$ and quenching rate constants k_q . The latter were calculated from known lifetimes of $^1\text{DCA}^*$ (15.2 ns in acetonitrile, 11.7 ns in cyclohexane) and $^1\text{DMA}^*$ (11.2 ns in acetonitrile, 13.3 ns in benzene) reported in the literature [3, 5, 6]. The value of τ_F for DMA in cyclohexane was assumed to be the same as in benzene.

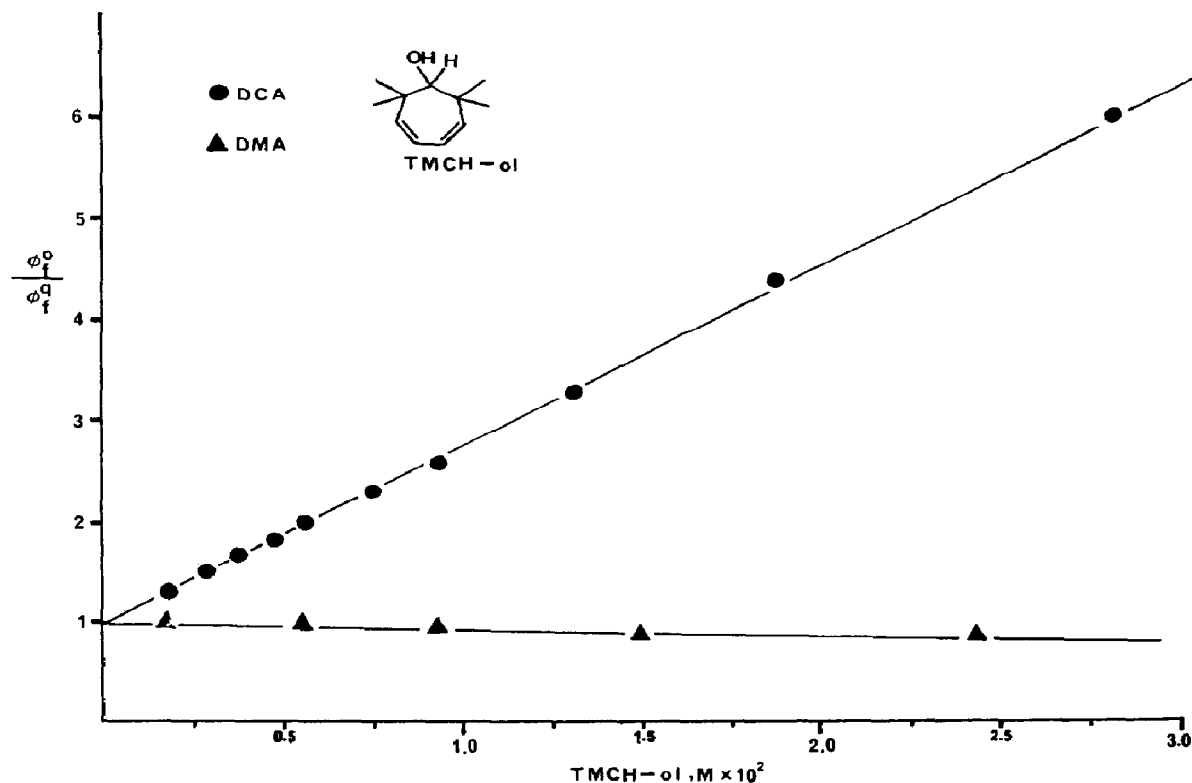


Fig. 3. Stern-Volmer plot for quenching of fluorescence of DCA and of DMA by 2,2,7,7-tetramethyl-3,5-cycloheptadien-1-ol (TMCH-ol) (7) in acetonitrile.

In general, the ability of compounds 1 - 11 to quench the fluorescence of DCA and DMA correlates with electron donor-acceptor properties. The electron deficient enones and dienones are, as expected, poor quenchers of $^1\text{DCA}^*$ compared with dienes 10 and 11. It is interesting that the cross-conjugated dienone 3 is a better quencher of $^1\text{DCA}^*$ than either the conjugated or homoconjugated enones 1, 2, 8 and 9, indicating some stabilizing interaction between the double bonds of 3 in the radical cation. There is a sixfold difference in k_q (DCA) between 7 and 5 in acetonitrile, compared with a less than threefold difference between 6 and 4; both trends are consistent with a change in electron donor ability of the diene moiety in the ketone as compared with the corresponding alcohol.

The dienes 10 and 11 and the simple enones 1, 2 and 8 are all poor quenchers of $^1\text{DMA}^*$, reflecting the poor electron-accepting ability of these systems. The reduction potential of 2 against the standard calomel electrode is -2.60 V [12], considerably more negative than values reported for a number of other enones (typically -2.1 to -2.3 V) [12]. Substituting this value in the Weller equation (see ref. 13)

$$\Delta G = E(\text{D}/\text{D}^+) - E(\text{A}^-/\text{A}) - e_0^2/a\epsilon - E_{0,0} \quad (1)$$

together with values of 0.98 V for the oxidation potential $E(\text{D}/\text{D}^+)$ of

TABLE 1

Fluorescence quenching of 9,10-dicyanoanthracene (DCA) and 9,10-dimethoxyanthracene (DMA) by unsaturated ketones and related compounds

Quencher	DCA		DMA	
	k_{qT} (M^{-1})	k_q ($M^{-1} s^{-1}$)	k_{qT} (M^{-1})	k_q ($M^{-1} s^{-1}$)
1	0.8 ^a	6.8×10^7	0.5 ^a	4.5×10^7
2	1.09 ^a	9.3×10^7	0.204 ^a	1.54×10^7
3 R = CH ₃	36.5 ^a 5.0 ^b	3.12×10^9 3.29×10^8	144 ^a 181 ^b	1.08×10^{10} 1.61×10^{10}
3 R = H			191 ^b 131 ^a	1.71×10^{10} 9.87×10^9
4	70.6 ^b	4.65×10^9	45.1 ^b	4.00×10^9
5	6.9 ^a 33 ^b 5.4 ^c	5.9×10^8 2.17×10^9	2.87 ^b	2.56×10^8
6	36.8 ^{a,d} 196.7 ^b 64.3 ^f 11.4 ^c	3.14×10^9 1.29×10^{10}	NQ ^{a,e} 3.70 ^{b,d}	3.30×10^8
7	179.7 ^b	1.18×10^{10}	NQ ^{b,e}	
8	0.18 ^b	1.21×10^7	NQ ^{b,e}	
9	0.39 ^b	2.59×10^7		
10	133.6 ^{a,g} 326.5 ^b	1.14×10^{10} 2.15×10^{10}	0.3 ^a	2.3×10^7
11	28.7 ^{a,g} 220 ^b 34.6 ^{c,g} 139 ^f	2.45×10^9 1.45×10^{10}	2.7 ^b	2.4×10^8

^aSolvent, cyclohexane.

^bSolvent, acetonitrile.

^cSolvent, benzene.

^dNon-linear quenching observed.

^eNQ, no quenching observed.

^fSolvent, ethyl ether.

^gExciplex fluorescence observed.

DMA [14], 74 kcal mol⁻¹ for the excitation energy $E_{0,0}$ of DMA [15] and 0.06 V for $e_0^2/\epsilon a$ [5, 13] (the energy associated with bringing a radical ion pair within encounter distance a in a solvent of dielectric constant ϵ), electron transfer from DMA to 2 is calculated to be endoergic by 7 kcal mol⁻¹. The corresponding free energy associated with electron transfer to 3, whose reduction potential was found to be -2.08 V [12], is calculated to be -5 kcal mol⁻¹. Thus, while 3 quenches ¹DMA* at close to the diffusion-controlled rate, the interaction of 2 (and by analogy the other enones) with

$^1\text{DMA}^*$ appears to be energetically unfavorable. For comparison, quenching of $^1\text{DMA}^*$ by tetracyanoethylene occurs in acetonitrile with $k_q = 6.0 \times 10^{10} \text{ M}^{-1} \text{ s}^{-1}$.

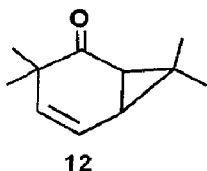
The fact that the cycloheptadienones 4 and 5 show activity both as electron donors and acceptors deserves some comment. Both ketones are surprisingly good quenchers of $^1\text{DCA}^*$, but it is clear that the four methyl groups on 5 inhibit effective interaction with the sensitizer compared with 4; an even more striking effect is seen when comparing the k_q values with respect to $^1\text{DMA}^*$, which differ by a factor of 15. The ionization and reduction potentials of these dienones and dienols have not been determined (the reduction potential of 5 could not be measured by standard methods) [12][†]. Nevertheless large enough differences in the values of ΔG (eqn. (1)) for the methylated and unsubstituted dienones to account for the observed changes in their reactivities would not be anticipated. Thus, steric effects associated with achieving proper orientation for electron transfer in encounter complexes appear to be significant in these donor-acceptor systems. Not surprisingly, the effect of the methyl groups is larger when the dienones act as electron acceptors (through the ketone moiety) rather than as donors (through the diene moiety), despite the homoconjugation in these systems [9, 10].

2.2. Photochemistry

Preparative irradiations were carried out with several of these systems, with the hope of obtaining new types of products derived from radical ion intermediates. Not surprisingly, given the poor ability of 8 and 9 to quench DCA fluorescence, extended irradiation at 400 nm of DCA in the presence of the acyclic enones 8 and a cyclic analog led to neither the disappearance of the enones nor the formation of new products, according to analysis by gas-liquid phase chromatography (GLPC)-mass spectroscopy (MS). The same result was found when biphenyl was added as a co-sensitizer [16] in the presence or absence of oxygen. Irradiation of DMA at 400 nm in the presence of dienone 3 for 112 h led to the appearance of several new products in small quantities, according to analysis by high performance liquid chromatography, thin-layer chromatography and gas chromatography (GC)-MS, but all attempts to isolate pure products were unsuccessful. It was established that the typical photoproducts of 3 [8] were not formed under these conditions. Similarly, a new unidentified product was formed on extended irradiation of DMA at 400 nm in the presence of enone 2.

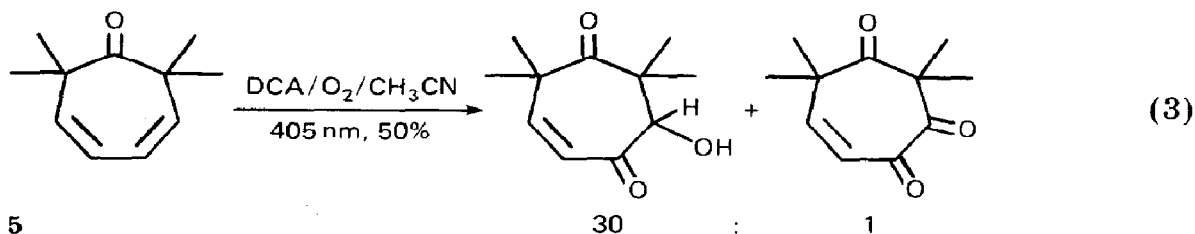
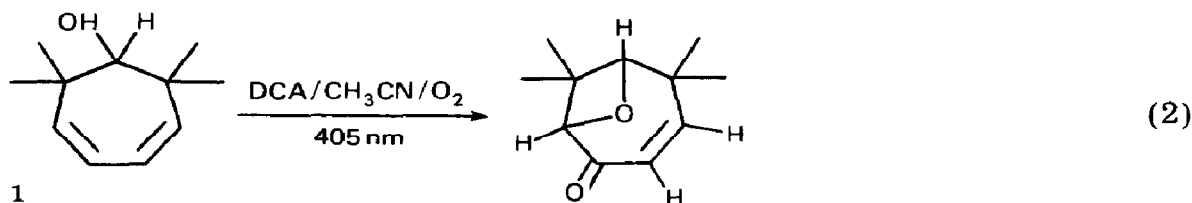
More definitive results were obtained using cycloheptadienone 5. When acetonitrile solutions of 5 containing either DCA or DMA were irradiated at 400 nm in the absence of oxygen, a single photoproduct was formed, identified as the bicyclic ketone 12. From studies of the direct and triplet-sensitized

[†]Reduction potentials of a number of compounds in this study were measured using cyclic voltammetry by Fox using acetonitrile solutions containing 0.1 M tetrabutylammonium perchlorate at room temperature. For details of procedure, see ref. 12.



excitation of **5** [9], **12** is known to originate from the lowest triplet π, π^* state of **5** by an oxa-di-pi-methane rearrangement [10]. Thus, it is likely that the formation of **12** on DCA- and DMA-sensitized excitation of **5** also involves the intermediacy of a $^3\pi, \pi^*$ state of **5**. Formation of triplets as a decay route of radical ion pairs is a well-known phenomenon [13, 17]. Indeed, 1,3-cyclohexadiene (CHD), which is a very poor quencher of DMA*, strongly quenched DMA-sensitized formation of **12**. This supports the intermediacy of a triplet state of **5**, produced via the initially formed radical ion pair. We cannot at this time exclude the possibility that CHD directly intercepts the radical anion of **5** before formation of the T_1 state by reverse electron transfer, but we regard this as a less likely quenching mechanism.

The most interesting reactions observed involved DCA-sensitized photooxygenation of **5** and **7** in acetonitrile to give the products shown in eqns. (2) and (3).



NO REACTION IN BENZENE
 NO REACTION OF **5** WITH 1O_2 SENSITIZERS RB, MB, TPP.
 NO SOLVENT ISOTOPE EFFECT

Full details of these reactions, including structure elucidations, are given elsewhere [18]. These transformations are not observed in benzene under the same conditions, or in acetonitrile using DMA as the sensitizer. The reaction in eqn. (3) was facilitated by the presence of biphenyl, but no reaction of **5** or **7** was observed using standard single-oxygen sensitizers, such as rose bengal, methylene blue, tetraphenylporphine and sodium hypochlorite-

H₂O₂. A review of the literature and primary references on singlet oxygen chemistry are given in ref. 19. Several attempts to induce reaction of 5 directly with potassium superoxide in the presence of [18]-crown-6 also failed. In mechanistic descriptions for these unusual photo-oxygenations, given in detail elsewhere [18], radical cations of 5 and 7 are the critical reaction intermediates.

3. Experimental details

3.1. Materials

DCA from Eastman Kodak was purified by recrystallization from ethanol and had a melting point of 335 - 337 °C. DMA was synthesized by the procedure of Meek *et al.* [20]. The material had a melting point of 201 - 202 °C (uncorrected) (literature value, 198 - 199 °C) [20] and had IR and ¹H nuclear magnetic resonance spectra consistent with published values [21]. The various enones and dienones were available from earlier studies in this laboratory, and were generally purified by preparative vapor chromatography prior to use. Acetonitrile (Aldrich spectrophotometric grade) was purified by refluxing over calcium hydride overnight, followed by distillation from P₂O₅, and was stored over molecular sieves. Benzene and cyclohexane (both Aldrich spectrophotometric grade) were usually used as received. In some runs, benzene was purified by stirring over calcium hydride at room temperature for 40 min and at reflux for 60 min, followed by distillation from P₂O₅ and storage over a 4 Å molecular sieve.

3.2. Fluorescence measurements

All fluorescence quenching experiments were carried out on a Spex Fluorolog spectrofluorometer using samples which had been deoxygenated by purging for 15 min with nitrogen. In a typical experiment, a 3 ml sample containing 10⁻³ - 10⁻⁵ M of either DCA or DMA in the solvent (see Table 1) was placed in a quartz cell with a glass stem capped with a septum. The sample was purged with extra pure oxygen-free nitrogen until the intensity of the fluorescence of the sensitizer was constant (usually within 15 min). Aliquots of the neat quencher or of a concentrated stock solution in cases of solid quenchers were then added to the cell using a syringe (1, 2 or 10 μl). The solutions were shaken prior to each measurement to assure even distribution of quencher in the solution.

3.3. Sensitized irradiations

Two experimental arrangements were used for these experiments. In one, the output of a 250 W lamp was passed through a series of three filter solutions (path length, 1 cm each) in a three-component cell to isolate light of 405 nm. The following filter solutions were used: (a) CuSO₄·5H₂O (44 g) in 100 ml aqueous NH₄OH (27 M); (2) iodine (0.75 g) in 100 ml CCl₄; (3) quinine hydrochloride (2.0 g) in 100 ml H₂O [22]. In the second config-

uration, the output of a water-cooled 450 or 550 W medium pressure mercury lamp in a Pyrex immersion well was passed through a surrounding filter solution of thickness 1 cm. The solution consisted of $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ (27 g), NaNO_2 (30 g) and 50 ml NH_4OH diluted with water to 1 l, which effectively isolates light of 405 and 430 nm [23].

In reactions in the absence of oxygen, the sample solutions were degassed by purging with oxygen-free nitrogen for at least 15 min. Following irradiation, often for long periods of time, the contents of the sample solution were analyzed by GLPC under conditions used previously in studies of products of direct irradiations of the ketones, and also by GC-MS using a capillary column (cross-linked methylsilicone OV-101). In a typical preparative-scale photo-oxygenation study, 400 ml of a solution containing 10^{-3} M DCA and 10^{-2} M **7** in purified acetonitrile was continuously purged with oxygen while being irradiated using the immersion lamp as described above. After 2 h, the starting material (**7**) was completely consumed. In analytical-scale studies of photo-oxygenation of **5** (about 0.1 M) in acetonitrile, DCA was used at 2.9×10^{-5} M and biphenyl (when present) at 10^{-2} M [16]. Oxygen was bubbled through the solution (0.25 ml) for 5 min prior to irradiation on the optical bench arrangement for 16 - 24 h. The reaction was monitored by GC-MS analysis.

Acknowledgments

This research was supported in part by grant CHE-8320154 from the National Science Foundation. Susan Chang is grateful to Simon Bolivar University for a sabbatical leave which allowed her participation in this project.

We are deeply grateful to Professor M. A. Fox, University of Texas, Austin, for the measurement of reduction potentials.

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