Electron-Transfer Photochemistry of Thianthrene. Nucleophile-Assisted Photooxidation to Sulfoxide

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The photochemistry of thianthrene (1) in the presence of a variety of electron acceptors in acetonitrile/water has been investigated. Diffusion-limited rates of fluorescence quenching were observed on excitation of 1 (with fumaronitrile and with methyl phthalate). Alternatively, addition of 1 led to quenching of the fluorescence emission of ketones, biacetyl, and fluorenone and to the quenching of the excited triplet states of quinones such as 2,5-dichloro-*p*-benzoquinone (5) and 9,10-anthraquinone (3). Steady irradiation of 1 with selected acceptors results in photooxidation yielding the sulfoxide (2) and the expected photoreduction products. The electron-transfer mechanisms were further studied by laser flash photolysis. The quenching of ketone triplets by 1 resulted in formation of the radical cation of 1 (λ_{max} 540 nm). The decay of this species and its dependence on the concentration of water present were determined; the bimolecular rate constant for trapping of $1^{\bullet+}$ by water in acetonitrile–water solutions is 4.9×10^4 M^{-1} s^{-1} under conditions in which 5 acts as a sensitizer. The nucleophilic trapping of the 1 radical cation by imidazole ($k = 3.6 \times 10^7$ M^{-1} s^{-1}) was also investigated. The mechanism of photoinduced two-electron oxidation of 1 and the role played by nucleophiles in facilitating the reaction are discussed in detail.

The chemical or electrochemical oxidation of thianthrene (1) has been the focus of numerous investigations.[1] In electrochemical experiments the first (one electron) oxidation occurs at a moderately positive potential ($E_{1/2}$ = 1.23 V vs SCE, acetonitrile); the oxidation wave is reversible in dry (nucleophile-free) solvent.[2]

The one-electron oxidation product ($1^{\bullet+}$) is stable and even isolable as the perchlorate salt,[3] and its ESR spectrum and paramagnetic properties have been reported.[4] Thianthrene is also known to participate in (ground state) charge-transfer complexation on combination with various electron acceptors in solution.[5]

There have been relatively few reports of the photochemistry of thianthrene. Investigations have so far revealed the fluorescence properties of the aromatic dithioether chromophore, along with the detection of the triplet state of 1.[6] Photolysis in the presence of benzoquinone provides an indication that electron-transfer intermediates are important (CIDEP experiments).[7] Electrogenerated chemiluminescence of 1 in the presence of the oxidant, peroxydisulfate ($S_2O_8^{2-}$), has been reported, as well as photoreaction on colloidal semiconductor surfaces.[8] The stability of the 1 radical cation permits routine handling so that the fluorescence emission properties of stable salts and their electron-transfer quenching can be observed.[9]

The trapping of moderately stable organic radical cations by nucleophiles has received considerable attention.[10] The role of nucleophilic groups as catalysts in the oxidation of sulfides in biological systems has been frequently considered.[11] Shine and his co-workers[12] carried out a series of early studies of the reaction of $1^{\bullet+}$ with nucleophiles and was able to provide a rationale for the formation of several different types of products that included sulfoxide derivatives of 1. The kinetics of chemical or electrochemical oxidation of 1, followed by trapping by nucleophiles including water, has been investigated in detail.[13–15]

In previous reports from this laboratory, the photochemistry of a dithioether, 1,5-dithiocyclooctane, was investigated under conditions of single-electron transfer with a photosensitizer.[16] The novel feature of reactions of this type involves the execution of a one-photon, two-electron redox process when a nucleophilic catalyst is present to facilitate the delivery of a second electron from an oxidized species (Scheme I). Proposals regarding the steps in oxidation of 1 in the presence of nucleophiles[13–15] have centered around several versions of a disproportionation type of mechanism, sometimes referred to as "half-

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Scheme I

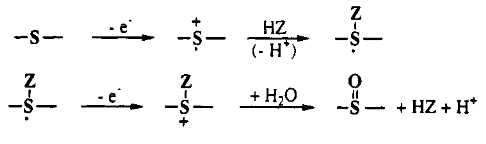

Table I. Fluorescence Quenching Associated with Electron-Transfer between Thianthrene (1) and Electron Acceptors[a]

acceptor	$E_{1/2}$(red) (V)[b]	ΔG_{et} (eV)[c]	$k_q\tau$ (M^{-1})	k_q (M^{-1} s^{-1})[d]
fumaronitrile	-1.29	-1.12	46	6.6×10^9
methyl phthalate	-1.83	-0.58	83	1.2×10^{10}
biacetyl	-1.28	-0.28	15	1.9×10^9
fluorenone	-1.30	-0.39	22	7.3×10^9

[a] Aerated 90% CH_3CN/10% H_2O solutions with 3.9 mM 1 (0.01 M biacetyl or fluorenone). [b] Half-wave reduction potentials for electron acceptors (CH_3CN); data from ref 18. [c] Calculated using the equation: $\Delta G_{et} = E_{1/2}(ox) - E_{1/2}(red) - E_{00} - E_c$, with terms including the half wave redox potentials of electron donor ($E_{1/2}(ox)$ = 1.23 V vs SCE for 1) and acceptor, the excitation energy of the fluorescent states (3.54, 2.69, and 2.82 eV for 1, biacetyl, and fluorenone, respectively), and E_c, a Coulomb interaction energy (0.1 eV for CH_3CN solvent) (ref 17). [d] Rate constants for the quenching of fluorescence obtained from the Stern–Volmer constants, $k_q\tau$, and measured fluorescence lifetimes (7.0 ns for 1 and 8.0 ns for biacetyl in 90% CH_3CN).

regeneration", requiring the essential elements of Scheme I. The hydrolytic decomposition of $1^{\bullet+}$, for example, involves trapping of the radical cation by water yielding a radical adduct that is a reducing species. The latter proceeds to react further with $1^{\bullet+}$ and the protonated form of the ultimate sulfoxide product results (vide infra).

In this work we report that 1 is a willing electron donor with a variety of sensitizing agents or photooxidants and in fact participates in two electron oxidation–reduction in the presence of nucleophiles under carefully specified conditions. Laser flash photolysis measurements allow the direct observation of $1^{\bullet+}$ as a phototransient and the direct determination of the kinetics of the trapping reaction involving the nucleophiles, water and imidazole.

Results

Fluorescence Quenching Studies. When dilute solutions of thianthrene in 90% CH_3CN/10% H_2O (λ_{max} 274 nm, $\epsilon = 3.53 \times 10^4$ M^{-1} s^{-1}) were irradiated at 280 nm in the presence of electron acceptors, fumaronitrile and methyl phthalate, the fluorescence observed for the sulfide at 435 nm[6] was quenched. The results of Stern–Volmer analysis of the quenching data including the bimolecular rate constants (k_q) are shown in Table I. The high rates of quenching ($>10^9$ M^{-1} s^{-1}) are near that expected for a diffusion-limited process and can be understood in terms of the favorable energetics that can be estimated[17] in terms of the free energy change, ΔG_{et}, for an electron transfer from thianthrene to electron acceptor following excitation (calculated values shown in Table I). The use of 1 as an electron-transfer quencher of excited states of potential photosensitizers, biacetyl and fluorenone, resulted in the efficient quenching of the relatively long-lived excited singlet states of the ketones. The quenching data for the ketones (Table I) are also consistent with a mechanism of electron transfer from 1 to sensitizer-excited species.

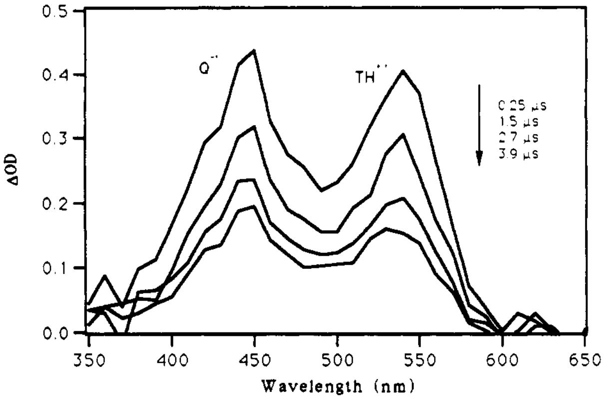

Figure 1. Transient absorption spectra for 2.0 mM 6 and 2.0 mM 1 in Ar-purged dry acetonitrile; Nd/YAG laser excitation at 355 nm. The 450- and 540-nm peaks are associated with $6^{\bullet-}$ and $1^{\bullet+}$ radical ion transients, respectively.

Laser Flash Photolysis and the Identification of Electron-Transfer Phototransients. Steady or flash irradiation of several combinations of 1 and various electron acceptors under conditions in which singlet (fluorescence) quenching was dominant were unsuccessful in revealing electron-transfer products. A preliminary study of biacetyl (BI) reactions showed that at concentrations of 1 in which BI triplets (but not singlets) are quenched, BI is converted into the biacetylpinacol.[19] In view of this result showing the effectiveness of triplet states to participate in electron transfer with 1, a series of quinones, known for their properties of near quantitative triplet formation.[21] and strong electron-acceptor tendencies, was chosen for further study using laser flash photolysis.

The frequency-tripled output of a Nd/YAG laser (355 nm, 60–100-mJ pulses of ca. 7-ns duration, fwhm) was used for excitation of samples of the quinones in the presence of 1. In all cases the radical cation, $1^{\bullet+}$, was readily observed (λ_{max} 540 nm)[3] in the time domain of 1–10 μs following the laser pulse. The transient spectra observed on quenching the triplets of two quinones are shown in Figures 1 and 2. Accumulated in Table II are phototransient data, including the peak absorptions that could be associated with the semireduced quinone (quinone radical anion) that accompanied $1^{\bullet+}$. For several of the quinones, the triplet transients could be distinguished sufficiently from quinone radical anions[21,22] (e.g., 370 and 440 nm for the triplet and the anion for 5, respectively) so that bimolecular quenching constants for the interception of quinone triplets by 1 could be determined (Table II). The decay times (half-lives) for the $1^{\bullet+}$ intermediates produced with various sensitizers are also reported.[23] The newly characterized quinone, 7, was of special interest as a high potential quinone having a reasonable water

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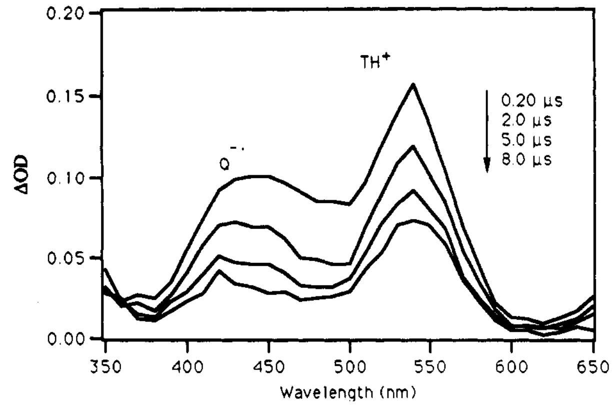
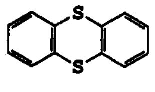


Figure 2. Transient absorption spectra for 0.1 mM **5** and 2.0 mM **1** in Ar-purged dry acetonitrile; excitation at 355 nm.

solubility, different states of protonation, and a group for attachment to polymers/peptides.[24]



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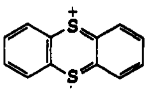
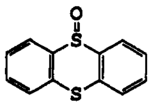


$\mathbf{1}^{+\cdot}$



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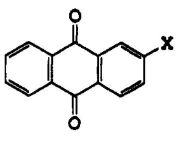
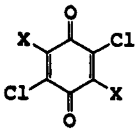
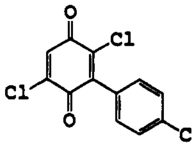


3, X=H
4, X=SO$_3$



5, X=H
6, X=Cl



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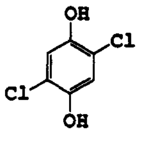

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When anthraquinone (**3**) or 2-anthraquinonesulfonate (**4**) was used as photosensitizer, the absorption bands of the radical anion transients appeared at 385 (and 540) nm for $3^{\cdot+}$ and 500 nm for 4^-,[22] respectively, overlapping the absorption of the thianthrene radical cation. However, if these solutions were purged with oxygen, the radical anion signal was quenched and the absorption band of the air-stable[3] thianthrene radical cation remained (Figure 3). A second kind of interception experiment was performed in which the electron acceptor, methyl viologen [$(CH_3C_5H_4N^+\text{-})_2$, 1.0 mM] was added to solutions of **3** and **1** in acetonitrile. In this case 355-nm laser excitation of **3** led to the characteristic transient signal for $1^{\cdot+}$ again, but the quinone anion band was replaced (100 ns to 10 µs time regime) with the well-known feature associated with the reduced species, the viologen radical ($MV^{\cdot+}$ 390 and 605 nm)[25] (Figure 4).

Table II. Electron-Transfer Quenching of Quinone Triplet States by 1 on Nd/YAG Laser Flash Photolysis in CH$_3$CN Solvent

acceptor	$E_{1/2}$(red)[a] (V vs SCE)	ΔG_{et}[b] (eV)	λ_{max} ($Q^{\cdot-}$)[c] (nm)	10^{-9} k_q[d] (M^{-1} s^{-1})	$\tau_{1/2}$[e] (µs)
6	0.01	-1.00	450		3.1
5	−0.18	-1.06	440	3.0	4.5
7	−0.24	-1.00	460	3.4	6.0
3	0.94	−0.54	540	3.1	8.8
4	−0.91	−0.63	500	2.8	8.9

[a] Quinone reduction potentials, from ref 18. [b] Free energy change for electron-transfer quenching of quinone triplets by **1** were calculated using the equation: $\Delta G_{et} = E_{1/2}(ox) - E_{1/2}(red) - E_\infty - E_c$, with terms including the redox potentials of electron donor and acceptor; the triplet-state energy for sensitizer (E_∞), 54.6 kcal/mol, was used for **5**[22a] and for **7**, along with 49, 62.4, and 61.6 kcal/mol for **6**,[22b] **3**,[22c] and **4**[21e] triplets, respectively; E_c = 0.1 eV for CH$_3$CN, from ref 17. [c] Absorption maxima for quinone radical anions (ref 22) that accompanied $1^{\cdot+}$ (540 nm) on 355-nm laser photolysis of degassed CH$_3$CN solution (0.1–2.0 mM quinone) (see Figures 1 and 2). [d] Rate constants for quenching quinone triplets by **1**. [e] Half-lives for $1^{\cdot+}$ (measured for 3% H$_2$O/97% CH$_3$CN solutions for sensitizers, **3** or **4**); all solutions were oxygen purged.

Product and Quantum Yield Studies on Thianthrene Oxidation and an Indication of the Role of Nucleophiles. Steady photolysis of **1** in the presence of the quinone sensitizers, **5** and **4**, was studied in detail. The products of irradiation of **5** and **1** in acetonitrile containing water were identified by HPLC comparison with authentic samples. Although the laser flash data confirmed the formation of the thianthrene radical cation and quinone anion, the production of the stable photoproducts of reduction (e.g., the hydroquinone, **9**) and the sulfoxide (**2**) depended markedly on the nature of the sensitizer, the amount of added nucleophiles, water or imidazole, and the presence of oxygen (aeration of samples). For example, irradiation of **5** and **1** (both 1.0 mM) in acetonitrile with up to 25% (13.9 M) water failed to produce more than trace amounts of **2**, although a slow rate of bleaching of the quinone was observed (UV).

On the other hand, anthraquinone was successful as a sensitizer for conversion of **1** to sulfoxide for runs with moderate concentrations of water [typically, 75% acetonitrile solutions]. Analysis for anthrahydroquinone (presumed to be unstable) was not carried out, but **2** was shown to accumulate in moderate yield (HPLC), see Table III), especially for runs in which oxygen was present. Quantum yields were measured for photoredox product formation for the system of **4** and **1** in the presence of the two nucleophilic species of interest, water and imidazole (366 nm, 25% H$_2$O/75% CH$_3$CN solvent, Ar or O$_2$ purged). When oxygen was used to quench the radical anion of quinone, the quantum yield of **2** is increased about 10-fold (Table III), compared with similar irradiation of Ar-purged solutions. Also, when the nucleophile, imidazole (**8**), was added, the quantum efficiency increased still more.

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(23) The kinetics of reaction of the quinone radical anion and $1^{\cdot+}$ phototransients in dry CH$_3$CN were not studied in detail. A reasonable second-order fit of the data for the decay of transients for sensitization by **5** could be obtained, however, and a rate constant of 2.2 × 10^{10} M^{-1} s^{-1} estimated. Although a simple back reaction of free radical ions is expected, other decay pathways are possible and the kinetics of the relatively slow decay in dry solvent could be more complicated. Formation and decay of radical ions from **5** and DCQB under conditions in which the different protonated forms of the quinone radical ions (quinone radical anion, semihydroquinone radical) could be distinguished are reported separately.[24]

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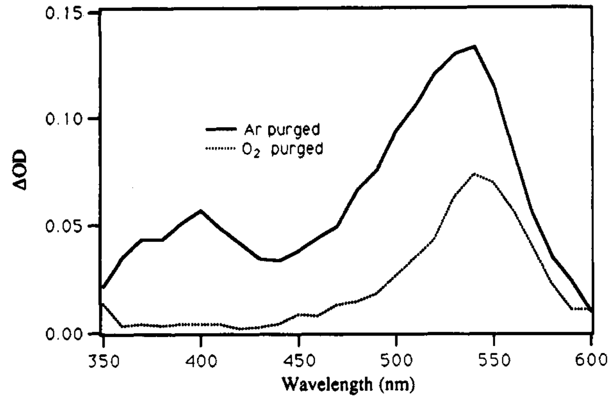

Figure 3. Transient absorption spectra of 0.05 mM **4** and 1.0 mM **1** in 3% H_2O/97% CH_3CN, with Ar or O_2, at 1.0-μs time delay; excitation at 355 nm.

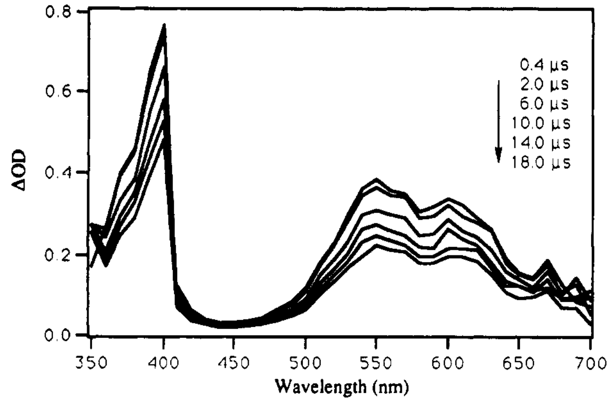

Figure 4. Transient absorption spectra of 1.0 mM **3**, 1.0 mM **1**, and 1.0 mM MV^{2+} in Ar-purged acetonitrile solution; excitation at 355 nm.

Table III. Quantum Yield of Photooxidation Product 2, Photosensitized by 4[a]

	Ar purged		oxygen purged	
	[8] = 0	[8] = 1.0 mM	[8] = 0	[8] = 1.0 mM
quantum yield	0.004	0.029	0.040	0.081

[a] [4] = 1.0 mM and [1] = 1.0 mM, in 25% H_2O/75% CH_3CN, irradiated at 366 nm.

Experiments were carried out to determine the fate of reduced species during photosensitized oxidation of **1**. The peroxidase-catalyzed oxidation of leuco crystal violet (LCV) to crystal violet (CV)[26] was used to test for the formation of the potential byproduct, H_2O_2. An O_2-purged solution of 0.04 mM **4** and 5.0 mM **1** in 75% CH_3CN was irradiated at 355 nm by laser photolysis for 10 min (90 mJ/pulse, 600 pulse/min). Analysis (HPLC) for the conversion of **1** to **2** was compared with the amount of H_2O_2 detected. A product ratio for **2**/H_2O_2 near 1:1 could be estimated.

The series of product and quantum yield experiments support a mechanism in which forward and back electron transfer reactions (Scheme II) operate efficiently[24] in the absence of significant concentrations of agents (nucleophile or oxygen) that trap one or the other of the photogenerated ions. In this scheme we include a probable step in which recombination of secondary ions (step 3) competes with the sequence of steps in $1^{\bullet+}$ hydrolysis (vide infra) and results in return to starting materials and reduced quantum efficiencies.

Scheme II

$$Q \xrightarrow{h\nu} {}^1Q^* \longrightarrow {}^3Q^* \qquad (1)$$

$$^3Q^* + TH \longrightarrow Q^{\bullet-} + TH^{\bullet+} \qquad (2)$$

$$Q^{\bullet-} + TH^{\bullet+} \longrightarrow Q + TH \qquad (3)$$

$$TH^{\bullet+} + N \longrightarrow THN^{\bullet+} \qquad (4)$$

$$Q^{\bullet-} + O_2 \longrightarrow Q + O_2^{\bullet-} \qquad (5)$$

$$THN^{\bullet+} + Q^{\bullet-} \longrightarrow TH + Q + N \qquad (6)$$

$$THN^{\bullet+} + O_2^{\bullet-} + H_2O \longrightarrow THO + H_2O_2 + N \qquad (7)$$

where Q = quinone (e.g., 3-7), TH = 1, N = nucleophile, THO = 2

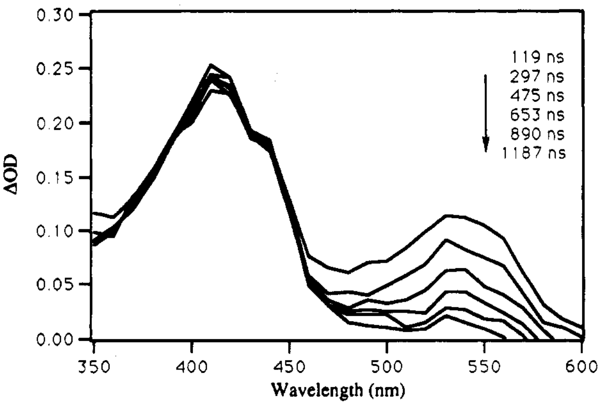

Figure 5. Transient absorption spectra of 1.0 mM **5** and 1.0 mM **1** in Ar-purged 75% CH_3CN/25% H_2O solution; excitation at 355 nm.

Kinetics of Thianthrene Radical Cation Trapping and the Mechanism of Nucleophile-Assisted Photooxidation. The course of photolysis that yields **2** sulfoxide and the role played by water in sulfide oxidation were fully expected, based on prior studies of the role of water in sulfide oxidation.[12,15] The present flash photolysis experiments further allowed the direct observation of the key step of trapping of the transient radical cation by water and potentially by other nucleophiles. With **5** acting as photosensitizer, the decay of the $1^{\bullet+}$ intermediate did not parallel the decay of quinone radical anion when >2.0 M water was present in acetonitrile solutions (Figure 5). The (millisecond) disappearance of the anion $5^{\bullet-}$ could be fit to a second order decay and, from the analysis (k/ϵ = 2.4 × 10^4 s^{-1} cm^{-1}), a rate constant for the probable disproportionation of the semiquinone[21] was calculated ($k = 1.3 \times 10^8$ M^{-1} s^{-1}, assuming $\epsilon_{435} = 5500$ M^{-1} cm^{-1}). The persistence of the radical anion is illustrated in Figure 6, along with a comparison with the faster processes of $1^{\bullet+}$ disappearance for solutions at high [H_2O]. The decay of the radical cation showed reasonably good first-order behavior (Figure 7) for solutions having [H_2O] = 2.0–10 M, and pseudo-first-order rate constants could be plotted against water concentration as shown in Figure 8.[27] A second-order rate constant $k = 4.9 \times 10^4$ M^{-1} s^{-1}, for the reaction of $1^{\bullet+}$ and H_2O was obtained from the slope of the best fit of the data to a straight line.

The decay of $1^{\bullet+}$ proved to be quite accelerated also when imidazole (**8**) was added as a trapping agent (and in the absence of water). Transient spectra for the micro-

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(26) (a) Motolla, H. A.; Simpson, B. E.; Gorin, G. *Anal. Chem.* **1970**, *42*, 410. (b) Chatterjee, S. Ph.D. Dissertation, Boston University, 1987.

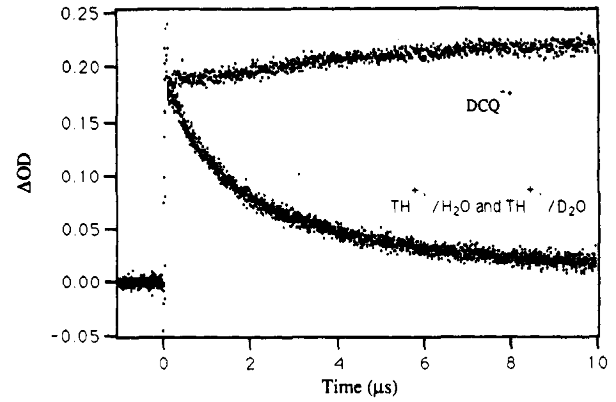

Figure 6. Transient decay curves for **5** radical anion (440 nm) and **1** radical cation (540 nm) generated in the presence of 25% (v/v) H_2O or D_2O in Ar-purged acetonitrile solution ([**5**] = 1.0 mM, [**1**] = 1.0 mM; excitation at 355 nm).

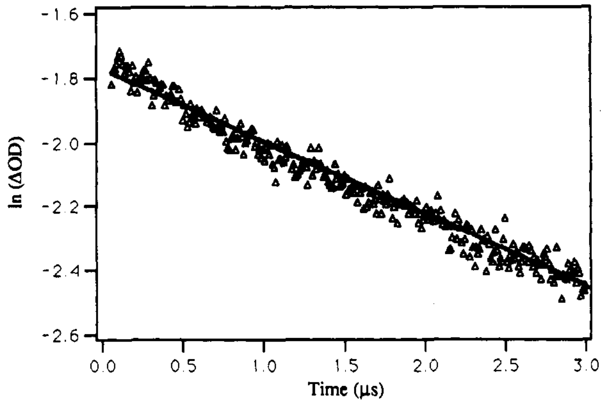

Figure 7. First-order decay of $1^{\cdot +}$ transient (540 nm) on flash photolysis of 2.0 mM **5** and 2.0 mM **1** in acetonitrile with 1.0 M H_2O (Ar-purged sample).

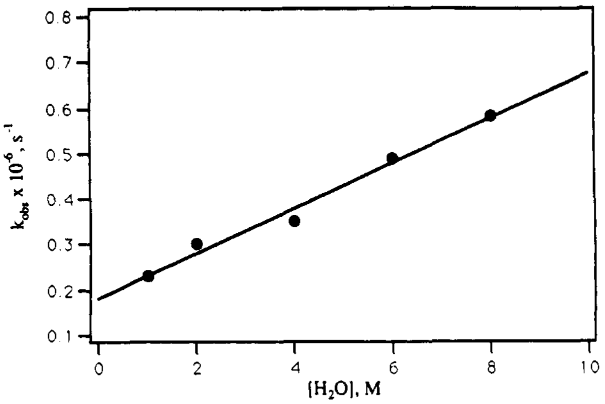

Figure 8. A plot of first-order rate constants of $1^{\cdot +}$ decay against water concentration (photosensitization by **5**, 2.0 mM in Ar-purged acetonitrile, with 2.0 mM **1**).

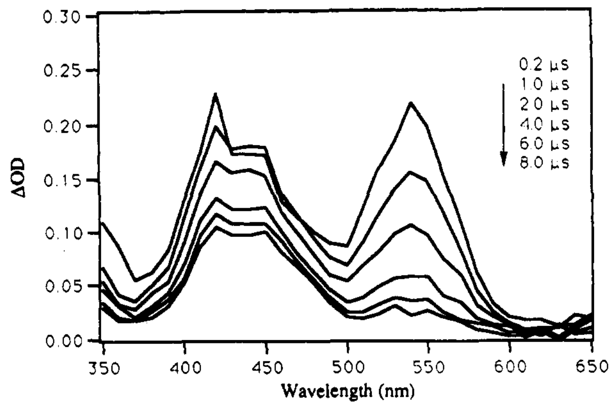

Figure 9. Transient absorption spectra of 1.0 mM **5**, 1.0 mM **1**, and 1.0 mM imidazole (**8**) in Ar-purged acetonitrile solution, Nd/YAG laser excitation at 355 nm.

second time regime are shown in Figure 9 for photolysis of **5** with **1** and **8**. The profile of rapid decay for $1^{\cdot +}$, which contrasted again with the disappearance of the quinone radical anion, is consistent with the pseudo-first-order mechanism of trapping by imidazole. When imidazole is present, the plot of k_{obs} for $1^{\cdot +}$ decay vs [**8**] provided a straight line with a slope of 3.6×10^7 M^{-1} s^{-1} for photooxidation initiated by **5** in acetonitrile (4.9×10^7 M^{-1} s^{-1} with **6** used as sensitizer).

The decay of $1^{\cdot +}$ in the presence of **8** was examined briefly as a function of pH. Thus, the pseudo-first-order decay constant following electron transfer of **1** with 0.05 mM **3** and 1.0 mM **8** was 1.3×10^5 s^{-1} for a solution composed of 75% CH_3CN and 25% of phosphoric acid buffer at pH 9.0, whereas use of an aqueous component buffered at pH 3.0 and 1.0 mM **8** yielded a rate constant for decay of only 2.4×10^4 s^{-1}. The alteration of the rate of $1^{\cdot +}$ trapping is consistent with the removal of the predominant nucleophile **8** via protonation (with solutions below the nominal p*K* for **8** of 6.0[28]). Also of mechanistic interest (vide infra) was the possibility that a solvent isotope effect on the rate of $1^{\cdot +}$ decay could be observed.[15] Included in the decay curves of Figure 6 is the plot of disappearance of the radical cation in acetonitrile with both H_2O and D_2O which reveals no measurable alteration in rate on deployment of deuterated solvent.

An interesting experiment was designed to investigate the possible reaction between ground-state quinone and thianthrene radical cation or a nucleophile-trapped radical, as follows:

$$Q + 1\text{-}Nu^{\cdot +} \rightarrow Q^{\cdot -} + 1\text{-}Nu^{2+}$$

The cation was generated by thermal reaction and mixed with quinones, or quinone and **8**, in 75% acetonitrile, and the products quantitatively analyzed by HPLC. In all cases investigated for reaction with $1^{\cdot +}$ (**5**, **3**, and **4**), no consumption of quinone was observed (and no hydroquinone was detected for **5**). When $1^{\cdot +}$ was hydrolyzed in water alone, an equal amount of **1** and **2** was obtained (HPLC).[14,15] The molar ratio of **1**/**2** was not changed significantly on the addition of quinones. Therefore, one possible mechanistic role for quinone in promoting "two-electron" thianthrene oxidation is thus eliminated.

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(27) Although we believe the pseudo-first-order kinetic data to be reliable, certain limits must be understood. It is clear that under conditions in which water is present in low concentration (<1 mM), the back reaction of radical ions will be favored and second-order decay will predominate. Another complicating feature is that $1^{\cdot +}$ decays return only to within about 5–10% of baseline (Figure 6); therefore, the first-order decay is reliable to no more than 3 half-lives. The origin of long-lived (weak) absorption at 540 nm is not known, but secondary bands associated with the much longer lived quinone radical anion or the appearance of other secondary intermediates (Schemes IV and V) are possibilities.

(28) Jencks, W. P.; Gilchrist, M. *J. Am. Chem. Soc.* **1968**, *90*, 2622.

(29) Parker[15a] prefers a mechanism in which nucleophile forms a complex with $1^{\cdot +}$ and not necessarily a covalent adduct as in Scheme III. An additional uncertainty, suggested by a referee, involves the site(s) of attack by two successive nucleophiles on oxidized intermediates (e.g., imidazole, then water in Scheme V); our option is to involve the two sulfurs rather than one so that aromaticity in the central ring is preserved.

Discussion

The mechanism of hydrolytic disposal of the radical cation of thianthrene has been the subject of some debate over the years. The original mechanism of Shine and Murata[13] involving the intermediacy of both radical cation and dication species was shown by Parker and Eberson[15d] to be inoperative since it is the monocation that is the principally reactive species with water, and the cation–dication equilibrium is highly disfavored.[10a,15] The mechanism of reaction of $1^{\bullet+}$ with water was shown by Evans and Blout[14] first to be second order in the radical cation, third order in water, and inhibited by acid. In a series of more detailed cyclic voltammetric studies by Parker and Hammerich,[15b,c] it was shown that the hydroxylation mechanism is even more complex and that as many as three rate laws may apply with variable orders for $1/1^{\bullet+}$ (e.g., order 1.3–1.6 for $1^{\bullet+}$ and up to 5 for water for oxidation in neutral acetonitrile), depending on the nature of the available bases/nucleophiles and pH. Furthermore, very large solvent isotope effects (k_{H_2O}/k_{D_2O} = 9–12) could be observed,[15a,b] consistent with the proposal that equilibria involving water protonation are involved in a complex series of reversible steps that lead ultimately to product, sulfoxide **2**.

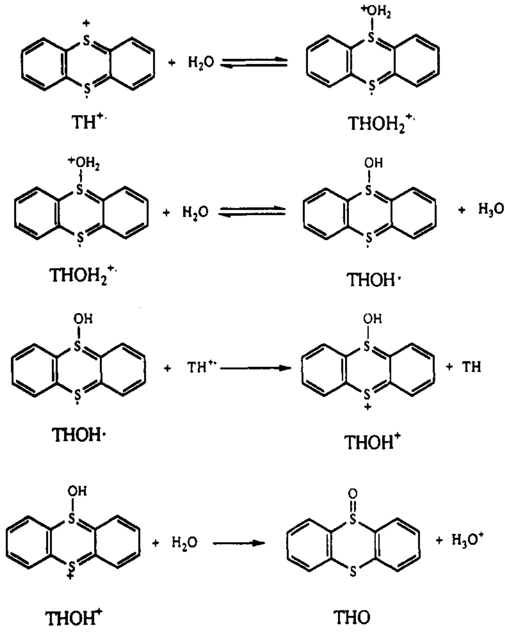
Our flash kinetic observations regarding $1^{\bullet+}$ disappearance can be understood in terms of the mechanism and conclusions of Parker et al.,[10a,15] with the proviso that it is only the early stage of the series of steps necessary for thianthrene oxidation that is inspected in the flash photolysis experiments. For initial consideration is the case in which nucleophile/base is present in low concentration (<1.0 mM water or <0.01 mM imidazole). The back reaction of photogenerated ions competes effectively with trapping of the radical cation; radical ion transients are readily observed, but net reaction is compromised (Figures 1 and 2 and steps 1–3, Scheme II).

For photolysis conditions in which water or imidazole are present in substantial amounts, the decays of radical ions are decoupled and the independent trapping of $1^{\bullet+}$ by nucleophile is readily discerned (Figures 5–9). This circumstance provided the opportunity to observe directly the radical cation decay and measure nucleophile trapping rates. The mechanism of Scheme III is that adopted by Parker,[10a] in which the steps of the "half-regeneration" sequence are delineated. Our analysis of $1^{\bullet+}$ decay kinetics is simplified with regard to kinetic order in that only the single step of water trapping (eq 1, Scheme III) is observable in the flash photolysis experiment. Also required if the reaction orders (first order each in $1^{\bullet+}$ and water) and the series of equilibria are to hold is that the equilibrium constant for the trapping step (Scheme II, eq 4, or Scheme III, eq 1) be relatively large (at least 10 M^{-1}) and that the appearance of other intermediates (e.g., THOH$^{\bullet}$) is not detected (no appreciable long-wavelength absorption, >500 nm, which could be readily resolved from Q transients).

If the decay curve in Figure 6 is carefully examined, one finds that the intermediate $1^{\bullet+}$ does not return completely to base line, indicating that some $1^{\bullet+}$ remains due to the equilibrium with water and ultimately participates in reaction step (3) (Scheme III). The first (predominant) decay of $1^{\bullet+}$ is pseudo-first-order, consistent with the nearly complete trapping by water of the cation. A slower secondary decay involves presumably the remaining $1^{\bullet+}$ species and the reducing radical, THOH$^{\bullet}$ (Scheme III, eq 3), an intermediate whose formation has been shown in electrochemical experiments to be overall rate limiting under certain conditions.[10a,15] When oxygen is present the trapped radical cation (1-Nu$^{\bullet+}$) donates its second electron to peroxide radicals to produce hydrogen peroxide as shown in Scheme II. Thus, the hydrogen peroxide test showed equal amounts of **2** and H_2O_2 as products in the event that solutions were purged by oxygen, consistent with a net reaction:

$$1 + O_2 + H_2O \rightarrow 2 + H_2O_2$$

Scheme III



Scheme IV

$$TH^{+\bullet} + NH \overset{K_1}{\rightleftharpoons} THNH^{+\bullet} \quad (1)$$

$$THNH^{+\bullet} + H_2O \overset{K_2}{\rightleftharpoons} THN^{\bullet} + H_3O^+ \quad (2)$$

$$THNH^{+\bullet} + THN^{\bullet} \xrightarrow{k_3} TH + THN^+ + NH \quad (3)$$

$$THN^+ + H_2O \xrightarrow{fast} THO + NH + H^+ \quad (4)$$

The mechanism of radical cation trapping and assistance in sulfoxide formation by a general nucleophile is abbreviated in Scheme IV. The case examined here in which the secondary nucleophile is employed is interesting in that imidazole proved the much superior trapping agent over water ($k_{rel} \sim 1000$). This result is in line with the known relative nucleophilicities for the two species.[30] The pseudo-first-order kinetic analysis for $1^{\bullet+}$ disappearance in the presence of imidazole requires the same assumptions applied to the reaction with water and further implicates the secondary steps shown in Scheme V. It is important to emphasize again the role of nucleophile which leads to reducing radical species, THN$^{\bullet}$, an intermediate which confers "two-electron" redox features on a process initiated by a single photoinduced electron transfer.[31]

In summary, thianthrene (**1**) can be induced to serve as a photochemical electron donor by a variety of means in which it acts as a quencher of excited states or as a sensitizer itself. Particularly effective is electron transfer with quinone triplets which can be observed directly by laser

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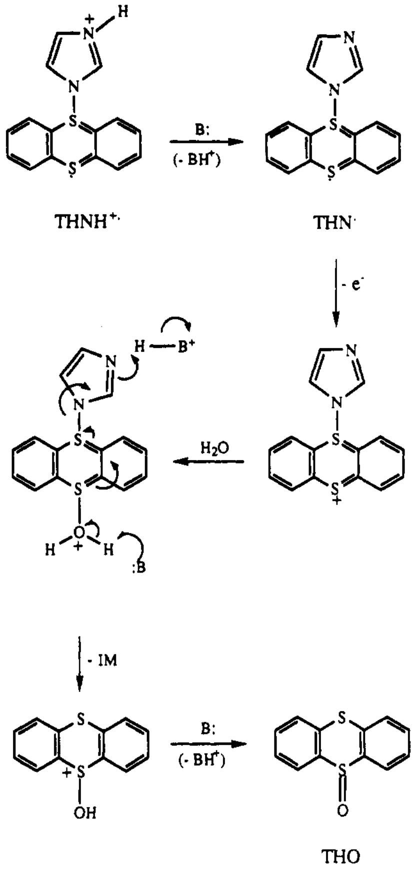
[30] Ritchie, C. D. *J. Am. Chem. Soc.* **1975**, *97*, 1170.

Scheme V



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lash photolysis. In the case of sensitization by **5** or **3**, lmost all of the decay for $1^{\bullet+}$ can be attributed to back lectron transfer involving the quinone radical anion, under ircumstances in which nucleophiles, such as water or midazole, are not present in significant concentration. A pseudo) first-order decay of the $1^{\bullet+}$ radical cation can be bserved on addition of these nucleophiles at appropriate evels. Useful rate constants for the trapping of the rototypical radical cation have been measured using flash inetic data. Thianthrene oxidation yielding sulfoxide epends on the nature of the sensitizer and the presence f nucleophile and/or oxygen to suppress unwanted radical ion) recombination steps. The detailed mechanism of lectron transfer leading to **1** and its subsequent hydrolysis s proposed to involve the sequence of Schemes II and III with modifications for use of a general nucleophile such s imidazole, Schemes IV and V).

Experimental Section

Materials. Anthraquinone (**3**) was commercially available from Aldrich and recrystallized from acetonitrile; sodium anthraquinone-2-sulfonate (**4**) (Aldrich) was recrystallized three times from water. Chloranil (**6**) was sublimed three times at 130 °C (1 mmHg), and 2,5-dichloro-1,4-benzoquinone (**5**) (Kodak) was recrystallized three times from ethanol. Thianthrene (**1**) (Aldrich) was recrystallized from ethanol three times; thianthrene 5-oxide (**2**) (mp 146 °C) was prepared by the method of Gilman and Swayampati.[37] Imidazole (**8**) was recrystallized from ethanol; 2,5-dichloro-1,4-dihydroxybenzene (**9**) and hydroquinone (Pfaltz & Bauer) were used without further purification. Type VI A-RZ peroxidase was commercially available from Sigma. Acetonitrile was HPLC grade and used as received from Fisher (no UV absorption > 200 nm).

2-(4-Carboxyphenyl)-3,6-dichloro-2,5-cyclohexadiene-1,4-dione (7). Based on a method reported for the preparation of 2,5-bis(4-ethylphenyl)-3,6-dichloro-2,5-cyclohexadiene-1,4-dione,[33] 2,5-dichloro-2,5-cyclohexadiene-1,4-dione (**5**) (4.50 g, 0.0254 mol) was dissolved in 160 mL of MeOH and 20 mL of Et_2O in a 500-mL round-bottom flask with stirring to prepare solution A. Sodium nitrite (5.0 g in 20 mL of H_2O) was added dropwise into a solution of 8.00 g (0.0583 mol) of 4-aminobenzoic acid in 20 mL of H_2O and 24 mL of concentrated HCl with stirring at 0 °C to obtain solution B; solution B was combined immediately with a solution C (20 g of NaOAc in 40 mL of H_2O) to provide solution D. The solution D was added dropwise into the solution A over 30 min with stirring. After 3 h, the resulting solution was heated at 40–50 °C for 20 min. The precipitate that formed was filtered, and the filtrate was evaporated under vacuum to about 15–20 mL. The product was extracted by addition of 150 mL of methylene chloride. The organic layer was washed with water three times. The organic fraction was dried ($MgSO_4$) and the solvent removed in vacuo. The resulting solid was washed with a portion of petroleum ether and then recrystallized from t-BuOH. The product obtained in this way still contained a small amount of **5** and therefore was washed by petroleum ether again and recrystallized from t-BuOH. The final product (2.5 g, mp 223–224 °C) was obtained in 33% yield: high-resolution mass spectrum, *m/e* 295.9649 ($C_{13}H_6Cl_2O_4$, calculated 295.9643); ^1H NMR (400 MHz, DMSO) δ 13.2 ppm (s, 1 H), 8.04 (d, J = 8.2 Hz, 2 H), 7.61 (s, 1 H), 7.45 (d, J = 8.2 Hz, 2 H); ^{13}C NMR (400 MHz, DMSO-d_6) δ 177.7, 176.5, 166.9, 143.4, 142.9, 139.5, 136.0, 132.9, 131.4, 129.8 (2 C), 128.9 (2 C); UV (in acetonitrile) ϵ_{298} = 5930 M^{-1} cm^{-1}, ϵ_{270} = 16 950 M^{-1} cm^{-1}, ϵ_{235} = 15 700 M^{-1} cm^{-1}.

Instrumentation and Methods. For determination of product quantum yields for steady-state photolysis, a quantum counting apparatus was used as previously described.[34] The light source, an Oriel 500-W lamp, was focused onto the entrance slit (2.68 mm) of a Bausch and Lomb high-intensity monochromator (maximum band-pass = 9.6 nm). Typical intensities of the irradiation source at 366 nm were 2.13 × 10^{-3} mEinsteins/h as determined from intergration areas for photodetected fluorescence for the rhodamine B quantum counter cell.[34] Typically, a 2-mL solution of sample was placed in a quartz cuvette holding a magnetic stir bar, sealed with a septum, and then purged with argon or oxygen for 20 min before irradiation at 366 nm. Photolysis product (thianthrene sulfoxide, **2**) was analyzed by HPLC with reference to a calibration curve of integrated area versus concentration determined for the pure substance by an average of at least two runs under identical conditions. The quantum counter was calibrated with reference to the 0.006 M potassium ferrioxalate actinometer, according to the literature method.[36] Samples were photolyzed to low conversion (<3.0%); irradiation times were 30–70 min. The quantum yields reported are an average of duplicate independent measurements.

HPLC and Photoproduct Analysis. The HPLC system consisted of a Rainin/Gilson HP/HPX with binary solvent delivery in conjunction with a Rainin Microsorb high-performance C_{18} reversed-phase column and Apple IIe microprocessor. Sample injections were made via a Rheodyne 725 injector; a KRATOS 757 variable-wavelength UV–vis detector was used (238 nm was selected). The HPLC solvent system was 100% Baker HPLC-

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(31) The peculiar feature of dependence of sulfoxide product formation ot only on the presence of nucleophile (and secondarily on the presence f oxygen for the trapping of quinone radical anion), but also on the ature of the sensitizer, can be understood in terms of alternate pathways ssociated with the quinones. Quinone **5** is not an active sensitizer for hianthrene conversion to sulfoxide, albeit a vigorous electron-transfer cceptor. The radical species for the benzoquinone derivative is more rone to undergo radical combination (i.e., reaction of **5** radical with a pecies such as THOH· with overall addition to the quinone), consistent ith the observation of quinone bleaching in our experiments and a variety f reported addition or substitution processes for chlorinated benzouinones.[21a,32]

(32) Jones, G., II; Haney, W. A.; Phan, X. T. *J. Am. Chem. Soc.* **1988**, *10*, 1923.

(33) Zee-Cheng, K.; Cheng, C. C. *J. Med. Chem.* **1970**, *13*, 264.

(34) Jones, G., II; Becker, W. G. *J. Am. Chem. Soc.* **1983**, *105*, 1269.

(35) Malba, V.; Jones, G., II; Poliakoff, E. D. *Photochem. Photobiol.* **985**, *42*, 451.

(36) Calver, J. G.; Pitts, J. N., Jr. *Photochemistry*; John Wiley & Sons, nc.: New York, 1966; Chapter 7.

(37) Gilman, H.; Swayampati, D. R. *J. Am. Chem. Soc.* **1955**, *77*, 3387.

grade CH_3CN mixed with millipore water (MilliQ system, with ion and carbon filters). A HP 3380A plotting integrator was used for recording sample retention times as well as quantifying peaks through their integrated areas with respect to a calibration curve of integration area versus concentration. For a solvent mixture of 30% H_2O/70% CH_3CN, typical retention times were 20.3, 6.45, 4.08, 2.81, and 2.17 min for **1**, **2**, **5**, **9**, and **4**, respectively.

Hydrogen Peroxide Test.[26] Leuco crystal violet (LCV) (37.4 mg) was dissolved in 100 mL of H_2O containing 5% (by volume) HCl to obtain a 1.0 mM stock solution. Buffer solution was prepared by mixing 2.0 M sodium acetate and 2.0 M acetic acid, and the solution was adjusted by acetic acid or NaOH to pH 4.9. The LCV stock solution was then diluted by addition of the buffer solution to a concentration of 1.0×10^{-5} M. The peroxidase solution was prepared by dissolving 5.0 mg of the enzyme in 5.0 mL of H_2O. In a control experiment, a solution of H_2O_2 (30% in water) was added to a solution of LCV (1.0×10^{-5} M) in a buffered medium (pH – 4.9), followed by addition of peroxidase solution.[26] A blue color characteristic of crystal violet (CV), the product of peroxide oxidation, developed immediately. At a pH of 4.9 the blue solution of pure CV had a λ_{max} at 590 nm with a shoulder at approximately 545 nm as obtained in the control experiment. The extinction coefficient (590 nm) of CV is reported[26] to be 7.5×10^4 M^{-1} cm^{-1}. According to Chatterjee,[26b] this method could be used for detection of H_2O_2 in an aqueous acetonitrile medium as well as water.

After oxygen purging, a quinone/1 solution (0.04 mM **4** and 5.0 mM **1** in 25% H_2O/75% CH_3CN) was laser irradiated (90 mJ/pulse, 600 pulse/min) at 355 nm for 10 min. A 10-μL aliquot of the solution was diluted by addition of 0.8 mL of LCV buffer solution and followed by about 0.2 mL of preoxidase aqueous solution to make a total volume of 1.0 mL. The absorbance of the solution at 590 nm corresponded to a concentration of 6.7×10^{-7} M crystal violet (6.7×10^{-5} M H_2O_2 product). For this sample, HPLC analysis showed a concentration of 5.5×10^{-5} M **2** produced in the photolysate.

Laser Flash Photolysis. The laser flash photolysis apparatus has been previously described.[34] It consists of a Quantel YG-581-10 Nd:YAG laser with frequency doubling (532 nm) and tripling (355 nm) capability, Lecroy Tr8818 100-megasample/s digitizer, an Oriel 150-W xenon monitoring lamp, and an RCA 4840 PMT. Also employed were a H-20 monochromator from Instruments SA, a Kinetics Systems stepping-motor controller for wavelength selection, a Kinetics Systems CAMAC interface crate, and a Macintosh II computer for data acquisition and manipulation. Samples employed CH_3CN or 75% CH_3CN/H_2O as solvent and were purged for at least 15 min with argon or oxygen prior to photolysis, depending on the requirement for cover gas. The path length of the (perpendicular) monitoring beam was 2.2 cm. Decay curves were generated from data points usually collected for 10 pulses (60–100 mJ/pulse at λ_{exc} = 355 nm); transient spectra were generated using data resulting from two pulses at each λ_{mon}. Correlation coefficients and standard deviations (point to slope, intercept, and slope), which were available from a linear least-squares analysis of data, were used in the evaluation of curve fitting and the kinetic order of reaction.

Fluorescence Quenching Measurements. Emission associated with sensitizers, biacetyl and fluorenone, was recorded on a PE MPF-44A fluorimeter (1-cm quartz cells, air-saturated samples). Solutions with absorbances of about 0.1 were excited at absorption maxima and fluorescence (maximum) intensities measured as a function of quencher concentration. From Stern–Volmer plots, $I_0/I = 1 + k_q\tau[Q]$, and linear regression analysis, slopes ($k_q\tau$ values) and intercepts (typically 1.00 + 0.02) were obtained.

Thermal Control Reaction of $1^{\bullet+}$ and Quinones. The perchlorate salt of $1^{\bullet+}$ was prepared following a literature method.[3] A fresh stock solution of $1^{\bullet+}$ ClO_4^- (1.0 mM) in dry acetonitrile was mixed and stirred with potential reactants, including water, quinones, and imidazole. The disappearance of the brown-red color of $1^{\bullet+}$ was observed in seconds. After the color disappeared completely, analysis for products (e.g., **2**, hydroquinones) was carried out by HPLC as described above.

Acknowledgment. Support of this research by the Office of Basic Energy Sciences, Department of Energy, is gratefully acknowledged.