

Photoinduced Electron Transfer for High Potential Quinone Sensitizers and
Thianthrenes. The Rate of Trapping of the Thianthrene Radical Cation by Water

Guilford Jones, II* and Bin Huang

Department of Chemistry, Boston University, Boston MA 02215

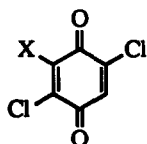
Abstract: Electron transfer properties of chlorinated benzoquinone triplet states are reported, including transient spectra and rates of electron transfer quenching by donor thianthrenes; a rate constant for the trapping of thianthrene radical cation by water has been measured.

The photochemistry of the halogenated 1,4-benzoquinones has been the focus of a number of investigations that reveal a variety of photoaddition and photoreduction pathways.¹ Chloranil (tetrachloro-1,4-benzoquinone), an exemplary oxidant ($E_{1/2} = 0.0$ V vs SCE), has been shown to be active in a number of photoinduced electron transfer reactions with arenes and olefins,² some proceeding by way of ground state charge-transfer complexes.³ A disadvantage in the deployment of the most reactive quinone derivatives is their ready reaction with nucleophiles and their instability in water.⁴ In an effort to use quinones of this type as sensitizers for electron transfer in aqueous media, including water solutions of photoactive peptides or acrylate polymers,^{5,6} we have investigated several 1,4-benzoquinone derivatives that are strong electron acceptors, but less powerful oxidizing agents than chloranil. We report here laser flash photolysis results for 2,5-dichloro-1,4-benzoquinone (1) and 2-(carboxyphenyl)-3,6-dichloro-1,4-benzoquinone (2), data encompassing the fundamental properties of quinone triplet and radical-anion intermediates. The electron donor, thianthrene (3) and a charged derivative (4) were selected as quenchers of quinone excited species. Although the electrochemistry of thianthrene and the stability of its radical-cation have been the focus of much attention,⁷ the photochemical electron transfer properties of 3 (or a derivative) have not been previously reported.

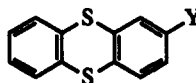
Commercial 1 (Aldrich) was used to prepare 2 by reaction with carboxyphenyldiazonium chloride, following the method of Cheng.⁸ Thianthrene derivative 4 was prepared from 2-acetylthianthrene according to the procedure of Charmas.^{9,10} The quinones displayed in their uv spectra the familiar strong (π,π^*) absorption at 250-260 nm and bands of lesser intensity at longer wavelengths (for 1, $\lambda_{max} = 327$, $\epsilon = 405$; for 2, $\lambda_{max} = 298$, $\epsilon = 5900$, CH_3CN , both bands indicative of mixed $n,\pi^*/\pi,\pi^*$ character^{1,11}). Quinones 1 and 2 were conveniently soluble in 25% water/75% acetonitrile and thermally stable in the mixed solvent medium for extended periods (> 24 hr, 25^o C). Redox potentials for the quinones (Table) were determined by cyclic voltammetry (dry CH_3CN solutions, Bu_4NPF_6 electrolyte).

Flash photolysis experiments were carried out using the Nd/YAG laser system ($\lambda/3$, 355 nm excitation, ca. 80 mJ / 7 nsec pulses) and detection methods previously described.¹² Quinone 1 (0.1 mM in dry, Ar-purged, acetonitrile) gave rise to a transient with features at 370 and 470 nm, while 2 provided a 440 nm intermediate, both of which resembled the 450 nm triplet transient associated with chloranil.^{2,3} A quantum efficiency near unity was assumed for formation of the quinone triplets.¹ The first order decays of quinone triplets (lifetimes, 10 μsec range) varied with quinone concentration. A plot of $1/\tau$ vs [Q] (0.5 - 4.0 mM) was

linear (the intercept, $1/\tau^0 = 3.4 \times 10^5 \text{ s}^{-1}$ for 1); the slopes provided rate constants for triplet "self quenching" ($T_1 + S_0 \rightarrow 2 S_0$), 1.5×10^8 and $2.3 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$ for 1 and 2, respectively, values reflecting a structural dependence similar to that observed before for a series of benzophenones and ascribed to bimolecular charge-transfer interaction.¹³



1, X = H
2, X = $\text{C}_6\text{H}_4\text{CO}_2\text{H}$



3, Y = H
4, Y = $\text{CH}_2\text{CO}_2\text{H}$

On addition of 3 to solutions of 1 in acetonitrile, the quinone triplet was replaced by transients shown in Fig 1. The spectra were ascribed to the quinone radical anion (ca. 450 nm)^{2,3} and the thianthrene radical-cation (540 nm).^{7,14} In a separate experiment 1 was photolyzed in the presence of 1.0 M isopropyl alcohol, a test that showed again the absence of triplet (at times > 200 ns) and the appearance of a sharper band at 420 nm, consistent with the formation of the semiquinone radical, QH.^{1,2} An acid-base equilibrium involving the quinone radical species (Q^\cdot , QH) ^{15,16} was implicated in experiments in which dilute acid or base was added to acetonitrile solutions (sample spectra, Fig. 1). Rate constants for electron transfer quenching of triplets for 1 and 2 with 3 (3.0×10^9 and $3.4 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$, respectively) reflected near diffusion limited rates, consistent with favorable electron transfer energetics (Table). Addition of 1.0 mM NaOH to CH_3CN solutions led to a two-fold reduction in electron transfer quenching rate for 2 and 4, consistent with the anticipated repulsion of negatively charged reactants (the $-\text{CO}_2^-$ conjugate bases). Quantum yields of net electron transfer (free radicals) falling in the range of 0.2 were obtained, based on a known absorptivity for 3^+ .¹⁹ A discernible effect of medium acidity on Φ_{et} was observed for the combination of 2 and 4 in $\text{CH}_3\text{CN}/\text{H}_2\text{O}$ solutions, an effect not readily accounted for on the basis of a simple consideration of charge type²² (carboxyl ionization).

The rate constant for the step in which water traps the radical-cation of 3, an important step in the pro-

Table Electrochemical data, spectral features for radical ions, and radical yields for quinone photoreduction

Compound	E_{red} (V vs SCE)	$\Delta G_{\text{et}}^{\text{a}}$ (k cal/mole)	$\lambda_{\text{max}} (\text{Q}^\cdot)$ (nm)	ϕ_{et}
1	-0.18	-21.9	440	
2	-0.24	-20.6	480	0.13 ^b 0.25 ^c

^aCalculated using the equation: $\Delta G_{\text{et}} = E_{\text{ox}} - E_{\text{red}} - E_{00} - E_{\text{c}}$ (ref 17), with terms including the redox potentials of electron acceptors and donor 3 ($E_{1/2} = 1.23 \text{ V vs SCE}$, CH_3CN ⁷), the triplet state energy of sensitizers ($E_{00} = E_{\text{T}} = 54.6 \text{ kcal/mol}$ reported for 1, ref 18) and Coulomb interaction energy (0.1 eV for CH_3CN); ^bfree radical yield measured for quenching by 4 (ref 19) in 25% (v/v) 0.1 M phosphosphate buffer solution (pH 5.4), 75% acetonitrile; ^cmeasured for 2 and 4 in 25% 0.1 M phosphosphate buffer solution (pH 3.0), 75% acetonitrile.

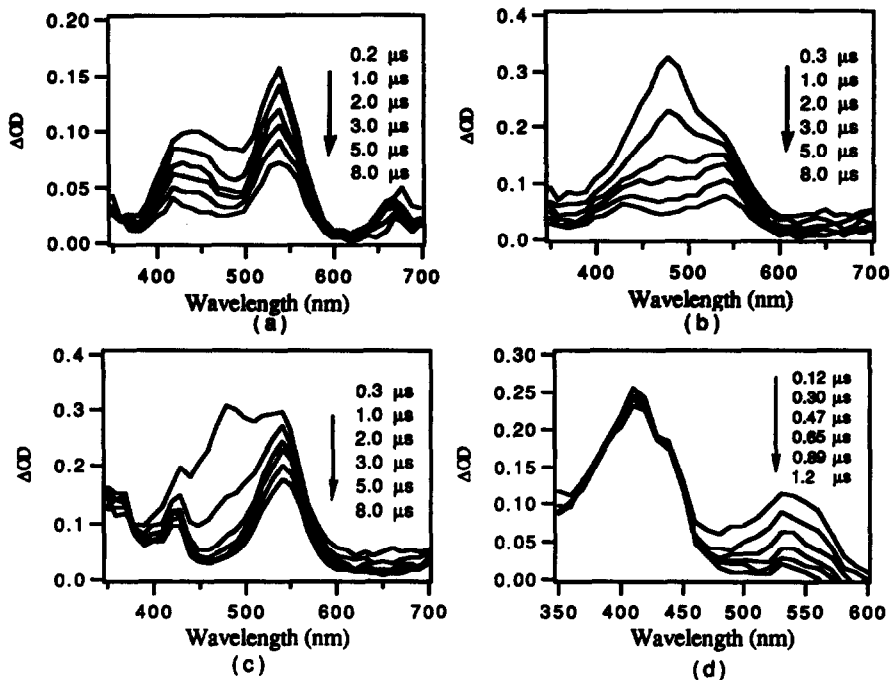


Figure 1. Transient absorption spectra for laser photolysis (355 nm) of quinones (Ar-purged acetonitrile solutions): (a) 0.1 mM 1 and 2.0 mM 3; (b) 0.1 mM 2 and 2.0 mM 3 with 0.3 mM NaOH; (c) 0.1 mM 2 and 2.0 mM 3 with 0.3 mM HCl; (d) 1.0 mM 1 and 1.0 mM 3 in 75% CH₃CN/25% H₂O.

posed mechanism of two-electron oxidation of 3 to its sulfoxide has been determined. As shown in Fig 1d, the 540 nm cation band is depleted rapidly, when water is present in significant concentration. The decay is pseudo-first order and from experiments in which water concentration varied (2-10 M), a rate constant, $k = 4.9 \times 10^4 \text{ M}^{-1} \text{ s}^{-1}$ for bimolecular trapping of 3⁺ by water can be computed. The kinetics of electrochemical oxidation in CH₃CN/H₂O have been shown⁷ to be quite complicated with a varied order of reaction in [H₂O] due to the importance of follow-up proton transfer steps. What is conveniently observed here is the initial step of cation interception by water, a reaction which is not necessarily rate-limiting overall in sulfide oxidation.

In summary, the triplet and radical-ion intermediates associated with dichlorobenzoquinones have been identified, along with intermediates from electron donor thianthrenes. The high potential quinones would appear to be suitable for use in a variety of media and will be attractive from the standpoint of their large excited state reduction potentials (ca. +2 V vs SCE). The quinones were employed as electron transfer sensitizers for the photooxidation of thianthrene and proved valuable in assessing the rate of trapping of photogenerated radical cations by nucleophile (water).

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10. For 2, the spectral data are: $m/e=295.9649$ ($C_{13}H_6Cl_2O_4$); 1H NMR (400 MHz, DMSO- d_6) δ 13.2 ppm (s, 1 H), δ 8.04 ppm (d, $J = 8.4$ Hz, 2 H), $\delta=7.61$ ppm (s, 1 H), $\delta=7.45$ ppm (d, $J = 8.0$ Hz, 2H); ^{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 (2C), 128.9 (2C). For 4, $m/e = 274.0117$ ($C_{14}H_{10}O_2S_2$); 1H NMR (400 MHz, DMSO- d_6) δ 7.57 (m, 2H), 7.49 (m, 2H), 7.34 (m, 2H), 7.23 (d, $J = 8.0$ Hz, 1H), 3.60 (s, 2H); ^{13}C NMR (400 MHz, DMSO- d_6): δ 172.3, 135.6, 134.6, 134.4, 134.3, 132.5, 129.7, 129.5, 128.8, 128.76, 128.5, 128.2 (2C), 32.0.
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14. The decays of the electron transfer intermediates (half-lives of ca. 4 μ s) could be reasonably fit to second-order plots, but the appearance of the QH \cdot secondary species in low yield suggested a more complicated kinetic scheme. Solutions were relatively stable but continued pulsing led to some coloration, indicating a net reaction of low quantum efficiency. The dominant pathway nonetheless is most likely the back reaction of radical (ions) as has been observed previously for quinone electron transfers.^{1,3} The oxidation potential for 4 ($E_{1/2} = 1.13$ V vs SCE, CH_3CN) was similar to that of 3.
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19. OD's were recorded at 200 ns, a time at which signals had not decayed appreciably, for solutions 0.1 mM in 1/2 and 1.0 mM in 3/4. The 4 $^{+}$ transient was recorded at 560 nm and the absorptivity value, $\epsilon = 8500$, established for 3 $^{+}$ was assumed.²⁰ For computation of quantum yields solutions were flashed in parallel with a benzophenone (CH_3CN) reference for which ϵ (520 nm) = 6500 was assumed.²¹
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