# Photochemical Oxidation of Water by 2-Methyl-1,4-benzoquinone: Evidence against the Formation of Free Hydroxyl Radical

**Aude Pochon, Pamela P. Vaughan, Daqing Gan, Peter Vath, Neil V. Blough,* and Daniel E. Falvey***

*Department of Chemistry and Biochemistry, University of Maryland, College Park, Maryland 20742-2021*

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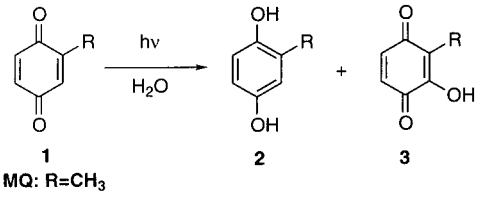
Photolysis of 2-methyl-1,4-benzoquinone (toluquinone) in aqueous solution results in the oxidation of water to create either hydroxyl radical or some species capable of transferring a hydroxyl radical. Trapping of the latter with dimethyl sulfoxide (DMSO) creates a methyl radical which in turn can be trapped by the stable radical 3-amino-2,2,5,5-tetramethyl-1-pyrrolidinyloxy. Competitive trapping studies using DMSO and either nitrite anion or salicylate anion show that the hydroxylating species is much more selective in its reactions than free hydroxyl radical. Laser flash photolysis experiments on toluquinone in aqueous solution show formation of a transient species immediately (<150 ns) following the excitation pulse that had previously been assigned to the excited triplet state of the quinone. This spectrum differs from the authentic triplet state spectrum generated in less reactive organic solvents (carbon tetrachloride and acetonitrile). The same intermediate is shown to react with the hydroxyl radical traps, cupric ions, and benzoate anion to yield the semiquinone radical. On the basis of these experiments it is argued that this transient species is a hydroxylating intermediate, probably best described as a complex between the semiquinone radical and the hydroxyl radical. It is further argued that this species is responsible for the hydroxyl radical trapping reactions.

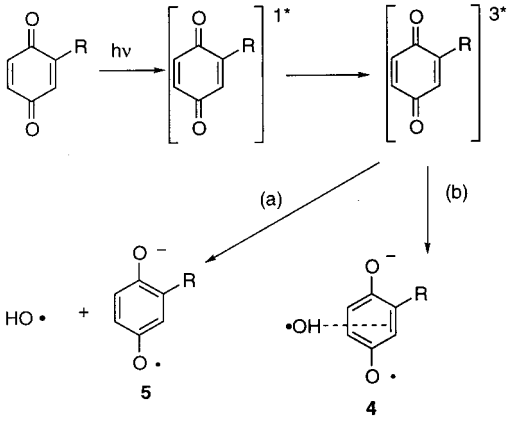
Benzoquinone and its derivatives show a rich array of photochemical behaviors that are highly dependent on the nature of the medium.[1−3] Like the aromatic ketones, 1,4-benzoquinone and its simple derivatives are characterized by n → $\pi^*$ triplet states, rapid and near-unity quantum yields for intersystem crossing. In relatively inert organic media the photochemistry is dominated by [2 + 2] cycloaddition processes giving either cyclobutane or oxetane rings. When photolyzed in the presence of substrates with weak C−H bonds, the major products are generally those derived from H atom transfer to the quinone triplet state followed by radical coupling processes. The quinones are much stronger excited-state oxidants than the ketones. Thus, in polar media and/or with electron-rich substrates, photoinduced electron-transfer reactions predominate.

While the aqueous photochemistry of various quinone derivatives has been studied for several decades,[4−17] a uniform description of the initial events remains elusive. It is widely agreed that the final products (under anaerobic conditions) include hydroxylated quinones and hydroquinones (Scheme 1).[4,6,7,18] Various chemical trapping experiments have confirmed that "•OH" is generated in these photolyses. (The use of quotation marks indicates either free •OH or any species capable of rapidly transferring •OH to another molecule). The simplest mechanism would have the excited triplet state of the quinone abstract a H atom from a molecule of water. This would produce a semiquinone anion (or, at low pH, its conjugate acid) along with a free hydroxyl radical (Scheme 2, pathway A).[11,13,15,17,19] An alternative view holds that the •OH radical remains bound to the semiquinone radical and it is this complex which is the source of "•OH" in the observed trapping reactions (Scheme 2, pathway B).[5,8,10,12,14] The distinction between these mechanisms has some practical consequences. The free •OH radical is expected to be more reactive and less kinetically selective in its reactions with various substrates. The •OH−semiquinone complex (**4** also referred to as a hydroxylating intermediate) is expected to exhibit reactivity that is somewhat attenuated relative to the free •OH and also more kinetically selective.

**SCHEME 1**




**SCHEME 2**




While these two pathways could, in principle, be distinguished through laser flash photolysis (LFP) experiments, a number of technical problems complicate the interpretation of LFP data

* Corresponding authors. Fax: 301-314-9121. E-mail (Falvey): df37@umail.umd.edu. E-mail (Blough): nb41@umail.umd.edu.

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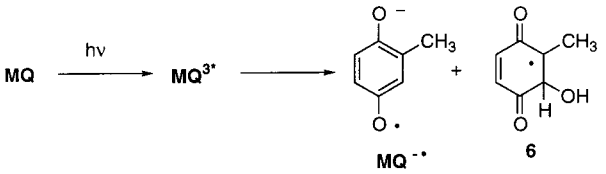
**SCHEME 3**




from these systems. First, the anticipated quinone-based intermediates (quinone triplet state,[20] semiquinone radical,[21] semiquinone anion,[22] and quinone−hydroxy adduct[23]) all have weak and overlapping absorption bands near 400 nm. Second, •OH itself has eluded direct detection in solution due to (1) its short lifetime, (2) its lack of a strong absorption band in the near UV or visible region of the spectrum, and (3) the high spin−orbit coupling that broadens its EPR line width.[24] Early LFP experiments by Bensasson[9] have attributed signals detected at times >500 ns following photolysis of 2-methyl-1,4-benzoquinone to a combination of semiquinone radical (QH•) and a hydroxyl adduct of an 2-methyl-1,4-benzoquinone (**6**). There is a distinct intermediate observed at times <500 ns which was attributed to the excited triplet state of the quinone ($Q^{3}$*) (Scheme 3).

2-Methyl-1,4-benzoquinone (**MQ** or 1,4-toluquinone) is an attractive compound to study for two reasons. First, unlike 1,4-benzoquinone, its photochemistry is less complicated due to the absence of [2 + 2] cycloaddition reactions. Second, H atom abstraction from water by its lowest excited triplet state (i.e., the net reaction illustrated by pathway (a) in Scheme 2) is predicted to be weakly exergonic at neutral pH.[25] Thus both pathway (a) and (b) in Scheme 2 are thermodynamically feasible. Through a combination of chemical trapping and LFP experiments, the aqueous photochemistry of **MQ** has been examined. The trapping experiments show that the "•OH" species generated in this way is far more selective in its trapping reactions than free •OH radicals. The LFP experiments identify a species formed within 40 ns of photolysis that is quenched by radical traps to generate the semiquinone radical. It is argued that this early transient signal is due primarily to an oxidizing semiquinone−•OH intermediate and that a free •OH radical is not formed.

## Results

**(1) Chemical Trapping Experiments.** The generation of "•OH" was probed using an approach described in detail in a series of earlier reports.[16,26−28] As shown in Scheme 4, addition of "•OH" to DMSO gives sulfinic acid with concomitant displacement of a methyl radical. The latter, in turn, is trapped with a nitroxyl radical, **3-AP**. Following reaction, the methyl adduct **9** is converted to a fluorescent derivative **11** by reaction with fluorescamine **10**. Quantification of the latter by HPLC with fluorescence detection allows for determination of the yield of "•OH" in a given run. We note that free •OH generated from nitrite photolysis and analyzed by this technique provided rate constant ratios from competitive trapping experiments (see below) that agree well with those obtained by pulse radiolysis experiments.[16]

Several control experiments were carried out in order to determine the optimal concentrations of trapping agents necessary to scavenge "•OH" generated from **MQ** photolysis. Shown in Figure 1 is the yield of the methyl adduct **9** at varying concentrations of DMSO from a photolysis of 5 $\mu$M MQ in the presence of 100 $\mu$M **3-AP**. The efficiency of trapping saturates near 50 mM and stays constant over a large concentration,

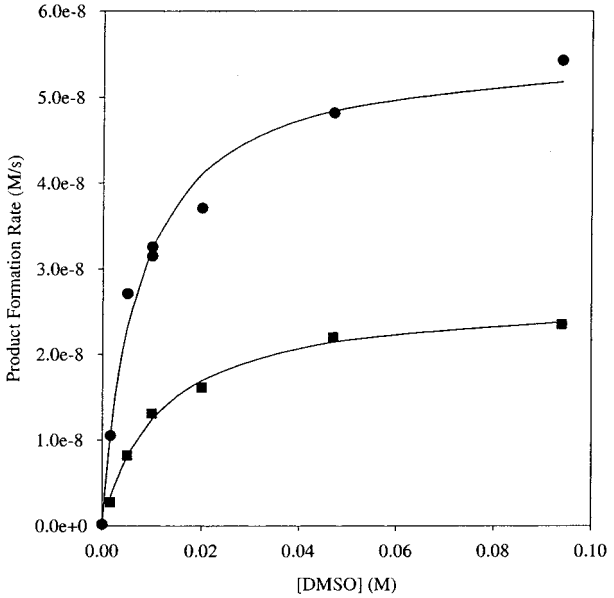
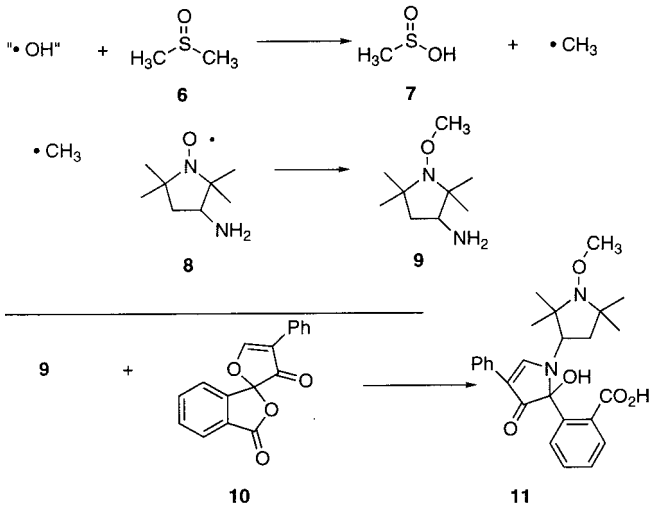



**Figure 1.** Yield of methyl adduct **9** from photolysis of aqueous solution of **MQ** (9 $\mu$M) in the presence of 50 $\mu$M **3-AP** and varying concentrations of DMSO (**6**). Circles show the reaction in the absence of any trap and the squares show the results when 0.48 mM nitrite is added. Product **9** was determined by derivatization with **10** followed by HPLC with fluorescence detection.

**SCHEME 4**




diminishing only at concentrations >1 M (for reasons that will be addressed later). A similar experiment (not shown) was carried out where the DMSO concentration was held at 230 mM and the concentration of the secondary trap, **3-AP**, was varied. It was found that, under anaerobic conditions, the yield of methyl adduct **9** was independent of the [**3-AP**] over the range 50−200 $\mu$M.

A detailed examination of the data in Figure 1 provides the first indication that the "•OH" species generated in this experiment is not the free hydroxyl radical. A DMSO concentration of $8.7 \pm 1.0 \times 10^{-3}$ M was found to be the half-saturation value ($[DMSO]_{1/2}$) under these conditions. At half-saturation the rate of "•OH" trapping by DMSO should be equal to the rate of •OH trapping by all of the other species in solution. The latter includes **3-AP**, **MQ**, and the phosphate buffer. Assuming that the rate constant for trapping by **MQ** is the same as the literature value for 1,4-benzoquinone ($k_{MQ} = 1.2 \times 10^{9}$ $M^{-1}$ $s^{-1}$),[21] that the reaction of •OH with **3-AP** occurs at the same rate constant as the related nitroxyl radical, TEMPO, ($k_{3AP}$

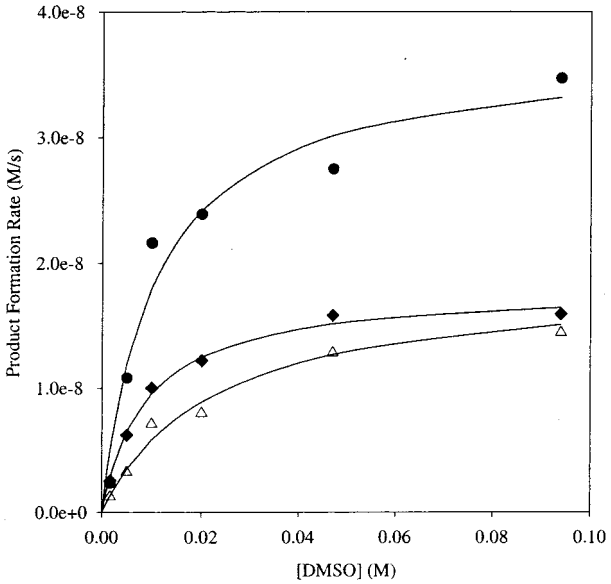



**Figure 2.** Effect of formate and salicylate on the yield of methyl radical from the photolysis of **MQ** in aqueous solution. Circles: no competitive trap; diamonds: 1 mM salicylate, triangles: 24 mM formate.

$= 3.4 \times 10^9\ M^{-1}\ s^{-1}$),[29] and using the conservative estimate that the rate constant for reaction of all of the phosphate species is the rate constant for reaction of •OH with the most reactive component, $HPO_4^{2-}$, ($k_{psho} = 1.5 \times 10^5\ M^{-1}\ s^{-1}$),[30] it is possible to calculate the rate constant for reaction of "•OH" with DMSO. Substituting these values into eq 1, along with the concentrations of each species provides a $k_{DMSO}$ value of $2.1 \times 10^7\ M^{-1}\ s^{-1}$. This value is more than 2 orders of magnitude lower than the reported rate constant for the reaction of free •OH with DMSO ($7 \times 10^9\ M^{-1}\ s^{-1}$).[29] Thus it appears the aqueous photolysis of **MQ** creates a species that is either less reactive toward DMSO than free •OH or is more reactive to the matrix than free •OH.

$$k_{DMSO} = \frac{k_{3AP}[3AP] + k_{MQ} + k_{phos}[totalPO_4]}{[DMSO]_{1/2}} \qquad (1)$$

Having established appropriate trapping conditions, the yields of methyl adduct **9** were examined under conditions where competitive •OH traps are added to the reaction mixtures. In particular, free •OH radicals are known to react rapidly with nitrite ($1.1 \times 10^{10}\ M^{-1}\ s^{-1}$), formate ($3.2 \times 10^9\ M^{-1}\ s^{-1}$), salicylate ($1.1 \times 10^{10}\ M^{-1}\ s^{-1}$), and DMPO ($4.3 \times 10^9\ M^{-1}\ s^{-1}$).[29] Figure 1 shows the DMSO dependence of the methyl yield in the absence of a trap and in the presence of 0.48 mM nitrite. Figure 2 shows similar experiments with 24 mM formate and 1 mM salicylate. Addition of these traps has two interesting effects. First, a greater quantity of DMSO is required to reach the half-saturation point. This is consistent with DMSO and nitrite interacting with a common intermediate, "[a]•OH". Interestingly the saturation level also diminishes with the addition of traps. This indicates non-competitive quenching where nitrite is intercepting some species that precedes "•OH". DMPO shows qualitatively similar behavior: both competitive and noncompetitive quenching are observed.

Scheme 5 shows the mechanistic model applied to the analysis, where $k_D$ is the rate constant for "•OH" reaction with DMSO, $k_W$ is the rate constant for the reaction of **MQ$^{3}$*** that leads to "•OH", $k_{OH}$ is the rate constant for the reaction of "•OH" with the quencher, $k_T$ is the rate constant for reaction of **MQ$^{3}$*** with the quencher, $k_o$ describes the sum of all triplet decay pathways in the absence of quencher, and $k_x$ describes the decay

**SCHEME 5**

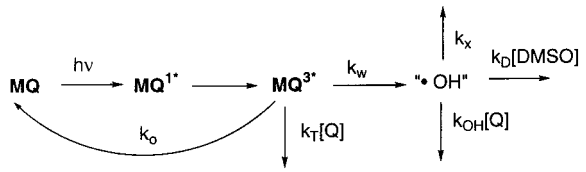



**TABLE 1: Rate Constant Ratios Obtained from Competitive Trapping Experiments Using MQ Photolysis in Aqueous Media and from Literature Values for •OH Radical Reactions**

| | nitrite | formate | salicylate | DMPO |
|---|---|---|---|---|
| $k_{OH}/k_D$ (**MQ**) | 9.2 | 0.46 | 8.0 | 0.65 |
| $k_{OH}/k_D$ (lit.) | 1.7 | 0.48 | 4.1 | 0.65 |

pathways for "•OH" in the absence of DMSO. The quantum yield for methyl adduct production, Φ, is the product of the quantum efficiencies of "•OH" formation and of DMSO trapping ($\Phi = \phi_{OH}\phi_{ME}$), assuming a unit quantum yield for formation of **MQ$^{3}$***. Equation 2 presents this in terms of the individual rate constants:

$$\Phi = \frac{\dfrac{k_w}{k_w + k_o + k_T[Q]}[DMSO]}{\dfrac{k_q[Q] + k_x}{k_D} + [DMSO]} \qquad (2)$$

A nonlinear least squares treatment of the data in Figure 2 provides optimal values for two parameters, $c_1$ and $c_2$ where,

$$c_1 = \frac{k_w}{k_w + k_o + k_T[Q]} \text{ and } c_2 = \frac{k_q[Q] + k_x}{k_D} \qquad (3)$$

The ratio of the DMSO and quencher trapping rate constants can be obtained by considering the difference between $c_2$ and $c_2^0$, where the latter refers to the case where [Q] = 0.

$$c_2 - c_2^{\,0} = \frac{k_q[Q]}{k_D} \qquad (4)$$

The above analysis allows for the determination of $k_q/k_D$ ratios in a way that does not depend on the level of noncompetitive quenching. Table 1 compares the ratios determined from the above analysis to predicted values, which were determined earlier for free •OH radicals derived from pulse radiolysis. With **MQ** photolysis two of the quenchers, nitrite and salicylate, show ratios that are significantly larger than those obtained when free •OH is unambiguously generated in the presence of the same traps. Thus, these trapping data are inconsistent with the free hydroxyl mechanism and support the argument that the "•OH" formed from **MQ** is actually a less reactive and more selective species than is free •OH.

Two of the traps, DMPO and formate anion, show the same ratios with **MQ** and free •OH and these data alone might be taken as evidence for the free hydroxyl mechanism. Indeed previous competition experiments by Alegría et al.[15] showed that DMPO and formate trap the "•OH" generated from **MQ** photolysis with ratios that did not differ significantly from free •OH. It is important, however to consider the reason that increased selectivity is expected in the hydroxyl transfer mechanism. The oxidizing intermediate is expected to exhibit lower rates for trapping with *all* substrates, presumably because the enthalpy required to break the HO•−semiquinone interaction

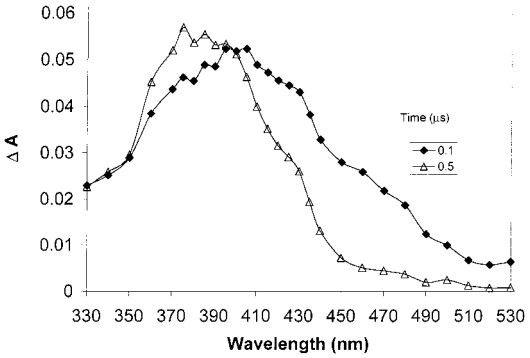



**Figure 3.** Transient absorption spectra from LFP (355 nm, 6 ns, 1−4 mJ/pulse) of **MQ** in aqueous solution (pH 7.2). Filled diamonds: spectrum measured 100 ns following the laser pulse; open triangles: spectrum measured 500 ns following the excitation pulse.

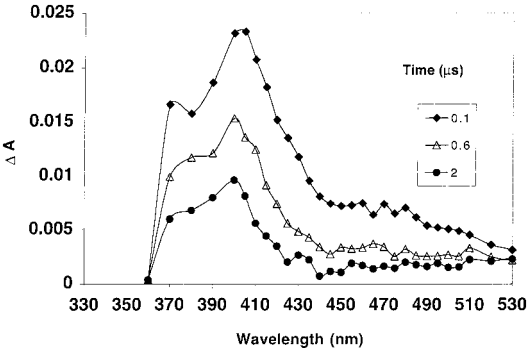


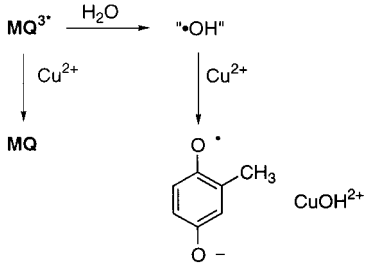

**Figure 4.** Transient absorption spectra from LFP of **MQ** in $CCl_4$. Spectra are measured at 100 ns (filled diamonds), 600 ns (open triangles), and 2 $\mu$s (filled circles) following the excitation pulse.

adds to the activation energy for each reaction. What is less clear is the extent to which this interaction will retard trapping by different quenchers. Some may be affected to a greater extent than DMSO, some to a lesser extent, and yet others to the same extent. Thus observation of the same trapping ratio in one case does not unequivocally prove that the same intermediate is being trapped. The ratios in Table 1 show that nitrite and salicylate are affected to a lesser extent than DMSO, whereas formate and DMPO are affected to about the same extent. This illustrates the dangers of relying on a single competition experiment.

**(2) Laser Flash Photolysis Studies.** Shown in Figure 3 are time-resolved spectra from LFP (355 nm, 6 ns, 1−4 mJ) of **MQ** in pH 7.2 aqueous solution. Immediately following the excitation pulse there is a broad absorption with a maximum at 410 nm. Within 400 ns this is converted to a narrower band with a maximum at 390 nm which persists for >500 $\mu$s. This behavior is largely consistent with the earlier report.[9] The long-lived species has been attributed to a **MQ** composite of the semiquinone anion and the hydroxyl−quinone radical adduct (**MQ**OH•). Addition of an H atom donor (EtOH) converts this spectrum into that of the semiquinone. Likewise, addition of the "•OH" scavenger, DMSO, also converts the long-lived spectrum to that of the semiquinone radical.

Earlier reports attributed the initial transient species at short times to the excited triplet state $\mathbf{MQ^{3}*}$.[9] However it is our argument that this species is the hydroxylating intermediate formed from the •OH radical and the semiquinone. To test this, we sought to generate the triplet state in a solvent less prone to oxidation (i.e., •OH formation). Figure 4 shows the transient spectra generated from LFP of **MQ** in $CCl_4$. The species formed immediately following the laser pulse shows a sharp maximum at 390 nm and a shoulder that extends from 430 to 520 nm. Its

**SCHEME 6**




decay fits well to a first-order rate expression and no detectable intermediates persist following its decay. The species is quenched by $O_2$. Addition of H atom donors (EtOH) quenches this spectrum and results in the formation of the **MQH•**. The spectrum in Figure 4 is therefore attributed the excited triplet state of **MQ**. To the extent that unreactive solvents can be identified, the triplet spectrum is not strongly altered when the solvent polarity is changed. The spectrum generated in $CH_3CN$ is virtually identical, except in this case there is a residual absorption for the semiquinone radical following the decay of the triplet state. The C−H bonds in this solvent are somewhat susceptible to abstraction.

It is significant that the spectrum seen at early times in aqueous solutions differs from the one seen in the less reactive organic solvents, $CCl_4$ and $CH_3CN$. The former is broader, with an ill-defined maximum at between 390 and 400 nm. The latter are more sharply defined and show maxima at 405 nm. Of course, this observation alone does not unequivocally demonstrate that there is a different species formed in aqueous solution than in the organic media. It is not unprecedented for a change in solvent to perturb a UV−vis spectrum. But at the very least these observations suggest that there is a significant interaction between $\mathbf{MQ^{3}*}$ and water that is not present in either $CH_3CN$ or $CCl_4$.

In a further attempt to distinguish the hydroxylating intermediate from the $\mathbf{MQ^{3}*}$, several quenching experiments were carried out. Cupric ions are paramagnetic and as such can physically quench the triplet state through a spin-exchange process. However it is also the case that $Cu^{2+}$ ions react with free •OH with a reported rate constant of $4 \times 10^8$ $M^{-1}$ $s^{-1}$.[31] It is reasonable to assume that Cu(II) would also react with a hydroxylating intermediate, through an OH transfer mechanism. Thus either assignment of the short-lived species predicts that $Cu^{2+}$ would quench it (Scheme 6). However, the two mechanisms differ in the predicted outcome of the quenching process. Physical quenching of $\mathbf{MQ^{3}*}$ should prevent formation of the semiquinone, **MQH•** and no persistent absorptions in the 400 nm region should appear. On the other hand, reaction of $Cu^{2+}$ with the hydroxylating intermediate will lead to formation of a semiquinone species (probably ion-paired with $Cu(OH)^{2+}$) that would be long-lived.

The results of the $Cu^{2+}$ experiment support the second mechanism. Addition of $Cu^{2+}$ ions to aqueous solutions **MQ** reduced the lifetime of the short-lived species. A pseudo-first-order treatment of this provides a rate constant of $2.8 \times 10^8$ $M^{-1}$ $s^{-1}$ for the quenching reactions. Shown in Figure 5 is the spectrum that results from LFP of aqueous solutions containing **MQ** (100 mM) and $CuSO_4$. Following decay of the short-lived intermediate, there is a long-lived species with $\lambda_{max}$ near 400 nm. This result cannot be readily reconciled with assignment of the initial transient to the excited triplet state $\mathbf{MQ^{3}*}$. We assign this long-lived species to the semiquinone anion ion paired to a $Cu(OH)^{2+}$ ion.

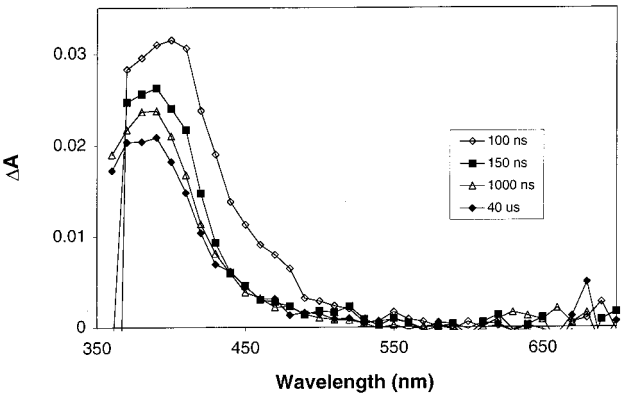



**Figure 5.** Transient absorption spectra from LFP of **MQ** in aqueous solvent containing 100 mM $CuSO_4$ taken at 100 ns (open diamonds), 150 ns (filled squares), 1 $\mu$s (open circles), and 40 $\mu$s following the excitation pulse.

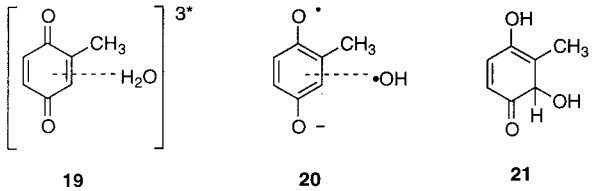
Quenching experiments were also carried out using benzoate anion as the trap, The latter is known to react with free •OH, showing a rate constant of $5.9 \times 10^9$ $M^{-1}$ $s^{-1}$.[29] Assuming that the initial transient is the hydroxylating intermediate, we would expect transfer of an •OH to the benzoate anion, generating the semiquinone anion along with a hydroxyl−benzoate adduct. This reaction should occur at a rate that is somewhat slower than that for the reaction of a free •OH with benzoate. The results of the experiment are consistent with this picture. Benzoate anion quenches the short-lived intermediate with a rate constant of $3 \times 10^8$ $M^{-1}$ $s^{-1}$. As expected, this quenching leads to the formation of the semiquinone anion seen at 410 nm.

A mechanism accounting for all of the trapping and LFP results is presented in Scheme 5. This model predicts two relevant intermediates. Excitation of the **MQ** gives its excited triplet state **MQ$^{3}$***. The lifetime of its presumed precursor the excited singlet state, **MQ$^{1}$*** is not known, but benzoquinone derivatives are known to intersystem cross with near unit efficiency. For this reason we assume that **MQ$^{1}$*** is too short-lived to play a significant role in the photochemistry. The traps nitrite, formate, and salicylate inhibit trapping by DMSO in a noncompetitive as well as a competitive fashion. Therefore the unreacted triplet state **MQ$^{3}$*** must live long enough to be intercepted by these traps. The lifetime of **MQ$^{3}$*** is not known. In fact some subtle shifts in the LFP transient spectrum in the time range 40−200 ns suggest to us that the spectrum immediately following the laser pulse may be a composite of the **MQ$^{3}$*** and the oxidizing intermediate. LFP experiments with faster time resolution could help resolve this issue.

The excited triplet **MQ$^{3}$*** then reacts with $H_2O$ to give the oxidizing intermediate. The latter species is detected at early times in the LFP experiment and is trapped by DMSO as well as the anions formate, salicylate, nitrite, and benzoate. In the absence of traps this intermediate transfers a hydroxyl radical to a ground state **MQ**, giving one **MQH•** and one quinone−OH adduct (**6**) as depicted in Scheme 3. The various traps all interact with the hydroxylating intermediate resulting in formation of semiquinone **MQ$^{-\bullet}$** and, depending on the trap, either the corresponding •OH adducts or hydroxide ion.

While these observations make it clear that the hydroxylating intermediate is distinct from free •OH, the structure of this species is not completely certain. Chart 1 illustrates a range of possibilities involving increasing levels of change relative to the structures of the reactants. The first possibility is a triplet exciplex where a largely intact $H_2O$ is specifically bound to

**CHART 1**




**19** **20** **21**

**MQ$^{3}$*** through a charge-transfer interaction. An intermediate situation would have a more fully transferred H atom and the •OH radical would remain nonspecifically bound to the semiquinone anion through a $\pi$-complex of the sort analogous to those seen in electrophilic aromatic substitution reactions. At the farthest extreme is a $\sigma$-complex whereby the OH is added to the semiquione to make a closed-shell photohydrate of **MQ**. The hydroxylating intermediate observed in this system is only slightly attenuated in its reactivity relative to free •OH. The attenuation is by only a factor of 2 in the case of cupric ion and a factor of ca. 10 in the case of benzoate. This seems more consistent with the $\pi$-complex as this complex should bear the most similarity to the free •OH. The photohydrate has a fully formed C−O $\sigma$-bond that would need to be broken in a transition state for •OH transfer and this would be expected to reduce its reactivity by a greater amount than is observed. Likewise, the exciplex would have to break an O−H bond in the transition state and again this would be expected to reduce its reactivity relative to free •OH beyond the modest amount that is observed. The current study has addressed only **MQ**. Preliminary studies on other simple benzoquinone derivatives show qualitatively similar behavior. Future studies will be directed at characterizing similar oxidizing species generated from related quinones.

## Experimental Section

**Trapping Experiments.** DMSO and nitroxyl trap **8** were systematically varied to determine optimal conditions. Typically, samples containing 50−500 $\mu$M **MQ** (in 10 mM phosphate buffer; pH = 7) were prepared in a 1 cm cuvette containing appropriate concentrations of DMSO (≥10 mM but less than 0.5 M) and 100 $\mu$M (**8**) under anaerobic conditions. All anaerobic samples were bubbled with argon or nitrogen for 5 min prior to irradiation and the headspace was continuously flushed during the irradiation. Following irradiation for an appropriate length of time (1−10 min) the pH was adjusted to 8.0, using 0.2 M borate buffer, prior to derivatization with fluorescamine **10**. Samples for HPLC analysis were prepared by adding 0.5 mL of 0.2 M borate buffer, 0.5 mL of reaction sample and 200 $\mu$L of 5 mM **10** and injected onto a 50 $\mu$L loop. Rates of methyl adduct production were acquired from the peak area of the fluorescent product (**11**) following subtraction of the peak area obtained for an irradiated blank containing identical concentrations of (**8**) and DMSO alone Apparent quantum yields ($\Phi$) were calculated using a previously published method.

A broadband irradiation system was used for some competition studies involving ethanol, methanol, nitrite, formate, salicylate, and 2-propanol. Light from a LX300UV broadband lamp was passed through a water column (9 in. in length) and a 418 nm Schott glass filter. Absorption spectra were obtained with a Hewlett-Packard 8452A diode array spectrophotometer. The HPLC system and chromatographic conditions were identical to those described previously.[16,26−28]

**Laser Flash Photolysis Experiments.** Laser flash photolysis experiments were performed using a Continuum Surelite II-10 Nd(:YAG) as the excitation source. The latter produces pulses

at 266 or 355 nm with a time duration of 4−6 ns and the Q-switch delay was adjusted to provide 2−5 mJ/pulse. A cylindrical lens was used to provide an excitation cross section at the front face of the sample cuvette of approximately 2 mm × 8 mm. The UV−Vis light source, probe beam, was produced by a CW 300 W Xe arc lamp. Transient waveforms were captured and stored using a Lecroy 9420 digital oscilloscope and transferred to a microcomputer for analysis. Typically, kinetic determinations were done on traces that were averaged over 20 shots. Samples were prepared in 10 mm × 10 mm quartz cuvettes, sealed with a rubber serum cap, and purged with $N_2$ for 10 min prior to the experiment. Unless otherwise stated, the **MQ** was dissolved in water which was buffered to pH 7.2 with 25 mM phosphate. Typical **MQ** concentrations were $(2-6) \times 10^{-4}$ M for 266 nm excitation and $(4-6) \times 10^{-3}$ M for 355 nm excitation.

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## References and Notes

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