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in 1,2-dichloroethane was mixed with a 0.27 M solution of cyclohexene in the same solvent using the mixing device of the stopped-flow apparatus in order to ensure reproducible mixing conditions without concentration gradients. After 5 or more minutes the reaction mixture was withdrawn and combined with that obtained from several identical shots. The concentration of *N*-(*trans*-2-bromocyclohexyl)pyridinium bromide in this solution was determined both spectrophotometrically, after appropriate dilution, at several wavelengths between 300 and 360 nm and by titration with 0.01 N aqueous $Hg(ClO_4)_2$ in the presence of diphenylcarbazone,[9,24] in comparison with a blank containing an

(24) Schöniger, W. *Mikrochim. Acta* **1955**, 123; **1956**, 869.

equal concentration of pyridine. A maximum difference of 3% was found between the two analytical methods.

Registry No. Cyclohexene, 110-83-8.

Supplementary Material Available: Description of the fitting algorithm by means of commented flow charts and a partial listing of a computer program (21 pages). Ordering information is given on any current masthead page.

Mechanism of the Photochemistry of *p*-Benzoquinone in Aqueous Solutions. 1. Spin Trapping and Flash Photolysis Electron Paramagnetic Resonance Studies[†]

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The primary photochemistry of *p*-benzoquinone (BQ) in aqueous solution has been investigated at pH 7 by steady-state and transient electron paramagnetic resonance (EPR) spectroscopy, using the spin trap 5,5-dimethyl-1-pyrroline 1-oxide (DMPO). The results strongly suggest a mechanism in which the triplet state of BQ abstracts a hydrogen atom directly from water forming *p*-benzosemiquinone (BQH•) releasing a free hydroxyl radical (OH•), which then reacts with another molecule of BQ to form the adduct BQ–OH•. The ultimate products are hydroquinone (BQH₂) and 2-hydroxy-*p*-benzoquinone (HO–BQ). A mechanism as in reactions 1–8 of Scheme III is proposed which accounts for the observations.

Introduction

Quinones are found widely in biological systems. In particular, substituted quinones, such as ubiquinone and plastoquinone are found in organelles in which electron transport occurs, e.g., photosynthetic and mitochondrial membranes. Many of these biological systems are exposed to sunlight. Thus, in addition to an inherent interest in the photochemistry of quinones in aqueous solutions, there is a need to rationalize the mechanism in view of the possible biological significance of quinone photochemistry.

Although the final products, I and II (see Scheme I), of the aqueous reactions of the unsubstituted *p*-benzoquinone (BQ) have long been identified,[1–4] there has been considerable disagreement[3–9] over the primary step that leads to the principal intermediate, the semiquinone radical (BQH•). The contention has been over the suggestion[10] that the primary step involves hydrogen abstraction from H_2O by excited BQ [which should lead to a free hydroxyl radical (OH•)]. Another conceivable mechanism is that of photosolvation of ³BQ to form a hydrated intermediate (BQ···H₂O) which could then react with BQ to form BQH• and BQ–OH•. Such a photosolvation process has been advanced[11,12] for the primary photochemistry of disodium anthraquinone-2,6-disulfonate in aqueous solutions and has been proposed as the primary process in the photochemistry of BQ.[7] The major problem has been the lack of convincing evidence to prove or disprove the presence of free OH• in this system. Doubts have also been cast as to whether the triplet of BQ has enough energy to oxidize water.[9]

We therefore began a study of the mechanism of this reaction with the objective of resolving the controversy that surrounds it. Our method of approach in this study involved performing experiments on a system which is known to yield free OH• radicals and then comparing the results with those obtained by carrying out similar experiments on the BQ system. The system chosen

SCHEME I: Illustration of the Products of the Photochemistry of *p*-Benzoquinone in Aqueous Solutions
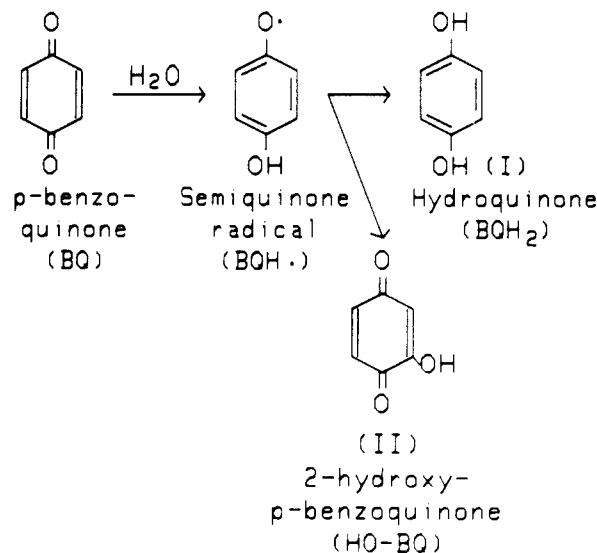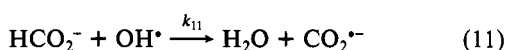

to generate free OH• radicals was the UV photolysis of a dilute solution (1% or less) of H_2O_2 in water.[13]

(1) Leighton, P. A.; Forbes, G. S. *J. Am. Chem. Soc.* **1929**, *51*, 3549–3561.
(2) Poupe, F. *Collect. Czech. Chem. Commun.* **1947**, *12*, 225–236.
(3) Joschek, H.-I.; Miller, S. I. *J. Am. Chem. Soc.* **1966**, *88*, 3273–3281.
(4) Kurien, K. C.; Robins, P. A. *J. Chem. Soc. (B)* **1970**, 855–859.
(5) Hashimoto, S.; Kano, K.; Okamoto, H. *Bull. Chem. Soc. Jpn.* **1972**, *45*, 966.
(6) Kano, K.; Matsuo, T. *Chem. Lett.* **1973**, 1127–1132.
(7) Shirai, M.; Awatsuji, T.; Tanaka, M. *Bull. Chem. Soc. Jpn.* **1975**, *48*, 1329–1330.

[†] Publication No. 358, Photochemistry Unit, University of Western Ontario.

In most practical applications, a radical concentration of 10^{-9}–10^{-8} M is required for steady-state electron paramagnetic resonance (EPR) detection.[14] However, for very reactive radicals such as the OH• radical, it is usually not possible to attain this concentration limit. In particular, the OH• radical has a $^2\Pi$ ground state with a correspondingly large spin–orbit coupling; the result is that the line width is so large that direct detection of the OH• radical by EPR is not possible in solution. One thus must use an indirect detection method such as the technique of spin trapping[15] in EPR. The spin trap used in this study was 5,5-dimethyl-1-pyrroline 1-oxide (DMPO), which has been shown to be an effective spin trap toward the OH• radical.[13,16] The spin adduct DMPO–OH• has a characteristic four-line EPR spectrum with a hyperfine splitting of 14.9 G.[13,17] Usually in systems where such a spectrum is obtained, the presence of free OH• is further investigated by use of a competition experiment involving OH• scavengers[16,18] such as the formate ion (HCO_2^-). This ion is known to react with free OH• to generate the formoyl radical ($CO_2^{•-}$),[17,19] which may then be trapped by DMPO to form DMPO–$CO_2^{•-}$ (see Scheme II); this spin adduct gives a characteristic six-line EPR spectrum. If a system contains free OH•, it will be expected to have a behavior toward the formate ion similar to that of the H_2O_2 system.

SCHEME II: Reactions Occurring in the Formate Competition Experiment

$$H_2O_2 \xrightarrow{h\nu} 2OH^\bullet \tag{9}$$

$$DMPO + OH^\bullet \xrightarrow{k_{10}} DMPO\text{–}OH^\bullet \tag{10}$$

$$HCO_2^- + OH^\bullet \xrightarrow{k_{11}} H_2O + CO_2^{\bullet-} \tag{11}$$

$$DMPO + CO_2^{\bullet-} \xrightarrow{k_{12}} DMPO\text{–}CO_2^{\bullet-} \tag{12}$$

Experimental Methods and Materials

A Varian E12 EPR spectrometer was employed. The output was digitized by means of a Nicolet Explorer 2090-III oscilloscope which was coupled to a Nicolet 1180 computer for signal averaging and data analysis.

The steady-state light source was a 200-W mercury–xenon lamp (Conrad Hanovia 901 B0011) with a Oriel power supply (Model 8500). Sample solutions were drawn through Teflon tubing into a flat cell in the EPR cavity by means of a flow apparatus[20] for steady-state photolysis. This method allowed for easy duplication of results and is therefore good for quantitative analysis. The EPR parameters were kept the same for both the H_2O_2 and BQ systems to permit a meaningful comparison of results.

Flash photolysis EPR measurements on flowing samples were carried out by using 100 kHz and 2 MHz modulated detection;
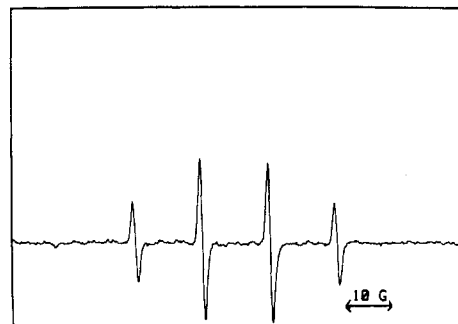

Figure 1. EPR steady-state spectrum of DMPO–OH• obtained by photolysis of a solution containing 0.04 mM BQ and 0.5 mM DMPO. Experimental conditions: microwave power = 10 mW, gain = 8×10^3, modulation amplitude = 2.0 G, pH 7, temperature $\sim$ 25 °C.

however, poor signal-to-noise ratios obtained with the latter did not yield usuable results. Continuous flow of sample solutions through the flat cell in the EPR cavity was maintained at the rate of $\sim$1.2 mL min^{-1}. The flashlamp used was an EG and G Electro-Optics xenon lamp, Model FX265 (flash duration of $\sim$1.5 μs fwhm) at 1 Hz with the Model PS 302 EG and G power supply.

UV–visible absorption spectra were measured on a Hewlett-Packard Model 8450A diode array spectrophotometer equipped with a Hewlett-Packard Model 9872C plotter. Quartz sample cells of 1 cm path length were used.

Some DMPO (97% pure) samples were obtained from Aldrich Chemical Co., but most samples were synthesized locally in a three-stage process following the method of Bonnett et al.[21] Analysis was carried out by NMR and UV spectroscopy and the final product was stored under nitrogen in the dark.

Commercial BQ from Aldrich Chemical Co. was purified by sublimation. Commercial grade 50% H_2O_2 was obtained from Fisher Scientific Co. and diluted as required.

In all the experiments performed, sample solutions were freshly prepared in the dark, buffered at pH 7 with phosphate (at 5 mM concentration except for control experiments in which artifacts that might be caused by the buffer were investigated), and continuously purged during experiments with prepurified nitrogen.

Results and Discussion

1. UV–Visible Absorption and Fluorescence Results. BQ in water (buffered at pH 7 with phosphate) has a major absorption at λ_{max} = 246 (ϵ = 2.2×10^4 M^{-1} cm^{-1}) and weaker bands at λ_{max} = 297 nm (ϵ = 3.5×10^2 M^{-1} cm^{-1}) and λ_{max} = 424 nm (ϵ = 24 M^{-1} cm^{-1}), respectively. These results agree with previously reported values.[4]

We could not detect any fluorescence emission from BQ in water or in nonpolar solvents such as hexane; this may be explained by the highly efficient ($\sim$100%),[22] and hence very rapid, intersystem crossing that usually occurs in excited quinones. Using nanosecond flash photolysis, Ronfard-Haret et al.[8] have reported detection of the BQ triplet decay in aqueous solution, and also detected the neutral semiquinone radical absorption as the first transient following the triplet decay. Hence, the photochemistry of BQ in aqueous solution almost certainly arises mainly from the triplet state, the lifetime of which is estimated to be <0.5 μs (in aqueous solutions).[8,9]

2. Steady-State Photolysis. Photolysis of a solution of BQ containing DMPO gives a four-line spectrum with a hyperfine splitting of 14.9 G (see Figure 1). This spectrum is identical with that obtained by photolysis of dilute (0.012%) H_2O_2 in the presence of DMPO. However, this observation is not sufficient to conclude that free OH• is involved in the BQ system, since DMPO–OH• can arise from systems which do not contain free OH•.[23,24] In

(8) Ronfard-Haret, J.-C.; Bensasson, R. V.; Amouyal, E. *J. Chem. Soc., Faraday Trans. 1* **1980**, *76*, 2432–2436.

(9) Beck, S. M.; Brus, L. E. *J. Am. Chem. Soc.* **1982**, *104*, 1103–1104.

(10) Bridge, N. K.; Porter, G. *Proc. R. Soc. London* **1958**, *A244*, 276–288.

(11) Clark, K. P.; Stonehill, H. I. *J. Chem. Soc., Faraday Trans. 1* **1972**, *68*, 577–590; **1972**, *68*, 1676–1686.

(12) Harriman, A.; Mills, A. *Photochem. Photobiol.* **1981**, *33*, 619–625.

(13) Harbour, J. R.; Chow, V.; Bolton, J. R. *Can. J. Chem.* **1980**, *52*, 3549–3553.

(14) Borg, D. C. In *Free Radicals in Biology*; Pryor, W. A., Ed.; Academic: New York, 1976; Vol. 1, pp 69–147.

(15) Janzen, E. G. *Acc. Chem. Res.* **1971**, *4*, 31–40.

(16) Marriott, P. R.; Perkins, M. J.; Griller, D. *Can. J. Chem.* **1980**, *58*, 803–807.

(17) Harbour, J. R.; Bolton, J. R. *Photochem. Photobiol.* **1978**, *28*, 231–234.

(18) Makino, K.; Mossoba, M. M.; Riesz, P. *J. Am. Chem. Soc.* **1982**, *104*, 3537–3539.

(19) Behar, D.; Fessenden, R. W. *J. Phys. Chem.* **1972**, *76*, 1710–1721.

(20) The flow apparatus was assembled in our laboratory by Dr. T. M. Chiu and the tubing was essentially an all-Teflon inlet (to the flat cell) and a Teflon-to-silicone outlet, the silicone end being connected to a Cole-Parmer 7520-00 Master Flex pump.

(21) Bonnett, R.; Brown, R. F. C.; Clark, V. M.; Sutherland, I. O.; Todd, A. *J. Chem. Soc.* **1959**, 2094–2102.

(22) Patai, S. In *The Chemistry of the Quinonoid Compounds*; Interscience: New York, 1974; Vol. 1, Chapter 9, pp 468.

(23) Finkelstein, E.; Rosen, G. M.; Rauckman, E. J. *Arch. Biochem. Biophys.* **1980**, *200*, 1–16.
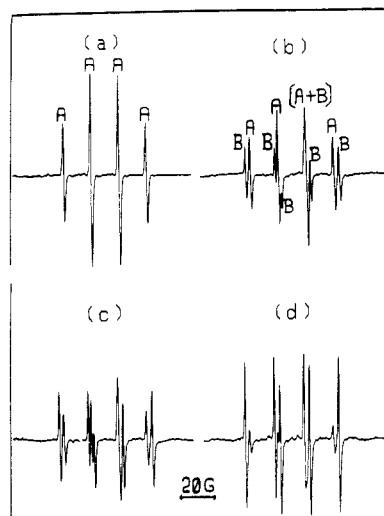
Figure 2. EPR steady-state results for the formate competition experiment in the H_2O_2 system (free OH• system) at pH 7. Experimental conditions: microwave power = 10 mW, gain = 8 × 10³, modulation amplitude = 2.0 G, temperature ~ 25 °C. (a) 0.012% H_2O_2 and 0.5 mM DMPO; (b) 0.012% H_2O_2, 0.5 mM DMPO, and 0.2 mM HCO_2^-; (c) 0.012% H_2O_2, 0.5 mM DMPO, and 0.4 mM HCO_2^-; (d) 0.012% H_2O_2, 0.5 mM DMPO, and 1.0 mM HCO_2^-. Peaks labeled A are due to DMPO–OH• while those labeled B are due to DMPO–$CO_2^{•-}$.
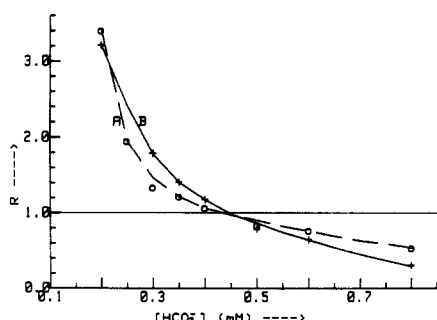

Figure 3. Plot of R vs. [HCO_2^-] for the H_2O_2 system (free OH• system); [DMPO] = 0.5 mM, 25 °C, pH 7. A is for 0.003% H_2O_2 while B is for 0.007% H_2O_2; COP of A = 0.43 mM and COP of B = 0.44 mM.

TABLE I: Variation of COP with [DMPO] for the H_2O_2 (Free OH•) System

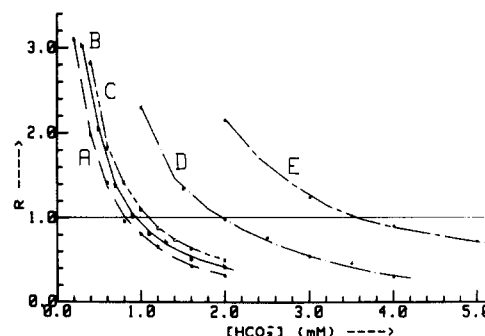| % H_2O_2	[DMPO], mM	COP, mM
0.005	0.20	0.21
0.010	0.20	0.21
0.005	0.35	0.34
0.010	0.35	0.34
0.003	0.50	0.43
0.007	0.50	0.44
0.002	0.70	0.71
0.010	0.70	0.66

Figure 4. Plot of R vs. [HCO_2^-] for the BQ system; [DMPO] = 0.5 mM, 25 °C, pH 7: A is for 0.02 mM BQ; B is for 0.03 mM BQ; C is for 0.05 mM BQ; D is for 0.10 mM BQ; E is for 0.20 mM BQ.
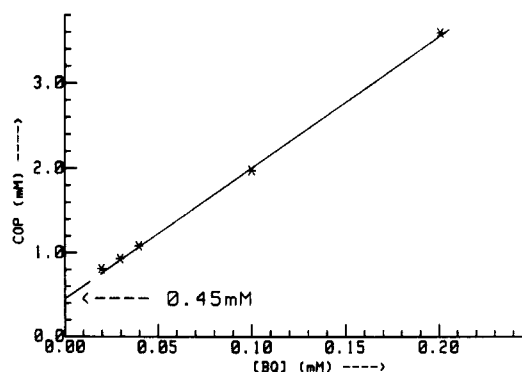

Figure 5. Plot of COP vs. [BQ] for [DMPO] = 0.5 mM, 25 °C, pH 7.

order to help resolve this problem, we carried out a competition experiment using the formate ion (HCO_2^-). In this experiment, HCO_2^- is added to compete with DMPO for any free OH• produced. The concentration of DMPO was kept constant while that of HCO_2^- was varied. The results for the H_2O_2 system are shown in Figure 2a–d. A quantitative analysis of the spectra (using the low-field line of either spin adduct) was then applied in the following manner.

The ratio R of the intensities for DMPO–OH• and DMPO–$CO_2^{•-}$ was calculated from the relation

$$R = I_{(DMPO-OH•)}/I_{(DMPO-CO_2•^-)} \qquad (15)$$

where I = intensity of first derivative of absorption line and is proportional to Y'_{max} $(\Delta H_{pp})^2$ where Y'_{max} is half the peak-to-peak amplitude of the first derivative line and ΔH_{pp} the peak-to-peak line width.[25] I is proportional to the spin adduct concentration.

Values of R were then plotted against [HCO_2^-] for a given DMPO concentration. The plots for the H_2O_2 (free OH•) system are shown in Figure 3. We define a cross-over-point (COP) as the concentration of HCO_2^- when $R = 1$; the plots in Figure 3 show that the COP is constant for a given concentration of DMPO. Also the COP values appear to be comparable with the concen-

tration of DMPO. To check if this trend is real, a concentration dependence study was carried out for various concentrations of DMPO; the results are given in Table I. This table shows clearly that a definite COP value can be established for a given DMPO concentration for the free OH• system, this value being close to the concentration of DMPO. Thus, we arrive at a quantitative condition for characterizing the free OH• system.

Photolysis of solutions of BQ in the presence of DMPO and varying amounts of formate yielded results which are quantitatively similar to those in Figures 2a–d. The R vs. [HCO_2^-] plots for the BQ system are given in Figure 4. The trend here is quite different from the H_2O_2 system in two striking respects:
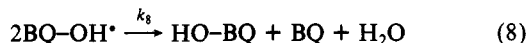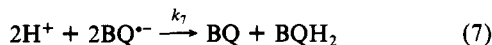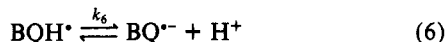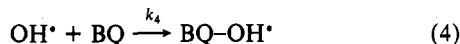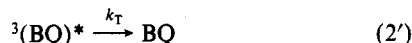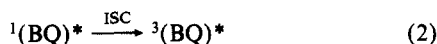
(a) The COP values differ for different concentrations of BQ and in all cases are higher than the concentration of DMPO.

(b) The COP values decrease as the concentration of BQ decreases.

This trend seems to imply that the BQ system may not involve free OH•. However, on extrapolating a plot of COP vs. [BQ] (Figure 5) to the limit of [BQ] → 0, the limiting COP value was found to be 0.45 mM which is almost the same as the COP value (0.44 mM) found for the free OH• system. This means that in the zero concentration limit, the BQ system does behave like a free OH• system.

With the above experimental background, we propose the mechanism given in Scheme III. According to this mechanism,

(24) Chew, V. S. F.; Bolton, J. R. *J. Phys. Chem.* **1980**, *84*, 1903–1908. Chew, V. S. F.; Bolton, J. R.; Brown, R. G.; Porter, G. *Ibid.* **1980**, *84*, 1909–1916.

(25) Wertz, J. E.; Bolton, J. R. *Electron Spin Resonance, Elementary Theory and Practical Applications*; McGraw Hill: New York, 1972; Chapter 2, p 21.

SCHEME III: The Proposed Mechanism for the Reactions of p-Benzoquinone in Aqueous Solutions

$$BQ \xrightarrow{h\nu} {}^1(BQ)^* \qquad (1)$$

$${}^1(BQ)^* \xrightarrow{ISC} {}^3(BQ)^* \qquad (2)$$

$${}^3(BQ)^* \xrightarrow{k_T} BQ \qquad (2')$$

$${}^3(BQ)^* + H_2O \xrightarrow{k_3} BQH^\bullet + OH^\bullet \qquad (3)$$

$$OH^\bullet + BQ \xrightarrow{k_4} BQ\text{-}OH^\bullet \qquad (4)$$

$$BQ\text{-}OH^\bullet + BQ \xrightarrow{k_5} HO\text{-}BQ + BQH^\bullet \qquad (5)$$

$$BQH^\bullet \xrightleftharpoons{k_6} BQ^{\bullet-} + H^+ \qquad (6)$$

$$2H^+ + 2BQ^{\bullet-} \xrightarrow{k_7} BQ + BQH_2 \qquad (7)$$

$$2BQ\text{-}OH^\bullet \xrightarrow{k_8} HO\text{-}BQ + BQ + H_2O \qquad (8)$$

In the presence of DMPO,

$$DMPO + OH^\bullet \xrightarrow{k_{13}} DMPO\text{-}OH^\bullet \qquad (13)$$

$$DMPO + BQ\text{-}OH^\bullet \xrightarrow{k_{14}} DMPO\text{-}OH^\bullet + BQ \qquad (14)$$

free OH$^\bullet$ is produced in reaction 3 in competition with the intersystem crossing of reaction 2′, but it quickly reacts with another molecule of BQ to form a quinone–hydroxy radical adduct (BQ–OH$^\bullet$) (the existence of such an adduct has previously been advanced in the literature).[8,11,26] This is probably the reason why previous workers have not been able to detect free OH$^\bullet$ in this system. In the presence of DMPO, the BQ–OH$^\bullet$ adduct reacts slowly to form the DMPO–OH$^\bullet$ adduct; this explains the high COP values observed for this system relative to that of the H$_2$O$_2$ system.

We have carried out a number of control experiments to check for artifacts:

1. A possible side reaction in the formate competition experiment for BQ is the complexation of formate ion with BQ to reduce the amount of HCO$_2^-$ available to produce the CO$_2^{\bullet-}$ radical. This possibility was checked by looking at the absorption spectra of BQ and HCO$_2^-$; the compound spectrum of the two was also taken. The difference spectrum obtained by subtracting the spectrum of HCO$_2^-$ from the compound spectrum showed that no such complexing occurs in the range of concentration investigated. The concentration of HCO$_2^-$ in this control experiment was 100-fold that of BQ, which more than covers the range of concentrations used in the steady-state experiment.

2. To ensure that, under our experimental conditions, DMPO does not undergo photolysis to produce any peaks that would interfere with the results, a steady-state photolysis of a solution of 1.0 mM DMPO in the buffer solution was carried out; the result showed no detectable artifact.

3. To be sure that the results obtained were independent of the buffer concentration, the actual buffer concentration in experiments was occasionally varied. For instance, in Figure 4, curve A was obtained at a buffer concentration of 5 mM while B was obtained at 2.5 mM, but the COP values are approximately the same.

3. Flash Photolysis of EPR with a Flowing Sample. In order to obtain more evidence for the mechanism that has been proposed (Scheme III), the rise kinetics of BQH$^\bullet$ and DMPO–OH$^\bullet$, respectively, were investigated by flash photolysis with EPR detection. A typical experiment involved flowing a sample solution through a flat cell in the EPR cavity and flashing the solution
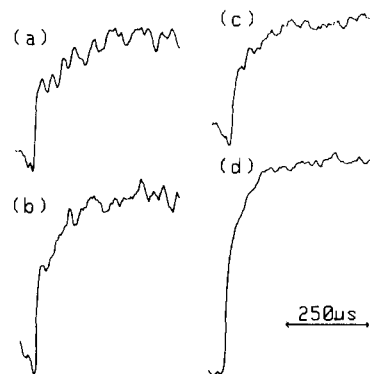
(26) Adams, G. E.; Michael, B. D. *Trans. Faraday Soc.* **1967**, *63*, 1171–1180.

Figure 6. Rise kinetics of BQ$^{\bullet-}$ obtained by flash photolysis of buffered solutions of BQ with EPR detection at 100 kHz modulation. Experimental conditions: microwave power = 10 mW, gain = 5 × 10^4, modulation amplitude = 0.63 G, pH 7, 25 °C. (a) 0.125 mM BQ, (b) 0.25 mM BQ, (c) 0.5 mM BQ, and (d) 1.0 mM BQ.
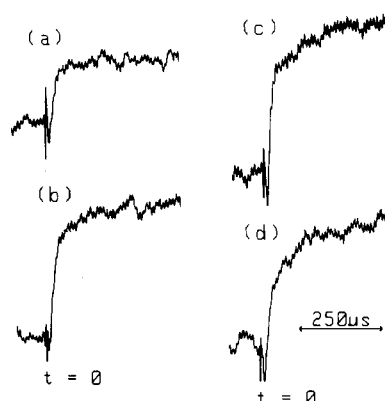

Figure 7. Rise kinetics of DMPO–OH$^\bullet$ obtained by flash photolysis of buffered solutions of BQ and DMPO with EPR detection at 100-kHz modulation. Experimental conditions: microwave power = 10 mW, gain = 8 × 10^3, modulation amplitude = 2.0 G, pH 7, 25 °C. (a) 1.0 mM BQ and 2.0 mM DMPO, (b) 5.0 mM BQ and 2.0 mM DMPO, (c) 10.0 mM BQ and 2.0 mM DMPO, and (d) 20.0 mM BQ and 2.0 mM DMPO. The spikes observed at the beginning of the rise curves (around $t = 0$) are flash artifacts.

as it passed through. The experiments were done with 100-kHz modulation of the magnetic field (instrument detection limit of $\sim$10 μs).

In the first experiment, solutions of BQ only were photolyzed and the semiquinone radical formation was monitored. The signal monitored was that of the more stable semiquinone radical anion (BQ$^{\bullet-}$) at a pH of 7 (the pK_a of BQH$^\bullet$ is 4.0);[26] the dissociation of BQH$^\bullet$ to BQ$^{\bullet-}$ is quite rapid (time constant of $\sim$1 μs)[26] on the time scale of our measurements. The concentration of BQ was varied to see how the kinetics would change. The results obtained are shown in Figure 6a–d; they show a clear biphasic rise at low concentrations of BQ with a fast instrument-limited rise followed by a slower component. As the BQ concentration is increased, the slower component can be seen becoming faster and finally the two are indistinguishable at [BQ] = 2 mM. This observation can be explained by considering eq 3 and 5 in the proposed mechanism; the fast component of the kinetic trace may be ascribed to the primary BQH$^\bullet$ formation in reaction 3 while the slower component arises from the secondary BQH$^\bullet$ formation in reaction 5. As the concentration of BQ increases, reaction 5 becomes faster and so explains the experimental observations.

In the second experiment, solutions of BQ containing DMPO were flashed and the formation kinetics of DMPO–OH$^\bullet$ was investigated. The results, which are given in Figure 7a–d, also suggest two sources of DMPO–OH$^\bullet$. However, the trend here is different in the sense that the kinetics appear to be a single component rise at low concentrations of BQ; but at higher concentrations, a biphasic rise becomes evident. Again this behavior can be explained by considering the proposed mechanism. At low concentrations of BQ, reaction 4 becomes insignificant and so most
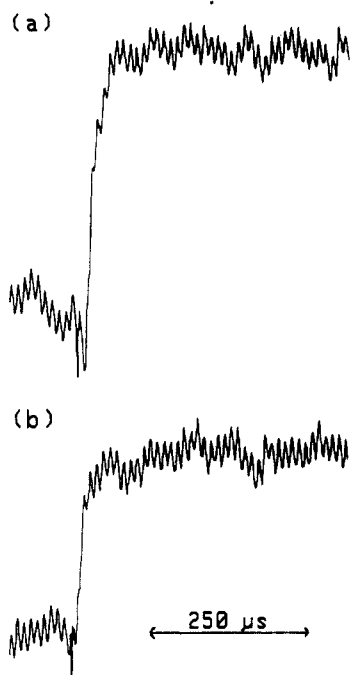
(a)

(b)

Figure 8. Rise kinetics of DMPO–OH• for the H_2O_2 system (free OH• system) obtained by flash photolysis EPR at 100-kHz detection. Experimental conditions: microwave power = 10 mW, gain = 8 × 10³, modulation amplitude = 2.0 G, pH 7, 25 °C. (a) 1% H_2O_2 and 2.0 mM DMPO, (b) 1% H_2O_2 and 1.0 mM DMPO.

of the OH• produced in reaction 3 becomes trapped in reaction 13 to give mainly a single component rapid rise; but at higher concentrations, reaction 4 and consequently reactions 5 and 14 become appreciable and hence the slower rising component appears. We have estimated the rate constant for the noninstru-

ment-limited rise corresponding to reaction 14 by least-squares curve fitting as k_{14} = (6.0 ± 0.7) × 10⁶ M^{-1} s^{-1}.

As a control, the rise kinetics of DMPO were monitored for the H_2O_2 (free OH•) system; the results given in Figure 8 show only a single component rise. Also a control flash photolysis experiment was carried out (to check if any artifact due to DMPO was present) on a buffered solution of 2 mM DMPO only; the result showed no detectable side reaction.

From the flash photolysis results of paper 2 we have found it necessary to add reaction 8 to Scheme III.

Conclusions

Through the use of flash photolysis and steady-state EPR and the spin trap DMPO we have provided strong evidence for a mechanism of the photochemistry of *p*-benzoquinone which involves the generation of free OH• radicals from water in the primary step. Other mechanisms, such as a photohydration mechanism, can be ruled out, although we cannot rule out the possibility that a fast photohydration reaction precedes the reaction which generates free OH• radicals.

We have assembled an optical flash photolysis unit and have used it to further investigate the rise kinetics of BQ•⁻. The results of that study, including a determination of key rate constants, are presented in the following paper.[27]

(27) Ononye, A. I.; Bolton, J. R. *J. Phys. Chem.*, following paper in this issue.

Mechanism of the Photochemistry of *p*-Benzoquinone in Aqueous Solutions. 2. Optical Flash Photolysis Studies[†]

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The mechanism of the photochemistry of *p*-benzoquinone (BQ) in aqueous solution has been investigated by using optical flash photolysis. The results agree very well with the mechanism developed from the EPR study in the preceding paper. The second-order rate constant for oxidation of water by triplet BQ at pH 7 is estimated to be ∼2 × 10⁵ M^{-1} s^{-1}, while a value of (6.5 ± 0.3) × 10⁷ M^{-1} s^{-1} is found for the secondary formation of the semiquinone radical (BQH•) according to BQ + BQ–OH• → BQH• + HO–BQ. The Arrhenius plot for this reaction gives an activation energy of 37 ± 2 kJ mol⁻¹. Also the rate constant of the reaction 2BQ•⁻ + 2H⁺ → BQH₂ + BQ is found to be (1.5 ± 0.1) × 10⁸ M^{-1} s^{-1}. The yield of semiquinone increases with increase in pH. This is explained by a decrease in the redox potential of the reaction OH• + H⁺ + e⁻ → H₂O with increase in pH which makes it more favorable for ³BQ* to oxidize H₂O. The quantum yield for BQ•⁻ formation at pH 7 was found to be 0.47 ± 0.04, independent of the initial concentration of BQ in the concentration range 0.3–1.0 mM.

Introduction

In the preceding paper,[1] we presented a detailed account of an EPR investigation of the mechanism of the photochemistry of

p-benzoquinone (BQ) in aqueous solution and proposed a mechanism to account for our observations (the mechanism is given here in Scheme I). However, in view of the long controversy (see

(1) Ononye, A. I.; McIntosh, A. R.; Bolton, J. R. *J. Phys. Chem.*, preceding paper in this issue.