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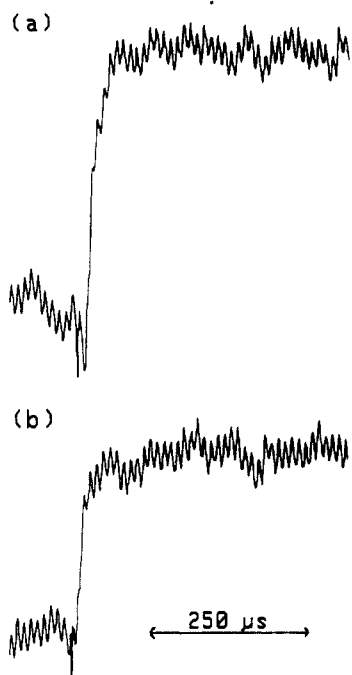


Figure 8. Rise kinetics of DMPO-OH* for the H₂O₂ system (free OH* system) obtained by flash photolysis EPR at 100-kHz detection. Experimental conditions: microwave power = 10 mW, gain = 8×10^3 , modulation amplitude = 2.0 G, pH 7, 25 °C. (a) 1% H₂O₂ and 2.0 mM DMPO, (b) 1% H₂O₂ and 1.0 mM DMPO.

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 $k_{14} = (6.0 \pm 0.7) \times 10^6 \text{ M}^{-1} \text{ s}^{-1}$.

As a control, the rise kinetics of DMPO were monitored for the H₂O₂ (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

Acknowledgment. This research was supported from a Research Grant to J.R.B. from the Natural Sciences and Engineering Research Council of Canada.

Registry No. I, 123-31-9; II, 2474-72-8; BQ, 106-51-4; BQH[•], 3225-29-4; DMPO, 3317-61-1.

(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[†]

A. Ike Ononye and James R. Bolton*

Photochemistry Unit, Department of Chemistry, University of Western Ontario, London, Ontario, Canada N6A 5B7 (Received: January 6, 1986; In Final Form: June 27, 1986)

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 $\sim 2 \times 10^5 \text{ M}^{-1} \text{ s}^{-1}$, while a value of $(6.5 \pm 0.3) \times 10^7 \text{ M}^{-1} \text{ s}^{-1}$ is found for the secondary formation of the semiquinone radical (BQH[•]) according to $\text{BQ} + \text{BQ-OH}^* \rightarrow \text{BQH}^* + \text{HO-BQ}$. The Arrhenius plot for this reaction gives an activation energy of $37 \pm 2 \text{ kJ mol}^{-1}$. Also the rate constant of the reaction $2\text{BQ}^{\bullet-} + 2\text{H}^+ \rightarrow \text{BQH}_2 + \text{BQ}$ is found to be $(1.5 \pm 0.1) \times 10^8 \text{ M}^{-1} \text{ s}^{-1}$. The yield of semiquinone increases with increase in pH. This is explained by a decrease in the redox potential of the reaction $\text{OH}^* + \text{H}^+ + \text{e}^- \rightarrow \text{H}_2\text{O}$ 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.

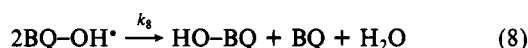
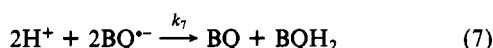
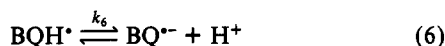
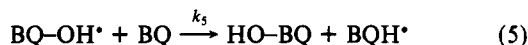
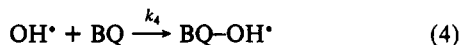
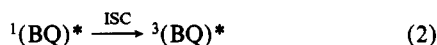
Introduction

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

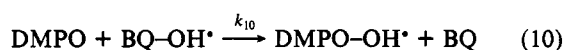
p-benzoquinone (BQ) in aqueous solution and proposed a mechanism to account for our observations (the mechanism is given here in Scheme I). However, in view of the long controversy (see

[†] Contribution No. 359, Photochemistry Unit, University of Western Ontario.

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

SCHEME I: Proposed Mechanism for the Reactions of *p*-Benzoquinone in Aqueous Solutions

In the presence of DMPO,



introduction given in paper 1)¹ surrounding this topic, we decided to employ a different technique, namely optical flash photolysis, as an independent means of obtaining further evidence for the mechanism we have advanced. A major advantage of this technique over EPR is that for transients with high extinction coefficients and where the absorption maxima are distinct, a much higher sensitivity is possible and a less distorted kinetic trace is easily obtained; consequently, a more quantitative and accurate analysis of the results is possible.

Bridge and Porter² were the first to carry out a flash photolysis study of quinones in aqueous solution. Most of their work was on duroquinone; however, they did mention briefly that photolysis of BQ gives rise to a transient, absorbing at 410 nm, which they did not assign. Kemp and Porter³ extended this work, using nanosecond flash photolysis, again mostly on duroquinone. As regards BQ, they simply commented that no short-lived absorption was observed in the region of 490 nm. The most extensive previous study of BQ in aqueous solution is that of Ronfard-Haret et al.⁴ using the nanosecond laser flash photolysis technique. They observed the first-order decay of the triplet-triplet absorption at 410 nm and reported a triplet lifetime of 530 ns. They also observed longer lived transients, which they ascribed to neutral *p*-benzosemiquinone (BQH^{*}) and a quinone-hydroxy radical adduct (BQ-OH^{*}), but they did not determine any rate constants for these intermediates.

In this paper, we report an extensive investigation of the formation kinetics of the semiquinone radical anion (BQ^{•−}) in the presence and absence of the spin trap 5,5-dimethyl-1-pyrroline 1-oxide (DMPO). The absorption of BQ^{•−} (rather than BQH^{*}) was monitored because BQH^{*} has a pK_a of 4.0 (determined by pulse radiolysis),⁵ and so at our working pH of 7, almost all of BQH^{*} is dissociated to BQ^{•−} during the time of the flash.

Experimental Methods and Materials

The optical flash photolysis unit used in these experiments was a Model FP1000 from PRA International configured in the kinetic

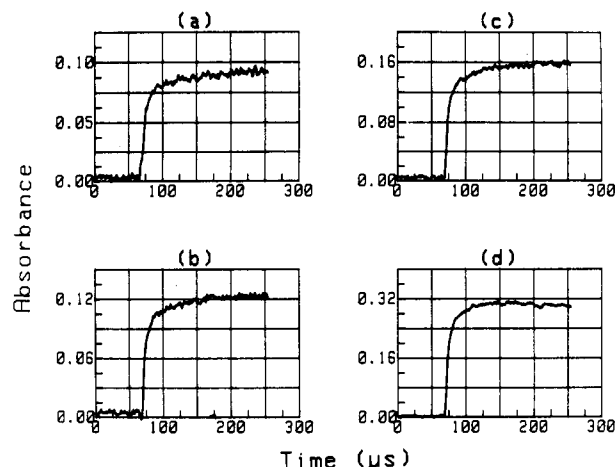


Figure 1. Optical flash photolysis curves for the rise kinetics of BQ^{•−} at pH 7, 25 °C. $\lambda_{\text{excitation}} \sim 300\text{--}380\text{ nm}$, $\lambda_{\text{observation}} = 430\text{ nm}$. (a) 0.3 mM BQ (b) 0.4 mM BQ (c) 0.5 mM BQ (d) 1.0 mM BQ.

mode. The photolyzing source was provided by two EG and G Electro-Optics 100-J xenon lamps, Model FX-141C-35, which were installed parallel to each other on either side of the sample chamber. The flash duration was $\sim 10\text{ }\mu\text{s}$ (fwhm) at 49-J discharge (7 kV and 2 μF capacitor), but the lamp profile showed a long tail extending out to $\sim 30\text{ }\mu\text{s}$. However, with the filter solution used in a jacketed sample cell, the effective flash duration was $\sim 8\text{ }\mu\text{s}$ while the lamp profile tailed off after $\sim 25\text{ }\mu\text{s}$. A quartz sample cell, 10 cm long and 1 cm internal diameter, was used.

The filter solution was prepared by the method described by Calvert and Pitts⁶ for isolating the 265-nm wavelength except that chlorine gas was not used and so a wider region 260–380 nm was isolated. All other samples were prepared as described in the previous paper.¹

The monitoring beam was provided by an Osram 75-W high-pressure xenon lamp with a PRA Model M303 power supply. A monochromator (with maximum error of $\pm 0.4\text{ nm}$) obtained from a Model 1700-II Czerny-Turner spectrometer (from Spex Industries Inc.) was employed together with a Model 1P28 photomultiplier obtained from Hamamatsu TV Co., Ltd. The output signal was digitized by means of a Nicolet Explorer III oscilloscope which was interfaced with a Hewlett-Packard 9816 microcomputer for direct computation of absolute absorbances.

The monochromator was set at the maximum ($\lambda_{\text{max}} = 430\text{ nm}$) absorption for BQ^{•−}. A Schott interference filter, Type AL 90174.18, which transmitted only light around 430 nm was employed to filter the monitoring beam entering the sample solution. This also minimized depletion of the sample solution by photolysis from the monitoring beam.

For quantum yield measurements, benzophenone, obtained from Fisher Scientific Co., was used in 2-propanol (obtained from Baker Chemical Co.) as the actinometer. A Corning glass filter CS 3-69 was employed to cut off light below 500 nm and allow monitoring of the benzophenone ketyl radical at 545 nm.

Sample solutions were always buffered at pH 7 with 5 mM phosphate. For other pH's, the buffer was adjusted to the desired pH with H₃PO₄ or HPO₄^{2−}. For all experiments, the sample solution was usually sealed up in the cell with a rubber septum and then purged with prepurified nitrogen for 30–35 min before photolysis. Only one flash was usually required to get a good trace for each sample solution in the cell.

Results and Discussion

1. *Formation Kinetics of BQ^{•−}*. The rise curves (absorbance vs. time) obtained at various concentrations of BQ are given in Figure 1a–d. These curves show a clear biphasic rise at low concentrations of BQ with the slower component becoming faster

(2) Bridge, N. K.; Porter, G. *Proc. R. Soc. London* **1958**, A244, 259–275, 276–288.

(3) Kemp, D. R.; Porter, G. *Proc. R. Soc. London* **1971**, A326, 117–130.

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

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(6) Calvert, J. G.; Pitts, Jr., J. N. *Photochemistry*; Wiley: New York, 1966.

as the concentration of BQ is increased. This trend is in complete agreement with that observed in the flash photolysis EPR experiments,¹ in which an authentic steady-state EPR spectrum of BQ^{•-} was first obtained and then monitored at a fixed magnetic field. The agreement of these two results, obtained by using different techniques, therefore gives more corroboration for the mechanism we have proposed.

A detailed analysis⁷ has been carried out by using the fitting function

$$F(t) = A_1[1 - \exp(-t/\tau_1)] + A_2[1 - \exp(-t/\tau_2)] \quad (11)$$

where A_1 and A_2 are preexponential factors, and τ_1 and τ_2 correspond to the rise times of the first and second rise components, respectively.

The basis of the fitting function is as follows.

The concentration $[BQH^*]_1$, produced from reaction 3 at any time t , is determined by both reaction 3 and the subsequent dissociation of BQH^{*} represented by reaction 6. Reaction 3 is pseudo first order in view of the high concentration of water. The pK_a of BQH^{*} is 4.0,⁵ and so at pH 7 the dissociation of BQH^{*} should proceed rapidly almost to completion. Thus reactions 3 and 6 can be approximated by two first-order reactions in series. Hence, under these assumptions, $[BQH^*]$ is given by

$$[BQH^*]_1 \approx \frac{A_1 k_3'}{k_6 - k_3'} [\exp(-k_3' t) - \exp(-k_6 t)] \quad (12)$$

where A_1 is the initial concentration of BQH^{*} (or final concentration of BQ^{•-} formed), k_3' is the pseudo-first-order rate constant for reaction 3, $k_3' = k_3[H_2O]$, and k_6 is the rate constant for reaction 6. Thus, the rate of formation, $d[BQ^{\bullet-}]_1/dt$, of BQ^{•-} from reaction 3 is given by

$$\begin{aligned} d[BQ^{\bullet-}]_1/dt &\approx k_6[BQH^*]_1 \\ &= \frac{A_1 k_3' k_6}{k_6 - k_3'} [\exp(-k_3' t) - \exp(-k_6 t)] \end{aligned} \quad (13)$$

From the results of previous workers,^{4,9} the lifetime of ³BQ* is much less than 1 μs [the time constant for reaction 6]; thus, k_3' is much greater than k_6 and eq 13 reduces to

$$d[BQ^{\bullet-}]_1/dt \sim A_1 k_6 [\exp(-k_6 t)] \quad (14)$$

and integration of eq 14 gives

$$[BQ^{\bullet-}]_1 \sim A_1[1 - \exp(-k_6 t)] \quad (15)$$

This is the approximate expression for describing the fast component rise; the rise time corresponds to $1/k_6$.

Considering reactions 5 and 6, we assume that k_6 is much greater than k_5' [k_5' is the pseudo-first-order rate constant for reaction 5] since the second component of the rise curve shows a fairly slow rise. Thus, the concentration, $[BQ^{\bullet-}]_2$, of BQ^{•-} from reaction 5 at any time t is similarly obtained as

$$[BQ^{\bullet-}]_2 \sim A_2[1 - \exp(-k_5' t)] \quad (16)$$

where A_2 is the initial concentration of BQH^{*} (or the final concentration of BQ^{•-} formed).

Equation 16 is the approximate expression for describing the second component rise. But since this rise is fairly slow compared to the first component, the two may be assumed parallel to each other and so eq 15 and 16 may be combined to give the single rate law

$$\begin{aligned} [BQ^{\bullet-}] &= [BQ^{\bullet-}]_1 + [BQ^{\bullet-}]_2 \\ &= A_1[1 - \exp(-k_6 t)] + A_2[1 - \exp(-k_5' t)] \end{aligned} \quad (17)$$

which is equivalent to eq 11 with

$$k_6 = 1/\tau_1 \text{ and } k_5' = 1/\tau_2$$

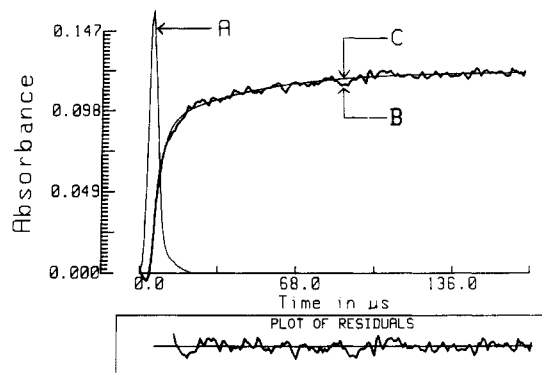


Figure 2. Iterative reconvolution curve fitting^{7,10} to experimental data for the rise kinetics of BQ^{•-}. The fit is shown for Figure 1b and the results for Figure 1a,c are given in Table I. A is the lamp profile, B is the experimental trace, and C is the theoretical fit.

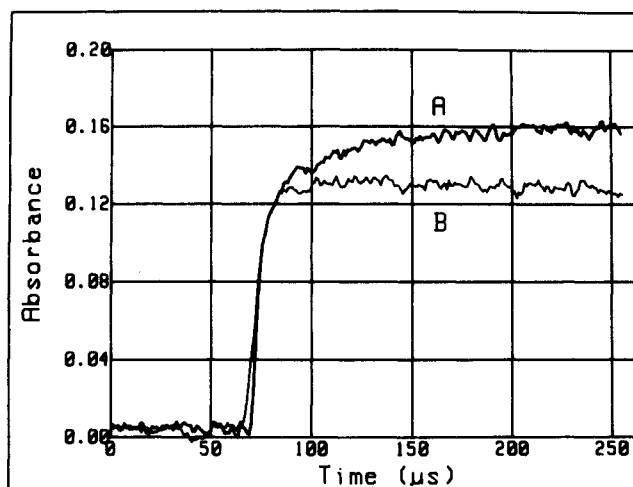


Figure 3. Influence of DMPO on the rise kinetics of BQ^{•-} at pH 7 and 25 °C. $\lambda_{\text{excitation}} \sim 300\text{--}380$ nm, $\lambda_{\text{observation}} = 430$ nm. Curve A obtained with 0.5 mM BQ only (no DMPO); curve B obtained with 0.5 mM BQ plus 0.5 mM DMPO.

TABLE I: Kinetic Fit for the Rise Kinetics of BQ^{•-} (Figure 1a-c)^a

[BQ], mM	τ_1 , μs	τ_2 , μs	A_1	A_2	k_5^b , M ⁻¹ s ⁻¹
0.3	1.8	54.0	0.081	0.024	6.17×10^7
0.4	1.6	41.0	0.105	0.038	6.08×10^7
0.5	1.6	30.0	0.125	0.050	6.67×10^7

^a Lifetimes 1 and 2 are indicated by τ_1 and τ_2 , respectively, while A_1 and A_2 indicate the corresponding preexponential factors. A_1 and A_2 are in absorbance units. ^b $k_5 = (\tau_2[BQ])^{-1}$. Average $k_5 = (6.5 \pm 0.3) \times 10^7$ M⁻¹ s⁻¹.

This theoretical expression was then fitted to the experimental curve by a deconvolution method (described elsewhere)⁷ which we developed for optical flash photolysis studies. This involves accounting for the finite pulse width of the exciting pulse while using the method of least-squares to obtain the best fit between theory and experiment.¹⁰ The analysis gives a very good fit, as may be seen from the sample result shown in Figure 2 for 0.4 mM BQ. The kinetic parameters obtained for various concentrations of BQ are given in Table I. The fast component rise is instrument limited (instrument detection limit with deconvolution being ~ 2 μs). From τ_2 , a value of $(6.5 \pm 0.3) \times 10^7$ M⁻¹ s⁻¹ is estimated for the second-order rate constant k_5 for reaction 5 (see Table I).

2. *Rise and Decay Kinetics of BQ^{•-} in the Presence of DMPO.* A further support for our proposed mechanism was obtained as follows.

(7) Ononye, A. I. Ph.D. Thesis, Department of Chemistry, University of Western Ontario, London, Canada, 1985.

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

(9) Beck, S. M.; Brus, L. E. *J. Am. Chem. Soc.* **1982**, *104*, 4789–4792.

(10) The computer program for the fit is contained in ref 7.

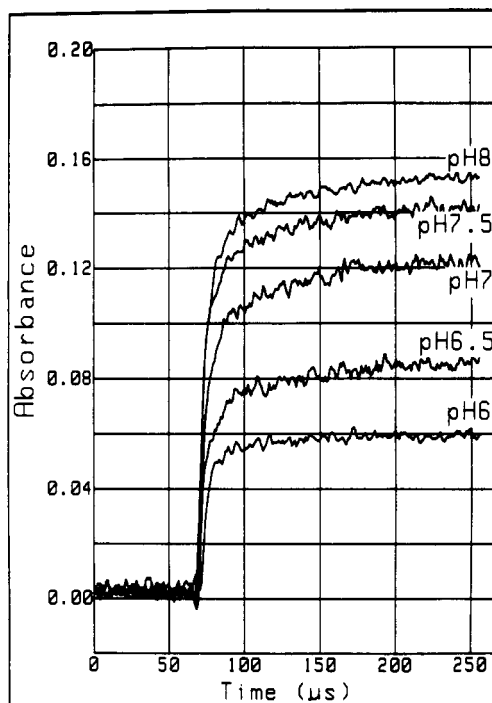


Figure 4. Rise kinetics of $BQ^{\bullet-}$ at various pH values for 0.4 mM BQ at 25 °C.

It is expected that if some DMPO is added to scavenge the free OH^{\bullet} produced in reaction 3, then reaction 4 and consequently reaction 5 will be greatly reduced. The rise kinetics of $BQ^{\bullet-}$ was therefore monitored with DMPO present in the solution of BQ. In Figure 3 the result is compared with that obtained from flash photolysis of a solution of equal concentration of BQ but with DMPO absent. It is quite evident that in the presence of DMPO, the slow rising component is absent and only the fast instrument-limited rise is observed.

To check if the decay observed in the presence of DMPO actually arises from the semiquinone radical anion bimolecular decay as given in reaction 7, the experiment was taken to a longer time scale and the trace observed fits very well to a one-component second-order decay (using an extinction coefficient of $7400 \text{ M}^{-1} \text{ cm}^{-1}$ for $BQ^{\bullet-}$)¹¹ with a decay rate constant of $(1.5 \pm 0.1) \times 10^8 \text{ M}^{-1} \text{ s}^{-1}$. This compares with the value of $1.7 \times 10^8 \text{ M}^{-1} \text{ s}^{-1}$ previously determined⁵ by pulse radiolysis for the bimolecular decay of $BQ^{\bullet-}$ at pH 7.

A control experiment was carried out by photolyzing a buffered solution of DMPO only in water (pH 7), but no artifact was observed.

We note from Table I that A_2 is always smaller than A_1 , whereas they should be similar in magnitude from reactions 1–5 of Scheme I. There are two possible side reactions which could explain this anomaly:

(1) Bimolecular recombination of OH^{\bullet} to form H_2O_2 . However, previous authors^{4,5,12} have not detected H_2O_2 as a product in this system. We believe that at the concentrations we have used reaction 4 effectively removes most of the OH^{\bullet} radicals from the system before recombination can take place.

(2) Disproportionation of $BQ-OH^{\bullet}$. We believe that the disproportionation reaction 8 is responsible for removing some of the $BQ-OH^{\bullet}$ before it can react to form $BQ^{\bullet-}$ via reactions 5 and 6. In the period of time ($\sim 100 \mu\text{s}$) in which $BQ-OH^{\bullet}$ has a significant concentration, a value of $k_8 \approx 10^8 \text{ M}^{-1} \text{ s}^{-1}$ would account for the reduced ratio of A_2/A_1 .

3. Effect of Changing pH. We now consider the effect of varying the pH of the reaction medium for BQ. The results given

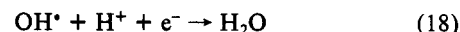
TABLE II: Quantum Yield (ϕ_{unk}) for the Formation of $BQ^{\bullet-}$ (Measured at pH 7 and 25 °C by Optical Flash Photolysis)

[BQ], mM	ϕ_{unk}
0.3	0.45 ± 0.04
0.4	0.48 ± 0.05
0.5	0.47 ± 0.05
1.0	0.51 ± 0.03
	av 0.47 ± 0.04

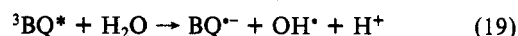
in Figure 4 were obtained from optical flash photolysis of 0.4 mM BQ at various pH values: the formation of $BQ^{\bullet-}$ was monitored.

These results show that the yield of $BQ^{\bullet-}$ is dependent on pH, being favored by an increase in pH. The kinetics do not seem to change as the rate constant calculated is approximately the same for the various pH traces. The observed increase in the yield of $BQ^{\bullet-}$ may be explained as follows:

The standard redox potential (vs. NHE) of the reaction



is 2.65 V.¹³ Hence at pH 7, the potential for reaction 18 drops to 2.24 V. The redox potential for $^3BQ^*$, calculated from the relation⁸ $E_0(T_1) = E_0[BQ(S_0)/BQ^{\bullet-}] + E_T$, is estimated to be 2.4 V. Thus at pH 7, the oxidation of water by $^3BQ^*$



is only slightly exergonic. An increase in pH will cause the redox potential of reaction 18 to decrease; hence, reaction 19 becomes more exergonic.

4. Quantum Yield Measurement. The quantum yield for the formation of $BQ^{\bullet-}$ was measured at pH 7. Benzophenone (BP) in 2-propanol was used as the standard actinometer since its absorption spectrum is similar to that of BQ in the region 290–360 nm (effective wavelength region of excitation). At a BP concentration $\leq 7 \times 10^{-5} \text{ M}$ in 2-propanol, the quantum yield (ϕ_{std}) for BP ketyl radical formation is 1.0.¹⁴ We therefore used $6.0 \times 10^{-5} \text{ M}$ BP and monitored the maximum yield of the ketyl radical at 545 nm. The extinction coefficient,¹⁴ $5.1 \times 10^3 \text{ M}^{-1} \text{ cm}^{-1}$, was used in calculating the number of moles of the radical produced.

The quantum yield (ϕ_{unk}) for $BQ^{\bullet-}$ formation was then obtained from the relation

$$\phi_{\text{unk}} = \phi_{\text{std}} (N_{\text{std}}^{\text{ph}}/N_{\text{std}}) (N_{\text{unk}}/N_{\text{unk}}^{\text{ph}}) \quad (20)$$

where $N_{\text{std}}^{\text{ph}}$ is the number of photons absorbed by benzophenone ($N_{\text{unk}}^{\text{ph}}$ for BQ) and N_{std} the number of molecules of the benzophenone ketyl radical produced (N_{unk} for $BQ^{\bullet-}$). $N_{\text{std}}^{\text{ph}}$ and $N_{\text{unk}}^{\text{ph}}$ were obtained by integration of the type

$$N^{\text{ph}} = \int_{290}^{360} N_{\lambda} T_{\lambda} f_{\lambda} d\lambda \quad (21)$$

where N_{λ} is the number of photons incident on the cell, T_{λ} the transmittance of the filter solution, and f_{λ} the fractional absorbance of the sample at wavelength band λ to $\lambda + d\lambda$. The expression for f_{λ} is given by

$$f_{\lambda} = (1 - 10^{-A_{\lambda}}) \quad (22)$$

where A_{λ} is the absorbance of the sample in the wavelength band λ to $\lambda + d\lambda$. Equation 21 was evaluated by numerical integration at intervals of 7 nm. A value of $7400 \text{ M}^{-1} \text{ cm}^{-1}$ was used as the extinction coefficient for $BQ^{\bullet-}$ in the calculation.¹¹

The final values of ϕ_{unk} calculated by eq 20 are given in Table II for four different concentrations of BQ at pH 7. ϕ_{unk} obtained (0.47 ± 0.04) appears to be independent of the initial concentration of BQ. Although the quantum yield results are specifically for $BQ^{\bullet-}$ formation, the same values could be assumed for the formation of BQH^{\bullet} (in the absence of interfering reactions), since almost all of BQH^{\bullet} would have dissociated to $BQ^{\bullet-}$ on the time

(11) Patel, K. B.; Willson, R. L. *J. Chem. Soc., Faraday Trans. 1* 1973, 69, 814–825.

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

(13) Schwartz, H. A. *J. Chem. Educ.* 1981, 58, 101–105.

(14) Beckett, A.; Porter, G. *Trans. Faraday Soc.* 1963, 59, 2038–2050.

TABLE III: Variation of Lifetimes and Preexponential Factors with Temperature in the Rise Kinetics of BQ^{•-} at pH 7^a

temp, °C	τ_1 , μ s	τ_2 , μ s	A_1	A_2	k_5 , $M^{-1} s^{-1}$
10	1.6	76.2	0.091	0.030	2.62×10^7
15	0.7	57.8	0.107	0.034	3.46×10^7
20	1.5	46.4	0.110	0.041	4.31×10^7
25	1.5	32.0	0.117	0.044	6.25×10^7
30	0.9	28.0	0.134	0.058	7.14×10^7

^a Analysis was done by iterative reconvolution. Values given are for 0.5 mM BQ. The preexponential factors A_1 and A_2 are in absorbance (abs) units.

scale and at the pH of our measurements (the pK_a of BQH[•] is 4.0).⁵

From Figure 4, if we assume that the plateau in each curve represents the relative quantum yield of formation of BQ^{•-}, we estimate that the limiting quantum yield at high pH is ~ 0.6 . Hence, even under the most favorable conditions, the quantum yield of formation of BQ^{•-} in water is significantly lower than that of the benzophenone ketyl radical in 2-propanol. This is a reasonable observation when we recall the small extent of exergonicity of reaction 19 at pH 7 and at higher pH. Therefore, we have included reaction 2' in Scheme I to account for those ³BQ* states which undergo intersystem crossing back to the ground state of BQ with no reaction.

Our quantum-yield results compare well with previous measurements: 0.53 ± 0.05 (366 nm);¹⁵ 0.31 ± 0.02 (253.7 nm);¹⁶ and 0.55 ± 0.05 (313 nm).¹⁷ In all these cases, the quantum yields are for the disappearance of BQ at pH 7.

5. Temperature Variation. As a final step in our series of experiments, we repeated the flash photolysis experiment for 0.5 mM BQ and monitored the formation of BQ^{•-} at various temperatures. The variation of temperature was achieved by cycling the filter solution in the cell jacket through a thermostat. A volume of 2 L of the filter solution was prepared and used as the temperature bath. For temperatures below 25 °C, the bath was cooled with ice.

The kinetic parameters computed are given in Table III. The short lifetime remains instrument limited but the long lifetime shows significant variations. The Arrhenius plot (see Figure 5) for k_5 , corresponding to the long lifetime, gives an activation energy of 37.2 ± 2.4 kJ mol⁻¹ for reaction 5.

Conclusions

The technique of optical flash photolysis has been used effectively in studying the mechanism of the photochemistry of *p*-

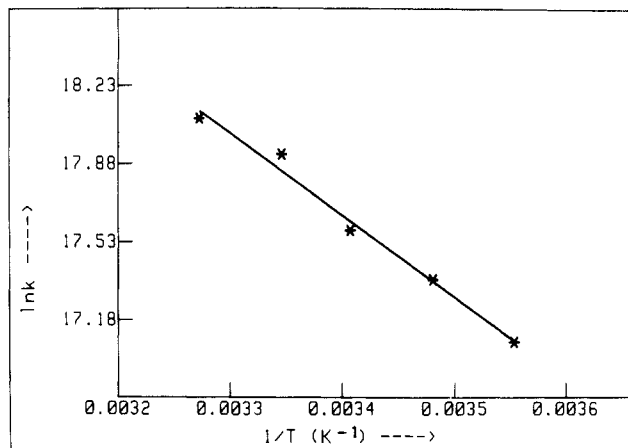


Figure 5. Arrhenius fit ($\ln k_5$ vs $1/T$) for the temperature variation of the rise kinetics of BQ^{•-} for reaction 5.

benzoquinone in aqueous solution. The semiquinone radical anion (BQ^{•-}) was followed by its optical absorption and the kinetics observed are in *pari passu* with those obtained by EPR detection, thus providing much stronger support for our mechanism.

From the results of other workers,^{3,4} we assumed the lifetime of ³BQ* to be much less than 1 μ s (0.2 μ s or less); this provided an approximate expression which resulted in a good fit to the kinetic traces observed. We may thus estimate that k_3' is $>10^7$ s⁻¹.

The kinetics observed for BQ^{•-} formation in the presence of DMPO provides good support for our interpretation of the fast component rise. It also supports the point that OH[•] produced in the primary reaction 3 is involved in a secondary reaction 4 which leads to a secondary formation of BQH[•] according to reaction 5. For this sequence of reactions to be plausible, reaction 4 must be fast; the value of 1.2×10^9 M⁻¹ s⁻¹ determined² for k_4 agrees with this expectation.

The results of our study of the photochemistry of *p*-benzoquinone in aqueous solution have considerable significance as regards the effect of sunlight on biological systems. If our mechanism can be shown to be a general one for quinonoid compounds, then it is likely that OH[•] radicals, with subsequent tissue damage, would be of concern in the effect of sunlight on skin tissue. Finally, it is hoped that this study will provide useful insight in studies involving the use of quinones in the area of photochemical conversion and storage of solar energy.

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