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Oxidation of Phenol by Singlet Oxygen Photosensitized by the Tris(2,2′-bipyridine)ruthenium(II) Ion

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The photochemical excitation of aqueous solutions of $Ru(bpy)_3^{2+}$ and phenol (PhOH) in the presence of air produces 1,4-benzoquinone (BQ) as the only organic product. In this study, we examined the $*Ru(bpy)_3^{2+}/PhOH/O_2$ system in terms of the dependence of the quantum yield of BQ formation (Φ_{BQ}) as a function of $[O_2]$, [PhOH], temperature, pH, and the composition of the solvent. The increase in Φ_{BQ} from its low value in acidic solution to its maximum at pH ∼ 9.4 is attributed to the increasingly competitive quenching of $*Ru(bpy)_3^{2+}$ by PhO^- and O_2. A maximum in Φ_{BQ} is also observed at ∼45 °C, an effect caused by the variation in the solubility of O_2 in solution as well as the activation energies of the competing steps in the mechanism. The proposed mechanism of the reaction, which could involve the formation of an endoperoxide intermediate from the reaction of $^1O_2$ by PhOH, is consistent with the observed decrease of Φ_{BQ} as a function of the mole fraction of H_2O in CH_3CN-H_2O solvent mixtures.

Introduction

The photooxidation of phenols is an important degradation mode of these pollutants in contaminated water. Previous studies have examined their direct excitation ($\lambda \sim 250$ nm),[1−8] organic dye,[9−21] and metal complex[22−24] photosensitization, radiolytically induced decomposition,[25] photocatalytic oxidation on TiO_2 surfaces,[26−33] and catalytic oxidation by transition metal complexes.[34,35] Organic and inorganic dye-sensitized solar photooxidation is of particular interest in wastewater treatment, especially for phenols that are resistant to biodegradation; oxidation in the presence of a sensitizer, visible light, and air can lead to photoproducts that are easily biodegradable, low molecular weight, oxygenated compounds.[9,36,37]

Energy transfer from an excited photosensitizer to ground-state dioxygen, O_2, produces singlet oxygen, $O_2(^1\Delta_g)$, which lies 94 kJ mol^{-1} above the ground state; the physical and chemical properties of $^1O_2$ have been very well documented.[38−42] Phenols can quench $^1O_2$, leading to the formation of quinones and coupling products.[41] The reductive quenching of an excited photosensitizer by phenols can also occur if the electron-transfer energetics are suitable and the reaction can kinetically compete with the natural decay of the excited species. The oxidation of phenols or phenolate ions results in the formation of phenoxyl radicals, which undergo very rapid dimerization in solution, especially if they are unsubstituted;[43] for the phenoxyl radical from phenol (PhOH; pK_a 9.98),[44] $2k = 2.6 \times 10^9$ M^{-1} s^{-1}.[45−47]

The archtypical metal complex photosensitizer, especially for aqueous solutions, is $Ru(bpy)_3^{2+}$ (bpy = 2,2′-bipyridine). With an excited-state standard reduction potential of 0.93 V (vs NHE),[48] $*Ru(bpy)_3^{2+}$ is reductively quenched by phenolate ion (PhO^-) in alkaline solution ($E_{ox}{}^o = -0.86$ V vs NHE),[49] yielding $Ru(bpy)_3^+$ and $PhO^\bullet$;[50,51] however, it is not quenched by PhOH in acidic and neutral solution ($E_{ox}{}^o = -0.86 - 0.0582(pK_a - pH)$ V vs NHE at 20 °C).[49]

In a previous publication,[52] we reported that the photochemical excitation of aqueous solutions of $Ru(bpy)_3^{2+}$ and PhOH in the presence of air produced 1,4-benzoquinone (BQ) as the only organic product; in the absence of O_2, no BQ or any other product was formed. Because the quantum yield of BQ formation (Φ_{BQ}) was significantly higher in D_2O, it was clear that the photooxidation mechanism involved $^1O_2$, which has a longer lifetime in D_2O than in H_2O.[38] On the basis of the knowledge of the rate constant for the quenching of $*Ru(bpy)_3^{2+}$ by O_2,[53] the rate constant for the quenching of $^1O_2$ by PhOH,[54] and the quantum yield of formation of $^1O_2$ from $*Ru(bpy)_3^{2+}$ ($\phi_\Delta = 0.5$),[55] we concluded that the reaction between $^1O_2$ and PhOH to form BQ occurs with approximately unitary efficiency.

If the $Ru(bpy)_3^{2+}$-photosensitized oxidation of PhOH by $^1O_2$ occurs as envisioned, Φ_{BQ} should be a function of the various experimental parameters in a predictable way. In this paper, we examine the $*Ru(bpy)_3^{2+}/PhOH/O_2$ system in detail in order to test the mechanism and its accompanying kinetics. We report here on the dependence of Φ_{BQ} as a function of $[O_2]$, [PhOH], temperature, pH, and the composition of CH_3CN-H_2O solvent mixtures.

Experimental Methods

Materials. $[Ru(bpy)_3]Cl_2 \cdot 6H_2O$ (GFS Chemicals) was recrystallized from water and dried over silica gel. Phenol was purchased from Aldrich and was purified by sublimation. Potassium ferrioxalate was prepared by the literature method.[56] Distilled water was further purified by passage through a Millipore purification train. Acetonitrile (Baker HPLC grade) was purified and dried as described in the literature.[57] Buffer solutions (pH 2−13) were prepared by literature methods.[58]

Continuous Photolysis. A 1000 W Xe lamp (Oriel) and monochromator (Bausch & Lomb) were used; the light intensity could be adjusted with the lamp power supply or with the monochomator slit. In a typical experiment, 4 mL of a magnetically stirred solution in a 1 × 1 cm cuvette within a

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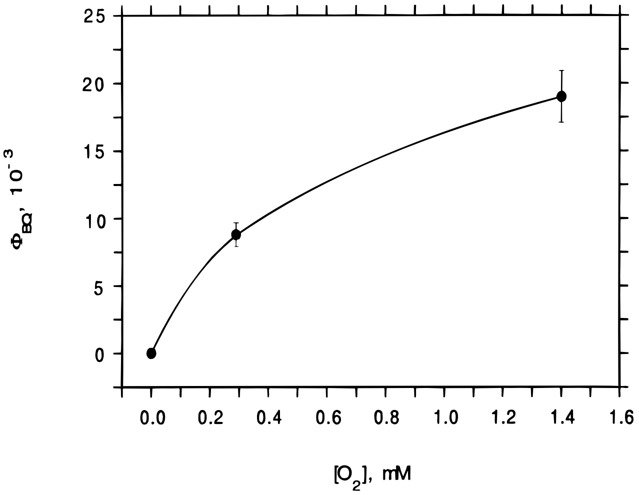


Figure 1. Φ_{BQ} as a function of [O_2] for aqueous solutions of 40 μM $Ru(bpy)_3^{2+}$ and 4.0 mM PhOH at 20 °C and pH 6.0. Error bars are ±10%. The solid curve is a fit of eq 6.

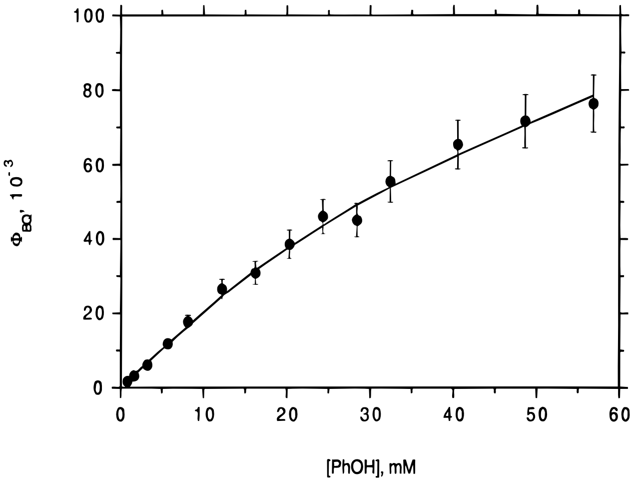


Figure 2. Φ_{BQ} as a function of [PhOH] for air-saturated aqueous solutions of 40 μM $Ru(bpy)_3^{2+}$ at 20 °C and pH 6.0. Error bars are ±10%. The solid curve is a fit of eq 6.

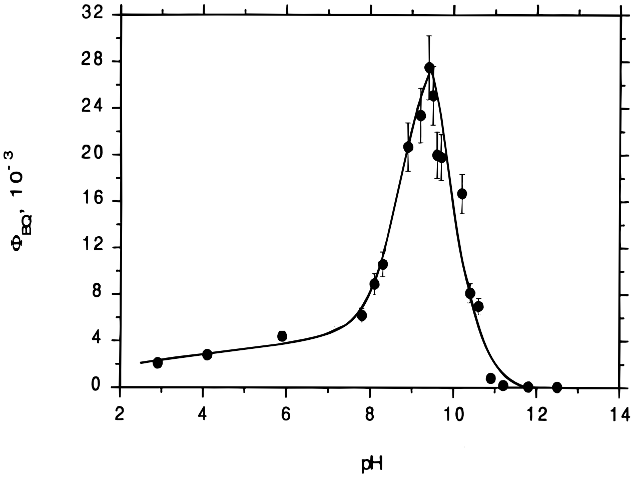


Figure 3. Φ_{BQ} as a function of pH for air-saturated aqueous solutions of 80 μM $Ru(bpy)_3^{2+}$ and 2.0 mM PhOH at 20 °C. Error bars are ±10%. The solid curve is a fit of eq 16.

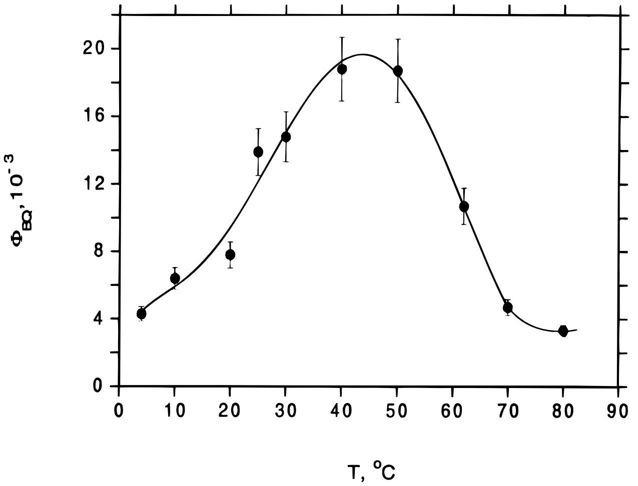


Figure 4. Φ_{BQ} as a function of temperature for air-saturated aqueous solutions of 80 μM $Ru(bpy)_3^{2+}$ and 3.2 mM PhOH at pH 6.0. Error bars are ±10%.

thermostated cell holder was irradiated at 450 nm. The light intensity incident on the cell ($I_o = (1.06 \pm 0.05) \times 10^{-5}$ ein L^{-1} s^{-1}) was monitored with a Rhodamine 6G photon counter, which was routinely calibrated against the potassium ferrioxalate chemical actinometer.

HPLC Analyses. A Waters HPLC system (C-18 reversed-phase column (3.9 × 300 mm), UV−vis photodiode array detector, and Millennium 2010 software) was used to identify quantitatively species from the continuous photolyses. Concentrations of possible photoproducts could be detected at concentrations of ≥ 0.01 μM.

Procedures. After the irradiation of solutions of $Ru(bpy)_3^{2+}$ and PhOH, a 20 μL sample of the photolyte was injected into the HPLC port; a 3:1 (v/v) H_2O/CH_3CN solution was used as the eluent with a flow rate of 1.0 mL/min, and the photodiode array detector was set at 254 nm. The photoproduct and starting materials were identified by comparison of their retention times and absorption spectra with those of authentic samples: $Ru(bpy)_3^{2+}$, 1.5 min; BQ, 5.8 min; PhOH, 10.3 min.

Results

The continuous photolysis ($\lambda_{ex} = 450$ nm) of air-saturated aqueous solutions of $Ru(bpy)_3^{2+}$ and PhOH yielded BQ as the only detectable photoproduct in the pH range 2.9−12.5; no hydroquinone (HQ) or 4,4′-biphenol were ever found. The slope of linear plots of the yield of BQ as a function of photolysis time (an example is shown in the Supporting Information) leads to values of Φ_{BQ}, which were reproducible to better than ±10% variation. For example, $\Phi_{BQ} = 8.6 \times 10^{-3}$ for solutions of 0.04−0.2 mM $Ru(bpy)_3^{2+}$ and 4.0 mM PhOH at 20 °C and pH 6.0.

Values of Φ_{BQ}, determined as a function of [O_2], [PhOH], pH, and temperature are shown in Figures 1−4, respectively; the data are given in the Supporting Information.

The value of Φ_{BQ} decreased with increasing mole fraction of acetonitrile (χ_{AN}) in CH_3CN-H_2O mixtures; no BQ was detected in neat CH_3CN. Figure 5 shows the dependence of Φ_{BQ} on χ_{AN}; the data are given in the Supporting Information.

Discussion

Reaction Mechanism. In its simplest terms, the reaction mechanism in acidic and neutral solution can be viewed as occurring via the excitation of the photosensitizer (reaction 1) followed by the decay of $^*Ru(bpy)_3^{2+}$ (reaction 2; $k_o = 1.6 \times 10^6$ s^{-1})[53] in competition with its energy-transfer quenching by O_2 (reaction 3; $k_q = 3.4 \times 10^9$ M^{-1} s^{-1});[55] the resultant $^1O_2$ decays in H_2O (reaction 4; $k_{de} = 2.7 \times 10^5$ s^{-1})[38] and reacts

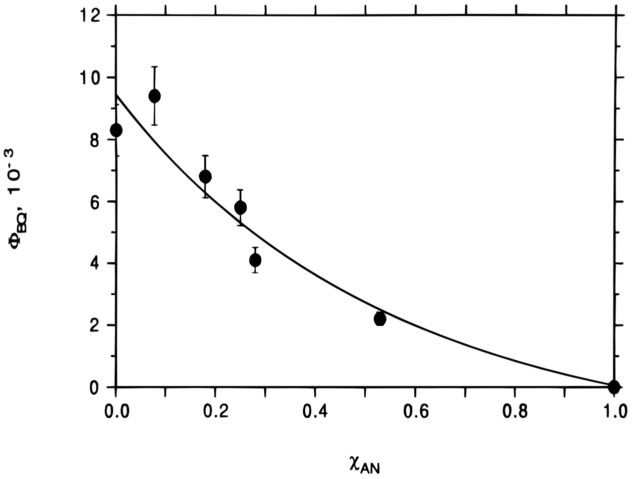


Figure 5. Φ_{BQ} as a function of χ_{AN} for air-saturated CH_3CN-H_2O solutions of 40 μM $Ru(bpy)_3^{2+}$ and 4.0 mM PhOH at 20 °C. Error bars are ±10%.

with PhOH (reaction 5; $k_{rx} = 2.6 \times 10^6$ M^{-1} s^{-1}) [54] to yield BQ ultimately with presumably unitary efficiency.

$$Ru(bpy)_3^{2+} \xrightarrow{h\nu} {}^*Ru(bpy)_3^{2+} \qquad (1)$$

$$^*Ru(bpy)_3^{2+} \rightarrow Ru(bpy)_3^{2+} + h\nu' \qquad (2)$$

$$^*Ru(bpy)_3^{2+} + O_2 \rightarrow Ru(bpy)_3^{2+} + {}^1O_2 \qquad (3)$$

$$^1O_2 \rightarrow O_2 + h\nu' \qquad (4)$$

$$^1O_2 + PhOH \rightarrow\rightarrow BQ \qquad (5)$$

For continuous irradiation at a known [$Ru(bpy)_3^{2+}$] and absorbance at 450 nm, application of the steady-state approximation for $^1O_2$ yields eq 6; use of the known values of k and ϕ_Δ leads to an excellent fit of the data in Figures 1 and 2.

$$\Phi_{BQ} = \frac{d[BQ]}{I_a\, dt} = \frac{\phi_\Delta k_q k_{rx}[O_2][PhOH]}{(k_o + k_q[O_2])(k_{de} + k_{rx}[PhOH])} \qquad (6)$$

Equation 6 also predicts that a plot of $1/\Phi_{BQ}$ vs 1/[PhOH] should be linear at constant [O_2] at low [PhOH] where $k_{de} \gg k_{rx}$[PhOH]. When the data from Figure 2 are treated in that way, an excellent linear plot (correlation coefficient 0.999) results (Supporting Information).

Effect of pH. The deprotonation of PhOH (reaction 7) changes the dynamics of the photosensitization. In the first place, the quenching of $^*Ru(bpy)_3^{2+}$ by PhO^- (reaction 8; $k_q' = 1.1 \times 10^8$ M^{-1} s^{-1}),[50] which will compete with reaction 3, must be included; the yield of the geminate redox pair, $Ru(bpy)_3^+$ and $PhO^\bullet$, into bulk solution upon escape from the quenching cage (η_{ce}) has been determined to be 0.40.[59] Because of the rapid electron-transfer reaction of $Ru(bpy)_3^+$ with O_2 (reaction 9; $k_{et} = 4.3 \times 10^9$ M^{-1} s^{-1}),[48] the back electron-transfer reaction between $Ru(bpy)_3^+$ and $PhO^\bullet$ (reaction 10; $k_{bt} = 5.3 \times 10^9$ M^{-1} s^{-1})[59] does not have a chance to compete; $O_2^{\bullet-}$ undergoes disproportionation with its conjugate acid.[60] $PhO^\bullet$ reacts slowly, if at all, with O_2; there does not seem to be any report of a measured rate constant, which is probably $<10^5$ M^{-1} s^{-1}. Although $PhO^\bullet$ undergoes dimerization to form dihydroxydiphenyls,[45-47] the anticipated rapid electron transfer with $O_2^{\bullet-}$ (reaction 11) would remove these radicals from any involvement in the production of BQ.

$$PhOH \rightleftarrows PhO^- + H^+ \qquad (7)$$

$$^*Ru(bpy)_3^{2+} + PhO^- \rightarrow Ru(bpy)_3^{+} + PhO^\bullet \qquad (8)$$

$$Ru(bpy)_3^{+} + O_2 \rightarrow Ru(bpy)_3^{2+} + O_2^{\bullet-} \qquad (9)$$

$$Ru(bpy)_3^{+} + PhO^\bullet \rightarrow Ru(bpy)_3^{2+} + PhO^- \qquad (10)$$

$$PhO^\bullet + O_2^{\bullet-} \rightarrow PhO^- + O_2 \qquad (11)$$

It is known from other studies that the interaction of $^1O_2$ with PhOH changes as a function of pH. Okamoto et al. found that the efficiency of photodegradation of PhOH by $^1O_2$ generated by rose bengal increased in the pH range 9.0−10.7, an effect attributed to a faster rate of reaction 12 compared to reaction 5;[9] Tratnyek and Hoigné determined $k_{rx}' = 1.6 \times 10^8$ M^{-1} s^{-1}.[54]

$$^1O_2 + PhO^- \rightarrow\rightarrow BQ \qquad (12)$$

If the reaction mechanism is modified to include reactions 8 and 12, and it is assumed that $PhO^\bullet$ and $O_2^{\bullet-}$ do not ultimately give rise to BQ, Φ_{BQ} can be written in terms of eq 13 through the application of the steady-state approximation for $^1O_2$ as before.

$$\Phi_{BQ} = \frac{\phi_\Delta k_q[O_2](k_{rx}[PhOH] + k_{rx}'[PhO^-])}{(k_o + k_q[O_2] + k_q'[PhO^-])(k_{de} + k_{rx}[PhOH] + k_{rx}'[PhO^-])} \qquad (13)$$

The [PhOH] and [PhO^-] terms are related to the initial concentration of phenol, $[PhOH]_0$, through reaction 7 and its K_a.

$$[PhOH] = [PhOH]_0\left(\frac{H^+}{H^+ + K_a}\right) \qquad (14)$$

$$[PhO^-] = [PhOH]_0\left(\frac{K_a}{H^+ + K_a}\right) \qquad (15)$$

By substituting eqs 14 and 15 into eq 13, an expression for Φ_{BQ} as a function of pH (eq 16) is obtained, where $A \equiv \phi_\Delta k_q' k_{rx}' K_a[O_2][PhOH]_0$; $B \equiv \phi_\Delta k_q' k_{rx}[O_2][PhOH]_0$; $C \equiv k_q K_a[PhOH]_0 + k_q K_a[O_2] + k_q' K_a[PhOH]_0$; $D \equiv k_o + k_q[O_2]$; $E \equiv k_{de}$; $F \equiv k_{rx}' K_a[PhOH]_0$; $G \equiv k_{rx}[PhOH]_0$; $H \equiv K_a$.

$$\Phi_{BQ} = \frac{A + B \times 10^{-pH}}{(C + D \times 10^{-pH})\left(E + \dfrac{F + G \times 10^{-pH}}{H + 10^{-pH}}\right)} \qquad (16)$$

Under the experimental conditions of Figure 3, where $[PhOH]_0$ and [O_2] are constant quantities, the data can be fitted to eq 16 quite satisfactorily, using the known values of the rate and equilibrium constants. In the pH 7−9 range, reaction 12 begins to compete more with reaction 4 than does reaction 5; the dramatic decrease in Φ_{BQ} beyond its maximum around pH 9.4 occurs as reaction 8 overwhelms reaction 3. The shallow upward slope of the low pH region of Figure 3 is undoubtedly due to contributions of reactions 8 and 12, which would compete somewhat with reactions 3 and 5 even at low [PhO^-].

However, an alternative explanation of the decrease in Φ_{BQ} in alkaline solution must be considered. Lipczynska-Kochany and Bolton reported that the yield of BQ as the principal primary product from the flash photolysis of PhOH in aqueous solution in the presence of air was constant at pH 3−8, increased at pH 8−10, and decreased at pH 10−11.[4] In addition, they observed secondary products, such as HQ and 2-hydroxy-*p*-benzoquinone, at pH >8. Their results were explained in terms of a lower stability of BQ at high pH. Indeed, it is known that BQ forms reversible adducts ($K = 8.3\ M^{-1}$) with OH^- in alkaline solution;[61] however, we demonstrated that the HPLC analysis for BQ was not affected by this interaction, leading us to believe that the values of Φ_{BQ} are not distorted by the analytical procedure.

Effect of Temperature. Okamoto et al. examined the yield of BQ as a function of temperature in the range 5−40 °C with rose bengal as the photosensitizer and found an activation energy for Φ_{BQ} of 17 kJ mol^{-1};[9] a plot of ln Φ_{BQ} vs $1/T$ for that temperature range with $Ru(bpy)_3^{2+}$ as the photosensitizer yields an activation energy of 31 kJ mol^{-1}. The difference in the temperature dependencies can be attributed in the first instance to the expected differences in the activation parameters of the photophysical and quenching processes of the excited states of the two photosensitizers. However, as Figure 4 shows for pH 6.0, Φ_{BQ} rises to a maximum at ∼45 °C that is about a factor of 5 higher than at its lower and higher temperature limits.

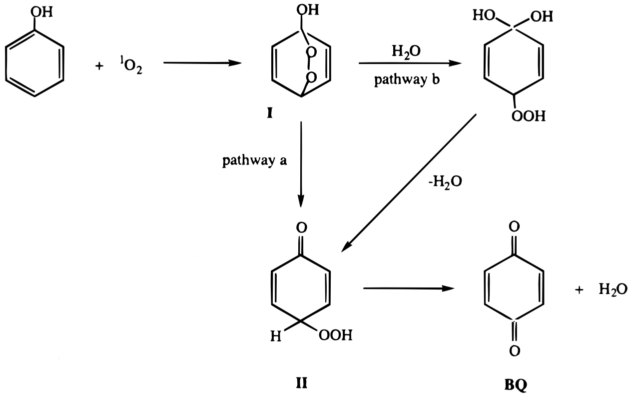
This complex dependence undoubtedly arises from the wide range of temperature dependencies of all the rate and equilibrium constants in eq 16, and of the solubility of O_2, which, in air-saturated aqueous solution, can be approximated by $[O_2]$ (in units of molarity) $= 0.025 \exp(-0.015T)$.[58] Clearly, without having all the information for all the activation parameters in eq 16, it is not possible to model the data in Figure 4 quantitatively. Nevertheless, it is probably safe to say that at low temperatures (5−40 °C), the generally positive temperature dependencies of the rate constants dominate, and Φ_{BQ} increases with increasing temperature; at high temperatures (50−80 °C), the negative temperature dependence of the solubility of O_2 dominates, and Φ_{BQ} decreases with increasing temperature.

Effect of Solution Medium. As χ_{AN} is increased at 20 °C, the lifetime of $^*Ru(bpy)_3^{2+}$ ($\tau_o = 1/k_o$) increases from 0.60 μs in H_2O to 0.97 μs in neat CH_3CN.[62] Similarly, the lifetime of $^1O_2$ ($\tau_{de} = 1/k_{de}$) increases from 3.7 μs in H_2O to 58 μs in neat CH_3CN.[38] In addition, the solubility of O_2 in organic solvents is generally greater than it is in H_2O.[63] If all the other parameters in eq 6 remained the same as the solution medium was changed, Φ_{BQ} would be expected to increase as χ_{AN} is increased. However, Figure 5 shows that not to be the case.

Clearly, reactions 5 and 12 are complex, and previous investigators have not reached complete agreement about their mechanisms or even stoichiometries. For example, Okamoto et al. found BQ to be the primary product from the reaction of $^1O_2$ with PhO^- in alkaline aqueous solution photogenerated from rose bengal.[9] However, Steenken et al. found HQ as the primary product from the reaction of $^1O_2$, generated photolytically from methylene blue or thermally from the decomposition of an endoperoxide, with PhOH in neutral aqueous solution;[19] in a secondary reaction, HQ was converted to BQ. In general, the evidence appears quite strong that the reaction of $^1O_2$ with aromatic compounds mainly involves cycloaddition to give initially an endoperoxide, which is transformed in a series of secondary steps into the final products.[41]

The conclusion must be reached from the results obtained here that H_2O is required for the formation of BQ; mechanistically, proton transfer is required for the formation of BQ or its quinoid precursors. A possible mechanism, admittedly speculative, is shown in Scheme 1, in which the first step involves 1,4-cycloaddition of $^1O_2$ to the aromatic ring of PhOH to yield endoperoxide **I**; this process has previously been postulated for the reaction of $^1O_2$ with para-substituted 2,6-di-*tert*-butylphenols[15] and could be operative here as well. In the second step, the peroxide-oxygen atom of **I** could undergo intramolecular H-abstraction to give hydroperoxycyclohexadienone **II** (pathway a) in competition with solvolysis (pathway b) to yield an unstable hydroperoxide, which could also lead to **II** through the loss of H_2O; similar pathways have been proposed earlier for the reaction of $^1O_2$ with 2,4-di-*tert*-butylresorcinol in CH_3OH.[13]

SCHEME 1



On the basis of the observed effect of the solution medium on Φ_{BQ}, we suggest that pathway b is the dominant process here; the reaction would be rapid in aqueous solution but would become slower as χ_{AN} is increased. Loss of H_2O from **II** would yield BQ. In neat CH_3CN, **I** could form, but pathway b would be inoperative; pathway a might be rendered slow due to the formation of a dipolar transition state. In this case, **I** could dissociate thermally to the original reactants[64,65] or directly to ground-state O_2.

Summary

Knowledge of the parameters in eqs 6 and 16 for the $Ru(bpy)_3^{2+}/PhOH/O_2$ system dictates that the following conditions should be employed in order to maximize Φ_{BQ} in the photosensitized oxidation of phenol to BQ: aqueous solution, preferably with D_2O as the solvent; $T \sim 45$ °C; pH ∼9.4; solution O_2-saturated, preferably at ≥1 atm pressure. The value of ϕ_Δ could be increased to ∼1 by the use of a different Ru(II) photosensitizer, such as $Ru(bpz)_3^{2+}$ (bpz = 2,2′-bipyrazine); however, PhOH as well as PhO^- quench $^*Ru(bpz)_3^{2+}$, yielding $Ru(bpz)_3^+$ and $PhO^\bullet$,[52] which would compete with the generation of $^1O_2$.

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Supporting Information Available: Tables of Φ_{BQ} as a function of $[O_2]$, [PhOH], temperature, pH, composition of CH_3CN-H_2O mixtures; plot of yield of BQ as a function of photolysis time; plot of $1/\Phi_{BQ}$ vs 1/[PhOH]. This material is available free of charge via the Internet at http://pubs.acs.org.

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