Oxidation of Phenols by Triplet Aromatic Ketones in Aqueous Solution

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Aromatic ketones efficiently mediate the photo-oxidative degradation of phenols in aerated aqueous solution, a process likely to be relevant in sunlit natural waters. Absolute bimolecular rate constants for the quenching of three model ketone triplets by nine phenols bearing various substituents, from electron-donating alkyl and alkoxy groups to the electron-withdrawing cyano group, were measured by nanosecond laser flash photolysis. Triplet benzophenone (BP) is quenched at nearly diffusion-controlled rates ($2.6-5.6 \times 10^9$ M^{-1} s^{-1}). Triplet state quenching of 3′-methoxyacetophenone (3′-MAP) and 2-acetonaphthone (2-AN) by the same set of phenols occurs more selectively, with rate constants spanning a range of 1 and more than 2 orders of magnitude, respectively. Quenching rate constants obey a Rehm−Weller relationship to the free energy of electron transfer from the phenol to the ketone triplet. By comparison of the quenching constants with overall photo-oxidation rates obtained by stationary irradiation in air-saturated aqueous solution, phenols bearing electron-donating substituents were found to be depleted with quantum yields generally exceeding 0.5, whereas parent phenol and, presumably, acceptor-substituded phenols are transformed at only ∼0.1 efficiency. The present quenching data were used to interpret the efficiency of photosensitized oxidation of phenols by dissolved natural organic matter (DNOM), an important sunlight absorber present in surface waters. The effective reduction potential of reactive excited triplet states in DNOM was estimated to be at least 1.36 V vs NHE.

Introduction

Excited triplet states of aromatic ketones are efficiently quenched by phenols in aprotic (polar and nonpolar) solvents[1,2] as well as in protic solvent mixtures[3] including pure water.[4] The quenching results in reduction of the triplet ketones to ketyl radicals or their conjugate bases, and the phenols are oxidized to phenoxyl radicals. Radical yields determined by laser flash photolysis were usually close to unity,[1,3,4] except when the phenols carried heavy-atom substituents such as bromine or iodine. We have shown that this process leads to efficient photo-oxidation of phenols in aerated aqueous solution and have proposed that the light-induced, abiotic degradation of phenol pollutants in natural waters may occur by a similar mechanism, whereby dissolved natural organic matter (DNOM), mainly consisting of humic and fulvic acids, acts as the sensitizer.[5] Furthermore, the same process may be important for the chemistry of atmospheric waters in the polluted and nonpolluted atmosphere, in particular for the production of hydrogen peroxide.[6]

We wished to obtain a quantitative structure−activity relationship for the quenching rate constants of triplet aromatic ketones by phenols in aqueous solution in order to predict the propensity of various substituted phenols toward photosensitized oxidation in sunlit natural waters. In the present study, we applied laser flash photolysis to determine absolute bimolecular rate constants for the quenching of three aromatic ketones, viz. benzophenone (BP), 3′-methoxyacetophenone (3′-MAP), and 2-acetonaphthone (2-AN), by nine substituted phenols, including the amino acid tyrosine and the water-soluble vitamin E analogue trolox. We compare these quenching rate constants with the relative rate constants for the depletion of substituted phenols that were obtained in a previous study.[5]

Experimental Section

Materials and Solutions. The aromatic ketones benzophenone (BP, Fluka, >99%), 3′-methoxyacetophenone (3′-MAP, Fluka, 99%), and 2-acetonaphthone (2-AN, Aldrich, 99%) were used as received. Except for 4-methylphenol (4-MP), which was vacuum distilled, all substituted phenols, viz. phenol (Merck, >99.5%), 4-cyanophenol (4-CNP, Fluka, >97%), 4-hydroxybenzoic acid (4-CBP, Fluka, 99%), 4-methoxyphenol (MOP, Merck, >98%), 3,4-dimethoxyphenol (DMOP, Aldrich, 99%), 2,4,6-trimethylphenol (TMP, EGA-Chemie, 99%), *rac*-6-hydroxy-2,5,7,8-tetramethylchroman-2-carboxylic acid (trolox, Fluka, >98%), and L-tyrosine (Fluka, >99%), were also used as received. Bidistilled water (dissolved organic carbon content ≤ 0.3 mg/L) was used throughout the experiments. Solutions containing a given aromatic ketone (50−200 μM) and variable concentrations of a specific phenol were prepared by adding 0.5−2.0% vol/vol of a 10 mM stock solution of the aromatic ketone in methanol and the appropriate amount of phenol aqueous stock solution (0.5−2 mM) to aqueous phosphate buffer (final phosphate concentration 50 mM). To keep dissociation of the phenols below 1%, the solutions containing 4-CNP were buffered at pH 6.0, those containing tyrosine and 4-CBP at pH 7.0, and all others at pH 8.0. The last pH was chosen in order to make direct comparisons with the previous study on photosensitized oxidation.[5] All solutions were equilibrated with air

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TABLE 1: Triplet State Quenching by Oxygen in Water, Reduction Potentials, and Triplet State Energies of Aromatic Ketones

aromatic ketone	triplet relaxation constant, k_0[a,b] (10^5 s^{-1})	rate constant for quenching by oxygen[c] (10^9 M^{-1} s^{-1})	reduction potential, E_{red}[d] (V vs NHE)	triplet state energy, $E_{0,0}$[e] (eV)	triplet state reduction potential, $E_{red} + E_{0,0}/F$ (V vs NHE)
BP	6.73 ± 0.17	2.6 ± 0.1	−1.31	3.00	1.69
3′-MAP	8.38 ± 0.54	3.3 ± 0.2	−1.50	3.14	1.64
2-AN	6.44 ± 0.12	2.5 ± 0.1	−1.48	2.58	1.10

[a] This study. In air-saturated water $T = 23 \pm 1$ °C, elevation 250 m. [b] Standard deviation from several (>6) independent measurements. [c] Calculated from k_0 assuming 100% triplet deactivation by oxygen at 255 μM concentration. [d] Half-wave potentials measured in 50% aqueous ethanol at pH 12.65 (ref 17), transformed from V vs SCE. [e] In polar solvents, ref 8.

at room temperature (22−24 °C) and were then filled into a quartz cell of 4.5 cm path length for flash photolysis.

Laser Flash Photolysis. The kinetic and spectrographic apparatus has been described elsewhere.[7] Transient absorption measurements were performed by excitation with 308 or 351 nm pulses (pulse width ~25 ns, 100−200 mJ per pulse) from an excimer laser (Lambda-Physik EMG 101 or COMPEX 205), which allowed selective excitation of the aromatic ketone. Neither the excitation wavelength nor the methanol content of the aqueous solutions (0.5−2.0% vol/vol) had an appreciable influence on the lifetimes of the triplet aromatic ketones. The following probe wavelengths were employed for observing the triplet decays: $\lambda_{obs} = 520$ nm for BP, 395 nm for 3′-MAP, and 440 nm for 2-AN. Analyses of transient absorbance decays, as well as fitting of the Marcus and Rehm−Weller equations to the data, were performed using the nonlinear fitting program Profit, version 5.0.0 for the Power Macintosh (Quantum Soft, Zürich, Switzerland).

Results

The transient absorbance decay curves generated by flash photolysis of the individual ketones in aerated aqueous solutions strictly obeyed the first-order rate law in the absence of phenols. These transients are due to the triplet states of the ketones which are formed within the duration of the laser pulse and with essentially unit quantum yield.[8] The observed triplet decay rate constants are given in Table 1, together with energetic parameters used in the discussion. Samples containing phenols mostly gave more complex decays. In particular, the absorption spectrum of the BP-ketyl radical is similar to that of triplet BP.[9] We analyze the decay curves using a biexponential rate law, with rate constants corresponding to the decay of the triplet, k^T, and of the ketyl radical, k^K. To extract the second-order quenching rate constant, $k_{q,P}$, from the dependence of the triplet decay on the phenol concentration [P], $k^T = k_0 + k_{q,P}[P]$, three independent decay traces, each run at a different phenol concentration, were simultaneously fitted using the biexponential function (see Figure 1). The decay rate constant of triplet BP in the absence of phenol, k_0, and the decay rate constant of the BP-ketyl radical (k^K, determined in a separate experiment, vide infra), were fixed in the nonlinear fitting procedure. For 3′-MAP and 2-AN, deviation from single-exponential decay was mostly due to absorbance of the phenoxyl radicals, and these traces were analyzed similarly, except that the second exponential decay rate constant was used as a fit parameter. The resulting quenching rate constants $k_{q,P}$ and their 95% confidence intervals are given in Table 2. The accuracy of these rate constants is satisfactory. Thus, the procedure adopted, which avoids the time-consuming operation of degassing the sample solutions, is adequate to the purpose of this study.

The selectivity of the triplet aromatic ketones decreases in the order: 2-AN > 3′-MAP > BP. Triplet BP gives quenching rate constants in the range of 2.6−5.6 × 10^9 M^{-1} s^{-1} with all phenols, whereas the triplet quenching rate constants for 3′-MAP and 2-AN vary over 1 and 2 orders of magnitude, respectively, with maximum values of ~3 × 10^9 M^{-1} s^{-1}.

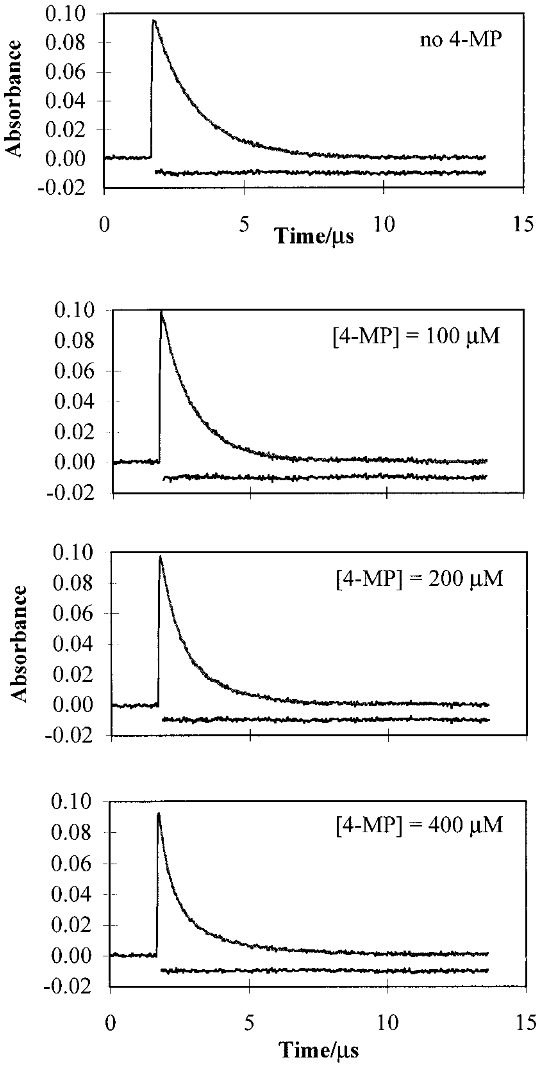

Figure 1. Transient absorption decays of triplet benzophenone (λ_{obs} = 520 nm) in air-saturated water in the absence and presence of the quencher 4-methylphenol at three different concentrations. The residuals of the fits (described in the text) are shown at the bottom of each diagram. The quenching constant was determined to be (4.2 ± 0.2) × 10^9 M^{-1} s^{-1}.

The decay constant of the BP-ketyl radical, $k^K = 5.8 \times 10^5$ s^{-1} at 24 °C, was obtained by fitting the transient absorbance trace of a solution containing BP and 300 μM TMP at λ_{obs} = 550 nm and at times greater than 1.2 μs after the laser pulse, whereby interference by the BP triplet was avoided. This value was confirmed in various kinetic traces obtained with BP (λ_{obs} = 520 nm) by fitting the tail of the transient decay with a single-

TABLE 2: Rate Constants for Quenching of Aromatic Ketone Triplet States by Phenols[a]

quencher	$k_{q,P}$(BP) ($M^{-1}\,s^{-1}$)	$k_{q,P}$(3′-MAP) ($M^{-1}\,s^{-1}$)	$k_{q,P}$(2−AN) ($M^{-1}\,s^{-1}$)
trolox	$(4.1 \pm 0.2) \times 10^9$	$(2.2 \pm 0.2) \times 10^9$	$(2.7 \pm 0.2) \times 10^9$
DMOP	$(5.6 \pm 0.2) \times 10^9$	$(2.4 \pm 0.3) \times 10^9$	$(3.1 \pm 0.1) \times 10^9$
TMP	$(5.1 \pm 0.9) \times 10^9$	$(2.6 \pm 0.3) \times 10^9$	$(7.2 \pm 0.1) \times 10^8$
4-MOP	$(4.2 \pm 0.6) \times 10^9$	$(2.7 \pm 0.3) \times 10^9$	$(1.8 \pm 0.1) \times 10^9$
4-MP	$(4.2 \pm 0.2) \times 10^9$	$(3.0 \pm 0.2) \times 10^9$	$(8.4 \pm 0.3) \times 10^7$
tyrosine	$(2.6 \pm 0.2) \times 10^9$	$(6.6 \pm 0.8) \times 10^8$	$(3.7 \pm 1.3) \times 10^7$
phenol	$(3.9 \pm 0.7) \times 10^9$	$(5.1 \pm 0.4) \times 10^8$	$(3.3 \pm 1.3) \times 10^7$
4-CBP	$(2.9 \pm 0.3) \times 10^9$	$(4.6 \pm 0.6) \times 10^8$	$(2.6 \pm 1.3) \times 10^7$
4-CNP	$(3.0 \pm 0.3) \times 10^9$	$(1.2 \pm 0.5) \times 10^8$	$(1.3 \pm 1.3) \times 10^7$

[a] Errors given as 95% confidence intervals estimated from data fits by the Levenberg−Marquardt method.

exponential function. Assuming that oxygen is the only significant scavenger of the ketyl radical under the experimental conditions used, a rate constant of $2.3 \times 10^9\ M^{-1}\ s^{-1}$ for the BP-ketyl radical reaction with oxygen is calculated using $[O_2] = 250\ \mu M$.[10]

Discussion

Absolute Quenching Rate Constants. The lifetimes of the ketone triplets were 1.2−1.6 μs in air-saturated water (Table 1). The lifetimes of the ketone triplets in degassed water were much longer (BP, 20 μs; 3′-MAP, 50 μs; 2-AN, 60 μs under our conditions) and the intrinsic decay rates would presumably be much higher in the absence of triplet−triplet annihilation which occurs only when high triplet concentrations are produced by flash photolysis. This implies that oxygen quenching is responsible for at least 93% of the triplet decay in air-saturated solution. One obtains a second-order rate constant for oxygen quenching of the ketone triplets of ca. $3 \times 10^9\ M^{-1}\ s^{-1}$ using $[O_2] = 255\ \mu M$.[10] This value compares well with those obtained for BP in acetonitrile and benzene ($2.3 \times 10^9\ M^{-1}\ s^{-1}$) and for 2-AN in benzene ($1.7 \times 10^9\ M^{-1}\ s^{-1}$).[8] The rate constant for the reaction of the BP-ketyl radical with oxygen ($2.3 \times 10^9\ M^{-1}\ s^{-1}$) is of the same order of magnitude. This reaction is expected to be very fast, owing to the highly negative reduction potential of BP (Table 1) and the slightly negative reduction potential of oxygen (−0.16 V vs NHE) that should render H atom or electron transfer from the ketyl radical or its conjugated base to oxygen highly exergonic.

Only few studies on triplet state quenching in solution have been performed using water as the solvent. The only rate constant for a ketone−phenol pair we are aware of concerns the quenching of triplet BP by tyrosine that was determined to be $3.6\times 10^9\ M^{-1}\ s^{-1}$.[4] The value of $2.6 \times 10^9\ M^{-1}\ s^{-1}$ determined here is between the latter value and the one measured in a 1:4 vol/vol acetonitrile/water mixture: $2.1 \times 10^9\ M^{-1}\ s^{-1}$.[11] Quenching of triplet BP by a series of para-substituted phenols in a 1:1 vol/vol acetonitrile/water mixture[3] exhibited a high selectivity, with rate constants increasing with the electron-donating strength of the para substituent from $4.0 \times 10^7\ M^{-1}\ s^{-1}$ (*p*-cyano, 4-CNP) to $4.9 \times 10^9\ M^{-1}\ s^{-1}$ (*p*-methoxy, 4-MOP). A smaller selectivity, with rate constants spanning a range of 1 order of magnitude, was observed for triplet BP quenching by the same series of phenols in benzene.[1] The present results, which show that triplet BP in water reacts unselectively with all substituted phenols, including 4-CNP, with rate constants close to the diffusion limit, demonstrate how strongly triplet quenching rate constants can be affected by the solvent.

There are still open questions regarding the mechanism of aromatic triplet ketone reduction by phenols in solution. The lack of a difference in reactivity between triplet ketones of n−π* and of π−π* character and the small deuterium isotope effect[1] exclude the hydrogen abstraction mechanism that is observed with aliphatic compounds. Formation of a complex by hydrogen bonding between the phenols and the excited triplet ketones was proposed[2] to enhance the efficiency of electron transfer upon excitation in polar, nonprotic solvents. In general, H atom transfer should be more favorable in nonpolar than in polar media, as demonstrated, for example, for the intramolecular hydrogen abstraction in triplet valerophenone,[12] whereas for electron transfer the opposite trend is expected. For the quenching of triplet aromatic ketones in aqueous solution, we expect that electron transfer should play an important role and that hydrogen bonding between the reactants should be largely eliminated by hydrogen bonding with the solvent. These predictions are confirmed by the above comparison of BP triplet quenching rate constants in different solvents.

Electron Transfer Modeling. Electron transfer from a phenol (PhOH) to the excited triplet state of a carbonyl compound $\{^3(R_1R_2{-}C{=}O)^*\}$ yields a protonated phenoxyl radical ($PhOH^{\bullet+}$) and a deprotonated ketyl radical ($R_1R_2{-}C^{\bullet}{-}O^-$), eq 1.

$$PhOH + {}^3(R_1R_2{-}C{=}O)^* \rightarrow PhOH^{\bullet+} + R_1R_2{-}C^{\bullet}\text{-}O^- \quad (1)$$

In the frame of various kinetic theories, such an intermolecular electron transfer reaction is usually described by a mechanism involving (a) formation of a precursor complex, (b) electron transfer to form a charge transfer (CT) complex, and (c) separation of the oxidized donor and reduced acceptor, as expressed by eq 2.

$$\begin{aligned} &PhOH + {}^3(R_1R_2{-}C{=}O)^* \rightleftharpoons \\ &\qquad [\,PhOH\cdots{}^3(R_1R_2{-}C{=}O)^*\,] \rightleftharpoons \\ &[PhOH^{\bullet+}\cdots R_1R_2{-}C^{\bullet}\text{-}O^-\,] \rightarrow PhOH^{\bullet+} + R_1R_2{-}C^{\bullet}\text{-}O^- \quad (2) \end{aligned}$$

Electron transfer theories provide a relationship between the rate of electron transfer from the precursor to the CT complex and the free energy change for this reaction step. Kinetic treatment of eq 2 leads then to expressions for the second-order rate constants for the overall reaction, eq 1. In the case of classical Marcus theory, the simplified eq 3[13] may be used

$$k^{obs} = \frac{k_d}{1 + \dfrac{k_d}{K_d Z}\exp\left\{\left[W + \dfrac{\lambda}{4}\left(1 + \dfrac{\Delta G^{\circ}_{el}}{\lambda}\right)^2\right]/RT\right\}} \quad (3)$$

where k^{obs} is the second-order rate constant for the intermolecular electron transfer reaction, k_d and k_{-d} are the rate constants for the formation and separation of the precursor complex, respectively, $K_d = k_d/k_{-d}$ is the equilibrium constant for precursor complex formation, Z is the universal collision frequency factor, W is the electrostatic work term, λ is the reorganization energy, ΔG°_{el} is the molar Gibbs free energy change for the electron transfer step, R is the universal gas constant, and T is the absolute temperature. For the present application, the work term W may be neglected due to the absence of charge on the reactants. Another frequently used expression for analyzing rate constants for excited state quenching induced by electron transfer is that derived empirically by

TABLE 3: Calculation of Oxidation Potentials for the Substituted Phenols

substituted phenol	$E_{ox}(PhO^-)$ (V vs NHE)	$pK_a(PhOH)^a$	$pK_a(PhOH^{+\bullet})$	$E_{ox}(PhOH)^b$ (V vs NHE)	$E_{ox}(PhOCH_3)^c$ (V vs NHE)
trolox	0.19^d	11.9^d	-0.9^e	0.95	
DMOP	0.50^f	9.9^g	-1.5^e	1.17	1.13
TMP	0.49^h	10.9	-1.5^e	1.22	
4-MOP	0.54^i	10.2	-1.4^j	1.23	1.30
4-MP	0.68^i	10.3	-1.6^j	1.38	
tyrosine	0.74^k	10.5	-1.6^e	1.46	
phenol	0.79^i	10.0	-2.0^j	1.50	1.62
4-CBP	0.90^i	9.2	-2.0^e	1.56	
4-CNP	1.12^i	8.0	-2.0^e	1.71	

[a] From ref 30 unless when noted. [b] Calculated using eq 6. [c] Reference 26. [d] Reference 20. [e] Estimated by comparison with values for other substituted phenols from refs 19 and 24. [f] Reference 21. [g] Canonica and Bader, unpublished results. [h] Reference 22. [i] Reference 23. [j] Reference 19. [k] Reference 31.

Rehm and Weller,[14,15] which in the present notation may be rewritten as

$$k_{obs} = \frac{k_d}{1 + \frac{k_d}{K_d Z}\left\{\exp\left[\left(\sqrt{\left(\frac{\Delta G^\circ_{el}}{2}\right)^2 + \left(\frac{\lambda}{4}\right)^2} + \frac{\Delta G^\circ_{el}}{2}\right)/RT\right] + \exp\left(\frac{\Delta G^\circ_{el}}{RT}\right)\right\}} \quad (4)$$

For fitting experimental data using eqs 3 or 4, the term $k_d/(K_dZ)$ is often used as a fixed parameter. Rehm and Weller[14,15] used the value of 0.25 for acetonitrile solutions, but Eberson[13] used the value of 0.1, noting that fits were not very sensitive to the value of this term. In this study, we will use the latter value. The free energy of electron transfer, used as an independent variable, is calculated from electrochemical and photophysical data, eq 5,[15]

$$\Delta G^\circ_{el} = -F[E_{red}(R_1R_2{-}C{=}O) - E_{ox}(PhOH)\,] - E_{0,0}[^3(R_1R_2{-}C{=}O)^*] + C \quad (5)$$

where F is the Faraday constant, E_{red} (E_{ox}) is the one-electron reduction (oxidation) potentials of the given species, $E_{0,0}$ is the electronic energy difference between the reacting excited state and the ground state (both including zero-point energies), and C is the electrostatic interaction energy, which, in our particular case, takes into account the attraction between the radical ions $PhOH^{\bullet+}$ and $R_1R_2{-}C^\bullet{-}O^-$. According to a model that assumes point charges in a dielectric continuum, C should only be ~ -2 kJ mol^{-1} (-0.02 eV) in aqueous solution at the ionic strength used in this study,[16] and we will, therefore, neglect it in the calculation of ΔG°_{el}. The experimental data required to estimate ΔG°_{el} are given in Tables 1 and 3. The quoted reduction potentials $E_{red}(R_1R_2{-}C{=}O)$ were measured in a 1:1 vol/vol ethanol/water mixture at high pH to avoid protonation of the ketyl radical anion.[17] The actual values in water may be somewhat less negative in view of the stronger stabilization of the ketyl radical anion in water than in the ethanol/water mixture. The choice of the oxidation potential for the phenols deserves particular attention. The electron transfer reaction (eq 1) requires that one uses $E_{ox}(PhOH/PhOH^{\bullet+}) = E_{red}(PhOH^{\bullet+}/PhOH)$ as the oxidation potential.[18] Unfortunately, this parameter cannot be measured directly in aqueous solution because of the very low pK_a of the protonated phenoxyl radicals, $PhOH^{\bullet+}$.[19] However, the oxidation potentials $E_{ox}(PhOH/PhOH^{\bullet+})$ may be calculated by combining the oxidation potentials of the anions, $E_{ox}(PhO^-/PhO^\bullet)$, which have been determined by pulse radiolytic measurements in aqueous solution at high pH for all phenols used here,[20–23] with the acidity constants of the corresponding phenols and phenoxyl radicals,[19,24] eq 6.

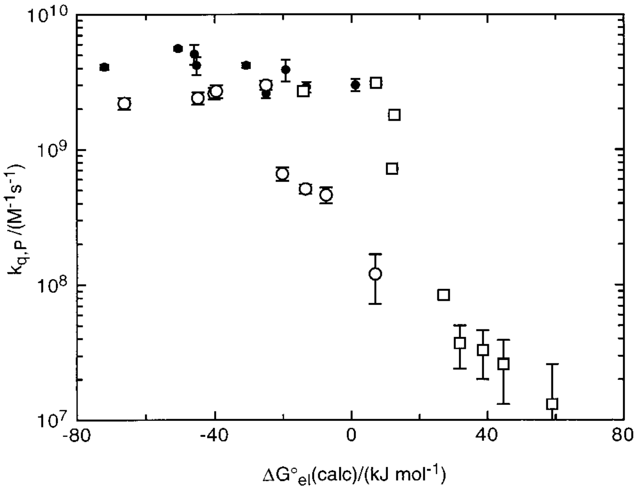

Figure 2. Quenching rate constant for the triplets of benzophenone (closed circles), 3′-methoxyacotophenone (open circles), and 2-acetonaphthone (open squares) plotted against the calculated free energy for one-electron transfer from the quencher to the triplet state of the aromatic ketone. Error bars represent 95% confidence intervals estimated from data fits by the Levenberg–Marquardt method.

$$E_{ox}(PhOH/PhOH^{\bullet+}) = E_{ox}(PhO^-/PhO^\bullet) + 2.303RT[pK_a(PhOH) - pK_a(PhOH^{\bullet+})]/F \quad (6)$$

The parameters used for evaluating eq 6 are given in Table 3. Parker and co-workers[25] have measured oxidation potentials for a few phenols in a very acidic 1:9 $HFSO_3/CH_2Cl_2$ mixture at -50 °C and noted that these were very close (within 0.1 V) to those for the corresponding anisoles. The oxidation potentials obtained here by means of eq 6 were found to be close (maximum deviation -0.12 V) to those of the corresponding anisoles in water solution[26] (last column in Table 3), which confirms the validity of our calculation.

The second-order quenching rate constants for all 27 ketone–phenol pairs (Table 2) are plotted in Figure 2 versus ΔG°_{el}(calc), which was calculated using eq 5 with $C = 0$ V and the parameters given in Tables 1 and 3. Quenching constants for triplet BP and 2-AN follow the same line and, with increasing ΔG°_{el}(calc), drop sharply below the diffusional limit at $\Delta G^\circ_{el}(calc) \approx 10$ kJ mol^{-1}. The data points for 3′-MAP approach those for BP and 2-AN at low ΔG°_{el}(calc) values, but the fall below the plateau starts already at $\Delta G^\circ_{el}(calc) \approx -20$ kJ mol^{-1} and is less steep than in the previous case.

At $\Delta G^\circ_{el}(calc) > 35$ kJ mol^{-1}, the quenching constants for 2-AN seem to level off and reach a value of about 1×10^7

M^{-1} s^{-1}. This unusual effect is attributed to partial (if minor) dissociation of the phenols at the experimental pH. The anions of all phenols studied here should quench the triplet of any of the three aromatic ketones at diffusional rate (~4 × 10^9 M^{-1} s^{-1}) owing to the high exergonicity of the reaction. The validity of such an assumption is corroborated by data on triplet BP quenching by phenoxide ions in a 1:1 vol/vol acetonitrile/water mixture.[3] For the pairs 2-AN/phenol, 2-AN/4-CBP, and 2-AN/4-CNP, the apparent rate constants at the experimental pH, considering only the phenoxide ion reactivity, are estimated to be 3−4 × 10^7 M^{-1} s^{-1}, which concurs well with the measured rate constants.

The BP and 2-AN data sets and the 3′-MAP data set were fitted separately to eqs 3 (Marcus model) and 4 (Rehm−Weller model), using $k_d/(K_dZ) = 0.1$ as a constant term. An additional fitting parameter, $\delta\Delta G°_{el}$, was introduced, eq 7, to compensate for the unknown (but relatively small) negative offset resulting from using ketone reduction potentials in a solvent mixture rather than in water for calculating $\Delta G°_{el}$.

$$\Delta G°_{el} = \Delta G°_{el}(\mathrm{calc}) + \delta\Delta G°_{el} \qquad (7)$$

For the BP and 2-AN data sets (excluding the 2-AN triplet quenching data by phenol, 4-CBP, and 4-CNP), fitting was performed using k_d, λ, and $\delta\Delta G°_{el}$ as the fit parameters. The Marcus equation has the well-known drawback of predicting a decrease in quenching rate constant with decreasing $\Delta G°_{el}$ at highly negative $\Delta G°_{el}$ values. For this reason, the four data points of lowest $\Delta G°_{el}$ were also neglected in the Marcus fit. Both models yielded comparable results (Figure 3a), with $\delta\Delta G°_{el} = -35$ and -27 kJ mol^{-1}, $k_d = 4.0 \times 10^9$ and 6.2×10^9 M^{-1} s^{-1}, and $\lambda = 75$ and 65 kJ mol^{-1}, for the Marcus and Rehm−Weller models, respectively. We noted that fits using the Marcus equation generally tend to give more negative values of $\delta\Delta G°_{el}$ and higher λ values at the same time, which is probably due to a higher correlation of these fitting parameters than for the Rehm−Weller model. We believe that the Rehm−Weller equation allows a better description of the present data set.

For fitting the 3′-MAP data to eqs 3 and 4 we used $\delta\Delta G°_{el}$ as a fixed parameter (value from the previous Rehm−Weller fit, -27 kJ mol^{-1}). This additional constraint was introduced in order to avoid an overestimation of both $-\delta\Delta G°_{el}$ and λ, because the mentioned correlation of these parameters increases with decreasing steepness of the curve at positive $\Delta G°_{el}$. We obtained $k_d = 2.9 \times 10^9$ and 5.8×10^9 M^{-1} s^{-1} and $\lambda = 103$ and 95 kJ mol^{-1} for the Marcus and Rehm−Weller models, respectively (Figure 3b). Both models yield λ values that are significantly higher than the values obtained for the BP and 2-AN data sets and might indicate a smaller delocalization of the unpaired electron in the 3′-MAP ketyl radical anion than in the BP and 2-AN ketyl radical anions. The λ values obtained for both data sets are typical of one-electron transfer reactions involving organic compounds,[13,16] and are in the same range as calculated solvent reorganization energies, which would support the hypothesis of an outer-sphere electron transfer.

The offset $\delta\Delta G°_{el} \approx -27$ kJ mol^{-1} would correspond to an underestimation of the reduction potentials of the aromatic ketones by ~0.28 V (~0.26 V if the electrostatic term C is also considered). This seems reasonable, since the reduction potential for BP increases by 0.28 V (from −1.59 to −1.31 V vs NHE) by changing the solvent from acetonitrile to a 1:1 vol/vol ethanol/water mixture.[17,27]

As opposed to an electron transfer mechanism, we now consider the possibility of a hydrogen atom transfer mechanism, although such a mechanism is expected to be less likely as indicated above. For the H atom transfer reaction, eq 8,

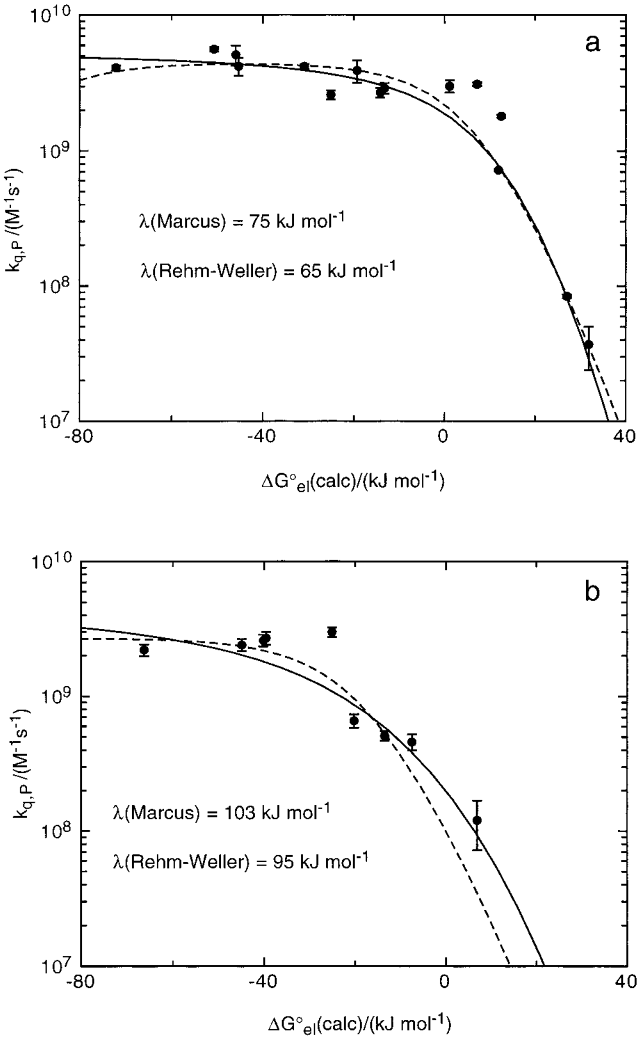

Figure 3. Rehm−Weller (—, eq 4) and Marcus (- - -, eq 3) fits of (a) the benzophenone and 2-acetonaphthone (three-parameter fit) and (b) the 3′-methoxyacetophenone (two-parameter fit) triplet quenching rate constants.

$$\mathrm{PhOH} + {}^3(\mathrm{R_1R_2{-}C{=}O})^* \rightarrow \mathrm{PhO}^\bullet + \mathrm{R_1R_2{-}C^\bullet{-}OH} \qquad (8)$$

the Gibbs free energy change can be written as

$$\Delta G°_H = -F[E_{red}(\mathrm{R_1R_2{-}C{=}O}) - E_{ox}(\mathrm{PhOH})] - E_{0,0}[{}^3(\mathrm{R_1R_2{-}C{=}O})^*] - 2.303RT[\mathrm{p}K_a(\mathrm{R_1R_2{-}C^\bullet{-}OH}) - \mathrm{p}K_a(\mathrm{PhOH}^{\bullet+})] \qquad (9)$$

Combining eqs 5 and 9, one obtains eq 10.[15]

$$\Delta G°_H - \Delta G°_{el} = -C - 2.303RT[\mathrm{p}K_a(\mathrm{R_1R_2{-}C^\bullet{-}OH}) - \mathrm{p}K_a(\mathrm{PhOH}^{\bullet+})] \qquad (10)$$

The pK_a of the ketyl radical is known only for BP (9.25),[28] but for 3′-MAP and 2-AN similar values are expected. The pK_a of the phenoxyl radical (Table 3) is in the range −2 to −1. This gives a value of about 11 for the term in square brackets in eq 10, which means that the H atom transfer reaction should be ~61 kJ mol^{-1} more exergonic than the electron transfer reaction. Fitting the quenching rate data to the Marcus and

Rehm–Weller models by replacing $\Delta G°_{el}$ with $\Delta G°_H$, and $\delta\Delta G°_{el}$ with $\delta\Delta G°_H$ (defined analogously as in eq 7), would thus result in $\delta\Delta G°_H$ values of $\sim$+34 kJ mol^{-1}, which is unreasonable. This discrepancy corroborates the hypothesis that quenching does occur by electron transfer and not by H atom transfer.

Comparison with Photosensitized Oxidation Rates. In our previous study,[5] we measured first-order rate coefficients, k^{eff}, for the photosensitized transformation of substituted phenols in aqueous solution using BP, 3′-MAP, and 2-AN as the sensitizers. Using monochromatic radiation and chemical actinometry we could determine the “quantum yield coefficients”, *f*, for such reactions as follows:

$$f = k^{eff}/(2.303Ia) \qquad (11)$$

where *I* is light fluence rate and *a* the decadic absorption coefficient of the solution (due to sensitizer absorption).[29] Assuming that the phototransformation is initiated by the excited triplet state of the sensitizer reacting with the phenol, the second-order rate constants for such transformation, $k_{r,P}$, is given by

$$k_{r,P} = f\frac{k_0}{\Phi_{isc}} \qquad (12)$$

where k_0 is the first-order deactivation rate coefficient of the triplet (in air-saturated solution) and Φ_{isc} the intersystem crossing quantum yield of the sensitizer. These constants may be related to the quenching rate constants of the triplet, $k_{q,P}$, by using the efficiency parameters $\eta_{P,PhO^\bullet}$, for the phenoxyl radical formation, and $\eta_{P,sec}$, for all secondary reactions transforming the phenoxyl radical into products that (on the experimental time scale) do not regenerate the parent compound.

$$k_{r,P} = k_{q,P}\eta_{P,PhO^\bullet}\eta_{P,sec} \qquad (13)$$

We may safely set the phenoxyl radical formation efficiency equal to 1, because it should correspond to that of the ketyl radical and ketyl radical anion formation efficiency, which was shown to be unity (within $\sim$20% experimental error) for most phenols in various solvents.[1,3,4] Thus, significant differences between $k_{r,P}$ and $k_{q,P}$ may be attributed to a low value of $\eta_{P,sec}$. In Figure 4, $k_{r,P}$ and $k_{q,P}$ are plotted versus the reduction potential of the phenoxyl radicals, $E_{red}(\text{PhO}^\bullet/\text{PhO}^-)$, for each sensitizer separately. Values of $k_{r,P}$ are not available for tyrosine, 4-CBP, and 4-CNP, and for the pair phenol/2-AN. One notes that both types of rate constants have basically the same values ($\eta_{P,sec} >$ 0.5), except for phenol, where $k_{r,P}$ is about an order of magnitude lower than $k_{q,P}$. A possible explanation for the reduced transformation rate of phenol ($\eta_{P,sec} \approx 0.1$) is that the phenoxyl radical is not further oxidized, for example by addition of superoxide and subsequent transformations,[22] but instead reduced by superoxide itself,

$$\text{PhO}^\bullet + {}^\bullet\text{O}_2{}^- \rightarrow \text{PhO}^- + \text{O}_2 \qquad (14)$$

a highly exergonic reaction which was shown to occur at increased efficiency with increasing reduction potential of the phenoxyl radical.[22] We thus expect that such reaction is also important for phenols bearing electron-withdrawing substituents. In addition, phenoxyl radicals with a relatively high reduction potential might also be reduced by other reaction intermediates or impurities present in solution.

DNOM photosensitization is an important process leading to the transformation of organic compounds in sunlit natural waters. We have suggested that the photosensitized transformation of phenols, and possibly of many other xenobiotics and natural products, in surface waters occurs through initial oxidation by reactive excited triplet states of the DNOM.[5] On the basis of the comparison of *f* values for DNOMs and aromatic ketones (Table 4 in ref 5), such reactive triplet states are most probably only a fraction of all DNOM triplets. If we assume that such reactivity of the DNOM can be explained in terms of electron transfer relationships, as shown in the present study for aromatic ketones, then it would be useful to estimate the reduction potential of DNOM reactive triplets, that would permit the prediction of transformation rates of various organic compounds by such an oxidative triplet mechanism. Comparison of the relative reactivity of various phenols for DNOM and aromatic ketone photosensitization lead to the conclusion that DNOM reactive triplets were clearly less selective than 2-AN triplets but more selective than BP triplets, whereas 3′-MAP triplets showed a comparable selectivity.[5] In terms of electron transfer theory, this would indicate that the effective value for the reduction potential of DNOM reactive triplets is comprised between $\sim$1.36 and $\sim$1.95 V vs NHE (calculated by adding $\sim$0.26 V, as previously discussed, to the triplet reduction potentials of 2-AN and BP from Table 1).

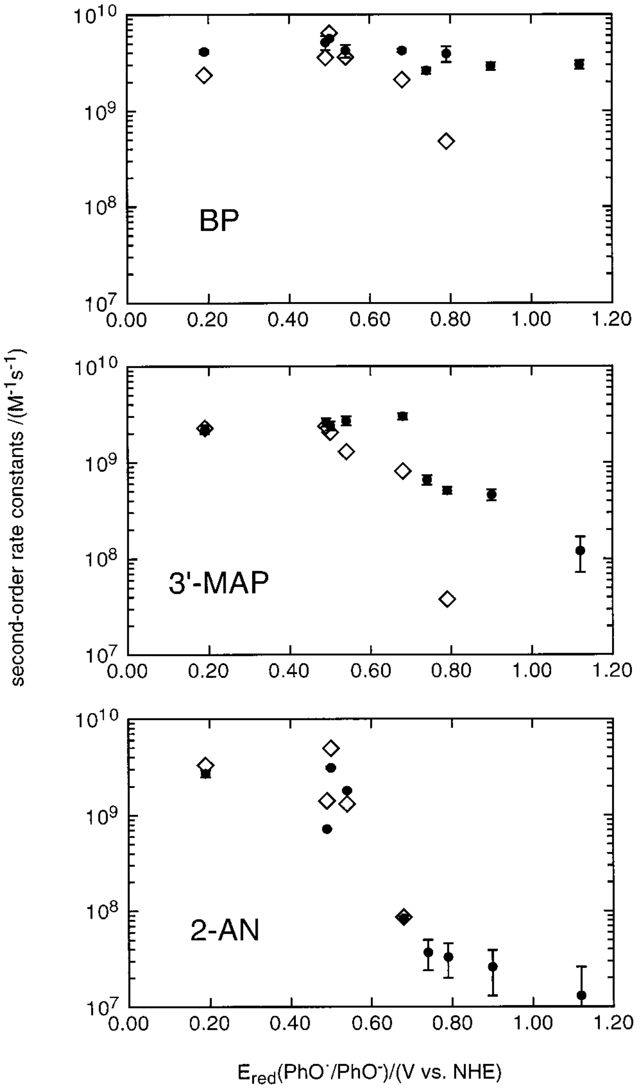

Figure 4. Second-order rate constants for quenching ($k_{q,P}$, ●) and photosensitized transformation ($k_{r,P}$, ◇), calculated from the values in ref 5 using eq 12, plotted against the reduction potential of the phenoxyl radicals.

Conclusions

Excited triplet states of aromatic ketones such as benzophenone, 3′-methoxyacetophenone, and 2-acetonaphthone are strong one-electron oxidants in aqueous solution and can efficiently initiate the oxidative degradation of substituted phenols. We have shown previously[5] that such a triplet state mechanism prevails over a singlet oxygen mechanism in air-saturated water solution. We expect that such a type I photosensitized oxidation mechanism may be relevant not only for phenols but also for any organic compound having a one-electron oxidation potential in the same range as or lower than those of phenols.

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