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Photoprocesses of *p*-Benzoquinones in Aqueous Solution

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The photochemistry of 1,4-benzoquinone (BQ) and several derivatives, for example, duroquinone, trimethyl-2,5- or 2,6-dimethyl-, and methyl-BQ in aqueous solution or mixtures with polar media, for example, acetonitrile or 2,2,2-trifluoroethanol, was studied by time-resolved UV−vis spectroscopy after pulses at 248 and 308 nm. The triplet state and the semiquinone radical (•QH/Q•$^-$) of BQs are spectroscopically and kinetically separated intermediates. The radical yield in the absence of H-atom donors is low and significantly increased in the presence of alcohols. Efficient photoinduced charge formation, because of Q•$^-$ and H$^+$ after H-atom transfer from 2-propanol to the triplet state, and small effects in the absence of a donor were observed by transient conductivity. The quantum yield of photodecomposition, $\lambda_{irr} = 254$ nm, is substantial for BQ, MeBQ, and Me_2BQs in aqueous solution, but small for Me_4BQ. To account for the efficient photoconversion of BQs into hydrobenzoquinones and 2-hydroxy-1,4-benzoquinones, a novel water-mediated reaction not involving free radicals is proposed as major step. This mechanism is consistent with the prediction that the observed triplet state is monomeric and the yield of Q•$^-$, detected by both transient absorption and conductivity, is low for sub-millimolar BQ, MeBQ, and Me_2BQs at pH 5−6. In addition, H-atom abstraction from a polar organic solvent or by self-quenching plays a role in mixtures with water or at enhanced quinone concentration, respectively.

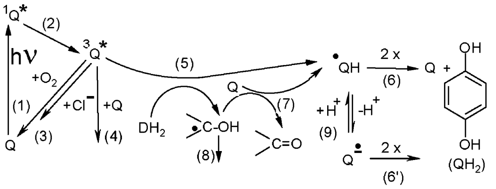
Introduction

Quinones function as electron carriers through the membrane of various proteins and enzymes.[1,2] The photochemistry of 1,4-benzoquinone (BQ) and derivatives, such as methyl-1,4-benzoquinone (MeBQ), 2,5- or 2,6-dimethyl-1,4-benzoquinones (Me_2BQs), or duroquinone (Me_4BQ)[3−25] as well as 1,4-naphthoquinone (NQ) and methyl-1,4-naphthoquinone,[26−30] has been intensively investigated. Often studied water-soluble 9,10-anthraquinone (AQ) derivatives are 1- or 2-sulfonated (1-SO_3-AQ^-, 2-SO_3AQ^-) and 2,6-disulfonated [2,6-$(SO_3)2AQ^{2-}$][30−42] which, however, reveal characteristic differences with respect to parent BQ.

Most quinones exhibit a high quantum yield of intersystem crossing (Φ_{isc}) in solution at room temperature.[3,4] The triplet state ($^3Q^*$) is the major species after pulsed excitation (steps 1 and 2, Scheme 1). For BQ and AQ, the maximum quantum yield of formation of hydroquinones (QH_2) in the presence of a H-atom donor, for example, 2-propanol, is close to unity.[5] The photoreduction of quinones by amines, such as triethylamine (TEA) or DABCO, is the subject of various investigations.[24,27−29,35,36] Triplet quenching by anions, 3, and oxygen, self-quenching, 4, and reaction 5 with H-atom donors are competing steps. The semiquinone radicals (•QH/Q•$^-$) play a key role in the photoreduction of quinones and eventually yield QH_2 (reaction 6). The alcohol radical may yield another semiquinone radical, 7, in competition to self-termination, 8 (Scheme 1). In neutral aqueous solution, the semiquinone radicals are present as radical anions because of equilibrium 9.[43−46]

The photoreactions of parent BQ in aqueous solution lead to 1,2,4-trihydroxybenzene (1,2,4-benzenetriol) as labile intermediate and eventually to 2-hydroxy-1,4-benzoquinone (Q′) and hydrobenzoquinone as stable products.[22,23] Formation of free OH radicals in the photolysis of quinones in aqueous solution has been considered by various groups.[13−19,37−40] This has been questioned for sulfonated AQs,[32] MeBQ,[21] and 2,6-Me_2BQ.[20] The mechanism is still under debate, but the free OH radical hypothesis has been excluded for parent BQ.[22]

SCHEME 1



Here, upon pulsed excitation at 248 and 308 nm and continuous irradiation at 254 nm, the reactions of 1,4-benzoquinones were studied in aqueous solution or 1:1 (vol) mixtures with polar organic solvents which do not favor H-atom transfer. The organic solvents as additives were acetonitrile, *tert*-butyl alcohol, 2,2,2-trifluoroethanol (TFE) or 1,1,1,3,3,3-hexafluoro-2-propanol (HFP). These fluoroalcohols are weakly nucleophilic and strongly polar solvents.[47] A series of quinones, such as parent BQ, MeBQ, 2,5-, 2,6-Me_2BQ, trimethyl-1,4-benzoquinone (Me_3BQ), Me_4BQ, 2,6-dimethoxy-BQ [$(OMe)_2BQ$], and phenyl-BQ (PhBQ), were chosen. The effects of quinoid structure and medium on the photoreactions were studied by time-resolved UV−vis spectroscopy and conductivity.

Experimental Section

The compounds (Merck, EGA/Aldrich, Sigma, Fluka) were purified by sublimation (Me_4Q) or recrystallization (BQ, 2,6-Me_2Q) or were used as received; TFE and HFP (EGA/Aldrich) and the other solvents (Merck, Uvasol quality) were checked for impurities, and water was from a Milli Q system. The absorption spectra were monitored on a UV−vis spectropho-

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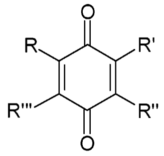
CHART 1



R	R'	R''	R'''	
Me	H	H	H	**MeBQ**
Me	H	Me	H	**2,5-Me$_2$BQ**
Me	Me	H	H	**2,6-Me$_2$BQ**
Me	Me	Me	H	**Me$_3$BQ**
Me	Me	Me	Me	**Me$_4$BQ**
OMe	OMe	H	H	**(OMe)$_2$BQ**
C$_6$H$_5$	H	H	H	**PhBQ**

tometer (HP, 8453) and for photoconversion the 254-nm line of a Hg lamp was used. Typically, absorbances of 1−3 were used for $\lambda_{irr} = 254$ nm. The conversion was carried out after vigorous bubbling by argon prior and during irradiation. For HPLC analyses, a 125 × 4.6 mm Inertsil ODS-3 5 μm column was used and MeOH-water 1:2 or 2:1 as eluents. The quantum yield of decomposition (Φ_d) was determined using the uridine/water/air actinometer.[48] The molar absorption coefficient of the Q′ form of BQ at the two maxima is $\epsilon_{260} = 4 \times 10^3$ and $\epsilon_{482} = 2.2 \times 10^3$ M^{-1}cm^{-1}.[46] Reaction of hydroquinones with oxygen fully reverses the quinones back in the cases of AQs in polar solvents,[42] but not for BQs.

Two excimer lasers (Lambda Physik, pulse width of 20 ns and energy <100 mJ) were used for excitation at 248 and 308 nm. The absorption signals were measured with two digitizers (Tektronix 7912AD and 390AD). Relative yields were obtained from the appropriate absorption signals using optically matched solutions. The experimental conditions were due to lower and higher concentrations for $\lambda_{exc} = 248$ and 308 nm, respectively. Absorbances of 0.2−3 were used, corresponding to concentrations of 0.02−0.1 mM for $\lambda_{exc} = 248$ nm and 1−8 mM for $\lambda_{exc} = 308$ nm, on the basis of molar absorption coefficients, for example, $\epsilon_{248} = 1.9 \times 10^4$ and $\epsilon_{308} = 2.6 \times 10^2$ M^{-1}cm^{-1} for BQ. For parent BQ, in contrast to several derivatives, the rate constant for quenching by 2-propanol could not be determined at a wavelength of triplet decay because of a too high absorption of the semiquinone radical with respect to the triplet signal. Instead, the grow-in kinetics were estimated. The molar absorption coefficient of Q•$^-$ and •QH for BQ in aqueous solution is $\epsilon_{430} = 6.1 \times 10^3$ and $\epsilon_{410} = 4.3 \times 10^3$ M^{-1}cm^{-1}, respectively; the values for 2,6-Me$_2$BQ are similar.[43] For Me$_4$BQ, the molar absorption coefficients of ^{3}Q*, Q•$^-$, and •QH are $\epsilon_{500} = 4.2 \times 10^3$, $\epsilon_{440} = 7.6 \times 10^3$, and $\epsilon_{420} = 4.7 \times 10^3$ M^{-1}cm^{-1}, respectively.[9] The fast (0.05−10 μs) and slow (5 μs to 1 s) conductivity signals were measured by DC and AC bridges as reported elsewhere.[25,42] The samples were freshly dissolved and all measurements refer to 24 ± 2 °C and deoxygenated solution, unless otherwise indicated.

Results

Continuous Irradiation. Irradiation at 254 nm of BQ in argon-saturated neat aqueous solution in relatively low concentration of 0.1 mM reveals two characteristic wavelengths at 228 and 256 nm which on examination can be denoted as isosbestic points as far as further conversion into secondary products is avoided. The absorption decreases between these wavelengths and increases below and above (Figure 1a). Comparable spectral changes were recorded for MeBQ or 2,6-Me$_2$BQ (Figure 1b), whereas for Me$_4$BQ (Figure 1c) and PhBQ (Figure 1d) the isosbestic points are red-shifted. Photodecomposition of the substrate was also measured by HPLC and hydroquinone, and one further species, 2-hydroxy-1,4-benzoquinone (Q′, see Scheme 2), was a major photoproduct absorbing above 250 nm. Photoconversion into the corresponding QH$_2$ in 2-propanol/acetonitrile and into QH$_2$ and Q′ in aqueous solution was observed by HPLC for BQ, MeBQ, Me$_2$BQs, or Me$_3$BQ.

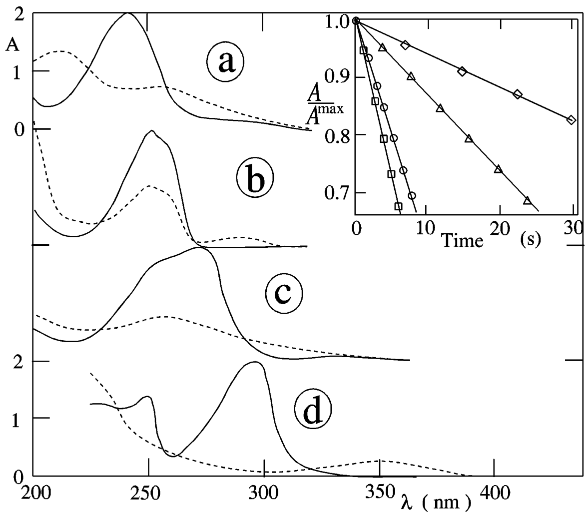


Figure 1. Absorption spectra of (a) BQ, (b) 2,6-Me$_2$BQ, (c) Me$_4$BQ, and (d) PhBQ in argon-saturated aqueous solution at pH 7 prior to (full) and after (dashed) irradiation at 254 nm; inset: absorption at maximum vs irradiation time for BQ (o), MeBQ (□), Me$_4$BQ (◇), and PhBQ (△).

SCHEME 2

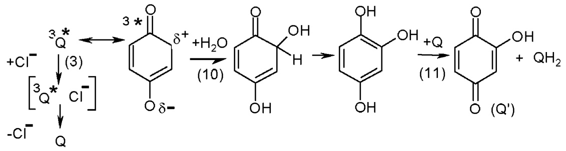


TABLE 1: Quantum Yields Φ_d of Decomposition of BQs[a]

quinone	MeCN	MeCN−H$_2$O[b]	2-propanol−H$_2$O[b]	H$_2$O
BQ	0.10 (<0.01)[c]	0.5	0.9	0.5 (0.4)
MeBQ	0.06 (<0.01)	0.8	0.9	0.8 (0.8)
2,5-Me$_2$BQ	0.06 (<0.02)	0.7	0.9	0.7 (0.5)
2,6-Me$_2$BQ	0.06 (<0.02)	0.7 (0.4)	0.9	0.7 (0.5)
Me$_3$BQ	0.01 (0.002)	0.1	0.6	0.1
Me$_4$BQ	0.005	0.1		
(OMe)$_2$BQ	0.002	0.03		
PhBQ	0.05 (0.02)	0.2		0.2 (0.2)

[a] In argon-saturated solution using $\lambda_{irr} = 254$ nm. [b] In 1:1 (vol) mixtures. [c] Values in parentheses refer to oxygen saturation.

The quantum yields of decomposition were obtained from plots of the absorption at the maximum versus irradiation time which are initially linear (inset of Figure 1). The Φ_d values of BQs (R: H, Me, Me$_2$) in acetonitrile are much smaller than in aqueous solution, where Φ_d is large but does not approach unity. Conditions of efficient photoconversion are also acetonitrile/water (1:1, vol) mixtures (Table 1); comparable effects were found in mixtures of *tert*-butyl alcohol and TFE with water. The photoconversion of BQ in aqueous solution is well characterized and the two photoproducts are QH$_2$ and Q′; the Φ values are equal and sum up to 0.42.[22] Another literature value is $\Phi_d = 0.5$ for 2,6-Me$_2$BQ in aqueous solution at pH 5.5, $\lambda_{irr} = 265$ nm.[20] Saturation by oxygen reduces Φ_d only moderately, in contrast to the absence of water. To further confirm the quite large Φ_d in aqueous solution, the values were also measured in 2-propanol/water (1:1) mixtures, where $\Phi_d = 1.0$ for BQ.[5]

Anions are known to quench the triplet state of BQ, NQ, and sulfonated AQs in aqueous solution.[12,23,30,33,34] Here, the quenching of Φ_d by Cl$^-$ and Br$^-$ was probed. In fact, when KCl was added to BQs, the slope of the absorption at the maximum versus irradiation time (inset of Figure 2) strongly

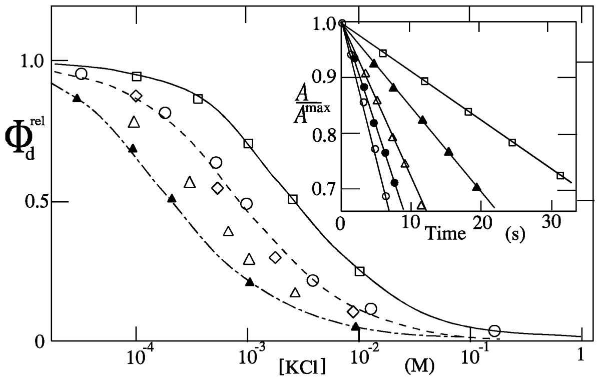


Figure 2. Plots of Φ_d as a function of [KCl] for BQ (circles), MeBQ (squares), 2,5-Me$_2$BQ (diamonds), and 2,6-Me$_2$BQ (triangles) in argon-saturated aqueous solution, $\lambda_{irr} = 254$ nm, pH 6−7; inset: absorption vs irradiation time for 2,6-Me$_2$BQ and [KCl] = 0 (○), 0.1 (●), 0.3 (△), 1 (▲), and 3 (□) mM.

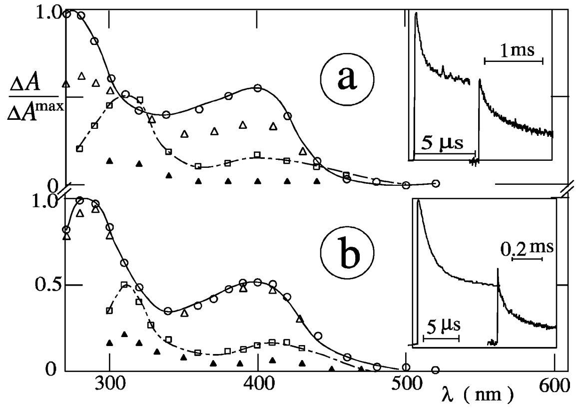


Figure 3. Transient absorption spectra of BQ (1 mM) in argon-saturated (a) aqueous solution at pH 7, (b) HFP-water (1:1) at 20 ns (○), 1 μs (△), 10 μs (□), and 1 ms (▲) after the 308-nm pulse; insets: triplet and radical decay at 420 nm.

decreases; plots of Φ_d as a function of log [KCl] are shown in Figure 2. The Cl$^-$ concentration, where Φ_d is 50% of the maximum value (half-concentration: [Cl$^-$]$_{1/2}$), can be compared with data from triplet quenching (see below).

Effects of Water on the Transient Properties upon Excitation at 308 nm. Transient absorption spectra of BQs (1−5 mM) in argon-saturated aqueous solution or 1:1 (vol) mixtures with organic solvents are presented in Figures 3−5. The spectra after the 308-nm pulse show the triplet state and subsequently the semiquinone radical. The T−T absorption spectrum of BQ in aqueous solution has two maxima at $\lambda_{TT} = 275$ and 400 nm (Figure 3a). For BQ in 1:1 (vol) mixtures with HFP (Figure 3b) or TFE, the triplet state can be separated from the semiquinone radical with maxima at $\lambda_{rad} = 320$ and 410 nm. Transient absorption spectra of 2,6-Me$_2$BQ show a red shift of λ_{TT} to 450 nm in water (Figure 4a) and mixtures with acetonitrile and HFP (Figure 4b). Further examples of the T−T absorption spectra in water/acetonitrile mixtures are shown for (OMe)$_2$BQ, $\lambda_{TT} = 480$ nm (Figure 5a) and PhBQ, $\lambda_{TT} = 550$ nm (Figure 5b). For MeBQ in acetonitrile and water, the absorption of the semiquinone radical dominates with respect to the triplet state.

The decay kinetics in most cases are first-order (rate constant: $1/\tau_T$), when the intensity is low enough and a second long-lived component due to radicals in the absence of oxygen was subtracted. The triplet lifetimes of the quinones examined in strongly polar media are compiled in Table 2. The triplet state is the major species after the pulse (steps 1 and 2 in Scheme 1), as supported by faster decay on addition of oxygen, similar to the case of various quinones in acetonitrile, where the rate constant for triplet quenching is $k_{ox} = (0.5−3) \times 10^9$ M^{-1}s^{-1}.[25] T−T annihilation was reduced or avoided by a low excitation intensity, whereby virtually no hydrated electron is formed, as monitored for BQ and 2,6-Me$_2$BQ in aqueous solution in the 600−700 nm range. In several cases, an effect of quinone concentration on τ_T was observed. The plots of $1/\tau_T$ versus [quinone] are linear for 2,6-Me$_2$BQ in aqueous solution and 1:1 (vol) mixtures with organic solvents (Figure 6) and the slope is k_4. This is also the case for BQ with exception of neat water, where the plot is downward curved. Thus, quenching of the triplet state by Q (self-quenching), reaction 4, has to be considered. The k_4 values are up to 2×10^9 M^{-1}s^{-1} (Table 3).

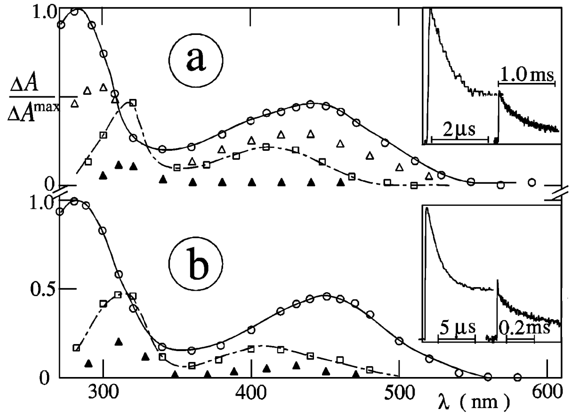


Figure 4. Transient absorption spectra of 2,6-Me$_2$BQ (1 mM) in argon-saturated (a) aqueous solution at pH 7, (b) HFP-water (1:1) at 20 ns (○), 1 μs (△), 10 μs (□), and 1 ms (▲) after the 308-nm pulse; insets: triplet and radical decay at 430 nm.

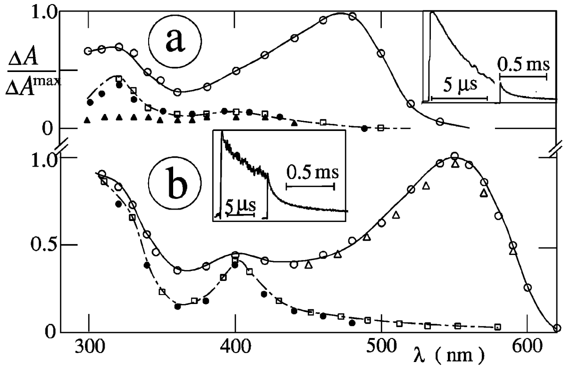


Figure 5. Transient absorption spectra in argon-saturated acetonitrile-water (1:1) of (a) (OMe)$_2$BQ and (b) PhBQ at 20 ns (○), 1 μs (△), 10 μs (□), 0.1 ms (●), and 1 ms (▲) after the 308-nm pulse; insets: triplet and radical decay at 350 nm.

The rate constant for triplet decay of BQs becomes larger on addition of 2-propanol as donor (DH$_2$) and the yield of the semiquinone radical is enhanced. Formation of •QH via step 5 depends on the quinone structure and nature of solvent and additives. For Me$_4$BQ in 2-propanol, the triplet with $\lambda_{TT} = 470$ nm as precursor and •QH as longer lived transient appear.[3] The long wavelength maximum of most BQs in aqueous solution is $\lambda_{rad} = 410−420$ nm and only slightly red-shifted for the Me$_4$, Ph, or (OMe)$_2$ derivatives.

The triplet decay is also accelerated on addition of amines, for example, DABCO or TEA. The quinone radical anion (Q•$^-$) and the triplet state are separated intermediates, whereas the radical cation (DH$_2$$^{•+}$) of several amines has a too low molar

TABLE 2: Triplet Lifetime τ_T (in μs) of BQs in the Absence and Presence of Water[a]

quinone	λ_{exc}(nm)	MeCN	MeCN−H_2O[b]	TFE−H_2O[b]	HFP−H_2O[b]	H_2O	D_2O
BQ	308	2.5	0.9	1	2	1−2	
	248	5	1.2	2		1.2	0.8
MeBQ	308	0.6	0.7	0.6	2	<0.2	
	248	1	0.5	0.6		0.2	0.3
2,5-Me_2BQ	248	3	1.2	0.5		1.0	1.0
2,6-Me_2BQ	308	<0.7	0.4	0.7	2	<0.5	
	248	3	1.4	1.2		1.2	1.4
Me_3BQ	248/308	8	4	5		1.8	
Me_4BQ	248/308	15	15	8	6	*c*	
$(OMe)_2BQ$	248/308	10	6	3	4		
PhBQ	248/308	3	2	1.5	2		

[a] In argon-saturated solution at low intensity. [b] The columns refers to 1:1 (vol) mixtures with water, pH 7−8. [c] Not transparent enough.

TABLE 3: Rate Constants for Triplet Quenching by BQs, 2-propanol, and Cl^-, and Cl^- Half-Concentrations[a]

quinone	solvent	k_4 ($\times 10^9$ M^{-1} s^{-1})	k_5 ($\times 10^6$ M^{-1} s^{-1})	k_3 ($\times 10^9$ M^{-1} s^{-1})	$1/(\tau_T \times k_3)$ (mM)	$[Cl^-]_{1/2}$ (mM)
BQ	H_2O			2.4 [4][b]	1	1.2
	MeCN−H_2O[c]	<1		1.4	0.5	0.5
MeBQ	H_2O	<2	>30	2.4 [4]	2	2.3
2,5-Me_2BQ	H_2O	2.0	20	2.5 [4]	0.4	0.5
2,6-Me_2BQ	H_2O	2.3	20	2.8 [4]	0.3	0.4
	MeCN−H_2O	1.6	40	3.5	0.2	0.2
Me_4BQ	MeCN−H_2O	<0.1	<1	0.008		
$(OMe)_2BQ$	MeCN−H_2O	<0.1	<1	0.3		>100
PhBQ	MeCN−H_2O	<0.1	<1	0.04		10

[a] In argon-saturated solution, H_2O, and <1% acetonitrile, at pH 6−8 using λ_{exc} = 248 nm. [b] In brackets: KCl is replaced by KBr. [c] In 1:1 mixtures with acetonitrile.

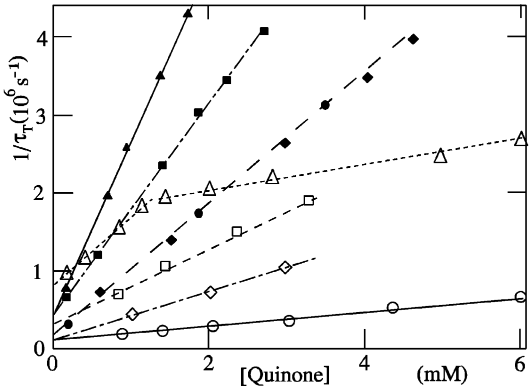


Figure 6. Plots of $1/\tau_T$ versus [quinone] for BQ (open) and 2,6-Me_2-BQ (full) in argon-saturated (circles), aqueous solution at pH 7 (triangles), acetonitrile−water (1:1) (squares), and TFE−water (1:1) (diamonds), λ_{exc} = 248 nm (<1mM) and 308 nm.

TABLE 4: Relative Absorbances of Radical Versus Triplet ($\Delta A_r/\Delta A_T$) of BQs in (1:1) Aqueous Mixtures[a]

quinone	MeCN	TFE	HFP	neat H_2O	neat D_2O[b]
BQ	0.5	0.6	0.2	0.15	0.2
MeBQ	0.5	0.4	0.5	0.5	0.5
2,6-Me_2BQ	0.1	0.15	0.1	0.1	0.2
Me_4BQ	0.2	0.2	0.2		

[a] In argon-saturated solution, λ_{exc} = 308 nm. [b] Using λ_{exc} = 248 nm.

absorption coefficient to be observed.[25] After reaction 5, the decay of •QH/Q•⁻ under argon is essentially second-order and radical termination 6 yields Q and QH_2. The first half-life ($t_{1/2}$) of BQs in acetonitrile is in the 0.1−10 ms range, depending on the system.[3,4,25] Reaction 7 is a second reduction step of the alcohol or amine radical which competes with reaction 8 of radical termination, not yielding QH_2 (Scheme 1).[42] Oxygen also quenches the decay of the semiquinone radical.[43−45] Both subsequent intermediates are also spectroscopically separated for $(OMe)_2BQ$ and PhBQ in the absence of H-atom donors (Figure 5) but not sufficiently separated for BQ in aqueous solution. The absorption signal at λ_{rad} (after triplet decay) with respect to T−T absorption at λ_{TT}, expressed by $\Delta A_r/\Delta A_T$, is taken as a measure of radical formation (Table 4). The absorption signal of the radical is largest for BQ in 1:1 mixtures of water with TFE.

Transient Properties for Low BQ Concentrations, λ_{exc} = 248 nm. The properties of the transients of BQs in argon-saturated aqueous solution or 1:1 (vol) mixtures with polar (rather inert) organic solvents change as concentration effects play a marked role. The much lower concentration applicable for λ_{exc} = 248 nm leads in most cases to longer τ_T values (Table 2). The triplet lifetime in the presence of water (>20 M), extrapolated to zero concentration, is 5−20 μs in most cases, but ca. 2 μs for BQ and Me_2BQs or <1 μs for MeBQ. The rate for quenching of triplet BQ by water can be estimated as 10^4 $M^{-1}s^{-1}$.

The spectra and maxima remain in principle the same, but the contribution of the semiquinone radical with respect to the triplet, just after the 248 nm pulse, is lower than for λ_{exc} = 308 nm. Examples are shown in Figure 7 for BQ, MeBQ, and Me_2-BQs. In particular, under the low-intensity conditions, no hydrated electron was observed for BQs in neat water. The triplet lifetime is virtually unchanged, when water is replaced by heavy water (Table 2). Variation of pH from 3 to 9 causes only minor changes in the spectra and kinetics of the triplet state and the semiquinone radical of BQ or 2,6-Me_2BQ.

The triplet lifetime of BQs becomes shorter on addition of anions. Linear dependences of $1/\tau_T$ on [KCl] were found in aqueous solution and 1:1 (vol) mixtures with acetonitrile (Figure 8). For AQs and selected quinones, a quenching reaction 3 of the triplet state by anions has been reported.[12,34] The rate constant for triplet quenching of Me_4BQ by Cl^-, $k_3 = 1 \times 10^7$ M^{-1} s^{-1}, is in agreement with the literature.[12] Larger values were found with the other BQs (Table 3) and $k_3 = 3 \times 10^9$ M^{-1} s^{-1} for NQ.[34] The half-concentration, where Φ_d is 50% of the maximum value, agrees with data from triplet quenching, $[Cl^-]_{1/2} = 1/(k_3 \times \tau_T)$, indicating mainly physical quenching.

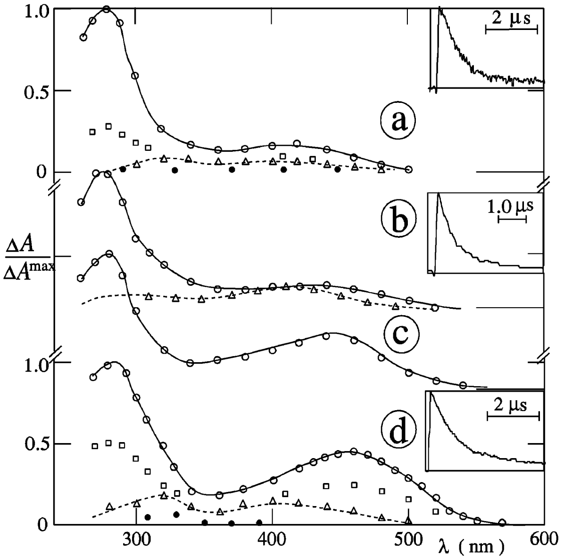


Figure 7. Transient absorption spectra of (a) BQ, (b) MeBQ, (c) 2,5-Me_2BQ, and (d) 2,6-Me_2BQ in argon-saturated aqueous solution at pH 6−7 at 20 ns (○), 1 μs (□), 10 μs (△), and 0.1 ms (●) after the 248-nm pulse; insets: triplet decay at 290 nm.

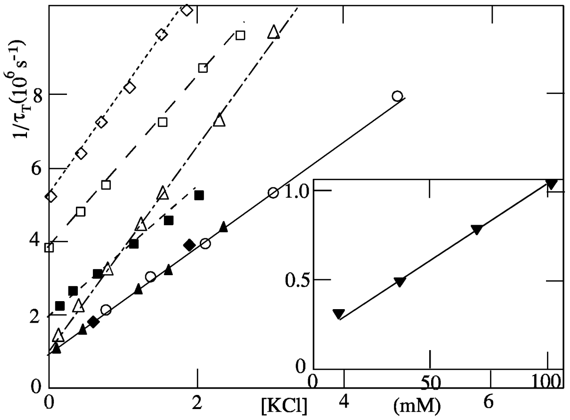


Figure 8. Plots of the inverse lifetime on [KCl], λ_{exc} = 248 nm, in argon-saturated aqueous solution (open) and mixed with acetonitrile (50%, full) for BQ (circles), MeBQ (squares), 2,6-Me_2BQ (triangles), and 2,5-Me_2Q (diamonds) at pH 7; insets: Me_4BQ.

For example, $[Cl^-]_{1/2}$ = 1 mM for BQ, larger for MeBQ and smaller for Me_2BQs; slightly smaller half-concentrations were measured with KBr (Table 3).

The rate constant k_5 for triplet quenching by 2-propanol of BQ in aqueous solution is 1.0×10^8 M^{-1} s^{-1} [22] and smaller for methylated BQs. In 1:1 (vol) mixtures with acetonitrile, k_5 is larger than in water (Table 3). Plots of ΔA_r after triplet decay versus [2-propanol] are shown in Figure 9 for BQ, MeBQ, and 2,6-Me_2BQ in aqueous solution and 1:1 (vol) mixtures with acetonitrile. The curves increase linearly from the initial $\Delta A_r{}^0$ value and approach saturation, $\Delta A_r{}^{max}$. The $\Delta A_r{}^0/\Delta A_r{}^{max}$ ratio, which is taken as a measure of radical formation in neat water with respect to the presence of H-atom donors (Table 5), is generally smaller for BQs in water/2-propanol than in acetonitrile in the presence of TEA or 2-propanol.

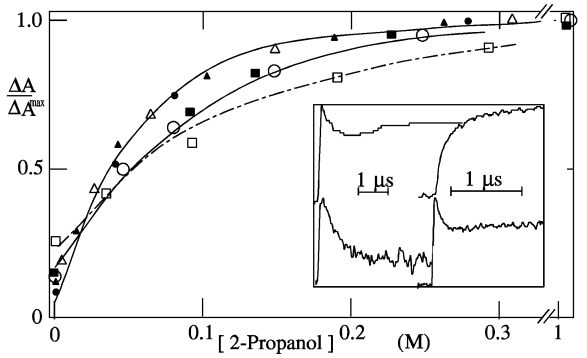


Figure 9. Plots of ΔA_{rad} vs [2-propranol] for BQ (circles), MeBQ (squares), and 2,6-Me_2BQ (triangles) in argon-saturated aqueous solution (open) and mixed with acetonitrile (50%, full) at pH 6−7, λ_{exc} = 248 nm; insets: signals for 2,6-Me_2BQ in the presence of 2-propanol 0.05 M (left) and 1 M (right) at 320 nm (upper) and 420 nm (lower).

TABLE 5: Relative Absorbances, $\Delta A_r{}^0/\Delta A_r{}^{max}$, of Radical Formation for BQs in the Presence of TEA and 2-Propanol[a]

quinone	MeCN/TEA[b]	MeCN/P[b]	MeCN−H_2O/P[c]	MeCN−H_2O/P[d]
BQ	0.2	0.17	0.5	0.1 (0.1)[e]
MeBQ	0.2	0.17	1	0.1
2,5-Me_2BQ			0.3	0.1
2,6-Me_2BQ	0.18	0.25	0.3	0.1
Me_4BQ	1	1	0.5	
$(OMe)_2BQ$		0.4	1	
PhBQ		2	0.3	

[a] Argon-saturated. [b] In acetonitrile, λ_{exc} = 308 nm, cf. ref 25. [c] For acetonitrile−water, 1:1, λ_{exc} = 308 nm. [d] For acetonitrile−water, 1:1, λ_{exc} = 248 nm. [e] Values in parentheses refer to relative conductivity signal, λ_{exc} = 248 nm.

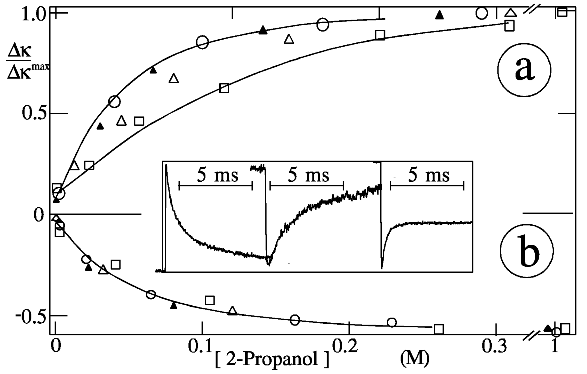


Figure 10. Dependences of the conductivity signal at 0.1 ms on [2-propanol] for BQ (circles), MeBQ (squares), and 2,6-Me_2BQ (triangles) in argon-saturated aqueous solution (open) and mixed with acetonitrile (1%, full) at (a) pH 5 and (b) pH 9, λ_{exc} = 248 nm; insets: conductivity signals for BQ at pH 5, 8, and 9.5 (from left to right).

Transient Conductivity. The conductivity signal of BQs in aqueous solution in the presence of 2-propanol (0.1−2 M) at pH 4−6 is substantial at a few μs after the pulse under both excitation conditions. To diminish the effects caused by self-quenching, data presented here refer to λ_{exc} = 248 nm. The signals decay by second-order kinetics with half-lives in the 1 ms range; examples are shown in Figures 10 and 11 (insets) for BQ and 2,6-Me_2BQ. The signal at 0.01−0.1 ms increases, when 2-propanol is added, from the initial $\Delta\kappa^0$ value to maximum reactivity, $\Delta\kappa^{max}$. In particular, for 2,6-Me_2BQ the peak signal increases by a factor of ca. 50. Similar dependences were found for several BQs (Figure 10a). This shows that photoreduction by alcohols leads to $Q\bullet^-$ and H^+ (see Scheme 3) and indicates that protons are virtually not formed in the absence of a donor. Neutralization at pH 8−10, thereby removing protons from the bulk of solution, causes negative signals (Figure 10b).

The conductivity signals of BQs in mixtures of water with 2-propanol (0.2 M) is substantial at pH 5−6 but low at pH <4.5 (Figure 11). This is due to formation of protons via step 9, forward. The pK_a values for the semiquinone radicals are 4.1,

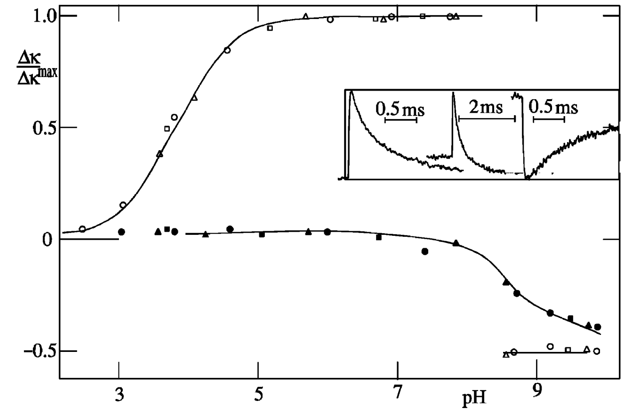


Figure 11. pH dependence of the conductivity signal in the presence of 0.2 M 2-propanol at 0.1 ms (open) and 0.1 s (full) after the 248-nm pulse for BQ (circles), MeBQ (squares), and 2,6-Me_2BQ (triangles) in argon-saturated aqueous solution; insets: signals for 2,6-Me_2BQ at pH 5, 8, and 9.5 (from left to right).

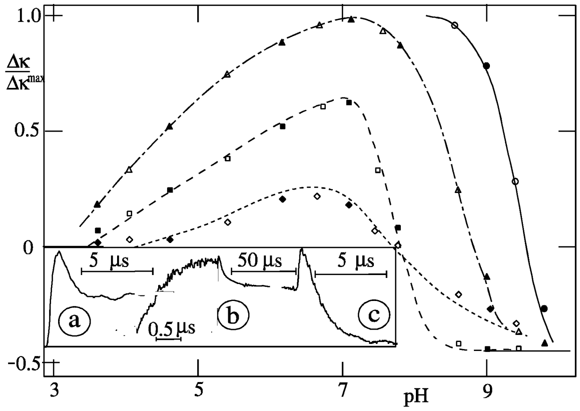
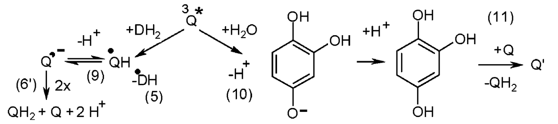


Figure 12. Conductivity signal vs pH for BQ (open) and 2,6-Me_2BQ (full) in argon-saturated aqueous solution in the absence of additives at 0.1 μs (circles), 1 μs (triangles), 10 μs (squares), and 100 μs (diamonds) after the 248-nm pulse; insets: signals for BQ at pH 3.8, 5, and 8 (a−c, respectively).

SCHEME 3



4.45, and 4.6 for BQ, MeBQ, and 2,6-Me_2BQ, respectively.[3,43−45] The neutralization kinetics at pH 8−10 (insets in Figure 11) indicate that a contribution from the radical anion is small.

For all BQs examined, for example, in 100:1 (vol) mixtures of aqueous solution at pH 5−7 with acetonitrile or in neat water, a conductivity signal could be detected on the 0.1−10 ms time scale which, however, is small, when compared to those in the presence of 2-propanol. For BQ, MeBQ, or Me_2BQs in neat aqueous solution, the signal (after triplet decay) is largest at 0.3 μs and pH 6 and becomes negative below pH 8. From the positive to negative conversion of the signal within a few μs in the slightly alkaline pH range a proton is identified as major conducting species (Figure 12). This proton appears for a few microseconds (insets of Figure 12), that is, proton formation is probably not fully resolved due to subsequent fast decay. As competing process, this fast proton intermediacy is also present, but the time resolution is not improved when 2-propanol is added in small concentration (Figure 13). Instead, the signals are much larger, in accordance with the dependence shown in Figure 10. On the other hand, the conductivity signal becomes smaller on addition of KCl, indicating competition of photoinduced proton formation with reaction 3.

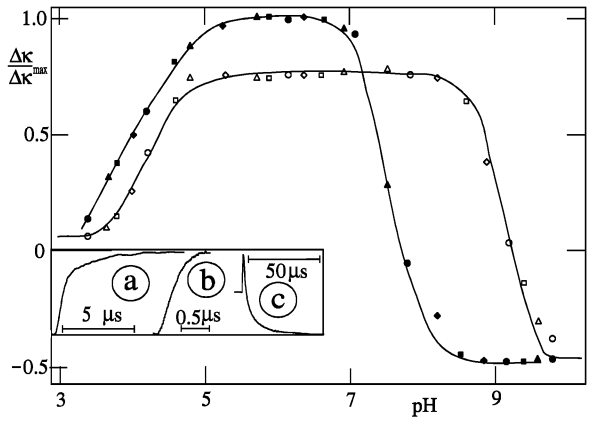


Figure 13. pH dependence of the conductivity signal of BQ (circles), MeBQ (squares), and 2,6-Me_2BQ (triangles) in argon-saturated aqueous solution in the presence of 2-propanol (0.2 M) at 500 ns (open) and 10 μs (full) after the 248-nm pulse; insets: signals for BQ at pH 3.8, 5, and 9 (a−c, respectively).

Discussion

Reactions of the Quinone Triplet with H-Atom Donors. The photoreduction of quinones leads to the semiquinone radical and the eventual products are hydroquinones, QH_2, and acetone, when 2-propanol is the H-atom donor.[3−5] With amines, photoinduced electron transfer yields $Q^{\bullet-}$ and $DH_2^{\bullet+}$ as secondary intermediates. The rate constant for triplet quenching (k_D) of NQ in acetonitrile by *N*,*N*-dimethylamine and TEA, because of appropriate redox properties, is close to the diffusion-controlled limit.[28] The concentration for 50% change, [2-propanol]$_{1/2}$, increases from 0.1 M for BQ or MeBQ to values larger than 10 M for Me_4BQ. For amines the half-concentrations are much smaller, for example, $[TEA]_{1/2} = 0.3$ mM for BQ, because of a larger rate constant.[25] Quenching of the triplet state by the hydroquinone[3,4,8] was avoided for a low overall conversion. Further pathways into $^{\bullet}QH$ are quenching of the triplet state by Q and T−T annihilation under pulsed excitation with $k = 2 \times 10^9$ M^{-1} s^{-1} for Me_4BQ.[8]

Where the triplet state and the semiquinone radical are spectroscopically well-enough separated, for example, for Me_4BQ,[25] PhBQ, and $(OMe)_2BQ$ (Figure 5), reaction 5 (Scheme 1) is accessible for variable donor concentration. In some cases, the absorption signal of the semiquinone radical is much larger than that of T−T absorption, at least in the presence of TEA and 2-propanol or related alcohols in appropriate concentrations.[25] The spectra of $^{\bullet}QH$ and $Q^{\bullet-}$ are only moderately shifted for BQ and derivatives.[3,43−46] The alcohol radical may yield via reaction 7 another semiquinone radical in competition to self-termination 8; the rate constant with 2-propanol is $k_7 = 1.6 \times 10^9$ M^{-1} s^{-1}.[35] Such a two-step reduction, because of reactions 5 and 7, is indicated by the absorption signal for 2,6-Me_2BQ (inset of Figure 9). This second increase was not always observable in mixtures with 2-propanol. The reason is probably that reaction 8 successfully competes under pulsed excitation, in contrast to steady-state conditions. Studies of BQs[25] and AQs[42] in acetonitrile in the presence of DABCO or TEA in appropriate concentrations have shown that the kinetics of conductivity increase, because of formation of H^+ and $Q^{\bullet-}$, and the triplet decay is in accord.

Effects of Water on the Photoreactions. The photoprocesses of BQs in aqueous solution deviate in several aspects from those in the organic phase. In particular, they have not been fully understood for parent BQ or most derivatives in the absence of H-atom donors. The quantum yield (Φ_Δ) of formation of singlet molecular oxygen, $O_2(^1\Delta_g)$ was reported to be ca. 0.1 for BQ and MeBQ in aqueous solution at pH 7.[19] Nevertheless, fluorescence plays virtually no role and Φ_{isc} of most BQs is expected to be large even in water.[3,4] For NQ, Φ_{isc} is not reduced on addition of water to acetonitrile.[28] This was also found for 2,5- or 2,6-Me_2BQ (not shown). The large Φ_d values of BQs at low concentration and in neutral aqueous solution (Table 1) are best interpreted by Φ_{isc} values close to unity. The weak T−T absorption for MeBQ and several BQ derivatives in neutral aqueous solution may be related to a spectroscopically hidden triplet state rather than to a low Φ_{isc} as concluded from the strongly increasing dependence of the ΔA_r values on [2-propanol] in mixtures of water with organic solvents (Figure 9 and Table 5).

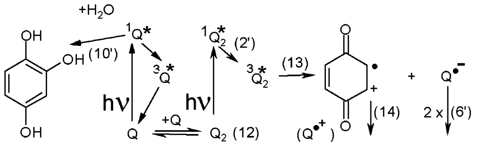
For Me_4BQ in 1:1 mixtures of water with ethanol, it has been reported that the kinetics of conductivity increase and triplet decay correspond.[11] Pulsed excitation of the semiquinone radical for 2-SO_3AQ^- in 2-propanol/water at 308 nm ejected an electron.[41] This ionization was avoided here by applying low enough pulse intensities and conversions, as monitored under conditions, for example, in the absence of acetonitrile, where the solvated electron is observable. The literature values for the triplet lifetime in aqueous solution are rather short, for example, 0.3 μs for MeBQ,[6−8] 0.8−1.2 μs for 2,3-Me_2BQ,[6,7] and 0.8 μs for 2,5-Me_2BQ.[8] Larger values at low concentrations of BQs (Figure 6 and Table 2) are due to better suppression of reaction 4 (Scheme 1). The low radical yield, as shown by the strongly increasing dependence of the ΔA_r and $\Delta\kappa$ values on [2-propanol] (Figures 9 and 10 and Table 5), indicates a different mechanism for BQ and several derivatives in water, not involving the free semiquinone radical.

Suggested Mechanism for Low BQ Concentrations. To account for the photoreactions of BQs at low concentration in the absence of a H-atom donor, a novel charge separation in the lowest triplet state followed by the water addition 10, formation of 1,2,4-trihydroxybenzene, and reaction 11 with Q (Scheme 2) are now suggested.[22] The water-mediated triplet reaction does not involve radicals at all. This mechanism is consistent with the results that the yield of $Q\bullet^-$ is low at pH 5−9 (Figure 9) and the prediction that the observed triplet state is monomeric. Reaction 10 has been proposed for BQ[13] and 2,6-Me_2BQ,[20] but without further details, for example, specification of the excited state.

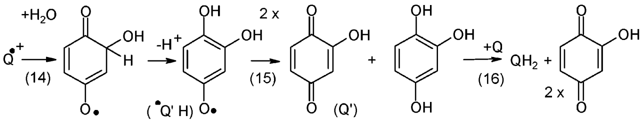
On the basis of the fast conductivity signals of BQ, MeBQ, or 2,6-Me_2BQ in aqueous solution at pH 4−8 (Figure 12), step 10 (Scheme 3) is accompanied by a fast proton intermediacy within a few microseconds. This holds also for those BQs which were examined in mixtures of water with acetonitrile. Moreover, the charge increase is essentially due to a proton, which adds within a few microseconds to the 1,2,4-trihydroxybenzene anion, the $pK_a = 9$.[49] The pK_a of 2-hydroxy-1,4-benzoquinone, Q′, which, however, is not formed in this time range, is 4.2.[46] As competing process, longer lived protons as major conducting species are produced via sequences 5 and 9 (Scheme 3) when 2-propanol is added (Figures 11 and 13). The dianion of trihydroxybenzene has been reported as a suggested intermediate of the hydroxide ion induced oxygenation of BQ to rhodizonate.[50]

The triplet state of BQs is quenched by anions, such as Cl^- (Figure 8). At Cl^- concentrations of <10 mM the effect is due to physical quenching 3 not yielding products in competition to reaction 10 plus 11 (Scheme 2). Moreover, Φ_d strongly decreases as a function of [Cl^-] (Figure 2). The similarity of the half-concentrations $[Cl^-]_{1/2}$ and the calculated $1/(k_3 \times \tau_T)$ values (Table 3) clearly show that the major route of BQs (<1 mM) in aqueous solution originates from the observed triplet state.

SCHEME 4



SCHEME 5



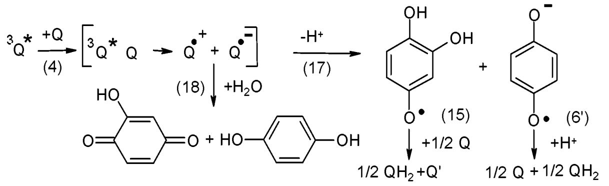
Mechanisms which Can Be Excluded. The most cited possibility for photoreduction in aqueous solution involves OH radicals.[2,3] The photochemistry of 2-SO_3AQ^- or 2,6-$(SO_3)_2AQ^{2-}$ was interpreted by involvement of OH radicals.[37−40] Formation of OH radicals has also been postulated in the photolysis of BQ and other quinones.[1,13−18] However, a free OH radical mechanism has been questioned, on the basis of results with 2,6-$(SO_3)_2AQ^{2-}$ and 2-SO_3AQ^-.[32] In a recent modification of the water oxidation mechanism, the results with MeBQ were interpreted by assuming a hydroxylating intermediate, different from the free OH radical.[21]

In this work, no indication was found for such an intermediate; the triplet state as initial species and the radicals are spectroscopically and kinetically separated. The $\Delta A_r/\Delta A_T$ values of BQ (Figure 3), MeBQ (Table 4), or 2,6-Me_2BQ (Figure 4) in aqueous solution are significantly suppressed with respect to the presence of H-atom donors, indicating less efficient formation of the semiquinone radical. This is supported by the low conductivity signal of BQs in aqueous solution and the increase on addition of 2-propanol (Figure 10). On the other hand, the Φ_d values of BQ, MeBQ, and Me_2BQs in aqueous solution at pH 7 are much larger than in neat acetonitrile (Table 1), indicating efficient nucleophilic water addition with $\Phi_d = 0.5-0.8$.

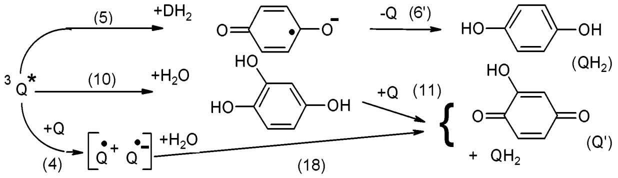
One possibility for the water addition is step 10′ (Scheme 4); it does not involve radicals at all and originates from either the excited singlet or a hidden upper excited triplet state. This reaction, however, is unlikely since fluorescence is not measurable at all[3,4] and the yield of the observed triplet state is virtually not affected by the amount of water (not shown). Even for MeBQ, where the triplet lifetime in aqueous solution is shorter than for other BQs, population of an upper excited triplet state should be excluded.

Involvement of OH radicals in the photolysis of parent BQ in aqueous solution has recently been excluded by von Sonntag and his group; instead, the suggested photoreactions lead via the semiquinone radical to Q and QH_2 and via the 2-hydroxy-1,4-semibenzoquinone radical (•Q′H) to the 2-hydroxy-1,4-benzohydroquinone and eventually into Q′ and QH_2.[22] The mechanism for BQ could involve a triplet exciplex and two radicals, $Q\bullet^-$/•QH and •Q′H. Decay of the latter occurs via reactions 15 and 16 (Scheme 5). However, a crucial point is the effect of concentration on the triplet decay. Two triplet

SCHEME 6



SCHEME 7



exciplexes with carbonyl and benzenoid ring adducts of electron-donating water molecules have been considered for 2,6-$(SO_3)_2$-AQ^{2-}.[40]

Another possibility is a monomer−dimer equilibrium 12; electron-transfer step 13 within the dimer triplet could account for formation of radical $Q\bullet^-$. This pathway via free radical ions is illustrated in Scheme 4 for a ground-state dimer. The products eventually derived from the radical cation are QH_2 and Q′. No indication for a dimer could be found in the absorption spectrum, when the BQ or 2,6-Me_2BQ concentrations were varied between 0.01 and 10 mM. At least for BQ derivatives at low concentrations (<0.3 mM), ground state and triplet dimers cannot play a role.

Possible Mechanism for Higher BQ Concentrations. A further possibility is an electron transfer 4 from Q to $^3Q^*$. An analogous pathway into radical ions is T−T annihilation under pulsed excitation, $^3Q^* + {}^3Q^*$, and this interaction has previously been considered for Me_4BQ.[8] The linear plots of $1/\tau_T$ versus [quinone] for 2,6-Me_2BQ and the curved dependence for BQ (Figure 6) accounts for the radical cation derived products at quinone concentrations larger than 1 mM. The possible pathway of BQs into free radical ions are steps 4 and 17 (Scheme 6). The radical cation/anion mechanism, however, conflicts with the findings that the yield of $Q\bullet^-$ is low. The eventual products are of QH_2 and Q′ type[22] and reaction 18 (Scheme 6) can be postulated. Reaction 18 competes successfully with electron back transfer, when the Φ_d values are as large as 0.5−0.8. In addition, the possibility of H-atom abstraction from the solvent, such as acetonitrile, 5 (Scheme 7), establishes another pathway, which however, should change the product pattern into higher amounts of QH_2 with respect to Q′.

A hypothesis via reaction 4 (Schemes 6 and 7) has been rejected for 2,6-$(SO_3)_2AQ^{2-}$[37−40] since no increasing dependence of $1/\tau_T$ versus [quinone] was found, that is, the rate constant k_4 is too low in aqueous solution. However, this is not generally the case, for example, the rate constant in aqueous solution is larger than 5×10^9 M^{-1} s^{-1} for BQ[22] and 4×10^9 M^{-1} s^{-1} for NQ.[28] This is in agreement with k_4 values (Table 3), obtained from the slopes of Figure 6. The model can account for products of BQs at moderate or higher concentrations, taking $k_4 = 1 \times 10^9$ M^{-1} s^{-1} or larger and a limiting τ_T of 10 μs. Then, a concentration of 0.1 mM is sufficient for more than 50% reaction of the observed triplet state under continuous irradiation. One could argue that for BQ or MeBQ, Φ_{isc} is low in water and an upper excited triplet is involved. However, the yield of observed triplet state in either water or acetonitrile is very similar in these and most other cases, Φ_d is up to unity in water and smaller than 0.1 in acetonitrile (Table 1). Therefore, the observed triplet state is an intermediate in the major part of the photoreaction of BQs in aqueous solution. Formation of separated radical cations and anions is inconsistent with the low yield of $Q\bullet^-$ as observable species for BQ, MeBQ, and Me_2BQs in water and 1:1 mixtures with polar solvents (Figures 3 and 4). Nevertheless, the overall photoreduction is efficient and the Φ_d values are much larger than in neat acetonitrile (Table 1).

Effects of Solvent and Substituent. Several attempts with organic solvents as additives to BQ in water, for example, dioxane, dimethyl sulfoxide, dimethylformamide, butyronitrile, or formamide, failed since H-atom abstraction is enhanced and absorption of the triplet is completely overlapped by that of the semiquinone radical. This is also gradually the case with acetonitrile, which for MeBQ has already been reported to be somewhat susceptible to abstraction.[21] For BQ and MeBQ even in neat acetonitrile, because of Φ_d values of 0.05−0.1 (Table 1), photoreduction has to be considered. On the other hand, *tert*-butyl alcohol does not behave as other alcohols, where H-atom abstraction is commonly efficient. Nevertheless, *tert*-butyl alcohol is not an inert solvent, as shown by semiquinone radical formation. The results with the two fluoroalcohols (Table 4) and *tert*-butyl alcohol are rather similar. The latter weakly nucleophilic polar solvents favor H bonds to oxygen and stabilize excited π,π states and ions.[47]

The reactivity of the triplet state of BQs with 2-propanol is quite large and the rate constant k_5 is strongly reduced by four methyl groups in acetonitrile[25] and also in water−acetonitrile. As indicators in the presence of water, both the triplet lifetime and the relative radical yield (Tables 4 and 5) as well as Φ_d (Table 1) can be used. The polarity may affect the triplet lifetime for BQ and 2,6-Me_2BQ, but the variation is only gradual for Me_4BQ. Me_3BQ and PhBQ are placed between and the smallest effects were obtained for $(OMe)_2BQ$. Generally, the effects of water on the triplet and radical properties are small for these BQs, in contrast to parent BQ, MeBQ, and the two Me_2BQs. The shortest triplet lifetime was found in water and a significant shortening on addition of water to “inert” organic solvents.

Conclusions

The suggested water-mediated photoprocesses of BQ and derivatives, such as MeBQ and Me_2BQs, are either step 10 (Scheme 7) of reaction of the lowest triplet state with water at low concentrations or one at high BQ concentrations which is induced by self-quenching of the triplet state followed by electron transfer 18. In both pathways, virtually no free radicals are involved for BQs. A third free radical pathway, 5 and 6′ (Scheme 7), as minor step contributes in mixtures with “nearly inert” organic solvents even in the absence of a H-atom donor.

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References and Notes

(1) Lubitz, W.; Lendzian, F.; Bittl, R. *Acc. Chem. Res.* **2002**, *35*, 313.

(2) Burie, J.-R.; Boussac, A.; Boullais, C.; Berger, G.; Mattioli, T.; Mioskowski, C.; Nabedryk, E.; Breton, J. *J. Phys. Chem.* **1995**, *99*, 4059 and references therein.

(3) Bruce, J. M. In *The Chemistry of the Quinoide Compounds*; Patei, S., Ed.; Wiley: New York, 1974; p 465.

(4) Maruyama, K.; Osuka, A. In *The Chemistry of the Quinoide Compounds*; Patei, S., Rappaport, Z., Eds.; Wiley: New York, 1988; p 737 and refs cited therein.

(5) Schulte-Frohlinde, D.; von Sonntag, C. *Z. Phys. Chem. N. F.* **1965**, *45*, 314.

(6) Kemp D. R.; Porter, G. *Proc. R. Soc. London, A* **1971**, *326*, 117.

(7) Nafisi-Movaghar, J.; Wilkinson, F. *J. Chem. Soc., Faraday Trans.* **1970**, *66*, 2268.

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

(9) Amouyal, E.; Bensasson, R. *J. Chem. Soc., Faraday Trans. 1* **1976**, *72*, 1274.

(10) Rossetti, R.; Brus, L. E. *J. Am. Chem. Soc.* **1986**, *108*, 4718.

(11) Scheerer, R.; Grätzel, M. *J. Am. Chem. Soc.* **1977**, *99*, 865.

(12) Scaiano, J. C.; Neta, P. *J. Am. Chem. Soc.* **1980**, *102*, 1608.

(13) Shirai, M.; Awatsuji, T.; Tanaka, M. *Bull. Chem. Soc. Jpn.* **1975**, *48*, 1329.

(14) Beck, S. M.; Brus, L. E. *J. Am. Chem. Soc.* **1982**, *104*, 1103; 4789.

(15) Ononye, A. I.; McIntosh, A. R.; Bolton, J. R. *J. Phys. Chem.* **1986**, *90*, 6264.

(16) Ononye, A. I.; Bolton, J. R. *J. Phys. Chem.* **1986**, *90*, 6270.

(17) Parker, A. W.; Hester, R. E.; Phillips, D.; Umapathy, S. *J. Chem. Soc., Faraday Trans.* **1992**, *88*, 2649.

(18) Alegría, A. E.; Ferrer, A.; Sepúlveda, E. *Photochem. Photobiol.* **1997**, *66*, 436.

(19) Alegría, A. E.; Ferrer, A.; Santiago, G.; Sepúlveda, E.; Flores, W. *J. Photochem. Photobiol., A: Chem.* **1999**, *127*, 57.

(20) Mazellier, P.; Bolte, M. *J. Photochem. Photobiol., A: Chem.* **1996**, *98*, 141.

(21) Pochon, A.; Vaughan, P. P.; Gan, D.; Vath, P.; Blough, N. V.; Falvey, D. E. *J. Phys. Chem. A* **2002**, *106*, 2889.

(22) von Sonntag, J.; Mvula, E.; Hildenbrand, K.; von Sonntag, C. *Chem. Eur. J.*, in press.

(23) Kurien, K. C.; Robins, P. A. *J. Chem. Soc. B* **1970**, 855.

(24) (a) Amouyal, E.; Bensasson, R. *J. Chem. Soc., Faraday Trans. 1* **1977**, *73*, 1561. (b) Sasaki, S.; Kobori, Y.; Aklyama, K.; Tero-Kubota, S. *J. Phys. Chem. A* **1998**, *102*, 8078.

(25) Görner, H. *Photochem. Photobiol.* **2003**, *8*, 440.

(26) (a) El'tsov, A. V.; Studzinskii, O. P.; Grebenkina, V. M. *Russ. Chem. Rev.* **1977**, *46*, 93. (b) Fisher, G. J.; Land, E. J. *Photochem. Photobiol.* **1983**, *37*, 27. (c) Amada, I.; Yamaji, M.; Sase, M.; Shizuka, H. *J. Chem. Soc., Faraday Trans.* **1995**, *99*, 2751. (d) Yamaji, M.; Kimura, M.; Shizuka, H. *Phys. Chem. Chem. Phys.* **1999**, *1*, 1859.

(27) Ci, X.; da Silva, R. S.; Goodman, J. L.; Nicodem, D. E.; Whitten, D. G. *J. Am. Chem. Soc.* **1988**, *110*, 8548.

(28) Amada, I.; Yamaji, M.; Tsunoda, S.; Shizuka, H. *J. Photochem. Photobiol., A: Chem.* **1996**, *95*, 27.

(29) Mac, M.; Wirz, J. *Photochem. Photobiol. Sci.* **2002**, *1*, 24.

(30) Loeff, I.; Goldstein, S.; Treinin, H.; Linschitz, H. *J. Phys. Chem.* **1991**, *95*, 4423.

(31) (a) Wilkinson, F. *J. Phys. Chem.* **1962**, *66*, 2569. (b) Hulme, B. E.; Land, E. J.; Phillips, G. O. *J. Chem. Soc., Faraday Trans.* **1972**, *68*, 1992. (c) Moore, J. N.; Phillips, D.; Nakashima, N.; Yoshihara, K. *J. Chem. Soc., Faraday Trans. 2* **1986**, *82*, 745. (d) Wakisaka, A.; Ebbesen, T. W.; Sakuragi, H.; Tokumaru, K. *J. Phys. Chem.* **1987**, *91*, 6547.

(32) Loeff, I.; Treinin, S.; Linschitz, H. *J. Phys. Chem.* **1983**, *87*, 2536.

(33) Loeff, I.; Treinin, A.; Linschitz, H. *J. Phys. Chem.* **1984**, *88*, 4931.

(34) Loeff, I.; Rabani, J.; Treinin, A.; Linschitz, H. *J. Am. Chem. Soc.* **1993**, *115*, 8933.

(35) Kausche, T.; Säuberlich, J.; Trobitzsch, E.; Beckert, D.; Dinse, K. P. *Chem. Phys.* **1996**, *208*, 375.

(36) Geimer, J.; Beckert, D. *Chem. Phys. Lett.* **1998**, *288*, 449.

(37) (a) Clark, K. P.; Stonehill, H. I. *J. Chem. Soc., Faraday Trans. 1* **1972**, *68*, 577. (b) Clark, K. P.; Stonehill, H. I. *J. Chem. Soc., Faraday Trans. 1* **1972**, *68*, 1676.

(38) Harriman, A.; Mills, A. *Photochem. Photobiol.* **1981**, *33*, 619.

(39) Phillips, D.; Moore, J. N.; Hester, R. E. *J. Chem. Soc., Faraday Trans. 1* **1986**, *82*, 2093.

(40) Moore, J. N.; Phillips, D.; Hester, R. E. *J. Phys. Chem.* **1988**, *92*, 5619.

(41) Goez, M.; Zubarev, V. *J. Phys. Chem. A* **1999**, *103*, 9605.

(42) Görner, H. *Photochem. Photobiol.* **2003**, *77*, 171.

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

(44) (a) Rao, P. S.; Hayon, E. *J. Phys. Chem.* **1973**, *77*, 2274. (b) Meisel, D.; Czapski, G. *J. Phys. Chem.* **1975**, *79*, 1503. (c) Steenken, S., Neta, P. In *The Chemistry of Phenols*; Rappaport, Z. Ed.; Wiley: New York, 2003; p 1107.

(45) Roginsky, V. A.; Pisarenko, L. M.; Bors, W.; Michel, C.; Saran, M. *J. Chem. Soc., Faraday Trans.* **1998**, *94*, 1835.

(46) Schuchmann, M. N.; Bothe, E.; von Sonntag, J.; von Sonntag, C. *J. Chem. Soc., Perkin Trans. 2* **1998**, 791.

(47) (a) Suzuki, T.; Lin, F.-T.; Priyadashy, S.; Weber, S. G. *J. Chem. Soc. Chem., Chem. Commun.* **1998**, 2685. (b) Ortica, F.; Romani, A.; Favaro, G. *J. Phys. Chem. A* **1999**, *103*, 1335.

(48) Fisher, G. J.; Johns, H. E. In *Photochemistry and Photobiology of Nucleic Acids*; Wang, S. Y., Ed.; Academic Press: New York, 1976; p 169.

(49) Qin, L.; Tripathi, G. N. R.; Schuler, R. H. *J. Phys. Chem.* **1987**, *91*, 1905.

(50) Fukuzumi, S.; Yorisue, T. *J. Am. Chem. Soc.* **1991**, *113*, 7764.