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ARTICLES

Oxygen Uptake upon Photolysis of 1,4-Benzoquinones and 1,4-Naphthoquinones in Air-Saturated Aqueous Solution in the Presence of Formate, Amines, Ascorbic Acid, and Alcohols

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The effects of oxygen in the photoreduction of 1,4-benzoquinone (BQ), 1,4-naphthoquinone (NQ), and a series of derivatives were studied in aqueous solution in the presence of acetonitrile and formate, aliphatic amines, e.g., EDTA or triethylamine, ascorbic acid, and alcohols, e.g., methanol or 2-propanol. The quinone triplet state is quenched, whereby the semiquinone and donor radicals are formed which react subsequently with oxygen. The overall reaction is oxidation of the donors and conversion of oxygen via the hydroperoxyl/superoxide radical into hydrogen peroxide. The quantum yield (Φ_{-O_2}) of this oxygen uptake changes in 2-propanol−water (1:10) from <0.01 for BQ to $\Phi_{-O_2} = 0.5-0.8$ for NQ. Generally Φ_{-O_2} increases with increasing donor concentration. The specific properties of quinone structure, the radical equilibria and reactivity, and the concentration dependences are discussed.

Introduction

Photoreduction of quinones takes place in a variety of solvents, whereby the semiquinone radical ($HQ^•$) and a solvent radical are formed via H atom transfer.[1−3] Amines function as donors for electron transfer with the radical anion ($Q^{•-}$) as intermediate.[4−6] The photochemistry of 1,4-benzoquinone (BQ), 1,4-naphthoquinone (NQ), 9,10-anthraquinone (AQ), and derivatives has been the subject of intensive investigations.[7−21] The photoreduction in nonaqueous solution leads from the quinone triplet state via the semiquinone radicals into hydroquinones: QH_2.[1−3] The photoreactions of parent BQ or 2,5-dimethyl-BQ (Me_2BQ) in aqueous solution are generally different, as they lead to both 2-hydroxy-1,4-benzoquinones (HOQs) and the corresponding QH_2s.[9,12,14,20] The OH radical was believed to be an intermediate in the photolysis of quinones in aqueous solution,[7,8] but this has been excluded for BQ, 2,6-dichloro-BQ, and Me_nBQ, $n = 1-3$.[12−15,20] Hydroxyquinones are also the additional photoproducts of NQ[16,17] and AQs[11] in aqueous solution.

The $HQ^•/Q^{•-}$ radicals of *p*-quinones have been characterized by radiation chemistry,[22−29] but the relationship between oxygen and the radicals has been described in the literature only for a few quinones. The photoinduced intermolecular H atom and/or electron transfer from ascorbic acid as one-electron reductant to the triplet state of suitable *p*-quinones in acetonitrile/water has been reported.[19,21] The features of the hydroperoxyl/superoxide ($HO_2^•/O_2^{•-}$) radicals are known from thermal reactions of QH_2s with oxygen and ascorbic acid in aqueous solution.[30−35] The photodynamic damage of a sensitizer by oxygen generally refers to electron transfer (type I) and energy transfer (type II) yielding $HO_2^•/O_2^{•-}$ radicals and singlet molecular oxygen, $O_2(^1\Delta g)$, respectively.[36]

Recently, the photoinduced O_2 uptake was studied for a series of ketones in air-saturated aqueous solution in the presence of H atom donors, such as alcohols and formate, and electron donors, such as ascorbic acid and aliphatic amines.[37] A close relationship was found between ketones and AQs,[38] as the radical anion is quenched by oxygen, in contrast to $Q^{•-}$ of parent BQ.[22−29] In fact, an equilibrium between $Q^{•-}$ and $O_2^{•-}$ radicals is established in aqueous solution and the position depends on the redox conditions. On the basis of a better understanding of the photochemical properties of BQs and NQs in aqueous solution it appears attractive to study the photodynamic action of oxygen toward donors, when sensitized by quinones.

Here, the photoinduced O_2 uptake was studied for Me_nBQ, $n = 0-4$, chloranil (Cl_4BQ) and several NQs in mixtures of water with 2-propanol, methanol, acetonitrile, and in the presence of formate, ethylenediaminetetraacetate (EDTA), triethylamine (TEA), and ascorbic acid. The quantum yields of O_2 consumption (Φ_{-O_2}), due to the conversion of O_2 into H_2O_2, are presented using continuous 280, 313, or 366 nm irradiation and compared with results from quenching of the triplet state of suitable *p*-quinones by these additives and the semiquinone radical by oxygen using time-resolved UV−vis spectroscopy at 248 or 308 nm. Oxygen interacts via quenching of the triplet state and scavenging of the semiquinone and donor radicals.

Experimental Section

Cl_2NQ, BrNQ, and MeONQ refer to substituted NQs: 2,3-dichloro-, 2-bromo-, and 2-methoxyNQ, respectively. The compounds (EGA, Sigma) and solvents (Merck, Fluka) were as received and/or the same as previously[6,19] and water was from a Millipore milliQ system. The absorption spectra were monitored on a UV/vis spectrophotometer (HP, 8453). For photoconversion the 254 nm line of a Hg low-pressure lamp

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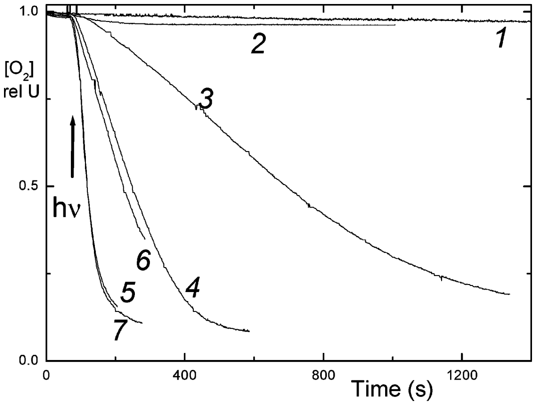


Figure 1. Plots of the O_2 concentration vs time for irradiation at 313 nm of Me_4BQ in air-saturated acetonitrile/water (1:1, vol, curve 1) and in the presence of formate (1 M, curve 2) and for NQ in acetonitrile/water (1:10) and formate (0.002, 0.02, and 0.2 M, curves 3−5) and for BrNQ/formate (0.03 and 1 M, curves 6 and 7).

and for irradiation at $\lambda_{irr} = 280$, 313, and 366 nm a 1000 W Hg−Xe lamp and a monochromator were used. The absorbances around 280 nm were larger than 3, corresponding to BQ concentrations of >0.3 mM. The molar absorption coefficients of BQ and NQ in acetonitrile at 254 nm are $\epsilon_{254} = 1.6 \times 10^4$ and 3×10^4 M^{-1} cm^{-1}, respectively. The oxygen concentration prior to and upon photolysis was determined by a Clark electrode (Hansatech). The air-saturated alcohol/water solutions were at pH 5−8 (unbuffered) and for the ascorbic acid solutions pH 2−3; alternatively, phosphate buffer was added. When the substrates in air-saturated aqueous solution are kept in the dark, the oxygen concentration remains constant. Virtually no increase was found, when the amount of added alcohol was below 10%, and the signal increased only by ca. 20% when mixed with acetonitrile (1:1, vol).[38] The relative yield of oxygen consumption was determined from the slope of the oxygen concentration vs irradiation time. As actinometers at 280 and 313/366 nm uridine and aberchrome-540 were used, respectively.[39] The error in this quantum yield is ± 30%. On the basis of competition kinetics of quenching of the acceptor triplet state by either oxygen or the donor it is appropriate to keep the ascorbic acid concentration low (at 1 or 10 mM) and the 2-propanol concentration high (in the 1−7 M range). For comparison, the photoinduced O_2 consumption was examined for benzophenone/2-propanol (1 M) in air-saturated aqueous solution. Quantum yields $\Phi_{-O_2} = 0.6$ and 0.8 were obtained from plots of the O_2 concentration vs time for irradiation at 280 and 313 nm, respectively.[38] 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) and an Archimedes 440 computer for data handling was used as in previous work.[17−19] The rate constants for triplet quenching by oxygen were obtained taking the inverse lifetimes under air and argon and 0.27 mM as oxygen concentration in air-saturated aqueous solution. The samples were air-saturated unless otherwise indicated, and the measurements refer to 24 °C.

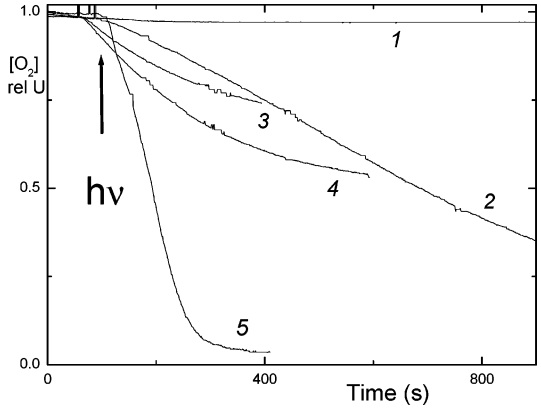


Figure 2. Plots of the O_2 concentration vs time for irradiation at 313 nm of Me_4BQ in air-saturated acetonitrile/water (1:1) in the presence of amines: (0.1 and 10 mM TEA, curves 1 and 2, and 10 mM EDTA, curve 3); curves 4 and 5 refer to NQ in acetonitrile/water (1:10) and 0.2 and 2 mM EDTA.

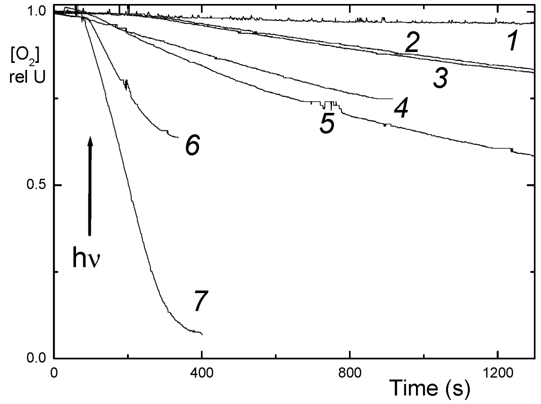


Figure 3. Plots of the O_2 concentration vs time for irradiation at 313 nm in air-saturated acetonitrile/water (1:10, vol) in the presence of ascorbic acid (10 mM, BQ, curve 1, MeBQ, curve 2, Me_2BQ, curve 3, Me_4BQ, curve 4), and 0.01, 0.1, and 1 mM for NQ (curves 5−7).

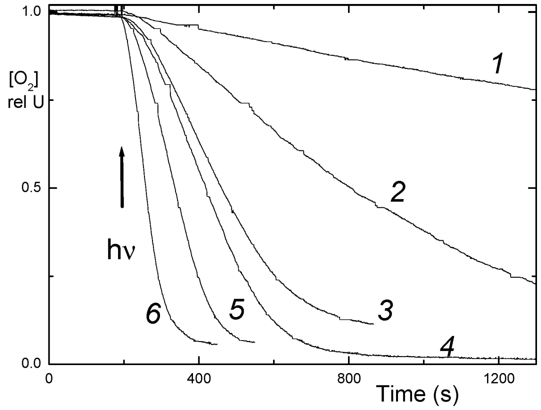


Figure 4. Plots of the O_2 concentration vs time for irradiation at 313 nm of NQ in air-saturated acetonitrile/water (1:10, curve 1) in the presence of 2-propanol (0.001 M, curve 2, 0.01 M, curve 3, 0.03 M, curve 4, 0.1 M, curve 5, and 1 M, curve 6).

Results and Discussion

Photoinduced Oxygen Consumption. The signal from the Clark electrode as measure of the O_2 concentration decreases with time upon UV irradiation at 280, 313, or 366 nm of quinones in air-saturated aqueous solution or in mixtures with acetonitrile in the presence of a donor. Examples of these plots are shown in Figures 1−5 for selected quinone/donor/concentration systems. The oxygen concentration is nearly constant in the dark and decreases upon photolysis in a specific way. The plot of the O_2 concentration vs irradiation time is initially downward curved, approaches a major linear part, and levels off. The slope of the linear part is taken to be proportional to the quantum yield of the O_2 consumption: Φ_{-O_2}. The values using $\lambda_{irr} = 280$, 313, or 366 nm are listed in Table 1. The results for $\lambda_{irr} = 254$ nm are not shown as they are virtually the same as for 280 nm. The dependence of Φ_{-O_2} as a logarithmic

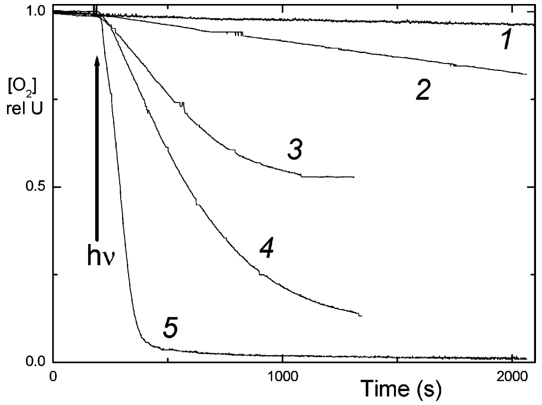
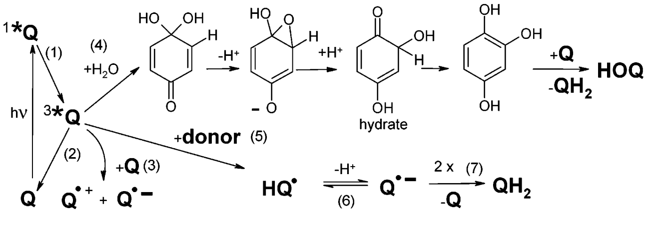


Figure 5. Plots of the O_2 concentration vs time for irradiation at 313 nm in air-saturated acetonitrile/water in the presence of alcohols: for Me_4BQ (1:1) 2-propanol (0.1 M, curve 1, 5 M, curve 2) for NQ (1:10) *tert*-butanol (10 M, curve 3), and for BrNQ (1:10) 2-propanol (0.1 M, curve 4, 5 M, curve 5).

function of the donor concentration is sigmoidal. Examples are shown in Figures 6 and 7 for characteristic cases. Generally, Φ_{-O_2} is markedly larger in the presence of a donor in an appropriate concentration than without the donor. The reason for the oxygen effect is the overall photoconversion of O_2 into hydrogen peroxide. This has recently been documented for AQ.[38]

Photoreactions in the Absence of Additives. The triplet lifetimes (τ_T) of Me_3BQ, Me_4BQ, Cl_4BQ, and most NQs in argon-saturated acetonitrile−water (1:10, vol) are a few microseconds at low concentrations (Table 2). However, for a few cases, e.g., BQ, MeBQ, and NQ, τ_T is shorter than 1 μs. Excitation of Me_nBQs in an acetonitrile/water mixture by 248 or 308 nm laser pulses produces the lowest triplet state ($^{3*}Q$) with a high quantum yield of intersystem crossing Φ_{isc} and absorption maxima at $\lambda_T = 320$ and 480 nm, $n = 3,4$.[13] Decay of the $^{3*}Q$ state in oxygen-free aqueous solution occurs via reaction 2, but several competing reactions may also be considered: reaction 3 with the quinone itself, quenching by water, reaction 4, and a donor via H atom abstraction or electron transfer, reaction 5, can play a role (Scheme 1). Equilibrium 6 is established in aqueous solution, having $pK_a = 4.2$ for parent BQ and many derivatives[29] The semiquinone radical was observed by photolysis and reacts via 7 into QH_2s.[4−6,9] Photoreaction 4 of nucleophilic water addition to the triplet state of BQ yields a hydrate and eventually HOQ without involving free radicals, apart from the last step, where the corresponding trihydroxybenzene reacts with the quinone via non-observable radicals into the two products.[13,14] Finally, the radical cation ($Q^{\bullet +}$), if formed, yields HOQ, e.g., for BQ.[14] Formation of OH radicals in the photolysis of quinones in aqueous solution had been considered,[7,8] but it has been excluded for BQs.[12−15,20] One striking result is that addition of *tert*-butanol, the typical scavenger of OH radicals, did not change the EPR spectrum after photolysis of BQ in the presence of a spin trap.[14] Quinone radicals, formed by the self-quenching reaction 3, could play a role at higher concentrations. Generally, this is not significant with respect to semiquinone radical formation via reaction 5, when an appropriate donor is applied. Oxygen and donors change the mechanism, see below.

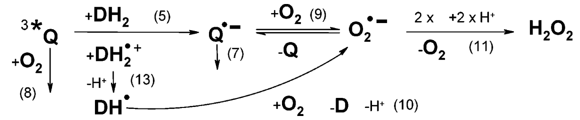
SCHEME 1



Photoreactions with Oxygen and Donors. The transient absorption spectra of various quinones in argon-saturated acetonitrile−water mixtures in the presence of 2-propanol[13,14] or ascorbic acid[19] are essentially comparable, as they reveal initially the triplet state and then the $HQ^{\bullet}/Q^{\bullet -}$ radical. The rate constants for reaction 5 of triplet quenching by a donor are compiled in Table 3. Scheme 2 illustrates the cases of electron transfer. In competition, oxygen quenches the $^{3*}Q$ state, reaction 8, whereby singlet molecular oxygen is formed.[6,8] The rate constants for quenching of the triplet state by oxygen change with structure, $k_8 = (0.3-1.5) \times 10^9$ M^{-1} s^{-1} in acetonitrile−water (1:1), corresponding to $\tau_T = 0.1-2$ μs under air (Table 2). Only for MeBQ is τ_T shorter than 0.3 μs. Reaction 8 and H atom abstraction or electron transfer, reaction 5, compete and can be influenced by the donor concentration. $P_D = k_5[D]/(k_5[D] + k_8[O_2])$ is a measure of the extent of triplet quenching by the donor in air-saturated aqueous solution. This defines a half-concentration $[D]_{1/2} = 1/(\tau_T \times k_5)$ for quenching by the donor (Table 4). In order to successfully compete with triplet quenching 8 by oxygen, the donor concentration should be larger than $[D]_{1/2}$. $P_D = 0.5$ for $[D] = [D]_{1/2}$.

Oxygen is also involved in quenching of the $Q^{\bullet -}$ radical, but equilibrium 9 has to be considered for quinones in aqueous solution. Pulsed 308 nm photolysis of semiquinone radicals of NQs and AQs reveals reaction 9 in competition to reaction 7. From pulse radiolysis studies quenching of the semiquinone radical by oxygen is well-known, the rate constant is $k_9 = 5 \times 10^4$, $(0.3-2) \times 10^8$, $(2-4) \times 10^7$, 4×10^7, 1×10^9, and 5×10^8 M^{-1} s^{-1} for BQ, Me_2BQs, NQ, MeNQ, AQ, and AQ-2-sulfonic acid, respectively.[10,23,24,26] The one-electron-transfer equilibria of a few quinone radicals are known, the rate constant k_{-9} is $(2-3) \times 10^8$ M^{-1} s^{-1} for Me_4BQ or MeNQ.[23] K_9 is <0.01 for BQ but large for NQ. The final reactions depend on pH, as $HO_2^{\bullet}/O_2^{\bullet -}$ has $pK_a = 4.7$.[32,33]

SCHEME 2



Photoreactions with Oxygen and Formate. Electron-transfer 5 yields $CO_2^{\bullet -}$, which reacts with oxygen via electron-transfer 10 in Scheme 3. One step for H_2O_2 formation is reaction 11, another is reaction 12.

$$Q^{\bullet -} + O_2^{\bullet -} + 2H^+ \rightarrow Q + H_2O_2 \qquad (12)$$

Reaction 10a occurs with $k_{10} = 4 \times 10^9$ M^{-1} s^{-1}.[40] Plots of the O_2 concentration vs irradiation time (313 nm) in presence of HCO_2^- are shown for Me_4BQ and NQs (Figure 1). The maximum quantum yield is $\Phi_{-O_2} = 0.6$ (Table 1). The Φ_{-O_2} values as a function of log [formate] have a sigmoidal shape (Figure 6). The reactions of formate ion with triplets of AQ-2-sulfonate, NQ, and benzophenones have been studied.[9,10] For quenching by formate using benzil and benzophenone $k_5 = 3 \times 10^7$ and 1×10^8 M^{-1} s^{-1}, respectively.[37] Similar k_5 values were found for NQ. Competing triplet quenching occurs via H atom transfer reaction 5 and energy transfer reaction 8.

Photoreactions with Oxygen and Amines. With aliphatic amines, electron-transfer reaction 5 is operative. The pH

TABLE 1: Quantum Yield of Oxygen Consumption in the Presence of Formate, Amines, Ascorbic Acid, and Alcohols[a]

quinone	λ_{irr} (nm)	none	formate	TEA	EDTA	ascorbic acid	2-propanol
BQ	313	<0.001	<0.01		0.01	0.04	0.02, 0.02[b]
Me_2BQ	313	<0.01				0.05	0.03
Me_3BQ	313	<0.01		0.1	0.1	0.06	0.03, 0.02[b]
Me_4BQ	313	<0.01			0.08	0.15	0.1
	366	0.01			0.06		0.07
NQ	280	<0.02		*d*		0.3	0.5 (0.3)[c]
	313	0.04	0.6	*d*		0.25	0.8 (0.6)
	366	0.06[e]		*d*	0.6	0.28	0.7
MeNQ	313	0.03	0.5	0.2	0.1	0.5	0.7 (0.6)
Cl_2NQ	313	0.01	0.1	0.4		0.4	0.1
BrNQ	313	0.01		0.3	0.3	0.3	0.2
MeONQ	313	0.01	0.1			0.3	0.4 (0.3)
AQ[f]	313	<0.02	0.08	0.2	0.5	0.6	0.6

[a] In air-saturated acetonitrile−water (1:10), pH 7 for formate (0.3 M), EDTA (0.03 M) and 2-propanol (7 M), 11.5−12.5 for TEA (0.03 M), and 2−3 for ascorbic acid (0.01 M). [b] Using 280 nm. [c] In parentheses: methanol. [d] Thermal reaction. [e] Same value in *tert*-butanol. [f] Taken from ref 38.

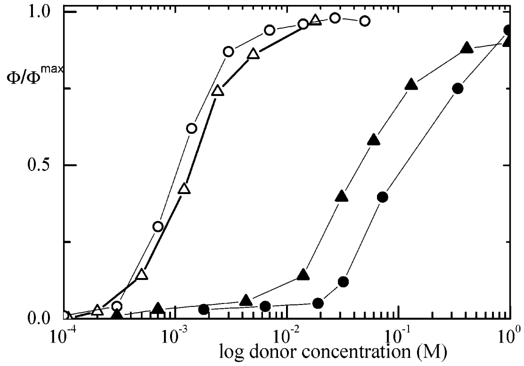


Figure 6. Semilogarithmic plots of the quantum yield Φ_{-O_2}. as a function of the formide (▲), ascorbic acid (○), and 2-propanol (●) concentrations (log scale) for NQ in air-saturated acetonitrile/water (1:10), λ_{irr} = 313 nm; open triangles refer to EDTA, λ_{irr} = 366 nm.

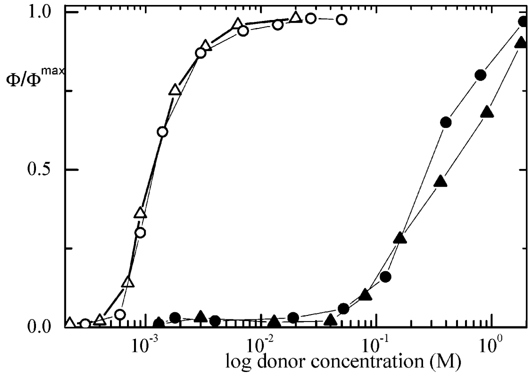


Figure 7. Semilogarithmic plots of the quantum yield Φ_{-O_2}. as a function of the ascorbic acid (open) and 2-propanol (full) concentrations (log scale) for BrNQ (triangles) and OMeNQ (circles) in air-saturated acetonitrile/water (1:10), λ_{irr} = 313 nm.

dependence of k_5 for Me_4BQ and TEA is well-known: the maximum value is in the alkaline range.[5] This has been confirmed for ketones.[37] The decrease of the O_2 concentration with time are shown in Figure 2. The maximum value of the NQs/amines system is $\Phi_{-O_2} = 0.6$ (Table 1). Note that the thermal stability becomes significant at pH 12. A similar value was obtained for NQ/EDTA when the pH was kept at 7. Step 9 of quenching of the quinone radical anion by oxygen may yield $O_2^{\bullet-}$.[38] The amine radical cation deprotonates at pH 7, reaction 13 (Scheme 2), and can be scavenged by oxygen.[41] Reaction 10 is another pathway to $O_2^{\bullet-}$ and eventually into H_2O_2. The Φ_{-O_2} values as a function of log [EDTA] have a sigmoidal shape (Figure 6).

TABLE 2: Triplet Lifetime and Rate Constant (10^8 M^{-1} s^{-1}) for Quenching by Oxygen[a]

	τ_T (μs)				
quinone	argon	air	k_8	k_9	k_{-9}
BQ	≥0.6	0.5	≥4	0.0005	10
MeBQ	<0.2	<0.1		0.01	8
Me_2BQ	2	0.3	12	0.3−2	2
Me_3BQ	4	0.3	12		
Me_4BQ	≥6	0.4	9	0.1	2−3
Cl_4BQ	≥4	1.6	2		
NQ	0.5	0.4	≥4	0.3	
MeNQ	2	0.3	12	0.4	2−3
BrNQ	1.5	0.3[b]	12		
MeONQ	1	0.3	12		

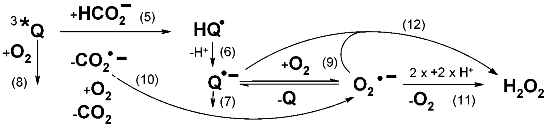
[a] In air-saturated acetonitrile−water (1:10, pH 7) solution, except for Me_4BQ and Cl_4BQ (1:1), λ_{exc} = 248 nm; k_9 and k_{-9} were taken from refs 10,23−26. [b] For Cl_2NQ under air: τ_T = 0.5 μs.

TABLE 3: Rate Constant k_5 (10^8 M^{-1} s^{-1}) for Quenching by Formate, Amines, Ascorbic Acid, and Alcohols[a]

quinine	formate	TEA	ascorbic acid	2-propanol
BQ	0.5		90	0.90
Me_2BQ		30 [20]	50	0.35 (0.2)[c]
Me_3BQ			34	0.002
Me_4BQ	0.01	3[d]	10	0.0005[e]
NQ		>20	>20	0.30 (0.2)
MeNQ	0.5		40	0.3
BrNQ			50	0.15
MeONQ	<0.1	30 [20]	40	0.1
AQ[f]	0.8	28 [30]	35	0.02

[a] In air-saturated acetonitrile−water (1:10) solution. [b] In brackets: EDTA. [c] In parentheses: methanol. [d] Taken from ref 5. [e] For Cl_4BQ $k_5 = 1 \times 10^5$ $M^{-1}s^{-1}$. [f] Taken from ref 38.

SCHEME 3



Photoreactions with Oxygen and Ascorbic Acid. Triplet quenching by ascorbic acid ($AscH_2/AscH^-$, pK_a = 4.1) occurs via electron transfer, reaction 5, Scheme 4; H atom transfer as previously assumed[19] does not operate in aqueous solution.[37,38] The triplet state of most BQs and NQs in air-saturated acetonitrile−water mixtures (1:1) is efficiently quenched, the rate constants are $k_5 = (1-9) \times 10^9$ M^{-1} s^{-1}.[19] The oxygen concentration decreases upon photolysis of BQs and NQs (Figure 3). In a few cases, e.g., for Cl_2NQ, a thermal reaction

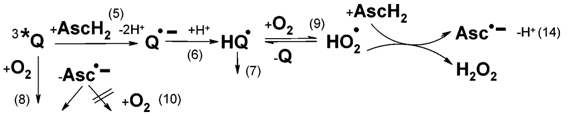
TABLE 4: Half-Concentration for Quenching by Formate, Ascorbic Acid, and 2-Propanol[a]

quinine	$[\text{formate}]_{1/2}$ (M)	$[\text{ascorbic acid}]_{1/2}$ (mM)	$[\text{2-propanol}]_{1/2}$ (M)
NQ	0.05	0.9	0.1/0.08
MeNQ	0.06/0.05	1/0.8	0.1/0.1
BrNQ		0.9/0.7	0.3/0.2
MeONQ		1.2/0.8	0.4/0.3

[a] In air-saturated acetonitrile−water (1:10) solution. Left/right: experimental/calculated.

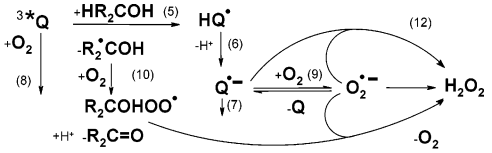
also occurs with ascorbic acid (0.1 M). The radical ($Asc^{\bullet-}$) terminates into dehydroascorbate and $AscH^-$ with $k = 2 \times 10^6$ M^{-1} s^{-1} at pH 7.[30] Photodamage occurs in the presence of both ascorbic acid and oxygen. This is mainly caused by formation of hydrogen peroxide via reaction 5 of the quinone triplet state with ascorbic acid and subsequent reaction 9 of $HQ^\bullet$ with oxygen. Reaction 14 with $k_{14} = (0.1-10) \times 10^6$ M^{-1} s^{-1} completes the conversion of oxygen into hydrogen peroxide. The effects of ascorbic acid concentration on Φ_{-O_2} are shown in Figures 6 and 7. The half-concentrations for quenching by ascorbic acid are low, $[D]_{1/2} = 1$ mM (Table 4) due to the much higher k_5 values compared to formate or alcohols (Table 3).

SCHEME 4



Triplet Quenching by Oxygen and Alcohols. Plots of the O_2 concentration vs irradiation time the in presence of an alcohol are shown in Figure 5 for Me_4BQ and NQs. The transient absorption spectra of Me_nBQ, $n = 2-4$, in air-saturated 2-propanol:water (1:1) show that triplet quenching by oxygen, step 8, competes with quenching 5 by 2-propanol, Scheme 5. For Me_2BQ in a 1:10 mixture of acetonitrile and water the rate constant is $k_5 = 4 \times 10^7$ M^{-1} s^{-1} and for 1 M 2-propanol reaction 5 is therefore much more efficient than reaction 8. For Me_4BQ is the case the opposite since $k_5 = 5 \times 10^5$ M^{-1} s^{-1} and thus reaction 8 successfully competes with reaction 5 even for 50% 2-propanol. The effects of 2-propanol concentration on Φ_{-O_2} are shown in Figures 6 and 7. For most quinones a much smaller concentration of 2-propanol is required. Only a slightly lower k_5 value with methanol leads to a similar plot of Φ_{-O_2} vs [alcohol] (not shown). With *tert*-butanol, however, k_5 is small and H atom abstraction does not occur. Therefore, no additional contribution to Φ_{-O_2} results (Table 1). An example for NQ is shown in Figure 4 (curve 2).

SCHEME 5



Alcohol radicals are involved in reaction 10 with oxygen, whereby a peroxyl radical is an intermediate and the rate constants of quenching are $(1-5) \times 10^9$ M^{-1} s^{-1}.[33,42] Release of $O_2^{\bullet-}$ could open a pathway to H_2O_2. From the *G* value (in radiolysis) for oxygen uptake from the 2-hydroxy-2-propyl-peroxide radical it can be concluded that oxygen is mainly consumed.[33] Acetone is the other photoproduct of quinones and aqueous 2-propanol under air.

Effects of Donor Properties and Quinones Structure. For BQs and NQs in aqueous solution Φ_{isc} is close to unity.[9,12−19] A small Φ_{-O_2} value for a given quinone/donor concentration combination has therefore two possible reasons: a low k_5 value or the condition $K_9 \ll 1$. In the case of electron transfer k_5 is related to the redox potential of the quinones.[4,6,13,19] In order to successfully compete with triplet quenching by oxygen, the donor concentration should be larger than $[D]_{1/2}$. For parent BQ and the donors examined $k_5 \geq 5 \times 10^7$ M^{-1} s^{-1} is large enough to fulfill the requirement of triplet quenching (Table 3). This is similar for NQ, MeNQ, and Me_2BQ, including electron transfer to TEA or EDTA in the latter case. For Me_3BQ and duroquinone with amines and ascorbic acid k_5 is relative large, $(0.3-3) \times 10^9$ M^{-1} s^{-1}, indicating that the free energy of electron transfer is sufficiently negative.[13,19] Quenching by H atom transfer to alcohols, however, is not efficient for Me_nBQ, $n = 3$, 4, and Cl_4BQ.[13]

Equilibrium 9 is crucial as it is shifted to the right side for AQs,[22,23] shifted to the left side for BQ, MeBQ, and Me_2BQ, and is in between for NQs, Me_3BQ, and Me_4BQ (see k_9 and k_{-9} in Table 2). The shift of equilibrium 9 to the left side is the main reason for the finding that Φ_{-O_2} is close to zero for Me_n-BQs, $n = 0$, 1, 2, Table 1. For AQ, 2-methyl-AQ, and 2,3-dimethyl-AQ, where $K_9 > 1$ and $k_5 = 2 \times 10^6$ M^{-1} s^{-1}, a 2-propanol concentration of 1 M is sufficient for 50% triplet quenching.[38] This is even more pronounced for most NQs, whereas for Me_4BQ with $k_5 = 5 \times 10^4$ M^{-1} s^{-1} step 8 is favored at 5 M 2-propanol or below. For ascorbic acid and amines k_5 is large enough for Me_3BQ and Me_4BQ, but Φ_{-O_2} is only ca. 0.1. One could argue that the electron transfer in the ^{3*}Q-donor complex is not necessarily 100%, otherwise, Φ_{-O_2} of the MeNQ/EDTA system should be larger, based on $\Phi_{-O_2} = 0.6$ for NQ/EDTA. Thus, the observed quantum yields are limited by electron back transfer.

Conclusion

The photoreactions of BQ, NQ, and a series of derivatives in water in the presence of formate, aliphatic amines, alcohols, or ascorbic acid can be analyzed by a common mechanism. Triplet quenching by H atom or electron transfer from the donor yield radicals, which convert oxygen into the superoxide radical which eventually dismutates into hydrogen peroxide. The equilibrium between $Q^{\bullet-}$ and $O_2^{\bullet-}$ radicals favors the pathway into H_2O_2 in the case of NQs, in contrast to BQ. This is reflected by the maximum Φ_{-O_2} values at appropriate donor concentration, which are substantial for NQs but low for BQs. Competition kinetics account for the concentration dependence of the quantum yield of this oxygen uptake.

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