

Photoinduced oxygen uptake for 9,10-anthraquinone in air-saturated aqueous acetonitrile in the presence of formate, alcohols, ascorbic acid or amines†

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The photolysis of 9,10-anthraquinone (AQ), 2-methyl- and 2,3-dimethyl-AQ was studied in air-saturated acetonitrile–water in the presence of various donors: formate, ascorbic acid, alcohols, *e.g.* 2-propanol or methanol, and amines, *e.g.* ethylenediaminetetraacetate (EDTA). The photoreaction is initiated by H-atom or electron transfer from the donor to the AQ triplet state. The conversion of oxygen into hydrogen peroxide occurs *via* the superoxide radical and its conjugate acid. The quantum yield of oxygen uptake (Φ_{-O_2}) increases with increasing donor concentration. $\Phi_{-O_2} = 0.3\text{--}0.6$ in the presence of 1 M 2-propanol and 3–10 mM ascorbic acid or EDTA. The properties of the quinone and donor radicals involved and the pH and concentration dependences of Φ_{-O_2} are described.

Introduction

The photochemical properties of 1,4-benzoquinone (BQ), 1,4-naphthoquinone (NQ) and 9,10-anthraquinone (AQ) in non-aqueous^{1–10} and aqueous^{11–20} solution are quite different. The photoreactions of BQ or 2,5-dimethyl-BQ in aqueous solution lead to the 2-hydroxy-1,4-benzoquinones (HOQs) in addition to the corresponding hydroquinones.^{15,16} Hydroxyquinones are the additional photoproducts in aqueous solution for BQ,^{15,16} NQ¹⁹ and AQ.¹¹ OH radicals were believed to be intermediates in the photolysis even for aqueous AQ,^{14,11} but this has been excluded for BQ and Me_nBQ, *n* = 1–3.^{15,16} The properties of the HQ[•]/Q^{•-} radicals of AQ have been characterized by radiation chemistry^{21–25} and the relationship between oxygen and semiquinone radicals has been studied for just a few quinones.²⁶

The photooxidative damage of a sensitizer generally refers to the electron transfer (Type I) and energy transfer (Type II) yielding the superoxide ion radical (O₂^{•-}) and singlet molecular oxygen, O₂(¹Δ_g), respectively. Rose Bengal has been widely used to photochemically generate O₂(¹Δ_g); the quantum yield is $\Phi_{\Delta} = 0.76\text{--}0.86$,^{27–30} whereas the quantum yield of formation of the superoxide radical is still under debate.³⁰ The quantum yield of oxygen uptake (Φ_{-O_2}) in the presence of *N,N*-diethylhydroxylamine (DHA) is up to 0.2.²⁹ Riboflavin is a related photochemical system, where the quantum yields of O₂^{•-} and O₂(¹Δ_g) formation in aqueous solution are 0.01 and 0.5, respectively.^{31,32} Ascorbic acid can enhance Φ_{-O_2} in the case of methylene blue.³³ The kinetics of dismutation of the ascorbate and superoxide radicals have characteristic pH dependences.^{34–40} The hydroperoxyl radical (HO₂[•]), the conjugate acid of O₂^{•-}, has $pK_a = 4.8$. Reactions of hydroquinones in aqueous solution with oxygen and ascorbic acid yield deoxyascorbate and H₂O₂.^{41–43} The photoinduced oxygen uptake was studied for benzophenone in benzene in the presence of amines.⁴⁴ Φ_{-O_2} is substantial for benzophenone and other ketones

in air-saturated aqueous solution in the presence of alcohols, formate, ascorbic acid, and amines; HO₂[•]/O₂^{•-} and eventually H₂O₂ can be generated by electron or H-atom transfer from the triplet state.⁴⁵ Thermal reactions of ascorbic acid with BQ, AQ and derivatives in the absence and presence of oxygen have been reported.^{41–43} It would therefore appear appropriate to examine the role and subsequent fate of oxygen in the photochemistry of quinones in aqueous solution. Little was found in the literature concerning photoinduced oxygen uptake,^{29,44} in particular there are as yet no quantum yields for quinones.

In this work, the photoinduced oxygen uptake/consumption was studied for AQ, 2-methyl-9,10-anthraquinone (MeAQ) and 2,3-dimethyl-9,10-anthraquinone (Me₂AQ) in mixtures of water with acetonitrile. AQs are attractive candidate for this study since the triplet state could serve as H-atom or electron acceptor and they exhibit a high quantum yield of intersystem crossing (Φ_{isc}) and a high Φ_{Δ} .^{1–7} Ascorbic acid and amines, *e.g.* triethylamine (TEA), DHA or ethylenediaminetetraacetate (EDTA) served as electron donors and 2-propanol, methanol or formate as H-atom donors. Φ_{-O_2} values, due to the conversion of O₂ into H₂O₂, are presented using continuous UV irradiation. Results from quenching of the triplet state of the three AQs by these additives or the radicals by oxygen are presented using time-resolved UV-vis spectroscopy at $\lambda_{exc} = 248$ nm. Oxygen interacts *via* quenching of the quinone triplet state and scavenging of the radicals derived from the electron or H-atom donors and/or the AQs.

Material and methods

The compounds (EGA, Sigma) and solvents (Merck, Fluka) were checked for impurities and used as received or purified by distillation (TEA). Water was from a Millipore MilliQ system. The absorption spectra were monitored on a UV/vis diode array spectrophotometer (HP, 8453). For photoconversion the 280 or 313 nm lines of a 1000 W Hg–Xe lamp and a monochromator were used, pathlength 1 cm. The absorbances around 280 nm were larger than 3, corresponding to AQ concentrations of 0.3–1 mM. The air-saturated (unbuffered) acetonitrile–water solutions (1 : 1, vol.) were at pH 6–8 prior to and after irradiation. A

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†Dedicated to Professor Kurt Schaffner on the occasion of his 75th birthday.

phosphate buffer (0.02 M) in these cases appeared to have no effect on Φ_{-O_2} . The pH was close to 7 also in the presence of formate and EDTA. The non-irradiated solutions in the presence of ascorbic acid have pH = 2–3. In the case of TEA and DHA the typical pH was 12–13. The oxygen concentration was measured by a Clark electrode (Hansatech). The relative yield of oxygen consumption was determined from the slope of the graph obtained by plotting $[O_2]$ vs. irradiation time.⁴⁵ The oxygen concentration in aqueous solution prior to photolysis is 0.27 mM and the signal increased only by *ca.* 20% when mixed with acetonitrile (1 : 1, vol.). The actinometers used at 280 and 313/366 nm were, respectively, uridine⁴⁶ and aberchrome-540⁴⁷. The experimental error in the quantum yield determination is $\pm 15\%$ for $\Phi_{-O_2} \geq 0.1$ and $\pm 30\%$ for the smaller values. Two excimer lasers (Lambda Physik, EMG 200 or 210 MSC), pulse width of 20 ns and energy <100 mJ, were used for excitation at 308 or 248 nm. The results refer to $\lambda_{exc} = 248$ nm owing to a lower substrate concentration and partly a better quality. 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 The rate constant for quenching by ascorbic acid was found to be the same for AQ in the presence and absence of air. The samples were air-saturated and the measurements refer to 24 °C.

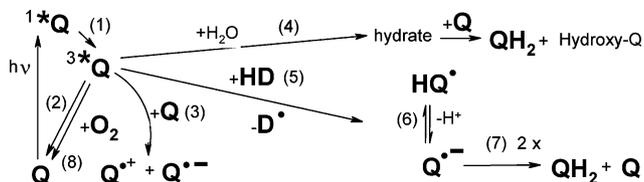
Results and discussion

Photoreactions of AQs without oxygen

The photoreactions are initiated by intersystem crossing into the triplet state (3Q).



The triplet decays *via* step (2) or reaction (3) with the quinone (Scheme 1). In the latter case which has been reported for BQs and NQs^{13,15,16,19} the triplet decays into a radical ion pair. The triplet lifetime (τ_T) of AQ in argon-saturated non-aqueous solution at room temperature is about 10 μ s and even longer, when the substrate concentration and laser intensity are low enough.¹⁰ Additional decay channels are reactions (4) and (5) with water and a donor, respectively. Four different donor types were chosen for irradiation of the AQ–water–air system: formate, 2-propanol as an example of a reactive alcohol, ascorbic acid as a unique radical scavenger and TEA as an example of an aliphatic amine. The rate constant k_5 was determined from the plots of $1/\tau_T$ vs. the donor concentration. The values range from $(1-2) \times 10^6$ M⁻¹ s⁻¹ for 2-propanol to $(2-4) \times 10^9$ M⁻¹ s⁻¹ for amines and ascorbic acid (Table 1).



Scheme 1 Showing reactions (1)–(8).

Transient absorption spectra upon pulsed excitation at 248 nm are shown in Fig. 1–4 for AQ and Me₂AQ in argon-saturated acetonitrile–water (1 : 1, vol.) in the presence of formate,

Table 1 Rate constants for quenching k_5 (10^9 M⁻¹ s⁻¹) by formate, 2-propanol, ascorbic acid and amines^a

Donor	AQ	MeAQ	Me ₂ AQ
Formate	0.08	0.04	0.06
2-Propanol	0.002	0.0015	0.001
Ascorbic acid	3.5		2.5
TEA	2.8		2.5
DHA	2.5		2.2
EDTA	3.0		2.5

^a In air-saturated acetonitrile–water (1 : 10, vol.) solution, $\lambda_{exc} = 248$ nm; pH 2.5–3.5 for ascorbic acid, 11.5–12.5 for TEA and DHA, otherwise pH 6–8.

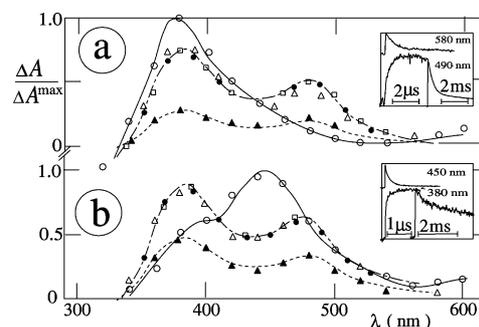


Fig. 1 Transient absorption spectra of (a) AQ and (b) Me₂AQ in argon-saturated acetonitrile–water (1 : 1, vol., pH 7) in the presence of formate ((a) 0.1 M, (b) 0.2 M) at 20 ns (○), 1 μ s (△), 10 μ s (□), 0.1 ms (●) and 1 ms (▲) after the 248 nm pulse; insets: kinetics of the triplet (upper) and radical (lower) using the wavelengths of observation as indicated.

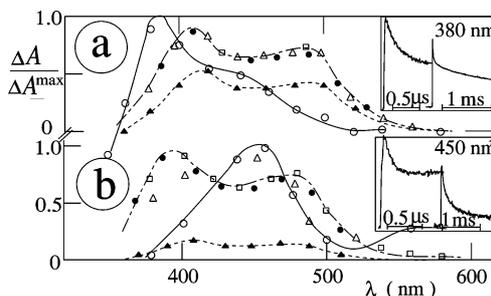


Fig. 2 Transient absorption spectra of (a) AQ and (b) Me₂AQ in argon-saturated acetonitrile–water (1 : 1, vol., pH 7) in the presence of 1 M 2-propanol at 20 ns (○), 1 μ s (△), 10 μ s (□), 0.1 ms (●) and 1 ms (▲) after the 248 nm pulse; insets: kinetics of the triplet and radical at 380/450 nm.

2-propanol, ascorbic acid and TEA, respectively. The spectra of the triplet state have a maximum at 380, 400 and 450 nm for AQ, MeAQ and Me₂AQ, respectively. AQ at pH >5 reveals initially the triplet state and then the Q^{•-} radical which has $pK_a = 4.5$ and terminates *via* step (7) into QH₂.^{21–25} The molar extinction coefficients of HQ[•] and Q^{•-} are $\epsilon_{390} = 8.9 \times 10^3$ and $\epsilon_{490} = 5.2 \times 10^3$ M⁻¹ cm⁻¹, respectively.²⁵ The semiquinone radical spectra of AQ and MeAQ are overlapping with the precursor, but the Q^{•-} radical has a second maximum at 490 nm. The triplet and radical spectra of Me₂AQ are specific and the maxima separated.

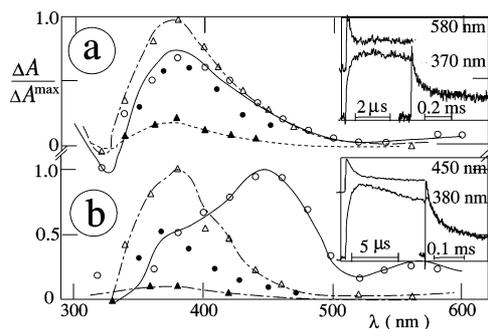


Fig. 3 Transient absorption spectra of (a) AQ and (b) Me₂AQ in argon-saturated acetonitrile-water (1 : 1, vol., pH 3.4) in the presence of 1 mM ascorbic acid at 20 ns (○), 1 μs (△), 0.1 ms (●) and 1 ms (▲) after the 248 nm pulse; insets: kinetics of the triplet (upper) and radical (lower) as indicated.

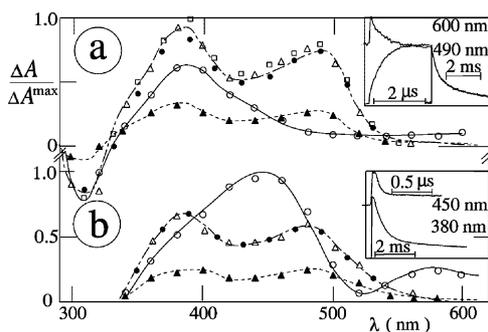


Fig. 4 Transient absorption spectra in argon-saturated acetonitrile-water (1 : 1, vol., pH 12) in the presence of 1 mM TEA for (a) AQ and (b) Me₂AQ at pH 12 at 20 ns (○), 1 μs (△), 10 μs (□), 0.1 ms (●) and 1 ms (▲) after the 248 nm pulse; insets: kinetics of the triplet (upper) and radical (lower) as indicated.

Photoreactions of AQs in the presence of air

Plots of the oxygen concentration vs. the irradiation time were obtained for the donors at various concentrations. Examples are shown as insets for AQ in the presence of HCO₂⁻ (Fig. 5), 2-propanol (Fig. 6), ascorbic acid (Fig. 7) and EDTA (Fig. 8). The quantum yield was taken from the slope of the decrease of the oxygen concentration vs. time. The maximum is close to unity (Table 2). The Φ_{-O_2} values as a function of log [donor] have a

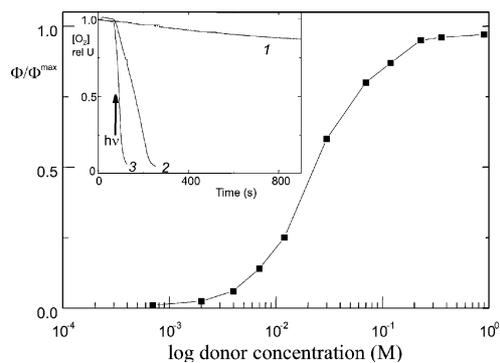


Fig. 5 Semilogarithmic plots of Φ_{-O_2} vs. the formate concentration for AQ in air-saturated acetonitrile-water (1 : 1, vol., pH 7–8) using $\lambda_{irr} = 313$ nm; inset: O₂ concentration vs. irradiation time in the presence of 0.001 (1), 0.02 (2) and 0.2 M (3) formate.

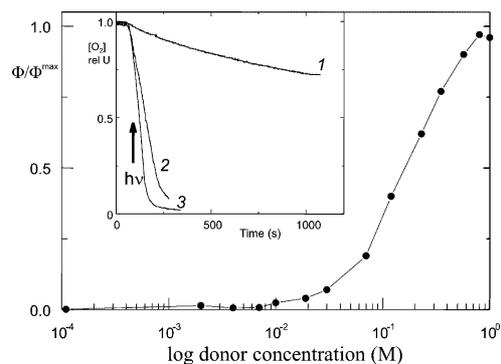


Fig. 6 Semilogarithmic plots of Φ_{-O_2} vs. the 2-propanol concentration for AQ in air-saturated acetonitrile-water (1 : 1, vol., pH 7–8) using $\lambda_{irr} = 313$ nm; inset O₂ concentration vs. irradiation time in the presence of 0.001 (1), 0.3 (2) and 2 M (3) 2-propanol.

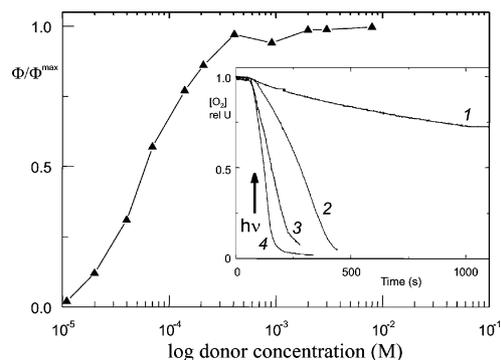


Fig. 7 Semilogarithmic plots of Φ_{-O_2} vs. ascorbic acid concentration for AQ in air-saturated acetonitrile-water (1 : 1, vol., pH 2.8–4) using $\lambda_{irr} = 313$ nm; inset O₂ concentration vs. irradiation time in the presence of 0.002 (1), 0.02 (2), 0.2 (3) and 3 mM (4) ascorbic acid.

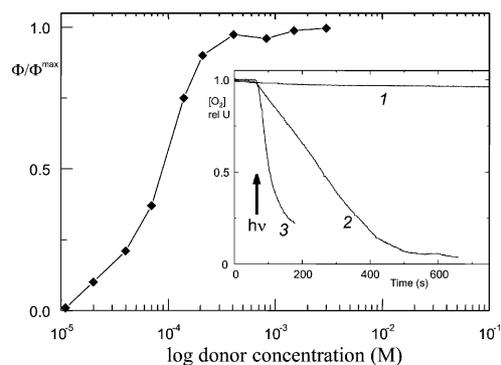


Fig. 8 Semilogarithmic plots of Φ_{-O_2} vs. EDTA concentration for AQ in air-saturated acetonitrile-water (1 : 1, vol., pH 10–12) using $\lambda_{irr} = 313$ nm; inset O₂ concentration vs. irradiation time in the presence of 0.01 (1), 0.03 (2) and 0.3 mM (3) EDTA.

sigmoidal shape, as shown in Fig. 5–8. The half-concentration, *i.e.* the donor concentration for 50% of the maximum Φ_{-O_2} value, is taken as a measure of the sensitivity of the AQ–donor system. The [donor]_{1/2} values range from 0.1 mM for ascorbic acid and amines to 0.2 M for 2-propanol (Table 3). The oxygen uptake photoreaction is not due to quenching reaction (8), illustrated in Scheme 1. Step (8) yields singlet molecular oxygen in substantial yield,^{6–8,14} but for AQs at the low concentrations used, practically

Table 2 Quantum yield of oxygen consumption for AQs in the presence of formate, alcohols, ascorbic acid and amines^a

Donor	$\lambda_{\text{irr}}/\text{nm}$	AQ	MeAQ	Me ₂ AQ
None	313	<0.02	<0.02	<0.02
Formate	313	0.08	0.06	0.05
<i>tert</i> -Butanol	313	<0.02		<0.02
2-Propanol	280	0.6 (0.4) ^b		0.5 (0.4)
2-Propanol	313	0.6 (0.4)	0.6	0.5
2-Propanol	366	0.6 [0.6] ^c		0.5 (0.4)
Ascorbic acid	313	0.6 [0.6] ^c	0.5	0.5
TEA	313	0.2	0.2	0.2
DHA	313	0.4	0.3	0.4
EDTA	313	0.5	0.4	0.3

^a In neutral air-saturated acetonitrile–water (1 : 1, vol.), except for ascorbic acid (pH 2.5–3.5) and TEA and DHA (pH 11–13); [donor] = 0.3, 2, 0.01 and 0.01 M for formate, alcohols, ascorbic acid, and amines, respectively.

^b In parentheses: methanol, 5 M. ^c In brackets: acetonitrile–water (1 : 10, vol.).

Table 3 Half-concentrations for quenching by formate, 2-propanol, ascorbic acid, TEA and EDTA^a

[Donor] _{1/2} /mM	AQ	Me ₂ AQ
Formate	30/40	100/85
2-Propanol	200/170	300/250 (400/300) ^b
Ascorbic acid	0.08/0.1	0.2/0.2
TEA	0.1/0.1	
EDTA	0.1/0.1	

^a In air-saturated acetonitrile–water (1 : 1, vol.), $\lambda_{\text{irr}} = 313$ nm, values: experimental and calculated: left and right, respectively. ^b For MeAQ.

no product is expected due to the short lifetime of $\text{O}_2(^1\Delta_g)$ in aqueous solution. The triplet lifetimes of Me₂AQ and AQ in air-saturated acetonitrile–water (1 : 1, vol., pH 6–8) are $\tau_T = 2.2$ and 3.0 μs , respectively. The rate constants for quenching of the triplet state by oxygen is $k_8 = (1-2) \times 10^8 \text{ M}^{-1} \text{ s}^{-1}$.¹⁰ This triplet quenching competes with the quenching by the respective donor (reactions (5a–d)). Oxygen is also involved in the scavenging of the acceptor radical, reaction (9) (forward), and termination of the $\text{HO}_2^*/\text{O}_2^{\cdot-}$ radicals leads eventually to H_2O_2 .

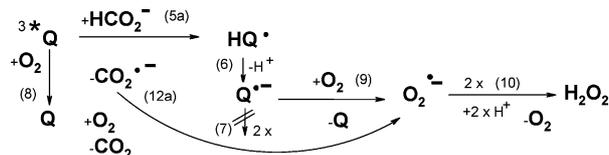


The semiquinone radical formed *via* reaction (5a) is essentially converted back into the AQ, reaction (9), and radical termination (7) does not take place. The rate constant for quenching of the semiquinone radical of AQ by oxygen is $k_9 = 3 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$.²² The subsequent reactions depend on the pH. One step for H_2O_2 formation is reaction (10). The rate constant is very small, $k_{10} < 0.3 \text{ M}^{-1} \text{ s}^{-1}$, for $\text{O}_2^{\cdot-}$ in the alkaline range and much larger, $k_{10} = 0.9 \times 10^6 \text{ M}^{-1} \text{ s}^{-1}$, for the HO_2^* radical.³⁷ Oxygen radicals could also be involved in reaction (11). Under air, however, reaction (11) cannot play an important role since reaction (9) is operative. For AQ in air-saturated solution back conversion ((9), forward) of the radical anion into intact quinone is efficient.^{22–26}



Photoreactions of AQs with oxygen and formate

The reactions of formate with triplets of AQs are illustrated in Scheme 2. Quenching occurs *via* H-atom transfer reaction 5a, followed by electron transfer reaction (12a), which occurs with $k_{12} = 4 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$.¹³



Scheme 2 Showing reactions (5a)–(10) and (12a).

Plots of the O_2 concentration *vs.* time under 313 nm irradiation are shown for AQ in the presence of HCO_2^- (insets of Fig. 5). The quantum yields increase with increasing of the formate concentration, approaching a maximum of $\Phi_{-\text{O}_2} = 0.08$ (Fig. 5 and Table 2). For AQ-2-sulfonate and NQ $k_5 = 3.5 \times 10^7 \text{ M}^{-1} \text{ s}^{-1}$.¹³ A similar k_5 was found for benzophenone, corresponding to $[\text{HCO}_2^-]_{1/2} = 0.01 \text{ M}$.⁴⁵ The half-concentration for AQ–formate is 0.03 M (Table 3). Reactions (5a) plus (6) in the absence of oxygen yield a peak at 490 nm due to the $\text{Q}^{\cdot-}$ radical, the kinetics of triplet decay at 580 nm and grow-in match (Fig. 1a). The termination of the $\text{Q}^{\cdot-}$ radicals has a half-life of 3 ms for Me₂AQ under our conditions (Fig. 1b) and 0.8 ms for AQ. The kinetics under air show a first-order decay of $\text{Q}^{\cdot-}$ with a lifetime of *ca.* 5 μs , corresponding to $k_9 = 1 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$.

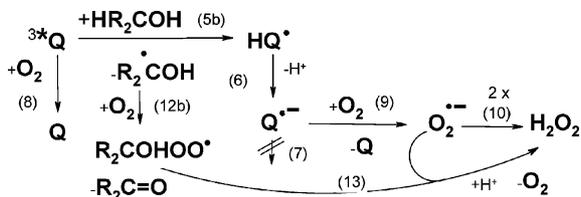
Photoreactions of AQs with oxygen and alcohols

The plots of the O_2 concentration *vs.* time in Fig. 6 (insets) refer to AQ in air-saturated 2-propanol–water and $\lambda_{\text{irr}} = 313$ nm. The maximum quantum yield is 0.6 and can be compared to $\Phi_{-\text{O}_2} < 0.01$ for AQ in acetonitrile–water. Upon irradiation at 280 nm the values are similar and larger than 0.5 also for irradiation at 366 nm (Table 2). The $\Phi_{-\text{O}_2}$ values show a sigmoidal shape as a function of \log 2-propanol concentration (Fig. 6). The half-concentrations are 0.2–0.4 M (Table 3). Triplet quenching by oxygen (reaction (8)) competes with the quenching reaction (5b) by 2-propanol. The $\text{p}K_a$ of the 2-hydroxy-2-propyl radical is 12.2. The AQ triplet state is the initial intermediate in the presence of oxygen and HR_2COH ; H-atom abstraction leads to the $\text{R}_2^{\cdot}\text{COH}$ radical and the semiquinone radical. Reaction (5b) successfully competes with reaction (2) in the case of 10–50% methanol, ethanol or 2-propanol. With *tert*-butanol, however, k_5 is small ($< 1 \times 10^6 \text{ M}^{-1} \text{ s}^{-1}$) and therefore $\Phi_{-\text{O}_2}$ is expected to be low. In fact, for AQ and 1–10 M *tert*-butanol $\Phi_{-\text{O}_2}$ is < 0.02 , a value which was also found for 1–10 M acetonitrile. Alcohol radicals are involved in reaction (12b) with oxygen, whereby a peroxy radical is an intermediate.



Eventually, $\text{O}_2^{\cdot-}$ is released and 2-propanol is oxidized into acetone. The rate constant of quenching the 2-hydroxy-2-propyl

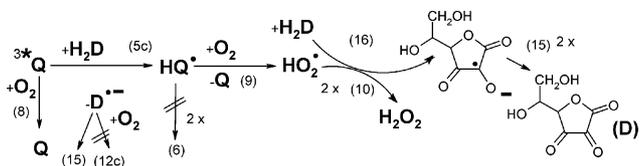
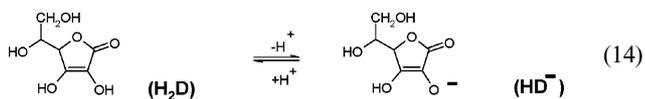
radical by oxygen is $k_{12} = 9 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$.^{48,49} The G value as a measure of the yield from radiolysis for oxygen uptake from the 2-hydroxy-2-propyl-peroxide radical is 3, it can therefore be concluded that oxygen is consumed.³⁸ $\text{O}_2^{\cdot-}$ elimination is base catalyzed and can be induced by a buffer.³⁹ Alternatively, termination of $\text{HO}_2^{\cdot}/\text{O}_2^{\cdot-}$ and the peroxide radical *via* reaction (13) could occur (Scheme 3). On the other hand, cross radical termination does not contribute under steady-state irradiation due to step (9) (forward). The decay of the triplet state and formation of the $\text{Q}^{\cdot-}$ radical (490 nm peak) match and the half-life of the radical termination is 0.4–1 ms (Fig. 2). Under air $\text{Q}^{\cdot-}$ has a lifetime of *ca.* 5 μs , as for other donors.



Scheme 3 Showing reactions (5b)–(10), (12b) and (13).

Photoreactions of AQs with oxygen and ascorbic acid

The quantum yield for irradiation of AQ at 313 nm using 0.01–0.1 M ascorbic acid is up to $\Phi_{-\text{O}_2} = 0.6$. The $\Phi_{-\text{O}_2}$ values as a function of log ascorbic acid concentration show a sigmoidal shape (Fig. 7) and curves of the O_2 concentration *vs.* time ($\lambda_{\text{irr}} = 313 \text{ nm}$) are shown as insets. For irradiation at 366 nm of AQ $\Phi_{-\text{O}_2}$ is similar to the value obtained at 313 nm. In the presence of ascorbic acid in aqueous solution equilibrium (14) is established. In the absence of oxygen the ascorbate radical ($\text{D}^{\cdot-}$) terminates *via* reaction (15) into deoxyascorbate (D) and HD^- with a strong pH dependence, at pH 7: $k_{15} = 2 \times 10^6 \text{ M}^{-1} \text{ s}^{-1}$.³⁶ In contrast to any other donors, the ascorbate radical is not quenched by oxygen, reaction (12c) (Scheme 4). Moreover ascorbic acid reacts with oxygen radicals *via* reaction (16).



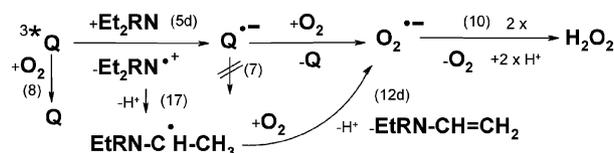
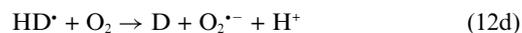
Scheme 4 Showing reactions (5c), (6), (8)–(10), (12c), (15) and (16).

The rate constants are $k_5 = (2.5\text{--}3.5) \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$ (Table 1) and $k_{16} = (0.1\text{--}1.2) \times 10^7 \text{ M}^{-1} \text{ s}^{-1}$ at pH 2–7.³⁶ Photodamage is mainly caused by formation of hydrogen peroxide *via* reaction (5c) of the triplet state with ascorbic acid, reaction (9) of the radical

with oxygen and reaction (16). Under air electron transfer from $\text{Q}^{\cdot-}$ to the ascorbate radical cannot play a role as step (9) competes successfully. Moreover, the ascorbyl radical does not react with the quinone. The photolytic and thermal H_2O_2 formation steps are clearly separated, as shown by the constant oxygen concentration in the time range prior to irradiation (Fig. 7) or by the nearly constant oxygen concentration at longer times. The photoinduced intermolecular H-atom/electron transfer reactions from the one-electron reductant to the triplet state of suitable *p*-quinones in acetonitrile–water have been reported.¹⁷ At pH < 4.5 the quinone radicals is present as HQ^{\cdot} (no peak at 490 nm). The triplet decay and radical formation match and the half-life is *ca.* 0.1 ms (Fig. 3). The kinetics under air are similar to those with the other donors.

Photoreactions of AQs with oxygen and amines

Plots of the O_2 concentration *vs.* irradiation time (313 nm) are shown in Fig 8 (insets) for AQ in the presence of EDTA. The $\Phi_{-\text{O}_2}$ values as a function of log EDTA concentration show a sigmoidal shape (Fig. 8) and the maximum for the amines is $\Phi_{-\text{O}_2} = 0.2\text{--}0.5$. Quenching by amines occurs *via* the electron transfer reaction (5d) (Scheme 5), the rate constants are $k_5 = (2\text{--}3) \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$ (Table 1). To keep these amines in aqueous solution reactive, a quite large pH is necessary.^{12,50} The radical cation forms the α -aminoaryl radical due to the deprotonation reaction (17) and could contribute to $\Phi_{-\text{O}_2}$ under air due to the scavenging reaction (12d).



Scheme 5 Showing reactions (5d), (7), (8), (10), (12d) and (17).

For trimethylamine the rate constant is $k_{12} = 3.5 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$.⁵¹ A reaction of TEA with $\text{O}_2^{\cdot-}$ radicals does not occur.⁴⁵ As in the case of ascorbic acid, the photolytic and thermal H_2O_2 formation steps are clearly separated, as shown by the constant oxygen concentration prior to irradiation (Fig. 8). The triplet decay and radical formation match and the $\text{Q}^{\cdot-}$ radicals have a half-life of *ca.* 1 ms (Fig. 4). The kinetics under air reveal a lifetime of *ca.* 5 μs , corresponding to $k_9 = 1 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$.

Effects of donors

The reactivity of the triplet state with each of the four donor types is similar for AQ, MeAQ and Me₂AQ, see k_5 in Table 1. This is mainly due to the small changes in the standard electrode potentials and the triplet energy level of the AQs. On the other hand, k_5 increases in the order 2-propanol, formate, amines and ascorbic acid, as for ketones.⁴⁵ The half-concentration for 50% quenching of $\Phi_{-\text{O}_2}$ should follow the opposite trend, as $[\text{donor}]_{1/2} = 1/(\tau_T \times k_5)$ is expected on the basis of the mechanistic schemes. For example, $[\text{ascorbic acid}]_{1/2}$ or $[\text{amine}]_{1/2}$ for AQ is

around 0.1 mM, whereas $[2\text{-propanol}]_{1/2} = 0.2 \text{ M}$. In fact the experimental and calculated values are in a reasonable agreement (Table 3). These results demonstrate that Type II photosensitized oxidation under the applied conditions does not uptake oxygen in measurable amounts.

Virtually the same results were found for AQ, when TEA was replaced by DHA. This is not the case for 1,4-diazabicyclo[2.2.2]octane (DABCO), where the rate constant is $5 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$, but Φ_{-O_2} is very low (< 0.01). The main reason is the efficient electron back transfer from $O_2^{\cdot-}$ (under air) or from $Q^{\cdot-}$ (under argon) to DABCO $^{+}$. In contrast to the other amines DABCO does not form a deprotonated radical, which can reduce oxygen *via* reaction (12d). It is worthwhile noting that protonation of the amino group in aliphatic amines causes a strong decrease in reactivity.^{45,50} This is also the case for the electron transfer from TEA or DHA to AQ, but not for EDTA which contains two nitrogens.

Φ_{isc} of AQ is close to unity¹⁻¹⁰ and a Φ_{-O_2} value of 2 could be possible, when each $O_2^{\cdot-}$ radical is converted into H_2O_2 . The maximum quantum yield in the presence of 2-propanol, ascorbic acid or EDTA is 0.5–0.6 (Table 2). In the 2-propanol case it follows that $\Phi_{-O_2} = 1$ only if the formation of both radicals (Scheme 3) and the termination step (13) of $Me_2COHO_2^{\cdot}$ and $HO_2^{\cdot}/O_2^{\cdot-}$ is effective since reactions (5b) and (10) alone would only give $\Phi_{-O_2} < 0.5$. In the ascorbic acid case where reaction (12c) is not operative, each hydroperoxyl radical may be converted into hydrogen peroxide *via* reaction (16) (Scheme 4), *i.e.* Φ_{-O_2} can be up to 1. The same should hold amines and the formate case where both radicals yield a hydroperoxyl radical. The experimental value of $\Phi_{-O_2} = 0.05\text{--}0.08$ for formate indicates an efficient physical quenching, *i.e.* the quenching reaction (5) does also lead back to the quinone and the donor.

Conclusion

The photoreactions of Me_nAQs ($n = 0,1,2$) in the presence of formate, alcohols, ascorbic acid or aliphatic amines follow the mechanism previously presented for several ketones.⁴⁵ Triplet quenching by H-atom or electron transfer from the donor yields AQ radicals, which convert oxygen into the superoxide radical which eventually dismutates into hydrogen peroxide. Competition kinetics of triplet quenching by oxygen not yielding oxygen radicals account for the concentration dependence of the quantum yield of this oxygen uptake. In contrast to BQ,²²⁻²⁶ equilibrium (9) of Me_nAQs is on the side of $Q/O_2^{\cdot-}$ rather than $Q^{\cdot-}/O_2$.

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