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Direct and ketone-sensitized photoconversion of 1-nitro-9,10-anthraquinone to 1-amino-9,10-anthraquinone mediated by donor radicals

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ABSTRACT

The full photoreduction of 1-nitro-2-R-9,10-anthraquinone (R = H: N1, methyl: N2) was studied in benzene, acetonitrile and acetonitrile–water mixtures in the presence of 2-propanol and triethylamine (TEA). The major photoproduct is the fluorescing 1-amino-2-R-AQ (A1, A2). The quantum yield of full reduction increases with the donor concentration, approaching $\Phi_{NH_2} = 0.1$. The intermediates involved are assigned on the basis of spectral and kinetic characteristics. The short-lived triplet state ($\leqslant$20 ns) of N2 can be intercepted by 2-propanol or TEA, thereby forming the spectroscopically hidden donor radicals and the nitroAQ radicals which absorb at 400 and 540 nm; the latter band is due to the radical anion. The triplet state of N1 was not observed at room temperature, but the radical properties and decay in the nitrosoAQ are similar for N1 and N2. For donors in lower concentrations Φ_{NH_2} is strongly increased in the presence of benzophenone, acetophenone or acetone, approaching 0.22. The results under direct and sensitized conditions are compared and major dependences and the effects of mixtures of acetonitrile with water are outlined.

1. Introduction

The photochemical features of 9,10-anthraquinone (AQ) and several derivatives in solution have been intensively studied [1–16]. The key-intermediate in the photoreduction of AQs is the semiquinone radical, the properties of which have been reviewed [17]. Two-photon ionization and subsequent electron transfer can take place for the 1,5-disulfonate of AQ [6]. The photoreactivity of AQs is lowered, when electron donating or accepting groups are substituted. For 2-aminoAQ in 2-propanol the quantum yield of reduction is close to zero, whereas it is 0.9 for the conversion of parent AQ to 9,10-dihydroanthraquinone (AQH_2) [1–3]. The low reactivity of aminoAQs is ascribed to a charge transfer process, leading to fast deactivation into the ground state. The photoprocesses of aminoAQs have been extensively studied [4,18–21], but concerning the reactions of nitroAQs only little is known [22–26].

The photoreduction of 1-nitro-2-R-AQ (R = H: N1, methyl: N2) to the corresponding 1-aminoAQs (A1, A2) in benzene and acetonitrile in the presence of phenylethylamine and 1- or 2-phenylethanol was the subject of a preceding study [27]. The triplet lifetime of N2 is τ_T = 5–20 ns at room temperature and that of N1 is shorter. The longer lifetime τ_T due to the methyl group in N2 therefore causes an enhanced reactivity at a given lower donor concentration. 1-Phenylethanol and ca. 0.01 mM acetophenone (as trace impurity) function as donor and sensitizer, respectively. The quantum yield (Φ_{NH_2}) of full conversion of N2 to A2, determined by photochemical means, is up to 0.2 in 1-phenylethanol [27]. Methanol, ethanol or 2-propanol are attractive H-atom donors, whereas amines, e.g. phenylethylamine and triethylamine (TEA), function as electron donors. A plausible photoreduction sequence of 1-nitroAQ would be H-transfer from the donor (DH_2) thereby forming nitrosoAQ; then further reduction leads to hydroxylaminoAQ and eventually to aminoAQ, Scheme 1. Radicals derived form 1-nitroAQ and the (H-atom or electron) donors are intermediates. An alternative pathway via the 1-nitrodihydroAQ (O_2NAQH_2), pathway b in Scheme 2, had been rejected [27]. For conversion of 1-nitroAQ and 2-nitroAQ in 2-propanol to NHOHAQs quantum yields of 0.0001 and 0.047 for λ_{irr} = 254 nm and 0.0001 and 0.0015 for λ_{irr} = 365 nm have been reported, respectively [25].

The photoconversion of a nitroarene to the aminoarene [28–36] is a rare process which requires six electrons. The formulation of a self-consistent mechanism accounting for the complete reduction by photochemical means has been achieved for nitrobenzene derivatives in the presence of perchloric acid and 10-methyl-9,10-dihydroacridine [32]. In another system, formate has been employed as an efficient reducing agent of various nitroarenes [33]. The relatively high efficiency for nitroAQs is based on the bi-functional AQ system, where both the 1-nitro group and one of the carbonyl groups are intermediate H-atom acceptor sites via a cascade-like mechanism.

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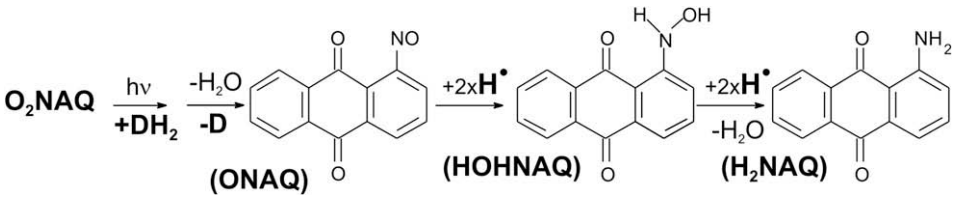
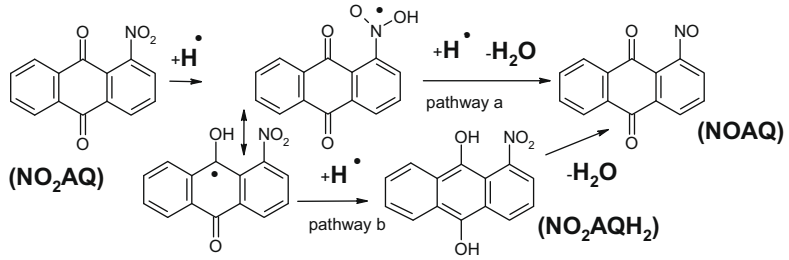


Scheme 1.



Scheme 2.

In the present work, the direct photolysis of N1 and N2, denoted here as nitro(methyl)AQ, was studied in solution in the presence of alcohols as H-donors or TEA as electron donor. Several intermediates were observed by time-resolved techniques. The second goal was to arrive at an understanding of the photosensitized reduction. For this purpose benzophenone, acetophenone or acetone were used. The benzophenone/acetonitrile/alcohol system has been employed for reduction of cationic dyes [37,38]. The third goal aimed at the reduction of 1-aminoAQ which is a subsequent photoreaction of 1-nitroAQ.

2. Experimental

The synthesized (A2 and N2) and the purchased (A1, N1, N2: Aldrich, TCI) AQs are the same as used previously [27]. The other compounds and the solvents were used as commercially available (Aldrich, Fluka, Merck) and checked for impurities. Acetonitrile was Uvasol quality, TEA was purified by distillation. Water was from a Millipore (milli Q) system. The molar absorption coefficient of N1 in acetonitrile is $\varepsilon_{329} = 4.6 \times 10^3\ M^{-1}\ cm^{-1}$ and that of A1 is $\varepsilon_{470} = 6.7 \times 10^3\ M^{-1}\ cm^{-1}$. For photoconversion a 1000 W Xe–Hg lamp and a monochromator was applied. Alternatively, irradiation was performed with the 254 nm line of a low pressure Hg lamp or a 250 W high pressure Hg lamp and a band-pass filter for 313 nm. The UV–Vis absorption spectra were recorded on a diode array spectrophotometer (HP, 8453). For various donor concentrations the quantum yield of conversion was obtained, keeping the initial absorbance at $\lambda_{irr} = 313$ nm constant. The quantum yields Φ_{H_2} and Φ_{NH_2} were determined using the aberchrome 540 actinometer and the identity of the products was checked by HPLC analysis [27]. These analyses were performed on a reverse phase ODS-3 (Perfect Target, 3 μm) column, 0.8 ml min^{-1}, with mobile phase gradient, composed of 0.5% trifluoroacetic acid and either acetonitrile–water (1:5) or neat acetonitrile as eluent. The retention times were $t_r = 18.5$ and 18.2 min for N1 and A1, respectively. For A2 and N2 the method fails since the retention times of are the same under our conditions, $t_r = 18.1$ min; the chromatograms could only be separated by different wavelengths. HydroxylaminoAQs were not observed by HPLC. The experimental error in the quantum yield determination is mostly ±15% and ±30% for values smaller than 0.01. A spectrofluorimeter (Cary, eclipse) was employed to measure the fluorescence and phosphorescence spectra. The fluorescence quantum yield (Φ_f) using rhodamine 101 in methanol, $\Phi_f = 0.9$, as reference. Two excimer lasers (Lambda Physik, pulse width of 20 ns and energy <100 mJ) were used for excitation at 308 and 248 nm (EMG 200, EMG 210 MSC); for simplicity, the results refer only to $\lambda_{exc} = 308$ nm. The absorption signals were measured with two digitizers (Tektronix 7912AD and 390AD) and an Archimedes 440 computer for data handling. All measurements, except for phosphorescence, refer to 24 °C.

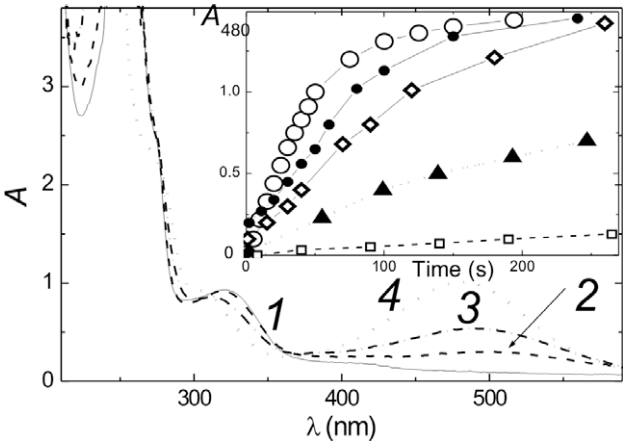


Fig. 1. Absorption spectra of N2 in argon-saturated acetonitrile in the presence of 0.1 M TEA at 0, 10, 30 and 200 s irradiation at 313 nm (1–4, respectively), insets: absorption at 480 nm as a function of time for 100 (○), 30 (●), 10 (◇), 3 (▲) and 1 mM (□) TEA.

3. Results and discussion

3.1. Iradiation of nitro(methyl)AQs

The absorption spectra of the two nitroAQs are similar, they have a major peak at 250 nm, e.g. in acetonitrile, and a second one at $\lambda_N = 330$ nm. A colored photoproduct with a band centered at $\lambda_A = 475$ nm appears upon irradiation at 313 nm in the presence of argon-saturated TEA. This is shown in Fig. 1 for N2. Based on analysis by HPLC, the product of N1 is attributed to A1. Comparable spectra were recorded using 2-propanol as donor. The absorption

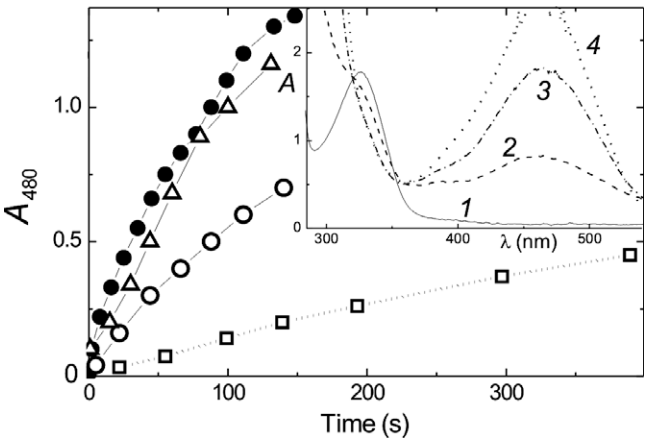


Fig. 2. Absorption at 480 nm of N2 in argon-saturated acetonitrile in the presence of 8 (●), 1 (Δ), 0.3 (○) and 0.1 M (□) 2-propanol vs time; insets: absorption spectra in the presence of 1 M 2-propanol at 0, 20, 50 and 200 s irradiation at 313 nm, 1–4, respectively.

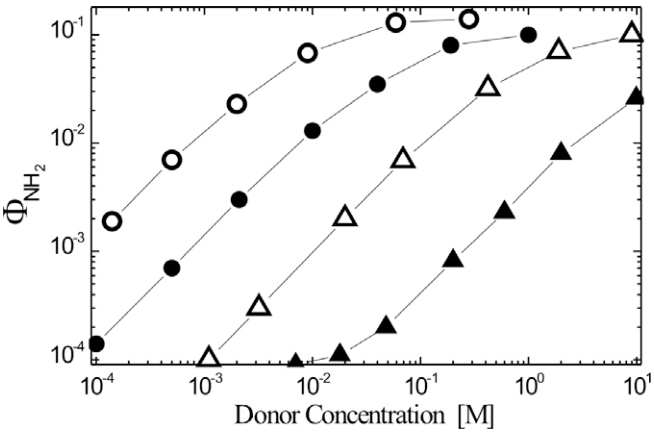


Fig. 3. Double-logarithmic plots of Φ_{NH_2} vs. the TEA (circles) and 2-propanol (triangles) concentration for N1 (full) and N2 (open) in argon-saturated acetonitrile.

spectra of irradiated N2 in the presence of 2-propanol (Fig. 2, inset) $\lambda_N = 330$ nm, $\lambda_A = 475$ nm, are similar to the N1 case. Close inspection of the spectra indicates a narrowing of the band (and a small shift to shorter wavelengths in some cases) as a function of the irradiation time. We attribute this to the enrichment of the hydroxylaminoAQ and the subsequent conversion to the slightly different band of the aminoAQ. Note that nitrosoAQs are not expected to absorb at 475 nm. In the presence of oxygen, the photoinduced 475 nm band does not appear at all. Prolonged irradiation leads to a further species with maximum at 390 nm. They are 1-aminodihydroAQs, H_2NAQH_2 and $H_2NMeAQH_2$ in the cases of A1 and A2, respectively.

3.2. Quantum yield of full reduction

The absorption of the nitro(methyl)AQs at 475 nm increases as a function of the time of irradiation at 313 nm. Plots of A_{480} for N2 as a function of the irradiation time are shown in the presence of TEA (Fig. 1, inset) and 2-propanol (Fig. 2). The slope of the initial linear part is a measure of the quantum yield, the values are compiled in Tables 1 and 2. Φ_{NH_2} in neat argon-saturated benzene or acetonitrile is below 10^{-3} and larger in mixtures with several alcohols, approaching $\Phi_{NH_2} = 0.04$ for N1 in neat 2-propanol and 0.13 for N2. The dependences of Φ_{NH_2} on the donor concentrations are

Table 1
Quantum yield of photoconversion of nitroAQs.[a]

Donor	Conc. (M)	N1:Φ_{NH_2}	N2:Φ_{NH_2}
1-Phenylethanol[b]	9	0.06	0.20
	Neat	0.09	0.22
TEA	0.5	0.08	0.14
2-Propanol	16 (Neat)	0.04	0.13

[a] In argon-saturated acetonitrile, $\lambda_{irr} = 313$ nm.
[b] Containing 0.01 M acetophenone, values taken from Ref. [27].

Table 2
Quantum yield of direct photoconversion of nitroAQs to aminoAQs.[a]

Solvent	Donor	Conc. (M)	N1:Φ_{NH_2}	N2:Φ_{NH_2}
Benzene	TEA	0.1	0.03	0.09
Acetonitrile	TEA	0.001	0.002	0.01
		0.01	0.01	0.06 (0.07)[b]
	2-Propanol	0.1	0.001	0.02
		2	0.008	0.09
MeCN–H_2O (4:1)	2-Propanol	2	0.005[c]	0.08[c]

[a] In argon-saturated solution, $\lambda_{irr} = 313$ nm.
[b] For $\lambda_{irr} = 254$ nm.
[c] Same value at pH 3 or 8, see text for pH 12.

shown in Fig. 3 in a double logarithmic presentation. The concentration, where $\Phi_{NH_2}/\Phi^{max}_{NH_2}$ is 50% of its maximum, $[donor]_{1/2}$, is characteristic for the efficiency, e.g. $[donor]_{1/2}$ is ca. 1 M for N2/2-propanol in acetonitrile solution. The Φ_{NH_2} values are similar in argon-saturated benzene or acetonitrile (Table 2). Φ_{NH_2} of N2 in neat ethanol and methanol is 0.06 and 0.04, respectively. The photochemical reduction of 1- and 2-nitroAQs in alcohols has earlier been studied by El'tsov and coworkers [23–25]. Φ_{NHOH} values of formation of 1-hydroxylaminoAQ upon irradiation of N1 in 2-propanol were 10^{-4} for both $\lambda_{irr} = 254$ and 365 nm [25]. They are too low and in our hands, Φ_{NH_2} as a minimum for Φ_{NHOH} is ca. 0.01 for N1.

The presence of 10–30% water has no significant effect on Φ_{NH_2} of N2 in 2-propanol at pH 3–8 (Table 2). At pH 12, however, the product spectrum shows no 475 nm peak as expected for amino(methyl) AQs, but a broad band around 710 nm. This is attributed to the deprotonated form of 1-hydroxylaminoAQ, in analogy to results with N1 in the presence of sodium methoxide [25]. Such a 710 nm band was also observed with aqueous TEA (not shown).

3.3. Sensitized reduction of nitro(methyl)AQs

The photoreduction of the nitroAQs is more efficient when benzophenone, acetophenone or acetone were employed as sensitizers. The absorption spectra of the nitro(methyl)AQs in argon-saturated acetonitrile at $\lambda < 330$ nm are overlapped by those of the sensitizer. The new colored photoproduct with a band centered at $\lambda_A = 475$ nm upon irradiation at 313 nm is the same as without sensitizers. Examples are shown for N1 in the presence of TEA (Fig. 4, inset). Comparable spectra were recorded using alcohols as donors. Recently, we found that Φ_{NH_2} is up to 0.2 (Table 1). 1-Phenylethanol and acetophenone, as already mentioned, function as donor and sensitizer, respectively [27].

A new band centered at $\lambda_H = 390$ nm appears upon further irradiation in the presence of 2-propanol, i.e. when N2 is completely converted to the photoproduct A2. This band is due to 1-amino-2-methyldihydroAQ [27]; the admission of air changes the 390 nm band back to that of A2 with $\lambda_A = 480$ nm. A 390 nm peak and a thermal step (a decrease in A_{400} within a few minutes or less) after admission of air could also be registered for N1 with 2-propanol as donor (not shown). For TEA (10 mM) as donor the

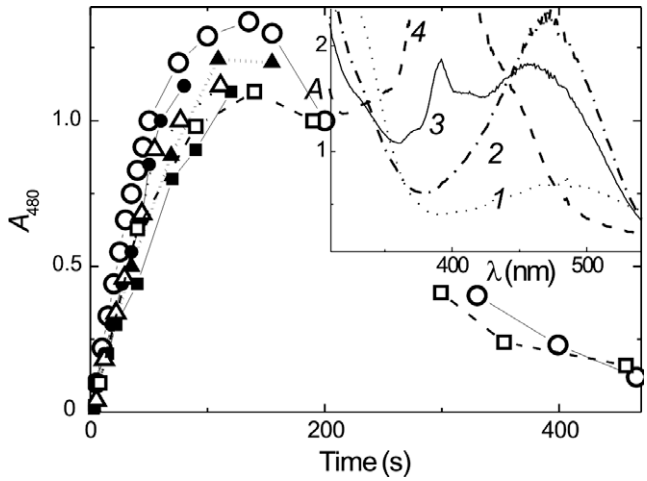


Fig. 4. Absorption at 480 nm of N1 in argon-saturated acetonitrile in the presence of 0.1 M 2-propanol (open) and 10 mM TEA (full) with benzophenone (circles), acetophenone (triangles) and acetone (squares); insets: absorption spectra for N1, benzophenone and TEA at 20, 130, 200 and 400 s irradiation at 313 nm 1–4, respectively.

Table 3
Quantum yield of sensitized photoconversion of nitroAQs to aminoAQs.[a]

Sensitizer	Donor	N1:Φ_{NH_2}	N2:Φ_{NH_2}
Acetone	2-Propanol	0.06	0.20
	Methanol	0.09	0.22
Benzophenone	TEA	0.1	0.11 [0.1][b]
	2-Propanol	0.12	0.12 [0.1]
	Ethanol	0.09	0.17
	Methanol	0.05	0.12
Acetophenone	TEA	0.12	0.22
	2-Propanol	0.10	0.20

[a] In argon-saturated acetonitrile, λ_{irr} = 313 nm. The donor concentration is 0.1 M for alcohols and 5–9 mM for TEA, respectively.
[b] In benzene.

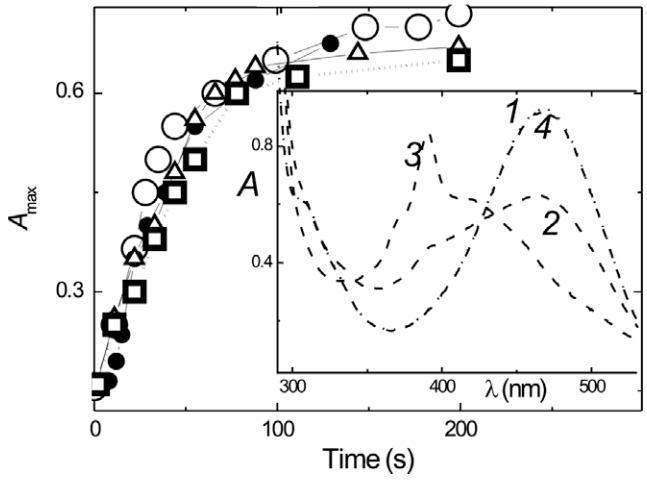


Fig. 5. Absorption at 390 nm of A1 in argon-saturated acetonitrile in the presence of 0.1 M 2-propanol (open) and 10 mM TEA (full) with benzophenone (circles), acetophenone (triangles) and acetone (squares); insets: absorption spectra for A1, benzophenone and 2-propanol at 0, 10 and 100 s irradiation at 313 nm 1–3, respectively and after admission of air (4).

conversion to A2 is similar (Fig. 4, inset). The time-dependence is shown in Fig. 4, the slope of the initial linear plot is taken as relative Φ_{NH_2} (see Table 3).

Table 4
Quantum yield of photoreduction of aminoAQs.[a]

Sensitizer	Donor	A1:Φ_{H_2}	A2:Φ_{H_2}
None[b]	TEA	0.002	<0.002
	2-Propanol	0.003	<0.002
Acetone	TEA	0.4	0.5
	2-Propanol	0.6	0.5
Acetophenone	TEA	0.4	0.4
Benzophenone	TEA	0.6	0.5
	2-Propanol	0.6	0.5

[a] In argon-saturated acetonitrile, λ_{irr} = 313 nm, the donor concentration is 0.1 M for alcohols and 5–9 mM for TEA.
[b] Using concentrations of 10 M 2-propanol or 0.5 M TEA.

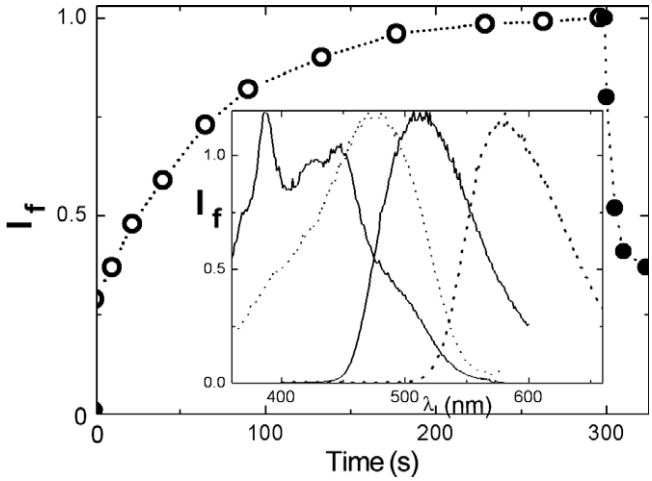


Fig. 6. Plots of I_f (λ_{ex} = 390 nm, λ_{em} = 590 nm) as a function of time of irradiation at 313 nm of A2 in argon-saturated acetonitrile in the presence of benzophenone and 0.1 M 2-propanol (○) and after admission of air (●); insets: Fluorescence spectra under argon at 200 s (full) and after admission of air (broken).

3.4. Photoreduction of amino(methyl)AQs

The absorption spectrum of A1 in argon-saturated acetonitrile has a major band centered at λ_A = 475 nm. A peak at λ_H = 390 nm appears upon irradiation at 313 nm in the presence of 2-propanol (Fig. 5, insets) or TEA. The photoproduct is attributed to 1-aminodihydroAQ (see above). The spectra are similar to those for A2, where the photoproduct is 1-amino-2-methyldihydroAQ. The slope of the initial linear increase of A_{390} is taken as measure of the quantum yield (Φ_{H_2}). Examples of the conversion to the dihydroAQs in the presence of TEA or 2-propanol are shown in Fig. 5, the values are listed in Table 4. The quantum yield of formation of 1-aminodihydroAQ in the presence of 2-propanol or TEA is small, $\Phi_{H_2} < 0.01$, and smaller for A2. The photochemical reduction of A1 in the acetonitrile–alcohol mixtures is enhanced on addition of benzophenone (<1 mM), acetophenone (5 mM) or acetone (0.3 M). It should be noted that the quantum yield of reduction of A1 in acetone–water (1:1, vol) is Φ_d = 0.06 at pH 3–11 [26]. The observed Φ_{H_2} values under sensitized conditions (Table 4) are much larger and only little smaller than unity, the maximum attainable value.

3.5. Fluorescence of the photoproducts

Nitro(methyl)AQs show no fluorescence, in contrast to aminoAQs [18–21]. However, fluorescence appears upon conversion of nitroAQs to the fully reduced aminoAQ photoproducts. The fluorescence emission of A1 or A2 with maximum at λ_f = 590–600 nm is a

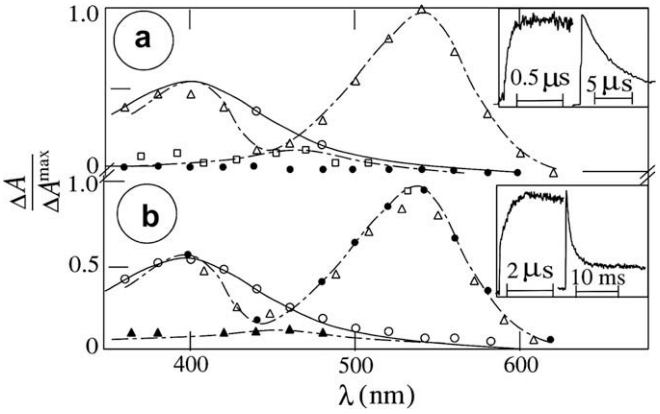


Fig. 7. Transient absorption spectra of N2 in (a) air- and (b) argon-saturated acetonitrile in the presence of 10 mM TEA at 20 ns (○), 1 µs (Δ), 10 µs (□), 0.1 ms (●) and 1 ms (▲) after the pulse; insets: kinetics at 500 nm.

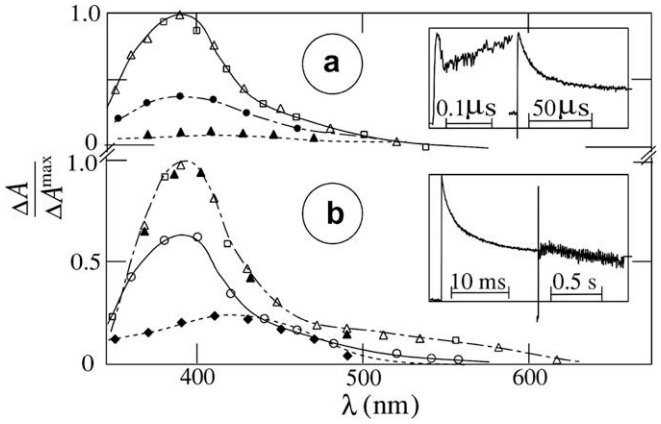


Fig. 8. Transient absorption spectra of N2 in (a) air- and (b) argon-saturated 2-propanol-acetonitrile (1:9) at 20 ns (○), 1 µs (Δ), 10 µs (□), 0.1 ms (●), 1 ms (▲) and 0.1 s (♦) after the pulse; insets: kinetics at 400 nm.

mirror image of the excitation spectrum and the latter resembles that of the absorption. Representative examples are shown in Fig. 6 (inset). The fluorescence quantum yield of A2 in acetonitrile and 2-propanol (1:1) is 0.02, in agreement with the literature value of $\Phi_f = 0.02$ in neat acetonitrile [20]. The observation of a green fluorescence immediately behind the entrance window during irradiation of the vigorously purged solution indicates reduction at the two carboxy groups and rapid disappearance, possibly by reaction with trace amounts of oxygen. The intensity (I_f) ($\lambda_{ex} = 390$ nm, $\lambda_{em} = 560$ nm) of N2 in 2-propanol increases as a function of the time of irradiation at 313 nm. Likewise, the fluorescence intensity of A2 in acetonitrile in the presence of 2-propanol or TEA and $\lambda_{ex} = 390$ of A1 can be used to measure the photoconversion to 1-amino-(2-methyl)dihydroAQs and the reversion upon admission of air. The latter is only partly under direct excitation and better under sensitized excitation. An almost complete reversible case for A2/benzophenone/2-propanol is shown in Fig. 6. Apparently, Φ_f of the aminodihydroAQs is larger than of the aminoAQs, an appropriate fluorescence study would however, be far beyond the scope of this work.

3.6. Triplet state

The short-lived transient of N2 with a lifetime of $\leqslant$20 ns at room temperature has been attributed to a triplet state [27]. No triplet quenching by oxygen could be found. The triplet state of N1 is too short-lived to be observed by our set-up upon excitation at 308 nm. Generally, the photoreactions are initiated by intersystem crossing, ^{1*}AQ-R is very short-lived, the triplet states of AQs have a much longer lifetime, $\tau_T = 3$–10 µs [14,15]. The triplet of N2 appears at 400 nm in acetonitrile even in the presence of either TEA (in low concentration) or 2-propanol (insets in Figs. 7a and 8a).

$$R - AQ + h\nu \rightarrow {}^{1*}R - AQ \rightarrow {}^{3*}R - AQ \qquad (1,2)$$

Upon excitation at 308 nm of A2 in argon-saturated acetonitrile, only a weak transient with maximum at 400 nm was found [27]. This is in agreement with the literature of low Φ_{isc} for animoAQs [19–21]. The triplet energy was found to be 220 kJ mol^{-1}; the onset of the phosphorescence peak in ethanol at −196 °C is at 480 nm for each: A1, A2, N1 and N2. A value of 250 kJ mol^{-1} has been reported for A1 [19]. Energy transfer from triplet benzophenone in argon-saturated acetonitrile showed only physical quenching, but no transient. This is in agreement with the short triplet lifetime of N1. On the other hand, the triplet state of benzophenone is quenched by N1, the rate constant in argon-saturated acetonitrile is $k_q = 6 \times 10^9$ M^{-1} s^{-1}.

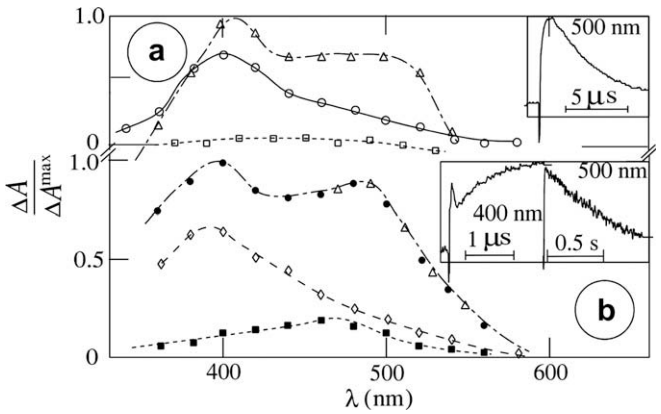


Fig. 9. Transient absorption spectra of N1 in (a) air- and (b) argon-saturated acetonitrile–water 3:1 in the presence of 2 M 2-propanol at 20 ns (○), 0.1 µs (◇), 1 µs (Δ), 10 µs (□), 0.1 ms (●) and 10 ms (■) after the pulse; insets: kinetics at 400 and 500 nm.

3.7. Radicals

In several solvents, e.g. alcohols, the triplet state of 1-nitro-2-methylAQ is overlapped by a second long-lived transient with maximum at $\lambda_R = 400$ nm. Examples of the spectra and kinetics in the presence of 2-propanol and TEA are shown for N2 in acetonitrile (Figs. 7 and 8, respectively). The long-lived species in the presence of an alcohol is attributed to the conjugate acid of the radical anion: $O_2NAQH^{\cdot}$. The spectra in the presence of TEA exhibit two broad bands with maxima at $\lambda_R = 400$ and 550 nm which are attributed to the radical anion. In this respect 1-nitroAQs are the same AQ [13,17]. The donor radicals are non-detectable under our conditions.

Owing to the triplet lifetime of $\tau_T < 20$ ns in argon-saturated acetonitrile, a relatively high donor concentration is required for effective radical formation. The half-lives ($t_{1/2}$) are 1 ms – 1 s (Table 5) and sensitive to trace amounts of oxygen. In air-saturated acetonitrile the radical yield is virtually the same, but $t_{1/2}$ is as short as 3–5 µs (Figs. 7a and 8a). The reactivity of the radicals toward scavening by oxygen in 1-phenylethanol was found to be two orders of magnitude lower than in acetonitrile [27]. Examples of the spectra and kinetics of N2 in the presence of aqueous 2-propanol at pH 8 are shown in Fig. 9. The half-lives under air and argon are $t_{1/2} = 5$ µs and ca. 0.5 s, respectively. The decay of the radical in the presence of water is slower (Table 5).

Table 5
Absorption maxima and half-live of the radicals of nitroAQs.[a]

Solvent	Donor	Conc. (M)	λ_R (nm)		$t_{1/2}$ (ms)	
			N1	N2	N1	N2
Benzene	TEA	0.1	420, 550	420,550	2	4
Acetonitrile	TEA	0.1	420, 550	420, 550	4	20
	1-Phenylethanol	4	400	400	1	1
	2-Propanol	8	390	400	10	15
MeCN-H_2O (3:1)	TEA, pH 13	0.1	420, 550	420, 550	30	40
	2-Propanol, pH 8	2		420, 500		>500
	pH 12	2		420, 550		>500

[a] In argon-saturated acetonitrile, λ_{exc} = 308 nm.

The TT absorption spectrum of benzophenone in argon-saturated acetonitrile is quenched by alcohols. The resulting ketyl radical reacts with N1 and N2, yielding a nitro(methyl)AQ radical with maximum at 400 nm. The same nitroAQ radical was formed upon excitation of acetophenone or acetone (not shown). The spectra of A2 and TEA in argon-saturated acetonitrile are shown in Fig. 10 for benzophenone-sensitized excitation conditions. Concerning the role of water on the transients: a significant effect is a delay of the radical termination (Table 5).

3.8. Reaction scheme of direct photoreduction of nitro(methyl)AQ

The proposed mechanism of photoreduction of the nitro(methyl)AQs is shown in Scheme 3. It involves the triplet state as the only reactive excited state and triggers a series of reduction steps via the donor radical. The first chemical step (3) is H-transfer to this triplet state yielding the acceptor and donor radicals [39–41]. Termination of the former radical, step (4a), yields the nitrosoAQ. Alternatively, nitrosoAQ results from H-transfer via (4b). DH· reacts by step (5) with nitrosoAQ to form the corresponding nitroso-derived radical and termination (6) yields hydroxylaminoAQ.

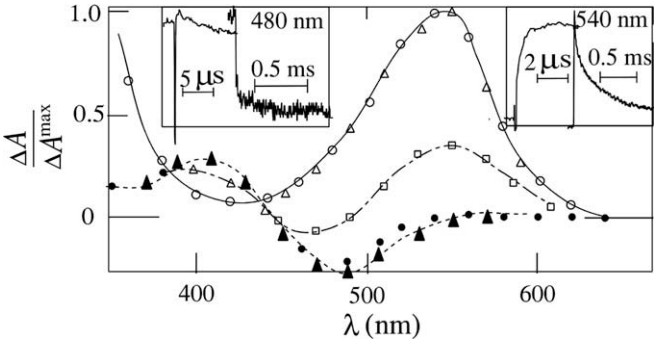


Fig. 10. Transient absorption spectra of A2 in argon-saturated acetonitrile in the presence of benzophenone and 10 mM TEA at 20 ns (○), 1 μs (Δ), 10 μs (□), 0.1 ms (●) and 1 ms (▲) after the pulse; insets: kinetics as indicated.

$$^{3*}O_2NAQ + DH_2 \rightarrow O_2NAQH^{\cdot}/O_2NAQ^{\cdot -} + DH^{\cdot}/DH_2^{\cdot +} \quad (3)$$

$$2 \times O_2NAQH^{\cdot} \rightarrow ONAQ + O_2NAQ + H_2O \quad (4a)$$

$$O_2NAQH^{\cdot} + DH_2 \rightarrow ONAQ + H_2O + DH^{\cdot} \quad (4b)$$

$$DH^{\cdot} + ONAQ \rightarrow D + ONAQH^{\cdot} \quad (5)$$

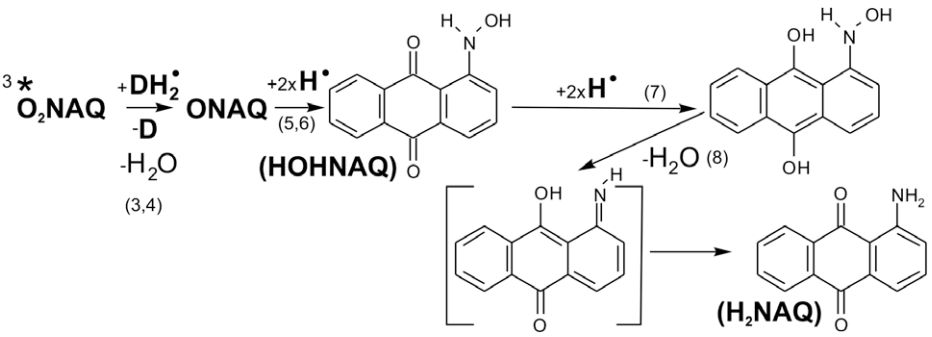
$$2 \times ONAQH^{\cdot} \rightarrow HOHNAQ + ONAQ \quad (6)$$

$$HOHNAQ + DH^{\cdot} \rightarrow HOHNAQH^{\cdot} + D \quad (7a)$$

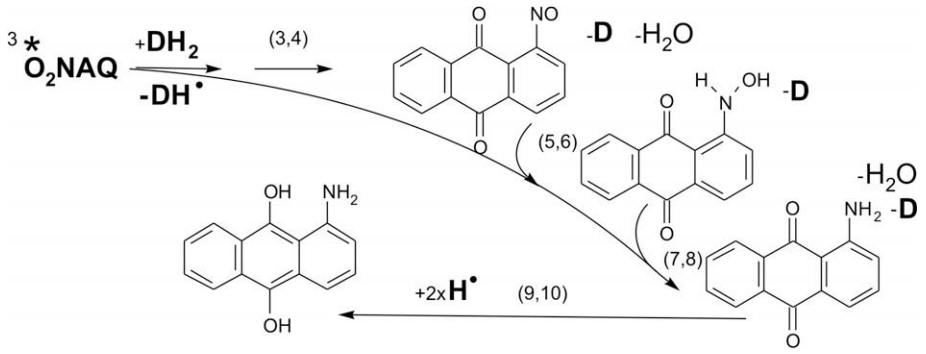
$$DH^{\cdot} + HOHNAQH^{\cdot} \rightarrow HOHNAQH_2 + D \quad (7b)$$

$$HOHNAQH_2 \rightarrow H_2NAQ + H_2O \quad (8)$$

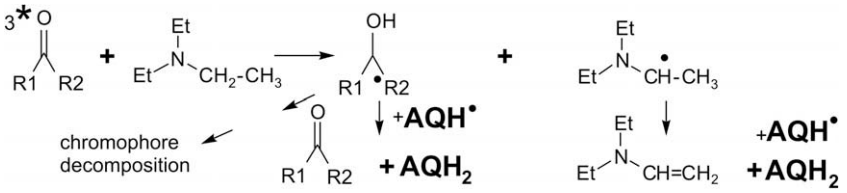
For the final two reduction steps the semiquinone radical is considered [27]. It is formed via step (7a) and converted into the product via (7b) plus (8), i.e. a radical self – coupling reaction is not required. This would explain why the reaction readily proceeds to the amino stage, in contrast to molecules which lack an H-accepting group in close proximity. The earlier proposed mechanism for N1 in 2-propanol contains three photoinduced steps: the first one involves H-transfer to an excited state of nitroAQ and leads to nitrosoAQ, the second photon leads to hydroxylaminoAQ as second non-radical species and the third photon leads to A1 [24,25]. However, the likelihood for the two light-induced steps to react efficiently with a donor is not high. The radical is efficiently quenched by oxygen, thereby forming superoxide radicals ($O_2^{\cdot -}/O_2H^{\cdot}$) which eventually react to hydrogen peroxide with a rate constant of $k_q = (0.5–1) \times 10^7\ M^{-1}\ s^{-1}$. Therefore, when trace amounts of air were admitted, nitrosoAQ could not be detected due to scavenging of the precursor by oxygen. According to the proposed mechanism, a minimum of three nitroAQ molecules in the triplet state is required for one aminoAQ: they give nitrosoAQs, reactions (3) plus (4), and hydroxylaminoAQs, reactions (5) plus (6), which reacts with a donor



Scheme 3.



Scheme 4.



Scheme 5.

radical via (7) plus (8). The observed Φ_{NH_2} (Tables 1 and 2) under non-sensitized conditions is much smaller than the maximum attainable value, this being $\Phi_{NH_2} = 0.33$.

3.9. Reactions of photoreduction of amino(methyl)AQs

Owing to the fact that during irradiation both DH· type radicals and aminoAQ molecules are present, further reduction steps (9) plus (10) of 1-aminoAQ to 1-aminodihydroAQ have to be taken into account, see Scheme 4. Thus prolonged irradiation of nitroAQs forms aminoAQs and finally their dihydro forms. Admission of oxygen, however, converts 1-aminodihydroAQ molecules back, reaction (11), a process being in common for all AQs.

$$H_2NAQ + DH^{\cdot} \rightarrow H_2NAQH^{\cdot} + D \quad (9)$$

$$2 \times H_2NAQH^{\cdot} \rightarrow H_2NAQH_2 + H_2NAQ \quad (10)$$

$$H_2NAQH_2 + O_2 \rightarrow\rightarrow H_2NAQ + H_2O_2 \quad (11)$$

The sensitized reduction occurs via photoreaction (1′), followed by the ketone triplet reaction step (2′) and reactions (9) and (10).

$$Sens + h\nu \rightarrow {}^{1*}Sens \rightarrow {}^{3*}Sens \quad (1')$$

$${}^{3*}Sens + DH_2 \rightarrow SensH^{\cdot}/Sens^{\cdot -} + DH^{\cdot}/DH_2^{+} \quad (2')$$

The radicals involved in the ketone/TEA system are shown in Scheme 5.

For A1 no triplet is populated on direct excitation and Φ_{H_2} is smaller than 10^{-3} even in the presence of an alcohol. This is due to the absence of any semiquinone radical. A CT triplet state of A1 which is inactive towards H-transfer and intramolecular hydrogen bonding, has been considered [20,21]. The proposed mechanism of photoreduction of the amino(methyl)AQs requires an initial radical, either from nitroAQ precursor, reaction (3), or a sensitizer, step (2′). An example with benzophenone as sensitizer is shown in Fig. 10. The important step is H-transfer (9) from the ketyl radical to the aminoAQ yielding the semiquinone radical. The subsequent termination (10) leads to 1-aminodihydroAQ within 1 ms. Therefore, the resulting absorption is larger around 390 nm and a bleaching occurs around 475 nm.

3.10. Reactions of photogenerated radicals with nitro(methyl)AQs

The radicals are efficiently formed via reactions (1′), (2′) and (9′).

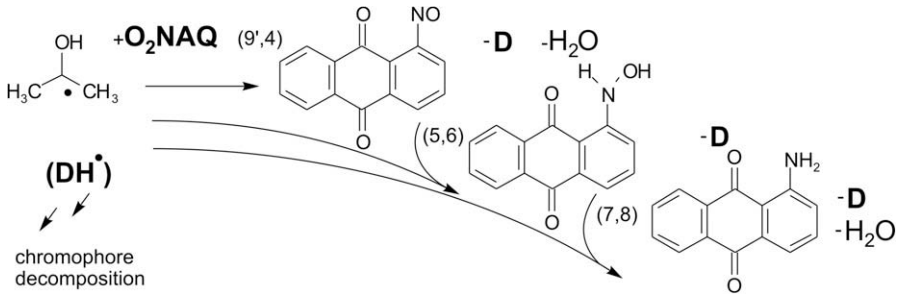
$$O_2NAQ + DH^{\cdot} \rightarrow O_2NAQH^{\cdot} + D \quad (9')$$

Sequence (4)–(8) is similar to that of direct photolysis, Schemes 4 and 6. The rate constant of reduction step (9′) can be estimated from a half-life of $t_{1/2} = 0.2$–1 ms. The rate constant of H-transfer from alcohols to triplet ketones is $k'_2 = (1–2) \times 10^6\ M^{-1}\ s^{-1}$ for 2-propanol [41] and smaller for methanol. For benzophenone/TEA $k'_2 = 1 \times 10^{10}\ M^{-1}\ s^{-1}$ [42]. Therefore, the expected alcohol concentration for 50% quenching is 0.01–1 M, whereas [TEA] is 3–4 orders of magnitude smaller. For acetone as sensitizer and 2-propanol as donor only one radical is involved: 2-hydroxypropyl. This is different for the other radical reactions because of the formation of ketyl and alcohol radicals in equal amount. The benzophenone/donor system has been employed for reduction of related dyes [37,38]. The rate constant of radical termination in aqueous solution is 2.4×10^9, 1.5×10^9 and $1.1 \times 10^9\ M^{-1}\ s^{-1}$ for methanol, ethanol and 2-propanol, respectively, and the rate constant of termination of 2-propanol radicals in acetonitrile is $1 \times 10^9\ M^{-1}\ s^{-1}$ [41,43,44].

3.11. Mechanistic aspects of the full photoreduction of nitro(methyl)AQs

The transient absorption spectra and kinetics of the nitro(methyl)AQs are shown in Figs. 7–9 and the half-lives are compiled in Table 5. They show the triplet state of N2 with a maximum around 400 nm and $\tau_T = 10$ ns and the detectable radicals with one or two bands in the 350–600 nm range as long-lived intermediates. They react via steps (4a) (4b) in nitroso(methyl)AQ or can be scavenged by oxygen. The radical of N1 is formed without observable triplet precursor.

The transient absorption signals after a few milliseconds are too weak to trace the subsequent steps from the nitrosoAQ to the aminoAQ. The photoreduction requires rigorous deoxygenation,



Scheme 6.

e.g. purging with argon (or nitrogen) since the Φ values are much lower when trace amounts of oxygen remain. The obvious reason is scavenging of the radicals by oxygen which prevents radical termination. Radical termination (4) takes place in the ms range and the remaining absorption is considerably reduced (Figs. 7–9). The results of continuous irradiation are in agreement.

4. Conclusion

The photochemical reactions of 1-nitroAQs were studied in acetonitrile in the presence of 2-propanol or other alcohols as H-donors and of triethylamine as electron donor. The triplet state of N2 is short-lived, but can be intercepted. Secondary radicals leading to the nitrosoAQ were observed for both N1 and N2 by flash photolysis. The conversion to the corresponding hydroxylamino form and eventually to A1/A2 is suggested to occur via nitroAQ and donor radicals. The photoreduction to aminoAQs is a cascade-like mechanism requiring six electron equivalents. Subsequent reduction to 9,10-dihydroxyaminoAQs takes place efficiently. The photoconversion of various non-quinone nitroarenes is blocked at the stage of the hydroxylamino form and diazaarenes are formed rather than the corresponding aminoarenes. The full photoreduction of nitroAQs is due to the bi-functional AQ system, where both the nitro group and one of the carbonyl groups are intermediate H-acceptor sites.

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