



Photoreduction of nitro-1,4-naphthoquinones in solution

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ABSTRACT

The photolysis of 2,3-dichloro-*n*-nitro-1,4-naphthoquinones (nitroN'Q, *n*: 5 and 6) was studied in benzene and acetonitrile. The triplet states of both nitroN'Qs, which can be quenched by H-atom donating solvents, e.g. 2-propanol or 1-phenylethanol, were characterized by flash photolysis. Formation and decay of nitronaphthoquinone radicals, due to H-atom transfer, were observed; the reactivities of the donors were examined and the mechanistic aspects discussed. The photoreduction of 6-nitroN'Q in the presence of the donors is efficient in contrast to 5-nitroN'Q. The major product is considered to be 6-hydroxylaminoN'Q.

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1. Introduction

The photolysis of 1,4-benzoquinone (BQ), 1,4-naphthoquinone (NQ) and 9,10-antraquinone (AQ) has been the subject of various studies [1–11]. A major process is photoreduction, e.g. in the presence of alcohols or electron donors, such as triethylamine (TEA). Efficient population of the triplet state is known for BQ, NQ and AQ, the quantum yield of intersystem crossing (Φ_{isc}) of the quinones is substantial [1–4]. For NQ and 2,3-dichloro-1,4-naphthoquinone (N'Q) in acetonitrile $\Phi_{isc} = 0.74$ and 0.90, respectively [11]. The quantum yield (Φ_{Δ}) of formation of molecular singlet oxygen, $O_2(^1\Delta_g)$, which can be regarded as a minimum for Φ_{isc} , is also substantial for NQs in several solvents, e.g. for N'Q in acetonitrile $\Phi_{\Delta} = 0.6$, and only low for cases in which a side chain is present [2–4,11]. A charge transfer band centered at 679 nm appears for N'Q in dimethyl sulfoxide and ethanol in the presence of 0.1–0.6 M TEA [12]. Quinones are known to react with ascorbate (vitamin C) thermally [13] and photochemically [14].

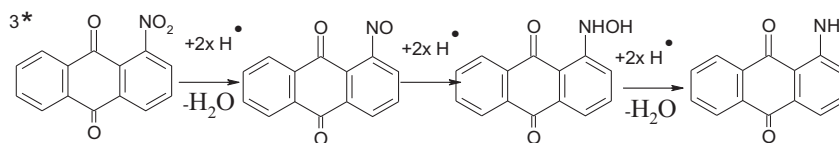
As to the photoreduction of quinonoid nitro-derivatives, 1-nitroAQ and 1-nitro-2-methylAQ have been studied [15–18], but neither nitroBQs nor nitroNQs. The major reduction photoproducts of the non-fluorescing nitroAQs are the fluorescing 1-aminoAQ and the 2-methyl derivative. The complete photoreduction in the presence of H-atom (2-propanol) or electron donors (TEA) leads to the aminoAQs due to transfer of six electron equivalents [15–18]. The

quantum yield (Φ_{red}) of reduction increases with the donor concentration, approaching $\Phi_{red} = 0.1$ [18]. The short-lived triplet state (≤ 20 ns) of 1-nitro-2-methylAQ can react with 2-propanol or TEA, thereby forming the spectroscopically hidden donor radicals and AQ radicals which absorb at 400 and 540 nm; the former and latter bands are due to the nitroAQ radical and its anion, respectively. The triplet state of 1-nitroAQ was not observed at room temperature, but the radical properties and the decay to the nitrosoAQs are similar for both nitroAQs [17,18]. A simplified pathway is shown in [Scheme 1](#).

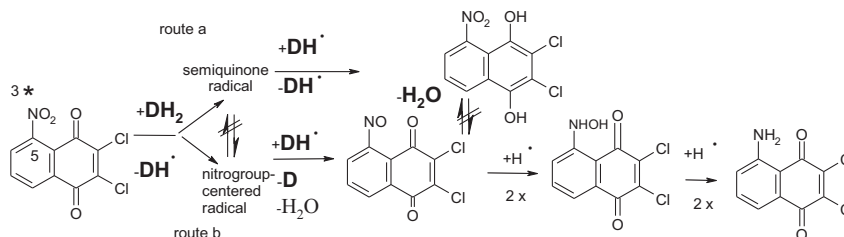
The literature for nitro-substituted NQs is scarce [19–29] and no information is available for nitroBQs as yet. 2,3-Dichloro-5-nitro-1,4-naphthoquinone (5-nitroN'Q) undergoes 1:2 acceptor–donor complex formation with aromatic amines [28]. For 5-nitroNQ conversion to 5-aminoAQ takes place via a Diels–Alder reaction [27].

Here, 5- and 6-nitroN'Q in the presence of an H-atom donor (DH_2) were examined. The photoprocesses and reduction products of nitroNQs are unknown. Two possible pathways of reduction of 5-nitroN'Q after excitation and formation of the triplet state are shown in [Scheme 2](#). Route (a) should yield the semiquinone radical and then the hydroquinone, while route (b) yields the nitrogroup-centered radical, the 5-nitrosoN'Q, 5-hydroxylaminoN'Q and eventually 5-aminoN'Q. Such a complete photoreduction mechanism, involving transfer of six reduction equivalents, has been proposed for 1-nitroAQ, where 1-hydroxylaminoAQ is one reduction product and 1-aminoAQ another [17,18]. However, one result of this study is that such an expectation of full and efficient photoreduction of 5-nitroN'Q is suggested not to be fulfilled.

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Scheme 1.



Scheme 2.

2. Experimental

5- and 6-NitroN'Q were purchased (TCI) and used as received. The other compounds and the solvents were used as commercially available (Aldrich, Merck) and checked for impurities. Acetonitrile was Uvasol quality, TEA was purified by distillation and 1- and 2-phenylethanol were from Fluka, 1-phenylethanol contains ca. 10 mM acetophenone. Water was from a millipore (milli Q) system. The molar absorption coefficient of 6-nitroN'Q in acetonitrile was determined to be $\epsilon_{340} = 4 \times 10^3 \text{ M}^{-1} \text{ cm}^{-1}$. For photoconversion a 1000 W Xe-Hg lamp and a monochromator were applied. Alternatively, irradiation was performed with a 250 W high pressure Hg lamp and a band-pass filter for 366 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 $\lambda_{\text{irr}} = 366 \text{ nm}$ constant. The quantum yields Φ_{red} were determined using $\Phi_{\text{red}} = 0.9$ of 2,3-dimethylAQ in an argon-saturated mixture of acetonitrile and 2-propanol (9:1) as actinometer [9]. The experimental error in the quantum yield determination is typically $\pm 15\%$ and $\pm 30\%$ for values smaller than 0.01. For 5- and 6-nitroN'Q a ground state reaction with TEA takes place, this prevents observation of a possible triplet quenching when the TEA concentration is larger than ca. 10 mM. Flash photolyses operated at $\lambda_{\text{exc}} = 355 \text{ nm}$ (Nd-YAG laser, GMU Lasertechnik), the absorption signals were measured by a Luzchem system. All measurements refer to 24°C .

3. Results and discussion

3.1. Ground state interaction

The absorption spectra of 5- or 6-nitroN'Q in benzene or acetonitrile solution have a band centered at $\lambda_a = 340 \text{ nm}$. A ground state reaction occurs for 6-nitroN'Q in air-saturated 1:1 (vol) mixtures of acetonitrile and water in the presence of ascorbate/ascorbic acid. The latter has a pK_a of 3. The spectral changes of 6-nitroN'Q with 10 mM ascorbate are shown in Fig. 1b. The process is attributed

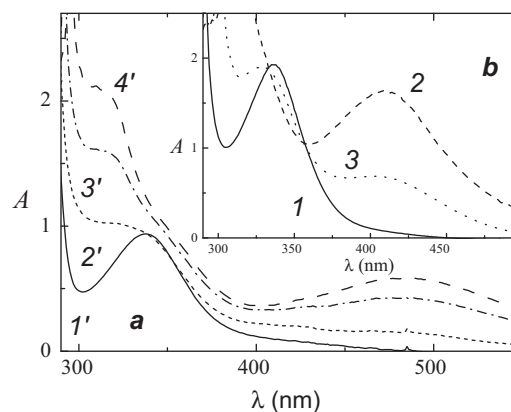
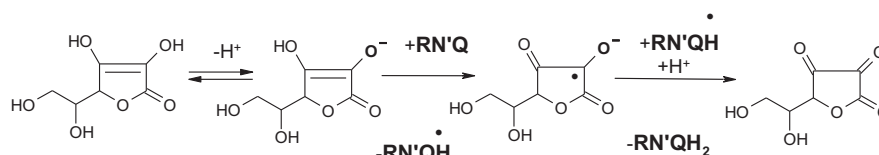


Fig. 1. Absorption spectra of 6-nitroN'Q in (a) argon-saturated acetonitrile in the presence of 0.01 M TEA at 0, 1, 3 and 7 min (1'–4', respectively) and (b) air-saturated, 50% water in the presence of 0.01 M ascorbate at 0, 3 and 30 min, 1–3, respectively.

to thermal reduction, see Scheme 3. One product of RN'Q (R: NO_2) is attributed to the nitroso form (nitrosoN'Q). Spectroscopically, it can probably not be distinguished from a dihydroquinone ($\text{nitroQH}_2 - \text{H}_2\text{O}$) as yet. Further reaction of nitrosoN'Q (R: NO) leads to hydroxylaminoN'Q (R: NHOH).

A similar reaction does not take place for 5-nitroN'Q, indicating different reduction potentials for the two nitroN'Qs. The thermal reaction of 6-nitroN'Q with ascorbate is unique and has not reported for nitroAQs. Interestingly, the time-dependence of thermal reduction of 6-nitroN'Q shows a reversibility, see curve 3 vs. 2 in Fig. 1b. This partial oxidation ($\text{hydroxylaminoN'Q} + 2\text{O}_2 \rightarrow \text{nitrosoN'Q} \rightarrow \text{nitroN'Q}$, see below) does not occur in the absence of oxygen.

Another ground state interaction was observed with TEA. The spectral changes of 6-nitroN'Q in argon-saturated mixtures of acetonitrile and water in the presence of 10 mM TEA are shown in Fig. 1a. For N'Q in dimethyl sulfoxide and ethanol the presence of 0.3 M TEA is required for the charge transfer band [12].



Scheme 3.

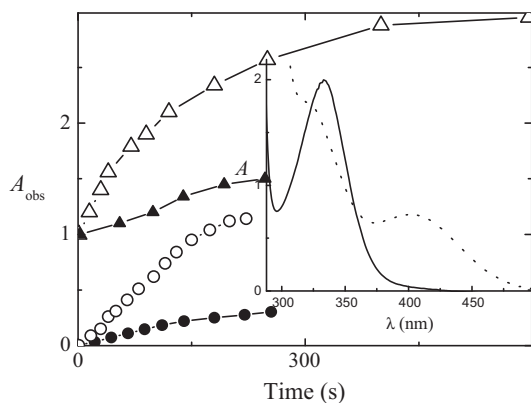


Fig. 2. Absorption at 300 (triangles) and 410 nm (circles) of 6-nitroN'Q in argon-saturated acetonitrile in the presence of 0.5 (full) and 8 M (open) 2-propanol as a function of time of irradiation at 366 nm; inset: spectra for 1 M 2-propanol at 0 (full) and 500 s (broken).

However, for 6-nitroN'Q in acetonitrile much lower TEA concentrations are required for the band at 500 nm. The low TEA concentration excludes charge transfer as origin of the observed band. Alternatively, a doubly deprotonated dihydroquinone is considered for nitroN'Qs. Moreover, upon irradiation of 6-nitroN'Q in argon-saturated acetonitrile in the presence of TEA, a new band centered at 620 nm appears. However, a separation between thermal and photochemical effects was not successful. Therefore, the effects of TEA on nitroN'Qs remain open as yet.

3.2. Irradiation of nitroN'Qs

Upon irradiation of 6-nitroN'Q at 366 nm in argon-saturated mixtures of acetonitrile and 2-propanol, a new band centered at $\lambda_a = 410$ nm appears. This is in contrast to neat argon-saturated acetonitrile, where no photoconversion occurs. The spectral changes of 6-nitroN'Q in the presence of 1 M 2-propanol are shown in Fig. 2 (inset). The corresponding A_{300} and A_{410} values as a function of time of irradiation at 366 nm are shown in Fig. 2. The slope is taken as a measure of the quantum yield of conversion of 6-nitroN'Q to a stable product. In a 1:1 mixture of acetonitrile and 2-propanol $\Phi_{red} = 0.06$, see Table 1. A_{410} as a function of time of irradiation at 366 nm is substantial for 6-nitroN'Q and relatively small for 5-nitroN'Q. Another example is shown for 1-phenylethanol as donor (Fig. 3). The corresponding spectral changes are shown for 6-nitroN'Q in argon-saturated mixtures of acetonitrile and 1-phenylethanol (inset of Fig. 3). The quantum yield increases with the donor concentration, approaching $\Phi_{red} = 0.16$ – 0.25 for 3 M 1-phenylethanol in benzene and acetonitrile. In contrast, Φ_{red} is markedly smaller in the presence of 2-phenylethanol. The same

Table 1
Quantum yield Φ_{red} of reduction of nitroN'Qs upon irradiation in the presence of donors.^a

Compound	Donor	Conc. (M)	Φ_{red}
5-NitroN'Q	2-Propanol	10	0.004
	1-Phenylethanol	3	0.004
6-NitroN'Q	2-Propanol	0.1	0.004
		1	0.016 (0.016) ^b
	10	0.06	
	1-Phenylethanol	0.03	0.016
		0.3	0.06
		1	0.11
	3	0.25 (0.15)	
2-Phenylethanol	3	0.006	

^a In argon-saturated acetonitrile, $\lambda_{irr} = 366$ nm.

^b In parentheses: benzene.

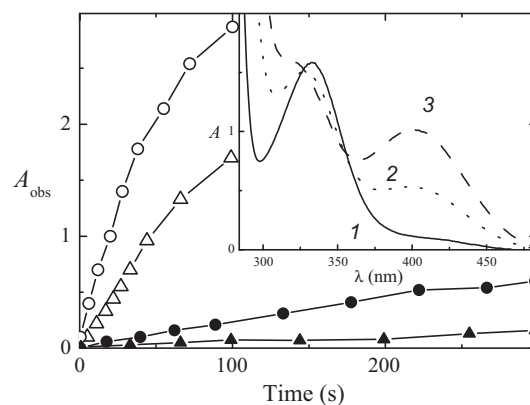


Fig. 3. A_{410} values of 5-nitroN'Q (full) and 6-nitroN'Q (open) in argon-saturated acetonitrile in the presence of 0.5 (triangles) and 8 M (circles) 1-phenylethanol as a function of time of irradiation at 366 nm; inset: absorption spectra of 6-nitroN'Q for 0.5 M 1-phenylethanol at 0, 30 and 200 s (1–3, respectively).

effect has previously been reported for 1-nitroAQ, where the much slower rate constant for H-abstraction has been attributed to the lower strength of the C–H bond of 2- vs. 1-phenylethanol [17].

The isosbestic points at 325 and 355 nm (inset of Fig. 3) indicate no significant secondary photolysis of 6-nitroN'Q. The product is assigned to the 6-hydroxylaminoN'Q on the basis of spectral characteristics, see below. For comparison, 1-nitroAQ has $\lambda_a = 360$ nm, 1-hydroxylaminoAQ $\lambda_a = 450$ nm and 1-aminoAQ $\lambda_a = 460$ nm [17,18]. Virtually no photoconversion occurs for 6-nitroN'Q, when oxygen is present. For 5-nitroN'Q in the presence of the two donors Φ_{red} is much lower (Table 1). A partial thermal reaction of the photoproduct to 6-nitroN'Q (5–40%) upon addition of air was found after a few days.

3.3. Reactions of the triplet state

The transient absorption spectra of 5- or 6-nitroN'Q in argon-saturated acetonitrile, $\lambda_{exc} = 355$ nm, are broad with a maximum at $\lambda_{TT} = 380$ – 400 nm and extending to 600 nm. They are attributed to the triplet state (${}^3Q^*$) since the species are formed within the pulse and due to quenching by oxygen. The decay kinetics in the absence of additives follow essentially a first-order law (rate constant: $1/\tau_T$) and the triplet lifetimes are $\tau_T = 6$ – 9 μ s, i.e. typical for quinones. As examples, the T–T absorption spectra of 6-nitroN'Q in benzene and acetonitrile are shown in Fig. 4a and b. The λ_{TT} and τ_T values of the nitroN'Qs examined are compiled in Table 2. The triplet properties

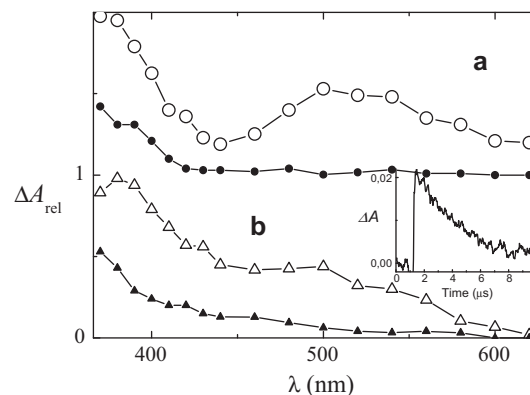


Fig. 4. Transient absorption spectra of 6-nitroN'Q in argon-saturated (a) benzene and (b) acetonitrile at 0.2 (open) and 100 μ s (full) after the 355 nm pulse; inset: kinetics at 500 nm.

Table 2
Absorption maximum, triplet lifetime and rate constants for quenching of triplet nitroNQs by 2-propanol^a and oxygen.

Compound	Solvent	λ_T (nm)	τ_T (μ s)	k_3 ($10^9 \text{ M}^{-1} \text{ s}^{-1}$)	k_4 ($10^6 \text{ M}^{-1} \text{ s}^{-1}$)
5-NitroNQ	Acetonitrile	380, 550	8	0.9	0.3 (3) ^b
6-NitroNQ	Benzene	380, 550sh	9	0.8	
NitroNQ	Acetonitrile	370, 530sh	9	1	0.3 (3)
N'Q ^c	Benzene	380, 470sh	15	0.6	
	Acetonitrile	380, 470sh	8	0.8	5 (40)

^a In argon-saturated solution, $\lambda_{\text{exc}} = 355 \text{ nm}$.

^b In parentheses: 1-phenylethanol.

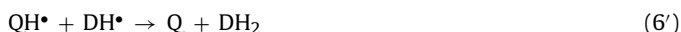
^c Taken from Ref. [11].

of both nitroNQ are rather similar. A minimum reaction sequence is (1)–(6), as for other NQs [9].



In most cases a minor longer lived transient appeared, which is attributed to a radical, formed by self-quenching (step 2) and/or triplet annihilation. The rate constant for triplet quenching by oxygen (3) is $k_3 = (0.8\text{--}1.0) \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$. The rate constant for triplet decay of 5- or 6-nitroNQ in argon-saturated acetonitrile becomes larger on addition of the donor. The rate constants k_4 for triplet quenching (reaction (4)) were obtained from the linear dependences of $1/\tau_T$ vs. the donor concentration. Note that this turned out to be difficult due to the similarities of the T–T and radical absorption spectra. The k_4 values for 5- and 6-nitroNQ are similar, $0.3 \times 10^6 \text{ M}^{-1} \text{ s}^{-1}$ for 2-propanol and $3 \times 10^6 \text{ M}^{-1} \text{ s}^{-1}$ for 1-phenylethanol (Table 2).

For NQ in acetonitrile the T–T absorption is overlapped by a weak longer lived transient with a maximum at $\lambda_{\text{rad}} = 375 \text{ nm}$, which is assigned to the semiquinone radical. In contrast, the absorption spectra of N'Q shows mainly the triplet state [9]. Transient absorption spectra of NQ in mixtures of acetonitrile and 2-propanol are due to the triplet state and the semiquinone radical which are both strongly absorbing and completely overlapping. After reaction (4) radical termination via (5) yields the corresponding dihydroquinone (QH₂). Further pathways into the semiquinone radical are quenching of the triplet state by Q (self-quenching, k_2) and T–T annihilation under pulsed excitation. For NQ in acetonitrile the literature value is $k_2 = 1 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$ [10]. After photoconversion, triplet quenching by dihydroquinone may take place. One out of several possibilities to account for a low reduction efficiency is step (6'), which may occur by electron transfer to DH[•] and protonation/deprotonation.



3.4. Reaction mechanism of nitroNQs

The transient absorption spectra of 6-nitroNQ in mixtures of acetonitrile and 2-propanol or 1-phenylethanol are presented in Figs. 5 and 6, respectively. The long-lived transient is attributed to the nitro-N'Q radical. An electron transfer from TEA yields the radical anion ($Q^{\bullet-}$), but this was not studied here (see above). Decay of the radical under argon occurs by second-order kinetics with a first half-life in the ms range under our conditions. In principle, the alcohol radical could yield educt Q and product QH₂ via reactions (6') and (6), respectively. Here D is acetone, when the donor is 2-propanol.

The photoconversion of a nitroarene to the aminoarene is a rare process which requires six electrons. Such a complete photo-reduction mechanism has been proposed for 1-nitroAQs [17,18]. A full reduction could be possible for 5-nitroNQ, where the last reduction step (hydroxylamino \rightarrow amino) involves the neighboring carbonylgroup, Scheme 2. However, Φ_{red} of 5-nitroNQ is too small. The two possibilities of reduction after excitation and formation of the triplet state remain also for 6-nitroNQ: route (a) via the nitroNQ[•]H radical to the dihydroquinone or route (b) via the nitrogroup-centered radical to the nitrosoquinone. The latter possibility and further reactions are shown in Scheme 4.

In principle, the reduction can lead to 6-hydroxylaminoNQ involving transfer of four reduction equivalents. Φ_{red} of 6-nitroNQ is substantial in optimized cases (Table 1). For 6-nitroNQ, a complete reduction is probably complex since the last reduction step lacks the neighboring carbonylgroup.

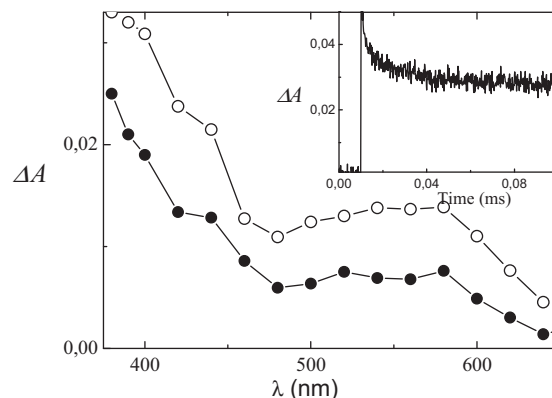


Fig. 5. Transient absorption spectra of 5-nitroNQ in argon-saturated acetonitrile in the presence of 3 M 2-propanol at 0.1 μ s (○) and 0.1 ms (●) after the 355 nm pulse; inset: kinetics at 400 nm.

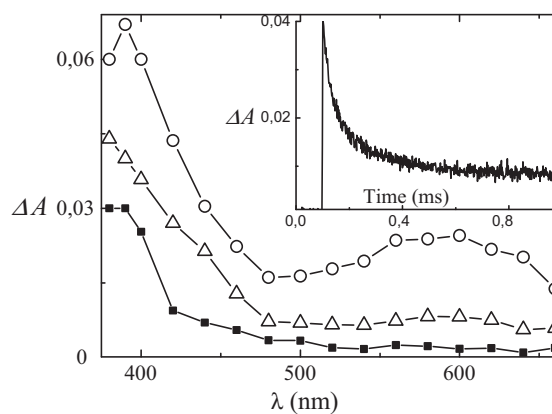
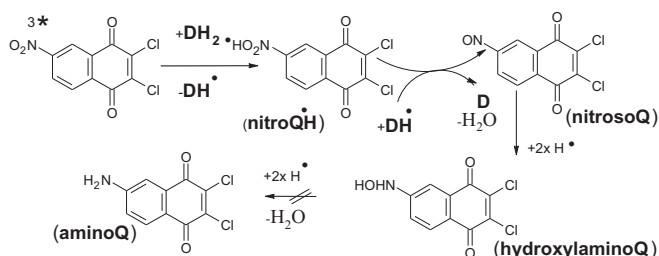
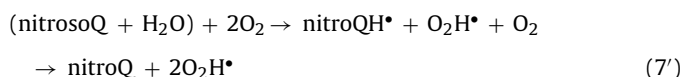
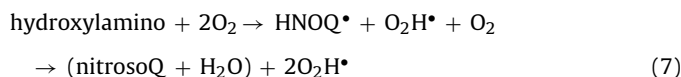


Fig. 6. Transient absorption spectra of 6-nitroNQ in argon-saturated acetonitrile in the presence of 0.1 M 1-phenylethanol at 1 μ s (○), 100 μ s (△) and 1 ms (■) after the 355 nm pulse; inset: kinetics at 420 nm.



Scheme 4.

Concerning the stability of the product of 6-nitroN'Q, admission of oxygen leads to a slow back-reaction. This is summarized in reactions (7) and (7').



There is some evidence for this reaction either photochemically in the presence of 1-phenylethanol (5–40% reversion upon addition of air after a few days, see Section 3.2) or thermally, see curve 3 vs. 2 in Fig. 1b.

A surprising finding of this work is $\Phi_{\text{red}} = 0.06\text{--}0.2$ for 6-nitroN'Q, but ≤ 0.004 for 5-nitroN'Q (Table 1). On the other hand, the triplet reactivities are similar for both nitroN'Qs (Table 2). The triplet state of nitroN'Qs can be intercepted by 2-propanol or 1-phenylethanol, thereby forming the donor radicals which absorb also at 400–600 nm. The strong difference in Φ_{red} indicates a deactivation step in the case of 5-nitroN'Q, not leading to permanent photoreduction. A twisting may occur for the 5-nitro group, but this is not expected for 6-nitroN'Q. The reason for this low reactivity could be the close proximity of the 5-nitro and the 4-carbonyl groups. A back-electron transfer is not possible for the radical of 6-nitroN'Q, but the details are unknown.

3.5. Properties of aromatic nitroso compounds

For nitrobenzene, a complete reduction is inefficient since a dimerization process is successful [30]. As to the properties of aromatic nitroso compounds, the nifedipine/nitrosophenyl couple is considered to be a good example. Nifedipine, a 4-(2-nitrophenyl)-1,4-dihydropyridine, is a calcium channel blocker and frequently used in the treatment of hypertension or cardiovascular diseases. It is sensitive to UV radiation and the photochemistry has therefore been the subject of various studies [31]. The intramolecular photoreduction of nifedipine into its nitrosophenyl product takes place within a few ns and the quantum yield of conversion is $\Phi_{\text{red}} = 0.3$ and does not depend significantly on the oxygen concentration and solvent properties. The photoconversion can be monitored in the UV range and is accompanied by the formation of an absorption band centered at 770 nm due to the nitrosophenyl entity, the molar absorption coefficient of which has been reported to be $\epsilon_{770} = 60 \text{ M}^{-1} \text{ cm}^{-1}$ [31].

For 1-nitrosoAQ a much lower absorption in the 300–500 nm range than the corresponding nitroAQ, hydroxylaminoAQ and aminoAQ has been postulated [17,18]. This is now also concluded for nitrosoN'Qs, thus excluding it as possible photoreduction product of 6-nitroN'Q with peak at 410 nm. Therefore, the observed photoreduction pathway is considered to lead to 6-hydroxylaminoN'Q rather than to end at the nitrosoN'Q stage.

3.6. Comparison between nitroN'Qs and nitroAQs

The ground state reactions of NQs or AQs with ascorbate/ascorbic acid has been reported to be slow [13,14], in contrast to that of 6-nitroN'Q (Fig. 1b). Moreover, no ground state reaction of quinones has been reported with TEA, except those with N'Q cited in the introduction.

The properties of nitroN'Qs and nitroAQs have similarities and differences. Similar for both is the multiplicity of the reactive intermediate: triplet state. However, the triplet state of nitroAQs is short-lived: ≤ 20 ns for 1-nitro-2-methylAQ, whereas that of 1-nitroAQ is probably much shorter since it has not been observed at room temperature [17,18]. The short triplet lifetime of nitroAQs is due to sterical reasons [18]. As a measure of triplet reactivity of nitroAQs, that of 2,3-dimethylAQ was used; $k_4 = 4 \times 10^7 \text{ M}^{-1} \text{ s}^{-1}$ for 1-phenylethanol and 50% smaller for 2-phenylethanol [17]. These values and those for 2-propanol are somewhat larger than for 6-nitroN'Q. For 1-nitroAQ the larger Φ_{red} in the presence of 1-phenylethanol with respect to 2-propanol is mainly due to the presence of ca. 10 mM acetophenone as sensitizer and irradiation at 308–313 nm [17,18]. A similar enhancement for 6-nitroN'Q in the presence of 1-phenylethanol cannot be ascribed to sensitization since irradiation was performed at 355–366 nm. The smaller Φ_{red} in the presence of 2-propanol may be due to reactions of type (6') in addition to (6).

4. Conclusions

The photoreduction processes of two 2,3-dichloro-*n*-nitro-1,4-naphthoquinones ($n=5,6$) in acetonitrile by 2-propanol or 1-phenylethanol were analyzed. The photoprocesses are governed by the nitro group, whereas a specific role of 2,3-dichloro substitution could not be found. The triplet state properties were characterized by transient UV–vis absorption spectroscopy and H-atom transfer from the donors to the triplet state was studied. The radical intermediates involved are assigned on the basis of spectral and kinetic characteristics. The photoreduction of the 6-nitro compound in the presence of H-atom donors is efficient, $\Phi_{\text{red}} = 0.06\text{--}0.2$, in contrast to the 5-nitronaphthoquinone. The major product is ascribed to the 6-hydroxylamionaphthoquinone which can also be achieved without UV light.

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