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Photoprocesses of *p*-naphthoquinones and vitamin K_1: effects of alcohols and amines on the reactivity in solution

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Received 11th June 2003, Accepted 8th September 2003
First published as an Advance Article on the web 30th September 2003

The photochemistry of 1,4-naphthoquinone (NQ), the 2-methyl, 2,3-dichloro and 2-bromo derivatives, and vitamin K_1 was studied in non-aqueous solvents by time-resolved UV-vis spectroscopy after ns laser pulses at 248 and 308 nm. The triplet state of the NQs reacts with alcohols and amines, *e.g.* triethylamine (TEA) and DABCO, yielding semiquinone radicals ($HQ^{\bullet}/Q^{\bullet-}$). They are the major intermediates and their second-order decay kinetics depend on the properties of the additives and the medium. Transient conductivity measurements suggest the occurrence of photoinduced electron transfer from amines to the triplet state of NQs in acetonitrile. The photoconversion (λ_{irr} = 254 nm) of NQs to the 1,4-dihydroxynaphthalenes (H_2Q) was measured in the absence and presence of varying concentrations of electron and H-atom donors, and the quantum yield was found to increase with increasing electron- or proton-donor concentration. The mechanisms of photoreduction of NQs by propan-2-ol and TEA in acetonitrile exhibit a number of similarities. Oxygen quenches the triplet state, thereby forming singlet molecular oxygen. Oxygen also reacts with the semiquinone radical, thereby forming $HO_2^{\bullet}/O_2^{\bullet-}$ radicals, and reacts with H_2Q, thereby re-forming the quinone. A different pattern, involving intramolecular H-atom transfer, holds for vitamin K_1, where 1,3-quinone methide (1,3-QM) diradicals were observed in acetonitrile prior to formation of two 1,2-QM tautomers, but a triplet was not. The decay of the 1,3-QM intermediates becomes faster in the presence of alcohols and amines due to proton-transfer reactions.

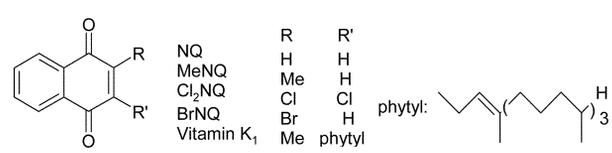
1 Introduction

Quinones are of great photobiological importance and serve as electron acceptors in photosynthesis.[1] The photoreduction of 1,4-benzoquinone and its derivatives, such as 1,4-naphthoquinone (NQ), 2-methyl-1,4-naphthoquinone (MeNQ) and 9,10-anthraquinone (AQ), has attracted widespread attention.[1–26] Generally, quinones exhibit a high quantum yield of intersystem crossing (Φ_{isc}), *e.g.* Φ_{isc} = 0.74 for NQ in acetonitrile.[2,10] MeNQ (vitamin K_3 or menadione) was frequently used to generate radical cations, especially the radical cation of thymine.[7] Cross-linking with a quantum yield of $<10^{-3}$ was reported for single-stranded DNA.[8] FTIR spectroscopic studies of quinones have suggested new avenues for investigation and yielded structural information.[1,12] This is important for the understanding of quinone–protein interactions in photosynthetic reaction centers.

The photochemistry of vitamin K_1 has been the subject of various studies.[27–34] In contrast to other quinones without isoprenoid side chains, vitamin K_1 undergoes intramolecular H-atom and proton-transfer processes. The products have been identified as the *E* and *Z* tautomers of 1,2-quinone methide (1,2-QM).[28–31] Two 1,3-quinone methide (1,3-QM) diradical intermediates have been characterized as the singlet and triplet states of 1,3-QM.[34]

The photoreduction of quinones by amines has been intensively studied.[11–15,21–23] The rate constant for triplet quenching (k_D) of NQ and MeNQ in acetonitrile by *N,N*-dimethylaniline (DMA) and triethylamine (TEA), due to appropriate redox properties, is close to the diffusion-controlled limit.[11,12] The photoreduction of quinones by propan-2-ol[4,19] or TEA leads, *via* the corresponding semiquinone radicals ($HQ^{\bullet}/Q^{\bullet-}$), to hydroquinones ($H_2Q$), 1,4-dihydroxynaphthalene in the case of NQ. The studies into the photochemistry of quinones are complemented by radiochemical studies.[35–37] The semiquinone radical plays a key role in the photoreduction of NQs, even when no donor is added. Photoinduced electron transfer from furan to the triplet state has been reported for 2,3-dichloro-1,4-naphthoquinone (Cl_2NQ).[9]

This paper aims to gain a deeper insight into the photoreduction reactions of NQ, MeNQ, 2-bromo-NQ (BrNQ) and Cl_2NQ in solution at room temperature in the presence of amines and alcohols. Time-resolved UV-vis spectroscopy and conductivity measurements with 248 and 308 nm pulses were applied and the secondary intermediates were produced by triplet quenching. Conversion of the NQs into hydroquinones and the quantum yield of decomposition were measured by continuous irradiation at 254 nm. The photoreduction pathways in acetonitrile–propan-2-ol, benzene–TEA and acetonitrile–TEA mixtures show a close relationship. In addition, the photochemical reactions of vitamin K_1 in acetonitrile in the absence and presence of amines and alcohols were studied. The data for vitamin K_1 are consistent with the modified reaction mechanism recently presented by Wirz *et al.*[34]



2 Materials and methods

All reagents were obtained from Aldrich and the solvents from Merck, benzene was Uvasol grade. NQ was purified by recrystallization and methylcyclohexane (MCH), 2-methyltetrahydrofuran (MTHF), TEA and DEA were distilled prior to use. All other reagents were used as received. Note that commercial vitamin K_1 (from Aldrich in our case) consists of *Z* and *E* isomer racemates in a ratio of 0.1–0.2.[34] The molar absorption coefficients of NQ are $\varepsilon_{254} = 1.7 \times 10^4$ M^{-1} cm^{-1} and $\varepsilon_{308} = 1.5 \times 10^3$ M^{-1} cm^{-1}. The absorption spectra were monitored on a HP 8453 UV-vis spectrophotometer. For photoconversion, the 254 nm line of a Hg lamp was used. The photoconversion was carried out with vigorous bubbling of argon through the solution prior to and during irradiation. The photodecomposition of the substrate was measured upon prolonged irradiation. Product analysis by HPLC was not

DOI: 10.1039/b306670n

successful due to the oxygen effect, as reported for AQs.[22] The emission and excitation spectra, and phosphorescence lifetime at −196 °C were measured on a Cary Eclipse spectrofluorimeter.

Relative yields were obtained using optically matched solutions (A_{254} = 1.5–2.0). The quantum yield of decomposition (Φ_d) was determined using the uridine–water–oxygen actinometer.[38] An excimer laser (Lambda Physik EMG 200, pulse width of 20 ns and energy <100 mJ) was used for excitation at 308 nm. For a few experiments, excitation at 248 nm was used. The absorption signals were measured with two digitizers (Tektronix 7912AD and 390AD). Typically, absorbances of 0.3–1.5 were used for λ_{exc}, corresponding to concentrations of 0.2–1 mM. The molar absorption coefficient of $HQ^{\bullet}$ for NQ in aqueous solution is $\varepsilon_{370} = 7 \times 10^3$ M^{-1} cm^{-1} that of $Q^{\bullet-}$ is $\varepsilon_{390} = 13 \times 10^3$ M^{-1} cm^{-1}.[35,36] For NQ in acetonitrile, the molecular absorption coefficient of T–T absorption and the semiquinone radical anion are $\varepsilon_{365} = 8.2 \times 10^3$ M^{-1} cm^{-1} and $\varepsilon_{403} = 8.8 \times 10^3$ M^{-1} cm^{-1}, respectively, and for MeNQ, the molar absorption coefficient of $Q^{\bullet-}$ is $\varepsilon_{405} = 7.5 \times 10^3$ M^{-1} cm^{-1}.[10,11] The value for $Q^{\bullet-}$ of Cl_2NQ in acetonitrile–water is $\varepsilon_{400} = 7.9 \times 10^3$ M^{-1} cm^{-1}.[9] The quantum yields of formation of singlet molecular oxygen (Φ_Δ) were measured as described previously.[39] The measurements were made at 24 ±2 °C in deoxygenated solutions, unless otherwise indicated.

3 Results and discussion

3.1 Reactions of the triplet state with oxygen and alcohols

The T–T absorption spectra of NQ in argon-saturated acetonitrile [Fig. 1(a)] and carbon tetrachloride (λ_{exc} = 308 nm) show a maximum at λ_{TT} = 370 nm. Efficient population of the triplet state (reaction 1) is known to occur from literature values of Φ_{isc} = 0.74, 0.86 and 0.90 for NQ, MeNQ and Cl_2NQ in acetonitrile, respectively.[9,10]

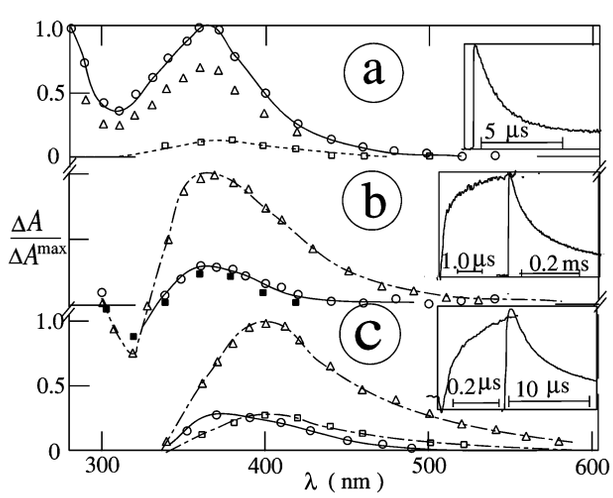


Fig. 1 Transient absorption spectra of NQ in argon-saturated acetonitrile (a) with no added donor, (b) in the presence of propan-2-ol (1 M) and (c) in the presence of DABCO (0.3 mM) at 20 ns (○), 1 µs (Δ), 10 µs (□) and 10 ms (■) after the 308 nm pulse Insets: radical formation and decay at 410 nm.

$$^1{}^*Q \longrightarrow {}^3{}^*Q \qquad (1)$$

The decay kinetics in the absence of additives follow essentially a first-order law (rate constant: $1/\tau_T$). Variation of the NQ or MeNQ concentration in acetonitrile shows a linear dependence of $1/\tau_T$ (reaction 2).[10]

$$^3{}^*Q + Q \longrightarrow 2\,Q \qquad (2)$$

Therefore, the lifetimes presented are for relatively low concentrations, corresponding to A_{308} = 0.5, where τ_T =1.9 µs. The triplet lifetime of Cl_2NQ is much longer, in agreement with τ_T = 7 µs in acetonitrile–water (4 : 1).[9] The λ_{TT} and τ_T values of the NQs examined are compiled in Table 1.

The rate constant for triplet quenching by oxygen (reaction 3) is k_{ox} = (0.3–1.5) × 10^9 M^{-1} s^{-1} (Table 1).

$$^3{}^*Q + O_2 \longrightarrow Q + O_2(^1\Delta_g) \qquad (3)$$

The decay of the triplet depends strongly on the kind of solvent and/or appropriate additives (H_2D). For NQ and MeNQ in acetonitrile, the T–T absorption is overlapped by a weak longer-lived transient with a maximum at λ_{rad} = 375 nm, which is assigned to the semiquinone radical ($HQ^{\bullet}$). In contrast, the absorption spectra of Cl_2NQ [Fig. 2(a)] and BrNQ show mainly the triplet state. After reaction 4, radical termination *via* reaction 5 yields Q and the corresponding hydroquinone (H_2Q).

$$^3{}^*Q + H_2D \longrightarrow HQ^{\bullet} + HD^{\bullet} \qquad (4)$$

$$2\,HQ^{\bullet} \longrightarrow Q + H_2Q \qquad (5)$$

Further pathways to 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 × 10^9 M^{-1} s^{-1}.[10] Transient absorption spectra of NQ in mixtures of acetonitrile and propan-2-ol are due to the triplet state and the semiquinone radical, which are both strongly absorbing and completely overlap each other [Fig. 1(b)]. For the NQs, the reactivity is rather high when compared to, for example, duroquinone.[2,5] After photoconversion, triplet quenching by hydroquinone also takes place, the rate constant for which is close to the diffusion-controlled limit.[40]

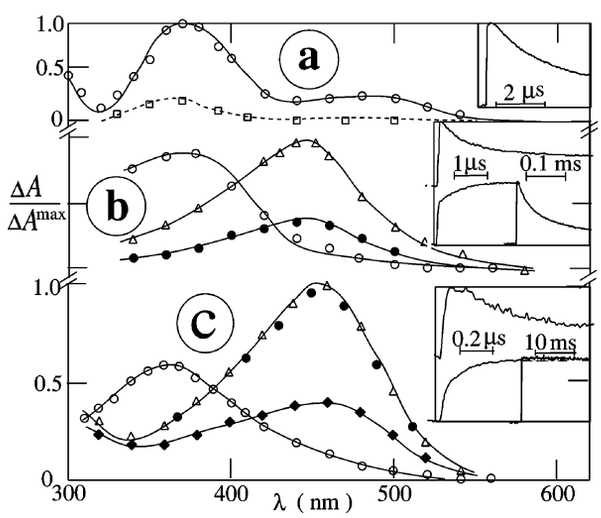


Fig. 2 Transient absorption spectra of Cl_2NQ in argon-saturated acetonitrile (a) with no added donor, (b) in the presence of propan-2-ol (0.1 M) and (c) in the presence of TEA (1 mM) at 20 ns (○), 1 µs (Δ), 10 µs (□), 0.1 ms (●) and 0.1 s (◆) after the 308 nm pulse. Insets: radical formation and decay at 410 nm.

The rate constant for triplet decay of NQs in argon-saturated acetonitrile becomes larger on addition of propan-2-ol. The rate constants for triplet quenching (reaction 4), obtained from the linear dependences of $1/\tau_T$ *vs.* [propan-2-ol], are specific for each quinone and medium. The value is $k_D = 3 \times 10^7$ M^{-1} s^{-1} for NQ and MeNQ, and lower for the other NQs (Table 2). In aqueous solution at pH 7, the semiquinone radical is present as a radical anion ($Q^{\bullet-}$) with pK_a = 4.0–4.5.[2,35–37]

$$HQ^{\bullet} \rightleftharpoons Q^{\bullet-} + H^+ \qquad (6)$$

In contrast to AQ, where the spectra of $HQ^{\bullet}$ and $Q^{\bullet-}$ are quite different, those of the NQs are only slightly shifted.[2,35] The

Table 1 Absorption maxima (λ_{TT}), triplet lifetimes (τ_T),[a] rate constants for quenching by oxygen (k_{ox}) and quantum yields of formation of singlet molecular oxygen (Φ_Δ) for the NQs

Quinone	Solvent	λ_{TT}/nm	τ_T/μs	$k_{ox}/10^9$ M^{-1} s^{-1}	Φ_Δ[b]
NQ	CCl_4	370	2.5	0.7	0.6
	C_6H_6	370	0.2	>0.8	0.07
	CH_2Cl_2	380	0.9	0.4	
	CH_3CN	370	1.9[c], 3[d]	0.3	0.4
MeNQ	CH_3CN	380	0.9[c]	1.5	
Cl_2NQ	C_6H_6	370, 470sh	15	0.6	0.6
	CH_3CN	370, 470sh	8, 8[d]	0.8	0.6
BrNQ	CCl_4	400	5		0.7
	CH_3CN	400	3, 3[d]	0.8	0.7

[a] In argon-saturated solution, λ_{exc} = 308 nm. [b] In oxygen-saturated solution. [c] For A_{308} = 0.5. [d] λ_{exc} = 248 nm.

Table 2 Rate constants for quenching by amines and propan-2-ol (k_D), absorption maxima (λ_{rad}) and half-lives ($t_{1/2}$) for the semiquinone radicals of the NQs[a]

Quinone	Solvent	Donor	k_D[b]/10^9 M^{-1} s^{-1}	λ_{rad}[c]/nm	$t_{1/2}$/ms
NQ	C_6H_6	TEA	3	380	0.002
	CH_3CN	DABCO	9 (15)[d]	360, 400	0.01
		TEA	16	370, 405	2
		Propan-2-ol	0.03	370	0.2
MeNQ	C_6H_6	TEA	3	380	0.02
	CH_3CN	TEA	12	380	2
		Propan-2-ol	0.03	375	1
Cl_2NQ	C_6H_6	TEA	2	460	0.005
	CH_3CN	TEA	10	460	>50
		Propan-2-ol	0.005	450	0.09
BrNQ[e]	CH_3CN	TEA	3	390	2
		Propan-2-ol	0.015	385	0.05

[a] In argon-saturated solution, λ_{exc} = 308 nm. [b] [Amine] = 0.2–10 mM, [propan-2-ol] = 0.02–1 M. [c] The first and second values correspond to [amine] = 0.3 and 20 mM, respectively. [d] With DEA. [e] λ_{exc} = 248 nm.

overall photoconversion leads to H_2Q and acetone. Transient absorption spectra of NQ in mixtures of acetonitrile and propan-2-ol are presented in Fig. 1(b). In contrast to NQ and MeNQ, the spectra of $^3Q^*$ and $HQ^\bullet$ are separated for Cl_2NQ [Fig. 2(b)] and BrNQ, since λ_{TT} is red-shifted with respect to λ_{rad}. Decay of the semiquinone 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 another semiquinone radical *via* reaction 7. A second reduction, due to reactions 4 and 7, became unobservable and self-termination (reaction 8) probably competes efficiently upon pulsed excitation, as already suggested for AQs.[22]

$$HD^\bullet + Q \longrightarrow D + HQ^\bullet \quad (7)$$

$$2\ HD^\bullet \longrightarrow \text{products} \quad (8)$$

3.2 Reactions of the quinone triplet state with amines

The triplet decay of NQs in argon-saturated acetonitrile (λ_{exc} = 308 nm) is accelerated on addition of TEA or DABCO (1,4-diazabicyclo[2.2.2]octane), and k_D = (0.3–1.6) × 10^{10} M^{-1} s^{-1} (Table 2). For NQ–TEA in acetonitrile, the literature value is k_D = 1.9 × 10^{10} M^{-1} s^{-1}.[10] The high rate constant for triplet quenching by amines is due to a negative free energy change, resulting from their low oxidation potentials and the reduction potentials (SCE) of $-E_{red}$ = 0.71, 0.77 and 0.45 V for NQ, MeNQ and Cl_2NQ in acetonitrile, respectively.[9,11] Triplet quenching by an amine occurs *via* reaction 4′, leading to $Q^{\bullet-}$ and the radical cation of the amine ($H_2D^{\bullet+}$).

$$^3{*}Q + H_2D \longrightarrow Q^{\bullet-} + H_2D^{\bullet+} \quad (4')$$

The molar absorption coefficient of the DMA radical cation in acetonitrile is ε_{465} = 6.3 × 10^3 M^{-1} cm^{-1}.[11] With DABCO, back electron transfer (reaction 9) accounts for the second-order decay of the semiquinone radical within *ca.* 10 μs, as shown in Fig. 1(c) for NQ.

$$Q^{\bullet-} + H_2D^{\bullet+} \longrightarrow Q + H_2D \quad (9)$$

Alternatively, a proton transfer could lead to neutral radicals ($HQ^\bullet$ and $HD^\bullet$); however, this does not occur.[22,23] The first half-life for the NQs–TEA–acetonitrile system is relatively large (Table 2). The dependence of the yield of the semiquinone radical of NQ *vs.* [TEA] can be fitted using the k_D and τ_T values (not shown).

The transient absorption spectra of NQ and Cl_2NQ in acetonitrile in the presence of TEA are shown in Fig. 3(a) and 2(c), respectively. For TEA in acetonitrile, equilibrium 10, with efficient formation of the α-aminoethyl radical is known to occur.[22,23,41]

$$Et_3N^{\bullet+} + NEt_3 \rightleftharpoons MeHC^\bullet\text{–}NEt_2 + HNEt_3^+ \quad (10)$$

Thus, it is conceivable that on increasing the TEA concentration, deprotonation is in competition with a second reaction leading to semiquinone radicals.

$$Q + MeHC^\bullet\text{–}NEt_2 \longrightarrow Q^{\bullet-} + CH_2{=}CHNEt_2 + H^+ \quad (11)$$

Reaction 11 accounts for the second grow-in of the absorption within a few μs, due to formation of $Q^{\bullet-}$ in the case of NQ [Fig. 3(a)]. The second reduction step *via* the α-aminoethyl radical was observed only at higher TEA concentrations, corresponding to a triplet lifetime of <50 ns.

3.3 Transient conductivity

An increase in conductivity (Δκ: positive signal) was observed within 1 μs after the pulse for NQ in argon-saturated neat

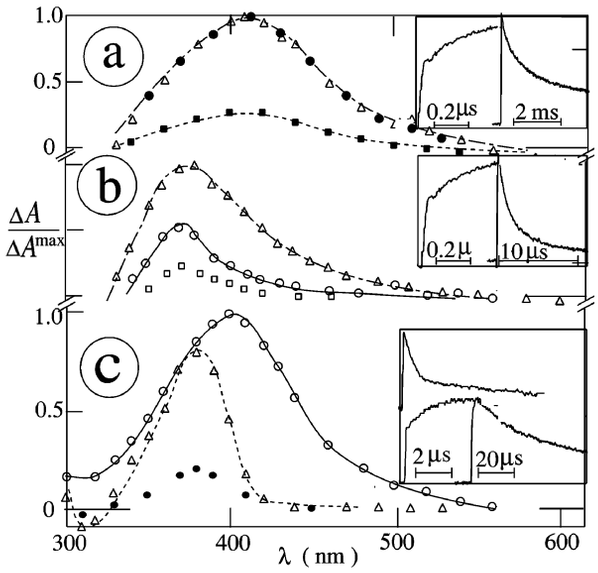


Fig. 3 Transient absorption spectra (in argon-saturated solution) of (a) NQ in acetonitrile in the presence of TEA (10 mM), (b) NQ in benzene in the presence of TEA (1 mM) (both with λ_{exc} = 308 nm) and (c) BrNQ in acetonitrile in the presence of propan-2-ol (0.1 M) (λ_{exc} = 248 nm) at 20 ns (○), 1 μs (Δ), 10 μs (□), 0.1 ms (●) and 10 ms (■) after the pulse. Insets: (a, b) radical formation and decay at 410 nm; (c) triplet (above) and radical (below) formation and decay at 400 nm.

acetonitrile in the presence of DABCO, TEA or DEA (>1 mM), λ_{exc} = 308 nm. The time dependences of representative cases are shown in Fig. 4. The rate constant of the fast increase depends linearly on [amine] and the signal approaches a maximum at an amine concentration of *ca.* 0.1 mM. The dependence of the conductivity yield of NQ *vs.* [TEA] is similar to that of the semiquinone radical (not shown). These findings are in full agreement with reactions 1 and 4′of photoinduced electron transfer. For DABCO (inset b in Fig. 4) or DEA, the conductivity signal decays by second-order kinetics within 10 μs due to back electron transfer (reaction 9). The conductivity signal of NQ in argon-saturated acetonitrile in the presence of TEA (>1 mM) is much longer lived. It decays by second-order kinetics, at least for the major part. After subtraction of the (minor) remaining part, the half-lives (in the 3–30 ms range) increased by a factor of *ca.* 5–8 when the laser intensity was decreased ten-fold. This is consistent with a termination process (reaction 5′) and subsequent protonation.

$$2\,Q^{\bullet-} \longrightarrow Q + Q^{2-} \qquad (5')$$

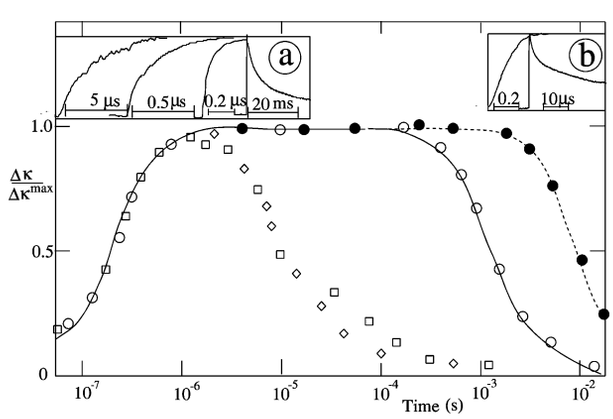


Fig. 4 Conductivity signals for NQ in argon-saturated acetonitrile in the presence of DABCO (1 mM; □), DEA (1 mM; ◇) and TEA [>1 mM; without (○) and with 5 M water (●)] after the 308 nm pulse. Insets: signals for (a) TEA (0.2, 0.8 and 5 mM, left to right) and (b) DABCO.

Interestingly, the radical termination of the NQ–TEA–acetonitrile system is slowed down on addition of water (Fig. 4), indicating a smaller rate constant for $Q^{\bullet-}$ than $HQ^{\bullet}$ radicals. The conductivity increase for NQ in wet acetonitrile (5 M water, pH 7) also depends also on the propan-2-ol concentration, and the signal, which is mainly due to proton release *via* reaction 6, approaches a maximum at about 1 M propan-2-ol. The conductivity signal at pH 3–4 is much lower, since H-atom transfer without deprotonation does not result in a conductivity change. Moreover, a delayed increase in conductivity due to reactions 10 and 11 was not observed in any case, even at higher TEA concentrations of 3–10 mM. The signals for MeNQ, BrNQ and Cl_2NQ in dry acetonitrile in the presence of DABCO or TEA (not shown) are comparable to those presented for NQ.

3.4 Reactions upon 248 nm excitation

When the wavelength of excitation was changed from 308 to 248 nm, lower NQ concentrations could be used and, apart from the triplet decay of NQ and MeNQ, essentially the same results were obtained. An example of the spectra and kinetics in argon-saturated acetonitrile in the presence of propan-2-ol is shown in Fig. 3(c) for BrNQ. Owing to the above-mentioned linear dependence of $1/\tau_T$ *vs.* NQ concentration, the longest triplet lifetime was achieved with λ_{exc} = 248 nm. However, this reaction seems to play no discernible role for BrNQ and Cl_2NQ (Table 1). Photoionization does not contribute at the applied low intensities, as no solvated electrons were detected for NQs in alcohols, where solvated electrons are not scavenged within the pulse width (as in acetonitrile). Note that the hydrated electron has been observed for MeNQ in aqueous solution.[25]

Examples of the transient absorption spectra and kinetics are shown for vitamin K_1 in acetonitrile [Fig. 5(a) and (b)], and in the presence of an alcohol [Fig. 5(c)] or amines (Fig. 6). These photolysis results, which were obtained under similar conditions, seem to resemble those of the four NQs. However, the detected primary and secondary transients of vitamin K_1 (1,3-QM and 1,2-QM, respectively, see section 3.9) and the NQs are not identical to those detected for NQs.

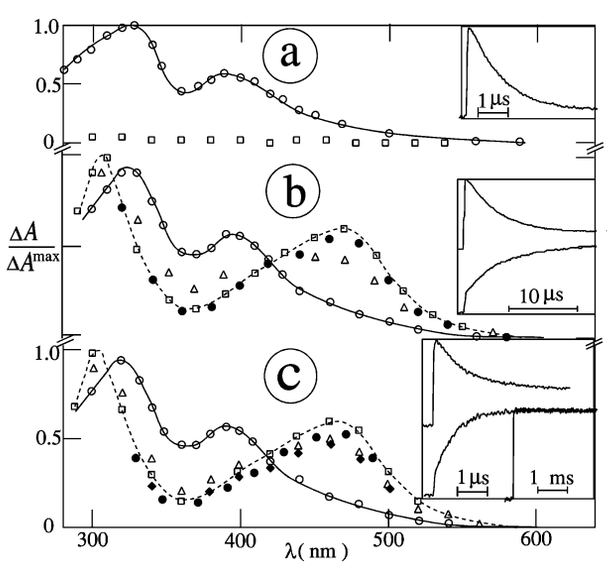


Fig. 5 Transient absorption spectra of vitamin K_1 in acetonitrile: (a) air-saturated, no added donor; (b) argon-saturated, no added donor; (c) argon-saturated, in the presence of propan-2-ol (0.2 M). Spectra were measured at 20 ns (○), 1 μs (Δ), 10 μs (□), 0.1 ms (●) and 0.1 s (◆) after the 248 nm pulse. Insets: decay kinetics at 390 nm (above) and grow-in at 470 nm (below).

3.5 Continuous irradiation

UV irradiation of NQ in argon-saturated acetonitrile leads to substrate decomposition, as shown by isosbestic points at 200, 245, 272 and 342 nm, a decrease in absorption between 245 and

342 nm, and above 342 nm, and increases in the other ranges (Fig. 7, inset). The photodecomposition of NQ (Fig. 8, inset), MeNQ and Cl_2NQ is more efficient in the presence of propan-2-ol (0.05–1 M). The spectral changes observed upon irradiation resemble those arising from intramolecular H-atom abstraction.[42] The molar absorption coefficient of the H_2Q form of Cl_2NQ in acetonitrile–water (4 : 1) is $\varepsilon_{328} = 5.8 \times 10^3$ $M^{-1}\,cm^{-1}$.[9]

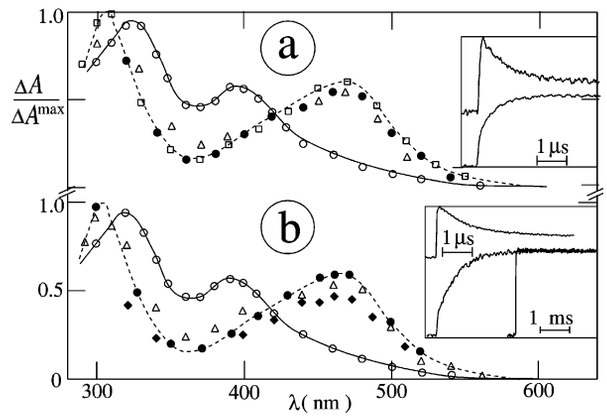


Fig. 6 Transient absorption spectra of vitamin K_1 in argon-saturated acetonitrile in the presence of (a) DABCO (0.5 mM) and (b) TEA (2 mM) at 20 ns (○), 1 μs (Δ), 10 μs (□), 0.1 ms (●) and 0.1 s (◆) after the 248 nm pulse; insets: decay kinetics at 390 nm (above) and grow-in at 470 nm (below).

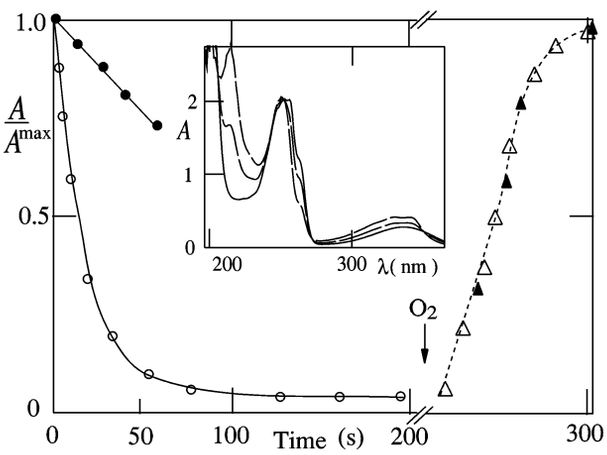


Fig. 7 Photoconversion of NQ; maximum change in A_{260} *vs.* time in argon-saturated acetonitrile without (blocked symbols) and with (open symbols) added propan-2-ol (1 M) during irradiation (circles) and without irradiation after addition of oxygen (triangles). Inset: spectra in neat acetonitrile at 0 (full line), 100 and 300 s (broken line).

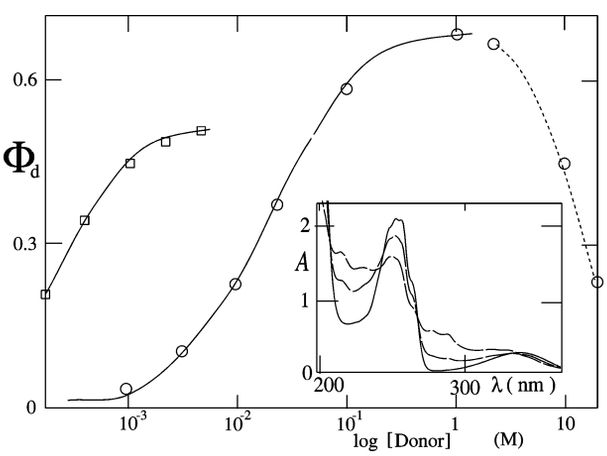


Fig. 8 Plots of Φ_d *vs.* [propan-2-ol] (○) and [TEA] (□) for NQ in argon-saturated acetonitrile. Inset: spectra in the presence of propan-2-ol (1 M) at 0 (full line), 10 and 50 s (broken line).

The quantum yield of decomposition (Φ_d) was obtained from the decrease in absorbance at an appropriate wavelength, *e.g.* 260 nm. Examples are shown in Fig. 7 for NQ in acetonitrile and in presence of propan-2-ol. For NQ and MeNQ in neat methanol or propan-2-ol, Φ_d is significantly smaller than in mixtures of acetonitrile and alcohol (Table 3). This is due to competing steps which do not yield H_2Q, *e.g.* reaction 8. Φ_d of NQ in acetonitrile increases with increasing propan-2-ol concentration; 50% of the maximum Φ_d value is reached at a half-concentration of *ca.* 0.02 M (Fig. 8). This is in line with the estimate of a half-concentration of 0.01 M obtained using a quenching rate constant of $k_D = 3 \times 10^7\ M^{-1}\,s^{-1}$ and a limiting triplet lifetime of 3 μs (Tables 1 and 2). For NQ in acetonitrile, the presence of TEA (0.05–1 mM) also leads to substrate decomposition and the spectral changes for NQs are reminiscent of those observed with alcohols. The Φ_d values of NQ increase with increasing TEA concentration, approaching a maximum value of $\Phi_d = 0.5$ (Fig. 8). The low half-concentration of *ca.* 0.02 mM is consistent with the high k_D value of $1.6 \times 10^{10}\ M^{-1}\,s^{-1}$ (Table 2).

3.6 Effects of oxygen

The above measurements were made in deoxygenated solutions, unless otherwise indicated. Triplet quenching of quinones by oxygen (reaction 3) yields singlet molecular oxygen, $O_2(^1\Delta_g)$.[16,43] The quantum yield of formation (Φ_Δ) of $O_2(^1\Delta_g)$ can be regarded as a minimum for Φ_{isc}. The values are substantial for NQs in several solvents (Table 1) and only low for vitamin K_1, where Φ_Δ in acetonitrile is below 0.02. The lower value for NQ in benzene, in contrast to Cl_2NQ in benzene, is due to the short triplet lifetime (see section 3.1). The literature value for NQ in aqueous solution is $\Phi_\Delta = 0.27$.[16]

In the presence of TEA or alcohols, reactions 4 and 4′ could compete successfully with triplet quenching by oxygen, *e.g.* for amine concentrations above 0.1 M in air-saturated acetonitrile. One important reaction of oxygen is trapping of the semiquinone radical (equilibrium 12, forward reaction).

$$HQ^{\bullet}/Q^{\bullet-} + O_2 \rightleftharpoons Q + HO_2^{\bullet}/O_2^{\bullet-} \qquad (12)$$

In fact, for duroquinone in aqueous solution, both rate constants for equilibrium 12 have been determined.[37] When 9,10-dihydroxyanthracene is exposed to oxygen, complete recovery of AQ can occur,[22] *i.e.* photodecomposition of AQ is thermally reversible. This was also found for NQ in the presence of TEA (Fig. 8) and the other NQs, in contrast to 1,4-benzoquinone.[23] Several possibilities may be considered; the most probable is reaction 13, based on the kinetics of oxidation of hydroquinones by molecular oxygen.[44]

$$H_2Q + O_2 \longrightarrow Q^{\bullet-} + O_2^{\bullet-} + 2\,H^+ \qquad (13)$$

Owing to the thermal reversibility, the Φ_d values are sensitive to trace amounts of oxygen. Examples of the reversibility are shown in Fig. 7 for NQ in the absence and presence of propan-2-ol. After photoconversion (in the absence of oxygen) into 1,4-dihydroxynaphthalene, reaction 13 (after addition of oxygen) completely restores NQ. Note that the time of recovery depends on the conditions, *e.g.* the amount of water present.

3.7 Effects of NQ structure and medium

The rate constant for the reaction of NQ and MeNQ in acetonitrile towards H-atom abstraction from propan-2-ol is $k_D = 3 \times 10^7\ M^{-1}\,s^{-1}$. The k_D value is the same for AQ[21,22] and lower for Cl_2NQ and BrNQ (Table 2). The secondary transients are shown for NQ in acetonitrile–propan-2-ol [Fig. 1(b)]. On the other hand, the reactivity for electron transfer from TEA is close to the diffusion-controlled limit for most NQs in

Table 3 Quantum yields of decomposition (Φ_d) of NQs in the absence and presence of TEA and propan-2-ol[a]

	Donor					
		TEA		Propan-2-ol		
Quinone	None	0.2 mM	2 mM	0.1 M	1 M	13 M
NQ	0.08 (0.006)[b]	0.2	0.45	0.6	0.7 (0.5)	0.2 [0.2][c]
MeNQ	0.06	0.3	0.42	0.6	0.7 (0.5)	0.3 [0.2]
Cl_2NQ	<0.002	0.2	0.3	0.08	0.12	0.2
BrNQ	0.005		0.3	0.06	0.1	

[a] In argon-saturated acetonitrile, λ_{irr} = 254 nm. [b] Values in parentheses are for oxygen-saturated solution. [c] Values in square brackets are for neat methanol.

acetonitrile, but lower in benzene and for BrNQ in acetonitrile. No triplet with τ_T >20 ns was detected for NQ and MeNQ in THF, which is an example of an H-atom donating solvent of medium polarity. Intermolecular H-atom abstraction prevails also in cyclohexane, toluene and butyronitrile, whereas in carbon tetrachloride and dichloromethane, the reaction yielding the semiquinone radical is negligible at low NQ concentrations. In principle, the substantial Φ_Δ (Table 1) and Φ_{isc} values for NQ and MeNQ[10] provide the possibility that up to two semiquinone radicals are formed per absorbed photon, thus giving Φ_d values between 0.5 and 1. Note that under otherwise the same conditions, the second reduction step, reaction 7 for alcohols or reaction 11 for TEA, which accounts for Φ_d >0.5, could kinetically be observed for AQs.[22]

In the presence of an amine in polar solvents, $Q^{\bullet-}$ and the radical cation of the amine are separate intermediates. The mechanism of photoreduction of NQs changes when the medium is less polar. In carbon tetrachloride, benzene and toluene, no free radical ions are present. An intermediate with a peak at 380 nm for the NQ–TEA–benzene system is formed by triplet quenching [Fig. 3(b)] and is attributed to the semiquinone radical. Reaction 4″ and electron back transfer, rather than formation of free radicals, accounts for the second-order decay occurring within a few μs.[13,22]

$$^3Q^* + NEt_3 \longrightarrow (Q^{\bullet-}/Et_3N^{\bullet+}) \qquad (4'')$$

For NQ and MeNQ, the spectra of $^3Q^*$ and $HQ^\bullet/Q^{\bullet-}$ are strongly overlapping, but the reactivity of a given solvent with the triplet state can be judged from the grow-in kinetics of the longer-lived semiquinone radical [Table 1, Fig. 1(b), (c) and 3(a), (b)]. In contrast, the λ_{TT} and λ_{rad} values are rather different for Cl_2NQ (Fig. 2) and BrNQ [Fig. 3(c)] and triplet decay and radical grow-in are both accessible. Benzene with τ_T <1 μs is not an 'inert' medium for NQ and MeNQ as well as for AQ,[22] in contrast to carbon tetrachloride. A specific triplet quenching reaction in benzene, known for NQ or MeNQ,[2,3] also takes place for BrNQ, but is less effective for Cl_2NQ.

3.8 Phosphorescence and transient absorption at low temperatures

The T–T absorption spectrum of Cl_2NQ in MTHF at −180 °C is shown in Fig. 9(a). The transient absorption spectra of NQs in glassy media at low temperatures (Table 4) resemble those at room temperature. This is different for vitamin K_1, where the species in fluid solution are not of triplet nature, see section 3.9. The relatively long lifetime in the case of vitamin K_1 at −180 °C [Fig. 9(b)] indicates formation of the lowest triplet state, as supported by phosphorescence. The maximum triplet lifetime of NQs in low temperature glasses is in the 0.4–6 ms range.

The emission and excitation spectra of vitamin K_1 in MCH at −196 °C are shown in Fig. 9(c). The major band centered at 580 nm is due to phosphorescence; however, fluorescence, centered at 440 nm, also seems to play a minor role. The phosphorescence lifetime (τ_p) is 3 ms and the phosphorescence onset

Table 4 Triplet lifetimes (τ) for the NQs and vitamin K_1 using emission and absorption

Quinone	Solvent	τ_p[a]/ms	λ_p[b]/nm	τ_T[c]/ms	λ_{TT}[d]/nm
NQ	MCH	0.4	475		
	MTHF	0.4	480	0.4	370
	Ethanol	0.4	480		
Cl_2NQ	MCH	6	530	6	380
	MTHF	6	540	6	380
BrNQ	MCH	0.4	505		
	MTHF	0.3	510	0.4	400
	Ethanol	0.4	520		
Vitamin K_1	MCH	3	520	3	360
	MTHF	3	520	4	370
	Ethanol	3	530		370

[a] Air-saturated at −196 °C. [b] Phosphorescence onset. [c] Argon-saturated at −180 °C, λ_{exc} = 248 nm. [d] Absorption maximum.

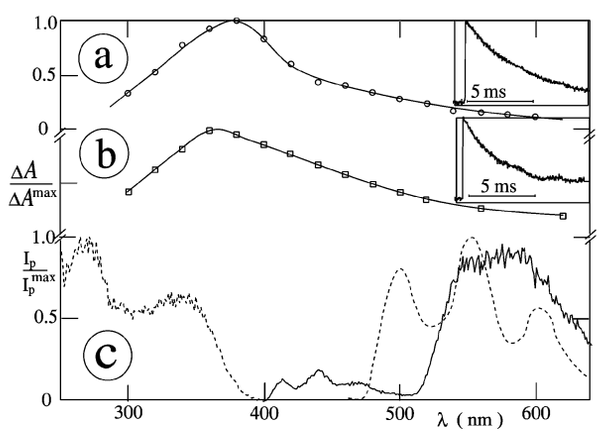


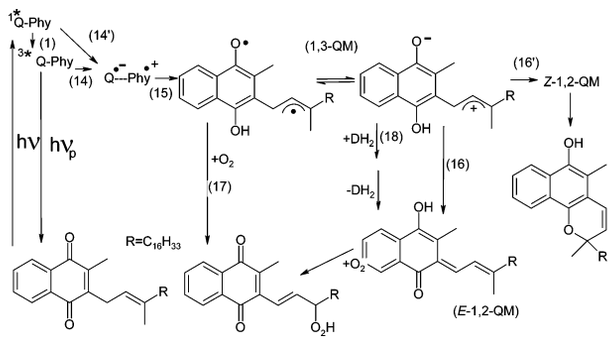
Fig. 9 Transient absorption spectra (in argon-saturated solution) of (a) Cl_2NQ and (b) vitamin K_1 in MTHF at −180 °C (0.1 μs, λ_{exc} = 248 nm). (c) Phosphorescence emission (right) and excitation (left) spectra of vitamin K_1 in air-saturated MCH (—) and NQ (· · ·) at −196 °C (λ_{exc} = 320 nm, λ_{em} = 600 nm).

(λ_p), as a measure of the triplet energy, is at 520 nm. The spectra, as well as the λ_p and τ_p values, of a given quinone are similar in the different glasses (Table 4) and the phosphorescence results are in agreement with the literature.[26,27]

3.9 Vitamin K_1

The photolysis results for vitamin K_1 do not fit in with the above discussion for the four NQs examined, which deals with intermolecular transfer processes. Intramolecular H-atom transfer from the olefinic side chain to the quinone moiety has been documented for plastoquinones and vitamin K_1.[28–34] The photochemistry of vitamin K_1 therefore differs completely from that of other quinones without side chains. Two 1,3-quinone methide (1,3-QM) diradicals have been suggested as observed intermediates, and a short-lived (non-observed) precursor ($Q^{\bullet-}$–$Phy^{\bullet+}$) can also be considered (reactions 14′ and 15,

Scheme 1).[34] The idea of a diradical existing prior to formation of the 1,2-QM tautomers (reaction 16) was first proposed by Porter and co-workers for plastoquinones.[28,29] The two 1,3-QM diradicals of vitamin K_1 in solution at room temperature are in equilibrium and can be quenched by oxygen (reaction 17).[34]



Scheme 1

The first intermediate on the ns timescale of vitamin K_1 in acetonitrile, in contrast to NQs without side chains, is the equilibrium of the 1,3-QM diradicals, which behave kinetically as single species.[34] The major and minor maxima (λ_{dir}) of the 1,3-QM diradicals of vitamin K_1 in acetonitrile are at 330 and 390 nm. The results are for λ_{exc} = 248 nm; no marked difference was found with λ_{exc} = 308 nm, except for faster decay of the 1,3-QM diradicals at higher laser intensities. The lifetime (τ_{dir}) under argon is up to 15 μs and the rate constant for quenching by oxygen (reaction 17, Scheme 1) is $k_{17} = 5 \times 10^8$ M^{-1} s^{-1}, in excellent agreement with the data from Wirz *et al.*[34] The corresponding values in benzene are λ_{dir} = 330 and 390 nm, τ_{dir} = 3 μs, and $k_{17} = 2.0 \times 10^8$ M^{-1} s^{-1}.

For vitamin K_1 in solution at room temperature, intersystem crossing seems to be too slow to compete with intramolecular proton transfer. It is therefore reasonable to propose reaction 14′, bypassing the triplet state, rather than reactions 1 and 14 (Scheme 1). On the other hand, phosphorescence was observed at −196 °C [Fig. 8(c)]. Radical intermediates of vitamin K_1 in acetonitrile have been reported based on time-resolved resonance Raman spectroscopy.[33] This identification may be doubtful and the postulated H-atom transfer from acetonitrile to the triplet state should be revised. The photochemical pathway is: excited singlet state ⟶ $Q^{\bullet -}$–$Phy^{\bullet +}$ ⟶ diradical ⟶ 1,2-QM tautomers *via* reactions 14′, 15 and 16 (Scheme 1), respectively.

In the presence of appropriate additives, τ_{dir} of vitamin K_1 in acetonitrile becomes shorter [Fig. 5(c) and 6]. Plots of $1/\tau_{dir}$ increases linearly with the amine concentration; the rate constants for quenching are 2×10^9 M^{-1} s^{-1} for DABCO and 4×10^8 M^{-1} s^{-1} for TEA. The conversion of 1,3-QM into 1,2-QM in the presence of 10 mM acetic acid occurs with $k_q = 2.5 \times 10^8$ M^{-1} s^{-1}, corresponding to τ_{dir} = 0.4 μs, which is in agreement with the literature value.[34] The presence of water and alcohols (including *tert*-butanol) in the acetonitrile also substantially enhanced the conversion, but the plots curve upward. Extrapolation of the initial linear dependence with k_q ≈ 3×10^6 M^{-1} s^{-1} to neat methanol would lead to τ_{dir} = 12 ns, which is much longer than the directly measured value of 0.7 ns.[34] The enhanced decay of the strong acid 1,3-QM in the presence of alcohols,[34] amines and water is due to proton transfer through these additives, where the k_q values refer to reaction 18 (Scheme 1).

4 Conclusion

The photoreduction of four NQs by propan-2-ol or TEA and related photoprocesses of vitamin K_1 were analyzed. Photoinduced electron transfer from amines to the triplet state of the NQs was studied by transient UV-vis absorption spectroscopy and conductivity measurements. In acetonitrile, no equilibrium between the $HQ^{\bullet}$ and $Q^{\bullet -}$ radicals is established. For Cl_2NQ and BrNQ, the spectra of the semiquinone radicals and T–T absorptions are different, in contrast to the parent NQ. The rather long half-life of the TEA-derived semiquinone radicals excludes back electron transfer as a major reaction, although it does occur in the presence of DABCO. The photoconversion to 1,4-dihydroxynaphthalenes is efficient for NQ and MeNQ in the presence of either propan-2-ol or TEA, and still moderate for the other NQs. Addition of oxygen reverts the dihydroxynaphthalenes back to the respective NQs. The photoreactions of vitamin K_1 involve two 1,3-quinone methide diradicals prior to formation of the *E* and *Z* tautomers of 1,2-QM. In the presence of alcohols and amines, proton transfer through these additives leads to faster conversion of 1,3-QM into 1,2-QM.

Acknowledgements

The author thanks Professor Wolfgang Lubitz for his support and Mrs Corinna Kesseler, Mr Leslie J. Currell and Lars Kalender for technical assistance.

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