

Photoreactions of 2-methyl-5-isopropyl-1,4-benzoquinone

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Abstract

The photochemistry of the title compound (thymoquinone: TQ) in solution was studied by time-resolved UV-Vis spectroscopy and 20 ns laser pulses at 248 nm. The results are compared with those of 2,5-dimethyl-1,4-benzoquinone (Me₂BQ). The triplet state of Me₂BQ reacts with amines, such as triethylamine (TEA) or 1,4-diazabicyclo[2.2.2]octane (DABCO) via electron transfer and with 2-propanol via H-atom transfer. The semiquinone radical of Me₂BQ is formed as the main intermediate and the second-order decay leads to the hydroquinone. The quantum yield of photodecomposition (Φ_d , $\lambda_{irr} = 254$ nm) of Me₂BQ is low in acetonitrile, but substantial in the presence of donors, where also the semiquinone radical is large. In contrast, Φ_d is substantial for TQ in neat acetonitrile even in the presence of oxygen. No triplet state was detected for TQ in any solvent at room temperature and the first transient (T_z) is assigned to a zwitterion, formed after an intramolecular H-atom transfer from the side chain. The lifetime of T_z in acetonitrile or *tert*-butanol is ca. 2 μ s and the decay is enhanced by water, acetic acid or 2,2,2-trifluoroethanol. Conversion of the zwitterion into hydroquinones, not involving free radicals, is proposed. In the presence of other alcohols or amines, however, conversion of T_z into radicals and their termination takes place. The effects of solvent polarity and other specific properties of intramolecular H-atom transfer with TQ are discussed.

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Keywords: Quinones; Photoreduction; Intramolecular H-atom transfer; Zwitterion; Radical

1. Introduction

Quinones are cofactors in photosynthetic reaction centers of photosystem I and II and act as electron carriers through the cell membrane [1,2]. The photochemistry of 1,4-benzoquinone (BQ) and derivatives, such as 1,4-naphthoquinone, and 9,10-anthraquinone, is the subject of various investigations [3–19]. Quinones in the presence of alcohols are photoreduced by intermolecular H-atom transfer leading to the semiquinone radical and eventually into hydroquinones (QH₂). The photoreduction by amines, such as *N,N*-dialkylamines, triethylamine (TEA) or 1,4-diazabicyclo[2.2.2]octane (DABCO), involves the semiquinone radical anion [10,15–19]. These processes can be efficient since the quantum yield of intersystem crossing (Φ_{isc}) of several quinones is close to unity [3]. The properties of the semiquinone radical (QH•/Q•⁻) have been documented by radiation chemistry [3,20–23].

In contrast to quinones without a side chain, photoinduced intramolecular H-atom transfer is possible for phyloquinones, e.g. Vitamin K₁ [24–26], and other appropriate quinones [27–32], in particular for 2-methyl-5-isopropyl-

1,4-benzoquinone (thymoquinone: TQ). The isopropyl group in the five position can act as an intramolecular H-atom donor [27–30]. The triplet state of TQ and the dibromo derivative, 2,5-dibromo-3-methyl-6-isopropyl-1,4-benzoquinone, is therefore expected to be short lived. Such a case without triplet reactivity is known for Vitamin K₁ [19,26]. A spirocyclopropyl intermediate has been proposed and four photoproducts have been identified for TQ in methanol [29]. For 2,5-dibromo-3-methyl-6-isopropyl-1,4-benzoquinone in ethanol 2,5-dibromo-3-allyl-6-methyl-1,4-hydrobenzoquinone as major photoproduct has been reported [32].

Photoinduced intramolecular H-atom transfer has also been considered for 2-*tert*-butyl-1,4-benzoquinone [29]. Alanine–BQ conjugates were reported to yield a biradical–zwitterion by intramolecular H-atom transfer [33]. A biradical–zwitterion has been proposed as the intermediate for vinylbenzo-1,4-benzoquinones [34]. For various suitable ketones photoinduced intramolecular H-atom transfer has been studied intensively [35]. *o*-Alkylarylketones, e.g. *o*-methylacetophenone, are known to form photoenols [36,37]. Related photoenolization reactions have been reported for 5-methyl-1,4-naphthoquinone [38–40] or 1-methyl-9,10-anthraquinone, whereby the latter photoproduct is 9-hydroxy-1,10-anthraquinone-1-methide [41,42].

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Here, the intramolecular H-atom transfer in TQ as well as the intermolecular H-atom abstraction reactions with suitable electron donors, such as TEA and alcohol, were studied by time-resolved UV-Vis spectroscopy in solution at room temperature. The quantum yields of decomposition (Φ_d) at $\lambda_{\text{irr}} = 254 \text{ nm}$ were measured and compared with those of 2,5-dimethyl-1,4-benzoquinone (Me_2BQ) as an example of a BQ without a substituent for β -H-atom transfer in the side chain. The properties of a zwitterion as first observable transient of TQ are outlined and the different results with Me_2BQ discussed.

2. Experimental details

The compounds and solvents (Merck, Sigma, Fluka) were used as received or purified by distillation: TEA, 2,2,2-Trifluoroethanol (TFE) and the other solvents (Merck, Uvasol quality where available) were checked for impurities and purified water was taken from a Milli-Q system. The absorption spectra were monitored on a UV-Vis spectrophotometer (HP, 8453). For photoconversion the 254 nm line of a Hg lamp was used. Typically, absorbances of 1–2 were used for $\lambda_{\text{irr}} = 254 \text{ nm}$, corresponding to concentrations of 0.1–0.3 mM. For HPLC analyses a 125 mm \times 4.6 mm Inertsil ODS-3 5 μm column was used and MeOH–water 1:2 or 2:1 as eluents; purity of TQ: 99.6%. The quantum yield of decomposition (Φ_d) was determined from the absorption versus irradiation time using the uridine/water/air actinometer [43]. An excimer laser (Lambda Physik, EMG 200, pulse width of 20 ns and energy <100 mJ) was used for excitation at 248 nm, for a few experiments at 308 nm, another excimer laser (EMG 200) was applied. The absorption signals were measured with two digitizers (Tektronix 7912AD and 390AD). Relative yields in argon-saturated acetonitrile were obtained using optically matched solutions, $\lambda_{\text{exc}} = 248 \text{ nm}$, absorbances of 0.20 mm^{-1} and benzophenone as reference. Absorbances of 0.4–0.6 mm^{-1} were used for the other measurements, corresponding to concentrations of 0.2–0.3 mM, based on the molar absorption coefficient of $\epsilon_{248} = 2 \times 10^4 \text{ M}^{-1} \text{ cm}^{-1}$ for TQ. The samples were freshly dissolved and all measurements refer to $24 \pm 2^\circ \text{C}$ and deoxygenated solution, unless otherwise indicated.

3. Results

3.1. Photoreduction of Me_2BQ

The triplet state with maxima at $\lambda_{\text{T}} = 285$ and 450 nm and a lifetime of $\tau_{\text{T}} = 4 \mu\text{s}$ (Table 1) is the major primary species of Me_2BQ in argon-saturated acetonitrile after the 248 nm pulse. The rate constant for triplet quenching by oxygen is $k_3 = 1.6 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$. The ^3Q state is formed via a short-lived singlet state according to Eqs. (1) and (2)

Table 1
Absorption maxima and lifetime of the transients of $\text{Me}_2\text{BQ}^{\text{a}}$

Solvent	$\lambda_{\text{T}}^{\text{b}}$ (nm)	$\tau_{\text{T}}^{\text{c}}$ (μs)	$\lambda_{\text{rad}}^{\text{b}}$ (nm)
Acetonitrile	285, 450	4 (1.6) ^d	320, 410 ^e
MeCN + 2-propanol (0.1 M)	285, 450	0.3	320, 410
MeCN + water (28 M)	285, 450	0.9	–
<i>tert</i> -Butanol	285, 450	1.5 (1.1) ^d	320, 410
2-Propanol	–	<0.01	320, 410 [1] ^f
TFE	285, 450	3	320, 410

^a Argon-saturated and $\lambda_{\text{exc}} = 248 \text{ nm}$.

^b Major peaks are in italics.

^c At low intensity and $A_{248} = 1$ –2.

^d In parentheses: rate constant for quenching by oxygen, k_{ox} ($\times 10^9 \text{ M}^{-1} \text{ s}^{-1}$).

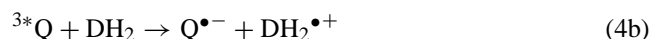
^e Weak signal.

^f Half-life $t_{1/2}$ (ms).

and quenched by oxygen (3), [3,4]:



Triplet quenching of BQs by 2-propanol (DH_2) occurs via reaction (4a), leading to the semiquinone radical and eventually to QH_2 according to (5) [3,12]. Reaction of the DH radical with Q can yield another $\bullet\text{QH}$ radical in competition to radical termination [6,7]. Triplet quenching by an amine leads via (4b) to the semiquinone radical anion:



The maxima at $\lambda_{\text{rad}} = 320$ and 420 nm for $\text{Q}\bullet^-$ of Me_2BQ are known from pulse radiolysis [22,23]. Electron back transfer accounts for the rather short half-life of the second-order decay of the DABCO derived $\text{Q}\bullet^-$ radical within 0.1 ms. For TEA in acetonitrile the α -aminoethyl radical reacts with Q to a second semiquinone radical and eventually into QH_2 . Addition of water (1:1, v/v) does not change the transient absorption spectra (Fig. 1a), but τ_{T} becomes shorter. Photoinduced electron transfer in acetonitrile as a relatively “inert” solvent takes place in the presence of either alcohols or amines, such as TEA or DABCO. An example is shown in Fig. 1b with 2-propanol. Equilibrium (6) is not established in dry acetonitrile [18].

3.2. Continuous irradiation

Irradiation at 254 nm of Me_2BQ in relatively low concentration (0.1 mM) in argon-saturated acetonitrile leads to isosbestic points at 230 and 270 nm, absorption increase is observed below and above and a decrease between these

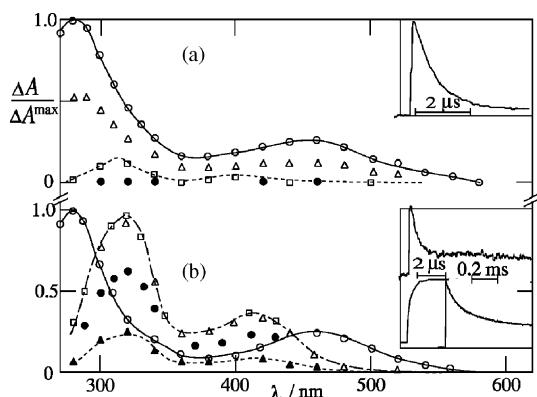


Fig. 1. Transient absorption spectra of Me₂BQ in argon-saturated (a) acetonitrile–water (1:1, v/v) and (b) in acetonitrile in the presence of 2-propanol (1 M) at 20 ns (○), 1 μs (△), 10 μs (□), 0.1 ms (●) and 1 ms (▲) after the 248 nm pulse; insets: decay at 450 nm (upper) and formation and decay at 320 nm (lower).

wavelengths. The quantum yield of decomposition (Φ_d) of Me₂BQ is low in argon-saturated acetonitrile, but large in the presence of either 2-propanol (0.01–16 M) or TEA (0.05–1 mM) (Table 2). Generally, Φ_d increases with increasing donor concentration the maximum change in Φ_d for quinones in acetonitrile–propanol mixtures is several orders of magnitude [12]. The major effect is the conversion of Me₂BQ into the corresponding hydroquinone as measured by HPLC, where one major photoproduct absorbing above 220 nm was observed. In oxygen-saturated acetonitrile or *tert*-butanol Φ_d is even lower (Table 2) because of triplet quenching by oxygen via (3).

Irradiation of TQ in acetonitrile leads to isosbestic points at 225 and 275 nm, an absorption decrease between these wavelengths and an increase below 225 nm and around 360 nm (Fig. 2d). The increase above 270 nm is different in aqueous solution, *tert*-butanol, 2-propanol or acetonitrile (Fig. 2a–d), indicating different products. UV irradiation at lower conversion in the presence of either 2-propanol or TEA leads also to efficient substrate decomposition and an absorption increase at 300–380 nm. The quantum yield Φ_d is substantial for TQ in the absence of an electron donor and even in oxygen-saturated acetonitrile or *tert*-butanol, in contrast to Me₂BQ (Table 2) and other quinones without side chain [12]. Photolysis of the initial products of TQ occurs already at a low conversion of ca. 10%, in contrast

Table 2
Quantum yields Φ_d of decomposition of quinones^a

Solvent	Me ₂ BQ/Ar	Me ₂ BQ/O ₂	TQ/Ar	TQ/O ₂
Acetonitrile	0.06	<0.02	0.6	0.5
MeCN + TEA ^b	0.4	0.01	0.5	
<i>tert</i> -Butanol	0.08	<0.02	0.6	0.5
2-Propanol	0.8	0.4	0.8	0.6
Water	0.8	0.7	0.8	0.7

^a In argon- or oxygen-saturated solution using $\lambda_{irr} = 254$ nm and HPLC.

^b TEA = 1 mM.

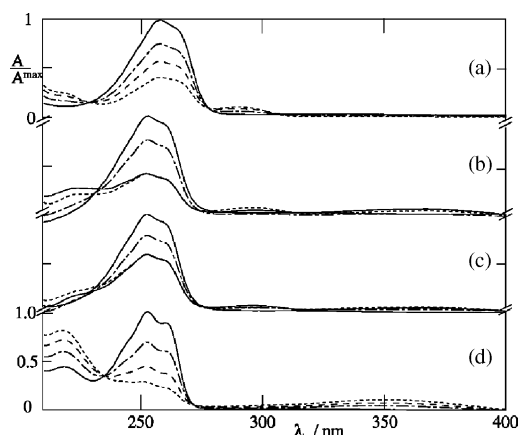


Fig. 2. Absorption spectra of TQ prior to (solid line) and after irradiation (broken line: 3, 10 and 30 s) in (a) neat aqueous solution, (b) *tert*-butanol, (c) 2-propanol and (d) acetonitrile.

to Me₂BQ where prolonged irradiation does not lead to secondary photolysis in significant amount.

3.3. Transient absorption with TQ

The transient absorption spectrum of TQ in acetonitrile after the 248 nm pulse has a major maximum at 295 nm and another weaker at 550 nm (Fig. 3a). The species at the end of the pulse (T_z) is not the triplet state, in contrast to other BQs without side chain, since no quenching by oxygen was found, the rate constant for quenching of T_z by oxygen is below $k_{ox} = 1 \times 10^7 \text{ M}^{-1} \text{ s}^{-1}$. The long-wavelength absorption maximum (λ_z) shows a blue-shifting trend on increasing the solvent polarity. The normalized Dimroth parameter E_T^N was used as a measure of the solvent polarity [44]. The shift in λ_z ranges from 550 nm in acetonitrile or 520 nm in *tert*-butanol with $E_T^N = 39$ –46 (Fig. 3b) to 440 nm in TFE with $E_T^N = 90$ (Fig. 3c). Further transient spectra are

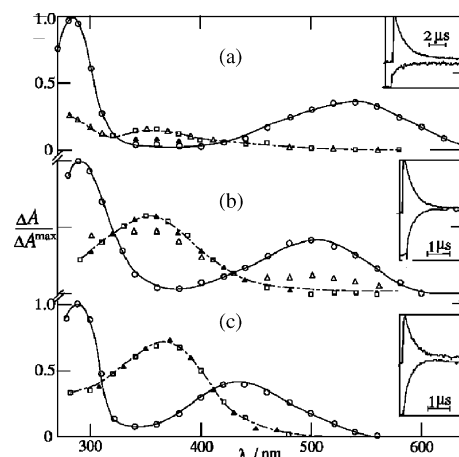


Fig. 3. Transient absorption spectra of TQ in argon-saturated (a) acetonitrile, (b) *tert*-butanol and (c) TFE at 20 ns (○), 1 μs (△), 10 μs (□) and 1 ms (▲) after the 248 nm pulse; insets: decay at 480–520 nm (upper) and formation at 360 nm (lower).

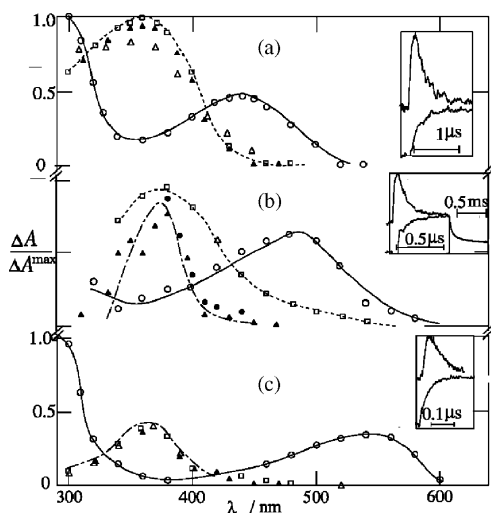


Fig. 4. Transient absorption spectra of TQ in argon-saturated (a) TFE–water (1:1), (b) acetonitrile–water (1:1) and (c) acetonitrile plus acetic acid (1 M) at 20 ns (○), 1 μs (△), 10 μs (□), 0.1 ms (●) and 1 ms (▲) after the 248 nm pulse; insets: (a, b) decay at 480–520 nm (upper) and formation at 360 nm (lower).

shown in acetonitrile in the presence of acetic acid (Fig. 4c) and in 1:1 mixtures of water with TFE (Fig. 4a) and acetonitrile (Fig. 4b). The rate constant for decay of T_z ($1/\tau_z$) shows a linear dependence on (acetic acid concentration) and the quenching rate constant is $k_q = 4 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$ (Fig. 5). The photoconversion into modified hydroquinone(s) is also efficient in aqueous solution at pH 7, but the dependence of $1/\tau_z$ versus $[\text{H}_2\text{O}]$ is not linear but upward curved.

The product of yield and coefficient, $\Phi_{\varepsilon_{550}}$, for T_z of TQ in neat acetonitrile is $6 \times 10^3 \text{ M}^{-1} \text{ cm}^{-1}$, i.e. similar to that of the triplet state of benzophenone at 520 nm as reference. T_z is converted into a weak permanent absorption at 300–400 nm in acetonitrile, due to a stable species (H_2Q_a , see below) which has a maximum (λ_p) at 360 nm. In several solvents, e.g. *tert*-butanol or TFE (Fig. 3b and c), T_z is converted into the stable species which has almost the same maximum

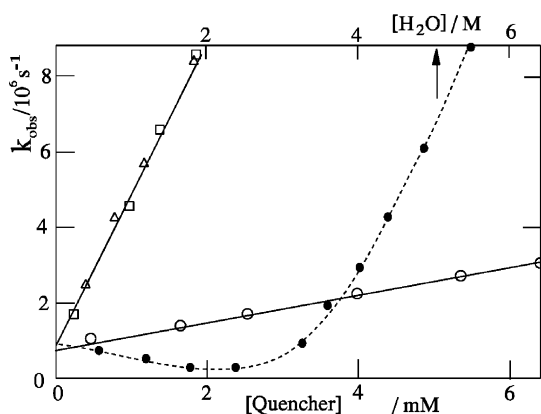


Fig. 5. Plots of $1/\tau_z$ vs. (additive) for DABCO (□), TEA (○), acetic acid (△) and H_2O (●).

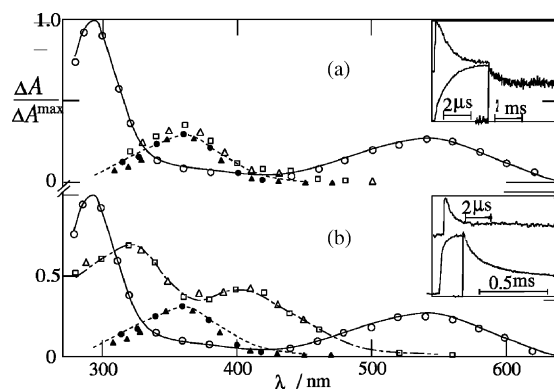


Fig. 6. Transient absorption spectra of TQ in (a) air-saturated acetonitrile/2-propanol (1:1) and (b) argon-saturated 2-propanol at 20 ns (○), 1 μs (△), 10 μs (□), 0.1 ms (●) and 1 ms (▲) after the 248 nm pulse; insets: decay at 550 nm (upper) and formation at 360 nm (lower).

$\lambda_p = 360 \text{ nm}$ but a stronger absorbance. The decay kinetics of T_z and grow-in kinetics of the product coincide. The decay kinetics of T_z in most cases and at low enough intensity follow a first-order law which, however becomes shorter at higher intensity. The limiting lifetime in argon-saturated acetonitrile is 3 μs. The λ_z , λ_p and τ_z values in the solvents examined are compiled in Table 3.

The transient absorption spectra of TQ in argon-saturated acetonitrile in the presence of 2-propanol (Fig. 6b), DABCO (Fig. 7a) or TEA (Fig. 7b) reveal close similarities. T_z is quenched by the amines (Fig. 5). The rate constant for quenching of T_z by DABCO and TEA is $k_q = 4 \times 10^9$ and $5 \times 10^8 \text{ M}^{-1} \text{ s}^{-1}$, respectively. T_z reacts into a longer lived species (T_{rad}) with $\lambda_{\text{rad}} = 320$ and 420 nm. T_{rad} can be quenched by oxygen and should be assigned to a radical (see below). Second-order decay of this radical results in stable products with an absorption increase at 360 nm. In the presence of oxygen, T_z is converted into the stable product without the intermediacy of T_{rad} (Fig. 6a).

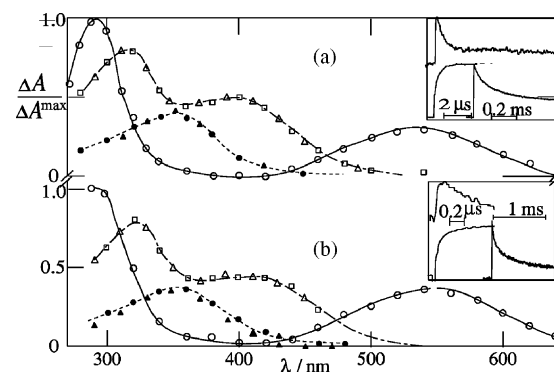


Fig. 7. Transient absorption spectra of TQ in argon-saturated acetonitrile and (a) DABCO (1 mM) and (b) TEA (1 mM) at 20 ns (○), 1 μs (△), 10 μs (□), 0.1 ms (●) and 1 ms (▲) after the 248 nm pulse; insets: decay at 550 nm (upper) and formation at 360 nm (lower).

Table 3
Absorption maxima and lifetime of the primary and secondary transients of TQ^a

Solvent	E_T^N	λ_z^b (nm)	τ_z^c (μ s)	λ_{rad} (nm)	$t_{1/2}$ (ms)	λ_p^d (nm)
<i>tert</i> -Butanol	39	<u>295</u> , 520	2–3	–	–	370
DMF ^e	40	540	0.5	410	0.08	350
Butyronitrile ^e		<300, 540	1.2	–	–	360
Acetonitrile	46	<u>295</u> , 550	2	–	–	360
MeCN + DABCO (1 mM)		<u>295</u> , 530	0.5	<u>320</u> , 410	0.06	360
MeCN + TEA (5 mM)		<u>295</u> , 530	0.2	<u>320</u> , 420	0.3	360
MeCN + Acetic acid (0.01 M)		550	0.1	–	–	370
MeCN + Water (4 M) ^f		480	0.2	–	–	360
2-Propanol	54	490	3–4	<u>320</u> , 410	0.2	370
Ethanol	65	<u>295</u> , 480	2–3	<u>320</u> , 410	0.2	370
Methylformamide ^e	72	<300, 500	1	–	–	360
Methanol	76	480	2	<u>320</u> , 410	0.2	370
Formamide	80	520	0.5	<340, 400	0.2	370
TFE	90	<320, 440	0.8	–	–	370
TFE + Water (28 M)		410	0.2	–	–	370

^a Argon-saturated and $\lambda_{exc} = 248$ nm.

^b Major peak underlined.

^c At low intensity and $A_{248} = 1$ –3.

^d Final product.

^e $\lambda_{exc} = 308$ nm.

^f See text.

3.4. Effects of temperature

To test for the lowest triplet state also in the case of TQ, phosphorescence was measured at -196 °C. The phosphorescence lifetime in ethanol is 0.5 ms for Me₂BQ and 0.4 ms for TQ. Literature values of the n, π triplet state of quinones are 0.3–1 ms, e.g. for 2-methyl-1,4-naphthoquinone or Vitamin K₁ [13,14]. While the triplet lifetimes of Me₂BQ and TQ in frozen media are similar and despite the efficient intersystem crossing for both quinones, this is not so in fluid solution at room temperature (see below). The transient absorption spectrum of TQ in ethanol at -180 °C is shown (Fig. 8, inset). The observed species, because of the phosphorescence, has to be assigned to the lowest triplet

state. The triplet lifetime is largest in glassy ethanol and the temperature dependence shows a strong decrease of τ_T and the triplet yield when the medium becomes fluid (Fig. 8).

4. Discussion

4.1. Phototransformation of BQs

Reactions of the triplet state of Me₂BQ with oxygen (3) and either an H-atom donating alcohol (4a) (Fig. 1b) or an amine (4b) are competing steps. The overall photoconversion of quinones without a β -H-atom in the side chain in acetonitrile in presence of TEA leads via ³Q* to the semiquinone radical anion and finally into QH₂ [3,6,7]. The properties of the semiquinone radical of 2-methyl-substituted BQs in aqueous solution by pulse radiolysis have been reported [20–23]. Equilibrium (9) between •QH and Q^{•-} in neat acetonitrile is not established, as it has been shown for the better spectroscopically resolved case of AQ [18]. With propanol, QH₂ and acetone result from termination of the semiquinone radical, as is known for various BQs [6,7]. Therefore, Φ_d is low in the absence of donors and substantial in argon-saturated acetonitrile only in the presence of donors at appropriate concentration (Table 2). Photoinduced charge separation after electron transfer from amines to ³Q* and the subsequent charge recombination or neutralization are supported by transient conductivity measurements [3,12]. The absorption spectra of Me₂BQ in aqueous acetonitrile solution show the semiquinone radical concomitant to triplet decay (Fig. 1a).

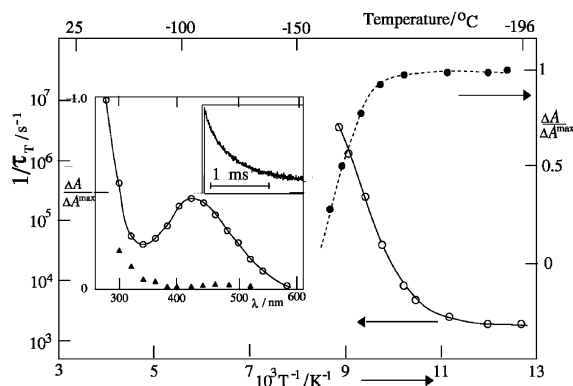
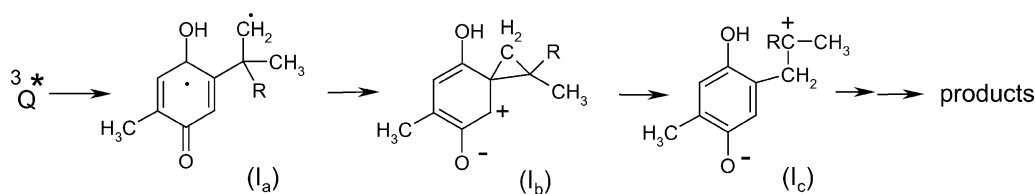


Fig. 8. Temperature dependence of the rate constant for decay (broken line) and transient absorption at 460 nm (solid line) for TQ (circles) in ethanol; inset: transient absorption spectra of TQ in ethanol at -180 °C at 20 ns (○), 0.1 ms (●) and 1 ms (▲) after the 248 nm pulse; insets: decay at 460 nm.



Scheme 1.

4.2. Intramolecular photoreactions of TQ

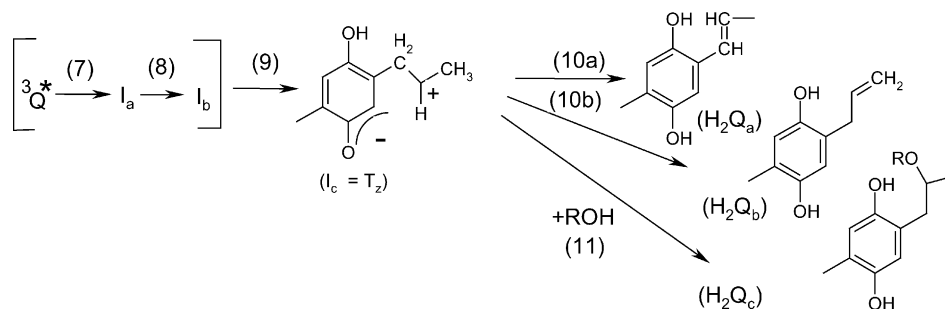
The photoreactions of BQs with and without a β -H-atom in the side chain are strikingly different. Based on product analysis of 1,4-benzohydroquinones with *tert*-butyl or isopropyl side chains, a zwitterion–diradical (I_a), a spirocyclopropyl intermediate (I_b) and a zwitterion prior to formation of stable products (Scheme 1) have been postulated [28–30]. In fact, the initial transient T_z cannot be assigned to the “normal” quinone triplet state which is efficiently quenched by oxygen, in contradiction to the observation for T_z for TQ. The long-wavelength absorption maximum λ_z of the spectrum of T_z is sensitive to solvent polarity, in contrast to the ${}^3Q^*$ state of BQs. On increasing the solvent polarity λ_z shifted from 550 nm in acetonitrile to 480 nm in alcohols and further to 410 nm in mixtures of TFE and water (Table 3 and Figs. 3 and 4). T_z cannot be the semiquinone radical, exhibiting maxima at 320 and 410 nm, based on pulse radiolysis of TQ in aqueous solution [23]. The solvent-dependent shift of the λ_z values is also not compatible with a non-ionic nature of T_z .

It is suggested for TQ in solution at room temperature that either Φ_{isc} is negligible or the lifetime of ${}^3Q^*$ is too short to be registered by nanosecond time resolution. T_z is therefore assigned to a zwitterionic species. It is, however, difficult to distinguish between that zwitterion, which is formed via the spirocyclopropyl I_b , or that zwitterion which is related to the precursor I_a . The lifetimes of I_a and I_b of TQ are probably too short to be registered by nanosecond time resolution and T_z is assigned to the second zwitterionic species, reactions (7)–(9). In acetonitrile the photoreaction should lead to the vinyl-hydroquinone derivative H_2Q_a , reactions (10a) and (10b), and possibly H_2Q_b (Scheme 2). The occurrence of intramolecular H-atom abstraction and the zwitterion as

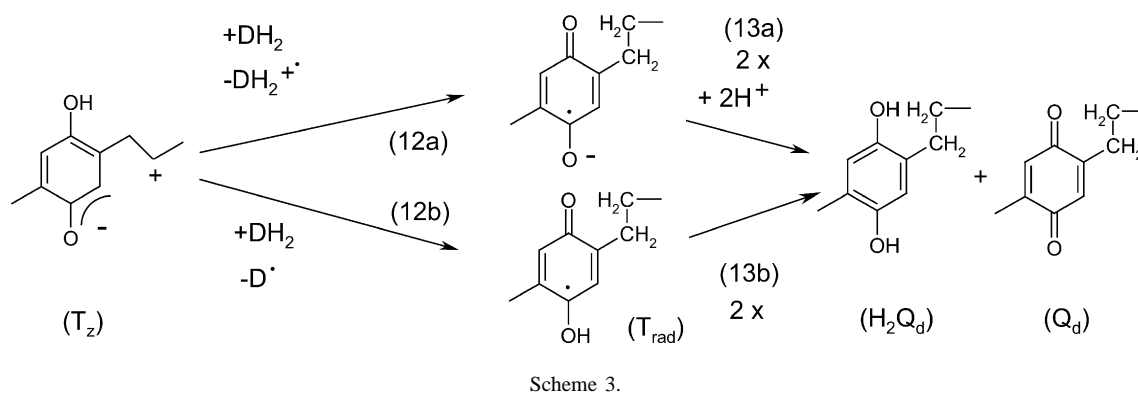
only accessible intermediate of TQ is in agreement with the substantial Φ_d value in neat argon-saturated acetonitrile, in contrast to other BQs without side chains. Interestingly, the zwitterion–diradical in the case of Vitamin K_1 in acetonitrile has a lifetime of up to 10 μ s and is quenched by oxygen, $k_{ox} = 0.5 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$ [19,26].

The results with TQ in *tert*-butanol and the fluoroalcohol are rather similar (Table 3). TFE as a weakly nucleophilic polar solvents, stabilizes ions and favors H-bonds to oxygen [45,46]. The observed conversion of T_z in TFE into the permanent 360 nm absorption is proposed to be due to an addition reaction (11), yielding a modified hydroquinone (H_2Q_c) (Scheme 2). The rate constant for conversion of T_z into H_2Q_c is similar in TFE and *tert*-butanol. This mechanism is supported by the finding that oxygen does not markedly decrease Φ_d , e.g. in *tert*-butanol (Table 2). One major effect is a prolongation of τ_z for low concentration of water and then a shortening which brings τ_z to a value lower than 30 ns for 20 M water. This latter dependence of $1/\tau_z$ versus $[H_2O]$ is not linear but upward curved (Fig. 5). The water addition may yield a H_2Q_c -type hydroquinone. So far, no radicals with a lifetime longer than a few nanosecond are involved.

Interestingly, T_z is quenched by amines (Fig. 8a and b) and 2-propanol (Fig. 7a), thereby T_z is converted into a longer lived radical species T_{rad} which subsequently decays by second-order kinetics into stable products with $\lambda_{max} = 360$ nm. The rate constant for quenching of T_z is largest for DABCO, $k_q = 4 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$, and much smaller for TEA. The spectrum of T_{rad} resembles that of the semiquinone radical of TQ in water [23]. T_{rad} is assigned to the semiquinone radical, formed by electron transfer from amines (12a) and H-atom transfer from alcohols (12b) and a (non-detectable) vinyl-type radical precursor (Scheme 3). The termination should yield a side chain modified TQ (Q_d) and its



Scheme 2.



hydroquinone (H_2Q_d). In the presence of oxygen the semiquinone radicals are quenched and the observed conversion, e.g. for alcohols (Fig. 7b), is proposed to be due to addition reaction (11) into products.

5. Conclusion

The photodeactivation pathways of 2,5-dialkyl-substituted BQs with and without a β -H-atom in the side chain are strikingly different. The triplet state of TQ escapes observation at room temperature. The isopropyl group in five positions acts as intramolecular H-atom donor and the first transient in fluid solution is assigned to a zwitterion T_z , formed after intramolecular H-atom transfer from the side chain. Decay of the zwitterion into modified hydroquinones, not involving free radicals, is proposed. In the presence of TEA or alcohols conversion of T_z into radicals and their termination takes place.

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