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Photoreactions of 2,5-dibromo-3-methyl-6-isopropyl-1,4-benzoquinone

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Abstract

The photochemistry of 2,5-dibromo-3-methyl-6-isopropyl-1,4-benzoquinone (Br_2TQ) in solution was studied by UV–vis spectroscopy using 20 ns laser pulses at 308 nm. The first transient with a lifetime of 0.06–0.2 μs is assigned to a triplet state. This triplet is converted into a short-lived zwitterion, which is formed after intramolecular H-atom transfer from the isopropyl substituent. The zwitterion has a lifetime of 0.1–2 μs and further conversion into 1,4-hydroquinones without involvement of free radicals is proposed. The properties of Br_2TQ differ from those of 2-*tert*-butyl-1,4-benzoquinone (BuBQ), where no intermediate could be detected under comparable conditions, and of 2-methyl-5-isopropyl-1,4-benzoquinone (thymoquinone: TQ), where the triplet state escapes observation at room temperature. The effects of solvent polarity and other specific properties of photoinduced intramolecular H-atom transfer in Br_2TQ are discussed. The mechanisms are specific for Br_2TQ, TQ and BuBQ, whereas the quantum yield of photodecomposition is large, e.g. in neat acetonitrile and several other solvents, even in the presence of oxygen.

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

1. Introduction

The photochemistry of 1,4-benzoquinone (BQ) and derivatives without side chain, e.g. 2,5-dimethyl-1,4-benzoquinone (Me_2BQ), is the subject of intensive investigations [1–13]. The quantum yield of intersystem crossing (Φ_{isc}) of several quinones, e.g. BQ and Me_2BQ, is close to unity [1–3]. Reaction of the triplet state with oxygen yields singlet molecular oxygen, the quantum yield is $\Phi_\Delta = 0.4$–0.9 for BQs in acetonitrile [8,9]. Intermolecular reactions of the triplet state with either an amine, such as *N*,*N*-dialkylamines, TEA or DABCO, or an H-atom donating solvent, e.g. an alcohol, yield hydroquinones (QH_2) [14–22]. The photoreduction of quinones in the presence of alcohols leads to the semiquinone radical ($^\bullet QH/Q^{\bullet -}$) and finally into QH_2. With propanol, QH_2 and acetone result from termination of the semiquinone radical, as known for various BQs [1–4,14]. The properties of the semiquinone radical have been characterized by both photochemistry [11–18] and radiation chemistry [23–26].

The mechanism of photoreaction changes completely, when intramolecular H-atom transfer is possible [27–32]. Thymoquinone (TQ: 2-methyl-5-isopropyl-1,4-benzoquinone) is an example of a photochemically reactive BQ derivative [33]. Upon photolysis of TQ a short-lived intermediate has been detected and attributed to a zwitterion, in contrast to quinones without a substituent for β-H-atom transfer in the side chain, e.g. BQ or Me_2BQ [33]. Other appropriate quinones are the 2,5-dibromo derivative (Br_2TQ: 2,5-dibromo-3-methyl-6-isopropyl-1,4-benzoquinone) and 2-*tert*-butyl-1,4-benzoquinone (BuBQ). A diradical (I_a), a spirocyclopropyl intermediate (I_b) and a zwitterion (I_c) have been postulated for 1,4-benzoquinones with *tert*-butyl or isopropyl side chains (Scheme 1) [28,32]. Phylloquinones, e.g. Vitamin K_1, are related systems with biological relevance [34–36].

Here, the photoinduced intramolecular H-atom transfer in Br_2TQ and BuBQ was studied by UV-vis spectroscopy in solution at room temperature. The quantum yield of

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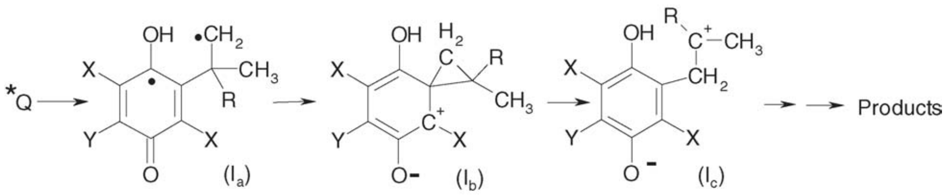
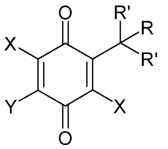


Scheme 1.

decomposition (Φ_d) at $\lambda_{irr} = 254$ nm is substantial in inert solvents, such as acetonitrile, in contrast to BQs without side chain. The properties of the triplet state and a zwitterion as first and second observable transient of Br_2TQ are outlined and the different results with respect to TQ are discussed. In contrast, no intermediate could be detected for BuBQ.

	R	R'	X	Y
TQ	H	Me	H	Me
Br_2TQ	H	Me	Br	Me
BuBQ	Me	Me	H	H
Me_2BQ	H	H	H	Me



2. Experimental details

The solvents, e.g. methyltetrahydrofuran: MTHF, acetonitrile (Uvasol quality) or 2,2,2-trifluoroethanol: TFE, and compounds (Merck, Sigma, Fluka) were used as received or purified by recrystallization, Me_2BQ or 1,4-diazabicyclo[2.2.2]octane: DABCO, or distillation, triethylamine: TEA. The absorption spectra were monitored on a UV–vis spectrophotometer (HP, 8453). For photoconversion the 254 nm line of a Hg lamp was applied. Typically, absorbances of 1–2 were used for $\lambda_{irr} = 254$ nm, corresponding to BQ concentrations of 0.1–0.3 mM. The molar absorption coefficient of Br_2TQ is $\varepsilon_{290} = 1.5 \times 10^4\ M^{-1}\ cm^{-1}$. The conversion was carried out after bubbling by argon prior to and during irradiation. For HPLC analyses a 125 × 4.6 mm Inertsil ODS-3.5 μm column was used and MeOH–water 1:2 or 2:1 as eluents. The quantum yield of decomposition Φ_d was determined using the uridine/water/air actinometer [37]. 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 at 248 nm, another excimer laser (EMG 201 msc) was applied. The absorption signals were measured with two digitizers (Tektronix 7912AD and 390AD). Relative yields were obtained using optically matched solutions. Absorbances of 1–4 were used for $\lambda_{exc} = 308$ nm, corresponding to concentrations of 0.05–0.2 mM for Br_2TQ. Formation of singlet molecular oxygen, $O_2(^1\Delta_g)$, was detected by a Ge-diode; The quantum yield (Φ_Δ) was obtained using phenazine in dichloromethane ($\Phi_\Delta = 0.89$) as reference [38]. The samples were freshly dissolved and all measurements refer to 24 °C and deoxygenated solution, unless otherwise indicated.

3. Results

3.1. Transient absorption at room temperature

The time-resolved UV–vis spectroscopy of Br_2TQ in acetonitrile (Fig. 1a), MTHF (Fig. 2c) and TFE (Fig. 3b) shows two transients after the 308 nm pulse. The short-lived species, which has a maximum at $\lambda_T = 470$ nm, decays by first-order kinetics and has a lifetime (τ_T) of 60–200 ns, is

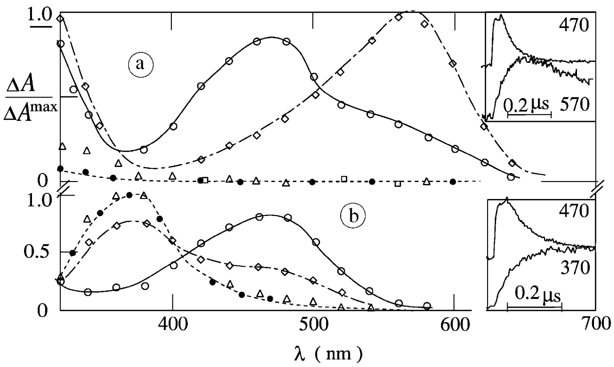


Fig. 1. Transient absorption spectra of Br_2TQ (argon) in (a) dry acetonitrile and (b) wet acetonitrile (1 M water) at 20 ns (○), 0.1 μs (◇), 1 μs (△), 10 μs (□) and 0.1 ms (●) after the 308 nm pulse; insets: kinetics at 470 nm (upper) and (a) 570 nm and (b) 370 nm (lower).

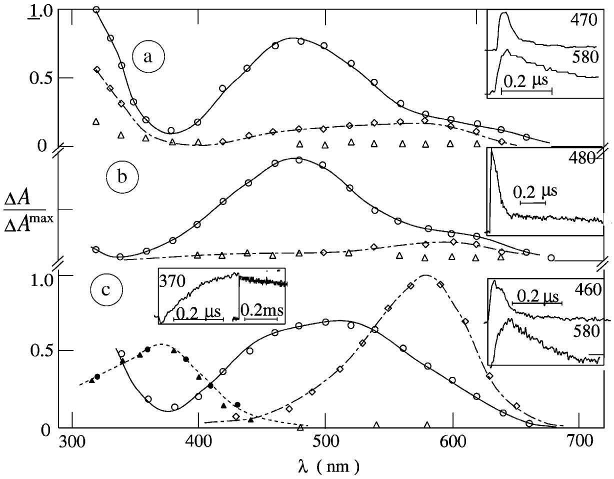


Fig. 2. Transient absorption spectra of Br_2TQ in (a) carbon tetrachloride; (b) toluene and (c) MTHF at 20 ns (o), 0.1 μs (◇), 1 μs (△), 0.1 ms (●) and 1 ms (▲) after the 308 nm pulse; insets: kinetics at 370 nm (left), 460–480 nm (upper) and 580 nm (lower).

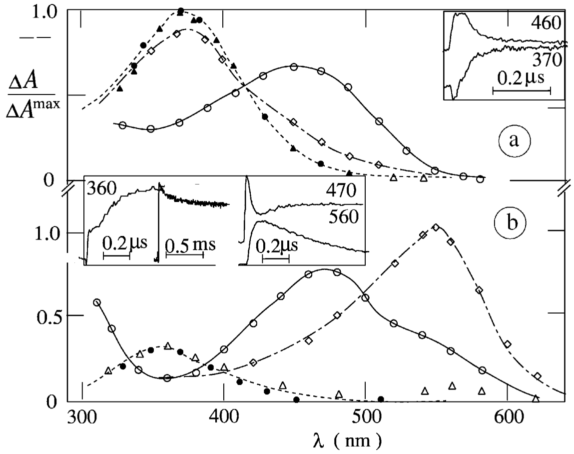


Fig. 3. Transient absorption spectra of Br_2TQ (argon) in (a) *tert*-butanol and (b) TFE at 20 ns (○), 0.1 µs (◇), 1 ms (△), 0.1 ms (●) and 1 µs (▲) after the 308 nm pulse; insets: kinetics at 460/470 nm (upper) and (a) 370 nm and (b) 360 and 560 nm.

converted into a secondary transient (T_z). T_z has a maximum at $\lambda_z = 550$–580 nm, decays also by first-order kinetics and has a lifetime (τ_z) of 0.1–2 µs. The initial species is assigned to the triplet state ($^{3*}Q$) and T_z to a zwitterionic species (see Section 4.2). The triplet state is formed within the pulse and the spectrum is only little influenced by solvent properties (Table 1). In most cases the triplet state is finally converted into one or several stable photoproducts (P_n) with maximum at $\lambda_p = 370$ nm. In MTHF (Fig. 2c) and TFE (Fig. 3b) this conversion takes place from $^{3*}Q$ via T_z into P_n. An example, where this conversion bypasses T_z, is shown for Br_2TQ in *tert*-butanol (Fig. 3a). A species with similar characteristics and conversion of $^{3*}Q$ directly into the stable 370 nm species was observed, when water was added to Br_2TQ in acetonitrile (Fig. 1b). The conversion of the triplet state via T_z into P_n may be too fast, as shown in Fig. 4b versus 4a for Br_2TQ in acetonitrile in the presence of 2-propanol in larger and smaller amount, respectively. Interestingly, no conversion into a detectable photoproduct takes place for Br_2TQ in solvents of lower polarity, such as carbon tetrachloride, benzene, toluene or dichloromethane. Apparently, τ_z depends on the medium (Table 2). In carbon tetrachloride (Fig. 2a) or toluene (Fig. 2b) T_z is only weakly absorbing at λ_z. On the other hand, T_z is substantial in MTHF and polar solvents, e.g. acetonitrile or TFE.

Table 1
Absorption maxima and triplet lifetime[a]

Quinone	Solvent	λ_T[b](nm)	τ_T (ns)
Br_2TQ	CCl_4[c]	<$\underline{310}$, 480	80
	Acetonitrile	$\underline{300}$, 460	80
	+Water (1 M)	460	60
	2-Propanol	300, $\underline{470}$	80
	Ethanol	300, $\underline{470}$	90
	Methanol	300, $\underline{470}$	100
	TFE	295, $\underline{460}$	200
	+Water (1 M)	290, $\underline{460}$	100
Me_2BQ[d]	Acetonitrile	$\underline{285}$, 450	4000
	+Water (28 M)	$\underline{285}$, 450	900

[a] Argon-saturated, $\lambda_{exc} = 308$ nm at low intensity and $A_{308} = 1$–2.

[b] Major peak underlined.

[c] Same maximum and comparable lifetime in benzene, toluene, MTHF, dichloromethane, methylformamide, dimethylformamide or butyronitrile.

[d] Taken from [33].

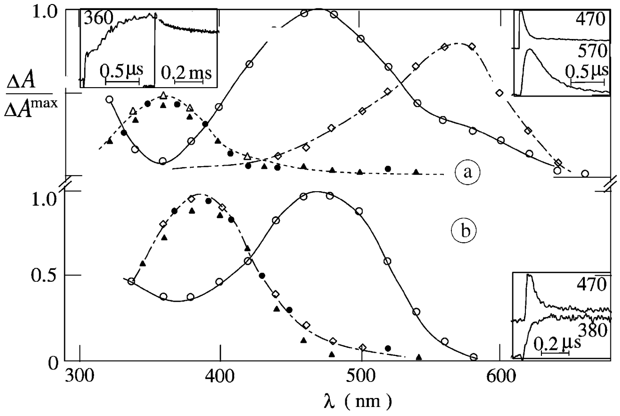


Fig. 4. Transient absorption spectra of Br_2TQ (argon) in acetonitrile plus 2-propanol (a) 0.3 M and (b) 3 M in 20 ns (o), 0.1 µs (◇), 1 µs (△), 0.1 ms (●) and 1 ms (▲) after the 308 nm pulse; insets: kinetics at 360 nm (left), 470 nm (upper) and (a) 570 nm and (b) 380 nm (lower).

A third transient (T_{rad}) with maximum at 435 nm was observed in the presence of the amines. The decay of T_z is quenched by DABCO or TEA. In acetonitrile $1/\tau_z$ depends linearly on the DABCO concentration and the slope, i.e. the rate constant for quenching of T_z, is $k_q = 2 \times 10^9\ M^{-1}s^{-1}$. At higher amine concentration T_z was too short-lived to be detected (Figs. 5a and b), in contrast to a TEA concentration of a few mM. T_z is converted into the longer lived T_{rad} species which subsequently decays by second-order kinetics either fast (DABCO) or slowly (TEA). The spectrum of T_{rad} differs only slightly from that of the semiquinone radical of Me_2BQ with $\lambda_{rad} = 440$ nm [19]. T_{rad} of Br_2TQ is

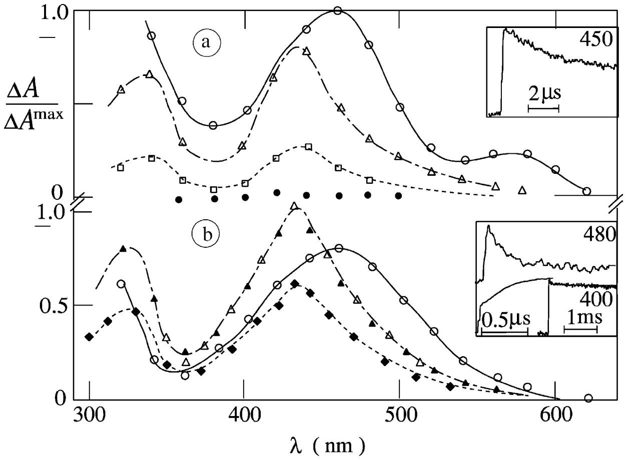


Fig. 5. Transient absorption spectra of Br_2TQ in argon-saturated acetonitrile in the presence of (a) DABCO 3 mM and (b) TEA 30 mM at 20 ns (○), 1 µs (△), 10 µs (□), 0.1 ms (●), 1 ms (▲) and 10 ms (◆) after the 308 nm pulse; insets: kinetics at 450/480 nm and (b) 400 nm (lower).

Table 2
Absorption maxima and lifetime of the secondary transient[a]

Quinone	Solvent	λ_z[b] (nm)	τ_z[c] (μs)	k_q ($\times 10^8$ $M^{-1}s^{-1}$)	λ_p[d] (nm)
Br_2TQ	Acetonitrile	<300, 580[e]	0.7	–	–
	+DABCO (5 mM)	<300, 580	0.1	20	–[f]
	+TEA (5 mM)		0.2	1	–[f]
	+*tert*-Butanol (1 M)		0.3	0.02	370
	+2-Propanol (2 M)		0.2	0.02	370
	+Ethanol (1 M)		0.2	0.04	370
	+Acetic acid (0.01 M)		0.2	5	360
	TFE	<300, 580	2	-	360
TQ[g]	Acetonitrile	295, 550	2	-	360
	+DABCO (1 mM)	295, 530	0.5	40	360
	+TEA (5 mM)	295, 530	0.2	5	360
	tert-Butanol	295, 520	2–3	<0.01	370
	2-Propanol	295, 490	3–4	<0.01	370
	+Acetic acid (0.01 M)	550	0.1	40	370
	+Water (4 M)	480	0.2	–[h]	360
	TFE	<320, 440	0.8	–	370

[a] Argon-saturated, $\lambda_{exc} = 308$ nm (Br_2TQ) and 248 nm (TQ).
[b] Major peak underlined.
[c] At low intensity and $A_{308} = 1–3$.
[d] Final product.
[e] Weak transient in benzene, toluene, dichloromethane, methylformamide, dimethylformamide or butyronitrile.
[f] Third transient T_{rad}.
[g] Taken from [33].
[h] Upward curved dependence.

tentatively assigned to a semiquinone radical (see Section 4.2). Note that the presence of DABCO converts the spectrum to a minor extent thermally that the colourless sample becomes yellow. The decay of T_z is also quenched by acetic acid and the rate constant is $k_q = 5 \times 10^8$ $M^{-1}s^{-1}$ (Table 2). The rate constants for quenching by 2-propanol and *tert*-butanol are similar, $k_q = 2 \times 10^6$ $M^{-1}s^{-1}$, indicating that radicals are not involved in these cases since the former is an efficient H-atom donor and the latter an OH radical scavenger.

In UV-transparent solvents, especially in acetonitrile and alcohols, excitation of Br_2TQ by 248 nm pulses led to comparable results. Virtually no transient absorption spectrum was observed for BuBQ in acetonitrile and 2-propanol at lower laser pulse intensity, $\lambda_{exc} = 248$ nm. At higher intensity a weak semiquinone radical was registered for BuBQ (not shown).

3.2. *Effects of oxygen and temperature on the triplet state*

The quantum yield of formation of singlet molecular oxygen is rather substantial for parent BQ or trimethyl-1,4-benzoquinone (Me_3BQ) in several air- or oxygen-saturated solvents, but small for TQ and close to zero for BuBQ (Table 3). For Br_2TQ Φ_Δ is also low in air-saturated solution, but significantly larger under oxygen. This strong dependence of Φ_Δ on the oxygen concentration is a consequence of the short triplet lifetime. The values of $\tau_T = 80$, 70 and 30 ns for Br_2TQ in argon-, air- and oxygen-saturated acetonitrile correspond to a rate constant for quenching by oxygen of 3×10^9 $M^{-1}s^{-1}$ and reveal that the amount of triplet quenching in air-saturated solution is only 10–20% (Table 3). The rate constant in TFE is much lower, $<5 \times 10^8$ $M^{-1}s^{-1}$.

To test for the triplet state as precursor in various cases, phosphorescence was measured at −196 °C. The phosphorescence lifetime in ethanol is $\tau_p = 0.5$, 0.4, 0.3 and 0.4 ms, for Me_2BQ, TQ, Br_2TQ and BuBQ, respectively. Literature values of the n,π triplet state of quinones are $\tau_p = 0.3–1$ ms, e.g. for MeNQ or Vitamin K_1 [6,7,21]. The transient absorption spectra of Br_2TQ (Fig. 6a) and TQ in ethanol at −180 °C have both $\lambda_T = 450$ nm. The observed species, because of the similar lifetime (Fig. 6b) to the phosphorescence signal, has to be assigned to the triplet state.

While the triplet lifetimes of Me_2BQ, TQ and Br_2TQ in frozen media are similar and the quantum yield of phosphorescence is comparable for these quinones, this is not so for τ_T and the quantum yield Φ_{isc} in fluid solution. The effect of temperature is shown in Fig. 6. The dependence of the rate constant for triplet decay versus $1/T$ is smooth for Br_2TQ, approaching the 90 ns value in ethanol at room temperature.

Table 3
Quantum yield (Φ_Δ) of formation of singlet molecular oxygen[a]

Quinone	CCl_4	C_6H_6	CH_3CN
BQ	0.7	0.1 (0.02)[b]	0.4
Me_3BQ	0.4	0.8	0.5
BuBQ	<0.02	<0.02	<0.02
TQ	0.02	0.03 (0.01)	<0.02
Br_2TQ	0.2 (0.04)	0.2[c] (0.02)	0.3 (0.03)

[a] Using oxygen-saturated solution, $\lambda_{exc} = 308$ nm.
[b] Values in parentheses: air-saturated solution.
[c] In CH_2Cl_2 $\Phi_\Delta = 0.1$.

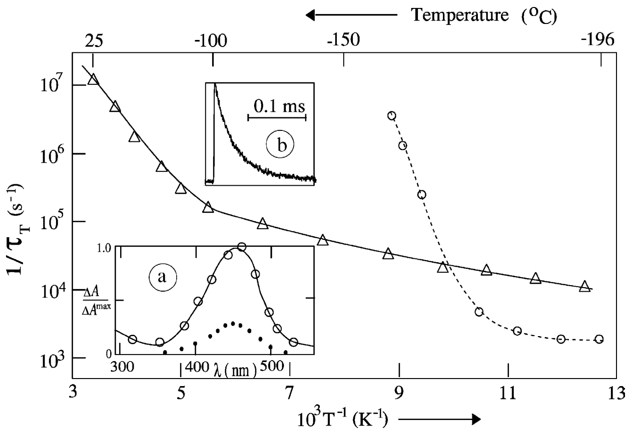


Fig. 6. Temperature dependences of the rate constants for triplet decay of TQ (circles) and Br_2TQ (triangles) in ethanol; insets for Br_2TQ in ethanol at −180 °C: (a) T–T absorption spectrum at (○) 1 μs and (●) 30 μs and (b) kinetics at 460 nm.

In contrast, the curve versus $1/T$ for TQ is steep and no triplet could be detected above −155 °C.

3.3. Continuous irradiation

Table 4
Quantum yield Φ_d of decomposition of quinones[a]

Quinone	Gas	CH_3CN	*tert*-BuOH	2-Propanol	H_2O[b]
Me_2BQ	Ar	0.06	0.08	0.8	0.8
	O_2	<0.02	<0.02	0.4	0.7
BuBQ	Ar	0.5	0.5	0.6	0.7
	O_2	0.5	0.5		0.7
TQ	Ar	0.6	0.6	0.8	0.8
	O_2	0.5	0.5	0.6	0.7
Br_2TQ	Ar	0.5	0.5	0.6	0.7
	O_2	0.5			0.6

[a] In Ar- or oxygen-saturated solution using $\lambda_{irr} = 254$ nm and HPLC.
[b] pH 6–7.

Irradiation of Br_2TQ in acetonitrile leads to isosbestic points at 260 and 300 nm, with an absorption decrease between and an increase below and around 360 nm (Fig. 7a). The changes in other solvents, e.g. *tert*-butanol or 2-propanol, are similar. The quantum yield Φ_d is substantial for Br_2TQ in the absence of an electron donor and even in oxygen-saturated acetonitrile or *tert*-butanol, in contrast to Me_2BQ (Table 4) and other quinones. Photodecomposition of Br_2TQ (retention time: $t_r = 21$ min) was measured by HPLC, where several photoproducts were observed depending on the medium and the degree of substrate decomposition. In acetonitrile the major peak (P_1) at low conversion was registered at $t_r = 14$ min, whereas further irradiation converts P_1 into P_2, $t_r = 17$ min. This conversion of the first into the secondary product is shown in Fig. 7c. In contrast, the major initial photoproduct in *tert*-butanol, 2-propanol, methanol, ethanol or in a mixture of one of these alcohols with acetonitrile is the same: P_3, $t_r = 19.2$ min. Prolonged photolysis of these samples yields essentially P_1 and P_2 as secondary products. The major peak P_3 in alcohols is attributed to the 3-allyl-6-methyl-1,4-hydrobenzoquinone, in accordance with the literature of the product of Br_2TQ in ethanol [32]. The two major peaks in mixtures of TFE or acetic acid with acetonitrile are P_4 with $t_r = 12.7$ min and P_1. Finally, the major product peaks in the presence of DABCO are P_5 with $t_r = 8$ min and P_4. The band of BuBQ in acetonitrile or other solvents is shifted to shorter wavelengths (Fig. 7b) and the photoconversion is likewise rather efficient (Fig. 7c), but HPLC analysis of the products was not very successful. Comparably large values of $\Phi_d = 0.5$ were also found for TQ and BuBQ in either argon- or oxygen-saturated acetonitrile (Table 4).

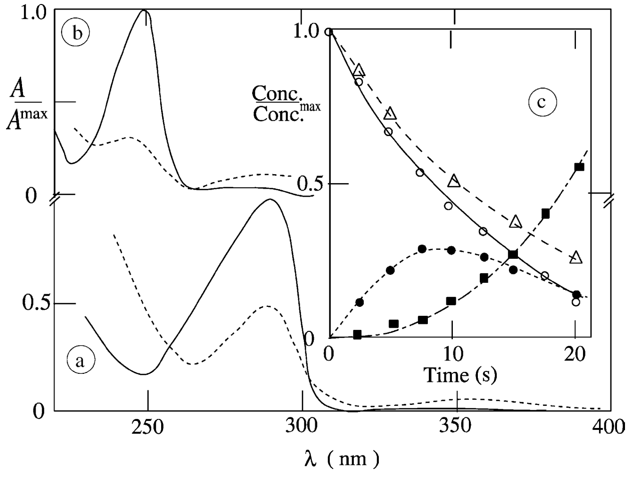
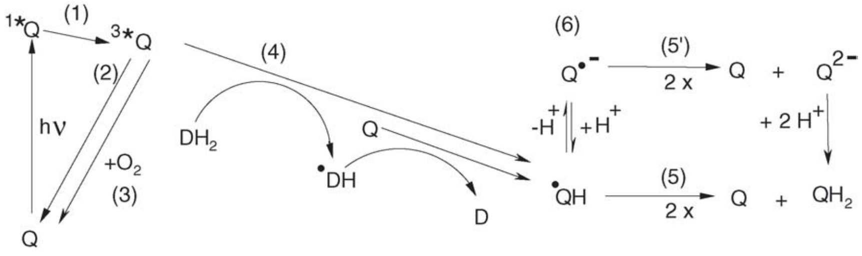


Fig. 7. Absorption spectra (a) of Br_2TQ in acetonitrile and (b) of BuBQ in aqueous solution prior to (full) and after (broken, 10 s) irradiation at 254 nm; (c) concentration vs. time in acetonitrile of Br_2TQ (○), two respective major products (P_1: ●) and P_2: ■) and BuBQ (△).

4. Discussion

4.1. Photoreactions of quinones

The intermolecular photoreactions of quinones are illustrated in Scheme 2. The triplet state, formed from $^{1*}Q$ by intersystem crossing (1), decays via (2) or by reaction with oxygen (3), thereby yielding singlet molecular oxygen in high yield, e.g. in acetonitrile, as literature values are $\Phi_\Delta = 0.4$ for BQ and 0.9 for Me_4BQ [8,9]. The photoreduction of quinones in the presence of H-atom donating alcohols leads via H-atom abstraction (4) to the semiquinone radical and finally via (5) into hydroquinones QH_2 [1–4,14]. The photoreduction steps by *N*,*N*-dialkylamines, TEA or DABCO (DH_2), are analogous, apart from electron transfer and involvement of the radical anion $Q^{\bullet-}$ step (5′) [15–18]. Φ_d is therefore substantial in argon-saturated acetonitrile in the presence of donors at appropriate concentration, but low in their absence [19–22]. Equilibrium (6) is not established in non-aqueous solution.



Scheme 2.

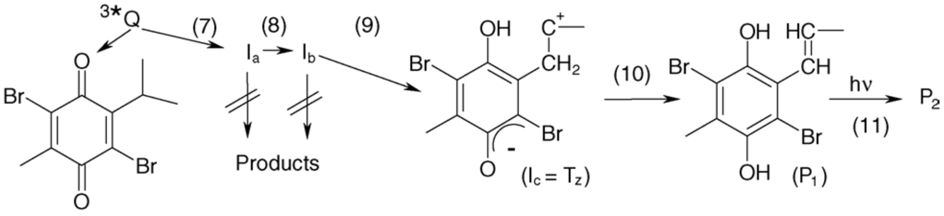
The photochemical properties of quinones with a side chain are generally complex [39,43] and they are not directly analogous to BQ or Me_2BQ. A photoinduced zwitterion-diradical has been observed in the case of Vitamin K_1 in acetonitrile; it has a lifetime of up to 10 μs and the decay is quenched by oxygen [19,36]. Alanine-BQ conjugates were reported to yield a biradical-zwitterion by intramolecular H-atom transfer [39]. A biradical-zwitterion has been proposed as intermediate for vinyl-1,4-benzoquinones [40]. For various suitable ketones photoinduced intramolecular H-atom transfer has been intensively studied [41]. *o*-Alkylarylketones, e.g. *o*-methylacetophenone, are known to form photoenols [42,43].

For TQ the initial transient within the 20 ns pulse is assigned to T_z, a zwitterionic species, and the lifetime of $^{3*}Q$ is too short to be registered [33]. A spirocyclopropyl intermediate and four photoproducts have been reported for TQ in methanol [29]. The side chain in BuBQ can act as intramolecular H-atom donor [27–29]. Based on product analysis of 1,4-benzoquinones with *tert*-butyl or isopropyl groups, I_a, I_b and zwitterion I_c (Scheme 1) were postulated [28,32]. The lack of any transient absorption for BuBQ in acetonitrile is in agreement with the postulation of efficient intramolecular H-atom transfer from the *tert*-butyl group in 5 position [28,29]. The weak semiquinone radical, registered in 2-propanol at higher intensity (not shown) may be due to secondary photolysis.

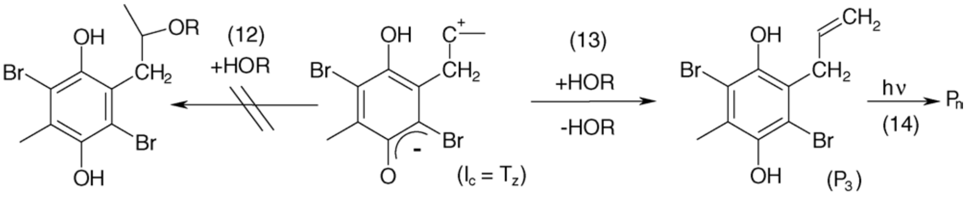
4.2. Photoreactions of Br_2TQ

The triplet state of Br_2TQ could be expected to be short lived in fluid solution. In fact, only in glassy media at low temperatures is the initial transient of TQ, which was attributed to the triplet state [33], observable by our means (Fig. 6). However, the triplet lifetime of Br_2TQ in solution at room temperature is much longer than that of TQ. The initial transient of Br_2TQ (Figs. 1–5) is now assigned to $^{3*}Q$ since it is formed during the excitation pulse and the quantum yield of formation of singlet molecular oxygen, which can be considered as minimum for Φ_{isc}, is $\Phi_\Delta = 0.2–0.3$ (Table 3). Apparently, the two heavy bromine atoms in 3 and 6 positions are favourable to enhance Φ_{isc} drastically. The triplet state of Br_2TQ in solvents of low polarity (Fig. 2a and b) is proposed to be non-reactive, i.e. intersystem crossing successfully competes with step (7), Scheme 3.

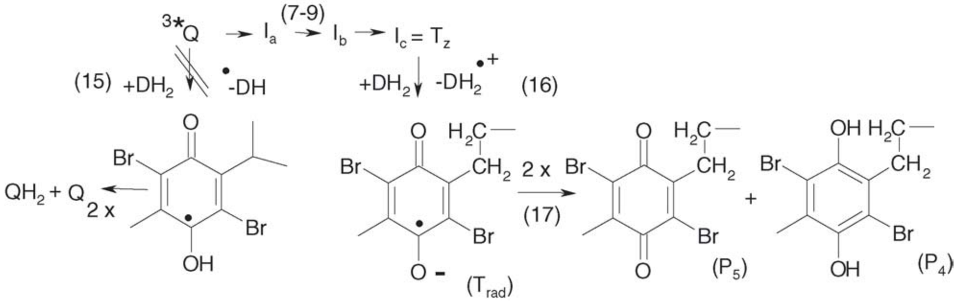
In MTHF and more polar solvents, however, the triplet state of Br_2TQ is reactive and transient T_z, formed via sequence (1) and (7)–(9), is assigned to the above mentioned zwitterion. For Br_2TQ in ethanol a zwitterionic intermediate had already been assumed [27]. Br_2TQ and TQ are comparable in the respects that T_z is an intermediate and no radicals (with a detectable lifetime) are involved. On the other hand, the effects of solvent polarity on λ_z and τ_z are smaller for Br_2TQ (Table 2) than for TQ [33]. The low conversion of T_z in acetonitrile into the permanent UV absorption (Fig. 1a)



Scheme 3.



Scheme 4.



Scheme 5.

is proposed to be due to reaction (10), yielding a vinyl-type hydroquinone as P_1 (Scheme 3). P_2, observed upon prolonged irradiation (Fig. 7c), reaction (11), is tentatively attributed to a hydroxycoumaran [28,29,40].

The observed conversion of T_z in TFE into the permanent 360 nm absorption (Fig. 3b) could be due to an addition reaction (12), yielding a modified hydroquinone (Scheme 4). Such a reaction with several alcohols (ROH) into several products containing the RO group has indeed been found for TQ [33]. For Br_2TQ, however, reaction (12) is not supported, as the HPLC product pattern is the same in either TFE, *tert*-butanol, 2-propanol, ethanol or methanol.

In contrast to TQ [33], no radical with absorption maxima at 320 and 410 nm was observed for Br_2TQ in 2-propanol (Fig. 4). Apparently, the major reaction in the absence of an electron donor does not yield free radicals with a detectable lifetime. Generally, a catalyzed pathway (7)–(9) and (13) from $^{3*}Q$ via T_z into hydroquinones and secondary photolysis (14) are proposed in polar media, whereas in solvents of low polarity the triplet decays predominantly without product formation.

The photoreduction mechanism of Br_2TQ in acetonitrile in the presence of a donor is totally different from that of intermolecular H-atom abstraction, as shown in Scheme 2 for BQs. H-atom transfer (15) or electron transfer from DH_2 to the triplet state of Br_2TQ to yield 2,5-dibromo-3-methyl-6-isopropyl-1,4-benzohydroquinone (QH_2) does not take place (Scheme 5), at least for TEA in the usual concentration range (<0.01 M). However, in the presence of amines T_z is converted via (16) into a semiquinone radical T_{rad} (Fig. 5a and b). T_{rad} decays via termination (17) and the products are tentatively assigned to a modified quinone (P_5) and the corresponding hydroquinone (P_4).

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 quinones without side chain. These intramolecular mechanisms are supported by the findings that oxygen does not markedly decrease Φ_d, e.g. for Br_2TQ, TQ and BuBQ in acetonitrile or *tert*-butanol (Table 4). Nevertheless, the effects of solvent polarity on Φ_{isc} and other specific properties of intramolecular H-atom transfer with TQ and Br_2TQ are complex and not yet fully understood.

5. Conclusion

The deactivation pathways of BQs with and without a β-H-atom in the side chain are strikingly different. For the three BQs under examination, the isopropyl or *tert*-butyl groups in 5 position act as an intramolecular H-atom donor. The short-lived triplet state of Br_2TQ is characterized, while that of TQ and BuBQ escapes observation. The second transient of Br_2TQ in solution at room temperature is assigned to a zwitterion, formed after intramolecular H-atom transfer. Decay of the zwitterion into modified hydroquinones of Br_2TQ, not involving free radicals, is proposed. In the presence of TEA or DABCO conversion of the zwitterion into radicals and their termination takes place. The transient properties of Br_2TQ differ strongly from those of either Me_2BQ (intermolecular transfer steps) or TQ (lack of triplet state).

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