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Photoprocesses of Chloro-Substituted *p*-Benzoquinones

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The photochemistry of chloro-(ClBQ), dichloro-(2,5- and 2,6-Cl_2BQ), and trichloro-1,4-benzoquinone (Cl_3BQ) was studied in aqueous solution and/or in mixtures with acetonitrile. Final products are the corresponding hydroquinones (QH_2s) and 2-hydroxy-1,4-benzoquinones (QOHs). Three transients were detected by UV−vis absorption spectroscopy. The triplet state appears within the 20 ns 248 nm pulse and is converted within 0.1−1 μs into a photohydrate (HI_{aq}). HI_{aq} which is spectroscopically and kinetically separated from the triplet state decays within 5 ms, whereas the anion of the hydroxyquinone (QO^-) grows in at ca. 500 nm in the 0.1−1 s time range. The proton formation and decay kinetics within 0.1−10 μs were observed by transient conductivity in the course of the reaction of the triplet state with water en route to HI_{aq} at pH 4−9. Formation of QO^- results in a permanent conductance. The efficient photoconversion of Cl_nBQs at low concentrations (<0.2 mM) into QH_2s and HOQs is due to a redox reaction of Q with rearranged HI_{aq}. The quantum yield of photoconversion at $\lambda_{irr} = 254$ nm is 0.8−1.2 for ClBQ or Cl_2BQs in aqueous acetonitrile and smaller (0.4) for Cl_3BQ. The yield of semiquinone radical ($^\bullet QH/Q^{\bullet -}$) of Cl_nBQs ($n = 1-4$) in acetonitrile-water (1:1) is low (<20%) at low substrate concentration but is significantly increased upon addition of an H-atom donor, for example, 2-propanol. Other mechanisms involving $^\bullet QH/Q^{\bullet -}$ radicals, such as quenching of the triplet state at enhanced Cl_nBQ concentrations and H-atom abstraction from an organic solvent in mixtures with water, have also to be considered.

Introduction

The photochemistry of 1,4-benzoquinone (BQ) and its derivatives, 1,4-naphthoquinone (NQ) or 9,10-anthraquinone (AQ), has been the subject of intensive investigations.[1−27] Generally, quinones exhibit a high quantum yield of intersystem crossing (Φ_{isc}) in solution at room temperature.[1] For BQ, NQ, and AQ, the maximum quantum yield of formation of hydroquinones (QH_2) in the presence of an H-atom donor, for example, 2-propanol, is close to unity.[3] The photoreduction of quinones by amines, such as triethylamine, occurs by electron transfer.[1,2,6−12] The properties of the semiquinone radical ($^\bullet QH/Q^{\bullet -}$), which plays a key role in the photoreduction of quinones, have been investigated by using radiation chemical techniques.[28−30]

The possibility of formation of $^\bullet OH$ radicals upon photolysis in aqueous solution has been postulated by several groups,[1,15−18] but a free $^\bullet OH$ radical mechanism has been questioned and is now excluded for BQ and its methyl derivatives Me_nBQs, $n = 2-4$.[22,23] The photoconversion of parent BQ and some of its derivatives in aqueous solution is well characterized and differs in several respects from the photoprocesses in the organic phase. The only photoproducts are QH_2 and 2-hydroxy-1,4-benzoquinone (QOH/QO^-), which are formed in equal amounts, $\Phi = 0.4-0.7$. For BQ and Me_nBQs, two pathways have to be considered: (i) via the semiquinone-type radicals and (ii) by water addition to the triplet state with the intermediacy of 1,2,4-trihydroxybenzenes (THBs). The latter pathway dominates at low BQ concentrations and does not involve radicals, apart from the last step, where the THBs react with the quinones (via nonobservable radicals) to the QH_2s and QOHs.[22,23] Similarly, in the photolysis of NQ in aqueous solution, trihydroxynaphthalenes are postulated as intermediates en route to the stable photoproducts, 5- and 7-hydroxy-1,4-naphthoquinone.[13,14]

As far as the chlorinated 1,4-benzoquinones are concerned, most papers refer to chloranil (Cl_4BQ) as sensitizer.[1,31,32] Only a few deal with the photochemical properties of Cl_nBQs, $n = 1-3$.[24−27] For Cl_2BQ, photoinduced electron transfer from 4,4-dimethoxydiphenylmethane and competitive decay pathways of the radical ions have been reported.[24] For 2,6-Cl_2BQ in aqueous solution, the corresponding photoproducts QOH/QO^- and QH_2 were detected, $\Phi = 1.5$.[26] Virtually no other time-resolved photochemistry of Cl_nBQs, $n = 1-3$ could be found in the literature.

In the present paper, the photochemical reactions of four chlorinated 1,4-benzoquinones, ClBQ, 2,5-Cl_2BQ, 2,6-Cl_2BQ, and Cl_3BQ, were studied by laser flash photolysis at 248 nm and continuous irradiation at 254 nm in aqueous solution and/or in 1:1 (vol) mixtures with acetonitrile, a polar organic solvent which does not favor H transfer. The photochemistry of Cl_nBQs in aqueous solution differs substantially from that of the parent BQ and Me_nBQs. The effects of chloro-substituents and medium on the photoreactions were studied by time-resolved UV−vis spectroscopy and conductivity at room temperature. For comparison, some experiments were carried out with Cl_4BQ.

Experimental Section

All compounds (Merck, Aldrich, Sigma, Fluka) were used as received. 2,2,2-Trifluoroethanol (TFE), a weakly nucleophilic and strongly polar solvent, was from Aldrich, and water was from a milli Q (Millipore) system. Absorption spectra were monitored on a UV−vis spectrophotometer (HP, 8453). The molar absorption coefficient of ClBQ in water is $\varepsilon_{254} = 1.4 \times 10^4$ $M^{-1}cm^{-1}$. For photoconversion, the 254 nm line of a low-pressure Hg lamp was used. Absorbances ranged between 1 and 2, corresponding to quinone concentrations of 0.1−1 mM. The solutions were vigorously bubbled with argon prior to and during

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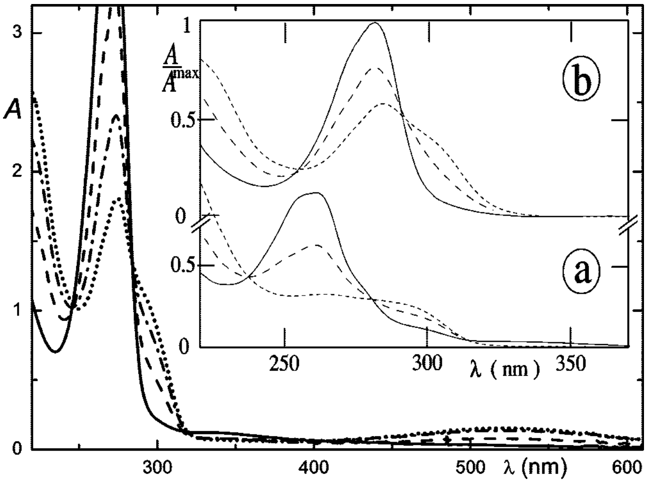


Figure 1. Absorption spectra of 2,6-Cl_2BQ in argon-saturated acetonitrile−water (1:10) at pH 7−8 prior to (full) and after irradiation (broken, 10 s interval) at 254 nm; (a) ClBQ and (b) Cl_3BQ in acetonitrile-water (1:1).

irradiation. The quantum yield Φ_d was determined by using the uridine/water/air actinometer.[33] For HPLC analyses, a 125 × 4.6 mm Inertsil ODS-3 5 μm column was used with methanol−water 1:2 or 2:1 as eluents. Oxygen concentrations were measured with a Clark electrode (Hansatech).[34] The molar absorption coefficients of QO^- of BQ at the two maxima are $\varepsilon_{260} = 4 \times 10^3$ and $\varepsilon_{482} = 2.2 \times 10^3$ $M^{-1}cm^{-1}$, and that of QOH is $\varepsilon_{400} = 2 \times 10^3$ $M^{-1}cm^{-1}$.[30] For $ClBQH_2$ and Cl_2BQH_2, $\varepsilon_{293} = 3.3 \times 10^3$ and $\varepsilon_{346} = 970$ M^{-1} cm^{-1}, respectively.[26,28] For the QO^- forms of 2,6-Cl_2BQ and Cl_3BQ, the reported molar absorption coefficients are $\varepsilon_{524} = 2.5 \times 10^3$ and $\varepsilon_{535} = 1.4 \times 10^3$ M^{-1} cm^{-1}.[26,35] Excimer lasers (Lambda Physik) provided 20 ns pulses at 248 and 308 nm (energy <100 mJ). The absorption and conductivity signals were measured with digitizers (Tektronix 7912AD and 390AD). Relative yields were obtained by using optically matched solutions. The results were found to be corresponding for excitation at either 248 or 308 nm, but for clarity and to keep the concentrations of Cl_nBQs ($n = 1-3$) as low as possible, the presented results refer to $\lambda_{exc} = 248$ nm throughout. The two Cl_2BQs were found to behave very similar. The fast (0.05−10 μs) and slow (5 μs−10 s) conductivity signals were measured by DC and AC bridges as reported elsewhere.[23] The detection of shorter-lived conductivity signals is restricted to the range pH 4−10. The samples were dissolved in acetonitrile and freshly mixed with water. All measurements refer to 24 °C and deoxygenated solution, unless stated otherwise.

Results and Discussion

Continuous Irradiation. Irradiation at 254 nm of Cl_nBQ, $n = 1-3$, in relatively low concentrations of 0.1 mM in argon-saturated water or in acetonitrile−water (1:10) leads to efficient conversion and initially to isosbestic points. Examples are shown for Cl_2BQ (Figure 1), ClBQ, and Cl_3BQ (insets a and b). In these cases, a red color appears because of the formation of QO^- anions. They are present as anions at pH 7 and share this property with the QOH/QO^- derivative of parent BQ, pK_a (QOH) = 4.[30] This photoconversion has been nicely illustrated in Figure 1b of ref 26 for a 20-times higher Cl_2BQ concentration. The isosbestic points of ClBQ are at 245, 280, and 310 nm. The maxima and the characteristic wavelengths are red-shifted in the order $n = 1-4$. The absorption changes at 260−280 nm for ClBQ, Cl_2BQs, and Cl_3BQ are shown in Figure 2a as a function of irradiation time. They are accompanied by a drop in pH, and examples are shown in Figure 2b. The photoconversion is not due to dechlorination, since no chloride ion was detected upon photolysis of 2,6-Cl_2BQ in aqueous solution.[26] Cl_4BQ is known to undergo substitution into trichlorohydroxyquinone at high pH and further into choranilic acid; a slow replacement of chlorine by hydroxide has also been observed in neutral solution.[36] On the other hand, thermal dechlorination of Cl_nBQ, $n = 1-3$, can be excluded.

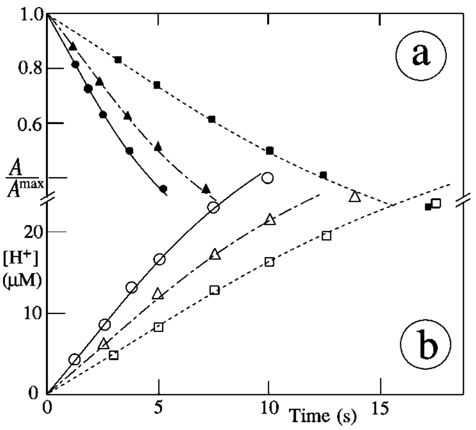


Figure 2. (a) Conversion and (b) proton concentration as a function of irradiation time for ClBQ (circles), 2,6-Cl_2BQ (triangles), and Cl_3BQ (squares) in argon-saturated acetonitrile−water (1:10), starting at pH 7, $\lambda_{irr} = 254$ nm.

TABLE 1: Quantum Yields of Decomposition Φ_d of 1,4-Benzoquinones in the Absence and Presence of Water[a]

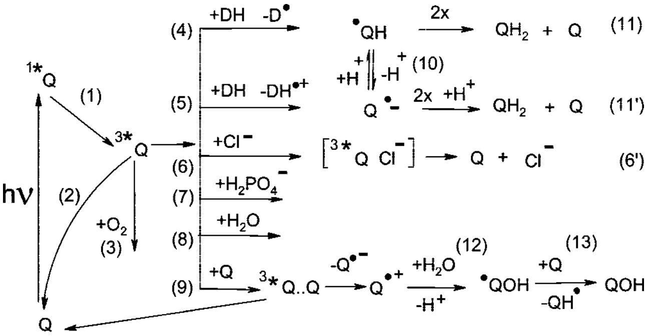
quinone	MeCN	MeCN/2-propanol[b]	MeCN/H_2O[c]	H_2O[d]
BQ	0.1 (<0.01)[e]	0.6	0.6 (0.5)	0.7 (0.5)
ClBQ	0.1 (<0.01)	0.7	1.2 (1.2)	1.3 (1.3)
2,5-Cl_2BQ	0.05 (<0.02)	0.6	0.9 (0.8)	0.9 (0.9)
2,6-Cl_2BQ	0.05 (<0.02)	0.6	0.9 (0.8)	0.9 (0.9)
Cl_3BQ	0.002		0.4	0.3
Cl_4BQ	0.002	0.01	0.1	

[a] In argon-saturated solution with $\lambda_{irr} = 254$ nm. [b] 10:1. [c] In 1:1 MeCN−H_2O. [d] pH 7, 1% MeCN. [e] Values in parentheses refer to oxygen saturation.

HPLC results of irradiated Cl_nBQs in aqueous solution show the formation of two classes of products: QH_2s and QOHs. From these chromatograms, the absorption spectra of the various chlorinated QO^- anions are obtained, $\lambda_{max} = 500$, 530, and 535 nm for $n = 1-3$, respectively. The other group of products, the QH_2s, elute notably later. For BQ, reference material was obtained by reduction, allowing the quantification (determination of quantum yields). QOH yields were obtained by a material balance that is from the difference of consumed educts and QH_2s formed.[22] For Cl_nBQs, the error is considerably higher, since no reference material of the products was available. A 1:1 ratio of dihydro- and 2-hydroxy-1,4-benzoquinones was measured for the two Cl_2BQs; the 30% deviation from the 1:1 ratio in a few cases is believed to be due to the error in absorption coefficients. On the basis of material balance considerations, the reported 1:2[26] QO^-/QH_2 ratio for 2,6-Cl_2BQ could not be rationalized.

The quantum yields of decomposition (Φ_d) of the Cl_nBQs in acetonitrile are low, whereas Φ_d approaches unity for ClBQ or 2,6-Cl_2BQs in aqueous solution at pH 7. Efficient photoconversion was also observed in acetonitrile−water, 1:1 (Table 1), and comparable effects were found in TFE−water, 1:1 (data not shown). Saturation with oxygen reduces Φ_d only moderately, in contrast to the absence of water.

SCHEME 1



Photoinduced oxygen formation (without explanation) has been reported for 2,6-Cl_2BQ.[26] In our hands, no marked change in the oxygen concentration, in particular no oxygen formation, was detected upon irradiation at 280 or 313 nm of ClBQ or Cl_2BQ in aqueous solution at pH 5−7 (data not shown). In contrast, efficient photoinduced oxygen consumption was measured for AQ, BQ, or NQ in acetonitrile−water (1:1 or 1:10, vol) under the same conditions.[34]

Reaction Scheme. The various reactions that excited BQs may undergo are shown in Scheme 1. The triplet state ($^{3*}Q$) is formed by intersystem crossing, reaction 1, and may decay to the ground state, reaction 2. In solution, $^{3*}Q$ can be quenched by oxygen, reaction 3, additives, such as 2-propanol or related alcohols, reaction 4, amines, such as triethylamine, reaction 5, halide ions such as chloride, reactions 6, phosphate, reaction 7, water, reaction 8, and by itself, reaction 9. Reactions 2, 3, and 9 and those with an H-atom donor 4 or an electron donor 5 are competing in organic solvents. The disproportionation of ${}^{\bullet}QH/Q^{\bullet -}$ into Q and QH_2, reaction 11, follows an H-atom or electron transfer as the primary step. The photoreduction of quinones by 2-propanol yields acetone as second product.[1−3] The 2-hydroxyprop-2-yl radical reduces Q to ${}^{\bullet}QH$, $k = 1.6 \times 10^9$ $M^{-1}s^{-1}$.[9] Thus, up to two ${}^{\bullet}QH/Q^{\bullet -}$ radicals can be generated per triplet state, and such a two-step reduction becomes observable under steady-state conditions, where the self-termination of 2-hydroxyprop-2-yl radicals is suppressed.[11,23]

In aqueous solution, reactions 6−8 and equilibrium 10 of the semiquinone radical and its anion also have to be considered. The semiquinone radicals are deprotonated at pH 5−7, $pK_a({}^{\bullet}QH) = 4-5$.[1,28,29] To account for the formation of QOH/QO^- in the presence of water, two pathways are conceivable: (i) a nonradical sequence via a water addition 8 and (ii) a free radical sequence, initiated by 9 via an excited complex ($^{3*}Q\cdots Q$) that can decompose into free radicals. The sequence, which is initiated by photoreaction 1 plus 8, is shown in Scheme 2 (see below).

Reactions of the Triplet State. Transient absorption spectra were studied in argon-saturated almost inert polar organic solvents and in 1:1 (vol) mixtures of acetonitrile and water. Examples are shown for ClBQ, Cl_2BQ, and Cl_3BQ in Figures 3−5, respectively. The spectra in acetonitrile−water show the triplet state just after the pulse, and then, the spectrum is dominated by a longer-lived intermediate. The effects of solvent polarity on the triplet properties are relatively small (Figures 3−5 and Table 2). The chlorine substitution leads to a red-shift of the absorption maxima. The triplet state of ClBQ has two maxima at $\lambda_{TT} = 290$ and 360–380 nm, and for Cl_4BQ, they are at $\lambda_{TT} = 310$ and 510 nm. The triplet state of ClBQ is difficult to detect: it is the main intermediate in carbon tetrachloride (Figure 3a), whereas in acetonitrile−water, the spectrum is overlapped by that of a long-lived transient (Figure 3b). The decay of the triplet state follows first-order kinetics, when T-T annihilation was largely avoided by a low excitation intensity. In the relatively inert solvent acetonitrile, triplet lifetimes (τ_T) range between 1 and 10 μs (Table 2). In the presence of water, the triplet lifetime reduces markedly, especially for ClBQ and Cl_2BQs (Table 3). A variation of pH (range 3−9) only changes a little the spectra and the kinetics of the triplet state, for example, of Cl_3BQ.

A decrease of the triplet lifetime with increasing quinone concentration has been observed for BQs.[7,22] Values of $k_9 = 2 \times 10^9$ M^{-1} s^{-1} have been obtained for Me_2BQs in aqueous solution and 1:1 mixtures with acetonitrile.[23] For the Cl_nBQs, linear dependences of $1/\tau_T$ on [quinone] were also found (Figure 6). The rate constant for self-quenching is $k_9 = 2 \times 10^9$ M^{-1} s^{-1} for Cl_3BQ in acetonitrile−water (1:1) but much smaller (1×10^8 M^{-1} s^{-1}) for Cl_4BQ. Self-quenching does not play a marked role when the quinone concentration is below 0.2 mM (with [quinone] = 0.1 mM and $k_9 = 2 \times 10^9$ M^{-1} s^{-1}, the limiting lifetime is 5 μs).

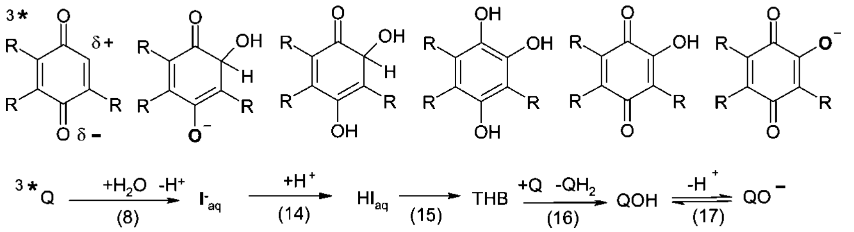
The increase of the triplet lifetime, 0.1, 0.6, and 0.8 μs (Table 3) in the respective order $n = 1$, 2, and 3 for the Cl_nBQs in acetonitrile−water (1:1), was also found for the Me_nBQs in the order $n = 0$, 1, 2, and 3, where the values under comparable conditions are 1, 0.6, 1.2, and 4 μs, respectively.[23] The most reactive triplet is that of ClBQ, being even more reactive than parent BQ.

The rather large Φ_d values of BQ and Cl_nBQs in aqueous solution and in acetonitrile−water (Table 1) are due to a substantial Φ_{isc}, nucleophilic attack of water on the triplet state, and eventual formation of the corresponding products: QH_2s and QO^-s. One could argue that Φ_{isc} is low for Cl_nBQs (n = 1,2), on the basis of the low observable triplet absorption in aqueous solution, and an upper excited triplet is involved. However, this can be excluded, because the yield of observed triplet state in either water or acetonitrile was found to be very similar.

Photohydrate as Intermediate. The long-lived transient of Cl_2BQ is spectroscopically and kinetically separated from the triplet state (Figure 4b). For ClBQ, however, the T-T absorption spectrum is largely overlapped by that of the subsequent species. The short-lived and long-lived transients in the cases of BQ and Me_nBQs in oxygen-free solutions have been attributed to the triplet state and the semiquinone radical, respectively; their spectra are similar, and the two maxima are only slightly shifted.[1,12] For parent BQ in aqueous solution, a long-lived intermediate was attributed to ${}^{\bullet}QH/Q^{\bullet -}$, which is characterized by a second-order decay, reaction 11. It has a yield of <10% of that in the presence of 2-propanol.[22,23] In addition, ${}^{\bullet}QOH$ radicals in low yield are formed, reactions 9 plus 12. The hydrate HI_{aq}, however, escaped observation.

For Cl_nBQs ($n = 1-3$) in aqueous solution, long-lived intermediates, denoted as HI_{aq}, were observed (Figure 7), which are distinctly different from the ${}^{\bullet}QH/Q^{\bullet -}$ radicals. These secondary transients, in contrast to the long-lived radical species of BQ or Me_nBQs, decay by first-order kinetics with a lifetime (τ_h) of 1−5 ms (Table 3). The nonradical nature of HI_{aq} of the Cl_nBQs ($n = 1-3$) is supported by the fact that τ_h shows no marked dependence on the pulse intensity. We therefore propose that HI_{aq} is the photohydrate and therefore the precursor of the corresponding Cl_nTHBs (Scheme 2). The lifetime is independent of the oxygen concentration. However, this is not an argument against a semiquinone radical nature, because quenching of this radical by oxygen is inefficient in the cases of BQs, in contrast to AQs.[29,34] At longer times, HI_{aq} is converted into THB and

SCHEME 2



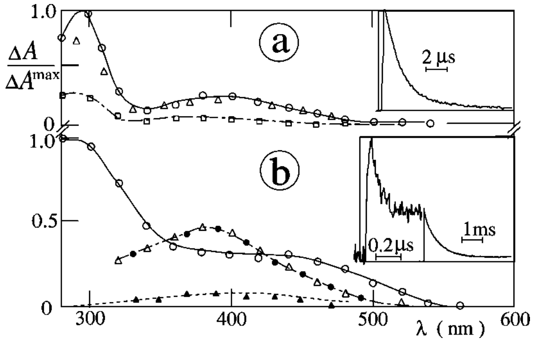


Figure 3. Transient absorption spectra of ClBQ in argon-saturated (a) carbon tetrachloride and (b) acetonitrile−water (1:1, pH 7−8) at 20 ns (○), 1 μs (△), 10 μs (□), 0.1 ms (●), and 1 ms (▲) after the 248 nm pulse; insets: decay at (a) 320 nm and (b) 460 nm.

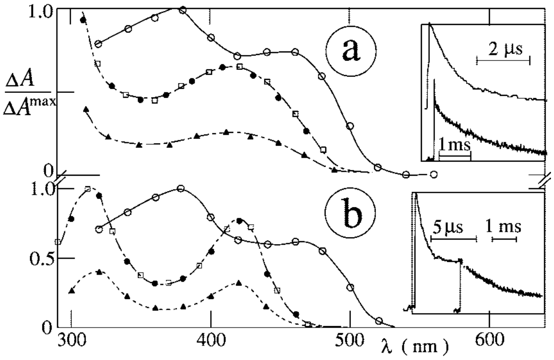


Figure 4. Transient absorption spectra of 2,6-Cl_2BQ at pH 6−8 in argon-saturated (a) acetonitrile−water (1:1) and (b) acetonitrile−2-propanol (1 M) at 20 ns (○), 10 μs (□), 0.1 ms (●), and 1 ms (▲) after the 248 nm pulse; insets: triplet decay at (a) 480 nm (upper) and (b) 400 nm (left) and kinetics of the long-lived transients at 400 nm.

TABLE 2: Triplet and Semiquinone Radical Properties[a]

quinone	solvent	λ_{TT} (nm)	τ_T (μs)	λ_{rad} (nm)	$\Delta A_{rad}/\Delta A_T$[b]
ClBQ	CCl_4	290, 380	5		<0.1
	acetonitrile	290, 360, 440	3	320, 400	0.2
	TFE	360, 430	2		<0.2
2,5-Cl_2BQ	acetonitrile	300, 460	4	320, 410	<0.2
2,6-Cl_2BQ	acetonitrile	300, 380, 460	4	320, 420	<0.2
	TFE	295, 360, 450	1	320, 420	<0.2
Cl_3BQ	acetonitrile	310, 490	10	320, 430	<0.1
Cl_4BQ	acetonitrile	310, 510	10	320, 440	<0.1

[a] In argon-saturated organic solvents at low intensity, λ_{exc} = 248 nm. [b] Relative absorbances.

TABLE 3: Triplet and Hydrate Properties[a]

quinone	λ_{TT} (nm)	τ_T (μs)	λ_h (nm)	τ_h (ms)	$\Delta A_h/\Delta A_T$[c]
ClBQ	300, 370	<0.1 (0.1)[b]	390	1	1 (1.2)[b]
2,5-Cl_2BQ	300, 450	<1 (0.6)	290, 420	1.2 (1)[b]	0.7 (0.9)
2,6-Cl_2BQ	300, 450	<1 (0.8)	290, 420	1.5 (1)	0.8
Cl_3BQ	<320, 460	1.6	<320, 420	5 (4)	0.2 (0.6)

[a] In argon-saturated aqueous solution, pH 7 at low intensity, λ_{exc} = 248 nm. [b] Values in parentheses refer to acetonitrile−water, 1:1. [c] Absorption ratio.

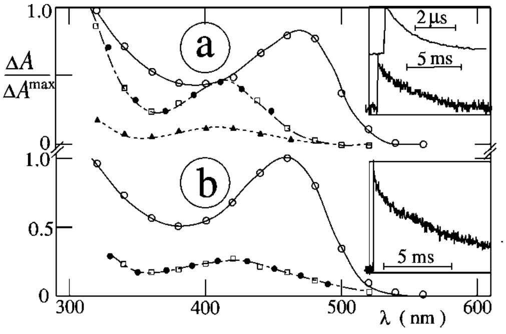


Figure 5. Transient absorption spectra of Cl_3BQ at pH 7 in argon-saturated (a) acetonitrile−water (1:1) and (b) aqueous solution at 20 ns (○), 1 μs (△), 10 μs (□), 0.1 ms (●), and 1 ms (▲) after the 248 nm pulse; insets: triplet decay at 480 nm (upper) and kinetics of the long-lived transients at 400 nm.

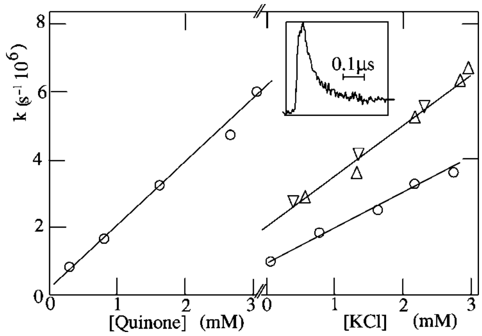


Figure 6. Inverse triplet lifetime on the Cl_3BQ concentration (left) in argon-saturated acetonitrile and KCl concentration (right) for 2,5-Cl_2BQ (△), 2,6-Cl_2BQ (▽), and Cl_3BQ (○) in acetonitrile−water (1:1, pH 7), inset: decay at 380 nm for Cl_3BQ and 3 mM KCl.

finally into the corresponding Cl_2QO^-, pK_a (Cl_2QOH) = 1.6.[26] The intermediacy of THB has to be postulated on the basis of the mismatch between the decay of HI_{aq} and the build-up of QO^- at 500 nm. Additional information concerning the mechanism is provided by conductometric measurements as presented next.

Transient Conductivity in the Absence of an H-Donor. A strong transient conductivity signal was observed in the microsecond time range for ClBQ, Cl_2BQ, and Cl_3BQ at pH 4−7 (Figure 8a). This was observed under both excitation conditions (308 and 248 nm); the results refer to λ_{exc} = 248 nm only. From the inversion of the signal in the slightly alkaline pH range of 8−9.5 (Figure 8a), a proton is identified as the major conducting species. This proton appears only for a few microseconds, that is, its formation is probably not fully resolved. Fast conductivity signals were also observed for ClBQ and Cl_2BQ in neat aqueous solution and 1:1 mixtures with acetonitrile. We interpret the formation of a short-lived proton as being due to nucleophilic addition of water to the triplet state, reaction 8, see Scheme 2. The resulting product (I_{aq}^-) has a

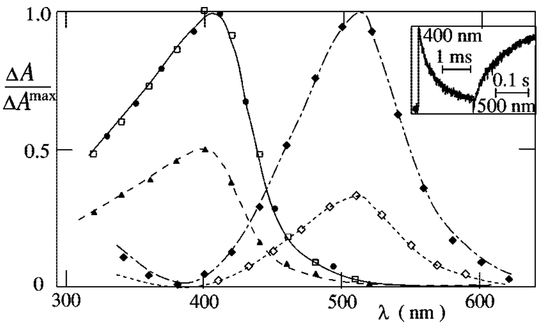


Figure 7. Transient absorption spectra of 2,6-Cl_2BQ in air-saturated acetonitrile−water (normalized 1:100, pH 7) at 10 μs (□), 0.1 ms (●), 1 ms (▲), 0.01 s (◇), and 1s (♦) after the 248 nm pulse; inset: decay at 400 nm and grow-in at 500 nm.

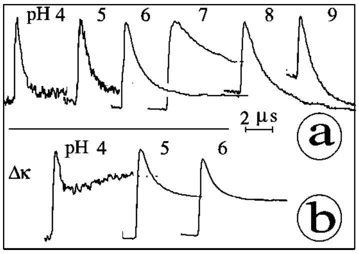


Figure 8. Conductivity signals of ClBQ in argon-saturated aqueous solution at various pH (1% acetonitrile) and in the 0−10 μs range (a) no additive and (b) in the presence of 2-propanol (0.5 M).

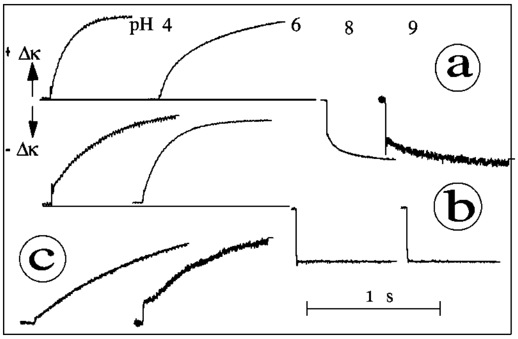


Figure 9. Conductivity signals of (a) ClBQ, (b) 2,6-Cl_2BQ, and (c) Cl_3BQ in argon-saturated aqueous solution (1% acetonitrile) at 0.01−1 s.

TABLE 4: Half-concentration and Rate Constants for Triplet Quenching by Cl^- and 2-propanol[a]

quinone	k_6 ($\times 10^9$ M^{-1} s^{-1})	$1/\tau_T k_6$ (mM)	$[Cl^-]_{1/2}$ (mM)	k_4 ($\times 10^6$ M^{-1} s^{-1})
ClBQ	2.0 1.4[b]	1.0 0.8[b]	2	
2,6-Cl_2BQ	2.4 [4][c]	2	2	>30
Cl_3BQ	2.5 [4]	0.4	0.3	20
Cl_4BQ			TR[d]	<0.1

[a] In argon-saturated aqueous solution (acetonitrile <1%) at pH 6−8 with λ_{exc} = 248 nm. [b] Values refer to mixtures, acetonitrile−water, 1:1. [c] In brackets: KCl is replaced by KBr. [d] TR, thermal reaction.

high pK_a value and is rapidly protonated in the acidic range, reactions 14. As a consequence, the species I_{aq}^- that gives rise to the first conductivity signal is very short-lived. The half-life is ca. 10 μs at pH 7 and shorter in the acidic and alkaline ranges. Similar results have been reported for BQ and Me_2BQ.[23]

Interestingly, a second conductivity component was observed for Cl_nBQs (Figure 9). This slow build-up signal is substantial and much larger in amplitude than that for parent BQ. The signals are due to formation of protons via reactions 8 and 14−17 into QO^- with pK_a(QOH) = 4.[30] Neutralization in the cases of Cl_nBQs (n = 1−3) at pH 8−11, thereby removing protons from the bulk of solution, slowly causes negative conductivity signals. Thus, the two conductivity parts are (i) formation and decay within a few microseconds of a proton, reactions 8 and 14, and (ii) release of a proton in the millisecond−second time range via equilibrium 17 (Scheme 2).

Transient Conductivity in the Presence of an H-Donor. The pathway to QOH and QH_2 in aqueous solution at low BQ or Me_nBQ concentrations does not involve radicals. The conductivity signals are therefore small, apart from either (i) the pulse-induced formation of a proton and decay within a few microseconds or (ii) the semiquinone radical conditions: when 2-propanol was added, protons were produced as major conducting species in the millisecond range, reactions 4 and 10.[23] Also for Cl_nBQs, n = 1−3, in argon-saturated aqueous solution or 10:1 (vol) mixtures with acetonitrile at pH 4−7, only a very small conductivity signal was detected in the 0.1−10 ms time range.

The conductivity signal appears after the pulse and increases, when 2-propanol is present (Figure 8b). The signal decays by second-order kinetics with half lives in the 1−10 ms range and is due to formation of protons via 10. In particular, for Cl_2BQ, the peak signal increases by a factor of ca. 10, indicating that photoreduction finally leads to H^+ and $Q^{\bullet -}$, whereby the contribution of the latter is minor because of the much lower equivalent conductivity. The signal of ClBQ or Cl_2BQs in argon-saturated 10:1 (vol) mixtures of aqueous solution with 2-propanol is substantial at 10−100 μs and pH 4−7 but low at pH <4.5. This is due to the dissociation of the semiquinone radical with pK_a ($ClQH^\bullet$) = 4−5. It is important to note that $Q^{\bullet -}$ is practically not formed in the absence of a donor. This implies that reactions 9 and 12 do not occur with chlorinated BQs.

Competing Photoreactions. When KCl was added to Cl_nBQs in aqueous solution or in 1:1 mixtures with acetonitrile, linear dependences of $1/\tau_T$ on $[Cl^-]$ were found (Figure 6). Anions are known to quench the triplet state of NQ and sulfonated AQs.[6,8] At low halide concentrations, physical quenching of the triplet state has been reported for Me_4Q, NQ, and sulfonated AQs.[8] The quenching rate constant by Cl^- is close to diffusion-controlled for all Cl_nBQs (Table 4). Φ_d strongly decreases as a function of $[Cl^-]$ because of the physical quenching reaction 6 (followed by reaction 6′) in competition to reactions 8 plus 12 (Scheme 1). The Cl^- concentration, where Φ_d is 50% of the maximum value, $[Cl^-]_{1/2}$, (Table 4), is in good agreement with data from triplet quenching, $1/[Cl^-]_{1/2} = k_6\tau_T$.

For Cl_2BQ in aqueous solution, the photoconversion into the corresponding QO^- is lowered in the presence of dimethylsulfoxide (DMSO); the half concentration $[DMSO]_{1/2}$, that is, the concentration for 50% change, is $[DMSO]_{1/2}$ = 20 mM.[26] The reason has been ascribed to a physical quenching with τ_T <1 μs and a rate constant of $k_q = 2 \times 10^9$ M^{-1} s^{-1}.[19] For BQ in aqueous solution, triplet quenching by phosphate yields 1,4-benzoquinone-2-phosphate with $k_7 = 5 \times 10^6$ M^{-1} s^{-1} at pH 5.[22]

Effects of Solvent. Generally, the three pathways initiated via 4/5, 8, or 9 have to be considered in aqueous solution. The free-radical sequence contributes in mixtures with nearly inert organic solvents as minor step, even in the absence of a H-donor. The possibility of H-abstraction from the solvent establishes an analogous pathway, which is also the case for MeBQ in acetonitrile.[21] For BQ and ClBQ, even in neat acetonitrile, because of Φ_d values of 0.05−0.1 (Table 1), photoreduction has to be considered. It remains open whether or not H-abstraction from the solvent is the only reaction. The $\Delta A_{rad}/\Delta A_T$ values of the BQs in aqueous solution are significantly suppressed with respect to the presence of H-donors, indicating inefficient formation of the semiquinone radical. This is supported by the low conductivity signal of Cl_nBQs in argon-saturated 10:1 (vol) mixtures of aqueous solution with acetonitrile and the increase upon addition of 2-propanol. The photoprocesses of Cl_nBQs in aqueous solution deviate significantly from those in the organic phase, for example, in the presence of H-atom donors.[11] In the absence of H-donors, the reactions have not been fully understood.[26] Φ_d smaller than 0.1 in acetonitrile are ascribed to population of the observable triplet state and without much $^{\bullet}QH/Q^{\bullet-}$ formation.[12] For Cl_nBQ ($n = 1-4$) in acetonitrile, the semiquinone radical does not play a significant role (Table 2). This is similar in benzene or TFE but in contrast to H-donating solvents.

Photoreactions Involving the Semiquinone Radical. One possibility for formation of QH_2 plus QO^-/QOH is the pathway outlined above (Scheme 2). The second possibility is formation of a complex initiated by electron transfer 9 from Q to $^3Q^*$ (Scheme 1). The rate constant in aqueous solution is $k_9 > 5 \times 10^9$ M^{-1} s^{-1} for BQ[22] and 4×10^9 M^{-1} s^{-1} for NQ.[8] This is in agreement with $k_9 = 2 \times 10^9$ M^{-1} s^{-1} for Cl_3BQ in acetonitrile−water (Figure 6) and accounts for products at high-to-moderate Cl_nBQs concentrations, by taking $k_9 = 1 \times 10^9$ M^{-1} s^{-1} or larger and a limiting τ_T of 10 μs. Then, a concentration of 0.1 mM is sufficient for more than a 50% reaction of the observed triplet state under continuous irradiation. The water-mediated reactions of quinones at high concentrations, involving radicals, are 9 plus 11, 12, and 13. The usual H-atom or electron transfer from the added donor also yields QH_2 but no formation of QO^-/QOH. An example for H-atom transfer from 2-propanol, resulting first in $^{\bullet}QH$ but actually during this abstraction process in $Q^{\bullet-}$, is shown in Figure 4b for Cl_2BQ. A molar absorption coefficient of $\varepsilon_{432} = 6 \times 10^3$ M^{-1} cm^{-1} has been reported for the semiquinone radical of Cl_2BQ.[37] When the triplet state and semiquinone radical are spectroscopically well-enough separated, for example, in the case of Cl_3BQ, the rate constant of reaction 4 can be measured by varying the donor concentration, $k_4 = 2 \times 10^7$ M^{-1} s^{-1}.

Role of the Photohydrate of BQs. The formation of a photohydrate upon irradiation of quinones has first been demonstrated in the case of NQ.[13] The nature of long-lived transients in aqueous solution in either the BQ/Me_nBQs or Cl_nBQs systems is different. For parent BQ, the hydrate is spectrocopically hidden, and the major species is the semiquinone radical, which is characterized by second-order decay.[22,23] The photohydrate of Me_nBQs was also not observed. This is in contrast to the Cl_nBQs $n = 1-3$, where the photohydrate is nicely resolved and the subsequent enolization is much slower than that for BQ. HI_{aq} of Cl_nBQs enolize by first-order kinetics with lifetimes of 1−5 ms (Table 3 and Figures 3b, 4a, 5, and 7). The resulting THBs do not absorb at $\lambda > 300$ nm. Their presence is concluded from the mismatch of the decay at 400 nm due to I_{aq}^-/HI_{aq} and grow-in at 500 nm due to QO^- (insets of Figure 7). The THBs are subsequently oxidized by the Cl_nBQs. This reaction gives rise to radicals, but because their steady-state concentration is very low, they are not detected. Upon their decay, the Cl_nQO^-s build up (the concomitant formation of the Cl_nQH_2s is not detected at $\lambda > 300$ nm). The rate of Cl_nQO^- formation depends on the Cl_nBQ concentration. As a consequence, the rate-limiting step in this sequence of events is the oxidation of the Cl_nTHBs by the Cl_nBQs.

A charge separation in the lowest triplet state, followed by water addition 8 yielding I_{aq}^-, is now suggested for the photoreaction of Cl_nBQs $n = 1-3$ at low concentration and in the absence of an H-atom donor (Scheme 2). This water-mediated triplet reaction, which does not involve radicals at all, is consistent with the results that the yield of $Q^{\bullet-}$ is low at pH 5−9. As for parent BQ, nonobservable radicals are involved in the last step 16, where Cl_nTHBs react with Cl_nBQs.

Chloranil. Cl_4BQ cannot undergo photohydration. Nevertheless, it is useful for comparison. In acetonitrile, Cl_4BQ serves as sensitizer, for example, for electron transfer from a donor to its triplet state.[31,32] The triplet state and semiquinone radical are spectroscopically well-enough separated; the maxima are $\lambda_{TT} = 310$ and 510 nm and $\lambda_{rad} = 320$ and 440 nm (Table 2). The decay of the semiquinone radical follows second-order kinetics. However, it turns out that triplet Cl_4BQ in aqueous solution is a poor H-abstractor. The concentration for 50% change, $[\text{2-propanol}]_{1/2}$, increases from 0.1 M for ClBQ to 10 M for Cl_4BQ, and the latter has $k_4 < 1 \times 10^5$ M^{-1} s^{-1}. In contrast, with solvents of low polarity, for example, in benzene, the rate constant is high, $k_4 = 7 \times 10^6$ M^{-1} s^{-1}.[32]

Conclusions

The effects of water on the photoreactions of Cl_nBQs, $n = 1-3$, in acetonitrile were investigated. The water-mediated reactions of 1,4-benzoquinones at low concentrations are nucleophilic addition to the triplet state and a sequence of reactions to two products: QH_2 and QOH. The mechanism involves the photohydrate I_{aq}^-/HI_{aq}, the corresponding (not spectroscopically registered) THBs, and the QO^- form but no detectable free radicals. Semiquinone radicals could result from triplet quenching or reactions with H-atom or electron-donating additives. Two conductivity parts were separated, formation of a proton and fast decay into HI_{aq} and slow release of a proton from QOH.

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