Competitive Decay Pathways of the Radical Ions Formed by Photoinduced Electron Transfer between Quinones and 4,4′-Dimethoxydiphenylmethane in Acetonitrile

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Abstract: The reactivity of the cation radical of $(4\text{-MeOC}_6\text{H}_4)_2\text{CH}_2$ photosensitized by 1,4-benzoquinone (BQ), 2,5-dichloro-1,4-benzoquinone (Cl_2BQ), and tetrachloro-1,4-benzoquinone (chloranil, CA) was investigated in acetonitrile. The main photoreaction products obtained by steady-state irradiation were identified to be: $(4\text{-MeOC}_6\text{H}_4)_2\text{CHOC}_6\text{H}_4\text{OH}$, sensitized by BQ; $(4\text{-MeOC}_6\text{H}_4)_2\text{CHCl}$, sensitized by Cl_2BQ; $(4\text{-MeOC}_6\text{H}_4)_2\text{CHOH}$, sensitized by CA. The mechanism of their formation was investigated by nanosecond laser flash photolysis that allowed transient species (radical ions, neutral radicals, and ions) to be detected and characterized in terms of absorption spectra, formation quantum yields, and decay

rate constants. For all systems, the interaction between the triplet quinone (Q) and $(4\text{-MeOC}_6\text{H}_4)_2\text{CH}_2$ produced the corresponding radical ions (quantum yield $\phi \geq 0.72$) which mainly decay by back electron transfer processes. Less efficient reaction routes for the radical ions $Q^{\bullet-}$ and $(4\text{-MeOC}_6\text{H}_4)_2\text{CH}_2^{\bullet+}$ were also: i) the proton-transfer process with the formation of the radical $(4\text{-MeOC}_6\text{H}_4)_2\text{CH}^{\bullet}$ by use of Cl_2BQ; ii) the hydrogen-transfer process with the formation of the cation $(4\text{-MeOC}_6\text{H}_4)_2\text{CH}^+$ in the case of CA. Instead, BQ sensitized

a much higher yield of $\text{BQH}^{\bullet}$ and $(4\text{-MeOC}_6\text{H}_4)_2\text{CH}^{\bullet}$, mainly by the direct interaction of triplet BQ with $(4\text{-MeOC}_6\text{H}_4)_2\text{CH}_2$. It was also shown that the presence of salts decreases significantly the rate of the back electron transfer process and enhances the quantum yields of formation of the neutral radicals and ions when Cl_2BQ and CA are used, respectively. The behavior of $\text{BQ}^{\bullet-}$, $\text{Cl}_2\text{BQ}^{\bullet-}$, and $\text{CA}^{\bullet-}$ appears to be mainly determined by the Mulliken charges on the oxygen atom obtained from quantum mechanical calculations with the model B3LYP/6-311G(d,p). Spin densities seem to be much less important.

Keywords: electron transfer · photochemistry · quinones · radical ions · radicals

Introduction

Upon light absorption, fast intersystem crossing with almost unitary efficiency[1] results in quinones so that the lowest excited triplet state (T_1) is populated. T_1 is a species with a significantly higher reduction potential with respect to the

ground state,[2] and it can decay either by a H-atom transfer process or, in the presence of aromatic substrates, by an electron-transfer process with the formation of the corresponding radical ions. The reactivity of the two radical ions is of great interest because these intermediates are involved in photoinduced processes of biological (photosynthesis and respiration) and industrial interest.[3, 4] In particular, the substantial electron affinity of quinones and the low dissociation energy of O−H bonds in their intermediates allow quinones to function as hydrogen-atom transporters.

Generally, when the substrate is an alkylaromatic compound, the corresponding radical cation is a strong carbon acid and heterolytic cleavage of the C−H bond in the side chain occurs (Scheme 1a).[5–8] The occurrence of homolytic cleavage of the same C−H bond (Scheme 1b) was rarely considered, and has not been experimentally investigated. Recently, we reported that this kind of bond breaking can be observed in the photoinduced electron-transfer reactions of $(4\text{-MeOC}_6\text{H}_4)_2\text{CH}_2$ and aryl alkyl sulfides sensitized by chloranil (CA).[9, 10] Flash photolysis experiments surprisingly indicated the occurrence of hydrogen-atom transfer from the

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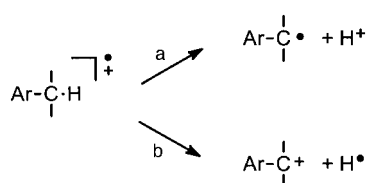
Scheme 1. The heterolytic cleavage of the C−H bond in a side chain and homolytic cleavage of the same bond.

Electron acceptors:

1,4-benzoquinone (BQ)

2,5-dichloro-1,4-benzoquinone (Cl₂BQ)

tetrachloro-1,4-benzoquinone (chloranil, CA)

Electron donor:

4,4'-dimethoxydiphenylmethane

aromatic radical cation to the radical anion $CA^{\cdot-}$. In this context, it appeared interesting to investigate this process in more detail by changing the molecular structure of the photosensitizer.

This work deals with steady-state and laser photolysis measurements carried out to investigate the influence of chlorine substitution on the quinone ring on the reactivity of the quinone/$(4\text{-MeOC}_6\text{H}_4)_2\text{CH}_2$ system in acetonitrile. In fact, the photochemical behavior induced by CA was compared with that of compounds sensitized by 1,4-benzoquinone (BQ) and 2,5-dichloro-1,4-benzoquinone (Cl₂BQ). The reactivity of the radical ions was compared with the Mulliken charges and spin densities of the radical anions obtained from quantum mechanical calculations by use of the model B3LYP/6-311G(d,p).[11] The reaction pathways of the radical ions were also investigated in the presence of salts; particular attention was paid to the effect of tetrabutylammonium perchlorate.

Experimental Section

Starting materials: The compound 4,4'-dimethoxydiphenylmethane [(4-MeOC₆H₄)₂CH₂] was prepared from the corresponding ketone by the Huang – Minlon modification of the Wolff – Kishner reduction and purified by recrystallization from hexane.[12] The quinones 1,4-benzoquinone (BQ, Aldrich), 2,5-dichloro-1,4-benzoquinone (Cl₂BQ, Aldrich), and tetrachloro-1,4-benzoquinone (chloranil, CA, Fluka), the absorption spectra of which are shown in Figure 1, were recrystallized before use. MeCN (Aldrich, HPLC grade) was distilled before use. Hydroquinone (BQH₂, Aldrich), 2,5-dichlorohydroquinone (Cl₂BQH₂, Aldrich), and Bu₄NClO₄ (Fluka) were used as received.

Methods: ¹H NMR spectra were recorded with the use of CDCl₃ on a Brucker AC 300 P spectrometer. MS analyses were performed on a Fisons Instruments VG-Platform Benchtop LC-MS (positive ion electrospray mass spectra, ESP⁺) spectrometer.
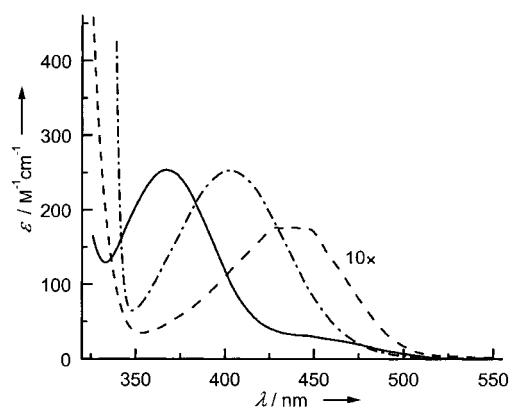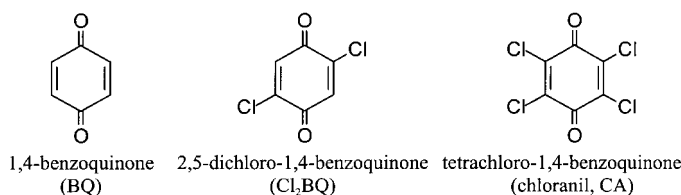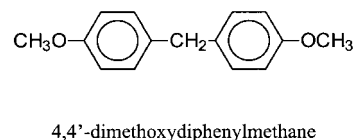

Figure 1. Absorption spectra of BQ (dash), Cl₂BQ (dash dot), and CA (solid) in MeCN.

Photochemical reactions: A solution of the quinone (5×10^{-3} M) in acetonitrile and $(4\text{-MeOC}_6\text{H}_4)_2\text{CH}_2$ (1×10^{-2} M), kept in a pyrex vessel capped with a rubber septum and fluxed with argon or oxygen, was irradiated without cooling at the instrument operating temperature in a Rayonet photoreactor ($\lambda_{exc} = 310 - 390$ nm). After irradiation for 15 min (BQ) or 10 min (Cl₂BQ or CA), an internal standard was added, and the raw photolysate was analyzed by ¹H NMR spectroscopy. All products formed were identified by comparison with authentic specimens. The compounds 4,4'-dimethoxybenzhydrol [(4-MeOC₆H₄)₂CHOH] (Aldrich), 4,4'-dimethoxybenzophenone (Aldrich), and tetrachlorohydroquinone (CAH₂, Sigma) were commercial products. The compound (4-MeOC₆H₄)₂CHCl was prepared by reaction of (4-MeOC₆H₄)₂CHOH with thionyl chloride; [(4-MeOC₆H₄)₂CH]₂O was prepared by reaction of (4-MeOC₆H₄)₂CHOH and (4-MeOC₆H₄)₂CHCl in pyridine/MeCN. The adduct (4-MeOC₆H₄)₂CHOC₆H₄OH was isolated from the oxidation on a preparative scale and characterized on the basis of the following spectral data.

¹H NMR (300 MHz, CDCl₃, 20 °C): δ = 7.3 – 6.6 (m, 12 H; ArH), 5.58 (s, 1 H; OH), 6.01 (s, 1 H; CH); ¹³C NMR (300 MHz, CDCl₃, 20 °C): δ = 158.9, 152.3, 149.7, 133.8, 128.1, 117.4, 115.8, 113.8, 81.8, 55.2. A dimer of Cl₂BQ with the loss of HCl (C₁₂H₃Cl₃O₄) was isolated from the oxidation on a preparative scale: ¹H NMR (300 MHz, CDCl₃, 20 °C): δ = 7.19 (s, 1 H), 7.05 (s, 1 H), 5.78 (s, 1 H); MS (15 V, ESP⁺): 317 [M+H]⁺.

Quantitative analysis of reaction products was performed by ¹H NMR spectroscopy. A good material balance was obtained in all experiments (> 80 %). Further irradiation was avoided to limit photosensitized reactions of the primary photoproducts. In the oxidation sensitized by BQ, the adduct (4-MeOC₆H₄)₂CHOC₆H₄OH was formed (7 %, yields referred to the starting material). In the presence of oxygen, 4,4'-dimethoxybenzophenone was formed (5 %). In the oxidation sensitized by Cl₂BQ, the main products observed were (4-MeOC₆H₄)₂CHCl (7 %), [(4-MeOC₆H₄)₂CH]₂O (2 %), and the dimer of the sensitizer (5 %). In the oxidation sensitized by CA, the main products observed were (4-MeOC₆H₄)₂CHOH (16 %), [(4-MeOC₆H₄)₂CH]₂O (2 %), and tetrachlorohydroquinone (14 %).

Laser flash photolysis: Excitation wavelengths of 355 nm from a Nd:YAG laser (Continuum Surelite II, third harmonic, pulse width approximately 7 ns and energy < 3 mJ per pulse)[13] and of 440 nm selected by a parametric oscillator (OPO, Continuum, pulse width approximately 4 ns and energy < 3 mJ per pulse) pumped by the Nd:YAG laser were used in nanosecond flash photolysis experiments. The transient spectra were obtained by a point-to-point technique, and the optical density changes (ΔA) were monitored after the flash at intervals of 5 – 10 nm over the spectral range 300 – 850 nm; there were on average at least ten decays at each wavelength. The lifetime values (the time at which the initial signal is reduced to $1/e$) and the $t_{1/2}$ values (the time at which the initial signal is halved) were reported for transients; these values showed first-order and second-order kinetics, respectively. The quantum efficiencies of transient formation were measured by calibrating the experimental setup with optically matched solutions of references: benzophenone (B) and CA in MeCN at excitation wavelengths of 355 and 440 nm, respectively. Transient quantum yields

(ϕ_{Tr}) were obtained by use of the relationship [Eq. (1)] between quantum yields (ϕ), absorption coefficients (ε), and changes of absorbance (ΔA), measured at the corresponding absorption maxima of the transient (Tr) and the reference (ref), namely triplet benzophenone ($\phi_T(B) = 1$ and $\varepsilon_T(B) = 6500\,M^{-1}cm^{-1}$ at 520 nm)[14] or triplet chloranil ($\phi_T(CA) = 1$ and $\varepsilon_T(CA) = 7700\,M^{-1}cm^{-1}$ at 520 nm).[15] The experimental errors on $t_{1/2}$ and ϕ_{Tr} were estimated to be $\pm 10\%$ and $\pm 15\%$, respectively.

$$\phi_{Tr} = \phi_T(ref)\frac{\varepsilon_T(ref)}{\varepsilon_{Tr}}\frac{\Delta A_{Tr}}{\Delta A(ref)} \qquad (1)$$

All solutions flowed through a quartz photolysis cell while argon was bubbled through them. All measurements were carried out at $22 \pm 2\,°C$.

Quantum mechanical calculations: The hybrid Hartree – Fock/DFT (density functional theory) method B3LYP was used to study the charge and spin distributions of the radical anions of quinones. In particular, the molecular structures were optimized by the B3LYP/6-31G method, and the Mulliken charges and spin densities of the radical anions were determined by the B3LYP/6-311G(d,p) method of the package Gaussian 98.[11]

Results and Discussion

Steady-state irradiation: The main photoproducts obtained by steady-state irradiation of the quinone/(4-MeOC$_6$H$_4$)$_2$CH$_2$ systems are shown in Table 1, together with the chemical yield (%) obtained after fifteen minutes (BQ) or ten minutes (Cl$_2$BQ or CA) of irradiation.
In particular, the adduct (4-MeOC$_6$H$_4$)$_2$CHOC$_6$H$_4$OH (7%, yield refers to the starting material) was formed in the oxidation of (4-MeOC$_6$H$_4$)$_2$CH$_2$ sensitized by BQ. In the presence of oxygen, 4,4′-dimethoxybenzophenone (5%) was formed. In the oxidation sensitized by Cl$_2$BQ, the main products formed were (4-MeOC$_6$H$_4$)$_2$CHCl (7%) and a dimer of the sensitizer (5%), which was probably derived from its decomposition. A smaller amount of [(4-MeOC$_6$H$_4$)$_2$CH]$_2$O (2%) was also observed. In the oxidation sensitized by CA, the main products observed were (4-MeOC$_6$H$_4$)$_2$CHOH

(16%), [(4-MeOC$_6$H$_4$)$_2$CH]$_2$O (2%), and tetrachlorohydroquinone (14%). It was shown that the ratio [(4-MeOC$_6$H$_4$)$_2$CHOH]/[[(4-MeOC$_6$H$_4$)$_2$CH]$_2$O] decreases significantly with the increase of the irradiation time, which suggests that the alcohol is formed first and then converted to the ether under the reaction conditions.

Laser flash photolysis

Triplet properties and quenching: The only transient formed by laser irradiation of quinones in MeCN in the absence of other additives was in the lowest triplet state T$_1$ and showed two broad absorption bands, one below 400 nm and the other in the 400 – 550 nm range; the triplet state decayed with a lifetime on the microsecond timescale (Table 2).

Addition of (4-MeOC$_6$H$_4$)$_2$CH$_2$ significantly quenched the state T$_1$ with rate constants close to the diffusional limit, at least for Cl$_2$BQ and CA, the quenching rate constants of which were measured. As shown in Table 2, these values are in agreement with the high reduction potentials of the triplet

Table 2. Triplet properties of quinones [absorption maxima, λ_{max}, and lifetimes, τ_T], together with the quenching rate constants (k_q) for (4-MeOC$_6$H$_4$)$_2$CH$_2$ in MeCN and the redox properties of quinones.

Q	λ_{max} [nm]	τ_T [µs]	k_q [$10^{10}\,M^{-1}s^{-1}$]	E°_{red} (Q/Q$^{\bullet-}$) [V vs SCE]	E°_{red} (^{3}Q*/Q$^{\bullet-}$) [V vs SCE]
BQ	360, 410	1	[a]	− 0.50	1.80
Cl$_2$BQ	390, 480	1	1.9	− 0.18	2.52
CA	370, 510	3.5	2.8	0.02	2.72

[a] The strong overlap between the absorption spectra of triplet BQ, BQH$^\bullet$, (4-MeOC$_6$H$_4$)$_2$CH$^\bullet$, and radical ions together with the high absorption coefficient of (4-MeOC$_6$H$_4$)$_2$CH$^\bullet$ prevented the determination of a reliable quenching rate constant (see text).

quinones. In the case of triplet BQ, this determination was prevented by the strong overlap between the absorption spectrum of T$_1$ and those of the radicals (4-MeOC$_6$H$_4$)$_2$CH$^\bullet$ and BQH$^\bullet$, which were also detected at low (4-MeOC$_6$H$_4$)$_2$CH$_2$ concentrations because of their high absorption coefficients (see below).

BQ/(4-MeOC$_6$H$_4$)$_2$CH$_2$: Upon irradiation of BQ in the presence of (4-MeOC$_6$H$_4$)$_2$CH$_2$ (1.5×10^{-2} M) in MeCN, signals at 330, 350, 420, and 450 nm were observed within the laser pulse (Figure 2). The signals at 330, 420, and 450 nm decay significantly (second-order kinetics with $t_{1/2} = 0.71$ µs and $2k_2 \approx 4 \times 10^{10}\,M^{-1}s^{-1}$, Table 3) between 0.16 to 1.3 µs after the laser pulse, whereas the absorption at 350 nm practically remains unchanged for the first 2 µs (see inset of Figure 2) and decays with second-order kinetics with $t_{1/2} = 23$ µs and $2k_2 \approx 6 \times 10^9\,M^{-1}s^{-1}$ (Table 3).

The short-lived transients produced within the laser pulse are assigned to the radical ions BQ$^{\bullet-}$ ($\lambda_{max} = 330$ and 420 nm)[16] and (4-MeOC$_6$H$_4$)$_2$CH$_2$$^{\bullet+}$ ($\lambda_{max} = 330$ and 450 nm)[8] by comparing their absorption spectra with those already reported. The electron-transfer process between triplet BQ and the ground state of (4-MeOC$_6$H$_4$)$_2$CH$_2$ occurs with a high efficiency ($\phi = 0.72$, Table 3). The long-lived transient at 350 nm is assigned to (4-MeOC$_6$H$_4$)$_2$CH$^\bullet$ ($\lambda_{max} =$

Table 1. Main photoproducts obtained by irradiation of Q in MeCN in the presence of (4-MeOC$_6$H$_4$)$_2$CH$_2$ (Ar-saturated solutions unless otherwise indicated).

Q	photoproduct	yield [%]
BQ	(4-MeOC$_6$H$_4$)$_2$CHOC$_6$H$_4$OH	7
	(4-MeOC$_6$H$_4$)$_2$CO[a]	5
Cl$_2$BQ	(4-MeOC$_6$H$_4$)$_2$CHCl	7
	C$_{12}$H$_3$Cl$_3$O$_4$	5
	[(4-MeOC$_6$H$_4$)$_2$CH]$_2$O	2
CA	(4-MeOC$_6$H$_4$)$_2$CHOH	16
	[(4-MeOC$_6$H$_4$)$_2$CH]$_2$O	2
	C$_6$Cl$_4$(OH)$_2$	14

[a] In oxygen-saturated solution.

Table 3. Spectral and kinetic properties of the transients of BQ, Cl$_2$BQ, CA, and (4-MeOC$_6$H$_4$)$_2$CH$_2$ (1.5×10^{-2} M) detected in MeCN, together with the quantum yields of formation.

Q	transient	λ [nm]	ε [M^{-1} cm^{-1}]	$t_{1/2}$ [µs]	$2k_2$ [M^{-1} s^{-1}]	ϕ
BQ[a]	BQ$^{\cdot-}$	330,*420*	6000	0.71	3.6×10^{10}	0.72
	(4-MeOC$_6$H$_4$)$_2$CH$_2^{\cdot+}$	330,*450*	1000	0.71	5.0×10^{10}	0.72
	BQH$^\cdot$	350,*410*	6000	23	5.3×10^{9}	0.15[b]
	(4-MeOC$_6$H$_4$)$_2$CH$^\cdot$	350	47000	23	6.6×10^{9}	0.15[b]
	(4-MeOC$_6$H$_4$)$_2$CH$^+$	505	120000	22[c]	$4.5 \times 10^{4[d]}$	≤ 0.006
Cl$_2$BQ[e]	Cl$_2$BQ$^{\cdot-}$	330,*430*	6000[f]	0.86	4.0×10^{10}	1.0
	(4-MeOC$_6$H$_4$)$_2$CH$_2^{\cdot+}$	450		0.86	4.0×10^{10}	1.0
	Cl$_2$BQH$^\cdot$	355,425		22		0.03
	(4-MeOC$_6$H$_4$)$_2$CH$^\cdot$	350		22	8.5×10^{10}	0.03
	(4-MeOC$_6$H$_4$)$_2$CH$^+$	505				≤ 0.007
CA[g]	CA$^{\cdot-}$	320,425,*450*	9700	0.80	6.0×10^{10}	1.0
	(4-MeOC$_6$H$_4$)$_2$CH$_2^{\cdot+}$	450		0.80	6.0×10^{10}	1.0
	(4-MeOC$_6$H$_4$)$_2$CH$^+$	505		23[c]	$4.4 \times 10^{4[d]}$	0.02
	(4-MeOC$_6$H$_4$)$_2$CH$^\cdot$					< 0.01

[a] [BQ] $= 2.8 \times 10^{-2}$ M. [b] This was ϕ of radicals produced within the laser pulse; a further amount corresponding to $\phi \approx 0.05$ (see text) was produced at longer delay times. [c] Lifetime in µs. [d] First-order decay rate constant in s^{-1}. [e] [Cl$_2$BQ] $= 1.2 \times 10^{-3}$ M. [f] Absorption coefficient of the analogous anion radical of 2,6-dichloro-1,4-benzoquinone taken from ref. [16]. [g] [CA] $= 3.2 \times 10^{-3}$ M.
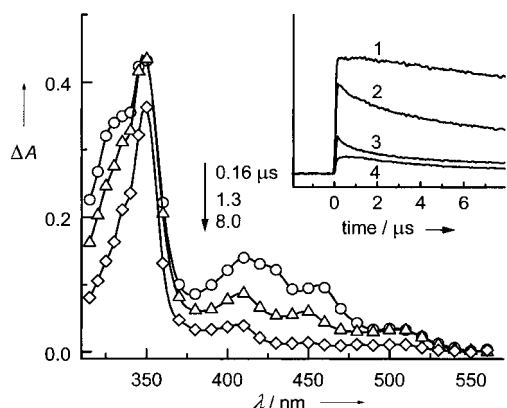
We suggest that the formation of BQH$^\cdot$ and (4-MeOC$_6$H$_4$)$_2$CH$^\cdot$ is mainly due to the occurrence of reaction (2), a direct H-atom transfer from the substrate to the triplet, rather than a proton-transfer reaction between the two radical ions [Eq. (3)]. This suggestion is supported by the oxygen effect on the kinetic properties of the transients recorded in air-equilibrated solution. In fact, the decay kinetics of the radical ions are practically unaffected by molecular oxygen, while the lifetime of the radicals BQH$^\cdot$ and (4-MeOC$_6$H$_4$)$_2$CH$^\cdot$ is shortened to approximately 100 ns. If the radicals were produced mainly by reactions of the radical ions, the upper limit of their lifetime would correspond to that of the precursors ($t_{1/2} = 0.71$ µs). Moreover, when 2.7×10^{-5} M (4-MeOC$_6$H$_4$)$_2$CH$_2$ was irradiated, a concentration at which the triplet lifetime of BQ ($\tau \approx 500$ ns) is much longer than the laser pulse, we could observe that the signal at 350 nm (λ_{max} for both radicals) and that of the radical ions (f.i. at 450 nm) grew with kinetics that correspond to the decay of triplet BQ measured at 380 nm (Figure 4). These kinetics clearly show that the triplet

Figure 2. Time-resolved absorption spectra obtained by laser photolysis of BQ (2.8×10^{-2} M) in the presence of (4-MeOC$_6$H$_4$)$_2$CH$_2$ (1.5×10^{-2} M) in MeCN ($\lambda_{exc} = 355$ nm). Inset: decay kinetics recorded at 350(1), 330(2), 410(3), and 500(4) nm.

350 nm, $\varepsilon_{max} = 47000$ M^{-1} cm^{-1})[17] and BQH$^\cdot$ ($\lambda_{max} = 350$ and 410 nm, $\varepsilon_{410} = 6000$ M^{-1} cm^{-1}; Figure 3).[18]
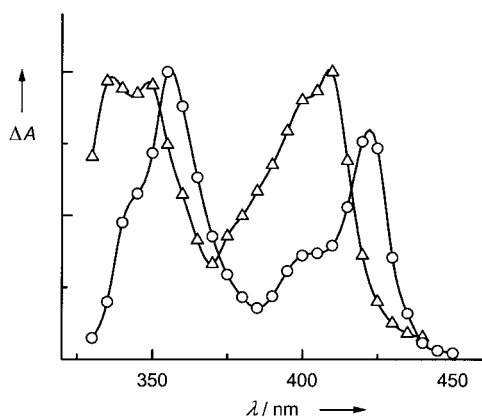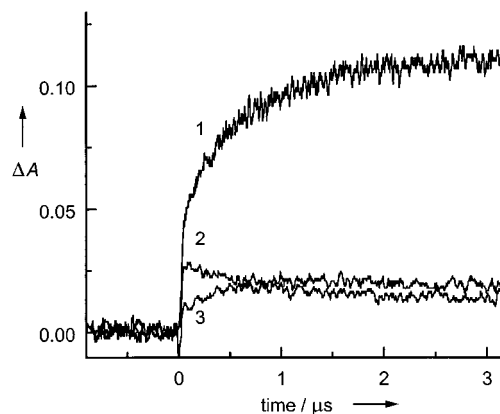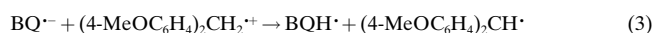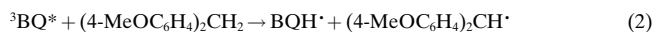

Figure 3. Normalized absorption spectra obtained by laser photolysis of *tert*-butylperoxide (1.0×10^{-3} M) in the presence of hydroquinone (triangles, 1.7×10^{-2} M) and of 2,5-dichlorohydroquinone (circles, 2.7×10^{-2} M) recorded in MeCN, 0.5 µs after the laser pulse ($\lambda_{exc} = 355$ nm).

Figure 4. Decay kinetics of BQ (2.8×10^{-2} M) in the presence of (4-MeOC$_6$H$_4$)$_2$CH$_2$ (2.7×10^{-5} M) in MeCN recorded at 350(1), 380(2), and 450(3) nm ($\lambda_{exc} = 355$ nm).

BQ is a precursor of both the neutral and charged radicals. The quantum yield of radicals directly produced by the triplet BQ is 0.15 (Table 3).

$$^3BQ^* + (4\text{-MeOC}_6H_4)_2CH_2 \rightarrow BQH^\cdot + (4\text{-MeOC}_6H_4)_2CH^\cdot \qquad (2)$$

$$BQ^{\cdot-} + (4\text{-MeOC}_6H_4)_2CH_2^{\cdot+} \rightarrow BQH^\cdot + (4\text{-MeOC}_6H_4)_2CH^\cdot \qquad (3)$$

However, it is probable that a small amount of BQH· and (4-MeOC$_6$H$_4$)$_2$CH· also comes from reaction (3). This is indicated by the observation that the signal at 350 nm (absorption maximum for both the radicals BQH· and (4-MeOC$_6$H$_4$)$_2$CH·) remains constant for about 2 μs and then decreases with a decay rate slower than the other transients. The latter kinetic behavior suggests that the decay of the radicals recorded at 350 nm is initially compensated by the increase of the absorption of BQH· and especially of (4-MeOC$_6$H$_4$)$_2$CH· formed by reaction (3). Accordingly, the best fit of the kinetics recorded at 350 nm for the BQ/(4-MeOC$_6$H$_4$)$_2$CH$_2$ system, carried out by use of the second-order laws that apply to the radicals produced directly from triplet BQ (growth within the laser pulse and decay with $t_{1/2} = 23$ μs) and those formed from the radical ions (growth with $t_{1/2} = 0.71$ μs and decay with $t_{1/2} = 23$ μs), results in a yield of radicals produced by radical ions of about 0.05 and therefore a quantum yield of about 0.07 (0.05/0.72) for the proton-transfer process. This value is significantly smaller than the quantum yield of radicals (0.15) formed through reaction (2); therefore, the proton-transfer process between radical ions seems to be only a minor route for radical formation. The quantum yield calculated for this process has to be considered as a rough estimate; nevertheless we feel that it can be used to compare the properties of BQ·$^-$ with those of the radical anions of the other quinones (see below).

The adduct (4-MeOC$_6$H$_4$)$_2$CHOC$_6$H$_4$OH formed in the photolysis experiment was likely to have been produced by coupling of the two radicals (4-MeOC$_6$H$_4$)$_2$CH· and BQH·. When the photolysis was carried out in the presence of O$_2$, a fast reaction of (4-MeOC$_6$H$_4$)$_2$CH· with O$_2$ led to 4,4′-dimethoxybenzophenone.

It is remarkable that the decay kinetics and the yield in radicals were about the same in the absence and in the presence of Bu$_4$NClO$_4$. Thus, it would seem that the salt does not significantly affect the reactivity of the two radical ions. It should be noted however that the huge absorption of the radical species produced by reaction (2) can mask the salt effect on the decay kinetics of this system.

Cl$_2$BQ/(4-MeOC$_6$H$_4$)$_2$CH$_2$: The laser photolysis of (4-MeOC$_6$H$_4$)$_2$CH$_2$ (1.5 × 10^{-2}M) sensitized by Cl$_2$BQ leads to the time-resolved spectra in Figure 5a. Signals at 330, 420, and 440 nm are observed and are attributable to the pair of radical ions (4-MeOC$_6$H$_4$)$_2$CH$_2$·$^+$ ($\lambda_{max} = 330$ and 450 nm) and Cl$_2$BQ·$^-$ ($\lambda_{max} = 330$ and 420 nm) formed with unitary efficiency.[20] These transients decay by second-order kinetics with a half-life of 0.86 μs and $2k_2 = 1 × 10^{10}$ M^{-1}s^{-1}. For longer delay times, absorption around 350 and 425 nm (Figure 3) is also observed, which is assigned to both (4-MeOC$_6$H$_4$)$_2$CH· and Cl$_2$BQH·,[18] formed by reaction (4); these radicals decay by second-order kinetics with a half-life of 22 μs and $2k_2 = 8.5 × 10^{10}$ M^{-1}s^{-1}.

$$Cl_2BQ^{·-} + (4\text{-}MeOC_6H_4)_2CH_2^{·+} \rightarrow Cl_2BQH^· + (4\text{-}MeOC_6H_4)_2CH^· \qquad (4)$$

Furthermore, it is to be noted that the decay time of the signal recorded at 350 nm, mainly due to the absorption of the
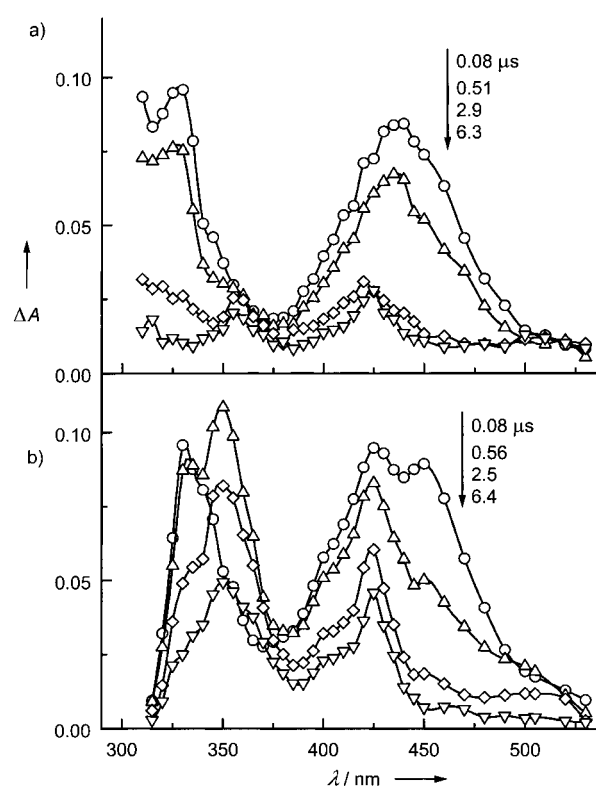

Figure 5. Time-resolved absorption spectra obtained by laser photolysis of Cl$_2$BQ (1.2 × 10^{-3}M) in the presence of (4-MeOC$_6$H$_4$)$_2$CH$_2$ (1.5 × 10^{-2}M) in MeCN, recorded in the absence (a) and in the presence of Bu$_4$NClO$_4$ (3.0 × 10^{-2}M) (b) ($\lambda_{exc} = 355$ nm).

radical (4-MeOC$_6$H$_4$)$_2$CH·, depends on the concentration of the ground state of the sensitizer Cl$_2$BQ; this behavior suggests the occurrence of a reaction (not investigated in detail) that is likely to result from the attack of the radical on the unsubstituted position of the ring of Cl$_2$BQ. This makes the Cl$_2$BQ/(4-MeOC$_6$H$_4$)$_2$CH$_2$ system much more complex than the other two, for which the interaction reaction between (4-MeOC$_6$H$_4$)$_2$CH· and the sensitizer was not observed. In fact, a quenching rate constant of $3 × 10^7$ M^{-1}s^{-1} was determined from the linear trend of the observed decay rate constant versus [Cl$_2$BQ]. Thus, the concentration of Cl$_2$BQ used in this work was kept low enough so that there was a negligible interaction with (4-MeOC$_6$H$_4$)$_2$CH·, especially for transient measurements, for which the quantum yields and the rate constants were determined.

Somewhat similar behavior was observed in the presence of Bu$_4$NClO$_4$ (Figure 5b). Formation of the two radical ions and of the two neutral radicals Cl$_2$BQH· and (4-MeOC$_6$H$_4$)$_2$CH· was again observed. Under such conditions, the yield of Cl$_2$BQH· and (4-MeOC$_6$H$_4$)$_2$CH· was sufficiently high ($\phi = 0.11$), and it was possible to see an increasing amount of these radicals coupled with the decay of the radical ions, according to reaction (4). The effect of the concentration of Bu$_4$NClO$_4$ on the yield of radicals is shown in Figure 6. These results contrast with those found for the BQ system, in which the yields of radicals are not affected by Bu$_4$NClO$_4$.

The radicals Cl$_2$BQH· and (4-MeOC$_6$H$_4$)$_2$CH· were expected to form the adduct (4-MeOC$_6$H$_4$)$_2$CHOC$_6$H$_2$Cl$_2$OH as in the previous case. However, no such adduct was observed in

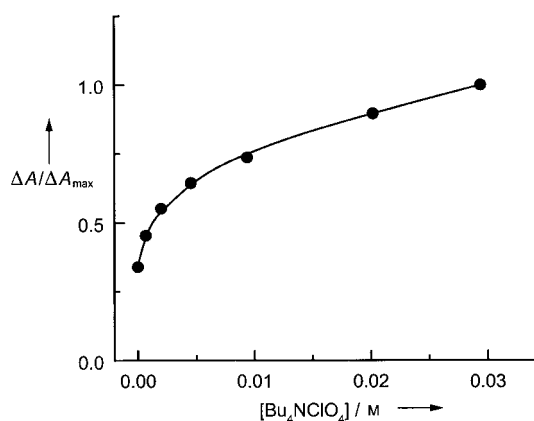Figure 6. Effect of the concentration of Bu_4NClO_4 on the absorbance changes recorded at 350 nm of Cl_2BQ (1.2×10^{-3} M) in the presence of (4-$MeOC_6H_4)_2CH_2$ (1.3×10^{-2} M) in MeCN ($\lambda_{exc} = 355$ nm).

the reaction products; the only observed products are (4-$MeOC_6H_4)_2CHCl$, $C_{12}H_3Cl_3O_4$, and $[(4-MeOC_6H_4)_2CH]_2O$. We suggest that under the reaction conditions the adduct decomposes mainly to form (4-$MeOC_6H_4)_2CHCl$ by reacting with HCl produced by decomposition of the sensitizer (indicated by the presence of the sensitizer dimer $C_{12}H_3Cl_3O_4$). However, it cannot be excluded that at the relatively high concentration of Cl_2BQ used in the photochemical experiments the products might be derived from the attack of (4-$MeOC_6H_4)_2CH^{\bullet}$ on Cl_2BQ.

CA/(4-$MeOC_6H_4)_2CH_2$: In the reaction of (4-$MeOC_6H_4)_2CH_2$ (1.5×10^{-2} M) photosensitized by CA we obtain time-resolved spectra (Figure 7a), in which the formation of the two radical ions $CA^{\bullet-}$[21] and (4-$MeOC_6H_4)_2CH_2^{\bullet+}$ ($\phi = 1.0$) is clearly observed just after the laser pulse ($\lambda_{max} = 330$, 420, and 450 nm); these transients decay by second-order kinetics with $t_{1/2} = 0.80$ μs and $2k_2 = 6 \times 10^{10}$ $M^{-1}s^{-1}$.

At longer delay times, a small absorption at 505 nm due to (4-$MeOC_6H_4)_2CH^+$ is present. The carbocation, formed with an efficiency of 0.016, decays with first-order kinetics ($\tau = 23$ μs).[22]

In the presence of Bu_4NClO_4, again the formation of the two radical ions is observed (Figures 7b and 8). Furthermore, their decay leads to the formation of an intense signal centered at 505 nm due to (4-$MeOC_6H_4)_2CH^+$ obtained in reaction (5); in fact, the decay of the ion radicals, recorded at 450 nm ($t_{1/2} = 2.7$ μs and $2k_2 = 1.8 \times 10^{10}$ $M^{-1}s^{-1}$, Figure 9), is coupled with an increase in the amount of the cation. Clearly, the reaction between the radical cation and the radical anion is a hydrogen atom transfer reaction [Eq. (5)], the efficiency of which appears to be significantly increased by the presence of the added salt ($\phi = 0.12$ at 3×10^{-2} M Bu_4NClO_4, Table 4).[22] The lifetime of the cation remains at approximately 23 μs, even in the presence of the salt. The absorption spectrum of the anion CAH^- ($\lambda_{max} = 320$ and 450 nm)[9, 10] was also obtained at long delay times, at which the radical ions were completely decayed.
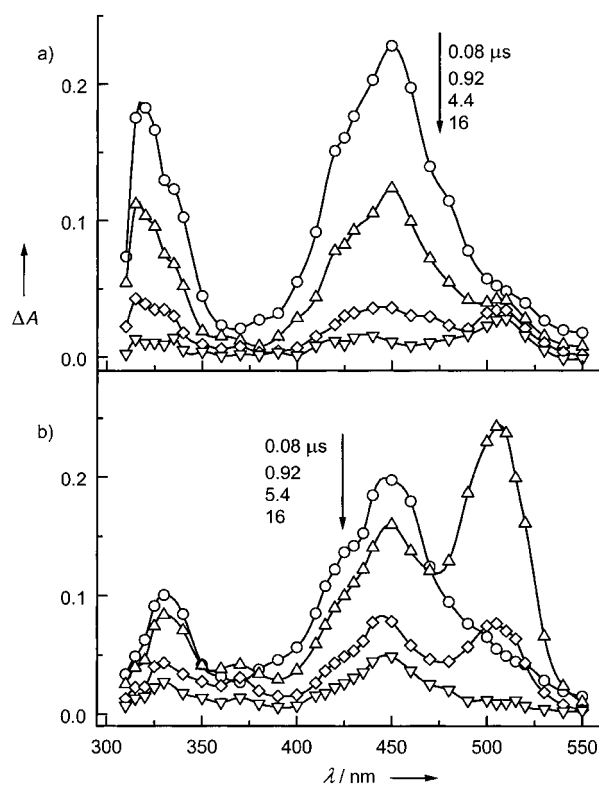
$$CA^{\bullet-} + (4\text{-}MeOC_6H_4)_2CH_2^{\bullet+} \rightarrow CAH^- + (4\text{-}MeOC_6H_4)_2CH^+ \qquad (5)$$

Figure 7. Time-resolved absorption spectra obtained by laser photolysis of CA (3.2×10^{-3} M) in the presence of (4-$MeOC_6H_4)_2CH_2$ (1.5×10^{-2} M) in MeCN, recorded in the absence (a) and in the presence of Bu_4NClO_4 (3.0×10^{-2} M) (b) ($\lambda_{exc} = 355$ nm).
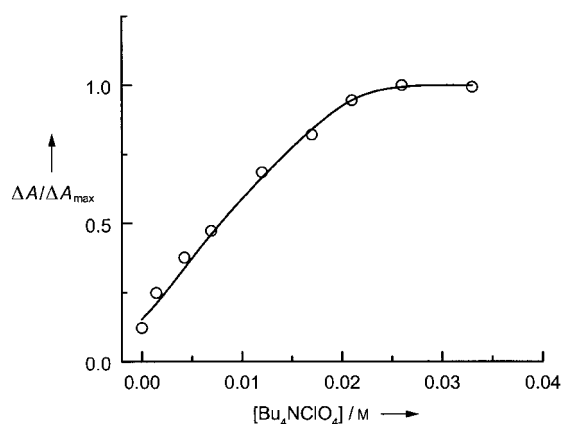

Figure 8. Effect of the concentration of Bu_4NClO_4 on the absorbance changes recorded at 505 nm of CA (3.2×10^{-3} M) in the presence of (4-$MeOC_6H_4)_2CH_2$ (1.5×10^{-2} M) in MeCN ($\lambda_{exc} = 355$ nm).

Reaction mechanism: The main reaction pathways of the quinone/(4-$MeOC_6H_4)_2CH_2$ systems, identified by both the steady-state and transient techniques in oxygen-free solution are summarized in Scheme 2. The decay rate constants and the formation quantum yields of the transients detected by laser flash photolysis allowed the second-order decay rate constants for the decay of the radical ions to be determined (Table 5).

The decay processes of radical ions corresponding to back electron transfer, proton transfer, and hydrogen transfer
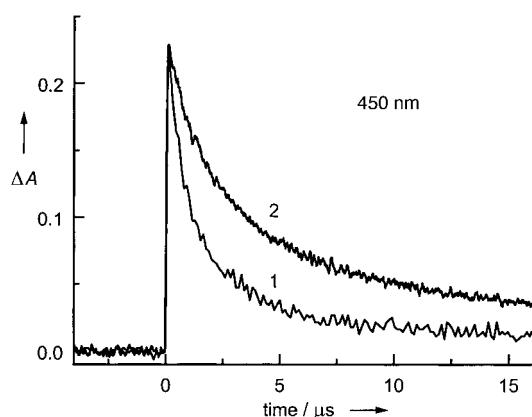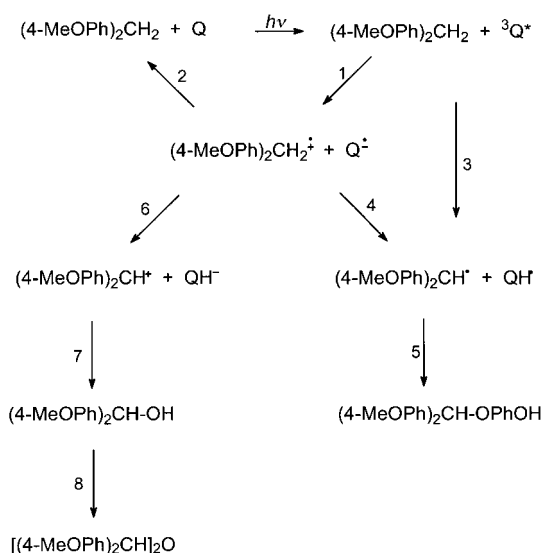
Figure 9. Decay kinetics obtained by laser photolysis of CA (3.2×10^{-3} M) in the presence of $(4\text{-MeOC}_6\text{H}_4)_2\text{CH}_2$ (1.5×10^{-2} M) in MeCN, recorded at 450 nm in the absence (1) and in the presence of Bu_4NClO_4 (3.0×10^{-2} M) (2) ($\lambda_{\text{exc}} = 355$ nm).

Table 4. Spectral and kinetic properties of the transients of Cl_2BQ, CA, and $(4\text{-MeOC}_6\text{H}_4)_2\text{CH}_2$ (1.5×10^{-2} M) detected in MeCN in the presence of Bu_4NClO_4 (3×10^{-2} M), together with the quantum yields of formation.

Q	transient	λ [nm]	$t_{1/2}$ [μs]	$2k_2$ [M^{-1}s^{-1}]	ϕ
Cl_2BQ[a]	$\text{Cl}_2\text{BQ}^{\cdot-}$	325, 430	2.2	1.1×10^{10}	1.0
	$(4\text{-MeOC}_6\text{H}_4)_2\text{CH}_2^{\cdot+}$	450	2.2	1.1×10^{10}	1.0
	$(4\text{-MeOC}_6\text{H}_4)_2\text{CH}^{\cdot}$	350	6.0	7.1×10^{10}	0.11
	$(4\text{-MeOC}_6\text{H}_4)_2\text{CH}^+$				< 0.007
CA[b]	$\text{CA}^{\cdot-}$	320, 425, 450	2.7	1.8×10^{10}	1.0
	$(4\text{-MeOC}_6\text{H}_4)_2\text{CH}_2^{\cdot+}$	450	2.7	1.8×10^{10}	1.0
	$(4\text{-MeOC}_6\text{H}_4)_2\text{CH}^+$	505	23[c]	$4.4 \times 10^{4[d]}$	0.10
	$(4\text{-MeOC}_6\text{H}_4)_2\text{CH}^{\cdot}$				< 0.03

[a] $[\text{Cl}_2\text{BQ}] = 1.2 \times 10^{-3}$ M. [b] $[\text{CA}] = 3.2 \times 10^{-3}$ M. [c] Lifetime in μs. [d] First-order decay rate constant in s^{-1}.

Scheme 2:

$(4\text{-MeOPh})_2\text{CH}_2 + \text{Q} \xrightarrow{h\nu} (4\text{-MeOPh})_2\text{CH}_2 + {}^3\text{Q}^*$

$(4\text{-MeOPh})_2\text{CH}_2^{\cdot+} + \text{Q}^{\cdot-}$

$(4\text{-MeOPh})_2\text{CH}^+ + \text{QH}^-$ $(4\text{-MeOPh})_2\text{CH}^{\cdot} + \text{QH}^{\cdot}$

$(4\text{-MeOPh})_2\text{CH-OH}$ $(4\text{-MeOPh})_2\text{CH-OPhOH}$

$[(4\text{-MeOPh})_2\text{CH}]_2\text{O}$

Scheme 2. A summary of the main reaction pathways of the quinone/$(4\text{-MeOC}_6\text{H}_4)_2\text{CH}_2$ system.

(steps 2, 4, and 6 of Scheme 2, respectively) were kinetically characterized for the three quinones by Equation (6).

$$2k_2(i) = 2k_2(\text{RI}) \times \phi(i)/\phi(\text{RI}) \qquad (6)$$

Table 5. Second-order decay rate constants [10^{10} M^{-1}s^{-1}] of Q$^{\cdot-}$ and $(4\text{-MeOC}_6\text{H}_4)_2\text{CH}_2^{\cdot+}$ in MeCN in the absence and in the presence of Bu_4NClO_4 (3×10^{-2} M) (see Scheme 2).[a]

Q	Without Bu_4NClO_4			With 3×10^{-2} M Bu_4NClO_4		
	$2k_2(2)$	$2k_2(4)$	$2k_2(6)$	$2k_2(2)$	$2k_2(4)$	$2k_2(6)$
BQ	(4.0)	(0.30)	≤ 0.04			
Cl_2BQ	3.9	0.12	≤ 0.03	0.98	0.12	≤ 0.02
CA	5.9	≤ 0.06	0.12	1.6	≤ 0.06	0.18

[a] Values in parentheses were calculated by using the formation quantum yield of radicals from radical ions ($\phi = 0.05$) estimated by fitting procedures (see text).

In this equation, $2k_2(\text{RI})$ stands for the overall second-order rate constant of the radical ions, and $\phi(i)$ and $\phi(\text{RI})$ represent the quantum yields of the i-fold step and of the formation of radical ions, respectively (Tables 3 and 4). The efficiency of step 2 was calculated by use of relationship (7); this is supported by the lack of transient species that provide evidence for further decay pathways of radical ions.

$$\phi(2) = 1 - \phi(4) - \phi(6) \qquad (7)$$

The interaction between triplet quinones and $(4\text{-MeOC}_6\text{H}_4)_2\text{CH}_2$ efficiently produces radical ions (step 1) with $\phi \geq 0.72$; only in the case of BQ does a parallel hydrogen-transfer process (step 3) occur with $\phi = 0.15$. In the absence of salts, the main decay process of the radical ions is the diffusion controlled back electron transfer process ($2k_2 = 3.9 - 5.9 \times 10^{10}$ M^{-1}s^{-1}), with slightly higher rate constants in the case of CA. The other decay processes (steps 4 and 6) have rate constants that are much smaller than that for step 2 by at least one order of magnitude: $2k_2(4) \leq 0.3 \times 10^{10}$ M^{-1}s^{-1} and $2k_2(6) \leq 0.12 \times 10^{10}$ M^{-1}s^{-1}. In fact, the proton-transfer process (step 4) is operative for BQ and Cl_2BQ, while the hydrogen-transfer process (step 6) is only for CA.

The second-order decay kinetics of the radicals produced by steps 3 and 4 suggest that their main decay process is the recombination (step 5) with formation of the adduct. This was also shown from steady-state experiments of BQ, in which irradiation of free-oxygen solutions allowed us to isolate the photoproduct $(4\text{-MeOC}_6\text{H}_4)_2\text{CHOC}_6\text{H}_4\text{OH}$. In the case of Cl_2BQ, the products isolated are probably derived from the decomposition of the first adduct formed $(4\text{-MeOC}_6\text{H}_4)_2\text{CHOC}_6\text{H}_2\text{Cl}_2\text{OH}$, which, however, was not observed among the photoproducts (see above).

Instead, the cation $(4\text{-MeOC}_6\text{H}_4)_2\text{CH}^+$ formed by CA through step 6 decays with first-order kinetics; this is likely to be through a reaction, with small traces of water still present in the solvent (step 7), to form the alcohol $(4\text{-MeOC}_6\text{H}_4)_2\text{CHOH}$. In an analogous way to the case of benzylic alcohols,[23] $(4\text{-MeOC}_6\text{H}_4)_2\text{CHOH}$ is likely to react with the cation $(4\text{-MeOC}_6\text{H}_4)_2\text{CH}^+$ to produce the ether $[(4\text{-MeOC}_6\text{H}_4)_2\text{CH}]_2\text{O}$.

For BQ in the presence of Bu_4NClO_4 (3×10^{-2} M), the decay processes were essentially unchanged with respect to those recorded in the absence of the salt, but small effects on the rate constants of steps 2 and 4 could be hidden by the high amount of radicals produced through triplet BQ.

On the other hand, for Cl$_2$BQ and CA in the presence of Bu$_4$NClO$_4$ (3×10^{-2} M), the quantum yields of the electron-transfer process were unchanged (unitary), while the half-life of the radical ions increased from approximately 0.8 µs to approximately 2.5 µs (Tables 3 and 4). This behavior is similar to that already found in the photoinduced electron transfer between 1,4-dicyanonaphthalene and *trans*-stilbene or 4,4′-dimethoxybiphenyl by addition of magnesium perchlorate.[24] The longer decay times recorded in the presence of salts suggest that the formation of complexes between the charged species (radical ions and salt ions) takes place. In our case, such complexes slow down the rate of the back electron transfer process by a factor of 4 (Table 5). This explains the significant increase in the quantum yields observed in the presence of Bu$_4$NClO$_4$ for the production of radicals from Cl$_2$BQ$^{•-}$ and (4-MeOC$_6$H$_4$)$_2$CH$_2^{•+}$ [Eq. (4)] and of ions from CA$^{•-}$ and (4-MeOC$_6$H$_4$)$_2$CH$_2^{•+}$ [Eq. (5)]. If we also took the experimental errors into account, a negligible salt effect was observed on the rate constants of the proton- and hydrogen-transfer processes (Table 5).

Quantum mechanical calculations: In order to try to understand the effect of chlorine atoms on the reactivity of the anion radicals of benzoquinone, ab initio quantum mechanical calculations were carried out to determine Mulliken charges and spin densities of the anion radicals by the model B3LYP/6-311G(d,p), after geometrical optimization with B3LYP/6-31G. The results of such calculations are compiled in Table 6 together with those already reported for BQ$^{•-}$. In practice, except for the charge on C1 and C4 (0.16 instead of 0.30) the present charge distribution and spin densities are very close to those already obtained by PWP86/6-311G(2d,p) calculations.[24] As shown in Table 6, the main effect of the increasing number of chlorine atoms in the quinone structure is to increase the positive charge on C1 and C4 (0.16 and 0.39 for BQ$^{•-}$ and CA$^{•-}$, respectively) and to reduce the negative charges on the oxygen atoms (-0.48 and -0.38 for BQ$^{•-}$ and CA$^{•-}$, respectively). Instead, the spin density shown in the last column of Table 6 is quite high and constant on the oxygen atoms (0.3) and relatively small on the other atoms. Thus, the

Mulliken charges are significantly affected by the presence and number of chlorine substituents, while the spin densities are not.

On the basis of these calculations, the different reactivity of the three radical anions of quinones appears therefore to be mainly due to the decrease of the negative charge on the oxygen atoms. In particular, the low negative charge on the oxygen of CA$^{•-}$ is probably responsible for the fact that this radical anion does not act as a base, but reacts with (4-MeOC$_6$H$_4$)$_2$CH$_2^{•+}$ by means of a hydrogen-transfer process (step 6 of Scheme 2); instead, for BQ$^{•-}$ and Cl$_2$BQ$^{•-}$ the charge is sufficiently high for a fast proton-transfer process (step 4 of Scheme 2). These properties were more evident in the presence of salts, for which the back electron transfer process was less efficient.

Conclusion

This study has shown that the compound (4-MeOC$_6$H$_4$)$_2$CH$_2$ is a suitable substrate to investigate the reactivity of radical ions because its transients (4-MeOC$_6$H$_4$)$_2$CH$_2^{•+}$, (4-MeOC$_6$H$_4$)$_2$CH$^{•}$, and (4-MeOC$_6$H$_4$)$_2$CH^{+} are easily detectable as a result of their well-separated absorption spectra and high absorption coefficients. In fact, the electron-transfer mechanism is operative with all sensitizers, as already found for CA$^{•-}$, even if the direct hydrogen-transfer reaction from the substrate to triplet BQ is a competitive process.

The results suggest that in CA$^{•-}$, the negative charge is so efficiently delocalized that hydrogen-atom transfer from the radical cation prevails over the most common proton-transfer process. Instead, for BQ$^{•-}$ and Cl$_2$BQ$^{•-}$ the negative charge on the oxygen atoms means that the basicity of the radical anion is sufficient and so the proton-transfer process is the dominant one (Table 5). This suggestion is supported by the Mulliken charges and spin densities obtained for the radical anions of quinones by ab initio calculations with the model B3LYP/6-311G(d,p).

The photoproducts sensitized by BQ and CA in steady-state experiments are in agreement with the nature of the transients (radicals and ions, respectively) detected by laser flash photolysis. In the case of Cl$_2$BQ, the photoreactivity appears much more complex probably because the stable products originate from the unstable primary photoadduct and substantial decomposition of the sensitizer took place.
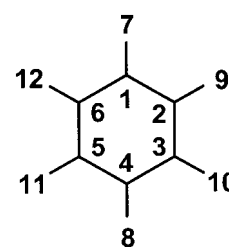
Table 6. Mulliken charges and spin densities of anion radicals of quinones calculated by B3LYP/6-311G(d,p) after geometrical optimization with B3LYP/6-31G.[a]

radical anion	element	n. atom	charge	spin
BQ$^{•-}$	C	1, 4	0.16(0.30)	0.05(0.07)
	C	2, 3, 5, 6	$-0.14(-0.13)$	0.08(0.10)
	O	7, 8	$-0.48(-0.49)$	0.30(0.25)
	H	9, 10, 11, 12	0.05	$-0.01(<0.01)$
Cl$_2$BQ$^{•-}$	C	1, 4	0.26	0.04
	C	2, 5	-0.26	0.08
	C	3, 6	-0.03	0.09
	O	7, 8	-0.42	0.30
	Cl	9, 11	-0.16	0.00
	H	10, 12	0.10	-0.01
CA$^{•-}$	C	1, 4	0.39	0.03
	C	2, 3, 5, 6	-0.17	0.08
	O	7, 8	-0.38	0.30
	Cl	9, 10, 11, 12	-0.08	0.00

[a] Values of charge and spin distributions in parentheses are taken from ref. [24].

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[18] Genuine absorption spectra of BQH· and Cl₂BQH· were obtained by photolysis of the *tert*-butylperoxide/hydroquinone (QH₂) system in MeCN, which produced the absorption spectra shown in Figure 3 (triangles and circles for BQ and Cl₂BQ, respectively), assigned to the doublet–doublet transitions of the radical QH·. As already reported,[19] irradiation of *tert*-butylperoxide with UV light promotes the formation of QH· by the following processes [Eqs. (8 a–c)].

$$(tBuO)_2 + h\nu \rightarrow (tBuO)_2^* \tag{8a}$$

$$(tBuO)_2^* \rightarrow 2tBuO^\bullet \tag{8b}$$

$$tBuO^\bullet + QH_2 \rightarrow tBuOH + QH^\bullet \tag{8c}$$

The absorption spectrum of BQH· shows two broad bands centered at approximately 350 and 410 nm with practically the same absorption coefficients. A value of the absorption coefficient of BQH· at λ_{max} corresponding to $6000 \, M^{-1} \, cm^{-1}$ was then obtained from the absorption spectrum of the radicals BQH· and (4-MeOC₆H₄)₂CH· recorded 8 μs after the laser irradiation of the BQ/(4-MeOC₆H₄)₂CH₂ system (Figure 2, diamonds). The following are also taken into account: i) the two radicals have the same concentration; ii) the absorption coefficient of (4-MeOC₆H₄)₂CH· at 350 nm is $47\,000 \, M^{-1} \, cm^{-1}$; iii) the absorption of (4-MeOC₆H₄)₂CH· at 410 nm is negligible; iv) the absorption of BQH· at 350 nm is equal to that recorded at 410 nm [Eq. (9)] $(\Delta A_{350}((4\text{-MeOC}_6H_4)_2CH^\bullet) = \Delta A_{350} - \Delta A_{410})$

$$\varepsilon_{410}(BQH^\bullet) = \varepsilon_{350}((4\text{-MeOC}_6H_4)_2CH^\bullet)$$
$$\times \Delta A_{410}(BQH^\bullet)/\Delta A_{350}((4\text{-MeOC}_6H_4)_2CH^\bullet) \tag{9}$$

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