FULL PAPER

Photohydroxylation of 1,4-Benzoquinone in Aqueous Solution Revisited

Justus von Sonntag,*[a] Eino Mvula,[a, b] Knut Hildenbrand,[b] and Clemens von Sonntag[a, b]

Abstract: In water, photolysis of 1,4-benzoquinone, **Q** gives rise to equal amounts of 2-hydroxy-1,4-benzoquinone **HOQ** and hydroquinone **QH$_2$** which are formed with a quantum yield of $\Phi = 0.42$, independent of pH and **Q** concentration. By contrast, the rate of decay of the triplet ($\lambda_{max} = 282$ and ~ 410 nm) which is the precursor of these products increases nonlinearly ($k = (2 \rightarrow 3.8) \times 10^6 \, s^{-1}$) with increasing **Q** concentration (($0.2 \rightarrow 10$) mM). The free-radical yield detected by laser flash photolysis after the decay of the triplet also increases with increasing **Q** concentration but follows a different functional form. These observations are explained by a rapid equilibrium of a monomeric triplet **Q*** and an exciplex **Q$_2$*** ($K = 5500 \pm 1000 \, M^{-1}$). While **Q*** adds water and subsequent enolizes into 1,2,4-trihydroxybenzene **Ph(OH)$_3$**, **Q$_2$*** decays by electron transfer and water addition yielding benzosemiqui-none **·QH** and **·OH** adduct radicals **·QOH**. The latter enolizes to the 2-hydroxy-1,4-semiquinone radical **·Q(OH)H** within the time scale of the triplet decay and is subsequently rapidly (microsecond time scale) oxidized by **Q** to **HOQ** with the concomitant formation of **·QH**. On the post-millisecond time scale, that is, when **·QH** has decayed, **Ph(OH)$_3$** is oxidized by **Q** yielding **HOQ** and **QH$_2$** as followed by laser flash photolysis with diode array detection. The rate of this pH- and **Q** concentration-dependent reaction was independently determined by stopped-flow. This shows that there are two pathways to photohydroxylation; a free-radical pathway at high and a nonradical one at low **Q** concentration. In agreement with this, the yield of **Ph(OH)$_3$** is most pronounced at low **Q** concentration. In the presence of phosphate buffer, **Q*** reacts with $H_2PO_4^-$ giving rise to an adduct which is subsequently oxidized by **Q** to 2-phosphato-1,4-benzoquinone **QP**. The current view that **·OH** is an intermediate in the photohydroxylation of **Q** has been overturned. This view had been based on the observation of the **·OH** adduct of DMPO when **Q** is photolyzed in the presence of this spin trap. It is now shown that **Q*/Q$_2$*** oxidizes DMPO ($k \approx 1 \times 10^8 \, M^{-1} s^{-1}$) to its radical cation which subsequently reacts with water. **Q*/Q$_2$*** react with alcohols by H abstraction (rates in units of $M^{-1} s^{-1}$): methanol (4.2×10^7), ethanol (6.7×10^7), 2-propanol (13×10^7) and tertiary butyl alcohol (~0.2×10^7). DMSO (2.7×10^9) and O_2 (~2×10^9) act as physical quenchers.

Keywords: excimer · hydroxylation · photochemistry · quinones · reaction mechanism

Introduction

In 1886 and 1888, Klinger published the first, and up until today still worth-reading, reports on the chemical effect of light on a quinone in solution.[1,2] Ever since, there has been a continuing interest in the photochemistry of quinones,[3–6] induced by the abundance of quinoid structures in nature and in technical products. For example, some *p*-quinone-based dyes show considerable photodegradation of the fabric while others do not.[6] This photo-tendering action is due to an H abstraction from the substrate, and therefore this type of reaction has been studied in detail in organic solvents and in aqueous solutions, not only with 1,4-benzoquinone, but also with substituted 1,4-benzoquinones including 1,4-naphtho- and 9,10-anthraquinones.[7–49]

1,4-Benzoquinone, **Q**, the parent of the quinones investigated, has three absorption bands at 250, 300 and 424 nm (in water, see Figure 1). The short-wavelength bands have been attributed to a π→π* transitions, while the long-wavelength band is due to an n→π* transition.[50] In a nonpolar solvent, the n→π* transition shows a vibrational fine structure.[18] In water, the n→π* transition is blue-shifted, and the vibrational fine structure is no longer observed (see

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Figure 1). **Q** does not show fluorescence of any importance, and it has been concluded that rapid intersystem crossing occurs, that is, the n→π* triplet **Q*** is rapidly populated and is the photochemically active species.[50] In fact, picosecond time-resolved Raman scattering experiments indicate that the triplet is present within 20 ps.[51] In the presence of a hydrogen donor, for example, 2-propanol, photoreduction occurs with a quantum yield close to unity [1 mol **QH₂**/Einstein, reactions (1)–(3)],[7,11,18] and the analogy to ketone photochemistry has been addressed.
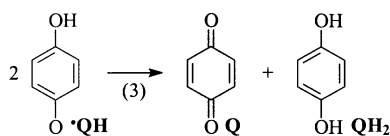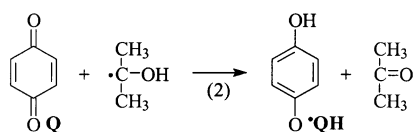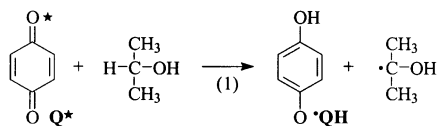
In the solid state and in inert organic solvents, quinones undergo cycloaddition reactions.[5] In water and in the absence of hydrogen donors, however, **Q** is efficiently photohydroxylated (quantum yield of photodecomposition $\Phi = 0.31$,[19] $\Phi = 0.5$,[37]), and as resulting products 2-hydroxy-1,4-benzoquinone, **HOQ**, and hydroquinone, **QH₂**, are formed in equal amounts ($\Phi = 0.25$).[37] This type of reaction is also given by other quinones, for example, anthraquinonesulfonates,[21,52–59] 2-methyl-1,4-benzoquinone,[60] 2-methoxy-1,4-benzoquinone[47] and 2,6-dimethylbenzoquinone.[61]

Photohydroxylation is suppressed by the addition of halide ions.[37,59,62,63] As short-lived intermediates CT-complexes have been suggested that can either decay to the ground state or, at elevated halide concentrations, form dihalide radical anions and a semiquinone radical anion, **Q·⁻**.[62] Oxidation of carbonate to $CO_3^{·-}$ has also been reported.[64,65] Electron transfer processes are also made responsible for the quinone-sensitized photooxidation of nucleobases.[66] This view is supported by EPR studies.[67–69]

Q·⁻ ($\Phi = 0.47$) is reported to be formed as a transient in the photolysis **Q** in water.[38] This is in contrast to data which indicate that in this system 1,4-benzosemiquinone-type radicals must be minor contributors to photohydroxylation ($<10\%$) compared with a non-radical pathway.[37] Based on spin-trapping experiments, it has been suggested[39,44,45] that the first step is an H-abstraction from water [reaction (4)}, that is, that the reaction is analogous to reaction (1).
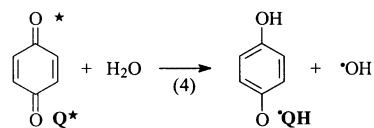
The view that ·OH are formed in the reaction of excited quinones with water is shared also by other authors.[32,52,53,58,64,70] However, it has been calculated that the reduction potential of the relaxed triplet state of **Q** is insufficient to oxidize water, and it has been suggested that the water oxidation (formation of 1,4-benzosemiquinone ·**QH** observed by time-resolved Raman spectroscopy) must be due to the reaction of an unrelaxed triplet state.[35] As another potential route to ·OH, electron transfer from a ground-state quinone to an excited quinone and oxidation of OH⁻ or water by the ensuing quinone radical cation has been considered.[4,54,55] In a recent study, the formation of a free ·OH has been rejected, and instead a kind of "krypto ·OH" (·OH complexed to ·**QH**) has been favoured.[60]

If ·OH were formed their addition to **Q** would indeed result in the formation of the observed products, **HOQ** and **QH₂** {reactions (5)–(7) and (3); for details of the complex kinetics see ref. [71]}.
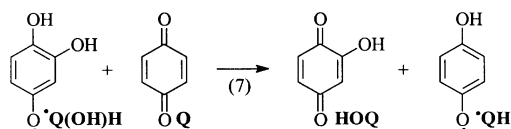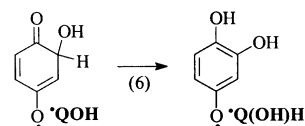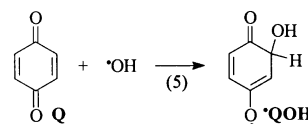
The observation of the typical four-line ·OH adduct to DMPO, when **Q** is photolyzed in the presence of this spin trap, has been taken as strong support for the H abstraction reaction (4).[39] However, it is well known that this ·OH-adduct radical can have other adduct radicals as precursor, for example, the superoxide radical, $O_2^{·-}$.[72] Moreover, excited states can oxidize spin traps,[73] and the ensuing spin trap radical cation may react with water resulting in an ·OH adduct. Thus, this evidence is not as strong as believed.[39]

There are, however, observations that are not compatible with free ·OH as intermediates. The addition of an excess of tertiary butyl alcohol that would have scavenged all free ·OH does not affect the spectral developments after a laser flash up to 200 μs.[32] Also a kind of warning is the fact that acetone in its triplet state does not abstract a hydrogen

atom from water, although its triplet energy ($322\ \text{kJ mol}^{-1}$) is higher than that of **Q** ($224\ \text{kJ mol}^{-1}$).[74]

In the present paper, we will show that neither a free ·OH radical nor an ·OH radical complexed to ·**QH** are intermediates in the photohydroxylation reaction, and evidence for an alternative mechanism will be given.

Experimental Section

1,4-Benzoquinone (Aldrich) was purified by sublimation. Hydroquinone and 1,2,4-trihydroxybenzene, **Ph(OH)₃** (both Aldrich) were available as reference material. Solutions were prepared in Milli-Q-filtered (Millipore) water and stored in the dark. To minimize any exposure to light, all glassware was covered with black cloth or aluminum foil. For product studies, the aqueous **Q** solutions were irradiated at 254 nm using a low-pressure Hg-arc, while kinetic studies employed the 308 nm light from an XeCl excimer laser (for the UV spectrum of **Q** in water see Figure 1; $\varepsilon(254\ \text{nm}) = 1500\ \text{m}^2\text{mol}^{-1}$, $\varepsilon(308\ \text{nm}) = 25\ \text{m}^2\text{mol}^{-1}$ in agreement with ref. [19])
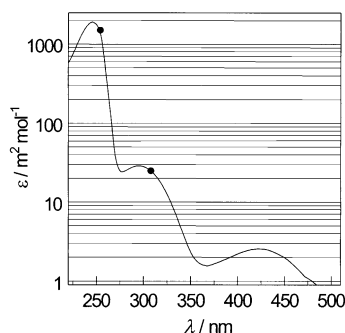

Figure 1. UV absorption spectrum of 1,4-benzoquinone in aqueous solution. The excitation wavelengths used in this study (low-pressure Hg-arc at 254 nm and XeCl excimer at 308 nm) are marked.

For UV irradiation at 254 nm, a low-pressure mercury lamp which does not emit 185 nm radiation (Heraeus Sterisol NN 30/89) was used. Actinometry was done using the ferrioxalate system.[75,76] The contribution to the bleaching of the ferrioxalate by wavelengths longer than 254 nm was determined by a separate measurement, blocking the UV light with a plate of ordinary glass. The effect of the 254 nm radiation was then obtained from the difference (5×10^{17} photons s^{-1} dm^{-3}). Irradiations were carried out in Suprasil cells (Hellma), $4 \times 1\ \text{cm}^2$ (face) $\times 1\ \text{cm}$, and lasted typically less than a minute requiring an automatic shutter (rise time 10 ms).

The products were identified by HPLC on a Nucleosil 5C18 column with water as eluent; retention times (min): **HOQ** (5.9), **Ph(OH)₃** (10.1), **QH₂** (15.5), 2-hydroxymethylhydroquinone (18.9), 2-hydroxymethyl-1,4-benzoquinone (36.6), **Q** (40.7). Under these conditions, **HOQ** was deprotonated. When an acidic eluent with 10% methanol was used, **HOQ** (14 min) eluted close to **Q** (15 min), and the separation was not as good. However, this eluent allowed us to separate well **HOQ** from 1,4-benzoquinone-2-phosphate **QP** (5 min) and also from **QH₂** (8.5 min). The reaction of **Ph(OH)₃** with **Q** led to a quantitative formation of **HOQ** (for details see below), and this method was used for the calibration of **HOQ**.

The formation of 2-hydroxymethylhydroquinone as well as 2-hydroxymethyl-1,4-benzoquinone in the photoreduction of **Q** by methanol (10% of the **QH₂** yield, confirming earlier pulse radiolysis data[77] on the reaction of ·CH₂OH with **Q**) was ascertained by gas chromatography combined with mass spectrometry after rotary evaporation of the irradiated solution and trimethylsilylation of the residue. The two hydroquinones were characterized by their mass spectra. Hydroquinone-bis-TMS (M_W

254 Da), m/z (%): 254 (84), 239 (100), 223 (4), 112 (8), 73 (82); 2-hydroxy-methylhydroquinone-tris-TMS (M_W 356 Da), m/z (%): 356 (44), 341 (13), 267 (15), 253 (9), 194 (33), 147 (14), 73 (100). 2-Hydroxymethyl-1,4-benzoquinone was reduced with 1,2,4-trihydroxybenzene to 2-hydroxy-methylhydroquinone. While the HPLC peak at 36.6 min disappeared, the peak at 18.9 min increased accordingly.

For the stopped-flow experiments, the Biologic SFM-3 setup equipped with a diode array detector (Tidas, J&M, Aalen, Germany) was used.

Methanesulfinic acid was readily detected by ion chromatography (Dionex DX100; column: AG14/AS14, eluent: water containing 4.5×10^{-4} M Na₂CO₃ and 4.25×10^{-4} M NaHCO₃) as described elsewhere.[78,79]

For the EPR experiments, a stock solution of 5,5-dimethylpyrroline-N-oxide (DMPO, Aldrich; 250 mg) in CH₃CN (5 mL) was kept under N₂ at $-18\,°\text{C}$. Spin-trapping experiments were carried out on 3.5 mM solutions of DMPO in 50 mM phosphate buffer, pH 7.2, containing either H₂O₂ or **Q** in the absence or presence of tertiary butyl alcohol. EPR spectra were recorded on a Varian E-9 X-band spectrometer equipped with an interface from Stelar s.n.c, Mede (PV), Italy and a PC. The spin adducts were generated by UV irradiation of the solutions in the cavity of the EPR instrument with unfiltered light from a Xenon short arc lamp (LX300UV, Cermax, ICL Technology, Sunnyvale, CA).

The laser photolysis set-up comprised a 308 nm XeCl-excimer laser (MINex, LTB Berlin, pulse train of three pulses (70, 20 and 10% of total energy, respectively, each with 5 ns half width, all three within 70 ns, total pulse train energy up to 15 mJ) as excitation source and a pulsed xenon short-arc lamp (XBO 450, Osram, power supply LPS 1200, lamp pulser MCP 2010, both Photon Technology International) supplying the analyzing light. The transient recording electronics, a photomultiplier (1P28, Hamamatsu, operated at 900 V, power supply: PS310, Stanford Research Systems) and a 500 MHz, 2.5 GS s^{-1} digitizing storage oscilloscope (TDS620b, Tektronix) guarantee a time resolution within the limits set by the excitation source. Further details have been published.[80]

The same 308 nm laser was also used for experiments in the minute time range (denoted as laser flash photolysis long time range detection LFP-LTRD). In this case, the laser beam was directed onto a Suprasil 10 mm fluorescence cell (Hellma, Germany) placed into a thermostated and stirred cell holder (Flash 100, QNW, USA). Transient spectra were recorded orthogonal to the laser beam with a fast diode array spectrometer (Tidas II, J&M, Aalen, Germany) via fiber optics and a home-made coupling to the cell holder. The trigger system of the laser flash photolysis[81] was modified and reprogrammed both to synchronize the spectrophotometer and the laser and to allow a burst of several laser pulses within a very short time to produce a stronger "pulse".

For pulse radiolysis the 11 MeV linear electron accelerator Electronika 003 (Thorium, Moscow) delivering 43 Gy pulses of 7 ns duration was used. Its recording optics and electronics were essentially identical to the laser flash photolysis set-up.

Simulations were performed on the complete 4D data matrix (time, wavelength, absorbance, concentration) with the specialized 4D data fitting software Pro-K II (Applied Photophysics, UK), see Figure 7. The models were double-checked with the Chemical Kinetics Simulator software, version 1.01, developed by IBM at the Almaden Research Center.

Results and Discussion

Final products and their quantum yields: In the preceding studies on the photolysis **Q** in aqueous solution, it has been suggested by a comparison of the UV spectra that the final products are **HOQ** and **QH₂**.[19] From this, a quantum yield of $\Phi(\textbf{Q}\ \text{consumption}) = 0.31$ was obtained.[19] The quantum yield was found to be independent of pH in the range of pH 0.4–8. We have recently shown that **HOQ** is a fairly strong acid (pK_a 4.2).[71] Its anion is characterized by a strong absorption at 482 nm ($\varepsilon = 200\ \text{m}^2\text{mol}^{-1}$), while the free acid has an absorption maximum at 380 nm ($\varepsilon = 140\ \text{m}^2\text{mol}^{-1}$). We had used the electrochemical oxida-

tion of 1,2,4-trihydroxybenzene (**Ph(OH)₃**) to generate **HOQ**,[71] but its oxidation by **Q**[19] (reaction 8; for the kinetics of this reaction see below) is an alternative and more convenient procedure that was now used for calibration.
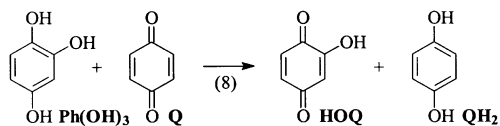
With **Q** in some excess, one mol **Ph(OH)₃** yields one mol **HOQ** and one mol **QH₂**. This quantitative conversion was ascertained by HPLC (see Experimental Section). The complete consumption of **Ph(OH)₃** is balanced by an equivalent formation of **QH₂**. Based on this calibration, it has now been shown that in the photolysis of **Q** in aqueous solution **QH₂** and **HOQ** are formed in equal yields (inset in Figure 2). No further products were detected by HPLC.

From Figure 2 (main graph), it can be seen that the yield of **HOQ** is neither dependent on pH (pH 2.1 and 7; confirming earlier observations[19]) nor on the concentration of **Q** (0.1 mM and 1 mM). Based on actinometry, quantum yields were determined at $\Phi = 0.42$ for the two products, **QH₂** and **HOQ**. This is in fair agreement with an earlier value[19] of $\Phi = 0.31$.
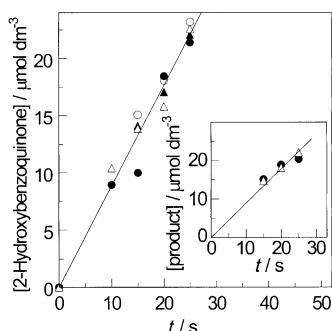

Figure 2. UV Photolysis (254 nm) of 1,4-benzoquinone in Ar-saturated aqueous solution. Formation of 2-hydroxy-1,4-benzoquinone as a function of time at pH 2.1 (△, ▲) and pH 7 (○, ●) at two different 1,4-benzoquinone concentrations (△, ●: 0.1 mM; ▲, ○: 1 mM). Inset: Formation of hydroquinone (●) and 2-hydroxy-1,4-benzoquinone (△: as a function of the irradiation time ([1,4-benzoquinone] = 1 mM).

To keep the pH constant, typically "inert" buffers such as phosphate are used. In the presence of high concentrations of phosphate buffer pH 4.6, however, a new product is observed that is attributed to 1,4-benzoquinone-2-phosphate, **QP**.
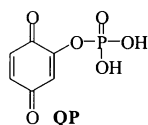
This product is characterized by absorption maxima at ~254 and 361 nm (HPLC, diode array, in agreement with the transient difference spectrum from LFP-LTRD experiments, see Figure 13). **QP** is unstable and fades away in neutral solution. It was thus impossible to collect sufficient material by preparative HPLC for its characterization by NMR spectroscopy.

Based on redox balance considerations, the quantum yield of **QH₂** must match that of the sum of **HOQ** and **QP**. The yields of the former two can be determined and thus the yield of the latter calculated. As can be seen from Figure 3, the quantum yield of **HOQ** is independent of the phosphate buffer concentration, while those of **QH₂** and **QP** rise with increasing buffer concentration.
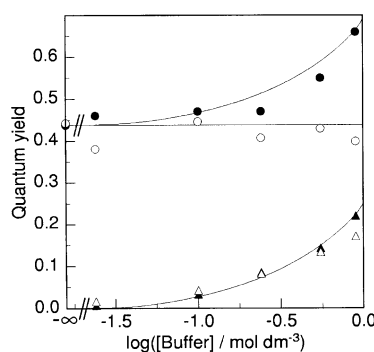

Figure 3. Photolysis of aqueous solutions of 1,4-benzoquinone at 254 nm. Quantum yields of the formation of 2-hydroxy-1,4-benzoquinone (○), hydroquinone (●) and 1,4-benzoquinonone-2-phosphate as a function of the phosphate buffer concentration pH 4.6 (▲) and pH 3.44 (△).

Identical data were obtained at pH 4.6 and 3.44. At these two pH values, the phosphate buffer is mainly present as $H_2PO_4^-$. Even at pH 4.66, the HPO_4^{2-} concentration is only 0.2 % of the total buffer concentration, and at the lower pH it drops to 0.016 %. If HPO_4^{2-} were the reactive species in the experiments shown in Figure 3 the **QP** yield at the highest phosphate buffer concentration (0.8 M) should be less than that found for 0.1 M phosphate buffer at pH 4.6. This not being the case, we conclude that the phosphate buffer effect observed here is given by the $H_2PO_4^-$ ions. Experiments at pH values noticeably above the ones studied and at high phosphate buffer concentrations (i.e., high concentrations of HPO_4^{2-}) were not feasible, since not only **QP** but also **Q** (to a lesser extent) are not sufficiently stable under these conditions.

It is noted that in contrast to phosphate, the quantum yield of photodecomposition of **Q** is greatly diminished by the addition of halide ions, chloride and bromide.[19]

Spin-trapping studies: That ·OH may be an intermediate in the photohydroxylation of **Q** is continuously suggested since the early work on this subject. The "proof" came from spin-trapping studies. In the presence of DMPO, a four-line EPR spectrum, typical for the DMPO–·OH adduct, has been obtained.[39,44] Competition with ethanol[39] and with formate[44] yielded data that were close to those calculated on the basis

of the known[82] rate constants of ·OH with DMPO and these substrates. Considering that these two substrates undergo ready photoreduction and thus this reasonable agreement could be due to an artefact, we set-up a competition with tertiary butyl alcohol, a substrate that is a very poor hydrogen donor, that is, not very reactive towards carbonyl excited states, but nevertheless readily reacts with ·OH ($k = 6 \times 10^8 \, \text{M}^{-1}\text{s}^{-1}$).[82] As can be seen from Figure 4, we also observe a four-line signal, identical to that obtained upon photolysis of H_2O_2. In such competitions, tertiary butyl alcohol is much more effective in reducing the four-line signal when it was generated via ·OH formed in the photolysis of H_2O_2 than when formed upon **Q** photolysis (Figure 4).
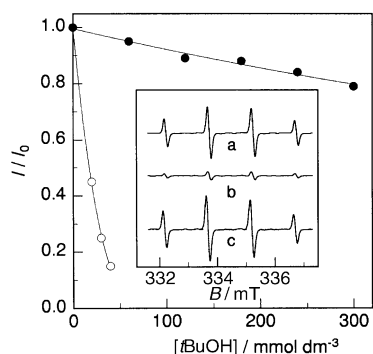

Figure 4. Normalized yields of the four-line EPR spectrum (cf. inset) in the photolysis of 1,4-benzoquinone (●: 0.5 mM) in the presence of DMPO (17.5 mM), and in the photolysis of H_2O_2 (○: 0.4%) as a function of the tertiary butyl alcohol concentration. Inset: photolysis of H_2O_2 in the absence (a) and in the presence of tBuOH (b, 40 mM) and in the photolysis of 1,4-benzoquinone in the presence of 120 mM tertiary butyl alcohol (c).

We thus conclude that in the case of the photolysis of **Q** the four-line signal must have another precursor. It has been estimated that the oxidation potential of the relaxed **Q*** may be around 2.4 V,[35] that is, very high but below the reduction potential of ·OH ($E^7 = 2.65$ V).[83] The oxidation potential of DMPO is around 1.7 V.[73] In analogy to experiments where photoexcited chloranil was reacted with DMPO in the presence of various acids as nucleophiles,[73] we suggest that an electron transfer from the spin trap to **Q*** occurs [reaction (9)]. This is followed by nucleophilic addition of water to the DMPO radical cation with the concomitant release of a proton [reaction (10)]. The rate constant for the reaction of **Q*** with tertiary butyl alcohol has been measured here (see below) at $\sim 2 \times 10^6 \, \text{M}^{-1}\text{s}^{-1}$ (for a compilation of rate constants see Table 1). From this value and the data shown in Figure 4, we estimate a rate constant in the order of $10^8 \, \text{M}^{-1}\text{s}^{-1}$ for the reaction of **Q*** with DMPO.
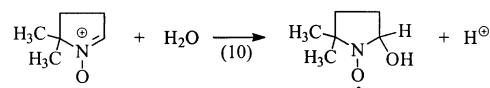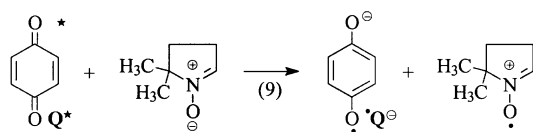

Table 1. Compilation of rate constants [$\text{M}^{-1}\text{s}^{-1}$] relevant for the present study.

Reaction	Rate constant	Reference
Q* + O_2	$\sim 2 \times 10^9$	this work
	2.4×10^9	[32]
Q* + **Q**	$> 5 \times 10^9$	this work
Q* + 2-propanol	1.3×10^8	this work
Q* + ethanol	6.5×10^7	this work
Q* + methanol	4.2×10^7	this work
Q* + tBuOH	2×10^6	this work
Q* + DMSO	2.7×10^9	this work
Q* + DMPO	$\sim 1 \times 10^8$	this work
Q + $Ph(OH)_3$	19 (pH 4.6)[a]	this work
Q + $Ph(OH)_2O^-$	8×10^5	this work
Q + ·OH → products	6×10^9	[71]
tBuOH + ·OH → products	6×10^8	[82]
DMSO + ·OH → products	7×10^9	[82]
·QOH → ·Q(OH)H	$2.5 \times 10^6 \, \text{s}^{-1}$	[71]
·Q(OH)H + Q → HOQ + ·QH	$\leq 2.4 \times 10^7$	[71]
·Q(OH)⁻ + Q → HOQ + Q·⁻	2×10^9	[71]

[a] Upper limit for the uncatalyzed reaction. For proton and buffer catalysis see text.

The 1,4-benzoquinone triplet state(s): The first transient observed by laser flash photolysis of **Q** has been assigned to its triplet state **Q*** (for the likely involvement of an excimer, **Q₂***, see below).[32] In this study,[32] where the UV absorption spectrum of the triplet was given in the range between 350 and 500 nm, the transient displayed a maximum at ~410 nm, but the much stronger one at 282 nm (cf. Figure 5) had been missed, and also in the more recent study on 2-methyl-1,4-benzoquinone,[60] no attempt has been made to measure the triplet spectrum below 330 nm. The shapes of the short-wavelength absorption band when put on an energy scale shows a good Gaussian distribution, and based on this analysis its maximum is located at 282 nm.

Upon the decay of **Q*** (and **Q₂***, see below), species with maxima at ~310 and 410 nm are formed (Figure 5). The rate of triplet decay has been reported at $k = 1.9 \times 10^6 \, \text{s}^{-1}$.[32] In
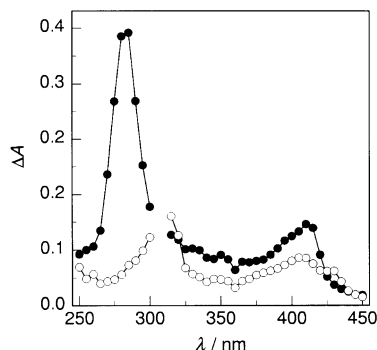

Figure 5. 308 nm laser flash photolysis of 1,4-benzoquinone (4 mM) in N_2-saturated aqueous solution. UV/Vis spectra recorded at 100 ns (●) and 1.4 µs (○) after the flash. The wavelengths close to the exciting wavelength had to be omitted.

this experiment, the **Q** concentration was 0.5 mM. We have now investigated the dependence of the lifetime of this species as a function of **Q** concentration which was varied in the range of $(0.2 \rightarrow 10)$ mM. As can be seen from Figure 6, at the lowest concentration used the rate of decay is $2 \times 10^6 \, \text{s}^{-1}$ and increases with increasing **Q** concentration, approaching at high **Q** concentration a constant value of $k = 3.8 \times 10^6 \, \text{s}^{-1}$.
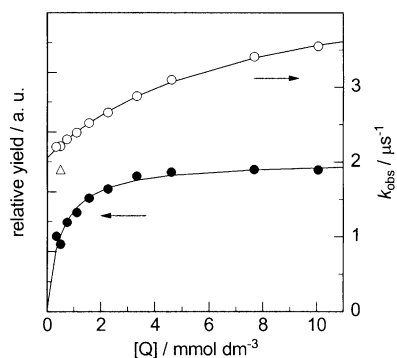

Figure 6. Laser flash photolysis at 308 nm of 1,4-benzoquinone in N_2-saturated aqueous solution at pH 2. Right scale ($\circ$): Rate of decay of the 1,4-benzoquinone triplet(s) at 285 nm as a function of the 1,4-benzoquinone concentration. The value obtained in ref. [32] has been included (triangle). Left scale ($\bullet$): Ratio of the initial absorption at 415 nm (assigned to the triple) to the final absorption at this wavelength (assigned to products, *for example*, free radicals) as a function of the 1,4-benzoquinone concentration. The solid lines have been calculated on the basis of the harmonic-mean approach to equilibrium kinetics.

Evidently, the **Q** concentration-dependence of the triplet lifetime is not compatible with a simple reaction of **Q**** with water, and at some point ground-state **Q** has to be involved as well. Without the yield data (lower curve in Figure 6), one would be tempted to ignore the curvature of the triplet decay rates (upper curve in Figure 6) and draw a straight line. This would result in a quenching rate of **Q**** by **Q** of $2 \times 10^8 \, \text{M}^{-1} \text{s}^{-1}$. However, fitting the yield data by conventional first-order competition kinetics results in a 20 times higher rate constant. Apparently, a more complex reaction Scheme is required.

It will be discussed below that **Q**** is most likely in rapid equilibrium with its dimer, **Q₂****, an exciplex consisting of two **Q** molecules [equilibrium (11)]. This can account for the data shown in Figure 6 and the other data to be reported next.
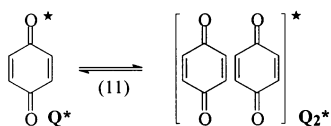
When the triplet has decayed, a noticeable absorption remains (cf. open circles in Figure 5). This has been attributed to the formation of free radicals.[32] Since only one **Q** concentration had been studied, it escaped attention[32,38] that

the radical yield is also a function of the **Q** concentration (Figure 6, lower curve, left scale).

In a flash photolysis study on duroquinone (2,3,5,6-tetramethyl-1,4-benzoquinone) in aqueous solution,[84] free-radical formation was only observed upon triplet–triplet annihilation, that is, at high triplet concentrations. Here, this process is excluded because the yield per dose was found to be independent of laser flash intensity, in agreement with the weak intensities of our laser flashes. The much shorter lifetime of **Q****/**Q₂**** as compared to that of the duroquinone triplet further reduces a potential contribution of triplet–triplet reactions.

The disappearance of free-radical intermediates at vanishing **Q** concentration together with the independence of Φ(photohydroxylation) on the **Q** concentration suggests that two processes occur side by side. We conclude that **Q**** reacts with ground state **Q** forming an exciplex, **Q₂****. While **Q**** hydrates without giving rise to a product that absorbs strongly at >300 nm, **Q₂**** gives rise to radical formation and hence to intermediates absorbing at long wavelengths. With **Q**** and **Q₂**** in rapid equilibrium ($k_{11} \approx 5 \times 10^9 \, \text{M}^{-1} \text{s}^{-1}$) and decay rates of $2 \times 10^6 \, \text{s}^{-1}$ for **Q**** and $3.8 \times 10^6 \, \text{s}^{-1}$ for **Q₂****, the stability constant $K_{11} = 5500 \pm 1000 \, \text{M}^{-1}$ is calculated from the data shown in Figure 6. The solid lines drawn through the data points of these figures were calculated on this basis.

With such a rapid equilibrium and fast decay rates, the differences in the UV absorption spectra of **Q**** and **Q₂**** can only be obtained by global analysis. The result is shown in Figure 7. According to this analysis, the absorption maxima of **Q**** and **Q₂**** do not differ much. However, compared with **Q****, **Q₂**** shows a lower absorption at the short-wavelength maximum.

Dioxygen quenches **Q****/**Q₂**** (see also ref. [32]), and consequently the ensuing free-radical yield is reduced. The rate constant derived from plotting k_{obs} versus the dioxygen concentration ($1.0 \times 10^9 \, \text{M}^{-1} \text{s}^{-1}$ at 2.2 mM **Q**, $1.1 \times 10^9 \, \text{M}^{-1} \text{s}^{-1}$ at 4.0 mM **Q**) does not agree with the rate constant derived from a Stern-Volmer plot based on the final free-radical yield using the same experimental data ($2.6 \times 10^9 \, \text{M}^{-1} \text{s}^{-1}$ at 2.2 mM **Q**, $1.9 \times 10^9 \, \text{M}^{-1} \text{s}^{-1}$ at 4.0 mM **Q**). This shows, that the mechanistic assumption behind the Stern-Volmer plot does
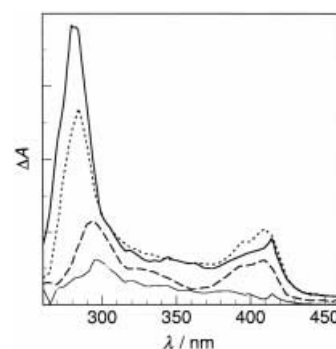

Figure 7. Global analysis of the transients. ——: 1,4-benzoquinone triplet, **Q****; ·····: triplet exciplex, **Q₂****; -----: decay product of **Q₂****, semiquinone radical ·**QH** products plus 2-hydroxy-1,4-benzoquinone, **QOH**; ——: decay product of **Q****, 1,2,4-trihydroxybenzene **Ph(OH)₃** and/or its precursors.

not hold, that is, simple competition kinetics do not take place. These marked difference indicate complex kinetics involving the quenching of more than one triplet state by O_2.

Alcohols also quench the 282 nm absorption ($[\mathbf{Q}] = (2 \rightarrow 4)$ mM in these experiments). The rate constants increase with increasing H-donating property of the alcohol from $\sim 0.2 \times 10^7 \, \mathrm{M^{-1} s^{-1}}$ (tertiary butyl alcohol, cf. Figure 8) to $13 \times 10^7 \, \mathrm{M^{-1} s^{-1}}$ (2-propanol), cf. Table 1.
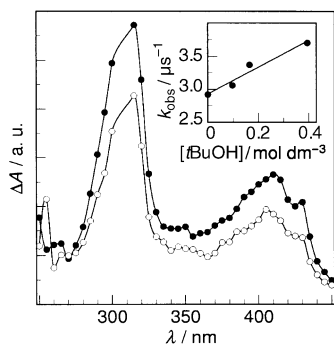

Figure 8. 308 nm laser flash photolysis UV of 1,4-benzoquinone (4 mM) in aqueous solution in the absence (●) and presence (○) of tBuOH (0.4 M). The spectra were recorded 1.4 µs after the flash. Inset: Observed rate constant of the decay at 285 nm of the 1,4-benzoquinone triplet as a function of the tertiary butyl alcohol concentration. The regression line yields a value of $k = (1.94 \pm 0.2) \times 10^6 \, \mathrm{M^{-1} s^{-1}}$.

In an earlier study,[32] experiments have also been carried out in the presence of 0.1 M tertiary butyl alcohol. The rather scattering data have been interpreted as being compatible with a *decrease* of the total semiquinone radical yield, and it has been suggested that tertiary butyl alcohol reacts with the ˙OH radicals formed according to reaction (4). The effect of tertiary butyl alcohol on the total semiquinone radical yield has been re-investigated here in somewhat more detail, and it is now clear that in fact the total semiquinone radical yield *increases* with increasing tertiary butyl alcohol concentration (cf. Figure 8 which shows two out of five data sets).

Dimethylsulfoxide (DMSO) is a much better triplet quencher than the alcohols (Table 1). This effective quenching cannot be attributed to hydrogen donation, since DMSO is a poor hydrogen donor. In agreement with this, free-radical formation is suppressed by DMSO. The lack of radical products also excludes an efficient electron transfer, that is, the formation of $\mathbf{Q}^{\bullet -}$ and a DMSO radical cation. The latter would be expected to react with water yielding the ˙OH adduct, which has been shown[85] to give rise to methanesulfinic acid and a methyl radical. Methanesulfinic acid (or its oxidation product methanesulfonic acid) is not formed, not even in low yields ($\Phi < 0.03$). Moreover, the methyl radical is known to react readily with $\mathbf{Q}$ yielding 2-methyl-1,4-benzoquinone.[86] We have also looked for this product, and did not find any indication for its formation. This is in contrast to a recent study on the photolysis of 2-methyl-1,4-benzoquinone in aqueous DMSO solutions.[60] There, the formation of methyl radicals was concluded based on fluorescent material formed in the presence of a nitroxyl radical trap.[60]

Our more stringent data suggest that DMSO acts overwhelmingly as a physical quencher. Such processes have been observed before with many other systems, and with optically active sulfoxides an isomerization is observed; an exciplex as a very short-lived intermediate has been postulated.[87,88]

The free-radical intermediates: The formation of free-radical intermediates has been noticed before and has been attributed to the formation of ˙$\mathbf{QH}$ and ˙$\mathbf{Q(OH)H}$,[32] or only to ˙$\mathbf{QH}$,[38] and, depending on pH, to their corresponding radical anions. From a flash photolysis study of a 0.4 mM $\mathbf{Q}$ solution at pH 7, it was concluded that $\Phi(\text{˙}\mathbf{QH}) = 0.47$.[38] In this calculation, the formation of $\mathbf{HOQ}$ that must have been formed upon the oxidation of ˙$\mathbf{Q(OH)H}$ by $\mathbf{Q}$ [cf. reaction (7)] at the time scale of these experiments (cf. ref. [71]) has not been accounted for, and thus $\Phi(\text{˙}\mathbf{QH})$ is lower. Radical formation is now suggested to be due to a reaction of $\mathbf{Q_2}^*$ with water (reaction 12) followed by a rapid conversion of ˙$\mathbf{QOH}$ into ˙$\mathbf{Q(OH)H}$ (reaction 6, $k = 2.6 \times 10^6 \, \mathrm{s^{-1}}$).
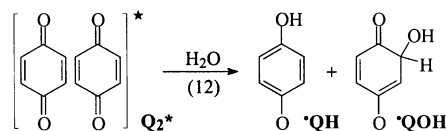
The same species can be generated in a pulse radiolysis experiment. There, solvated electrons and ˙OH are formed in about equal yields with a contribution of some 10% hydrogen atoms. In their reaction with $\mathbf{Q}$, solvated electrons (and potentially also ˙H) give rise to ˙$\mathbf{QH}$, while ˙OH yield ˙$\mathbf{Q(OH)H}$ (via ˙$\mathbf{QOH}$) (cf. reactions (5)–(7), ref. [71], and references therein).

In Figure 9, the spectra obtained by pulse radiolysis of N_2-saturated aqueous $\mathbf{Q}$ solutions at neutral and low pH are compared with corresponding laser experiments. The pK_a value of ˙$\mathbf{QH}$ is at 4.0,[89] (4.1),[90] and that of ˙$\mathbf{Q(OH)H}$ is at 4.9.[71] In view of the fast oxidation of ˙$\mathbf{Q(OH)}^-$ by $\mathbf{Q}$ at pH 7 ($k = 2 \times 10^9 \, \mathrm{M^{-1} s^{-1}}$),[71] 1–2 µs after the laser/electron pulse we deal with a 2:1 mixture of ˙$\mathbf{QH}$ and $\mathbf{HOQ}$. $\mathbf{HOQ}$ also absorbs in the same wavelength region as ˙$\mathbf{QH}$, and its spectrum also changes with pH ($pK_a(\mathbf{HOQ}) = 4.1$).[71] At low pH, the oxidation of the now no longer deprotonated ˙$\mathbf{Q(OH)H}$ is much slower ($k \leq 2.4 \times 10^7 \, \mathrm{M^{-1} s^{-1}}$). The rate of reaction is governed by the rate of oxidation of ˙$\mathbf{Q(OH)}^-$ in equilibrium,[71] and at the pH and $\mathbf{Q}$ concentrations of Figure 9 $\mathbf{HOQ}$ formation is negligible under acidic conditions at 1 µs.

Because in the present system we deal with two products (˙$\mathbf{QH}$ and $\mathbf{HOQ}$), the spectral differences between low and high pH are less pronounced here than in systems containing only[89,90] ˙$\mathbf{QH}$. However, the good agreement of these two data sets clearly shows that free radicals are indeed formed upon the decay of $\mathbf{Q_2}^*$. In contrast to the earlier pulse radiolysis study,[71] the intermediate ˙$\mathbf{QOH}$ cannot be detected in the laser flash experiment, because its conversion into ˙$\mathbf{Q(OH)H}$ takes place at the same rate as the decay of $\mathbf{Q}^*/\mathbf{Q_2}^*$.
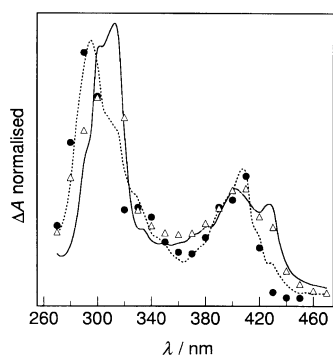
Figure 9. UV photolysis (symbols) and pulse radiolysis (lines) of 1,4-ben-zoquinone (**Q**) in deoxygenated aqueous solutions. UV/Vis absorption spectra of the intermediates present 1 µs after the laser flash/electron pulse. Solid line ([**Q**] = 1.8 mM) and triangles (4 mM) neutral solutions, dotted line (pH 3.3, [**Q**] = 0.1 mM), circles (pH 2, [**Q**] = 4 mM).

At pH 7, the decay of **Q***/**Q**$_2$* occurs at a similar time scale as the deprotonation of **·QH**. Optically, this is reflected as an increase in the absorption at 315 nm (Figure 10), the only wavelength where the products (semiquinone-type radicals) show a stronger absorption than the triplets (cf. Figure 5). As expected, at low pH, where this deprotonation no longer takes place, no increase at 315 nm is observed on this time scale.
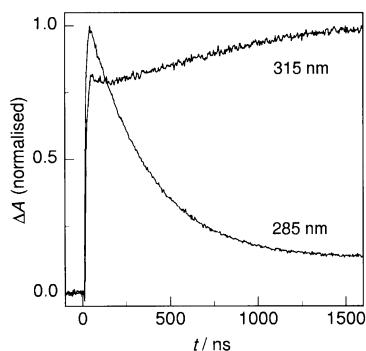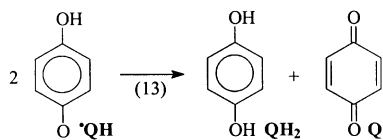

Figure 10. 308 nm laser flash photolysis of 1,4-benzoquinone (4 mM) in aqueous solution at pH ~7. Normalized absorptions at 288 nm and at 315 nm as a function of time.

As discussed above, after a few µs only **·QH** remains. It decays by second-order kinetics into **Q** and **QH**$_2$ [reaction (13)].

The self-termination rate constant of **·QH** is $1.09 \times 10^9\,\mathrm{M^{-1}\,s^{-1}}$, while **Q**$^{·-}$ self-terminates somewhat more slowly $(1.7 \times 10^8\,\mathrm{M^{-1}\,s^{-1}})$.[89] As a consequence of the rapid oxidation of **·Q(OH)H** by **Q**, **·Q(OH)H** is not reduced into **Ph(OH)**$_3$

in free-radical disproportionation reactions, for example, with **·QH** or itself.

Formation of 1,2,4-trihydroxybenzene and its oxidation by 1,4-benzoquinone: Although **Ph(OH)**$_3$ cannot be formed via the free-radical pathway, it is a likely intermediate, when the monomeric triplet, **Q***, reacts with water [reaction (14) followed by the enolization reaction (15)].
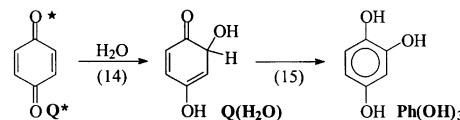
The oxidation of **Ph(OH)**$_3$ by **Q** gives rise to the final products, **HOQ** and **QH**$_2$ [reaction (8)]. An oxidation of the precursor of **Ph(OH)**$_3$, **Q(H$_2$O)**, by **Q** [reaction (16)] must also be envisaged (for discussion see below).
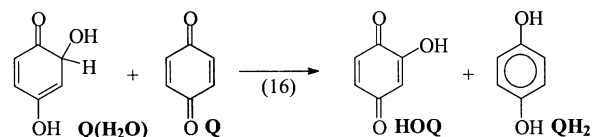
Using electrochemical oxidation of **Ph(OH)**$_3$ to generate **HOQ**, we have recently shown that **HOQ** is a fairly strong acid (pK_a 4.2) and that its anion is characterized by a strong absorption at 482 nm ($\varepsilon = 200\,\mathrm{m^2\,mol^{-1}}$), while the free acid has an absorption maximum at 380 nm ($\varepsilon = 140\,\mathrm{m^2\,mol^{-1}}$).[71] The oxidation of **Ph(OH)**$_3$ by **Q** has been used before as a spectral reference for the formation of **HOQ**.[19] With the help of the stopped-flow technique (spectrophotometrical detection), we now show that the rate of reaction depends on pH and at a given pH on the phosphate buffer concentration. With **Ph(OH)**$_3$ in large excess over **Q**, the kinetics of the formation of **HOQ** is of (pseudo) first order. The rapid autoxidation of the anion of **Ph(OH)**$_3$ prevented us from extending our studies to pH values above those given in Figure 11. These data are compatible with a slow oxidation of the fully protonated **Ph(OH)**$_3$ (at low pH) and a much faster one of its monoanion (pK_a 9.1)[91] From the data one estimates that **Ph(OH)**$_3$ is oxidized with $k = 14\,\mathrm{M^{-1}\,s^{-1}}$ and its anion with $k = 8 \times 10^5\,\mathrm{M^{-1}\,s^{-1}}$ (for a compilation of rate constants see Table 1). However, the situation is more complex. In acid solution, the rate of reaction increases again, and upon addition of H$_2$PO$_4^-$ (pH 4.66) the rate increases with increasing phosphate buffer concentration (inset in Figure 11). Under these conditions, the rate of reaction is described by $k_{obs} = (19 + 170 \times [\mathrm{H_2PO_4^-}])\,\mathrm{M^{-1}\,s^{-1}}$. A maximum in the rate of reaction between pH 3 and 5.5, as has been reported before,[19] is not apparent from our data.

The increase in the rate of the oxidation of **Ph(OH)**$_3$ by **Q** at low pH is somewhat unexpected. Two potential interpretations are envisaged. At low pH, **Q** and its protonated form, **QH**$^+$, are in equilibrium, and **QH**$^+$ is a stronger oxi-
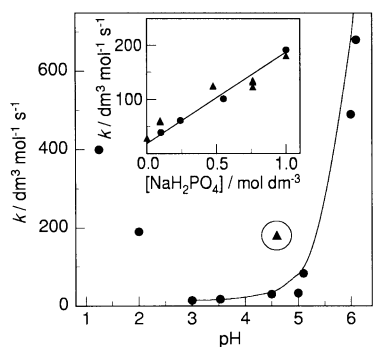
Figure 11. Observed second-order rate constant of the oxidation of 1,2,4-trihydroxybenzene by 1,4-benzoquinone as a function of pH (●) and in the presence of 1 M NaH$_2$PO$_4$ (▲). Data by stopped-flow. The solid line is calculated on the basis on the values given in the text. Inset: rate of the phosphate catalyzed oxidation as a function of the phosphate concentration at pH 4.66, laser flash photolysis LFP-LTRD (●) and stopped-flow (▲).

dant than **Q**. The proton affinity of **Q** has not yet been determined, but the pK_a of acetoneH$^+$ which may serve as a guide is at -3.06.[92] Alternatively, **Q** and **Ph(OH)$_3$** could be in equilibrium with a CT complex, a kind of quinhydrone. Protonation of this "quinhydrone" would speed-up the oxidation of **Ph(OH)$_3$** by **Q**. We favor the latter mechanistic concept, because at pH 4.66 phosphate buffer (cf. triangle in Figure 11) would not increase the **QH$^+$** concentration in equilibrium but could protonate the "quinhydrone".

Above, it has been shown that in the free-radical pathway a few μs after the flash **·QH** and **HOQ** are the products (in the absence of phosphate buffer; for the effect of phosphate buffer see below). After this, radicals **·QH** decay by disproportionation into **QH$_2$** and **Q** [reaction (10)]. This reaction is completed within a few ms.

Thus, any formation of **HOQ** observed in the post-millisecond time range must be due to another process, that is, the non-radical pathway [reactions (14)–(16), (8)]. As shown in Figure 12, a biphasic buildup of **HOQ** (for its UV spectrum see inset) is indeed observed. The slow part follows the very characteristic pH dependent kinetics of the oxidation of **Ph(OH)$_3$** by **Q** as discussed above.

The ratio of the fast/slow components increases with increasing **Q** concentration (data not shown), substantiating
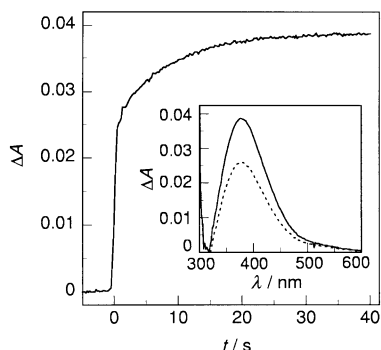

Figure 12. 308 nm laser flash photolysis of 1,4-benzoquinone (0.5 mM) at pH 2.5. The laser flash was directed into a cuvette of a diode array spectrophotometer, and spectra were recorded every 0.2 s. Main graph: kinetics at 390 nm. Inset: Spectra at 1 s (·····) and at 39 s (——).

that the free-radical pathway requires a reaction of **Q*** with **Q**. The fast component also gains in importance upon lowering the pH. Since this change in mechanism is not connected with a change in the rate of the decay of **Q***/**Q$_2$***, it cannot be due to an increase of the rate of radical formation upon protonation of **Q$_2$***. We, therefore, tentatively suggest that **Q(H$_2$O)** is oxidized by **Q** [reaction (16)] in competition with its rearrangement to **Ph(OH)$_3$** [reaction (15)]. Being of higher energy than **Ph(OH)$_3$**, **Q(H$_2$O)** may be oxidized by **Q** (H$^+$-catalyzed, again via a CT complex) much faster than **Ph(OH)$_3$**. In case this process occurred at times <1 s, it would be recorded together with the free-radical pathway. Our setups do not allow us to monitor times between 1 ms and 1 s, and testing this mechanistic proposal experimentally was not possible.

Reactions involving phosphate: In the presence of phosphate buffer, the overall product quantum yield is increased, and a new product, attributed to 2-phosphato-1,4-benzoquinone **QP** is formed (see above). Its yield increases with increasing phosphate concentration. Concomitantly, the **Q** triplets as monitored at 285 nm decay faster with $\sim4\times 10^6$ M^{-1}s^{-1} at 0.3 mM **Q** and $\sim5\times10^6$ M^{-1}s^{-1} at 8.3 mM **Q** (data not shown). At both **Q** concentrations, the addition of phosphate seems to increase only little if at all the free radical yield. We hence suggest, that phosphate mainly reacts with **Q***, and a reaction with **Q$_2$*** must be minor in comparison.

In analogy to reactions (14) and (15), the reaction of **Q*** with H$_2$PO$_4^-$ is given by reactions (17) and (18).
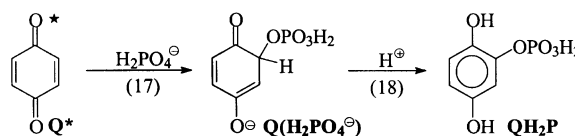
The subsequent oxidation of **QH$_2$P** by **Q** to **QP** [reaction (19)] is analogous to that of **Ph(OH)$_3$** to **HOQ** [reaction (8)].
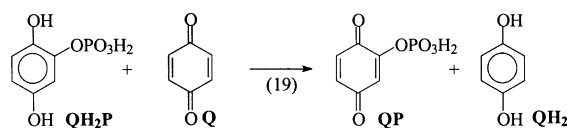
In the presence of 1 molar phosphate at pH 4.66, following the buildup of **HOQ**, a further buildup between 300 and 450 nm is observed (Figure 13). Subtraction of the spectrum measured after 5 s from that after 98 s yields a spectrum with $\lambda_{max} = 361$ nm (when put on an energy scale, this peak shows a perfect Gaussian distribution allowing the exact determination of its maximum). It agrees with the spectrum of **QP** observed by HPLC.

The oxidation of **QH$_2$P** by **Q** is notably slower ($k_{obs} = 7$ M^{-2}s^{-1}) than that of **Ph(OH)$_3$** ($k_{obs} = 190$ M^{-2}s^{-1}) under equal conditions (1 M phosphate).
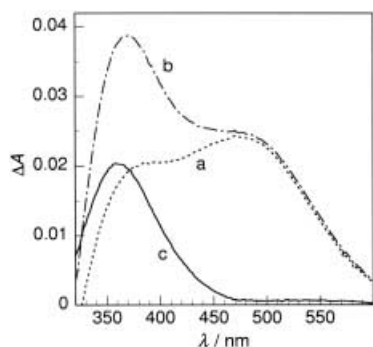
Figure 13. Laser flash photolysis (LFP-LTRD) at 308 nm of 1,4-benzoquinone (5.5 mM, air-saturated) in the presence of 1 M $H_2PO_4^-$. a) 5 s after the flash (assigned to 2-hydroxybenzoquinone); b) 98 s after the flash; c) difference spectrum (assigned to 2-phosphato-1,4-benzoquinone).

Summary of the photohydroxylation mechanism: It has been shown above that no free ·OH is formed. The intermediacy of an ·OH complexed to $Q^{·-}$ as has been proposed recently[60] has likewise to be rejected not only on the basis of the above experiments that exclude the formation of significant amounts of methyl radicals in the presence of DMSO but also as a potential concept in general. π-Complexes of radicals to aromatic compounds are known, and even for a radical as reactive as ·OH it has been shown that such a complex has to be postulated as an intermediate in its reaction with benzene to the hydroxycyclohexadienyl radical.[93] However, a π-complex of a strongly oxidizing radical such as ·OH with a strongly reducing radical such as $·QH/Q^{·-}$ (as postulated in ref. [60]) will immediately collapse either by electron transfer of by recombination. We therefore have to come up with another mechanism.

This mechanism has to accommodate two important aspects: i) the increase in rate of the decay of the triplet with increasing **Q** concentration and ii) the observation that the free-radical yield increases with increasing **Q** concentration despite the fact that the product quantum yields are independent of the **Q** concentration. Furthermore, the incorporation of phosphate in the presence of phosphate buffer with a concomitant increase in the total quantum yield of product formation has to be taken into account.

Observation ii) requires that excited **Q** has two pathways for its decay towards the products **QH₂** and **HOQ**, one at low **Q** concentrations without the intermediacy of free radicals and one at high **Q** concentrations via free-radical intermediates. This can be accounted for if **Q*** reacts with water yielding an adduct, **Q(H₂O)** [reaction (14); see Scheme 1, below], which is oxidized by **Q** straight away [reaction (16)], or re-arranges into **Ph(OH)₃** [reaction (15)] and is then oxidized by **Q** to **HOQ** [reaction (8)]. In competition with this, **Q*** reacts with ground-state **Q** and the ensuing exciplex **Q₂*** decays by electron transfer into $Q^{·-}$ and $Q^{·+}$. $Q^{·+}$ is expected to react "immediately" with water. Benzene-derived radical cations have lifetimes >1 ns only when substituted by more than two (electron donating) methyl substituents,[94, 95] and $Q^{·+}$ with its two electron-withdrawing carbonyl groups may be even shorter-lived. One also may consider that the radical cation never materializes, and the reaction of the ex-

ciplex with water may proceed directly to $Q^{·-}$ and ·QOH. ·QOH isomerizes rapidly ($k = 2.5 \times 10^6 \, s^{-1}$) into **·Q(OH)H**.[71]

In the presence of phosphate buffer, **Q*** decays faster without enhancing the free-radical yield [reaction (17)], eventually giving rise to **QP** [reactions (18) and (19)].
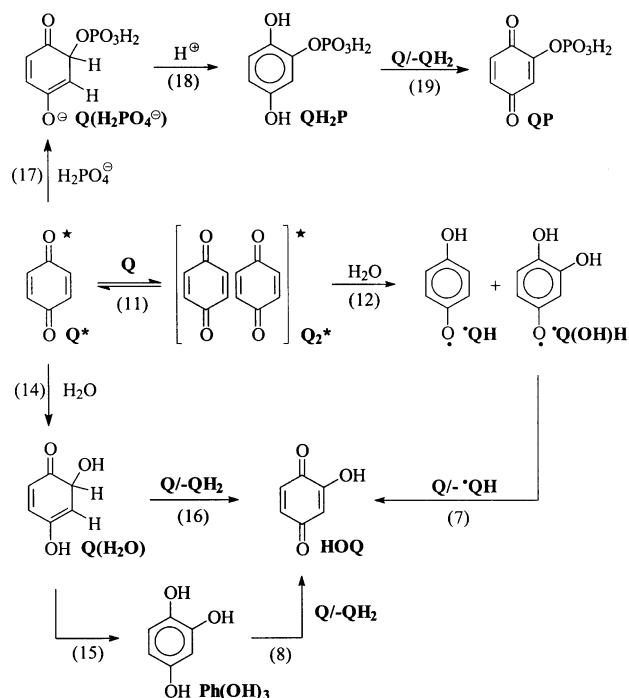
Scheme 1.

Conclusion

The formation of an exciplex, **Q₂***, en route to **QH₂** and **HOQ** via free radicals has been investigated in the present paper. Exciplexes with **Q*** seem to be more general. The photoinduced hydroxylation of benzene by **Q** in aqueous solution[64] will have a **Q***–benzene exciplex and upon its decay a hydroxycyclohexadienyl radical as the most likely precursors. The quenching of **Q*** by halide ions, X^-, is thought to pass through an exciplex, $Q^*–X^-$, which must have a certain lifetime, since it gives rise to radical formation at high Cl^- concentrations ($Q^*–X^- + X^- \rightarrow Q^{·-} + X_2^{·-}$).[62] Exciplexes are postulated for the quenching of **Q*** by dioxygen and by DMSO, but these reactions do not lead to observable products such as quenching of **Q*** by X^- at low X^- concentrations. Exciplexes are, of course, not restricted to quinones but an abundant phenomenon in photochemistry. In analogy to the present system, we have recently shown that in photochemistry of maleimide in aqueous solution the maleimide exciplex gives not only rise to a dimer biradical but also to the formation of free radicals via electron transfer.[96]

Acknowledgement

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