

Reaction of OH radicals with benzoquinone in aqueous solutions. A pulse radiolysis study



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Hydroxyl radicals have been generated by pulse radiolysis in N₂O-saturated aqueous solutions. Their addition to 1,4-benzoquinone BQ ($k_3 = 6.6 \times 10^9 \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$ by competition with thiocyanate) in neutral solution leads to a build-up of optical absorption that shows different rates at wavelengths at around 330 and at >400 nm. At 330 nm the rate of build-up is proportional to the benzoquinone concentration, and its rate constant agrees with the value (k_3) obtained by competition. At the longer wavelengths, it becomes independent of benzoquinone concentration beyond $4 \times 10^{-4} \text{ mol dm}^{-3}$ ($k_6 = 6.9 \times 10^5 \text{ s}^{-1}$). Kinetic analysis in the ns time-range show that the primarily-generated benzoquinone-OH-adduct radical 1 undergoes rapid ($k_4 = 2.5 \times 10^6 \text{ s}^{-1}$) keto-enol tautomerization yielding the 2,4-dihydroxyphenoxy radical 2. To gain support for this proposed reaction, radical 2 [$\text{p}K_a(2) \approx 4.9 \pm 0.2$] has been independently generated by one-electron oxidation of 1,2,4-trihydroxybenzene using $\cdot\text{OH}$ in acidic or N₃ \cdot in neutral and basic solution. Its absorption characteristics compare favourably with those observed in the benzoquinone system. On the basis of spectrophotometric and conductometric data it is proposed that in neutral solution the radical anion 2a is rapidly oxidized by benzoquinone itself ($k_{15} \geq 2 \times 10^9 \text{ dm}^3 \text{ mol}^{-1}$) into the end product 2-hydroxy-1,4-benzoquinone anion 4a [$\text{p}K_a(4) = 4.1 \pm 0.1$; $\lambda_{\text{max}}(4) = 380 \text{ nm}$; $\lambda_{\text{max}}(4a) = 482 \text{ nm}$] and the semibenzoquinone radical anion 3a. The latter decays bimolecularly into benzoquinone and hydroquinone ($2k_{16} = 3.1 \times 10^8 \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$). In acidic solution the rate of oxidation of 2 by benzoquinone is considerably slower ($k_{13} \leq 2.4 \times 10^7 \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$). The assignment of the final product to 2-hydroxy-1,4-benzoquinone 4 has been confirmed by the absorption characteristics and $\text{p}K_a$ value of the authentic material obtained by the two-electron electrochemical oxidation of 1,2,4-trihydroxybenzene.

Quinones and phenoxy radicals have been studied extensively since the early days of radiation chemistry because of their involvement in many biologically important processes such as photosynthesis, electron transport (see ref. 1 for a collection of references) and in the antioxidant properties of such vitamins as A, E and K as well as of many natural phenolic substances in plants.^{2–4} Benzoquinone is employed in certain cases to increase the shelf-life of industrial polymerizable monomers.

The reaction of the OH radical with 1,4-benzoquinone has been investigated by Adams and Michael by pulse radiolysis, and the observed transient has been attributed to the benzoquinone-OH-adduct radical.⁵ In a more recent study of the reaction of the methyl radical with benzoquinone, Veltwisch and Asmus have proposed that the benzoquinone methyl adduct radical tautomerizes to the methyl semiquinone.⁶ This initial process is then followed by the reaction of this semiquinone-type radical with a second molecule of benzoquinone to produce 2-methyl-1,4-benzoquinone (identified as a final product) and the unsubstituted semibenzoquinone radical. Due to the slowness of the reaction of the methyl radical with benzoquinone the kinetics of the tautomerization and the subsequent oxidation could not be resolved.

In the present paper it will be shown that the benzoquinone-OH-adduct radical is very short-lived; it rapidly tautomerizes and is further oxidized by excess benzoquinone. Since all these reactions occur early on the μs timescale, the absorption reported by Adams and Michael is in fact already due to a mixture of the semiquinone radical anion and 2-hydroxy-1,4-benzoquinone.

Experimental

1,4-Benzoquinone (Fluka) was purified by fractional sublimation under argon. Hydroquinone (Fluka, >99%), 1,2,4-trihydroxybenzene (Aldrich, 99%), sodium azide (Fluka, >99.5%) and other chemicals used were available commercially. Water was purified by a Millipore Milli-Q system. Solutions of benzoquinone and of 1,2,4-trihydroxybenzene were freshly prepared by dissolving the solid substance in oxygen-free N₂O-saturated water immediately before each experiment and were kept from exposure to either light or air during the experiment.

Pulse radiolysis was carried out using 0.4 μs electron pulses generated by a 2.8 MeV van-de-Graaff electron accelerator at the Max-Planck-Institut für Strahlenchemie. The pulse radiolysis apparatus and the set-up of the optical and AC-conductance detection methods as well as the corresponding computer-assisted data processing arrangement have been described elsewhere.⁷ The experiments with the higher 1,4-benzoquinone concentrations were carried out with the 11 MeV linear accelerator (Elektronika, Torium, Moscow) at the Institut für Oberflächenmodifizierung using 17 Gy pulses of 5 ns duration. Thiocyanate dosimetry was used in the optical measurements, and dimethyl sulfoxide in N₂O-saturated solution at pH 4 was used for dose determination in the conductance measurements.⁸ For the evaluation of the conductivity signals the equivalent conductance of the anions was assumed to be equal to that of the methyl sulfinate anion formed in the dimethyl sulfoxide dosimeter system.

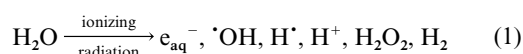
In the absence of authentic 2-hydroxy-1,4-benzoquinone, a putative product, which was unavailable commercially, an

N_2 -saturated aqueous solution of 1,2,4-trihydroxybenzene ($5 \times 10^{-4} \text{ mol dm}^{-3}$) in 0.1 mol dm^{-3} KCl was electrolysed in an electrochemical set-up.⁹ This consists essentially of a closed coulometric cell with two platinum electrodes and a SCE as reference.¹⁰ The potential drop across the cell is kept constant by means of a EG & G 273A potentiostat. During the electrolysis small samples (typically 10^{-3} dm^{-3}) of the reaction solution are taken from the cell at regular intervals *via* a syringe-pump arrangement into an optical cell (0.1 cm pathlength) in a Hewlett-Packard 8452A spectrophotometer for analysis. Each sample is then returned to the electrolysis cell after the spectrum is recorded. The pH of the 1,2,4-trihydroxybenzene solution was adjusted by using $5 \times 10^{-3} \text{ mol dm}^{-3}$ acetate, phosphate or borate buffers between pH 3 and 8.

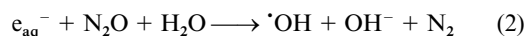
Results and discussion

Radical-generating system

Hydroxyl radicals have been generated in the radiolysis of water [reaction (1)]. The radiation chemical yields (G values) of these

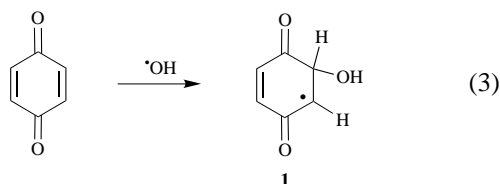


primary water radicals are $G(\text{e}_{\text{aq}}^-) \approx G(\cdot\text{OH}) = 2.9 \times 10^{-7} \text{ mol J}^{-1}$ and $G(\text{H}^\cdot) = 0.6 \times 10^{-7} \text{ mol J}^{-1}$. N_2O is used to convert the solvated electrons into $\cdot\text{OH}$ [reaction (2)].¹¹



Rate constant of the reaction of the OH radical with benzoquinone

Pulse radiolysis of an N_2O -saturated aqueous solution of benzoquinone (BQ) at pH 6.2 (natural pH) produces a transient spectrum (represented by ● in Fig. 1) which agrees with the one reported by Adams and Michael.⁵ For the determination of the rate constant of the addition of OH radicals to BQ [reaction (3)] they monitored the absorbance build-up at 450



nm from which a rate constant of $k_3 = 1.2 \times 10^9 \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$ was calculated.⁵ At the time, the mechanistic complexities (see below) were not realized. We have now redetermined this rate constant by competition kinetics with thiocyanate and obtained $k_3 = 6.6 \times 10^9 \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$. Corrections have been made for the absorbance of the transient species resulting from reaction (3) at 480 nm where $(\text{SCN})_2^{\cdot-}$ has its maximum. Further data presented below support the new (higher) value.

The most conspicuous feature of the transient spectrum observed in the BQ solution (represented by ● in Fig. 1) is that the rate of absorbance build-up is several times higher when monitored at around 330 nm (inset A in Fig. 1, $k_{\text{obs}} = 2.1 \times 10^6 \text{ s}^{-1}$) than at 400 nm and above (*cf.* inset B in Fig. 1, $k_{\text{obs}} = 6.9 \times 10^5 \text{ s}^{-1}$). These two distinct kinetic processes represent the formation of two different species. Evidently only the build-up at 330 nm is sufficiently fast to reflect reaction (3), since k_3 is known from competition kinetics (see above).

Fig. 2 shows some aspects of the kinetic behaviour of the system in near neutral solution. To show that the above observed fast absorbance build-up at 330 nm represents the initial addition of OH radicals to BQ [reaction (3)], k_{obs} moni-

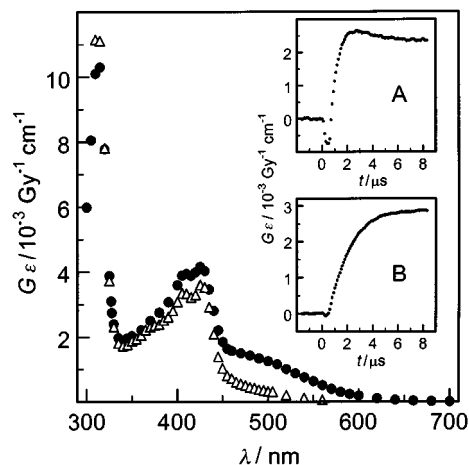


Fig. 1 Transient spectrum (●) obtained 8 μs after electron pulse irradiation (*ca.* 6 Gy/pulse) of N_2O -saturated solution of BQ ($4 \times 10^{-4} \text{ mol dm}^{-3}$) at pH 6.2. Inset A: absorbance build-up at 330 nm; inset B: absorbance build-up at 440 nm. For comparison the spectrum of the semibenzoquinone radical anion (Δ) obtained 8 μs after electron pulse irradiation (*ca.* 5 Gy/pulse) of an N_2O -saturated solution of NaN_3 ($5 \times 10^{-2} \text{ mol dm}^{-3}$) and hydroquinone ($10^{-3} \text{ mol dm}^{-3}$) at pH 7.6 is also shown.

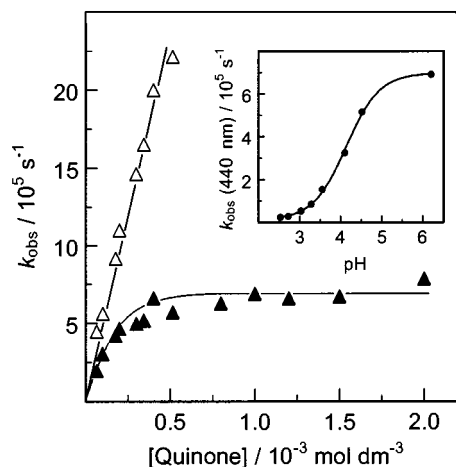


Fig. 2 Dependence of the observed first-order rate constants of absorbance build-up at 330 (Δ) and at 440 nm (\blacktriangle) on BQ concentration in N_2O -saturated solution at pH 6.2 (conditions as in Fig. 1). Inset: pH dependence of k_{obs} of absorbance build-up at 440 nm in $10^{-3} \text{ mol dm}^{-3}$ BQ solution.

tored at this wavelength has been plotted against the BQ concentration (Δ in Fig. 2). Indeed, according to this linear plot, $k_3 = 5.0 \times 10^9 \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$ is obtained. This is in good agreement with the value of $6.6 \times 10^9 \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$ obtained independently from competition kinetics.

Unlike the fast build-up at 330 nm, the slower absorbance build-up at 440 nm represents a much more complicated process. Its first-order rate constant (\blacktriangle in Fig. 2) increases with the BQ concentration only up to about $4 \times 10^{-4} \text{ mol dm}^{-3}$, at higher BQ concentration k_{obs} reaches a plateau value of $6.9 \times 10^5 \text{ s}^{-1}$, independent of the BQ concentration up to $2 \times 10^{-3} \text{ mol dm}^{-3}$. Pulse radiolysis experiments carried out at the Institut für Oberflächenmodifizierung have shown that k_{obs} remains constant up to a BQ concentration of $6 \times 10^{-3} \text{ mol dm}^{-3}$ (data not shown). Furthermore, when the pH of the BQ solution is varied (at a fixed BQ concentration of $10^{-3} \text{ mol dm}^{-3}$) this plateau value of k_{obs} decreases with increasing acidity of the solution (from 6.9×10^5 at pH 6.2 to $2.4 \times 10^4 \text{ s}^{-1}$ at pH 2.5). This pH dependence is a sigmoidal curve with an inflection point at pH 4.2 (inset in Fig. 2).

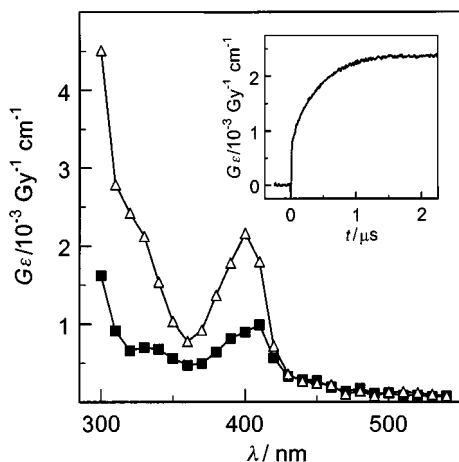


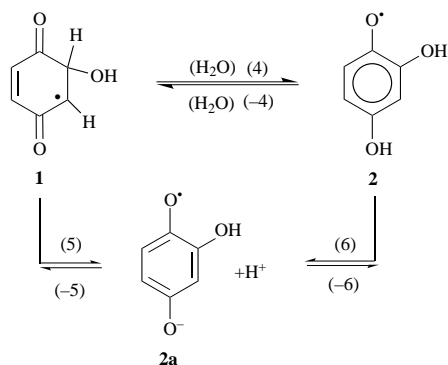
Fig. 3 Pulse radiolysis (5 ns pulses of *ca.* 17 Gy/pulse) of N_2O -saturated BQ solution ($5 \times 10^{-3} \text{ mol dm}^{-3}$) at pH 2. Spectra recorded 80 (■) and 750 ns (△) after the pulse. Inset: the absorption build-up at 330 nm.

To obtain further information concerning the OH-adduct radical **1** and its subsequent transformation the ns pulse radiolysis facilities were used to extend our kinetic measurements into the very short time of $<1 \mu\text{s}$ after the pulse.

Enolization of the benzoquinone–OH-adduct radical

Fig. 3 shows the transient absorption spectra in $5 \times 10^{-3} \text{ mol dm}^{-3}$ BQ solution at pH 2 (spectra recorded in neutral solution are distorted considerably by the semiquinone radical anion which is produced at this high BQ concentration by direct scavenging of about 40% of solvated electrons by BQ and are not shown here). Under these conditions the reactions of OH radicals, H atoms and about one-fifth of solvated electrons with BQ are completed within 50 ns after the pulse. The spectrum recorded 80 ns after the pulse (■ in Fig. 3) is thus essentially the spectrum of the OH-adduct radical **1** (with minor contributions from the H-adduct and the semiquinone radical). As shown in Fig. 3, radical **1** undergoes a transformation reaction to produce a new transient species, the spectrum of which (recorded 750 ns after the pulse, △ in Fig. 3) has a maximum at 400 nm. The inset in Fig. 3 shows the absorption build-up at 330 nm with $k_{\text{obs}} = 2.5 \times 10^6 \text{ s}^{-1}$.

We suggest that the OH-adduct radical **1** undergoes a very rapid, possibly water-assisted keto–enol tautomerization to give the 2,4-dihydroxyphenoxyl radical **2** [equilibrium (4),



$k_4 = 2.5 \times 10^6 \text{ s}^{-1}$). Not surprisingly, reaction (4) is much faster than the enolization of non-radical enone species.^{12,13} The spectrum obtained in Fig. 3 (△) is attributed to radical **2**. This is likely to have its first $\text{p}K_{\text{a}}$ value in the pH region of 4–5 as found for other hydroxyphenoxyl radicals of similar type.^{14,15} In neutral solution it dissociates into the 2,4-dihydroxyphenoxyl radical anion **2a** [equilibrium (6)]. The formation of **2a** from **1** directly [reaction (5)] is considered insignificant as

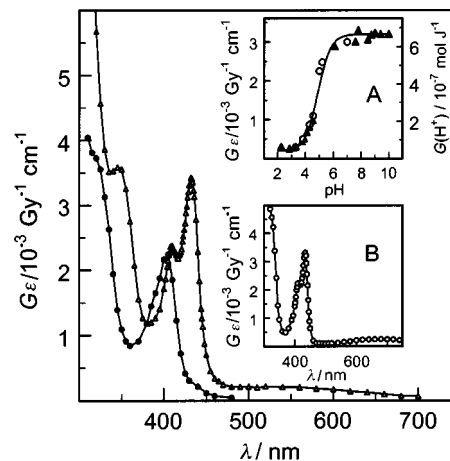
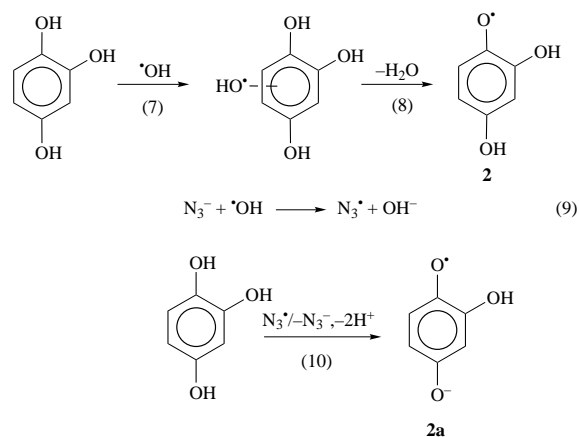


Fig. 4 Pulse radiolysis of 1,2,4-trihydroxybenzene ($10^{-3} \text{ mol dm}^{-3}$) in N_2O -saturated solution, *ca.* 3 Gy/pulse. Experiments for $\text{pH} > 7$ were carried out in the presence of NaN_3 ($5 \times 10^{-2} \text{ mol dm}^{-3}$). The spectrum of the 2,4-dihydroxyphenoxyl radical **2** at pH 3.3 (●) was obtained 30 μs after the pulse. The spectrum of the 2,4-dihydroxyphenoxyl radical anion **2a** at pH 7.6 (△) was obtained 16 μs after the pulse. Inset A: pH dependence of the absorbance at 430 nm (▲) and of $G(\text{H}^+)$ (○) obtained by conductance measurements. Inset B: Spectrum of **2a** obtained 16 μs after the pulse at pH 10 in the presence of $10^{-2} \text{ mol dm}^{-3}$ borate buffer.

deprotonation/protonation processes in C–H-acid systems are comparatively slow.¹⁶

2,4-Dihydroxyphenoxyl radical

To support the above reaction mechanism we have taken a closer look at the 2,4-dihydroxyphenoxyl radical **2** which can be readily generated directly from 1,2,4-trihydroxybenzene independent of the BQ system. This can be achieved either by addition of the hydroxyl radical [reaction (7)] followed by water elimination [reaction (8)] of the tetrahydroxycyclohexadienyl radical in acidic solution (spectrum ● in Fig. 4), similar to the case of hydroquinone and other polyhydroxycyclohexadienyl radicals,^{5,17} or by the reaction of the azide radical [reaction (9)]



in basic solution [reaction (10)] [spectra at pH 7.6 (△) and at pH 10 (inset B) in Fig. 4].

A comparison of the authentic spectrum of radical **2** (● in Fig. 4) with the spectrum obtained above in $5 \times 10^{-3} \text{ mol dm}^{-3}$ BQ solution (△ in Fig. 3) confirms our assignment of the latter to that of radical **2**.

Fig. 4 also shows the shift of the absorption maximum of radical **2** at 400 nm in acidic solution to 430 nm at pH 7.6. In the inset A of Fig. 4 the absorbance at 430 nm as well as the value of $G(\text{H}^+)$ obtained by conductometric measurements are plotted as functions of pH. From this sigmoidal curve the first $\text{p}K_{\text{a}}(\mathbf{2}) = 4.9 \pm 0.2$ is obtained [equilibrium (6)]. With this $\text{p}K_{\text{a}}$

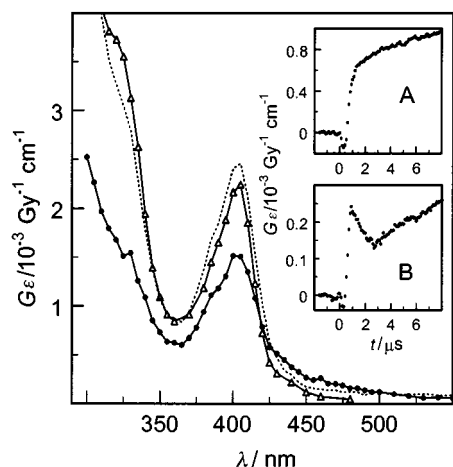


Fig. 5 Pulse radiolysis of 1,4-benzoquinone (10^{-3} mol dm $^{-3}$) in N $_2$ O-saturated solution at pH 3.1, *ca.* 3 Gy/pulse. Rapid conversion of radical **1** into the 2,4-dihydroxyphenoxyl radical **2**. Spectra of the transients taken 1 (●) and 2 μs (Δ) after the pulse. Inset A: absorption build-up at 370 nm. Inset B: absorption build-up at 470 nm. For comparison, the spectrum taken 30 μs after the pulse in the radiolysis of 1,2,4-trihydroxybenzene (10^{-3} mol dm $^{-3}$) in N $_2$ O-saturated solution at pH 3.3 is also shown (main graph, dotted line).

value the acid dissociation [reaction (6)] of radical **2** has a rate constant of $k_6 = 6.3 \times 10^5$ s $^{-1}$ if one assumes $k_{-6} = 5 \times 10^{10}$ dm 3 mol $^{-1}$ s $^{-1}$.

The assignment of the second pK $_a$ value of radical **2** is more difficult. From neutral to basic pH (*cf.* inset B in Fig. 4) the main absorption of radical anion **2a** appears unchanged at 430 nm (with a shoulder at 410 nm). Between pH 8 and 9 there is a sharp reduction of the absorbance at 360 nm. This is accompanied by a very weak increase at the longer wavelength region 650–700 nm. However, since these changes appear not to follow a smooth sigmoidal curve pattern, other possible factors such as a base-catalysed tautomerization of **2a** to a dienone radical anion (*cf.* ref. 17) might bring about these changes rather than the deprotonation of the radical anion **2a** to the corresponding dianion.

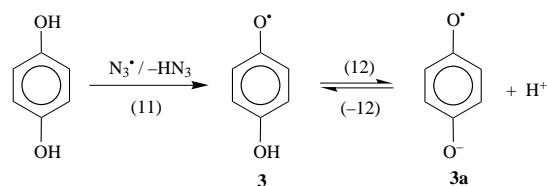
Radiolysis in acidic solution

Further confirmation of the above reaction mechanism was obtained in μs pulse radiolysis of low concentration of BQ in acidic solution. As shown in Fig. 5 the situation here is similar to that observed in the ns timescale for a high concentration of BQ (*cf.* Fig. 3). The initial spectrum taken 1 μs after the pulse (● in Fig. 5, attributed to **1**), is transformed rapidly into spectrum Δ which resembles closely that of the authentic 2,4-dihydroxyphenoxyl radical **2** (dotted line in Fig. 5 is taken from the spectrum in Fig. 4). This transformation is best observed in the wavelength region >430 nm where radical **1** shows stronger absorption than radical **2**. In the inset B of Fig. 5 the initial fast build-up immediately after the pulse [reaction (3)] is followed by an absorption decay as **1** tautomerizes into **2** [reaction (4)]. This absorption decay is too fast here for kinetic evaluation, but its rate is comparable to the rate of reaction (4) determined above.

The second (slower) absorption build-up observed after 2 μs (*cf.* insets in Fig. 5) represents the subsequent reaction of radical **2** which is much slower in acidic solution than in neutral solution as already mentioned above (*cf.* inset in Fig. 2).

Oxidation of the 2,4-dihydroxyphenoxyl radical by benzoquinone

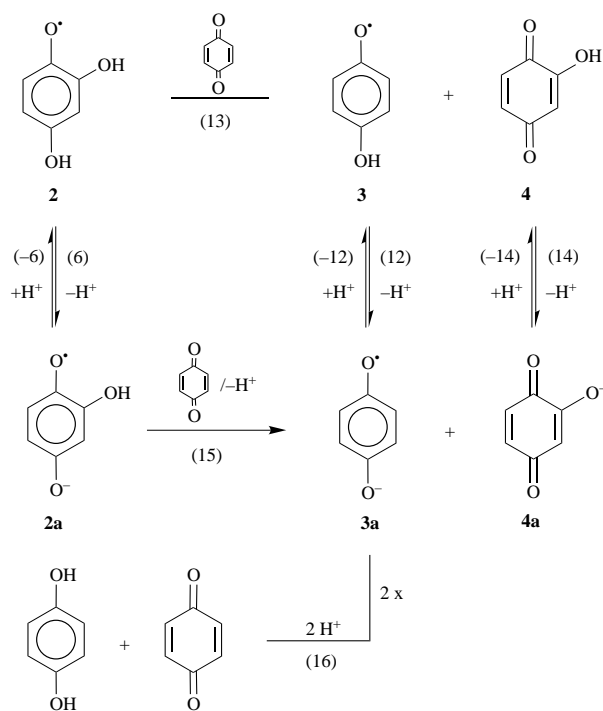
At the end of a build-up process with $k_{\text{obs}} = 6.9 \times 10^5$ s $^{-1}$ the spectrum recorded 8 μs after the pulse (● in Fig. 1) shows that the transient here is neither the radical **2** nor its anion **2a** (*cf.* Fig. 4). On the other hand, if this spectrum is compared with the spectrum of the well-known semibenzoquinone radical



anion **3a** (Δ in Fig. 1) [pK $_a$ (**3**) = 4.0, equilibrium (12)]⁵ produced by the reaction of the azide radical with hydroquinone [reactions (9) and (11)], the close similarity of these two spectra in the wavelength region 300–450 nm is obvious.

The divergence of the two spectra in Fig. 1 in the wavelength region above 450 nm suggests the presence of an additional species besides the semibenzoquinone radical anion **3a**. Indeed, whereas the absorbance < 320 nm disappears (bimolecular rate constant, $2k_{16} = 3.1 \times 10^8$ dm 3 mol $^{-1}$ s $^{-1}$), the absorbance between 320–500 nm decays only partly, and that above 500 nm does not change at all, even at 0.1 s after the pulse, *i.e.* the absorption at 500 nm can be ascribed to a permanent product with an absorption maximum at 480 nm at pH 6.2 as shown in Fig. 6.

The explanation of these phenomena is as follows. At pH 6.2, the 2,4-dihydroxyphenoxyl radical **2** is deprotonated to the corresponding semiquinone radical anion **2a** [equilibrium (6)]. This is rapidly oxidized by BQ [reaction (15)] to produce the semiquinone radical anion **3a** and the 2-hydroxy-1,4-benzoquinone anion **4a**. The former subsequently decays bimolec-



ularly producing hydroquinone and BQ [reaction (16)]. The final product observed 0.1 s after the pulse with an absorption maximum at 480 nm is therefore attributed to **4a** (Fig. 6).

Reaction (15) is similar to the rapid oxidation of the methylsemiquinone radical by BQ reported previously.⁶ This results in the quantitative formation of methylbenzoquinone.

Returning to Fig. 2, one observes that at BQ concentrations < 4×10^{-4} mol dm $^{-3}$, k_{obs} at 440 nm (▲) increases with BQ concentration. Reaction (15) is responsible for this build-up. From the slope of this plot, $k_{15} \approx 2 \times 10^9$ dm 3 mol $^{-1}$ s $^{-1}$ can be estimated. At BQ concentrations > 4×10^{-4} mol dm $^{-3}$ k_{obs} reaches the limit at 6.9×10^5 s $^{-1}$ which is the same as k_6 calculated for the acid dissociation reaction of radical **2**. In other words, under these conditions the rate of formation of the products in reaction (15) is limited by k_6 .

The value estimated above for reaction (15) is not unusual for rate constants of electron transfer for semiquinones to benzoquinones² since the difference in one-electron reduction potentials (the driving force) of such a reaction, $\Delta E \approx 210$ mV [the reduction potential of benzoquinone² $E(Q/Q^{\cdot-}) = 99$ mV at pH 7 and that of the 2,4-dihydroxyphenoxyl radical¹⁸ **2** (or anion **2a**) $E(\text{ArO}^{\cdot-}/\text{ArO}^-) = -110$ mV at pH 13.5], is sufficiently high. The rate constant for the analogous reaction by methyl-semiquinone has been estimated to be *ca.* 4×10^8 dm³ mol⁻¹ s⁻¹ on the basis of $\Delta E = 76$ mV.⁶

In acidic solution the equilibrium (6)/(-6) lies increasingly to the side of radical **2**. The latter is oxidized by BQ [reaction (13)] with more difficulty than its anion.¹⁸ Under these conditions reaction (13) becomes the rate-determining step. Since k_{obs} (440 nm) is reduced to 2.4×10^4 s⁻¹ at pH 2.5 (*cf.* inset of Fig. 2), it follows that $k_{13} \leq 2.4 \times 10^7$ dm³ mol⁻¹ s⁻¹.

From the above reaction scheme, where the subsequent reactions of radical **2** depend on its state of dissociation [equilibrium (6)/(-6)], it can be readily shown that at the inflection point of the kinetic-pK plot shown in the inset of Fig. 2, $[\text{H}^+] = (k_6 + k_{15} \times [\text{BQ}]) / k_{-6}$. Under these conditions $k_{15} \times [\text{BQ}] = 2 \times 10^9 \times 10^{-3} = 3 k_6$. Hence, $[\text{H}^+] = 4 k_6 / k_{-6}$, $\text{pH} = -0.6 + \text{p}K_a = -0.6 + 4.9 = 4.3$. The actual inflection point found at pH 4.2 neatly confirms the above reaction scheme.

Further support of the proposed mechanism by conductance measurements

Additional evidence in favour of the foregoing mechanism is

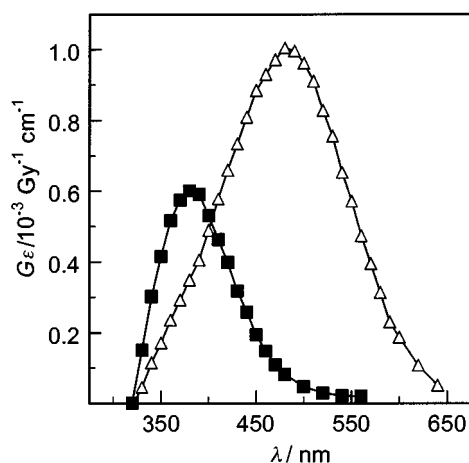


Fig. 6 Pulse radiolysis of N₂O-saturated solution of BQ (10^{-3} mol dm⁻³; *ca.* 15 Gy/pulse). Spectra of the final products taken 0.1 s after the pulse at pH 2.5 (■, 2-hydroxy-1,4-benzoquinone) and at pH 6.2 (△, anion of 2-hydroxy-1,4-benzoquinone).

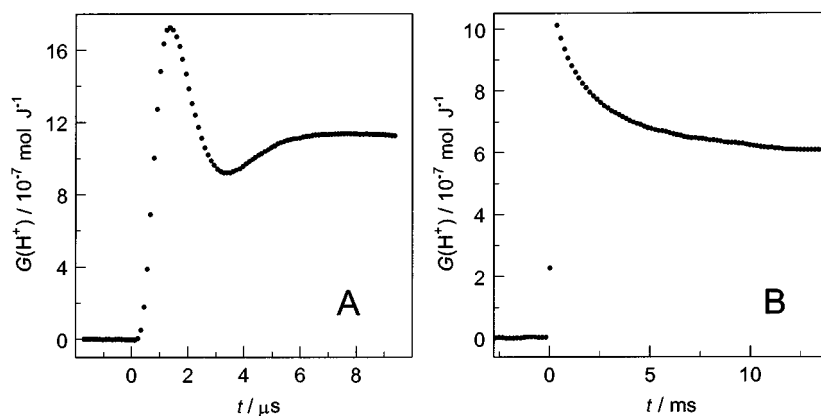


Fig. 7 Pulse radiolysis of N₂O-saturated solution of BQ (10^{-3} mol dm⁻³) at pH 6.2. Conductance changes in the μs (A), and ms (B) time ranges. The initial spike appearing during the first 3 μs after the pulse arises from interference of the pulse with the detection devices and does not reflect the actual conductance change.

provided by the measurement of conductance changes. In an N₂O-saturated solution of BQ at pH 6.2 (natural) irradiated with an electron pulse, following the initial jump caused by the formation and subsequent neutralization of H⁺ within the pulse [reaction (1)] a transient conductance build-up equivalent to $G(\text{H}^+) = 11.8 \times 10^{-7}$ mol J⁻¹ is observed several μs after the pulse (Fig. 7A). This conductance increase subsequently decays *via* second-order kinetics to a lower and permanent level (monitored up to 0.1 s after the pulse) equivalent to $G(\text{H}^+) = 5.5 \times 10^{-7}$ mol J⁻¹ (Fig. 7B).

At neutral pH, radical **3** is fully deprotonated [equilibrium (12)/(-12); $\text{p}K_a(\mathbf{3}) = 4.0$]. The G value of proton formation observed at twice the value of $G(\mathbf{2}) = G(\cdot\text{OH}) = 5.8 \times 10^{-7}$ mol J⁻¹ 6 μs after the pulse (Fig. 7A), indicates that product **4** is also fully deprotonated at pH 6. After the disappearance of the semibenzoquinone radical anion by bimolecular decay [reaction (16)], the remainder of the conductance increase is solely due to the final product, the anion of 2-hydroxy-1,4-benzoquinone, **4a**.

In acidic solution, the pattern of conductance change in the N₂O-saturated solution of BQ is similar to that observed at pH 6.2, except that the magnitude of the conductance increase [*i.e.* $G(\text{H}^+)$] becomes smaller in more acidic solution (Fig. 8). Both curves in Fig. 8, measured 20 μs and 0.1 s after the pulse, show their inflection points at pH *ca.* 4.3. The curve measured at 20 μs reflects the sum of the semibenzoquinone radical **3** and 2-hydroxy-1,4-benzoquinone **4**, whereas the value measured at 0.1 s, *i.e.* after all radicals have disappeared by bimolecular decay, must reflect $\text{p}K_a(\mathbf{4}) = 4.3$ [equilibrium (14)].

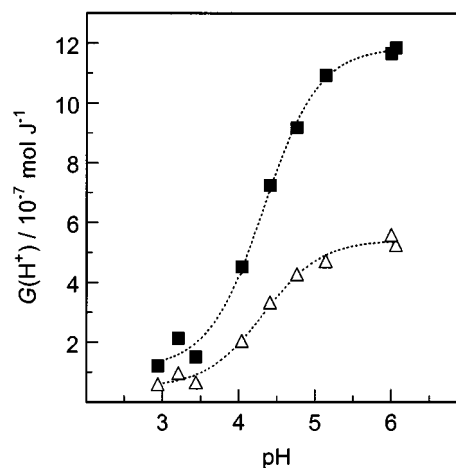


Fig. 8 Dependence of proton formation monitored as conductance increase 20 μs (■) and 0.1 s (△) after the pulse (6–8 Gy/pulse) in N₂O-saturated solutions of BQ (10^{-3} mol dm⁻³)

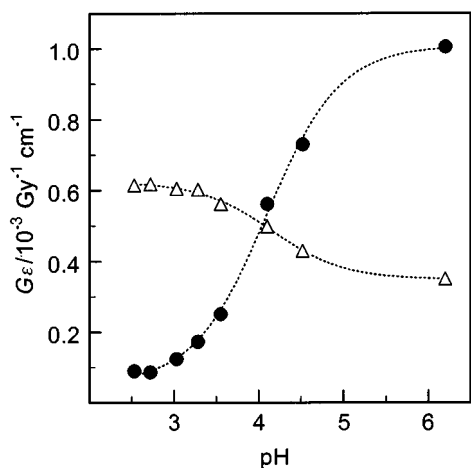


Fig. 9 Pulse radiolysis of N_2O -saturated solutions of BQ (10^{-3} mol dm^{-3}), pH dependence of the absorbance at 380 nm (Δ) and at 480 nm (\bullet) of the final product (2-hydroxy-1,4-benzoquinone **4**) monitored 0.1 s after the pulse.

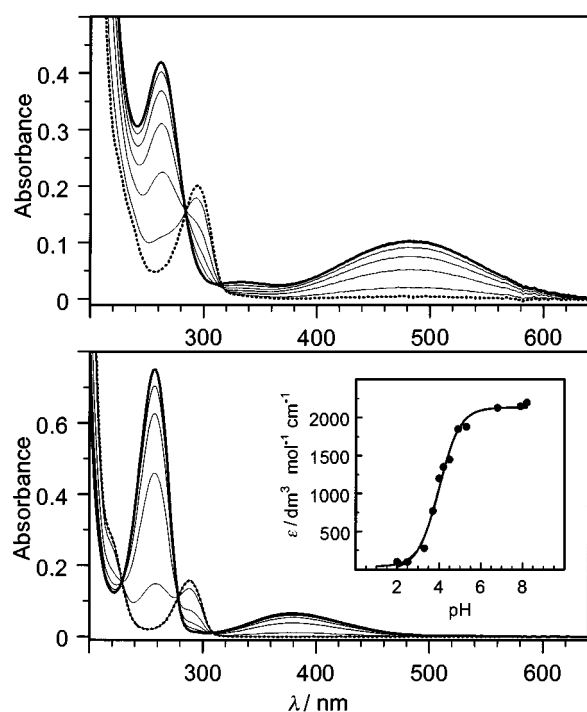


Fig. 10 Time-dependent spectra taken during the two-electron oxidation of 1,2,4-trihydroxybenzene (5×10^{-4} mol dm^{-3}). Dotted lines represent the spectrum of the starting material. The final spectra (bold) were taken at the end of the electrolysis process (typically after 180 s). Upper: experiment carried out at pH 8.2. Lower: experiment carried out at pH 2.0. Inset: pK_a plot of the absorbance monitored at 482 nm.

pK_a value of product **4** determined by optical and spectro-electrochemical measurements

It has been shown in Fig. 6 that the absorption characteristics of the final product assigned to 2-hydroxy-1,4-benzoquinone **4** change from acidic pH to neutral solution. The absorption maximum at 480 nm ($\epsilon = 1800$ dm^3 mol^{-1} cm^{-1} assuming a G value of 5.6×10^{-7} mol J^{-1} for **4a**) in neutral solution is replaced by a maximum at 380 nm at pH 2.5 ($\epsilon = 1080$ dm^3 mol^{-1} cm^{-1} , for **4**). The changes in absorbance of the BQ solution at these two wavelengths with pH result in the two pK_a curves shown in Fig. 9. From the intercept of these two curves,

$pK_a(\mathbf{4}) = 4.0$ is obtained, which is in good agreement with the value determined by the conductometry method.

The assignment of the final product as 2-hydroxy-1,4-benzoquinone **4** receives further support from the results of an electrochemical oxidation of 1,2,4-trihydroxybenzene to give the product **4**.¹⁹ The cyclic voltammograms of 1,2,4-trihydroxybenzene exhibit irreversible waves at 0.2–0.4 V vs. SCE, depending on pH. The electrolysis was carried out at 0.5 V. In Fig. 10 the spectral changes during the anodic oxidation process are shown at pH 8.2 (upper) and at pH 2.0 (lower). After about 180 s the current dropped to background level, and two electrons per molecule of the starting material were transferred. The final product 2-hydroxy-1,4-benzoquinone **4** thus obtained (spectra shown in bold) has an absorption maximum at 482 nm ($\epsilon = 2200$ dm^3 mol^{-1} cm^{-1}) at pH 8.2 while in acid solution its maximum is shifted to 380 nm ($\epsilon = 1400$ dm^3 mol^{-1} cm^{-1}).

The absorption characteristics of product **4** are thus identical to those of the final product obtained by pulse radiolysis (Fig. 6). The pH dependence of the absorption of this product monitored at 482 nm (inset in Fig. 10) shows an inflection point at pH 4.1 which is attributed to $pK_a(\mathbf{4})$. This value is in good agreement with that determined by pulse radiolysis (conductance and optical measurements, see above).

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