Pulse Radiolytic One-electron Oxidation of some Dihydroxy-substituted Anthraquinones

Haridas Pal, Dipak K. Palit, Tulsi Mukherjee* and Jai P. Mittal

Chemistry Division, Bhabha Atomic Research Centre, Bombay 400 085, India

The spectroscopic characteristics and the kinetic parameters associated with the transients formed on oneelectron oxidation of quinizarin (1,4-dihydroxy-9,10-anthraquinone), quinizarin 2- and 6-sulfonates, 1,5dihydroxy-9,10-anthraquinone and 1,8-dihydroxy-9,10-anthraquinone have been studied by pulse radiolysis and kinetic spectrophotometric techniques, using OH^{*}, O^{*-}, N₃^{*}, Br₂^{*-} and ^{*}CH₂CHO as the oxidising radicals. The pK_a and the disproportionation equilibria of the semi-oxidised quinones have been studied for the water-soluble sulfonates. In contrast to the complex decay of the semi-oxidised naphthazarin (5,8-dihydroxy-1,4-naphthoquinone), the semi-oxidised anthraquinone derivatives decay by simple second-order kinetics. The pK_a values of the latter are also much higher (ca. 8) compared to the former (ca. <4). The differences observed are attributed to the loss in symmetry in the free radical structures of the semi-oxidised anthraquinone derivatives.

The chemistry of semiquinone radicals, produced by oneelectron reduction of dihydroxy quinones has been studied in great detail.¹⁻⁷ One-electron oxidation of dihydroxy quinones at their phenolic OH site can also produce semioxidised quinone as free radicals.⁸⁻¹² The oxidation of dihydroxy quinones, already having one quinone moiety, will introduce a benz-semiguinone moiety into the compound and thus their properties are expected to differ from those produced by simple phenol oxidation. The 1,4-dihydroxy quinones constitute the main chromophoric part of the quinonoid antitumour drugs,13 such as adriamycin and daunomycin, and one-electron oxidation of adriamycin has been implicated to be associated with its physiological activity by Pietronigro et al.¹⁴ The sulfonate derivatives of anthraquinones have important photochemical and redox applications.⁵ The corresponding 1,5- and 1,8-dihydroxy anthraquinones are also interesting chemicals, the study of which provides important information on the effect of intra-e. molecular hydrogen bonding as well as the substitution effect. In this paper the one-electron oxidation of a number of dihydroxy anthraquinones has been reported with special reference to their absorption characteristics and the kinetics of formation and decay. Since all the simple dihydroxy anthraquinones, except their sulfonate derivatives, are almost insoluble in aqueous media below ca. pH 10.5, and since no oxidation studies have so far been carried out in organic or aqueous-organic mixed solvents, these one-electron oxidation

studies could be carried out only in aqueous alkaline (pH > 10.5) solutions. For the sulfonate derivatives of the 1,4dihydroxy anthraquinones, however, the one-electron oxidation has been studied for a wide pH range of *ca.* 1–14 using OH[•], ^{8,15} O^{•-}, ^{8,15} N[•]₃, ^{8,16–18} Br⁻₂ ^{-19,20} or [•]CH₂CHO^{21,22} [at the strong acid (*ca.* pH 1) condition] as the oxidising agents. The dihydroxy anthraquinones and their sulfonate derivatives investigated in the present work are given in Scheme 1.

Experimental

1,4-QH₂ and 1,8-QH₂ were obtained from Aldrich (USA) and 1,5-QH₂ from Tokyo Kasei Kogyo (TCI, Japan) and were purified by repeated crystallisation from water-methanol mixtures (1,4-QH₂) or hexane (1,5-QH₂ and 1,8-QH₂). 1,4-QH₂-2S and 1,4-QH₂-6S were donated by Dr. J. M. Bruce of Manchester University and further purified by repeated crystallisation from water. All other chemicals used [NaN₃, KBr, (CH₂OH)₂, KSCN, NaH₂PO₄, Na₂HPO₄, NaOH, HCIO₄] were the purest grade available from Fluka, Merck or BDH and were used without further purification. All solutions were made in triply distilled water. The oxygen-free gases used for deaeration or other specific purposes were nitrogen from Indian Oxygen Ltd. and N₂O from British Oxygen Co. The solutions were made strongly alkaline with 1 mol dm⁻³ NaOH for studies at *ca*. pH 14.

R^4 R^3 R^2 R^2						
		structure				
compounds	abbreviations	R ¹	R ²	R ³	R ⁴	R ⁵
1,4-dihydroxy-9,10-anthraquinone quinizarin-2-sulfonate quinizarin-6-sulfonate 1,5-dihydroxy-9,10-anthraquinone 1,8-dihydroxy-9,10-anthraquinone	(1,4-QH ₂) (1,4-QH ₂ -2S) (1,4-QH ₂ -6S) (1,5-QH ₂) (1,8-QH ₂)	H SO ₃ H H H	ОН ОН ОН Н Н	Н Н Н ОН Н	H H SO₃ H H	H H H H OH

Details of the pulse radiolysis arrangements are as described earlier.^{23,24} A Shimadzu model UV-160 A spectrophotometer and an Orion ionalyser model 901 fitted with a combination electrode were used for absorption and pH measurements.

The dose absorbed was measured by thiocyanate dosimetry²⁵ (10^{-2} mol dm⁻³ KSCN, air-saturated) using $\xi_{(SCN)_2}^{500 nm} = 710 \text{ m}^2 \text{ mol}^{-1}$ and G, defined as the number of moles formed per Joule (or molecules formed per 100 eV) of energy absorbed, as $3.005 \times 10^{-7} \text{ mol J}^{-1}$ [or 2.9 molecules (100 eV)⁻¹].

Unless otherwise specified, NaN₃ ($5 \times 10^{-2} \text{ mol dm}^{-3}$), KBr ($10^{-1} \text{ mol dm}^{-3}$), ethylene glycol (1 mol dm^{-3}) were used to generate the oxidising radicals N₃, Br₂⁻ and 'CH₂CHO, respectively.

Results and Discussion

When an electron pulse is delivered to an N_2O -saturated solution of a dihydroxyquinone or its sulfonate derivatives (in general abbreviated as QH_2) the following reactions take place, producing a transient radical formed by one-electron oxidation of the quinones. The oxidation generally takes place by the reaction of the OH[•] radical at one of the two phenolic OH sites of the dihydroxy quinones, followed by elimination of water.⁸⁻¹² The reactions taking place can be shown as,

$$H_2O \rightarrow e_{aq}^-, H^{\bullet}, OH^{\bullet}, other products$$
 (I)

$$e_{aq}^{-} + N_2 O \rightarrow [N_2 O]^{\bullet -} \xrightarrow{H_2 O} N_2 + OH^{\bullet} + OH^{-}$$
(II)

$$QH_2 + OH^{\bullet} \rightarrow QH^{\bullet} + H_2O \text{ (or, } Q^{\bullet-} + H_3O^+\text{)}$$
 (III)

In alkaline solutions (pH > 12) OH[•] will be replaced^{8,15} by O^{-} .

$$OH' + OH^{-} \xrightarrow{pK_{a} = 11.9} O'^{-} + H_{2}O \qquad (IV)$$

Apart from normal electron removal (oxidation) shown in reaction (III), OH[•] could partially add to the benzenoid ring containing OH substituents, to produce cyclohexadienyl-type radicals, which could subsequently be converted into the thermodynamically more stable oxygen-centred radicals (semi-oxidised quinones) by elimination of a molecule of water.⁵⁻¹² Moreover, OH[•] could also add on to the other aromatic rings of the quinones to produce quinone-OH[•] adducts.⁸⁻¹² To avoid this, an excess of additives such as NaN₃, KBr or (CH₂OH)₂ was used in N₂O-saturated solutions of the dihydroxy quinones where OH[•]/O^{•-} radicals were quantitatively replaced by the weaker but selective secondary oxidising agents, N^{*}₃, ^{8,16-18} Br^{*-}₂ ^{-19,20} and

 $^{\circ}CH_{2}CHO$,^{21,22} respectively, and these secondary oxidising agents in turn oxidised the quinones selectively at their phenolic OH sites.

$$OH'(O^{*-}) + N_3^{-} \longrightarrow OH^{-}(O^{2-}) + N_3^{*}$$
(V)

$$OH^{\bullet} + Br^{-} \longrightarrow OH^{-} + Br^{\bullet} \xrightarrow{Br^{-}} Br_{2}^{\bullet-}$$
(VI)

$$OH^{\bullet}(H^{\bullet}) + (CH_2OH)_2 \xrightarrow{H^+} 2H_2O(H_2) + CH_2CHO$$
(VII)

 $QH_2 + N_3^{\bullet}$ (or $Br_2^{\bullet-}$ or CH_2CHO)

$$\rightarrow$$
 QH[•] (or, Q^{•-} + H⁺) + N₃⁻ (or 2Br⁻ or CH₃CHO) (VIII)

One-electron reduction of the quinones by H[•] may occur to a small extent at pH < 11 by reduction of the quinone moiety by addition of H[•], followed by deprotonation. However, as the contribution of this process is very small (<10%) in comparison to reactions (III) and (VIII), it is not considered further.

Neglecting the delocalisation of the electron, the structures of the neutral forms of the semi-oxidised quinones (QH^{*}) produced by one-electron oxidation can be represented as shown in Scheme 2. Depending on the pH of the solution, the semioxidised quinones can also exist in their monoanionic form, where the phenolic OH group will be deprotonated. As the protonation of the SO₃⁻ group occurs at very low pH (<1), it is not considered here.

One-electron Oxidation of 1,4-QH₂-2S and 1,4-QH₂-6S

Difference absorption spectra, representing the difference in absorbance between the semi-oxidised quinone and the parent quinone, produced on oxidation of 1,4-QH₂-2S and 1,4-QH2-6S by N3, OH, O' or 'CH2CHO radicals under appropriate conditions, were obtained after the completion of reactions (III) or (VIII). The difference absorption spectra of the transients produced at ca. pH 1 (using 'CH₂CHO as the oxidising agent) and at pH 11 (using N₃ as the oxidising agent) for 1,4-QH₂-2S and 1,4-QH₂-6S are shown in Fig. 1 and 2. Since the parent quinones do not have any absorption in the wavelength range 650-760 nm, a careful investigation of the difference spectra (Fig. 1 and 2) in this wavelength region clearly suggests that for both the quinones the ionic form of the semi-oxidised quinone existing at ca. pH 1 is different from that existing at pH 11. An attempt was made to determine the pK_a of the semi-oxidised quinones by observing the change in absorbance with pH at 720 nm where the

R ⁵ O O'	semi-oxidised quinone (neutral form) (QH')	R ¹	R ²	R ³	R ⁴	R ⁵
	(a) 1,4-QH*	H	ОН	Н	H	H
	(b) 1,4-QH-2S	SO ₃	ОН	Н	H	H
	(c) 1,4-QH-6S	H	ОН	Н	SO ₃	H
	(d) 1,5-QH*	H	Н	ОН	H	H
	(e) 1,8-QH*	H	Н	Н	H	OH



Fig. 1 Difference absorption spectra of the semi-oxidised 1,4-QH₂-2S at *ca*. pH 1 (\bigcirc) and 11 (\bigcirc). The oxidising agents were 'CH₂CHO (*ca*. pH 1) and N₃ (pH 11). *Inset*: Variation of ΔA with pH at 720 nm (using N₃ as the oxidising agent). Dose = 9.4 Gy; [quinone] = 10⁻⁴ mol dm⁻³; [ethylene glycol] = 1 mol dm⁻³ and [N₃⁻] = 5 × 10⁻² mol dm⁻³

parent quinones do not absorb. The pH range 6–11 was investigated using N₃ as the oxidising radical. The sigmoid curves thus obtained are shown in the insets of Fig. 1 and 2, resulting in radical pK_a s of 7.9 and 8 for 1,4- \dot{Q} H-2S and 1,4- \dot{Q} H-6S, respectively. As the protonation of the N₃⁻ ion starts below *ca.* pH 5.5 (the pK_a of HN₃ is 4.7) reactions (V) and (VIII) become very slow, rendering the conversion $(QH_2 \rightarrow QH^{-})$ incomplete. Thus the sigmoid pK_a curves could not be extended below this pH. Considering the probable structures of the semi-oxidised quinones produced by the one-electron oxidation of the dihydroxy quinones (Scheme 2) it is expected that these pK_a values correspond to the protolytic equilibria between the neutral and monoanionic forms of the semi-oxidised quinones. Note that the pK_a values of 7.9 (1,4- \dot{Q} H-2S) and 8 (1,4- \dot{Q} H-6S) as estimated in this work



Fig. 2 Difference absorption spectra of the semi-oxidised 1,4-QH₂-6S at *ca*. pH 1 (\bigcirc) and 11 (\bigcirc). The oxidising agents were 'CH₂CHO (*ca*. pH 1) and N'₃ (pH 11). *Inset*: Variation of ΔA with pH at 720 nm (using N'₃ as the oxidising agent). Dose = 9.4 Gy; [quinone] = 10⁻⁴ mol dm⁻³; [ethylene glycol] = 1 mol dm⁻³ and [N'₃] = 5 × 10⁻² mol dm⁻³

are much higher than that reported $(pK_a < 4)$ for the semioxidised naphthazarin (5,8-dihydroxy-1,4-naphthoquinone).⁸ Differences in the properties of the semi-oxidised quinones produced from naphthoquinone and anthraquinone derivatives are due to the presence of the extra aromatic ring. In naphthazarin, one-electron oxidation leads to structures A (neutral) and B (anionic) as shown in Scheme 3. In the anionic form, the electron can be delocalised over the entire double ring system, giving it a high degree of symmetry and consequent stability. On the other hand, in the corresponding semi-oxidised anthraquinone derivatives, the presence of a third ring perturbs the symmetry. While the neutral form has a hydrogen-bonded structure (C), the anionic form (D) attains more phenolic character due to the resonance structures shown, causing an increase in the pK_a . The presence of sulfonate group and also its position in the ring appears to have no significant effect on the radical properties, since the pK_a of 2- and 6-sulfonate derivatives are virtually identical.

The true or corrected absorption spectra of the neutral and the monoanionic forms of the semi-oxidised quinones of 1,4-QH₂-2S and 1,4-QH₂-6S were obtained by correcting the corresponding difference spectra at *ca.* pH 1 and 11 (Fig. 1 and 2) for the parent quinone depletion. If a single form of



the semi-oxidised quinone is present, then at any wavelength λ , the absorption coefficient ($\varepsilon_{\rm R}/{\rm m}^2~{\rm mol}^{-1}$) of the semi-oxidised quinone is given by:

$$\varepsilon_{\mathbf{R}} = \varepsilon_{\mathbf{p}} + \frac{[\Delta A][G_{(\mathrm{SCN})_{2}^{-}}][\varepsilon_{(\mathrm{SCN})_{2}^{-}}]}{[A_{(\mathrm{SCN})_{2}^{-}}]G_{\mathbf{R}}}$$
(1)

where ε_p is the absorption coefficient in m² mol⁻¹ for the parent quinone absorption at wavelength λ , ΔA is the observed difference in absorbance of the semi-oxidised quinone at wavelength λ , $A_{(SCN)_2^{-1}}$ is the observed absorbance at 500 nm of the $(SCN)_2^{-1}$ radical produced in the dosimeter solution under isodose condition and $G_{\mathbf{R}}$ is the G value of the semi-oxidised quinone. The corrected absorption spectra of the semi-oxidised quinones were obtained applying eqn. (1) to the corresponding difference spectra and using the $G_{\mathbf{R}}$ value of 6.5 molecules per 100 eV for both the cases of N_3^{\bullet} and 'CH₂CHO as the oxidising agents.⁸ The true absorption spectra thus obtained for the neutral and monoanionic forms of semi-oxidised quinones of 1,4-QH2-2S and 1,4-QH2-6S are shown in Fig. 3 and 4 and the list of the radical absorption peaks and the corresponding absorption coefficient values are given in Table 1 for comparison.



Fig. 3 Corrected absorption spectra of the semi-oxidised 1,4-QH₂-2S at *ca.* pH 1 (\bigcirc) and 11 (\bigcirc)



Fig. 4 Corrected absorption spectra of the semi-oxidised 1,4-QH₂-6S at *ca.* pH 1 (\bigcirc) and 11 (\bigcirc)

Table 1 Spectroscopic characteristics of the semi-oxidised quinones of 1,4-QH₂, 1,4-QH₂-2S, 1,4-QH₂-6S, 1,5-QH₂ and 1,8-QH₂

	$\frac{\lambda/\mathrm{nm}}{\epsilon/10^2}\mathrm{m^2}\mathrm{mol^{-1}}$		
semi-oxidised quinone from	neutral (QH [*])	monoanion (Q ^{·-})	pK _a
1,4-QH ₂	a	390 (3.0)	a
1,4-QH ₂ -28	465 (8.0)	540 (7.0) 390 (2.9)	8.0 ± 0.1
1,4-QH ₂ -6S	468 (7.4)	420 (4.0) 600 (5.8)	7.9 ± 0.1
1,5-QH ₂ 1,8-QH ₂	a a	472 (10.5) 482 (8.3)	a a

a The absorption maxima and pK_a of the neutral semi-oxidised quinones could not be estimated due to insufficient solubility of the quinones in water at pH < 10.5.

The difference absorption spectra (not shown in the figure) obtained at pH 11 by using OH[•] or Br_2^{-} as the oxidising agents and at *ca*. pH 14 using O^{•-} or Br_2^{-} as the oxidising agents were nearly identical to those obtained using N₃[•] radical at these two pH. A little difference between the absorption spectra obtained by using N₃[•] and OH[•] in the 350–400 nm region may be due to the formation of a very small amount of quinone-OH[•] adduct.⁸⁻¹² However, the absorbance of the latter was so small that it was not possible to characterise the species unambiguously.

Since the parent quinones exist in two different ionic forms at pH 11 and ca. 14 $[pK_a(1) \text{ and } pK_a(2) \text{ for } 1,4-QH_2-2S \text{ are } 9.1 \text{ and } 12.6 \text{ and those for } 1,4-QH_2-6S \text{ are } 9.1 \text{ and } 11.6 \text{ respectively}^5]$ it was not possible to compare the difference absorption spectra obtained at these two pH values for all the wavelength range used. However, a comparison of these two difference absorption spectra for both the quinones at the longer wavelength region (650–760 nm), where the parent quinones do not absorb, indicate that it could be the same form of the semi-oxidised quinones existing at pH 11 and ca. 14. This was however, unambiguously proved by applying correction for the parent quinone depletion to the difference absorption spectra [eqn. (1)], when the same corrected absorption spectra were obtained at pH 11 and ca. 14 for both the quinones.

The different rate constants for the formation of the semioxidised quinones of 1,4-QH2-2S and 1,4-QH2-6S with different oxidising agents (OH[•], O^{•-}, N₃[•], Br₂^{•-} and [•]CH₂CHO) at different pH were determined by observing the growth of the absorbance of the transients at the longer wavelength region (>650 nm) in N₂O-saturated [N₂-bubbled in the case of (CH₂OH)₂ as the additive] solutions of the quinones $(5 \times 10^{-5} - 1.0 \times 10^{-4} \text{ mol dm}^{-3})$ and the appropriate additive in proper concentration. The second-order rate constants were obtained following the linear variation of the observed pseudo-first-order rate constant with the quinone concentration and the values thus obtained are given in Table 2. The N₃ radicals reacted three-four times faster at pH 11 or ca. 14 than at ca. pH 6. This may be attributed to the simple charge-transfer nature of the reaction at alkaline pH values. The decay of the semi-oxidised quinones of 1,4-QH₂-2S and 1.4-OH₂-6S were observed following the disappearance of their absorbance (ΔA) in the longer (>650 nm) wavelength region. At ca. pH 1 and 14 the rate of disappearance of radical absorption followed bimolecular second-order kinetics. The decay rate constants obtained at ca. pH 1 and 14 for both the semi-oxidised guinones are listed in Table 2.

Table 2 Kinetic parameters of the semi-oxidized quinones of 1,4-QH₂-2S and 1,4-QH₂-6S in aqueous solution

reaction	pН	$k/dm^3 mol^{-1} s^{-1}$
1,4-QH ₂ -2S + OH'	11	$(9.7 \pm 0.3) \times 10^9$
1,4-QH,-6S + OH'	11	$(1.1 \pm 0.1) \times 10^{10}$
$1,4-QH_{2}-2S+N_{3}$	6	$(1.4 \pm 0.1) \times 10^9$
	11	$(4.4 \pm 0.2) \times 10^9$
	ca. 14	$(4.4 \pm 0.2) \times 10^9$
$1,4-QH_{2}-6S+N_{3}$	6	$(1.3 \pm 0.1) \times 10^9$
	11	$(5.6 \pm 0.2) \times 10^9$
	ca. 14	$(5.7 \pm 0.2) \times 10^9$
$1,4-QH_2-2S + CH_2CHO$	ca. 1	$(1.2 \pm 0.2) \times 10^{10}$
$1,4-QH_2-6S + CH_2CHO$	ca. 1	$(2.0 \pm 0.2) \times 10^{10}$
$1,4-QH_2-2S + Br_2^{-1}$	11	$(1.3 \pm 0.1) \times 10^9$
· •	ca. 14	$(2.3 \pm 0.1) \times 10^9$
$1,4-QH_2-6S + Br_2^{-1}$	11	$(7.7 \pm 0.3) \times 10^8$
	ca. 14	$(1.1 \pm 0.1) \times 10^9$
$1,4-QH_2-2S+O^{-1}$	ca. 14	$(1.7 \pm 0.3) \times 10^9$
$1,4-QH_{2}-6S+O^{-1}$	ca. 14	$(1.5 \pm 0.2) \times 10^9$
2(1,4-QH-2S)	ca. 1	$(5.7 \pm 0.2) \times 10^9$
2(1,4-Q ^{•-} -2S)	<i>ca.</i> 14	$(5.5 \pm 0.2) \times 10^{8}$
2(1,4- QH-6S)	ca. 1	$(4.4 \pm 0.3) \times 10^9$
2(1,4-Q ^{•-} -6S)	ca. 14	$(4.3 \pm 0.3) \times 10^8$

The decay could be assigned to the disproportionation of the transient semi-oxidised quinones to the diquinone and the parent dihydroxy quinone as shown in Scheme 4 for semi-oxidised quinones of 1,4-QH₂-2S at *ca.* pH 14.

In the pH range ca. 6-13, the decay of the semi-oxidised quinones of both 1,4-QH₂-2S and 1,4-QH₂-6S were incomplete due to the attainment of an apparent equilibrium following the initial decay. Presumably, in this pH range, an equilibrium as in eqn. (2) was attained.

2 semi-oxidised quinone

$$\underset{k_{\rm b}}{\overset{k_{\rm f}}{\longrightarrow}} \text{diquinone} + \text{dihydroxy quinone} \quad (2)$$

The equilibrium constant K_{eq} (= k_f/k_b) was measured at different pH values for the semi-oxidised quinones of both 1,4-



Scheme 4



Fig. 5 Variation of log K_{eq} with pH for the semi-oxidised 1,4-QH₂-2S (\bigcirc) and 1,4-QH₂-6S (\bigcirc)

 QH_2 -2S and 1,4- QH_2 -6S, observing the initial and the equilibrium concentration of the transients and applying eqn. (3)

$$K_{\rm eq} = \frac{[A_0 - (R_0 + R_{\rm eq})/2][(R_0 - R_{\rm eq})/2]}{R_{\rm eq}^2}$$
(3)

where, A_0 is the initial concentration of the quinones, and R_0 and R_{eq} are the concentrations of the semi-oxidised quinones produced immediately after the completion of reaction (VIII) and after the attainment of equilibrium (2), respectively. Fig. 5 shows the variation of log K_{eq} vs. pH for the semi-oxidised quinones of 1,4-QH₂-2S and 1,4-QH₂-6S for the pH range ca. 6-13. Above and below this pH range $k_{\rm b}$ becomes so slow compared to $k_{\rm f}$ that the radicals appear to decay by secondorder kinetics. It is interesting at this point to compare Fig. 5 with similar plots for the corresponding reduced semiquinones.⁵ Such a comparison clearly indicates that the disproportionation reactions of the semiquinones and the semi-oxidised quinones are similar, though they are formed by two different methods (the former by one-electron reduction and the latter by one-electron oxidation) and their basic structures are also different. Reaction of the diquinones with water, as observed in the case of naphthazarin,⁸ was not apparent in the present systems. This reaction, even if it takes place at all, must be quite slow compared to that of naphthazarin. The differences in the properties of the semi-oxidised forms of naphthoquinone and anthraquinone derivatives may be attributed to the loss in symmetry in the structures of the latter, leading to more phenolic character, as discussed earlier for the pK_a values (Scheme 3).

One-electron Oxidation of 1,4-QH2, 1,5-QH2 and 1,8-QH2

Owing to the very low solubility of $1,4-QH_2$, $1,5-QH_2$ and $1,8-QH_2$ in water at pH < 10.5, one-electron oxidation studies were performed in N₂O-saturated quinone solutions at pH 11 and *ca*. 14, in presence and absence of 5×10^{-2} mol dm⁻³ sodium azide (NaN₃). At pH 11, OH[•] as well as N₃[•] were used as the oxidizing agents while at *ca*. pH 14, O^{•-} and N₃[•] were the oxidising agents. The radiation chemical reactions were as given in reactions (I)–(VIII), and produced the semi-oxidised quinone, QH[•] or Q^{•-}.

The resultant (semi-oxidised quinone – quinone) difference absorption spectra on completion of reactions (III) or (VIII)

were measured as in the case of 1,4-QH₂-2S and 1,4-QH₂-6S. The absorption spectra of the semi-oxidised quinones were obtained after correcting for the depletion of the parent quinone following eqn. (1) considering $G_{\mathbf{R}} = 6.5$ molecules per 100 eV.⁸ The (semi-oxidised quinone – quinone) difference absorption spectra as obtained using N_3 as the oxidising radical and the corresponding corrected semi-oxidised quinone spectra at pH 11 for 1,4-QH₂, 1,5-QH₂ and 1,8-QH₂ are shown in Fig. 6 and 7. Similar absorption spectra were obtained for the 1,4-QH2, 1,5-QH2 and 1,8-QH2 semioxidised quinones using the other oxidizing radicals (OH, O'- at pH 11 and 14) and also N₃ at ca. pH 14, showing that the same ionic form of the semi-oxidised guinones does exist at the two pH values. A little qualitative difference in the corrected absorption spectra of the semi-oxidised guinone at pH 11, with OH' as the oxidising agent, as in the case of the other two sulfonates, may be due to the formation of a small amount of quinone-OH' adduct,8-12 which could not be characterised definitely owing to its very small absorption. By comparison with related systems such as 1,4- QH2-2S,1,4-QH2-6S and naphthazarin,8 the semi-oxidised quinones of 1,4-QH₂, 1,5-QH₂ and 1,8-QH₂ in the alkaline solutions (pH 11 to ca. 14) could be characterised as the monoanionic form (Q^{-}) and their structures could be assigned as in Scheme 5.



Fig. 6 Difference absorption spectra of the semi-oxidised 1,4-QH₂ (\bigcirc), 1,5-QH₂ (\triangle) and 1,8-QH₂ (\bigoplus) at pH 11. The oxidising agent was N₃[•]. Dose = 9.4 Gy. [quinone] = 10⁻⁴ mol dm⁻³ and [N₃⁻] = 5 × 10⁻² mol dm⁻³



Fig. 7 Corrected absorption spectra of the semi-oxidised $1,4-QH_2$ (\bigcirc), $1,5-QH_2$ (\triangle and $1,8-QH_2$ (\bigcirc) in aqueous solution at pH 11

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Scheme 5

On applying the correction according to eqn. (1), corrected spectra as shown in Fig. 7 were obtained. The absorption maxima and the corresponding absorption coefficients for the semi-oxidised quinone monoanions (Q^{-}) of $1,4-QH_2$, $1,5-QH_2$ and $1,8-QH_2$ are listed in Table 1 along with those of the semi-oxidised quinones of $1,4-QH_2-2S$ and $1,4-QH_2-6S$. Owing to solubility restrictions in water as well as in aqueous ethylene glycol,⁸ the absorption spectra of the neutral semi-oxidised quinone (QH[•]) could not be obtained for the present systems.

The different rate constants for the formation of the semioxidised quinones with different oxidising agent (OH', O'and N₃) at pH 11 and ca. 14 were determined by observing the growth of the absorbance at the longer wavelength region (>650 nm, where the parent quinones do not have any absorption) in N₂O-saturated solutions of the quinones $(5 \times 10^{-5} - 1.0 \times 10^{-4} \text{ mol } \text{dm}^{-3})$ with or without 5×10^{-2} mol dm^{-3} NaN₃. The second-order rate constants thus obtained are given in Table 3 along with the bimolecular decay rate constants of the semi-oxidised quinones observed following the decay of their absorbance at the longer (>650nm) wavelength region. It is interesting to note that the rate of disappearance of radical absorption follows bimolecular second-order kinetics in the present system (like those of 1,4-QH₂-2S and 1,4-QH₂-6S), unlike the complications observed⁸ in the case of semi-oxidised naphthazarin. The third aromatic ring in the present system possibly renders all secondary reactions very slow in comparison with the timescale of the radical decay, most likely due to disproportionation to the diquinone and the parent dihydroxyquinone (Scheme 4).

Table 3 Kinetic parameters of the semi-oxidized quinones of 1,4- QH_2 , 1,5- QH_2 and 1,8- QH_2 in aqueous alkaline solution

reaction	pН	$k/dm^3 mol^{-1} s^{-1}$
$1,4-QH_2 + N_3$	11	$(6.5 \pm 0.2) \times 10^9$
	ca. 14	$(7.0 \pm 0.2) \times 10^9$
$1,5-QH_2 + N_3^{-1}$	11	$(1.2 \pm 0.2) \times 10^{10}$
	ca. 14	$(1.4 \pm 0.2) \times 10^{10}$
$1,8-QH_2 + N_3$	11	$(1.0 \pm 0.2) \times 10^{10}$
	ca. 14	$(1.0 \pm 0.2) \times 10^{10}$
$1,4-QH_2 + OH^*$	11	$(1.3 \pm 0.2) \times 10^{10}$
$1,5-QH_2 + OH^*$	11	$(4.1 \pm 0.3) \times 10^{10}$
$1,8-QH_2 + OH$	11	$(2.1 \pm 0.2) \times 10^{10}$
$1,4-QH_2 + O^{-}$	ca. 14	$(3.7 \pm 0.2) \times 10^9$
$1,5-QH_2 + O^{-}$	ca. 14	$(1.4 \pm 0.2) \times 10^{10}$
$1,8-QH_2 + O^{-}$	ca. 14	$(0.5 \pm 0.1) \times 10^{10}$
2(1,4-Q ^{•-})	11	very slow ($< 10^7$)
	ca. 14	$(6.0 \pm 0.5) \times 10^8$
2(1,5-Q ^{•-})	11	$(6.0 \pm 0.5) \times 10^{8}$
	ca. 14	$(1.3 \pm 0.4) \times 10^{10}$
2(1,8-Q ^{•-})	11	$(4.1 \pm 0.6) \times 10^9$
	<i>ca</i> . 14	$(1.4 \pm 0.4) \times 10^9$

Conclusion

The spectroscopic and kinetic characteristics of the semioxidised quinones of a number of dihydroxy derivatives of 9,10-anthraquinone have been investigated. The pK_a of the semi-oxidised quinones of 1,4-QH2-2S and 1,4-QH2-6S are higher than that of the semi-oxidised 5,8-dihydroxy-1,4-naphthoquinone,⁸ indicating that the extra aromatic ring in the present systems substantially alters the properties of the semioxidised quinones over that of semi-oxidised dihydroxy naphthoquinone. The most interesting aspects of the semioxidised quinones of dihydroxy anthraquinones is that they undergo a simple bimolecular disproportionation to the diquinone and the parent dihydroxy quinone, whereas the semi-oxidised 5,8-dihydroxy naphthoquinone decays by a very complicated mechanism.8 The difference in the behaviour of the semi-oxidised forms of dihydroxy anthraquinones and 5,8-dihydroxy naphthoquinone is difficult to explain though it can be stated undoubtedly that the extra aromatic ring in the present semi-oxidised quinone systems and the consequent loss in symmetry and increase in phenolic character largely alter the reactivity, rendering the complicated secondary processes, reported⁸ for semi-oxidised 5,8-dihydroxy naphthoquinone, very slow in comparison to the rate of disproportionation into the diquinone and dihydroxy quinone.

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