Redox Reactions of 8-Hydroxyquinoline. A Pulse Radiolysis Study

D. B. Naik, P. Dwibedy, G. R. Dey, K. Kishore, and P. N. Moorthy*

*Applied Chemistry Division, Bhabha Atomic Research Centre, Trombay, Mumbai 400 085, India*

Received: June 5, 1997; In Final Form: September 22, 1997

Pulse radiolysis technique was used to study the reactions of e_{aq}^-, H atoms, and other reducing radicals such as $COO^-/COOH$, $(CH_3)_2COH$, CH_3CHOH, and CH_2OH radicals with 8-hydroxyquinoline (8HQ) at various pH's. e_{aq}^- reacts with 8HQ with high rate constants ($k_2 = 3 \times 10^{10}$ at pH 7 and 2.6×10^{10} at pH 12). Absorption spectra of the transient species were recorded in the wavelength region 300−800 nm. Semireduced species formed by the reaction of e_{aq}^- with 8HQ as well as that formed by H atom reaction were found to be strong reductants and were found to transfer an electron to methylviologen. $COO^-/COOH$ and alcohol radicals were found to react with 8HQ by addition reactions. The rate constants for the reactions were much higher at acidic pH's ($\approx 10^9$ dm^3 mol^{-1} s^{-1}), where 8HQ is in the protonated form, as compared to those at neutral pH ($\approx 10^8$ dm^3 mol^{-1} s^{-1}), where it is present in the neutral form. These adduct radicals were also found to be reducing in nature. The rate constant for OH radical reaction with 8HQ was estimated to be 7.6×10^9 dm^3 mol^{-1} s^{-1} at pH 7 and 1.3×10^{10} dm^3 mol^{-1} s^{-1} at pH 0; a cyclohexadienyl type of radical is formed in both the cases. These adducts react with oxygen ($k = 3.2 \times 10^9$ dm^3 mol^{-1} s^{-1} at pH 7) to give peroxyl radicals. Br_2^- and N_3 radicals react with 8HQ by electron transfer at pH 13 giving a phenoxyl-type radical. At pH 7, N_3 and SO_4^- radicals react with 8HQ by electron transfer whereas the reaction of the Br_2^- radical is quite slow. Only SO_4^- is able to oxidize 8HQ in its protonated form existing at acidic pH.

Introduction

8-Hydroxyquinoline (8HQ) is a versatile molecule because of its amphoteric and zwitterionic properties, as shown in Scheme 1. It is one of the well-known complexants used for the estimation of Mg, Zn, Al, Cu, and so forth, and also for the separation of Be from Al. Complexants are also important ingredients of dilute chemical decontamination formulations in aqueous medium used for dissolving out oxide deposits on the heat-transfer surfaces of water-cooled nuclear reactors.[1,2] Because of its good complexing ability, 8HQ can be used as a complexant in such formulations. During the process of decontamination, the formulation components also get exposed to high radiation doses as they circulate through the reactor core. Therefore, the radiation stability of these components is of relevance, and this is largely governed by the reactivity of the formulation components with the primary species of water radiolysis, namely, e_{aq}^-, H atoms, and OH radicals. There are no reports on such studies carried out on this compound in the literature. Earlier, pulse radiolysis studies were carried out on pyridinol isomers.[3−6] 8HQ is expected to show behavior similar to that of pyridin-3-ol because of the positions of the N atom and OH group in both the molecules. In fact pK_a's of these two molecules are quite close to each other. In the case of most pyridine derivatives the e_{aq}^- reaction is quite fast and leads to the formation of pyridinyl-type of radicals,[7] which are strong reductants. The same is true of pyridinols. OH radicals usually react with these compounds by addition to the ring, giving OH adducts at electron-rich positions.[8] One-electron oxidation of these pyridine derivatives is rather difficult. However, in the case of pyridinols, one-electron oxidation does take place at high pH's where the OH group is deprotonated.[4,5] It is also known that reducing radicals such as $COO^-/COOH$ and $(CH_3)_2$-COH react with pyridin-3-ol by addition rather than by an electron-transfer mechanism.[3] This is not so in the case of other

SCHEME 1
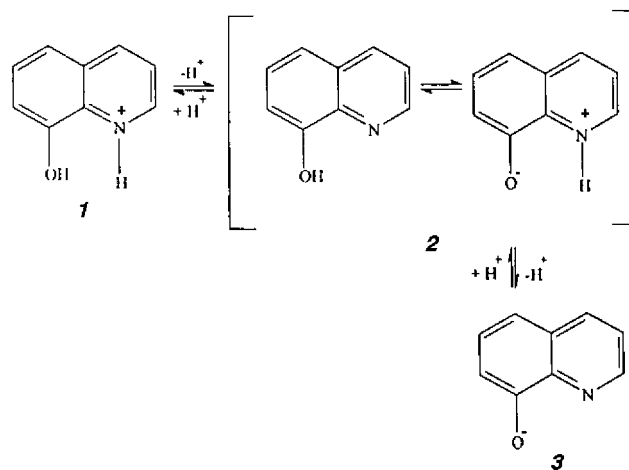
pyridine derivatives. Although radiation chemistry of 8HQ should be similar to that of pyridin-3-ol, the possibility of hydrogen bond formation in 8HQ may give different reactions. We have studied the reactions of 8HQ with e_{aq}^-, H atoms, OH/ O^- radicals, and reducing radicals such as $COO^-/COOH$, $(CH_3)_2COH$, CH_3CHOH, and CH_2OH and oxidizing radicals Br_2^-, N_3, and SO_4^- at different pH's and the results are discussed in this paper.

Experimental Section

8-Hydroxyquinoline from Qualigens Fine Chemicals, Bombay, India, was used after recrystallizing twice from water, and its absorption spectrum matched well with that reported in the literature.[9] All the other chemicals used were of the highest purity available. The solutions were prepared in water having a conductivity of <0.1 μS/cm, obtained from a Barnstead
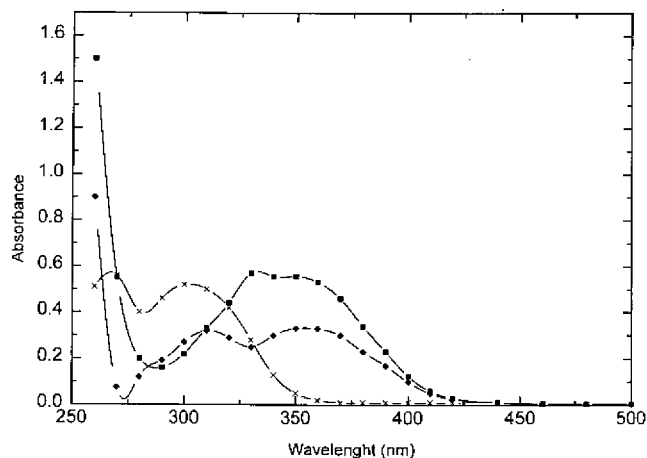
Redox Reactions of 8-Hydroxyquinoline

J. Phys. Chem. A, Vol. 102, No. 4, 1998 **685**

Figure 1. Absorption spectra of 2×10^{-4} mol dm^{-3} 8HQ at pH 1 (◆), pH 7 (×), and pH 13 (■).
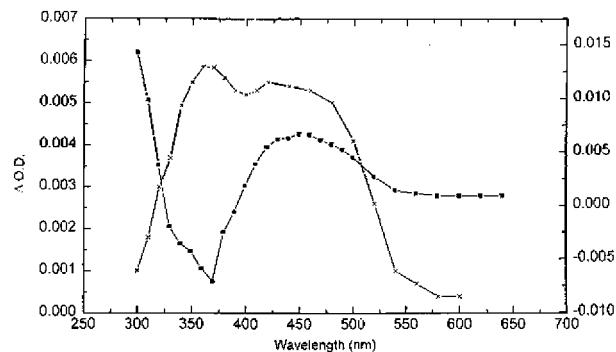

Figure 2. Transient spectra formed by reaction of e$_{aq}^-$ with 8HQ at pH 7 (×) and pH 12 (■) in N$_2$-purged solutions containing 2×10^{-4} mol dm^{-3} 8HQ and 0.1 mol dm^{-3} *tert*-butyl alcohol.
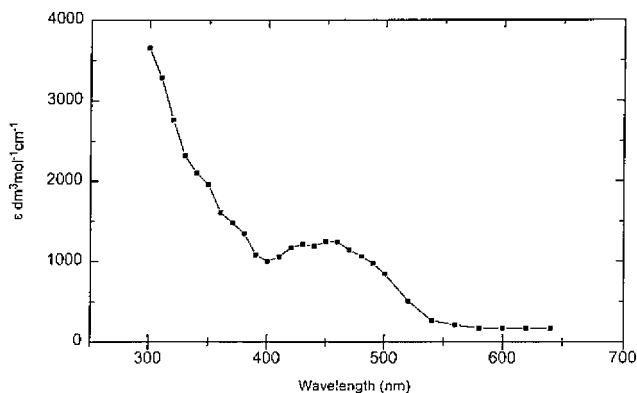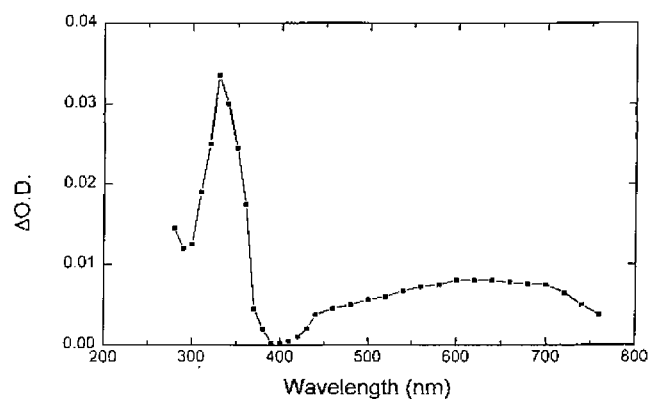

Figure 3. Absorption spectrum of the semireduced 8HQ corrected for parent absorption.

"Nanopure" system. The solutions were purged with Iolar grade (Indian Oxygen Ltd.) N$_2$O and N$_2$ gases. The pH's of the solutions were adjusted using H$_2$SO$_4$, KH$_2$PO$_4$, Na$_2$HPO$_4$·2H$_2$O, Na$_2$B$_4$O$_7$·10H$_2$O, and NaOH solutions in appropriate proportions. Details of the pulse radiolysis setup used have been discussed elsewhere.[10] Single pulses of 7-MeV electrons of 50-ns duration from a linear electron accelerator were used for the irradiation of samples. Pulse dose was in the range 15–20 Gy/pulse. Dosimetry was carried out using aerated decimolar potassium thiocynate solutions using a value of 21 520 dm^3 mol^{-1} cm^{-1} for $G\epsilon$ at 500 nm.[11] To study the reactions of e$_{aq}^-$ and H atoms, *tert*-butyl alcohol was used as a OH radical scavenger. To study the reactions of alcohol radicals, a matrix containing respective alcohol (1 mol dm^{-3}) was used at all the pH values, the solutions were purged with N$_2$ at acidic pH's and N$_2$O at neutral pH to convert e$_{aq}^-$ into OH radicals, then both OH radicals and H atoms react with alcohols by H abstraction reaction to give alcohol radicals. Typically

$$CH_3OH + H/OH \rightarrow CH_2OH + H_2/H_2O \qquad (1)$$
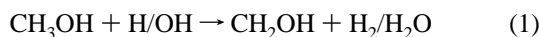
At neutral pH, CO$_2^-$ radicals were generated by reaction of formate ions with H atoms and OH radicals, whereas at acidic pH formic acid was used for generating COOH radicals by similar reactions. For studying the reactions of OH radicals at pH 7 and O$^-$ radicals at pH 13, solutions were purged with N$_2$O. For studying the reactions of OH radicals at acidic pH, solutions were purged with O$_2$ wherein H atoms are converted into HO$_2$ radicals, which were found to be unreactive toward 8HQ. N$_3$ and Br$_2^-$ radicals were generated by the reaction of N$_3^-$ and Br$^-$, respectively with OH radicals, whereas SO$_4^-$ radicals were obtained by the reaction of e$_{aq}^-$ with S$_2$O$_8^{2-}$ in the presence of *tert*-butyl alcohol as OH radical scavenger.

$$S_2O_8^{2-} + e_{aq}^- \rightarrow SO_4^- + SO_4^{2-} \qquad (2)$$
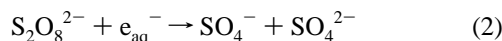
Results and Discussions

Reactions of 8HQ with e$_{aq}^-$. 8HQ has two pK_a values at 5.02 and 9.81 (ref 12). Different conjugate acid base forms of 8HQ are shown in Scheme 1, and their absorption spectra are given in Figure 1. The reactions of form (2) at pH 7 and form 3 at pH 12 with hydrated electrons were found to be very fast. The rate constant values were determined by following the decay of the e$_{aq}^-$ absorption at 720 nm and were found to be 3×10^{10} and 2.6×10^{10} dm^3 mol^{-1} s^{-1} at pH 7 and 12, respectively. The values at pH 7 and 12 are comparable, showing that

deprotonation does not lead to any significant decrease in the rate constant. In pyridinols[3,5] and phenol[13] deprotonated forms have much lower reactivity with e$_{aq}^-$ as compared to that of their respective neutral forms. The reason for this can be that e$_{aq}^-$ is more reactive with the pyridine moeity in 8HQ and addition of e$_{aq}^-$ to the pyridine part of the molecule is not affected much because of deprotonation on the other ring; also the presence of an additional ring in 8HQ can increase the e$_{aq}^-$ reaction rate constant. The absorption spectra obtained in pulse-irradiated N$_2$-purged 2×10^{-4} mol dm^{-3} 8HQ solutions containing 0.1 mol dm^{-3} *tert*-butyl alcohol (as OH radical scavenger) at pH 7 and 12 are shown in Figure 2. These spectra were corrected for the parent compound absorption, and it was seen that the corrected spectra at both the pH's are almost identical (Figure 3). The transients formed at both pH 7 and 12 decayed by second-order kinetics. Spectral and kinetic parameters of these transients are given in Table 1. The semireduced species formed in e$_{aq}^-$ reaction with 8HQ at pH 7 was found to be strongly reducing in nature, and it could transfer an electron to methylviologen to produce MV$^+$ radical cations having absorption at 600 nm. The electron-transfer reaction rate constant for the semireduced species with MV^{2+} was determined to be 3.2×10^9 dm^3 mol^{-1} s^{-1}. From kinetic salt effect experiments it was observed that the semireduced species at pH 7 was a charged species, showing that at pH 7 addition of e$_{aq}^-$ to 8HQ (neutral form) leads to the formation of a monoanion. Possibly, the negative charge is on the O atom; as in the zwitterionic form of 8HQ, the electron will add to the protonated nitrogen. At pH 12, the semireduced species formed by the reaction of e$_{aq}^-$ with 8HQ was also found to be strongly reducing in nature since it also reduced methylviologen. The rate constant for the reaction of the 8HQ-e$_{aq}^-$ adduct with MV^{2+} at pH 12 was determined to be 4×10^9 dm^3 mol^{-1} s^{-1}.

TABLE 1: Kinetic and Spectral Parameters for the Reaction of Reducing Radicals with 8HQ

| species	pH	$k_{formation}$ (dm^3 mol^{-1} s^{-1})	λ_{max} (nm)	ϵ (dm^3 mol^{-1} cm^{-1})	decay $2k/\epsilon l$ (s^{-1})
e_{aq}^-	7	3×10^{10}	370, 450	1500 (450 nm)	1.1×10^6
e_{aq}^-	12	2.6×10^{10}	450	1500 (450 nm)	
H	0	5.6×10^9	600−620		4.2×10^6
CO_2^-	7	1.5×10^8	400−430		4.9×10^5 (at 400 nm)
COOH	0	1.5×10^9	420−460		1.3×10^6 (at 440 nm)
$(CH_3)_2COH$	7	6.7×10^7	360−370		6.4×10^4
$(CH_3)_2COH$	0	1.2×10^9	430		1.2×10^6
CH_3CHOH	7	4.8×10^7	370		1×10^5
CH_3CHOH	0	1.1×10^9	570		1.6×10^5
CH_2OH	7		370		
CH_2OH	0	2×10^8	570		2.6×10^5

Figure 4. Absorption spectrum of the transient species formed by H atom reaction with 8HQ at pH 0 in N$_2$-purged solution containing 2×10^{-4} mol dm^{-3} 8HQ and 0.1 mol dm^{-3} *tert*-butyl alcohol.

As the corrected spectra at both pH 7 and 12 are identical, it is suggested that at pH 12 also the species is monoanionic.

Reaction with H Atoms. H atoms were found to react with the protonated form (1) of 8HQ at pH 0 with a rate constant of 5.5×10^9 dm^3 mol^{-1} s^{-1}. The absorption spectrum (Figure 4) exhibited one band with λ_{max} at 600 nm, and absorption was increasing continuously below 400 nm. The species formed by H atom reaction decayed by second-order kinetics with a $2k/\epsilon l$ value of 4.2×10^6 s^{-1} at 600 nm. This species was also found to be reducing in nature and could transfer electrons to methylviologen and thionine. H atoms can react with 8HQ either by addition to the nitrogen atom or at other sites on the π-rings. Thus in principle it can give rise to more than one transient species. The H-adduct at the N atom is expected to be reducing in nature, as in the case of pyridine derivatives.[7] It was observed that the G-value for semireduced methylviologen or semithionine formation was around 35% of that of G_H. Thus, it can be concluded that 35% of the H atoms react with 8HQ by addition at the N atom.

Reactions with One-Electron-Reducing Species. Reactions of CO$_2^-$/COOH and alcohol radicals, namely, (CH$_3$)$_2$COH, CH$_3$-CHOH, and CH$_2$OH, were studied at pH 0 and 7. Rate constants for these reactions were determined by following the buildup of transient absorption at the absorption maxima of the respective species. These rate constant values are given in Table 1. It can be seen that at pH 7 these radicals react with 8HQ rather slowly with $k = 10^7−10^8$ dm^3 mol^{-1} s^{-1}. Earlier, in the case of pyridin-3-ol also, it was observed that (CH$_3$)$_2$COH and CO$_2^-$ radicals react slowly, with rate constants on the order of 10^7 dm^3 mol^{-1} s^{-1}. At pH 0, where 8HQ is present in the protonated form, rate constants were found to be higher by an order of magnitude, which was also true in the case of pyridin-3-ol.[3] Reactions of CH$_3$CHOH and CH$_2$OH radicals also showed similar pH dependence, as can be seen from Table 1.
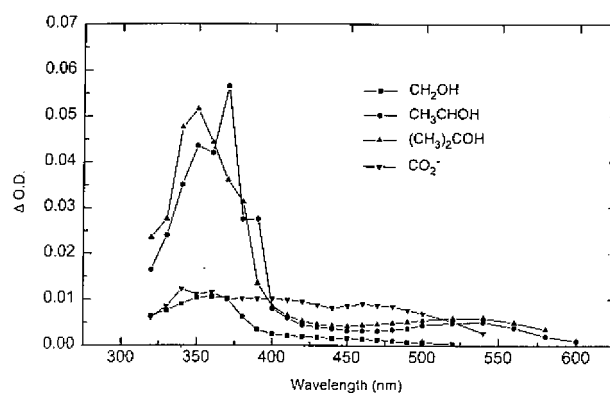
Figure 5. Absorption spectra of the transient species formed by the reactions of CO$_2^-$, (CH$_3$)$_2$COH, CH$_3$CHOH, and CH$_2$OH radicals with 8HQ at pH 7 in N$_2$O-saturated solutions containing 1×10^{-3} mol dm^{-3} 8HQ and 0.1 mol dm^{-3} HCOONa or 1 mol dm^{-3} of respective alcohol.
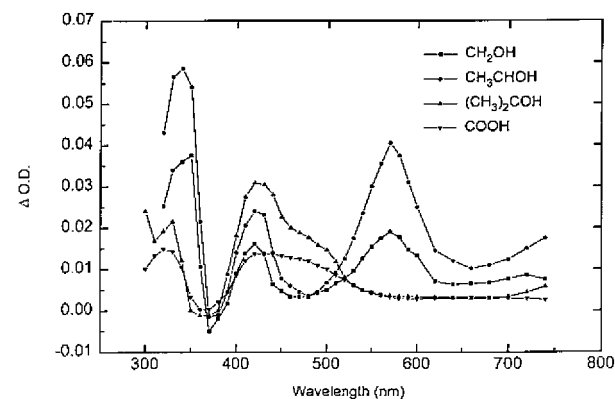
Figure 6. Absorption spectra of the transient species formed by the reactions of COOH, (CH$_3$)$_2$COH, CH$_3$CHOH, and CH$_2$OH radicals with 8HQ at pH 0 in N$_2$-saturated solutions containing 1×10^{-3} mol dm^{-3} 8HQ and 1 mol dm^{-3} of formic acid or respective alcohol.

Absorption spectra of the transient species formed by the reactions of CO$_2^-$/COOH and alcohol radicals at pH 7 and 0 are given in Figures 5 and 6, respectively. At pH 7, these spectra are different from that of the semireduced species formed by e_{aq}^- reaction at the same pH. As in the case of pyridin-3-ol, we can conclude that CO$_2^-$ and alcohol radicals add to the 8HQ molecule and do not react by electron transfer. In the case of pterin and also pterin-6-carboxylate ions CO$_2^-$ has been reported to react partly by addition.[14] Also at pH 0, COOH and alcohol radicals react with 8HQ by addition to the rings. It is known that for an electrophilic reaction the rate constant decreases with protonation of nitrogen.[15] Accordingly, it could be expected that the protonation of nitrogen in 8HQ increases its reactivity toward nucleophiles such as (CH$_3$)$_2$COH and other alcohol radicals. At pH 12, where 8HQ is present in the

Redox Reactions of 8-Hydroxyquinoline

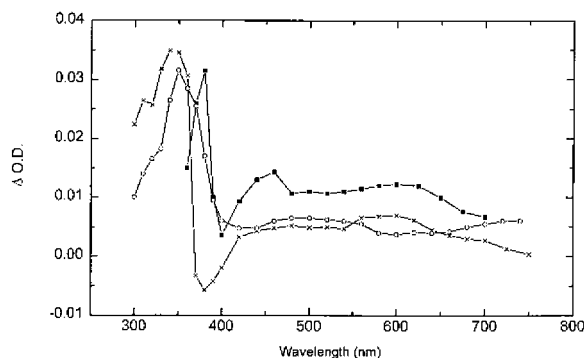*J. Phys. Chem. A, Vol. 102, No. 4, 1998* **687**

Figure 7. Transient absorption spectra of the species formed by the reactions of OH radicals with 8HQ at pH 7 (○) and O[−] radicals with 8HQ at pH 13 (■) in N$_2$O-saturated solutions containing 1×10^{-3} mol dm^{-3} 8HQ and by the reactions of OH radicals with 8HQ at pH 0 (×) in O$_2$-saturated solution containing 2×10^{-4} mol dm^{-3} 8HQ.

deprotonated form, the reactions of alcohol radicals were not observed. We also looked into the nature of these adducts. It was found that at pH 0 the adducts fomed by the reaction of 8HQ with COOH and alcohol radicals were able to transfer electrons to thionine and methylviologen with rate constants on the order of 3×10^9 dm^3 mol^{-1} s^{-1}, and thus are reducing in nature.

Reaction of 8HQ with OH/O[−] Radicals. Absorption spectrum of the transient species formed by the reaction of OH radicals at pH 7 with 8HQ is given in Figure 7. The rate constant for this reaction was determined by following the buildup of absorbance at 370 nm and found to be 7.4×10^9 dm^3 mol^{-1} s^{-1}. The absorption spectrum corrected for ground-state absorption shows a maximum at 330−340 nm, suggesting that the transient species is a hydroxycyclohexadienyl type of radical. This is also supported by observations on reactions of specific oxidants with 8HQ, which are discussed later. The transient species was found to decay by second-order kinetics and the decay rate was unaffected by increasing ionic strength, suggesting that the species is neutral. Also it was not able to oxidize ascorbate ion.

At pH 0, OH radicals were found to react with 8HQ with a rate constant of 2×10^{10} dm^3 mol^{-1} s^{-1} as determined by competition kinetics using KSCN as competing solute. The species formed has a strong absorption band in the 330−350-nm region and weak absorption in the 600-nm region (Figure 7). The spectrum corrected for parent absorption has a strong peak at 340 nm, suggesting that at this pH also a hydroxycyclohexadienyl type of radical is formed.

The O[−] radical anion reaction with 8HQ was studied at pH 13. The transient absorption spectrum is given in Figure 7 and shows maxima at 360 and 460 nm and a broad band in the 520−620 nm region. The rate constant for this reaction as determined by monitoring buildup of absorption at 600 nm was found to be 4.5×10^9 dm^3 mol^{-1} s^{-1}.

Formation of Peroxyl Radicals. In 8HQ solutions containing both N$_2$O (10 mM) and O$_2$ (0.5 mM) at pH 7, it was found that the initial OH adduct reacted with O$_2$ to give another transient species. The absorption spectrum recorded 40 μs after the electron pulse is given in Figure 8. After correction for parent absorption it exhibits a hump at 350−360 nm, where the extinction coefficient is around 700 dm^3 mol^{-1} cm^{-1} (Figure 8). This spectrum can be assigned to peroxyl radicals formed by the reaction of O$_2$ with the OH adduct of 8HQ. These radicals were quite stable and did not decay appreciably in 1 ms. We could not observe any reaction of peroxyl radicals with ascorbate ions. It is quite possible that the rate constant for
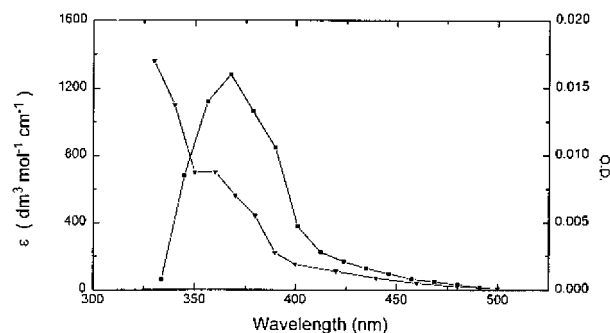

Figure 8. Absorption spectrum of the peroxyl radicals formed by the reaction of O$_2$ with OH adduct of 8HQ at pH 7 (■) in a solution containing 4×10^{-4} mol dm^{-3} 8HQ, 0.01 mol dm^{-3} N$_2$O, and 5×10^{-4} mol dm^{-3} O$_2$ and the absorption spectrum of the peroxyl radicals corrected for parent absorption (▼).
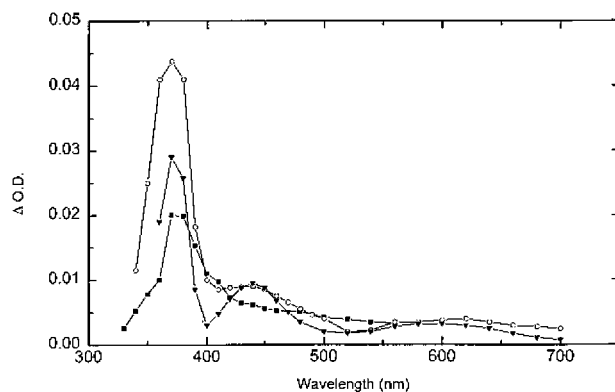

Figure 9. Absorption spectra of the transient species formed by the reaction of N$_3$ radicals with 8HQ at pH 7 (○) and at pH 13 (▼) in N$_2$O-saturated solution containing 5×10^{-4} mol dm^{-3} 8HQ and 0.02 mol dm^{-3} NaN$_3$ and by reaction of SO$_4^-$ radicals with 8HQ at pH 3.5 (■) in N$_2$-purged solution containing 2×10^{-4} mol dm^{-3} 8HQ, 0.1 mol dm^{-3} *tert*-butyl alcohol, and 0.02 mol dm^{-3} K$_2$S$_2$O$_8$.

such a reaction may be quite low. Earlier OH adducts of DNA and its bases have been reported to form peroxyl radicals.[16,17] The rate constant for the reaction of O$_2$ with the 8HQ-OH adduct was determined to be 3.2×10^9 dm^3 mol^{-1} s^{-1} by following its initial decay at 380 nm as a function of O$_2$ concentration. At pH 0 also, the adduct formed by OH radical reaction with 8HQ reacted with oxygen, but the rate constant was lower (9×10^7 dm^3 mol^{-1}s^{-1}). At this pH, no new absorption band due to peroxyl radicals could be observed above 300 nm.

Reactions of Specific One-Electron Oxidants. The absorption spectrum of the transient species formed by the reaction of N$_3$ radicals with 8HQ at pH 7 shows an absorption maximum at 370 nm (Figure 9). The rate constant for the reaction was determined by buildup of the absorption signal at 370 nm and was found to be 1.2×10^9 dm^3 mol^{-1} s^{-1}. This spectrum is quite different from that of the transient species formed by OH radical reaction with 8HQ at pH 7. Reaction of SO$_4^-$ radicals with 8HQ at pH 7 also gave a similar transient spectrum. Hence, we can ascribe this spectrum to the one-electron oxidized species of 8HQ. The species decayed by second-order kinetics with $2k/\epsilon l$ value of 3.6×10^5 s^{-1} at 370 nm. Br$_2^-$ radicals were not able to oxidize 8HQ at a measurable rate. In the case of pyridin-3-ol also, it was oberved that N$_3$ radicals bring about one-electron oxidation, whereas reaction with Br$_2^-$ radicals at pH 7 was immeasurably slow.

At pH 13, where 8HQ is in the deprotonated form, both N$_3$ and Br$_2^-$ radicals react with fairly high rate constant to give the same transient species, whose absorption spectrum is given
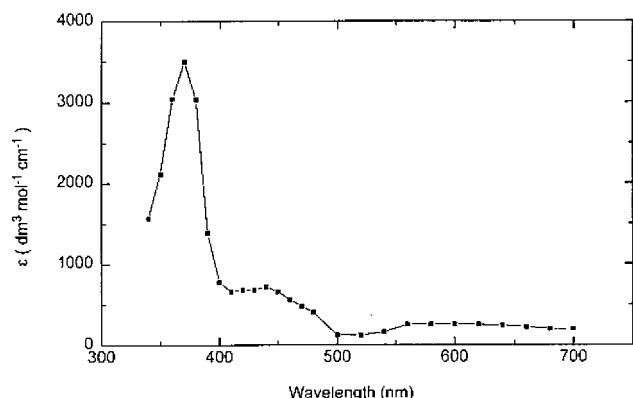
Figure 10. Spectrum of the species formed by the reaction of N_3 radicals with 8HQ corrected for the parent compound absorption.

TABLE 2: Kinetic and Spectral Parameters for the Reaction of Oxidizing Radicals with 8HQ

species	pH	$k_{formation}$ (dm^3 mol^{-1} s^{-1})	λ_{max} (nm)	ϵ (dm^3 mol^{-1} cm^{-1})	decay $2k/\epsilon l$ (s^{-1})
OH	7	7.4×10^9	360		2.8×10^5
OH	0	2×10^{10}	450		
O$^-$	13	4.5×10^9	450, 600		
N$_3$	7	1.2×10^9	370	3500	3.6×10^5
N$_3$	13	5.2×10^9	440	650	2.3×10^4 (first order)
Br$_2^-$	13	3×10^9	440	650	2.3×10^4 (first order)
SO$_4^-$	7	6.3×10^9	370	2700	9.1×10^5
SO$_4^-$	3.5	5.5×10^9	370		5.6×10^5 (at 440 nm)

in Figure 9. It has peaks at 370 and 440 nm. The spectrum is different from the one obtained on reaction of O$^-$ radical anions with 8HQ at this pH. The spectra of species formed in reactions of N$_3$ radicals with 8HQ at pH 7 and 13 when corrected for parent compound absorption were identical (Figure 10) showing that the same species is formed at both pH's, which can be phenoxyl-type radicals. At pH 13, these radicals decayed by first-order kinetics, and the rate was dependent on OH$^-$ ion concentration. The bimolecular rate constant for this reaction was determined to be 1.6×10^5 dm^3 mol^{-1} s^{-1}. The rate constant for the reaction of N$_3$ radicals with 8HQ at pH 13 was determined by following absorption buildup at 450 nm, whereas that for Br$_2^-$ radical reaction was determined following its pseudo-first-order decay at 370 nm. Kinetic and spectral parameters for the reaction of oxidizing radicals with 8HQ are given in Table 2.

At acidic pH's, where 8HQ is in the protonated state, its oxidation was quite difficult. Both Br$_2^-$ and Cl$_2^-$ radicals did not react with 8HQ under these conditions. Reaction of SO$_4^-$ radicals was studied at pH 3.5, and the absorption spectrum of the transient species formed is given in Figure 9. The species decays by good second-order kinetics with a $2k/\epsilon l$ value of 5.6×10^5 s^{-1} at 440 nm. This spectrum is ascribed to that of semioxidized species of 8HQ at pH 3.5.

Radiation Stability. Decontamination formulations contain a chelant (generally EDTA), a reductant (ascorbic acid, AA), and a buffering agent (citric acid) in millimolar concentrations. 8HQ, being a good chelant, can be used in place of EDTA. The pH of the formulation is usually kept around 3, where e$_{aq}^-$ will be converted into H atoms. Hence, under the effect of radiation at this pH, reactions of H atoms and OH radicals are of importance. The reactivity of both H and OH radicals with 8HQ is quite high, as discussed earlier. In the presence of AA, only a part of these radicals will be reacting with 8HQ because

of the high reactivity of AA with both H ($k = 1.3 \times 10^8$ dm^3 mol^{-1} s^{-1}) and OH radicals ($k = 1.2 \times 10^{10}$ dm^3 mol^{-1} s^{-1}).[18] Citric acid, however, has very low reactivity with these radicals. Although 8HQ is highly reactive as compared to EDTA, its aromatic structure gives it stability because its reaction with H and OH radicals will give only dihydro and dihydroxy derivatives of 8HQ. This may not impair its chelating ability. On the other hand, in the case of EDTA, although its reactivity is less ($k \approx 10^8$ dm^3 mol^{-1} s^{-1}),[18] there is permanent damage to the molecule due to decarboxylation, leading to destruction of its chelating sites.

Conclusion

It was observed that reaction of 8HQ with e$_{aq}^-$ and H atoms gives strong reducing radicals. COOH/CO$_2^-$ and alcohol radicals, namely, (CH$_3$)$_2$COH, CH$_3$CHOH, and CH$_2$OH radicals, add on to the 8HQ molecule. However, at the same time these adducts were found to transfer electrons to acceptors such as thionine. OH/O$^-$ radicals react with 8HQ by addition and OH adducts form peroxyl radicals in the presence of oxygen, as in the case of OH adducts of uracil and thymine. One-electron oxidation of 8HQ shows strong pH dependence. Both Br$_2^-$ and N$_3$ radicals can oxidize the deprotonated form of 8HQ, whereas N$_3$ and SO$_4^-$ radicals are able to oxidize the neutral form. Oxidation of the protonated form is possible only through SO$_4^-$ radicals, whereas Cl$_2^-$ is not able to bring about oxidation. In its reactions with radiolytic species, the behavior of 8HQ is akin to that of pyridin-3-ol.

References and Notes

(1) Ayres, J. *Decontamination of Nuclear Reactors and Equipments*; Ronald Press Co.: New York, 1970.

(2) Velmurugan, S.; Narasimhan, S. V.; Mathur, P. K.; Venkateswaralu, K. S. *Nucl. Technol.* **1991**, *96*, 248.

(3) Naik, D. B.; Moorthy, P. N. *J. Chem. Soc., Perkin Trans. 2* **1990**, 705.

(4) Naik, D. B.; Moorthy, P. N. *J. Radioanal. Nucl. Chem.* **1991**, *148*, 403.

(5) Naik, D. B.; Moorhty, P. N. *Proc. Indian Acad. Sci. (Chem. Sci.)* **1991**, *103*, 667.

(6) Steenken, S.; O'Neill, P. *J. Phys. Chem.* **1979**, *83*, 2407.

(7) Solar, S.; Solar, W.; Getoff, N.; Holcman, J.; Sehested, K. *Radiat. Phys. Chem.* **1988**, *32*, 585.

(8) Anbar, M.; Meyerstein, D.; Neta, P. *J. Phys. Chem.* **1966**, *70*, 2660.

(9) Mason, S. F. *J. Chem. Soc.* **1957**, 5010.

(10) Guha, S. N.; Moorthy, P. N.; Kishore, K.; Naik, D. B.; Rao, K. N. *Proc. Indian Acad. Sci.* **1987**, *99*, 261.

(11) Fielden, E. M. Chemical Dosimetry of Pulsed Electron and X-ray Sources in the 1−20 MeV Range. In *The Study of Fast Processes and Transient Species by Electron Pulse Radiolysis*; Baxendale, J. H., Busi, F., Eds.; Riedel Publishing Co.: Dordrecht, Holland, 1982; pp 49−62.

(12) Perrin, D. D. In *Dissociation Constants of Organic Bases in Aqueous Solutions*; Butterworth: London, 1965.

(13) Anbar, M.; Hart, E. J. *J. Am. Chem. Soc.* **1964**, *86*, 5633.

(14) Farhani, M.; Surdhar, P. S.; Allen, S.; Armstrong, D. A.; Schoneich, C.; Mao, Y.; Asmus, K. D. *J. Chem. Soc., Perkin Trans. 2* **1991**, 1687.

(15) Simic, M.; Neta, P.; Hayon, E. *Int. J. Radiat. Phys. Chem.* **1971**, *3*, 309.

(16) Willson, R. L. *Int. J. Radiat. Biol.* **1970**, *17*, 349.

(17) Fujita, S.; Steenken, S. *J. Am. Chem. Soc.* **1981**, *103*, 2540.

(18) Buxton, G. V.; Greenstock, C. L.; Helman, W. P.; Ross, A. B. *J. Phys. Chem. Ref. Data* **1988**, *17*, 513.