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Different Channels of Hydroxyl Radical Reaction with Aryl Sulfides: Effect of the Substituents

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In a neutral aqueous solution of (phenylthio)acetic acid, the hydroxyl radical is observed to react with a bimolecular rate constant of 7.2×10^9 dm^3 mol^{-1} s^{-1}, and the transient absorption bands are assigned to $^{\bullet}$OH radical addition to benzene and sulfur with rough estimated values of 50 and 40%, respectively. The reaction of the $^{\bullet}$OH radical with diphenyl sulfide ($k = 4.3 \times 10^8$ dm^3 mol^{-1} s^{-1}) is observed to take place with the formation of the solute radical cation, OH-adduct at sulfur, and benzene with rough estimated values of 12, 28, and 60%, respectively. The transient absorption bands observed on reaction of the $^{\bullet}$OH radical, in neutral aqueous solution of 4-(methylthio)phenyl acetic acid, are assigned to solute radical cation ($\lambda_{max} = 550$ and 730 nm), OH-adduct at sulfur ($\lambda_{max} = 360$ nm), and addition at benzene ($\lambda_{max} = 320$ nm). The fraction of $^{\bullet}$OH radical reacting to form a solute radical cation is observed to increase with increasing concentration of acid, and in highly acidic solutions, the solute radical cation is the only transient species formed on reaction of $^{\bullet}$OH radical with these sulfides.

Introduction

The studies on the radicals and radical ions derived from organic sulfides have been the subject of active interest as sulfur-centered radical species play an important in understanding the biological systems with sulfur-containing compounds.[1−3] These studies are also useful in understanding the electron-transfer and redox reactions of bio-molecules.[4−8] Hydroxyl radical and specific one-electron oxidants are known to bring about one-electron oxidation of dialkyl sulfides (R_2S), resulting in the formation of sulfur centered radical cations ($R_2S^{\bullet+}$) either directly or via a complex sequence of reactions involving an OH-adduct, an α-thio radical, and monomer radical cation.[9] The oxidized sulfur has a high tendency to be stabilized by coordination with a free p-electron pair of a second sulfur atom or a hetroatom (O, N, P, halogen) both by intra- and intermolecular association.[10] Simple sulfur centered radical cations have been observed only in the case of di-*tert*-butyl sulfide and aryl sulfides and explained due to steric influence and adjacent π system, respectively. Direct evidence for the involvement of OH-adduct, α-thio radical, and monomer radical cation could be obtained from functionalized sulfides.[11,12] Evidence for the formation of sulfur-centered species has come from ESR and optical absorption spectroscopic studies.[9−13] Sulfur centered cationic species are represented by a three-electron bond containing two bonding σ and one antibonding σ^* electron. These three-electron bonded (2c-3e) species have been the subject of active interest in both experimental and theoretical investigations.[9−14]

The kinetic, spectroscopic, and redox properties of the transient species formed on reaction of the $^{\bullet}$OH radical with substituted alkyl sulfides have been reasonably well understood and mainly one channel (sulfur site) is observed in most of the cases. On the other hand, only a few studies have been made on aryl-substituted sulfur compounds.[15] The benzene ring would act as an additional site for reaction with the $^{\bullet}$OH radical, and spin delocalization would reduce the tendency of the solute radical cation to form dimer radical cation. The present studies on (phenylthio)acetic acid, diphenyl sulfide, and 4-(methylthio)-phenyl acetic acid have been carried out with the objective of investigating the possibility of different channels of $^{\bullet}$OH radical reaction. with aryl-substituted sulfur compounds. It is important to know the conditions under which the radical cation is formed as this information is essential to determine its reactivity.

Experimental Section

(Phenylthio)acetic acid, (PTA), 4-(methylthio)phenyl acetic acid (MPA), and diphenyl sulfide (DPS) obtained from Aldrich Chemicals were used without further purification. All other chemicals used were also of high purity. The solutions were prepared in deionized “Nanopure” water, and freshly prepared solutions were used for each experiment. The pH of the solution was adjusted with NaOH/$HClO_4$ in Na_2HPO_4/KH_2PO_4 phosphate buffers. All other experimental details are described elsewhere.[12] The pulse radiolysis experiments were carried out with high-energy electron pulses (7 MeV, 50 ns) obtained from a linear electron accelerator, whose details are given elsewhere.[16] An aerated aqueous solution of KSCN (1×10^{-2} mol dm^{-3}) was used for determining the dose delivered per pulse using $G\epsilon_{500} = 21520$ dm^3 mol^{-1} cm^{-1} per 100 eV for the transient $(SCN)_2{\bullet}^-$ species. G denotes the number of species per 100 eV of absorbed energy ($G = 1$ corresponds to 0.1036 μmol J^{-1}), and ϵ is the molar absorptivity of the $(SCN)_2{\bullet}^-$ species at 500 nm. The dose per pulse was close to 15 Gy (1 Gy = 1 J kg^{-1}) except for kinetic experiments, which were carried out at a lower dose of about 10 Gy.

The transient species formed on pulse radiolysis were detected by optical absorption method using a 450 W pulsed xenon arc lamp and Kratos (GM-252) monocromator. The photomultiplier

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output was digitized with a 100 MHz storage oscilloscope interfaced to a computer for kinetic analysis.[17] The bimolecular rate constants were determined from the linear regression plots of k_{obs} versus solute concentration for at least three independent experiments, and the variation was within 15%.

Radiolysis of the N_2-saturated neutral aqueous solution leads to the formation of three highly reactive species ($^{\bullet}H$, $^{\bullet}OH$, and e_{aq}^-) in addition to the less reactive or inert molecular products (H_2, H_2O_2, and H_3O^+).

$$H_2O \rightarrow {}^{\bullet}H, {}^{\bullet}OH, e_{aq}^-, H_2, H_2O_2, \text{and } H_3O^+ \tag{1}$$

The reaction with $^{\bullet}OH$ radical was carried out in N_2O-saturated solutions, where e_{aq}^- is quantitatively converted to $^{\bullet}OH$ radicals with $G(^{\bullet}OH) = 5.6$ and $^{\bullet}OH$ radical is the main species to react with the solute.

$$N_2O + e_{aq}^- \rightarrow {}^{\bullet}OH + OH^- + N_2 \tag{2}$$

The reaction of specific one-electron oxidants were carried out under conditions such that $^{\bullet}OH$ radicals do not react with the solute initially and only the one-electron oxidants react with the solute. These one-electron oxidants were generated as reported in the literature, and the procedure is briefly mentioned in the text.[18]

Results and Discussion

The ground-state optical absorption spectrum of neutral and acidic aqueous solutions of PTA showed an absorption band at 248 nm with very little absorption at $\lambda > 300$ nm. In basic solution (pH >10), an aqueous solution of PTA showed an absorption band at 254 nm with very little absorption at $\lambda > 300$ nm. Therefore, PTA is present in the protonated form ($C_6H_5SCH_2COOH$) in neutral and acidic solutions and in the deprotonated form ($C_6H_5SCH_2COO^-$) in basic solutions. The aqueous solution of DPS showed an absorption band at 250 nm with very little absorption at $\lambda > 300$ nm and its absorption spectrum remained unchanged in pH 1−11 region. The aqueous solution of MPA showed an absorption band at 255 nm, without any appreciable absorption at $\lambda > 300$ nm. These studies indicate that pulse radiolysis studies with optical absorption detection could be used without any correction for the ground-state absorption in 300−700 nm region.

Pulse Radiolysis Studies on (Phenylthio)acetic Acid. *Reaction of •OH Radicals in Neutral Solution.* Pulse radiolysis of N_2O-saturated neutral aqueous solution of (phenylthio)acetic acid (PTA, 1.5×10^{-3} mol dm^{-3}) showed the formation of transient absorption bands at 330 and 360 nm (Figure 1a). In the presence of *tert*-butyl alcohol (0.3 mol dm^{-3}), an efficient $^{\bullet}OH$ and weak $H^{\bullet}$ atom scavenger, a small absorption band with $\lambda_{max} = 360$ nm (Δ O.D. = 0.005) was observed, suggesting that the contribution of $H^{\bullet}$ atom reaction with the solute is negligible and the transient absorption spectrum (Figure 1a) is mainly due to the reaction of the $^{\bullet}OH$ radical with the solute. The decay of the transient bands at 330 and 360 nm showed mixed kinetics and time-resolved studies (Figure 1b,c) showed that the transient band at 360 nm decay faster than that at 330 nm and that only one band at 330 nm was observed 90 μs after the pulse. Time-resolved studies have not shown the formation of a transient absorption band with the decay of 330 and 360 nm bands. It appears from Figure 1 that the transient absorption bands are sharp, and the contribution of 360 nm band at 300 nm and that of 330 nm band at 390 nm may be negligible. The transient absorptions at 300 and 390 nm decayed by second-order kinetics with $2k/\epsilon l = 1.1 \times 10^4$ s^{-1} and by first-order kinetics with $k = 5.2 \times 10^4$ s^{-1} (inset of Figure 1), respectively. Under these conditions, the decay rates may be considered for 330 and 360 nm bands, respectively. The rate constant for the reaction of the $^{\bullet}OH$ radical with PTA was determined by formation kinetic studies at 330 and 360 nm. The pseudo-first-order rate increased linearly with solute concentration, and the bimolecular rate constant at both the wavelengths was determined to be $(7.2 \pm 0.8) \times 10^9$ dm^3 mol^{-1} s^{-1} (Table 1).

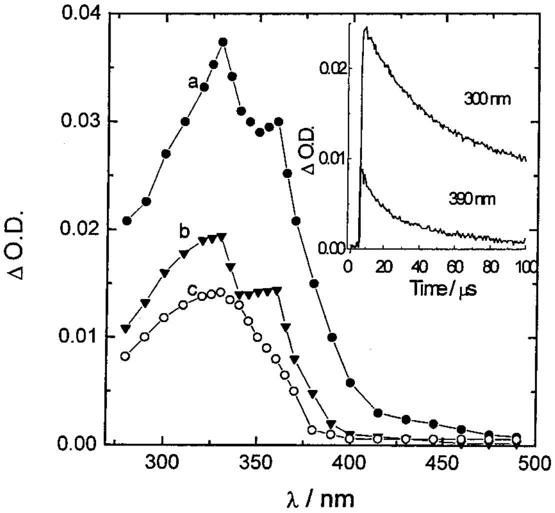


Figure 1. Transient absorption spectra obtained on pulse radiolysis of N_2O-saturated neutral aqueous solution of PTA (1.5×10^{-3} mol dm^{-3}) 1.5 (a), 40 (b), and 90 μs (c) after the pulse. Inset show absorption−time profiles at 300 and 390 nm.

TABLE 1: Kinetic and Spectral Parameters of the Transient Species Formed from Aryl Sulfides[a]

reaction	λ_{max}/nm	pH	K_f/ dm^3 mol^{-1} s^{-1}	K_d/s^{-1}	% of SRC[a]
PTA + •OH	330, 360	7	7.2×10^9	3.2×10^{4b} 1.1×10^{4c}	0
PTA + •OH	310, 540	*d*	3.8×10^9	4.6×10^3	100
DPS + •OH	340, 350−370, 750	7	4.3×10^8	2.9×10^{4e}	12
DPS + •OH	340, 750	*f*	5.5×10^8	1.4×10^4	100
MPA + •OH	320, 360, 550, 730	7	7.5×10^9 9.2×10^9	1.3×10^5	55
MPA + •OH	320, 550, 730	*g*		1×10^4	100

[a] SRC, solute radical cation in neutral solution. k_d, decay by first-order kinetics. [b] At 390 nm. [c] At 300 nm (second-order kinetics). [d] $HClO_4$ = 7.8 mol dm^{-3}. [e] At 750 nm. [f] [$HClO_4$] 1 mol dm^{-3}. [g] $HClO_4$ = 0.5 mol dm^{-3}.

In aerated solutions, pulse radiolysis studies showed only one band at 360 nm (Figure 2). The decay at 390 nm showed first-order kinetics with $k = 6.8 \times 10^4$ s^{-1}, close to the value observed in N_2O-saturated condition. The relative decrease in the absorbance at 360 nm, in aerated solutions, was much less than that observed at 330 nm (Figures 1 and 2). These studies suggest that the band at 330 nm has high reactivity with oxygen and is not seen in aerated conditions. Therefore, the band at 330 nm may be due to a C-centered radical, whereas the band at 360 nm is due to some other species. The available literature on organic sulfur compounds suggest that the band at 330 nm is due to a species formed on addition of the $^{\bullet}OH$ radical to a benzene ring (a, Scheme 1), and the band at 360 nm is due to a sulfur-centered OH adduct (b, Scheme 1).

The molar absorption coefficient of the sulfur centered OH-adduct of dialkyl sulfides is in the region of 4500−5500 dm^3 mol^{-1} cm^{-1}.[19] Because the peak position of the OH adduct of

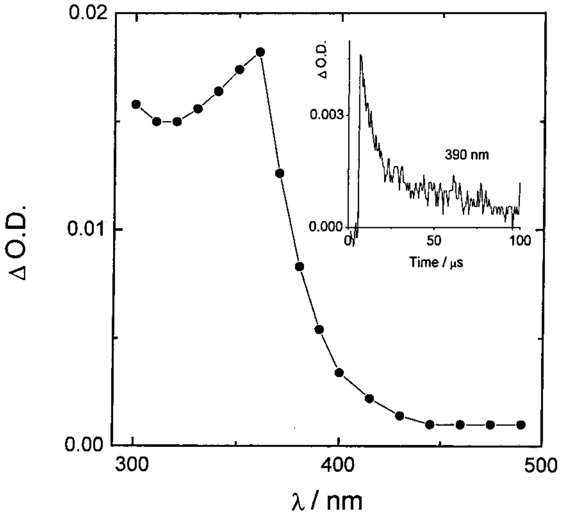


Figure 2. Transient absorption spectra obtained on pulse radiolysis of aerated neutral aqueous solution of PTA (1.5×10^{-3} mol dm^{-3}) 1.5 μs after the pulse. Inset show absorption−time profile at 390 nm.

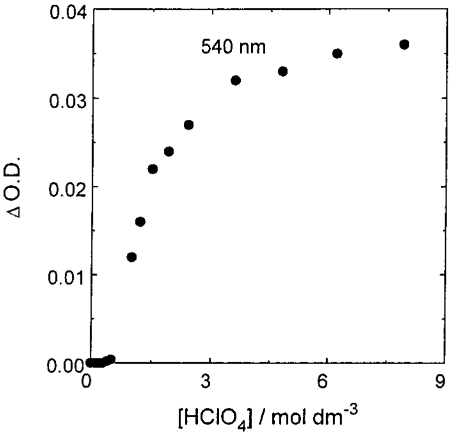


Figure 3. Variation of absorbance at 540 nm for the transient species formed on pulse radiolysis of aerated acidic aqueous solution of PTA (1.5×10^{-3} mol dm^{-3}) as a function of [$HClO_4$].

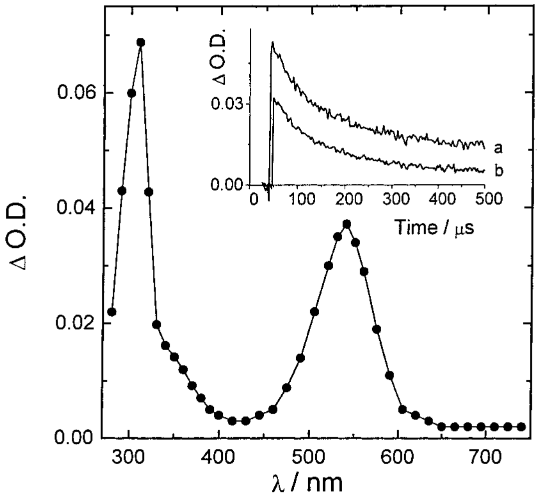
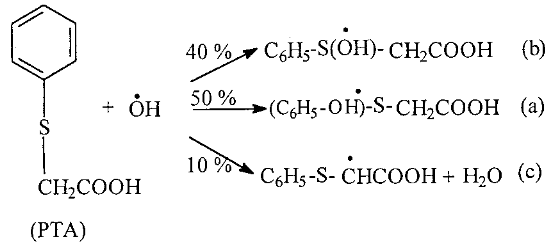


Figure 4. Transient absorption spectra obtained on pulse radiolysis of aerated acidic ($HClO_4$ = 7.8 mol dm^{-3}) aqueous solution of PTA (1.5×10^{-3} mol dm^{-3}). Inset show absorption−time profiles at 310 (a) and 540 nm (b).

SCHEME 1



PTA is in the same region, and assuming that the aromatic ring has a small effect on this band intensity, the average value of 5000 dm^3 mol^{-1} cm^{-1} could be taken as the molar absorption coefficient for the transient species absorbing at 360 nm. Under these conditions, the concentration of the transient species is calculated to be 3.5×10^{-6} mol dm^{-3}. However, the actual concentration of •OH radicals, under the present experimental conditions, is 9×10^{-6} mol dm^{-3}. Therefore, about 40% of the •OH radicals are reacting to form the transient species absorbing at 360 nm (sulfur centered OH adduct).

The reaction of •OH radicals with dialkyl sulfides is mainly by one-electron oxidation with a small fraction (~10%) by H-abstraction forming α-thio radicals, which absorb in the 280−290 nm region. Considering that ~10% of the •OH radicals are reacting with PTA to form α-thio radicals, the remaining fraction (~50%) of •OH radicals would be adding to the benzene ring (Scheme 1).

Pulse radiolysis studies with $N_3^•$, a specific one-electron oxidant, did not show any transient absorption in the 300−600 nm region, indicating that the transient absorption (Figure 1) is not due to solute radical cation or $N_3^•$ is not reacting with PTA. To confirm this, the studies were carried out with $Cl_2^{•-}$, a powerful one-electron oxidant. The transient absorption band of $Cl_2^{•-}$ (λ = 345 nm), formed on pulse radiolysis of aerated acidic (pH = 1) aqueous solution of Cl^- (4×10^{-2} mol dm^{-3}), was observed to decay faster on addition of a low concentration of PTA (0.4×10^{-3} mol dm^{-3}), indicating electron transfer from PTA to $Cl_2^{•-}$. The pseudo-first-order rate constant (k_{obs}) was found to increase linearly with PTA concentration, and the bimolecular rate constant was determined to be 1.3×10^9 dm^3 mol^{-1} s^{-1}. The time-resolved studies did not show the formation of any new band in the 300−600 nm region. These studies suggest that although electron transfer is taking place from PTA to $Cl_2^{•-}$, the solute radical cation (PTA$^{•+}$) is either not stable under these conditions or has no transient absorption bands in the 300−600 nm region. $SO_4^{•-}$, another strong one-electron oxidant ($E°$ = 2.4 V), was also able to undergo electron transfer with PTA with a bimolecular rate constant of 2.1×10^9 dm^3 mol^{-1} s^{-1}, without formation of any transient absorption band in the 300−700 nm region. These studies suggest that •OH radicals are not reacting with PTA, under neutral conditions, to form the solute radical cation (see text also).

Reaction of •OH Radicals in Acidic Solution. The nature of the transient absorption spectrum remained same in pH 1−10. However, pulse radiolysis in highly acidic solutions ($HClO_4 \geq$ 0.5 mol dm^{-3}) showed formation of another transient absorption at 540 nm with increasing concentration of $HClO_4$. Figure 3 shows the variation of absorbance at 540 nm as a function of $HClO_4$ concentration. The band at 540 nm was seen only when [$HClO_4$] was more than 0.5 mol dm^{-3}. The absorbance was seen to reach saturation value when the $HClO_4$ concentration was in the 6−8 mol dm^{-3} region. The transient absorption spectrum (Figure 4) obtained on pulse radiolysis of aerated acidic ($HClO_4$ = 7.8 mol dm^{-3}) aqueous solution of PTA (1.5 $\times$ 10^{-3} mol dm^{-3}) exhibits absorption bands at 310 and 540 nm. Both of the bands decayed by first-order kinetics with $k = (4.6 \pm 0.2) \times 10^3$ s^{-1} (inset of Figure 4), suggesting the formation of one transient species. The rate constant for the

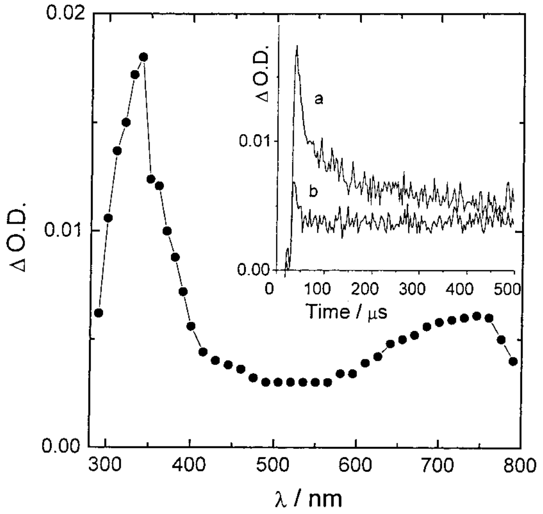
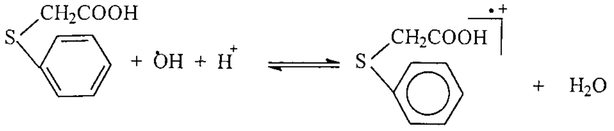


Figure 5. Transient absorption spectra obtained on pulse radiolysis of N_2O-saturated aqueous solution of DPS (1.5×10^{-3} mol dm^{-3}, pH = 10) 9 μs after the pulse. Inset show absorption−time profiles at 340 nm in N_2O (a) and aerated (b) conditions.

SCHEME 2



reaction of •OH radicals with PTA was determined by formation kinetic studies at 310 and 540 nm, and the bimolecular rate constant value (3.8×10^9 dm^3 mol^{-1} s^{-1}) was same at both the wavelengths. The yield and the lifetime of the 540 nm band was observed to increase with $HClO_4$ concentration. The transient absorption at 540 nm remained independent of solute concentration (0.2−2) $\times 10^{-3}$ mol dm^{-3}, showing the formation of monomeric species. Sulfur centered monomer radical cations absorb in the region of 300 nm but have a high tendency to form dimer radical cations. Therefore, the transient absorption spectrum (Figure 4) could not be due to sulfur-centered monomer radical cation. The positive charge is expected to be delocalized over the entire molecule, because of the presence of the benzene ring. The intermediate OH adducts and their reaction with H^+ could not be observed under the present experimental conditions. Therefore, the formation of the solute radical cation is represented in an overall reaction as shown in Scheme 2.

Pulse Radiolysis Studies on Diphenyl Sulfide. *Reaction of •OH Radical in Neutral Solution.* Pulse radiolysis of N_2O-saturated aqueous solution of DPS (1.5×10^{-3} mol dm^{-3}, pH = 10) showed the formation of a transient absorption band with λ_{max} = 340 nm, a shoulder in the 350−370 nm region, and a broad band in the 700−780 nm region with λ_{max} at 750 nm (Figure 5). The transient absorption was not seen in the presence of *tert*-butyl alcohol, an efficient •OH radical and weak H• atom scavenger, suggesting that the transient spectrum (Figure 5) is due to the reaction of •OH radicals, and the contribution of H• atom reaction is negligible. The bimolecular rate constant for the reaction of the •OH radical with DPS, forming a 340 nm band, was determined by formation kinetic studies and the value was (4.3 ± 0.2) $\times 10^8$ dm^3 mol^{-1} s^{-1}. The band at 750 nm decayed by first-order kinetics with $k = 2.9 \times 10^4$ s^{-1}. The band at 340 nm showed mixed kinetics, with the initial portion decaying by first-order kinetics with $k = 2.6 \times 10^4$ s^{-1}. The latter portion still showed mixed kinetics, indicating the presence of more than one transient species. The decay of the 750 nm band and the initial portion of the band at 340 nm remained unaffected in aerated conditions, whereas the latter portion of the band at 340 nm was appreciably quenched in aerated conditions (inset of Figure 5). These studies suggest that the reaction of the •OH radical with DPS results (1) in the formation of more than one transient species immediately after the pulse and without any transformation to another transient species. (2) The transient species absorbing at 750 nm has absorption in the 340 nm region and is not affected in aerated conditions. (3) The transient absorbance in the 300−400 nm region is affected in aerated conditions and is due to more than one transient species.

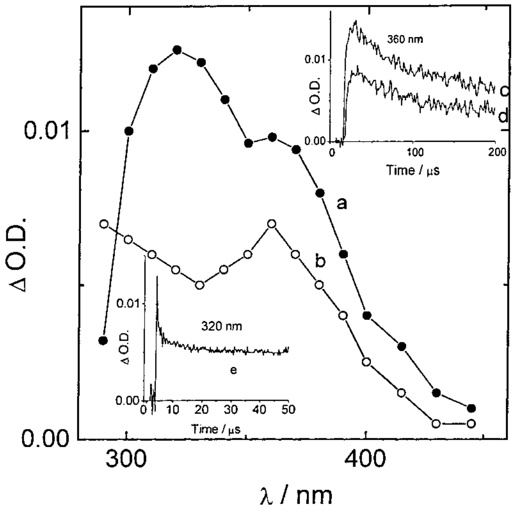


Figure 6. Transient absorption spectra obtained on pulse radiolysis of aqueous solution of DPS (1.5×10^{-3} mol dm^{-3}, pH = 10) 100 μs after the pulse in N_2O (a) and 5 μs after the pulse in O_2-saturated conditions (b). Inset show absorption−time profiles at 360 nm in N_2O (c) and O_2-saturated conditions (d) and at 320 nm in O_2-saturated conditions.

The transient absorption at 750 nm has completely decayed within 100 μs; therefore, the absorption in the 300−400 nm region 100 μs after the pulse would be due to species other than absorbing at 750 nm. Figure 6a shows the transient absorption spectrum obtained on pulse radiolysis of DPS (1.5 $\times 10^{-3}$ mol dm^{-3}, pH = 10), 100 μs after the pulse, in N_2O conditions. The transient absorption spectrum showed a band at 320 nm with a shoulder at 360 nm. The decay of transient absorption bands at 320 and 360 nm was different and showed mixed kinetics, suggesting that both the bands are due to different species. The decay kinetics at 360 nm remained the same in N_2O and O_2-saturated conditions (inset of Figure 6).

Figure 6b shows the transient absorption spectrum obtained on pulse radiolysis of an O_2-saturated aqueous solution of DPS (1.5×10^{-3} mol dm^{-3}) 5 μs after the pulse, which exhibits an absorption band at 360 nm and increasing absorption at $\lambda <$ 320 nm. The absorption−time profile at 320 nm (inset of Figure 6) showed very fast initial decay, which should be due to the reaction of a carbon centered radical with O_2. The transient absorption 5 μs after the pulse should therefore be due to the sulfur-centered OH adduct, with very little contribution of the 320 nm band. Taking an average value of 5×10^3 dm^3 mol^{-1} cm^{-1} for the molar absorption coefficient for the transient species absorbing at 360 nm (sulfur centered OH adduct), the concentration of the transient species is calculated to be 1.4×10^{-6} mol dm^{-3}. Under the present experimental conditions, the actual concentration of •OH radicals is 5×10^{-6} mol dm^{-3}.

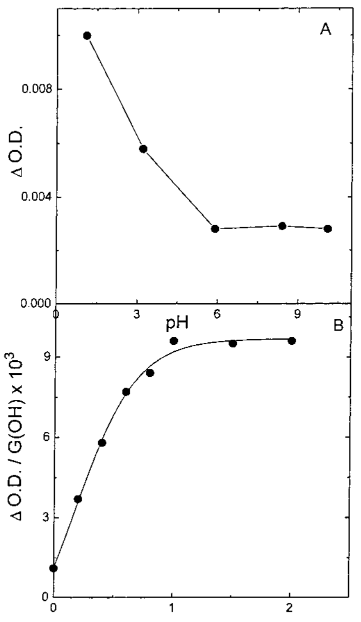


Figure 7. Variation of absorbance (750 nm) as a function of pH (A) and concentration of $HClO_4$ (B) formed on pulse radiolysis of aerated aqueous solution of DPS (1.5×10^{-3} mol dm^{-3}).

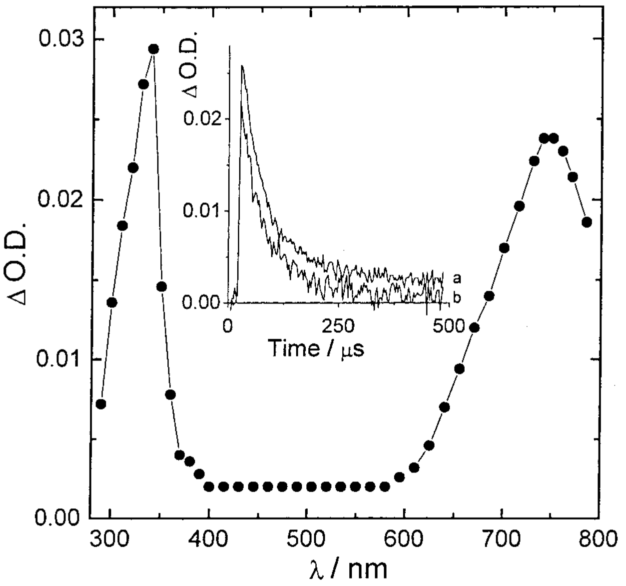
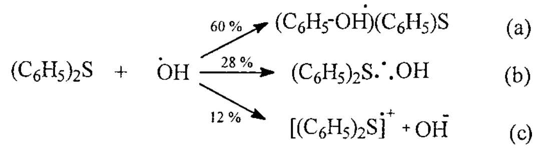


Figure 8. Transient absorption spectrum obtained on pulse radiolysis of aerated acidic ($HClO_4 = 1$ mol dm^{-3}) aqueous solution of DPS (1.5×10^{-3} mol dm^{-3}) 6 μs after the pulse. Inset show absorption–time profiles at 340 (a) and 750 nm (b).

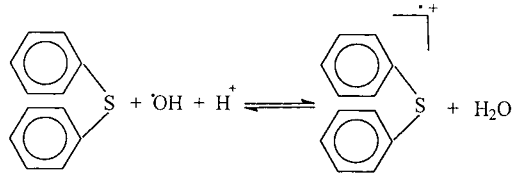
Therefore, ~ 28% of •OH radicals are reacting with DPS to form sulfur centered OH-adduct (360 nm band).

Reaction of •OH Radicals in Acidic Solution. The nature of the transient absorption spectrum and decay kinetics remained same in the pH 6–10 region. However, in acidic solutions, the absorbance at 750 nm was observed to increase with H^+ concentration (Figure 7), reaching saturation when [$HClO_4$] was in the range of 1–2 mol dm^{-3}. Figure 8 shows the transient absorption spectrum obtained on pulse radiolysis of aerated acidic ($HClO_4 = 1$ mol dm^{-3}) aqueous solution of DPS (1.5×10^{-3} mol dm^{-3}), which exhibits absorption bands at 340 and 750 nm. The entire spectrum decayed by first-order kinetics with $k = 1.4 \times 10^4$ s^{-1}. The rate constant for the reaction of the •OH radical with DPS in acidic solution ($HClO_4 = 1$ mol dm^{-3}), determined by formation kinetic studies at 340 and 750 nm, gave similar results, and the bimolecular rate constant value was 5.5×10^8 dm^3 mol^{-1} s^{-1}. The absorbance at 340 and 750 nm remained independent of solute concentration, suggesting the formation of a monomeric species and complete reaction of •OH radicals with DPS. The molar absorption coefficient at 750 nm was determined to be 5.6×10^3 dm^3 mol^{-1} cm^{-1}. On the basis of the molar absorption coefficient value of 5.6×10^3 dm^3 mol^{-1} cm^{-1} for 750 nm band, the fraction of •OH radicals reacting with DPS, in N_2O-saturated solutions at pH = 10 to form the transient species absorbing at 340 and 750 nm bands, was determined to be about 12%. It should be due to the formation of the solute radical cation (Scheme 3).

SCHEME 3



SCHEME 4



Therefore, •OH radicals can be concluded to react with DPS, under neutral conditions, with the formation of (1) •OH addition to the benzene ring (a, Scheme 3, ~60%), (2) sulfur centered OH adduct (b, Scheme 3, ~28%), and (3) the solute radical cation with an absorption band at 750 nm and in the region of 340 nm (c, Scheme 3, ~12%).

In highly acidic solutions ($HClO_4 \geq 1$ mol dm^{-3}), OH-adducts (a,b, Scheme 3) are converted to solute radical cation. Because the decay of OH adducts (320 and 360 nm) has not followed the formation of tye solute radical cation (750 nm), the bimolecular rate constant for the reaction of •OH radicals with DPS was high (5.5×10^8 dm^3 mol^{-1} s^{-1}). The reaction of •OH radicals with DPS in acidic solutions could be represented as shown in Scheme 4. The intermediate OH adducts would be highly unstable and could not be observed under our experimental conditions. The equilibrium would shift toward the right as the concentration of H^+ is increased. The increase in the absorbance at 750 nm and the lifetime of the solute radical cation with H^+ concentration support this observation. The confirmative evidence for the assignment of the transient absorption spectrum (Figure 8) to the solute radical cation has been obtained from similarity of transient spectrum with that obtained on reaction of $Cl_2^{\bullet-}$ with DPS.

Pulse Radiolysis Studies on 4-(Methylthio)phenyl Acetic Acid. *Reaction of •OH Radical in Neutral Solution.* Figure 9a shows the transient optical absorption spectrum obtained on pulse radiolysis of the N_2O-saturated neutral aqueous solution of MPA (1.5×10^{-3} mol dm^{-3}), which exhibits absorption bands at 320, 360, and 550 nm with a broad absorption in the 690–750 nm region. The transient absorption at 550 and 730 nm showed first-order decay with $k = 1.3 \times 10^5$ s^{-1}. The transient absorption at 320 and 360 nm showed different kinetics and suggests the formation of more than one species. The transient absorption at 550 and 730 nm has completely decayed within 40 μs. The transient absorption spectrum (Figure 9b), 40 μs after the pulse, should therefore be due to species other

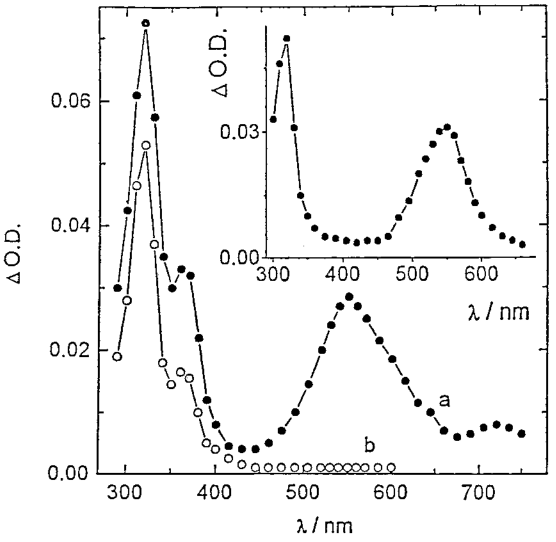


Figure 9. Transient absorption spectrum obtained on pulse radiolysis of N_2O-saturated aqueous solution of MPA (1.5×10^{-3} mol dm^{-3}) 2 (a) and 40 μs (b) after the pulse. Inset shows transient absorption spectrum obtained on reaction of $Cl_2^{\bullet-}$ with MPA.

than that showing absorption bands at 550 and 730 nm. The decay of these absorption bands still showed mixed kinetics. The bimolecular rate constant for the reaction of the $^{\bullet}$OH radical with MPA, determined by formation kinetic studies at 320 and 360 nm, gave a value of 7.5×10^9 dm^3 mol^{-1} s^{-1}.

To determine the various channels of $^{\bullet}$OH radical reaction, the reaction of $Cl_2^{\bullet-}$ was carried out with MPA, and transient absorption bands at 320 and 550 nm were observed (shown up to 660 nm, inset of Figure 9). The bimolecular rate constant for the reaction of $Cl_2^{\bullet-}$ with MPA was determined both from the decay of $Cl_2^{\bullet-}$ and formation of the 550 nm band, and similar results were obtained (2×10^9 dm^3 mol^{-1} s^{-1}). The transient absorption spectrum (λ_{max} = 320, 550, and 730 nm) should be due to solute radical cation. The molar absorption coefficient at 550 nm is determined to be 5.4×10^3 dm^3 mol^{-1} cm^{-1} (see text). Using this value of the molar absorption coefficient, the concentration of the solute radical cation formed in N_2O-saturated neutral aqueous solution (Figure 9a) is determined to be 0.52×10^{-6} mol dm^{-3}, corresponding to ~55% of the $^{\bullet}$OH radical concentration.

A small fraction of $^{\bullet}$OH radicals (~10%) may be reacting by H abstraction forming α-thio radicals, which absorb in the 280−290 nm region. The transient absorption band at 360 nm remained unaffected in aerated conditions, whereas the transient absorption band at 320 nm was appreciably quenched. The transient absorption, which is quenched in aerated conditions, should be due to a species other than the solute radical cation. In analogy with the studies reported earlier, the transient absorption bands at 320 and 360 nm are assigned to OH addition at the benzene ring and sulfur, respectively. Using the molar absorption coefficient value of 5×10^3 dm^3 mol^{-1} cm^{-1}, for the OH adduct at sulfur (λ = 360 nm), ~25% $^{\bullet}$OH radicals are observed to react to form the OH adduct at sulfur. The remaining fraction of $^{\bullet}$OH radical may be reacting to form the OH adduct at the benzene ring. The reaction of $^{\bullet}$OH radical with MPA, in neutral conditions, may be represented as shown in Scheme 5.

Reaction of $^{\bullet}$OH Radicals in Acidic Solution. The transient absorbance at 550 nm was observed to increase with $HClO_4$ concentration (Figure 10) reaching a saturation value when [$HClO_4$] was close to 0.5 mol dm^{-3}. Pulse radiolysis of aerated acidic ($HClO_4$ = 0.5 mol dm^{-3}) aqueous solution of MPA (1.5×10^{-3} mol dm^{-3}) showed the formation of transient absorption bands at 320, 550, and 730 nm (Figure 11). The spectrum matched with that obtained on reaction of $Cl_2^{\bullet-}$ with MPA. Therefore, the transient absorption spectrum obtained in acidic solution (Figure 11) should be due to solute radical cation. The entire spectrum decayed by first-order kinetics with $k = 1 \times 10^4$ s^{-1} (inset of Figure 11). Under the present experimental conditions, the molar absorption coefficient at 550 nm is determined to be 5.4×10^3 dm^3 mol^{-1} cm^{-1}.

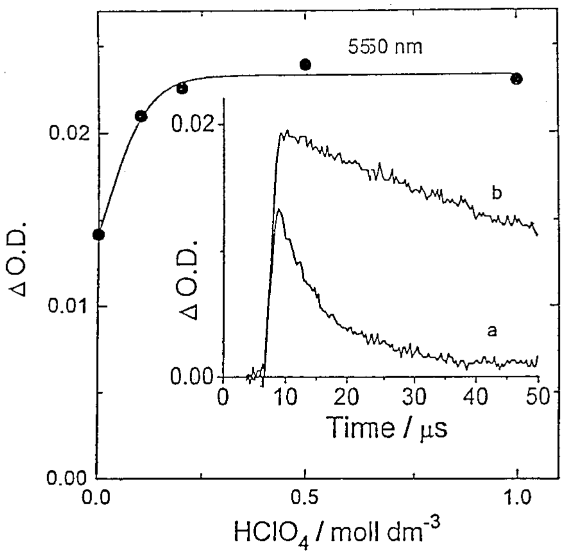


Figure 10. Variation of absorbance at 550 nm, formed on pulse radiolysis of aerated aqueous solution of MPA (1.5×10^{-3} mol dm^{-3}) as a function of $HClO_4$ concentration. Inset show absorption−time profiles at 550 nm in absence (a) and presence of $HClO_4$ (0.5 mol dm^{-3}).

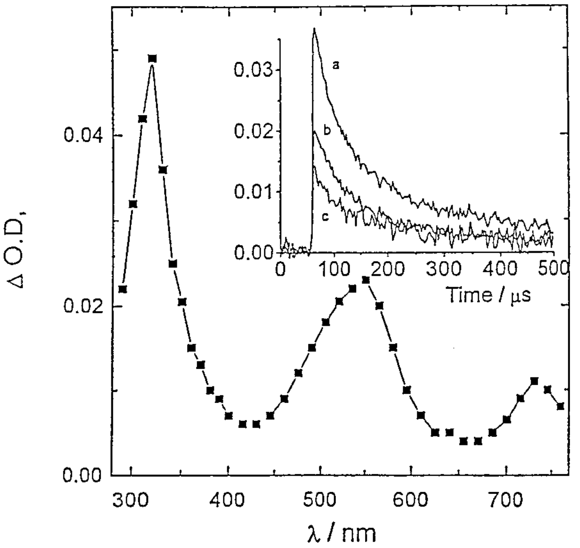
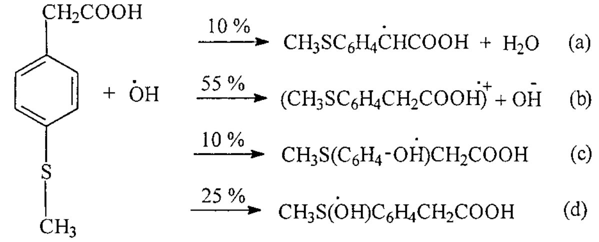
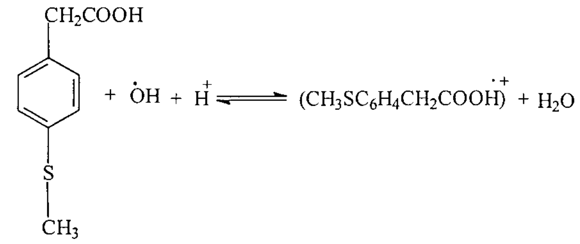


Figure 11. Transient absorption spectrum obtained on pulse radiolysis of aerated acidic ($HClO_4$ = 0.5 mol dm^{-3}) aqueous solution of MPA (1.5×10^{-3} mol dm^{-3}). Inset shows absorption−time profiles at 320 (a), 550 (b), and 730 nm (c).

SCHEME 5



SCHEME 6



In acidic solutions, only one transient species (solute radical cation) is formed, and its absorbance and lifetime were observed to increase with $HClO_4$ concentration (inset of Figure 10). The rate constant for the reaction of the •OH radical with MPA in acidic solution is high. The overall reaction of the •OH radical with MPA is shown in Scheme 6. The equilibrium would shift toward the right as the concentration of $HClO_4$ is increased. The increase in the absorbance and the lifetime support the existence of the equilibrium.

Conclusions

The nature of hydroxyl radical reaction with aryl sulfides is observed to depend strongly on the nature of the substituted group present in the molecule. In a neutral aqueous solution of (phenylthio)acetic acid, hydroxyl radical is unable to undergo electron-transfer reaction, whereas 55% of the •OH radicals react with 4-(methylthio)phenyl acetic acid by solute radical cation formation. The fraction of the solute radical cation formed in acidic solution is observed to increase with increasing concentration of acid as the electron withdrawing power of the •OH radical is increased in the presence of H^+.[20] The other channels available for reaction of •OH radicals with aryl sulfides, in neutral aqueous solutions, are not taking place in highly acidic solutions, and the solute radical cation is the only transient species formed.

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