

Effect of electron-withdrawing power of the substituted group on $\cdot\text{OH}$ radical reaction with substituted aryl sulphides: A pulse radiolysis study

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Abstract. In neutral aqueous solution of (phenylthio)acetic acid, hydroxyl radical is observed to react with a bimolecular rate constant of $7.2 \times 10^9 \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$ and the transient absorption bands are assigned to $\cdot\text{OH}$ radical addition to benzene and sulphur with a rough estimated values of 50 and 40% respectively. The reaction of the $\cdot\text{OH}$ radical with diphenyl sulphide ($k = 4.3 \times 10^8 \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$) is observed to take place with formation of solute radical cation, OH-adduct at sulphur and benzene with estimated values of about 12, 28 and 60% respectively. The transient absorption bands observed on reaction of $\cdot\text{OH}$ radical, in neutral aqueous solution of 4-(methylthio)phenyl acetic acid, are assigned to solute radical cation ($\lambda_{\text{max}} = 550$ and 730 nm), OH-adduct at sulphur ($\lambda_{\text{max}} = 360 \text{ nm}$) and addition at benzene ring ($\lambda_{\text{max}} = 320 \text{ nm}$). The fraction of $\cdot\text{OH}$ radical reacting to form solute radical cation is observed to depend on the electron-withdrawing power of substituted group. In acidic solutions, depending on the concentration of acid and electron-withdrawing power, solute radical cation is the only transient species formed on reaction of $\cdot\text{OH}$ radical with the sulphides studied.

Keywords. Pulse radiolysis; aryl sulphides; hydroxyl radicals; aqueous solution.

1. Introduction

Chemistry of radicals and radical ions derived from organic sulphides has been a subject of active interest as sulphur-centred radical species play an important role in understanding the biological systems with sulphur-containing compounds.^{1–4} These studies are also useful in understanding the electron-transfer and redox reactions of bio-molecules.^{4–7} Hydroxyl radicals and specific one-electron oxidants are known to bring about one-electron oxidation of dialkyl sulphides (R_2S), resulting in the formation of sulphur-centred radical cations ($\text{R}_2\text{S}^{\bullet+}$) either directly or via a complex sequence of reactions involving an OH-adduct, an α -thio radical and a monomer radical cation.^{8–10} The oxidized sulphur has a high tendency to be stabilized by co-ordination with a free p -electron pair of a second sulphur atom or a hetroatom (O, N, P, halogen) both by intra- and inter-molecular association. Direct evidence for the involvement of an OH-adduct, α -thio radical and monomer radical cation could be obtained from functionalized sulphides. Sulphur-centred cationic species are represented by a three-electron bond containing two bonding σ and one anti-bonding σ^* electron. These three-electron bonded ($2c-3e$) species have been the subject of active interest in both experimental and theoretical investigations.^{8–13}

Kinetic, spectroscopic and redox properties of the transient species formed on reaction of $\bullet\text{OH}$ radical with substituted alkyl sulphides have been reasonably well understood and mainly one channel (sulphur site) is observed in most of the cases. On the other hand, only a few studies have been made on aryl-substituted sulphur compounds.^{14–16} The benzene ring acts as an additional site for reaction with $\bullet\text{OH}$ radical and spin delocalization reduces the tendency of the solute radical cation to form dimer radical cation. The present studies on (phenylthio)acetic acid, diphenyl sulphide and 4-(methylthio)phenyl acetic acid have been carried out with in order to understand the effect of electron-withdrawing power of substituted groups on the nature of $\bullet\text{OH}$ radical reaction with aryl-substituted sulphur compounds. It is important to know the conditions under which radical cation is formed as this information is essential to determine its reactivity.

2. Experimental

(Phenylthio)acetic acid (PTA), 4-(methylthio)phenyl acetic acid (MPA) and diphenyl sulphide (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/HClO₄ in Na₂HPO₄/KH₂PO₄ 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.¹⁷ Aerated aqueous solution of KSCN (1×10^{-2} mol dm⁻³) was used for determining the dose delivered per pulse, which 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 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 N₂-saturated neutral aqueous solution leads to the formation of three highly reactive species ($\bullet\text{H}$, $\bullet\text{OH}$, e_{aq}^-) in addition to the less reactive or inert molecular products (H₂, H₂O₂, and H₃O⁺). The reaction with $\bullet\text{OH}$ radical, in neutral aqueous solutions was carried out in N₂O-saturated solutions, where e_{aq}^- is quantitatively converted to $\bullet\text{OH}$ radicals ($e_{\text{aq}}^- + \text{N}_2\text{O} \rightarrow \bullet\text{OH} + \text{OH}^- + \text{N}_2$). In acidic solutions, the reaction was carried out in aerated conditions to scavenge H \bullet and e_{aq}^- ($\text{H}\bullet + \text{O}_2 \rightarrow \text{HO}_2\bullet$; $e_{\text{aq}}^- + \text{H}^+ \rightarrow \text{H}\bullet$).

3. Results and discussion

3.1 Pulse radiolysis studies on (phenylthio)acetic acid

3.1a *Reaction of $\bullet\text{OH}$ radicals in neutral solution:* Pulse radiolysis of N₂O-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 *t*-butyl alcohol (0.3 mol dm⁻³), an efficient $\bullet\text{OH}$ and weak H \bullet atom scavenger, a small absorption band with $\lambda_{\text{max}} = 360$ nm ($\Delta\text{OD} = 0.005$) 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 $\bullet\text{OH}$ radical with the solute. The decay of the transient bands at 330 and 360 nm showed mixed kinetics. Time-resolved studies showed that the transient band at 360 nm decays faster than that at 330 nm and only one band at 330 nm was observed 90 μs after the pulse. It appears from figure 1a

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 $2k/\epsilon l = 1.1 \times 10^4 \text{ s}^{-1}$ and by first-order kinetics with $k = 5.2 \times 10^4 \text{ s}^{-1}$ respectively. Under these conditions, the decay rates may be considered for 330 and 360 nm bands respectively. The rate constant for the reaction of $\bullet\text{OH}$ 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 $(7.2 \pm 0.8) \times 10^9 \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$.

In aerated solutions, pulse radiolysis studies showed only one band at 360 nm, which decayed by first-order kinetics with $k = 6.8 \times 10^4 \text{ s}^{-1}$, 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. These studies suggest that the species showing a 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-centred radical whereas the band at 360 nm is due to some other species. The available literature on organic sulphur compounds suggests that the band at 330 nm is due to a species formed on addition of $\bullet\text{OH}$ radical to benzene ring (scheme 1a) and the band at 360 nm is due to sulphur-centred OH-adduct (scheme 1b). The molar absorption coefficient of sulphur-centred OH-adduct of dialkyl sulphides is in the region of $4500\text{--}5500 \text{ dm}^3 \text{ mol}^{-1} \text{ cm}^{-1}$.¹⁸ Since the peak position of the OH-adduct of PTA is in the same region and assuming that the aromatic ring has small effect on this band intensity, the average value of

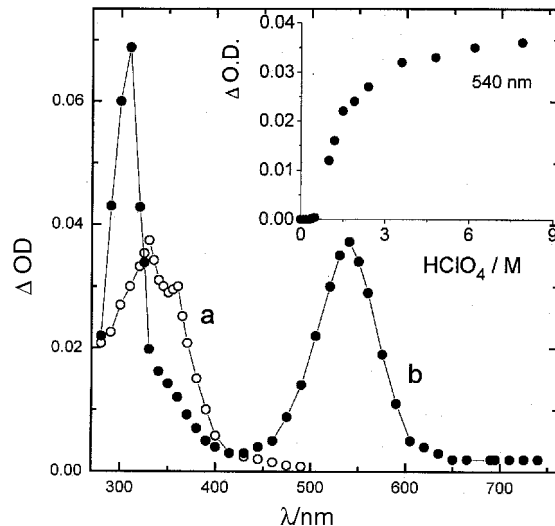
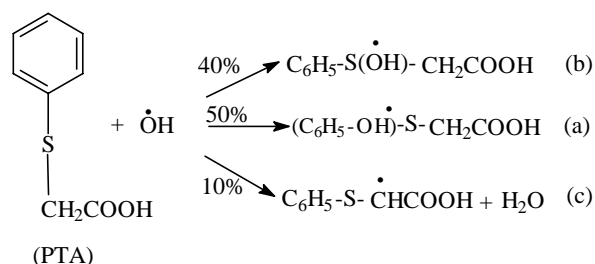


Figure 1. Transient absorption spectra obtained on pulse radiolysis of N_2O -saturated neutral aqueous solution of PTA ($1.5 \times 10^{-3} \text{ mol dm}^{-3}$) (a) and aerated acidic ($\text{HClO}_4 = 7.8 \text{ mol dm}^{-3}$) aqueous solution of PTA ($1.5 \times 10^{-3} \text{ mol dm}^{-3}$) (b) Inset shows variation of absorbance at 540 nm for the transient species formed on pulse radiolysis of aerated acidic aqueous solution of PTA ($1.5 \times 10^{-3} \text{ mol dm}^{-3}$) as a function of $[\text{HClO}_4]$.



Scheme 1.

$5000 \text{ dm}^3 \text{ mol}^{-1} \text{ cm}^{-1}$ could be taken as the molar absorption coefficient for the transient species absorbing at 360 nm. Under these conditions, about 40% of $\bullet\text{OH}$ radicals are reacting to form the transient species absorbing at 360 nm (sulphur-centred OH-adduct).

The reaction of $\bullet\text{OH}$ radicals with dialkyl sulphides is mainly by one-electron oxidation with a small fraction ($\sim 10\%$) by H-abstraction forming α -thio radicals, which absorb in 280–290 nm region. Considering that $\sim 10\%$ of $\bullet\text{OH}$ radicals are reacting with PTA to form α -thio radicals, the remaining fraction ($\sim 50\%$) of $\bullet\text{OH}$ radicals would be adding to benzene ring. Under neutral conditions, the formation of solute radical cation, was not observed (see text also).

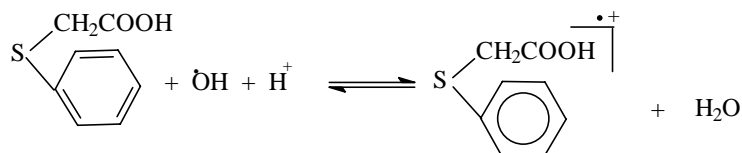
The transient absorption band of $\text{Cl}_2^{\bullet-}$ ($\lambda = 345 \text{ nm}$), formed on pulse radiolysis of aerated acidic ($\text{pH} = 1$) aqueous solution of Cl^- ($4 \times 10^{-2} \text{ mol dm}^{-3}$) was observed to decay faster on addition of low concentration of PTA ($0.4 \times 10^{-3} \text{ mol dm}^{-3}$), indicating electron transfer from PTA to $\text{Cl}_2^{\bullet-}$. 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 $1.3 \times 10^9 \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$. The time-resolved studies did not show the formation of any new band in 300–600 nm region. These studies suggest that although electron transfer is taking place from PTA to $\text{Cl}_2^{\bullet-}$, the solute radical cation ($\text{PTA}^{\bullet+}$) is not stable under these conditions. The solute radical cation was observed only in acidic solutions (see text).

3.1b Reaction of $\bullet\text{OH}$ radicals in acidic solution: The nature of the transient absorption spectrum remained same in $\text{pH} 1\text{--}10$. However, pulse radiolysis in highly acidic solutions ($\text{HClO}_4 \geq 0.5 \text{ mol dm}^{-3}$) showed formation of another transient absorption band at 540 nm with increasing concentration of HClO_4 (inset of figure 1). The absorbance was seen to reach saturation value when HClO_4 concentration was in 6–8 mol dm^{-3} region. The transient absorption spectrum (figure 1b) obtained on pulse radiolysis of aerated acidic ($\text{HClO}_4 = 7.8 \text{ mol dm}^{-3}$) aqueous solution of PTA ($1.5 \times 10^{-3} \text{ mol dm}^{-3}$) exhibits absorption bands at 310 and 540 nm. Both the bands decayed by first order kinetics with $k = (4.6 \pm 0.2) \times 10^3 \text{ s}^{-1}$, suggesting the formation of one transient species. The rate constant for the reaction of $\bullet\text{OH}$ radicals with PTA was determined by formation kinetic studies at 310 and 540 nm and the bimolecular rate constant value ($3.8 \times 10^9 \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$) was same at both the wavelengths. The yield and the life time of 540 nm band was observed to increase with HClO_4 concentration. The transient absorption at 540 nm remained independent of solute concentration ($0.2\text{--}2 \times 10^{-3} \text{ mol dm}^{-3}$), showing the formation of monomeric species. Sulphur-centred monomer radical cations

absorb in the region of 300 nm, but have high tendency to form dimer radical cation. Therefore, the transient absorption spectrum (figure 1b) could not be obtained due to sulphur-centred monomer/dimer radical cation. The positive charge is expected to be delocalized over the entire molecule, due to the presence of benzene ring and the formation of solute radical cation is represented in an overall reaction as shown in scheme 2. Since the solute radical cation has absorption bands in 300–600 nm region, the absence of these bands suggest that it is not formed on reaction of \cdot OH radicals with PTA in neutral conditions.

3.2 Pulse radiolysis studies on diphenyl sulphide

3.2a *Reaction of \cdot OH radical in neutral solution:* Pulse radiolysis of N_2O -saturated aqueous solution of DPS ($1.5 \times 10^{-3} \text{ mol dm}^{-3}$, $\text{pH} = 10$) showed the formation of a



Scheme 2.

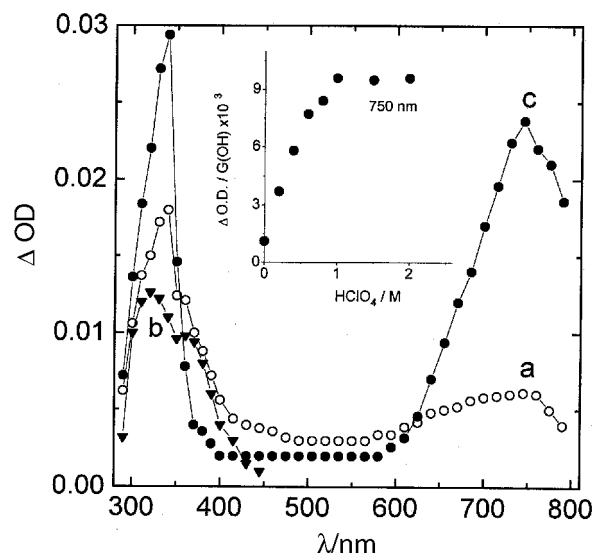
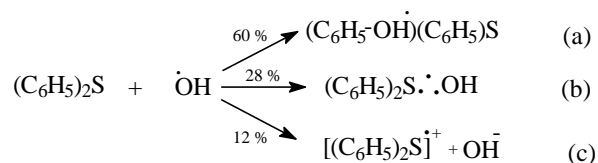


Figure 2. Transient absorption spectra obtained on pulse radiolysis of N_2O -saturated aqueous solution of DPS ($1.5 \times 10^{-3} \text{ mol dm}^{-3}$, $\text{pH} = 10$) $9 \mu\text{s}$ after the pulse (a) and $100 \mu\text{s}$ after the pulse (b). Aerated acidic ($\text{HClO}_4 = 1 \text{ mol dm}^{-3}$) aqueous solution of DPS ($1.5 \times 10^{-3} \text{ mol dm}^{-3}$) $6 \mu\text{s}$ after the pulse (c). Inset shows variation of absorbance (750 nm) as a function of $[\text{HClO}_4]$, formed on pulse radiolysis of aerated aqueous solution of DPS ($1.5 \times 10^{-3} \text{ mol dm}^{-3}$).

transient showing absorption band at $\lambda_{\text{max}} = 340$ nm, with a shoulder in 350–370 nm region and a broad band in 700–780 nm region with λ_{max} at 750 nm (figure 2a). The bimolecular rate constant for the reaction of $\bullet\text{OH}$ radical was determined by formation kinetic studies (340 nm) and the value is $(4.3 \pm 0.2) \times 10^8 \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$. The band at 750 nm decayed by first order kinetics with $k = 2.9 \times 10^4 \text{ s}^{-1}$. The band at 340 nm showed mixed kinetics, initial portion decaying by first order kinetics with $k = 2.6 \times 10^4 \text{ s}^{-1}$. The latter portion still showed mixed kinetics, indicating the presence of more than one transient species. The decay of 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. These studies suggest that the reaction of $\bullet\text{OH}$ 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 340 nm region and is not affected in aerated conditions. (3) The transient absorbance in 300–400 nm region is affected in aerated conditions and is due to more than one transient species.

The transient absorption at 750 nm has completely decayed within 100 μs , therefore the absorption in 300–400 nm region, 100 μs after the pulse would be due to species other than absorbing at 750 nm. Figure 2b shows the transient absorption spectrum obtained on pulse radiolysis of DPS ($1.5 \times 10^{-3} \text{ mol dm}^{-3}$, $\text{pH} = 10$), 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 same in N_2O and O_2 -saturated conditions whereas the band at 330 nm was appreciably quenched in aerated solutions. In analogy with the earlier studies the transient absorption band at 360 nm is assigned to sulphur-centred OH-adduct. Taking an average value of $5 \times 10^3 \text{ dm}^3 \text{ mol}^{-1} \text{ cm}^{-1}$ for molar absorption coefficient for the transient species absorbing at 360 nm (sulphur-centred OH-adduct), $\sim 28\%$ of $\bullet\text{OH}$ radicals are reacting with DPS to form sulphur-centred OH-adduct (scheme 3).

3.2b Reaction of $\bullet\text{OH}$ radicals in acidic solution: The nature of the transient absorption spectrum and decay kinetics remained same in pH 6–10 region. However, in acidic solutions, the absorbance at 750 nm was observed to increase with H^+ concentration (inset of figure 2), reaching saturation when $[\text{HClO}_4]$ was in the range of 1–2 mol dm^{-3} . Figure 2c shows the transient absorption spectrum obtained on pulse radiolysis of aerated acidic ($\text{HClO}_4 = 1 \text{ mol dm}^{-3}$) aqueous solution of DPS ($1.5 \times 10^{-3} \text{ mol dm}^{-3}$), which exhibits absorption bands at 340 and 750 nm. The entire spectrum decayed by first order kinetics with $k = 1.4 \times 10^4 \text{ s}^{-1}$. The rate constant for the reaction of $\bullet\text{OH}$ radical with DPS in acidic solution ($\text{HClO}_4 = 1 \text{ mol dm}^{-3}$), determined by formation kinetic studies at 340 and 750 nm gave similar results and the bimolecular rate constant value was $5.5 \times 10^8 \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$. The absorbance at 340 and 750 nm remained independent of solute concentration, suggesting the formation of a monomeric species and complete reaction of $\bullet\text{OH}$ radicals with DPS. The molar absorption coefficient at 750 nm was determined to be $5.6 \times 10^3 \text{ dm}^3 \text{ mol}^{-1} \text{ cm}^{-1}$. Based on the molar absorptivity value of $5.6 \times 10^3 \text{ dm}^3 \text{ mol}^{-1} \text{ cm}^{-1}$ for 750 nm band, the fraction of $\bullet\text{OH}$ radicals reacting with DPS, in N_2O -saturated solutions at $\text{pH} = 10$ to form the transient species absorbing at 340 and 750 nm bands, was determined to be about 12% (scheme 3c).

**Scheme 3.**

Therefore, it can be concluded that $\dot{\text{O}}\text{H}$ radicals react with DPS, under neutral conditions, with the formation of (1) $\dot{\text{O}}\text{H}$ addition to benzene ring (scheme 3a, ~60%). (2) Sulphur-centred OH-adduct (scheme 3b, ~28%). (3) The solute radical cation with absorption bands at 340 and 750 nm (scheme 3c, ~12%).

The confirmative evidence for the assignment of transient absorption spectrum (figure 2c) to solute radical cation has been obtained from similarity of transient spectrum with that obtained on reaction of $\text{Cl}_2^{\bullet-}$ with DPS. In highly acidic solutions, the formation of solute radical cation may be represented by a mechanism similar to that shown in scheme 2. The intermediate OH-adducts could not be observed in highly acidic solutions.

3.3 Pulse radiolysis studies on 4-(methylthio)phenyl acetic acid

3.3a Reaction of $\dot{\text{O}}\text{H}$ radical in neutral solution: Figure 3a shows the transient optical absorption spectrum obtained on pulse radiolysis of N_2O -saturated neutral aqueous solution of MPA ($1.5 \times 10^{-3} \text{ mol dm}^{-3}$), which exhibits absorption bands at 320, 360 and 550 nm with a broad absorption in 690–750 nm region. The transient absorption at 550 and 730 nm showed first order decay with $k = 1.3 \times 10^5 \text{ s}^{-1}$. 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 and the transient absorption spectrum (figure 3b), should therefore be due to species other 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 $\dot{\text{O}}\text{H}$ radical with MPA, determined by formation kinetic studies at 320 and 360 nm gave a value of $7.5 \times 10^9 \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$.

The transient absorption band of $\text{Cl}_2^{\bullet-}$ was observed to decay faster in the presence of low concentration of MPA and time resolved studies showed the formation of transient absorption bands at 320 and 550 nm (shown up to 660 nm, inset of figure 3). The bimolecular rate constant for the reaction of $\text{Cl}_2^{\bullet-}$ with MPA, was determined both from the decay of $\text{Cl}_2^{\bullet-}$ and formation of 550 nm band and similar results were obtained ($2 \times 10^9 \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$).

A small fraction of $\dot{\text{O}}\text{H}$ radicals (~10%) may be reacting by H-abstraction forming α -thio radicals (scheme 4a). 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 specie other than solute radical cation. By analogy with the studies reported earlier, the transient absorption bands at 320 and 360 nm are assigned to OH addition at benzene ring and sulphur respectively. Using the molar absorptivity value of $5 \times 10^3 \text{ dm}^3 \text{ mol}^{-1} \text{ cm}^{-1}$, for the OH-adduct at sulphur ($\lambda = 360 \text{ nm}$), ~25% $\dot{\text{O}}\text{H}$ radicals are observed to react to form OH-adduct at sulphur (scheme 4d). The remaining fraction of $\dot{\text{O}}\text{H}$ radical may be reacting to form OH-adduct at benzene ring (scheme 4c).

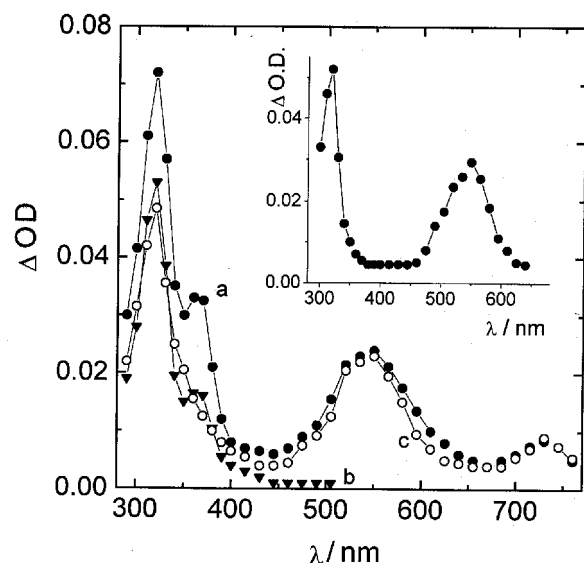


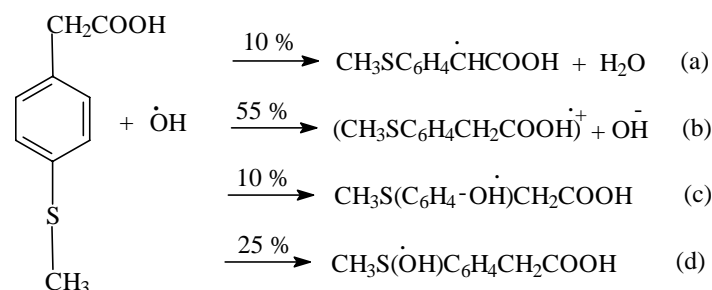
Figure 3. Transient absorption spectrum obtained on pulse radiolysis of N_2O -saturated aqueous solution of MPA ($1.5 \times 10^{-3} \text{ mol dm}^{-3}$) $2 \mu\text{s}$ after the pulse (a) and $40 \mu\text{s}$ after the pulse (b). Aerated acidic ($\text{HClO}_4 = 0.5 \text{ mol dm}^{-3}$) aqueous solution of MPA ($1.5 \times 10^{-3} \text{ mol dm}^{-3}$) $2 \mu\text{s}$ after the pulse (c). Inset shows transient absorption spectrum obtained on reaction of $\text{Cl}_2^{\bullet-}$ with MPA.

The transient absorbance at 550 nm was observed to increase with HClO_4 concentration reaching saturation value when $[\text{HClO}_4]$ was close to 0.5 mol dm^{-3} . Pulse radiolysis of aerated acidic ($\text{HClO}_4 = 0.5 \text{ mol dm}^{-3}$) aqueous solution of MPA ($1.5 \times 10^{-3} \text{ mol dm}^{-3}$) showed the formation of transient absorption bands at 320, 550 and 730 nm (figure 3c). The spectrum matched with that obtained on reaction of $\text{Cl}_2^{\bullet-}$ with MPA. Therefore the transient absorption spectrum obtained in acidic solution (figure 3c) should be due to solute radical cation. The entire spectrum decayed by first order kinetics with $k = 1 \times 10^4 \text{ s}^{-1}$. Under the present experimental conditions, the molar absorptivity at 550 nm was determined to be $5.4 \times 10^3 \text{ dm}^3 \text{ mol}^{-1} \text{ cm}^{-1}$. Using this value of molar absorptivity, the concentration of the transient species ($\lambda = 550 \text{ nm}$) formed in N_2O -saturated neutral aqueous solution (figure 3a) was determined to be $\sim 55\%$. The reaction of $\bullet\text{OH}$ radical with MPA, in neutral conditions, may be represented as shown in scheme 4.

In acidic solutions, only one transient species (solute radical cation) is formed whose absorbance and lifetime were observed to increase with HClO_4 concentration. Intermediate OH-adducts could not be observed. The reaction of $\bullet\text{OH}$ radical with MPA in highly acidic solution may be represented as shown in scheme 2. The equilibrium would shift towards right as the concentration of HClO_4 is increased. The increase in the absorbance and the lifetime support the existence of the equilibrium.

3.4 Effect of electron-withdrawing power of substituted group

The fraction of $\bullet\text{OH}$ radicals reacting by electron transfer reaction with the aryl sulphides studied, is observed to depend on the nature of the substituted group. The presence of



Scheme 4.

acidic group having very high electron withdrawing power (σ^*)¹⁹ is found to eliminate the chance of solute radical cation formation. Nearly 12% of $\cdot\text{OH}$ radicals react by electron transfer reaction when C_6H_5 group, with lower σ^* , is present and the fraction is increased to 55% when CH_3 group is present. As the concentration of acid is increased, the fraction of solute radical formed is also observed to increase. The amount of acid required to achieve complete radical cation formation is also observed to increase with electron withdrawing power of the solute molecule. Both the fraction of solute radical cation formed in neutral solution and concentration of acid required for complete formation of solute radical cation is observed to depend on the electron withdrawing power of the substituted group present in the solute molecule.

4. Conclusions

The nature of hydroxyl radical reaction with substituted aryl sulphides is observed to depend strongly on the nature of substituted group present in the molecule. In neutral aqueous solution of (phenylthio)acetic acid, hydroxyl radicals are unable to undergo electron transfer reaction, whereas 55% of $\cdot\text{OH}$ radicals react with 4-(methylthio)phenyl acetic acid by solute radical cation formation. The fraction of solute radical cation formed in acidic solution is observed to increase with increasing concentration of acid.

Acknowledgements

Thanks are due to Drs J P Mittal and T Mukherjee for encouragement and support to this work.

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