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Spectral, Kinetics, and Redox Studies on the Transients Formed on Pulse Radiolysis of Aqueous Solution of (4-Methylthiophenyl)methanol

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Pulse radiolysis technique has been employed to investigate the nature and the redox properties of the transient species generated on radiolysis of aqueous solution of (4-methylthiophenyl)methanol (MTPM). Pulse radiolysis in 1,2-dichloroethane, reaction with specific one-electron oxidants ($Cl_2^{\bullet -}$, $SO_4^{\bullet -}$, Tl^{2+}, $Br^{\bullet}$) and reaction of $^{\bullet}OH$ radicals in acidic solution showed absorption bands at 320 and 545 nm; these are assigned to solute radical cation with positive charge on the benzene ring. OH-adduct was observed in neutral solution. The oxidation potential for MTPM/MTPM$^{\bullet +}$ couple is determined to be 1.55 ± 0.04 V vs NHE. e_{aq}^- reacts with a bimolecular rate constant of 1.5×10^9 dm^3 mol^{-1} s^{-1} and the transient absorption bands (λ_{max} = 320, 470 nm) are assigned to the solute radical anion. E^0 value for MTPM/MTPM$^{\bullet -}$ couple is determined to be -1.84 ± 0.04 V vs NHE. The redox properties of the transient species formed on reaction with $^{\bullet}OH$, $^{\bullet}H$, and $O^{\bullet -}$ have been evaluated.

The oxidation mechanism of the sulfur-containing organic compounds has been the subject of recent radiation and photochemical investigations.[1–7] The studies on the radical and radical ions of organic sulfides have gained importance as sulfer-centered radical species are the possible key intermediates in the biological systems with sulfur-containing comounds.[8–12] One-electron oxidation of dialkyl sulfides (R_2S) by $^{\bullet}OH$ radical leads to the formation of sulfur-centered dimer radical cation, $(R_2S)_2^{\bullet +}$, via a complex sequence of reactions involving OH-adduct, α-thio radicals, and monomer radical cation for which no direct evidence exists in the literature.[13] Some experimental evidence for the formation of these intermediates could be obtained in functionalized dialkyl sulfides.[14,15] The nature of the functional group, chain length from sulfur, and pH have been shown to play an important role in the final stabilization of the oxidized sulfur. Oxidized sulfur has a high tendency to stabilize with the free p-electron pair of another heteroatom (S, N, P, halogen) forming a 3-electron bonded species, except in the case of *t*-butyl sulfide in which solute radical cation was observed to have an absorption band at 285 nm, stabilized mainly due to the steric hindrance provided by the solute molecule.[10,16–19] Two-center three-electron (2σ–$1\sigma^*$) bonding has been subject of both experimental and theoretical investigations.[20,21] Aryl substitution is also expected enhance the stabilization of monomer radical cation due to delocalization of the positive charge on the benzene ring.[22,25] The effect of substituents on the nature and reactivity of transients produced from alkyl sulfides has been reasonably well understood and a large number of publications have come in recent years. The effect of aryl substitution on the nature of the transients formed is still lacking.[22–25] CH_2OH and CH_3 groups have Hammett parameters[26] (σ^*) of 0.56 and 0, respectively. It would be of interest to study the sites of attack in the presence of alkyl and aryl groups present in the same molecule and compare the results with thioanisole and 2-(phenylthio)ethanol, which have a group in common. The present investigations are aimed in this direction and the properties of the transient species formed on radiolysis of (4-methylthiophenyl)methanol (MTPM) are discussed.

Experimental

(4-methylthiophenyl)methanol (MTPM, scheme 1), obtained from Aldrich Chemicals, was of high purity and was used without any further purification. Freshly prepared solutions were used for each experiment. The solutions were prepared in 1×10^{-3} mol dm^{-3} phosphate buffer using "nanopure" water. The pH was adjusted with $NaOH/HClO_4$. High purity gases (N_2, N_2O, O_2) were used for purging the solutions. All other chemicals used were also of high purity. The optical adsorption studies in the ground state were carried out with Hitachi 330 spectrophotometer. All other experimental details are described elsewhere.[15]

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.[27] The dose delivered per pulse was determined with aerated aqueous solution of KSCN (1×10^{-2} mol dm^{-3}) with $G\varepsilon$ = 21,520 dm^3 mol^{-1} cm^{-1} per 100 eV at 500 nm for the transient $(SCN)_2^{\bullet -}$ species.[28] The G denotes the number of species per 100 eV of absorbed energy and ε is the molar absorptivity of $(SCN)_2^{\bullet -}$ species at 500 nm. The dose per pulse was close to 15 Gy except for kinetic experiments, which were carried out at a lower dose of about 10 Gy.

Radiolysis of N_2-saturated neutral aqueous solution leads to the formation of three highly reactive species ($^{\bullet}H$, $^{\bullet}OH$, e_{aq}^-) in addition to the formation of less reactive or inert molecular products (H_2, H_2O_2).[29]

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$$H_2O \rightarrow {}^{\bullet}H, {}^{\bullet}OH, e_{aq}^{-}, H_2, H_2O_2, H_3O^{+} \qquad (1)$$

The reaction with $^{\bullet}OH$ radicals was carried out in N_2O-saturated solution where e_{aq}^{-} is quantitatively converted to $^{\bullet}OH$ radicals with G($^{\bullet}OH$) = 5.6 and $^{\bullet}OH$ radical is the main reactive species to react with the solute. The reaction with $O^{\bullet-}$ was carried out in N_2O-saturated solution at pH = 13, where $^{\bullet}OH$ is converted to $O^{\bullet-}$ with a pK_a value of 11.9. The reaction with e_{aq}^{-} was carried out in N_2-saturated solution in presence of *t*-butyl alcohol to scavenge $^{\bullet}OH$ radical. The reactions with specific one-electron oxidants ($N_3^{\bullet}$, $CCl_3OO^{\bullet}$, $Br^{\bullet}$, $I_2^{\bullet-}$) 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.[30–32]

The radiolysis of a solute in aqueous solution is carried out to investigate the reaction of e_{aq}^{-}, $^{\bullet}H$, and $^{\bullet}OH$ radicals, whereas in a non-polar solvent such as aliphatic, alicyclic, and also halo-alkanes, such reactions yield parent and free ions which can be easily used for the time-resolved study of electron transfer processes.[33–35] 1,2-Dichloroethane (DCE) has been employed as a solvent for the study of solute radical cations due to its high ionization potential (11.1 eV).[34] The yield of solvent cations is increased because the electrons produced by ionizing radiations are scavenged by the parent molecule and undergo dissociative electron capture reaction. The ionization potential of organic sulfur compounds is in the range of 8–9 eV and the solvent cations can easily transfer their charge to solute molecules. The rate constant values were taken from that kinetic analysis, for which very good correlation was obtained between the experimental and calculated results.[36] The bimolecular rate constant were determined from the linear regression plots of k_{obs} vs solute concentration for at least three experiments and the variation was within ±10%.

Results and Discussion

The ground state optical absorption spectrum of aqueous solution of MTPM showed an absorption band at 255 nm ($\varepsilon = 1.2 \times 10^4$ dm^3 mol^{-1} cm^{-1}) with very little absorption at $\lambda >$ 300 nm, suggesting that optical absorption detection technique can be used for pulse radiolysis studies without any correction for the ground state absorption. The absorption spectrum remained independent of pH in 1–13, showing the absence of any pK_a in this region.

Reaction of $^{\bullet}$OH Radical in Neutral Solution. Figure 1a shows the transient absorption spectrum obtained on pulse radiolysis of N_2O-saturated neutral aqueous solution of MTPM (1.5×10^{-3} mol dm^{-3}), which exhibits absorption bands at 320, 360, and 545 nm. In the presence of t-butyl alcohol (0.3 mol dm^{-3}), an efficient $^{\bullet}OH$ radical and weak $^{\bullet}H$ atom scavenger, very little absorption was observed in 350–390 nm region (Fig. 1b), indicating that the contribution of $H^{\bullet}$ atom reaction is negligible. The transient spectrum (Fig. 1b) should be due to the reaction of $H^{\bullet}$ atom with the solute (see text). The bimolecular rate constant for the reaction of $^{\bullet}OH$ radical, measured by formation kinetic studies at 320 and 545 nm (B, inset of Fig. 1), gave similar results: $(4.5 \pm 0.8) \times 10^9$ dm^3 mol^{-1} s^{-1}. The band at 545 nm and the initial portion of the band at 320 nm showed first order decay with k = 3.8×10^4 s^{-1}. (A, inset of Fig. 1). The band at 360 nm and the latter portion of the band at 320 nm showed mixed and different kinetics. The transient absorption spectrum, in aerated conditions, also showed absorption bands at 320, 360, and 545 nm (Fig. 1c) with similar decay of 545 nm band (k = 4.2×10^4 s^{-1}) and accelerated decay of 320 nm band. Since the bands at 320 and 360 nm are close to each other, their true decay rates could not be determined. These studies suggest that (1) the reaction of $^{\bullet}OH$ radical with MTPM results 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 545 nm has absorption in 320 nm region, and (3) the transient species formed on addition/abstraction by $^{\bullet}OH$ radical have absorption in 320/360 nm region without any contribution in 545 nm region.

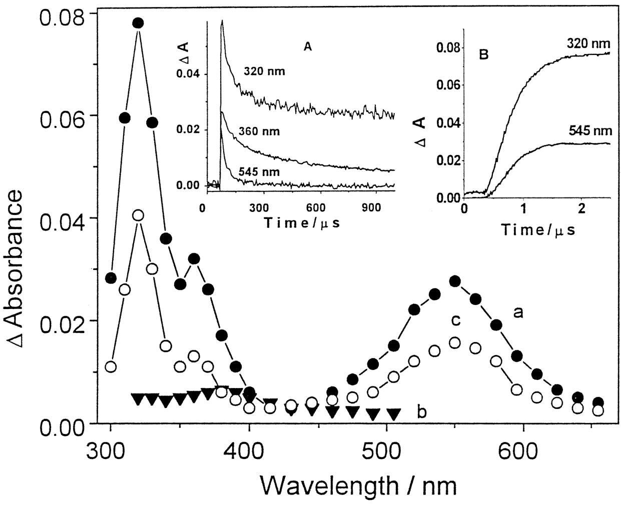


Fig. 1. Transient optical absorption spectra obtained on pulse radiolysis, 1.5 μs after the pulse, of aqueous solution MTPM (1.5×10^{-3} mol dm^{-3}, pH = 7) in N_2O-saturated (a), in presence of *t*-butyl alcohol (0.3 mol dm^{-3}) (b), and in aerated conditions in absence of *t*-butyl alcohol (c). Inset shows absorption time-profiles for the spectrum (a) at different wavelengths for decay (A), and formation (B).

Identification of Transient Species. The hydroxyl radicals are known to react with organic compounds by $H^{\bullet}$ atom abstraction, addition, and electron transfer mechanism. In order to establish the nature of $^{\bullet}OH$ radical reaction, pulse radiolysis studies were carried out with a number of specific one-electron oxidants.

Reaction with $Cl_2^{\bullet-}$. The transient absorption band of $Cl_2^{\bullet-}$ (345 nm) was observed to decay faster in the presence of low concentrations of MTPM (0.8–3) $\times 10^{-4}$ mol dm^{-3}, indicating electron transfer from MTPM to $Cl_2^{\bullet-}$ (reaction 2). The time resolved studies showed the formation of transient absorption bands at 320 and 545 nm (Fig. 2).

$$Cl_2^{\bullet-} + MTPM \rightarrow MTPM^{\bullet+} + 2Cl^{-} \qquad (2)$$

The biomolecular rate constant for reaction (2), determined from the decay of $Cl_2^{\bullet-}$ band at 345 nm as a function of solute concentration, gave a value of 3.1×10^9 dm^3 mol^{-1} s^{-1}, close to that determined from the growth of the band at 545 nm ($k = 4.2 \times 10^9$ dm^3 mol^{-1} s^{-1}). Since $Cl_2^{\bullet-}$ is a specific one-electron oxidant (E^0 = 2.1 V vs NHE), the transient absorption spectrum (Fig. 2b) should be due to solute radical cation ($MTPM^{\bullet+}$). The entire spectrum decayed by first order kinet-

Table 1. Kinetic and Spectral Parameters of the Transient Species Formed on Reaction of $^{\bullet}H$, $^{\bullet}OH$, $O^{\bullet-}$, e_{aq}^-, and Specific One-electron Oxidants and Reductants with MTPM

Reaction	pH	λ_{max}	k/dm^3 mol^{-1} s^{-1}	k_d/s^{-1}	ε/dm^3 mol^{-1} cm^{-1}	Transient species
MTPM + $^{\bullet}OH$	7	320	4.5×10^9	—		
		360		—		
		545		3.8×10^4		
MTPM + $Cl_2^{\bullet-}$	1	320	3.1×10^9	2.5×10^4	8.3×10^3	radical
		545			5.5×10^3	cation
MTPM + Tl^{2+}	1	320	2.2×10^9	2.1×10^4	—	radical
		545				cation
MTPM + $Br^{\bullet}$	1	320	4.1×10^9	4.1×10^4	—	radical
		545				cation
MTPM + $NO_3^{\bullet}$	1	320	4.5×10^9	2.6×10^4	—	radical
		545				cation
MTPM + $SO_4^{\bullet-}$	7	320	2.5×10^9	—	—	radical
		545				cation
MTPM + $Br_2^{\bullet-}$	1	320	—	—	—	radical
		545				cation
MTPM + $^{\bullet}OH$ + H^+	—	320	—	2.3×10^4		radical
		545		2.5×10^4		cation
MTPM + $H^{\bullet}$	1	360	2.2×10^9	4.3×10^5 [a]	5.8×10^3	H-adduct
MTPM + $O^{\bullet-}$	13	330	3.1×10^9	2.5×10^4 [a]	26.3×10^3	
		485			1.9×10^3	
MTPM + e_{aq}^-	7	320	1.5×10^9	1.4×10^4	11.5×10^3	anion
		470			—	radical
MTPM + $COO^{\bullet-}$	7	320	—	2.2×10^4	—	radical
		470				anion

a) Second order kinetics ($2k/\varepsilon l$).

ics with $k = 3.6 \times 10^4$ s^{-1}, close to the value observed for the decay of 545 nm band in N_2O-saturated solutions. Under the present experimental conditions, the molar absorptivity at 320 and 545 nm bands were determined to be 8.3×10^3 and 5.5×10^3 dm^3 mol^{-1} cm^{-1}, respectively (Table 1).

Reaction with Other Oxidizing Agents. One-electron oxidation of MTPM has also been investigated with a number of oxidizing agents (Table 1) and the transient absorption spectrum obtained in each case was similar to that obtained on reaction with $Cl_2^{\bullet-}$ in comparable yield. $Br_2^{\bullet-}$ was also able to undergo electron transfer with MTPM, but with ~65% yield. $N_3^{\bullet}$ radical ($E^0 = 1.3$ V vs NHE) was not able to undergo electron transfer with MTPM. These studies suggest that the oxidation potential of MTPM/MTPM$^{\bullet+}$ couple is in the range of 1.3 and 2.1 V.

Pulse Radiolysis in DCE. The transient absorption spectrum obtained on pulse radiolysis of N_2-saturated solution of MTPM (4×10^{-3} mol dm^{-3}) in DCE showed the formation of transient bands at 320 and 545 nm (Fig. 3), similar to those obtained on reaction of specific one-electron oxidants (Table 1) and $^{\bullet}OH$ radicals with MTPM in acidic solution (see text). The transient absorption spectrum (Fig. 3) is assigned to solute radical cation (reactions 3 and 4). Since the exact yield of solvent radical cation (DCE$^{\bullet+}$) is not known, the molar absorptivity of solute radical cation (MTPM$^{\bullet+}$) in DCE could not be determined.

$$\mathrm{DCE} \rightarrow \mathrm{DCE}^{\bullet+} + e^- \tag{3}$$

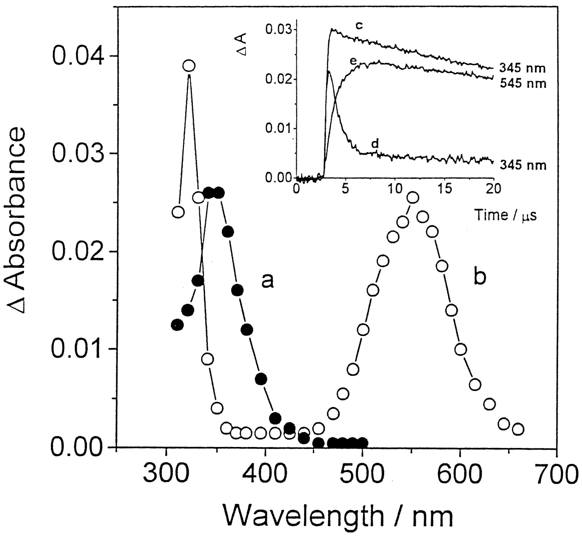


Fig. 2. Transient optical absorption spectrum obtained on pulse radiolysis of aerated aqueous solution of Cl^- (4×10^{-2} mol dm^{-3}, pH = 1) in presence of MTPM (3×10^{-4} mol dm^{-3}), immediately (a), and 5.5 μs after the pulse (b). Inset shows absorption time profiles at 345 nm in absence (c), and presence of MTPM (d), and at 545 nm (e).

$$\mathrm{DCE}^{\bullet+} + \mathrm{MTPM} \rightarrow \mathrm{MTPM}^{\bullet+} + \mathrm{DCE} \tag{4}$$

Different Channels for Reaction of $^{\bullet}$OH Radical. The nature of the transient absorption band at 545 nm formed on

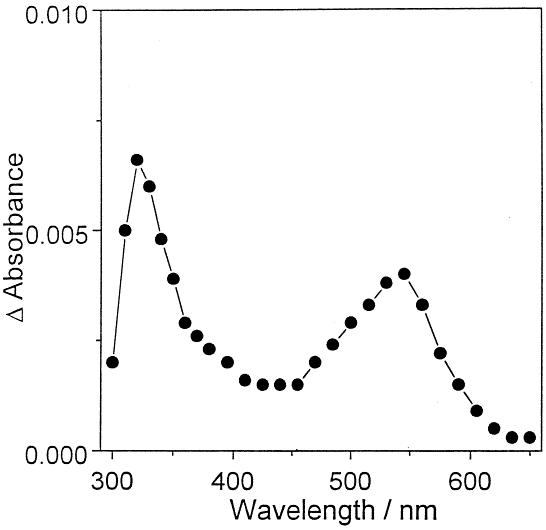


Fig. 3. Transient absorption spectrum obtained on pulse radiolysis of N_2-saturated solution of MTPM (4×10^{-3} mol dm^{-3}) in DCE 1.5 μs after the pulse.

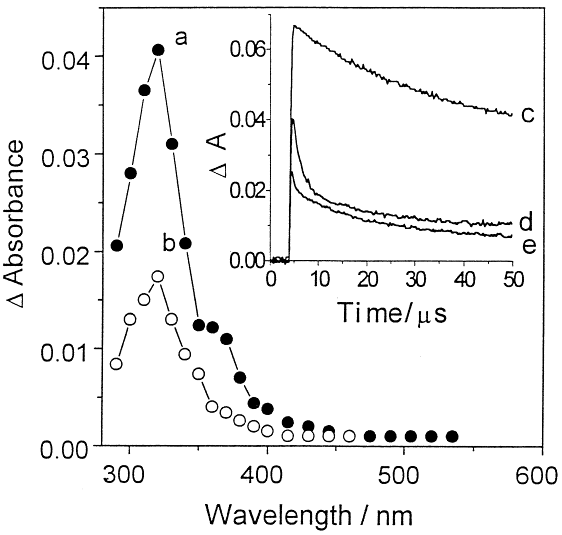


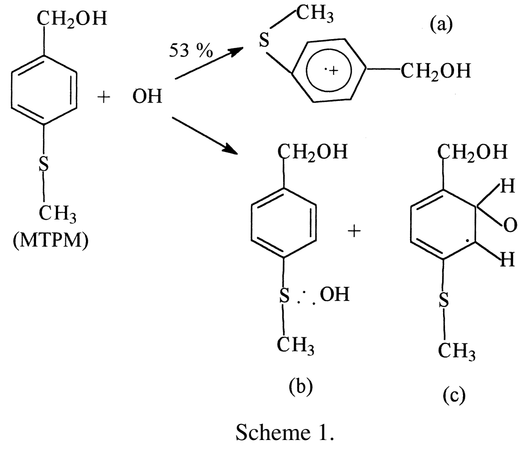
Fig. 4. Transient absorption spectra obtained on pulse radiolysis of MTPM (1×10^{-3} mol dm^{-3}) 190 μs after the pulse in N_2O (a), and aerated conditions (b). Inset show absorption-time profiles at 320 nm in N_2O (c), aerated (d), and O_2-saturated conditions (e).

reaction of Cl$_2^{\bullet-}$ and $^\bullet$OH radicals with MTPM was similar, and is assigned to the same species (MTPM$^{\bullet+}$). Using the molar absorptivity at 545 nm = 5.5×10^3 dm^3 mol^{-1} cm^{-1}, we observed that ~53% of $^\bullet$OH radicals react with MTPM by electron transfer mechanism and the remaining react by some other mechanism (addition/abstraction). The ratio of the absorbance at 320/545 nm bands formed on reaction of Cl$_2^{\bullet-}$ with MTPM is 1.5 whereas that formed on reaction with $^\bullet$OH radicals in N_2O-saturated solutions (Fig. 1a) is 2.8. These results suggest that $^\bullet$OH radical is also reacting with MTPM to form transient species with absorption in 320 nm regions.

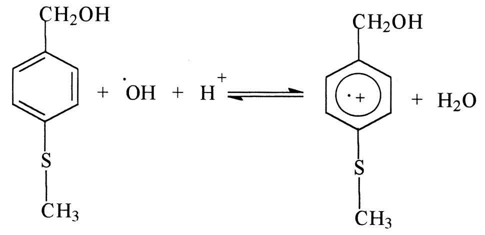
The transient absorption spectrum (Fig. 4a), obtained on pulse radiolysis of N_2O-saturated neutral aqueous solution of MTPM (1×10^{-3} mol dm^{-3}), 190 μs after the pulse, exhibits an absorption band at 320 nm with a shoulder in 350–370 nm region. During this time, the transient absorption due to the solute radical cation ($\lambda_{\max}$ = 320 and 545 nm) has completely decayed and this spectrum (Fig. 4a) should be due to some transient species other than solute radical cation. The absorption at 320 nm decayed by second order kinetics with $2k/\varepsilon l = 1.9 \times 10^5$ s^{-1}. In aerated conditions, the absorption-time profile showed accelerated decay (inset of Fig. 4), the initial portion decaying by first order kinetics with $k = 9 \times 10^4$ s^{-1} (Fig. 4d) but the nature of the absorption spectrum remained the same (Fig. 4b).

α-Thio radical and sulfur-centered OH-adduct of dialkyl sulfides have absorptions in 290–310 nm region and at 360 nm, respectively.[10] $^\bullet$OH radical addition to the benzene ring results in the formation of a transient absorption band in 310–330 nm region.[37] The fact that the nature of the transient absorption spectrum remained the same in aerated conditions (Fig. 4), suggests that it is not due to α-thio radical formed on abstraction of H$^\bullet$ atom from CH_3/CH_2OH groups. Therefore the transient absorption band at 320 nm may be due to the addition of $^\bullet$OH radicals to the benzene ring (Scheme 1c) and the shoulder at 360 nm to sulfur-centered OH-adduct (Scheme 1b). The addition of $^\bullet$OH radicals to the benzene ring could be at any position. The contribution of α-thio radicals may be negligible. Lower yield (Fig. 4b) may be due to lower $^\bullet$OH radical yield in the aerated solution. The faster decay of the 320 nm band in presence of oxygen (inset of Fig. 4) may be due to the addition of oxygen to carbon centered radical (Scheme 1c) and the biomolecular rate constant was calculated to be ~4×10^8 dm^3 mol^{-1} s^{-1}. The contribution of individual reactions (Scheme 1b and 1c) could not be determined due to the close proximity of these absorption bands.

The absorbance of the transient band at 545 nm remained independent of solute concentration, indicating it to be due to a monomer species. Sulfur-centered monomer radical cations have absorption in 300 nm region and are highly unstable, but have a high tendency to coordinate with another solute molecule, forming a 3-electron bonded sulfur-centered dimer radical cation.[10] These dimer radical cations of dialkyl sulfides have absorption in 400–500 nm region. Therefore the transient absorption bands at 320 and 545 nm could not be due to a sulfur-centered cationic species. On the other hand, the reaction



Scheme 1.



Scheme 2.

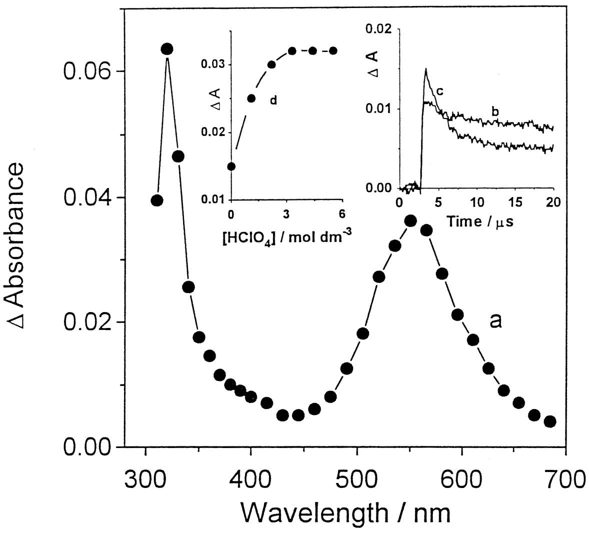


Fig. 5. Transient absorption spectrum obtained on pulse radiolysis of aerated acidic ($HClO_4 = 5.5$ mol dm^{-3}) aqueous solution of MTPM (1.5×10^{-3} mol dm^{-3}), 2.5 μs after the pulse (a). Inset show absorption-time profiles at 360 nm in aerated (b), acidic ($HClO_4 = 1$ mol dm^{-3}) (c), and variation of absorbance at 545 nm as a function of [$HClO_4$] (d).

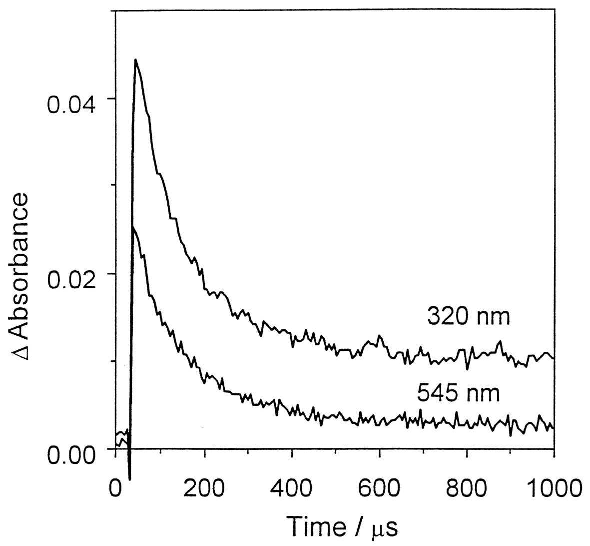


Fig. 6. Absorption-time profiles obtained on pulse radiolysis of aerated acidic ($HClO_4 = 5.5$ mol dm^{-3}) aqueous solution of MTPM (1.5×10^{-3} mol dm^{-3}) at 320 and 545 nm.

of $^{\bullet}$OH radicals with aryl substituted sulfides have absorption bands in 310 and 530 nm region and are assigned to solute radical cation with positive charge on the benzene ring.[22,23,25] Therefore the transient absorption bands at 320 and 545 nm are assigned to solute radical cations with positive charge on the benzene ring (Scheme 1a). Under the present experimental conditions, the contribution of sulfur-centered dimer radical cations may be negligible and such cations may be formed only at very high solute concentrations.

Reaction of $^{\bullet}$OH Radical in Acidic Solution. The decay of the transient absorption band at 360 nm (inset of Fig. 5) was observed to increase from 9.5×10^3 s^{-1} to 1.5×10^5 s^{-1} when the $HClO_4$ concentration was increased from 0 to 1 mol dm^{-3}. Simultaneously, the absorbance of 545 nm band increased, reaching a saturation value when [$HClO_4$] was in the region of 5–6 mol dm^{-3} (Fig. 5d). The transient absorption spectrum showed bands at 320 and 545 nm (Fig. 5a), similar to those obtained on reaction of $Cl_2^{\bullet -}$ and other specific one-electron oxidants with MTPM. The entire spectrum decayed by first order kinetics with $k = 2.4 \times 10^4$ s^{-1} (Fig. 6). The increase in the absorbance may be due to the fact that the equilibrium (Scheme 2) shifts towards the right in acidic solutions. Under these conditions, only one channel (Scheme 1a) is being used for the reaction of $^{\bullet}$OH radical with MTPM. The other transient species, formed in neutral solution are converted to solute radical cations in acidic solution. The overall reaction of $^{\bullet}$OH radical with MTPM in acidic solutions can be represented by Scheme 2.

Oxidation Potential of MTPM/MTPM$^{\bullet +}$ Couple. The transient absorption band of $Br_2^{\bullet -}$ ($\lambda = 360$ nm), formed on pulse radiolysis of N_2O-saturated neutral aqueous solution of Br^- (4×10^{-2} mol dm^{-3}) was observed to decay more quickly on addition of low concentration of MTPM (1×10^{-4} mol dm^{-3}), indicating electron transfer from MTPM to $Br_2^{\bullet -}$. The pseudo-first-order rate (k_{obs}) of $Br_2^{\bullet -}$ was observed to depend on [Br^-]. The transient band of MTPM$^{\bullet +}$ ($\lambda = 545$ nm), formed on pulse radiolysis of aerated acidic ($HClO_4 = 5.5$ mol dm^{-3}) aqueous solution of MTPM (1.5×10^{-3} mol dm^{-3}) was observed to decay faster on addition of low concentration of Br^-, indicating electron transfer from Br^- to MTPM$^{\bullet +}$. These studies and the fact that the yield of the 545 nm band, formed on reactions of $Br_2^{\bullet -}$ with MTPM, was ~65%, suggest the existence of the following equilibrium. It is assumed that there is no reversible nucleophilic addition of the bromide ion to the ring of the solute radical cation, as time-resolved studies have not shown the formation of any band other than that of solute radical cation.

$$Br_2^{\bullet -} + \mathrm{MTPM} \leftrightharpoons \mathrm{MTPM}^{\bullet +} + 2Br^- \qquad (5)$$

$$\frac{1}{\Delta A} = \frac{1}{K\varepsilon[\mathrm{R}]}\,\frac{[\mathrm{Br}^-]^2}{[\mathrm{MTPM}]} + \frac{1}{\varepsilon[\mathrm{R}]} \qquad (6)$$

The transient absorption of MTPM$^{\bullet +}$ at 545 nm where $Br_2^{\bullet -}$ has negligible absorption (path length = 1 cm), is related to the equilibrium constant (K) in Eq. 6, where [R] is the radical concentration, which was kept constant at a given dose, and ε is the molar absorptivity of the transient at 545 nm. The saturation value of the absorbance (ΔA) was measured at 545 nm and the plot of $1/\Delta A$ vs $[\mathrm{Br}^-]^2/[\mathrm{MTPM}]$ was linear (Fig. 7A). The absorbance was measured for low concentrations of

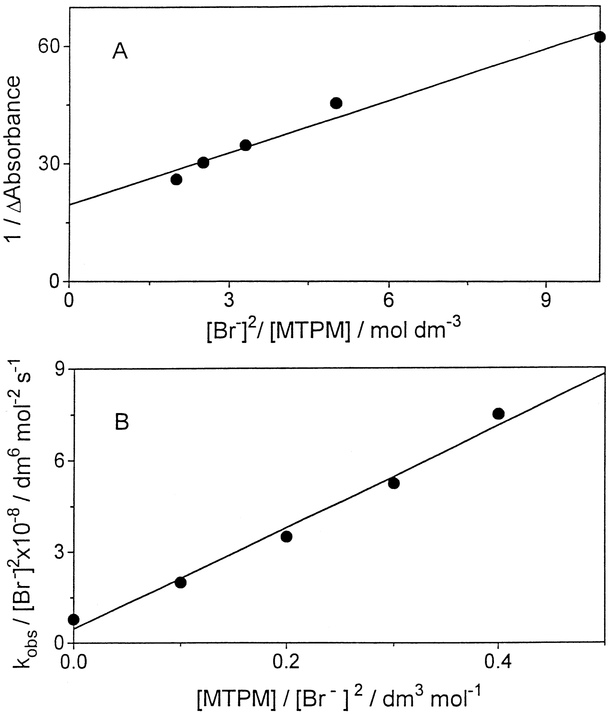


Fig. 7. (A) Plot of $1/\Delta A$ (545 nm) as a function of $[Br^-]^2/[MTPM]$ and (B) $k_{obs}/[Br^-]^2$ (360 nm) as a function of $[MTPM]/[Br^-]^2$ obtained on pulse radiolysis of N_2O-saturated aqueous solution for various concentrationsof Br^- (0.4–2) × 10^{-4} mol dm^{-3} and MTPM (1–3) × 10^{-2} mol dm^{-3}.

MTPM (0.4–2) × 10^{-4} mol dm^{-3}, so that any depletion in the absorbance due to the partial decay of $MTPM^{\bullet +}$ is negligible. The equilibrium constant (K) = intercept/slope was determined to be 4.45. Under the present experimental conditions, G($^\bullet$OH) = 5.6 and [R] = 0.93 × 10^{-5} mol dm^{-3}, the molar absorptivity at 545 nm was determined to be 5.5 × 10^3 dm^3 mol^{-1} cm^{-1}.

The equilibrium constant can also be determined from the following kinetic equations:

$$k_{obs} = k_f[MTPM] + k_r[Br^-]^2 \quad (7)$$

$$\frac{k_{obs}}{[Br^-]^2} = k_f\frac{[MTPM]}{[Br^-]^2} + k_r \quad (8)$$

The pseudo-first-order rate (k_{obs}) was determined on monitoring the decay of the transient band of $Br_2^{\bullet -}$ (λ = 360 nm) for various concentrations of Br^- = (2–4) × 10^{-2} mol dm^{-3} and MTPM = (0–2) × 10^{-4} mol dm^{-3}. The plot of $k_{obs}/[Br^-]^2$ vs $[MTPM]/[Br^-]^2$ gave a straight line (Fig. 7B) with slope (k_f) = 16.7 × 10^8 and intercept (k_f) = 0.465 × 10^8. The equilibrium constant ($K = k_f/k_r$) was determined to be 35.9. It is related to the difference (ΔE^0) of the oxidation potential of two couples by the following relationship:

$$0.059 \log K = E^0 (Br_2^{\bullet -}/2Br^-) - E^0 (MTPM/MTPM^{\bullet +}) \quad (9)$$

Using the average value of equibrium constant (K) = 20.2 and the value of 1.63 V vs NHE for E^0 ($Br_2^{\bullet -}/2Br^-$) couple, the oxidation potential value for $MTPM/MTPM^{\bullet +}$ couple was determined to be 1.55 ± 0.04 V vs NHE.

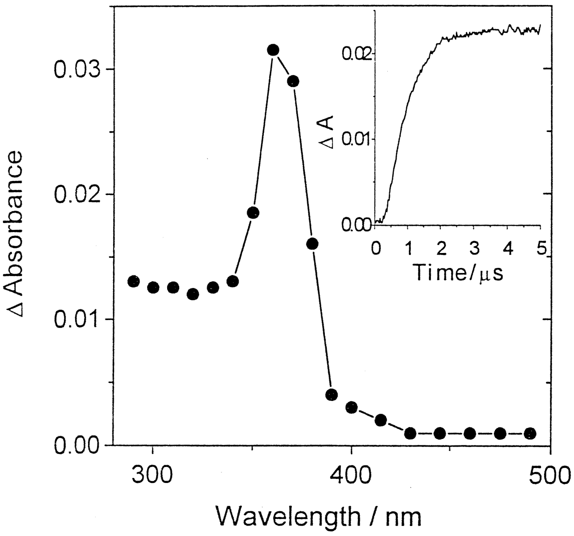
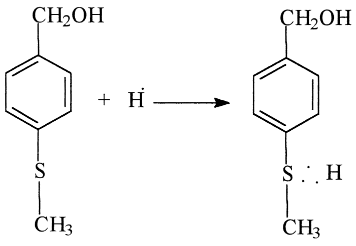


Fig. 8. Transient absorption spectra obtained on pulse radiolysis of N_2-saturated acidic (pH = 1) aqueous solution of MTPM (1 × 10^{-3} mol dm^{-3}) in presence of t-butyl alcohol (0.3 mol dm^{-3}) 1.5 µs after the pulse. Inset show absorption-time profiles at 360 nm.



Scheme 3.

Reaction with $H^\bullet$ Atoms. Figure 8 shows the transient absorption spectrum obtained on pulse radiolysis of N_2-saturated acidic (pH = 1) aquesous solution of MTPM (1 × 10^{-3} mol dm^{-3}) in the presence of *t*-butyl alcohol (0.3 mol dm^{-3}), which exhibits a band at 360 nm. Since the position of this band matched with that obtained on reaction of $^\bullet$OH radical with MTPM and assigned to the sulfur-centered OH-adduct, the transient species (Fig. 8) is therefore assigned to the sulfur-centered H-adduct (Scheme 3). The rate constant for the reaction of $H^\bullet$ atom with the solute was determined by formation kinetic studies and is shown in Table 1. In the absence of knowledge about the nature of stable products formed, the exact decay mechanism could not be given at this stage.

Reaction with $O^{\bullet -}$. Pulse radiolysis on N_2O-saturated basic (pH = 13) aqueous solution of MTPM (1 × 10^{-3} mol dm^{-3}) showed the formation of transient absorption bands at 330 and 485 nm (Fig. 9). The kinetic parameters are shown in Table 1. The adducts formed on addition of $O^{\bullet -}$ and $^\bullet$OH radicals to the benzene ring are expected to give similar spectra. But the nature of the spectra in the two cases was different. Therefore, the transient species (Fig. 9) may not be due to $O^{\bullet -}$-adduct but to a radical species formed on abstraction of $H^\bullet$

Table 2. Second Order Rate Constants and Yields of $MV^{\bullet +}$ and $TMPD^{\bullet +}$ Formed on Reaction of Transient Species Generated from MTPM under Different Conditions

Reaction	pH	$MV^{\bullet +}$		$TMPD^{\bullet +}$	
		$k/10^9$ dm^3 mol^{-1} s^{-1}	G($MV^{\bullet +}$)	$k/10^9$ dm^3 mol^{-1} s^{-1}	G($TMPD^{\bullet +}$)
MTPM/N_2O	13	8.9	4.8	—	0.2
MTPM/N_2/*t*-butyl alcohol	1	—	0.5	—	< 0.1
MTPM/N_2O	7	4.1	1.9	4.2	2.2

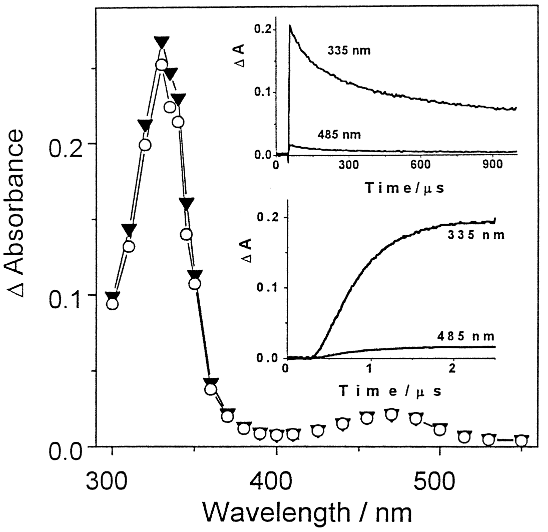


Fig. 9. Transient absorption spectra obtained on pulse radiolysis of N_2O-saturated aqueous (pH = 13) solution of MTPM (1 × 10^{-3} mol dm^{-3}) ▼ 1 μs, and ○ 8 μs after the pulse. Inset shows formation and decay of transient absorption bands at 335 and 485 nm.

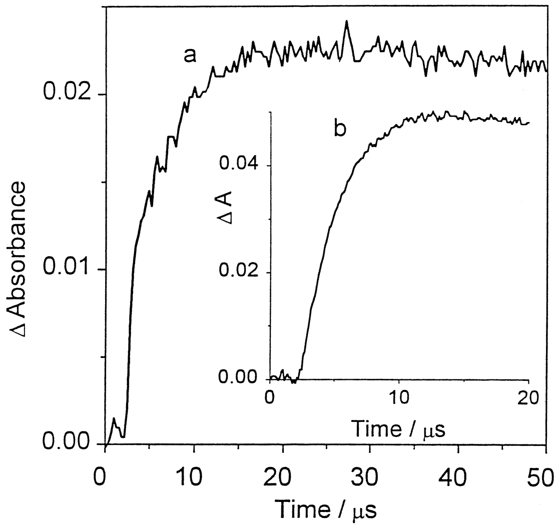


Fig. 11. Absorption-time profiles obtained on pulse radiolysis of N_2O-saturated aqueous solution of MTPM (1.7 × 10^{-3} mol dm^{-3}) containing TMPD (4 × 10^{-5} mol dm^{-3}), λ = 610 nm, pH = 6 (a), and MV^{2+} (4 × 10^{-5} mol dm^{-3}), λ = 605 nm, pH = 13 (b).

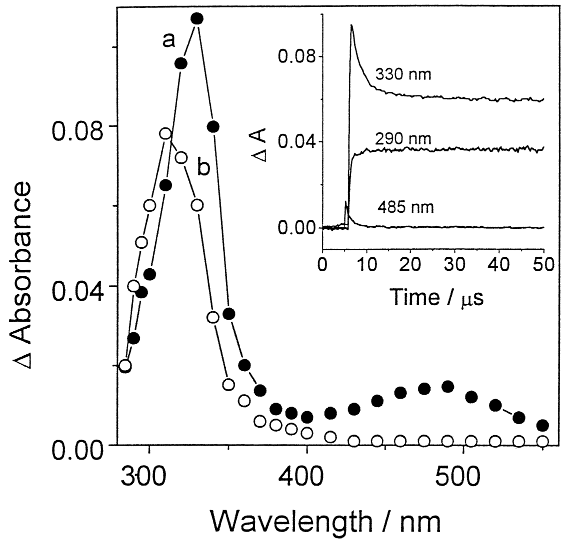


Fig. 10. Transient absorption spectra obtained on pulse radiolysis of aerated aqueous (pH = 13) solution of MTPM (1 × 10^{-3} mol dm^{-3}), 1 μs (a), and 8 μs (b), after the pulse. Inset show absorption-time profiles at 330, 485 and 290 nm.

atom by $O^{\bullet -}$. In aerated solutions, time-resolved studies showed the formation of a transient band at 310 nm (Fig. 10b). The band at 485 and the initial portion of the band at 330 nm decayed by first order kinetics with $k = 4.8 \times 10^{-5}$ s^{-1} matching with the formation of the band at 310 nm. The transient absorption spectrum (Fig. 10a), matched with that formed under N_2O-saturated conditions (Fig. 9). The accelerated decay should be due to the reaction of the radical species with oxygen; the bimolecular rate constant was determined to be 2.4 × 10^9 dm^3 mol^{-1} s^{-1}. The transient absorption spectrum obtained 8 μs after the pulse (Fig. 10b) should be due to a transient species formed on addition of oxygen to the radical species and assigned to a peroxyl radical decaying by second order kinetics with $2k/\varepsilon l = 1.5 \times 10^4$ s^{-1}.

Redox Reactions of Transient Adducts. The oxidant methylviologen (MV^{2+}) and the reductant *N*,*N*,*N*′,*N*′-tetramethyl-*p*-phenylenediamine (TMPD) were used to evaluate the nature of radicals produced in reactions of $^{\bullet}OH$, $^{\bullet}H$, and $O^{\bullet -}$ with MTPM. The reaction rate was monitored at 605 nm (ε = 12 800 dm^3 mol^{-1} cm^{-1}) in the case of MV^{2+} and at 610 nm (ε = 12 000 dm^3 mol^{-1} cm^{-1}) for TMPD. These redox experiments were carried out at a lower dose 10 Gy per pulse, to minimize the effect of biomolecular radical recombination reactions. The concentrations of TMPD and MV^{2+} were kept constant at 4 × 10^{-5} mol dm^{-3} and of MTPM at 1.7 × 10^{-3} mol dm^{-3}. The bimolecular rate constants and G value obtained under different experimental conditions are given in Table 2. The typical absorption-time profiles obtained with MV^{2+} and

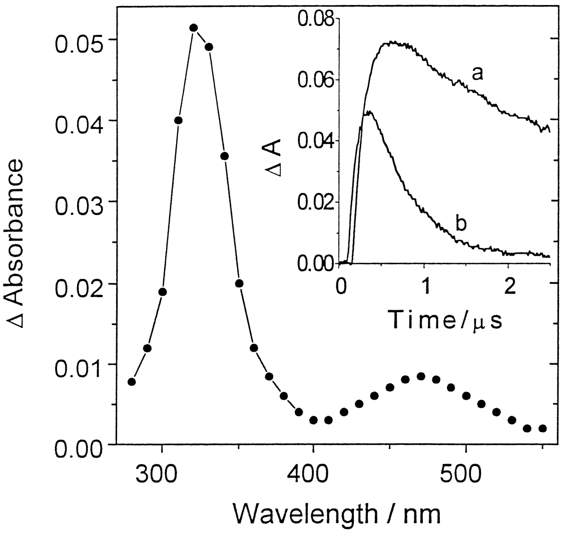


Fig. 12. Transient absorption spectrum obtained on pulse radiolysis of N_2-saturated aqueous solution of MTPM (1×10^{-3} mol dm^{-3}) containing *t*-butyl alcohol (0.3 mol dm^{-3}) 3 μs after the pulse. Inset shows absorption-time profile at 700 nm in the absence (a), and presence of MTPM (b).

TMPD are shown in Fig. 11. The reactions of $^{\bullet}$OH radicals with MTPM produce radical cations and neutral radicals (Scheme 1). The radical cations would be able to oxidize TMPD to TMPD$^{\bullet+}$ because the oxidation potential of solute radical cations (1.55 V) is higher than that of TMPD$^{\bullet+}$/TMPD couple. The neutral radicals are reducing MV^{2+} to $MV^{\bullet+}$. The pulse radiolysis of N_2O-saturated aqueous solution of MTPM (1×10^{-3} mol dm^{-3}) in presence of $[Fe(CN)_6]^{3-}$ (1×10^{-3} mol dm^{-3}), did not show any bleaching at 420 nm, indicating that the OH-adduct is not able to oxidize $[Fe(CN)_6]^{3-}$.[38,39]

Reaction with e_{aq}^{-}. The decay of e_{aq}^{-} (inset of Fig. 12) at 700 nm was observed to become faster in the presence of low concentrations of MTPM (0.8×10^{-3} mol dm^{-3}). The rate constant for reaction (10) was investigated on monitoring its decay at 700 nm as a function of MPTM concentration (0–1) $\times 10^{-3}$ mol dm^{-3} and the biomolecular rate constant was determined to be 1.5×10^{9} dm^3 mol^{-1} s^{-1}. The time-resolved studies showed the formation of transient absorption bands at 320 and 470 nm (Fig. 12). The entire spectrum decayed by first order with $k = 1.5 \times 10^{4}$ s^{-1}.

$$\mathrm{MTPM} + e_{aq}^{-} \rightarrow (\mathrm{MTPM})^{\bullet -} \tag{10}$$

The nature of the transient absorption spectrum, its decay and formation kinetics remained the same at pH = 11, suggesting the absence of any acid-base equilibrium. Therefore, the transient absorption spectrum obtained at pH 7 (Fig. 12) should be due to an anion radical (MTPM)$^{\bullet-}$ and not due to a H-adduct formed on protonation of radical anion. The differences of the transient absorption spectrum (Fig. 12) from that of H-adduct (Fig. 8) also support these results.

Reaction with Other Reducing Agents. Isopropyl ketyl radical, formed on pulse radiolysis of N_2-saturated acidic (pH = 1) aqueous solution of 2-propanol (1 mol dm^{-3}) in the presence of a low concentration of MTPM, failed to produce any transient absorption band in 300–600 nm region, showing that the reduction potential of MTPM/MTPM$^{\bullet-}$ couple is quite high. COO$^{\bullet-}$ radical anion ($E^0 = -1.9$ V) formed on pulse radiolysis of N_2O-saturated aqueous solution of sodium formate (4×10^{-2} mol dm^{-3}) in the presence of a low concentration of MTPM (1×10^{-3} mol dm^{-3}) showed the formation of transient absorption bands at 320 and 470 nm, similar to that obtained on reaction with e_{aq}^{-}. Therefore, the COO$^{\bullet-}$ radical anion is able to transfer electron (reaction 11).

Reduction Potential of MTPM/MTPM$^{\bullet-}$. The yield of the transient bands, formed on reaction of COO$^{\bullet-}$ with MTPM was only about 50%, indicating that complete electron transfer is not taking place. The yield and the pseudo-first-order rate (k_{obs}), was found to depend on the concentrations of MTPM and formate ion, indicating the existence of the following equilibrium:

$$\mathrm{COO}^{\bullet -} + \mathrm{MTPM} \rightleftarrows \mathrm{MTPM}^{\bullet -} + \mathrm{CO_2} \tag{11}$$

The transient absorbance of MTPM$^{\bullet-}$ at 320 nm (optical path length = 1 cm), where COO$^{\bullet-}$ has negligible absorption, was determined for various concentrations of formate ions (2–6) $\times 10^{-2}$ mol dm^{-3} and MTPM (0.6–3) $\times 10^{-3}$ mol dm^{-3} under conditions such that $^{\bullet}$H/$^{\bullet}$OH radicals would initially react with formate ions and COO$^{\bullet-}$ formed would then react with MTPM. The transient absorption of MTPM$^{\bullet-}$ is related to the equilibrium constant *K* by the following relationship:

$$\frac{1}{\Delta A} = \frac{1}{K\varepsilon[\mathrm{R}]}\,\frac{[\mathrm{Formate}^{-}]}{[\mathrm{MTPM}]} + \frac{1}{\varepsilon[\mathrm{R}]} \tag{12}$$

where [R] is the radical concentration, which was maintained constant at a given dose, and ε is the molar absorptivity at 320 nm. The saturation value of the absorbance was measured at 320 nm. The plot of $1/\Delta A$ vs [Formate$^-$]/[MTPM] was linear (Fig. 13A), with slope = 3.63 and intercept = 8.7. The equilibrium constant (*K*) = intercept/slope was determined to be 2.4. Under the present experimental conditions with [R] = 0.95×10^{-5} mol dm^{-3}, the molar absorptivity was determined to be 1.2×10^{4} dm^3 mol^{-1} cm^{-1}.

The equilibrium can also be determined from the following kinetic equation:

$$k_{obs} = k_f[\mathrm{MTPM}] + k_f[\mathrm{Formate}^{-}] \tag{13}$$

$$\frac{k_{obs}}{[\mathrm{Formate}^{-}]} = k_f\frac{[\mathrm{MTPM}]}{[\mathrm{Formate}^{-}]} + k_r \tag{14}$$

The pseudo-first-order rate (k_{obs}) was determined on monitoring the formation of the transient absorption band of MTPM$^{\bullet-}$ at 320 nm for various concentrations of [MTPM] = (0.7–3) $\times 10^{-3}$ mol dm^{-3} and formate ion (2–6) $\times 10^{-2}$ mol dm^{-3}. The plot (Fig. 13B) of k_{obs}/[Formate−] vs [MTPM]/[Formate$^-$] gave a straight line with slope (k_f) = 1.66×10^{9} and intercept (k_r) = 0.84×10^{8}. The equilibrium constant was determined to be 19.8. The equilibrium constant is related to the difference (ΔE^0) of the redox potential value of both the couples by the following relationship:

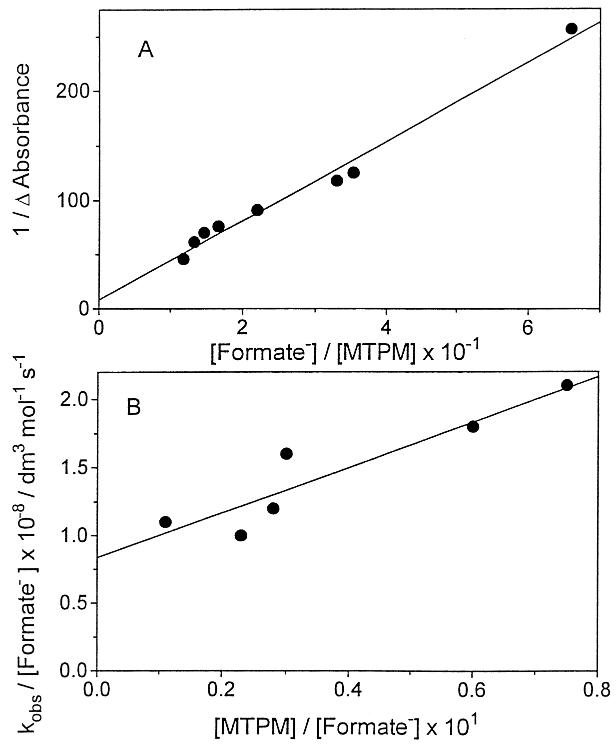


Fig. 13. (A) Plot of $1/\Delta A$ at 320 nm as a function of [Formate$^-$]/[MTPM]. (B) Plot of k_{obs}/[Formate$^-$] as a function of [MTPM]/[Formate$^-$] obtained on pulse radiolysis of N_2-saturated aqueous solution containing different concentrations of MTPM (0.7–3) × 10^{-3} mol dm^{-3} and formate$^-$ (2–6) × 10^{-2} mol dm^{-3}.

$$0.059 \log K = \Delta E^0 = E^0\ \mathrm{COO^{\bullet -}/COO} - E^0\ \mathrm{MTPM/MTPM^{\bullet -}} \quad (15)$$

Taking the average of $K = 11.1$ and using the value of -1.9 V for E^0 $\mathrm{COO^{\bullet -}/COO}$ couple, the reduction potential value for $\mathrm{MTPM/MTPM^{\bullet -}}$ couple was determined to be -1.84 ± 0.04 V.

Electron Transfer Reactions with Organic Compounds. The transient species formed on reaction of e_{aq}^- with MTPM was able to transfer electrons to MV^{2+}, as investigated by monitoring the formation of $MV^{\bullet +}$ at 605 nm. The biomolecular rate constant was determined to be 4.6×10^9 dm^3 mol^{-1} s^{-1} and G($MV^{\bullet +}$) was 2.5, close to G(e_{aq}^-), showing complete electron transfer from anion radical of MTPM to MV^{2+}. The reaction with other organic compounds was also investigated and the rate constant values determined from the decay of the radical anion at 320 nm are summarized in Table 3. The rate constant values decreased with increase in the reduction potential value of the organic compound.

Reaction with Inorganic Ions. The radical cation can react with an anionic nucleophile by addition and/or electron transfer.[40,41] Solvent polarity and redox potential of the nucleophile have a strong effect on the relative contributions of these two pathways. In order to estimate the relative contributions of these processes, we have determined the bimolecular rate constant values for the reaction of solute radical cation with a number of inorganic ions. The values are summarized in Table 4. The rate constant values are observed to decrease with increase in the oxidation potential value of the inorganic ion. Based on the rate constant of a number of nucleophiles with CH_3I in methanol at 25 °C, the relative nucleophilic reactivity parameter (ηCH_3I) is available in the literature.[42] The rate constants obtained were observed to remain insensitive to the relative nucleophilicity of the anion. The bimolecular rate constant for the reaction of radical cation with NO_2^- (7.8×10^9 dm^3 mol^{-1} s^{-1}) was comparable with that of I^- (9×10^9 dm^3 mol^{-1} s^{-1}) although the nucleophilicity increased from 5.35 to 7.42 eV. Therefore the reaction of solute radical cation is mainly by electron transfer mechanism and not by the nucleophilic addition and could be accounted for by the difference in their redox potential values.

Table 3. Bimolecular Rate Constant for the Reaction of Solute Radical Anion with Organic Compounds

Compound	Rate constant/dm^3 mol^{-1} s^{-1}	E^0/V
MV^{2+}	4.6×10^9	-0.44
C_6H_5CN	5.3×10^8	-1.45
$C_6H_5COCH_3$	5.2×10^8	-1.36
CH_3COCH_3	2.8×10^8	-1.50

Table 4. Bimolecular Rate Constant for the Reaction of Solute Radical Cation with Inorganic Ions

Reaction	Rate constant/ dm^3 mol^{-1} s^{-1}	E^0/V	ηCH_3I/eV
$MTPM^{\bullet +} + I^-$	9×10^9	1.03	7.42
$MTPM^{\bullet +} + N_3^-$	7×10^9	1.33	5.78
$MTPM^{\bullet +} + NO_2^-$	7.8×10^9	1.04	5.35
$MTPM^{\bullet +} + SCN^-$	5×10^8	1.63	6.70
$MTPM^{\bullet +} + Cl^-$	$< 3 \times 10^6$	2.05	4.37

Effect of Substituents. The reaction of $^{\bullet}OH$ radical with substituted aryl sulfides is observed to depend on the nature of the substituents. Monomer radical cations with positive charge on the benzene ring have been observed with diaryl sulfides.[23] The reaction of $^{\bullet}OH$ radical with thioanisole showed the formation of OH-adduct and monomer radical cations with positive charge on the benzene ring. In acidic solutions, the OH-adduct is converted to monomer radical cation and a small fraction to sulfur-centered dimer radical cations.[25] The reaction of $^{\bullet}OH$ radicals with 2-(phenylthio)ethanol has shown the formation of α-thio radicals, OH-adduct and benzene centered monomer radical cations. In highly acidic solutions, only monomer radical cations are observed. The presence of CH_3 and CH_2OH groups (in thioanisole and 2-(phenylthio)ethanol) have resulted in the formation of OH-adduct and α-thio radical respectively. On the other hand, the presence of CH_2OH group on the benzene ring (in MTPM) has not shown any effect. Only OH-adduct is observed, which should be due to the presence of CH_3 group. The -OH group on the benzene ring as in the case of 4,4′-thiodiphenol, resulted in the formation of phenoxyl radicals on fast deprotonation of solute radical cation. Due to high electron density at sulfur in dialkyl sulfides, the bimolecular rate constant for the reaction of e_{aq}^- is quite low. The aryl-substituted sulfides have shown higher reactivity with e_{aq}^-. These results clearly demonstrate that the substituents and their relative position with reespect to sulfur plays an important role on the nature of the transient species formed on reaction fo •OH radical and e_{aq}^- with substituted sulfur compounds.

Conclusions

•OH radical in neutral aqueous solution of (4-methylthiophenyl)methanol is observed to react by electron transfer mechanism (53%) and by addition at sulfur and benzene ring. In highly acidic solutions, only solute radical cation with positive charge on the benzene ring is observed. The oxidation potential for the formation of solute radical cation is determined to be 1.55 V. The transient species formed on reaction of •OH radicals by addition at sulfur and benzene ring have reducing nature. e_{aq}^- has high reactivity and forms radical anions with negative charge on the benzene ring. The reduction potenttial is determined to be −1.84 V.

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