

## Investigations on the nature of the transient species formed on pulse radiolysis of a aqueous solution of 4-(methylthio)benzoic acid

V. B. GAWANDI, H. MOHAN and J. P. MITTAL \*

*Radiation Chemistry and Chemical Dynamics Division, Bhabha Atomic Research Centre, Trombay, Mumbai 400 085, India*

Received 2 November 2001; accepted 12 June 2002

**Abstract**—The transient absorption spectrum ( $\lambda_{\max} = 320, 400$  and  $550$  nm) obtained on reaction of  $\bullet\text{OH}$  radicals with 4-(methylthio)benzoic acid is assigned to a solute radical cation with a positive charge on the benzene ring. The reaction with specific one-electron oxidants also produced similar spectrum and the oxidation potential for the formation of solute radical cation is estimated to be between  $1.4$  and  $1.6$  V vs NHE. The reaction of  $e_{\text{aq}}^-$  with the solute showed the formation of a transient absorption band at  $320$  nm and is assigned to solute radical anion with reduction potential more negative than  $-1.5$  V.

*Keywords:* Pulse radiolysis; 4-(methylthio)benzoic acid; transient species.

### INTRODUCTION

Hydroxyl radicals and specific one-electron oxidants are known to bring about one-electron oxidation of dialkyl sulfides ( $\text{R}_2\text{S}$ ), leading to the formation of sulfur-centered radical cations  $\text{R}_2\text{S}^{\bullet+}$  [1–8]. Simple sulfur centered radical cation of dialkyl sulfides have been observed only in some cases such as di-*tert*-butyl sulfide as oxidized sulfur has high tendency to stabilize by co-ordination with free p-electron pair of another sulfur or a heteroatom (O, N, P, halogen) both by inter- and intra-molecular association [9–13]. These interactions are represented by a three-electron bond containing two bonding  $\sigma$  and one antibonding  $\sigma^*$  electrons. The formation of sulfur centered three-electron bonded species has been inferred to take place via a complex sequence of reactions involving  $\alpha$ -thioalkyl radicals, OH-adduct and monomer radical cations. Evidence for the formation of sulfur-centered

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\*To whom correspondence should be addressed.

species has come from ESR and optical spectroscopic studies [14–24]. Three-electron bonded species have been the subject of active interest both experimentally and theoretical investigations [25–27]. The knowledge of chemistry involved in the reactions of radicals and radical ions of organic molecules is very important in understanding electron transfer reactions. These studies are also important as they act as intermediates in many organic reactions in biological and organic synthesis [28–30]. These studies are also of relevance because of the formation of sulfur-centered radicals as possible intermediates in redox reactions of biomolecules [16–18, 31, 32]. Although a large amount of information on the nature of the transient species and kinetic parameters is available for different alkyl derivatives of organic sulfur compounds, only a few studies have been made on aryl-substituted compounds [33–36]. Therefore, it is of interest to investigate the nature of the transient species formed from aryl-substituted organic sulfur compounds. The delocalization in the aromatic ring is expected to stabilize the radical cations. With this objective, the nature of the transient species formed on pulse radiolysis of 4-(methylthio)benzoic acid is investigated and reported in this manuscript.

## EXPERIMENTAL

4-(Methylthio)benzoic acid (MTBA, Aldrich Chemicals) was of high purity and used without any further purification. Freshly prepared solutions were used for each experiment. The solutions were prepared in 1 mM phosphate buffer using ‘nanopure’ water. The pH was adjusted with NaOH/HClO<sub>4</sub>. Iolar grade, high purity gases (N<sub>2</sub>, N<sub>2</sub>O, O<sub>2</sub>) were used for purging the solutions. All other chemicals used were also of high purity. The optical absorption studies in the ground state were carried out with Hitachi 330 spectrophotometer. All other experimental details are described elsewhere [35, 36].

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 [37, 38]. The dose delivered per pulse was determined with aerated aqueous solution of KSCN (10 mmol/dm<sup>3</sup>) with  $G\varepsilon = 21\,520\text{ dm}^3/\text{mol per cm per }100\text{ eV}$  at 500 nm for the transient (SCN)<sub>2</sub><sup>•-</sup> species.  $G$  denotes the number of species per 100 eV of absorbed energy ( $G = 1$  corresponds to 0.1036 μmol/J) and  $\varepsilon$  is the molar absorptivity of (SCN)<sub>2</sub><sup>•-</sup> species at 500 nm. The dose per pulse was close to 15 Gy (1 Gy = 1 J/kg), except for kinetic experiments, which were carried out at a lower dose of about 10 Gy. The rate constant values were taken from that kinetic analysis for which very good correlation was obtained between the experimental and calculated results [39]. The bimolecular rate constant was determined from the linear regression plots of  $k_{\text{obs}}$  versus solute concentration for at least three experiments and the variation was within ±10%.

Radiolysis of N<sub>2</sub>-saturated neutral aqueous solution leads to the formation of three highly reactive species (<sup>•</sup>H, <sup>•</sup>OH, e<sub>aq</sub><sup>-</sup>) in addition to the formation of less reactive or inert molecular products (H<sub>2</sub>, H<sub>2</sub>O<sub>2</sub>). The reaction with <sup>•</sup>OH radicals was carried

out in N<sub>2</sub>O-saturated solutions where e<sub>aq</sub><sup>-</sup> is quantitatively converted to <sup>•</sup>OH radicals. The reaction with O<sup>•-</sup> was carried out in N<sub>2</sub>O-saturated solutions at pH 13, where <sup>•</sup>OH radicals are converted to O<sup>•-</sup> with a pK<sub>a</sub> value of 11.9. The reaction with e<sub>aq</sub><sup>-</sup> was carried out in N<sub>2</sub>-saturated solutions in presence of *t*-butyl alcohol to scavenge <sup>•</sup>OH radicals.

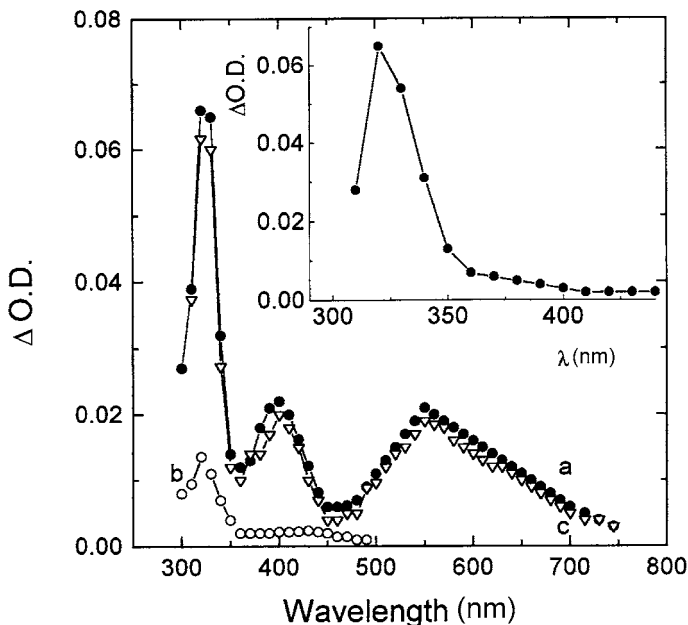
Radiolysis of a solute in aqueous solution is carried out to investigate the reaction of e<sub>aq</sub><sup>-</sup>, H<sup>•</sup> and <sup>•</sup>OH radicals whereas in a non-polar solvent such as halo-alkanes, solvent cations can be used for electron-transfer studies. 1,2-Dichloroethane (DCE) has been frequently employed as a solvent for the study of solute radical cations of organic compounds due to the high ionization potential of DCE (11.1 eV) [40]. The yield of solvent cations is increased because the solvent molecule scavenges the electrons produced by ionizing radiations.

## RESULTS AND DISCUSSION

The ground-state optical absorption spectrum of MTBA (pH 7.7) showed a band at 270 nm ( $\epsilon = 14\,000 \text{ dm}^3/\text{mol per cm}$ ). In acidic solutions (pH 2.4), the optical absorption spectrum showed bands at 220 and 280 nm ( $\epsilon_{280} = 17\,500 \text{ dm}^3/\text{mol per cm}$ ) with a pK<sub>a</sub> of 4. The absorption in the entire pH range (1–12) showed very little absorption at  $\lambda > 300 \text{ nm}$ . Pulse radiolysis studies, using an optical absorption detection technique, can therefore be used without any ground state correction in the 300–750 nm region. The solute is in the protonated form (CH<sub>3</sub>SC<sub>6</sub>H<sub>4</sub>COOH) in the acidic solution and deprotonated form (CH<sub>3</sub>SC<sub>6</sub>H<sub>4</sub>COO<sup>-</sup>) in basic solutions.

### *Pulse radiolysis studies in neutral solution*

Figure 1a shows the transient absorption spectrum obtained on pulse radiolysis of N<sub>2</sub>O-saturated neutral aqueous solution of MTBA, which exhibits absorption bands at  $\lambda_{\text{max}} = 320, 400 \text{ and } 550 \text{ nm}$ . In the presence of *t*-butyl alcohol (0.3 mol/dm<sup>3</sup>), an efficient <sup>•</sup>OH radical and weak <sup>•</sup>H atom scavenger, very small absorption was observed in 300–350 nm region (Fig. 1b), indicating that the transient absorption spectrum (Fig. 1a) is mainly due to the reaction of <sup>•</sup>OH radicals with the solute and the contribution of H<sup>•</sup> atom reaction with the solute is negligible. The rate constant for the reaction of <sup>•</sup>OH radicals with the solute was determined by formation kinetic studies at 320 and 400 nm and the pseudo-first-order ( $k_{\text{obs}}$ ) rate was observed to increase with solute concentration from  $2 \times 10^{-4} \text{ mol/dm}^3$  to  $6 \times 10^{-4} \text{ mol/dm}^3$ . The bimolecular rate constant was determined from the linear plot of  $k_{\text{obs}}$  versus solute concentration and the value was same at both the wavelengths ( $(6.4 \pm 0.4) \times 10^9 \text{ dm}^3/\text{mol per s}$ , Table 1). The entire spectrum decayed by first-order kinetics with  $k = 2.1 \times 10^4 \text{ s}^{-1}$  (Table 1). The absorbance of transient absorption bands remained independent of solute concentration  $(0.3\text{--}0.8) \times 10^{-3} \text{ mol/dm}^3$ , indicating the formation of a monomeric species and suggests that the entire yield of <sup>•</sup>OH radicals have reacted with the solute. Under these conditions, the molar



**Figure 1.** Transient absorption spectra obtained on pulse radiolysis of  $N_2O$ -saturated neutral aqueous solution of MTBA ( $8 \times 10^{-4}$  mol/dm) in the (a) absence and (b) presence of *t*-butyl alcohol ( $0.4$  mol/dm<sup>3</sup>). (c) Transient absorption spectrum obtained on reaction of  $Br^\bullet$  with MTBA ( $4 \times 10^{-4}$  mol/dm<sup>3</sup>). Inset: transient absorption spectrum on pulse radiolysis of  $N_2$ -saturated solution of MTBA ( $8 \times 10^{-4}$  mol/dm<sup>3</sup>) containing *t*-butyl alcohol ( $0.3$  mol/dm<sup>3</sup>) at pH 1.

**Table 1.**

Kinetic and spectral parameters of the transients formed from MTBA on reaction with oxidizing radicals at pH 7

Reaction	$\lambda_{\max}$ (nm)	Formation rate constant ( $\times 10^{-9}$ dm <sup>3</sup> /mol per s)	Decay ( $s^{-1}$ )
MTBA + $Br^\bullet$	320, 400, 550	6.5	$1.8 \times 10^4$
MTBA + $SO_4^{\bullet-}$	320, 400, 550	4.9	$2.5 \times 10^4$
MTBA + $Br_2^{\bullet-}$	320, 400, 550	3.2	$2.8 \times 10^4$
MTBA + $N_3^\bullet$	no reaction		
MTBA + $CCl_3OO^\bullet$	no reaction		

absorptivity at 400 nm was determined to be  $2.4 \times 10^3$  dm<sup>3</sup>/mol per cm. The nature of the transient absorption spectrum remained same in aerated conditions, suggesting that the transient spectrum is not due to a carbon centered radical.

The transient absorption spectrum observed in the presence of *t*-butyl alcohol (Fig. 1b) may be due to the reaction of  $H^\bullet$  atom with the solute, as *t*-butyl alcohol radicals formed on abstraction of  $H^\bullet$  atom from *t*-butyl alcohol do not absorb in this region. In order to confirm this, pulse radiolysis studies were carried out in  $N_2$ -saturated solutions at pH 1 in the presence of *t*-butyl alcohol ( $0.3$  mol/dm<sup>3</sup>) to

**Table 2.**

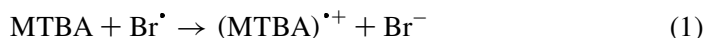
Kinetic and spectral parameters of the transients formed from MTBA on reaction with primary radiolytic species of water radiolysis

Reaction	pH	$\lambda_{\max}$ (nm)	Formation rate constant ( $\times 10^{-9}$ dm <sup>3</sup> /mol per s)	Decay (s <sup>-1</sup> )
MTBA + e <sub>aq</sub> <sup>-</sup>	7	320	17	$1.5 \times 10^4$
MTBA + H <sup>•</sup>	1	320	3.2	$1.6 \times 10^4$
MTBA + O <sup>•-</sup>	13	345, 480	4.5	$1.5 \times 10^9$ <sup>a</sup>
MTBA + <sup>•</sup> OH	7	320, 400, 550	6.4	$2.1 \times 10^4$

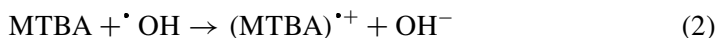
<sup>a</sup> Second-order kinetics (2k).

scavenge <sup>•</sup>OH radicals. The transient absorption spectrum (Fig. 1, inset) showed a transient absorption band at 320 nm, thus supporting the earlier observation that the small transient absorption (Fig. 1b) is due to the reaction of H<sup>•</sup> with the solute. The kinetic parameters of the transient species formed on reaction of H<sup>•</sup> atom with MTBA are shown in Table 2.

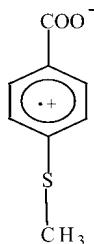
<sup>•</sup>OH radicals are known to react with organic compounds by addition, abstraction and electron-transfer reaction mechanism. The transient absorption bands formed on reaction of <sup>•</sup>OH radicals with MTBA (Fig. 1a) could not be due to H<sup>•</sup> abstraction reaction as the transient absorption spectrum was not quenched in oxygen. In order to distinguish between electron transfer and addition reactions, pulse radiolysis studies were carried out with specific one-electron oxidants. The Br<sup>•</sup> atom is a specific one-electron oxidant with  $E^0 = 1.9$  V and is formed on pulse radiolysis of a N<sub>2</sub>O-saturated neutral aqueous solution of 1,2-dibromoethane ( $4 \times 10^{-2}$  mol/dm<sup>3</sup>). Reaction of Br<sup>•</sup> with MTBA showed the formation of transient absorption bands at 320, 400 and 550 nm (Fig. 1c). The bimolecular rate constant for the reaction of Br<sup>•</sup> with the solute, determined by formation kinetics, gave a value of  $6.5 \times 10^9$  dm<sup>3</sup>/mol per s and the entire spectrum decayed by first-order kinetics with  $k = 1.8 \times 10^4$  s<sup>-1</sup>. The spectrum is assigned to solute radical cation formed according to reaction 1:



Since the transient absorption spectrum obtained on reaction of <sup>•</sup>OH radicals with the solute (Fig. 1a) is similar to that formed on reaction with Br<sup>•</sup> (Fig. 1c) and assigned to solute radical cation, therefore the transient absorption spectrum (Fig. 1a), obtained on reaction of <sup>•</sup>OH radicals with MTBA is also assigned to solute radical cation (reaction 2).



The yield of the transient species in both the cases was nearly same, suggesting that complete electron transfer has taken from MTBA to Br<sup>•</sup> (reaction 1) and the oxidation potential of MTBA/MTBA<sup>•+</sup> is less than that of the Br<sup>•</sup>/Br<sup>-</sup> couple (1.9 V).



Scheme 1.

One-electron oxidation of MTBA has been carried out with a number of specific one-electron oxidants (Table 1). The kinetic and spectral parameters of the transient species, in each case, were similar to those obtained on reaction with  $\cdot\text{OH}$  radicals. The yield of the transient species formed on reaction of  $\text{SO}_4^{\bullet-}$  with the solute was comparable to that obtained on reaction with  $\cdot\text{OH}$  radicals, thus suggesting that complete electron transfer has taken place. However, the yield of the transient species formed on reaction of  $\text{Br}_2^{\bullet-}$  with the solute was approx. 80% of that obtained on reaction with  $\cdot\text{OH}$  radicals. This shows that complete electron transfer is not taking place and the oxidation potential is close to that of  $\text{Br}_2^{\bullet-}/\text{Br}^-$  couple (1.6 V). The oxidation potential of the  $\text{N}_3^{\bullet}/\text{N}_3^-$  couple is 1.3 V and it failed to undergo electron transfer reaction with the solute, suggesting that the oxidation potential of the solute is more than that of the  $\text{N}_3^{\bullet}/\text{N}_3^-$  couple. The  $\text{CCl}_3\text{OO}\cdot$  radical, which is also a specific one-electron oxidant with oxidation potential close to 1.4 V, failed to undergo electron transfer reaction with MTBA, thus supporting the earlier observation that the oxidation potential of  $\text{MTBA}/\text{MTBA}^{\bullet+}$  is high. These studies suggest that the oxidation potential of the solute is between 1.4 and 1.6 V.

Sulfur-centered monomer radical cations of dialkyl sulfides are highly unstable, absorb at approx. 300 nm and have a high tendency to stabilise on coordination with another molecule to form the dimer radical cation. The dimer radical cations of dialkyl sulfides, with positive charge on sulfur, are known to absorb in the 450–550 nm region. On the other hand, the radical cation of aryl sulfides, with positive charge on the benzene ring, is reported to have absorption bands in the 300–350 and 500–550 nm regions [33, 34]. The kinetic and spectral parameters of the transient species formed on reaction of  $\cdot\text{OH}$  radicals and specific one-electron oxidants with MTBA suggest it to be due to a monomeric species. Therefore, the transient species is assigned to solute radical cation with a positive charge on the benzene ring (Scheme 1).

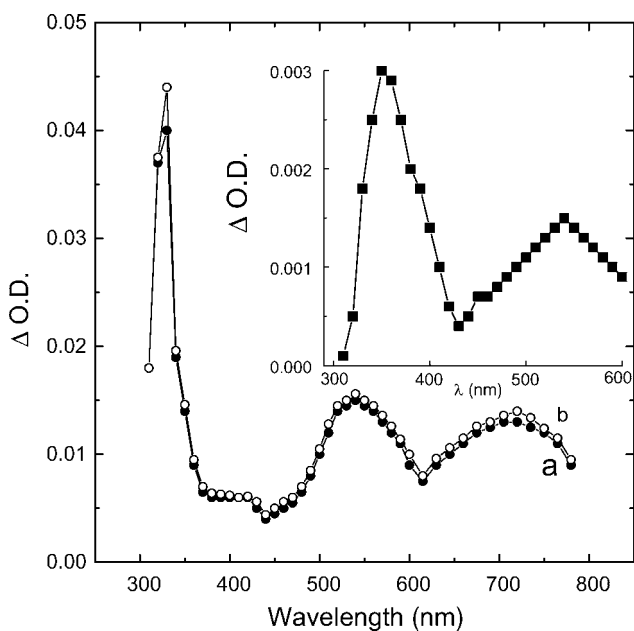
#### *Pulse radiolysis studies in acidic solutions*

$\text{Cl}_2^{\bullet-}$  is also a strong one-electron oxidant with an oxidation potential for  $\text{Cl}_2^{\bullet-}/2\text{Cl}^-$  couple equal to 2.1 V. The transient absorption band of  $\text{Cl}_2^{\bullet-}$  ( $\lambda = 345$  nm), formed on pulse radiolysis of a aerated acidic (pH = 1) aqueous solution of  $\text{Cl}^-$  ( $4 \times 10^{-2}$  mol/dm<sup>3</sup>) showed accelerated decay in the presence of a low concentration

**Table 3.**

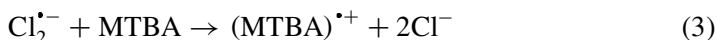
Kinetic and spectral parameters of the transients formed from MTBA

Reaction	pH	$\lambda_{\max}$ (nm)	Formation rate constant ( $\times 10^9$ dm <sup>3</sup> /mol per s)	Decay (s <sup>-1</sup> )
MTBA + Cl <sub>2</sub> <sup>•-</sup>	1	330, 540	2.5	$2.1 \times 10^4$
MTBA + Br <sup>•</sup>	1	330, 540	4.3	—
MTBA in DCE		330, 540	—	—

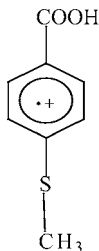


**Figure 2.** (a) Transient absorption spectra obtained on pulse radiolysis of aerated acidic (pH 1) aqueous solution of Cl<sub>2</sub><sup>•-</sup> ( $4 \times 10^{-2}$  mol/dm<sup>3</sup>) and MTBA ( $2 \times 10^{-4}$  mol/dm<sup>3</sup>), 6  $\mu$ s after the pulse. (b) Transient absorption spectrum obtained on reaction of Br<sup>•</sup> with MTBA ( $4 \times 10^{-4}$  mol/dm<sup>3</sup>). Inset: transient absorption spectrum obtained on pulse radiolysis of N<sub>2</sub>-saturated solution of MTBA ( $2 \times 10^{-4}$  mol/dm<sup>3</sup>) and 1,2-dibromoethane in DCE.

of MTBA ( $2 \times 10^{-4}$  mol/dm<sup>3</sup>), indicating electron transfer (reaction 3).



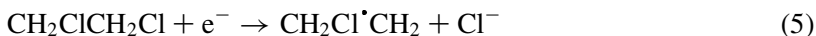
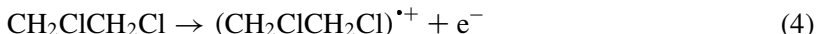
The bimolecular rate constant for reaction 3, determined from the decay of the 345 nm band at various concentrations of MTBA ( $(0.5-3) \times 10^{-4}$  mol/dm<sup>3</sup>) gave a value of  $2.5 \times 10^9$  dm<sup>3</sup>/mol per s (Table 3). Time-resolved studies showed the formation of transient bands at 330 and 540 nm with a broad band in the 660–780 nm region (Fig. 2a). The entire spectrum decayed by first-order kinetics with  $k = 2.1 \times 10^4$  s<sup>-1</sup>. Although the transient species formed on reaction with Cl<sub>2</sub><sup>•-</sup> is expected to be a solute radical cation, the nature of the transient spectrum



### Scheme 2.

was different from that obtained at pH 7 (Fig. 1a). It may be due to the fact that at pH 7 the solute is present in the protonated form. In order to confirm this, the reaction of  $\cdot\text{OH}$  radical with MTBA was carried out at pH 1 and the transient absorption spectrum (Fig. 2b) was similar to that obtained on reaction with  $\text{Cl}_2^{\bullet-}$  (Fig. 2a). The yield of the transient species was same in both the cases, indicating complete electron transfer (reaction 3).

In 1,2-dichloroethane (DCE), the solute is expected to be in the protonated form and the pulse radiolysis of  $\text{N}_2$ -saturated solution of MTBA in DCE showed (shown up to 600 nm) bands at 330 and 540 nm (Fig. 2, inset). These bands should be due to solute radical cations formed according to reactions 4–6:

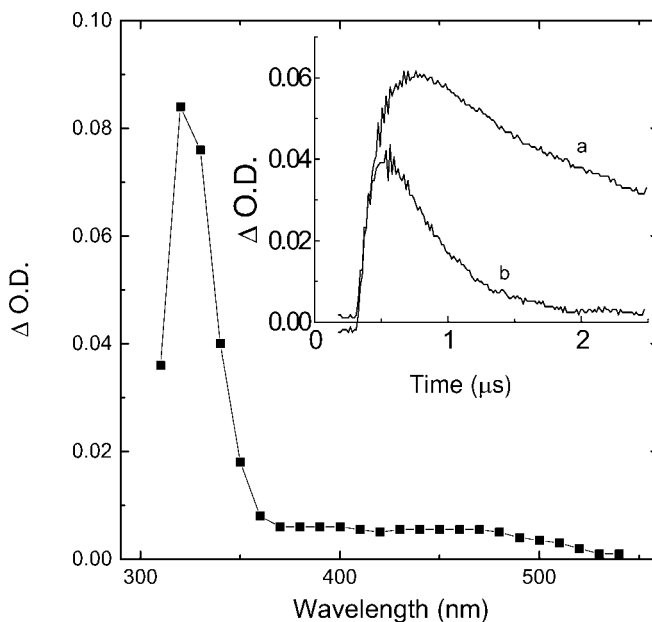


These results support the assignment of the transient absorption spectra (Fig. 2a) to solute radical cation. One-electron oxidation of MTBA, in acidic solution, has also been carried out with other specific one-electron oxidants (Table 3) and the nature of the transient absorption spectrum in each case was similar to that obtained on reaction with  $\cdot\text{OH}$  radicals. Therefore the transient absorption spectrum (Fig. 2) is assigned due to solute radical cation (protonated form) as shown in Scheme 2.

### Reaction with $e_{\text{aq}}^-$

The reaction of  $e_{\text{aq}}^-$  with the solute was studied on monitoring the decay of  $e_{\text{aq}}^-$  at 700 nm as a function of solute concentration. The decay of  $e_{\text{aq}}^-$  was observed to become faster (Fig. 3, inset) on addition of a low concentration of the solute and increased linearly with solute concentration ( $(0.3\text{--}1.8) \times 10^{-4}$  mol/dm<sup>3</sup>). The bimolecular rate constant, determined from the linear plot of  $k_{\text{obs}}$  versus solute was found to be  $1.7 \times 10^{10}$  dm<sup>3</sup>/mol per s. Time-resolved studies showed the formation of a transient absorption band at 320 nm (Fig. 3). The absorption band was observed to decay by first-order kinetics with  $k = 1.6 \times 10^4$  s<sup>-1</sup>. The bimolecular rate constant for the reaction of  $e_{\text{aq}}^-$  with MTBA, determined from the formation kinetics at 320 nm gave a value of  $1 \times 10^{10}$  dm<sup>3</sup>/mol per s, which is close to that determined for the decay of  $e_{\text{aq}}^-$  at 700 nm. The nature of the transient absorption spectrum





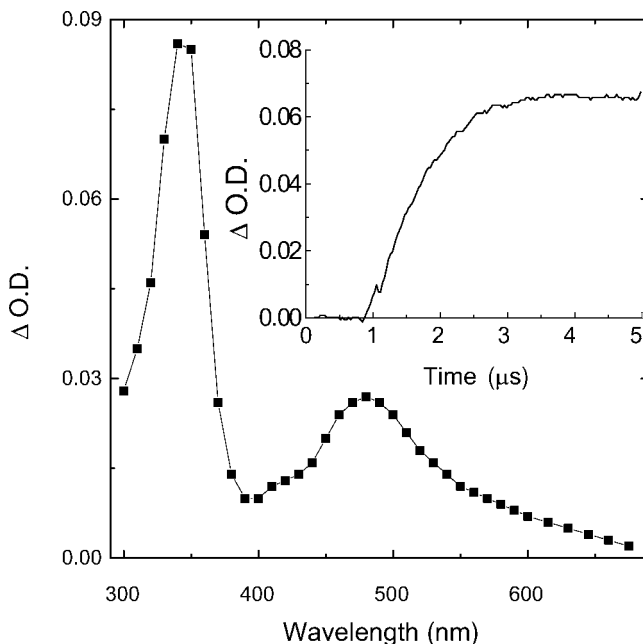
**Figure 3.** Transient absorption spectra obtained on pulse radiolysis of  $\text{N}_2$ -saturated neutral aqueous solution of MTBA ( $8 \times 10^{-4} \text{ mol/dm}^3$ ) containing *t*-butyl alcohol ( $0.3 \text{ mol/dm}^3$ ). Inset: absorption *versus* time profiles ( $\lambda = 700 \text{ nm}$ ) obtained on pulse radiolysis of  $\text{N}_2$ -saturated aqueous solution containing *t*-butyl alcohol ( $0.3 \text{ mol/dm}^3$ ) in the (a) absence and (b) presence of MTBA ( $5 \times 10^{-4} \text{ mol/dm}^3$ ).

remained independent of pH in the range 7–10, indicating the absence of reversible protonation in this region.

Acetone ketyl radicals,  $(\text{CH}_3)_2\dot{\text{C}}\text{OH}$ , formed on pulse radiolysis of  $\text{N}_2\text{O}$ -saturated neutral aqueous solution of isopropanol ( $1 \text{ mol/dm}^3$ ) failed to undergo electron transfer with MTBA, suggesting that the reduction potential of the MTBA/MTBA $^{\bullet-}$  couple is more negative than that of the  $(\text{CH}_3)_2\dot{\text{C}}\text{OH}/(\text{CH}_3)_2\text{CO}, \text{H}^+$  couple (approx. 1.1 V).

#### Reaction with $\text{O}^{\bullet-}$

Pulse radiolysis of  $\text{N}_2\text{O}$ -saturated aqueous solution (pH = 13) of MTBA ( $0.8 \times 10^{-3} \text{ mol/dm}^3$ ) showed the formation of transient absorption bands at 345 and 480 nm (Fig. 4). The rate constant for the reaction of  $\text{O}^{\bullet-}$  with the solute, determined by formation kinetic studies (Fig. 4, inset) at 345 and 480 nm gave similar results and the bimolecular rate constant value was  $4.5 \times 10^9 \text{ dm}^3/\text{mol per s}$ . The absorbance of the transient absorption bands remained independent of solute concentration, showing that the entire yield of  $\text{O}^{\bullet-}$  has reacted with the solute. The molar absorptivity of the transient absorption band at 345 nm was determined to be  $9.2 \times 10^3 \text{ dm}^3/\text{mol per cm}$ . The entire spectrum decayed by second-order kinetics with  $2k = 1.5 \times 10^9 \text{ dm}^3/\text{mol per s}$ . In aerated conditions the bands showed faster



**Figure 4.** Transient absorption spectra obtained on pulse radiolysis of  $N_2O$ -saturated aqueous solution (pH 13) of MTBA ( $8 \times 10^{-4}$  mol/dm<sup>3</sup>) immediately after the pulse. Inset: absorption *versus* time profile at 345 nm.

decay. The band at 345 nm showed first-order decay with  $k = 7.4 \times 10^5$  s<sup>-1</sup>. Considering the high reactivity of the transient species with oxygen, it is suggested to be due to a carbon-centered radical.

#### *Reaction with inorganic ions*

$N_3^*$  failed to undergo electron transfer reaction with MTBA in neutral solutions and indicated that the oxidation potential of the MTBA/MTBA<sup>•+</sup> couple is more than that of the  $N_3^*/N_3^-$  couple (1.3 V). Therefore, it should be possible that the solute radical cation may be able to undergo electron transfer with  $N_3^-$ . The transient absorption band of solute radical cation ( $\lambda = 550$  nm) was observed to decay faster on addition of low concentration of  $N_3^-$  ( $(1-5) \times 10^{-5}$  mol/dm<sup>3</sup>). The bimolecular rate constant was determined to be  $1.3 \times 10^9$  dm<sup>3</sup>/mol per s.

## CONCLUSIONS

The reaction of  $\cdot OH$  radicals with aryl-substituted sulfides is observed to depend strongly on the nature of the substituents present in the molecule. While the reaction of  $\cdot OH$  radicals in the neutral aqueous solution of 2-(phenylthio)ethanol and thianisole showed formation of approx. 22 and 73% of solute radical cation, respectively, complete electron transfer was observed in the present case.

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