Spectral, Kinetic, and Redox Studies on the Transients Formed on Reaction of Hydroxyl Radicals with Thioanisole

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The hydroxyl radicals are observed to react with thioanisole (TA) with a bimolecular rate constant of 3.5 × 10^9 dm^3 mol^{-1} s^{-1} and form transient optical absorption bands with λ_{max} = 310, 365, 530, and 740 nm. The transient absorption bands at 310, 530, and 740 nm are also formed on reaction of specific one-electron oxidants such as $CCl_3OO^\bullet$, $Br_2^{\bullet-}$, and $Cl_2^{\bullet-}$ with thioanisole and are assigned to solute radical cations with positive charge on the benzene ring. Based on the studies with specific one-electron oxidants, ≈73% of $^\bullet$OH radicals are inferred to react with thioanisole by electron transfer and 27% by OH-adduct formation. The oxidation potential for the TA/$TA^{\bullet+}$ couple, based on the equilibrium established with the $Br_2^{\bullet-}$ / $2Br^-$ couple, is determined to be 1.53 V vs NHE. The OH-adduct (λ_{max} = 365 nm) is observed to undergo acid-catalyzed dehydration and form a solute radical cation. A small fraction of it is converted to sulfur-centered dimer radical cations and the major fraction into the monomer radical cations with the positive charge on the benzene ring. The monomer radical cations, formed in neutral aqueous solutions, are a strong one-electron oxidant and are able to oxidize I^- with a bimolecular rate constant value of 6.4 × 10^9 dm^3 mol^{-1} s^{-1}.

1. Introduction

One-electron oxidation of alkyl sulfides (R_2S) by $^\bullet$OH radicals and specific one- electron oxidants leads to the formation of the sulfur-centered radical cation ($R_2S^{\bullet+}$).[1−4] The oxidized sulfur has a high tendency to coordinate with another sulfur or other heteroatoms (O, N, halogen) and form dimer radical cations absorbing in the 450−550 nm region.[5−8] The formation of the sulfur-centered dimer radical cation takes place via a complex reaction mechanism involving the OH-adduct and α-thio radical which absorb in the region 350−370 and 280−300 nm, respectively.[9,10] The reaction of $^\bullet$OH radicals with alkyl sulfides and substituted derivatives has been a subject of recent interest.[11−13] It has been shown that both the nature and the relative position of the substituent group with respect to sulfur play an important role in the formation of transient intermediate species. Such studies have also gained importance due to the formation of the sulfur-centered radical species as the possible intermediates in the biological systems with sulfur-containing compounds.[14] 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.[15] Recently, the reactions of $^\bullet$OH radicals and specific one-electron oxidants on $(C_6H_5)_2S$ have shown the formation of a radical cation, $[(C_6H_5)_2S]^{\bullet+}$, with absorption bands at 360 and 740 nm.[16] The dimer radical cations were not observed. The radical cations of aromatic thioethers have been generated on reaction of specific one-electron oxidants such as $SO_4^{\bullet-}$ and Tl^{2+}, and the reactivity with a number of solutes has been determined.[17] Therefore, it is of interest to examine the nature of $^\bullet$OH radical reactions with phenyl-substituted derivatives, and the results of the reaction of $^\bullet$OH radicals and specific one-electron oxidants with $C_6H_5SCH_3$ are described in this paper.

2. Experimental Section

Thioanisole (TA, purity = 99%) obtained from Aldrich Chemicals was used without further purification. The solutions were prepared in deionized Nanopure water, and freshly prepared solutions were used for each experiment. 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.[18] Aerated aqueous solutions of KSCN was used for determining the dose delivered per pulse using $G\epsilon_{500}$ = 21 520 dm^3 mol^{-1} cm^{-1} per 100 eV for the transient $(SCN)_2^{\bullet-}$ species and the dose per pulse was close to 15 Gy per pulse.[19] All other experimental details are described elsewhere.[12] The reaction of $^\bullet$OH radicals was carried out in N_2O-saturated solutions where e_{aq}^- is quantitatively converted to $^\bullet$OH radicals ($N_2O + e_{aq}^- \rightarrow N_2 + {}^\bullet OH + OH^-$).

The transient absorption as a function of time was recorded on a storage oscilloscope interfaced to a computer for kinetic analysis. The first-order rate constant (k_{obs}) values were determined from the plot of ln(OD) vs time. The points back calculated from the slope and intercept of the plots were found to fit the actual decay curves quite well.[20] The bimolecular rate constant values were determined from the slope of the linear plot of k_{obs} vs solute concentration. The rate constant values were the average of at least three experiments, and the variation was within ±10%.

3. Results and Discussion

Reaction of $^\bullet$OH radicals in neutral solutions. Figure 1 shows the transient optical absorption spectrum obtained on pulse radiolysis of N_2O-saturated neutral aqueous solution of TA (3 × 10^{-3} mol dm^{-3}), which exhibits absorption bands with λ_{max} = 310, 365, 530, and 740 nm. These absorption bands were not observed in the presence of *tert*-butyl alcohol (0.3 mol dm^{-3}), an efficient $^\bullet$OH radical and weak $^\bullet$H atom scavenger, suggesting that the absorption spectrum is due to the reaction of $^\bullet$OH radicals with TA. The bimolecular rate constant for

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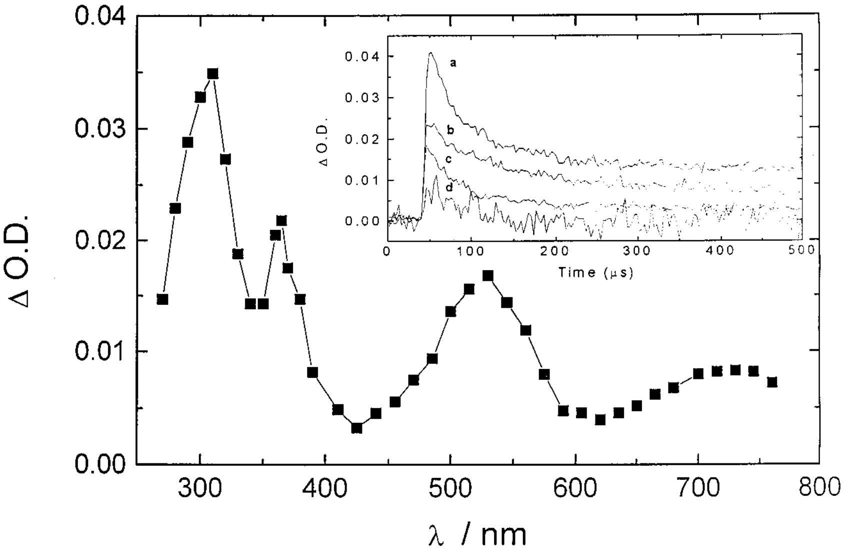


Figure 1. Transient optical absorption spectrum obtained on pulse radiolysis of neutral N_2O-saturated aqueous solution of TA (3×10^{-3} mol dm^{-3}), 2μs after the pulse. Inset shows the absorption−time signal at (a) 310, (b) 365, (c) 530, and (d) 740 nm.

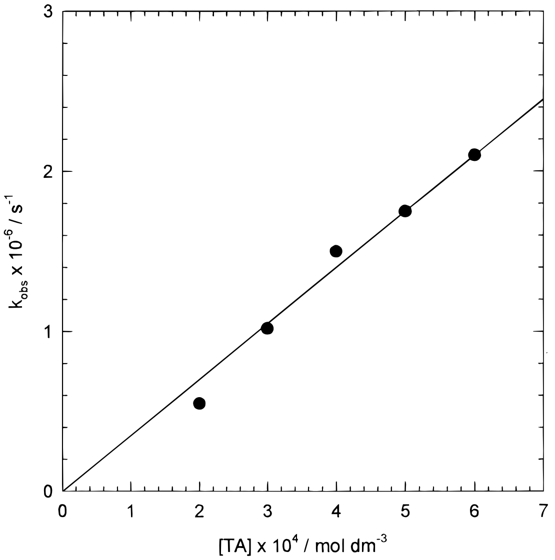


Figure 2. Plot of observed first-order rate constant with thioanisole concentration (λ = 310 nm).

the reaction of •OH radicals with the solute was determined on monitoring the growth of the transient absorption as a function of solute concentration (2−6) × 10^{-4} mol dm^{-3}. The pseudo-first-order rate constant (k_{obs}) was found to increase linearly in this concentration range (Figure 2), which gave the bimolecular rate constant value of (3.5 ± 0.5) × 10^9 dm^3 mol^{-1} s^{-1}. The bimolecular rate constant determined at different wavelengths (310, 365, 530 nm) gave the same value. The absorbance of these transient bands remained independent of solute concentration, (0.3−3) × 10^{-3} mol dm^{-3}, suggesting that the transient bands are due to a monomeric species. The decay of the bands at 310, 530, and 740 nm followed similar kinetics, first order with k = (1.08 ± 0.1) × 10^4 s^{-1}. The decay of the 365 nm band also followed first-order kinetics, but its decay rate (k = 5.5 × 10^3 s^{-1}) was different from those of other bands, suggesting the presence of more than one species (inset of Figure 1). The residual absorbance at longer times (300 μs) may be due to some stable products formed on radiolysis. Since the rate of •OH radical reaction was the same at these wavelengths, and the time-resolved studies do not show any transformation, all the transient species must have formed immediately after the pulse.

Reaction with Specific One-Electron Oxidants. The •OH radicals are known to undergo •H abstraction, addition, and electron-transfer reaction with a number of organic solutes. To distinguish among various modes of reaction of the •OH radicals with TA, pulse radiolysis studies were carried out with specific one-electron oxidants. $CCl_3OO^•$ is known to be a strong one-electron oxidant and has very little absorption at λ > 280 nm. The pulse radiolysis of aerated aqueous solution of CCl_4 (3 × 10^{-2} mol dm^{-3}) + *tert*-butyl alcohol (0.3 mol dm^{-3}) would generate $CCl_3OO^•$ radicals, which in the presence of TA would react to form solute radical cations.

$$CCl_4 + e_{aq}^- \rightarrow {}^•CCl_3 + Cl^- \tag{1}$$

$${}^•CCl_3 + O_2 \rightarrow CCl_3OO^• \tag{2}$$

$$CCl_3OO^• + TA \rightarrow CCl_3OO^- + TA^{•+} \tag{3}$$

Figure 3 shows the transient optical absorption spectrum obtained on pulse radiolysis of aerated aqueous solution of CCl_4 (3 × 10^{-2} mol dm^{-3}) + *tert*-butyl alcohol (0.3 mol dm^{-3}) + TA (2.9 × 10^{-3} mol dm^{-3}), 45 μs after the pulse. This exhibits absorption bands with λ_{max} = 310, 530, and 740 nm. The entire spectrum was observed to decay by the same kinetics, first order with k = (4.2 ± 0.7) × 10^3 s^{-1}. This suggests the formation of one species, which should be due to the solute radical cation $(TA)^{•+}$. The growth of the transient band with λ_{max} = 310 nm was found to increase with solute concentration (1−4) × 10^{-3} mol dm^{-3} (Figure 3A). The bimolecular rate constant, determined from the linear plot of k_{obs} vs solute concentration was 0.9 × 10^8 dm^3 mol^{-1} s^{-1}.

Figure 3B shows variation of absorbance (λ = 310 nm) as a function of solute concentration, which increased linearly for low concentration (<10^{-3} mol dm^{-3}) and reached saturation value for TA concentration ≥ 2 × 10^{-3} mol dm^{-3}. Under the present experimental conditions, the entire yield of e_{aq}^- has reacted with CCl_4, and $CCl_3OO^•$ radicals formed have reacted completely with the solute. Therefore, the concentration of the transient species formed on reaction of $CCl_3OO^•$ radicals with TA could be taken equal to the concentration of e_{aq}^-. Under these conditions, the molar absorptivity at 310 and 530 nm was determined to be 4.56 × 10^3 and 2.42 × 10^3 dm^3 mol^{-1} cm^{-1}, respectively.

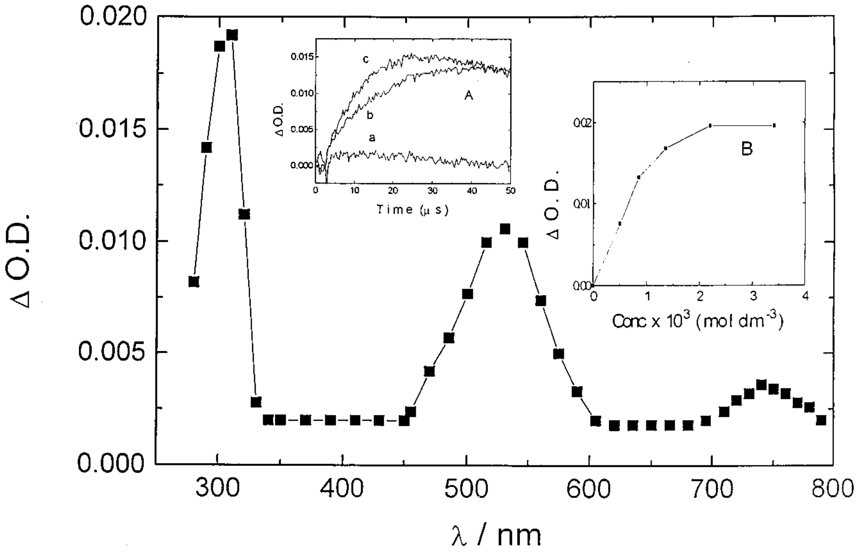
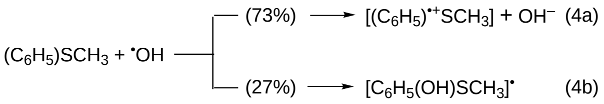


Figure 3. Transient optical absorption spectrum obtained on pulse radiolysis of aerated aqueous solution of CCl_4 (3×10^{-2} mol dm^{-3}) + *tert*-butyl alcohol (0.3 mol dm^{-3}) + TA (2.9×10^{-3} mol dm^{-3}) 45 μs after the pulse. Inset shows (A) absorption−time signal (310 nm) for (a) 0; (b) 1.7×10^{-3} and (c) 3.4×10^{-3} mol dm^{-3} of TA; (B) variation of absorbance (310 nm) as a function of solute concentration.

The nature of the transient spectrum (λ = 310, 530, 740 nm) formed on reaction of $^{\bullet}OH$ radicals with TA (Figure 1) was similar to that formed on reaction of $CCl_3OO^{\bullet}$ radicals with TA (Figure 3). These transient bands (λ = 310, 530, 740 nm) are therefore assigned to the same species, i.e., the solute radical cation. The decay of the solute radical cations formed on reaction of $CCl_3OO^{\bullet}$ radicals was slower than that observed with $^{\bullet}OH$ radicals. The possible reason may be due to the lower value of the formation rate constant observed with $CCl_3OO^{\bullet}$ radicals as compared to the value obtained with $^{\bullet}OH$ radicals. The OH-adducts of alkyl sulfides are known to have absorption bands with λ_{max} in the 360−370 nm region.[2−4] Therefore, the band observed at 365 nm in the present case (Figure 1) may be due to the OH-adduct. The sulfur-centered monomer radical cations are short-lived and absorb in the region of 300−310 nm.[2−4] The dimer radical cations, whose transient absorbance shows concentration dependence, absorb in the region of 400−550 nm.[2−4] Therefore the bands observed at 310, 530, and 740 nm could not be due to sulfur-centered monomer/dimer radical cations as (1) the absorbance of the transient bands remained independent of solute concentration, (2) the bands are relatively long-lived, and (3) the positions of the transient bands do not match with those of monomer /dimer readical cations reported in the literature. The oxidized sulfur has a high tendency to stabilize on coordination with another sulfur, but in the presence of a phenyl ring, the oxidized molecule may be stabilized as a monomeric species with positive charge on the phenyl ring due to resonance stabilization with the adjacent π system. Therefore, the transient absorption bands with λ = 310, 530, and 740 nm (Figure 1, 3) could be due to monomer radical cation with positive charge on the benzene ring. The absorbance of these bands remained independent of solute concentration, which also supports the assignment of the bands to monomer species.

Using the molar absorptivity ($\epsilon = 2.42 \times 10^3$ dm^3 mol^{-1} cm^{-1}) of the transient band (λ = 530 nm) formed on reaction of $CCl_3OO^{\bullet}$ radical with TA, the concentration of the transient species (λ = 530 nm) formed on reaction of $^{\bullet}OH$ radicals with TA is determined to be 6.8×10^{-6} mol dm^{-3}. But the actual concentration of the $^{\bullet}OH$ radicals under these conditions was 9.3×10^{-6} mol dm^{-3}, suggesting that ≈73% of $^{\bullet}OH$ radicals are reacting with the solute to form solute radical cations (λ = 310, 530, 740 nm). The remaining fraction of $^{\bullet}OH$ radicals, ≈27%, must have reacted to form the OH-adduct, which absorbs at 365 nm (Scheme 1).

SCHEME 1:



The transient band of $Cl_2^{\bullet-}$ formed on pulse radiolysis of aerated acidic aqueous solution of Cl^- (2×10^{-2} mol dm^{-3}, pH = 1) was found to decay faster in the presence of low concentrations of TA, (0−4) $\times 10^{-5}$ mol dm^{-3}, showing electron transfer from TA to $Cl_2^{\bullet-}$ (reaction 5).

$$Cl_2^{\bullet-} + TA \rightarrow TA^{\bullet+} + 2Cl^- \qquad (5)$$

The pseudo-first-order rate constant (k_{obs}) was found to increase linearly with solute concentration, (0−4) $\times 10^{-5}$ mol dm^{-3}, and the bimolecular rate constant was determined to be 4.8×10^9 dm^3 mol^{-1} s^{-1}. Time-resolved studies showed the formation of transient bands with λ_{max} = 310, 530, and 740 nm, similar to those observed on reaction of $CCl_3OO^{\bullet}$ radicals with TA. This is expected, as the oxidation potential for $Cl_2^{\bullet-}$/$2Cl^-$ couple is higher than that of the $CCl_3OO^{\bullet}$/CCl_3OO^- couple.

The decay of the transient band of $I_2^{\bullet-}$, formed on pulse radiolysis of N_2O-saturated solution of I^- (4×10^{-2} mol dm^{-3}), was not affected on addition of low concentrations of TA, suggesting that electron transfer from TA to $I_2^{\bullet-}$ is not taking place and that the oxidation potential of the TA/$TA^{\bullet+}$ couple is higher than that of the $I_2^{\bullet-}$/$2I^-$ couple (1.03 eV vs SCE). The $N_3^{\bullet}$ was also found to be unreactive toward TA. These studies suggest that the oxidation potential for the TA/$TA^{\bullet+}$ couple is even higher than that of the N_3^-/$N_3^{\bullet}$ couple (1.33 eV vs SCE).

The transient band of $TA^{\bullet+}$ at 310 nm was found to decay faster on addition of low concentration of I^-, (0−3) $\times 10^{-5}$ mol dm^{-3}, suggesting electron transfer from I^- to $TA^{\bullet+}$, supporting the above conclusion on the redox potentials. The bimolecular rate constant was determined to be 6.4×10^9 dm^3 mol^{-1} s^{-1} (Table 1).

Oxidation Potential of theTA/$TA^{\bullet+}$ Couple. The transient band of $Br_2^{\bullet-}$, formed on pulse radiolysis of N_2O-saturated neutral aqueous solution of Br^- (4×10^{-2} mol dm^{-3}) was

TABLE 1: Spectral and Kinetic Parameters for the Transients Formed on Reaction of • OH Radicals and Specific One-Electron Oxidants with Thioanisole

reaction	pH	λ_{max}/ nm	k_f/dm^3 mol^{-1} s^{-1}	decay/s^{-1}	ϵ/dm^3 mol^{-1} cm^{-1}
TA + •OH	7	310	3.5×10^9	1.08×10^4	
		365		5.5×10^3	
		530			
		740			
TA + $CCl_3OO^•$	7	310	0.9×10^8	4.2×10^3	4.56×10^3
		530			2.42×10^3
		740			
TA + $Cl_2^{•-}$	1	310	4.8×10^9		
		530			
		740			
TA + •OH	high H^+	310	4.1×10^9	9×10^3	
		410			
		530			
		740			
$TA^{•+}$ + I^-	7	380	6.4×10^9		

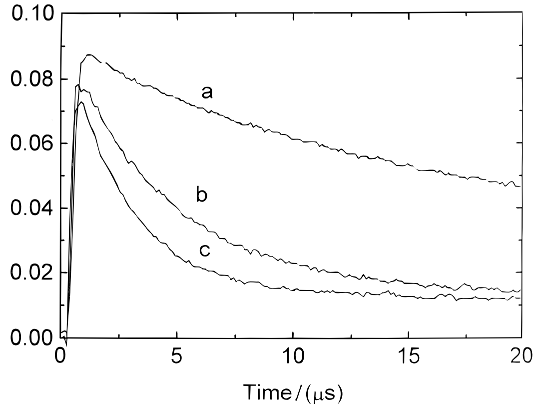


Figure 4. Absorption−time signal (λ = 360 nm) obtained on pulse radiolysis of N_2O-saturated solution of Br^- (4×10^{-2} mol dm^{-3}) in the presence of TA: (a) 0; (b) 1×10^{-3}; and (c) 1.8×10^{-3} mol dm^{-3}.

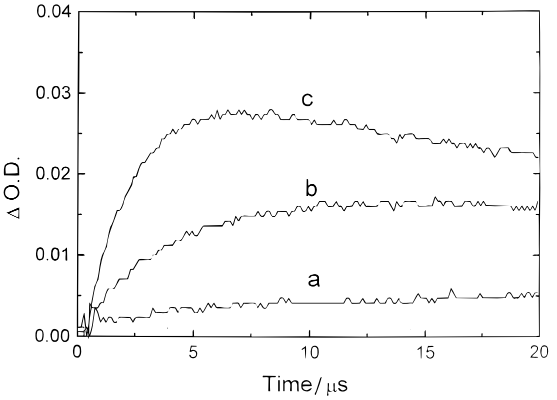


Figure 5. Absorption−time signal (λ = 530 nm) obtained on pulse radiolysis of N_2O-saturated solution of Br^- (4×10^{-2} mol dm^{-3}) in the presence of TA: (a) 0; (b) 1×10^{-3}; and (c) 1.8×10^{-3} mol dm^{-3}.

observed to decay faster on addition of low concentrations of TA (Figure 4). The decay of the transient band of $TA^{•+}$, formed on pulse radiolysis of N_2O saturated neutral aqueous solution of TA, was also affected in the presence of low concentrations of Br^-, suggesting the existence of the following equilibrium.

$$Br_2^{•-} + TA \rightleftharpoons TA^{•+} + 2Br^- \tag{6}$$

Simultaneous to the faster decay, the transient absorption at 530 nm was observed to grow (Figure 5). Time-resolved studies showed the formation of transient bands with λ_{max} = 310, 530, and 740 nm, thus supporting the formation of $TA^{•+}$. The

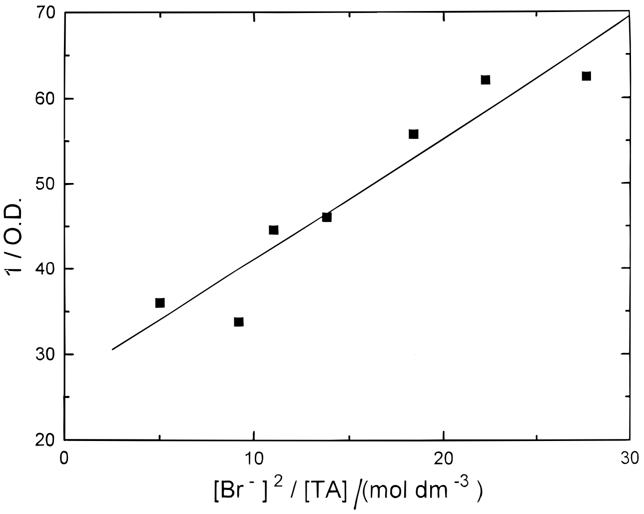


Figure 6. Plot of 1/OD at 530 nm as a function of $[Br^-]^2$/[TA}.

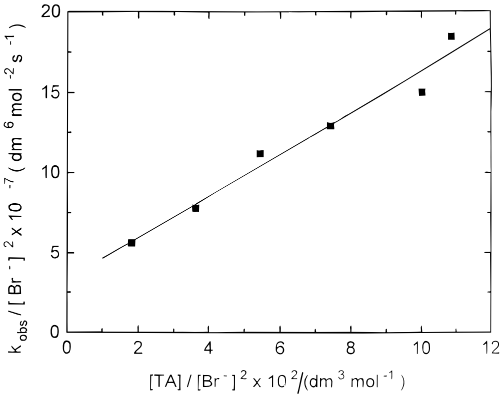


Figure 7. Plot of k_{obs} /$[Br^-]^2$ as a function of [TA]/$[Br^-]^2$.

transient absorbance of $TA^{•+}$ at 530 nm (optical path length = 1 cm), where $Br_2^{•-}$ has negligible absorbance, is related to the equilibrium constant K by the following relationship:

$$\frac{1}{OD} = \frac{1}{K\epsilon[R]}\frac{[Br^-]^2}{[TA]} + \frac{1}{\epsilon[R]} \tag{7}$$

where [R] is the radical concentration, which was maintained constant at a given dose, and ϵ is the molar absorptivity of the transient at 530 nm. The maximum value of the absorbance (OD) was measured at 530 nm, and the plot of 1/OD vs $[Br^-]^2$/[TA] was linear (Figure 6). The absorbance was measured for low concentrations, (0.6−4) × 10^{-4} mol dm^{-3}, of TA so that any depletion in the absorbance due to the partial decay of $TA^{•+}$ is negligible. The equilibrium constant (K) = intercept/slope was determined to be 23.1. Under the present experimental conditions, G(•OH) = 5.6 and [R] = 1.1×10^{-5} mol dm^{-3}, the molar absorptivity at 530 nm was determined to be 3.2×10^3 dm^3 mol^{-1} cm^{-1}. The value is slightly higher than that determined directly.

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

$$k_{obs} = k_f[TA] + k_r[Br^-]^2 \tag{8}$$

$$\frac{k_{obs}}{[Br^-]^2} = k_f\frac{[TA]}{[Br^-]^2} + k_r \tag{9}$$

The pseudo-first-order rate (k_{obs}) was determined on monitoring the decay of the transient band of $Br_2^{•-}$ (λ = 360 nm) for

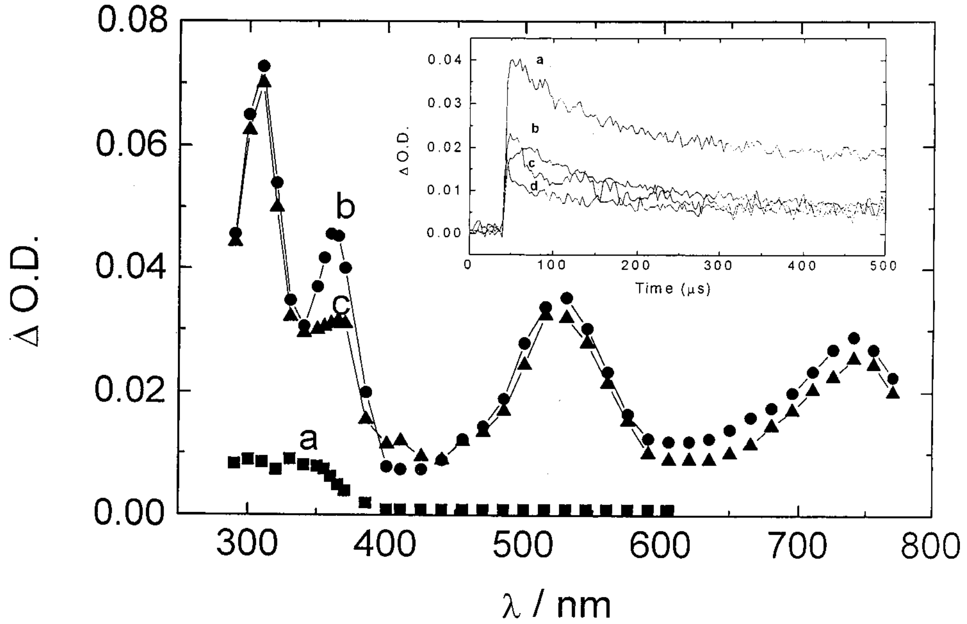


Figure 8. Transient optical absorption spectra obtained on pulse radiolysis of aerated acidic aqueous solution of TA (2×10^{-3} mol dm^{-3}) (a) in the presence of *tert*-butyl alcohol (0.3 mol dm^{-3}) and in the absence of *tert*-butyl alcohol (b) 2 μs and (c) 15 μs after the pulse. Inset shows the absorption-time signal at different wavelengths.

various concentration of $Br^- = (1-4) \times 10^{-2}$ mol dm^{-3} and TA = $(0-1.8) \times 10^{-3}$ mol dm^{-3}, under conditions such that $^•OH$ radicals would react initially with Br^- and $Br_2^{•-}$ would then react with TA. The plot of k_{obs} /[Br$^-$]^2 vs [TA]/[Br$^-$]^2 gave a straight line (Figure 7) with slope (k_f) = 1.125×10^9 and intercept (k_r) = 4.75×10^7. The equilibrium constant, K, was determined to be 23.7, close to the value determined by absorbance method. It is related to the difference ($\Lambda E°$) of the oxidation potential of the two couples by the following relationship:

$$0.059 \log K = \Lambda E° = E_{Br_2^{•-}/2Br^-} - E_{TA/TA^{•+}} \qquad (10)$$

Using the value of 1.63 V for $E_{Br_2^{•-}/2\,Br^-}$, the oxidation potential for the $E_{TA/TA^{•+}}$ couple was determined to be 1.53 ± 0.03 V vs NHE.

Reaction of $^•OH$ Radicals in Acidic Solutions. It is known that OH-adducts of a number of organic compounds can undergo acid-catalyzed dehydration to form the solute radical cation.[11,12,21] But the nature of the transient spectrum and the formation and decay kinetics remained independent of pH in the range 1−11, suggesting that acid-catalyzed dehydration of OH-adducts is not taking place in this pH range. Depending upon the electron-donating/withdrawing power of the substituents, acid-catalyzed dehydration of OH-adducts is observed at different acid concentrations. In organic compounds containing highly electron withdrawing groups, it may take place in the presence of high acid concentration.[12] In highly acidic solutions, $HClO_4 \geq 1$ mol dm^{-3}, the yield of $^•H$ atoms would increase due to the reaction of e_{aq}^- with H^+ ($e_{aq}^- + H^+ \rightarrow {}^•H + H_2O$). Therefore, to investigate the reaction of $^•OH$ radicals with the solute in highly acidic solutions, the contribution of $^•H$ atom reaction with the solute should be known or $^•H$ atoms should be scavenged. In aerated acidic solutions, $^•H$ atoms would be scavenged by oxygen ($^•H + O_2 \rightarrow HO_2^•$) and $^•OH$ radicals would be the main reactive species to react with the solute. Figure 8a shows the transient optical absorption spectrum obtained on pulse radiolysis of acidic ($HClO_4$ = 6.9 mol dm^{-3}) aqueous solution of TA (2×10^{-3} mol dm^{-3}) in the presence of *tert*-butyl alcohol (0.3 mol dm^{-3}). The small absorption in the 290−330 nm region suggests that the contribution of $HO_2^•$ radicals to TA is negligible and $^•OH$ radical reaction with TA can be investigated in aerated solutions.

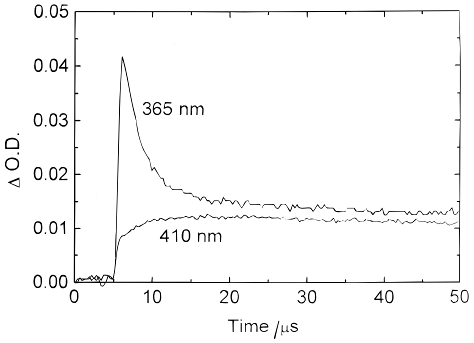


Figure 9. Absorption-time signal obtained on pulse radiolysis of aerated acidic solution ($HClO_4$ = 6.9 mol dm^{-3}) of TA (2×10^{-3} mol dm^{-3} at (a) 365 nm and (b) 410 nm.

In aerated acidic solutions ($HClO_4$ = 6.9 mol dm^{-3}, TA = 2×10^{-3} mol dm^{-3}), the initial portion of absorption at 365 nm was found to decay faster ($k = 2.3 \times 10^5$ s^{-1}, Figure 9). Simutaneouly, the absorption at 410 nm showed slow growth ($k = 3.1 \times 10^5$ s^{-1}), similar to the initial faster decay at 365 nm (Figure 9). The absorption at both these wavelengths decayed by similar kinetics ($k = 9 \times 10^3$ s^{-1}) at longer time scale. These studies show that the transient species absorbing at 365 nm is reacting with H^+ to form another transient species, which absorbs at 410 nm. Time-resolved studies (Figure 8b,c) also showed appreciable decrease in absorption at 365 nm and small growth at 410 nm. The decay at other wavelengths (310, 530, 740 nm) was very small and followed similar kinetics, first order with $k = 9 \times 10^3$ s^{-1} (inset of Figure 8). The bimolecular rate constant for the reaction of $^•OH$ radicals with TA in acidic solutions ($HClO_4$ = 6.9 mol dm^{-3}), determined by formation kinetic studies at 310 nm, was 4.3×10^9 dm^3 mol^{-1} s^{-1}.

The absorbance of the transient species at λ = 310 and 530 nm remained independent of solute concentration, $(0.8-3) \times 10^{-3}$ mol dm^{-3}, whereas at 410 nm a slight increase was observed. From these studies, it appears that the OH-adduct is reacting with H^+ to form the sulfur-centered radical cation. A small fraction of it is converted to the sulfur-centered dimer

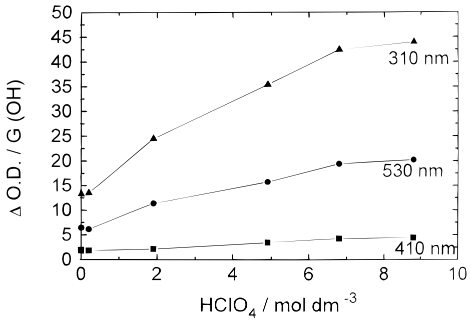
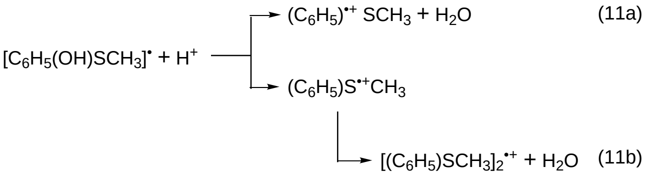


Figure 10. :Variation of absorbance at 310, 410, and 530 nm as a function of {$HClO_4$].

SCHEME 2:



radical cation absorbing at 410 nm. Since the decay of the transient absorption band at 365 nm matched the growth at 410 nm, the monomer radical cation is rapidly converted to the dimer radical cation (Scheme 2). The remaining fraction of sulfur-centered radical cations is converted to monomer radical cations with positive charge on the benzene ring, absorbing at 310, 530, and 740 nm (Scheme 2). Since the nature of the transient bands at 310, 530, and 740 nm was similar to those observed at neutral pH (Figures 1, 3), the bands in the acidic solutions (Figure 8) are also assigned to solute radical cations with positive charge on the benzene ring. The band at 410 nm should be due to sulfur-centered dimer radical cation (Scheme 2).

The reaction of $^\bullet$OH radicals with $HClO_4$ has been reported to produce ClO_3 radicals, which has small absorption at 350 nm.[22] $HClO_4^{\bullet +}$ is formed only when [$HClO_4$] is greater than 10 mol dm^{-3} and absorbs at 440 nm.[22] Therefore, the absorption changes observed in the presence of $HClO_4$ (Figures 8, 9) should be due to the reaction of $^\bullet$OH radicals with TA in the presence of H^+ (Scheme 2) and not due to transient species formed on radiolysis of $HClO_4$. These changes are also not due to the reaction of radiolytic products of $HClO_4$ with TA, as a similar transient optical absorption spectrum was also observed in the presence of H_2SO_4.

At higher concentrations of $HClO_4$, part of the radiation energy would be absorbed by $HClO_4$. The absorption of radiation energy by $HClO_4$ would decrease $^\bullet$OH radical yield as the radiolysis of $HClO_4$ does not produce $^\bullet$OH radicals.[22] Based on electron density variation, the absorbance at 310, 410, and 530 nm is normalized with respect to $^\bullet$OH radical yield for various concentrations of $HClO_4$ and is shown in Figure 10. The absorbance increased with $HClO_4$ concentration, reaching a plateau value when [$HClO_4$] was in the range of 9−10 mol dm^{-3}. These studies suggest that the OH-adduct is almost completely converted to the solute radical cation in this concentration range of $HClO_4$.

4. Conclusion

The hydroxyl radicals, in neutral aqueous solution of thioanisole, are observed to react by OH-adduct (27%) formation and by an electron-transfer mechanism (73%). In highly acidic solutions, the OH-adduct is converted to monomer radical cations with positive charge on the benzene ring and sulfur-centered dimer radical cations.

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