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Evidence for the Role of Electron-Withdrawing Power of Functional Groups and [H^+] for Electron-Transfer Reaction in Substituted Alkyl Sulfides

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The pulse radiolysis technique has been employed to demonstrate the effects of the electron-withdrawing power of functional groups and the H^+ concentration on the nature of $^{\bullet}OH$ radical reaction with substituted alkyl sulfides. The intermediate OH adduct and α-thioalkyl radical could be detected in substituted sulfides having a functional group of high electron-withdrawing power. The concentration of H^+ required for the formation of solute radical cations appears to correlate with the electron-withdrawing power of the functional group. The reactivity of e_{aq}^- toward dialkyl sulfides increases upon the introduction of strongly electron-withdrawing groups which effectively reduce the electron density at sulfur. The transient absorption band ($\lambda_{max} = 310$ nm) observed from the reaction of $^{\bullet}OH$ radicals with methyl thioacetic acid (MTA) is assigned to the α-thioalkyl radical formed via an intermediate OH adduct. In highly acidic solutions ($[HClO_4] \geq 3$ mol dm^{-3}), $^{\bullet}OH$ radicals are able to react with MTA to form dimer radical cations ($\lambda_{max} = 490$ nm). The specific one-electron oxidants ($Cl_2^{\bullet-}$, $Br_2^{\bullet-}$, and $SO_4^{\bullet-}$) undergo electron-transfer reaction with the solute; however, the transient absorption band of the dimer radical cation at 490 nm could not be observed, which may be due to unstable nature of the transient species in neutral and slightly acidic solutions. The oxidation potential is determined to be 1.56 V. The decay kinetics of the solute dimer radical cation is discussed in detail, and deprotonation of the solute radical cation is found to be the rate-determining step. The stability constant for the dimer radical cation has been determined to be 10 dm^3 mol^{-1} at 25 °C. The transient species ($\lambda_{max} = 390$ nm, $k = 3.3 \times 10^9$ dm^3 mol^{-1} s^{-1}), formed from the reaction of $Br^{\bullet}$ atom with the solute, is assigned to a three-electron-bonded $Br^{\bullet}$ adduct.

Introduction

Radicals and radical ions derived from sulfur-containing organic compounds have been the subjects of active interest because they play an important role in understanding the chemistry of biological systems containing sulfur.[1−3] Knowledge of the chemistry involved in the reactions of radicals and radical ions of organic molecules is very important to understanding electron-transfer reactions. These studies are also important because they act as intermediates in many organic reactions in biological and organic synthesis.[4−6] These studies are also of relevance because of the formation of sulfur-centered radicals as possible intermediates in the redox reactions of biomolecules.[7−11]

Hydroxyl radicals and specific one-electron oxidants are known to bring about the one-electron oxidation of dialkyl sulfides (R_2S), leading to the formation of sulfur-centered radical cations $R_2S^{\bullet+}$.[8,12] Simple sulfur-centered radical cations of dialkyl sulfides have been observed only in some cases such as di-*tert*-butyl sulfide because oxidized sulfur has high tendency to stabilize by coordination with the free p electron pair of another sulfur or a heteroatom (O, N, P, or halogen) both by inter- and intramolecular association.[8,12,13] These interactions are represented by a three-electron bond containing two bonding σ and one antibonding σ^* electrons. The formation of sulfur-centered three-electron-bonded species have been inferred to take place via a complex sequence of reactions involving α-thioalkyl radicals, OH adducts, and monomer radical cations. These intermediates are generally very short-lived and are converted into sulfur-centered radical cations.[12,13] Direct evidence for the involvement of these species could be obtained from functionalized sulfides.[3,8,12−14] Evidence for the formation of sulfur-centered species has come from ESR and optical spectroscopic studies.[3,7−9,12−15] Three-electron-bonded species have been the subject of active interest in both experimental and theoretical investigations.[16] In the presence of an electron-withdrawing group (−COOH), hydroxyl radicals failed to undergo one-electron oxidation of substituted alkyl sulfides in neutral solutions and required relatively high H^+ concentration to form the dimer radical cations.[17] One-electron oxidation of substituted alkyl sulfides is reported to depend on the nature of the substituted group.[14] Therefore, it is of interest to examine the nature of the $^{\bullet}OH$ radical reaction with methyl thioacetic acid, which contains both electron-withdrawing (−COOH) and electron-releasing ($-CH_3$) groups. The pulse radiolysis investigations on an aqueous solution of methyl thioacetic acid and the effect of an additional CH_3 group in methyl thiomethyl acetate on the nature of the transient species formed are reported in this manuscript.

The stabilization of an OH adduct at sulfur in substituted organic sulfides has been reported by the formation of an internal hydrogen bond between hydroxyl hydrogen and an oxygen located either in an adjacent carbonyl or in an adjacent methoxy group.[13e] This explanation holds well for the formation of the OH adduct of methyl thiomethyl acetate due to a favorable six-membered ring configuration but could not explain the formation

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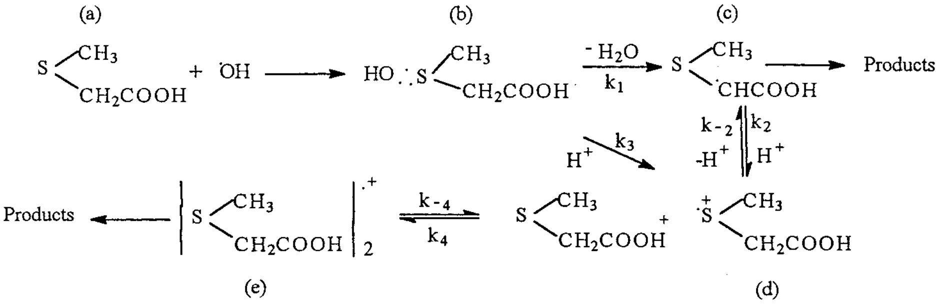
SCHEME 1



and/or absence of OH adducts of other substituted alkyl sulfides.[14,17] Moreover, the formation of sulfur-centered radical cations of substituted alkyl sulfides is observed to depend on the concentration of H^+. The formation of intermediate OH adduct and the α-thioalkyl radical and their subsequent transformation into a sulfur-centered radical cation have been investigated for substituted alkyl sulfides and are discussed in this manuscript with respect to the electron-withdrawing power of the functional group.

Experimental Section

Methyl thioacetic acid (MTA, Scheme 1a) obtained from 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 1×10^{-3} mol dm^{-3} phosphate buffer using "nanopure" water. The pH was adjusted with $NaOH/HClO_4$. Iolar-grade, high-purity gases (N_2, N_2O, and O_2) 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 a Hitachi 330 spectrophotometer. All other experimental details are described elsewhere.[14]

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] The dose delivered per pulse was determined with aerated aqueous solutions of KSCN (1×10^{-2} mol dm^{-3}), with $G\epsilon = 21\,520$ dm^3 mol^{-1} cm^{-1} per 100 eV at 500 nm for the transient $(SCN)_2^{\bullet-}$ species.[19] G denotes the number of species per 100 eV of absorbed energy ($G = 1$ corresponds to 0.1036 μmol J^{-1}), and ϵ is the molar absorptivity of the $(SCN)_2^{\bullet-}$ species at 500 nm. The dose per pulse was close to 15 Gy (1 Gy = 1 J kg^{-1}) except for kinetic experiments, which were carried out at a lower dose of about 10 Gy.

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

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

The reaction with $^\bullet$OH radicals was carried out in N_2O-saturated solutions, where e_{aq}^- is quantitatively converted to $^\bullet$OH radicals with $G(^\bullet OH) = 5.6$ and the $^\bullet$OH radical is the main species to react with the solute ($N_2O + e_{aq}^- \rightarrow {}^\bullet OH + OH^- + N_2$). The reaction with $O^{\bullet-}$ was carried out in N_2O-saturated solutions at pH 13, where $^\bullet$OH radicals are converted to $O^{\bullet-}$ with a pK_a value of 11.9 ($^\bullet OH + OH^- \rightarrow O^{\bullet-} + H_2O$). The reaction with e_{aq}^- was carried out in N_2-saturated solutions in the presence of *tert*-butyl alcohol to scavenge $^\bullet$OH radicals ($(CH_3)_3COH + {}^\bullet OH \rightarrow {}^\bullet CH_2(CH_3)_2COH + H_2O$). The reaction of specific one-electron oxidants were carried out under conditions such that $^\bullet$OH radicals do not react with the solute initially and only the one-electron oxidants react with the solute. These one-electron oxidants were generated as reported in the literature, and the procedure is briefly mentioned in the text.[20]

The transient species formed from pulse radiolysis were monitored using a 450 W pulsed xenon arc lamp, a monochromator (Kratos, GM-252), and a Hamamatsu R-955 photomultiplier as the detector. The photomultiplier output was digitized with a 100 MHz storage oscilloscope interfaced to a computer for kinetic analysis.[21] The rate constant values were taken from that kinetic analysis for which very good correlation was obtained between the experimental and calculated results. The bimolecular rate constant was determined from the linear regression plots of k_{obs} versus solute concentration for at least three experiments, and the variation was within ±10%.

Results and Discussion

The ground-state optical absorption spectrum of acidic (pH 1) aqueous solutions of MTA (Scheme 1a) showed an absorption band at 235 nm ($\epsilon = 260$ dm^3 mol^{-1} cm^{-1}) with very little absorption at $\lambda > 280$ nm. In neutral and basic solutions, the optical absorption spectrum showed increasing absorption at $\lambda < 270$ nm without any band at 235 nm. The solute is in the protonated form (CH_3SCH_2COOH) in acidic solution and deprotonated form ($CH_3SCH_2COO^-$) in neutral and basic solutions, with a pK_a of 3.5. The pulse radiolysis studies can be carried out with an optical absorption technique without any correction for the ground-state absorption in 300−700 nm regions.

Reaction with $^\bullet$OH Radicals. Figure 1a shows the transient absorption spectrum obtained from the pulse radiolysis of an N_2O-saturated neutral aqueous solution of MTA (2.3×10^{-3} mol dm^{-3}), which exhibits an absorption band with $\lambda_{max} = 310$ nm (Table 1). The band was completely quenched in the presence of *tert*-butyl alcohol (0.3 mol dm^{-3}), an efficient $^\bullet$OH radical, and a weak H$^\bullet$ atom scavenger, suggesting that it was mainly due to the reaction of $^\bullet$OH radicals with MTA. The transient absorption was appreciably quenched in aerated conditions. The band was observed to decay by second-order kinetics with $2k/\epsilon l = 5.4 \times 10^6$ s^{-1}. The absorbance of the band at 310 nm remained independent of solute concentration ($1-4 \times 10^{-3}$ mol dm^{-3}), showing that $^\bullet$OH radicals have completely reacted with MTA. Under these conditions, the molar absorptivity at 310 nm was determined to be 1.1×10^3 dm^3 mol^{-1} cm^{-1}. The second-order rate constant for the reaction of $^\bullet$OH radicals with MTA, as determined by formation kinetic studies at 310 nm, gave a value of 2.5×10^{10} dm^3 mol^{-1} s^{-1}. The competition kinetic studies using KSCN as the standard solute gave a value of 2.3×10^{10} dm^3 mol^{-1} s^{-1}, close to the value determined by formation kinetic studies. These studies suggest that $^\bullet$OH radicals are essentially reacting with MTA to form a transient band with $\lambda_{max} = 310$ nm.

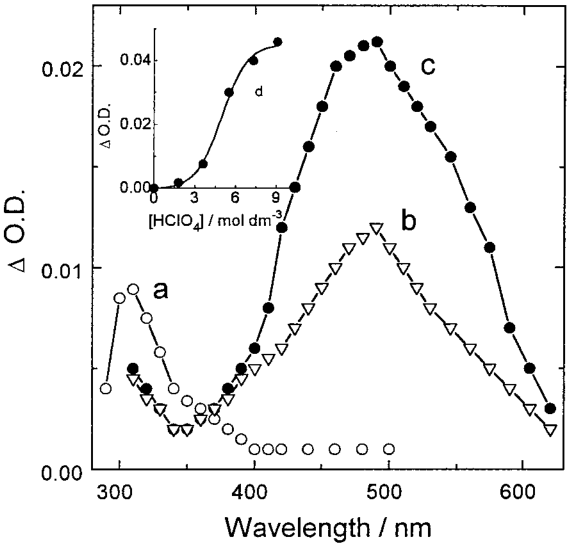


Figure 1. Transient absorption spectra obtained from the pulse radiolysis of an N_2O-saturated aqueous solution of MTA (line a, pH 6, [MTA] = 2.3×10^{-3} mol dm^{-3}) and aerated aqueous solutions of MTA (line b, [HClO$_4$] = 3.7 mol dm^{-3}, [MTA] = 9.2×10^{-3}; line c, [MTA] = 2.3×10^{-2} mol dm^{-3}). Inset (d) shows the variation of absorbance at 490 nm as a function of HClO$_4$ concentration.

TABLE 1: Kinetic and Spectral Parameters of the Transient Species Formed from the Reaction of Primary and Secondary Reactive Species with MTA

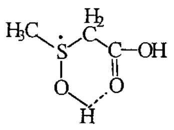
reaction	pH	λ_{max}/ nm	k_f/dm^3 mol^{-1} s^{-1}	k_d/dm^3 mol^{-1} s^{-1}	ϵ/dm^3 mol^{-1} cm^{-1}
MTA + $^{\bullet}$OH	6	310	2.5×10^{10}	5.9×10^{9}	1.1×10^{3}
MTA + H$^{\bullet}$	1	310	- - -	- - -	- - -
$Cl_2^{\bullet -}$ + MTA	1		2.8×10^{9}	- - -	- - -
$I_2^{\bullet -}$ + MTA	6		no reaction		
$N_3^{\bullet}$ + MTA	6		no reaction		
$SO_4^{\bullet -}$ + MTA	6		1.3×10^{9}		
Br$^{\bullet}$ + MTA	1	390	3.3×10^{9}	1×10^{5} [a]	
MTA + O$^{\bullet -}$	13	300	2.3×10^{9}	7.4×10^{9}	2.9×10^{3}
MTA + e_{aq}^{-}	6		8.1×10^{9}		

[a] First-order decay (s^{-1}).

The position of the transient absorption band obtained from the reaction of $^{\bullet}$H atoms with MTA at pH 1 (in the presence of 0.3 mol dm^{-3} *tert*-butyl alcohol) was at $\lambda_{max} = 310$ nm. Due to a very low signal (ΔOD = 0.004), the rate constant for the reaction of an H$^{\bullet}$ atom with MTA was not determined by formation kinetic studies; instead, it was carried out by competition kinetic studies using tetracycline (TC) as a reference solute.[22] The absorbance of the TC−H adduct ($\lambda = 440$ nm), formed from the pulse radiolysis of an N_2-saturated solution (pH 1) of tetracycline (4×10^{-4} mol dm^{-3}) containing *tert*-butyl alcohol (0.3 mol dm^{-3}), was determined for varying concentrations of MTA ($0-1 \times 10^{-3}$ mol dm^{-3}). Using $k_{TC+H} = 2.5 \times 10^9$ dm^3 mol^{-1} s^{-1}, we determined the rate constant for the reaction of the H$^{\bullet}$ atom with MTA to be 4.5×10^9 dm^3 mol^{-1} s^{-1}. The reaction of O$^{\bullet -}$ at pH 13 showed an absorption band at 300 nm, which decayed by second-order kinetics with $2k/\epsilon l = 4.9 \times 10^6$ s^{-1}. The rate constant for the reaction of O$^{\bullet -}$ with MTA, determined by formation kinetic studies, was 2.3×10^9 dm^3 mol^{-1} s^{-1}.

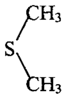
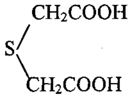
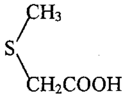
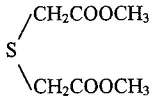
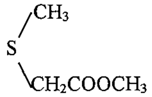
The nature of the transient absorption spectra obtained from the reaction of H$^{\bullet}$, $^{\bullet}$OH, and O$^{\bullet -}$ with MTA was similar, but the rate constant for the reaction of the $^{\bullet}$OH radical was higher than that obtained for the reaction of H$^{\bullet}$ and O$^{\bullet -}$ with MTA. The α-thioalkyl radicals absorb in the region of 290−310 nm, whereas OH adducts of dialkyl sulfides absorb in 340−360 nm region. On the basis of data available in the literature and the experimental results, we assigned the transient absorption band obtained from the reaction of the $^{\bullet}$OH radical with MTA to α-thioalkyl radicals (Scheme 1c). The high value of the rate constant for the reaction of $^{\bullet}$OH radicals with MTA may suggest that $^{\bullet}$OH radicals are not reacting directly by H$^{\bullet}$ atom abstraction because these reactions are normally slow. The $^{\bullet}$OH radicals may be reacting with MTA via an intermediate OH adduct (Scheme 1b), which is converted to α-thioalkyl radical in a very fast process. The high reactivity of the transient band ($\lambda = 310$ nm) with oxygen also supports its assignment to a carbon-centered radical. The lifetime of the intermediate OH adduct may be too low to observe. The low value of the rate constant for the reaction of O$^{\bullet -}$ and H$^{\bullet}$ with MTA shows that H$^{\bullet}$ atom abstraction is taking place without any intermediate adducts.

SCHEME 2



The OH adducts of alkyl sulfides are generally very short-lived and are converted to sulfur-centered radical cations and/or α-thioalkyl radicals.[12,13] However, in substituted organic sulfides, the OH adduct at sulfur is reported to be stabilized by the formation of an internal hydrogen bond between the hydroxyl hydrogen and an oxygen located in the adjacent group. An example of a stabilized OH adduct with λ_{max} at 330 nm was first reported with methyl thiomethyl acetate at pH 3.7.[13e] This adduct is subsequently converted into sulfur-centered dimer radical cation with λ_{max} at 470 nm. If the stabilization of the OH adduct is taking place with the formation of an internal hydrogen bond resulting a favorable six-membered ring configuration as observed for methyl thiomethyl acetate, then such an OH adduct should also be observed for methyl thioacetic acid (Scheme 2). To ensure that our pulse radiolysis system is sensitive enough to detect very low lived transients and that the OH adduct of methyl thioacetic acid has not been missed, we carried out the pulse radiolysis studies with methyl thiomethyl acetate, and the transient absorption band at 330 nm was observed immediately after the pulse with transformation to another transient band at 470 nm (Figure 2), similar to the process reported in the literature (see text). Therefore, the absence of a transient absorption band at 330 nm from the OH adduct of methyl thioacetic acid could not be due to some defect in our experimental facility. This could not be explained on the basis of an internal hydrogen bonding between the hydroxyl hydrogen an oxygen located in the adjacent functional group, as reported for methyl thiomethyl acetate. Similarly, $^{\bullet}$OH radicals can also form an OH adduct with 2,2′-thiodiethanoic acid and 2,2′-thiodiethanol with a favorable six-membered ring by internal hydrogen bonding. However, α-thioalkyl radical was observed from the reaction of $^{\bullet}$OH radical with these compounds.[14e,17a] Seven-membered ring configuration is expected to be unfavorable for the OH adduct of the diester of 3,3′-thiodipropionic acid, formed with an internal hydrogen-bonded structure. But the intermediate OH adduct could be observed for this solute.[17c] However, the favorable six-membered structure for the OH adduct was observed for diester of 2,2′-thiodiethanoic acid.[14a] Therefore, internal hydrogen bonding for the formation of the OH adduct of substituted alkyl sulfides could not be the only factor for their stabilization. It is possible that the difference in the electron density at sulfur, created by the presence of functional groups having high electron-withdrawing power, may

TABLE 2: Effect of Substituents on the Nature of Transients Species Formed from the Reaction of •OH Radicals with Substituted Sulfides

Solute	Neutral solutions		Acidic solutions		$[H^+]$ required for the formation of DRC / mol dm^{-3}	σ*
	λ_{max} / nm	transient species	λ_{max} / nm	transient species		
 $S(CH_3)_2$	465	DRC	465	DRC	0	0
 $S(CH_2COOH)_2$	285	α-thio radical	520	DRC	> 6	2.94
 $S(CH_3)(CH_2COOH)$	310	α-thio radical	490	DRC	> 3	1.47
 $S(CH_2COOCH_3)_2$	340	OH-adduct	485	DRC	0.1	---
 $S(CH_3)(CH_2COOCH_3)$	330	OH-adduct	470	DRC	10^{-3}	---

DRC - Dimer radical cation

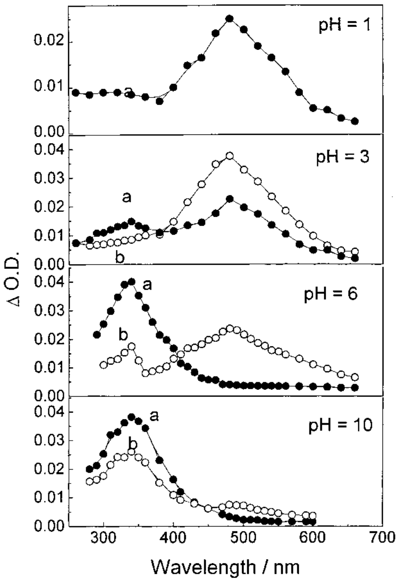
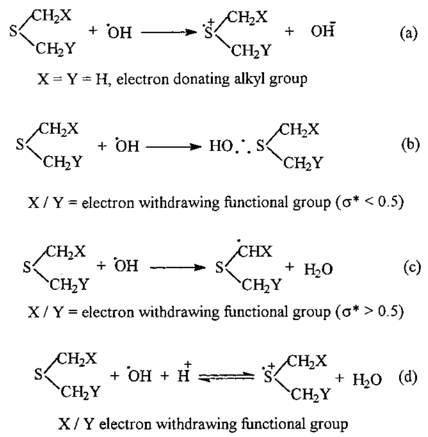


Figure 2. Transient absorption spectra obtained from the pulse radiolysis of an N_2O-saturated aqueous solution of methyl thiomethyl acetate (1.8×10^{-3} mol dm^{-3}) (a) immediately after the pulse and (b) 5, 3, and 1 μs after the pulse at pH 10, 6, and 3, respectively.

be playing an important role in the nature of •OH radical reaction with alkyl sulfides.

In dialkyl sulfides, the electron density at sulfur is very high due to the presence of electron-releasing alkyl groups and electrophilic •OH radicals immediately removing an electron to form the solute radical cation (Scheme 3a) without forming any intermediate OH adduct or α-thioalkyl radical. The lifetime of these intermediates is extremely short. In the presence of electron-withdrawing functional groups, electron density at sulfur is expected to be reduced, and the intermediate OH adduct or the α-thioalkyl radical, depending on the electron-withdrawing power of the functional group, can be observed (Scheme 3b,c); •OH radicals are not removing an electron in the initial process. In acidic solutions, •OH radicals may be able to remove an electron, since the removal of H_2O is facilitated in comparison with the removal of OH^-.[23] An equilibrium is established for the formation of the solute radical cation (Scheme 3d). The concentration of H^+ required for the electron-transfer process would depend on the electron-withdrawing power of the functional group, and the equilibrium would shift toward the right in high H^+ concentrations. The solute radical cation would then be observed even for substituted sulfides with a functional group having high electron-withdrawing power. The following examples demonstrate the role of the electron-withdrawing power of the functional groups.

SCHEME 3



Effect of Electron-Withdrawing Functional Groups. The reaction of •OH radicals with dimethyl sulfides result in the formation of dimer radical cations at pH 7. On the other hand, α-thioalkyl radicals are observed from the reaction of •OH radicals with 2,2′-thiodiethanoic acid even at pH 1, which may be due to the high electron-withdrawing power of $-COOH$ ($\sigma^* = 2.94$) compared to that of $-CH_3$ ($\sigma^* = 0.0$).[24] The presence of the $-CH_2OH$ group ($\sigma^* = 0.56$) has also produced an α-thioalkyl radical from the reaction of •OH radicals with 2,2′-thiodiethanol. The presence of electron-releasing CH_3

groups in the diester of 2,2′-thiodiethanoic acid has increased the electron density on sulfur, and the OH adduct could be observed as the first intermediate.

Effect of [H$^+$]. The nature of the transient absorption spectrum, obtained from the reaction of $^{\bullet}$OH radicals with MTA, remained the same in pH 1−7. However in highly acidic solutions ([$HClO_4$] $\geq$ 3 mol dm^{-3}), pulse radiolysis studies showed the formation of a transient absorption band at 490 nm. The absorbance of this band was observed to increase with solute concentration (Figure 1b,c) and also with the concentration of $HClO_4$ (inset of Figure 1), reaching a saturation value when [$HClO_4$] was close to 9 mol dm^{-3}. Since the intensity and the lifetime of the transient species absorbing at 490 nm were seen to increase with solute concentration, the transient absorption band is therefore assigned to the dimer radical cation (Scheme 1e). The nature of the transient absorption spectrum and the absorbance value remained the same in aerated and N_2-saturated conditions, thus supporting the cationic nature of the transient species and the negligible contribution of the $^{\bullet}$H/$HO_2^{\bullet}$ radical reaction with the solute. As determined by formation kinetic studies at 490 nm, the bimolecular rate constant for the reaction of $^{\bullet}$OH radicals with MTA ([$HClO_4$] = 5.5 mol dm^{-3}) forming the 490 nm band was 1.2×10^9 dm^3 mol^{-1} s^{-1}. Under these conditions, the band was observed to decay by first-order kinetics with $k = 2.3 \times 10^4$ s^{-1}.

The high concentration of $HClO_4$ is required to reach the saturation of the 490 nm band, and the entire radiation energy would not be absorbed by H_2O alone. Therefore, the yield of $^{\bullet}$OH radicals is reduced, since radiolysis of $HClO_4$ will not yield $^{\bullet}$OH radicals. On the basis of electron density distribution in H_2O and $HClO_4$, G(OH) is expected to be ~1.4. Under these conditions, the molar absorptivity of $(MTA)_2^{\bullet+}$ at 490 nm is estimated to be 21 700 dm^3 mol^{-1} cm^{-1}. This value of molar absorptivity is quite high compared to the molar absorptivity of the dimer radical cations of dialkyl sulfides.[12] At high the concentration of $HClO_4$ used in the present experiments, radiolysis of $HClO_4$ would result in the formation of ClO_2, ClO_3, and ClO_4 radicals.[25] ClO_3 radicals oxidize in nature with a potential between 1.6 and 2.4 V vs NHE.[25] $HClO_4^{\bullet+}$ is formed only when [$HClO_4$] > 10 mol dm^{-3}. The species generated from the radiolysis of $HClO_4$ can also contribute to the oxidation of MTA, and therefore, the actual value of molar absorptivity of $(MTA)_2^{\bullet+}$ should be lower. The actual concentration of $(MTA)_2^{\bullet+}$ formed from the reaction of the radiolysis products of $HClO_4$ with MTA is difficult to assess. Considering that the radiolysis of $NaClO_4$ could also produce products similar to those obtained from the radiolysis of $HClO_4$ ([$HClO_4$] < 10 mol dm^{-3}), we find in the pulse radiolysis of an aqueous solution of $NaClO_4$ (5 mol dm^{-3}) containing MTA (2×10^{-3} mol dm^{-3}) the absence of transient absorption at 490 nm, suggesting the absence of any contribution from the radiolysis products of $NaClO_4$ toward the formation of the solute dimer radical cation. This, however, does not prove that the contribution from the radiolysis products of $HClO_4$ in forming the dimer radical cation is negligible. Depending on the contribution of radiolysis products toward the formation of dimer radical cation, the molar absorptivity at 490 nm may be lowered.

The presence of the $-CH_3$ group has a marked effect on the concentration of H$^+$ required for the formation of the solute radical cation of substituted dialkyl sulfides, as shown by comparing the results of methyl thioacetic acid and methyl thiomethyl acetate. $^{\bullet}$OH radicals react with methyl thioacetic acid in pH 1−10 by forming α-thioradical (λ = 310 nm) without any transformation (Figure 1a). On the other hand, the reaction of $^{\bullet}$OH radicals with methyl thiomethyl acetate is pH-dependent (Figure 2). At pH 10, the transient absorption band observed immediately after the pulse (λ_{max} = 330 nm) is inferred to be due to the OH adduct, and it showed a little transformation at 470 nm. The band at 470 nm is due to the dimer radical cation. The transformation of the OH adduct to the dimer radical cation could be distinctly seen at pH 6 with $k = 1.2 \times 10^6$ s^{-1}. The saturation value was attained 3 μs after the pulse. The transformation becomes faster with decreasing pH. At pH 3, appreciable absorption at 470 nm is seen immediately after the pulse and attained saturation value 1 μs after the pulse. At pH 1, the transformation is complete within the pulse duration, and the only band observed was at 470 nm (Figure 2). $Cl_2^{\bullet-}$ was observed to react with methyl thiomethyl acetate with a bimolecular rate constant of 1.8×10^9 dm^3 mol^{-1} s^{-1}. Time-resolved studies showed the formation of a transient absorption band at 470 nm, unlike in methyl thioacetic acid, where $Cl_2^{\bullet-}$ reacts but time-resolved studies have not shown the transient absorption band of the dimer radical cation. As stated previously, the dimer radical cation of methyl thioacetic acid is not stable at pH 1 and is therefore not seen from the reaction with $Cl_2^{\bullet-}$, but with methyl thiomethyl acetate, the transient absorption band of dimer radical cation could be seen.

Dimer radical cations of 2,2′-thiodiethanoic acid are observed only in highly acidic conditions ([$HClO_4$] > 6 mol dm^{-3}), which should be due to the very high electron-withdrawing power of the $-COOH$ group (σ^* = 2.94). The electron density at sulfur is reduced appreciably, and $^{\bullet}$OH radicals require a very high concentration of H$^+$ for the formation of solute radical cations. The presence of a $-CH_2OH$ group with lower electron-withdrawing power (σ^* = 0.56) has required lower concentration of H$^+$ to form the solute dimer radical cations of 2,2′-thiodiethanol.[14e] The presence of electron-releasing $-CH_3$ groups increases the electron density at sulfur and lowers [H$^+$].

It may be possible that the OH adduct ($>S\therefore OH$), upon protonation, yield an intermediate complex $(>S\therefore OH_2)^+$ which, with a second sulfide molecule, is converted to a three-electron-bonded ($>S\therefore{}^+S<$) dimer radical cation from water elimination. The water may be easily removed in comparison to OH$^-$ elimination in the nonprotonated OH adduct. It is also possible that α-thioalkyl radicals, formed from H$^{\bullet}$ atom abstraction, may undergo protonation to yield the monomer radical cation (Scheme 1d) and then associate with a second sulfide molecule to form the dimer radical cation (Scheme 1e). If these processes were mainly responsible for the formation of the dimer radical cation, then very high concentration of H$^+$ would not have been required. These processes should also not depend on H$^+$ concentration, as observed for substituted alkyl sulfides having functional groups of different electron-withdrawing power. The contribution from such processes to form monomer/dimer radical cation is expected to be small.

Reaction with e_{aq}^-. The bimolecular rate constant for the reaction of e_{aq}^- with dimethyl sulfide is very low (2×10^7 dm^3 mol^{-1} s^{-1}) due to high electron density at sulfur.[20c] In the presence of electron-withdrawing functional groups, the electron density at sulfur would be reduced, and e_{aq}^- is expected to have a high rate constant value. The reaction of e_{aq}^- with MTA was studied by monitoring the decay of e_{aq}^- at 700 nm as a function of MTA concentration. The decay was observed to become faster upon addition of a low concentration of MTA. The bimolecular rate constant, determined from the linear plot of the pseudo-first-order rate (k_{obs}) versus solute concentration, gave a value of 5.7×10^9 dm^3 mol^{-1} s^{-1} and thus support the conclusion that the functional groups change the electron density at sulfur. The reaction of e_{aq}^- with the solute was also studied at pH 10.5, and the bimolecular rate constant was determined to be 4.5×10^9 dm^3 mol^{-1} s^{-1}.

Time-resolved studies showed very little absorption in 300−600 nm region, but absorption increased at $\lambda < 300$ nm. Time-resolved studies showed a transient absorption band at 310 nm with very low absorbance (∇OD ≤ 0.002). Due to very small absorption, kinetic studies could not be carried out, but the nature of the transient spectra at these pH's was different.

Reaction with Specific One-Electron Oxidants The reaction of specific one-electron oxidants have been carried out with MTA. The transient absorption band of $Cl_2^{\bullet-}$ ($E^0 = 2.03$ V), formed on the pulse radiolysis of aerated acidic (pH 1) aqueous solution of Cl^- (4×10^{-2} mol dm^{-3}, $\lambda = 345$ nm), was observed to decay faster in low concentrations of MTA ($(1-6) \times 10^{-5}$ mol dm^{-3}), indicating electron transfer from MTA to $Cl_2^{\bullet-}$

$$\mathrm{Cl_2^{\bullet-} + MTA \rightarrow MTA^{\bullet+} + 2\,Cl^-} \qquad (2)$$

The pseudo-first-order rate constant (k_{obs}) was found to increase linearly with MTA concentration, and the bimolecular rate constant, determined from the linear plot of k_{obs} versus the MTA concentration, was 2.8×10^9 dm^3 mol^{-1} s^{-1} . Time-resolved studies did not show the formation of any transient absorption band in the 370−550 nm region. These studies suggest that while electron transfer is taking place, the solute radical cation is decaying very fast, thus supporting the earlier results that solute dimer radical cations are observed only in highly acidic solutions. Pulse radiolysis studies have been carried out with other specific one-electron oxidants. The transient absorption band of $SO_4^{\bullet-}$ ($E^0 = 2.43$ V, $\lambda = 460$ nm), formed from the pulse radiolysis of an N_2-saturated solution of $S_2O_8^{2-}$ (4×10^{-2} mol dm^{-3}) containing *tert*-butyl alcohol (0.3 mol dm^{-3}), showed accelerated decay in low concentrations of MTA ($(1-6) \times 10^{-4}$ mol dm^{-3}), indicating electron transfer from MTA to $SO_4^{\bullet-}$. The bimolecular rate constant was determined to be 1.3×10^9 dm^3 mol^{-1} s^{-1}. In this case also, the time-resolved studies did not show any transient absorption in the 370−550 nm region after the complete decay of $SO_4^{\bullet-}$. These studies suggest that the solute radical/dimer radical cation is not stable under these conditions. The transient absorption band of $I_2^{\bullet-}$ ($E^0 = 1.02$ V), formed from the pulse radiolysis of an N_2O-saturated aqueous solution of I^- (4×10^{-2} mol dm^{-3}), was not affected inlow concentrations of MTA, suggesting the absence of electron transfer from MTA to $I_2^{\bullet-}$. Pulse radiolysis studies have also not shown the formation of any transient absorption band in the 450−550 nm region from the reaction of $N_3^{\bullet}$ ($E^0 = 1.35$ V) with MTA. These studies suggest that the oxidation potential for the formation of the solute radical cation is between 1.35 and 2.03 V.

The transient absorption band of $Br_2^{\bullet-}$ ($E^0 = 1.63$ V), formed from the pulse radiolysis of an N_2O-saturated aqueous solution of Br^- (4×10^{-2} mol dm^{-3}), showed accelerated decay in low concentrations of MTA, indicating electron transfer from MTA to $Br_2^{\bullet-}$. The decay of $Br_2^{\bullet-}$, in low concentrations of MTA was observed to depend on Br^- concentration. The decay of the transient band, formed from the pulse radiolysis of an aerated acidic ($[HClO_4] = 3.8$ mol dm^{-3}) aqueous solution of MTA (1×10^{-2} mol dm^{-3}), was also observed to become faster in low concentrations of Br^-, indicating electron transfer from Br^- to $MTA^{\bullet+}$. These studies suggest the existence of the following equilibrium:

$$\mathrm{Br_2^{\bullet-} + MTA \rightleftharpoons MTA^{\bullet+} + 2\,Br^-} \qquad (3)$$

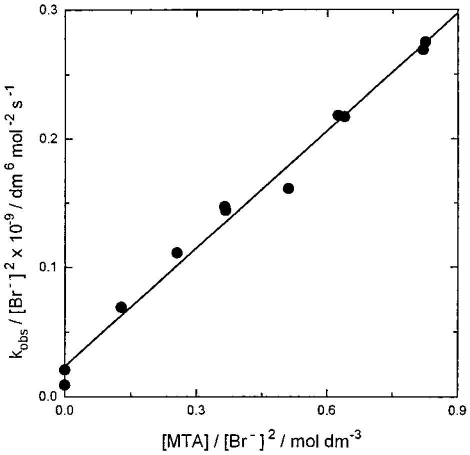


Figure 3. Plot of $k_{obs}/[Br^-]^2$ as a function of $[MTA]/[Br^-]^2$.

It has been mentioned previously that $MTA^{\bullet+}$ is not stable under these conditions and time-resolved studies do not show transient absorption in the 450−550 nm region. The optical absorption method could not be used to determine the equilibrium constant. However, it can be determined from the following kinetic equation:

$$k_{obs} = k_f[\mathrm{MTA}] + k_r[\mathrm{Br}^-]^2 \qquad (4)$$

$$\frac{k_{obs}}{[\mathrm{Br}^-]^2} = k_f\frac{[\mathrm{MTA}]}{[\mathrm{Br}^-]^2} + k_r \qquad (5)$$

The pseudo-first-order rate (k_{obs}) was determined from monitoring the decay of the transient band of $Br_2^{\bullet-}$ ($\lambda = 360$ nm) for various concentrations of Br^- ($(2-6) \times 10^{-2}$ mol dm^{-3}) and MTA ($(0.4-2.3) \times 10^{-3)}$ mol dm^{-3} under conditions such that $^{\bullet}$OH radicals would react initially with Br^- and the $Br_2^{\bullet-}$ formed would then react with MTA. The plot of $k_{obs}/[Br^-]^{2-}$ versus $[MTA]/[Br^-]^2$ gave a straight line (Figure 3) with a slope (k_f) of 0.304×10^9 and an intercept (k_r) of 0.0238×10^9. The equilibrium constant, K (k_f/k_r), was determined to be 12.8. It is related to the difference of the oxidation potential of two couples by the following relationship:

$$0.059 \log K = \Delta E^0 = E^0(\mathrm{Br_2^{\bullet-}/2Br^-}) - E^0(\mathrm{MTA/MTA^{\bullet+}}) \qquad (6)$$

Using the value of 1.63 V for $E^0(Br_2^{\bullet-}/2Br^-)$, we determined the oxidation potential for $E^0(MTA/MTA^{\bullet+})$ to be 1.56 ± 0.3 V vs NHE. Since the monomer radical cation ($MTA^{\bullet+}$) is in equilibrium with the dimer radical cation $(MTA)_2^{\bullet+}$, the redox potential value may apply to the latter or at least to both of the radical cations.

Decay Kinetics. The formation of the OH adduct (Scheme 1b) may be considered as an elementary step for the reaction of $^{\bullet}$OH radicals with the solute. The OH adduct of alkyl sulfides is known to absorb in the 350−360 nm region. The absence of such a band shows that the OH adduct is not stable and is immediately converted to α-thioradicals (Scheme 1c). Simple sulfur-centered monomer radical cations are highly unstable and absorb in 300 nm region. The monomer radical cations have a strong tendency to stabilize from coordination with another solute molecule to form a dimer radical cation (Scheme 1e). It has been shown that the decay kinetics of the dimer radical cations of dialkyl sulfides in neutral aqueous solutions is associated with the kinetics of the back reaction of equilibrium (k_{-4}) and with the deprotonation of the solute radical cation

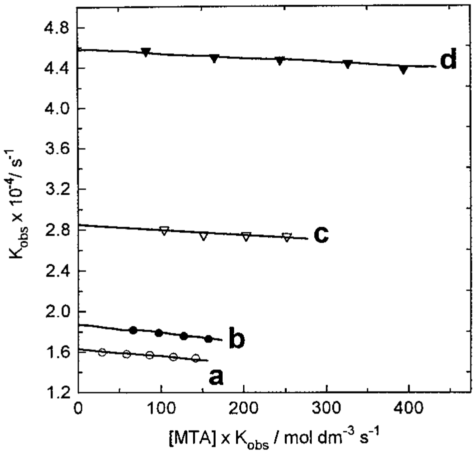


Figure 4. Plots of first-order rate (k_{obs}) vs k_{obs}[MTA] for the decay of 490 nm band when [$HClO_4$] = 6.4 (a), 5.5 (b), 3.7 (c), and 2.7 mol dm^{-3} (d).

(k_{-2}).[26] Using different proton acceptor concentrations to accelerate the deprotonation reaction of the radical cation, it has been shown from the plots of observed rate constants for the decay of dimer radical cation, k_{obs} versus k_{obs} × [solute], that the rate determining step would be deprotonation if plots have the same slope (k_4) but different intercepts (k_{-2} + deprotonation rate constant × [proton acceptor]). The decay by back-reaction of the equilibrium would give same intercept (k_{-4}) and different slopes $k_4/(k_{-2}$ + deprotonation rate constant × [proton acceptor]). This method of analysis for various absolute rate constants associated with the decay of dimer radical cations is not applicable in our case because a high concentration of $HClO_4$ was employed and k_{obs} as a function of different proton concentration could not be studied.[17b] However, plots of k_{obs} versus k_{obs}[solute] at different [$HClO_4$]'s gave straight lines (Figure 4) with the same slope (10 dm^3 mol^{-1}) and different intercepts. Therefore, deprotonation could be the rate-determining step, and the stability constant of the dimer radical cation would be equal to 10 dm^3 mol^{-1} at 25 °C. From the formation rate constant (k_4) value of 1.2 × 10^9 dm^3 mol^{-1} s^{-1}, we calculated k_{-4} to be 1.2 × 10^8 s^{-1}.

The intercept is found to depend on the H^+ concentration, which may be due to fact that at lower H^+ concentration, the OH adduct would decay to α-thio radicals and at high H^+ concentration, OH adduct would decay to the solute radical cation. It is also possible that at higher [$HClO_4$], α-thioradicals may combine with H^+ to form the solute radical cation. At low concentrations of $HClO_4$, α-thioradicals may subsequently decay to a stable end product. The intercept is represented by a complex function, which makes it difficult to determine the deprotonation rate constant.

It has been reported that the dimer radical cation of diisopropyl sulfide decays by the deprotonation mechanism with a stability constant of 540 dm^3 mol^{-1}, whereas the stability constant of the dimer radical cation of dimethyl sulfide is 2 × 10^5 dm^3 mol^{-1}.[26] A much lower value observed for dimer radical cations of MTA would explain their lack of stabilization. As the stability constant of the dimer radical cation decreases, the decay mechanism shifts from the back reaction of the equilibrium to the deprotonation mechanism.

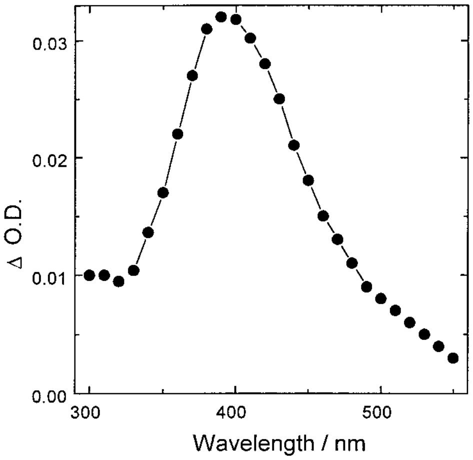
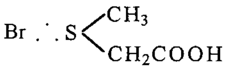


Figure 5. Transient absorption spectrum obtained from the pulse radiolysis of an N_2-saturated acidic (pH 1) aqueous solution of 1,2-dibromoethane (2 × 10^{-2} mol dm^{-3}) containing MTA (0.6 × 10^{-3} mol dm^{-3}).

SCHEME 4



Reaction with Br$^•$ Atoms. Br$^•$ atoms (E^0 = 1.9 V for the Br$^•$/Br$^-$ couple), formed from the pulse radiolysis of an N_2-saturated solution of 1,2-dibromo ethane (2 × 10^{-2} mol dm^{-3}, pH 1) are also one-electron oxidant and were observed to react with MTA to form a transient absorption band with λ_{max} = 390 nm (Figure 5). The band at 390 nm was observed to decay by first-order kinetics with k = 1 × 10^5 s^{-1}. The bimolecular rate constant for the reaction of Br$^•$ with MTA, as determined by formation kinetic studies at 390 nm, gave a value of 3.3 × 10^9 dm^3 mol^{-1} s^{-1}. The nature of the transient absorption spectrum (Figure 5) does not match with that of dimer radical cation (Figure 1b), and moreover, dimer radical cations are not expected to be stable at pH 1. The absorbance of the transient band at 390 nm remained independent of solute concentration (0.5−2 × 10^{-3} mol dm^{-3}) and, thus, indicate it to be due to a monomeric species. Therefore, it (Figure 5) could not be assigned to a dimer radical cation. Simple sulfur-centered monomer radical cations are highly unstable and absorb in the region of 300 nm.[12] An intramolecular radical cations formed from p-orbital overlap between oxidized sulfur and oxygen would have a four-member ring configuration and is expected to be unstable. Moreover, such a transient species was not observed from the reaction of $^•$OH radical and other specific one-electron oxidants. The absorption spectrum (Figure 5) is due to a transient species formed from the reaction of Br$^•$ with MTA, since Br$^•$ has no absorption in this region. The band is assigned to a three-electron-bonded Br adduct (Scheme 4). Three-electron-bonded species between halogen and alkyl sulfides are reported to absorb in this region.[12h] I$^-$ was also observed to react with MTA$^{•+}$ to form a transient absorption band with λ_{max} = 390 nm (see text) and is assigned to a similar three-electron-bonded I adduct. The three-electron-bonded adduct between the Cl$^•$ atom and MTA was not observed because Cl$^•$, formed from the reaction of $^•$OH radicals with Cl$^-$, has high reactivity with Cl$^-$ and is converted to $Cl_2^{•-}$. Cl$^-$ was not observed to undergo an electron-transfer reaction with MTA$^{•+}$ (see text), and therefore, a three-electron-bonded species between Cl$^•$ and MTA could not be observed.

Reaction of MTA$^{•+}$ with Inorganic Ions. The high oxidation potential value for a MTA/MTA$^{•+}$ couple (1.56 V) suggests that the radical cation would be able to undergo electron-transfer reactions with inorganic ions having low oxidation potential values. The decay of $(MTA)_2^{•+}$ formed from the pulse radiolysis of an aerated acidic ([$HClO_4$] = 5.5 mol dm^{-3}) aqueous solution of MTA (9.5 × 10^{-3} mol dm^{-3}) was observed to decay faster in low concentrations of I^- (1×10^{-4} mol dm^{-3}), indicating electron transfer from I^- to $MTA^{\bullet+}$. Simultaneously, time-resolved studies showed the formation of the transient absorption band at 390 nm with a rate constant of 6×10^9 dm^3 mol^{-1} s^{-1}. The bimolecular rate constant determined from the decay at 490 nm for different concentrations of I^- ($1-8 \times 10^{-5}$ mol dm^{-3}) gave a value of 4.6×10^9 dm^3 mol^{-1} s^{-1}, close to that obtained from the growth of the 390 nm band. The band is assigned to the three-electron-bonded adduct between the $I^\bullet$ atom and MTA and not to $I_2^{\bullet-}$ because the near-infrared absorption band of $I_2^{\bullet-}$ at 740 nm was not seen. Similarly, the transient absorption band of $(MTA)_2^{\bullet+}$ was observed to decay faster in low concentrations of Br^-, and the bimolecular rate constant was determined to be 3.1×10^8 dm^3 mol^{-1} s^{-1}. The decay of the transient absorption band of the dimer radical cation at 490 nm was not affected by the addition of low concentrations of Cl^- (4×10^{-5} mol dm^{-3}), indicating the absence of electron transfer between $(MTA)_2^{\bullet+}$ and Cl^- and thus supporting the lower oxidation potential value for the $MTA/MTA^{\bullet+}$ couple (1.56 V) than for the $Cl^\bullet/Cl^-$ couple (2.4 V) and the absence of a three-electron-bonded adduct between Cl and MTA.

Redox Nature of the Transient Species. The redox nature of the transient species formed from the reaction of $^\bullet$OH radicals in a highly acidic solution of MTA is established (cationic), and its oxidation potential was determined to be 1.56 V. The oxidant methyl viologen (MV^{2+}) and reductant N,N,N′,N′-tetramethylene-*p*-phenylenediamine (TMPD) were used to determine the nature of α-thioradical formed in a neutral solution of MTA. The reduced form ($MV^{\bullet+}$) of the oxidant has two well-defined absorption bands at 395 and 605 nm. The oxidized form ($TMPD^{\bullet+}$) has absorption band at 610 nm. Pulse radiolysis of an N_2O-saturated neutral aqueous solution of MTA (2×10^{-3} mol dm^{-3}) in low concentrations (4×10^{-5} mol dm^{-3}) of either MV^{2+} or TMPD failed to give transient absorption at the respective λ_{max}, indicating that the α-thio radical is unable to undergo electron-transfer reaction with MV^{2+} and TMPD. The transient species formed from the reaction of e_{aq}^- with MTA also failed to give the transient absorption due to $MV^{\bullet+}$, indicating that either the reduction potential of radical anion is low (less than -0.46 V) or the radical anion has undergone fast protonation to form a neutral H adduct which is unable to transfer electrons to $MV^{2+}.^{\bullet}$

Conclusions

$^\bullet$OH radicals are able to undergo electron-transfer reaction with methyl thioacetic acid under high acid concentrations to form dimer radical cations. The decay of the dimer radical cation is controlled by the deprotonation of the radical cation. The dimer radical cation is a strong one-electron oxidant ($E^0 = 1.56$ V). The substituent group is observed to play an important role in the nature of $^\bullet$OH radical reaction and the concentration of H^+ required for the formation of solute radical cation.

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