Structure–reactivity studies on $^\bullet$OH radical reaction with substituted dialkyl sulfides

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Received (in Cambridge) 1st February 1999, Accepted 12th May 1999

The results of the reaction of an $^\bullet$OH radical with a number of functionalized organic sulfides reported here demonstrate that the pH, the nature of the functional group and the chain length affect the nature of the $^\bullet$OH radical reaction with sulfides. The transient absorption spectrum (λ_{max} = 295 nm), formed on reaction of $^\bullet$H atoms and $^\bullet$OH radicals with an aqueous solution of 2-(methylthio)ethanol and 2-(ethylthio)ethanol is assigned to the α-thio radical. It decayed by second order kinetics with $2k = 5.2 \times 10^9$ dm^3 mol^{-1} s^{-1} and was quenched by oxygen. The transient absorption spectra (λ_{max} = 480 and 500 nm respectively), obtained on reaction with $^\bullet$OH radicals (pH = 1), are assigned to a sulfur centered dimer radical cation. The variation of the transient absorbance with pH showed an inflection point at pH = 2.1. The reaction of $^\bullet$OH radicals (pH = 6) with 2,2′-thiodiethanoyl chloride showed the formation of α-thio radicals (λ_{max} = 300 nm) and an OH-adduct (λ = 350–380 nm), whereas in acidic solutions, the transient spectrum (λ_{max} = 340 nm, τ = 0.8 μs) is assigned to an intra-molecular radical cation with a 4-membered ring configuration. The transient species (λ_{max} = 370 nm, τ = 17 μs) formed on reaction of $^\bullet$OH radicals with a 3,3′-thiodipropionyl chloride is assigned to a 5-membered intra-molecular radical cation and remained independent of pH. The OH-adduct (λ_{max} = 350 nm, pH = 11) of 3,3′-thiodipropionamide is observed to undergo transformation to an intra-molecular radical cation (λ_{max} = 370 nm). The transformation is not observed in acidic solutions and only an intra-molecular radical cation (λ_{max} = 370 nm) is observed immediately after the pulse. The contribution of α-thio radicals of 2,2′-thiodiethanamide decreased with pH, and in neutral solutions $^\bullet$OH radicals are observed to react mainly by OH-adduct formation whereas in acidic solutions (pH = 1), as intra-molecular radical cation (λ_{max} = 335 nm) with a 4-membered ring configuration is inferred to be the transient species.

Introduction

The reaction of the hydroxyl radical ($^\bullet$OH) in aqueous solutions of dialkyl sulfides (R_2S) and their substituted derivatives has been the subject of recent interest.[1–4] These studies have gained in importance as sulfur centered radical species are considered to be possible intermediates in redox reactions of biomolecules.[5–7] These studies are also important in understanding the physico-chemical processes taking place in biological systems as radicals and radical ions derived from sulfur containing compounds play an important role in the chemistry of biological systems.[8]

Hydroxyl radicals and specific one-electron oxidants, on reaction with organic sulfur compounds produce sulfur centered radical cations either directly or *via* a complex sequence of reactions involving an OH-adduct, an α-thio radical and monomer radical cations.[3,9,10] The OH-adduct and α-thio radicals absorb in the 345–360 and 290–310 nm regions respectively. Sulfur centered monomer radical cations are highly unstable and absorb at 300 nm. Oxidized sulfur has a high tendency to stabilize itself by coordinating with the free p-electron pair of a second sulfur or other hetero atom such as O, P, N or a halogen, both inter- and intra-molecularly.[1–3,11,12] Such interactions are represented by a 2c–3e bonded species containing two bonding σ electrons and one antibonding σ* electron. The nature of the $^\bullet$OH radical reaction with substituted alkyl sulfides is observed to depend on the nature of the substituents, the pH of the solution and the chain length between sulfur and the substituent group. Sulfur in dialkyl sulfides has a high electron density due to the presence of two lone pairs of electrons and electron releasing alkyl groups. As the $^\bullet$OH radical is a strong electrophile, it would immediately remove an electron from the dialkyl sulfide and the intermediate OH-adduct would be highly unstable. In the presence of electron withdrawing substituents, the electron density at sulfur would decrease and the OH-adduct and α-thio radicals may have long enough life times to be observed as the intermediates. With this objective, the nature of the $^\bullet$OH radical reaction with substituted alkyl sulfides has been investigated using pulse radiolysis and it is shown that the reaction is influenced by the substituents, the pH and the chain length between sulfur and the substituted group.

Experimental

Synthesis of thiodialkanoyl chlorides

The dry acids (2,2′-thiodiethanoic acid and 3,3′-thiodipropionic acid) were converted to thiodialkanoyl chlorides by treating with an excess of thionyl chloride (reaction (1)) and

$$\mathrm{R(COOH)_2 + SOCl_2 \longrightarrow R(COCl)_2 + SO_2 + HCl} \quad (1)$$

$$\mathrm{R = S(CH_2)_2;\ S(CH_2CH_2)_2}$$

refluxing the mixture for 80 min.[13] The excess of thionyl chloride was removed on distillation at 78 °C.

Synthesis of thiodialkanamides

Concentrated ammonia solution was added to thiodialkanoyl chlorides at 0 °C. The reaction mixture was heated to dryness. The thiodialkanamide formed (reaction (2)) was recrystallised

$$\mathrm{R(COCl)_2 + 2\,NH_3 \longrightarrow R(CONH_2)_2 + 2\,HCl} \quad (2)$$

from ethanol. The purity of the compounds was determined with NMR and IR analysis.

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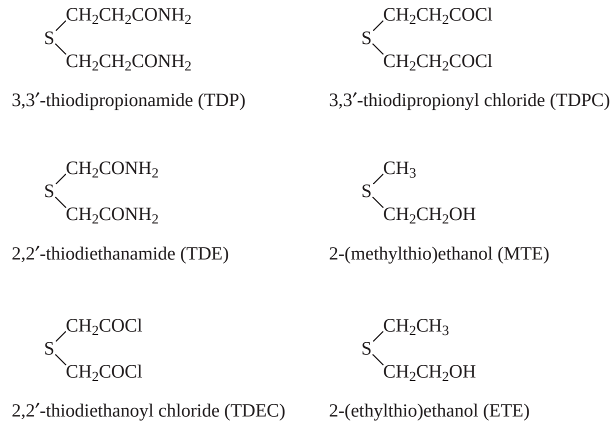
2-(Methylthio)ethanol (MTE) and 2-(ethylthio)ethanol (ETE) obtained from Aldrich Chemicals were of high purity and were used without further purification. All other chemicals were also of high purity. The solutions in deionized 'nanopure' water were prepared in 1×10^{-3} mol dm^{-3} phosphate buffer using Na_2HPO_4 and KH_2PO_4. Freshly prepared solutions were used for each experiment. The pH was adjusted with NaOH–$HClO_4$.

Pulse radiolysis experiments were carried out with high energy electron pulses (7 MeV, 50 ns) obtained from a linear electron accelerator whose details are described elsewhere.[14] The dose delivered per pulse was determined by the use of an aerated aqueous solution of KSCN (1×10^{-2} mol dm^{-3}) and it was close to 12–15 Gy. All other experimental details are described elsewhere.[4] The transient absorption as a function of time was recorded on a storage oscilloscope (100 MHz) interfaced to a computer for kinetic analysis.[15] The transient species were monitored using a 450 W pulsed xenon arc lamp, monochromator (Kratos, GM-252) and Hamamatsu R-955 photomultiplier as the detector. The rate constant values were taken from those kinetic analyses for which a very good correlation was observed between experimental and calculated results. The rate constant values are the average of three experiments and the variation was within 15%. The structures of various compounds used in this study are shown in Scheme 1.


3,3′-thiodipropionamide (TDP)
3,3′-thiodipropionyl chloride (TDPC)
2,2′-thiodiethanamide (TDE)
2-(methylthio)ethanol (MTE)
2,2′-thiodiethanoyl chloride (TDEC)
2-(ethylthio)ethanol (ETE)

Scheme 1

Radiolysis of N_2-saturated neutral aqueous solution leads to the formation of three highly reactive species ($^{\bullet}H$, $^{\bullet}OH$, e_{aq}^-) in addition to the formation of less reactive or inert molecular products (H_2, H_2O_2).[16] The reaction of $^{\bullet}OH$ radicals in neutral

$$H_2O \longrightarrow {}^{\bullet}H, {}^{\bullet}OH, e_{aq}^-, H_3O^+, H_2, H_2O_2 \tag{3}$$

aqueous solutions was carried out under N_2O-saturated conditions where e_{aq}^- are quantitatively converted to $^{\bullet}OH$ radicals (reaction (4)). In acidic solutions, the reaction of $^{\bullet}OH$ radicals

$$N_2O + e_{aq}^- \longrightarrow {}^{\bullet}OH + OH^- + N_2 \tag{4}$$

was carried out in aerated solutions to scavenge $^{\bullet}H$ atoms (reaction (5)) and e_{aq}^- are converted to $^{\bullet}H$ atoms (reaction (6)).

$$^{\bullet}H + O_2 \longrightarrow HO_2^{\bullet} \tag{5}$$

$$e_{aq}^- + H^+ \longrightarrow H^{\bullet} + H_2O \tag{6}$$

The reaction of $^{\bullet}H$ atoms was carried out at pH = 1 in the presence of 0.3 mol dm^{-3} *tert*-butyl alcohol to scavenge $^{\bullet}OH$ radicals.

$$(CH_3)_3COH + {}^{\bullet}OH \longrightarrow {}^{\bullet}CH_2(CH_3)_2COH + H_2O \tag{7}$$

The reaction with a specific one-electron oxidant ($Br^{\bullet}$) was carried out under conditions such that the primary radiolytic species of water radiolysis do not react with the solute initially and only the specific one-electron oxidant reacts with the solute. $Br^{\bullet}$ atoms were generated on pulse radiolysis of a N_2O-saturated aqueous solution of 1,2-dibromoethane (2×10^{-2} mol dm^{-3}) *via* reactions (8) and (9).

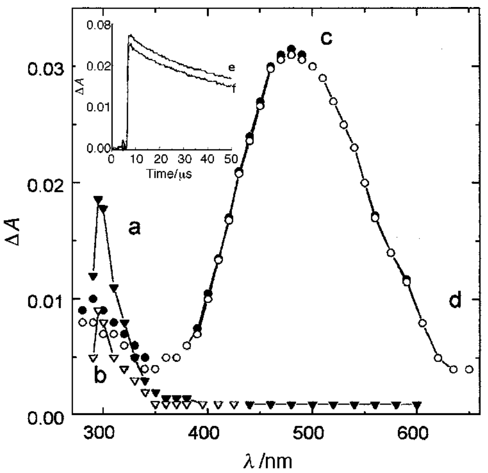


Fig. 1 Transient absorption spectrum obtained on pulse radiolysis of MTE (4.6×10^{-3} mol dm^{-3}) (a) N_2O-saturated, pH = 6; (b) N_2-saturated, pH = 1, *tert*-butyl alcohol = 0.3 mol dm^{-3}; (c) N_2-saturated, pH = 1 and (d) aerated (pH = 1). Inset shows absorption–time profiles at 480 nm in (e) N_2 and (f) aerated solutions.

$$CH_2BrCH_2Br + {}^{\bullet}H/{}^{\bullet}OH \longrightarrow CH_2Br^{\bullet}CHBr + H_2/H_2O \tag{8}$$

$$CH_2Br^{\bullet}CHBr \longrightarrow CH_2{=}CHBr + Br^{\bullet} \tag{9}$$

The rate constant for the reaction of radiolytic species with the solute was determined by monitoring the growth of the transient absorption at λ_{max} as a function of solute concentration (2–8) $\times 10^{-4}$ mol dm^{-3} and the pseudo-first order rate (k_{obs}) was observed to increase with solute concentration. The bimolecular rate constant was determined from the linear plot of k_{obs} *vs.* solute concentration. The molar absorptivity of the transient species was determined under conditions such that the radiolytic species had completely reacted with the solute and only one pathway was available for the reaction.

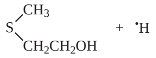
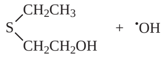
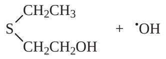
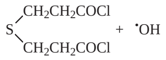
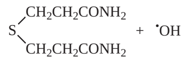
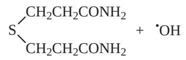
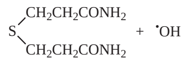
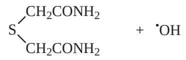
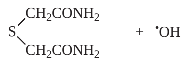
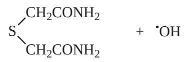
Results

The ground state optical absorption spectra of various substituted sulfides in aqueous solutions, used in the present studies, showed absorption maxima at $\lambda < 280$ nm with a very small absorption at $\lambda > 300$ nm and remained the same at pH = 1–11. The absorption spectra of 2,2′-thiodiethanoyl chloride and 3,3′-thiodipropinoyl chloride were different from those of the corresponding acids, indicating that these acyl chlorides are not hydrolysed under the present experimental conditions, within the experimental time. These results suggest that pulse radiolysis investigations with optical absorption as the detection technique can be employed without any correction for the ground state absorption in the pH 1–11 region.

2-(Methylthio)ethanol

Fig. 1a shows the transient optical absorption spectrum obtained on pulse radiolysis of an N_2O-saturated neutral aqueous solution of MTE (4.6×10^{-3} mol dm^{-3}), which exhibits an absorption band with $\lambda_{max} = 295$ nm. The kinetic parameters of the transient absorption band are shown in Table 1. The band was observed to decay by second order kinetics with $2k = 5.2 \times 10^9$ dm^3 mol^{-1} s^{-1}. Fig. 1b shows the transient absorption spectrum obtained on pulse radiolysis of an N_2-saturated acidic (pH = 1) aqueous solution of MTE (4.6×10^{-3} mol dm^{-3}, *tert*-butyl alcohol = 0.3 mol dm^{-3}), which also showed an

Table 1 Kinetic and spectral parameters of the transient formed on reaction of ${}^{\bullet}OH$ radicals with different substituted sulfides

No.	Reaction	pH	λ_{max}/ nm	ε_{max}/dm^3 mol^{-1} cm^{-1}	k_f/dm^3 mol^{-1} s^{-1}	k_d/dm^3 mol^{-1} s^{-1}
1	 $CH_3SCH_2CH_2OH + {}^{\bullet}OH$	6	295	1.8×10^3	5×10^9	5.2×10^{9}[a]
2	 $CH_3SCH_2CH_2OH + {}^{\bullet}H$	1	295	1.7×10^3	—	—
3	 $CH_3SCH_2CH_2OH + {}^{\bullet}OH$	1	480	6.6×10^3	3.2×10^9	1×10^{4}[b]
4	 $CH_3CH_2SCH_2CH_2OH + {}^{\bullet}OH$	6	295	1.7×10^3	4.5×10^9	5.1×10^{9}[a]
5	 $CH_3CH_2SCH_2CH_2OH + {}^{\bullet}OH$	1	500	6.8×10^3	3.8×10^9	3.7×10^{4}[b]
6	 $S(CH_2COCl)_2 + {}^{\bullet}OH$	6	300 350–380	— —	6.5×10^9	6.2×10^{6}[c]
7	 $S(CH_2COCl)_2 + {}^{\bullet}OH$	1	340	5.1×10^3	1.0×10^{10}	1.2×10^{6}[b]
8	 $S(CH_2CH_2COCl)_2 + {}^{\bullet}OH$	6	370	3.4×10^3	2.4×10^9	4.9×10^{4}[b]
9	 $S(CH_2CH_2CONH_2)_2 + {}^{\bullet}OH$	11	350 370	1.5×10^3 —	7.3×10^9	1.4×10^{5}[b] 3.1×10^{4}[b]
10	 $S(CH_2CH_2CONH_2)_2 + {}^{\bullet}OH$	5.5	370	—	—	4.5×10^{4}[b]
11	 $S(CH_2CH_2CONH_2)_2 + {}^{\bullet}OH$	1	370	3.6×10^3	6.1×10^9	3.7×10^{4}[b]
12	 $S(CH_2CONH_2)_2 + {}^{\bullet}OH$	11	310 340	— 1.7×10^3	—	2.3×10^{4}[b] 2.3×10^{5}[b]
13	 $S(CH_2CONH_2)_2 + {}^{\bullet}OH$	6	345 310–330	—	—	3.5×10^{5}[b] 8.2×10^{3}[b]
14	 $S(CH_2CONH_2)_2 + {}^{\bullet}OH$	1	335	—	2.4×10^9	2.7×10^{5}[b]

[a] Second order decay ($2k$). [b] First order decay (s^{-1}). [c] Second order decay ($2k/\varepsilon l$)/s^{-1}.

absorption band at 295 nm. Pulse radiolysis of an N_2-saturated acidic (pH = 1) aqueous solution of MTE (4.6×10^{-3} mol dm^{-3}) showed an absorption band with λ_{max} = 480 nm and a small shoulder in the 290–310 nm region (Fig. 1c). The nature of the spectrum and decay kinetics remained the same in an aerated solution (Fig. 1d and inset of Fig. 1) indicating that the spectrum is due to the reaction of ${}^{\bullet}OH$ radicals and the contributions of the ${}^{\bullet}H$ atom is negligible. The variation of absorbance at 480 nm as a function of pH showed an inflection point at pH = 2.1. The yield and the life-time of the transient absorption band were observed to increase with solute concentration.

2-(Ethylthio)ethanol

Fig. 2a shows the transient absorption spectrum obtained on pulse radiolysis of N_2O-saturated neutral aqueous solution of ETE (3.8×10^{-3} mol dm^{-3}), which exhibits an absorption band at 295 nm. At pH = 1, the transient absorption spectrum showed a peak at 500 nm with a small shoulder in the 290–310 nm region (Fig. 2b). The kinetic parameters are shown in Table 1. The variation of absorbance at 500 nm, in aerated solutions, showed an inflection point at pH = 2.1 (inset of Fig. 2). The variation of the absorbance (500 nm) and decay rate with ETE concentration are shown in Fig. 3 and the saturation value was attained when the solute concentration was in the range of (6–7) × 10^{-3} mol dm^{-3}.

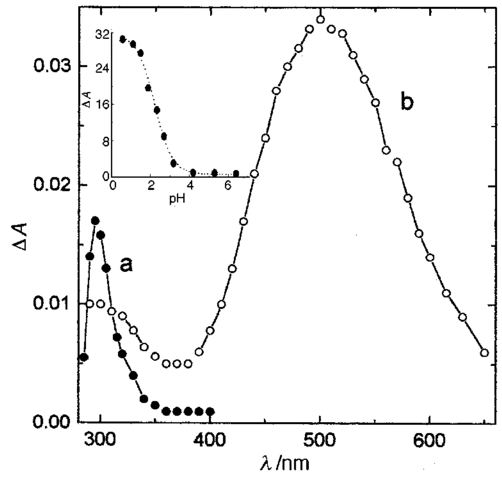


Fig. 2 Transient absorption spectrum obtained on pulse radiolysis of an aqueous solution of ETE (3.8×10^{-3} mol dm^{-3}) (a) N_2O-saturated at pH = 6 and (b) N_2-saturated (pH = 1). Inset shows variation of absorbance at 500 nm as a function of pH.

2,2′-Thiodiethanoyl chloride

Fig. 4a exhibits the transient absorption spectrum obtained on pulse radiolysis of an N_2O-saturated neutral aqueous solution

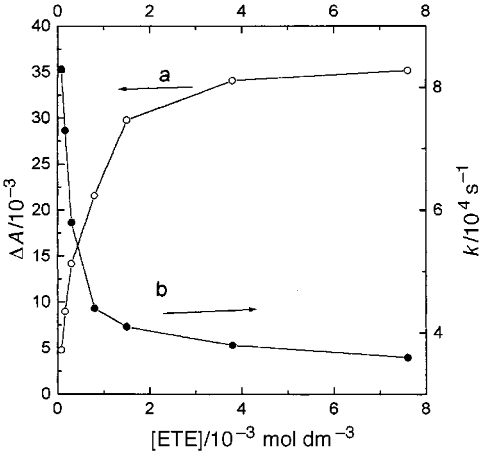


Fig. 3 Variation of (a) absorbance and (b) first order rate constant at 500 nm as a function of ETE concentration, formed on pulse radiolysis of aerated aqueous solution of ETE at pH = 1. Dose = 16 Gy per pulse.

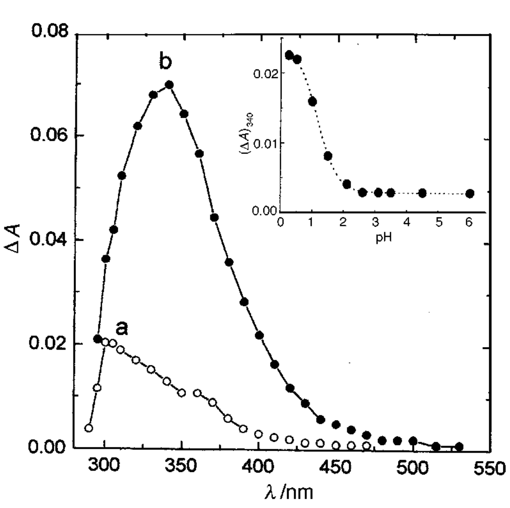


Fig. 4 Transient absorption spectra obtained on pulse radiolysis of an aqueous solution of TDEC (2.6 × 10^{-3} mol dm^{-3}) (a) N_2O-saturated at pH = 6 and (b) N_2-saturated (pH = 1). Inset shows variation of absorbance at 340 nm as a function of pH.

of TDEC (2.6 × 10^{-3} mol dm^{-3}) with an absorption band at 300 nm and a small shoulder in the 350–380 nm region. The transient absorbance at 300 nm remained independent of solute concentration in the (1–5) × 10^{-3} mol dm^{-3} region and decayed by second order kinetics with $2k/\varepsilon l = 6.2 \times 10^6$ s^{-1}. The decay kinetics in the 350–380 nm region could not be studied accurately due to the very small size of the signal. As the pH of the solution was decreased, the transient absorption was observed to increase. Fig. 4b (pH = 1) shows the transient absorption spectrum having an absorption band at 340 nm, decaying by first order kinetics with $k = 1.2 \times 10^6$ s^{-1}. The absorbance at 340 nm remained independent of solute concentration, suggesting it to be due to a monomeric species. The variation of absorbance (340 nm) as a function of pH gave an inflection point at pH = 1.2 (inset of Fig. 4). All other kinetic parameters are shown in Table 1.

3,3′-Thiodipropionyl chloride

Fig. 5a shows the transient absorption spectrum obtained on pulse radiolysis of an N_2O-saturated neutral aqueous solution of TDPC (2.6 × 10^{-3} mol dm^{-3}), which exhibits an absorption band with $\lambda_{max} = 370$ nm. The kinetic parameters of this band are shown in Table 1. The nature of the transient absorption spectrum remained independent of pH (1–11) and of solute concentration (inset of Fig. 5).

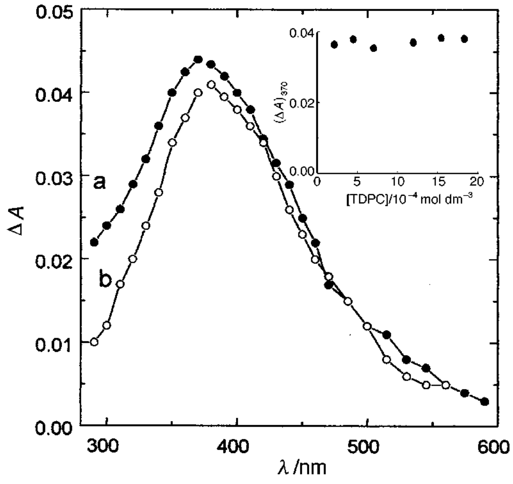


Fig. 5 (a) Transient absorption spectrum obtained on pulse radiolysis of an N_2O-saturated aqueous solution of TDPC (2.6 × 10^{-3} mol dm^{-3}) at pH = 6. Dose = 58 Gy per pulse. (b) Transient absorption spectrum obtained on pulse radiolysis of aerated acidic (pH = 1) solution of 1,2-dibromoethane (4 × 10^{-2} mol dm^{-3}) containing TDPC (1 × 10^{-3} mol dm^{-3}). Dose = 18 Gy. Inset shows variation of absorbance at 370 nm as a function of solute concentration. Dose = 45 Gy per pulse.

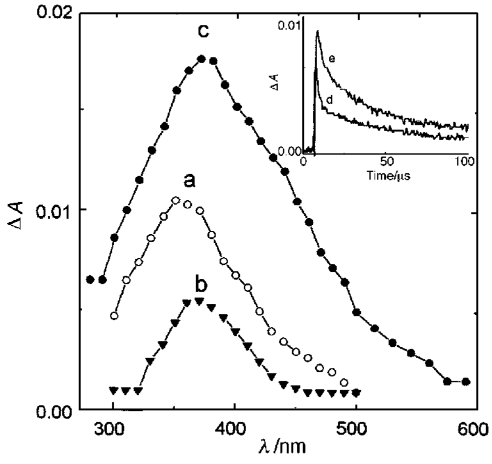


Fig. 6 Transient absorption spectra obtained on pulse radiolysis of an N_2O-saturated aqueous solution of TDP (1 × 10^{-3} mol dm^{-3}, pH = 11) (a) 1 μs and (b) 7 μs after the pulse and (c) at pH = 6. Inset shows absorption–time profiles at (d) 350 nm (pH 11) and (e) 370 nm (pH 6).

3,3′-Thiodipropionamide

Fig. 6a shows the transient absorption spectrum obtained on pulse radiolysis of an N_2O-saturated basic (pH = 11) aqueous solution of TDP (1 × 10^{-3} mol dm^{-3}), which exhibits an absorption band with $\lambda_{max} = 350$ nm. The analysis of the absorption–time profile (Fig. 6d) revealed that the transient absorption has two different types of decay. The initial portion decayed by first order kinetics with $k = 1.4 \times 10^5$ s^{-1} and the latter portion with $k = 3.1 \times 10^4$ s^{-1}. Time-resolved studies showed the formation of another transient absorption band with $\lambda_{max} = 370$ nm (Fig. 6b). The absorbance of this band remained independent of solute concentration and the rate constant was determined to be equal to 7.3 × 10^9 dm^3 mol^{-1} s^{-1}. Fig. 6c shows the transient absorption spectrum obtained on pulse radiolysis of N_2O-saturated aqueous solution of TDP (1 × 10^{-3} mol dm^{-3}, pH = 5.5). The absorption band at 370 nm decayed by first order kinetics with $k = 4.5 \times 10^4$ s^{-1}. Pulse radiolysis of N_2-saturated aqueous solution of TDP (1 × 10^{-3} mol dm^{-3}) at pH = 1, also showed one transient absorption band at 370 nm which decayed by first order kinetics with $k = 3.7 \times 10^4$ s^{-1}. The absorbance at 370 nm remained independent of solute concentration (0.6–4) × 10^{-3} mol dm^{-3}. The molar absorptivity

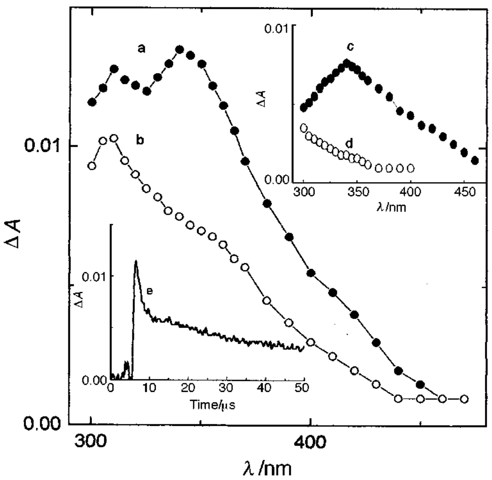


Fig. 7 Transient optical absorption spectra obtained on pulse radiolysis of an N_2O-saturated aqueous solution of 2,2′-thiodiethanoamide (1.4×10^{-3} mol dm^3, pH = 11) (a) 1.5 μs and (b) 6 μs after the pulse. Transient absorption spectra under aerated conditions (c) 1.5 μs and (d) 6 μs after the pulse and (e) absorption–time profile at 350 nm.

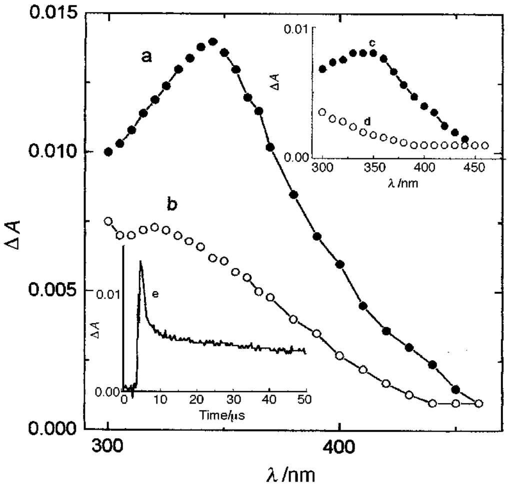


Fig. 8 Transient absorption spectrum obtained on pulse radiolysis of an N_2O-saturated aqueous solution of 2,2′-thiodiethanoamide (1.4×10^{-3} mol dm^3, pH = 6) (a) 1.5 μs and (b) 6 μs after the pulse and transient absorption spectra under aerated conditions (c) 1.5 μs and (d) 6 μs after the pulse and (e) absorption–time profile at 345 nm.

was determined to be 3.6×10^3 dm^3 mol^{-1} cm^{-1} and other kinetic parameters are given in Table 1.

2,2′-Thiodiethanamide

Fig. 7a shows the transient absorption spectrum obtained on pulse radiolysis of an N_2O-saturated aqueous solution of TDE (1×10^{-3} mol dm^{-3}, pH = 11), which exhibits absorption bands at 310 and 340 nm. The time resolved studies revealed that the absorption at 340 nm decays faster ($k = 2.3 \times 10^5$ s^{-1}) than that at 310 nm ($k = 2.3 \times 10^4$ s^{-1}) and only one band (310 nm) with a small shoulder in the 330–370 nm region was observed 5 μs after the pulse (Fig. 7b). The absorption–time profile also suggests the presence of two types of species (Fig. 7e). The transient absorption spectra in aerated solution showed the presence of only one band at 340 nm (Fig. 7c). The transient absorption spectrum of TDE under N_2O-saturated conditions at pH = 6, showed only one band at 345 nm (Fig. 8a) with some absorption in the 310–330 nm region (Fig. 8b) which could be seen 5 μs after the pulse. The spectrum in aerated conditions (Fig. 8c) showed only one band at 345 nm. The transient absorption spectrum at pH = 1, showed only one band at 335 nm (Fig. 9a) which decayed by first order kinetics with $k = 2.7 \times 10^5$ s^{-1} (Fig. 9c). The variation of absorbance at 335 nm showed an inflection point at pH = 1.4 (Fig. 9d).

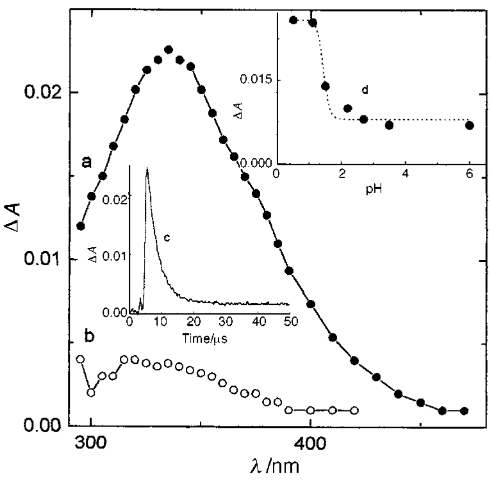
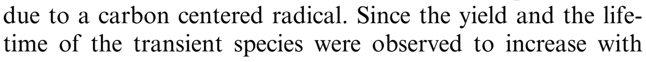


Fig. 9 Transient absorption spectrum obtained on pulse radiolysis of aerated aqueous solution of 2,2′-thiodiethanoamide (1.4×10^{-3} mol dm^3, pH = 1) (a) 1.5 μs and (b) 12 μs after the pulse. Inset shows (c) the absorption–time profile at 335 nm and (d) the variation of absorbance (335 nm) as a function of pH.

Discussion

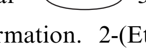
Reactions with MTE and ETE

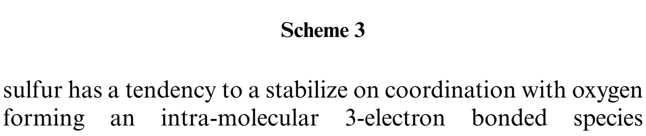
The nature of the transient spectrum, obtained on reaction of $^\bullet$OH radicals (pH = 6) and $^\bullet$H atoms with MTE, and its decay and formation kinetics, were similar for both MTE and ETE (Fig. 1). The band was completely quenched by oxygen and is therefore assigned to a carbon centered α-thio radical formed on $^\bullet$H atom abstraction by $^\bullet$H/$^\bullet$OH (reaction (10), Scheme 2).



$$\mathrm{S}(\mathrm{CH_3})\mathrm{CH_2CH_2OH} + {}^\bullet\mathrm{H}/{}^\bullet\mathrm{OH} \longrightarrow \mathrm{S}(\mathrm{CH_3}){}^\bullet\mathrm{CHCH_2OH} + \mathrm{H_2/H_2O} \quad (10)$$

Scheme 2

In analogy with these studies, the transient absorption band formed on reaction of $^\bullet$OH radicals with ETE at neutral pH is also assigned to α-thio radicals. In acidic solutions, the nature of the spectrum and the decay kinetics observed on reaction of $^\bullet$OH radicals with MTE and ETE remained the same in N_2 and aerated conditions indicating that the transient species is not due to a carbon centered radical. Since the yield and the lifetime of the transient species were observed to increase with solute concentration (Fig. 3), it is probably a dimer radical cation (reaction (11), Scheme 3). It is also known that oxidized sulfur has a tendency to a stabilize on coordination with oxygen forming an intra-molecular 3-electron bonded species ().[1] The large difference in the electronegativity of S and O (1.06 eV) and the relatively unstable nature of a 4 membered ring for the intra-molecular  3-electron bonded species, may prevent its formation. 2-(Ethylthio)-ethanol is similar in structure to MTE and pulse radiolysis



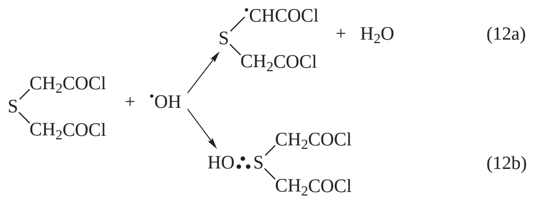
$$\mathrm{S}(\mathrm{CH_3})\mathrm{CH_2CH_2OH} + {}^\bullet\mathrm{OH} + \mathrm{H^+} \longrightarrow {}^{\bullet+}\mathrm{S}(\mathrm{CH_3})\mathrm{CH_2CH_2OH} \xrightleftharpoons{\mathrm{S}(\mathrm{CH_3})\mathrm{CH_2CH_2OH}} \left[\mathrm{S}(\mathrm{CH_3})\mathrm{CH_2CH_2OH}\right]_2^{\bullet+} \quad (11)$$

Scheme 3

studies at pH = 1 also showed similar results and thus support the reaction mechanism. In case of ETE, the transient absorption band of the dimer radical cation (500 nm) showed a red shift, which is due to the presence of an additional electron releasing methyl group. The life-time of the dimer radical cation of ETE (27 µs) was shorter than that of MTE (100 µs), which may be due to the bulkier ethyl group present in the molecule. The reaction of the $^{\bullet}$Br radical, which is a specific one-electron oxidant (E^{o} for $Br^{\bullet}/Br^{-}$ couple = 1.9 V), with MTE and ETE also produced transient absorption spectra similar to those observed on reaction of $^{\bullet}$OH radicals with MTE and ETE at pH = 1, thus supporting the assignment of the transient absorption band to cationic species. The OH-adduct formed in an acidic medium may be too short lived to detect under our experimental conditions.

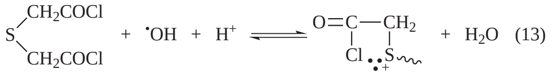
Reactions with TDEC and TDPC

As mentioned earlier, the α-thio radicals formed on abstraction of $^{\bullet}$H atoms by $^{\bullet}$H/$^{\bullet}$OH radicals from dialkyl sulfides absorb in the 290–310 nm region. Therefore, the transient absorption band at 300 nm (Fig. 4a) formed on reaction of $^{\bullet}$OH radicals with TDEC at pH = 6 is assigned to α-thio radicals. The small shoulder in the 350–380 nm region may be due to the OH-adduct as the OH-adducts of dialkyl sulfides absorb in the 350–370 nm region. The reaction of $^{\bullet}$OH with TDEC is represented by Scheme 4.



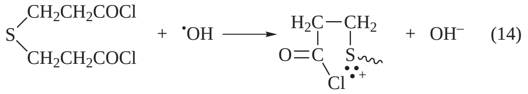
Scheme 4

The contribution of individual processes could not be determined. The absorbance of the transient absorption band at 340 nm at pH = 1 remained independent of solute concentration, suggesting the formation of a monomeric species. Simple sulfur centered monomer radical cations of dialkyl sulfides are very unstable and are known to stabilize on coordination with another heteroatom. Therefore, the transient absorption could not be due to a simple sulfur centered monomer radical cation. The small difference in the electronegativity of S and Cl (0.39 eV) may favour the formation of an intra-molecular radical cation ($S \therefore^{+} Cl$) in competition with the formation of the dimer radical cation. The larger difference in the electronegativity of S and O (1.06 eV) may not favour the formation of an intra-molecular radical cation between sulfur and oxygen. In acidic solutions, the transient absorption band at 340 nm is therefore assigned to the intra-molecular radical cation formed on p-orbital overlap of oxidized sulfur and Cl forming a 4-membered ring (Scheme 5). The reaction of $Br^{\bullet}$ atoms with TDEC also showed the formation of a transient absorption spectrum similar to that obtained on reaction of $^{\bullet}$OH radicals at pH = 1. The nature of the transient absorption spectrum remained the same in aerated and deaerated solutions suggesting that the contribution of the $H^{\bullet}$ atom reaction is negligible and the transient species is not due to a carbon centered radical. These studies support the assignment of the transient absorption spectrum (Fig. 5b) to a cationic species. The OH-adduct and α-thio radicals if formed in acidic conditions may be too short lived to detect under our experimental conditions.



Scheme 5

The reaction of $^{\bullet}$OH radicals with TDPC showed the formation of one transient absorption band at 370 nm and remained independent of pH (1–11) and solute concentration (inset of Fig. 5). The nature of the transient absorption spectrum also remained the same in aerated solutions. These studies suggest that the transient absorption band is due to a monomeric cationic species. The band is assigned to the intra-molecular radical cation forming a 5-membered ring on p-orbital overlap of oxidized S and Cl (Scheme 6).

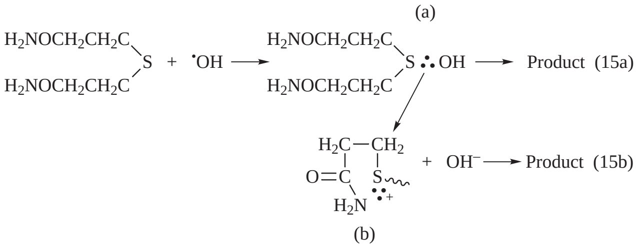


Scheme 6

A 5-membered ring configuration is expected to have higher stability as compared to the 4-membered ring configuration observed in the case of TDEC. The higher stability is reflected in the increased life-time of the intra-molecular radical cation of TDPC (20 µs) as compared to that of TDEC (0.8 µs). The intra-molecular radical cation of TDPC (Fig. 5a) was formed even at pH = 11, which also supports the expectation that the 5-membered ring is more stable, unlike the 4-membered ring configuration of TDEC which was formed in acidic solutions. The transient absorption spectrum obtained on reaction of $Br^{\bullet}$ atoms with TDPC (Fig. 5b) was similar to that obtained on reaction of $^{\bullet}$OH radicals, thus supporting the formation of the cationic species. Br^{-} formed an oxidation of these acyl chlorides by $Br^{\bullet}$ may react with a solute radical cation ($>S^{\bullet +}$) to form a 3-electron bonded species $>S \therefore Br$. But the transient absorption band obtained on reaction of $Br^{\bullet}$ atom with TDEC and TDPC were similar to those obtained on reaction with $^{\bullet}$OH radicals at pH = 1, suggesting that the formation of $>S \therefore Br$ is not taking place.

Reactions with TDP and TDE

In analogy with earlier studies and with those reported in the literature, the transient absorption band at 350 nm, formed on the reaction of $^{\bullet}$OH radicals with TDP (Fig. 6a) is assigned to the OH-adduct. The transient band with λ_{max} = 370 nm (Fig. 6b) is assigned to the intra-molecular radical cation formed with a 5-membered ring configuration. The 5-membered ring can be formed by bonding between S and O or N. But the difference in the electronegativity between S and N (0.63 eV) is less than that between S and O (1.06 eV). Therefore, it is expected that the intra-molecular radical cation is formed between S and N (Scheme 7). Intra-molecular radical cations formed between S and N are known to absorb in this region.[1,3,9]



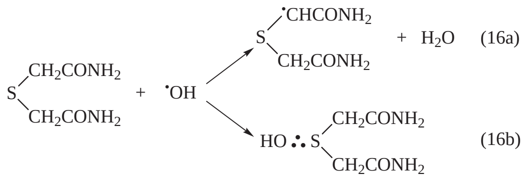
Scheme 7

It is possible that either (1) the OH-adduct and the monomer radical cation are formed simultaneously or (2) the OH-adduct is converted on decay to the intramolecular radical cation as shown in Scheme 7. If the second mechanism is operative, then the decay of the OH-adduct should be affected by pH and the OH-adduct should not be observed at lower pH. Only one band at 370 nm was observed at pH = 5.5 (Fig. 6c), which showed one component decay by first order with $k = 4.5 \times 10^{4}\ s^{-1}$ (Fig. 6e).

Therefore, $^\bullet$OH radicals are reacting with the solute to form the OH-adduct, which on decay is converted to an intra-molecular radical cation absorbing at 370 nm as shown in Scheme 7. The OH-adduct would decay very fast at lower pH. At pH = 1 only one band at 370 nm was observed. The decay of this band was not affected in aerated solutions and the nature of the transient absorption spectrum was similar to that observed on reaction of Br$^\bullet$ atoms with TDP at pH = 1, thus supporting its assignment to the solute radical cation.

The normalized absorbance [$\Delta A/G(\mathrm{OH})$]‡ of the transient band (370 nm) observed on pulse radiolysis of N_2O-saturated aqueous solution of TDP at pH = 6 was 3.1×10^3, much less than that obtained on reaction of $^\bullet$OH radicals with TDP at pH = 1 [$\Delta A/G(\mathrm{OH}) = 5.3 \times 10^{-3}$] and also on reaction of specific one-electron oxidant $^\bullet$Br atoms with TDP [$\Delta A/G(\mathrm{OH}) = 5 \times 10^{-3}$]. It may be due to the fact that at pH = 6, some of the OH-adduct may be decaying by reaction (15a). At pH = 6 removal of OH^- may not be favoured as compared to removal of H_2O in acidic solutions. The remaining fraction of OH-adduct may decay to a stable product at this pH. The transformation of the OH-adduct to solute radical cation at this pH may be too fast to observe distinctly as at pH = 11. The transformation would slow down at higher pH.

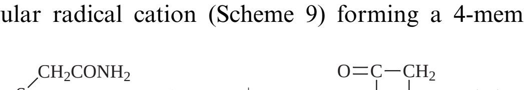
In case of 2,2′-thiodiethanoamide (TDE), the time resolved studies at pH = 11 revealed the formation of two transient species absorbing at 310 nm and 340 nm. The absorption at 310 nm was not seen in aerated solutions whereas the absorption at 340 nm was still present in aerated solutions and is assigned to the OH-adduct. The band at 310 nm is assigned to a carbon centered radical (α-thio radicals) as these are known to have a high reactivity with oxygen. Both the species might be formed simultaneously (Scheme 8) as time resolved studies do not show the formation of a band with decay of another band.



Scheme 8

The contribution of individual processes could not be determined as the bands are close together. Based on the absorbance at 340 nm in aerated solutions and $G(\mathrm{OH}) = 2.7$, the molar absorptivity at 340 nm was determined to be 1.7×10^3 dm^3 mol^{-1} cm^{-1}. At pH = 6, the contribution of α-thio radicals is observed to be less than at pH = 11 as the transient absorption spectrum (Fig. 8a) showed only one band at 345 nm with a small contribution by α-thio radicals. In aerated solutions only one band at 345 nm was observed.

In acidic solutions (pH = 1), only one band at 335 nm was observed (Fig. 9a) and its absorption time profile was different from those at pH = 6 and 11. This band was observed when the pH was less than 3. Its molar absorptivity was also different from that of the OH-adduct. The band is assigned to the intra-molecular radical cation (Scheme 9) forming a 4-membered ring on p-orbital overlap of oxidized sulfur with nitrogen. The nature of the transient absorption spectrum at pH = 1 remained the same in aerated solutions and was also similar to that obtained on reaction of Br$^\bullet$ atoms with TDE, thus supporting the assignment to the solute radical cation.



Scheme 9

The 4-membered ring configuration is expected to be less stable than the 5-membered ring configuration and this is supported by the decreased life-time (4 μs) for the radical cation of TDE in comparison to that of TDP (27 μs). The spectral changes observed on reaction of $^\bullet$OH radicals with these two amides are not due to the reaction with the amide group as the observed absorption spectra are different from those observed with various simple amides.[17] The OH-adduct, if formed, may be too short lived to observe under our experimental conditions.

Effect of pH

The acid-catalysed oxidation of a number of organic compounds has been reported in the literature.[4,18] Since the decay of OH-adduct or α-thio radicals do not follow the formation of the radical cation in acidic solutions, the acid-catalysed oxidation of substituted sulfides cannot be taking place on reaction of H^+ with OH-adduct or α-thio radicals. The rate constant for the reaction of $^\bullet$OH radicals remained independent of pH, showing that $^\bullet$OH radicals react directly with the solute (in the presence of H^+) to form the radical cation. The increase in the absorbance with decreasing pH is due to the fact that more $^\bullet$OH radicals are reacting by the acid-catalysed mechanism than by OH-adduct or α-thio radical formation. The saturation value at lower pH represents the complete formation of radical cations. The variation of absorbance with pH does not represent a thermodynamic equilibrium but shows the existence of different processes at different pHs. The electron transfer reaction, at neutral pH, would take place with the removal of OH^-, which may not be a favourable process in comparison with the removal of H_2O in acidic solutions.[19] Therefore $^\bullet$OH radicals may react with different mechanisms at different pHs.

Conclusions

The hydroxyl radicals react with dialkyl sulfides to form a 3-electron bonded sulfur centered ($>S \therefore {}^+S<$) dimer radical cation. In the presence of a functional group containing a heteroatom (Cl, N, O), the nature of the transient species formed on reaction of $^\bullet$OH radicals depends strongly on the nature of the substituent group, the pH of the solution and the chain length of the functional group. The presence of the $-CH_2CH_2OH$ group results in the formation of α-thio radicals and dimer radical cations in neutral and acidic solutions respectively. In the case of the $-CH_2CH_2CH_2OH$ group, an intra-molecular radical cation with p-orbital overlap between oxidized sulfur and O forming a 5-membered ring is observed in neutral solutions.[4c] The reaction of $^\bullet$OH radicals with 2,2′-thiodiethanoyl chloride leads to the formation of α-thio radicals in neutral solutions. An intra-molecular radical cation forming a 4-membered ring between oxidized sulfur and chlorine is inferred to be the transient species in acidic solutions. In the case of 3,3′-thiodipropionyl chloride, an intra-molecular radical with a 5-membered ring is observed even in neutral solutions. The reaction of $^\bullet$OH radicals with 2,2′-thiodiethanoamide forms α-thio radicals and OH-adduct/intra-molecular radical cation in neutral and acidic solutions respectively. The OH-adduct formed on reaction of $^\bullet$OH radicals with 3,3′-thiodipropionamide is observed to undergo transformation to the intra-molecular radical cation in basic solutions and the intra-molecular radical cation without any transformation from OH-adduct in acidic solutions. Thus the nature and the chain length of the substituent group play important roles in the nature of the $^\bullet$OH radical reaction with substituted alkyl sulfides.

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‡ $G(\mathrm{OH})$ denotes the number of $^\bullet$OH radicals per 100 eV of absorbed energy.

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Paper 9/00830F