Pulse Radiolysis Investigations on Electron-transfer Reactions in Aqueous Solutions of Substituted Alkyl Sulfides

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The transient optical absorption band (λ_{max} = 345 nm, $t_{\frac{1}{2}}$ = 4.0 μs, $\varepsilon = 2.6 \times 10^3$ dm^3 mol^{-1} cm^{-1}) formed on pulse radiolysis of N_2O-saturated dilute neutral aqueous solutions of dimethyl 3,3′-thiodipropionate (DTDP) is assigned to an ˙OH-adduct. The rate constant for the reaction of ˙OH radicals has been determined to be 1.4×10^{10} dm^3 mol^{-1} s^{-1}. At higher solute concentrations the ˙OH-adduct is converted to sulfur-centred dimer radical cations (λ_{max} = 510 nm, $\varepsilon = 4.9 \times 10^3$ dm^3 mol^{-1} cm^{-1}, $t_{\frac{1}{2}}$ = 14.0 μs). In acidic solutions, only dimer radical cations are formed. In neutral aqueous solutions of 3,3′-thiodipropanol (TDP) ˙OH radicals are able to bring about one-electron oxidation, forming intramolecular radical cations with p-orbital overlap between the oxidized sulfur and oxygen (λ_{max} = 420 nm, $t_{\frac{1}{2}}$ = 17 μs, $\varepsilon = 2.6 \times 10^3$ dm^3 mol^{-1} cm^{-1}). In acidic solutions, sulfur-centred dimer radical cations are formed (λ_{max} = 510 nm, $t_{\frac{1}{2}}$ = 12 μs, $\varepsilon = 6.3 \times 10^3$ dm^3 mol^{-1} cm^{-1}). In the presence of halide ions, the oxidized sulfur in DTDP and TDP stabilizes by formation of an $>S\therefore X$ type species.

The initial stage in the reaction of ˙OH radicals with alkyl sulfides is the formation of an ˙OH-adduct, which is converted to sulfur-centred radical cations and α-thioradicals either directly or *via* a complex reaction scheme.[1–5] Simple sulfur-centred radical cations have been observed only in the case of some of the sulfides such as thioanisole, di-*tert*-butyl sulfides *etc.* Their relative stability is explained as being due to the resonance of the unpaired p-electron of the oxidized sulfur with the adjacent π system, or due to steric influence.[6–8] These $R_2S^{\cdot+}$ type radical cations absorb at *ca.* 300 nm and for most aliphatic substituents show a strong tendency to coordinate with the free p-electron pair of the second sulfur atom or with other heteroatoms such as N, O, Cl, Br and I.[8–12] Such interactions are represented by a three-electron bond containing two bonding σ electrons and one antibonding σ* electron and can take place both by inter- and intra-molecular association.[13–15] The reaction of the ˙OH-adduct to form the sulfur-centred radical cation is generally a fast process and the intermediate sequence of proposed reactions are difficult to follow.[1,2] The nature of ˙OH radical reactions are influenced by the nature of substituents and their distance from sulfur in substituted alkyl sulfides.[12,16–21] Therefore, it is of interest to study the nature of ˙OH radical reactions and the redox properties of various organic sulfur compounds containing different substituents.

Studies on the oxidizing behaviour of organic sulfur compounds are important for the understanding of the physicochemical processes taking place in amino acids, sulfur drugs and other biological systems which contain sulfur. These studies are of relevance because of the formation of sulfur-centred radicals as possible intermediates in redox reactions of biomolecules.[22] In substituted alkyl sulfides, the neighbouring groups may affect electron-transfer reactions at sulfur. Depending upon the orbital interaction of the oxidized sulfur with neighbouring groups, the oxidized sulfur may be stabilized by forming an intramolecular solute radical cation. The different electron-withdrawing power of substituted groups may also affect the nature of electron-transfer reactions.[23,24] With this objective, the nature of ˙OH radical reactions, redox properties and the effect of substituents on the oxidation of sulfur in dimethyl 3,3′-thiodipropionate and 3,3′-thiodipropanol are studied and reported in this paper.

Experimental

Dimethyl 3,3′-thiodipropionate (DTDP, 99%) and 3,3′-thiodipropanol (TDP, 98%) were obtained from Aldrich Chemicals and used without any further purification. All solutions were prepared in 'nanopure' deionized water and fresh solutions were used for each experiment. The pH of the solution was adjusted with $HClO_4$ and NaOH. Indian Oxygen 'IOLAR' grade N_2O, O_2 and N_2 gases were used for purging the solutions. The experimental details for pulse radiolysis experiments employing 50 ns pulses of 7 MeV electrons from a linear accelerator have been described elsewhere.[16] An aerated aqueous solution of KSCN (10 mmol dm^{-3}) was used to monitor the dose delivered per pulse using $G\varepsilon$ = 21 522 dm^3 mol^{-1} cm^{-1} for 100 eV at 500 nm for the transient $(SCN)_2^{\cdot-}$ species.[25] The dose per pulse was *ca.* 1.2×10^{17} eV cm^{-3}. The AC conductivity changes produced on pulse radiolysis (pH = 3.7) were monitored in the dual functional cell arrangement and electronic detection system obtained from the Hahn–Meitner–Institut, Berlin.[26] A potential of 10 V was applied between the electrodes. The reaction of ˙OH radicals was studied in N_2O-saturated solutions in which e_{aq}^- are quantitatively converted to ˙OH radicals ($N_2O + e_{aq}^- \longrightarrow {}^{\cdot}OH + OH^- + N_2$, $k = 9.1 \times 10^9$ dm^3 mol^{-1} s^{-1}) with G(OH) = 5.6 (species for 100 eV of absorbed energy).[27] The pulse radiolysis experiments were carried out at a temperature of 23 °C. Error limit for rate constant values are within ±10%.

Results and Discussion

Hydroxyl Radical Reactions with DTDP.—Fig. 1(*a*) shows the transient optical absorption spectrum obtained on pulse radiolysis of an N_2O-saturated aqueous solution of DTDP (2.3×10^{-4} mol dm^{-3}, pH = 6.0, dose = 1.4×10^{17} eV cm^{-3} per pulse). It exhibits an absorption band with λ_{max} = 345 nm, decaying by first-order kinetics with $t_{\frac{1}{2}}$ = 4.0 μs. From the dependence of the rate of formation of this transient, as monitored at 345 nm, on DTDP concentration (1.0–3.0 × 10^{-4} mol dm^{-3}), the rate constant for the reaction of ˙OH radicals with this substrate is measured as 1.8×10^{10} dm^3 mol^{-1} s^{-1}. Since the conductivity of the solution does not change upon irradiation [Fig. 2(*a*)], the transient must be of neutral character. Out of three possible reaction modes of ˙OH radicals

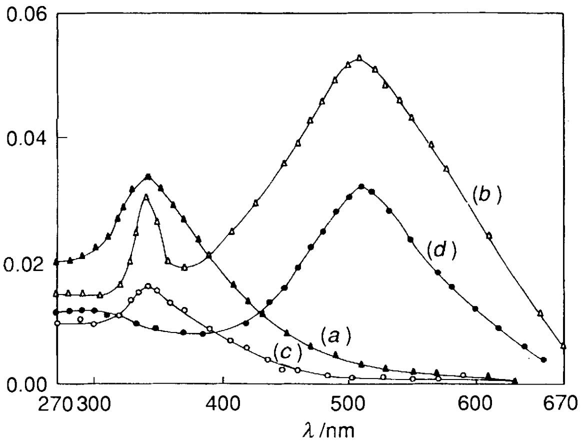


Fig. 1 Transient optical absorption spectrum obtained immediately after pulse radiolysis of aqueous solution of DTDP (*a*) N_2O-saturated, pH = 6.0, 2.3 × 10^{-4} mol dm^{-3}; (*b*) N_2O-saturated, pH = 6.0, 1.2 × 10^{-2} mol dm^{-3}; (*c*) O_2-saturated, pH = 6.0, 2.3 × 10^{-4} mol dm^{-3} and (*d*) O_2-saturated, pH = 1.5, 2.9 × 10^{-2} mol dm^{-3}

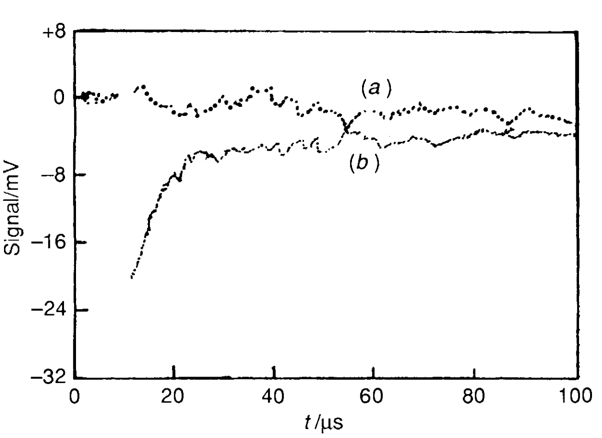


Fig. 2 Conductivity–time curves obtained on pulse radiolysis of an N_2O-saturated aqueous solution (pH = 3.7) of (*a*) DTDP (2.3 × 10^{-4} mol dm^{-3}) and (*b*) DTDP (1.2 × 10^{-2} mol dm^{-3})

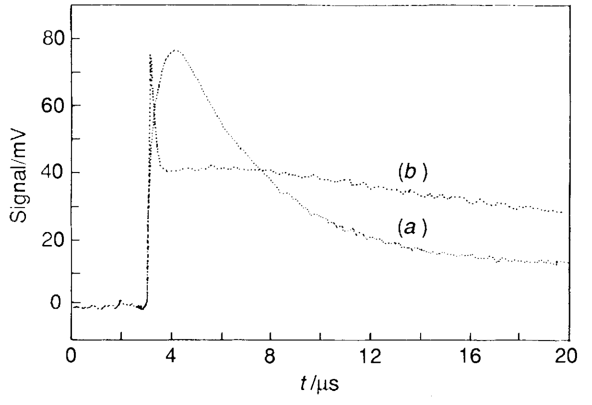


Fig. 3 Absorption–time curves obtained on pulse radiolysis of an N_2O-saturated aqueous solution of DTDP (pH = 6.0, λ = 345 nm); (*a*) 2.3 × 10^{-4} mol dm^{-3} and (*b*) 1.2 × 10^{-2} mol dm^{-3}

(abstraction, addition, electron transfer), the high rate constant value and neutral nature suggest the transient band to be due to an ˙OH radical addition reaction. This is likely to occur at sulfur, eqn. (1).

$$>S + {}^{\bullet}OH \longrightarrow >S{\therefore}OH \qquad (1)$$

Under the experimental conditions employed in Fig. 1(*a*), the reactivity (rate constant × concentration) of ˙OH radicals towards DTDP and ˙OH radicals is 4.1 × 10^6 and 7.2 × 10^4 s^{-1}, respectively, suggesting that *ca.* 98% of ˙OH radicals have reacted with DTDP to form the transient band at 345 nm. Therefore, the concentration of ˙OH radicals (1.3 × 10^{-5} mol dm^{-3}) would be equal to the concentration of the transient species absorbing at λ_{max} = 345 nm. The extinction coefficient is thus determined to be 2.6 × 10^3 dm^3 mol^{-1} cm^{-1}. The rate constant for the reaction of ˙OH radicals with DTDP, and the extinction coefficient of the 345 nm band was also determined by competition kinetic studies using KSCN as the standard solute ($K_{SCN^- + {}^{\bullet}OH}$ = 1.1 × 10^{10} dm^3 mol^{-1} s^{-1}, ε_{500} = 7200 dm^3 mol^{-1} cm^{-1}).[28] The competition kinetic studies were performed at low DTDP concentrations (0.5–1.0 × 10^{-4} mol dm^{-3}) to avoid possible interference by the absorption of the dimer radical cations, eqn. (2), with the 500 nm band of $(SCN)_2^{\bullet -}$. That there is also no interference from the 345 nm band of ˙OH-adduct, the decrease in the absorbance of $(SCN)_2^{\bullet -}$ species on addition of equimolar concentration of DTDP has been taken as the concentration of ˙OH radicals reacting with DTDP while the corresponding increased absorbance at 345 nm would be due to the formation of ˙OH-adduct. The values thus obtained are k_1 = 0.9 × 10^{10} dm^3 mol^{-1} s^{-1} and ε ($>S{\therefore}OH$) = 2.9 × 10^3 dm^3 mol^{-1} cm^{-1}, respectively. The somewhat lower rate constant obtained by a pulse radiolysis competition kinetic method using SCN^- as standard solute may reflect the possibility of oxidation of SCN^- to $(SCN)_2^{\bullet -}$ by the species formed from the reaction of ˙OH radicals with DTDP, resulting in too high a $(SCN)_2^{\bullet -}$ yield. The higher redox potential for the species (see below) formed on reaction of ˙OH radicals with DTDP in comparison with the $(SCN)_2^{\bullet -}/2SCN^-$ couple (1.32 V) may support this observation.

The ˙OH radicals are known to react with alkyl sulfides to produce two transient bands typically located around 290 nm and between 460–550 nm (depending on the alkyl group). These bands are assigned to α-thioradicals and dimer radical cations, respectively.[5] However, in the analysis of the signal during and immediately after pulse radiolysis of an aqueous solution of ethyl sulfide, a very short lived transient band with λ_{max} = 340 nm was observed and assigned to an ˙OH-adduct.[1] The electron-withdrawing power (σ^*) of $-CO_2CH_3$ is +2.0.[23,24] This group is separated by two methylene groups from sulfur and may not lower the electron density at sulfur in comparison with the $-CH_3$ group whose electron-withdrawing power is zero. Consequently the $-CO_2CH_3$ group would not exert any significant influence on λ_{max}. The high rate constant value for the addition of the electrophilic ˙OH group may also suggest that the electron density at sulfur is not appreciably reduced by the $-CO_2CH_3$ group. The ˙OH-adduct is expected to be formed by p-orbital overlap of the unpaired electron of the ˙OH radical with the free p-electrons of sulfur in DTDP forming a neutral three-electron bonded species $(CH_2CH_2CO_2CH_3)_2S{\therefore}OH$ (with, presumably, a polarized sulfur–oxygen bond). The absence of a transient band with λ_{max} = 290 nm suggests that α-thioradicals (by hydrogen atom abstraction) are not formed in competition with the ˙OH-adduct. The high rate constant for the ˙OH reaction with DTDP suggests the formation of the ˙OH-adduct as the primary process. The ˙OH-adduct may decay to α-thioradicals either directly or through solute radical cations.[2]

As the concentration of DTDP is increased, the lifetime of the 345 nm band is observed to decrease. Simultaneously, another absorption band with λ_{max} = 510 nm is observed to grow. Fig. 3 shows typical traces at 345 nm for 2.3 × 10^{-4} and 1.2 × 10^{-2} mol dm^{-3} concentration of DTDP. The absorbance at 510 nm is directly determined from the transient absorbance observed immediately after the pulse since the 345 nm band has very little absorbance at 510 nm. Fig. 4 shows the variation in the absorbance at 510 nm as a function of DTDP concentration.

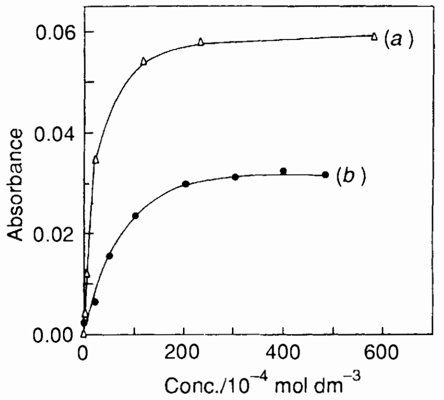


Fig. 4 Variation in the absorbance of transient band (510 nm) with solute concentration; (*a*) pH = 6.0, N_2O-saturated and (*b*) pH = 1.5, O_2-saturated

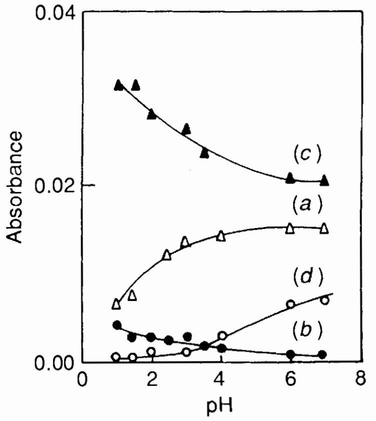


Fig. 5 Variation in the absorbance of transient bands formed immediately after pulse radiolysis of O_2-saturated solutions with pH; (*a*) 345 nm, 2.3 × 10^{-4} mol dm^{-3}; (*b*) 510 nm, 2.3 × 10^{-4} mol dm^{-3}; (*c*) 510 nm, 1.2 × 10^{-2} mol dm^{-3} and (*d*) 345 nm, 1.2 × 10^{-2} mol dm^{-3}

The increase in the absorbance and growth of the 510 nm band is complementary to the faster decay of the 345 nm band. This shows the reaction of DTDP with the $^{\bullet}$OH-adduct (345 nm band) which is pseudo first-order with respect to the solute concentration. Time-resolved conductivity studies at high solute concentration (1.2 × 10^{-2} mol dm^{-3}, pH = 3.7) show that the formation of the optically absorbing species is accompanied by a loss in conductance [Fig. 2(*b*)]. The formation of radical cations is associated with OH^- ions, eqn. (2).[1,7] In acidic solutions, the neutralization of OH^- with H^+, eqn. (3), results in a decrease in conductance as the highly

$$>S\therefore OH + >S \longrightarrow >S\overset{+}{\therefore}S< + OH^- \qquad (2)$$

$$OH^- + H^+ \longrightarrow H_2O \qquad (3)$$

conducting H^+ ions are replaced by a normal cationic species. The transient conductivity signal is similar to the optical signal and suggests that the optically absorbing species is cationic in nature. Therefore, the 510 nm band is assigned to dimer radical cations since it is formed at high solute concentrations *via* eqn. (2) and its intensity is found to increase with solute concentration.

The dimer radical cations of alkyl sulfides absorb in this region,[5] thus supporting the assignment of the 510 nm band to dimer radical cations. The position of this band is on the red side of λ_{max} (450–550 nm) observed for dimer radical cations of various alkyl sulfides. It has been shown that a red shift is generally associated with a weakening of the three-electron bond.[5,13] Since the $-CO_2CH_3$ group has only a small, if any, electron-withdrawing effect on sulfur the red shift is likely to reflect steric hindrance.

Fig. 1(*b*) shows the transient optical absorption spectrum obtained on pulse radiolysis of an N_2O-saturated aqueous solution of DTDP (1.2 × 10^{-2} mol dm^{-3}, pH = 6.0). The variation in the intensity of the 345 and 510 nm bands as a function of pH could not be studied in N_2O-saturated solutions since at lower pH values, e_{aq}^- would also react with H^+ ions in addition to its reaction with N_2O, and *G*(OH) would not remain constant in N_2O-saturated solutions at pH < 3.0. This difficulty is overcome by carrying out the experiments in O_2-saturated solutions which scavenges both H^+ and e_{aq}^-. Fig. 5 shows the variation in the absorbance of the 345 and 510 nm bands formed on pulse radiolysis of an O_2-saturated aqueous solution of DTDP (2.3 × 10^{-4} mol dm^{-3}) as a function of pH. The intensity of the 345 nm band decreases with decrease in the pH of the solution suggesting the reaction of the $^{\bullet}$OH-adduct with H^+ ions, eqn. (4). Simultaneously, the absorbance of the 510 nm band increased slightly showing the formation of dimer radical cations, eqn. (5). The increase in the absorbance at 510 nm was small owing to a low solute concentration. Lack of an absorption band in the 400 nm region suggests that the oxidized sulfur is not able to co-ordinate with oxygen intramolecularly to form a three-electron bonded species, **I**, between the oxidized sulfur and oxygen, although such interactions result in the formation of a five-membered ring configuration which is expected to be reasonably stable. Such transient species have been shown to absorb at wavelengths around 400 nm.[3,10] Intramolecular radical cations, if formed in the present case, appear to be highly unstable. Bulky or electron-donating alkyl groups attached to sulfur are shown to lower the stability of intramolecular radical cations from 1,*n*-bis(alkylthio)alkanes.[15] Therefore, sulfur-centred radical cations formed *via* eqn. (4) may instead be converted to dimer radical cations. Figs. 1(*c*) and 1(*d*) show the transient optical absorption spectrum obtained on pulse radiolysis of an O_2-saturated aqueous solution of DTDP (2.3 × 10^{-4} mol dm^{-3}, pH = 6.0) and (2.9 × 10^{-2} mol dm^{-3}, pH = 1.5), respectively. The decay of the 345 and 510 nm bands is not affected by molecular oxygen, suggesting that the transient bands are not due to carbon-centred radicals which could be expected to react readily with O_2. Compared to N_2O-saturated solutions, the absorbance of the transient bands in O_2-saturated solutions was low due to lower *G*(OH) values. At high solute concentration (1.2 × 10^{-2} mol dm^{-3}), the intensity of the 345 nm band decreases with pH [Fig. 5(*d*)] and that of the 510 nm band increases [Fig. 5(*c*)]. At 1.0 × 10^{-2} mol dm^{-3}, the 510 nm band was observed to decay by first-order kinetics with $t_{\frac{1}{2}}$ = 14 μs. The absorbance of the 510 nm band increases with solute concentration and reaches a plateau value above 4.0 × 10^{-2} mol dm^{-3} concentration of DTDP. At this concentration the reactivity of $^{\bullet}$OH radicals towards DTDP and $^{\bullet}$OH radical is 7.2 × 10^8 and 6.3 × 10^4 s^{-1}, respectively, showing that almost all the $^{\bullet}$OH radicals react with DTDP to form the transient band with λ_{max} = 510 nm. Therefore, the concentration of $^{\bullet}$OH radicals (0.65 × 10^{-5} mol dm^{-3}) may be taken to be equal to the concentration of the transient species. The extinction coefficient thus determined (4.9 × 10^3 dm^3

$$>S\therefore OH + H^+ \longrightarrow >S^{\bullet +} + H_2O \qquad (4)$$

$$>S^{\bullet +} + >S \longrightarrow >S\overset{+}{\therefore}S< \qquad (5)$$

I

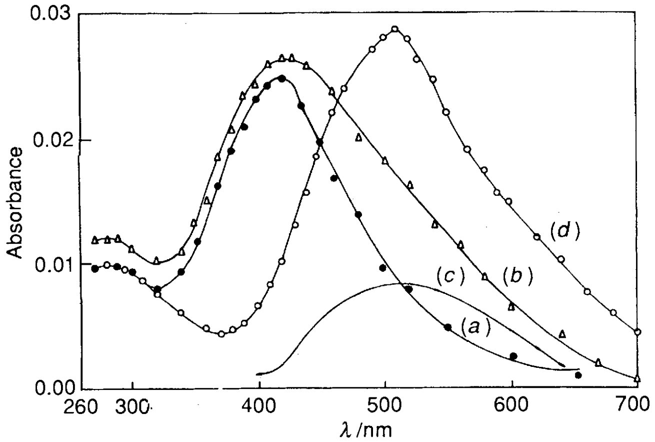


Fig. 6 Transient optical absorption spectrum obtained immediately after pulse radiolysis of an aqueous solution of TDP; (*a*) N_2O-saturated, pH = 6.0, 1.5×10^{-4} mol dm^{-3}; (*b*) N_2O-saturated, pH = 6.0, 1.5×10^{-2} mol dm^{-3}; (*c*) difference in spectrum of (*b*) and (*a*); and (*d*) O_2-saturated, pH = 1.5, 1.5×10^{-2} mol dm^{-3}. Dose = 1.2×10^{17} eV cm^{-3} per pulse.

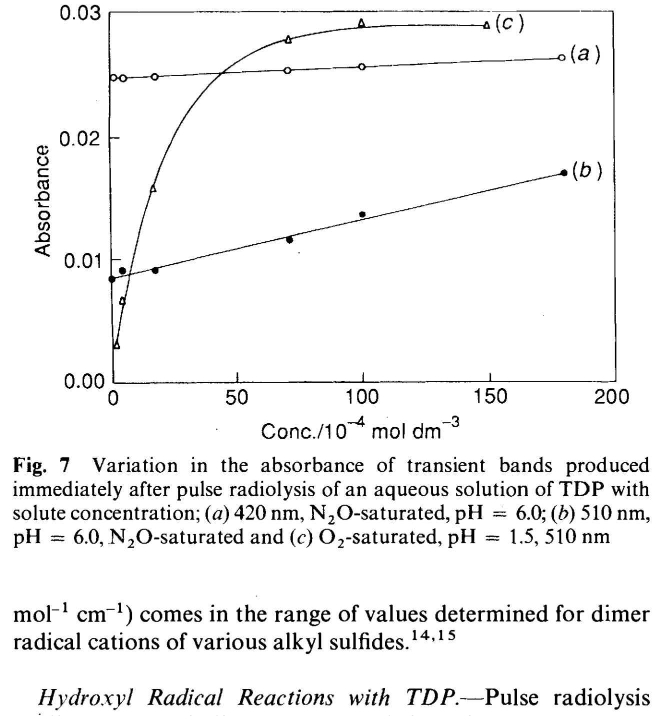
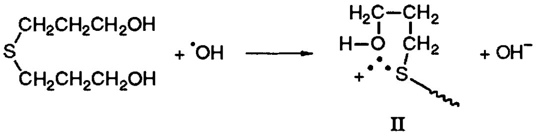


Fig. 7 Variation in the absorbance of transient bands produced immediately after pulse radiolysis of an aqueous solution of TDP with solute concentration; (*a*) 420 nm, N_2O-saturated, pH = 6.0; (*b*) 510 nm, pH = 6.0, N_2O-saturated and (*c*) O_2-saturated, pH = 1.5, 510 nm

mol^{-1} cm^{-1}) comes in the range of values determined for dimer radical cations of various alkyl sulfides.[14,15]

Hydroxyl Radical Reactions with TDP.—Pulse radiolysis studies on 3,3′-thiodipropanol (TDP), in which the $-CO_2CH_3$ group of DTDP is replaced by $-CH_2OH$, show different results. Fig. 6(*a*) shows the transient optical absorption spectrum obtained on pulse radiolysis of an N_2O-saturated aqueous solution of TDP (1.5×10^{-4} mol dm^{-3}, pH = 6.0). It exhibits an absorption band with λ_{max} = 420 nm and a small shoulder in the region of 280–300 nm. The band in the 280–300 nm region may be due to α-thioradicals, formed on hydrogen atom abstraction by $^{\bullet}OH$ radicals. The 420 nm band is observed to decay by first-order kinetics with $t_{\frac{1}{2}}$ = 17 μs. The rate constant for the reaction of $^{\bullet}OH$ radicals with the TDP, as measured from the formation kinetic studies, is 1.4×10^{10} dm^3 mol^{-1} s^{-1}.

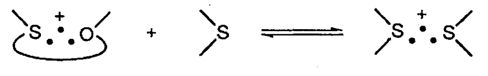
The time-resolved conductivity signal is similar to that shown in Fig. 2(*b*), suggesting the formation of positively-charged species. The intensity of this band remained nearly independent of solute concentration (2.0×10^{-4}–2.5×10^{-3} mol dm^{-3}). The simple sulfur-centred radical cations are very short lived and absorb at 300 nm. The yield of dimer radical cations depends on solute concentration. This band is therefore assigned to intramolecular three-electron bonded species formed on p-orbital overlap of oxidized sulfur with oxygen (**II**). Intramolecular



(6)

three-electron bonded species between sulfur and oxygen have been shown to absorb around 400 nm,[3,10] thus supporting this assignment in the present case. Time-resolved studies do not indicate the formation of a 420 nm band *via* another transient species *e.g.* an $^{\bullet}OH$-adduct. This shows that an $^{\bullet}OH$-adduct if formed must be highly unstable. The high rate constant for the formation of the 420 nm band also supports this conclusion.

When the concentration of TDP is increased (2.5×10^{-3}–1.5×10^{-2} mol dm^{-3}), the absorbance of the 420 nm band also increased slightly, Fig. 7(*a*), but a small shoulder appeared in the 450–550 nm region. Fig. 6(*b*) shows the transient optical absorption spectrum obtained on pulse radiolysis of an N_2O-saturated aqueous solution of TDP (1.5×10^{-2} mol dm^{-3}, pH = 6.0). The difference in the absorption spectra of Figs. 6(*a*) and 6(*b*) shows a band with λ_{max} = 510 nm, Fig. 6(*c*). The absorbance at 510 nm is observed to increase with solute concentration [Fig. 7(*b*)]. At high solute concentration, the dimer radical cations may be formed by the reaction of TDP with intramolecular radical cation **II** accordingly to eqn. (7).



(7)

Therefore, the small increase in the absorption at 420 nm must be due to absorption from the 510 nm band. At low solute concentration (1.5×10^{-4} mol dm^{-3}), the contribution of the 510 nm band at 420 nm is expected to be negligible. The $-CH_2OH$ group, being separated from sulfur by two methylene groups, may not affect the electron density at sulfur appreciably. Therefore, the fraction of $^{\bullet}OH$ radicals reacting with TDP to form radical cations may be taken to be equal to 80% (found for normal alkyl sulfides).[12] Taking this fraction of $^{\bullet}OH$ radicals to form the 420 nm band, the extinction coefficient of the $S\therefore O$ bonded species is determined to be 2.6×10^3 dm^3 mol^{-1} cm^{-1}.

As the pH of the solution is decreased, the absorbance of the 420 nm band also decreases, whilst simultaneously the absorbance of the 510 nm band increases. This shows that dimer radical cations are formed at lower pH and intramolecular p-orbital overlap between the oxidized sulfur and oxygen does not occur at low pH. The intensity of the 510 nm band is observed to increase with solute concentration [Fig. 7(*c*)]. Fig. 6(*d*) shows the transient optical absorption spectrum obtained on pulse radiolysis of an O_2-saturated aqueous solution of TDP (1.5×10^{-2} mol dm^{-3}, pH = 1.5). This exhibits the characteristic absorption band of a dimer radical cation with λ_{max} = 510 nm, decaying by first-order kinetics with $t_{\frac{1}{2}}$ = 12 μs. The extinction coefficient at 510 nm was determined to be 6.3×10^3 dm^3 mol^{-1} cm^{-1}.

Redox Properties of Radical Cations of DTDP and TDP.—The redox properties of radical cations of DTDP and TDP are studied by observing electron-transfer reactions with specific one-electron oxidants having known redox potentials. These reactions are studied by following the decay/growth curves of transient species. For example, Tl^{2+}, formed on pulse radiolysis of an O_2-saturated aqueous solution of Tl^+ (1.0×10^{-2} mol dm^{-3}, pH = 1.5) is observed to oxidize DTDP and form dimer radical cation, $(DTDP)_2^{\bullet+}$. The pseudo first-order rate constant, determined from the growth of the band at 510 nm is observed to depend linearly on solute concentration (0.4–1.1×10^{-3} mol

Table 1 Rate constants for the formation of $>$S∴X

Reaction	Rate constant/10^{-9} dm^3 mol^{-1} s^{-1}
$Cl_2^{\cdot-}$ + DTDP	1.2
$(DTDP)_2^{\cdot+}$ + Br^-	2.1
$(DTDP)_2^{\cdot+}$ + I^-	7.9
$Cl_2^{\cdot-}$ + TDP	2.6
$Br_2^{\cdot-}$ + TDP	1.9
$(TDP)_2^{\cdot+}$ + I^-	7.0

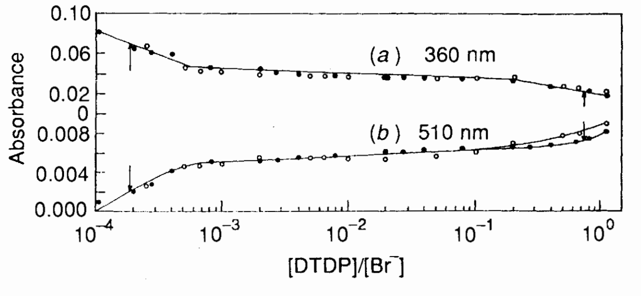


Fig. 8 Variation of absorbance at (*a*) 360 nm and (*b*) 510 nm as a function of the DTDP/Br^- concentration ratio, formed on pulse radiolysis of an N_2O-saturated aqueous solution of DTDP (●, 2.0×10^{-4}; ○, 5.0×10^{-4} mol dm^{-3}) and varying concentrations of Br^- (2.0×10^{-4}–2.0 mol dm^{-3}) 5 μs after the pulse

dm^{-3}), from which the bimolecular rate constant is determined to be 1.7×10^9 dm^3 mol^{-1} s^{-1}. Tl^{2+} is also observed to undergo an electron-transfer reaction with TDP with a rate constant of 2.0×10^9 dm^3 mol^{-1} s^{-1}. $N_3^{\cdot}$ radicals formed on pulse radiolysis of N_2O-saturated aqueous solutions of N_3^- (1.0×10^{-2} mol dm^{-3}, pH = 6.0) are not able to oxidize DTDP and TDP. From these studies, a rough estimate for the redox potential value for DTDP/DTDP$^+$ and TDP/TDP$^+$ couples is in the range 1.33–1.98 V.

The decay of $Cl_2^{\cdot-}$, formed on pulse radiolysis of an O_2-saturated aqueous solution of Cl^- (2.5×10^{-2} mol dm^{-3}, pH = 1.5), becomes faster and first-order in the presence of low concentrations (1.0×10^{-4}–6.0×10^{-4} mol dm^{-3}) of DTDP. Time-resolved studies showed the formation of a new band with λ_{max} = 380 nm. This λ_{max} value is different from that of DTDP$^{\cdot+}$ and $(DTDP)_2^{\cdot+}$. On the other hand, it is close to the λ_{max} of three-electron bonded neutral species formed with $^{\cdot}$Cl and alkyl sulfide.[9] Therefore, in the present case, the transient band formed with λ_{max} = 380 nm is assigned to $>$S∴Cl species formed *via* eqn. (8). The rate constant for eqn. (8) was

$$Cl_2^{\cdot-} + {>}S \longrightarrow {>}S{\therefore}Cl + Cl^- \qquad (8)$$

determined to be 1.2×10^9 dm^3 mol^{-1} s^{-1}. Decay of $Br_2^{\cdot-}$ and $I_2^{\cdot-}$, formed on pulse radiolysis of an N_2O-saturated aqueous solution of 1.0×10^{-2} mol dm^{-3} Br^- and I^-, respectively, is not affected in presence of low concentrations (10^{-3}–10^{-4} mol dm^{-3}) of DTDP, suggesting that the reaction of $Br_2^{\cdot-}$ and $I_2^{\cdot-}$ with DTDP is very slow. On the other hand, the decay of dimer radical cations of DTDP at 510 nm, formed on pulse radiolysis of an O_2-saturated aqueous solution of DTDP (1.5×10^{-2} mol dm^{-3}, pH = 1.5), becomes faster in presence of small concentrations of Br^- (0.5–2.5×10^{-4} mol dm^{-3}) and I^- (0.4–1.0×10^{-4} mol dm^{-3}). The time-resolved studies showed the formation of new bands with λ_{max} = 390 and 400 nm, respectively. These are assigned to $>$S∴Br and $>$S∴I species formed according to eqns. (9) and (10), respectively. The rate constants for eqns.

$$({>}S)_2^{\cdot+} + Br^- \longrightarrow {>}S{\therefore}Br + {>}S \qquad (9)$$

$$({>}S)_2^{\cdot+} + I^- \longrightarrow {>}S{\therefore}I + {>}S \qquad (10)$$

(9) and (10) are 2.1×10^9 and 7.8×10^9 dm^3 mol^{-1} s^{-1}, respectively.

The oxidation reactions with halide ions have also been studied with TDP, and rate constants for the formation of three-electron bonded species, $>$S∴X, are shown in Table 1. From these studies it appears that the rate constant for $>$S∴X formation is nearly the same both for DTDP and TDP. The three-electron bonded species can either be formed by the reaction of $>$S with $X_2^{\cdot-}$ or $(>S)_2^{\cdot+}$ with X^-. It has been reported previously that $>$S∴X exists in the equilibria given in eqns. (11) and (12). Fig. 8 shows the variation of absorbance at

$$X_2^{\cdot-} + {>}S \rightleftharpoons {>}S{\therefore}X + X^- \qquad (11)$$

$${>}S{\therefore}X + {>}S \rightleftharpoons ({>}S)_2^{\cdot+} + X^- \qquad (12)$$

360 and 510 nm, observed on pulse radiolysis of N_2O-saturated aqueous solutions of DTDP (2.0×10^{-4}, 5.0×10^{-4} mol dm^{-3}) and varying concentrations of Br^- (2.0×10^{-4}–2.0 mol dm^{-3}). These measurements are carried out at 5 μs after the pulse, during which time equilibrium conditions have been established. At low and high ratios of DTDP/Br^-, $Br_2^{\cdot-}$ and $(DTDP)_2^{\cdot+}$ species, respectively, are predominantly present while in the intermediate range, $>$S∴Br species are present. The inflection points correspond to equilibrium constants K_{11} and K_{12} of 5.3×10^4 and 1.38, respectively. These values are slightly lower than those observed for $Et_2S{\therefore}Br$ species.[9]

The $^{\cdot}HO_2$ radicals, formed in O_2-saturated acidic aqueous solutions are also oxidizing in nature and their possible contribution to the oxidation of DTDP and TDP was studied in the following two ways: (*a*) The intensity of the 510 nm band remained the same in N_2- and O_2-saturated solutions suggesting that $^{\cdot}HO_2$ radicals do not contribute towards oxidation of DTDP and TDP. If $^{\cdot}HO_2$ radicals were contributing towards the oxidation, the intensity would have been reduced in N_2-saturated solutions in which $^{\cdot}HO_2$ radicals would not be formed. (*b*) The 510 nm band is not observed in the presence of *tert*-butanol (1.0 mol dm^{-3}) also suggesting that $^{\cdot}HO_2$ radicals do not contribute to the oxidation of DTDP and TDP since $^{\cdot}HO_2$ radicals do not react with this alcohol.

The redox potential of $^{\cdot}HO_2$ radicals (1.0 V)[29] is lower than the expected value of the redox potential of DTDP and TDP, thus supporting the observation that $^{\cdot}HO_2$ radicals do not oxidize DTDP and TDP.

Conclusions

Hydroxyl radicals fail to undergo direct one-electron transfer reactions in neutral dilute solutions of dimethyl 3,3′-thiodipropionate but instead form a relatively long-lived adduct radical. This $^{\cdot}$OH-adduct is converted to sulfur-centred dimer radical cations at high solute concentration. The $^{\cdot}$OH radicals are able to undergo a one-electron transfer reaction, however, in neutral aqueous solutions of 3,3′-thiodipropanol, resulting in the formation of intramolecular radical cations **II** due to p-orbital overlap between the oxidized sulfur and oxygen. In acidic pH region, dimer radical cations of dimethyl 3,3′-thiodipropionate and 3,3′-thiodipropanol are formed.

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