Oxidation Reactions of Thiodiglycolic Acid:† A Pulse Radiolysis Study

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The transient optical absorption spectrum produced on pulse radiolysis of an N_2O saturated aqueous solution (pH 3.0–10.0) of thiodiglycolic acid has been assigned to the α-thio radical, $HO_2CH_2C{-}S{-}\dot{C}HCO_2H$, formed by hydrogen atom abstraction from the parent compound by hydroxyl radicals. The absorption maximum (285 nm) and extinction coefficient (1.6×10^3 dm^3 mol^{-1} cm^{-1}) are found to be independent of solute concentration over the range 8.0×10^{-5}–8.0×10^{-2} mol dm^{-3} and pH (1.0–10.0) of the solution. The rate constant for the reaction of hydroxyl radicals with thiodiglycolic acid has been determined to be 4.1×10^9 dm^3 mol^{-1} s^{-1} and the product species decays by second-order kinetics with a rate constant of 1.6×10^9 dm^3 mol^{-1} s^{-1}. Strong oxidizing agents such as $(CH_3I)_2^{+\bullet}$, $Cl_2^{-\bullet}$, $CH_3\dot{I}OH$, and $SO_4^{-\bullet}$ have been found to oxidize thiodiglycolic acid with the formation of a transient species with λ_{max} 280 nm, the rate constants being 6.7×10^9, 4.9×10^8, 6.9×10^9, and 2.7×10^9 dm^3 mol^{-1} s^{-1}, respectively. The transient optical absorption spectrum (λ_{max} = 280, 380 nm) obtained on pulse radiolysis of a nitrogen saturated solution of thiodiglycolic acid in 1,2-dichloroethane has been assigned to a radical cation derived from this solute.

Pulse radiolysis investigations on the reactions of hydroxyl radicals with organic sulphides in aqueous solution have revealed the formation of the radical cations of these compounds.[1–4] Simple radical cations have been observed only in the case of some of the sulphides such as thioanisole, di-t-butyl sulphide, *etc.* These cations absorb at *ca.* 300 nm and their relative stability is explained as being due to the resonance of the unpaired p electron of the oxidized S atom with the adjacent π system or due to steric influences.[5–7] The radical cations show a strong tendency to stabilize by co-ordination with a free electron pair from another S atom. Depending on the substituents, they absorb in the region 400–600 nm and have lifetimes of several ms in aqueous solution.[8] Evidence for the formation of such sulphur-centred cations has come from ESR and optical spectroscopy in aqueous, non-aqueous, and solid systems.[9–12] The intermolecular and intramolecular p orbital overlap of the oxidized S atom with the free p electrons of the S or other hetero atom has been represented by a three-electron bond containing two bonding σ electrons and one antibonding σ* electron.[2,3] The stability depends on the electron-donating properties of the substituents at S and the other hetero atom, the pH of the solution, and the geometry of the species which influence the orbital overlap required for the formation of three-electron bonded species.[13–15] The present studies on thiodiglycolic acid (TDGA)† are aimed at understanding the effect of a substituted carboxyl group on the susceptibility of the S atom to oxidation. The studies are also important because TDGA is a urine metabolite in humans who are exposed to vinyl chloride.[16]

Experimental

Thiodiglycolic acid (TDGA) was Fluka, Purum grade (purity >98%). The solutions were prepared in deionized 'nanopure' water. The pH of the solutions was adjusted with $HClO_4$ or NaOH. Indian Oxygen IOLAR grade N_2O, N_2, or O_2 were used for purging the solutions. The pulse radiolysis experimental set up, employing 25 ns or 2 μs pulses of 7 MeV electrons from a linear accelerator has been fully described elsewhere.[17] An aerated aqueous solution of KSCN was used for monitoring the dose delivered per pulse assuming $G\varepsilon$ = 21 522 dm^3 mol^{-1} s^{-1} per 100 eV at 500 nm for the transient $(CNS)_2^{-\bullet}$ species.[18] The reaction of OH radicals was studied by using N_2O saturated solutions to convert e_{aq}^- into OH radicals ($N_2O + e_{aq}^- \longrightarrow N_2 + OH^\bullet + OH^-$). The reaction of H atoms was studied using a nitrogen saturated matrix (pH = 1.0) containing 0.1 mol dm^{-3} t-butyl alcohol in order to convert e_{aq}^- into H atoms and scavenge the OH radicals [$e_{aq}^- + H^+ \longrightarrow H + H_2O$; $(CH_3)_3COH + OH \longrightarrow \dot{C}H_2(CH_3)_2COH + H_2O$). The charge state of the transient species formed on pulse radiolysis was studied by conductivity measurements.[19] In all cases, fresh solutions were used for each measurement.

Results and Discussions

Figure 1(*a*) shows the transient optical absorption spectrum obtained on pulse radiolysis of an N_2O-saturated aqueous solution of TDGA (5.3×10^{-2} mol dm^{-3}, pH = 6.0, dose = 5.5×10^{17} eV cm^{-3} per pulse). The transient band (λ_{max} = 285 nm) was found to decay with second order kinetics (Figure 2) with $2k/\varepsilon l = 1.02 \times 10^6$ s^{-1}. From the inset in Figure 2 it is apparent that the decay does not follow first order kinetics whereas the $1/A$ *versus* time plot is linear. The points back-calculated from the slope and intercept of this reciprocal plot fit the actual decay curve quite well [Figure 2(*a*)]. There was no relative change in the conductivity of the solution as a result of pulse radiolysis, indicating the formation of a neutral species. Under the experimental conditions employed, the concentration of hydroxyl radicals produced per pulse is *ca.* 5.5×10^{-5} mol dm^{-3}. This is much lower than the concentration of TDGA (5.3×10^{-2} mol dm^{-3}). Assuming that all the hydroxyl radicals have reacted with TDGA giving rise to the transient species, with λ_{max} at 285 nm, the extinction coefficient was calculated to be 1.6×10^3 dm^3 mol^{-1} cm^{-1}. The kinetics of formation of the product species was studied by following the signals at 285 nm at different concentrations of TDGA (1.0–4.5×10^{-3} mol dm^{-3}). From the linear plot of the first-order rate constant *versus* the TDGA concentration, the bimolecular rate constant for the reaction of hydroxyl radicals with TDGA was determined to be

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† IUPAC recommended: 2,2′-thiodi(ethanoic acid).

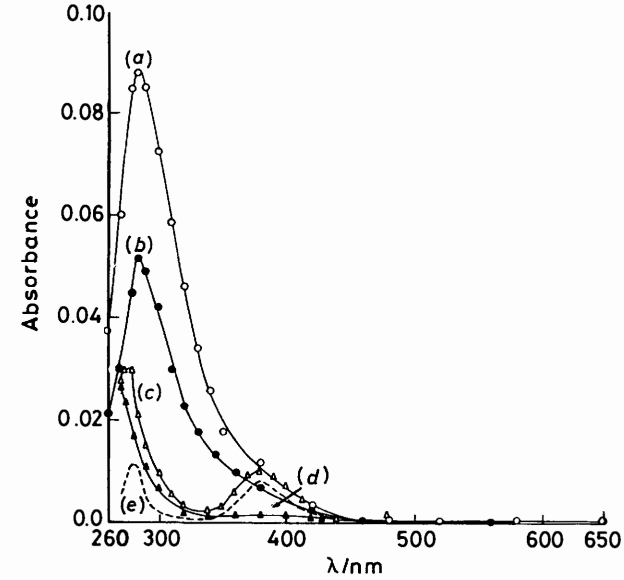

Figure 1. Transient optical absorption spectrum obtained on pulse radiolysis (dose per pulse 5.5 × 10^{17} eV cm^{-3}) of TDGA (*a*) in an N_2O saturated aqueous solution (5.3 × 10^{-2} mol dm^{-3}, pH = 6.0); (*b*) in nitrogen saturated aqueous solution (4.3 × 10^{-2} mol dm^{-3}, pH = 1.0, t-butyl alcohol = 0.1 mol dm^{-3}); (*c*) nitrogen saturated solution (1.0 × 10^{-4} mol dm^{-3}) in DCE; (*d*) nitrogen saturated DCE; and (*e*) difference absorption spectrum of (*d*) and (*c*).

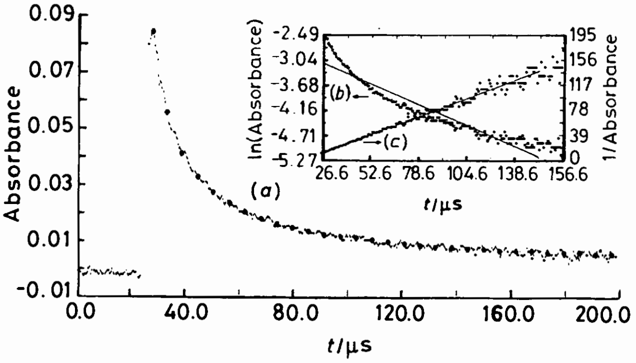

Figure 2. (*a*) Decay of the transient band (285 nm) formed on pulse radiolysis of an N_2O saturated aqueous solution of TDGA; (*b*) first-order plot; and (*c*) second-order plot. The closed circles on curve (*a*) represent points back-calculated from the slope and intercept of (*c*).

4.1 × 10^9 dm^3 mol^{-1} s^{-1}. This is close to the value of 3.6 × 10^9 dm^3 mol^{-1} s^{-1} determined by the competition kinetic method.[20]

Figure 1(*b*) shows the transient optical absorption spectrum obtained on pulse radiolysis of a nitrogen saturated aqueous solution of TDGA (4.3 × 10^{-2} mol dm^{-3}, pH = 1.0, dose = 5.3 × 10^{17} eV cm^{-3} per pulse) containing 0.1 mol dm^{-3} of t-butyl alcohol. Under these conditions, the transient absorption spectrum would be due to the reaction of H atoms with TDGA. This band was also found to decay with second order kinetics with the same $2k/\varepsilon l$ value. Since the decay kinetics and the position of the band maximum are the same in the two cases, the species can be assigned to the α-thio radical HO_2CH_2C–S–$\dot{C}HCO_2H$ formed on hydrogen atom abstraction by H/OH radicals. α-Thio radicals formed on hydrogen atom abstraction from organic sulphides have been shown to absorb at *ca.* 290 nm.[4] The t-butyl radicals, $\dot{C}H_2(CH_3)COH$, formed on hydrogen abstraction by hydroxyl radicals were found to be unreactive towards TDGA, as observed by the absence of any transient band on pulse radiolysis of an N_2O saturated neutral aqueous solution of TDGA (2.5 × 10^{-4}) containing 0.1 mol dm^{-3} t-butyl alcohol.

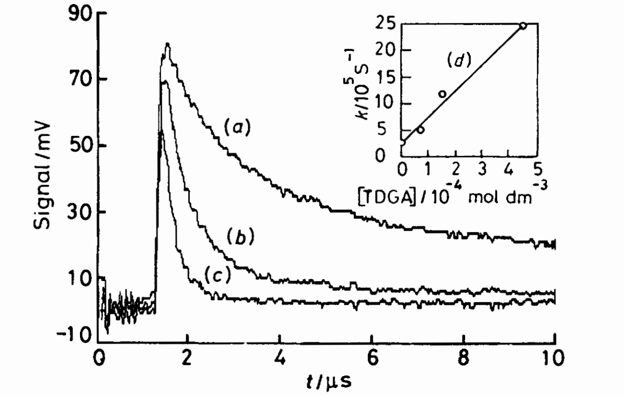

Figure 3. Decay of the transient absorption band formed on pulse radiolysis of an N_2O saturated aqueous solution of CH_3I (8.0 × 10^{-3} mol dm^{-3}, pH = 3.0) in presence of TDGA (*a*) 0; (*b*) 1.5 × 10^{-4}; and (*c*) 4.5 × 10^{-4} mol dm^{-3}. Dose per pulse = 1.0 × 10^{17} eV cm^{-3}. (*d*) Plot of observed first order rate constant with TDGA concentration.

The absorbance of the transient band formed on reaction of H atoms with TDGA [Figure 1(*b*)] was much lower than that formed with hydroxyl radicals [Figure 1(*a*)]. This is due to the lower yield of H atoms (*G* = 3.6) at pH = 1.0 as compared with the yield of hydroxyl radicals (*G* = 6.0 in an N_2O saturated solution at pH = 6.0). The extinction coefficient of the transient band [Figure 1(*b*)] was calculated to be the same as that of the transient band formed on reaction with hydroxyl radicals [Figure 1(*a*)].

The nature of the transient optical absorption spectrum and its decay kinetics were observed to be independent of solute concentration (8.0 × 10^{-2}–8.0 × 10^{-5} mol dm^{-3}) and pH of solution (1.0–10.0). Even in strong acid solutions (1.0 mol dm^{-3} $HClO_4$), the transient optical absorption spectrum was similar to that shown in Figure 1(*a*). No absorption in the region 400–600 nm was observed. The dimer radical cations of organic sulphides are known to absorb in the region 400–600 nm.[13] Hence the absence of absorption in this region indicates that the dimer radical cations of TDGA are not formed, even in 1.0 mol dm^{-3} $HClO_4$. Therefore it can be inferred that hydroxyl radicals are not able to oxidize TDGA; instead they abstract H atoms to form the α-thio radicals.

Experiments were carried out in order to study the oxidation of TDGA by using specific one-electron oxidants. This was done by observing the decay of the transient band of different oxidizing species in the presence of a low concentration of TDGA (10^{-6}–10^{-4} mol dm^{-3}). The decay of the transient bands of $Br_2^{-\bullet}$, $I_2^{-\bullet}$, and $Tl^{2+\bullet}$ formed on pulse radiolysis of N_2O saturated aqueous solutions of Br^- (4.5 × 10^{-2} mol dm^{-3}, pH = 6.0), I^- (4.0 × 10^{-2} mol dm^{-3}, pH = 6.0), and Tl^+ (2.0 × 10^{-2} mol dm^{-3}, pH = 3.0) were not affected on addition of TDGA (4.0 × 10^{-4} mol dm^{-3}). This shows that these oxidizing species are not able to oxidize TDGA. The $(CH_3I)_2^{+\bullet}$ formed on pulse radiolysis of an N_2O saturated aqueous solution of CH_3I (8.0 × 10^{-3} mol dm^{-3}, pH = 3.0) has been shown to be a strong oxidizing agent.[21] The oxidation of TDGA by $(CH_3I)_2^{+\bullet}$ was studied by following the decay of the $(CH_3I)_2^{+\bullet}$ band at 415 nm in the presence of different concentrations of TDGA [Figure 3(*a*)–(*c*)]. The band was found to decay progressively faster. The bimolecular rate constant for the oxidation of TDGA by $(CH_3I)_2^{+\bullet}$ was determined from the slope of the linear plot of pseudo-first-order rate constant *vs.* TDGA concentration [Figure 3(*d*)] and was found to be 6.7 × 10^9 dm^3 mol^{-1} s^{-1}. Pulse radiolysis of N_2O saturated aqueous solutions of CH_3I (8.0 × 10^{-3} mol dm^{-3}) and TDGA

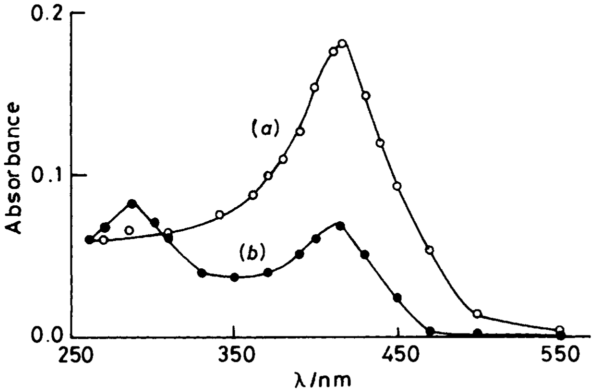

Figure 4. Optical absorption spectrum obtained on pulse radiolysis of an N_2O saturated aqueous solution of (*a*) CH_3I (8.0×10^{-3} mol dm^{-3} and (*b*) CH_3I (8.0×10^{-3} mol dm^{-3}) and TDGA (4.5×10^{-4} mol dm^{-3}). Dose per pulse 5.5×10^{17} eV cm^{-3}, pH = 3.0.

(4.5×10^{-4} mol dm^{-3}) showed the presence of a transient band at 290 nm (Figure 4), which must be due to the radical cation of TDGA formed on oxidation by $(CH_3I)_2{}^{+\cdot}$. $Cl_2{}^{-\cdot}$, $CH_3\dot{I}OH$, and $SO_4{}^{-\cdot}$ are also known to be strong one electron oxidants and have also been found to be able to oxidize TDGA. The transient bands of $Cl_2{}^{-\cdot}$, $CH_3\dot{I}OH$, and $SO_4{}^{-\cdot}$ formed on pulse radiolysis of Cl^- (2.0×10^{-2} mol dm^{-3}, pH = 1.5, O_2 saturated), CH_3I (8.0×10^{-3} mol dm^{-3}, pH = 6.0, N_2O saturated) and $SO_4{}^{2-}$ (6.0×10^{-3} mol dm^{-3}, pH = 6.0, t-butyl alcohol = 0.05 mol dm^{-3}, N_2 saturated) were found to decay progressively faster in the presence of increasing concentrations of TDGA. The bimolecular rate constant for the oxidation of TDGA was determined as in the case of $(CH_3I)_2{}^{+\cdot}$ and the values were found to be 4.9×10^8, 6.9×10^9, and 2.7×10^9 dm^3 mol^{-1} s^{-1}, respectively. In these cases also, increased absorption was observed in the region 280–300 nm, which can be attributed to the formation of the radical cation of TDGA. The radical cation of dimethyl sulphide hbeen shown to absorb at 285 nm.[22] These studies suggest that only those oxidizing species with oxidation potential $\geqslant 2.1$ V *vs.* NHE are able to oxidize TDGA. Therefore, the reduction potential of the $TDGA^+$/TDGA couple should be close to 2.0 V *vs.* NHE. The α-thio radical (λ_{max} = 285 nm) formed on pulse radiolysis of an N_2O saturated aqueous solution of TDGA [Figure 1(*a*)] was not able to oxidize Br^-, I^-, and dimethyl disulphide. Since hydroxyl radicals are not able to oxidize TDGA in aqueous solutions, the oxidation reactions of the radical cation of TDGA with other additives could not be investigated. The fact that the 285 nm band observed on pulse radiolysis of an N_2O saturated solution of TDGA was not able to oxidize Br^- *etc.*, shows that this is due to a species different from the one formed on oxidation of TDGA by the above oxidizing species. If both the bands were due to the same species, it should also have oxidized species such as Br^- with an oxidation potential (1.6 V *vs.* NHE) lower than that of the $TDGA^+$/TDGA couple.

Formation of Radical Cations in 1,2-*Dichloroethane*.—1,2-Dichloroethane (DCE) has been recommended and used as a solvent for the study of radical cations of organic compounds.[23] In this solvent, the yield of matrix cations is increased due to reaction of the electrons with matrix molecules (Scheme).

$$CH_2Cl\text{–}CH_2Cl \longrightarrow CH_2Cl\text{–}CH_2Cl^+ + e^-$$
$$CH_2Cl\text{–}CH_2Cl + e^- \longrightarrow CH_2Cl\text{–}CH_2 + Cl^-$$

Scheme.

Figure 1(*c*) shows the transient optical absorption spectrum of a nitrogen saturated solution of TDGA (1.0×10^{-4} mol dm^{-3}) in DCE. It shows an absorption band at 380 nm and increased absorption in the region 270–290 nm. Pulse radiolysis of nitrogen saturated DCE also gives rise to an absorption in the region 270–290 nm [Figure 1(*d*)]. Figure 1(*e*) shows the difference absorption spectrum and this should be due to species formed from TDGA. The absorption band at 280 nm, which was also observed on oxidation of TDGA by different oxidizing species, should be due to the radical cation of TDGA. The decay kinetics could not be studied due to the presence of an absorption band due to the transient species formed from DCE itself in this region. The band at 380 nm may also belong to the radical cation of TDGA. It is also possible that a complex between Cl^- and $TDGA^+$ may be formed, giving rise to a neutral three-electron bonded species $(HO_2CH_2C)_2S\therefore Cl$. This species may show absorption in this region. The complex between Cl^- and the radical cations of organic sulphides has been shown to form neutral three-electron bonded species which absorb in the region 380 nm.[24] In this case also, the decay of the 380 nm band could not be studied due to low absorption and interference from transient species resulting from DCE [Figure 1(*d*)].

Conclusions

Hydroxyl radicals react with TDGA by hydrogen atom abstraction to form α-thio radicals but are unable to effect oxidation even in strongly acidic solutions. The oxidation of TDGA can be brought about by strong one electron oxidants such as $(CH_3I)_2{}^{+\cdot}$, $Cl_2{}^{-\cdot}$, $CH_3\dot{I}OH$, and $SO_4{}^{-\cdot}$. The formation of radical cations of TDGA is also observed in 1,2-dichloroethane.

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