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Electron Transfer Reactions of 2,2′-Thiodiethanoic Acid in Aqueous Solutions: A Pulse Radiolysis Study

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OH radicals are observed to react with 2,2′-thiodiethanoic acid in aqueous solutions containing a high concentration of $HClO_4$ by an inner-sphere electron transfer reaction mechanism to form solute dimer (λ_{max} = 520 nm) radical cations at high solute concentrations. The stability constant for the dimer radical cation has been determined to be 68 $dm^3\ mol^{-1}$ at 25 °C. The decay kinetics of solute dimer radical cation is discussed in detail and deprotonation of the solute radical cation is found to be the rate-determining step. The solute dimer radical cations are able to undergo electron transfer reactions with Br^- and form a transient band (λ_{max} = 385 nm) which is assigned to a bromine–solute adduct.

OH-radical-induced reactions in aqueous solutions of alkyl sulfides and their substituted derivatives have been the subject of much interest.[1-5] The reaction of •OH radicals and specific one-electron oxidants produces sulfur-centred radical cations either directly or *via* a complex sequence of reactions.[5-7] Oxidized sulfur has high tendency to stabilize itself by co-ordination with the free p electron pair of a second sulfur or with other heteroatoms such as O, P, N and halogens, both inter- and intra-molecularly.[2,8-12] Such interactions are represented by a three-electron bond containing two bonding σ electrons and one antibonding σ^* electron.[1] Unlike simple alkyl sulfides, the nature of •OH radical reactions with substituted alkyl sulfides depends on the nature of the substituent, chain length between the sulfur and the substituent and the pH of the solution.[4,10,13-15] Therefore, it is interesting to study the nature of OH-radical-induced reactions with a variety of sulfur compounds, under different pH conditions.

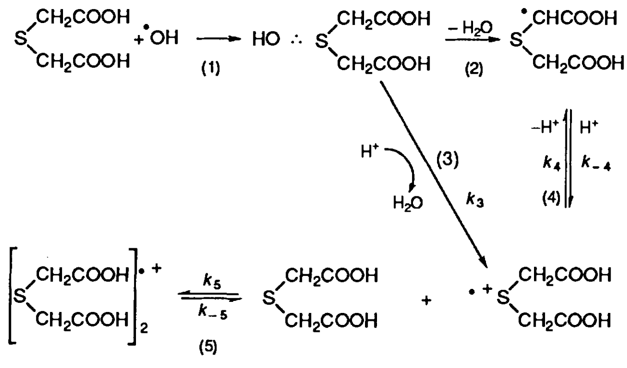
The studies on the reaction of •OH radicals with organic sulfur compounds have gained much importance because sulfur-centred radical species are considered to be possible intermediates in redox reactions of biomolecules.[16] Such studies are also important for the understanding of the physicochemical processes that take place involving amino acids, sulfur drugs and other biological systems that contain sulfur. Although the OH radicals are known to react with thiodiglycolic acid by H-atom abstraction,[13] we are now able to generate conditions under which •OH radicals are able to react by inner-sphere electron transfer to form sulfur-centred radicals and dimer radical cations. The formation, stabilization and redox properties of dimer radical cations of thiodiglycolic acid are reported in this paper. An attempt is also made to analyse the essence of the conditions required for the •OH-radical-induced dimer radical cation formation of thiodiglycolic acid.

Experimental

2,2′-Thiodiethanoic acid (thiodiglycolic acid, TDGA) obtained from Fluka was used without further purification. Perchloric acid (70%, sp. gr. = 1.67) was obtained from Merck. Aqueous solutions were prepared in deionized 'nanopure' water. Indian oxygen 'iolar' grade N_2 or O_2 gases were used for purging the solutions. Freshly prepared solutions were used in each experiment. The pulse radiolysis experiments were carried out with high energy (7 MeV, 50 ns) electron pulses generated from a linear accelerator.[17] An aerated aqueous solution of KSCN (10^{-2} mol dm^{-3}) was used for monitoring the dose delivered per pulse using $G\varepsilon$ (at 500 nm) = 21 522 $dm^3\ mol^{-1}\ cm^{-1}$ per 100 eV for the $(SCN)_2^{\bullet -}$ species.[18] The dose per pulse was determined to be 1.0×10^{17} eV cm^{-3}. The rate constant values are an average of at least three independent experiments and the variation in the data is to within ± 10%. The reaction of •OH radicals, in acidic solutions, was carried out in O_2-saturated solutions where H atoms and e_{aq}^- are converted into HO_2 radicals ($e_{aq}^- + H^+ \rightarrow H + H_2O$; $H + O_2 \rightarrow HO_2$). At the high concentration of $HClO_4$ employed in the present experiments, the entire radiation energy would not be absorbed by water alone and the *G*(OH) value available for water radiolysis is not applicable in the present case. The extinction coefficient value of the transient species formed under these conditions could not be evaluated as the *G*(OH) value is not known at high [$HClO_4$]. All the experiments were carried out at 25 °C.

Results and Discussion

The reaction of •OH radicals in neutral aqueous solutions of TDGA forms a transient band with λ_{max} = 285 nm.[13] Optical absorption[6] and electron spin resonance studies[19] have shown that the reaction of •OH radicals with alkyl sulfides forms a neutral radical which absorbs in the region 280–300 nm. This neutral radical can be formed by H-atom abstraction from the OH-adduct [step (2), Scheme 1]. The band observed on reaction of •OH radicals with TDGA in neutral aqueous solution was assigned to α-thio radicals.[13]



Scheme 1

The nature of transient optical absorption spectrum remained same in the pH range 0–10. However, if [H^+] was increased by addition of $HClO_4$, a broad absorption band with λ_{max} = 520 nm was observed when [$HClO_4$] was

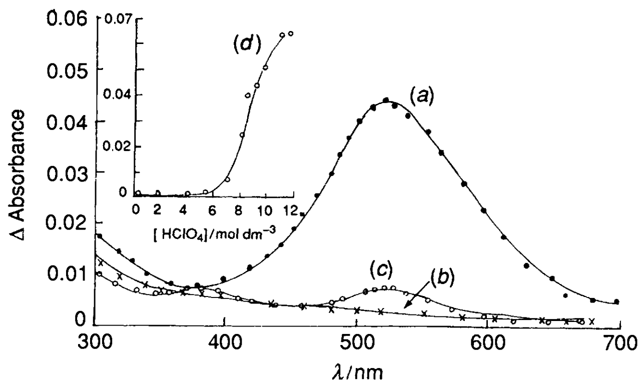


Fig. 1 Transient optical absorption spectrum obtained immediately after a 50 ns pulse in O_2-saturated aqueous solutions containing (*a*) TDGA (2.1×10^{-2} mol dm^{-3}), $HClO_4$ (9.3 mol dm^{-3}); (*b*) $HClO_4$ (9.3 mol dm^{-3}); (*c*) TDGA (3.1×10^{-4} mol dm^{-3}), $HClO_4$ (9.3 mol dm^{-3}); (*d*) variation in the absorbance of the 520 nm band as a function of [$HClO_4$]; [TDGA] = 2.1×10^{-2} mol dm^{-3}. Dose = 1.0×10^{17} eV cm^{-3} per pulse.

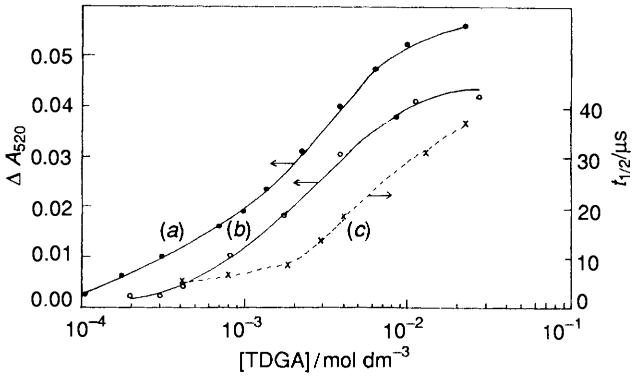


Fig. 2 Variation in the absorbance of the transient band (520 nm) formed on pulse radiolysis of O_2-saturated solutions of TDGA in (*a*) $HClO_4$ (10.8); (*b*) $HClO_4$ (9.1 mol dm^{-3}) as a function of [TDGA]; (*c*) variation of $t_{\frac{1}{2}}$ as a function of [TDGA] ([$HClO_4$] = 9.8 mol dm^{-3}). Dose = 1.1×10^{17} eV cm^{-3} per pulse.

more than 4.0 mol dm^{-3}. Fig. 1(*a*) displays the transient optical absorption spectrum obtained on pulse radiolysis of an O_2-saturated aqueous solution of TDGA (2.1×10^{-2} mol dm^{-3}) in 9.3 mol dm^{-3} $HClO_4$. Under these conditions, this band was observed to decay by first-order kinetics with a half-life of 36 μs.

The intensity of the transient band ($\Delta A = 0.039$) formed on pulse radiolysis of an O_2-saturated solution ([TDGA] = 2.1×10^{-2} mol dm^{-3}; [$HClO_4$] = 8.8 mol dm^{-3}; $\lambda = 520$ nm) reduced considerably ($\Delta A = 0.005$) in the presence of *tert*-butyl alcohol (0.5 mol dm^{-3}), which is a relatively strong •OH radical and weak H-atom scavenger. The intensity of the transient band (520 nm) remained same for N_2- and O_2-saturated solutions. This transient band was not observed on pulse radiolysis of an O_2-saturated aqueous solution of 9.3 mol dm^{-3} $HClO_4$ [Fig. 1(*b*)]. The bimolecular rate constant for the reaction of •OH radicals with TDGA forming the 520 nm band was determined from formation kinetic studies. In the concentration range 5×10^{-4}–2×10^{-3} mol dm^{-3}, the band was found to grow with *pseudo*-first-order kinetics and the bimolecular rate constant was determined to be 1.9×10^{9} dm^{3} mol^{-1} s^{-1}.

Effect of Solute Concentration.—The intensity and the lifetime of the transient optical absorption band (520 nm) formed on pulse radiolysis of O_2-saturated aqueous TDGA increased with increasing solute concentration (Fig. 2). A plateau value was observed at 2×10^{-2} mol dm^{-3}. The intensity and the lifetime of the transient band (520 nm) increased with [solute], but the nature of the transient optical absorption spectrum remained same for different [TDGA] (1.0×10^{-3}–2.0×10^{-2} mol dm^{-3}). When [TDGA] < 4.0×10^{-4} mol dm^{-3}, a broad absorption band of low intensity was observed with $\lambda_{max} = 360$ nm [Fig. 1(*c*)]. This was observed in the 1.0×10^{-4}–4.0×10^{-4} mol dm^{-3} region and its intensity and lifetime remained unchanged. The bimolecular rate constant for the formation of 360 nm band, as determined from formation kinetics, was 6.4×10^{9} dm^{3} mol^{-1} s^{-1}, and it decayed by first-order kinetics with $t_{\frac{1}{2}} = 20.4$ μs.

Effect of [H^+].—The formation of the 520 nm transient optical absorption band was observed to require a high concentration of $HClO_4$. Fig. 1(*d*) shows the variation in the absorbance of the 520 nm band as a function of [$HClO_4$]. The absorbance increased in intensity with increased [$HClO_4$]. The plateau value could not, however, be obtained experimentally although it appears to level off at [$HClO_4$] = 11.0 mol dm^{-3}. The optical absorption band (360 nm) observed at low solute concentration was also observed only when [$HClO_4$] > 4.0 mol dm^{-3}.

Assignment of Transient Species.—The primary reactive species produced on radiolysis of acidic aqueous solution are H and OH radicals. Under our experimental conditions, (O_2-saturated), H atoms would be converted into HO_2 radicals which are weak oxidizing agents with a redox potential of +1.0 V.[20] The absence of the transient band in the presence of an OH-radical scavenger and presence in N_2-saturated solution show that the band is due to a reaction of •OH with the solute and not to HO_2 radicals. The formation of the OH-adduct [step (1), Scheme 1] can be considered as an elementary step for the reaction of •OH with TDGA. The OH-adducts of alkyl sulfides absorb in the region of 340 nm[3]. Simple sulfur-centred radical cations are highly unstable and absorb in the region of 300 nm.[1] Since the transient optical absorption band due to OH-adduct (~340 nm) or solute radical cation (*ca.* 300 nm) could not be observed on pulse radiolysis of a neutral aqueous solution of TDGA, these transient species must be highly unstable and decay during the pulse duration. Since the absorbance at 520 nm increases with solute concentration, it should be due to a dimeric species. Asmus *et al.*[21] have shown the formation of $(CH_3)_2S^{\bullet+}$ on acid-assisted oxidation of the H-adduct of $(CH_3)_2SO$ in presence of high [$HClO_4$] (> 1.0 mol dm^{-3}). The OH radicals are also known to undergo acid-induced oxidation of iodo,[22,23] bromo[24,25] and a number of other organic compounds.[26,27] Therefore, it is possible that acid-induced oxidation of the OH-adduct of TDGA may also take place in the present case. The transient band observed on pulse radiolysis of an O_2-saturated aqueous solution of high [TDGA] and [$HClO_4$] could be assigned to dimer radical cations of TDGA formed according to reactions (3) and (5) (Scheme 1). The dimer radical cations of alkyl sulfides absorb in the region 450–550 nm and therefore support this assignment.[1]

It has been shown[21] that deaerated aqueous solutions containing high [$HClO_4$] form a transient band with λ_{max} = 335 nm, which is assigned to ClO_4 radicals formed on reaction of H and OH radicals with ClO_4^-. This radical has very little absorption at $\lambda > 400$ nm. Therefore the 520 nm band should not be due to ClO_4 radicals. Under our present experimental conditions (O_2-saturated), H-atoms would be scavenged and the formation of ClO_4 radicals would be reduced [Fig. 1(*b*)]. In order to confirm that the transient optical absorption band [Fig. 1(*a*)] is not due to the reaction of ClO_4 radicals with TDGA, pulse-radiolysis studies were carried out on O_2-saturated aqueous $NaClO_4$ (8.7 mol dm^{-3}) containing 2.1×10^{-2} mol dm^{-3} TDGA. The transient band at 520 nm was

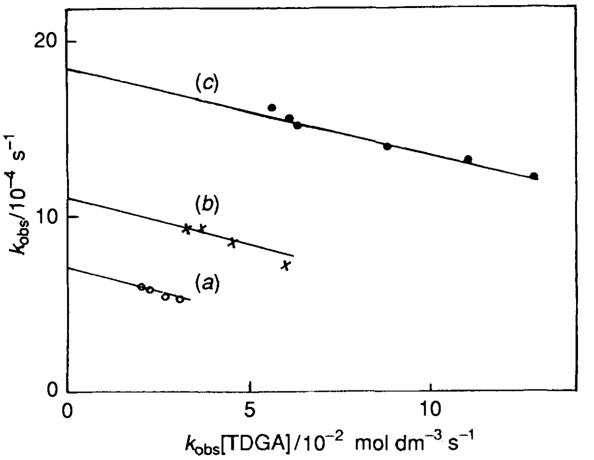


Fig. 3 Plots of first-order rate (k_{obs}) *versus* k_{obs}[TDGA] for the decay of 520 nm band at (*a*) 9.8; (*b*) 8.8; (*c*) 7.8 mol dm^{-3} $HClO_4$

not observed although appreciable absorption at 520 nm was observed when 8.7 mol dm^{-3} $HClO_4$ was used [Fig. 1(*d*)]. Therefore, 520 nm band could not be due to the reaction of ClO_4 radicals with TDGA. It has also been shown[21] that, owing to a competitive process, the formation of ClO_4 radical would be reduced in the presence of the solute. Additional evidence in support of the assignment of the 520 nm band to the dimer radical cation came when pulse radiolysis studies were carried out on H_2SO_4 systems instead of $HClO_4$. Pulse radiolysis (dose = 1.0 × 10^{17} eV cm^{-3} per pulse) of O_2-saturated aqueous solutions of TDGA (2.0 × 10^{-2} mol dm^{-3}) in H_2SO_4 (10.0 mol dm^{-3}) showed the presence of a band with λ_{max} = 520 nm. A lower value of ΔA at 520 nm, observed in the presence of 10.0 mol dm^{-3} H_2SO_4 (0.027) as compared with ΔA = 0.052 in 10 mol dm^{-3} $HClO_4$, may be due to the fact that the Hammett acidity function (H_0) is lower for H_2SO_4 (−4.89) than for $HClO_4$ (−5.79).[28] The actual [H^+] in 10 mol dm^{-3} H_2SO_4 would therefore be lower than in 10 mol dm^{-3} $HClO_4$. A small difference in dose (1.0 × 10^{17}, 1.2 × 10^{17} eV cm^{-3} per pulse) may also contribute to the lower ΔA value observed in the presence of H_2SO_4. To the best of our knowledge, the Hammett acidity function values for [$HClO_4$] > 10 mol dm^{-3} are not available in the literature,[28] therefore variations in ΔA of the 520 nm band are plotted as a function of [$HClO_4$]. One can easily see the similar qualitative features of the ΔA *versus* H_0 plot at acid concentrations < 10.0 mol dm^{-3}. The 520 nm band could not be due to $SO_4^{\cdot-}$, formed on reaction of $\cdot$OH radicals with HSO_4^- as the bimolecular rate constant for this reaction is very low (8 × 10^5 dm^3 mol^{-1} s^{-1}) and the transient species has λ_{max} = 450 nm.[29] Therefore, it can be concluded that the transient bands observed in presence of high [$HClO_4$] are due to the reaction of H^+ with the OH-adduct. At high solute concentration, dimer radical cations are formed. The increase in the intensity and lifetime of this transient band with solute concentration suggests the existence of equilibrium (5) (Scheme 1), which is expected to be shifted more and more to the left. At low solute concentration (1.0 × 10^{-4}–4.0 × 10^{-4} mol dm^{-3}), the intensity and lifetime of the broad absorption band observed at 360 nm [Fig. 1(*c*)] remained the same. The intramolecular radical cation formed on p-orbital overlap of oxidized sulfur with oxygen are reported to absorb in the region of 400 nm.[10] The strained structure of the four-membered ring, if formed, in the present case is expected to be unstable. Simple sulfur-centred radical cations from alkyl sulfides absorb in the region of 300 nm.[1] Therefore, the exact nature of the transient corresponding to this band cannot be assigned at present.

Decay Kinetics.—Fig. 1(*d*) shows that the transient optical absorption band at 520 nm, even at high solute concentration, is observed only when [$HClO_4$] > 4.0 mol dm^{-3}. Therefore, under these conditions, the OH-adduct must decay to α-thio radicals. At higher [$HClO_4$], the OH-adduct decays to the solute radical cation [step (3)], which is converted into dimer radical cation *via* equilibrium (5). The intensity of 520 nm band appears to level off when [$HClO_4$] = 11.0 mol dm^{-3}. Asmus *et al.*[30] have shown that the decay kinetics of dimer radical cations of alkyl sulfides in neutral aqueous solution is associated with the kinetics of the back reaction of equilibrium (5) and by deprotonation of the solute radical cation (4). 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}) *vs.* k_{obs}[solute], that the rate-determining step would be deprotonation if plots have same slope (k_5) but different intercepts (k_4 + deprotonation rate constant [proton acceptor]). The decay by back-reaction of the equilibrium would give same intercept (k_{-5}) and different slopes $k_5/(k_4$ + 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 as a high concentration of $HClO_4$ was employed and k_{obs}, as a function of different proton acceptor concentration could not be studied. However, plots of k_{obs} *vs.* k_{obs}[solute] at different [$HClO_4$] gave straight lines (Fig. 3) with the same slope (68 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 68 dm^3 mol^{-1} at 25 °C. From the formation rate constant (k_5) value of 1.9 × 10^9 dm^3 mol^{-1} s^{-1}, k_{-5} was calculated to be 2.4 × 10^7 s^{-1}.

It has been reported[21] that the dimer radical cation of di-isopropyl 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 2.0 × 10^5 dm^3 mol^{-1}. A much lower value observed for dimer radical cations of TDGA 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.

The intercept is found to depend on H^+ ion concentration, which may be due to the fact that, at lower [H^+], the OH-adduct would decay to α-thio radicals (2) and at high [H^+] the OH adduct would decay to solute radical cations (3). It is also possible that at higher [$HClO_4$], α-thio radicals may combine with H^+ to form the solute radical cation whereas at low [$HClO_4$], α-thio radicals may combine with oxygen and subsequently decay to stable products. The solute radical cations formed at high [$HClO_4$] are unreactive towards oxygen. It appears that the intercept is represented by a complex function, which makes it difficult to determine the deprotonation rate constant. The ratio of the intercept for two values of [$HClO_4$] is much higher than that of [$HClO_4$]. This may be due to the increased contribution of reaction (2) at lower [$HClO_4$].

Effect of Substituents.—In the case of alkyl sulfides, dimer radical cations are formed at neutral pH whereas, in the case of TDGA, very high [H^+] (> 4.0 mol dm^{-3}) is required. The electron-withdrawing power of the COOH group is very high (+2.94)[31] compared with that for the CH_3 group (0.0) and therefore the electron density on the sulfur might be reduced considerably and OH radicals may not be able to remove an electron from the sulfur at neutral pH. At high acid concentration, the transient OH-adduct can combine with H^+ to form a solute radical cation. It is also possible that the neutral α-thio radical, at high [$HClO_4$], may also combine with H^+

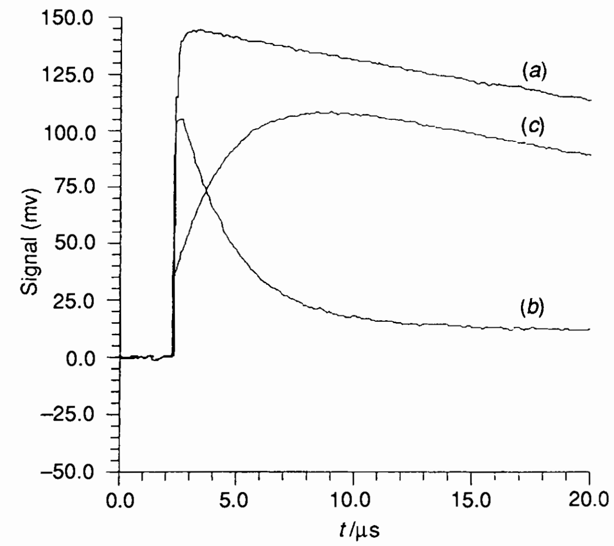


Fig. 4 Absorption–time signal obtained on pulse radiolysis of O_2-saturated solutions of TDGA (2.1×10^{-2} mol dm^{-3}, $[HClO_4] = 9.6$ mol dm^{-3}) + Br^- (4.5×10^{-4}) (*a*) in the absence of Br^- at 520 nm; (*b*) the presence of Br^- at 520 nm; (*c*) at 385 nm

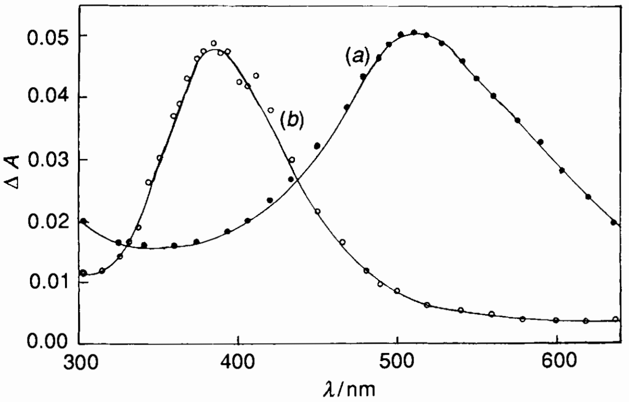


Fig. 5 Time-resolved optical absorption spectrum obtained on pulse radiolysis of O_2-saturated solutions of TDGA (2.1×10^{-2}) and Br^- (4.5×10^{-4} mol dm^{-3}) in 9.6 mol dm^{-3} $HClO_4$: (*a*) immediately after and (*b*) 10 μs after the pulse

to form solute radical cations. In the case of 3,3′-thiodipropionic acid, the electron-withdrawing power of the COOH group would be lowered owing to increased chain length and OH radicals have been observed to undergo inner-sphere electron transfer reactions even at neutral pH.[23]

The electron-withdrawing power of the CH_2OH group is +0.56.[31] The OH-radical-induced reactions with 2,2′-thiodiethanol,[14] have been shown to involve inner sphere electron transfer at pH = 2.0. The lower electron-withdrawing power of CH_2OH group would require low $[H^+]$ for inner-sphere electron transfer by •OH radicals with 2,2′-thiodiethanol. Therefore, the high $[H^+]$ required for inner-sphere electron transfer reaction by •OH radicals with TDGA must be due to the high electron-withdrawing power of the COOH group in TDGA. Additional evidence for the requirement of high acid concentration in the presence of a group of high electron-withdrawing power has also come from OH-radical-induced reactions with chloro-, iodo- and bromo-alkanes,[23–25] where it has been shown that the presence of high electron-affinity groups render acid-induced oxidation by OH radicals a more difficult process.

Oxidation Reactions.—$SO_4^{\bullet -}$ and $Cl_2^{\bullet -}$ radical anions are strong one-electron oxidants with redox potential values of 2.4 and 2.1 V, respectively.[32] These radical anions have been found to undergo one electron-transfer reactions with bimolecular rate constants of 2.7×10^9 and 4.9×10^8 dm^3 mol^{-1} s^{-1}, respectively.[13] However, the transient band at $\lambda_{max} = 520$ nm was not observed even in presence of high [TDGA] (1×10^{-2} mol dm^{-3}). This shows that radical cations of TDGA formed at neutral pH or pH 1.5 are not stable and immediately decay by deprotonation. Only in presence of high acid concentration would TDGA radical cations be stabilized to dimer radical cations at high solute concentration. Attempts to study the electron-transfer reactions between $Cl_2^{\bullet -}$ and TDGA at high $[HClO_4]$ (>4.0 mol dm^{-3}) were not successful owing to solubility limitations.

The transient decay of $Br_2^{\bullet -}$ ($\lambda = 360$ nm) remained unaffected in the presence of small concentrations of TDGA (1.0×10^{-4} mol dm^{-3}) showing that $Br_2^{\bullet -}$ ($E_o = 1.62$ V)[32] is unable to oxidize TDGA. Therefore, the redox potential value for the $(TDGA)_2^{\bullet +}$/2 TDGA couple should be between 1.62 and 2.1 V. These studies further confirm that HO_2 radicals, the oxidation potential of which is +1.0 V,[20] are not the source of the 520 nm band because even $Br_2^{\bullet -}$ (oxidation potential is 1.62 V) is unable to undergo one-electron transfer with TDGA.

The redox properties of dimer radical cations of TDGA were studied by observing the electron-transfer reactions in presence of small concentrations of I^-, Br^- and Cl^-. The transient decay of $(TDGA)_2^{\bullet +}$ remained unaffected in the presence of different concentrations of Cl^- (1.0×10^{-5}–1.0×10^{-3} mol dm^{-3}) showing that $(TDGA)_2^{\bullet +}$ is not able to transfer an electron to Cl^-. Therefore, the redox potential for the $(TDGA)_2^{\bullet +}$/2 TDGA couple should be less than that of the $Cl_2^{\bullet -}$/2 Cl^- couple = + 2.1 V *vs.* NHE.[32]

The transient decay of 520 nm band becomes faster (Fig. 4) in the presence of low concentrations of Br^- (4.5×10^{-4} mol dm^{-3}). The bimolecular rate constant for reaction (6) is

$$(TDGA)_2^{\bullet +} + Br^- \longrightarrow Br + 2\,TDGA \qquad (6)$$

determined from the slope of linear plot of k_{obs} *vs.* $[Br^-]$, and the value is 6.1×10^8 dm^3 mol^{-1} s^{-1}. Time-resolved studies reveal the formation of a new band with $\lambda_{max} = 385$ nm (Fig. 5). The bimolecular rate constant for reaction (6) was also determined from the build-up of the 385 nm band and the value is 8.9×10^8 dm^3 mol^{-1} s^{-1}. The band at $\lambda_{max} = 385$ nm does not match that of $Br_2^{\bullet -}$. This band (385 nm) could be assigned to a species of the type $S \therefore Br$, formed on reaction of Br with TDGA. Such species with Br atoms and alkyl sulfides are reported to be formed and have $\lambda_{max} = 380$–390 nm.[11]

The transient decay of dimer radical cations of TDGA (520 nm) was not affected on addition of small amounts of riboflavin, RF (1.0×10^{-4} mol dm^{-3}) showing that electron transfer is not possible from $(TDGA)_2^{\bullet +}$ to RF. Therefore, the oxidation potential of the $(TDGA)_2^{\bullet +}$/2 TDGA couple should be less than that of the $RF^{\bullet +}$/RF couple = 2.28 V *vs.* NHE.[33] These studies further support the earlier conclusion that the redox potential value of the $(TDGA)_2^{\bullet +}$/2 TDGA couple should be between 1.62 and 2.1 V.

The stability of TDGA and other solutes under conditions of high acid concentration was studied by monitoring the optical absorption of TDGA as a function of time. The solutions for pulse radiolysis experiments were always freshly prepared and used for a short time (< 5 min), whereas even up to 10 min, detectable changes were not observed. This shows the stability of the system within the experimental time limits. However, the study of electron-transfer reaction between $(TDGA)_2^{\bullet +}$ and I^- was not successful as I^- was found to be unstable in $HClO_4$.

Solvation of Ions.—It is now well established that oxidized sulfur centres have a high tendency to co-ordinate with a second sulfur or hetero atom having a free p-electron pair.[1] The radical cation of TDGA may associate with a $HClO_4$–H_2O molecule and form a three-electron bonded species with an S∴O bond.[21] The relative weakness of this bond would convert it into a much stronger S∴S bond at high solute concentration. Thefore the 520 nm band observed at high solute concentration may be due to the dimer radical cation and not due to solvation of the solute radical cation. The transient band (360 nm) observed at low solute concentration may have contributions due to solvation of the solute radical cation with $HClO$–H_2O. The transient band observed on puse radiolysis of TDGA (2.1×10^{-2} mol dm^{-3}) containing Br^- (4.5×10^{-4} dm^{-3}) is assigned to the S∴Br species. It is possible that it may be converted into the $(S\therefore BrH)^+$ radical cation at high acid concentration.[21]

Conclusions

OH radicals are able to undergo inner-sphere electron transfer reactions with TDGA under conditions of high acid concentration. Solute dimer radical cations are formed at high solute concentration. Dimer radical cations participate in a fast equilibrium with radical cations and solute. The decay of dimer radical cation is controlled by the deprotonation of the radical cation. The dimer radical cations are observed to be strong one-electron oxidants. The dimer radical cations are able to oxidize Br^- with a bimolecular rate constant of 7.5×10^8 dm^3 mol^{-1} s^{-1}.

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