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# Intra- and Inter-molecular Electron Transfer Reactions in 3,3′-Thiodipropionic Acid

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The transient optical absorption band ($\lambda_{max}$ 390 nm, $t_{\frac{1}{2}}$ 38 μs, ε 3.13 × $10^3$ dm$^3$ mol$^{-1}$ cm$^{-1}$) produced on pulse radiolysis of $N_2O$-saturated aqueous solution of 3,3′-thiodipropionic acid (pH 6.0–10.0) has been assigned to intramolecular 3-electron-bonded species formed on p-orbital overlap of sulphur and oxygen. The absolute rate constant for the reaction of OH radicals forming a 390 nm band has been determined to be 1.1 × $10^{10}$ dm$^3$ mol$^{-1}$ s$^{-1}$. An intermolecular dimer radical cation ($\lambda_{max}$ 500 nm, $t_{\frac{1}{2}}$ 17 μs, ε 7.20 × $10^3$ dm$^3$ mol$^{-1}$ cm$^{-1}$) is formed on pulse radiolysis of an $O_2$-saturated aqueous solution of 3,3′-thiodipropionic acid (pH 1.0–3.5, concentration >3.0 × $10^{-4}$ mol dm$^{-3}$). $Tl^{2+}$ and $Cl_2^-$ are able to oxidize 3,3′-thiodipropionic acid with a bimolecular rate constant of 3.8 × $10^9$ and 5.5 × $10^9$ dm$^3$ mol$^{-1}$ s$^{-1}$ respectively. The dimer radical cation of 3,3′-thiodipropionic acid $(TDPA)_2^{+\bullet}$, is able to oxidize $I^-$ to $I_2^-$ with a bimolecular rate constant of 5.5 × $10^9$ dm$^3$ mol$^{-1}$ s$^{-1}$. An equilibrium is established between dimer radical cation $(TDPA)_2^{+\bullet}$ and $Br^-$ from which the one-electron redox potential for the $TDPA^+$/TDPA couple has been determined to be 1.81 V *versus* normal hydrogen electrode (NHE).

Hydroxyl radicals are known to bring about one-electron oxidation of organic sulphides, $R_2S$, leading to the formation of sulphur-centred radical cations, $R_2S^{+\bullet}$.[1–3] The oxidized sulphur has a high tendency to be stabilized by co-ordination with a free p-electron pair of a second sulphur atom or a heteroatom (O, N, halogen) both by intra- and inter-molecular association.[4–7] Simple sulphur-centred radical cations have been observed only for some sulphides such as thioanisole, di-t-butyl sulphide, *etc.*, and can be explained as being due to resonance of the unpaired p-electron of the oxidized sulphur atom with the adjacent π-system or due to steric influences.[8–10] Evidence for the formation of sulphur-centred radical cations has come from ESR, optical spectroscopy, and pulse radiolysis studies.[1–3,11–14] The intra- and inter-molecular association of the p-electrons of oxidized sulphur with a free p-electron pair of a second sulphur or heteroatom has been represented by a three-electron bond containing two bonding σ and one antibonding σ* electron.[1] Recently, it was shown that hydroxyl radicals fail to bring about one-electron oxidation of sulphur in 2,2′-thiodiacetic acid.[15] Carboxylic groups being electrophilic in nature, lower the electron density at sulphur and prevent its oxidation by OH radicals. The OH radicals react with this compound by H-atom abstraction thus forming α-thio radicals. The lowering of electron density at sulphur in 2,2′-thiodiacetic acid may be compensated by the presence of electron-releasing $CH_2$ groups and a larger separation of carboxylic groups from sulphur in 3,3′-thiodipropionic acid.

Studies of oxidation reactions of sulphur-containing organic compounds have gained importance in helping us to understand the physicochemical processes taking place in amino acids and other biological systems which contain sulphur.[16] In this paper, the results of oxidation reactions on 3,3′-thiodipropionic acid are reported. It is demonstrated that substituents play an important role in the oxidation of sulphur and in its subsequent reactions forming intra- and inter-molecular species. These studies may also help us to understand the physicochemical changes taking place on reaction of oxidizing species with sulphur drugs, which are used for the treatment of a number of diseases.

## Experimental

3,3′-Thiodipropionic acid (TDPA), obtained from Aldrich Chemicals (purity 99%), was used without further purification. All solutions were prepared in triply distilled water. The pH of the solution was adjusted with $HClO_4$ or NaOH. Indian Oxygen IOLAR grade $N_2$, $O_2$, or $N_2O$ gases were used for purging of the solutions. The experimental details for pulse radiolysis experiments employing 50 ns pulses of 7 MeV electrons from a linear accelerator have been described earlier.[15] An aerated, aq. solution of KSCN was used to monitor the dose delivered per pulse assuming $G\varepsilon$ 21 522 dm$^3$ mol$^{-1}$ cm$^{-1}$ per 100 eV at 500 nm for the transient $(CNS)_2^-$ species.[17] The dose per pulse was ~1.0 × $10^{17}$ eV cm$^{-3}$. The conductivity changes in the solutions produced on pulse radiolysis were monitored in a dual-function cell.[18,19] The observed signal ($\Delta V$) is related to the equivalent molar conductance change ($\Lambda$) by equation (1)[19] where $V$ is the

$$\Delta V = \frac{VR_a}{10^3 K_c}\sum_n C_n \Lambda_n Z_n \qquad (1)$$

applied voltage between the two electrodes (10 V), $R_a$ the working load resistance (1 kΩ), $K_c$ the cell constant (0.177 cm$^{-1}$), $C_n$ the concentration of the $n$th charged species (mol dm$^{-3}$) formed after the pulse, and $Z_n$ the net change in its charge (1 for one-electron oxidation). 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 $O_2$-saturated aq. solution of TDPA (2.8 × $10^{-3}$ mol dm$^{-3}$, pH 6.0) immediately after the pulse. The spectrum exhibits a broad band with $\lambda_{max}$ 390 nm and a small shoulder in the region 270–310 nm. The $e_{aq.}^-$ and H-atoms would be scavenged by $O_2$. The lack of absorption spectrum in the presence of t-butyl alcohol (0.6 mol dm$^{-3}$), in the region 280–650 nm shows that $O_2^-$ and $HO_2$ formed are not reacting with TDPA to give the transient species shown in

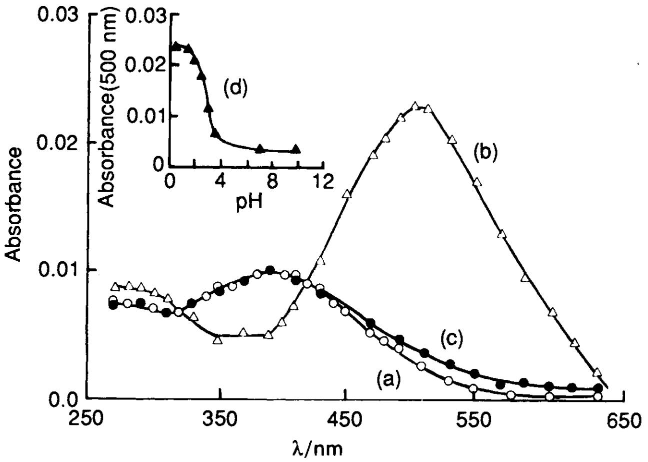


**Figure 1.** Transient optical absorption spectrum obtained on pulse radiolysis of $O_2$-saturated aq. (a) TDPA ($2.8 \times 10^{-3}$ mol dm$^{-3}$, pH 6.0); (b) TDPA ($2.8 \times 10^{-2}$ mol dm$^{-3}$, pH 1.5); (c) TDPA ($2.8 \times 10^{-4}$ mol dm$^{-3}$, pH 1.5); (d) variation of absorbance of 500 nm band of $(TDPA)_2^{+}$ formed on pulse radiolysis of $O_2$-saturated aq. TDPA ($2.8 \times 10^{-2}$ mol dm$^{-3}$) with pH.

Figure 1(a). Therefore, the transient optical absorption spectrum shown in Figure 1(a) is due to reaction of OH radicals with TDPA. The 390 nm absorption band was observed to decay by first-order kinetics with $t_{\frac{1}{2}}$ 38 μs. The rate constant for the reaction of OH radicals with TDPA, giving rise to the 390 nm band, was determined by formation kinetics. The band was observed to grow by first-order kinetics, the pseudo-first-order rate constant increasing linearly with TDPA concentration. The bimolecular rate constant, determined from the slope of pseudo-first-order rate with TDPA concentration, was $1.1 \times 10^{10}$ dm$^3$ mol$^{-1}$ s$^{-1}$. The high rate-constant value suggests that the reaction of OH radicals with TDPA is a diffusion-controlled reaction and excludes the possibility of this band due to H-atom abstraction, a process which generally is relatively slow.[20] In $N_2O$-saturated solutions, the absorbance of the 390 nm band increased by a factor of two [due to higher $G$(OH) yield], whereas the nature of the spectrum remained unchanged.

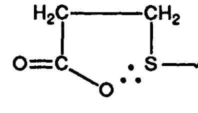
The decay of the transient absorption band at 290 nm was different from that at 390 nm, indicating that this band was due to a different species. OH Radicals are known to react with alkyl sulphides by H-atom abstraction and to form α-thio radicals absorbing in the region 280–300 nm.[4] Therefore, the small shoulder observed in the region 280–300 nm could be due to an α-thio radical. Pulse radiolysis of $N_2$-saturated aq. TDPA ($1.0 \times 10^{-3}$ mol dm$^{-3}$, t-butyl alcohol 0.2 mol dm$^{-3}$, pH 1.5) showed the formation of a transient band absorbing in the region 280–300 nm. Owing to its low absorbance, quantitative analysis of its decay and formation kinetics could not be carried out but the $\lambda_{max}$ of this band matched that formed on reaction with OH radicals. This suggests that the band is due to H-atom abstraction forming α-thio radicals.

The rate constant for the reaction of $e_{aq.}^-$ with TDPA is very low ($5.8 \times 10^7$ dm$^3$ mol$^{-1}$ s$^{-1}$)[21] as compared with the rate-constant value with $O_2$ ($2.0 \times 10^{10}$ dm$^3$ mol$^{-1}$ s$^{-1}$).[20] This suggests that the electrons would be scavenged by $O_2$ even at high solute concentrations ($1.0 \times 10^{-2}$ mol dm$^{-3}$). Therefore, the observed bands could not be due to reaction of $e_{aq.}^-$ with TDPA.

The p$K$-value of 3,3′-thiodipropionic acid is ~4,[21] therefore at pH ≥ 6.0 it would be present as $TDPA^{2-}$. On pulse radiolysis of $N_2O$-saturated aq. TDPA ($2.8 \times 10^{-3}$ mol dm$^{-3}$, pH 10.0), an increase in the conductivity of 12 mV was observed as compared with the conductivity of $N_2O$-saturated water (pH 10.0), thus suggesting that reaction (2) occurs. The increase in the equivalent conductance would be equal to

$$TDPA^{2-} + {}^{\bullet}OH \longrightarrow TDPA^{-} + OH^{-} \qquad (2)$$

$\Lambda_{OH^-} + \Lambda_{TDPA^-} - 2\Lambda_{TDPA^-}$. The equivalent conductance of $OH^-$ at 25 °C is 197 $\Omega^{-1}$ cm$^2$. The equivalent conductance of $TDPA^-$ at 25 °C is taken as 33.1 $\Omega^{-1}$ cm$^2$, being the average value of the equivalent conductance of propylsulphonate anion (37.1 $\Omega^{-1}$ cm$^2$)[22] and octylsulphonate anion (29.0 $\Omega^{-1}$ cm$^2$), since the molecular weight of TDPA is close to the average molecular weight of these ions (166) and therefore may have the same mobility. Therefore, the net change in the equivalent conductance would be 163.9 $\Omega^{-1}$ cm$^2$. The increase in the conductivity of 12 mV corresponds to the $G$-value of the 390 nm band being 4.3. This is less than $G$(OH) = 6.0 in $N_2O$-saturated solutions, indicating that ~70% of OH radicals are able to react with TDPA to form the 390 nm band. Remaining OH radicals may be reacting by H-atom abstraction to form the 290 nm band of α-thio radicals. In normal alkyl sulphides, *ca.* 80% of OH radicals are able to bring about one-electron oxidation of alkyl sulphides.[4] The slightly lower value obtained here (~70%) suggests that the extent of electron-transfer reaction by OH radicals is reduced when carboxylic groups are present in alkyl sulphides. The sulphur-centred radical cations of alkyl sulphides absorb at *ca.* 300 nm and are very short-lived species.[23] Therefore, the long-lived absorption band at 390 nm formed on reaction of OH radicals with TDPA could not be due to a simple sulphur-centred species. The possibility that this absorption band is due to a dimer radical cation, $(TDPA)_2^{+}$, is excluded since the intensity and life-time of this absorption band were observed to remain independent of solute concentration ($1.5 \times 10^{-2}$–$4.5 \times 10^{-4}$ mol dm$^{-3}$). Therefore, this band is assigned to the intramolecular 3-electron-bonded species (**1**). Such intramolecular p-orbital overlaps between S and O, S and N, S and halogen have been reported.[4,6,24–26] The position of $\lambda_{max}$ for intramolecular p-orbital overlap forming a 3-electron bond between S and N and between S and O, is in the region 380–400 nm. Therefore, the assignment of the 390 nm band, formed on reaction of OH radicals with TDPA, to S ∴ O, three-electron-bonded species is not unreasonable. On the basis that 70% reaction of OH radicals with TDPA forms the 390 nm band, the extinction coefficient for this species was estimated to be $3.13 \times 10^3$ dm$^3$ mol$^{-1}$ cm$^{-1}$.



(**1**)

The nature of the transient optical absorption spectrum and decay kinetics of the band at 390 nm were independent of both solute concentration ($1.5 \times 10^{-2}$–$4.5 \times 10^{-4}$ mol dm$^{-3}$) and pH of the solution (6.0–10.0). However, when the pH of the solution was lowered, the spectrum and the decay kinetics were observed to depend both on the pH and on solute concentration. At pH 1.5, the intensity of the 390 nm band was observed to decrease for concentrations > $4.0 \times 10^{-4}$ mol dm$^{-3}$ (Figure 2). Simultaneously, another band appeared at 500 nm. Figure 1(b) shows the transient optical absorption spectrum obtained on pulse radiolysis of $O_2$-saturated aq. TDPA ($2.8 \times 10^{-2}$ mol dm$^{-3}$, pH 1.5). The transient band at 500 nm was observed to decay by first-order kinetics with $t_{\frac{1}{2}}$ 17 μs. The intensity and the life-time of the 500 nm band was observed to depend on [TDPA]. The band was formed at the expense of that at 390 nm. At pH 1.5, OH radicals would react with TDPA forming $TDPA^{+}$, equa-

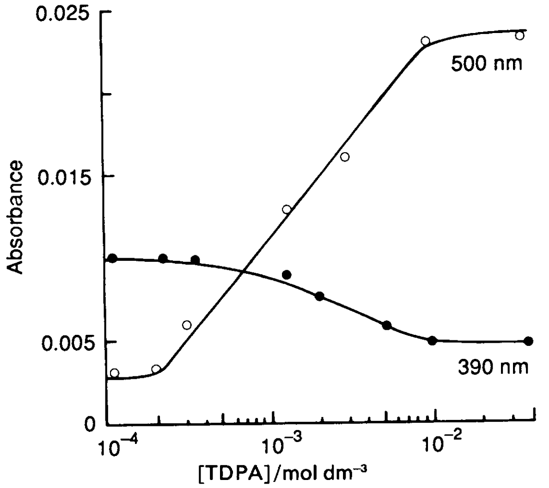


**Figure 2.** Variation in the absorbance of transient bands formed on pulse radiolysis of $\mathrm{O_2}$-saturated aq. solutions (pH 1.5) at different concentrations of TDPA.

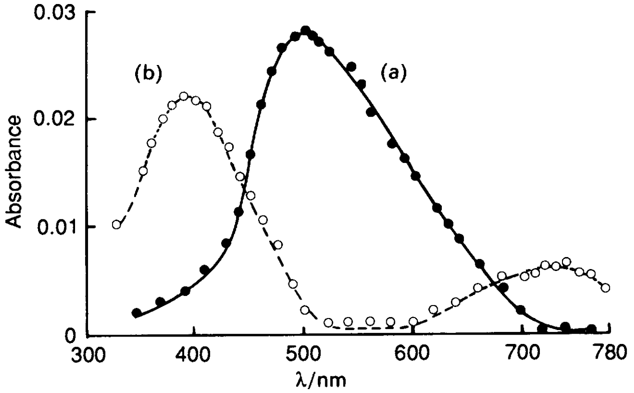


**Figure 3.** Transient optical absorption spectrum on pulse radiolysis of $\mathrm{O_2}$-saturated aq. (pH 1.5) TDPA ($2.8 \times 10^{-2}$ mol dm$^{-3}$) and $\mathrm{I^-}$ ($9.0 \times 10^{-5}$ mol dm$^{-3}$) (a) immediately; (b) 7 μs after the pulse.

tion (3), this product would be converted into $(\mathrm{TDPA})_2^{+}$ at high

$$\mathrm{TDPA} + {}^{\cdot}\mathrm{OH} \longrightarrow \mathrm{TDPA}^{+} + \mathrm{OH}^{-} \qquad (3)$$

solute concentration. Therefore, the 500 nm band is assigned to dimer radical cation $(\mathrm{TDPA})_2^{+}$. The dimer radical cations of alkyl sulphides are known to absorb in the region 450–600 nm.[27] Figure 1(c) shows the transient optical absorption spectrum obtained on pulse radiolysis of $\mathrm{O_2}$-saturated aq. TDPA ($2.8 \times 10^{-4}$ mol dm$^{-3}$, pH 1.5). This band is assigned to the intramolecular 3-electron-bonded radical cation formed on p-orbital overlap between S and O. Figure 1(d) shows the variation in the absorbance of the 500 nm band formed on pulse radiolysis of $\mathrm{O_2}$-saturated aq. TDPA ($2.8 \times 10^{-2}$ mol dm$^{-3}$) as a function of pH. The inflexion point is observed at pH 3.0. These studies suggest that dimer radical species are formed at pH $< 3.0$ and TDPA concentration $> 3.0 \times 10^{-4}$ mol dm$^{-3}$. The intramolecular radical species is formed at low solute concentrations, $< 3.0 \times 10^{-4}$ mol dm$^{-3}$, and when the pH is $< 3.0$.

The conductivity studies could not be carried out at pH $< 3.0$ due to inherent limitations.[19] Therefore, direct estimation of yield and extinction coefficient for the dimer radical cation was not possible. The 500 nm band is supplementary to the 390 nm band. At high solute concentrations, the 390 nm band is completely converted into the 500 nm band. Taking the yield of the 500 nm band compound to be equal to that of the 390 nm band compound, the extinction coefficient of the 500 nm band was estimated to be $7.20 \times 10^{3}$ dm$^{3}$ mol$^{-1}$ cm$^{-1}$.

*Oxidation of TDPA by Specific One-electron Oxidants*.—The oxidation of TDPA by various specific one-electron oxidants was studied in order to estimate the redox potential of the $\mathrm{TDPA^{+}/TDPA}$ couple and the redox properties of $(\mathrm{TDPA})_2^{+}$. The decay of $\mathrm{I_2^{-}}$ formed on pulse radiolysis of $\mathrm{N_2O}$-saturated aq. $\mathrm{I^-}$ ($2.0 \times 10^{-2}$ mol dm$^{-3}$, pH 7.0) was not affected by the presence of TDPA ($6.0 \times 10^{-4}$ mol dm$^{-3}$), indicating that TDPA could not be oxidized by $\mathrm{I_2^{-}}$. Therefore the redox potential of the $\mathrm{TDPA^{+}/TDPA}$ couple should be $> 1.03$ V *versus* NHE.[28,29] On the other hand, the decay of $(\mathrm{TDPA})_2^{+}$ was affected by the presence of $\mathrm{I^-}$, indicating the oxidation of $\mathrm{I^-}$ to $\mathrm{I_2^{-}}$ [equation (4)]. The decay of $(\mathrm{TDPA})_2^{+}$, formed on pulse

$$(\mathrm{TDPA})_2^{+} + 2\mathrm{I}^{-} \longrightarrow \mathrm{I_2^{-}} + 2\mathrm{TDPA} \qquad (4)$$

radiolysis of $\mathrm{O_2}$-saturated aq. TDPA ($2.8 \times 10^{-2}$ mol dm$^{-3}$, pH 1.5; $\lambda_{\max}$ 500 nm) was studied as a function of $[\mathrm{I^-}]$ ($1.5 \times 10^{-5}$–$1.5 \times 10^{-4}$ mol dm$^{-3}$). The decay was faster and of first order. The bimolecular rate constant was determined from the slope of the linear plot of pseudo-first-order rate constant with $[\mathrm{I^-}]$ and was $5.4 \times 10^{9}$ dm$^{3}$ mol$^{-1}$ s$^{-1}$.

The time-resolved studies on pulse radiolysis of $\mathrm{O_2}$-saturated aq. TDPA ($2.8 \times 10^{-2}$ mol dm$^{-3}$, pH 1.5) containing $\mathrm{I^-}$ ($9.0 \times 10^{-5}$ mol dm$^{-3}$) showed two new bands at 385 and 740 nm (Figure 3). These bands are characteristic of $\mathrm{I_2^{-}}$ formed on oxidation of $\mathrm{I^-}$ by $(\mathrm{TDPA})_2^{+}$. The bimolecular rate constant for the oxidation of $\mathrm{I^-}$ by $(\mathrm{TDPA})_2^{+}$ was also determined from the formation kinetics of the 385 and 740 nm bands, and the values are $5.5 \times 10^{9}$ and $6.1 \times 10^{9}$ dm$^{3}$ mol$^{-1}$ s$^{-1}$, respectively. These values are close to that determined from the decay of $(\mathrm{TDPA})_2^{+}$.

$\mathrm{TDPA^{+}}$ formed on pulse radiolysis of $\mathrm{O_2}$-saturated aq. TDPA ($2.8 \times 10^{-4}$ mol dm$^{-3}$, pH 1.5) was also observed to be an equally strong oxidant and to oxidize $\mathrm{I^-}$ to $\mathrm{I_2^{-}}$ with a bimolecular rate constant of $5.9 \times 10^{9}$ dm$^{3}$ mol$^{-1}$ s$^{-1}$ as determined from the growth of the $\mathrm{I_2^{-}}$ band at 740 nm. Owing to the close proximity of the transient bands of $\mathrm{TDPA^{+}}$ (390 nm) and that of $\mathrm{I_2^{-}}$ (385 nm), our studies could not be carried out by following the decay of the 390 nm band and the growth of the 385 band.

$\mathrm{Cl_2^{-}}$ formed on pulse radiolysis of $\mathrm{O_2}$-saturated aq. $\mathrm{Cl^-}$ ($3.5 \times 10^{-2}$ mol dm$^{-3}$, pH 1.5) was observed to oxidize TDPA with a bimolecular rate constant of $5.5 \times 10^{9}$ dm$^{3}$ mol$^{-1}$ s$^{-1}$. Similarly, $\mathrm{Tl^{2+}}$ formed on pulse radiolysis of $\mathrm{O_2}$-saturated aq. $\mathrm{Tl^{+}}$ ($2.0 \times 10^{-3}$ mol dm$^{-3}$, pH 1.5) also oxidized TDPA, with a bimolecular rate constant of $3.8 \times 10^{9}$ dm$^{3}$ mol$^{-1}$ s$^{-1}$. In these studies, the characteristic absorption band of $\mathrm{TDPA^{+}}$ was observed at 390 nm. $\mathrm{N_3^{\cdot}}$ formed on pulse radiolysis of $\mathrm{N_2O}$-saturated $\mathrm{N_3^{-}}$ ($4.5 \times 10^{-3}$ mol dm$^{-3}$, pH 7.0) failed to oxidize TDPA. These studies suggest that the redox potential of the $\mathrm{TDPA^{+}/TDPA}$ couple lies in the range 1.3–1.9 V *versus* NHE.

The decay of $(\mathrm{TDPA})_2^{+}$, formed on pulse radiolysis of $\mathrm{O_2}$-saturated aq. TDPA ($2.8 \times 10^{-2}$ mol dm$^{-3}$, pH 1.5), was observed to accelerate in the presence of $\mathrm{Br^-}$ $4.6 \times 10^{-4}$ mol dm$^{-3}$. The decay of the initial portion of the curve was of first order and depended on $[\mathrm{Br^-}]$. The plot of pseudo-first-order rate constant, determined from the exponential part of the $(\mathrm{TDPA})_2^{+}$ decay, as a function of $[\mathrm{Br^-}]$ does not pass through the origin (Figure 4). It was also observed that the absorption did not decay to its baseline. Even the decay of $\mathrm{Br_2^{-}}$ formed on pulse radiolysis of $\mathrm{N_2O}$-saturated aq. $\mathrm{Br^-}$ ($4.5 \times 10^{-2}$ mol dm$^{-3}$, pH 7.0) was affected by $6.5 \times 10^{-5}$ mol dm$^{-3}$ TDPA. Looking at these results, it appears that oxidation of $\mathrm{Br^-}$ by $(\mathrm{TDPA})_2^{+}$ is a reversible process [equation (5)]. The equilibrium

$$(\mathrm{TDPA})_2^{+} + 2\mathrm{Br}^{-} \rightleftharpoons \mathrm{Br_2^{-}} + 2\mathrm{TDPA} \qquad (5)$$

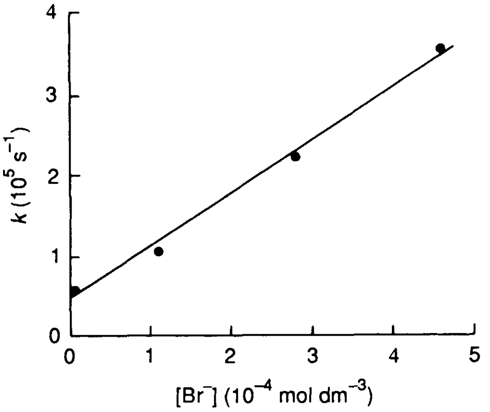


**Figure 4.** Variation of pseudo-first-order rate constant with $[Br^-]$.

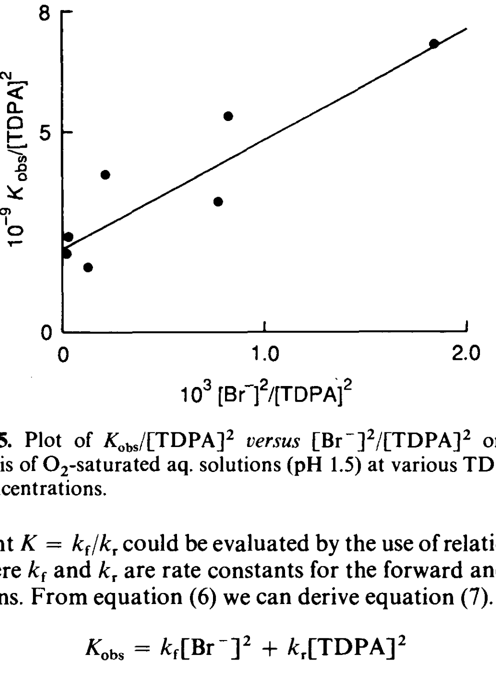


**Figure 5.** Plot of $K_{obs}/[TDPA]^2$ *versus* $[Br^-]^2/[TDPA]^2$ on pulse radiolysis of $O_2$-saturated aq. solutions (pH 1.5) at various TDPA and $Br^-$ concentrations.

constant $K = k_f/k_r$ could be evaluated by the use of relationship (6) where $k_f$ and $k_r$ are rate constants for the forward and back reactions. From equation (6) we can derive equation (7). A plot

$$K_{obs} = k_f[Br^-]^2 + k_r[TDPA]^2 \qquad (6)$$

$$\frac{K_{obs}}{[TDPA]^2} = k_f\frac{[Br^-]^2}{[TDPA]^2} + k_r \qquad (7)$$

of $K_{obs}/[TDPA]^2$ *versus* $[Br^-]^2/[TDPA^2$ (Figure 5) gives a straight line. The rate constants $k_f$ and $k_r$ are determined from the slope and intercept, respectively. The value of the equilibrium constant was determined to be $1.28 \times 10^3$.

The difference in the redox potentials of $E^\circ_{TDPA^+/TDPA}$ and $E^\circ_{Br_2^-/2Br^-}$ couple is equal to the value of $RT/F \ln K = 0.059 \log K$. Hence equation (8) holds. In this way, the redox potential

$$\begin{aligned} E^\circ_{TDPA^+/TDPA} &= E^\circ_{Br_2^-/2Br^-} + 0.059 \log K \\ &\doteq 1.63 + 0.059 \log K \end{aligned} \qquad (8)$$

of the $TDPA^+/TDPA$ couple was determined to be 1.81 V *versus* NHE. The redox potential of the $MeSSMe^+/MeSSMe$ couple has been determined to be 1.39 V *versus* NHE.[29] From the oxidation of $Me_2S_2$ by $Me_2S^+$, the redox potential of the $Me_2S^+/Me_2S$ couple was suggested to be $>1.4$ V *versus* NHE.[29] Since the extent of oxidation of TDPA by OH radicals (*ca.* 70%) is slightly lower than that of $Me_2S$ (*ca.* 80%), due to presence of carboxylic groups, the redox potential of the $TDPA^+/TDPA$ couple may be slightly higher than that of the $(Me_2S^+/(Me)_2S$ couple.

*Conclusions.*—Hydroxyl radicals are able to bring about one-electron oxidation of 3,3′-thiodipropionic acid. An intramolecular three-electron-bond is formed between the sulphur and oxygen atoms. The intermolecular dimer radical cation is formed at low pH and high solute concentration. The redox potential for the $TDPA^+/TDPA$ couple has been determined to be 1.81 V *versus* NHE.

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