

One-electron reduction of thionine studied by pulse radiolysis

S N GUHA, P N MOORTHY*, K KISHORE, D B NAIK and
K N RAO

Chemistry Division, Bhabha Atomic Research Centre, Trombay, Bombay 400 085, India

MS received 25 May 1987; revised 26 August 1987

Abstract. One-electron reduction of thionine has been studied by using the technique of nanosecond pulse radiolysis and kinetic spectrophotometry. H , e_{aq}^- as well as radicals derived from methanol, ethanol, isopropanol, THF, dioxane and *t*-butanol by H atom abstraction were used as reductants. The rate constants for the transfer of electrons from these radicals to thionine were directly determined from the pseudo first-order formation rates of the product, semithionine and the one-electron reduction potential of thionine estimated. The absorption spectrum of semithionine in its different conjugate acid-base forms was found to be in agreement with previously reported spectra and the decay of the species was second order. By monitoring transient absorbance changes as a function of pH, two pK_a values were observed and, based on the effect of ionic strength on the second-order decay constants of the species were assigned to the equilibria described.

Keywords. One-electron reduction of thionine; pulse radiolysis; kinetic spectrophotometry; semithionine; thionine.

1. Introduction

Thionine and other thiazine dyes have been used in photogalvanic cells to convert light to electrical energy (Rabinowitch 1940; Kamat *et al* 1979). Because of this, many studies have been reported in the past concerning its photoreduction by ferrous ions and other reducing agents, both by steady-state and flash-photolytic techniques (Ainsworth 1960; Hatchard and Parker 1961; Fischer *et al* 1970; Bonneau and Pereyre 1975; Guha *et al* 1979). The intermediate product of photoreduction has been identified as the short-lived species semithionine, which in certain pH ranges and in surfactant-free solutions has been shown to form a complex with Fe^{2+} ions (Guha *et al* 1985). In order to study the spectra and kinetics of formation of this species in aqueous solutions in the absence of complex forming ions, we have employed the technique of pulse radiolysis and kinetic spectrometry (Hunt and Thomas 1967). In this technique, a dilute aqueous solution containing the compound to be studied is subjected to a short duration (a few nanoseconds) burst of energetic electrons which by primary interaction with the solvent water generate strongly reducing species, viz. hydrated electrons (e_{aq}^-) and hydrogen atoms (H), and oxidizing species, viz. hydroxyl radicals (OH). By the choice of suitable reagents (see §2) it is possible to investigate exclusively the reactions of the reducing or oxidizing species. We have studied aqueous solutions of thionine under the former conditions and the results of this study are reported here.

* To whom all correspondence should be addressed.

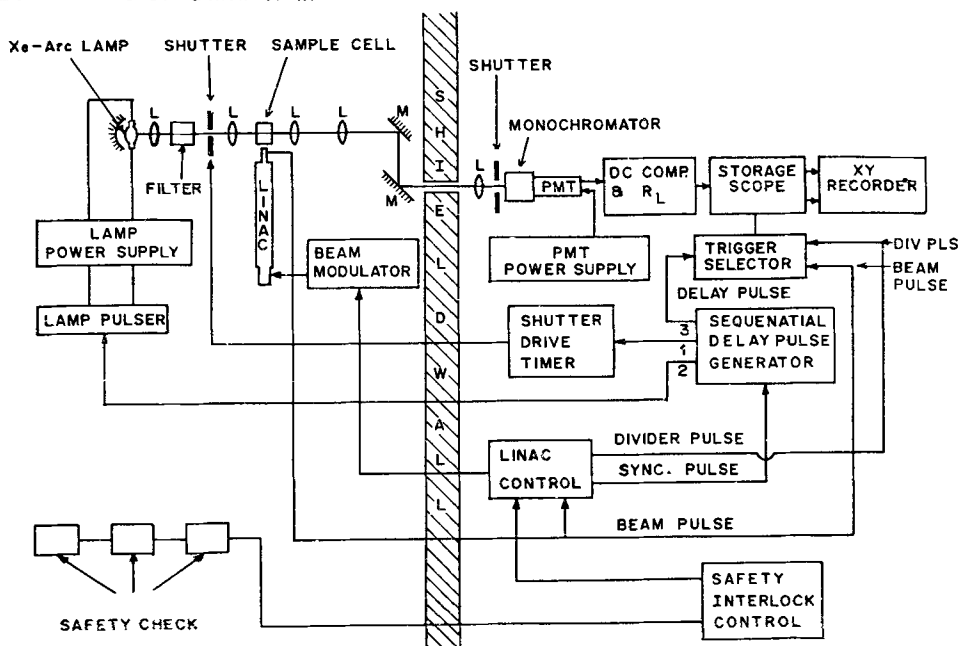


Figure 1. Schematic diagram of pulse radiolysis set-up.

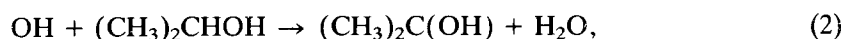
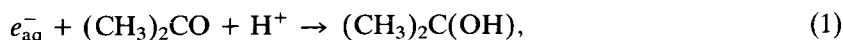
2. Experimental

The pulse radiolysis apparatus is shown schematically in figure 1. It consists of an electron linear accelerator (Viritech Ltd., England) capable of giving single shots of 5–25 ns, 7 MeV electron pulses at peak current of ~ 1 A. The pulse irradiates the sample contained in a 1 cm \times 1 cm 'Suprasil' square cuvette kept at a distance of ~ 12 cm. from the electron beam window, where the beam diameter is ~ 1 cm. The transient changes in the absorbance of the solution caused by the electron beam pulse are monitored with the help of a collimated light beam from either a steady 250 Watts tungsten halogen lamp (for slow signals) or a pulsed 450 W Xenon arc lamp (for fast signals). The accelerator, sample cell and monitoring light source are housed in a shielded cave and the monitoring light beam, after passing through the sample cell is directed to the detection room through a tunnel in the shield wall* with the help of fused silica lenses and front aluminium coated mirrors. The light beam is finally focussed on to the entrance slit of a grating monochromator (Kratos Analytical Instruments Inc., USA, model GMA 252) over the exit slit of which is fixed a photomultiplier tube (PMT-Hamamatsu TV Co., Japan, Model R-955) with uniform spectral response in the region 185–900 nm. The voltage to the PMT is supplied from a high voltage power supply (Electronics Corporation of India, Model HV 4800 D). The PMT voltage divider network is similar to the one described by Hunt and Thomas (1967) for nanosecond response. The output signal from the PMT is fed through a manual DC offset circuit to the Y input of a 100 MHz storage scope (Iwatsu Electric Co., Japan, Model TS 8123). An electrically operated shutter (Vincent Associates, USA, Model 225-L) interposed

* 1.5 m thick concrete.

between the monitoring light source and the sample cell is normally kept closed to prevent the photolysis of the sample and can be opened for a duration of ~ 50 ms covering the electron beam pulse period. Within this time period, the intensity of the Xenon arc lamp light output is increased 20–100 times for a duration of ~ 5 ms to achieve improved S/N ratio. Synchronisation of the electron beam pulse with the shutter opening, pulsing of the arc lamp and triggering of the base line of the storage scope is accomplished with an indigenously developed sequential delay pulse generator. Appropriate cut-off filters are interposed before the monochromator entrance slit to eliminate artifacts from second-order diffracted light of shorter wavelengths.

Thionine used was Fluka 'Puriss' grade and was further purified as described by Guha *et al* (1982). Other chemicals were all BDH 'Analar', S Merck 'GR' or J T Baker 'Analysed' grade and were used without further purification. Solutions were prepared in triply distilled water. For pH adjustments H_2SO_4 , Na_2HPO_4 , KH_2PO_4 , $Na_2B_4O_7 \cdot 10H_2O$ and $NaOH$ were used in suitable combinations, keeping the total ionic strength equivalent to that of ~ 0.04 mol dm^{-3} 1:1 electrolyte. Indian Oxygen Ltd. 'IOLAR' grade N_2 and Matheson 'Research' grade N_2O were used for purging of solutions. For measuring the electron pulse dose, 0.05 mol dm^{-3} aerated KCNS solution was used, taking $G\epsilon$, for the $(CNS)_2^-$ species generated in this system, to be 21522 $dm^3 mol^{-1} cm^{-1}$ per 100 eV at 500 nm (Fielden 1984). Doses generally used were 1.5×10^{17} eV cm^{-3} per pulse. For extinction coefficient measurements a lower dose (1/5 th of the above) was employed. For studying reactions of e_{aq}^- at pH 6, the solutions contained 0.1 mol dm^{-3} *t*-butanol to scavenge OH radicals, the reaction products of which were first shown to be unreactive towards thionine. Reactions of H atoms were studied in acidic solutions (pH ~ 3) where the e_{aq}^- are quantitatively converted to H by reaction with H^+ ions within the electron pulse duration; 0.1 mol dm^{-3} *t*-butanol served as OH scavenger. A matrix containing 1.0 mol dm^{-3} isopropanol and 0.1 mol dm^{-3} acetone served to convert all of e_{aq}^- , H and OH to reducing $(CH_3)_2C(OH)$ radicals over the entire pH range from ~ 0.1 to 13. This is possible because at pH 5 where H^+ concentration is too low to convert e_{aq}^- to H and then to $(CH_3)_2C(OH)$, acetone reacts with e_{aq}^- to give the same species within the electron pulse duration:

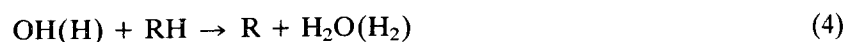


$$(k_1 = 5.9 \times 10^9 \text{ and } k_2 = 2 \times 10^9 \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}).$$

Radicals of other organic compounds (viz. ethanol, methanol, glucose, dioxane and tetrahydro furan) were generated in N_2O saturated solutions at pH 6 via reactions 3 and 4.



$$(k_3 = 8.7 \times 10^9 \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}),$$



$$(k_4 = 10^9 \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1} \text{ for the compounds used}).$$

In calculating the extinction coefficients of the semithionine species produced by pulse radiolytic reduction, the fraction of H atoms reacting with thionine by processes other than electron transfer was taken as 11% (Solar *et al* 1982). Corrections were also made to account for the fraction of e_{aq}^- , H and other radicals being lost by mutual reaction, and for the percentage of non-reducing $\text{CH}_2\text{CH}(\text{OH})\text{CH}_3$ radicals formed in (4) in the acetone-isopropanol system. G -values for e_{aq}^- , H and OH as reported by Draganic and Draganic (1971) were used.

3. Results and discussion

The well-known absorption band of the hydrated electron with λ_{max} at 720 nm (Keene 1964), which decays predominantly by second-order kinetics in an electron beam pulsed deoxygenated $10^{-1} \text{ mol dm}^{-3}$ *t*-butanol matrix (pH 9.6), was found to decay much faster and by first-order kinetics in the presence of thionine, the rate constant depending on thionine concentration, thus indicating the high reactivity of this compound with e_{aq}^- . The bimolecular rate constant for this reaction evaluated from such pseudo first-order decay traces was $2.6 \times 10^{10} \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$. On monitoring transient absorbance over the entire spectral region barring that covering the absorption bands of thionine itself, a well-defined spectrum with absorption maximum at 400 nm was observed. Typical signals showing the disappearance of e_{aq}^- at 720 nm and formation of product species at 400 nm are given in figure 2. The build-up of absorbance after the electron pulse at this wavelength occurred over the same time period as the decay of the hydrated electron and was pseudo first order with respect to thionine concentration. The bimolecular rate constant ($k_{e_{aq}^-} + \text{thionine}$) evaluated from such build-up traces was $3 \times 10^{10} \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$. This value is $\sim 15\%$ higher than the one obtained by following e_{aq}^- decay because of the error introduced by the subsequent decay of the species. However, even the latter value is much higher (nearly twice) than the

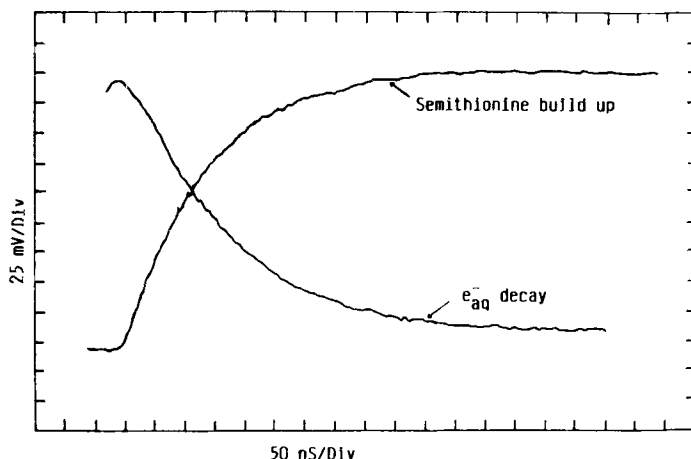
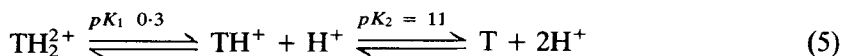


Figure 2. Decay of hydrated electron absorption (720 nm) and build up of semithionine absorption (400 nm) in aqueous solution at pH 9.6 (0.1 mol dm^{-3} *t*-butanol, $2 \times 10^{-4} \text{ mol dm}^{-3}$ TH^+ , O_2 -free system).

values reported for the rate constant of this reaction by Solar *et al* (1982): 1.1 and $1.4 \times 10^{10} \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$, respectively, at pH 7.6 and 12.6. The presence of impurities in the thionine employed could be causing the lower values, for we found that unpurified thionine gave $1.9 \times 10^{10} \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$ for this rate constant at pH 7.6. It is also to be noted that thionine itself is rather unstable in highly alkaline solutions. Its pK_a values are ~ 0.3 and 11 (Kramer and Maute 1972), the conjugate acid-base forms involved being:



Because of its instability in the highly alkaline medium, the reactivity of the fully deprotonated form (T) could not be determined. But at pH 11 where both TH^+ and T forms are present in equimolar concentrations the observed rate constant was, within limits of experimental error, the same as that at pH 9.6 where thionine is predominantly present in the TH^+ form. It is therefore to be inferred that the two forms TH^+ and T have almost identical reactivity with e_{aq}^- . Further the disappearance of the hydrated electron (monitored at 720 nm) and formation of a transient species absorbing at 400 nm are both due to the same process, viz., the one-electron reduction of thionine by e_{aq}^- , and therefore the species absorbing at 400 nm must be the one-electron reduction product, semithionine. This inference is supported by the observation that the transient absorption at 400 nm was absent if an oxygen-saturated solution was pulsed under otherwise identical conditions. O_2 has a very high reactivity towards e_{aq}^- ($k_{\text{aq}}^- + \text{O}_2 = 2 \times 10^{10} \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$) and in an oxygen-saturated solution where $[\text{O}_2] \approx 10^{-3} \text{ mol dm}^{-3}$, the e_{aq}^- reacts exclusively with O_2 and not with the thionine present at a concentration of $< 10^{-4} \text{ mol dm}^{-3}$. This observation also shows that O_2^- the product of e_{aq}^- scavenging by O_2 is not capable of reducing thionine.

The complete absorption spectrum of the transient species at this pH (figure 3a) was recorded in electron beam pulsed oxygen-free $8 \times 10^{-5} \text{ mol dm}^{-3}$ thionine solution containing 1.0 mol dm^{-3} isopropanol and 0.1 mol dm^{-3} acetone. A well-defined absorption band with λ_{max} at 400 nm and another merging into the thionine absorption band at 630 nm were observed. The absorbances at these wavelengths were found to build up to a maximum at $\sim 3 \mu\text{s}$ after the electron pulse, and decayed by second-order kinetics on a time scale similar to the 400 nm absorption in the *t*-butanol matrix referred to earlier. From this it is inferred that the species formed in the two matrices are the same. Further, for the same dose, the absorbance in the isopropanol acetone matrix where the e_{aq}^- , H and OH are almost quantitatively converted to the reducing $(\text{CH}_3)_2\text{C}(\text{OH})$ radicals, and $G (= 5.95)$, was almost double that found in the *t*-butanol matrix $G_{e_{\text{aq}}^-} (= 2.63)$. These observations suggest that thionine undergoes one-electron reduction by $(\text{CH}_3)_2\text{C}(\text{OH})$ radicals to give semithionine. As expected on this basis, in O_2 -saturated solutions where the $(\text{CH}_3)_2\text{C}(\text{OH})$ radicals are converted to the non-reducing peroxy radicals, the transient spectrum of semithionine was not observed on electron beam pulsing. At lower pH values the 630 nm band was appreciably red-shifted (to 770 nm). Monitoring absorbance changes at 770 nm as a function of pH in electron beam pulsed oxygen-free 1 mol dm^{-3} isopropanol, 0.1 mol dm^{-3} acetone matrix containing $5 \times 10^{-5} \text{ mol dm}^{-3}$ thionine revealed two inflexion points at pH 1.8 and 8.1 (figure 4). Therefore, three conjugate acid-base

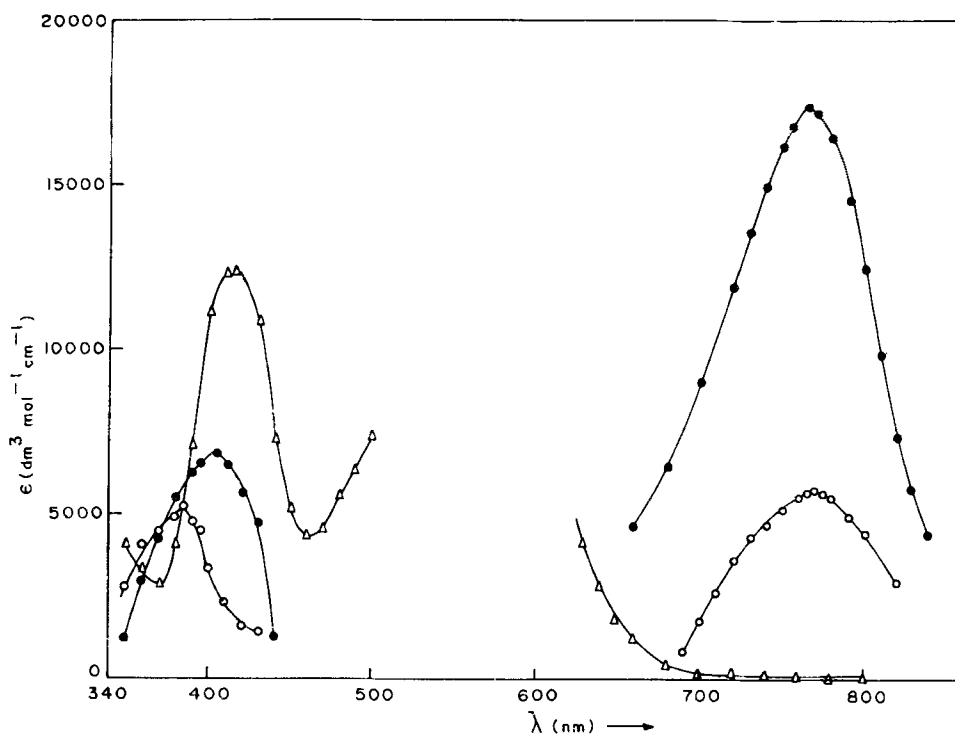
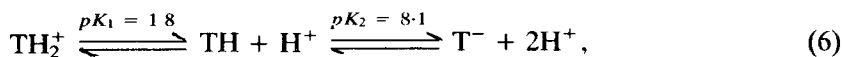
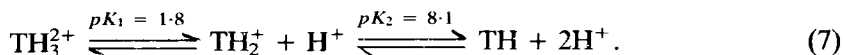


Figure 3. Absorption spectrum of transient semithionine species in e -pulse irradiated aqueous solutions: pH 0.25 (○), 6 (●) and 9.6 (△).

forms of semithionine are indicated. If we represent the neutral thionine molecule as T, the above equilibria for the one-electron reduction product semithionine could be one of the following.



or



The spectra of the three forms as monitored at $\sim 3 \mu\text{s}$ after the electron pulse in matrices of 1 mol dm^{-3} isopropanol and 0.1 mol dm^{-3} acetone, pH 0.25, 6.0 and 9.6 are given in figure 3, and values of λ_{max} and ϵ_{max} of semithionine at these pH values are given in table 1. It may be noted that these spectra agree with those reported by Solar *et al* (1982); however, our detection system was not sensitive enough to enable us to observe the peaks in the region $\lambda < 300 \text{ nm}$. Also the gap in the region of $\lambda \sim 480\text{--}620 \text{ nm}$ is due to strong absorption by thionine itself. It is seen that all the forms are characterized by a band in the 400 nm region with small shifts in the λ_{max} . The other band in the longer wavelength region has λ_{max} around 770 nm at pH values 0.25 and 6.0 but at 9.6 it is appreciably blue-shifted and merges with the absorption band of thionine itself. The spectrum at pH 13 was

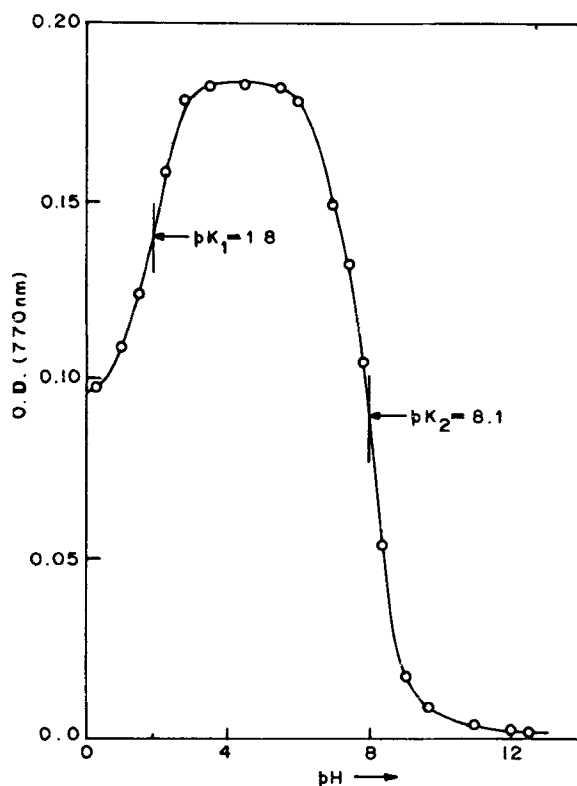


Figure 4. pK of semithionine species.

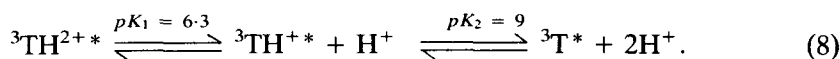
Table 1. Absorption maxima, extinction coefficients and decay kinetics of the semithionine radical.

pH	Protonated form of semithionine	λ_{max} (nm)	ϵ_{max} ($dm^3 mol^{-1} cm^{-1}$)	$2k$ ($dm^3 mol^{-1} s^{-1}$)*	
				No added salt	In the presence of added salt
0.25	TH_3^{2+}	385	5,220	2.1×10^9	—
		770	5,785		
6.0	TH_2^+	400	6,826	2.1×10^9	3.0×10^9 (0.1M Na_2SO_4)
		770	17,200		3.5×10^9 (0.1M $NaClO_4$)
9.6	TH	400	12,380	1.8×10^9	1.8×10^9 (0.1M Na_2SO_4)
		630	—		

* Second-order rate constant for the dismutation of semithionine

identical to the one at pH 9.6, except that the longer wavelength band was better defined, as at this pH the corresponding spectral band of thionine is also appreciably blue-shifted and hence does not interfere with that of the product species; hence a clear maximum at 630 nm was evident.

In order to distinguish between the two protolytic equilibria, (6) and (7), for semithionine, the effect of ionic strength on the second-order decay constant of the species present at pH 9.6 and 6 was investigated. The results (table 1) clearly indicate that the species at pH 9.6 is neutral whereas the one at pH 6 is charged. The increase in rate constant at high ionic strength at pH 6 is close to that expected for reaction between two singly-charged species. Hence the scheme represented by (7) must be correct. A similar conclusion has been arrived at by Bonneau *et al* (1968) in their work on the flash-photolytic reduction of thionine using phenylene diamine as photoreductant. In this connection it may be noted that although Solar *et al* (1982) have reported $pK_1 = 1.8$ for semithionine they have not reported the second pK value. An earlier report (Kramer and Maute 1972) of $pK_2 = 8.1$ for this species as due to the equilibrium between TH_2^+ and TH forms was based on photoreduction of thionine in the presence of organic reducing agents. In such experiments the initially formed thionine triplet which has two pK values (Kramer and Maute 1972) corresponding to the equilibria:



accepts an electron from the organic compound to give semithionine. Inference of a $pK_2 = 8.1$ for the product semithionine from such experiments is somewhat ambiguous in view of the two pK values of the thionine triplet in close proximity; also the organic reductant used, viz. EDTA, has pK values in the same region further complicating the interpretation. On the other hand, the observation of pK_1 and pK_2 in the present pulse radiolysis experiments is not subject to such limitations as the reducing species $(\text{CH}_3)_2\text{COH}$ used has a $pK = 12$ (Moorthy and Hayon 1974). Besides, the assignment of the different conjugate acid base forms of semithionine on the basis of ionic strength effect on the second-order decay constants of these different forms is also unambiguous.

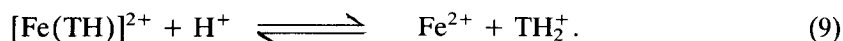
3.1 Reaction with H-atoms

In the oxygen-free 0.1 mol dm^{-3} *t*-butanol matrix at $\text{pH} \sim 3$ where the e_{aq}^- are quantitatively converted to H atoms by reaction with H^+ ions and the OH radicals are scavenged by *t*-butanol, the transient species formed by reaction of H atoms was found to be identical to the one produced by reduction with $(\text{CH}_3)_2\text{C}(\text{OH})$ radicals at the same pH with respect to both λ_{max} and decay kinetics. This suggests that the H atom preferentially acts as a one-electron reductant rather than add on to the heteroaromatic ring of thionine. By computer analysis of their pulse radiolysis data Solar *et al* (1982) have indirectly inferred that only about 11% of H atoms add on to the ring and the rest bring about reduction of thionine to semithionine. From the pseudo first order rate constant for build-up of transient semithionine at 770 nm in the oxygen free 0.1 mol dm^{-3} *t*-butanol matrix ($\text{pH} \sim 3$)

containing different concentrations of thionine we have deduced the bimolecular rate constant for its reaction with H atoms to be $9.9 \times 10^9 \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$ which may be compared with the value of $8.5 \times 10^9 \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$ reported by Solar *et al* (1982). Again our value is higher than the latter for the same reason as discussed for the e_{aq}^- reaction rate constant.

3.2 Comparison with the results of photoreduction studies

In our earlier studies on the photoreduction of thionine by ferrous ions (Guha *et al* 1979, 1985) it was observed that the spectrum of the product transient semithionine species was characterised by a fine structure in the longer wavelength band. This fine structure became predominant at high Fe^{2+} concentration and at higher pH, say 3.5 and was attributed to the complexed semithionine species and an equilibrium of the type:



In the present study, where the system does not contain Fe^{2+} ions, it is significant that the spectra are devoid of fine structure, thus indirectly supporting the earlier conclusions.

3.3 Reactions of thionine with other reducing radicals

H and OH radicals formed in electron pulsed aqueous solutions react very fast with organic molecules such as ethanol, methanol, glucose, dioxane and tetrahydrofuran by hydrogen abstraction (4) to give radicals which are reducing in nature as in the case of $(\text{CH}_3)_2\text{C}(\text{OH})$ radicals from isopropanol. In N_2O saturated neutral aqueous solutions where e_{aq}^- are quantitatively converted to OH, the electron beam pulsed aqueous solutions of these compounds contain only the above reducing radicals. In order to determine their effectiveness as one-electron reducing agents N_2O saturated, neutral 0.1 mol dm^{-3} solutions of these compounds containing $10^{-4} \text{ mol dm}^{-3}$ thionine were subjected to the same dose of 25 ns electron pulses and the maximum transient absorbances reached $\sim 10 \mu \text{ s}$ after the pulse were determined. The transient spectra obtained were identical to the ones observed in similar isopropanol matrices. From the transient build-up traces the rate constants for the corresponding one-electron reductions were evaluated. The results, along with those for isopropanol, are given in table 2 and figure 5. It is seen that the reducing efficiency of these radicals more or less follows the trend in their known one-electron reduction potentials. From the inflexion point of the curves in figure 5 the one-electron reduction potential of thionine is inferred to be $+0.05 \text{ V}$ (vs NHE). This value therefore explains the ability of thionine to undergo easy one-electron reduction by H atoms. In the past, indirect estimate of the one-electron reduction potential of thionine had been made (Rabinowitch 1940), the value at pH 2 ranging from 0.25 to 0.35 V. Taking into consideration the involvement of a proton in the reduction step:



the above value leads to -0.045 to $+0.055 \text{ V}$ for the reduction potential at pH 7.

Table 2. Rate constant for the one-electron reduction of thionine by organic radicals (pH 6.8).

Organic radical derived from	* $E^{\circ 1}$ (vs. NHE) (neutral pH)	k_{II}^{\ddagger} ($\text{dm}^3 \text{mol}^{-1} \text{s}^{-1}$)
1. Isopropanol	-1.05	4.6×10^9
2. EtOH	-0.95	4.9×10^9
3. MeOH	-0.73	4.6×10^9
4. THF	-0.55	4.6×10^9
5. Dioxane	+0.05	2.7×10^9
6. Glucose	+0.06**	1.6×10^9
7. <i>t</i> -Butanol	+0.15	0.0
8. Cytosine	-0.12 [†]	4.2×10^9

[‡] Bimolecular rate constant; * Litte *et al* (1971); Henglein (1976);

** This value is for ribose radicals (Rao and Hayon 1974); [†] Rao and Hayon (1974)

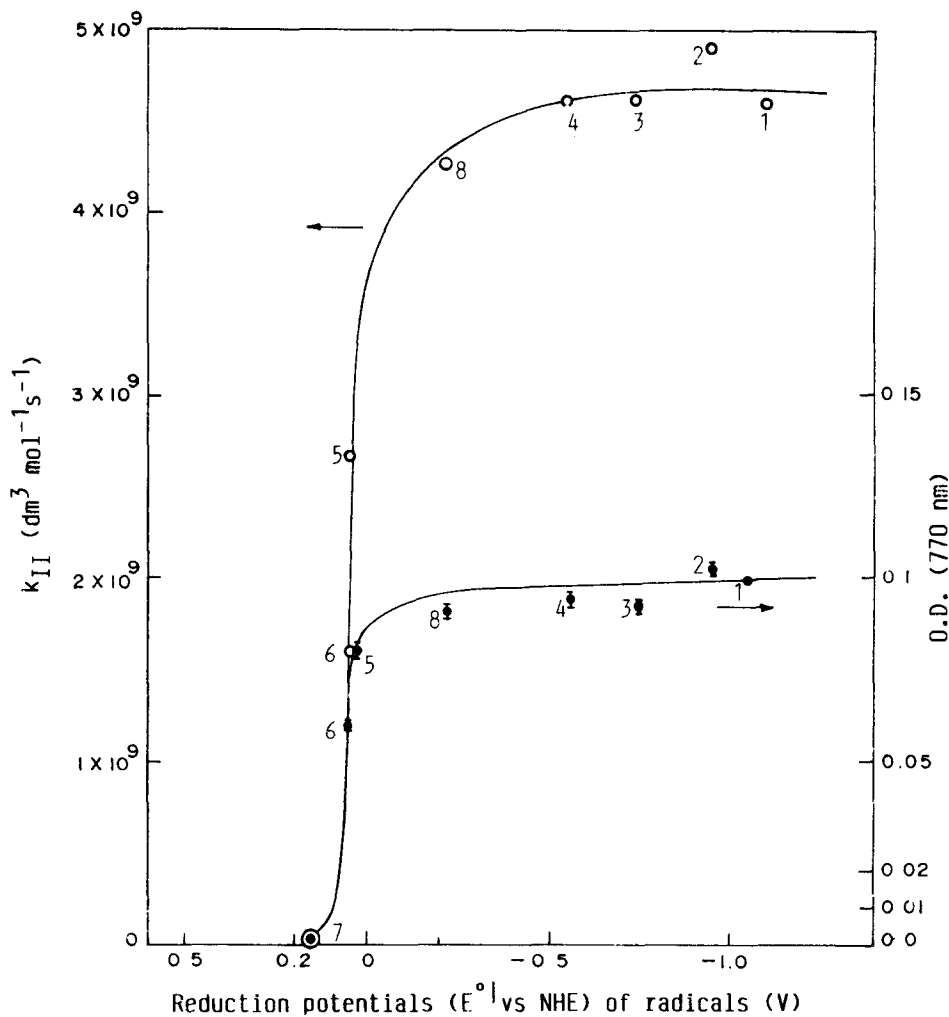


Figure 5. Redox titration curve for semithionine species (numbers on the curves correspond to those in table 2).

Our directly determined value based on redox titration with radicals of known redox potential is closer to the upper limit of the above estimated range.

Acknowledgements

We are grateful to Drs J P Mittal and R M Iyer for useful discussions.

References

- Ainsworth S 1960 *J. Phys. Chem.* **64** 715
Bonneau R, Faure J and Jousset-Dubien J 1968 *Ber. Bunsenges Phys. Chem.* **72** 267
Bonneau R and Pereyre J 1975 *Photochem. Photobiol.* **21** 173
Draganic I G and Draganic Z D 1971 *Radiation chemistry of water* (New York: Academic Press)
Fielden E M 1984 in *The study of fast processes and transient species by electron pulse radiolysis* (eds) J H Baxendale and F Busi (Boston: D Reidel) p. 59
Guha S N, Moorthy P N and Rao K N 1979 *Mol. Photochem.* **9** 183
Guha S N, Moorthy P N and Rao K N 1982 *Proc. Indian Acad. Sci. (Chem. Sci.)* **91** 73
Guha S N, Moorthy P N and Rao K N 1985 *J. Photochem.* **28** 37
Hatchard C G and Parker C A 1961 *Trans. Faraday Soc.* **57** 1093
Henglein A 1976 in *Electroanalytical chemistry* (ed.) A J Bard (New York: Marcell Decker) p. 163
Hunt J W and Thomas J K 1967 *Radiat. Res.* **32** 149
Kamat P V, Karkhanavala M D and Moorthy P N 1979 *Indian J. Chem.* **A18** 206, 210
Keene J P 1964 *Radiat. Res.* **22** 1
Kramer H E A and Maute A 1972 *Photochem. Photobiol.* **15** 7
Lilie J, Beck G and Henglein A 1971 *Ber. Bunsenges. Phys. Chem.* **71** 458
Moorthy P N and Hayon E 1974 *J. Phys. Chem.* **78** 2615
Rabinowitch E 1940 *J. Chem. Phys.* **8** 551, 560
Rao P S and Hayon E 1974 *J. Am. Chem. Soc.* **96** 1287, 1295
Solar S, Solar W and Getoff N 1982 *Radiat. Phys. Chem.* **20** 165