# Nature of the Transient Species Formed in the Pulse Radiolysis of Some Thiourea Derivatives

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Kinetic and spectral characteristics of the transients formed by the reaction of diethylthiourea and thiosemicarbazide with $e^-_{aq}$, H atom and OH radicals and some one-electron reductants and oxidants have been studied by the pulse radiolysis technique. Reactions of $e^-_{aq}$ and H atom with diethylthiourea produced transient species which were strong reductants, whereas in the case of thiosemicarbazide this was not so. The OH radical reaction in both cases led to the formation of transient species which have absorption bands in the visible region. $CO_2H$ and isopropyl ketyl radicals were found to react with these compounds by H abstraction in the presence of acid to give species similar to those formed by reaction with OH radicals under similar conditions.

Thiourea derivatives such as thiosemicarbazide (TSC), phenylthiourea (PTU), diethylthiourea (DTU), 2-mercaptobenzimidazole, *etc.* are well known corrosion inhibitors[1-4] which may be used along with dilute chemical decontaminant formulations for minimising corrosion of the base metal during decontamination of coolant circuits of nuclear reactors. In this process they will be subjected to high radiation doses, and hence there is interest in the radiation chemistry of such compounds. There are a few reports on pulse radiolysis studies on thiourea in the literature,[5,6] but no work has been reported on the radiation chemistry of its derivatives. We have carried out pulse radiolysis studies on PTU[7] and reported the formation of an intramolecular three-electron bonded species by OH radical reaction, similar to that formed in the case of methionine.[8] Alternatively, the transient absorption in the visible region can be due to resonance stabilization of the S–C–N bond and the delocalisation of the unpaired electron over this bond. Similar species have been observed in the cases of other thiourea derivatives *viz.* TSC and DTU. In acidic solutions, H atoms, acetone ketyl radicals and $CO_2H$ radicals also react with these compounds by H abstraction as in the case of selenourea.[9] A study of the reactions of TSC and DTU with primary species of water radiolysis *viz.* $e^-_{aq}$, H atoms, OH radicals and some specific one-electron oxidants and reductants using the pulse radiolysis technique is reported in this paper.

## Experimental

TSC from LOBA Chemie and DTU from Aldrich, USA, were purified by repeated crystallisation. All other chemicals were of AnalaR grade. Water from 'Barnstead Nanopure System' having conductivity < 0.1 μS $cm^{-1}$ was used for preparing all the solutions. Gases, *viz.* $N_2O$, $N_2$ and $O_2$ used for saturating the solutions were of IOLAR/Instrument grade, from Indian Oxygen. The pH of the solutions was adjusted by using phosphate and borate buffers or by adding plain $H_2SO_4$ of appropriate strength. The details of the pulse radiolysis set-up have been reported earlier.[10] A 7 MeV linear electron accelerator (Ray Technologies, England) giving 50 ns single pulses of dose *ca.* 15 Gy per pulse was used for irradiating the samples. Decimolar potassium thiocyanate solution was used for determining the absorbed dose employing a value of 21 500 $dm^3$ $mol^{-1}$ $cm^{-1}$ per 100 eV for Gxε of $(CNS)_2^{\bullet -}$ radical species at 500 nm.[11] Spectral and kinetic data acquisition and analysis were carried out with an IBM compatible PC-XT computer.[12] The one-electron oxidants employed *viz.* $Br_2^{\bullet -}$, $N_3^{\bullet}$, $Cl_2^{\bullet -}$ were produced by the reaction of OH radicals with $Br^-$, $N_3^-$ and $Cl^-$ ions and $SO_4^{\bullet -}$ radicals were produced by the reaction of $e^-_{aq}$ with persulfate ions.

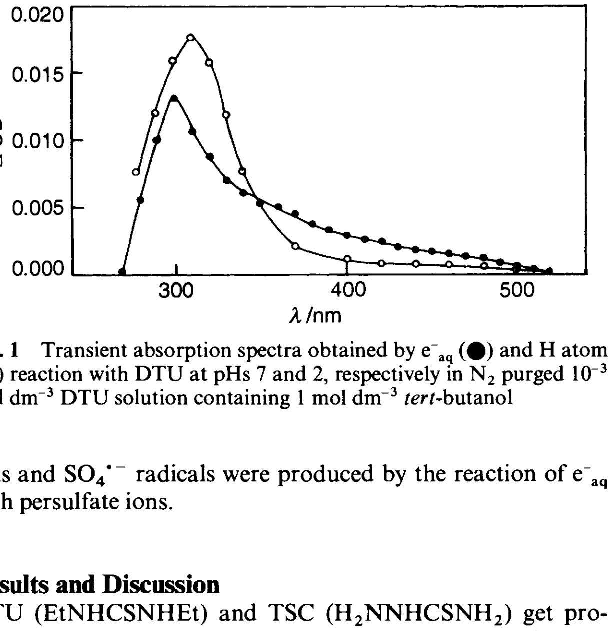


Fig. 1 Transient absorption spectra obtained by $e^-_{aq}$ (●) and H atom (○) reaction with DTU at pHs 7 and 2, respectively in $N_2$ purged $10^{-3}$ mol $dm^{-3}$ DTU solution containing 1 mol $dm^{-3}$ *tert*-butanol

## Results and Discussion

DTU (EtNHCSNHEt) and TSC ($H_2NNHCSNH_2$) get protonated only at pHs < 0 and their p*K*s for protonation are − 1.7 and − 2.01, respectively.[13,14] They have no p$K_a$ in the pH region 0–10. These compounds are reactive towards all the primary species of water radiolysis *viz.* $e^-_{aq}$, H and OH radicals and also with some one-electron oxidants. One-electron reductants such as $CO_2H$ and $(CH_3)_2COH$ radicals were found to be reactive with these compounds only in highly acidic medium (3.6 mol $dm^{-3}$ $H_2SO_4$). All these reactions are discussed below in detail.

*Reaction of* $e^-_{aq}$.—The transient absorption spectrum obtained by the reaction of $e^-_{aq}$ with DTU at pH 7 ($10^{-3}$ mol $dm^{-3}$ DTU + 1 mol $dm^{-3}$ *tert*-butanol, $N_2$ purged solutions) is shown in Fig. 1. It shows a band in the UV region with absorption maximum at 300 nm which is assigned to a carbon centred radical anion, $(EtNH)_2C–S^-$ as in the case of thiourea[15] and phenylthiourea.[7] The rate constant for the reaction of $e^-_{aq}$ with DTU was determined by following the decay of $e^-_{aq}$ absorption at 720 nm and is given in Table 1. The transient species *viz.* the electron adduct of DTU decayed by first-order kinetics. A change in pH or concentration of DTU did not have any effect on the yield of the transient species, its spectrum and its first-order decay rate. Thus, the first-order decay of the electron adduct of DTU is probably not due to

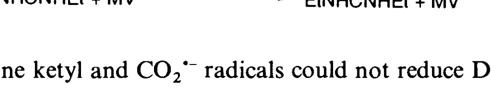
**Table 1** Spectral and kinetic parameters for the transient species formed by the reaction of one-electron reducing radicals

| Species | pH | $\lambda_{max}$/ nm | $\varepsilon$/ $dm^3\ mol^{-1}\ cm^{-1}$ | $k_f$/ $10^8\ dm^3\ mol^{-1}\ s^{-1}$ | $2k\varepsilon^{-1}\ l^{-1}$/ $10^5\ s^{-1}$ |
|---|---|---|---|---|---|
| With DTU | | | | | |
| $e^-_{aq}$ | 7 | 300 | 2500 | 5.0 | 0.2[a] |
| H | 2 | 310 | 3530 | 7.1 | 15.0 |
| | < 0 | 425 | 9500[b] | 6.6 | 2.0 |
| $CO_2H$ | < 0 | 425 | — | 5.5 | 2.0 |
| $(CH_3)_2COH$ | < 0 | 425 | — | 3.5 | 2.1 |
| With TSC | | | | | |
| $e^-_{aq}$ | 7 | 300 | 400 | 10.9 | 33.0 |
| H | 2 | 500 | 500 | 22.0 | 10.0 |
| | < 0 | 400 | 4000[b] | 10.0 | 17.0 |
| $CO_2H$ | < 0 | 400 | — | 5.0 | 18.0 |
| $(CH_3)_2COH$ | < 0 | 400 | — | 2.0 | 18.0 |

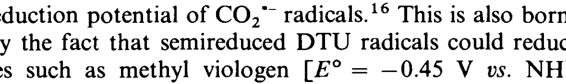
[a] First-order decay. [b] For $G_H$ = 3.65.

protonation/deprotonation or due to its interaction with the parent molecule. It is possible that the radical anion breaks up to give another species which either has very weak absorption or no absorption in the wavelength region 300–800 nm (*e.g.* breaking up of the C–N bond to give $EtNH_2$ and EtNHC=S radical or $EtNHCS^-$ and EtNH radical).

The initial electron adduct (semireduced DTU) was found to be a strong reductant as in the cases of semireduced phenylthiourea[7] and was found to transfer electron to solutes such as methyl viologen, safranine-T and thionine at pH 7. The rate constants for the reaction of semireduced DTU with these solutes were determined by following the build up of the product species at its absorption maximum and are given in Table 2. To determine the charge on the initial electron adduct of DTU, the electron-transfer reaction from this adduct to $MV^{2+}$ ions was studied at different ionic strengths of the solution. The rate-constant value was found to decrease with increasing ionic strength, *e.g.* the rate constants were 6.5 × $10^9$ and 4 × $10^9$ $dm^3\ mol^{-1}\ s^{-1}$, respectively at ionic strengths of 0.01 and 0.05 mol $dm^{-3}$. This suggested that the reacting species are oppositely charged and the product of $Z_A \times Z_B$ was estimated from a plot of $k$ *vs.* $\mu^{\frac{1}{2}}$ which had a slope of $-2$ indicating that the semireduced DTU species has charge of $-1$ (as methyl viologen is present as $MV^{+2}$). Hence the initial $e^-_{aq}$ adduct of DTU must be negatively charged. The reaction scheme can be written as shown in eqns. (1) and (2) (where Et = ethyl).



$$\text{EtNH}\overset{\overset{\text{S}}{\|}}{\text{C}}\text{NHEt} + e^-_{aq} \longrightarrow \text{EtNH}\overset{\overset{\text{S}^-}{|}}{\dot{\text{C}}}\text{NHEt} \quad (1)$$



$$\text{EtNH}\overset{\overset{\text{S}^-}{|}}{\dot{\text{C}}}\text{NHEt} + MV^{2+} \dashrightarrow \text{EtNH}\overset{\overset{\text{S}}{\|}}{\text{C}}\text{NHEt} + MV^{+\bullet} \quad (2)$$

Acetone ketyl and $CO_2^{\bullet -}$ radicals could not reduce DTU at neutral pH. This indicates that the one-electron reduction potential of DTU may be more negative than −2.0 V *vs.* NHE, the reduction potential of $CO_2^{\bullet -}$ radicals.[16] This is also borne out by the fact that semireduced DTU radicals could reduce solutes such as methyl viologen [$E^\circ = -0.45$ V *vs.* NHE (NHE = normal hydrogen electrode)][16] with diffusion controlled rates.

The reaction of $e^-_{aq}$ with TSC was also studied at neutral pH in $N_2$ saturated $10^{-3}$ mol $dm^{-3}$ TSC solutions containing 1 mol $dm^{-3}$ *tert*-butanol (OH radical scavenger). The absorption spectrum of the transient (corrected for depletion of the parent compound) is shown in Fig. 2. It shows a weak shoulder band around 300 nm which may be attributed to a carbon-centred radical. The above spectrum was recorded using 2 µs single pulses (dose *ca.* 80 Gy) as the transient species has very weak absorption ($\varepsilon_{300}$ *ca.* 400 $dm^3\ mol^{-1}\ cm^{-1}$) and hence its absorbance was below the detection limit of our apparatus when 50 ns pulses were used (dose 15 Gy) and the species concentration is only about 5 × $10^{-6}$ mol $dm^{-3}$. The rate constant for the reaction of $e^-_{aq}$ with TSC was determined by following the decay of $e^-_{aq}$ absorbance at 720 nm and the value is given in Table 1. Unlike the electron adducts of DTU and PTU,[7] the transient species from TSC was found to be unreactive towards solutes such as methyl viologen, safranine-T, thionine, *etc.*, suggesting that it is non-reducing in nature. It decayed by second-order kinetics at 300 nm (where the parent

**Table 2** Rate constants for the reaction of electron and H adducts of DTU with various solutes at pH 7 and 2, respectively[a]

| Solute | $\lambda_{max}$[b]/nm | $k/10^9\ dm^{-3}$ mol s <br> $e^-_{aq}$ Adduct | <br> H Adduct |
|---|---|---|---|
| Methyl viologen | 600[17] | 3.9 | 1.4 |
| Safranine-T | 645[18] | 2.6 | 1.0 |
| Thionine | 740[10] | 4.4 | 2.3 |

[a] System: $N_2$ saturated 2–5 × $10^{-3}$ mol $dm^{-3}$ *tert*-butanol + solute; solute concentration 1–5 × $10^{-5}$ mol $dm^{-3}$; build-up kinetics of solute radical followed at its $\lambda_{max}$. [b] Of the radical.

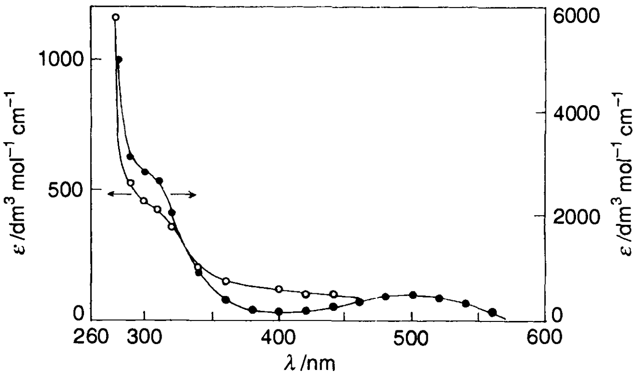


**Fig. 2** Transient absorption spectra (corrected for parent molecule bleaching) obtained by $e^-_{aq}$ (○) and H atom (●) reaction with TSC at pHs 7 and 2, respectively in $N_2$ purged $10^{-3}$ mol $dm^{-3}$ TSC solutions containing 1 mol $dm^{-3}$ *tert*-butanol

molecule absorption is negligible). The decay rate was unaffected when the ionic strength of the solution was changed indicating that the transient species was neutral. It is possible that in this case the electron addition to C=S bond is followed by very fast cleavage of the C–N bond leaving behind a neutral species as shown in eqn. (3).

$$NH_2NHCSNH_2 + e^-_{aq} + H^+ \longrightarrow NH_2NHCS^{\bullet} + NH_3 \quad (3)$$

It is difficult to measure $NH_3$ produced in this reaction as all urea and thiourea derivatives give test for ammonia. $NH_3$ specific electrodes also could not be used as in this method solutions have to be made alkaline to convert ammonium ions into ammonia and TSC decomposes in alkaline solutions. Protonation of the electron adduct could also give a neutral species but as seen later in the case of the H-atom reaction, the transient spectra as well as extinction coefficients are quite different in the two cases. The differences in the behaviour of the electron adducts of PTU, DTU and TSC can be explained in terms of inductive effect as well as the size of the molecules. In the case of PTU, the electron is stabilized by delocalisation over the phenyl group. Both ethyl and $-NH_2$ groups are electron donating in nature and increase the electron density at the $>$C=S bond, making it more susceptible to protonation in its reduced form. As the degree of delocalisation will be less in the neutral radical (as compared to the anionic form) this may lead to shorter lifetimes for the adduct, *i.e.* the bond cleavage is very fast leading to a neutral species.

The spectral and kinetic parameters of the transients formed by $e^-_{aq}$ reaction with DTU and TSC are given in Table 1. The rate constant values are lower in the case of DTU and TSC as compared to that in the case of thiourea[4] and PTU[7] which can be attributed to the presence of electron-donating groups such as –Et and $-NH_2$ in these compounds.

*Reaction of OH Radicals*.—The transient absorption spectra obtained by the reaction of OH radicals with DTU at pH *ca.* 0 ($O_2$ saturated) and 7 ($N_2O$ saturated) in $10^{-3}$ mol dm$^{-3}$ DTU solutions were found to be identical and only the spectrum obtained at pH 7 is shown in Fig. 3. $HO_2$ was found to be unreactive towards DTU. The absorption spectrum shows a single band in the visible region with $\lambda_{max}$ at 425 nm. OH radicals can react with DTU by either hydrogen abstraction from the –NH– group or addition to the $>$C=S group and subsequent elimination of a water molecule to give sulfur centred radicals in both cases. In the case of the OH radical reaction with thiourea a band at 400 nm was observed,[15] which was assigned to an S-centred radical and it was concluded that the species contains a three-electron bond.[15] In the case of PTU,[7] the OH radical reaction led to the formation of a transient species whose absorption falls in the visible region (590 nm) and it was attributed to the formation of an intramolecular three-electron bond between sulfur and nitrogen atoms. However, absorption in the visible region can also be attributed to a resonance stabilized radical as shown in eqn. (4).

$$EtNH-\overset{\overset{\displaystyle S}{\|}}{C}-NHEt + OH \longrightarrow EtNH-\overset{\overset{\displaystyle S^{\bullet}}{|}}{C}-NEt + H_2O \quad (4)$$

Although the absorption maximum is quite close to that of the intramolecular transient species formed between S and N atoms in the case of methionine (400 nm),[8] a similar intramolecular bond formation will be difficult in the case of DTU because of the geometry involved. In a triangular configuration overlapping of $\pi$ orbitals will be very weak. Thus the absorption is more likely to be due to the resonance stabilized radical shown above with unpaired electron delocalised over the S–C–N bond. This may be true in the case of thiourea and PTU also. The species was found to be neutral as seen from kinetic salt effects studies carried out at pH 7. As there was no change in the spectra obtained at pH 0 and 7, the species has no p$K_a$ in this pH range. However, at pH < 0 (3.6 mol dm$^{-3}$ $H_2SO_4$), although there was no change in the absorption maximum of the species, there was an increase in the extinction coefficient at 425 nm (Fig. 3). It is proposed that the increase in extinction coefficient is due to protonation of the transient species at this pH [eqn. (5)]. The semioxidised species

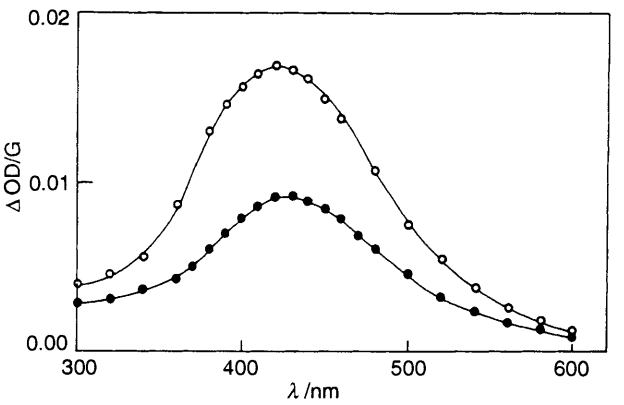


**Fig. 3** Transient absorption spectra obtained by OH radical reaction with DTU at pHs 7 (●) and < 0 (3.6 mol dm$^{-3}$ $H_2SO_4$) (○) in $N_2O$ saturated and $O_2$ saturated $10^{-3}$ mol dm$^{-3}$ DTU solutions

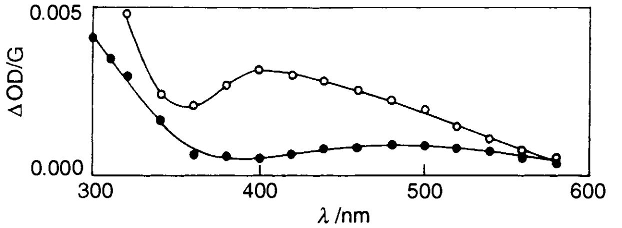
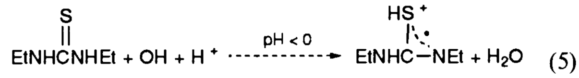


**Fig. 4** Transient absorption spectra obtained by OH radical reaction with TSC at pHs 7 (●) and < 0 (3.6 mol dm$^{-3}$ $H_2SO_4$) (○) in $N_2O$ saturated and $O_2$ saturated $10^{-3}$ mol dm$^{-3}$ TSC solutions



$$EtNH\overset{\overset{\displaystyle S}{\|}}{C}NHEt + OH + H^+ \xrightarrow{pH < 0} EtNH\overset{\overset{\displaystyle HS^{+\bullet}}{|}}{C}-NEt + H_2O \quad (5)$$

was found to be non-oxidising in nature as in the case of PTU.[7] Its decay followed second-order kinetics at pH 7. However, in the presence of oxygen the species decayed by first-order kinetics due to reaction with oxygen.

In the case of TSC also the OH radical reaction was studied at pHs < 0, 0 ($O_2$ saturated) and 7 ($N_2O$ saturated) using $10^{-3}$ mol dm$^{-3}$ TSC solutions. In this case also $HO_2$ was found also to be unreactive towards TSC. The absorption spectra at pH 0 and 7 were similar and showed a band in the visible region with absorption maximum at 500 nm (Fig. 4). Here the OH radicals also react by H abstraction from the $-NH_2$ group or by addition to –C=S double bond followed by elimination of water molecule to give a resonance stabilised species similar to that formed in the case of DTU and PTU. At pH < 0, the transient species gave a spectrum with $\lambda_{max}$ at 400 nm which can again be attributed to the protonated form of the above species. The transient species decayed by second-order kinetics at pH 7, but showed first-order decay at pH < 0 due to reaction with oxygen. The decay rate at pH 7 was unaffected by an increase in ionic strength of the solution suggesting that the transient species is neutral at this pH. Thus at lower pHs *i.e.* below zero, the species can be expected to be in the protonated form. The kinetic and

**Table 3** Spectral and kinetic parameters of the transient species formed by the reaction of one-electron oxidising radical

| Species | pH | $\lambda_{max}$/nm | $\varepsilon$/dm$^3$ mol$^{-1}$ cm$^{-1}$ | $k_f/10^9$ dm$^3$ mol$^{-1}$ s$^{-1}$ | $2k\varepsilon^{-1} l^{-1}/10^4$ s$^{-1}$ |
|---|---|---|---|---|---|
| With DTU | | | | | |
| OH | 7 | 425 | 5250 | 0.8 | 11.0 |
| | 0 | 425 | 6000 | 0.76 | 2.4[a] |
| | < 0 | 425 | 9000 | 0.8 | 2.0[a] |
| $Br_2^{\bullet -}$ | 7 | 425 | 6600 | 3.1 | 8.0 |
| | 0 | 425 | 6730 | 3.6 | 2.0[a] |
| $Cl_2^{\bullet -}$ | 0 | 425 | 6600 | 4.0 | 3.0[a] |
| With TSC | | | | | |
| OH | 7 | 500 | 600 | 13.0 | 55.0 |
| | < 0 | 400 | 4000 | 5.0 | 2.0[a] |
| $BR_2^{\bullet -}$ | 7 | 500 | 600 | 3.9 | — |
| $SO_4^{-}$ | 7 | 500 | 600 | 9.2 | — |
| $N_3^{\bullet}$ | 7 | 500 | 600 | 1.3 | — |

[a] First-order decay.

spectral data for the semioxidised species from DTU and TSC are given in Table 3.

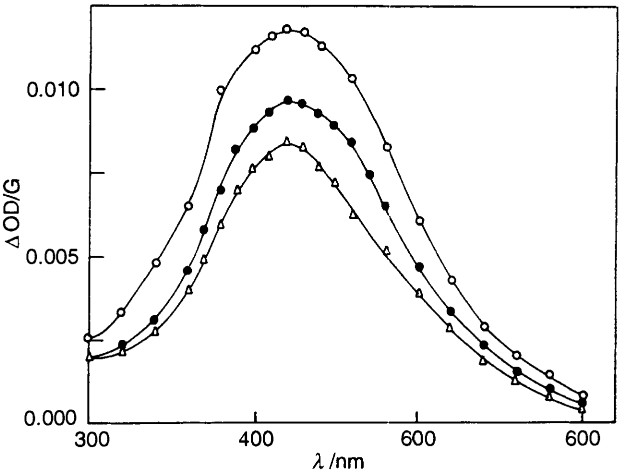
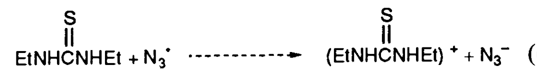
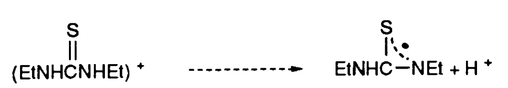


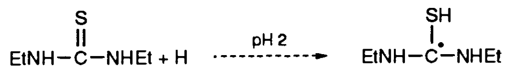
**Fig. 5** Transient absorption spectra obtained by the reaction of H atoms (○), $CO_2H$ (●) and $(CH_3)_2COH$ (△) radicals with DTU at pH < 0 (3.6 mol dm$^{-3}$ $H_2SO_4$) using $10^{-3}$ mol dm$^{-3}$ DTU solutions containing 1 mol dm$^{-3}$ *tert*-butanol, formate and propan-2-ol, respectively for the above three systems

*Reactions with Other Oxidising Radicals*.—One-electron oxidation of DTU and TSC was studied at different pHs using $Br_2^{\bullet -}$, $SO_4^{\bullet -}$, $N_3^{\bullet}$ and $Cl_2^{-}$ radicals. The transient absorption spectra produced by the reactions of these species with DTU and TSC were identical to those obtained by the OH radical reaction with these compounds at the same pHs. The rate constants were determined by following the formation of the transient or decay of the oxidant radical and the values are listed in Table 3. The decay rates of the species were also similar to those obtained in the case of transients produced by OH radical reaction. It appears that the cation radical species formed by the reaction of these one-electron oxidants with thiourea derivatives undergoes fast deprotonation to give a species identical to that obtained in the case of the reaction of OH radicals. The reaction mechanism in the case of the reaction of DTU with azide radicals is shown in eqns. (6) and (7).


$$\mathrm{EtNH\overset{\overset{S}{\|}}{C}NHEt} + N_3^{\bullet} \dashrightarrow (\mathrm{EtNH\overset{\overset{S}{\|}}{C}NHEt})^{+} + N_3^{-} \quad (6)$$

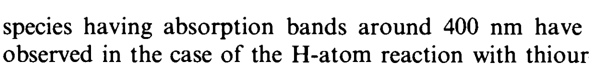

$$(\mathrm{EtNH\overset{\overset{S}{\|}}{C}NHEt})^{+} \dashrightarrow \mathrm{EtNH\overset{\overset{S}{|^{\bullet}}}{C}{\overset{\cdot\cdot}{-}}NEt} + H^{+} \quad (7)$$

*Reaction of H Atoms*.—Reaction of H atoms with DTU was studied at pHs 2, and < 0 (in 3.6 mol dm$^{-3}$ $H_2SO_4$), using deoxygenated ($N_2$ purged) $10^{-3}$ mol dm$^{-3}$ DTU solutions containing 1 mol dm$^{-3}$ *tert*-butanol. The transient spectra obtained at these pHs are shown in Figs. 1 and 5, respectively. At pH 2, the H-atom reaction gave a transient spectrum with absorption maximum at 310 nm which can be attributed to the addition of H atom to the C=S double bond and formation of a carbon centred radical [eqn. (8)]. This radical species was found


$$\mathrm{EtNH{-}\overset{\overset{S}{\|}}{C}{-}NHEt} + H \xrightarrow{\text{pH } 2} \mathrm{EtNH{-}\overset{\overset{SH}{|}}{\dot{C}}{-}NHEt} \quad (8)$$

to be a good reductant and could reduce solutes such as methyl viologen.

In the presence of 3.6 mol dm$^{-3}$ $H_2SO_4$, *i.e.* pH < 0 however, the reaction of H atoms with DTU gave a transient spectrum with $\lambda_{max}$ at 425 nm. The rate constants for the reaction of H atoms at pHs 2 and < 0 were determined by following the growth of absorbance at the respective maxima. The rate-constant value was lower at pH < 0 as compared to that obtained at pH 2 due to protonation of the ground state of the compound as in the case of PTU.[7] The species decayed by second-order kinetics at both the pHs. The change in absorption spectrum with pH indicates the formation of a different species. In fact the absorption spectrum is identical to that of the species obtained by OH radical reaction at pH < 0 with same extinction coefficient. It is proposed that the H-atom reaction at pH < 0 leads to the H-abstraction reaction as in the case of selenourea[9] to give a species similar to that formed by the OH radical reaction *i.e.* H abstraction [eqn. (9)]. Similar


$$\mathrm{EtNH{-}\overset{\overset{S}{\|}}{C}{-}NHEt} + H + H^{+} \xrightarrow{\text{pH} < 0} \mathrm{EtNH{-}\overset{\overset{HS^{+}}{|^{\bullet}}}{C}{\overset{\cdot\cdot}{=}}NEt} + H_2 \quad (9)$$

species having absorption bands around 400 nm have been observed in the case of the H-atom reaction with thiourea as well as PTU[7] in highly acidic solutions. Although in the case of selenourea,[9] the spectrum was attributed to the formation of a dimer anion radical, no concentration effect was observed on the yield of the species in the case of DTU. Hence, the absorption band around 400 nm cannot be ascribed to an intermolecular three-electron bonded species.

The reactions of H atoms with TSC were studied at pHs 2 and < 0 (3.6 mol dm$^{-3}$ $H_2SO_4$) in deoxygenated ($N_2$ purged) $10^{-3}$ mol dm$^{-3}$ TSC solutions containing 1 mol dm$^{-3}$ *tert*-

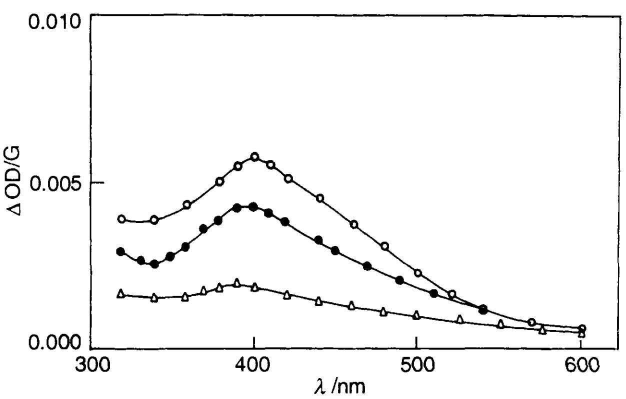


**Fig. 6** Transient absorption spectra obtained by the reaction of H atoms (○), $CO_2H$ (●) and $(CH_3)_2COH$ (△) radicals with TSC at pH $< 0$ (3.6 mol $dm^{-3}$ $H_2SO_4$) using $10^{-3}$ mol $dm^{-3}$ TSC solutions containing 1 mol $dm^{-3}$ *tert*-butanol, formate and propan-2-ol, respectively for the above three systems

butanol. The spectrum at pH 2 is shown in Fig. 2 and has been corrected for the parent molecule absorption at this pH. It shows a shoulder at 310 nm and a weak band in the 500 nm region. The spectrum is quite different from that of the transient species formed by $e^-_{aq}$ reaction with TSC and is similar to that obtained by the OH radical reaction with this compound at pH 7 (see Fig. 6). It appears that even at pH 2, H atoms react with TSC by H abstraction to give a resonance stabilised radical species similar to that obtained by the OH radical reaction. At pH $< 0$, the transient spectrum (Fig. 4) showed a band with an absorption maximum at 400 nm similar to the one obtained in the case of H-atom reaction with thiourea, PTU[7] and DTU at pH $< 0$ and it can be attributed to the formation of the protonated form of the radical obtained at pH 2. The kinetic and spectral data on the reactions of H atoms with DTU and TSC are given in Table 1.

*Reactions of One-electron Reductants in Acidic Solutions.*—Acetone ketyl radicals as well as $CO_2^{\bullet -}$ and $CO_2H$ radicals were found to be unreactive towards TSC and DTU in neutral as well as in weakly acidic solutions. But in highly acidic solutions (3.6 mol $dm^{-3}$ $H_2SO_4$), they reacted with DTU and TSC to give transient species ($\lambda_{max}$ = 425 nm) whose spectra (shown in Figs. 3 and 4) were similar to those of the species formed by the H-atom reaction under similar acidic conditions. Similar spectra were also obtained by the reactions of H, $CO_2H$ and $(CH_3)_2COH$ radicals at pH $< 0$ with PTU[7] except for a slight shift in absorption maximum (400 nm). This suggests that acetone ketyl and $CO_2H$ radicals also react with DTU and TSC by H abstraction as in the case of the H-atom reaction at this pH. The same should be true in the case of PTU.[7] It appears that H-abstraction reactions are facile with the protonated forms of the thiourea derivatives as compared to that with the neutral forms. In acidic media, protonation first takes place at the S site (as in the case of TSC[14]) and the H abstraction takes place from the amino groups. The kinetic and spectral data pertaining to the reaction of these one-electron reductants with DTU and TSC are given in Table 1. The yields of the transient species were maximum in the case of the H-atom reaction as seen from Figs. 3 and 4. It is mostly owing to incomplete scavenging of these radicals by the solute due to low reactivity. However, it is possible that $CO_2H$ and $(CH_3)_2COH$ radicals react not only by H abstraction but by other modes also, possibly addition.

## Conclusion

Both TSC and DTU are highly reactive towards the primary radiolytic species *viz.* $e^-_{aq}$, H atom and OH radicals. The electron and H adducts of DTU are strong reductants. However, in the case of TSC, hydrated electron reactions led to the formation of a neutral, non-reducing species. Reaction of OH as well as some one-electron oxidants with these two compounds led to the formation of resonance stabilised species with characteristic absorption in the visible region. The semioxidised species, however, were found to be non-oxidising. The reaction of H atom, $CO_2H$ and acetone ketyl radicals at pH $< 0$ gave rise also to a similar species with absorption in the visible region.

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