Nature of the Transient Species in the One-electron Oxidation of Diethyl Dithiocarbamate as Studied by Pulse Radiolysis

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One-electron oxidation of the diethyl dithiocarbamate(DDC) anion by oxidising radicals such as $^{\bullet}OH$, $N_3^{\bullet}$, $Br_2^{\bullet -}$ *etc.* has been studied employing the pulse radiolysis technique. The transient species absorbing in the visible region (λ_{max} 570 nm) has been identified as the dimer anion radical formed by the interaction of the initial neutral radical ($Et_2NCS_2^{\bullet}$) with the parent anion. This species was found to be rather unreactive towards other solutes and decayed, with second-order kinetics, to give disulfiram. The reaction of disulfiram with hydrated electrons (e^-_{aq}) gave rise to the same transient spectrum as obtained in the case of one-electron oxidation of DDC. The reaction of e^-_{aq} with DDC at pH 9 gave a transient spectrum with λ_{max} 340 nm which has been attributed to a carbon-centred radical dianion ($Et_2NCS_2^{\bullet 2-}$).

Diethyl dithiocarbamate is known to be a good anti-oxidant.[1] It has been used as a protective agent against radiation in mice,[2] and also as a radiation sensitizer because of its ability to deactivate superoxide dismutase.[3] Recently it has also been used to enhance light-energy conversion efficiency of Cd-X based photoelectrochemical cells.[4,5] Its oxidation product is either disulfiram or a sulphoxide depending on the oxidant.[1] Kamat and Dimitrijevic[6] have recently studied its reaction with $^{\bullet}OH$ and $Br_2^{\bullet -}$ radicals and observed a transient absorption with λ_{max} 580 nm, which has been attributed to the formation of $Et_2NCS_2^{\bullet}$ radical. We have conducted a detailed pulse radiolysis study of this compound in aqueous solution which suggests the transient species to be a dimer anion radical. These results, along with other data on its one-electron reduction and the reactivity of the transients, are presented in this paper.

Experimental

All chemicals employed in the study were the purest commercially available and were used as such without further purification. Water from 'Barnstead Nanopure System' was used for preparing all solutions. Gases employed to saturate the solutions, *viz.* N_2O, N_2 and O_2, were Iolar/Instrument grade from Indian Oxygen Ltd. Borate buffer was used to adjust the pH of the solutions in the range 9.0–9.5, except in conductivity studies where NaOH was employed. The pulse radiolysis apparatus has been described in detail previously.[7] Electron pulse dose was measured using aerated decimolar thiocyanate solutions taking $G\varepsilon$ for $(CNS)_2^-$ species to be 21 520 dm^3 mol^{-1} cm^{-1} per 100 eV at 500 nm.[8] The average dose per pulse was *ca.* 15 Gy. Spectral and kinetic data acquisition and analysis were carried out with an IBM-PC-XT using the program ABIWAT.[9] A dual cell[10] was used for pulse radiolysis conductivity studies. Steady state radiolysis was carried out in a ^{60}Co γ-source having a dose rate of 16 Gy cm^{-3} min^{-1}.

Results and Discussion

The solubility of sodium diethyl dithiocarbamate(DDC) in water is *ca.* 7 × 10^{-4} mol dm^{-3}. At pH < 8 it decomposes[11] to give CS_2 and Et_2NH. Therefore all experiments were conducted at pH 9–9.5.

Reaction with $^{\bullet}OH$ radicals.—Fig. 1 shows the transient absorption spectrum obtained by the reaction of $^{\bullet}OH$ radicals with DDC in pulse irradiated, N_2O saturated, 2 × 10^{-4} mol dm^{-3} solutions at pH 9.2. The spectrum with λ_{max} 570 nm agrees with that reported by Kamat and Dimitrijevic.[6] The shape of the absorption spectrum was time-independent indicating the presence of only one light-absorbing species. According to Kamat and Dimitrijevic,[6] the transient species is the $Et_2NCS_2^{\bullet}$ radical. If we consider DDC to be similar to thiolate ion (RS^-) it would react with $^{\bullet}OH$ radicals by electron transfer to give $RS^{\bullet}$ radicals. This reaction usually proceeds *via* formation of an adduct ($RSOH^{\bullet -}$) which, in the presence of H^+, undergoes elimination of water to give the $RS^{\bullet}$ radical. However at pH 9 the concentration of H^+ is low and therefore only a direct electron transfer reaction between OH and RS^-, as in eqn. (1), can be considered.

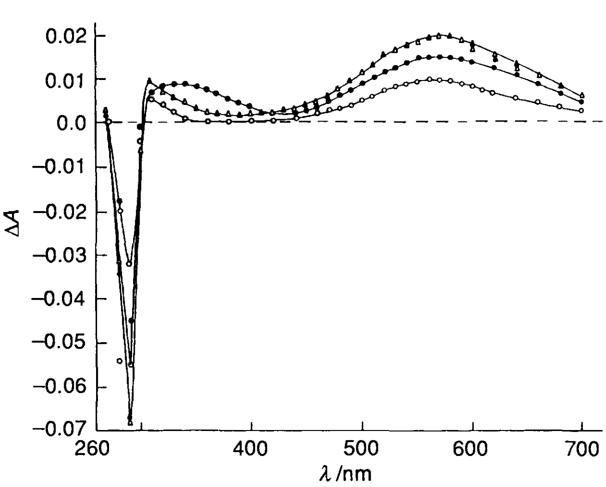


Fig. 1 Absorption spectra of the transient species produced by the reaction of DDC with various oxidising radicals at pH 9.2. $^{\bullet}OH$ (△), $N_3^{\bullet}$ (▲) and $Br_2^{\bullet -}$ (●), in N_2O saturated solutions, and $^{\bullet}OH$ in air saturated solutions (○). [DDC] = 2 × 10^{-4} mol dm^{-3}.

$$RS^- + OH \longrightarrow RS^{\bullet} + OH^- \qquad (1)$$

However, simple sulphur-centred radicals derived from thiols or alkyl sulphides do not absorb in the visible region.[12] In such systems the transient absorption in the visible region is usually due to the formation of either intermolecular 3-electron-bonded species of the type $(RS \therefore SR)^-$ as in the case of thiols and $(R_2S \therefore SR_2)^+$ as in the case of dialkyl sulphides, or intramolecular 3-electron bonded species of the type $(RS \,\underline{\therefore}\, SR)^+$ as in the case of one-electron oxidation of dialkyl disulphides.

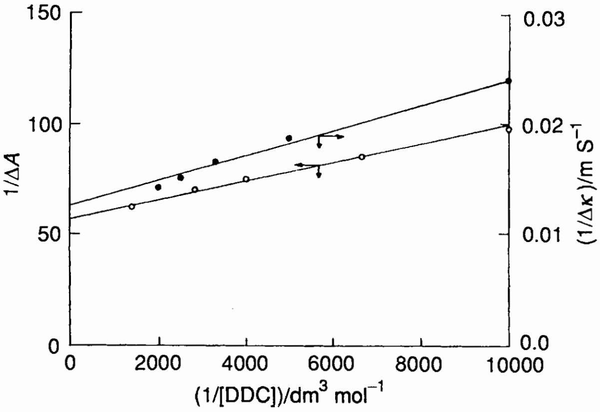


Fig. 2 Effect of concentration of DDC on the yield of the transient as shown by the plot of $1/\Delta A$ and $1/\Delta\kappa$ *vs.* 1/[DDC] for pulse irradiated N_2O saturated DDC solutions

Pulse radiolysis ac conductivity studies carried out with N_2O saturated 5×10^{-4} mol dm^{-3} DDC solutions at pH 9.5 gave rise to a positive conductivity signal of *ca.* 52 mV as compared to a negative signal of 200 mV observed in the case of N_2O saturated thiocyanate solution at pH 4. A positive conductivity signal indicates the release of OH^- ions on pulse irradiation, as required by eqn. (1). This shows that $^{\bullet}OH$ radicals react by electron transfer, and not by an addition reaction *i.e.* $RSOH^{\bullet -}$ is not formed. However, a positive conductivity signal may be due to the formation of $RS^{\bullet}$ or $(RS \therefore SR)^-$ formed by the intermolecular interaction between $RS^{\bullet}$ and the parent anion RS^-, as shown in eqn. (2).

$$RS^{\bullet} + RS^- \rightleftharpoons (RS \therefore SR)^- \qquad (2)$$

The formation of the intermolecular 3-electron-bonded species, similar to that observed in the case of thiols,[13] was confirmed when the effect of the concentration of DDC(RS^-) on the yield of the transient species was studied by both absorption and conductivity techniques. Both ΔA and $\Delta\kappa$ were found to increase with increasing DDC concentration. This increase in the yield of the transient could be explained only by an equilibrium reaction of the type shown in eqn. (2). This result also ruled out the formation of intramolecular 3-electron-bonded species, as changes in the concentration of DDC would not have any effect on the yield of transient in that case.

The plots of $1/\Delta A$ and $1/\Delta\kappa$ *vs.* 1/[DDC] are shown in Fig. 2. These are linear and the intercept values give the maximum values of ΔA and $\Delta\kappa$ respectively. Values of 13 000 and 11 000 ± 1000 dm^3 mol^{-1} for the equilibrium constant, *K*, were calculated from the slope and intercept of the absorbance and conductivity plots respectively. The *G*-value for the $(RS \therefore SR)^-$ species was evaluated from the conductivity signal using eqn. (3), where $G(SCN)_2^- = 5.5$, $\Lambda_{\text{thiocyanate syst.}}$[10] $= -360$

$$\frac{G(SCN)_2^- \times \Lambda_{\text{thiocyanate syst.}}}{G(RS \therefore SR)^- \times \Lambda_{\text{DDC system}}} = \frac{\Delta\kappa_{\text{thiocyanate syst.}}}{\Delta\kappa_{\text{DDC system}}} \qquad (3)$$

S cm^2 mol^{-1} and $\Lambda_{\text{DDC system}} = \Lambda_{OH^-} - \Lambda_{RS^-} = 170 - 45 = 125$ S cm^2 mol^{-1}. (It is assumed that $\Lambda_{RS^-} = ca.\ \Lambda_{(RS \therefore SR)^-} = 45$ S cm^2 mol^{-1}.)

$G(RS \therefore SR)^-$ was estimated to be *ca.* 5 from the maximum conductivity value extrapolated from Fig. 2. Knowing the values of *G* and ΔA_{max} the extinction coefficient for the species $(RS \therefore SR)^-$ at 570 nm was estimated to be *ca.* 2500 dm^3 mol^{-1} cm^{-1}. This value is somewhat higher than that reported by Kamat and Dimitrijevic.[6] However the above authors have not specified the pH at which they carried out the pulse radiolysis experiments. If the pH was <9, the concentration of DDC would not remain constant during the time of the experiment, leading to a lower yield of the transient and, consequently, a lower apparent value of the extinction coefficient (1800 dm^3 mol^{-1} cm^{-1}).

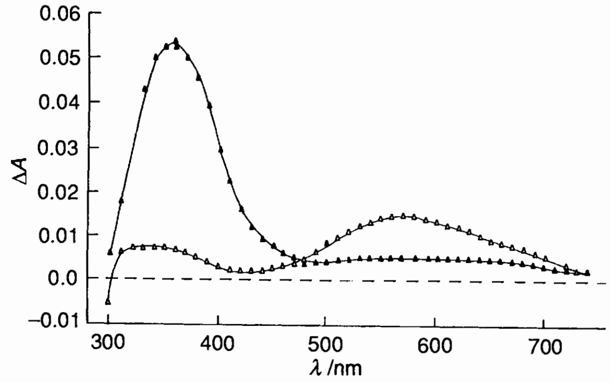


Fig. 3 Time resolved transient spectra obtained in the pulse radiolysis of N_2O saturated solutions of 0.01 mol dm^{-3} Br^- containing 2×10^{-4} mol dm^{-3} DDC, pH 9.2, immediately after the pulse (▲) and 8 µs after the pulse (△)

The rate constant for the reaction of $^{\bullet}OH$ radicals with DDC estimated from the formation of the $(RS \therefore SR)^-$ species, was found to be $(1.0 \pm 0.1) \times 10^{10}$ dm^3 mol^{-1} s^{-1}. The transient species decayed with second-order kinetics with a rate constant of $2k = (7 \pm 1) \times 10^9$ dm^3 mol^{-1} s^{-1} which is similar to the value reported by Kamat and Dimitrijevic.[6]

Reactions of other oxidising radicals with DDC.—Reactions of other oxidizing radicals ($N_3^{\bullet}$, $Br_2^{\bullet -}$, $I_2^{\bullet -}$, $(SCN)_2^{\bullet -}$ and $CCl_3O_2^{\bullet}$) were studied under appropriate conditions. With the exception of $CCl_3O_2^{\bullet}$ all the radicals were produced by the reaction of $^{\bullet}OH$ radicals with N_2O saturated 10^{-2} mol dm^{-3} azide, halide and thiocyanate solutions. $CCl_3O_2^{\bullet}$ radicals were produced by the reaction of e_{aq}^- with 10^{-2} mol dm^{-3} CCl_4 in air saturated 2 mol dm^{-3} *tert*-butyl alcohol solutions. These radicals react with DDC(RS^-) by electron transfer giving $RS^{\bullet}$ which immediately combines with RS^- to give $(RS \therefore SR)^-$. Transient spectra recorded in all these systems were similar to that obtained in the case of $^{\bullet}OH$ radical reaction. Some of these are shown in Fig. 1. Time resolved transient spectra in the case of reaction of $Br_2^{\bullet -}$ with DDC are shown in Fig. 3. The decay of $Br_2^{\bullet -}$ absorption at 360 nm is followed by the appearance of the $(RS \therefore SR)^-$ transient band with λ_{max} *ca.* 570 nm and another weak band in the 350–400 nm region. In these systems also an increase in DDC concentration led to an increase in the yield of the transient species indicating the existence of equilibrium (2). The yield of the transient species was lower in the case of oxidation by $Br_2^{\bullet -}$, $I_2^{\bullet -}$ and $(SCN)_2^{\bullet -}$, indicating that these radicals react only partly by electron transfer. Halides are known to form 3-electron-bonded species with sulphur-centred radicals[14] and the weak band in the 350–400 nm region seen in the case of halides could be due to such a species. The increase in the concentration of halide (*e.g.* Br^-) led to a small decrease in the yield of the transient species with λ_{max} 570 nm and a corresponding increase in absorption in the 350–400 nm region. However the effect is not so pronounced, indicating that the equilibrium constant of the $(RS \therefore Br)^-$ species is much lower than that of the $(RS \therefore SR)^-$ species.

The rate constants for the reaction of the above oxidising radicals with DDC were determined by following the formation of $(RS \therefore SR)^-$ in all cases, and confirmed by following the decay of the oxidant radical wherever possible (Table 1). These

Table 1 Rate constants for the one-electron oxidation of diethyl dithiocarbamate by various oxidising radicals at pH 9, measured by observing product formation at 570 nm

Oxidising radical	$k/10^9$ dm^3 mol^{-1} s^{-1} [a]
$^{\bullet}OH$	10
$N_3^{\bullet}$	7.0
$Br_2^{\bullet -}$ [b]	2.5
$(SCN)_2^{\bullet -}$	2.5
$I_2^{\bullet -}$ [c]	2.4
$CCl_3O_2^{\bullet}$	2.0

[a] Values of k are within ±10%. [b] Also measured by observing decay of $Br_2^{\bullet -}$ at 360 nm. [c] Also measured by observing decay of $I_2^{\bullet -}$ at 380 nm.

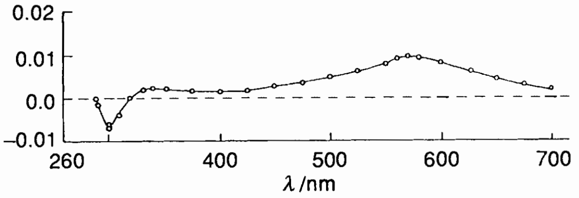


Fig. 4 Transient spectrum produced by the reaction of e^-_{aq} with DSF in N_2 saturated 10^{-4} mol dm^{-3} DSF soltuions containing 1 mol dm^{-3} *tert*-butyl alcohol at pH 9.2

results indicate that DDC is readily oxidised. In cyclic voltammetric experiments the oxidation potential of DDC has been reported[15] to be 0.05 V *vs.* SCE (in acetonitrile medium) which is in agreement with the above result.

Reaction of e^-_{aq} *with Disulfiram.*—Disulfiram(DSF) is the oxidation product of DDC. Its structure is similar to a disulphide(RSSR) where R = Et_2NCS. Thus its reaction with e^-_{aq} should lead to the formation of $(RS \therefore SR)^-$ species, as in the case of alkyl disulphides.[16] Pulse radiolysis of N_2 saturated 10^{-4} mol dm^{-3} DSF solutions in 1 mol dm^{-3} *tert*-butyl alcohol at pH 9.2 gave a transient spectrum very similar to that obtained in the one electron oxidation of DDC (Fig. 4). The reaction is shown in eqn. (4). The absorption at 570 nm was unaffected by

$$RSSR + e^-_{aq} \longrightarrow (RS \therefore SR)^- \qquad (4)$$

the change in pH in the region 4–10, indicating that the pK_a value for this species does not lie in this region. The rate constant for the reaction of e^-_{aq} with DSF at pH 9.2 estimated by following the decay of the e^-_{aq} absorption at 720 nm, was $(1.1 \pm 0.1) \times 10^{10}$ dm^3 mol^{-1} s^{-1}. The second-order rate constant for bimolecular decay of the transient was the same as that observed in the case of the transient produced by the reaction of $^{\bullet}OH$ with DDC. DSF could not be reduced by isopropyl ketyl radicals indicating its reduction potential to be highly negative.

Nature of the Transient Species.—All the above experiments indicate that the transient species with λ_{max} 570 nm is a dimer anion radical of the type $(RS \therefore SR)^-$, the observed transition being 2σ–σ^*, similar to that observed in the one-electron oxidation of thiols or dialkyl sulphides.[12] The spectrum obtained in the one-electron oxidation of DDC by $^{\bullet}OH$ radical was unaffected by the presence of oxygen (*ca.* 10^{-3} mol dm^{-3}), except for a reduction in yield (as compared with the N_2O saturated solutions) due to scavenging of e^-_{aq} by O_2 (Fig. 1). The decay of the transient dimer anion radical was second order, in contrast to the mixed order decay[17] in the case of the dimer cation radical $(R_2S \therefore SR_2)^+$. This decay was not affected by the presence of oxygen. This is generally expected in the case of electron deficient species. It was also unreactive towards other solutes such as ABTS, safranine-T, thionine *etc.* Thus it was found to be neither reducing nor oxidising in nature. The inertness of this radical may explain why DDC can act as a good protective agent. The second-order bimolecular decay led to the formation of disulfiram [eqn. (5)] which was identified

$$2(RS \therefore SR)^- \longrightarrow RSSR + 2RS^- \qquad (5)$$

as the main product in γ-irradiated, N_2O-saturated DDC solutions at pH 9.2.

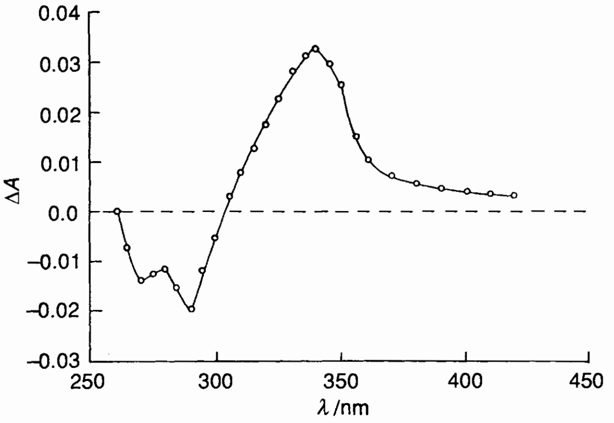
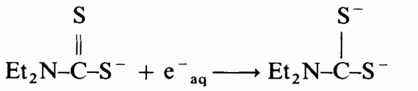


Fig. 5 Transient spectrum produced by the reaction of e^-_{aq} with DDC in N_2 saturated 2 × 10^{-4} mol dm^{-3} DDC solutions containing 0.01 mol dm^{-3} *tert*-butyl alcohol at pH 9.2

Reaction of e^-_{aq} *with DDC.*—Pulse radiolysis of N_2 saturated DDC solutions containing 0.01 mol dm^{-3} *tert*-butyl alcohol gave a transient spectrum with λ_{max} 340 nm (Fig. 5). The rate constant for the reaction of e^-_{aq} with DDC, evaluated by following the decay of e^-_{aq} absorption at 720 nm as well as the formation kinetics of the transient at 340 nm, was $(2.5 \pm 0.2) \times 10^9$ dm^3 mol^{-1} s^{-1}. The extinction coefficient at 340 nm was estimated to be 5600 dm^3 mol^{-1} cm^{-1}. Isopropyl ketyl radicals and $CO_2^{\bullet -}$ radicals were not able to reduce DDC. The electron adduct of DDC may be a carbon-centred radical formed by the addition of the electron to the double bond between carbon and sulphur [eqn. (6)].



$$Et_2N\text{–}\overset{\overset{\displaystyle S}{\|}}{C}\text{–}S^- + e^-_{aq} \longrightarrow Et_2N\text{–}\overset{\overset{\displaystyle S^-}{|}}{C}\text{–}S^- \qquad (6)$$

This radical decayed with second-order kinetics with $2k = (1.0 \pm 0.1) \times 10^9$ dm^3 mol^{-1} s^{-1}. Decay of the radical was very fast in presence of air, indicating a reaction with oxygen. pK values and the reaction with hydrogen atom could not be studied, as DDC is not stable at pH < 9.

Conclusion

The transient species produced by the one-electron oxidation of DDC using various oxidant radicals is a dimer anion, radical of the type $(RS \therefore SR)^-$ and not a monomeric species such as $Et_2NCS_2^{\bullet}$ radical as reported in the literature.[6] The ease of oxidation of DDC and the inertness of the transient species may explain its radiation protection properties. The electron adduct of DDC has an absorption in the UV region and may be a carbon-centred radical.

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Paper 0/04961A
Received 5th *November* 1990
Accepted 23rd *January* 1991