Formation of a Sulphur-Sulphur Bridged Radical Cation During the Oxidation of 1,4-Dithian by Hydroxyl Radicals

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Summary A transient radical cation with a three-electron bond between the two sulphur atoms in the 1,4-positions is formed upon oxidation of 1,4-dithian by OH radicals in aqueous solutions at low solute concentration.

THE formation of transient radical cations, $(R_2S)_2^+$, during the oxidation of sulphides by hydroxyl radicals in aqueous solutions has been established recently.[1-4] The structure of this species is best described in terms of a three-electron bond between the sulphur atoms of the two sulphide molecules involved.[2]

We report here an intramolecular 'complexation' during the oxidation of 1,4-dithian. The reaction of OH· radicals with 1,4-dithian was investigated by irradiation of an aqueous, N_2O-saturated 10^{-4} M solution of 1,4-dithian with a *ca.* 2 μs electron pulse. Under these conditions *ca.* 5×10^{-6}M OH· radicals are produced. Their reaction with 1,4-dithian is a diffusion controlled process,[5] *i.e.* is complete during the pulse. The transient formed in this process can be detected by conductivity and optical absorption measurements.

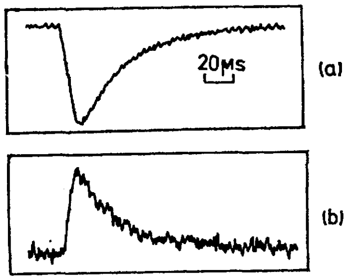


FIGURE 1 (a) Change in conductivity as a function of time in a pulse-irradiated, N_2O-saturated aqueous solution, pH 4·5, 10^{-4}M in 1,4-dithian. (b) Optical absorption at 680 nm as a function of time in the same solution. Same time scale.

Figure 1(a) shows a trace of the conductivity as a function of time in a pulsed solution of pH 4·5. The signal decreases during the pulse and then recovers at longer times. The initial decrease indicates the formation of a positively charged species.[4] The net result of reactions (1) and (2) is that a highly conducting proton (specific conductivity 315 Ω^{-1} cm^2) is effectively replaced by a less conducting 'normal' positive ion (specific conductivity *ca.* 70 Ω^{-1} cm^2).

$$OH\cdot + \text{1,4-dithian} \rightarrow \text{1,4-dithian}^+ + OH^- \quad (1)$$

$$OH^- + H^+_{aq} \rightarrow H_2O \quad (2)$$

The subsequent increase in conductivity results from deprotonation of the positive ion, *i.e.* the highly conducting proton is liberated again.

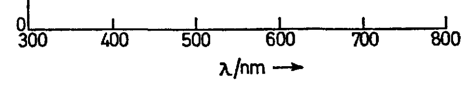
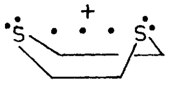


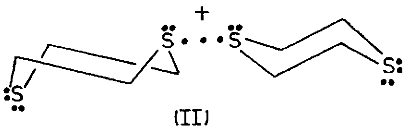
FIGURE 2. (A) Spectrum of the transient formed at low (10^{-4}M) 1,4-dithian concentration. (B) Spectrum of the transient formed at higher (10^{-3}M) 1,4-dithian concentration. The extinctions of (A) and (B) are normalized to the same transient concentration.

A simultaneous tracing of the optical absorption at 680 nm in the pulsed solution is shown in Figure 1(b). It shows a fast initial increase and then a decay corresponding to the conductivity signal. The absorption is therefore attributed to the positive 1,4-dithian ion. The optical spectrum obtained from the absorption immediately after the pulse is given by curve (A) in Figure 2. It has a maximum at 660 nm and an estimated extinction coefficient of *ca.* 2×10^3 l mol^{-1} cm^{-1}.[5]

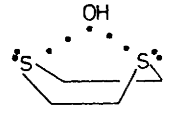
With increasing 1,4-dithian concentration the yield of positive ions as calculated from the initial decrease in the conductivity signal does not change. Significant changes are observed, however, for the optical absorption. The spectrum of the transient positive ion is now shifted towards shorter wavelengths with a maximum at 500 nm, *e.g.* the spectrum obtained at 10^{-3}M 1,4-dithian is given by curve (B) in Figure 2. It is typical for complexed $(R_2S)_2^{+\cdot}$ type radical cations.[4] Its yield increases with 1,4-dithian concentration and even at 10^{-3}M saturation has not yet been achieved.



(I)



(II)



(III)

Differences in the decay kinetics also indicate the formation of positive ions of different structure at low and high 1,4-dithian concentration, respectively. The decay of both the conductivity and the optical signal at low concentration is purely exponential indicating a unimolecular deprotonation process for species (I) giving curve (A). From the half-life, $t_{\frac{1}{2}}$ 24·6 μs, a rate constant k_1 2·8 × 10^4 s^{-1} is calculated. Species (II) giving curve (B) is much longer lived, the lifetime depends on the solute concentration, and the decay kinetics are complex.

The above results indicate that the transient radical cation (I) requires only one 1,4-dithian molecule. The electron structure of (I) is described by a three-electron bridge between the two sulphur atoms in the 1,4-positions, *i.e.* the radical cation results from intramolecular 'complexation.' This conclusion is also based on the fact that radical cations containing only one sulphur atom, *e.g.* R_2S^+ from Bu^t_2S, exhibit different optical and chemical properties.[6]

At higher 1,4-dithian concentration an intermolecular complex (II) is formed where the two binding sulphur atoms could approach more closely and also both molecules could exist in the chair configuration. From kinetic analysis of the optical data it does not appear, however, that (II) is directly produced by reaction of (I) with an unaffected 1,4-dithian molecule. The immediate precursor of both (I) and (II) seems rather to be the OH radical adduct (III) on account of a short-lived absorption ($t_{\frac{1}{2}} < 1\,\mu s$) observable at 360 nm. An essentially identical absorption has been observed for the complexed $(R_2S)_2OH\cdot$ radical from simple sulphides,[4] which has a similar structure.

The formation of the two radical cations is then described by the kinetics of the competing reactions (3) and (4)

$$(III) \rightarrow (I) + OH^- \qquad (3)$$

$$(III) + \text{1,4-dithian} \rightarrow (II) + OH^- \qquad (4)$$

Irrespective of the mechanism of their formation (I) and (II) may be expected to exist in the equilibrium: (I) + 1,4-dithian $\rightleftharpoons$ (II).

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