Formation of Positive Ions and Other Primary Species in the Oxidation of Sulphides by Hydroxyl Radicals

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The oxidation of simple aliphatic sulphides [MeSMe, EtSEt, $(CH_2)_4S$] by hydroxyl radicals occurs *via* a complex reaction mechanism. The first step is addition of the OH· to sulphur to form R_2SOH radicals. At low sulphide concentrations ($<10^{-4}$M) R_2SOH rapidly eliminates H_2O to form a RSR($-$H)· radical which may be described by the mesomeric forms $-CH-\underline{S}-$ and $-CH=\dot{S}-$. This radical is ultimately also formed at higher sulphide concentrations but *via* a different pathway. R_2SOH increasingly reacts with another R_2S molecule to form a short lived $(R_2S)_2OH·$ radical complex which dissociates to $(R_2S)_2^+$ and OH^-. The $(R_2S)_2^+$ complex ion seems to be relatively stable and decays essentially *via* equilibration to the molecular cation R_2S^+. This ion in its reaction with the solvent, OH^- ions, and through a bimolecular process with another R_2S^+ cation is effectively deprotonated to form the RSR($-$H)· radical. The reaction route at high concentration includes the formation of transient species with oxidizing properties; $Fe(CN)_6^{4-}$ is rapidly oxidized by $(R_2S)_2^+$ [and possibly $(R_2S)_2OH·$]. The RSR($-$H)· radical partially disproportionates to negative and long lived (>1 ms) positive ions. The stable oxidation product, sulphoxide, has been identified.

THE formation of positive ions during the oxidation of a sulphide (MeSMe) by OH· radicals in aqueous solutions was initially suggested by Henglein and his co-workers from the results of a pulse radiolytic study.[1] Evidence was also presented that the structure of the positive ion was a complex $(Me_2S)_2^+$ rather than the molecular cation Me_2S^+. The life time of $(R_2S)_2^+$ was reported to be in the 10^{-4} s range and a strong optical absorption at 470 nm was assigned to this species.

Further evidence for the existence of positive sulphide ions has been published by Norman and his co-workers.[2,3] In their e.s.r. study of the oxidation of sulphides by ·OH radicals generated in solutions containing Ti^{III}–H_2O_2 they were able to identify $(R_2S)_2^+$ ions which they suggest

to be formed *via* reaction (1). They also discuss the

$$R_2S^+ + R_2S \longrightarrow (R_2S)_2^+ \qquad (1)$$
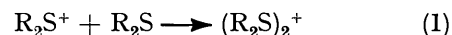
R_2S^+ ion as an important intermediate in the oxidation process.

Positive ions have also been identified as primary oxidation products of organic sulphur compounds in pulse radiolysis conductivity experiments on the oxidation of disulphides [4] [reaction (2)].

$$RSSR + OH· \longrightarrow RSSR^+ + OH^- \qquad (2)$$

[1] G. Meissner, A. Henglein, and G. Beck, *Z. Naturforsch.*, 1967, **22b**, 13.

[2] B. C. Gilbert, D. K. C. Hodgeman, and R. O. C. Norman, *J.C.S. Perkin II*, 1973, 1748.

[3] B. C. Gilbert, J. P. Larkin, and R. O. C. Norman, *J.C.S. Perkin II*, 1973, 272.

[4] H. Möckel, M. Bonifačić, and K.-D. Asmus, *J. Phys. Chem.*, 1974, **78**, 282.

In addition to R_2S^+ and $(R_2S)_2^+$ ions, some neutral radicals were also discussed as oxidation intermediates of sulphides, in particular the addition product $R_2\dot{S}OH$ and an $R\dot{C}H-SR$ radical which formally results from hydrogen atom abstraction.[1-3] In Norman's work,[2,3] however, it is indicated that the latter radical is probably formed by deprotonation of a positive R_2S^+ ion.

In the present study direct evidence for the $(R_2S)_2^+$ ion is presented by pulse radiolysis conductivity measurements. This technique has been shown to be suitable for the observation of short lived charged species.[5-7] In addition optical pulse radiolysis and some steady state γ-radiolysis studies were carried out to characterize some physico-chemical properties of the intermediate species and to establish a complete mechanism of the primary events in the oxidation process of MeSMe, EtSEt, and tetrahydrothiophen, $(CH_2)_4S$, in aqueous solution.

EXPERIMENTAL

Commercially available dimethyl sulphide, diethyl sulphide, and tetrahydrothiophen were purified by fractional distillation to $\geqslant 99\%$. Other chemicals [$HClO_4$, $NaClO_4$, NaOH, and $K_4Fe(CN)_6$] were of analytical grade and were used without further purification. The solvent was triply distilled water which was bubbled with argon for ca. 1 h to remove dissolved oxygen.

During the irradiation of water, reducing and oxidizing species (hydrated electrons e_{aq}^- and hydroxyl radicals OH· respectively) are formed simultaneously with approximately equal yields of G 2·75.* In order to study exclusively the oxidation processes initiated by the OH· radicals, the solutions were saturated with N_2O after the argon treatment. In such solutions all hydrated electrons are converted to hydroxyl radicals [reaction (3), $k = 8 \times 10^9$ l mol^{-1} s^{-1},

$$N_2O + e_{aq}^- \longrightarrow OH· + OH^- + N_2 \qquad (3)$$
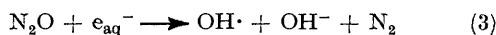
solubility of N_2O $2·6 \times 10^{-2}M$]. Traces of oxygen present in the N_2O were removed by bubbling the nitrous oxide gas through a solution of freshly prepared Cr^{2+} ions.

The required sulphide concentrations were obtained by injecting either a stock solution or the pure compound into the N_2O saturated solution through a rubber seal. Since the sulphides dissolve rather slowly in water the solutions were stirred for ca. 1—2 h prior to use.

The pulse radiolysis experiments were carried out with a 1·6 MeV (10 mA) Van de Graaff apparatus using electron pulses of 0·5—4 μs. The absorbed dose rate was ca. 1700 rad (μs pulse)$^{-1}$. The experimental set-up and the analysis of optical absorption— and conductivity–time curves has already been described.[6-8] Absolute measurements of the irradiation induced changes in conductivity are based on equation (4) [5-7] where ΔV_s is the signal voltage observed on

$$\Delta V_s = \frac{VR}{k10^3} \sum_i \Delta c_i |z_i| \Lambda_i \qquad (4)$$

the oscilloscope as a result of the formation or destruction of charges in the solution, V is the voltage between the two

* The G-value represents the number of species formed or destroyed per 100 eV absorbed energy.[8a]

[5] K.-D. Asmus, G. Beck, A. Henglein, and A. Wigger, *Ber. Bunsengesellschaft Phys. Chem.*, 1966, **70**, 869.

[6] G. Beck, *Internat. J. Radiation Phys. Chem.*, 1969, **1**, 361.

electrodes in the irradiation cell (30 V), R is a working resistance (1 kΩ), and k is the cell constant in cm^{-1}. Δc_i is the change in concentration of the ith charged species, $|z_i|$ its net change in charge number (1 for a one electron oxidation), and Λ_i its equivalent conductivity in Ω^{-1} cm^2.

Dosimetry was based on simultaneous optical and conductivity measurement of $C(NO_2)_3^-$ ions which are formed with G 5·6 in irradiated aqueous, argon saturated solutions of $10^{-3}M$-$C(NO_2)_4$ and $10^{-1}M$-isopropyl alcohol [maximum absorption of $C(NO_2)_3^-$ at 350 nm with ε 1·5 × 10^4 l mol^{-1} cm^{-1}, and equivalent conductivity of a $C(NO_2)_3^-$-H_{aq}^+ ion pair Λ 360 Ω^{-1} cm^2].[7,9]

γ-Radiolysis experiments were performed with a ^{60}Co source of ca. 1500 Ci and an absorbed dose rate of 1·2 × 10^5 rad h^{-1}.

Analysis for $Fe(CN)_6^{3-}$ ions were carried out spectrophotometrically on the Zeiss RPQ 20A instrument. G.l.c. was performed with a Varian 2860 chromatograph using a SE 30 column for the analysis of sulphoxides and a Porapak P-S column to test the purity of the sulphides.

All experimental data refer to room temperature.

RESULTS AND DISCUSSION

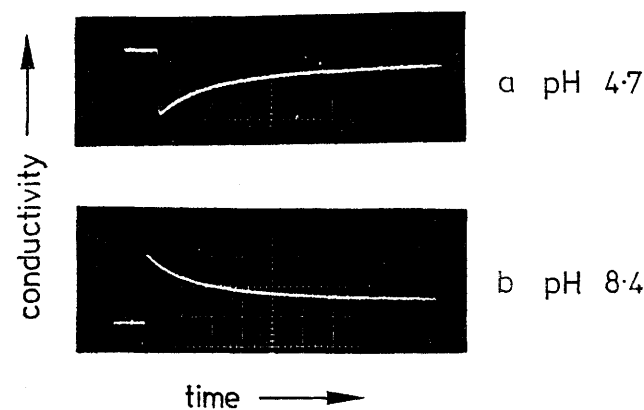*Formation of Positive Ions.—Conductivity measurements.* Figure 1 shows typical examples of conductivity–

FIGURE 1 Conductivity–time curves of pulse-irradiated aqueous N_2O saturated solutions of $5 \times 10^{-4}M$-Me_2S. Pulse length ca. 1 μs; time scale: 200 μs per large division; sensitivity: 20 mV per large division: a pH 4·7, dose 955 rad (5·96 × 10^{16} eV g^{-1}); b pH 8·4, dose 1050 rad (6·55 × 10^{16} eV g^{-1})

time curves observable in pulse irradiated, N_2O saturated, aqueous solutions of sulphides. In particular the diagrams refer to a solution of $5 \times 10^{-4}M$-MeSMe at pH 4·7 and 8·4. Similar diagrams were observed for the other sulphides discussed in this paper.

In the slightly acid solution (Figure 1a) the conductivity is seen to have decreased immediately after the pulse. At longer times the signal increases again with a half-life of ca. 150 μs to ca. 75% of its original value. In the ms time range therefore a net decrease in conductivity remains.

[7] K.-D. Asmus, *Internat. J. Radiation Phys. Chem.*, 1972, **4**, 417.

[8] (a) A. Henglein, W. Schnabel, and J. Wendenburg, in' Einführung in die Strahlenchemie,' Verlag Chemie, Weinheim, 1969; (b) A. Henglein, *Allg. prakt. Chem.*, 1966, **17**, 296.

[9] K.-D. Asmus, H. Möckel, and A. Henglein, *J. Phys. Chem.*, 1973, **77**, 1218.

In the slightly basic solution (Figure 1b) the conductivity increases immediately after the pulse; it then decreases again, levelling off at *ca.* 70% of its pre-pulse value.

The reaction of MeSMe with ·OH radicals is known to be an essentially diffusion controlled process (see ref. 1 and below). At this sulphide concentration the reaction is thus complete within the time-span of the pulse, and the observed changes in conductivity have to be attributed to the ·OH–sulphide oxidation reaction.

The initial decrease in conductivity clearly indicates the formation of positive ions in the reaction of the sulphide with hydroxyl radicals. The oxidation of the sulphide, *i.e.* the removal of an electron, necessarily leads to a simultaneous formation of an OH^- ion as the negative counter ion [reaction (5)]. In the acid solution

$$\text{sulphide} + \text{OH·} \longrightarrow \text{sulphide}^+ + \text{OH}^- \quad (5)$$
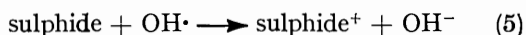
the OH^- ion will, of course, immediately be neutralized [reaction (6)] thereby removing a proton from the solution, *i.e.* the net effect is a substitution of a H_{aq}^+ ion by a

$$\text{OH}^- + \text{H}_{aq}^+ \longrightarrow \text{H}_2\text{O} \quad (6)$$

positive sulphide ion. Since the specific conductivity of a proton in aqueous solution (Λ 315 Ω^{-1} cm^2) is much higher than that of a ' normal ' positive ion (Λ *ca.* 60—70 Ω^{-1} cm^2) [10] the overall effect of the sulphide oxidation will be a decrease in conductivity. The exact nature of the positive ion formed from the sulphide cannot be deduced from a single conductivity experiment. Owing to the similarity of specific conductivities of singly charged positive ions no distinction can be made between the simple MeSMe^+ ion, a complexed $(\text{MeSMe})_2^+$, or any other positive ion. Identification of the positive ion is however possible by additional optical and conductivity pulse radiolysis experiments as seen below.

In basic solution the hydroxide ion formed in reaction (5) is stable with respect to neutralization by protons. Consequently, the conductivity signal increases owing to the formation of the positive ion (Λ *ca.* 60—70 Ω^{-1} cm^2) and the OH^- ion (Λ 180 Ω^{-1} cm^2) [10] (Figure 1b).

Any mechanism which does not include the formation of hydroxide ions and a positive ion cannot explain the observed changes in conductivity. Radical anions associated with protons (*e.g.* from acid–base dissociation of an ·OH radical adduct to the sulphide) would necessarily lead to a reversed situation, *i.e.* increase in conductivity in acid solution, and decrease in basic solution. The latter is due to immediate neutralization of the proton and effective substitution of an OH^- ion (Λ 180 Ω^{-1} cm^2) by a less conducting negative ion (Λ *ca.* 60 Ω^{-1} cm^2).[10]

The yield of positive ions can be calculated from the decrease or increase in conductivity immediately after the pulse.[5-7] From Figure 1a (the signal obtained in acid solution), an initial decrease in conductivity cor-

responding to $G \times \Delta\Lambda = 1000$ [see equation (4)] is derived.* $\Delta\Lambda$ is the difference between the specific conductivity of a proton and the less conducting positive ion, *i.e.* $\Delta\Lambda = \Lambda_{\text{H}_{aq}^+} - \Lambda_{\text{pos. ion}}$. The specific conductivity of the radical positive ion formed in the oxidation process [equation (5)] is unknown. It is expected, however, to be in the range of other normal singly charged positive ions of similar size [10] and is taken as $\Lambda_{\text{pos. ion}} = (65 \pm 10)\ \Omega^{-1}$ cm^2. With the known $\Lambda_{\text{H}_{aq}^+} = 315\ \Omega^{-1}$ cm^2 $\Delta\Lambda$ is estimated to be 250 Ω^{-1} cm^2 and thus $G(\text{pos. ion}) = 4\cdot0$.

The same yield is obtained by analysis of Figure 1b. In basic solution the initial conductivity increase is produced by positive sulphide ions and OH^- ions with a total $\Lambda = \Lambda_{\text{pos. ion}} + \Lambda_{\text{OH}^-} = 65 + 180 = 245\ \Omega^{-1}$ cm^2. The observed signal corresponds to a $G \times \Lambda = 950$. Hence $G(\text{positive ions}) = 3\cdot9$ and amounts to essentially the same value as in slightly acid solution. In fact the yield of positive ions as determined from the conductivity experiments is found to be independent of pH within the range 3—8·5. At higher pH, neutralization of the positive ions by OH^- occurs. This aspect is treated in more detail below.

The slower increase in conductivity following the initial decrease (Figure 1a) in acid solution is explained by slow chemical conversion of the positive sulphide ion back to highly conducting protons. This liberation of H_{aq}^+ in basic solution leads to the observed decrease after the initial increase (immediate neutralization by OH^-).

The remaining net change in conductivity after *ca.* 1 ms indicates that some long lived positive ions are formed as well.

Conductivity changes very similar to those discussed above for MeSMe were also observed in solutions of EtSEt and $(\text{CH}_2)_4\text{S}$ pulse irradiated under the same conditions. Again, the formation of transient positive ions is clearly indicated.

For all three sulphides the yield of positive ions is found to be strongly dependent on the sulphide concentration. As can be seen from Figure 2, $G(\text{positive ion})$ steadily increases, reaching a plateau value of G *ca.* 5·5 at concentrations of several 10^{-3}M. Two important conclusions can be drawn from this finding. (1) The formation of the conducting positive ion cannot be a single step process and seems to involve more than one sulphide molecule. Since the reactions of the sulphides with ·OH radicals are essentially diffusion controlled, *ca.* 10^{-4}M-solute will be sufficient for complete scavenging of the hydroxyl radicals.[8] Our finding is therefore in agreement with the conclusions of Henglein [1] and Norman [2] on the more complex nature of the positive ion. (2) The yield of positive ions formed at high concentrations equals the yield of oxidizing hydroxyl radicals [$G(\text{OH}) = 5\cdot5$ in irradiated N_2O saturated aqueous solutions]. This suggests that only one species is formed in the initial reaction of ·OH + R_2S. Depending on the sulphide concentration, this species will then either form positive

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* $\Delta c \times \Lambda$ is calculated using equation (4). G is directly proportional to the concentration, $G = \Delta c \times N_L \times 10^2/\text{dose} \times 10^3$ (dose in eV g^{-1}).[8a]

[10] Landolt-Börnstein, ' Zahlenwerte und Funktionen,' Springer–Verlag, Berlin, 1960, vol. II/7.

ions or react *via* a different pathway. Since the three possible reaction modes of an OH radical (abstraction, addition, electron transfer) would lead to completely
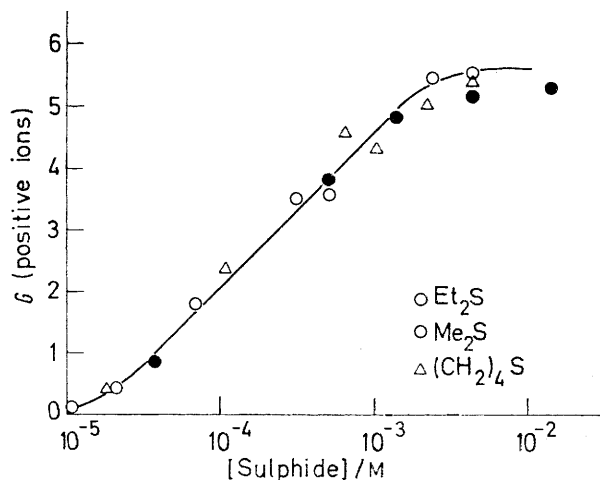

FIGURE 2   Yield of positive ions $[(R_2S)_2^+]$ as a function of sulphide concentration determined by conductivity measurements

different primary species our results also indicate that only one of these mechanisms occurs as a primary process.

Optical absorption spectra. Two main transient absorptions peaking at 280 and 470 nm have been observed in pulse irradiated neutral, N_2O saturated solutions of MeSMe in a previous study.[1]   In ref. 1 the two absorptions were attributed to the $\dot{C}H_2SMe$ radical (280 nm) and the positive ion (470 nm).   In view of the concentration dependence of the yield and the lifetime the latter was assumed to be the complexed $(MeSMe)_2^+$ ion.

Very similar observations were now made for solutions of EtSEt and $(CH_2)_4S$.   The spectrum of the transient absorptions from EtSEt ($10^{-3}M$; N_2O saturated) 5 μs after a 1 μs pulse is shown by the solid curve in Figure 3.
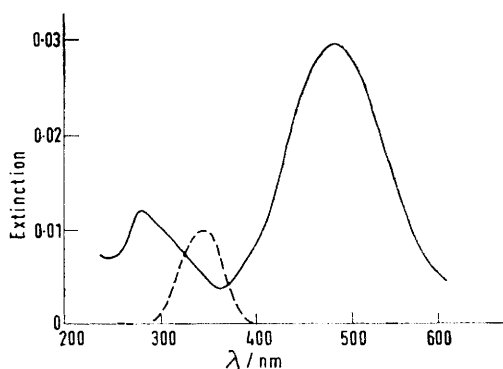

FIGURE 3   Spectrum of transient species from the reaction OH· + Et_2S: solid line, absorption at 5 μs after 1 μs pulse; dashed line, short lived absorption at the end of the 1 μs pulse. The extinction is generally normalized to an absorbed dose of 10^3 rad ($6·24 \times 10^{16}$ eV g^{-1})

The dashed line refers to another, very short lived, absorption observed during and immediately after the pulse.   Its half-life is <5 μs and the maximum absorp-

tion occurs at 340 nm.   The three absorption maxima are attributed to different species on account of differences in the rates of formation and decay, kinetic salt effects, and concentration dependences.

The concentration dependence of the optical absorptions is shown in Figure 4.   The yield of the 280 nm absorption measured immediately after the pulse increases at low concentration reaching a maximum value at $<10^{-4}M$-EtSEt.   This is to be expected if the absorption is formed by a diffusion controlled process by reaction of the sulphide with hydroxyl radicals, *i.e.* the curve essentially describes the competition $R_2S + OH·$ and $OH· + OH·$.

The short lived 340 nm absorption (measured immediately after the pulse) grows in at comparatively much higher concentration.   Significant yields are detectable at concentrations $>10^{-4}M$.   The increase in 340 nm absorption also appears to coincide with a slight decrease in yield of the 280 nm absorption.
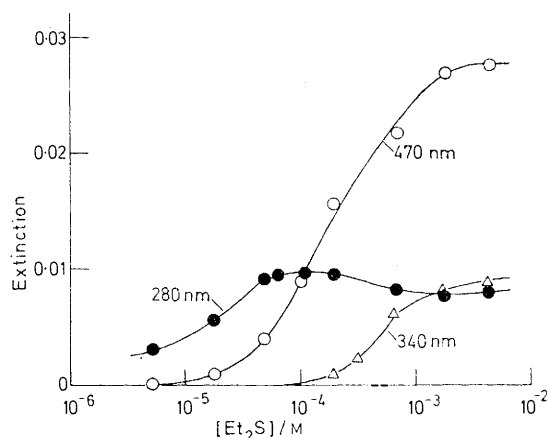

FIGURE 4   Yield of the transient 280, 340, and 470 nm absorption as a function of Et_2S concentration (extinction normalized to 10^3 rad)

The concentration dependence of the 470 nm absorption (measured *ca.* 5 μs after the pulse) essentially parallels that of the 340 nm absorption and also the yield of positive ions shown in Figure 2.   Maximum yield is achieved at a concentration $>10^{-3}M$-sulphide.

Kinetic analysis also shows different pictures for the various absorbing species.   The 280 nm species is formed *via* a pseudo-first-order process at low concentrations, the rate being dependent on the sulphide concentration. An overall second-order rate constant for its formation in the ·OH + R_2S reaction is derived as k *ca.* $(1·4 \pm 0·5) \times 10^{10}$ 1 mol^{-1} s^{-1}.   At concentrations $>5 \times 10^{-5}M$, the 280 nm product is formed during the 1 μs pulse.   The decay of the transient essentially occurs *via* a second-order process.   The first half-life, as seen in Figure 5, stays constant over most of the concentration range. The increase in $t_{1/2}$ at very low concentrations is explained by a lower transient concentration (see Figure 4) due to incomplete OH· scavenging.

The formation of the short lived 340 nm absorption cannot be resolved.   It is always formed within the

pulse, *i.e.* $t_{1/2} < 1$ μs. The decay of the absorption occurs by a first-order process with $t_{1/2}$ 1—2 μs essentially independent of sulphide concentration.

A direct relation seems to exist between the 340 and the 470 nm species. As the 340 nm absorption decays,
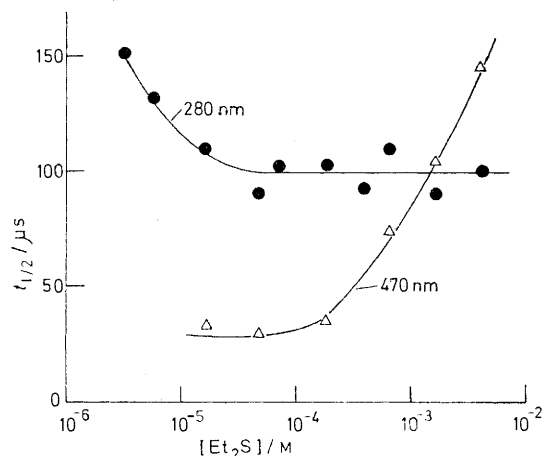
FIGURE 5 Half-lives for the decay of the optical absorption at 280 and 470 nm as a function of Et₂S concentration at an absorbed dose of *ca.* 10³ rad

the 470 nm absorption increases. Two typical oscilloscope traces of the optical absorption at these two wavelengths as a function of time are shown in Figure 6 for a solution of 5×10^{-4}M-EtSEt. (The long lived component in the 340 nm trace originates from the 470 nm species which has a broad absorption extending into the u.v. region.) The half-life of the 470 nm formation is identical with that for the 340 nm decay. Only at low sulphide concentrations where the 340 nm species cannot be detected, does the rate of the 470 nm formation become dependent on the sulphide concentration.

Quite different decay kinetics are observed for the 470 nm species. The decay is of mixed first and second order and will be treated in detail below. Two important
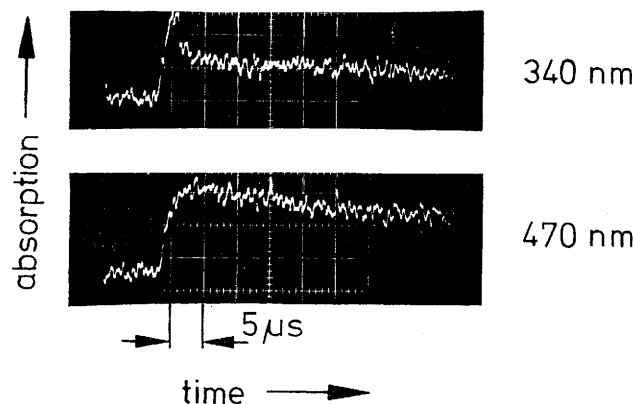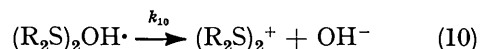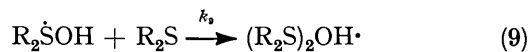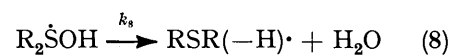
FIGURE 6 Absorption–time curves at 340 and 470 nm in pulsed (1 μs), N₂O saturated solutions of 5×10^{-4}M-Et₂S (pH 5)

features relevant to the identification of the species involved in the mechanism should be noted however at this point. (1) The lifetime considerably increases with sulphide concentration (Figure 5). (2) At low sulphide

concentrations where only small yields of the 470 nm species are formed the first half-life seems to level off at a lower limit of *ca.* 30 μs.
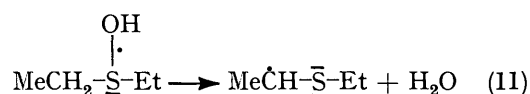
Kinetic salt effect experiments show no influence of the ionic strength of the solution on the 280 and 340 nm decay. The 470 nm decay rate, however, increases with ionic strength ($NaClO_4$) as expected for a bimolecular reaction of two charged species of the same sign.

Reaction Mechanism.—On the basis of the experimental results presented above the 470 nm absorption is assigned to the positive ion and that at 340 nm to its immediate precursor. The concentration dependence of yield and kinetics implies that the formation of the 340 nm product involves a second sulphide molecule, and that both the 340 and 280 nm species have a common nonabsorbing precursor. Furthermore, from the conductivity experiments it is evident that the precursors of the 470 nm positive ion are neutral species. Taking into account the previous conclusion, *i.e.* that the ˙OH radical undergoes only one specific type of reaction with the sulphide, the mechanism (7)—(10) for the primary steps of the sulphide oxidation may be derived. The first step

$$R_2S + OH \cdot \xrightarrow{k_7} R_2\dot{S}OH \qquad (7)$$

$$R_2\dot{S}OH \xrightarrow{k_8} RSR(-H)\cdot + H_2O \qquad (8)$$

$$R_2\dot{S}OH + R_2S \xrightarrow{k_9} (R_2S)_2OH\cdot \qquad (9)$$

$$(R_2S)_2OH\cdot \xrightarrow{k_{10}} (R_2S)_2^+ + OH^- \qquad (10)$$
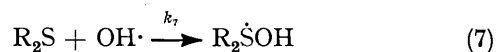
is the diffusion controlled addition reaction of the ˙OH radical to sulphur. Since sulphur can accept additional electrons in its d orbitals, an $R-\dot{S}(OH)-R$ structure appears reasonable. It is also known that this type of radical does not exhibit any absorption in the visible and near u.v. range.[1]

$R_2\dot{S}OH$ then eliminates H_2O in a fast process ($t_{1/2} < 1$ μs, *i.e.* $k_8 > 7 \times 10^5$ s⁻¹) by reaction (11). Since the

$$\text{MeCH}_2-\overset{\overset{\displaystyle OH}{|\cdot}}{\underline{S}}-\text{Et} \longrightarrow \text{Me}\overset{\cdot}{C}H-\underline{\underline{S}}-\text{Et} + H_2O \qquad (11)$$

resulting radical probably exists in mesomeric forms the

$$\text{Me}\overset{\cdot}{C}H-\underline{\underline{S}}-\text{Et} \longleftrightarrow \text{MeCH}=\underline{\dot{S}}-\text{Et} \qquad (12)$$

gain in energy may facilitate the fast water elimination from the OH adduct. The 280 nm absorption is attributed to this mesomeric radical. At low sulphide concentrations it is virtually the only absorbing species.

At higher sulphide concentrations $R_2\dot{S}OH$ reacts to an increasing extent with an undamaged sulphide molecule to form the complexed radical $(R_2S)_2OH\cdot$ which is thought to be responsible for the 340 nm 'spike' absorption. [The absorption of an $(R_2S)_2OH\cdot$ complex should be shifted towards the red compared with that of $R_2\dot{S}OH$.] Since its rate of formation could not be resolved even at the lowest concentration at which the absorption is

observable, k_9 can only be estimated as of the order of diffusion controlled rate constants.

The $(R_2S)_2OH\cdot$ radicals then decay via a first-order process to form $(R_2S)_2^+$ and OH^- ions, the former being responsible for the 470 nm absorption. The rate constant k_{10} is calculated to be $(4 \pm 1) \times 10^5$ s^{-1}. At low R_2S concentrations the rate-determining step of $(R_2S)_2^+$ formation is the complexation reaction (9), i.e. the rate of growth of the 470 nm absorption becomes dependent on R_2S concentration. From this $k_9 = (5\cdot3 \pm 1\cdot5) \times 10^9$ l mol^{-1} s^{-1} is derived.

Further evidence for the suggested mechanism is provided by the following observations. The dissociation of $(R_2S)_2OH\cdot$ into ions is certainly expected to be enhanced by H_{aq}^+. And indeed the lifetime of the 340 nm absorption decreases with decreasing pH and no $(R_2S)_2OH\cdot$ absorption can be observed below pH 3. In basic solution at pH > 9 the absorption becomes longer lived, up to $t_{1/2}$ 10 μs at pH ca. 11.

Table 1 summarizes various rate constants (k_7, k_9, k_{10}), the half-life of the optical absorption at 470 nm at low sulphide concentrations, and the extinction coefficients of the $(R_2S)_2^+$ ions at 470 nm. The latter were calculated from the optical density at this wavelength in solutions of high sulphide concentration, i.e. complete conversion of $\cdot$OH radicals into positive ions. Maximum absorptions always occurred at the same wavelengths for all three sulphides, i.e. for the $RSR(-H)\cdot$ radical at 280 nm, for the $(R_2S)_2OH\cdot$ radical at 340 nm, and for the $(R_2S)_2^+$ radical ion at 470 nm.

Decay of the Transients.—$(R_2S)_2^+$ *Decay.* The decay of the transient 470 nm absorption cannot be described in terms of simple first- or second-order kinetics. The first half-life generally decreases with increasing dose, i.e. increasing transient concentration, and the usual second-order plots of the reciprocal optical density (at 470 nm) versus time yield reasonable straight lines. The second-order rate constants thus derived, however, decrease with

<div align="center">TABLE 1</div>

Rate constants k_7, k_9, and k_{10}, maximum extinction coefficients for the $(R_2S)_2^+$ ion at 470 nm, and minimum half-life of the 470 nm absorption at low sulphide concentrations

R_2S	k_7/l mol^{-1} s^{-1}	k_9/l mol^{-1} s^{-1}	k_{10}/s^{-1}	$\varepsilon_{(R_2S)_2^+}$/l mol^{-1} cm^{-1} at 470 nm	$t_{1/2}$/μs at at 470 nm
Me$_2$S	$(1\cdot9 \pm 0\cdot5) \times 10^{10}$	$(1\cdot3 \pm 0\cdot4) \times 10^{10}$	$\approx 4 \times 10^5$	$(6\cdot2 \pm 0\cdot4) \times 10^3$	≈ 60
Et$_2$S	$(1\cdot4 \pm 0\cdot4) \times 10^{10}$	$(5\cdot3 \pm 2\cdot0) \times 10^9$	$\approx 4 \times 10^5$	$(6\cdot5 \pm 0\cdot3) \times 10^3$	≈ 30
(CH$_2$)$_4$S	$(1\cdot4 \pm 0\cdot4) \times 10^{10}$	$(6\cdot3 \pm 2\cdot0) \times 10^9$	$\geqslant 4 \times 10^5$	$(6\cdot4 \pm 0\cdot3) \times 10^3$	≈ 50

The $(R_2S)_2^+$ absorption in basic solution decays increasingly rapidly with increasing pH, indicating the neutralization of the positive ion by hydroxide ions. Further, kinetic salt effect experiments on the decay of the 470 nm absorption show that the reaction of the OH^- ion occurs with a positively charged species. At high ionic strength of the solution ($>10^{-1}$M-NaClO$_4$) the rate of decay decreases. In addition, as the yield and the lifetime of the $(R_2S)_2^+$ absorption decrease with increasing pH a strong new absorption appears with a maximum at 350 nm. This well known absorption is due to the radical anion $R_2\dot{S}O^-$,[1] which is much more stable than its neutral $R_2\dot{S}OH$ form. In our high pH solutions $R_2\dot{S}O^-$ is formed directly by dissociation of the OH adduct.

The fact that the competition between reactions (8) and (9) does not lead to a complete elimination of the 280 nm absorption at high sulphide concentrations may be explained as follows. (1) The decay of the $(R_2S)_2^+$ ion eventually yields the 280 nm radical again (see below). (2) The decay kinetics at 280 and 470 nm become increasingly similar with increasing sulphide concentration. A significant part of the 280 nm absorption therefore seems to be due to u.v. tailing of the $(R_2S)_2^+$ absorption.

The mechanism derived above for diethyl sulphide applies in principle to dimethyl sulphide and tetrahydrothiophen. The only significant difference was that the 340 nm spike could not be observed for tetrahydrothiophen. The lifetime of the $(R_2S)_2OH\cdot$ seems to be shorter (i.e. <1 μs), and in addition a possibly smaller extinction coefficient could preclude distinction from the other absorbing species.

increasing concentration of the reacting species (k_2 should be independent of concentration for a pure second-order process). Such a finding is typical for mixed first- and second-order processes. Assuming that the $(R_2S)_2^+$ ion disappears by a mixed reaction path, the decay kinetics are described by the differential equation (13) where the

$$-\mathrm{d}c/\mathrm{d}t = 2k_2c^2 + k_1c \qquad (13)$$

second-order term pertains to the bimolecular reaction of two positive ions and the first-order term describes a pure or pseudo-first-order reaction of the positive ion. The latter could, for example, be a reaction with the solvent water molecule. Integration of this equation leads to (14) [c_0 = initial concentration of $(R_2S)_2^+$ ions]. For

$$\frac{1}{c} = \frac{2k_2}{k_1}(e^{k_1t} - 1) + \frac{1}{c_0}e^{k_1t} \qquad (14)$$

convenience this expression can be simplified by expanding the e^{k_1t} term.[11] Under the condition that $k_1t \leqslant 1$, which is met in our experiments, this leads to the approximation (15). A plot of $1/c$ versus time accordingly yields a straight line whose slope however is

$$\frac{1}{c} \sim \left(2k_2 + \frac{k_1}{c_0}\right)t + \frac{1}{c_0} \qquad (15)$$

dependent on c_0, i.e. the initial concentration of the reacting positive ion.

The apparent second-order rate constant k_{II} derived from the experimental result by the usual second-order

[11] K.-D. Asmus and I. A. Taub, *J. Phys. Chem.*, 1968, **72**, 3382.

$1/c$ versus t plots is therefore given by equation (16).

$$k_{\mathrm{II}} = 2k_2 + k_1/c_0 \qquad (16)$$

Substitution of c_0 by $E_0/\varepsilon d$ (E_0 = extinction at 470 nm at $t = 0$, ε = extinction coefficient, and $d = 1$ cm = optical path length) leads to expression (17) for the measured apparent second-order rate constant.[11] Accordingly a

$$k_{\mathrm{II}}/\varepsilon = 2k_2/\varepsilon + k_1/E_0 \qquad (17)$$

plot of $k_{\mathrm{II}}/\varepsilon$ versus $1/E_0$ should give a straight line with $2k_2/\varepsilon$ as intercept and k_1 as the slope. Figure 7 shows such plots for the decay of the 470 nm absorption in pH 4·7 solutions of 4·2 × 10^{-3}M-dimethyl and -diethyl sulphide, and -tetrahydrothiophen. The good straight lines obtained support the suggested mechanism. From the intercepts and the extinction coefficients (Table 1) the second-order rate constants, $2k_2$, are calculated as 4·65 × 10^8, 4·8 × 10^8, and 6·15 × 10^8 l mol^{-1} s^{-1} for Me$_2$S, Et$_2$S, and (CH$_2$)$_4$S, respectively. Although the second-order rate constants do not differ very significantly for the three sulphides, larger differences are noted for the first-order terms. From the slopes, k_1, 0·4 × 10^3, 1·8 × 10^3, and 3·5 × 10^3 s^{-1}, are derived for Me$_2$S, (CH$_2$)$_4$S, and Et$_2$S, respectively, i.e. an appreciably higher first-order contribution is observed for the diethyl compound than for tetrahydrothiophen and dimethyl sulphide.

Changes in the ionic strength of the solution affect only the second-order term (pH < 8·5). The first-order rate constant on the other hand is strongly dependent on the sulphide and OH$^-$ ion concentration.

Figure 8 shows, for example, plots of $k_{\mathrm{II}}/\varepsilon$ versus $1/E_0$ for various concentrations of Et$_2$S. The gradient, k_1, increases by a factor of ca. 10 with a ca. 25-fold decrease in sulphide concentration. Further, the intercept, $2k_2$,
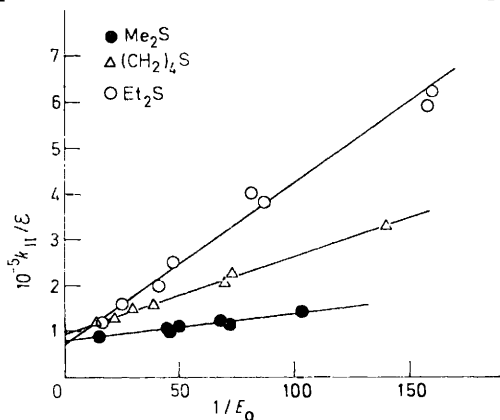
FIGURE 7   Plots of $k_{\mathrm{II}}/\varepsilon$ (derived from second-order $1/E$ against t plots) against $1/E_0$ (E = extinction at 470 nm at time t, E_0 = maximum extinction at 470 nm at $t = 0$): concentration of sulphides 4·2 × 10^{-3}M; pH 4·7

seems to increase at lower Et$_2$S concentrations. It may be noted, however, that even slight differences in gradient lead to large differences in $2k_2$ and thus no meaningful quantitative conclusions may be drawn from the apparent changes in the second-order rate constant.

Such a concentration dependence together with the

dependence of the (R$_2$S)$_2^+$ ion yield on the sulphide concentration suggests that it is not the (R$_2$S)$_2^+$ ion itself which reacts but another species which forms (R$_2$S)$_2^+$ ions with increasing sulphide concentration. According to
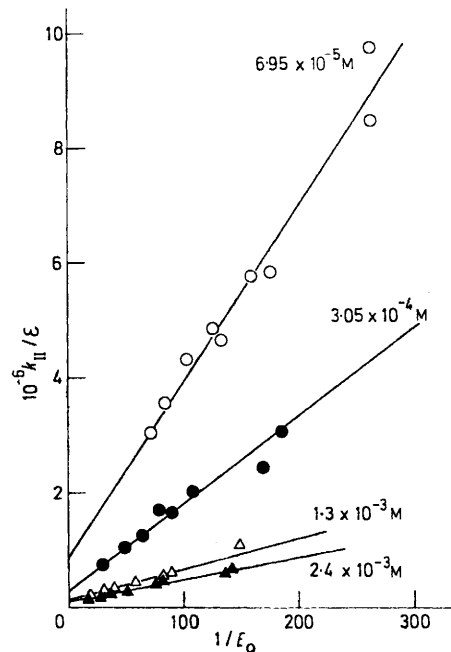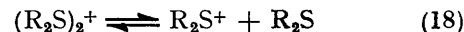
FIGURE 8   Plots of $k_{\mathrm{II}}/\varepsilon$ against $1/E_0$ for various concentrations of Et$_2$S: pH 4·7

the kinetic salt effect this species should also be a positive ion. The simplest and most reasonable hypothesis

$$(\mathrm{R_2S})_2^+ \;\rightleftharpoons\; \mathrm{R_2S^+} + \mathrm{R_2S} \qquad (18)$$

would be equilibrium (18) where the R$_2$S$^+$ ion is the reactive species and (R$_2$S)$_2^+$ has a comparatively long lifetime.

The disappearance of positive ions by a first-order process is now given by equation (19) where $c =$

$$-\mathrm{d}c/\mathrm{d}t = k[\mathrm{R_2S^+}] \qquad (19)$$

$[(\mathrm{R_2S})_2^+] + [\mathrm{R_2S^+}]$, i.e. the total positive ion concentration, and k is the true [R$_2$S]-independent, first-order decay rate constant. Where equation (20) applies

$$K = [\mathrm{R_2S^+}][\mathrm{R_2S}]/[(\mathrm{R_2S})_2^+] \qquad (20)$$

then (21) and (22) follow. Inspection of equation (22)

$$[\mathrm{R_2S^+}] = Kc/(K + [\mathrm{R_2S}]) \qquad (21)$$

$$-\mathrm{d}c/\mathrm{d}t = kKc/(K + [\mathrm{R_2S}]) \qquad (22)$$

shows that the experimentally measured first-order rate constant, k_1, for the decay of positive ions may be expressed as (23). Rearrangement leads to (24). A plot

$$k_1 = kK/(K + [\mathrm{R_2S}]) \qquad (23)$$

$$1/k_1 = 1/k + [\mathrm{R_2S}]/kK \qquad (24)$$

of the reciprocal of k_1 (as derived from the $k_{\mathrm{II}}/\varepsilon$ against $1/E_0$ plots) against sulphide concentration accordingly is expected to yield a straight line. Figure 9 shows such a

treatment for the Et_2S results. Similar diagrams are obtained for Me_2S and $(CH_2)_4S$. The true first-order rate constants and the equilibrium constants K as calculated from the intercepts and slopes of the respective curves are listed in Table 2.

TABLE 2

True first-order rate constant for the decay of the R_2S^+ ion and equilibrium constant for $(R_2S)_2^+ \rightleftharpoons R_2S^+ + R_2S$

R_2S	k/s^{-1}	$K/mol\ l^{-1}$
Me_2S	$(2\cdot5 \pm 0\cdot5) \times 10^3$	$(1\cdot8 \pm 0\cdot5) \times 10^{-3}$
$(CH_2)_4S$	$(6\cdot9 \pm 2\cdot0) \times 10^3$	$(1\cdot1 \pm 0\cdot5) \times 10^{-3}$
Et_2S	$(33\cdot3 \pm 5\cdot0) \times 10^3$	$(0\cdot29 \pm 0\cdot07) \times 10^{-3}$

The dissociation constants, K, decrease from Me_2S through $(CH_2)_4S$ to Et_2S, $i.e.$ the strongest complex, $(R_2S)_2^+$, exists for the diethyl compound. Since the concentration dependence of the yield of $(R_2S)_2^+$ ions (Figure 2) was found to be independent of the nature of the sulphide, these differences in K would indicate that the $(R_2S)_2^+$ ion is not formed via an intermediate R_2S^+ in the oxidation process, thereby supporting our mechanism with $(R_2S)_2OH\cdot$ as immediate precursor of the complex cation.

The first-order rate constant for the R_2S^+ decay is also highest for Et_2S. This value ($k\ 3\cdot3 \times 10^4\ s^{-1}$) which refers to infinitely low sulphide concentrations corresponds to a half-life of 21 μs. Since the kinetic analysis of the 470 nm absorption decay in Et_2S solutions shows a considerable first-order contribution [much more than for Me_2S and $(CH_2)_4S$] and the first half-life at low Et_2S concentrations is $ca.$ 30 μs, this may be considered as further support for the complex kinetic treatment above.

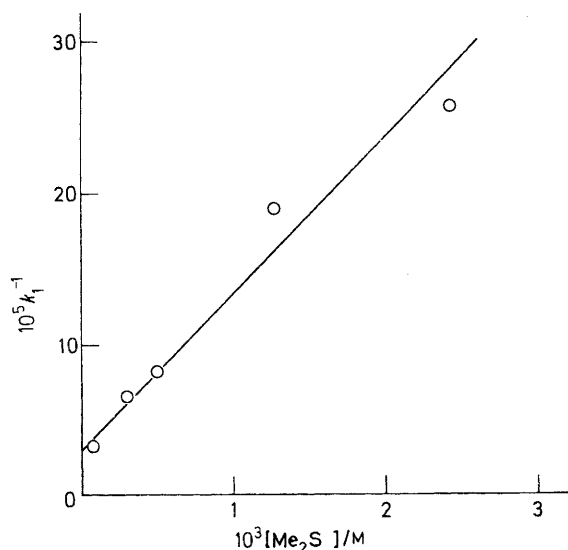The decay kinetics of the positive ions are essentially invariant with pH within the range 3—8·5. At higher

FIGURE 9 Plot of $1/k_1$ (k_1 = first-order rate constant for the decay of the 470 nm absorption as derived from k_{II}/ε against $1/E_0$ plots) as a function of Et_2S concentration

pH, the rate of the 470 nm decay increases. Plots of k_{II}/ε against $1/E_0$ for solutions of 5×10^{-3}M-Et_2S and different OH^- ion concentrations are shown in Figure 10.

From these curves it is concluded that it is mainly the first-order decay which is affected by the hydroxide ion concentration.

The results presented above suggest that the chemical reactions leading to the decay of the $(R_2S)_2^+$ ion absorption at 470 nm are the pseudo-first-order processes of the
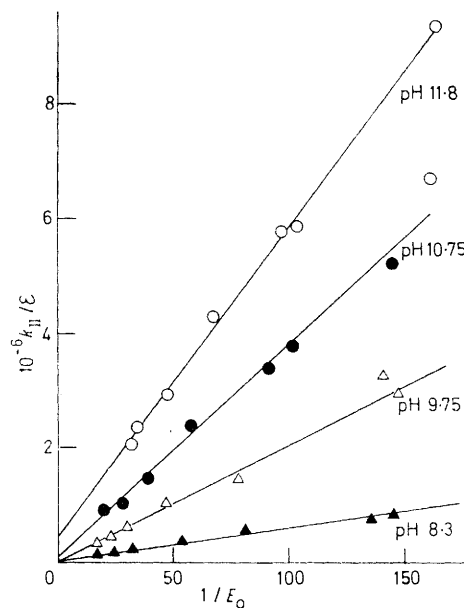
FIGURE 10 Plots of k_{II}/ε against $1/E_0$ for the decay of the 470 nm absorption at various pH values. Concentration of $Et_2S = 5 \times 10^{-3}$M

R_2S^+ with H_2O and OH^-. The most likely processes are the proton transfer reactions (25) and (26) directly forming the radical, thought to be responsible for the 280 nm

$$R_2S^+ + H_2O \longrightarrow RSR(-H)\cdot + H_3O^+ \quad (25)$$

$$R_2S^+ + OH^- \longrightarrow RSR(-H)\cdot + H_2O \quad (26)$$

absorption. The first-order rate constant derived from the results in slightly acid solution then describes the reaction of the positive ion with the solvent. In basic solution the additional reaction with hydroxide ions shows the kinetic salt effect. The bimolecular rate constants for reaction (26) derived from the results in Figure 10 and similar results for solutions of Me_2S and $(CH_2)_4S$ are of the order of $10^7\ l\ mol^{-1}\ s^{-1}$, $i.e.$ considerably lower than expected for a simple neutralization reaction. A neutralization of R_2S^+ to form R_3SOH therefore appears less likely. Furthermore an R_2SOH radical would, by reaction with R_2S [equation (9)] immediately re-enter the cycle to eventually produce $(R_2S)_2^+$ ions again. At high concentrations of R_2S ($>10^{-3}$M) where R_2SOH quantitatively reacts with R_2S the lifetime of the $(R_2S)_2^+$ ion is thus expected to be infinite, $i.e.$ practically much longer than the experiment shows. The direct formation of the $RCHSR$ radical from the positive ion is also in agreement with Norman's suggestions.[2,3]

The second order rate constant $2k_2$ is attributed to

reaction (27) yielding either a dimer ion or leading to disproportionation.

$$R_2S^+ + R_2S^+ \longrightarrow (R_2S)_2{}^{2+} \text{ or } R_2S + R_2S^{2+} \quad (27)$$
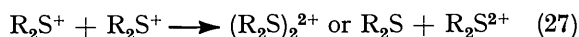
The complex $(R_2S)_2{}^+$ ion could of course also contribute to a small extent to the decay of the 470 nm absorption though our results would indicate high stability of this ion compared to the R_2S^+ ion.

It would be expected, however, that in basic solution the $(R_2S)_2{}^+$ ion would also be neutralized by OH^- ions.

Decay of the conductivity signals. The reaction of R_2S^+ with H_2O leads to the liberation of a free proton. This process accounts for the partial recovery of the conductivity signal in the μs—ms time range as discussed already in the conductivity measurements section. The decay kinetics of the curves (see Figure 1) are of a similar complex nature as those of the 470 nm absorption (a higher first-order contribution is indicated). The lifetime of the conductivity is, however, generally longer than that of the optical absorption. For Et_2S, $t_{1/2}$ (cond.) exceeds $t_{1/2}$ (opt.) by up to 25%, for $(CH_2)_4S$ and Me_2S by up to 50%. This is easily explained by the second-order contribution to the positive ion decay. The reaction of two R_2S^+ ions *via* equation (27) again yields positive ions [R_2S^{2+} or $(R_2S)_2{}^{2+}$] with the same net charge. This reaction therefore does not lead to a change in conductivity though it contributes to the decay of the 470 nm absorption. Secondary reactions of these new ions, *e.g.* with H_2O, will produce protons and thus contribute to the (delayed) decay in conductivity. It might be noted that differences in lifetime between conductivity and optical signal are smallest for Et_2S which also showed the relatively smallest contribution to the second-order part of the overall decay.

The residual (long lived) change in conductivity is explained below together with the decay of the species absorbing at 280 nm, *i.e.* the RSR($-$H)· radical. As will be seen it is not related to any of the positive ions discussed so far.

RSR($-$H)·*Radical decay.* The 280 nm absorption has been attributed to the RSR($-$H)· radical. It appears to be formed by a fast irreversible H_2O elimination from the OH· radical adduct to the sulphide, $R_2\dot{S}OH$, and as a neutralization product of the $(R_2S)_2{}^+$ and R_2S^+ ions. Its decay kinetics are best evaluated at low sulphide concentrations where yields of $(R_2S)_2{}^+$ ions are small or non-existent. The decay of the 280 nm absorption is found to be second-order and shows neither kinetic salt effect nor dependence on the sulphide concentration. At doses of *ca.* 10^3 rad per pulse the first half-life is *ca.* 100 μs (for all three sulphides). Assuming that $G[RSR(-H)\cdot] \approx G(OH)$ at low R_2S concentrations this gives a bimolecular rate constant for the decay of RSR($-$H)· of $2k_2$ *ca.* 2×10^9 l mol^{-1} s^{-1}. The extinction at 280 nm generally amounts to *ca.* 1/3 of the maximum absorption at 470 nm, indicating an extinction coefficient of *ca.* 2×10^3 l mol^{-1} cm^{-1} for the RSR($-$H)· radicals.

A trace of the 280 nm absorption as a function of time

in a pulsed solution of $1\cdot5 \times 10^{-5}M$-$(CH_2)_4S$ (500 rad per pulse; pH $4\cdot7$) is shown in the upper part of Figure 11. The 280 nm absorption does not decay completely. At longer times (>1 ms) a permanent, *i.e.* long lived absorption remains. The spectrum of this product shows, however, no distinct peaks and was not identified. The simultaneous tracing of the 470 nm absorption in the bottom diagram of Figure 11 indicates that only very little $(R_2S)_2{}^+$ is formed at this sulphide concentration and further, that the $(R_2S)_2{}^+$ lifetime is comparatively small ($t_{1/2(470)}$ *ca.* 60 μs; $t_{1/2(280)}$ *ca.* 200 μs). A most interesting result is revealed from the simultaneously recorded conductivity signal (middle curve in Figure 11).

280 nm
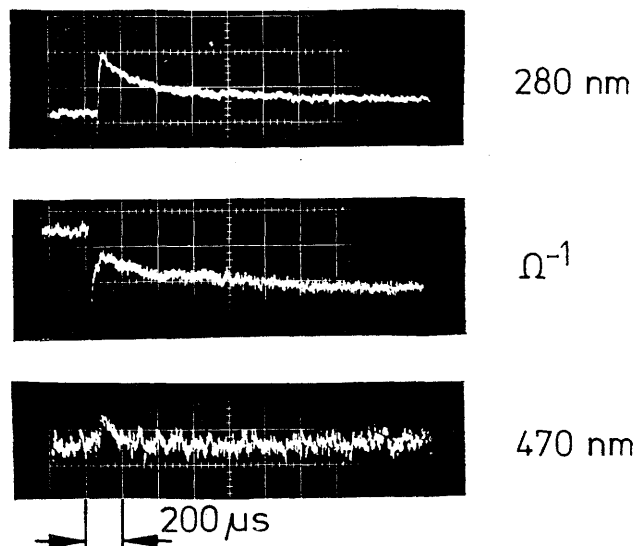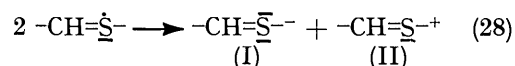
Ω^{-1}

470 nm

200 μs

FIGURE 11 Absorption– and conductivity–time curves for pulsed, N_2O saturated solutions of $1\cdot5 \times 10^{-5}M$-$(CH_2)_4S$ at pH $4\cdot7$. Upper curve: 280 nm; middle curve: conductivity; bottom curve: 470 nm

An initial decrease in conductivity is followed by a fast increase corresponding to the 470 nm decay. The signal then decreases again indicating the formation of a stable, *i.e.* long lived positive ion. The kinetics of this second slow decrease in conductivity are identical with that of the decay of the 280 nm optical absorption. This indicates that the disproportionation of the RSR($-$H)· radical leads to the formation of ions and also that this reaction is responsible for the residual permanent (on this time-scale) change in conductivity (see also Figure 1).

The following mechanism is proposed. The RSR($-$H)· radical, which seems to be best described in terms of two mesomeric forms, $-\overset{\cdot}{C}H-\overline{\underline{S}}-$ and $-CH=\overset{\cdot}{\underline{S}}-$, undergoes a disproportionation reaction, e.g. (28).

$$2 -CH=\overset{\cdot}{\underline{S}}- \longrightarrow -CH=\overline{\underline{S}}-^- + -CH=\underline{S}-^+ \quad (28)$$
$$\qquad\qquad\qquad\quad (I) \qquad\qquad (II)$$

Both ions (I) and (II) probably also exist in several mesomeric forms. The negative ion (I) will presumably pick up a proton (in acid solution) and/or react with the solvent and rearrange to a sulphide molecule. This

means a substitution of a proton by a normal positive ion (II) which, as has been discussed already, leads to a decrease in conductivity in acid solution or an increase in basic solution.

The positive ion is thought to be the long-lived species. It might be expected that the ion with the positive charge at the sulphur atom will predominate rather than a carbonium ion. Further, the H_2O adduct formed via reaction (29) could have a lifetime much longer than

$$-CH=\underline{S}-^+ + H_2O \longrightarrow [-CH_2-\overset{\overset{\displaystyle OH}{|}}{\underline{S}}-]^+ \qquad (29)$$
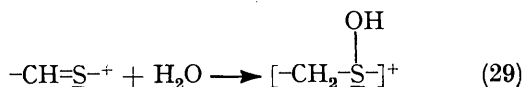
milliseconds. {Similarly the water adduct to the carbonium ion $[-(OH)CH-\overline{S}H-]^+$, if formed at all.} This ion is a protonated sulphoxide which will eventually yield free protons and the sulphoxide. The latter has in fact been positively identified by g.l.c. analysis of γ-irradiated, N_2O saturated solutions of the sulphides.

According to the stoicheiometry of the above mechanism two RSR($-H$)· radicals yield one long-lived positive ion. Destruction of the RSR($-H$)· radicals exclusively by disproportionation via reaction (29) should thus lead to a 50% decrease of the initial conductivity signal at longer times. The experimental result (Figure 1) shows however that only ca. 20—30%, i.e. half of the expected yield, remains in the ms time range. Further the yield of sulphoxide from the γ-radiolysis experiments amounts to only ca. half that expected if the RSR($-H$)· radical decay occurred solely according to reaction (29). A reaction which would possibly account for the remainder would be simultaneous non-ionic disproportionation or combination of two RSR($-H$)· radicals, e.g. by the mesomeric C-radical form, $-\overset{\cdot}{C}H-\overline{S}-$. Although g.l.c. analysis of γ-irradiated solutions indicate the formation of other stable products besides sulphoxide positive identification of these has not yet been accomplished.

Formation of Oxidizing Species.—A number of pulse and continuous γ-radiolysis experiments with solutions containing sulphides and hexacyanoiron(II) were carried out in order to obtain information on the chemical properties of the $(R_2S)_2^+$ ions.

In a pulsed N_2O saturated solution of 10^{-3}M-sulphide and various concentrations of $Fe(CN)_6^{4-}$ the 470 nm $(R_2S)_2^+$ absorption is seen to decay by a pseudo-first-order process, the half-life of which decreases proportionately to increasing hexacyanoiron(II) concentration.

$$(R_2S)_2^+ + Fe(CN)_6^{4-} \longrightarrow 2R_2S + Fe(CN)_6^{3-} \qquad (30)$$
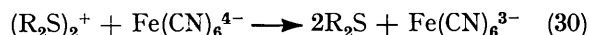
This indicates the electron transfer reaction (30). [Hexacyanoiron(III) has also been identified in appropriate γ-radiolysis experiments.] The $(R_2S)_2^+$ ion therefore has oxidizing properties. The rate constants for the electron transfer process derived from the kinetic analysis are listed in Table 3. They are seen to be quite similar for all three sulphides and imply an essentially diffusion controlled process.

γ-Radiolysis experiments carried out with similar solutions also show the formation of oxidizing inter-

mediates in the reaction of sulphides with hydroxyl radicals. Figure 12a shows, for example, the yield of

TABLE 3

Rate constants for the reaction of $(R_2S)_2^+$ ions with hexacyanoiron(II), measured pulse radiolytically at 470 nm

R_2S	$k[Fe(CN)_6^{4-} + (R_2S)_4^+]$ / l mol^{-1} s^{-1}
Me_2S	$(8\cdot5 \pm 1\cdot5) \times 10^9$
Et_2S	$(7\cdot5 \pm 1\cdot0) \times 10^9$
$(CH_2)_4S$	$(9\cdot3 \pm 1\cdot0) \times 10^9$

$Fe(CN)_6^{3-}$ formed in N_2O saturated solution (pH ca. 5·0) of 1×10^{-4}M-$Fe(CN)_6^{4-}$ and various concentrations of MeSMe. At low sulphide concentrations the yield of
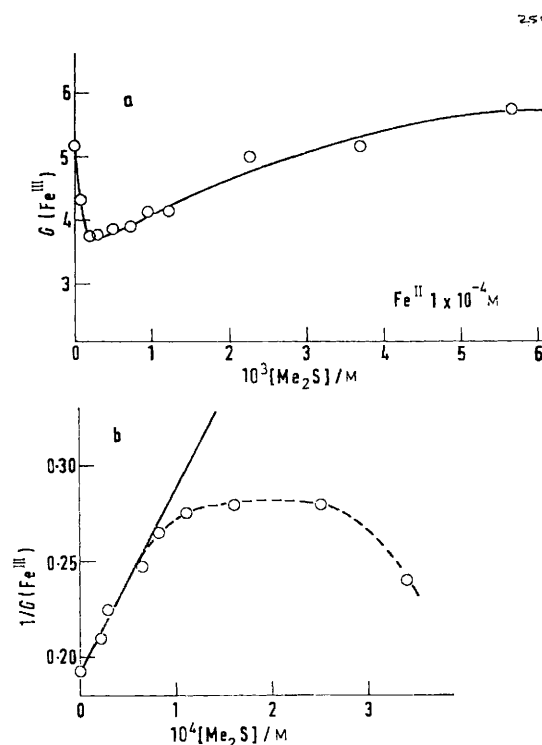
Figure 12   a, Yield of hexacyanoiron(III) in γ-irradiated, N_2O saturated solutions of 10^{-4}M-$Fe(CN)_6^{4-}$ and various concentrations of Me_2S (pH = 5·0); b, Plot of $1/G(Fe^{III})$ against $[Me_2S]$

$Fe(CN)_6^{3-}$ first decreases owing to competition between reactions (7) and (31). The curve then goes through a

$$Fe(CN)_6^{4-} + OH· \longrightarrow Fe(CN)_6^{3-} + OH^- \qquad (31)$$

minimum and increases again, at higher MeSMe concentrations, to $G[Fe(CN)_6^{3-}] \approx G(OH·)$. This shows that with increasing sulphide concentration species are formed which oxidize $Fe(CN)_6^{4-}$. From our experiments, however, it cannot be determined whether only $(R_2S)_2^+$ or also $(R_2S)_2OH·$ and possibly R_2S^+ are able to oxidize $Fe(CN)_6^{4-}$. Certainly the RSR($-H$)· radical does not seem to react with the hexacyanoiron(II).

The decay of the curve at low sulphide concentrations is quantitatively described by the usual competition

kinetics, *i.e.* equation (32). Rearrangement gives (33).

$$G[\text{Fe(CN)}_6{}^{3-}] =$$

$$G(\text{OH}\cdot) \cdot \frac{k_{31}[\text{Fe(CN)}_6{}^{4-}]}{k_{31}[\text{Fe(CN)}_6{}^{4-} + k_7[\text{R}_2\text{S}]} \quad (32)$$

$$\frac{1}{G[\text{Fe(CN)}_6{}^{3-}]} = \frac{1}{G(\text{OH}\cdot)} \left(1 + \frac{k_7[\text{R}_2\text{S}]}{k_{31}[\text{Fe(CN)}_6{}^{4-}]} \right) \quad (33)$$

A plot of the reciprocal yield of $\text{Fe(CN)}_6{}^{3-}$ *versus* the sulphide concentration in fact yields a straight line for low sulphide concentrations as seen in Figure 12b. Taking $G(\text{OH}\cdot) = 5\cdot5$ and $k_{31} = 1 \times 10^{10}$ l mol^{-1} s^{-1},[12] k_7 is calculated from the slope as 5×10^9 l mol^{-1} s^{-1}. Similar experiments for the other sulphides gave k_7 8×10^9 and 9×10^9 l mol^{-1} s^{-1} for the reaction of $\cdot$OH radicals with Et_2S and $(\text{CH}_2)_4\text{S}$, respectively. These values, particularly the latter two, are in fair agreement with the rate constants measured directly in the pulse radiolysis experiments.

At higher sulphide concentrations the yield of $\text{Fe(CN)}_6{}^{3-}$ can no longer be described by the simple competition reactions. Accordingly the $1/G[\text{Fe(CN)}_6{}^{3-}]$ against $[\text{R}_2\text{S}]$ curve levels off and eventually decreases again. Very similar results were obtained for solutions containing Et_2S and $(\text{CH}_2)_4\text{S}$. For these two compounds however no significant increase in $G[\text{Fe(CN)}_6{}^{3-}]$ after the minimum in the curve of the type given in Figure 12a could be determined. One of the reasons for this was that the lower solubility did not allow such high sulphide concentrations. On the other hand differences by a factor of two or more in the rate constants of the various reactions involved could also be responsible.

Conclusions.—The formation of complex $(\text{R}_2\text{S})_2{}^+$ ions as relatively long-lived intermediates is clearly shown by our experiments. This substantiates the previous findings of Henglein [1] and Norman [2] and their co-workers. A likely structure (A) for the complex ion has been suggested by Norman and involves a quasi-three electron
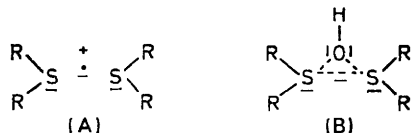

bond between the two sulphur atoms.[2] For the immediate precursor of this ion, the $(\text{R}_2\text{S})_2\text{OH}\cdot$ radical, structure (B) is suggested with the OH group probably perpendicular to the S–S bond.

The overall oxidation mechanism is represented in the Scheme. The dashed lines indicate possible reaction pathways which could not, however, be proven for the sulphides investigated here.

The consideration of the complexing properties of sulphur leads to the interesting conclusion that, depending on the sulphide concentration, the $\text{RSR}(-\text{H})\cdot$ radical (which then decays to the final products) is either formed

in a fast two step process or *via* a multi-step reaction sequence involving several equilibria. It also appears worth noting that the ' long ' route includes the formation of an intermediate with oxidizing properties whereas the direct route does not.
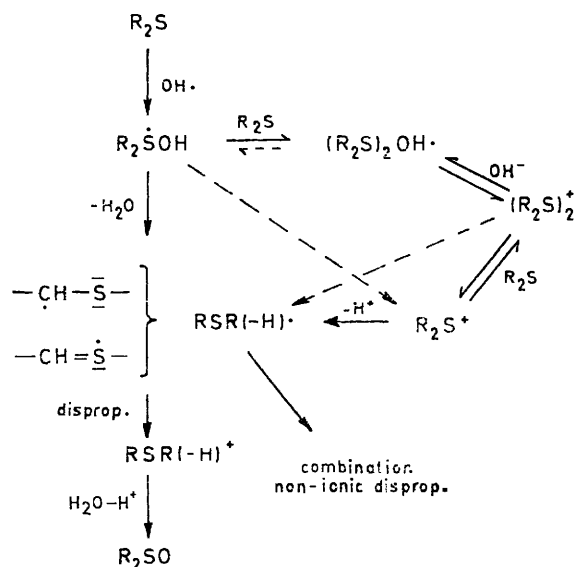
SCHEME

For different sulphides the actual pathways will certainly depend on the relative reaction rate constants which again to a certain extent will reflect the three dimensional structure of the reacting species. Such steric effects were also discussed by Norman in the interpretation of his results.[2,3]

Failure to observe the $(\text{R}_2\text{S})_2\text{OH}\cdot$ radical for tetrahydro-thiophen may in fact be explained by steric considerations whereby the OH group is prevented from making a close approach to the S–S bond between the two $(\text{CH}_2)_4\text{S}$ molecules. Even more striking in this respect would seem to be the observations made for the oxidation of di-t-butyl sulphide by $\cdot$OH radicals. (A detailed paper on this subject will be published separately.[13]) The t-butyl group in this case clearly prevents the formation of the complex $(\text{R}_2\text{S})_2\text{OH}\cdot$ radical and the $(\text{R}_2\text{S})_2{}^+$ ion. On the other hand the molecular cation R_2S^+ ($\text{Bu}^t\text{--}\dot{\text{S}}^+\text{--}\text{Bu}^t$) seems to be formed directly from the $\cdot$OH radical adduct. This R_2S^+ has a lifetime of several tens of microseconds. It also undergoes reaction with another sulphide molecule but does not form $(\text{R}_2\text{S})_2{}^+$ ions in this reaction. One of the reaction products rather seems to be the sulphonium ion R_3S^+.

[12] M. Anbar and P. Neta, *Internat. J. Appl. Radiation and Isotopes,* 1967, **18,** 493 and references cited therein.
[13] H. Möckel, M. Bonifačić, and K.-D. Asmus, to be published.