Unstable Intermediates. Part 179.[1] Electron Spin Resonance Studies of Radicals formed in Irradiated Organic Sulphides and Disulphides

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Various organic sulphides, including dimethyl and di-t-butyl sulphide and methionine, together with disulphides, including dimethyl and dibutyl disulphides, cystine and lipoic acid have been exposed to ^{60}Co γ-rays at 77 K, both in the pure state and in various solvents. E.s.r. and, in selected cases, optical spectra of the resulting intermediates are reported and discussed. In particular, the reaction $R_2S^{\cdot+} + R_2S \longrightarrow R_2S\dot{-}SR_2^+$ is considered and it is suggested that certain species, previously identified as $R_2S^{\cdot+}$, are better identified as $R_2S\dot{-}SR_2^+$. The structure of species having g values close to 2.058, 2.025, and 2.001 is also discussed.

In a previous paper we described our studies of the effect of high energy radiation on a wide range of thiols.[1] The major aim of the present work was to extend this to include organic sulphides and disulphides. As with the thiols, partly because of their biological significance, these compounds have been widely studied by radiation chemists.[2] Pulse radiolysis studies have given information on the optical spectra of various intermediates, whilst largely solid-state e.s.r. studies have revealed structural information.[2] Related redox and photochemical studies have given liquid-phase e.s.r. spectra for some of these intermediates [3] which, because of their relatively small line-widths are subject to less ambiguity in interpretation and hence have been of great help in the task of interpreting solid-state spectra. An important aspect of our previous study [1] was the observation that the nature of the intermediates, and hence the overall course of reaction, was a function of the environment of the thiol. This means that, for example, irradiation of the pure materials at 4.2 K does not of necessity give intermediates that are relevant to the reactions that occur under biological conditions. This aspect is probed further in the present study.

EXPERIMENTAL

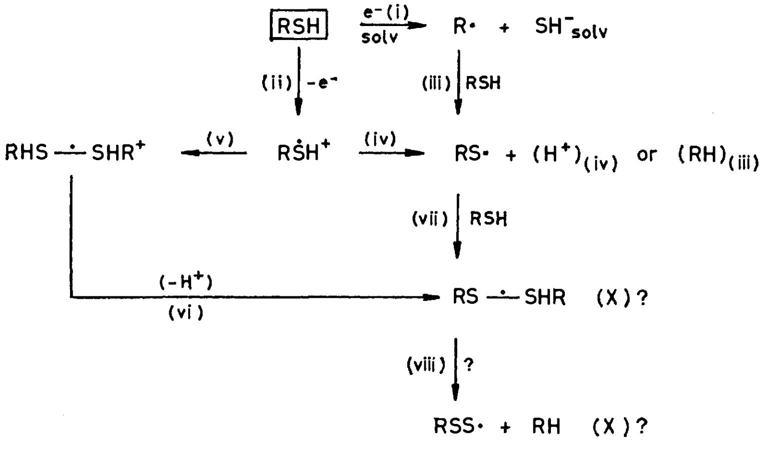
All materials were of the highest available grades. Their purity was checked by n.m.r. spectroscopy and found to be satisfactory. Samples for irradiation were in the form of fine powders, or, for dilute solution in the deoxygenated solvents used (mainly CD_3OD, 6M-H_2SO_4–H_2O, and 6M-D_2SO_4–D_2O), in the form of small spherical beads. They were exposed to ^{60}Co γ-rays in a Vickrad cell at a dose rate of *ca.* 2 Mrad h^{-1} for between 0.1 and 2.0 h.

E.s.r. spectra were measured on X-band Varian E2 and E109 spectrometers.

RESULTS AND DISCUSSION

Our results are summarised in the Tables and Figures. Before describing the results for each compound, we discuss various general aspects, in terms of Schemes 2 and 3, which give our expectations for the electron-gain and -loss processes which normally comprise the major primary effects of γ-irradiation.

In Scheme 1, we summarise, for comparative purposes, our conclusions for thiols. Process (i) was dominant for methanolic solutions but electron capture took other routes in the absence of protic media. Step (ii) was not detected, but RS· radicals were formed in most cases at 77 K. However, step (v) was thought to be an alternative in certain cases. A species X, having three distinct principal g values (*ca.* 2.058, 2.025, and 2.001) was formed from RS· and possibly $RHS\dot{-}SHR^+$ on annealing. This is thought to be either $RS\dot{-}SHR$



SCHEME 1

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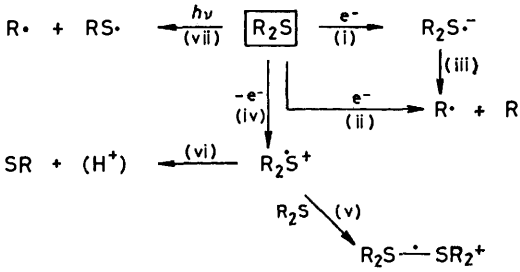
[1] Part 178, D. J. Nelson, R. L. Petersen, and M. C. R. Symons, *J.C.S. Perkin II*, 1977, 2005.

[2] J. E. Packer, in ' The Chemistry of the Thiol Group,' ed. S. Patai, Wiley, New York, 1973, p. 482.

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

formed by (vii), or RSS• formed by (vii) and (viii). In addition, a variety of carbon centred radicals were detected, especially those having the SH group α to the radical centre ($R_2\dot{C}SH$). These are thought to be formed by secondary radical reactions.

In Scheme 2, we summarise our expectations for dialkyl and related sulphides. We have obtained no evidence for electron attachment [step (i)]. Anions of type $R_2S^{\cdot -}$ have never been authenticated as intermediates. The species $H_2S^{\cdot -}$ was proposed by Bennett *et al.*,[4] but others [5,6] have pointed out that the structure $HS\dot{-}SH^-$ would fit the e.s.r. data more satisfactorily. We stress that there is a major difference between electron capture by RS–SR molecules and by R_2S molecules, since the former have low-lying σ* orbitals, whereas the latter have no readily available vacant orbitals. The most distinguishing feature expected for $R_2S^{\cdot -}$ and related anions would be a large isotropic hyperfine coupling to ^{33}S. Although powder spectra have not revealed features for radicals containing ^{33}S in which the excess electrons are largely in 3*p* orbitals on sulphur,[7,8] we would have expected to be able to detect features for radicals having large isotropic coupling constants. Such features have never been detected in these studies. Recently, Hadley and Gordy [9] have suggested that a centre having the properties that we would assign to RS• radicals is in fact due to $R\dot{S}H^-$ (or $R\dot{S}H_2$ molecules). Our reasons against their representation have been given in our paper on thiols,[1] and we will use the RS• representation in the following discussion.



SCHEME 2

Comparison with our thiol results [1] suggested that step (ii) in Scheme 2 would occur provided the medium had a high anion solvating power. This has been confirmed for glassy methanolic solutions, evidence being obtained for both $R^{1\cdot}$ and $R^{2\cdot}$ radicals from R^1SR^2 compounds. However, these were not in general trapped in the absence of the protic solvent. Radicals R• might also be formed by (i) + (iii) rather than by (ii) directly. Also, (vii) is a possible route, since electron return commonly yields excited states that can suffer homolysis. This is, however, improbable for glassy methanol, since this medium traps electrons and holes efficiently.

For molecules such as methionine, reaction (ii) is in competition with electron addition to the carboxy-group and with loss of NH_3. These reactions are favoured for the pure material, but evidently not in methanolic solution.

Electron loss (iv) should give the parent cation $R_2\dot{S}^+$ unless there are other groups from which loss is more facile. Although there have been several reports of the formation of $R_2S^{\cdot +}$ cations in the solid-state,[10,11] we are not convinced that they have been correctly identified (see below). The cations $R_2S^{\cdot +}$ are isoelectronic with phosphinyl radicals, $R_2P^{\cdot}$, which have been studied in the solid [12] and liquid [13,14] states. These radicals have their unpaired electrons almost entirely confined to a $3p_z$ orbital on phosphorus [$A_{iso}(^{31}P)$ *ca.* 96 G]. Unfortunately, although g_z (*ca.* 2.002) and A_z (*ca.* 296 G) are well defined, the *x* and *y* features are usually poorly defined and the *g* values are not accurately known. From g_{av} 2.009, an apparent value for $g_\perp$ is 2.012 5, but in fact g_x and g_y are not expected to be equal. The isotropic proton coupling for such radicals is expected to be in the region of 20 G for freely rotating alkyl groups but may be greater or smaller if there are preferred conformations for steric reasons. Thus, for $(Me_2CH)_2\dot{P}$ we found two equivalent protons, with $A(^1H)$ 13 G.[12] Similar proton coupling constants are expected for $R_2S^{\cdot +}$. This contention can be supported by analogy with RS•. For these radicals, ^1H coupling constants in the region of 20—30 G have been recorded.[1,15,16] For $R_2S^{\cdot +}$ a slight increase in $A(\alpha\text{-}H)$ is expected because of the positive charge effect.[17] In fact, the values for $A(^1H)$ measured for the species previously identified as $R_2S^{\cdot +}$ have been in the 5—10 G region, and generally the number of lines has been far greater than predicted.

One reason why $R_2S^{\cdot +}$ radicals have been elusive is probably the high efficiency of reaction (v). This reaction is well authenticated for liquid-phase reactions,[3] but although we [18] have postulated its occurrence in irradiated thiodiglycolic acid,[19] this postulate has been firmly refuted.[20] Another reaction that may lead to loss of $R_2S^{\cdot +}$ radicals is (vi). Radicals of the type ($R_2\dot{C}$–SR) are frequently encountered both in

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[4] J. E. Bennett, B. Mile, and A. Thomas, *Chem. Comm.*, 1966, 182.

[5] M. C. R. Symons, *Adv. Chem. Series*, 1968, **82**, 1.

[6] M. J. Lin and J. H. Lunsford, *J. Phys. Chem.*, 1976, **30**, 2015.

[7] J. H. Hadley and W. Gordy, *Proc. Nat. Acad. Sci. U.S.A.*, 1974, **71**, 3106.

[8] A. Naito, K. Akasaka, and H. Hatano, *Chem. Phys. Letters*, 1975, **32**, 247.

[9] J. H. Hadley and W. Gordy, *Proc. Nat. Acad. Sci. U.S.A.*, 1977, **74**, 216.

[10] S. Kominami, K. Akasaka, H. Umegski, and H. Hatano, *Chem. Phys. Letters*, 1971, **9**, 510.

[11] H. C. Box, H. G. Freund, and E. E. Budzinski, *J. Chem. Phys.*, 1968, **49**, 3874.

[12] B. Fullam, S. P. Mishra, and M. C. R. Symons, *J.C.S. Dalton*, 1974, 2145.

[13] D. Griller, B. P. Roberts, A. G. Davies, and K. U. Ingold, *J. Amer. Chem. Soc.*, 1974, **96**, 554.

[14] M. J. S. Gynane, A. Hudson, M. F. Lappert, and P. P. Power, *J.C.S. Chem. Comm.*, 1976, 623.

[15] K. Akasaka, *J. Chem. Phys.*, 1965, **43**, 1182.

[16] H. C. Box, H. G. Freund, and E. E. Budzinski, *J. Chem. Phys.*, 1966, **45**, 809.

[17] R. Hulme and M. C. R. Symons, *J. Chem. Soc.*, 1965, 1120.

[18] M. C. R. Symons, *J.C.S. Perkin II*, 1974, 1618.

[19] H. C. Box, H. G. Freund, and E. E. Budzinski, *J. Chem. Phys.*, 1968, **49**, 3974.

[20] H. C. Box and E. E. Budzinski, *J.C.S. Perkin II*, 1976, 553.

liquid- and solid-state studies as secondary products, but they may, of course, be formed by radical attack on α-hydrogen atoms rather than by processes (iv) + (vi).

We now examine the cases for the $R_2S^{\cdot +}$ and $R_2S\dot{-}SR_2^+$ formulations for species previously identified as $R_2S^{\cdot +}$ in solid-state studies. The properties of these centres, listed in Table 1, are: *g* values in the regions of 2.02, 2.01, 2.00, and hyperfine coupling to α-protons in the 5—10 G region. The number of hyperfine lines detected in single-crystal studies is sometimes greater than can be accounted for in terms of the $R_2S^{\cdot +}$ formulation. Frequently, a violet-blue colour has been associated with these centres (*i.e.* a band in the 500—600 nm region).

The *g* values are close to those observed for $RS\dot{-}SR^-$ radicals, with g_x and g_y ($g_{\text{max.}}$ and $g_{\text{int.}}$) slightly greater than those for the anions. Since for steric reasons, we expect the S–S bond to be somewhat longer and weaker in the cations than in the anions, this small increase in *g* values is exactly what is expected. Also, g_{av} is close to the liquid-phase value for $R_2S\dot{-}SR_2^+$ radicals.[3] However, these values are also quite reasonable for $R_2S^{\cdot +}$ radicals.

The proton hyperfine coupling constants are again close to those for the dimer anions, and to those obtained from liquid-phase studies.[3] However, they are far smaller than those found for RS· and $R_2P\cdot$ radicals and we are unable to devise any explanation for their magnitude if the species really are $R_2S^{\cdot +}$ radicals.

Again, we are unable to understand how $R_2S^{\cdot +}$ radicals could have an allowed electronic transition in the 500—600 nm region. There is no liquid-phase evidence for such a low lying transition, nor is there any theoretical justification of which we are aware. However, $RS\dot{-}SR^-$ radicals have an allowed transition in the 400—430 nm region which, by analogy with the isostructural radical Cl_2^-,[21] we have identified as $\sigma \longrightarrow \sigma^*$.[1] Examination of the results for $RS\dot{-}SR^-$ radicals suggests that, as the bulk of the R groups increases, so the band shifts to low frequencies. This accords with the $\sigma \longrightarrow \sigma^*$ assignment if we postulate a slight stretching of the weak three-electron S–S bond. For $R_2S\dot{-}SR_2^+$ this effect will be greater and hence we predict an intense band at lower energies, which displays a greater sensitivity to the size of the R groups. Asmus and his co-workers[22] have assigned a band in the 500 nm region to $R_2S{-}SR_2^+$ radicals which fits in well with these predictions.

These considerations lead firmly to the conclusions that the species listed in Table 1 are better described as $R_2S\dot{-}SR_2^+$ ions rather than $R_2S^{\cdot +}$. In refuting this postulate[18] for the species formed in thiodiglycolic acid, Box *et al.*[20] used an argument based upon crystal symmetry requirements. Thus for the cation $(HO_2CCH_2)_2S\dot{-}S(CH_2CO_2H)_2^+$ they predict the detection of two sets of four equivalent protons, whereas they detected four sets of two equivalent protons. Since the formation of a S–S bond will involve some movement of one or both sulphur atoms, and since the CO_2H groups are strongly held by hydrogen bonds, there must be some twisting of the CH_2 groups to facilitate bonding. Unless this movement is identical for both molecule and cation, this equivalence will be lost. Minimisation of steric interactions may also be favoured by the required loss of symmetry. This postulate seems to us to be far more reasonable than that of Box and Budzinski who assign the extra features to ' interactions involving protons of neighbouring molecules '.[20]

TABLE 1

E.s.r. and optical parameters for species identified[a] as $R_2S\dot{-}SR_2^+$ cations

Substrate	Radical	*g*	^{1}H hyperfine coupling (G)[b]	$\lambda_{\text{max.}}$/nm
Thiodiglycolic acid	$(HO_2CCH_2)_2S\dot{-}S(CH_2\overset{+}{C}O_2H)_2$	2.022, 2.011, 2.004	15.3(4), 8.9(2), 5.7(2)[c]	600,700
DL-Acetylmethionine	$\{[CH_3CONHCH(CO_2H)CH_2CH_2]\dot{S}Me\}_2^+$	2.023, 2.013, 2.004	*ca.* 6.5[d]	725
DL-Methionine	$[(H_3^+NCH(CO_2^-)CH_2CH_2)\dot{S}Me]_2^+$	2.022, 2.013, 2.002	*ca.* 8[e]	700
Me_2S	$Me_2S\dot{-}SMe_2^+$	2.010 3 (av)	6.3 (iso)	500,600
2-Methyltetrahydrothiophen[f]	$MeHC[CH_2]_3S\dot{-}S[CH_2]_3CHMe^+$	[g]		625

[a] Identification given herein: for alternative identifications, see text. [b] G = 10^{-4} T. [c] Ref. 20. [d] Ref. 10. [e] Ref. 24. [f] Ref. 25. [g] Not assigned in ref. 25.

It is noteworthy that the optical spectra now assigned to cation dimers in the solid-state come at somewhat lower energies than those observed in solution (also g_{av} values are slightly greater). This may well reflect the inability of these rather cumbersome cations to achieve an ideal conformation in the crystalline solids. Thus the S–S bonds are forced to be slightly longer than the equilibrium lengths, $\lambda_{\text{max.}}$ moves to longer wavelengths and g_{av} increases. That the former effect is reasonable is nicely illustrated by the observation that the cation (I) has $\lambda_{\text{max.}}$ 680 nm.[23]

(I)

Similarly, we postulate that the blue radical studied by Kominami[24] in DL-methionine crystals was really the dimer cation, and possibly the species detected by Dismukes and Willard[25] in irradiated 2-methyltetrahydrothiophen with $\lambda_{\text{max.}}$ 625 nm was also an $R_2S\dot{-}$

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[21] C. J. Delbecq, B. Smaller, and P. H. Yuster, *Phys. Rev.*, 1958, **111**, 1235.

[22] M. Bonifačić, H. Möckel, D. Bahnemann, and K.-D. Asmus, *J.C.S. Perkin II*, 1975, 676.

[23] D. Bahnemann and K.-D. Asmus, *J.C.S. Chem. Comm.*, 1975, 238.

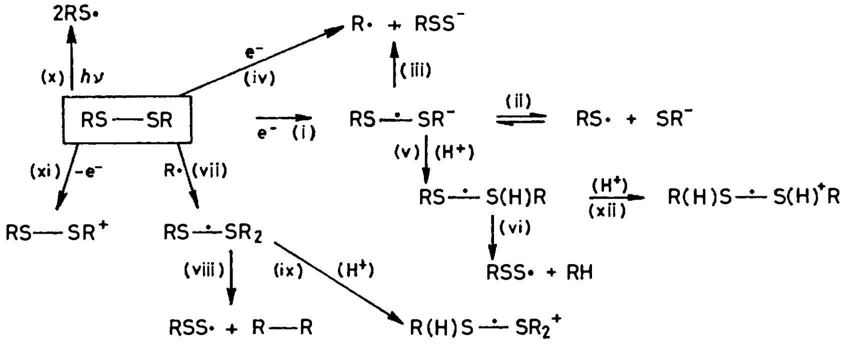
[24] S. Kominami, *J. Phys. Chem.*, 1972, **76**, 1729.

[25] G. C. Dismukes and J. F. Willard, *J. Phys. Chem.*, 1976, **80**, 2072.

SR_2^+ cation. This was attributed to $R_2\dot{S}^+$ radicals by Dismukes and Willard.[25]

The only dialkyl sulphide that gave detectable yields of species X (g 2.058, 2.025, 2.001) was methionine. This species was formed slowly at room temperature. after irradiation at 77 K, and it was never a major product. It has been studied in single crystals of methionine by Cadena and Rowlands,[26] who identified it as RS•. Hyperfine coupling to two inequivalent ^{33}S atoms was observed for this species formed from the acetyl derivative irradiated at room temperature,[27] which was identified as RSS•. The nature of species X was discussed extensively in our foregoing paper,[1] and is considered further below.

In Scheme 3, both primary anions, $RS\dot{-}SR^-$, and cations, $RSSR^+$, are well defined and relatively stable. Properties for the anions are similar to those discussed above and given in Table 1 for the σ* cations, $R_2S\dot{-}SR_2^+$. Examples of e.s.r. parameters for the electron-loss centres, $RSSR^+$, are given in Table 2. They probably have an electronic transition at *ca.* 420 nm (ε *ca.* 2 × 10^3 l mol^{-1} cm^{-1}).[28] Solid-state radiolysis of the pure materials usually results in formation of these two species. However, in the liquid-phase, equilibrium (ii) sets in rapidly, and reactions characteristic of RS• radicals ensue. We now find that, in CD_3OD glasses, reaction (iv) also occurs to a minor extent, but there is no sign of features for RS• radicals for these solutions. Although, in most cases, the dialkyl sulphides gave no detectable yield of species X, this species is usually formed from disulphides either directly at 77 K, or on annealing. Thus, for example, MeS–SMe gave MeS–SMe^+, MeS–SMe^-, and species X at 77 K. In CD_3OD, high yields of MeS–SMe^- together with $•CH_3$ and some X were formed at 77 K.



SCHEME 3

TABLE 2

E.s.r. parameters assigned to RS–SR+ cations

Substrate	Radical	*g*			^1H Hyperfine coupling (G)
MeS–SMe	MeS–SMe^+	2.036	2.001 7	2.002	9, 7, 7
MeS–SMe	MeS–SMe^+ [a]	2.032		2.002	9.1,
$C_5H_{11}S$–SC_5H_{11}	$C_5H_{11}S\dot{\pm}SC_5H_{11}$ [b]	2.035	2.018	2.003	
Cystine	RCH_2S–SCH_2R^+ [c]	2.033	2.038	2.005	7.6, 6.25, 5.9 [d] 5.1, 2.0, 1.5

[a] Ref. 29. [b] F. K. Truby, *J. Chem. Phys.*, 1964, **40**, 2768. [c] H. C. Box and H. G. Freund, *J. Chem. Phys.*, 1964, **41**, 2571. [d] A. Naito, K. Akasaka, and H. Hatano, *J. Magnetic Res.*, 1976, **24**, 53.

Results for MeS–SMe in aqueous 6M-sulphuric acid (or D_2SO_4) were revealing. Species X was not formed, even on annealing. However, two species were detected one, α, being lost during the annealing process, and the

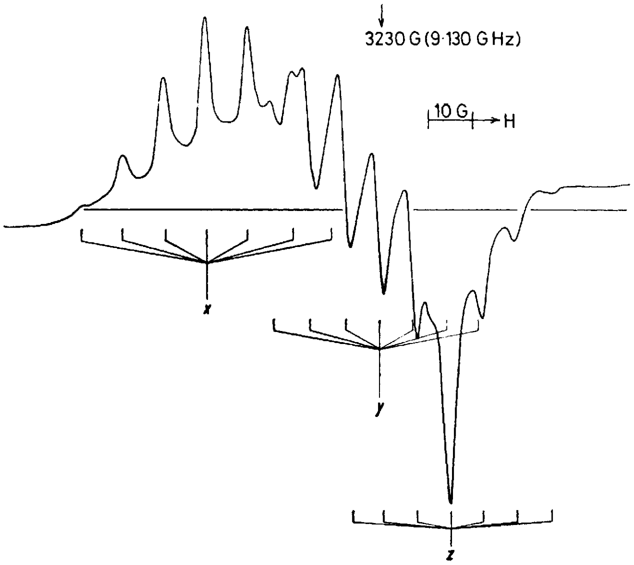


FIGURE 1 First derivative X-band e.s.r. spectrum from dimethyl disulphide in 6M-D_2SO_4–D_2O after exposure to ^{60}Co γ-rays at 77 K, and annealing until features for $SO_4^{•-}$ and $•SO_3^-$ were lost showing features assigned to MeS–SMe^+ radicals

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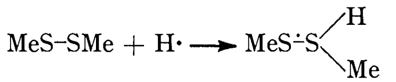
[26] D. G. Cadena and J. R. Rowlands, *J. Chem. Soc.* (*B*), 1968, 488.

[27] J. H. Hadley and W. Gordy, *Proc. Nat. Acad. Sci. U.S.A.*, 1975, **72**, 3486.

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

other, β, being gained. The spectrum for α was never well defined, being seriously overlapped by features for $SO_4^{\cdot -}$ and $\cdot SO_3^-$ from the solvent. However, the low-field lines for α were similar to those expected for the anion, $MeS\dot{-}SMe^-$. The β features, shown in Figure 1, are undoubtedly due to the parent cations, $MeS\dot{-}SMe^+$, the resulting data, given in Table 2, being close to those derived by Gillbro [29] from single crystal studies. It is significant that the normally high yield of trapped hydrogen (or deuterium) atoms was greatly reduced by added MeS–SMe. This suggests reaction (1) is efficient. Since it is probable [1] that species X is either $RS\dot{-}SR_2$ or RSS· formed therefrom, the absence of X when sulphuric acid is employed is puzzling. We suggest that $MeS\dot{-}S(H)Me$ [$MeS\dot{-}S(D)Me$] is indeed formed, but is rapidly protonated to give $[Me(H)S\dot{-}S(H)Me]^+$, or $[Me(D)S\dot{-}S(D)Me]^+$, and that this is responsible for the α-features. As stressed above, this is reasonable, but it does require that the two S–H protons give rise to undetectably small hyperfine couplings. We have already drawn this conclusion from our studies of thiols, which are thought to yield $R(H)S\dot{-}S(H)R^+$ cations by the dimerisation process (v) in Scheme 1. Formation of the cations $MeS\dot{-}SMe^+$ on annealing coincided with loss of $\cdot SO_4^-$, suggesting reaction (2).



$$MeS{-}SMe + H\cdot \longrightarrow MeS\dot{-}S\begin{smallmatrix}H\\Me\end{smallmatrix} \qquad (1)$$

$$SO_4^- + MeS{-}SMe \longrightarrow SO_4^{2-} + MeS\dot{-}SMe^+ \qquad (2)$$

In our study of thiols, we concluded that species X was most probably $RS\dot{-}SR_2$ rather than RSS·.[1] This conclusion is reinforced by our present results. Thus X is frequently formed from RSSR directly at 77 K. This is quite reasonable for reactions such as (vii) in Scheme 3, but most unreasonable for (vii) + (viii) to give RSS·, since (viii) is known to be slow at ambient temperatures.[30] Also formation of the $R(H)S\dot{-}S(H)R^+$ cations, if correctly identified, supports the formation of $RS\dot{-}S(H)R$ intermediates. We stress that this conclusion does not mean that RSS· radicals are not formed under other circumstances, nor that they, fortuitously, have e.s.r. data similar to those now assigned to $RS\dot{-}SR_2$ radicals. It does mean, however, that $RS\dot{-}SR_2$ radicals do have e.s.r. spectra of the type associated with species X. Thus unless there is compelling reason for postulating reactions such as (viii) in Scheme 3, species X would seem to be better formulated as $RS\dot{-}SR_2$.

Although $RS\dot{-}SR^-$ and $RS\dot{-}SR_2$ radicals form RS· radicals reversibly in solution, this does not appear to be an important reaction in solids, since RS· radicals have not been detected in the present work. These radicals are characterised by a g_z feature of 2.158 when formed in methanolic glasses, and such features are absent in all our spectra. This also suggests that excited-state dissociation [(x) in Scheme 3)] is not important in these solid-state studies.

Comments on Individual Compounds.—Dimethyl sulphide. The pure material gave a dominating e.s.r. spectrum from $H_2\dot{C}SCH_3$ radicals, showing an anisotropic coupling to two α-protons (*ca.* 17 G) and a small coupling (*ca.* 3 G) to the methyl group. Some evidence for a species with *g* values in the range 2.02—2.00 with $A(^1H)$ *ca.* 6—7 G was obtained using high microwave powers, but although we believe this to be the $Me_2S\dot{-}SMe_2^+$ radical, the spectra were too poor to be definitive. The irradiated material was dark purple after irradiation. In methanol (CD_3OD), clear features for $\cdot CH_3$ radicals were superimposed upon those for $\dot{C}D_2OD$ and weak features for $H_2\dot{C}SMe$. No features for MeS· radicals or species X were detectable.

In sulphuric acid (D_2SO_4) broad features possibly assignable to $Me_2S^{\cdot +}$ were obtained after annealing to remove $SO_4^{\cdot -}$ and $\cdot SO_3^-$ features, but again the spectra were too broad to be properly interpreted. Evidently, if $Me_2S^{\cdot +}$ species were present, the methyl groups are not freely rotating. A similar lack of resolution was observed for $Me_2P\cdot$ radicals,[12] so this is not surprising. Further annealing gave a well resolved set of 13 lines [$A(^1H)$ 6.3 G; g_{av} 2.010] which are clearly identifiable as belonging to $Me_2S\dot{-}SMe_2^+$ radicals. Recooling to 77 K gave only a broad singlet covering the expected range for *g* values in the 2.02—2.00 region. Again, we interpret this reversible loss of resolution as indicating loss of rotation by the methyl groups (*cf.* for $MeS\dot{-}SMe^+$, resolution was good at 77 K, which is in accord with the absence of steric hindrance to rotation for this cation.) Very similar results were obtained for $Pr^n{}_2S$. Well defined features for $CH_3CH_2\dot{C}H_2$ radicals were obtained from solutions in CD_3OD. A species thought to be $(Pr_2S\dot{-}SPr_2)^+$ was obtained both from the pure compound and after annealing D_2SO_4 solutions, but this evidence was not definitive.

Di-t-butyl sulphide. In contrast with Me_2S and Pr_2S, the pure material was colourless after irradiation at 77 K. At low microwave power, features for $Me_3C\cdot$ radicals were dominant. However, at high powers, a broad line showing defined features at *g* 2.034 and 2.000 was dominant. We tentatively assign these to the cation $(Bu^t)_2S^{\cdot +}$. This is unable to form a dimer cation because of steric factors, and the absence of any colouration is in accord with this. Similar features were obtained, after annealing, from sulphuric acid solutions. Solutions in CD_3OD gave only $Me_3C\cdot$ radicals.

Tetrahydrothiopyran-4-one. This gave very poorly defined spectra in the pure state. Solutions in CD_3OD gave a spectrum assignable to a radical $H_2\dot{C}{-}CH_2R$, which we presume to be $H_2\dot{C}CH_2O(CH_2CH_2S^-)$.

DL-*Methionine.* This important sulphide and its *N*-acetyl derivative have been extensively studied as single crystals,[10,24,26,27] and our work on the pure materials simply seems to confirm previous results. The multi-line

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[29] T. Gillbro, *Chem. Phys.*, 1974, **4**, 476.

[30] T.-L. Tung and J. A. Stone, *J. Phys. Chem.*, 1974, **78**, 1130.

spectrum assigned to $R_2S^{\cdot +}$ cations by others [10,24] and to $R_2S\dot{-}SR_2^+$ cations by us, was not resolved in the powder spectra, which only gave a broad envelope with occasional hints of a 6—8 G splitting. This splitting was interpreted as stemming from two equivalent protons giving 33.2 G coupling, one giving 16.6 G and two giving 8.3 G. We suggest that there are two equivalent groups of methyl protons giving *ca.* 8 G coupling and four methylene protons giving *ca.* 14 G coupling. This reproduces the recorded spectra quite satisfactorily, and is reasonable provided the four methylene protons are fixed in a favourable conformation to give a large coupling. We stress that this species has an intense purple colour (λ *ca.* 700 nm). The species identified by Cadena and Rowlands [26] as $MeS\dot{C}HCH_2CH_2CH(NH_3^+)CO_2^-$ was well defined in the powder spectrum and our derived data are close to those obtained from single crystals. Solutions in D_2SO_4 gave a very broad singlet after annealing, covering the range expected for $R_2S\dot{-}SR_2^+$ radicals, but individual features were not resolved. Solutions in CD_3OD gave well resolved features for $\cdot CH_3$ radicals, but no features for $RS\cdot$, $R_2S\dot{-}HSR^+$, or species X were obtained even after annealing. We were only able to obtain evidence for species X after extensive exposure of methionine at room temperature. This strongly suggests that X is formed from radiolysis of one of the initial radiolysis products. Hence it seems to us unsafe to attempt any specific assignment. We stress that X was not obtained from any other of the dialkyl sulphides studied herein.

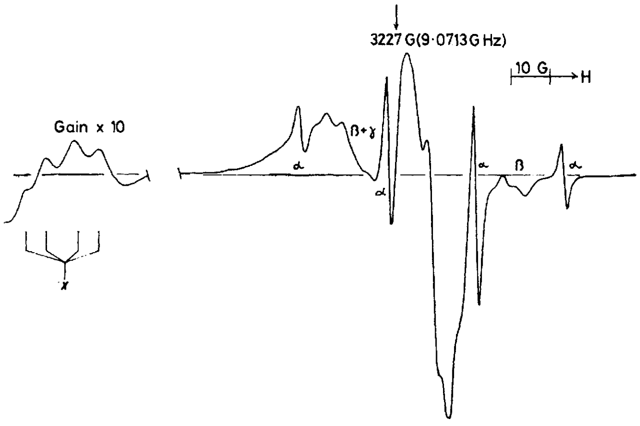


FIGURE 2 First derivative X-band e.s.r. spectrum for dimethyl disulphide in CD_3OD after exposure to ^{60}Co γ-rays at 77 K, showing features for $\cdot CH_3$ (α), $H_2\dot{C}SSMe$ (β), $D_2\dot{C}OD$ (central line), $MeS\dot{-}SMe^-$ (γ), and species X

Dimethyl disulphide. The pure material gave results similar to those described by Gillbro.[29] Clear features for species X (described as $CH_3S\cdot$ by Gillbro), $MeS-SMe^+$, and $MeS\dot{-}SMe^-$ radicals were obtained, together with features assigned to $H_2\dot{C}SSCH_3$ radicals. In CD_3OD solution, features for $MeS\dot{-}SMe^-$ anions were obtained together with the characteristic quartet for $\cdot CH_3$ radicals, and species X (Figure 2). It is noteworthy that some dissociative electron capture occurred [reaction (3)] despite the prevalence of electron addition.

$$MeS-SMe + e^- \longrightarrow Me\cdot + MeSS^- \qquad (3)$$

Also note that species X was formed directly at 77 K. This is reasonable for reactions such as (4) but surely

$$D\cdot + MeS-SMe \longrightarrow MeS\dot{-}S(D)Me \qquad (4)$$

unreasonable if X is $MeSS\cdot$. Solutions in D_2SO_4 have been discussed above.

DL-*Cystine.* This compound, usually as the hydrochloride, has been widely studied. Our purpose in studying the pure material as a powder was to satisfy ourselves that we could derive the correct hyperfine and *g* values from the powder spectra. This proved to be the case, and gave us confidence in the other analyses reported herein.

Solution in CD_3OD again gave some dissociative electron capture to give $\cdot CH_2CH(NH_3^+)CO_2^-$ radicals [$A(\alpha\text{-H})_{av}$ *ca.* 22 G; $A(\beta\text{-H})$ *ca.* 8 G], together with species X. Solutions in sulphuric acid gave higher yields of X, which showed a 10 G proton hyperfine coupling, but other features were too poorly defined to warrant interpretation.

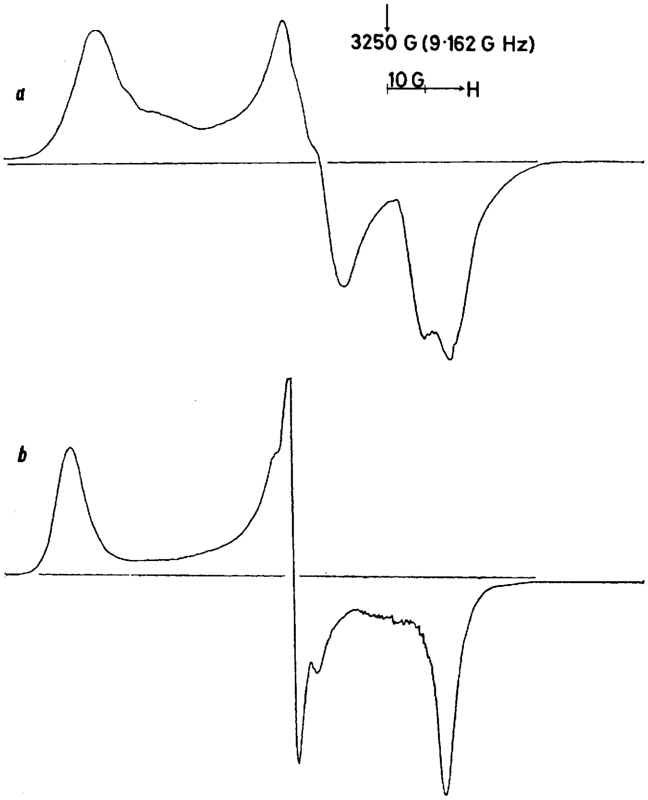


FIGURE 3 First derivative X-band e.s.r. spectra for lipoic acid after exposure to ^{60}Co γ-rays showing features for species X; *a* for the pure acid irradiated at ambient temperature and *b* for solutions in CD_3OD irradiated at 77 K

DL-*Lipoic acid.* This disulphide (II) is unsymmetrical, and should therefore give rise to two species X. This

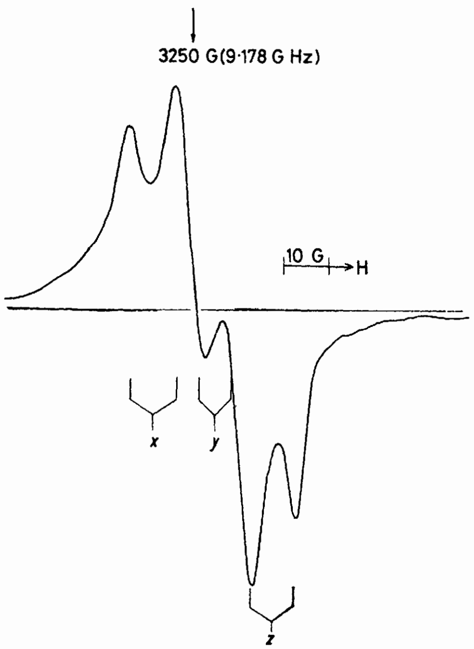
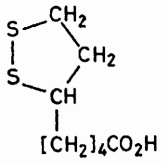


FIGURE 4 First derivative X-band e.s.r. spectrum for lipoic acid after exposure to ^{60}Co γ-rays at 77 K, showing features assigned to the parent radical anion

seems to be true in that the pure material gave a species exhibiting the familiar 9—10 G doublet, whilst solutions in CD_3OD gave a major singlet species with very weak doublet satellites (Figure 3). This difference is curious, and may reflect different attacking radicals. Possibly one is formed from the anion by protonation and the other by radical attack.



(II)

The disulphide anions, formed both from the pure material and its solutions in CD_3OD had normal *g* values but apparently only one proton coupling of *ca.* 10 G (Figure 4). This suggests that the preferred conformation places only one of the three protons in a favourable position for coupling to the unpaired electron.

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