Unstable Intermediates. Part 178.[1] The Structure of Intermediates formed in the Radiolysis of Thiols

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A wide range of thiols have been exposed to ^{60}Co γ-rays at 77 K both in the pure state and in dilute methanolic or aqueous glasses. Spectra assigned to RS· radicals had g_z values (z is along the $C{-}\dot{S}$ bond) which varied with the environment, but which were all close to 2.158 in methanol. Dissociative electron capture at sulphur ($RSH + e^- \rightarrow R\cdot + SH^-$) was only observed in methanolic or aqueous glasses, and it is postulated that solvation of the ejected SH^- ion plays an important role. The structure of a species (X) containing two sulphur atoms and having g values close to 2.058, 2.025, and 2.001 is discussed. Two rival structures, $RS\cdot{-}SR_2$ and RSS· are considered in depth and it is concluded that the former is most probable unless both species have very similar properties. Electron loss to give $R\dot{S}H^+$ followed by reaction to give $R(H)S\cdot{-}S(H)R^+$ cations is postulated to explain certain features in the e.s.r. spectra, as an alternative to proton loss to give RS· radicals.

RADIATION chemists have made extensive studies of thiols, both as pure compounds and as aqueous solutions partly because of their general biological significance and partly because aminothiols in particular are important for *in vivo* radiation protection. For example, cysteine, $HSCH_2CH(NH_3^+)CO_2^-$, and cysteamine, $HSCH_2CH_2NH_2$, are both highly protective and have been extensively studied.[2]

Since the pioneering work of Gordy and his co-workers,[3] e.s.r. spectroscopy has been extensively used on the pure compounds, irradiated at room temperature or at 77 K,[4] and, more recently by Box *et al.*, after exposure at 4.2 K.[5] These studies revealed a wide spectrum of sulphur-centred radicals, many of which were identified as thiyl radicals, RS·. In particular, a species which we will designate X, with g values in the region 2.058, 2.025, and 2.001, formed from thiols and disulphides, was almost invariably identified as RS·. One of us [6] has given a variety of reasons why this identification, still widely used,[7] must be wrong, and suggested the structure $RS\cdot{-}SR_2$. Simultaneously, Hadley and Gordy [8] by studying ^{33}S satellite features for radical X in irradiated cystine hydrochloride, showed that this species does indeed contain two non-equivalent sulphur atoms. However, they formulated these radicals, (X), as RSS·, and later [9] expressed the view that Symons' formulation ($RS\cdot{-}SR_2$) must be incorrect. Unfortunately, they gave no specific reasons for this firm conclusion, so the issue must be treated as still open. One of the purposes of this work is to examine these two theories in depth.

Of the other centres identified as thiyl radicals, several with one very large g value are probably correctly identified. These include two radicals in irradiated cysteine with g_z 2.321 and 2.312, identified as RS· by Akasaka,[10] and one in irradiated penicillamine hydrochloride with g_z 2.295, identified as RS· by Budzinski and Box.[11] These solid-state studies have revealed a variety of species other than those identified as RS· radicals. They include $R_2\dot{C}SH$ radicals, and species formed by loss of NH_3 or by electron addition to carboxy-groups. Products vary with temperature in some cases, but it is claimed that studies performed at 4.2 K will reveal the nature of the primary products.[11,12] Thus, for example, Kou and Box [12] found that, for cysteine hydrochloride irradiated at 4.2 K, electron addition to the carboxy-group was the only reaction with electrons, the electron loss centres being RS·, and a radical formed from the chloride ions. These are therefore thought to be the primary products of irradiation. However, care must be exercised in extrapolating such results to room temperature, and even more so to other environments. We have found that changes in environment can make major changes in the nature of primary radiation products,[13] and hence another aim of this study was to compare results for pure compounds and their solutions at 77 K. Methanol was selected as solvent since it closely resembles water, but in contrast with water, its solutions form good glasses at 77 K. Also, in its perdeuteriated form, solvent radicals only contribute narrow central features which do not greatly overshadow those of interest.

Another factor that makes the use of such a solvent significant, is that the g_z value (z is along the C–S bond) for RS· radicals is determined by the environment, and hence in order to obtain a value that will characterise RS· radicals and distinguish them from others, a constant environment is needed. This is provided satisfactorily by methanol.[14]

Liquid-phase studies have also been bedevilled by

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[3] W. Gordy, W. B. Ard, and H. Shield, *Proc. Nat. Acad. Sci. U.S.A.*, 1955, **41**, 983.

[4] See, for example, Y. Kurita and W. Gordy, *J. Chem. Phys.*, 1961, **34**, 282; T. Henriksen, *ibid.*, 1962, **36**, 1258; K. Akasaka, S. Kominami, and H. Hatano, *J. Phys. Chem.*, 1971, **75**, 3747.

[5] H. C. Box, H. G. Freund, K. T. Lilga, and E. E. Budzinski, *J. Phys. Chem.*, 1970, **74**, 40.

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

[7] H. R. Falle, F. S. Dainton, and G. A. Salmon, *J.C.S. Faraday I*, 1976, 2014.

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

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

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

[11] E. E. Budzinski and H. C. Box, *J. Phys. Chem.*, 1971, **75**, 2564.

[12] W. W. H. Kou and H. C. Box, *J. Chem. Phys.*, 1976, **64**, 3060.

[13] S. P. Mishra, M. C. R. Symons, and B. W. Tattershall, *J.C.S. Faraday I*, 1975, 1772.

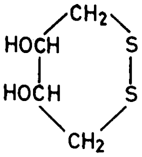
[14] D. J. Nelson and M. C. R. Symons, *Chem. Phys. Letters*, 1975, **36**, 340.

incorrect identifications of thiyl radicals. In fact, these radicals are unlikely to give rise to detectable liquid-phase e.s.r. signals, because of the solvent control of the *g* values and consequent rapid modulation thereof. In particular, a species formed by hydroxyl radical attack in aqueous solutions having g_{av} *ca.* 2.01 [15] previously identified as RS· is now known to be the oxy-derivative, RSO.[16] This species, also studied in the solid state,[17,18] has g_1 2.023, g_2 2.011, and g_3 2.003. Optical spectra assignments have again varied widely. There seems to be complete agreement that the disulphide radical anion, formed from RS· by reaction (1), has an intense band in

$$RS\cdot + RS^- \rightleftharpoons RSSR^- \qquad (1)$$

the 410 nm region with ε *ca.* 7 × 10^3 l mol^{-1} cm^{-1}.[2,19] Several workers agree that RS· radicals give rise to a somewhat weaker band in the 330 nm region, but this is less sure. The only reasonable transition of such low energy is $\sigma \rightarrow \pi$, which is not strongly allowed since it contains a major $3p \leftarrow 3p$ element, and hence the oscillator strength should be relatively small. Whilst a form of charge transfer to solvent transition is possible, this should be at higher energy than that for RS^- ions, which occurs (for HS^-) at *ca.* 230 nm in aqueous solution.[20]

Others have reported a band in the 380 nm region which has been assigned to RS· radicals.[6,21] We feel that this would certainly be better assigned to an adduct of RS·. In the particular case of dithiothreitol [21] evidence has been presented for a reversible protonation as the link between the 410 nm band for $RSSR^-$ and the 380 nm peak. This molecule can form the cyclic disulphide anion (I), which on protonation could give either RS·, as postulated,[21] or the cyclic adduct RS ··· S(H)R. We have accordingly investigated this system in glassy solutions as a function of pH.



(I)

$$RSH + e^- \longrightarrow R\cdot + HS^- \qquad (2)$$

$$HS^- + H_2O \rightleftharpoons H_2S + OH^- \qquad (3)$$

A reaction detected in fluid solution but, curiously, never reported in solid-state radiolyses is dissociative electron capture leading to HS^- and hence, H_2S [reactions (2) and (3)].[22,23] This seems to occur with high efficiency in aqueous solution [2] provided the pH is not too high, since S^{2-} is not displaceable. Another of our aims was to understand why this reaction has not been reported in solid-state studies.

Radicals of type $R_2\dot{C}SH$ have been well characterised by e.s.r. spectroscopy.[24-27] The optical spectrum has not been so well characterised, but it seems probable that they give rise to a band in the 280 nm region.[28]

EXPERIMENTAL

All compounds used in this study were commercially available and were used without further purification. Their purity was checked by proton resonance measurements. Deuteriation was achieved by exchange with deuterium oxide through aeration (MeSH) or recrystallisation.

Glassy beads, prepared by pipetting liquid samples, either neat or as solutions, directly into liquid nitrogen, were irradiated in the dark at 77 K in a ^{60}Co Vickrad source for up to 1 h at a dose rate of 2 Mrad h^{-1}. Solid samples were finely pulverised before irradiation in the dark at the temperatures specified. X-Band e.s.r. spectra were recorded at 77 K and higher temperatures on a Varian E3 or E109 spectrometer. In selected cases Q-band spectra were measured using a superheterodyne spectrometer constructed in these laboratories.

The optical spectrum of the stable radical remaining at room temperature following the 77 K irradiation of solid (−)-D-penicillamine hydrochloride was recorded on a Beckman DK-2A spectrophotometer equipped with a diffuse reflectance attachment.

RESULTS AND DISCUSSION

Thiyl Radicals.—Irradiation of pure thiols gave well defined low-field resonances in several instances, which we identify as the parallel (*z*) features for RS· (Table 1 and Figure 1). The values for g_z are clearly dependent upon the environment, being variable even within the same crystal. However, all the thiols studied (Table 1) gave the same g_z value in CD_3OD. This value (2.158) is closer to the free-spin value (2.0023) than any example in the pure materials, which suggests that hydrogen bonding is maximised in this solvent. We stress that, in order to detect a well defined *z*-feature, hydrogen bonding must be strong and must generate a well defined difference between the *x* and *y* axes. This will automatically occur if there is only one donor proton, which is likely to be the case for thiols [see (II)]. That the

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[15] W. Wolf, J. C. Kertesz, and W. C. Landgraf, *J. Magnetic Resonance*, 1969, **1**, 618; 1974, **15**, 427.

[16] B. C. Gilbert, H. A. H. Lane, and R. C. Sealy, *J.C.S. Perkin II*, 1975, 892.

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[20] M. J. Blandamer, J. M. Gross, and M. C. R. Symons, *Trans. Faraday Soc.*, 1964, **60**, 494.

[21] P. C. Chan and H. J. Bielski, *J. Amer. Chem. Soc.*, 1973, **95**, 5504.

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[23] P. Neta and R. W. Fessenden, *J. Phys. Chem.*, 1971, **75**, 2277.

[24] J. W. Wells and E. E. Budzinski, *J. Chem. Phys.*, 1973, **59**, 5211.

[25] P. J. Krusic and J. K. Kochi, *J. Amer. Chem. Soc.*, 1971, **93**, 846.

[26] J. Q. Adams, *J. Amer. Chem. Soc.*, 1970, **92**, 4535.

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

[28] M. Nonijaĕić, H. Möckel, D. Bahnemann, and K.-D. Asmus, *J.C.S. Perkin II*, 1975, 675.

definition of such bonding is more precise in the pure crystals than in CD_3OD is shown by the narrow z-features for the pure materials and the broad, unresolved z-features from RS· radicals in CD_3OD. Hyperfine coupling from protons in $RCH_2\dot{S}$ or $R_2CH\dot{S}$ radicals was never resolved for RS· radicals in this solvent. It is possible that this arises not only because of variable hydrogen-bond strengths in the glass, but also because of variable torsional angles, θ, between the directions of the C–H bonds and that of the hydrogen bond that serves to define x and y. These angles are normally well defined in the crystalline materials, but could well be variable in a methanol glass. (This could also be one reason why RO· radicals have never been detected in irradiated glassy alcohols, despite the fact that they give well defined features when formed in certain crystalline biomolecules.[29]) Attempts to detect RS· radicals in various aprotic solvents at 77 K failed, as expected, and they were not usually detected from pure thiols in the absence of hydrogen-bonding groups such as NH_3^+ or CO_2H. These results confirm the concept that well defined hydrogen bonding is necessary for the observation of a narrow g_z feature, whose value is dependent upon the strength of this bonding.[7]

TABLE 1

Selected g values for thiyl radicals (RS·)

Substrate	Medium	g_z	Comments
MeSH	MeSH		No resolved proton coupling
	CD_3OD	2.158	
EtSH	EtSH		
	CD_3OD	2.158	No resolved proton coupling
$HSCH_2CO_2H$	$HSCH_2CO_2H$		Either no RS· or a very poorly defined feature
	CD_3OD	2.158	
	$NAOH–H_2O$	2.134	
$HSCH(Me)CO_2H$	$HSCH(Me)CO_2H$		Broad ill defined shoulder
	CD_3OD	2.158	
$HSCH_2CH_2CO_2H$	$HSCH_2CH_2CO_2H$		Broad ill defined shoulder
	CD_3OD	2.158	
$HSCH_2CH_2NH_2$	$HSCH_2CH_2NH_3^+Cl^-$	2.230	A_z [H(1)] 15, A_z [H(2)] 28 G
	CD_3OD	2.158	
	EtOH	2.159	
	Pr^iOH	2.200	
	$NaOH–H_2O$	2.134	
$HSCH_2CH(OH)CH_2Cl$	$HSCH_2CH(OH)CH_2Cl$		
	CD_3OD	2.158	
$HSCH_2(CHOH)_2CH_2SH$			Broad ill defined shoulder
	CD_3OD	2.158	
$HSCH_2CH(NH_3^+)CO_2^-$	$HSCH_2CH(NH_3^+)CO_2HCl^-$	2.321, 2.312	Proton splitting not resolved in powder spectra
	CD_3OD	2.158	
$HSC(Me)_2CH(NH_3^+)CO_2^-$	$HSC(Me)_2CH(NH_3^+)CO_2HCl^-$	2.295	On anneal ⟶ 2.220
	CD_3OD	2.158	

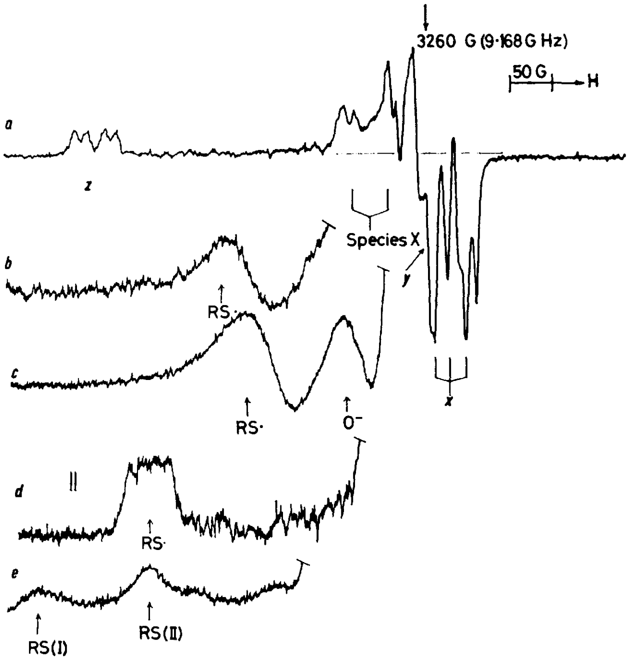
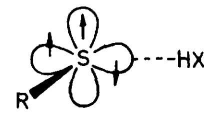


FIGURE 1 First derivative X-band e.s.r. spectra for various thiols after exposure to ^{60}Co γ-rays, showing features assigned to RS· radicals: *a*, cysteamine hydrochloride, showing x, y, and z features; *b*, cysteine hydrochloride in CD_3OD; *c*, thioglycolic acid in aqueous alkali, showing the z feature for RS· and the perpendicular O⁻ feature; *d*, penicillamine hydrochloride; *e*, cysteine hydrochloride. Only the z (parallel) features are shown for *b*—*e*



(II)

Thiyl radicals are probably formed by electron ejection followed by proton transfer to a nearby base. $R\dot{S}H^+$ cations have not been clearly detected, but a competing reaction in which $R\dot{S}H^+$ ions react with neighbours to give the dimer cations $R(H)S^{\cdot}–S(H)R^+$ is a probable alternative to proton transfer when the geometric arrangement is correct (see below).

Although we are satisfied that these species are all RS· radicals, this theory has recently been disputed by

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[29] H. C. Box and E. E. Budzinski, *J. Chem. Phys.*, 1975, **62**, 197.

Hadley and Gordy.[30] They studied the ^{33}S hyperfine coupling for a species with g values (2.214, 2.006, and 1.990) formed in irradiated *N*-acetyl-L-cysteine and decided that it was formed by electron capture to give $R\dot{S}H^-$ or $R\dot{S}H_2$ radicals. A major reason for this was the g value of 1.990, which they state rules out RS• radicals. However, such a low g value shift is readily accommodated for RS• in our view and can be linked with the large positive shift in g_z. We would certainly expect the appearance of large ^1H coupling for either of these species and none was observed. The ^{33}S data fit in well with expectation for $R\dot{S}$ radicals. The isotropic coupling to ^{33}S was small, showing the species to be π rather than σ and this alone seems to rule out the suggested structures.[30]

Dissociative Electron Capture.—As stressed above, the way in which thiols interact with electrons seems to vary widely, and reaction to give HS^- has not, apparently, been detected by e.s.r. spectroscopy in solid-state studies, despite its prevalence in the liquid phase. We have shown in previous work that the role of the medium can be crucial in controlling the mechanism of an electron capture process.[13,31] It therefore seemed possible that loss of HS^- may require the presence of a good anion solvent such as water or methanol. The solvent in liquid-phase studies that gives HS^- from electron capture has always been water. We now have found that the similar solvent, CD_3OD, also gives loss of HS^- as a major process, even at 77 K.

A good example is that of penicillamine. Solid-state studies on crystalline material at 4.2 K have shown that electron addition to the carboxy-group is the major electron-capture step.[11] At higher temperatures, dissociative electron capture to give NH_3 has also been observed,[11] but not electron capture to give HS^-. However, in methanol, the major step seems to be loss of HS^-, giving the radical $Me_2\dot{C}CH(NH_2^+)CO_2^-$, which is readily characterised by its e.s.r. spectrum (Figure 2). Thus, of the three possible reactions, loss of HS^- clearly dominates in protic media. Similar results were obtained for the other thiols (Figure 2 and Table 2). These are discussed separately below.

We conclude that protic solvents encourage HS^- formation, and consider that the over-riding factor is hydrogen bonding which remains an integral part of the solvation of the ejected anion. This seems to tip the scales from NH_3 formation to HS^- formation. Electron capture at CO_2^- or CO_2H groups dominates at 4.2 K probably because this involves less movement of nuclei than the dissociative electron capture processes. These carboxylate anions are pyramidal at the carboxy-carbon, but the distortion is small.[32] When more thermal energy is available we conclude that C–S bond stretching competes directly, or possibly that addition to the carboxy-group is reversible. In other words, electron donation from CO_2^{2-} or CO_2H^- groups may occur.

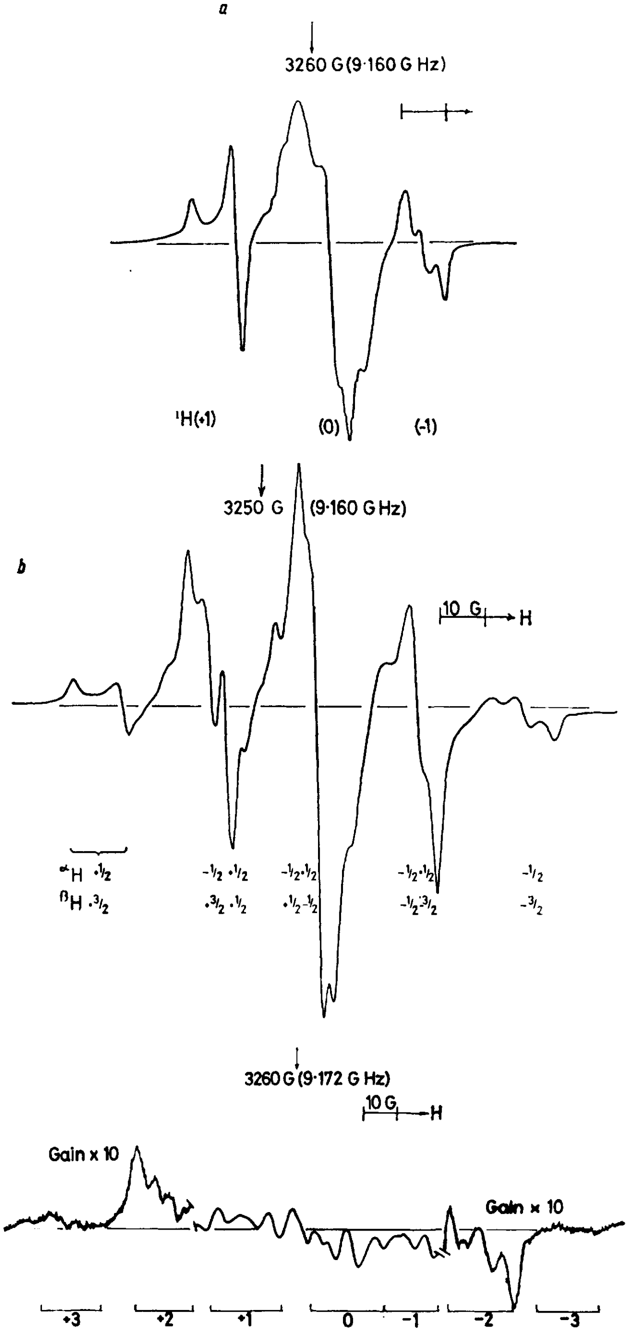

FIGURE 2 First derivative X-band e.s.r. spectra for various thiols in CD_3OD after exposure to ^{60}Co γ-rays at 77 K, showing features assigned to radicals formed by loss of HS^- anions: *a*, thioglycolic acid, showing features assigned to $H_2\dot{C}CO_2^-$ radicals; *b*, thiolactic acid, showing features assigned to $Me\dot{C}HCO_2^-$ radicals; *c*, penicillamine, showing features assigned to $Me_2\dot{C}CH(NH_3^+)CO_2^-$ radicals

General absence of radicals formed by HS^- loss in the pure materials is thus interpreted in terms of the absence of strong hydrogen bonding. However, in the particular case of thioglycolic acid, we have detected

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

[31] D. J. Nelson and M. C. R. Symons, *J.C.S. Perkin II*, 1977, 286.

[32] J. E. Bennett and L. H. Gale, *Trans. Faraday Soc.*, 1968, **64**, 1174.

$H_2\dot{C}CO_2H$ radicals, which suggests that in this case the required bonding is present in the crystalline material.

TABLE 2

Radicals formed by loss of HS^- from a variety of thiols in CD_3OD at 77 K

Thiol	Radical	E.s.r. features
MeSH	$\cdot CH_3$	3 H (23G): Rotating
EtSH	$\cdot CH_2CH_3$	2α-H (22 G_{av}), 2β-H (25.5 G)
$HSCH_2CO_2^-$	$\cdot CH_2CO_2^-$	2α-H (21 G_{av})
$HSCH(Me)CO_2^-$	$\cdot CH(Me)CO_2^-$ [a]	1α-H (21 G) 3β-H (24 G)
$HSCH_2CH_2CO_2^-$	$\cdot CH_2CH_2CO_2^-$	2α-H (22 G), β-H(1) (15 G), β-H(2) (10 G)
$HSCH_2CH_2NH_2$	$\cdot CH_2CH_2NH_2$	2α-H (21 G) 2β-H (33 G)
$HSCH_2(CHOH)_2CH_2SH$	$\cdot CH_2(CHOH)_2CH_2SH$	2α-H (23 G) 1β-H (38 G)
$HSCH_2CH(NH_3^+)CO_2^-$	$\cdot CH_2CH(NH_3^+)CO_2^-$	2α-H (22 G) 1β-H (37 G)
$HSCME_2CH(NH_3^+)CO_2^-$	$\cdot CMe_2CH(NH_3^+)CO_2^-$	6β-H (24 G) 1β-H (6 G) 1N, 5G

[a] Also formed by irradiation of the pure compound.

The 3*g Value Species X*.—In all cases, species having 3*g* values in the region of 2.058, 2.025, and 2.001 were obtained. The data are summarised in Table 3, and some examples given in Figure 3. Before considering the merits and disadvantages of the two rival theories,[7-9] pertinent information is summarised. We will begin by making the simplifying assumption that only one type of radical is responsible for these features, but stress that this may well be incorrect.

TABLE 3

Radicals labelled X in the text (? RSS· or $RS^{\cdot}$–SR_2) [a]

Substrate	*g* Tensor components g_x	g_y	g_z	^1H Hyperfine coupling (G) [b]
CH_3SH	2.056	2.025	2.000	Quartet, 7.2
C_2H_5SH	2.059	2.026	2.002	Doublet, 8
$HSCH_2CO_2H$				No clear features for species X
$HSCH(Me)CO_2H$	2.059	2.025	2.000	Singlet
$HSCH_2CH_2CO_2H$	2.061	2.025	2.001	Doublet, 9
$HSCH_2CH_2NH_3^+Cl^-$	2.058	2.025	2.001	Doublet
$HSCH_2CH(OH)CH_2Cl$	2.059	2.025	2.001	Doublet, 8
$HSCH_2(CHOH)_2CH_2SH$ [c]	2.060	2.025	2.001	Doublet, 9
$HSCH_2CH(NH_3^+)CO_2HCl^-$ [d]	2.055	2.024	2.000	Doublet, 10
$HSCME_2CH(NH_3^+)CO_2HCl^-$	2.057	2.025	2.001	Singlet
Average	2.058	2.025	2.001	

[a] Values obtained from concentrated solutions in CD_3OD were all close to these values. [b] Isotropic within ±1 G. [c] Date for dithiothreitol and dithioerithritol were very similar. [d] The first species formed from RS· had g_x 2.066, g_y 2.010, and g_z 2.000 with two protons having $A(^1H) \approx 17.2$ G (*cf*. ref. 10).

Proton hyperfine coupling is usually between 5 and 10 G (Table 3). Whilst MeSH gave a radical with coupling to three equivalent protons, all other primary thiols (RCH_2SH) gave radicals with coupling to a single proton. This can be explained in terms of one specific configuration in which the second proton of the methylene group lies fortuitously close to the nodal plane and hence exhibits no hyperconjugative coupling.[33,34] However, it does suggest that there must be very precise steric requirements, which seem to be independent of the nature of R. Secondary and tertiary thiols (R_2CHSH and R_3CSH) exhibit no resolved ^1H coupling when they form species X.

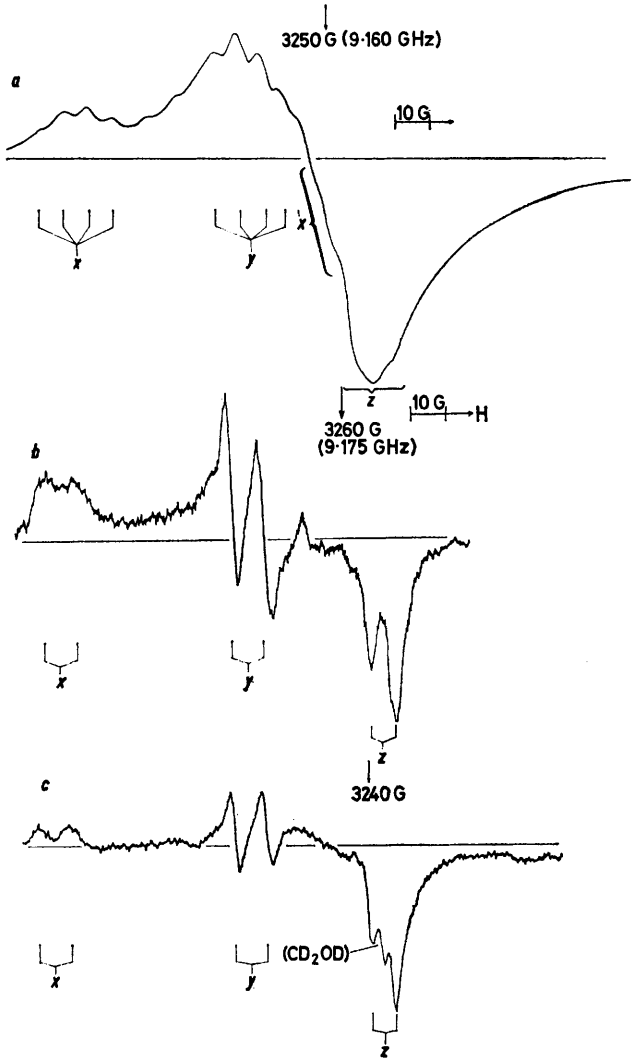

FIGURE 3 First derivative X-band e.s.r. spectra for various thiols after exposure to ^{60}Co γ-rays at 77 K and partial annealing to remove RS· radicals, showing features assigned to species X (possible RSS· or $RS^{\cdot}$–SR_2): *a*, methanethiol (extra features marked α); *b*, 3-mercaptopropionic acid; *c*, 1,4-dithiothreitol

In the particular case of penicillamine hydrochloride, Budzinski and Box [11] observed a small doublet splitting for certain orientations, but this was assigned to weak interactions with neighbouring molecules. We have carefully examined the powder spectrum for species X in penicillamine hydrochloride in the expectation that the very narrow *x*, *y*, and *z* features should give some indication of coupling to the S–H proton, if it is present. In fact, at low power and low modulation amplitude,

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[33] J. Gibson, D. J. E. Ingram, M. C. R. Symons, and M. G. Townsend, *Trans. Faraday Soc.*, 1957, **53**, 914.

[34] M. C. R. Symons, *J. Chem. Soc.*, 1959, 277.

both the x and z features showed extra splitting, which was totally lost for the deuteriated material. This is shown in Figure 4 for the $g_{min.}$ feature, which appears as a triplet. This is reasonable for a single coupled proton, if the coupling is weak but anisotropic, since the normally forbidden '$\Delta M_I = \pm 1$' features are expected to be relatively strong. We therefore interpret the triplet of Figure 4 as arising from a single proton with $A(^1H)$ *ca.* 3.3 G for this orientation.

The range of g values covered in Table 3 is quite large for $g_{max.}$, which suggests either that species X is still somewhat affected by the environment or that more than one species is involved.

The orientations of the g and A tensors relative to the crystal structures should be informative. Unfortunately, it seems that considerable movement needs to be postulated in order to fit the results with particular theories, so that nothing definitive can be deduced. This presumably arises because the species contains two sulphur atoms and movement is required to form the sulphur–sulphur bond.

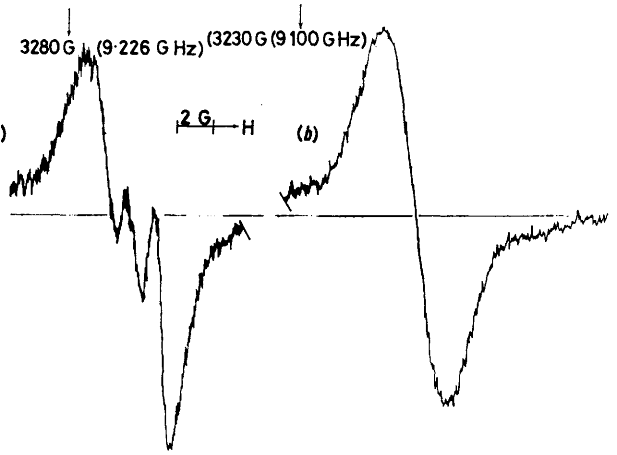

FIGURE 4 Second derivative X-band e.s.r. spectra at 77 K for $HSC(Me)_2CH(NH_3^+)CO_2HCl^-$ (*a*) and $DSC(Me)_2CH(ND_3^+)$-CO_2DCl^- (*b*) after exposure to ^{60}Co γ-rays at 77 K and annealing to yield radical X only. Only the $g_{min.}$ feature is illustrated

The ^{33}S hyperfine coupling constants demonstrate the inequivalence of the two sulphur atoms conclusively. The values for $A_{\parallel}$ (*ca.* 51 and 33 G)[9] are well defined, but those for $A_{\perp}$ (*ca.* 21 and 13 G) are less certain since they have to be obtained by a curve-fitting procedure. However, if these values are accepted, the calculated $3p$ characters for S(1) and S(2) are *ca.* 0.36 and 0.54 respectively,[9] with small $3s$ contributions of 0.013 and 0.022 respectively. The principle directions of the two ^{33}S interaction tensors seem to be the same, and to lie approximately along those for the principle g tensor components, with $A_{\parallel}$ along $g_{min.}$ (g_x).

These results can now be compared with expectation for the two current theories, namely that X is $RS\dot{S}$ [8,9] or $RS\cdot\!-\!SR_2$.[7] Strongly in favour of $RS\dot{S}$ is the almost complete absence of proton coupling from any protons in the $-SR_2$ group. Indeed, we would be inclined to take this as conclusive evidence against the $RS\cdot\!-\!SR_2$ theory were it not for other evidence, which seems to be at variance with the $RS\dot{S}$ theory. In order to retain the $RS\cdot\!-\!SR_2$ concept it is necessary to say that the expected proton coupling is invariably small. Two factors make this possible if not probable. One is that the spin density on S(1) (the more weakly coupled sulphur atom) is relatively low, and the other is that there may be more $3s$ character in the orbital of the unpaired electron on this atom. [These statements are not based on the ^{33}S results, since, especially for S(1) the $3p$ and $3s$ populations are very uncertain: they are based on expectation that the $-S(1)R_2$ sulphur atom will have more $3s$ character in its bonding orbitals than the $-S(2)R$ sulphur atom.] It is well established that as s admixture increases, the isotropic hyperfine coupling to both α- and β-protons diminishes. A good example is the near-zero value for $H\dot{N}O_2$.[35] However, even if this is the case, some anisotropic coupling should be observed for certain orientations in the case of $RS\cdot\!-\!SHR$ radicals. It is unfortunate that there are no informative liquid-phase data for species X, since the solid-state features are usually broad, and could conceal hyperfine splitting in the 0—2 G region. The only liquid-phase result for species X of which we are aware is that obtained by Davies and Roberts,[36] for a radical derived from photolysis of di-n-butyl disulphide in iso-octane. A species with g_{av} 2.0262 and width 11.5 G was thought to be $Bu\dot{S}$, but as we have stressed, this is improbable. The large width, reflecting an efficient spin–lattice relaxation process, precludes the possibility of solving this problem by liquid-phase studies. In principle, proton ENDOR spectroscopy could prove the presence or absence of the $-SR_2$ group, but no results have been reported, and our own attempts to obtain proton ENDOR spectra for species X have failed.[37]

However, in the particular case of penicillamine hydrochloride, the e.s.r. spectrum for species X does display an extra coupling (Figure 4). This is small, and can be interpreted as an intermolecular effect, but it at least means that the $RS\cdot\!-\!S(H)R$ structure, with A_{iso}(α-H) *ca.* 0, cannot be dismissed. The anisotropic coupling for $RS\cdot\!-\!SHR$ radicals should be small because of the low spin density but, in the absence of the principle hyperfine components and A_{iso}, all we can conclude is that this structure remains reasonable.

The form of the g tensor components is in satisfactory agreement with either theory. For $RS\dot{S}$ radicals, $g_{max.}$ should lie close to the S–S bond direction, and stem mainly from spin on S(2). The direction for $g_{min.}$ should be approximately along the normal to the R–S–S plane (III). In contrast, for $RS\cdot\!-\!SR_2$, provided the electronic structure is essentially σ^*, as previously envisaged,[7] $g_{min.}$ should be close to the S–S bond, as for $RS\text{–}SR^-$ radicals, and $g_{max.}$ is likely to lie close to the C–S bond

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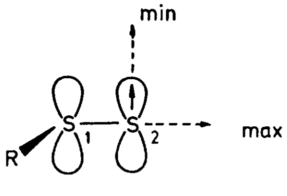
[35] F. J. Adrian, E. L. Cochran, and V. A. Bowers, *J. Chem. Phys.*, 1969, **51**, 1018.

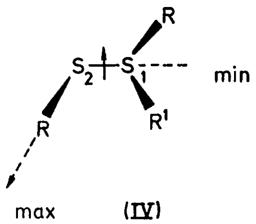
[36] A. G. Davies and B. P. Roberts, *J. Chem. Soc.* (*B*), 1971, 1830.

[37] J. Hüttermann and M. C. R. Symons, unpublished results.

direction of the RS^- group (IV), though this is not a necessary requirement.



(III)



(IV)

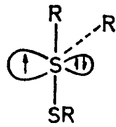
In most cases, these requirements cannot be readily checked because of the movements that have to occur when the S–S bond is formed. There is, however, one species that does seem to fit the requirements for the $RS^{\cdot}$–SR_2 structure quite well. This is a species formed not from a thiol, but from the disulphide, cystine hydrochloride. This species, designated α_2 by Akasaka *et al.*[38] and by Hadley and Gordy,[8] has $g_{\text{max.}}$ 2.066, $g_{\text{int.}}$ 2.010, and $g_{\text{min.}}$ 2.000, and exhibits strong ^{33}S coupling to one sulphur atom [8] and to two equivalent protons (17—21 G). This radical was identified as an $R\dot{S}$ radical,[8,38] but the low value of $g_{\text{max.}}$ makes this identification improbable. Since it is clearly formed from $RSSR^-$ radicals, it could well be the adduct $RS^{\cdot}$–S(H)R, as previously surmised,[7] provided delocalisation onto S(2) is small. This interpretation agrees well with the principle directions of the *g* tensor, since $g_{\text{min.}}$ is along the S–S bond direction and $g_{\text{max.}}$ is along the C–S direction of the RS^- group. Hence the RS–SR_2 formulation is satisfactory. This species is clearly different from the usual X species (Table 3), and hence again one can argue strongly in favour of the RSS· formulation for X, on the grounds that X is formed from the $RS^{\cdot}$–SR_2 adduct on annealing [reaction (4)]. If it is accepted that radical α_2 is $RS^{\cdot}$–S(H)R,

$$RS^{\cdot}\text{–}S(H)R \longrightarrow RSS^{\cdot} + RH \qquad (4)$$

and if one wishes to retain the $RS^{\cdot}$–SR_2 formulation for species X, it is necessary to postulate some alteration in structure for $RS^{\cdot}$–SR_2 on annealing. That this should be so is quite reasonable, but constitutes yet another limitation on the $RS^{\cdot}$–SR_2 theory.

The ^{33}S hyperfine data for species X seem to fit either theory. They do require an axial coupling, which is not required by the symmetry of either species. However, as already stressed, the 'perpendicular' coupling constants are most unsure and hence the coupling may not be axial. They also require that S(1) and S(2) have the same axis for $A_{\parallel}$, but this is satisfied by both models.

We have examined the idea that the structure for $RS^{\cdot}$–SR_2 deviates from the suggested σ^* structure towards the 'sulphuranyl' radical structure shown in (V). Here the lone pair on S(2) is taken to be stereochemically active. Variation of structure of exactly this type has been recently found for phosphoranyl radicals,[39] so the suggestion is not unreasonable. However, we would have expected, in this case, to have observed a greater isotropic coupling for $^{33}S(2)$, in contrast with the results reported by Hadley and Gordy.[8,9] Also, there would now be no requirement for S(1) and S(2) to share a common direction for the ^{33}S parallel coupling. We are therefore inclined to favour the σ^* structure originally envisaged.[7]



(V)

Thus the e.s.r. structural evidence favours the RSS· structure, without excluding $RS^{\cdot}$–SR_2. The most direct method of confirming this would be to prepare RSS· radicals unambiguously by a different route. Unfortunately, our attempts to do this have not resulted in definitive results. Thus studies of RSSH compounds certainly gave species resembling X, but other sulphur-centred radicals were also formed and assignment to RSS· radicals remains ambiguous. We have also studied RS_4R compounds in the hope that the thermal dissociation (5) would be detectable, but so far these studies have also been unsuccessful.

$$RS_4R \rightleftharpoons 2RS_2^{\cdot} \qquad (5)$$

We now turn to chemical evidence. It is generally agreed that radiolysis of thiols (RSH) gives RSSR and some H_2S as the only sulphur containing products.[2] Only in the apparently special case of penicillamine have polysulphides been obtained. Thus Purdie *et al.*[40] found that under certain conditions irradiated penicillamine gave the trisulphide (RSSSR) and valine (RH) as significant products. They suggested that this is formed by reactions (6) and (7). Reaction (7) was

$$RS + RS^- \rightleftharpoons RSSR^- \qquad (6)$$

$$RSSR^- + H_2O \longrightarrow RSS^{\cdot} + RH + OH^{-\cdot} \qquad (7)$$

favoured at low $[RSSR^-]$ and high concentrations of penicillamine, which are the conditions that prevail in the solid-state. Subsequently, reaction (8) takes place.

$$RSS^{\cdot} + RS^{\cdot} \longrightarrow RSSR \qquad (8)$$

One would expect the dimerisation (9) to occur also,

$$2RSS^{\cdot} \longrightarrow RS_4R \qquad (9)$$

but only traces of RS_4R were detected.[40] Goyal and Armstrong also detected the trisulphide and valine as major radiation products.[41] Following this study, Tung

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[38] K. Akasaka, S. I. Ohnishi, T. Suita, and J. Nitta, *J. Chem. Phys.*, 1964, **40**, 3110.

[39] M. C. R. Symons, *Phys. Chem. Letters*, 1976, **40**, 226.

[40] J. W. Purdie, H. A. Gillis, and N. V. Klassen, *Canad. J. Chem.*, 1973, **51**, 3132.

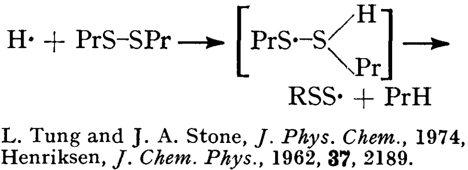
[41] G. C. Goyal and D. A. Armstrong, *Canad. J. Chem.*, 1976, **54**, 1938.

and Stone[42] postulated a similar reaction scheme to explain certain aspects during the flash photolysis and pulse radiolysis of cysteine. However, as yet, there is no evidence for RSSSR or alanine as final products.

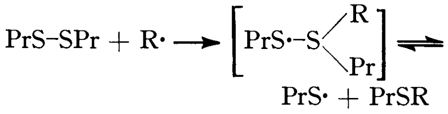
There is a major difference between these two compounds however, in that step (7) for penicillamine had a rate constant *k* of $2.3 \times 10^3\ s^{-1}$, whilst that for cysteine was *ca.* $2 \times 10^{-3}\ s^{-1}$. A possible explanation of this large difference in rates lies in the relatively high stability of the radical ·R for penicillamine, $Me_2\dot{C}CH(NH_3^+)CO_2^-$, compared with that for cysteine, $H_2\dot{C}CH(NH_3^+)CO_2^-$, since complete or at least incipient formation of these radicals is probably required for step (7). We and others have observed the formation of species X at 77 K. It could be objected that this might involve the reactions of ' hot ' intermediates, but even when X is produced thermally, its growth is sometimes detected at low temperatures. For example, Henriksen found that for penicillamine and its hydrochloride irradiated at 77 K, the e.s.r. spectrum showed a strong growth in [X] in the 160—240 K region.[43] For glutathione this growth occurred in the 240—300 K region and for cysteine growth began in the 160 K region. These solid-state low temperature reactions are not directly comparable with those occurring in water, but nevertheless the efficiency for the formation of species X is most surprising if it is RSS·, especially for cysteine.

In our studies, concentrated solutions of thiols in methanol glasses gave only RS· radicals at 77 K, but these were generally lost on annealing to *ca.* 130 K with the simultaneous growth of the signal from species X. This seems to require an impossibly high rate-constant for a process such as (7). It is also significant that species X formed in methanol gave the same variable g_z values for different substrates as has been found for the pure solids. In other words, the *g* values are controlled by the nature of R, not of the solvent. If, as suggested by Hadley and Gordy,[9] and as seems to be required by the RSS· theory, these variations are due to solvation differences, this result is difficult to understand. For $RS^{\cdot}\text{–}SR_2$ however, we expect a steric contribution to the length of the weak S–S bond and hence a variation in g_z.

A good example in which the expected products from RSS· radicals (RS_3R and RH) were specifically not obtained is for the γ radiolysis of cyclohexane solutions of di-n-propyl disulphide.[44] E.s.r. results for such systems show conclusively that room temperature radiolysis should have given species X as a major product. Nevertheless neither PrSSSPr nor propane were detected as products. The authors found that both electrons and hydrogen atoms were efficiently scavenged, so that reaction (7) or, for example (10), cannot have occurred. The major sulphur-containing product proved to be cyclohexyl propyl sulphide, presumably formed by (11). Thus the adduct $RS^{\cdot}\text{–}SR_2$ is a



$$H\cdot + PrS\text{–}SPr \longrightarrow \left[PrS^{\cdot}\text{–}S\begin{matrix}H\\Pr\end{matrix}\right] \longrightarrow RSS\cdot + PrH \qquad (10)$$



$$PrS\text{–}SPr + R\cdot \longrightarrow \left[PrS^{\cdot}\text{–}S\begin{matrix}R\\Pr\end{matrix}\right] \rightleftharpoons PrS\cdot + PrSR \qquad (11)$$

reasonable intermediate, but RSS· is most improbable as the major species detected by e.s.r. spectroscopy.

Many other such studies seem to require that RS· radicals are of major importance in the reaction of thiols, but not RSS· radicals. One vital difference between the RSS· and $RS^{\cdot}\text{–}SR_2$ theories is that $RS^{\cdot}\text{–}SR_2$ is a ready source of RS· radicals in the liquid-phase, whereas RSS· cannot be. We stress that even $RS^{\cdot}\text{–}SR^-$ radicals form RS· reversibly in solution[2] and the S–S bond is certain to be weaker in $RS^{\cdot}\text{–}SR_2$. Thus if RSS· is the most important high-temperature intermediate in solid-state radiolyses, it is puzzling that RS· is the most important species in liquid-phase studies.

Spin-trapping.—In order to test this point further, we have endeavoured to utilise the spin-trapping technique. Several groups have shown that RS· radicals can be characterised by the use of spin-traps.[27,45,46] For example, Wargen and Williams used BuNO as a trap and found the radical $MeS\text{–}(Bu)\dot{N}O$ was characterised by a 1.2 G quartet from the methyl group protons and a ^{14}N triplet of 18.9 G.[46] In our experiments, BuNO (*ca.* 10^{-3}M) was incorporated in methanol glasses containing RSH in high concentration. After radiolysis at 77 K, the glasses were carefully warmed until a maximum yield of species X was detected by e.s.r. spectroscopy, and other radical signals, especially that for RS· radicals, had been lost. The glasses were then allowed to melt and the liquid-phase spectrum was obtained. These gave characteristic signals from RS· adducts, and in the particular case of MeSH, clear quartets with $A(^1H)$ 1.3 G were detected. The inference that species X is a thermal source of RS· radicals seems difficult to avoid.

Absorption Spectra.—There can be no doubt that $RS^{\cdot}\text{–}SR^-$ radicals have an intense absorption band in the 400—450 nm region.[2,19] This intense transition ($\varepsilon_{max.}$ *ca.* 10^4 l mol^{-1} cm^{-1}) is, in our view, probably the $\sigma \rightarrow \sigma^*$ band corresponding to the 365 nm band for the isostructural radical $Cl_2{}^{\cdot -}$.[47] We would expect to find a corresponding transition for the $RS^{\cdot}\text{–}SR_2$ adducts, which could equally well be shifted to high or low energies of the $RS^{\cdot}\text{–}SR^-$ band. The HS· radical in the gas phase has a weak band in the 310—320 nm region comprising a set of vibrational components, and the $HS_2\cdot$ radical has a similar band at *ca.* 330 nm.[48] In acidic solutions the $RSSR^-$ peak is lost, and a transient, low intensity

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

[43] T. Henriksen, *J. Chem. Phys.*, 1962, **37**, 2189.

[44] J. A. Stone and J. Esser, *Canad. J. Chem.*, 1974, **52**, 1253.

[45] W. H. Davis and J. K. Kochi, *Tetrahedron Letters*, 1976, **21**, 1761.

[46] J. A. Wargen and F. Williams, *J.C.S. Chem. Comm.*, 1975, 947.

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

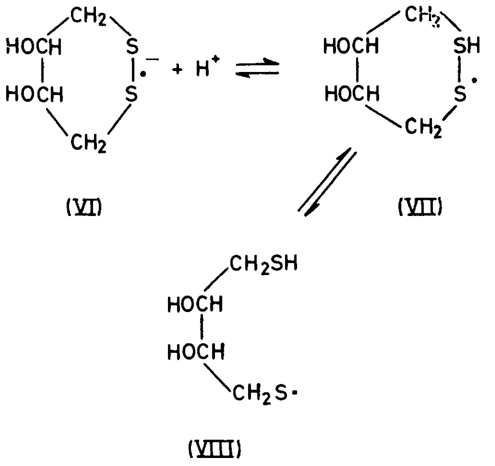
[48] R. K. Gosavi, M. DeSorgo, H. E. Gunning, and O. P. Strausz, *Chem. Phys. Letters*, 1973, **21**, 318.

band at *ca.* 330 nm appears.[49] There are strong reasons for assigning this to RS•, formed by protonation (12).

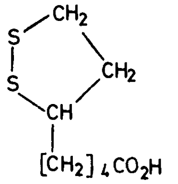
$$\mathrm{RSSR^- + H^+ \overset{a}{\rightleftharpoons} RS{\cdot}\text{–}SHR \overset{b}{\rightleftharpoons} RS{\cdot} + RSH} \qquad (12)$$

This fits the gas-phase results well, but if RSS• radicals were also present, they might not be detected separately. However, they are far less reactive than RS• radicals and hence a long-lived component should appear in the 330 nm region. This does not seem to have been detected.

These results suggest that in the liquid-phase at ambient temperatures equilibrium (12*b*) is far to the right and hence RS•–SHR radicals are not detected. However, in two instances involving cyclic structures that prevent the gross separation of RS• and RSH, a new, intense band was found in the 380 nm region. Thus Chan and Bielski [21] found that dithiothreitol gave a band at 380 nm which they assigned to the neutral species (VII) or (VIII). Since RS• radicals do not have an intense band in this region, and since this new species is formed by a reversible protonation of the cyclic RS•–SR⁻ anions (VI), assignment to RS•–SHR seems to be unavoidable. Similarly, thioctic acid (IX) gave an absorption at 450 nm assigned to the anion, and an equally intense band at 385 nm assigned to the protonated anion.[49] The 385 nm peak was present at ' zero time ' which rules out any slow processes such as (7).



(VI) (VII) (VIII)



(IX)

The recent results of Falle *et al.*[7] are also pertinent to this problem. They studied a range of thiols and disulphides in 6M-sulphuric acid glasses containing $\mathrm{Fe^{II}}$, which was photolysed (253.7 nm) to give hydrogen atoms [reaction (13)]. They found that disulphides such as cystine gave an immediate growth of a species with the three *g* values characteristic of X, together

$$\mathrm{Fe^{II} + h\nu + H^+ \longrightarrow Fe^{III} + H{\cdot}} \qquad (13)$$

with an intense absorption band at *ca.* 375 nm. Since they were under the misapprehension that this species was RS•, and since the reaction was rapid at 77 K, they concluded than an electron transfer was involved [reaction (14)]. We would re-interpret this reaction as

$$\mathrm{RSSR + e + H^+ \longrightarrow RS{\cdot} + RSH} \qquad (14)$$

(15). Again, the link between X and the 375 nm band

$$\mathrm{RSSR + H{\cdot} \longrightarrow RS{\cdot}\text{–}S(H)R} \qquad (15)$$

is very strong, and the likelihood of forming $\mathrm{RS_2{\cdot}}$ radicals at 77 K is small.

We conclude that the $\mathrm{RS{\cdot}\text{–}SR_2}$ species almost certainly has an intense absorption band at *ca.* 380 nm, but that except for cyclic species, dissociation in the liquid-phase is fast and nearly complete so that it is usually not detected. In order to test if species X has such an absorption band, we irradiated finely powdered penicillamine hydrochloride with γ-rays at 77 K and warmed to room temperature, the only detectable paramagnetic species being X. The room temperature diffuse-reflectance spectrum was dominated by an intense band at 375 nm. Thus, unless some other non-magnetic intermediate has such an absorption, it seems safe to conclude that species X has a band at *ca.* 375 nm. This is again satisfactory if X is $\mathrm{RS{\cdot}\text{–}SR_2}$. However, the RSS• radical should not have an intense absorption in this region, but only a relatively weak band at higher energies.

Conclusions.—It is difficult to know what to conclude, since, as we have shown, there are arguments for and against both theories. On balance, we favour the $\mathrm{RS{\cdot}\text{–}SR_2}$ structure for species X, but it remains possible that both species, fortuitously, have *g* values in the same region. It should be possible to prepare an unambiguous sample of RSS• radicals, and despite our current failures, we are still pursuing this possibility.

Other Paramagnetic Centres.—Methanethiol. The irradiated solids, MeSH and MeSD, display an extremely complicated powder spectrum which suggests the presence of at least two species of type X. The species detected by Gillbro in single crystals of MeSH [50] is clearly present, as shown in Figure 3, and the derived parameters agree with those obtained from the crystal. Unfortunately, overlap is such that we have been unable to obtain good data for the other centre. The Q-band spectra were still too complicated for satisfactory interpretation. It seems possible that both RSS• and $\mathrm{RS{\cdot}\text{–}SR_2}$ centres may have been formed in this case. The major X-centre was identified as MeS• by Gillbro,[50] who also identified two other poorly defined centres as

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[49] M. Z. Hoffman and E. Hayon, *J. Amer. Chem. Soc.*, 1972, **94**, 7950.

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

$Me\dot{S}H^+$ and $Me\dot{S}H^-$. In our view, both these identifications are somewhat improbable. $Me\dot{S}H^+$ should give $Me\dot{S}$ very rapidly, or alternatively should give the dimer $Me(H)S{\cdot}{-}S(H)Me^+$, since $Me_2S^{\cdot+}$ radicals are known to dimerise rapidly in this manner.[51] The anion $Me\dot{S}H^-$ belongs to a class of electron excess centres that have not yet been detected. Since in good anion solvating media, $Me{\cdot} + SH^-$ are formed, and since the isostructural molecule, MeCl, gives only $Me{\cdot} + Cl^-$, and since no species resembling methyl radicals was formed, we are against this formulation. (The anion $H_2S^{\cdot-}$ has been reported,[52] but there are good reasons for describing this as $HS{\cdot}{-}SH^-$.[53,54]) Our powder spectra display features in the free-spin region which suggest the presence of $H_2\dot{C}SH$ radicals, the data [$A_{av}(^1H)$ 21 G] being those expected for this species. This may have been one of the species detected by Gillbro. The other species absorbing in the free-spin region could be studied most readily at high microwave powers since the features for $H_2\dot{C}SH$ were selectively saturated. The spectrum obtained was similar to the powder spectrum for $MeS{\cdot}{-}SMe^-$ radicals (unpublished result), but since this anion is not expected, we assign the spectrum to the cation dimer, $Me(H)S{\cdot}{-}S(H)Me^+$. The data derived on this basis give average values for g and A(Me) close to those for $Me_2S{\cdot}{-}SMe_2^+$ (Table 4). If this tentative identification is correct it has an important implication, since the hyperfine coupling to the two S–H protons is not resolved. This supports our contention that the coupling to S–H protons in $RS{\cdot}{-}SHR$ complexes is small.

TABLE 4

E.s.r. parameters for species formed from irradiated thiols, tentatively identified as $RHS{\cdot}{-}SHR^+$ cations

Substrate	Postulated radical	g Value	^{1}H Coupling (G) (no. of features)	Comments
Me_2S	$(MeS-)_2^+$ [a]	g_{av}, 2.01	6.5 (13)	Liquid phase
MeSH	$(MeHS-)_2^+$	Not defined	5 (?7)	One g feature *ca.* 2.02 and one close to 2.000
$HSCH_2CO_2H$	$[HO_2CCH_2(H)S-]_2^+$	Not defined	*ca.* 5 (?3 or 5)	g Values between 2.02 and 2.000, always concealed by other lines
$HSCH(Me)CO_2H$	$[HO_2CCHMe(H)S-]_2^+$	*ca.* 2.02, 2.01, 2.00	Not resolved	Broad features at high powers
$HS(CH_2)_2NH_3^+Cl^-$	$[H_3^+NCH_2CH_2(H)S-]_2^+$	*ca.* 2.02, 2.01, 2.00	*ca.* 5 G (5)	Only resolved during anneal
$HSCH_2CO_2^-$ (NaOH glass)	$(^-O_2CCH_2S-)_2^-$ [b]	2.020, 2.011, 2.000	Not resolved	Suggest the ^{1}H coupling is broadened from a range of conformations

[a] Ref. 52. [b] $RS{\cdot}{-}SR^-$ included for comparison.

Ethanethiol. Very similar results were obtained for this thiol. The central (g 2) region showed poorly resolved features assignable to $Me\dot{C}HSH$ radicals, the broadening being typical of radicals containing a single α-proton. Elliot and Adam [55] studied this thiol in hydrocarbon glasses and in the pure state, both by e.s.r. and u.v. spectroscopy after u.v. irradiation. They postulate that $EtS{\cdot}$ radicals are responsible for an intense 400 nm peak and for a broad e.s.r. absorption at g 2.00. They also suggest that species X is $EtSS{\cdot}$. It does seem probable that aggregation occurred in the hydrocarbon glasses and that the photoactive species were dimers or oligomers of EtSH. The results of this study and their interpretation seems to us to be somewhat obscure.

Thioglycolic acid ($HSCH_2CO_2H$). The central spectrum for the pure compound shows hyperfine coupling to two inequivalent protons (*ca.* 22 and 4 G) and we suggest that this is the parent anion, $HSCH_2CO_2H^-$ with the excess electron in the pseudo π^* orbital of the carboxy-group. On annealing a species with anisotropic coupling to a single proton of *ca.* 16 G is identified as $HS\dot{C}HCO_2H$. This had g and $A(^1H)$ values of 2.009 (18 G), 2.005 (15 G), and 2.001 (15 G). It is likely that only one of these is a principle value because these tensors share only one principle direction. Solutions in aqueous sodium hydroxide (and D_2O + NaOD) glasses were studied, because we wished to confirm the formation of $RSSR^-$ radicals and to obtain typical powder spectra thereof. After annealing, concentrated solutions gave loss of $RS{\cdot}$ features and concomitant growth of features clearly assignable to the dimer anions $\bar{O}_2CCH_2S{\cdot}{-}SCH_2CO_2^-$. Simultaneously, the samples acquired an intense orange colouration, indicative of a band in the 420 nm region. Formation of the dimer anion in the presence of RS^- ions is, of course, expected, but the marked similarity of this process to those in which $RS{\cdot}$ radicals are converted into X is noteworthy.

Thiolactic acid [$HSCH(Me)CO_2H$]. The central region for irradiated CD_3OD solutions comprised a quintet with $A(^1H)$ *ca.* 21 G and the outermost lines displaying outer shoulders indicative of a $\dot{C}H_2$ group. We therefore favour a species $R\dot{C}HMe$, which could be either $HS\dot{C}HMe$ formed by loss of e^- and carbon dioxide, or $Me\dot{C}HCO_2^-$ formed by electron attachment and loss of SH^-. Since this species was formed in CD_3OD, which would suppress the former but encourage the latter reaction, we favour the radical $Me\dot{C}HCO_2^-$. On annealing to near the softening point of CD_3OD, the quintet gave way irreversibly to a quartet (*ca.* 15 G), which showed clear signs of g anisotropy with one g value in the 2.008 region. We suggest that this is the radical $Me\dot{C}(SH)CO_2^-$.

3-Mercaptopropionic acid ($HSCH_2CH_2CO_2H$). The

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central region of the e.s.r. spectrum for the pure material was too poorly defined to warrant consideration. However, solutions in CD_3OD gave a spectrum characteristic of the radical $H_2\dot{C}{-}CH_2CO_2^-$ (Table 2). Thus dissociative electron capture was again facilitated in this medium, but other species formed in the pure material could not be identified.

Cysteamine ($HSCH_2CH_2NH_2$). In addition to a strong signal from RS• radicals characterised by a feature at *g* 2.22, the pure hydrochloride gave an asymmetric feature in the central region which we tentatively assign to the dimer cation, $R(H)S{\cdot}{-}S(H)R^+$. At *ca.* 130 K this became better defined, and we clearly identify a set of three or five components (*A ca.* 8 G) centred on *g* 2.02. Other sets, probably also comprising three or five lines were at *ca.* 2.01 and 2.00. Thus, we postulate formation of $R\dot{S}H^+$ followed by weak bonding to a neighbouring RSH molecule. If this is correct, then we again conclude that coupling to the two α-protons is very small. (The alternative $RS{\cdot}{-}SR^-$ formulation for this species is considered to be most improbable in such an acidic environment.)

In CD_3OD glasses, in addition to RS• radicals, a species $H_2\dot{C}{-}CH_2R$ was detected having A(α-H) *ca.* 22 G (anisotropic) and A(β-H) *ca.* 33 G (isotropic). The structure having R = SH is extremely unlikely, since groups such as SH normally strongly prefer an out-of-plane configuration such that A(β-H) = *ca.* 13 G.[56] Thus we identify this radical as $H_2\dot{C}{-}CH_2NH_3^+$, with the NH_3^+ group in the radical plane.

In an aqueous alkali glass, cysteamine gave, on annealing, features assignable to the anion $RS{\cdot}{-}SR^-$.

$ClCH_2CH(OH)CH_2SH$. The pure material gave broad features of the type assigned above to the dimer cations. Also species X appeared on annealing. The material was an intense violet colour after exposure at 77 K, and the colour changed to orange as species X was formed on annealing. These colour changes accord with the assignment made above, since $R_2S{\cdot}{-}SR_2^+$ cations absorb strongly in the 500—600 nm region. In CD_3OD glass a species $H_2\dot{C}CHR$ having A(α-H) *ca.* 22 G and A(β-H) *ca.* 28 G was obtained. In this case we cannot distinguish between loss of Cl^- and loss of SH^- since the resulting radicals should have almost identical e.s.r. spectra.

Dithioerythritol and dithiothreitol [$HSCH_2CH(OH)CH(OH)CH_2SH$]. These compounds also gave species with three or possibly five components (*A ca.* 7—8 G) that we think are characteristic of the dimer cations. Again the α protons gave no detectable hyperfine coupling. These species were not formed in CD_3OD solution, but instead, a species $H_2\dot{C}CH_2R$ was formed with a β-proton coupling of *ca.* 34 G. Since β-OH groups are expected to tend towards the in-plane position,[57] which is indicated by the large β-proton coupling, we suggest that these radicals are $H_2\dot{C}{-}CH(OH)R$ formed by loss of SH^-.

Cysteine [$H\dot{S}CH_2CH(NH_3^+)CO_2^-$]. For the pure material, features for RS• radicals were very well defined (Figure 1) implying precise hydrogen bonding, but for CD_3OD solutions, despite the smaller *g* shift, the proton hyperfine structure was not resolved on the parallel component. Central features expected for RCO_2H^- and for $HSCH_2\dot{C}HCO_2H$ radicals were poorly defined in the pure material; however, CD_3OD solutions gave well defined features for $H_2\dot{C}CHR_2$ radicals [A(α-H) *ca.* 22 G, anisotropic and A(β-H) *ca.* 37 G, isotropic] formed by loss of SH^-.

Penicillamine [$HSC(Me)_2CH(NH_3^+)CO_2^-$]. Very similar results were obtained to those for cysteine, including the formation of two RS• centres. Solutions in CD_3OD or D_2O gave $Me_2\dot{C}CH(ND_3^+)CO_2^-$ radicals which were clearly identifiable. These are not detected in the pure compound or in the hydrochloride, which gave the $R\dot{C}O_2H^-$ anion [$A(^1H)$ *ca.* 15 G]. As reported by Budzinski and Box [11] a chlorine-centred radical is also formed in the latter salt. This was identified as a chlorine atom,[11] but we prefer the concept that the species is $ClOH_2$. The radical $ClOH^-$ has been identified previously in irradiated strontium chloride [58] and in aqueous chloride glasses,[59] and the parameters are quite similar. Hyperfine coupling to two equivalent protons strongly supports this identification.

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