On the Electron Spin Resonance Detection of $R\dot{S}$ Radicals in Irradiated Solids: Radicals of Type $RSSR^-$, $RS{-}SR_2$, and $R_2SSR_2^+$

By **Martyn C. R. Symons,** Department of Chemistry, The University, Leicester LE1 7RH

It is suggested that radicals previously identified as $R\dot{S}$, having *g* tensor components in the 2·002, 2·025, and 2·060 regions are better described as $RS\dot{-}SR_2\,\sigma^*$ radicals, structurally similar to the established radical anions, $RS\dot{-}SR^-$. Furthermore, a radical in irradiated thiodiglycolic acid previously thought to be $(HO_2CCH_2)_2\dot{S}^+$ is almost certainly the dimer-cation $(HO_2CCH_2)_2S\dot{-}S(CH_2CO_2H_2)^+$. The type of spectrum expected for $R\dot{S}$ radicals including $H\dot{S}$ is discussed, together with possible assignments.

THE literature abounds in references to e.s.r. spectra assigned to $R\dot{S}$ (thiyl) radicals,[1-5] and with one notable exception,[5] these all have three distinct *g* values close to the averaged values of 2·002, 2·025, and 2·060. (A selection is given in the Table.) In many instances nearly isotropic proton hyperfine splittings are also reported. Spectra assigned to $H\dot{S}$ radicals in the solid state have the same set of features [1,4] (Table). The aim of this work is to outline reasons why it seems that these data are incorrectly assigned, and to suggest an alternative assignment.

First, thiyl radicals are isostructural with alkoxyl radicals, $R\dot{O}$. Despite repeated claims, I am unaware of any authentic example of an e.s.r. spectrum for $R\dot{O}$ radicals, in either the fluid or solid state,[6] with the exception of the hydroxyl radical in ice or salt hydrates.[7,8] The reason for this is the degeneracy of the p–π orbitals and consequent orbital angular momentum about the molecular (z) axis, which has to be largely quenched if a solid-state e.s.r. spectrum is to be observed. This quenching, perforce, must come from the surrounding medium, and a detectable spectrum will only result, even in the presence of strong interaction, provided this is sufficiently asymmetric to lift the degeneracy of the π-levels, and sufficiently precise to give a well defined set of e.s.r. features. (In principle, $R\dot{O}$ or $R\dot{S}$ radicals other than $H\dot{O}$ or $H\dot{S}$ can undergo a Jahn–Teller distortion to lift the orbital degeneracy, but this will surely be insufficient to give rise to a well defined e.s.r. spectrum in the free-spin region.) For $\dot{O}H$ in ice, this is satisfied by the strong hydrogen bonding provided by neighbouring water molecules. However, for $R\dot{O}$ radicals in alcohol glasses for example, hydrogen bonding is not sufficiently precise to give well defined spectra.

Since $R\dot{S}$ radicals have the same π-degeneracy, the same limitations should apply. Indeed, the experimental limitations should be greater and the probability of detection smaller, since on the one hand sulphur in RSH forms far weaker hydrogen bonds than oxygen in ROH, and on the other, the spin–orbital coupling constant for sulphur is very much greater than that for oxygen and so angular momentum will be less readily quenched and the positive g_z shift greater. The results assigned to $R\dot{S}$ radicals (Table) are not compatible with these conclusions since the *g* values are precisely defined for a wide range of matrices, both hydrogen bonding and

---

[1] D. H. Volman, J. Wolsenholme, and S. G. Hadley, *J. Phys. Chem.*, 1967, **71**, 1798.

[2] Y. Kurita and W. Gordy, *J. Chem. Phys.*, 1961, **34**, 282.

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

[4] D. A. Stiles, W. J. R. Tyerman, O. P. Strausz, and H. E. Gunning, *Canad. J. Chem.*, 1966, **44**, 2149.

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

[6] M. C. R. Symons, *J. Amer. Chem. Soc.*, 1969, **91**, 5924.

[7] J. A. Brivati, M. C. R. Symons, D. J. A. Tinling, H. W. Wardale, and D. O. Williams, *Trans. Faraday Soc.*, 1967, **63**, 2112.

[8] G. H. Dibdin, *Trans. Faraday Soc.*, 1967, **63**, 2098.

non-hydrogen bonding. Furthermore, deviation from axial symmetry, which can only be induced by a strong environmental interaction, is precise and the same for a wide range of environments. (We stress that axial symmetry, which might at first sight be expected for $R\dot{S}$, will not in fact be observed since any environmental interaction capable of quenching the orbital angular momentum will always remove axial symmetry both for the g and A tensor components.)

Magnetic data for some sulphur radicals

Medium	Radica	g Tensor components g_x	 g_y	 g_z	^{1}H Hyperfine coupling (G) [a]
H_2S [b]	$HS\text{–}\dot{S}H_2$	2·061	2·024	2·003	*ca.* 7
$H_2S + H_2O$ [c]	$HS\text{–}\dot{S}H_2$	2·060	2·025	2·003	*ca.* 9·5
RSH [d]	$RS\text{–}\dot{S}HR$	$2{\cdot}055_2$	$2{\cdot}024_6$	$2{\cdot}003_2$	
L-Cystine HCl [e]	$RX\text{–}\dot{S}HR$ (i)	2·066	2·010	2·000	*ca.* 17·20 G (2H)
	(ii)	2·052	2·025	2·002	*ca.* 10·5 (1H)
EtSH–3-MP [f]	$EtS\text{–}\dot{S}HEt$	2·063	2·027	1·999	^{1}H coupling not resolved
$Me_2S\text{–}H_2O$ [g]	$Me_2S\text{–}SMe_2{}^+$	g_{av} 2·0103			a_{iso} 6·8 (12H)

[a] 1 G = 10^{-4} T. [b] Ref. 4: described as HS· therein. [c] Ref. 1: described as HS· therein (g values, not quoted in this ref. are taken from our own studies.) [d] Y. Kurita, *Bull. Chem. Soc. Japan*, 1967, **40**, 94. [e] Ref. 17: described as $R\dot{S}$ therein (ii) formed from (i) on annealing, probably *via* twisting about the S–S bond. [f] J. Skelton and F. C. Adam, *Canad. J. Chem.*, 1971, **49**, 3536. Described as EtS· therein. 3-MP = 3-methylpentane. [g] Ref. 15.

Similar objections relate to the magnitude of the ^{1}H coupling of 7—9 G assigned to ' HS· ' radicals. This value has been justified[1,4] by comparison with gas-phase data for $H\dot{S}$.[9] However, for gaseous $H\dot{S}$ radicals, the observed electron spin–nuclear spin coupling of 5·4 G [9] is not the Fermi contact coupling because of the very large orbital magnetic contribution. Indeed, comparison with a range of isostructural π-radicals leads to the empirical value of *ca.* −20 to −25 G [*cf.* $\dot{O}H$ (−26 G), $\dot{N}H_2$ (−25 G), $\dot{P}H_2$ (−18 G)]. It is, however, possible to calculate both the true isotropic hyperfine coupling and the dipolar coupling from the gas-phase data,[10] and this yields the values −23·2 and 4·3 G for A_{iso} and B respectively. These considerations once again cast grave doubts upon the assignments since the observed coupling is both too small and also too isotropic for $H\dot{S}$ radicals.

It is therefore postulated that solid-state e.s.r. spectra for $H\dot{S}$ radicals have not yet been detected, and that the reported spectra for $R\dot{S}$ radicals having g values close to 2·002, 2·025, and 2·060 are due to secondary radicals. These are thought to be ' dimer ' species of general formula $RS\dot{-}SR_2$, having the unpaired electron predominantly in the S–S σ^* orbital. These radicals are similar to the negative ions $RS\dot{-}SR^-$ formed from disulphides [11] and, less directly, to the V_K centres such as $Cl_2{}^-$ formed from halide ions.

This postulate fulfils the requirement of precision in the e.s.r. parameters since these are no longer dictated by environmental interaction. However, it requires justification on two main counts, the ability of $R\dot{S}$ to react in the solid state and the appropriateness of the measured e.s.r. parameters to this structure.

That reaction (1) should occur in the pure solids is

$$RS\cdot + SR_2 \longrightarrow RS\dot{-}SR_2 \qquad (1)$$

quite reasonable and indeed is to be expected. Thus, halogen atoms react efficiently with halide ions to form $Hal_2{}^-$ even in aqueous glasses,[12,13] and $R_3P\cdot^+$ radicals readily react with R_3P molecules to give $R_3P\text{–}PR_3{}^+$ radicals.[14] It is noteworthy that Volman *et al.*[1] needed to anneal their aqueous glasses of H_2S to 195 K for 13 days after photolysis at 77 K in order to observe good spectra of the type under consideration. This strongly supports our view that a secondary process is involved, the initially formed HS· radicals being undetectable. It could be argued that this ' dimerisation ' should not have occurred in a 1% solution of H_2S in Xe.[1] However, at 77 K species are often able to diffuse in solid Xe, and the fact that another species described as the polymer radical $(S)_n\cdot$ exhibited a strong absorption at 77 K during photolysis of this solid solution [1] confirms that diffusion to form $HS\text{–}SH_2$ is a reasonable postulate.

Very recently, Gilbert *et al.*[15] have shown that $R_2S\cdot^+$ radical cations formed by reaction between ·OH radicals and organic sulphides readily react with an excess of sulphide to give $R_2S\dot{-}SR_2{}^+$ dimers. This lends very strong support to the present postulate, since the family of radicals $RS\dot{-}SR^-$, $RS\dot{-}SR_2$, and $R_2S\dot{-}SR_2{}^+$ are all isostructural.

The results for the radical anions $RS\dot{-}SR^-$ [11] show that, as expected, the unpaired electron is in the S–S σ^* orbital, the g value in this direction (g_z) being 2·004 and those perpendicular to this direction (g_x and g_y) being in the 2·010—2·014 region.[11] In the particular case of cystine dihydrochloride, on annealing, the e.s.r. spectrum assigned to the anion was lost, being replaced by a

---

[9] H. E. Radford and M. Linzer, *Phys. Rev. Letters*, 1963, **10**, 443; C. C. McDonald, *J. Chem. Phys.*, 1965, **39**, 2587.

[10] M. Tanimoto and H. Uehara, *Mol. Phys.*, 1973, **25**, 1193.

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

[12] I. Marov and M. C. R. Symons, *J. Chem. Soc.* (*A*), 1971, 201.

[13] I. S. Ginns and M. C. R. Symons, *J.C.S. Dalton*, 1972, 143.

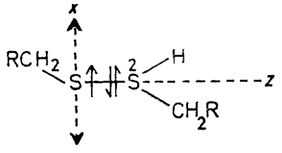
[14] A. R. Lyons and M. C. R. Symons, *J.C.S. Faraday II*, 1972, **68**, 1589.

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

spectrum assigned to $RCH_2\dot{S}$ radicals.[11,16] [The cation spectrum was also lost on annealing and Box *et al.*[11] postulated process (2) to explain this. However, the

$$RCH_2SSCH_2R^+ \longrightarrow RCH_2S^+ + RCH_2\dot{S} \quad (2)$$

g values for this new species differ markedly from those assigned to $RCH_2\dot{S}$ obtained from the anion. This dissociation (2) is most unlikely in the light of the extreme reactivity to be expected from the electron-deficient cation RCH_2S^+ and the fact that the S–S bond in the parent cation $(RCH_2S{-}SCH_2R)^+$ should be stronger than that in the original sulphide.] We propose that the fate of the parent anion $(RCH_2S\dot{-}SCH_2R)^-$ is not homolytic bond fission but protonation to give (I).



(I)

This molecule still has the unpaired electron in the S–S σ^* orbital, but this is now asymmetric, having a greater contribution from the atomic orbitals of S(1) than those of S(2) for electronegativity reasons. The S–S bond will probably be weaker than that in the anion, and this will bring the σ^* level closer to the π-level and hence increase g_x. More significantly, the loss of symmetry will enable the σ^* level to couple with the filled 'π' level and hence g_x should be greatly enhanced as observed. (These considerations depend upon the preferred conformation of the $RS\dot{-}SR_2$ radicals. This is unknown but must be quite precise since the form of the *g* tensor will be strongly dependent upon conformation.)

It is well established theoretically and experimentally that as *s* character is added to the orbital of an unpaired electron, originally in a π-orbital, the negative α-proton coupling of the π-radical decreases in magnitude and eventually changes sign. Thus, for example, the ^1H coupling for pyramidal $\cdot SiH_3$ radicals is *ca.* (+)7·9 G.[17,18] We therefore predict a smaller proton coupling than that for $H\dot{S}$ radicals, and the observed value of *ca.* ± 8 G is quite acceptable. The fairly isotropic nature of this coupling can also be understood since the powder spectrum is expected to be dominated by the *g* tensor components and hence the ^1H *A* values will not be principal components. Since the spin density on the H_2S fragment of $HS\dot{-}SH_2$ is reduced, the proton coupling is expected to be $< \pm 8$ G so might well not be resolved. However, in several published spectra wing lines are present and the spectra could be doublets of triplets with the outer lines broadened by anisotropic effects.

The results for L-cystine dihydrochloride ($RCH_2S{-}SCH_2R$) reported by Akasaka *et al.*[16] can be accommodated well on this model. Thus we suggest that their $RCH_2\dot{S}$ radical is really $RCH_2S\dot{-}SHCH_2R$ formed by protonation of the parent anion, which is known from pulse radiolysis studies to be a rapid process.[19] The coupling of 17—20 G for two equivalent protons is then rather large for the σ^* radical unless the major spin density is on S(1) and the two coupled protons are in the most favourable conformation for overlap between the C–H orbitals and that of the unpaired electron. [However, at least two other radicals with similar *g* values were detected, one having a 5-line pattern with $A(^1H)$ 6·5 G. It is possible that selective line broadening is masking intermediate lines in the first radical.] Again, that the free spin *g* value direction lies along the S–S bond and the direction of $g_{\max.}$ is in the C–S–S plane, provides strong support for our model.[10]

These considerations, together with the results of Gilbert *et al.*[15] lead to the conclusion that a radical described as $(HO_2CCH_2)_2S^{\cdot+}$ in irradiated thiodiglycolic acid at 4·2 K[20] is really the dimer-cation $(HO_2CCH_2)_2S\dot{-}S(CH_2CO_2H)_2^+$. The g_{av} value is close to those reported by Gilbert *et al.*,[15] and the form of the *g* tensor components is remarkably similar to that for the isostructural anions. Furthermore, the *X*-ray crystal structure study of Paul[21] shows that the S · · · S separation is only 3·78 Å in the parent crystal, so that only slight movement will provide the required bond.

Having concluded that the great majority of so-called thiyl radicals are $RS\dot{-}SR_2$ species, it seems that a radical reported to have $g_{\parallel}$ 2·29 and $g_{\perp}$ 1·99 in irradiated cysteine hydrochloride really is a thiyl radical, $HO_2CCH(NH_3^+)CH_2S\cdot$, as postulated by Akasaka.[5] This species is quite different from all the others discussed above, and the high $g_{\parallel}$ value is much more in line with expectation. Furthermore, the ^1H coupling constants of *ca.* 38 and 14 G are in good accord with expectation for thiyl radicals, again in marked contrast with the results discussed above. Clearly, this radical must have a precise conformation in order to have a precise $g_{\parallel}$ value. This probably involves intra- or inter-molecular hydrogen bonding. The change on annealing, to a species of the $RS{-}SR_2$ type, is then just reaction (1) which in this case cannot occur readily at 77 K. I stress that these *g* values should not be taken as characteristic of $R\dot{S}$ radicals or even of this particular $R\dot{S}$ species since the value of $g_{\parallel}$ is largely governed by the particular environment involved.

[4/995 *Received, 21st May*, 1974]

---

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

[17] S. W. Bennett, C. Eaborn, A. Hudson, R. A. Jackson, and K. D. J. Root, *J. Chem. Soc. (A)*, 1970, 348.

[18] J. H. Sharp and M. C. R. Symons, *J. Chem. Soc. (A)*, 1970, 3084.

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

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

[21] S. Paul, *Acta Cryst.*, 1967, **23**, 491.