Electron Spin Resonance Detection of Radicals $R\dot{S}$, $R\dot{O}$, and R^1 $S{-}R^{2+}$ in Irradiated Solids

By **Harold C. Box*** and **Edwin E. Budzinski**, Dept. of Biophysics, Roswell Park Memorial Institute, Buffalo, New York 14263, U.S.A.

The tensors describing the proton hyperfine couplings in thiodiglycolic acid cation were deduced from ENDOR measurements on single crystals *X*-irradiated at 4·2 K. The *g* tensors for $R^1{-}S{-}R^{2+}$, $R\dot{S}$, and $R\dot{O}$ radicals are compared.

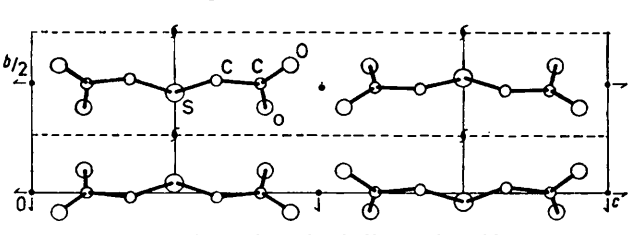
E.S.R. spectroscopy has been employed extensively to study radicals produced by irradiation of solids; however the identification of radicals by this method has not always been unequivocal. This is particularly true of radicals in which the unpaired electron is mainly localized on an oxygen or sulphur atom as a recent survey of the literature by Symons [1] makes evident. Some additional data has been obtained from ENDOR (electron nuclear double resonance) measurements on sulphur radicals and from low temperature studies of radical generation which clarify some of the problems highlighted by Symons.

TABLE 1

Principal values of *g* tensors in radicals attributed to species R^1-S-R^{2+}. Measurements on single crystals irradiated at 4.2 (ref. 3) or at 77 K (refs. 6 and 7)

Crystal	Radical	Principal values			Reference
Thiodiglycolic acid	$HO_2CCH_2\dot{S}^+CH_2CO_2H$	2.022	2.011	2.004	3
(±)-Acetylmethionine	$CH_3CONHCH(CO_2H)CH_2CH_2\dot{S}^+CH_3$	2.023	2.013	2.004	6
(±)-Methionine	$NH_2CH(CO_2^-)CH_2\dot{C}H_2S^+CH_3$	2.022	2.013	2.002	7

One of the interesting sulphur radicals formed in irradiated sulphides has been reported as having the structure $R^1{-}S{-}R^{2+}$ in which the unpaired electron is localized mainly on the sulphur atom. The absorption of one such radical, namely the oxidized species found in thiodiglycolic acid has been re-examined in single crystal *X*-irradiated at 4.2 K. Thiodiglycolic acid crystals belong to the space group P_{nam} with four molecules per unit cell.[2] The two halves of the thiodiglycolic acid molecule are related by a plane of mirror symmetry perpendicular to *c* and passing through the sulphur atom as shown in the Figure. The four molecules in the unit cell are related by two-fold screw axes parallel to the crystal axes. The e.s.r. absorption exhibits a large variation in *g* value described by the *g* tensor whose principal values are listed in Table 1. One of the principal axes of the *g* tensor is parallel to the *c* crystal axis.[3] The hyperfine pattern of this absorption is generated by eight protons. There are four sets of two equivalently coupled protons. The complete coupling tensors have now been determined from ENDOR measurements and are listed in Table 2.



Crystal packing of thiodiglycolic acid

TABLE 2

Proton hyperfine coupling tensors for the oxidized species in thiodiglycolic acid *X*-irradiated at 4.2 K as determined from ENDOR measurements. Principal values are given in MHz. The e.s.r. absorption is generated from eight proton couplings; these four couplings and a symmetry related set

	a	*b*	*c*
47.90	0.654	0.408	0.636
42.42	−0.704	0.634	0.316
40.22	−0.274	−0.655	0.703
45.70	0.677	0.662	0.319
42.96	0.045	−0.471	0.880
40.02	0.733	−0.582	−0.350
29.70	0.361	0.827	0.429
23.00	0.259	−0.531	0.806
22.42	0.895	−0.179	−0.407
21.18	0.881	0.104	0.459
14.74	−0.198	0.906	0.160
14.30	−0.427	−0.233	0.873

The suggestion that an absorption having these characteristics should be attributed to a cation dimer [1] must be rejected. Should a dimer be formed one would expect that the symmetry present in the thiodiglycolic acid structure would be retained in the dimer cation. Preservation of symmetry has been noted in the formation of primary oxidation and reduction products in a number of other organic crystals irradiated at 4.2 K.[4] The fact that the e.s.r. absorption of the oxidation product in irradiated thiodiglycolic acid has a principal axis of its *g* tensor

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

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

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

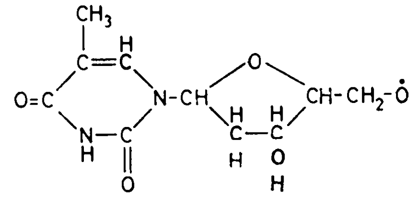
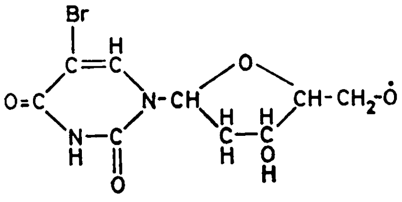
[4] H. C. Box, E. E. Budzinski, and W. Potter, *J. Chem. Phys.*, 1971, **55**, 315; H. C. Box, H. G. Freund, and G. W. Frank, *ibid.*, 1968, **48**, 3825.

parallel to *c* indicates that symmetry is indeed preserved. ENDOR studies show clearly that the oxidation product gives rise to a *single* absorption in the *ac* and *bc* planes (in contrast to the reduction product which gives rise to two symmetry-related absorptions). One expects therefore that two sets of four equivalent hyperfine couplings arising from the methylene protons would be observed from a dimer cation. In fact, ENDOR measurements show that the oxidation product absorption in thiodiglycolic acid irradiated at 4.2 K has four sets of two equivalent hyperfine couplings. In retaining the simple cation interpretation one is obliged to assign the extra four proton couplings observed experimentally to hyperfine interactions involving protons of neighbouring molecules. Even the lesser two couplings in Table 2 seem large to be attributed to neighbouring molecules; however this phenomenon is not peculiar to thiodiglycolic acid alone. The oxidation product absorption in irradiated α-aminoisobutyric acid also exhibits unexpectedly large proton couplings arising from neighbouring molecules.[5]

It should be noted that at least two other radicals are reported in the literature as having the structure R^1–S–R^{2+} with the unpaired electron localized on sulphur.[6,7] These radicals and the cation observed in irradiated thiodiglycolic acid all have remarkably similar *g* tensors as shown in Table 1.

TABLE 3

Principal values of *g* tensors reported for $R\dot{S}$ and $R\dot{O}$ radicals. Measurements on single crystals irradiated at 4.2 K except in refs. 8 and 11 where crystal, was maintained at 77 K

Crystal	Radical	Principal values			τ·τ′	Reference
Cysteine hydrochloride	ClNH$_3$–CH(CO$_2$H)–CH$_2\dot{S}$	2.29	1.99	1.99		8
		2.251	2.004	1.985	1.00	9
Penacillamine hydrochloride	ClNH$_3$–CH(CO$_2$H)–C(CH$_3$)$_2$–$\dot{S}$	2.297	2.037	1.921	1.00	10
Acetylcysteine	CH$_3$–CONH–CH(CO$_2$H)–CH$_2$–$\dot{S}$	2.216	2.006	1.990		11
Serine	NH$_2$–CH(CO$_2$$^-$)–CH$_2$–$\dot{O}$	2.079	2.005	1.998	0.918	12
Thymidine		2.0831	2.0052	1.9999	0.993	13
Bromodeoxyuridine		2.087	2.006	1.999	0.823	Unpublished results

Another purpose of this report is to point out similarities between $R\dot{S}$ radicals and $R\dot{O}$ radicals both of which have in fact [1] been observed experimentally. If the unpaired electron is assigned to a non-degenerate sulphur 3*p* orbital or to a non-degenerate oxygen 2*p* orbital in these radicals respectively, the maximum *g* value is predicted to occur when the magnetic field is parallel to the direction of the C–S or C–O bond. The minimum *g* value is expected to be approximately the free spin value (2.0023). The *g* tensors listed at the top of Table 3 are attributed to $R\dot{S}$ radicals which were generated in single crystals of sulphhydryls by irradiation at low temperature.[8-11] At low temperature one anticipates little reorientation of the C–S bond direction upon formation of the radical. The quantity τ·τ′ in Table 1 is the dot product of two unit vectors; one in the direction of maximum *g* value and the other in the direction of the C–S bond as calculated from crystal structure. The fact that these dot products are unity supports the interpretation that these absorptions arise from $R\dot{S}$ radicals.

Recently analogous $R\dot{O}$ radicals have been reported in single crystals of serine [12] and thymidine [13] *X*-irradiated at 4.2 K. More recently an analogous radical was discovered in bromodeoxyuridine irradiated at 4.2 K. Table 3 contains a description of the *g* tensors in these

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[5] A. Minegishi, Y. Shimozaki, and G. Meshitsuka, *J. Chem. Phys.*, 1972, **56**, 2481.

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

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

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

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

[11] G. Saxebøl and Ø. Herskedal, *Radiation Res.*, 1975, **62**, 395.

[12] J. Y. Lee and H. C. Box, *J. Chem. Phys.*, 1973, **59**, 2509.

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

radicals. Perhaps because of the lower mass of oxygen compared to sulphur the values of $\tau \cdot \tau'$ are found to be somewhat less than unity suggesting that a slight reorientation of the C–O bond occurs. The e.s.r. spectra associated with each of the radicals in Table 1 is lost at higher temperatures; the changes being variously attributed to conformational changes and/or secondary reactions. The $R\dot{O}$ radical produced in *X*-irradiated serine is transient even at 4.2 K.[12]

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