Electron Spin Resonance Studies of Radicals derived from Dithionate, Tetrathionate, and Thiosulphate Anions*

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Exposure of sodium dithionate to ^{60}Co γ-rays at 77 K gives a centre having hyperfine coupling to ^{33}S ($A_{\parallel}$ = 165 G, $A_{\perp}$ = 135 G) which is thought to be the primary electron-capture centre $[S_2O_6]^{3-}$ having the extra electron confined to the S–S σ^* orbital. This assignment is supported by the observation that ^{33}S features characteristic of $[^{33}SO_3]^-$ radicals grew in as those assigned to $[S_2O_6]^{3-}$ anions were lost on annealing. The major electron-loss centre is identified as the hydroxyl radical formed from hydrate water molecules. Sodium thiosulphate gives a radical having a large isotropic hyperfine coupling to ^{33}S. This centre, previously thought to be $[S_2O_3]^-$, is now identified as $[S_2O_3]^{3-}$. In anhydrous $Na_2[S_2O_3]$ this centre exhibits hyperfine coupling to ^{23}Na. This salt and $K_2[S_2O_3]{\cdot}5H_2O$ give a new species having one very high g value, identified as $[S_2O_3]^-$. Two sets of ^{33}S features are obtained from $[S_2O_6]^{3-}$ suggesting an asymmetric environment. In accord with this, two slightly different $[^{\bullet}SO_3]^-$ radicals are obtained on annealing. The anion $[O_3SS{-}SSO_3]^{3-}$ is a primary product in irradiated sodium tetrathionate, but is not detected in thiosulphate even after annealing. A second centre formed from tetrathionate exhibits a large g value variation and extra hyperfine coupling to ^{23}Na.

THE $[^{\bullet}SO_3]^-$ radical anion was characterised early in the history of e.s.r. studies of inorganic radicals.[1,2] It has been formed in a wide range of substrates,[3] and possible factors governing the effect of the environment on the ^{33}S hyperfine components have been discussed.[4] One possible source of $[^{\bullet}SO_3]^-$ radicals is the dithionate ion [equation (1)]. However, there are good reasons for

$$[S_2O_6]^{2-} + e^- \longrightarrow [^{\bullet}SO_3]^- + [SO_3]^{2-} \qquad (1)$$

supposing that the reverse of reaction (1) might be favourable at low temperatures,[5,6] and, indeed, that initial electron addition would not break the S–S σ bond, but give, instead, the σ^* radical $[O_3S\dot{-}SO_3]^{3-}$.[7,8] A major aim of the present study was to check on this possibility.

Another aspect of the radiation chemistry of oxo-anions of sulphur relates to the thiosulphate anion. This has already been extensively studied, especially in single crystals of $Na_2[S_2O_3]{\cdot}5H_2O$.[9-11] After room-temperature irradiation, a radical thought to be $[^{\bullet}S(S)O_2]^-$ has been characterised by e.s.r. spectroscopy, and evidence for $[O\dot{S}S]^-$ radicals has also been adduced. However, after exposure at 77 K only one species was detected, which has been assumed to be the electron-loss centre, $[S_2O_3]^-$.[9-11] I think that this centre is more likely to be $[S_2O_3]^{3-}$, and another aim was to verify and justify this postulate.

It seemed possible that if $[S_2O_3]^-$ radicals are formed, they would tend to react to give S–S σ^* radicals [equation (2)]. This radical should be formed by electron addition

$$[\dot{S}{-}SO_3]^- + [S_2O_3]^{2-} \longrightarrow [O_3S{-}S\dot{-}S{-}SO_3]^{3-} \qquad (2)$$

to tetrathionate ions, $[O_3S{-}S{-}S{-}SO_3]^{2-}$, so I have exposed sodium tetrathionate to γ-rays in the hope of obtaining e.s.r. parameters for the electron adduct.

Organosulphur radicals have recently been widely studied by e.s.r.[7,12,13] and optical [6,14,15] techniques. In reactions with $^{\bullet}$OH and RO$^{\bullet}$ radicals, certain oxysulphur radicals have been obtained,[16,17] and the present work serves, in part, as a link between the organic and earlier inorganic e.s.r. studies.

EXPERIMENTAL

Materials were of the highest available grades and were used directly after being received. Samples recrystallised from purified water gave identical results. Largely per-deuteriated hydrates were obtained by recrystallisation from 98% D_2O.

Samples were irradiated as fine powders or as glassy beads (in $CD_3OD + D_2O$) at 77 K in a Vickrad ^{60}Co γ-ray source for up to 1 h at a dose rate of *ca.* 1 Mrad h^{-1}.†

E.s.r. spectra were recorded at 77 K on a Varian E-109 spectrometer, calibrated with a Hewlett–Packard 5246L frequency counter and a Brüker B-H12E field probe. Samples were annealed at >77 K in the insert Dewar flask, and recooled to 77 K whenever significant spectral changes were observed.

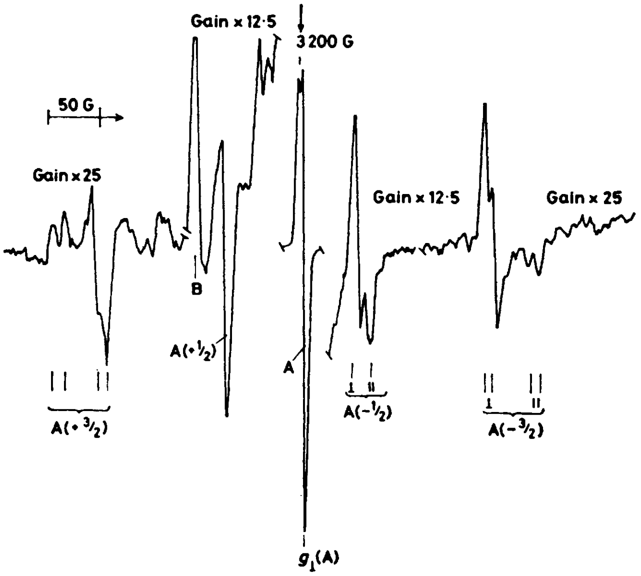

FIGURE 1 First-derivative X-band e.s.r. spectrum for $Na_2[S_2O_6]{\cdot}2H_2O$ after exposure to ^{60}Co γ-rays at 77 K, showing features for radical A, thought to be $[S_2O_6]^{3-}$

RESULTS AND DISCUSSION

Dithionate Ions.—After exposure at 77 K the spectrum shown in Figure 1 was obtained. E.s.r. parameters derived therefrom are given in Table 1. Radical A has ^{33}S hyperfine features quite similar to those expected for

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* Taken as Unstable Intermediates, Part 185.

† Throughout this paper: 1 rad = 10^{-2} J kg^{-1}; 1 G = 10^{-4} T.

TABLE 1

E.s.r. parameters for radicals derived from dithionate, tetrathionate, and thiosulphate anions, and related species

Host	Radical		^{33}S Hyperfine coupling/G			*g* Values		
$Na_2[S_2O_6]$	$[S_2O_6]^{3-}$ A		165,	135,	135	2.0025		
			158,	130,	130			
	$^{\bullet}OH$ B		*ca.* 0,	34,	34 (^{1}H)	2.074	2.007	2.007
	$[SO_3]^-$ C_1		155.7,	112,	112	2.003		
	$[SO_3]^-$ C_2		[a]	105,	105	2.003		
$Na_2[S_2O_3]$	$[S_2O_3]^{3-}$ D	S_1	144.5,	122,	122	2.024	2.024	2.002
		S_2	66,					
	(or $[S_2O_3]^-$) [b]	(*b*) S_1	143.5,	122.4,	121.9 (*b*)	2.0239	2.0228	2.0021
		(*b*) S_2	65.5,	21.4,	16.0			
	$[S_2O_2]^-$ [b] (or $[S_2O_3]^{3-}$)		183,	146.4,	144.1	2.0093	2.0051	2.0026
$Na_2[S_4O_6]$	$[S_4O_6]^{3-}$ E		70,	[c]	[c]	2.002	2.0115	2.0160
	F		[d]			2.054	2.026	*ca.* 2.002
$H_3\overset{+}{N}CH_2CH_2SO_3^-$ [e]	$[^{\bullet}SO_3]^-$		135,	99,	99	2.003		

[a] Not clearly resolved. [b] Ref. 12. [c] $\leqslant 20$ G. [d] No ^{33}S features detected. [e] Ref. 3.

$[^{33}\dot{S}O_3]^-$, and this would be a natural assignment. However, as discussed below, I suggest that this species is really the electron adduct, $[O_3S\dot{-}SO_3]^{3-}$. The parallel and perpendicular $M_I = \pm\frac{3}{2}$ features for radical A appear as doublets, but this splitting is not apparent on the $\pm\frac{1}{2}$ features. This means either that there are two subtly different radicals (A_1 and A_2) formed with almost equal probability, or, more probably, that $[O_3{}^{33}S\dot{-}SO_3]^{3-}$ differs slightly from $[O_3S\dot{-}{}^{33}SO_3]^{3-}$.

TABLE 2

Orbital populations derived from the ^{33}S hyperfine data in Table 1

Radical		a_{3s}^2	a_{3p}^2	$a_{3s}^2 + a_{3p}^2$	a_{3p}^2/a_{3s}^2
$[S_2O_6]^{3-}$	A 1	0.15	0.353	0.503	2.35
	A 2	0.144	0.33	0.474	2.29
$[\cdot SO_3]^-$	C_1	0.13	0.514	0.644	3.95
	a	0.114	0.425	0.539	3.73
$[S_2O_3]^{3-}$	D	0.132	0.265	0.397	2.01
(or $[S_2O_3]^-$)	*b*				

[a] Ref. 3. [b] Ref. 12.

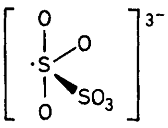
A second radical, B, was also formed at 77 K. This has a parallel feature at $g_{\parallel} = 2.074$ and a perpendicular feature on the low-field edge of the central components. When $Na_2[S_2O_6]\cdot 2D_2O$ was used the parallel feature narrowed and the low-field perpendicular feature was lost. This must mean that this feature is a component of a ^{1}H hyperfine multiplet, and hence $^{\bullet}OH$ radicals are strongly implicated. In fact, two of the expected perpendicular triplet features for $^{\bullet}OD$ were seen in the deuteriated sample, giving $A_{\perp}(^2H) = 6.7$ G and $g_{\perp} = 2.007\,0$, in good agreement with expectation.[18] Thus the major electron-loss centre seems to be $^{\bullet}OH$ (from $[H_2O]^{+\cdot}$) rather than $[S_2O_6]^-$.

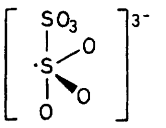
On annealing, the A features were lost, and appeared to be replaced by other features C_1 and C_2. The C_1 features were relatively broad. Those for C_2 were narrow, but only the perpendicular features were clearly defined. The parameters, for both, given in Table 1, are typical of $[^{\bullet}SO_3]^-$ as can be seen by comparison with other results quoted in Table 1. Clearly the two radicals are in different environments, with C_1 probably close to one or more Na^+ ions. I suggest that these species are the two alternative $[^{33}\dot{S}O_3]^-$ radicals formed from the parent anion.

Identity of Radical A.—I think that the σ* formulation, $[O_3S\dot{-}SO_3]^{3-}$, for this species is the most probable for the following reasons.

(*i*) Radical A is lost when radicals C_1 and C_2 appear: since the data for C_1 are very close to previous results for $[^{\bullet}SO_3]^-$ it seems most reasonable that electron capture gives $[O_3S\dot{-}SO_3]^{3-}$ and that this subsequently dissociates, as in equation (1).

(*ii*) The e.s.r. parameters for A can be analysed in the usual way[1] to give approximate orbital populations. These are given in Table 2. These results show that the *p* : *s* ratio is less for radical A than for normal $[^{\bullet}SO_3]^-$ radicals, and the total spin density on sulphur ($3s + 3p$) is also less. These trends are as expected if A is $[O_3S\dot{-}SO_3]^{3-}$. The reduced *p* : *s* ratio means, on the usual argument that bond angle and hybridisation are closely linked,[19,20] that the co-ordination around sulphur is more pyramidal in A than in $[^{\bullet}SO_3]^-$. This is to be expected for both sulphur atoms in $[O_3S\dot{-}SO_3]^{3-}$. The same result was obtained for $[R_3P\dot{-}PR_3]^+$ radicals relative to $[^{\bullet}PR_3]^+$ radicals.[5] Also, since the species concerned must be $[O_3{}^{33}S\dot{-}{}^{32}SO_3]^{3-}$ the sum of the two sets of spin densities should be close to unity. It is, in fact, *ca.* 0.98 (Table 2). This shows that the unpaired electron is much more strongly localised on sulphur in $[O_3S\dot{-}SO_3]^{3-}$ than in $[^{\bullet}SO_3]^-$. This important result supports the concept of localised σ bonds, and accords with our observations on other radicals.[5,21]


(I)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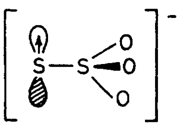
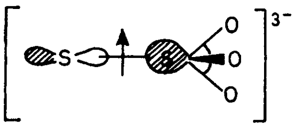

(III)

In this discussion, I have made the tacit assumption that the electron-excess radical will have a σ* structure. The alternative sulphuranyl structures (I) or (II) could not account for the two almost equivalent sets of ^{33}S coupling constants, and are therefore rejected.

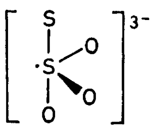
Thiosulphate Ions.—I have checked that e.s.r. powder spectroscopy for $Na_2[S_2O_3]\cdot 5H_2O$ gives the same results as those reported for single crystals.[9-11] The data are identical within experimental error (Table 1). I have also ascertained that on annealing the species identified as $[{}^{\bullet}S_2O_3]^-$ (D) decays, and that identified as $[{}^{\bullet}S_2O_2]^-$ grows in simultaneously. No other well defined features were detected. Results for $K_2[S_2O_3]{\cdot}5H_2O$ were similar for species D (Table 1 and Figure 2). However, for anhydrous $Na_2[S_2O_3]$ features clearly belonging to D were all split into quartets. These must stem from coupling to ^{23}Na nuclei which have $I = \frac{3}{2}$. The coupling of *ca.* 10 G is unusually large for an ' ion pair ',[22] and must mean that orbital overlap is large, and that there is an unusually large degree of electron transfer (*ca.* 3%).

The spectra for both the potassium and anhydrous sodium salts show an extra, narrow, low-field feature marked α in Figure 2. This feature, which was not obtained from the hydrated sodium salt, was lost during annealing prior to the loss of the D features.

Identity of D.—All previous workers concluded that D was $[S_2O_2]^-$, and a theoretical calculation in support of this has appeared.[23] However, I favour the electron-capture centre $[S_2O_3]^{3-}$ for D. First-order structures for these species are: (IV), $[S_2O_3]^{3-}$ having a σ* structure; (V) and (VI), $[S_2O_3]^{3-}$ with trigonal-bipyramidal structures; and (III), $[S_2O_3]^-$. (The hole may be delocalised slightly onto the oxygen atoms.) I favour $[S_2O_3]^{3-}$ with structure (IV) for the following reasons.



(IV)



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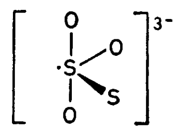


(VI)

(*i*) The single-crystal results show that $A_{max.}$ for both ^{33}S tensors and $g_{min.}$ lie close to the S–S bond direction of the parent ion. This is only expected for (IV). In particular, for (III) $[S_2O_3]^-$ I expect $g_{max.}$ and $A_{min.}$ to lie along this direction.

(*ii*) In the anhydrous salt there is a large hyperfine coupling to ^{23}Na. Since this is one of the largest coupling constants recorded for ion pairs, I conclude that the anion must donate an electron readily. This strongly favours $[S_2O_3]^{3-}$ over $[S_2O_3]^-$.

(*iii*) For (IV), the central sulphur atom should contribute an sp^3-hybridised orbital and the ligand atom should contribute primarily a $3p$ orbital to the wavefunction of the unpaired electron. Since this is an antibonding orbital, the electron density should be greater on the less electronegative component, namely the ligand sulphur atom. This is exactly what is found (Table 2). For structures (V) and (VI) delocalisation onto the ligand sulphur is again *via* the $3p_z$ (σ) orbital, but the directions of the two $A_{max.}$ values should

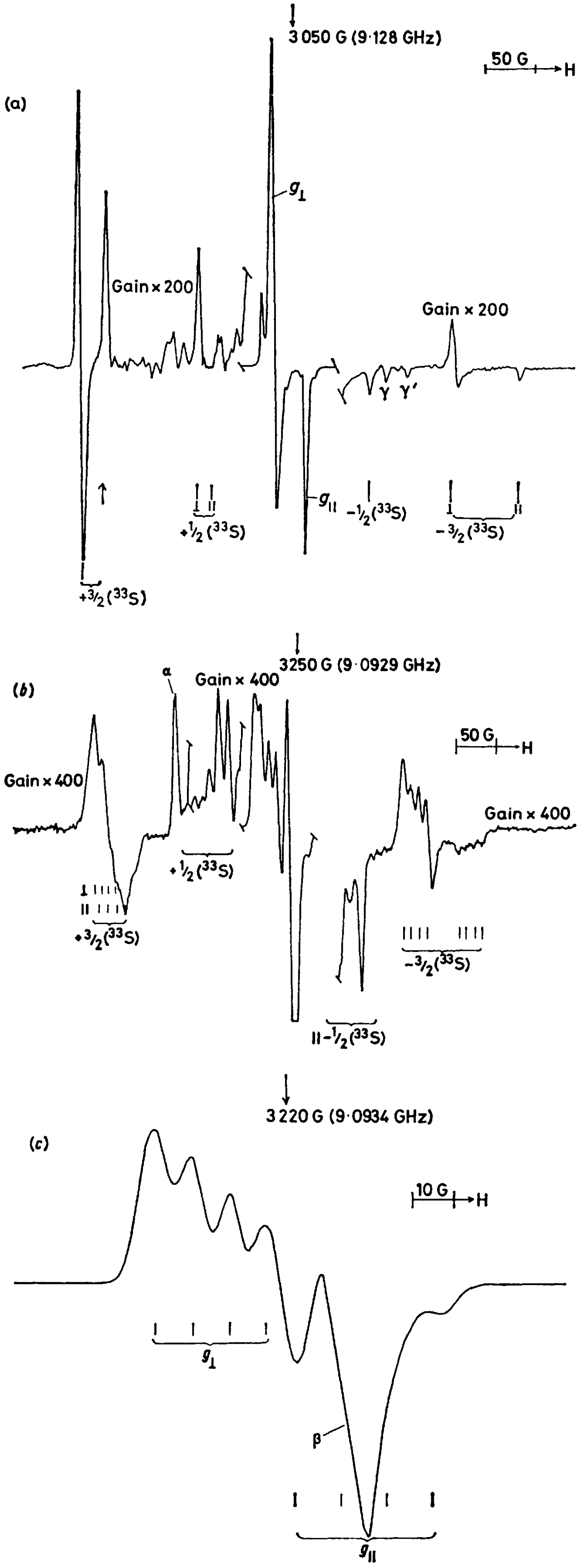


FIGURE 2 First-derivative *X*-band e.s.r. spectra for (*a*) $K_2[S_2O_3]{\cdot}5H_2O$ and (*b*), (*c*) $Na_2[S_2O_3]$ (anhydrous) after exposure to ^{60}Co γ-rays at 77 K. For spectrum (*c*) the sample was annealed to *ca.* 120 K to reduce the intensity of the central line (β). One of the parallel features marked γ is from a second type of ^{33}S nucleus (the ligand sulphur in $[{}^{\bullet}S_2O_3]^{3-}$): the other feature is not identified

not be the same. Also, the major spin density should now reside on the central atom. For (III) $[S_2O_3]^-$ virtually all the spin density is expected on the ligand atom, the central atom acquiring (negative) spin density only *via* spin polarisation of the σ-bonding electrons.[24]

(*iv*) Species D was formed in relatively good yield from dilute solutions in CD_3OD-D_2O solvents at 77 K. It is common experience that electron-excess centres are more readily formed than electron-loss centres in such media. I conclude firmly that D is $[S_2O_3]^{3-}$, and that the σ^* structure (IV) is most probable.

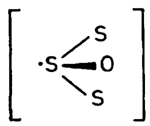
In that case, I would expect that, on annealing, the usually more favoured trigonal-bipyramidal structures (V) or (VI) would be formed. In fact, this may well be so, since the data assigned to $[S_2O_2]^-$ [structure (VII)] (Table 1) could equally well be for (V) or (VI). The principle directions for the g and $A(^{33}S)$ tensors are also correct for (V) or (VI) if the two large sulphur atoms do not move, but only one or more oxide ligands move during the pseudo-rotation of (IV) ⟶ (V) or (VI). The magnitudes of the ^{33}S coupling constants are reasonable for all three structures. I therefore do not think that a distinction can be made on physical grounds.

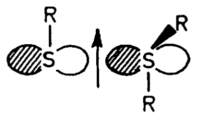
On chemical grounds, formation of (V) or (VI) is to be expected. However, formation of $[S_2O_2]^-$ requires loss of O if it is formed from $[S_2O_3]^-$, or loss of O^{2-} if it is formed from $[S_2O_3]^{3-}$. Since there are no good oxygen-atom acceptors, the former reaction is highly improbable at low temperatures. The latter, requiring protonation of $[S_2O_3]^{3-}$ and loss of $[OH]^-$, is certainly possible, but I would have expected that loss of sulphur would be more likely than loss of oxygen. I therefore suggest that the annealed species is more likely to be $[S_2O_3]^{3-}$ with structures (V) or (VI).

Identification of Species α.—Radical (III) $[S_2O_3]^-$ is expected to have its unpaired electron largely confined to the ligand sulphur atom. In that case it can be classed with the sulphanyl radicals, $RS^{\cdot}$. A characteristic feature of these radicals is a very large g_z value (z is along the R–S bond).[12] The magnitude of g_z is variable, being dependent on the extent to which the local fields lift the degeneracy of the $3p_\pi$ orbitals on the ligand sulphur. We found, in particular, that the value of g_z was always 2.158 for $RS^{\cdot}$ radicals in glassy methanol.[12]

The g value for feature α is indeed a variable (Table 1), and is 2.154 for concentrated solutions in aqueous methanol. The species responsible for α seems to be only a minor component from the intensity of this feature, but I stress that the signal, if this identification is correct, spreads from α to the centre of the spectrum, and hence α is by no means a minor component. I therefore suggest that α is due to $[S_2O_3]^-$ radicals. It is not clear why this species was not formed in $Na_2[S_2O_3]\cdot 5H_2O$.

On annealing, feature α was lost, and new features in the region of 2.065 and 2.026 grew in. By comparison with similar sulphur radicals,[12] I presume that the third g value is close to 2.002. This change is often observed when $RS^{\cdot}$ radicals are lost, and there are two quite distinct theories for the structure of the new species (X in ref. 12). My own postulated structure [12] is the σ^* species $RS-SR_2$ (VIII), and that of Hadley and Gordy [13] is $RSS^{\cdot}$ (IX). It is becoming increasingly probable that both types of radical have g values in the 2.05—2.06, 2.025, and 2.002 regions. In the present case, species (VIII) could be formed from $[\dot{S}-SO_3]$ [equations (3) and (4)]. Alternatively, species (IX) could be formed as in (5). The dimer anion $[O_3S-S\dot{-}S-S-SO_3]^{3-}$ was not detected. However, it has been detected in irradiated tetrathionate systems and found to be thermally unstable (see below).


(VII)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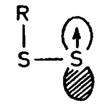
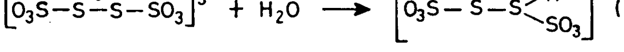

(IX)

$$[\cdot S-SO_3]^- + [S_2O_3]^{2-} \longrightarrow [O_3S-S\dot{-}S-SO_3]^{3-} \quad (3)$$


$$[O_3S-S\dot{-}S-SO_3]^{3-} + H_2O \longrightarrow \left[O_3S-S\dot{-}S\begin{smallmatrix}H\\SO_3\end{smallmatrix}\right]^{2-} \quad (4)$$

Tetrathionate Anions.—A typical spectrum obtained after exposure at 77 K is shown in Figure 3. One major species, E, has three distinct g values, and well defined ^{33}S parallel features centred on the high-field g feature (2.002). No perpendicular ^{33}S features were detected.

$$[^{\cdot}S-SO_3]^- + [S_2O_3]^{2-} \longrightarrow [O_3S-S-\dot{S}]^- + [SO_3]^{2-} \quad (5)$$

These results accord well with expectation for the σ^* anion $[O_3S-S\dot{-}S-SO_3]^{3-}$, which is expected to have its extra electron in an orbital which is primarily composed of sulphur $3p_z$ orbitals (X). The g values and ^{33}S parameters are close to those reported for the isostructural alkyl disulphide anions.[13]

Another radical detected at 77 K (F) has a low-field feature at $g_x = 2.051$, and a cross-over feature at $g_y = 2.024$. Almost certainly this centre has a g_z feature in the free-spin region, obscured by the more intense E features. The intensity of the F features were enhanced on slight annealing, but were too low for the detection of ^{33}S satellites. [Yet another centre (G) had features at $g = 2.028\,8$ and $g = 2.021\,2$, which were rapidly lost on annealing. These are probably due to $^{\cdot}OH$ radicals and are not further discussed.]

Centre F has g values similar to the radical obtained from the thiosulphate ion, discussed above. These are again reminiscent of the centre obtained in irradiated organic sulphides and known as species X.[12] The g_x values (2.065 and 2.051) for these two centres are sufficiently different that we cannot be sure that the identification should be the same in both cases. Possibly one is the protonated electron adduct (VIII) and the other the

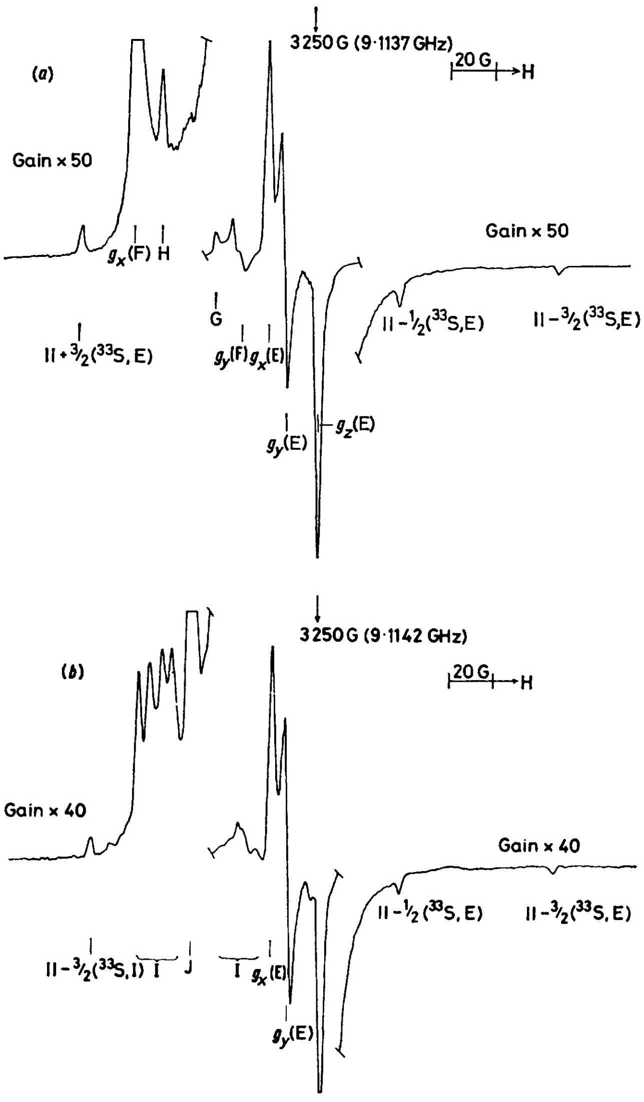
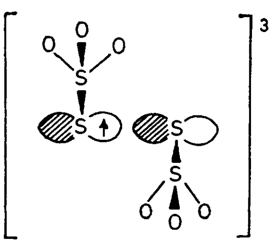


FIGURE 3 First-derivative X-band e.s.r. spectrum for $Na_2[S_4O_6]$ after exposure to ^{60}Co γ-rays at 77 K, showing (*a*) features for radical E and F and (*b*), after momentary annealing, features for radical I discussed in the text

RSS' radical (IX). I am unable to make a clear assignment in either case.

The feature marked H in Figure 3(*a*) was absent when the tetrathionate was recrystallised from D_2O. It was replaced by two features just on the low-field side of the low-field g feature. If this is treated as a triplet from hyperfine coupling to ^{2}H, then the resulting ^{1}H and ^{2}H coupling constants (36 and 5.5 G respectively) agree well and hence feature H is the $(+\frac{1}{2})$ component of a hyperfine doublet centred on $g_{\parallel} = 2.031\,2$. No other features could be assigned definitively to this species. The coupling of 36 G is large for a sulphur radical, and I am unable at present to suggest a reasonable structure for this centre.



(X)

On annealing, the features marked F in Figure 3(*a*) appeared to change into quartet features with about the same g values [I in Figure 3(*b*)]. After recrystallisation from D_2O these same features grew in on annealing, and I therefore assign the splitting to ^{23}Na ($A \approx 5.1$ G). Probably the same radical is involved, and some irreversible movement has brought a sodium ion into a region of good overlap. Yet another feature (J) grew in during the annealing process at $g = 2.037\,5$. This also remains unidentified.

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