Electron-gain and -loss Centres in Oxyanions containing S–S Bonds: An Electron Spin Resonance Study†

Shuddhodan P. Mishra[a] **and Martyn C. R. Symons***[,b]
[a] *Nuclear and Radiation Chemistry Laboratory, Department of Chemistry, Baneras Hindu University, Varanasi – 221005, India*
[b] *Department of Chemistry and Biological Chemistry, University of Essex, Wivenhoe Park, Colchester CO4 3SQ, UK*

The oxyions $S_2O_4{}^{2-}$, $S_2O_5{}^{2-}$ and $S_2O_6{}^{2-}$ have been exposed to ionizing radiation at 77 K in the hope of trapping the primary electron-gain and -loss centres for study by ESR spectroscopy. In order to distinguish features for the electron-capture centres uniquely, dilute glasses containing these anions were also irradiated at 77 K and their spectra studied. In all cases, in addition to central features for the normal ^{32}S centres, various species containing one ^{33}S have been detected. Possible structures for these species are proposed. Changes that occurred on warming to room temperature are discussed in the light of these identifications.

In our early studies of the action of ionizing radiation on inorganic salts, using ESR spectroscopy in attempts to identify and study 'primary' radiolysis products, the pure compounds were generally used.[1,2] A wide range of radicals were detected, and in many cases identified, but there were often ambiguities because of the dual nature of radiation damage. Thus electron-loss and -gain centres are expected to be the primary products, but one or both of these often break down unimolecularly to give other products, or they may react with neighbouring ions. Another complication is that electron return may result either in very low yields or in bond homolysis, to give pairs of radicals trapped in close proximity. Even more confusing is the fact that, during the process of ionization and electron trapping, both the loss centres (holes) and the gain centres may migrate by electron transfer, and if there are suitable impurities present in trace amounts these may act as hole or electron traps, giving radicals from unknown precursors.

We therefore tried to make use of this migration propensity by deliberate doping. These studies showed that doping with anions having one less charge than the host usually resulted in specific electron capture at the dopant, electron loss being confined to the host. The opposite occurred if the dopant had one extra charge. For example, $PO_4{}^{3-}$ in a $SiO_4{}^{4-}$ lattice gave $PO_4{}^{\bullet 4-}$ anions[3] whilst $BO_3{}^{3-}$ ions gave $BO_3{}^{\bullet 2-}$ radical anions when doped into calcium carbonate,[4] and $ClO_3{}^-$ gave $ClO_3{}^{\bullet 2-}$ in this host.[5] These results usually gave reliable values for the specific gain or loss centres, enabling us to return to the pure irradiated compounds and identify both centres.[4,5]

A further development was the use of ionizing solvents such as methanol, which can be frozen to give glassy solids. Since such glasses are well depicted as being infinitely viscous liquids the solute remains dilutely dispersed, and on exposure to ionizing radiation many solutes capture electrons exclusively.[6]

We have recently helped to develop a technique used originally by Hamill,[7] and by Shida and Takemura,[8] forming exclusively electron-loss centres from solutes. The most widely used solvent is $CFCl_3$. In these solvents, solvent molecules rapidly scavenge ejected electrons, but the hole centres are mobile *via* electron transfer and hence can reach dilute solute molecules which will transfer an electron to the solvent reactions, if their ionization potentials are less than that of the solvent.[9] Unfortunately, this system is only suitable for neutral solutes.

One of the most important results of these studies has been the discovery that electron addition into σ bonds, giving σ* radicals often occurs.[10] Although the bonding is weak, such radicals are now being recognized as important intermediates in many reactions.[11,12] σ* Radicals can be formed either by electron capture, equation (1), or by electron loss followed by bond formation [equations (2) and (3)]. The most stable species

$$A{-}B + e^- \longrightarrow A\dot{-}B^- \qquad (1)$$

$$A^- \longrightarrow A^\bullet + e^- \qquad (2)$$

$$A^\bullet + B^- \longrightarrow A\dot{-}B^- \qquad (3)$$

seen to be those in which A = B (*i.e.* $A\dot{-}A^-$, say), and when the σ bonding is between atoms of the second or higher rows in the Periodic Table.

Our aim herein was to probe the three sulfur–sulfur bonded ions $S_2O_4{}^{2-}$, $S_2O_5{}^{2-}$ and $S_2O_6{}^{2-}$, the main interest being in the mixed species, $S_2O_5{}^{2-}$, because few mixed σ and σ* radicals are known. Here, if bond breaking occurs after electron gain or loss, we would expect to detect $SO_2{}^{\bullet -}$ or $SO_3{}^{\bullet -}$ from these dimer anions. We have studied the pure compounds in the hope of detecting primary electron-gain and -loss centres and, on annealing, the expected breakdown products, $SO_2{}^{\bullet -}$ and $SO_3{}^{\bullet -}$. As a check on identification, we have used dilute solutions in CD_3OD to induce electron capture selectively.

Experimental

Sodium dithionate (BDH), dithionite (Lancaster) and μ-oxo-tetraoxodisulfate (Fisons) were the highest grades available and were used as received. Salt solutions in CD_3OD and $CD_3OD + D_2O$ were *ca.* 0.1–1.0 mol dm^{-3}. The pure salts were cooled, as very fine powders, to 77 K, and irradiated with ^{60}Co γ-rays or with 150 MeV (2.4 × 10^{-16} J) X-rays at this temperature, to doses of up to 10 kGy. The solutions were deuteriated and frozen as very small glassy beads. The salts were also irradiated at room temperature at higher doses in order to study low yields of secondary products. Since the natural abundance of ^{33}S is only 0.74%, and since it has $I = \frac{3}{2}$, the major central features are

---

† *Non-SI unit employed:* G = 10^{-4} T.

due to ^{32}S radicals and it is necessary to study the other regions at high gain in order to detect centres containing one ^{33}S. Those containing two ^{33}S are too dilute to detect.

Results and Discussion

Pertinent results are summarized in the Tables and compared with data from other sources therein. Some typical spectra are shown in the Figures. The room-temperature samples gave well defined spectra of $SO_3{}^{\cdot -}$, or parallel ^{33}S features for $SO_2{}^{\cdot -}$, or both (Fig. 1). These results give us bench-mark parameters for the present matrixes. (One of us has previously shown that ESR data for $SO_3{}^{\cdot -}$ and related species vary slightly from one matrix environment to another.[13])

The $SO_2{}^{\cdot -}$ radical anion, which is isoelectronic with the remarkably stable radical, $ClO_2{}^{\cdot}$, is itself quite stable, and is formed reversibly when $S_2O_4{}^{2-}$ ions are dissolved in protic solvents such as water.[14] It is a π radical, the ^{33}S hyperfine coupling showing large $A_{\parallel}$ values and small $A_{\perp}$ values (Table 1).[15]

The $SO_3{}^{\cdot -}$ radical has a pyramidal structure, the singly occupied molecular orbital (SOMO) on sulfur being hybridized, with considerable 3s character.[16,17] It is far more reactive than $SO_2{}^{\cdot -}$, and there is no tendency for its dimer, $S_2O_6{}^{2-}$, to dissociate at ambient temperatures.

Sulfur-centred σ^* radicals have been studied extensively, and the electron adducts of organic disulfides, $RS\overset{\cdot}{-}SR^-$, are thought to be important intermediates in the interconversion of sulfhydryl compounds into disulfides.[18] Also, the corresponding σ^*-radical cations, $R_2S\overset{\cdot}{-}SR_2{}^+$, are well characterised by ESR and optical spectroscopy and are remarkably stable.[18a,19,20] The mixed disulfide, $R_2S\overset{\cdot}{-}SR$ is also thought to be important,[21] but there is some controversy regarding its identification.[22] This species is of interest in relation to our present study of $O_3S–SO_2{}^{3-}$ centres.

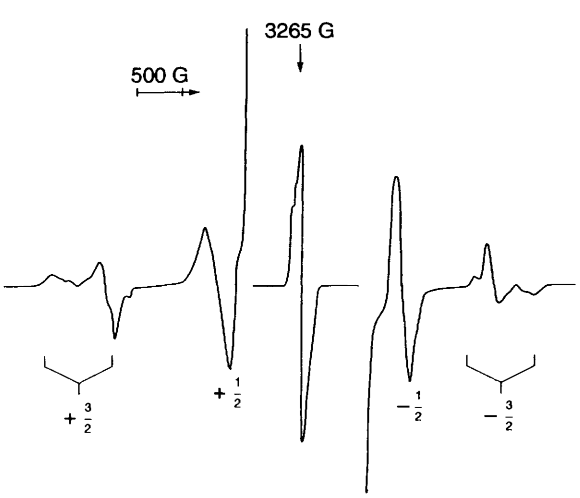

Fig. 1 First-derivative ESR spectrum for $Na_2S_2O_5$ after exposure to ionizing radiation at 77 K and warming to room temperature, showing features assigned to radicals containing ^{33}S, identified as $^{33}SO_3{}^{\cdot -}$ radicals

Table 1 The ESR parameters for $^{33}SO_2{}^{\cdot -}$ and $^{33}SO_3{}^{\cdot -}$ in various matrices

		^{33}S hyperfine coupling/G				
Radical	Ref.	$A_{\parallel}$	$A_{\perp}$	A_{iso}	$g_{\parallel}$	$g_{\perp}$
$^{33}SO_2{}^{\cdot -}$	*a*	58	(−)7	15	2.011	2.003
	b	59	(−)8	14	2.009	2.002
	c	—	—	15	—	—
$^{33}SO_3{}^{\cdot -}$	*d*	153	115.5	128	2.0035	2.0035
	e	150	120	130	2.0034	2.0034
	a	155	117	130	2.0034	2.0034

[a] This work. [b] Ref. 15. [c] Ref. 14. [d] Ref. 16. [e] Ref. 17.

Table 2 The ESR parameters for various σ^1 and σ^* radicals formed from irradiated $S_2O_6{}^{2-}$, $S_2O_5{}^{2-}$ and $S_2O_4{}^{2-}$ ions.

		^{33}S hyperfine coupling/G			
Radical	Matrix	$A_{\parallel}$	$A_{\perp}$	A_{iso}	$g_{\parallel}, g_{\perp}$
$O_2{}^{33}S\overset{\cdot}{-}SO_3{}^{3-}$	$Na_2S_2O_5$	122	90	101	2.002, 2.004
$O_2{}^{33}S\overset{\cdot}{-}SO_3{}^{3-}$	$Na_2S_2O_4$	121	89	100	2.002, 2.004
$O_3{}^{33}S\overset{\cdot}{-}SO_3{}^{3-}$	$Na_2S_2O_6$	158	135	143	2.0025, 2.0025
$O_3{}^{33}S{\cdot}SO_3{}^-$	$Na_2S_2O_6$	165	130	142	2.0025, 2.0025

Table 3 Approximate orbital populations for the 3s and 3p sulfur orbitals deduced from the isotropic and anisotropic ^{33}S data given in Tables 1 and 2

Radical	p:s ratio	(p + s) (%)
$^{33}SO_2{}^{\cdot -}$	32	70
$^{33}SO_3{}^{\cdot -}$	4.2	54.5
$O_3{}^{33}S\overset{\cdot}{-}SO_3{}^{3-}$	2.3	37.6 (75.2[a])
$O_3{}^{33}S{\cdot}SO_3{}^-$	3.7	51 (102[a])
$O_2{}^{33}S\overset{\cdot}{-}SO_3{}^{3-}(\alpha)$	4.6	45[b]

[a] Total spin density on the two sulfur atoms. [b] The alternative, $O_2S–{}^{33}SO_3{}^{3-}$, was not clearly defined.

Sodium Dithionate.—At 77 K there are two well defined sets of ^{33}S features, as previously observed.[23] We originally identified both these centres as the σ^* adduct, $[O_3S\overset{\cdot}{-}SO_3]^{3-}$, which was thought to be asymmetrically located in the crystal such that the SOMO was unequally distributed, giving a ^{33}S coupling of $A_{\parallel} = 165$ G, $A_{\perp} = 135$ G for one and $A_{\parallel} = 158$ G, $A_{\perp} = 130$ G for the other. This seems to be quite reasonable, but it leaves the corresponding electron-loss centre unidentified. This could be a centre, similar to $SO_4{}^-$ ions,[1,2] having a SOMO confined to one or more of the oxygen ligands on one side of the anion, as in $^{\cdot}OSO_2–SO_3{}^-$. This would only give a small ^{33}S coupling, but large positive g shifts are expected. In fact, there is only one intense central feature for ^{32}S radicals, centred at $g = 2.0025$, showing little or no g anisotropy. Hence oxygen-centred species seem to be unlikely. The alternative, not previously considered, is electron loss from the S–S σ bond giving the one-electron radical, $[O_3S{\cdot}SO_3]^-$. Such one-electron-bonded centres are much less common than their three-electron analogues, but they should have comparable stability. Known σ^1 centres include $Ag{\cdot}Ag^+$, $Me_3C{\cdot}CMe_3{}^+$ and $H_3B{\cdot}BH_3{}^-$.[24–26] If only one of the centres is the σ^* species and the other is a σ^1 centre, then we propose that the data be reassigned such that the larger $A_{\parallel}$ is taken with the smaller $A_{\perp}$ and *vice versa*. This combination is given in Table 2. The reasoning behind this reassignment is that the σ^* anion should dissociate to give $SO_3{}^{\cdot -} + SO_3{}^{2-}$ whilst the σ^1 centre would give $SO_3{}^{\cdot -}$ and SO_3. In the former, the second product, $SO_3{}^{2-}$, is markedly pyramidal, whilst SO_3 is planar. Hence we infer that the SO_3 units in the σ^* centre should be more pyramidal than those in the σ^1 unit. This is the case using these alternative combinations of data. Also, the SOMO for the species assigned the σ^1 structure is strongly confined to the two sulfur atoms, whilst there is greater delocalization for the σ^* SOMO (Table 3). This contrast is again reasonable when comparing the lower and upper σ orbitals. The values for 3s and 3p character given in Table 3 were computed in the usual way,[27] using the $(3s)^0$ values of 1237 G given by Morton and Preston[28] but the $(3p)^0$ value of 57 G recommended in ref. 27. We have previously found that this choice gives the most reasonable results for a wide range of radicals.

We conclude that the two sulfur centres, detected in equal yields for irradiated $Na_2S_2O_6$, may well be the primary σ^1 and σ* centres. To check the σ* assignment, we studied $S_2O_6^{2-}$ ions as dilute solutions in a methanol glass. The features were poorly defined, but were in reasonable agreement with the results for the σ* species given (Table 2).

It is perhaps surprising that the data for $^{33}SO_3^{\bullet-}$ radicals (Table 1) are quite similar to those assigned to $S_2O_6^{\bullet 3-}$ and $S_2O_6^{\bullet-}$ since in the latter only 50% of the SOMO is associated with each $^{33}SO_3$ unit. However, the same behaviour is found for phosphorus centres, where the spectra are far better defined and hence more reliably interpreted. For example, the radical cation $P(OMe)_3^{\bullet+}$ has $A_{\parallel} \approx 900$ G and $A_{\perp} \approx 713$ G, whilst the σ* dimer $(MeO)_3P\text{–}P(OMe)_3^{+}$ has $A_{\parallel} \approx 727$ G and $A_{\perp} \approx 619$ G.[29] Again, the trends are the same: the $P(OR)_3$ units become more pyramidal in the dimer, the p:s ratio falling from 3.9 to 2.6:1, and the SOMO is far more confined to phosphorus in the dimer. No clear ^{33}S-containing species were obtained for frozen methanolic solutions.

Sodium μ-Oxo-tetraoxodisulfate.—The asymmetric anion $[O_2S\text{–}SO_3]^{2-}$ is considered before $[O_2S\text{–}SO_2]^{2-}$ because our interpretation of results for the latter hinge on those for the former. In this case, considering the σ^1 and σ* species as probable primary centres, there will be two distinct sets of ^{33}S satellite lines, one for $O_2{}^{33}S\text{–}SO_3$ species and one for $O_2S\text{–}{}^{33}SO_3$ species. If some dissociation also occurs, then both $SO_3^{\bullet-}$ and $SO_2^{\bullet-}$ are expected to form. Since the electron affinity of the SO_3 unit is greater than that for the SO_2 unit, we expect the SOMO for the σ^1 centre to be centred more on the SO_3 unit, whilst that for the σ* species will be centred more on the SO_2 half of the radical anion. Hence there should be four sets of features. One is identified as belonging to the σ* anion, and because of the form of the parameters is tentatively assigned to $[O_2{}^{33}S\dot{-}SO_3]^{3-}$. This is because the p:s ratio is relatively large (4.6:1) (Table 3), as expected for the SO_2 unit, since this gives $SO_2^{\bullet-}$ on dissociation. The spin density is *ca.* 45% on sulfur, which is relatively high, since $SO_2^{\bullet-}$ itself has a spin density of only *ca.* 65% on sulfur,[15] using the same atomic parameters.

This centre (α) is of importance, since it is also clearly formed in irradiated dithionite (Fig. 2). We suggest that $O^{\bullet-}$ radicals are formed in this system and that these add to one side of the $S_2O_4^{2-}$ units to give $[O_2S\dot{-}SO_3]^{3-}$. It seems that the species most readily detected is the $O_2{}^{33}S$ derivative. If this is correct, both sets of spectra must also contain features for $[O_2S\dot{-}{}^{33}SO_3]^{3-}$. There are indeed other common features, but these are poorly defined, and overlap with the $\pm\frac{1}{2}$ features of the other centres. Thus, we are satisfied that the required features are present, but hesitate to attempt to produce ^{33}S-hyperfine data therefrom.

It seems certain that the σ* species is formed, as expected, but the identities of the electron-loss centres are less sure. There is a weak feature in the g 2.01 region which is probably the g_{max} feature for $SO_2^{\bullet-}$ radicals formed in relatively low abundance. The expected 40 G doublet for $^{\bullet}OH$ radicals is definitely absent. We therefore suggest that, as with $S_2O_6^{2-}$, electron loss is from the S–S bond, giving an asymmetric σ^1 structure which contributes to the central broad line. This centre, for reasons given above, should have a SOMO biased towards the SO_3 unit and hence should show a large ^{33}S hyperfine splitting. Apart from the features already assigned, there are no resolved features of the type expected. The σ^1 centre would dissociate to give SO_2 and $SO_3^{\bullet-}$. Features for $^{33}SO_3^{\bullet-}$ clearly grow on annealing to room temperature, suggesting that the σ^1 radical is present, but are not evident at 77 K.

The results for methanolic glasses containing $S_2O_5^{2-}$ ions confirm the identification of α as the electron-capture centre.

Sodium Dithionite.—The ESR spectrum for this salt, irradiated at 77 K, shows a central asymmetric singlet, a g_{max} feature at 2.021, and several sets of ^{33}S components in the wings (Fig. 2). Prior to irradiation this salt gave a very weak signal from $SO_2^{\bullet-}$ radicals, but it was less than 1% of that given on irradiation. The structure of the $S_2O_4^{2-}$ ion is as shown in Fig. 3. The oxygen ligands eclipse, implying weak bonding *via* oxygen, whilst the S–S bond is unusually long. Hence we had expected primary electron loss and gain to occur at this weak bond giving $S_2O_4^{\bullet-} + S_2O_4^{\bullet 3-}$. However, the S–S bonds in these radicals will be even weaker, and we had therefore expected to observe dissociation to give $SO_2^{\bullet-} + SO_2$ and $SO_2^{\bullet-} + SO_2^{2-}$. Certainly $SO_2^{\bullet-}$ is a product. If the other ^{33}S features are due to the primary loss and gain (σ^1 and σ*) species, then there is a surprising degree of orbital hybridization in the SOMO of both. Addition of $O^{\bullet-}$ to $S_2O_4^{2-}$ would give the σ* radical anion $[O_2S\dot{-}SO_3]^{3-}$. This is the species, α, that is common to both $S_2O_4^{2-}$ and $S_2O_5^{2-}$ systems, and we consider the identification to be firm. After allowing for the two sets of quartets that this σ* radical anion generates, there are no other well defined ^{33}S features remaining. Hence we suggest that α is, effectively, the electron-loss centre. The electron-gain centre is then presumed to be $SO_2^{\bullet-}$ formed together with SO_2^{2-} by dissociative electron capture. Studies using methanol were conducted by cooling to just above the glass temperature to remove $SO_2^{\bullet-}$, followed by cooling to 77 K and irradiating. Only features for $SO_2^{\bullet-}$ were detected. Thus, our search for the σ^1 and σ* centres for this ion have failed.

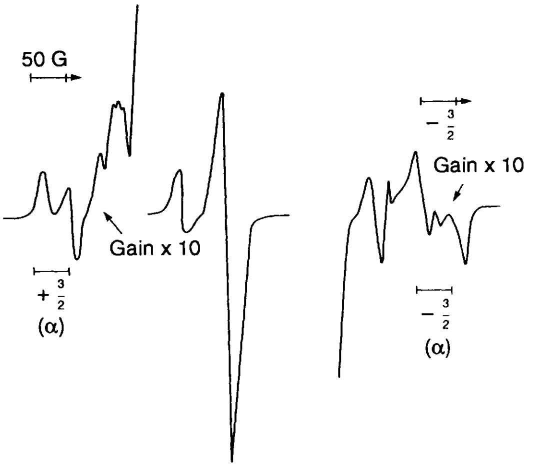

Fig. 2 First-derivative ESR spectrum for $Na_2S_2O_4$ after exposure to ionizing radiation at 77 K, showing ^{33}S features also assigned to $[O_2S\dot{-}SO_3]^{3-}$ radicals (α)

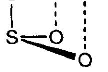

Fig. 3 Structure for the $S_2O_4^{2-}$ anion showing possible weak bonding between the oxygen ligands

We conclude that, for $S_2O_5^{2-}$ and $S_2O_6^{2-}$, both σ^1 and σ* species are formed on electron-loss and -gain, but that dissociation to give $SO_2^{\bullet-} + SO_2$ or SO_2^{2-} occurs even at 77 K for $S_2O_4^{2-}$ ions.

Acknowledgements

We thank the Commission for the European Communities for a contract with India supporting this study.

References

1 P. W. Atkins and M. C. R. Symons, *The Structure of Inorganic Radicals*, Elsevier, Amsterdam, 1967.
2 M. C. R. Symons, *Adv. Chem.*, 1968, **82**, 1.
3 M. C. R. Symons, *J. Chem. Phys.*, 1970, **53**, 857.
4 R. S. Eachus and M. C. R. Symons, *J. Chem. Soc. A*, 1968, 2438.

5 R. S. Eachus and M. C. R. Symons, *J. Chem. Soc. A*, 1968, 2433.

6 M. C. R. Symons, in *Radicaux Libres Organiques*, Centre National de la Recherche Scientifique, Paris, 1977, vol. 287, p. 105.

7 W. H. Hamill, in *Radical Ions*, eds. E. T. Kaiser and L. Kevan, Wiley, New York, 1968, p. 239.

8 T. Shida and Y. Takemura, *Radiat. Phys. Chem.*, 1983, **21**, 157.

9 M. C. R. Symons, *Chem. Soc. Rev.*, 1984, **13**, 393.

10 A. Abu-Raqabah and M. C. R. Symons, *J. Chem. Soc., Faraday Trans.*, 1990, 3293.

11 R. Breslow, M. Brandl and A. D. Adams, *J. Am. Chem. Soc.*, 1987, **109**, 3799.

12 A. Abu-Raqabah and M. C. R. Symons, *J. Am. Chem. Soc.*, 1990, **112**, 8614.

13 M. C. R. Symons, *J. Chem. Soc. A*, 1970, 1998.

14 P. W. Atkins, A. Horsfield and M. C. R. Symons, *J. Chem. Soc.*, 1964, 5220.

15 D. Schoemaker and C. T. Shirkey, *Phys. Rev.*, 1972, **136**, 1562.

16 G. Lind and R. Kewley, *Can. J. Chem.*, 1972, **50**, 43.

17 M. J. Lin and J. H. Lunsford, *J. Phys. Chem.*, 1975, **79**, 892.

18 D. J. Nelson, R. L. Petersen and M. C. R. Symons, *J. Chem. Soc., Perkin Trans. 2*, (*a*) 1977, 2005; (*b*) 1978, 1978.

19 B. C. Gilbert, D. K. C. Hodgemann and R. O. C. Norman, *J. Chem. Soc., Perkin Trans. 2*, 1973, 1748.

20 D. M. R. Rao, M. C. R. Symons and B. W. Wren, *J. Chem. Soc., Perkin Trans. 2*, 1982, 1681.

21 M. C. R. Symons, *J. Chem. Soc., Perkin Trans. 2*, 1976, 908.

22 J. H. Hadley and W. Gordy, *Proc. Natl. Acad. Sci. USA*, 1975, **72**, 3486.

23 M. C. R. Symons, *J. Chem. Soc., Dalton Trans.*, 1979, 1468.

24 I. G. Smith and M. C. R. Symons, *J. Chem. Res.*, 1979, (*S*) 382.

25 P. H. Kasai and D. McLeod, *J. Chem. Phys.*, 1969, **51**, 1250.

26 T. A. Claxton, R. E. Overill and M. C. R. Symons, *Mol. Phys.*, 1974, **27**, 701.

27 M. C. R. Symons, *Chemical and Biochemical Aspects of Electron Spin Resonance Spectroscopy*, Van Nostrand Reinhold, London, 1978.

28 J. R. Morton and K. F. Preston, *J. Magn. Reson.*, 1978, **50**, 577.

29 A. Hasegawa, G. D. G. McConnochie and M. C. R. Symons, *J. Chem. Soc., Faraday Trans. 1*, 1984, 1005.

Received 9th December 1993; *Paper* 3/07294K