Electron Spin Resonance Studies of a Range of Stannane Radical Cations †

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Exposure of dilute solutions of stannanes in freon ($CFCl_3$) at 77 K to ^{60}Co γ-rays gave the parent radical cations. SnH_4 gave two well defined centres, both exhibiting very large hyperfine coupling to ^{117}Sn and ^{119}Sn. One, with C_{3v} symmetry, showing strong coupling to a unique proton, is thought to have the unpaired electron confined to one σ Sn–H orbital with a large 5*s* contribution from tin. The other (C_{2v} symmetry), with strong coupling to two equivalent protons, and formed initially in almost equal yield, is slowly converted into the C_{3v} form. The main cations $SnMeH_3^+$, $SnMe_2H_2^+$, and $SnMe_3H^+$ have comparable C_{2v} structures with strongly *s–p* hybridised tin orbitals, but that for $SnMe_4$ has its major spin density on a single methyl group, with almost no 5*s*-orbital character on tin. In this case, the $SnMe_3$ unit appears to have become planar. Studies using $^{13}CH_3$ labelling confirm that this radical has extensive $Me_3Sn^+ \cdots \dot{C}H_3$ character. In accord with this, methyl radicals were detected on annealing above 77 K. This agrees with the well established tendency for such organometallic compounds to give alkyl radicals in the liquid phase on chemical or electrochemical reduction. When methyl groups were progressively replaced by chlorine, good yields of methyl radicals were obtained at 77 K. For $SnMe_3Cl^+$ the parent cation spectrum closely resembled that of $SnMe_4$, showing that electron loss from chlorine is disfavoured relative to loss from a tin–carbon σ bond. Other stannanes studied in this way include $SnMe_3Et$, which gave high yields of ethyl radicals at 77 K. The t-butyl derivative gave a stable cation at 77 K, having a nearly planar $SnMe_3$ unit but a pyramidal $-CMe_3$ unit. This signal was lost reversibly on annealing, in contrast with that for $SnMe_4^+$ cations, with the reversible growth of broad features assigned to $^{\cdot}CMe_3$ radicals.

Some years ago we studied the effect of ionizing radiation on a range of organotin compounds at low temperatures, using e.s.r. spectroscopy to detect the trapped radical species formed therein.[1] A range of radicals, including $SnR_3^{\cdot}$, $SnR_4^{\cdot -}$, $Me_2Sn^{\cdot -}SnMe_3$, and possibly $SnMe_5^{\cdot}$ were detected, but no clear evidence was obtained for the parent radical cations, SnR_4^+. One aim of the present study was to prepare these ions unambiguously, and to characterise them by e.s.r. spectroscopy.

These cations have been extensively studied by photoelectron spectroscopy (p.e.s.), the first ionisation being interpreted in terms of electron loss from the $3t_2$ set of orbitals, which can be viewed as localised Sn–C σ orbitals.[2,3] Unfortunately, these results are not really informative about the most stable distortion adopted by the resulting cations. Such information can, however, be gleaned from solid-state e.s.r. studies, provided there are no strong interactions with the matrix molecules.[4]

It now seems certain that, by suitable choice of solvent, neutral solute molecules (S) can often be selectively converted either into their radical anions ($S^{\cdot -}$) or cations ($S^{\cdot +}$) or into breakdown products thereof.[5] For the latter, solvents such as trichlorofluoromethane are used, the key reactions on irradiation being given by equations (1)—(4). The ejected electrons

$$CFCl_3 \xrightarrow{\gamma} CFCl_3^+ + e^- \qquad (1)$$

$$e^- + CFCl_3 \longrightarrow CFCl_3^- \longrightarrow Cl^- + \dot{C}FCl_2 \qquad (2)$$

$$CFCl_3^+ + CFCl_3 \longrightarrow CFCl_3 + CFCl_3^+ \qquad (3)$$

$$CFCl_3^+ + S \longrightarrow CFCl_3 + S^{\cdot +} \qquad (4)$$

are rapidly and irreversibly captured [equation (2)], but the ' holes ' can migrate [equation (3)] and react with solute molecules provided these have ionization potentials less than that for the solvent molecules. In some cases, weak σ bonding occurs, as in $S^{\cdot +}-ClCFCl_2$, so that the hole is shared between solute and solvent,[4] but this is relatively rare.

Various tin-centred cations have been studied by this technique, namely $SnMe_4^+$,[6] $Sn_2Me_6^+$,[7] SnH_4^+,[8] and some $SnMe_3R^+$ cations.[9] This paper brings together and extends our own studies.[6-8] The results are of particular interest from a mechanistic viewpoint since MR_4^+ cations of the Group 4B metals are known to act as good sources of alkyl radicals [equation (5)].[10]

$$SnR_4^{\cdot +} \longrightarrow R^{\cdot} + SnR_3^+ \qquad (5)$$

Results and Discussion

E.S.R. Spectra.—Typical spectra are given in Figures 1—3. Spectra for SnH_4^+ cations show the initial formation of two different species with large ^{117}Sn and ^{119}Sn and ^1H splittings [Figure 1(*a*)]. When SnD_4 was used the proton multiplets indicated in Figure 1(*a*) became broad singlets. We are certain that these features, together with central lines due to radicals with non-magnetic tin isotopes (^{117}Sn has $I = \frac{1}{2}$ and is 7.67% abundant whilst ^{119}Sn also with $I = \frac{1}{2}$, is 8.68% abundant) are all a property of SnH_4^+ cations. The technique used herein has been very widely used,[11-15] the processes involved being summarised in equations (1)—(4). We feel fully justified in assuming that primary cations are responsible for the spectra observed (except when unimolecular decomposition has occurred) and this is tacitly assumed in the following discussion.

Clearly there are two different structures for the SnH_4^+ cations, formed initially in comparable yields, one having two equivalent strongly-coupled hydrogen atoms with C_{2v} sym-

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

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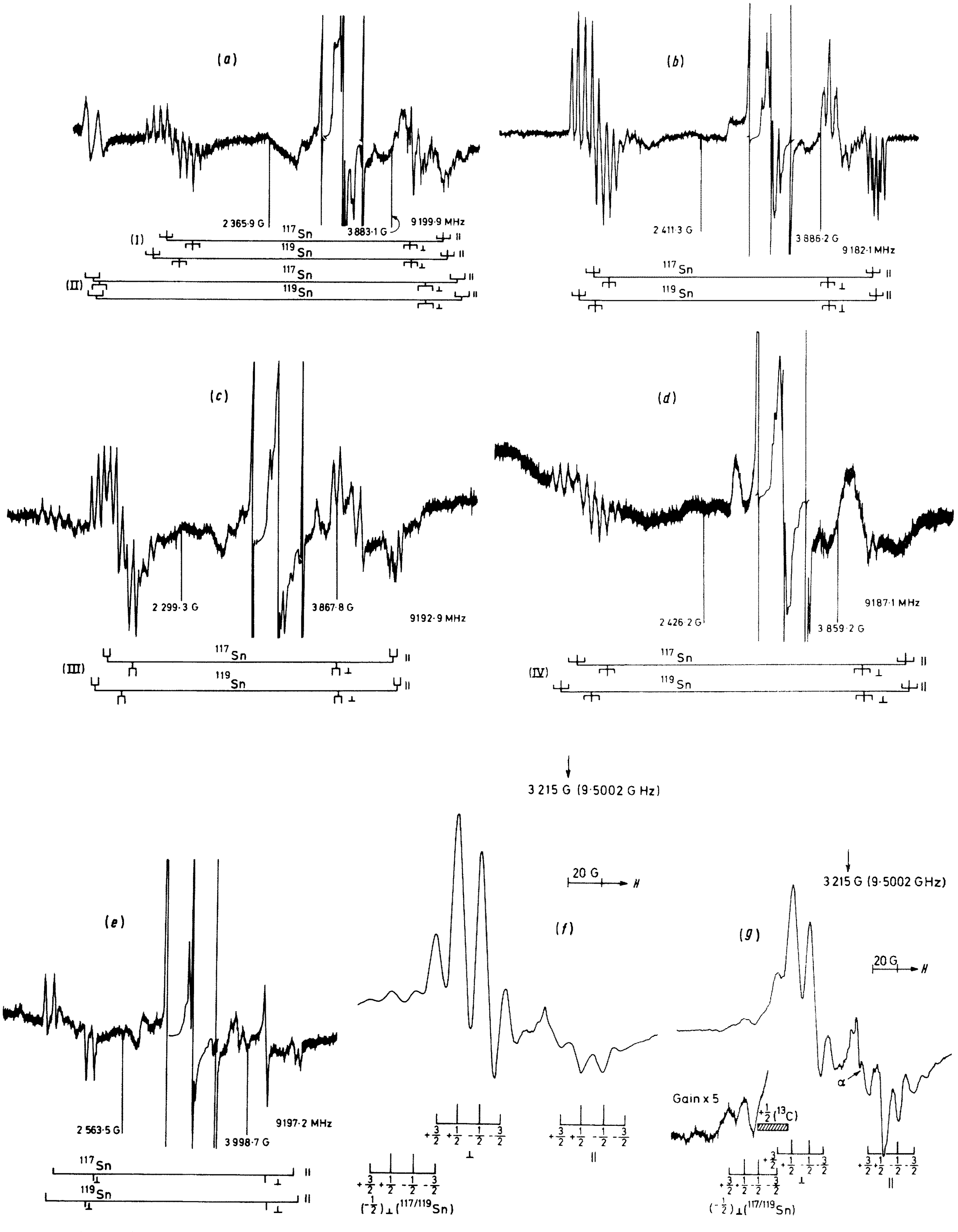
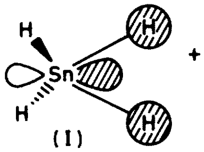


Figure 1. First derivative *X*-band e.s.r. spectra for (*a*) SnH_4, (*b*) $SnMeH_3$, (*c*,*d*) $SnMe_2H_2$, (*e*) $SnMe_3H$ and (*f*,*g*) $SnMe_4$ in $CFCl_3$ after exposure to ^{60}Co γ-rays at 77 K showing features assigned to (*a*) SnH_4^+ cations in two alternative conformations [(I) and (II)] (the low-field feature occurs at a field of 107 G), (*b*) $SnMeH_3^+$, (*c*) $SnMe_2H_2^+$ cations in their initial conformation (III), (*d*) $SnMe_2H_2^+$ after storage (IV), (*e*) $SnMe_3H^+$, (*f*) $SnMe_4^+$ and (*g*) $Me_3Sn{-}^{13}CH_3^+$ + $Me_3Sn{-}^{12}CH_3^+$ cations showing the range for the $+\frac{1}{2}$ ^{13}C component. [Lines marked α are assigned to impurity cations.] All solid solutions were in the 0.1—2.0 mol% range

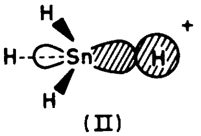
Table. E.s.r. parameters for $SnMe_xH_{4-x}$ (x = 0—4) radical cations

Radical	$g_\perp$ [a]	$g_\parallel$ [a]	Nucleus [b]	Coupling constants [c]/G $A_\perp$	$A_\parallel$	Spin densities [d] ρ_s	ρ_p	Structure (stability)
SnH_4^+ (I)	2.020	1.991	^{119}Sn	−2 370	−3 100	0.17	0.93	C_{2v}
			^{117}Sn	−2 270	−2 960	0.17	0.93	(unstable)
			H(2)	85	85	0.17		
SnH_4^+ (II)	2.016	1.984	^{119}Sn	−3 180	− 3650	0.21	0.60	C_{3v}
			^{117}Sn	−3 040	− 3490	0.21	0.60	(stable)
			H(1)	175	175	0.34		
$SnMeH_3^+$	2.027	1.976	^{119}Sn	−2 380	−3 150	0.17	0.98	C_{2v}
			^{117}Sn	−2 270	−3 010	0.17	0.98	
			H(2)	85	85	0.17		
$SnMe_2H_2^+$ (III)	2.046	1.972	^{119}Sn	−1 190	−2 700	0.14	0.90	C_{3v} [e] or C_{2v} [e]
			^{117}Sn	−1 900	−2 580	0.14	0.90	(unstable)
			H(1)	68	68	0.13		
$SnMe_2H_2^+$ (IV)	2.026	1.975	^{119}Sn	−2 380	−3 220	0.17	1.08	C_{2v} [e]
			^{117}Sn	−2 270	−3 080	0.17	1.08	(stable)
			H(2)	85	85	0.17		
$SnMe_3H^+$	2.027	1.960	^{119}Sn	−1 670	−2 420	0.12	0.95	
			^{117}Sn	−1 600	−2 310	0.12	0.95	C_{3v} or C_{2v}
$SnMe_4^+$	2.044	1.999	^{119}Sn, ^{117}Sn	−78	−210	0.01	0.17	C_{3v}
			H(3)	−13.5	−13.5	−0.03		
			^{13}C	53	120	0.067	0.70	

[a] Evaluated from intense central signals. [b] Numbers in parentheses refer to the number of equivalent strongly-coupled H atoms. [c] Evaluated from tin satellites. [d] Calculated using atomic parameters listed by J. R. Morton and K. F. Preston (*J. Magn. Reson.*, 1978, **30**, 577) and the procedure given in ref. 16. [e] Effective symmetries in terms of the SnH_2 unit.



(I)



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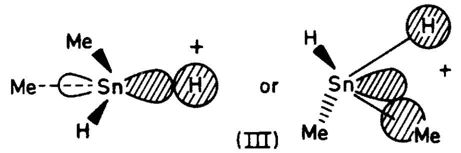

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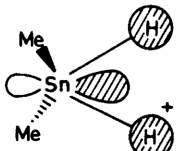


(IV)

metry, (I), the other having one very strongly-coupled hydrogen with C_{3v} symmetry, (II). On annealing, or on storage at 77 K, (I) is converted into (II), which is therefore the thermodynamically favoured structure. Although a third (D_{2h}) structure is expected to be of comparable stability, no species with four equivalent protons was detected.

The methyl-substituted derivatives (except $SnMe_4^+$) also showed very large hyperfine splittings for the tin nuclei, as shown in Figure 1(*b*)—(*e*). For $SnMeH_3^+$ one species with two equivalent strongly-coupled protons dominates, which resembles the C_{2v} SnH_4^+ cation (I). There are weak features for a species with a smaller $^{117/119}Sn$ coupling visible on the low-field side of the spectrum [Figure 1(*b*)], which have not been assigned.

For $SnMe_2H_2$ two species with strongly-coupled tin nuclei were initially detected [Figure 1(*c*)], that with the smaller splitting, (III), being slowly converted to the other, (IV), on storage at 77 K [Figure 1(*d*)]. The more stable of the two major cations [Figure 1(*d*)] again shows coupling to two equivalent protons of *ca.* 85 G. This species (IV) is closely similar to the C_{2v} SnH_4^+ species (I) (Table), and we consider an effective C_{2v} structure most probable. However, the second species (III), with the smaller tin coupling has only one strongly-coupled proton. (Assignment of features was aided by studying oriented samples, in capillary tubes, which showed intense perpendicular lines, free of the parallel components.) This species could have a pseudo-C_{2v} structure or, equally probable, an effective C_{3v} structure. However, the low symmetry suggests that something between these limiting conformations may be closer to the correct structure.

A similar ambiguity arises for the only species with a large tin coupling obtained from $SnMe_3H$ [Figure 1(*e*)]. In this case there is no resolved proton coupling either for the Sn–H or methyl protons. Again, pseudo-C_{2v} or -C_{3v} arrangements are possible, but some compromise between these limiting structures is most likely. [A feature closer to the free-spin region (α) ' grew-in ' during the annealing process: this has not yet been assigned.]

The e.s.r. spectra for $SnMe_4^+$ cations [Figure 1(*f*)], are less well defined, and it is necessary to make certain assumptions in order to extract $^{117/119}Sn$ coupling constants. The low-field ' perpendicular ' feature showing quartet splitting from one strongly-coupled set of methyl protons is clear. Close to this is a second quartet which is assigned to the $M_I = +\frac{1}{2}$ perpendicular component for $^{117/119}Sn$ species. Its proximity to the main quartet establishes that the tin isotropic coupling is now very small, in marked contrast with the other cations with C_{2v} and C_{3v} structures. High-field lines indicated in Figure 1(*f*) were persistently present in all our spectra and were lost on annealing when the major $SnMe_4^+$ features decayed. Using these, the parameters given in the Table were extracted. We also studied $SnMe_4$ labelled with ^{13}C. In our experiment only one $^{12}CH_3$ was replaced by $^{13}CH_3$ (*i.e. ca.*

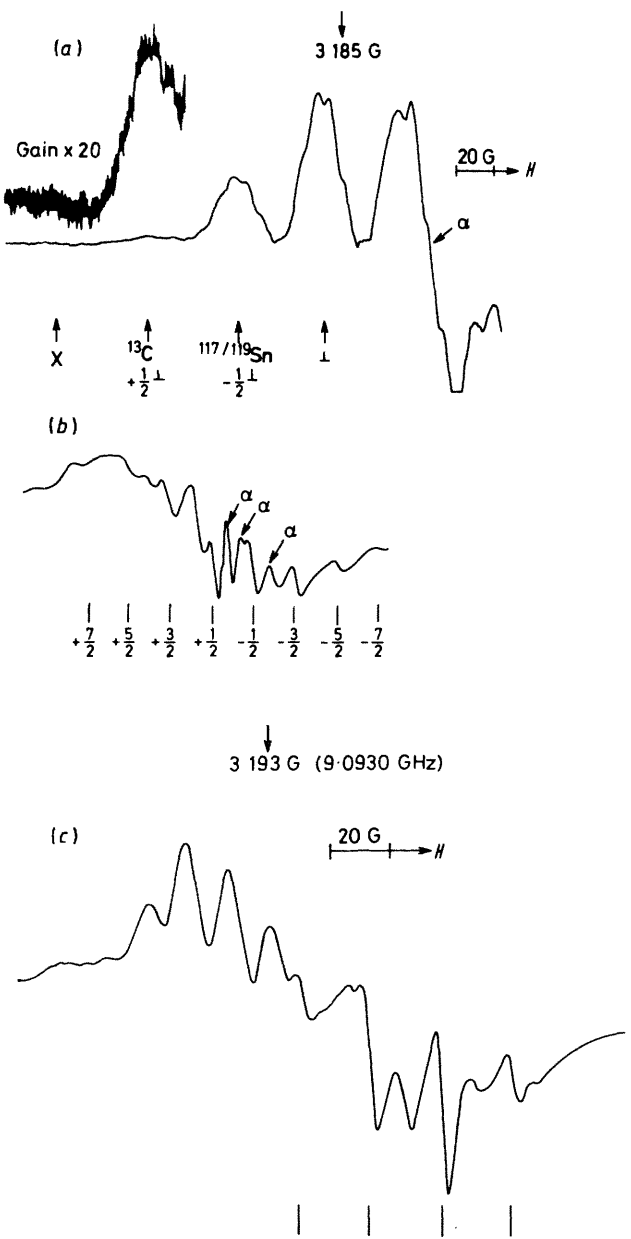


Figure 2. First derivative *X*-band e.s.r. spectra obtained using various $\mathrm{Me_3Sn{-}R}$ derivatives in $\mathrm{CFCl_3}$ at 77 K after exposure to $^{60}\mathrm{Co}$ γ-rays: (*a*) R = $\mathrm{CMe_3}$, showing $^{13}\mathrm{C}$ satellite lines for the parent cation (X shows the predicted region for a $^{13}\mathrm{C}$ feature for $\mathrm{Me_3{}^{117/119}Sn{-}^{13}CMe_3{}^+}$ and (*b*) as for (*a*), showing the reversible loss of $\mathrm{Me_3Sn{-}CMe_3{}^+}$ cations and formation of $\mathrm{{}^{\bullet}CMe_3}$ radicals during the annealing process (the $M_I = \pm\frac{9}{2}$ lines are too weak to detect), (*c*) R = Me, showing features for $\mathrm{{}^{\bullet}CH_3}$ radicals formed during the annealing process [Lines α are from extraneous radical cations]

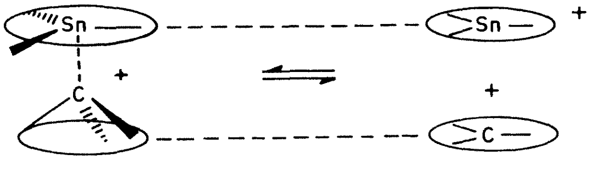
25% enrichment). The resulting e.s.r. spectrum is shown in Figure 1(*g*). Unfortunately, the $^{13}\mathrm{C}$ hyperfine splitting is small, and no well-defined $^{13}\mathrm{C}$ satellites were resolved outside the $^{117/119}\mathrm{Sn}$ satellites. Nevertheless, the low-field ($M_I = +\frac{1}{2}$) line must fall roughly in the region indicated in Figure 1(*g*), and from this knowledge we have been able to extract approximate coupling constants using the same procedure as that for the $^{117/119}\mathrm{Sn}$ features.[5]

A variety of alkyl-substituted species, $\mathrm{SnMe_3R}$ were also studied. For $\mathrm{SnMe_3Et}$, the major product at 77 K was the ethyl radical as was observed by Kochi and co-workers,[9] who also obtained isopropyl radicals directly from $\mathrm{SnMe_3Pr^i}$. In marked contrast, as was also found previously,[9] the t-butyl derivative gave no $\mathrm{{}^{\bullet}CMe_3}$ radicals at 77 K. Instead, features typical of the parent cation, $\mathrm{Me_3Sn{-}CMe_3{}^+}$ were obtained [Figure 2(*a*)]. There is definite structure from the methyl protons of the $\mathrm{{-}CMe_3}$ moiety apparent on the main perpendicular component and also on the $^{117/119}\mathrm{Sn}$ satellites. Yet another satellite multiplet exhibiting the same proton splitting was detected, which is probably due to radicals containing $^{13}\mathrm{C}$.[9] [We always obtained extra features (α) in these spectra which, unfortunately, conceal the expected parallel lines for the tin cation. These are assigned to the cations of impurities, which we have been unable to remove.]

We previously reported that trapped methyl radicals were detected by e.s.r. spectroscopy during the process of annealing samples containing $\mathrm{SnMe_4{}^+}$. This discovery was seriously called into question by Walther *et al.*,[9] who state categorically that methyl radicals are not detectable on annealing. Since it is unusual to make such a clear criticism without being on sure ground, we decided to repeat this work. As can be seen in Figure 2(*c*), well defined features unambiguously assignable to $\mathrm{{}^{\bullet}CH_3}$ radicals do indeed appear on annealing. We are unable to explain this difference, but are fully satisfied with our positive identification.

Walther *et al.*[9] also failed to detect $\mathrm{{}^{\bullet}CMe_3}$ radicals on annealing samples containing $\mathrm{Me_3Sn{-}CMe_3{}^+}$ cations. In our view, broad features assignable to $\mathrm{{}^{\bullet}CMe_3}$ ' grow-in ' reversibly on annealing. At the same time, the e.s.r. features assigned to the cation are lost reversibly [Figure 2(*b*)]. This cycle was repeated with gradual loss in intensity. This reversible change occurred at temperatures (*ca.* 130 K) at which there was no major loss of signal from $\mathrm{SnMe_4{}^+}$ cations, and indeed, there was no reversible loss of cation signal for $\mathrm{SnMe_4{}^+}$. This result establishes that the loss of the $\mathrm{Me_3Sn{-}CMe_3{}^+}$ signal is unlikely to be due to the onset of extensive librational or rotational motion, since this would surely be more favourable for $\mathrm{SnMe_4{}^+}$.

We are therefore led to the postulate that there is a reversible thermolysis of the Sn–C bond. We show below that the $\mathrm{{-}CMe_3}$ unit in the cation is pyramidal, so, in effect, our postulate is of a reversible flattening of the $\mathrm{{-}CMe_3}$ unit, without any major separation of the two halves of the molecule, as shown in equation (6). From the temperature corresponding to loss of *ca.* 50% of the cation signal (*ca.* 130 K), we obtain an approximate value of the Sn–C bond strength of *ca.* 6 kcal mol^{-1} (*ca.* 25.1 kJ mol^{-1}).



(6)

We have also studied various chloro-derivatives. $\mathrm{SnMe_3Cl}$ gave e.s.r. features similar to those for $\mathrm{SnMe_4{}^+}$ cations, but with a reduced quartet splitting (12 G) [Figure 3(*a*)]. As with $\mathrm{SnMe_4{}^+}$ cations, methyl radicals were readily formed on annealing. We were unable to detect any $\mathrm{\dot{C}l{-}SnMe_3{}^+}$ type centre with electron loss from the chlorine π level.

A major radiation product from $\mathrm{SnMe_2Cl_2}$ and $\mathrm{SnMeCl_3}$ was methyl [Figure 3(*b*)]. Again, no features characteristic of electron loss from chlorine were obtained, but broad central features, possibly assignable to the parent cations, were observed for $\mathrm{SnMeCl_3}$, in the same general regions as those for

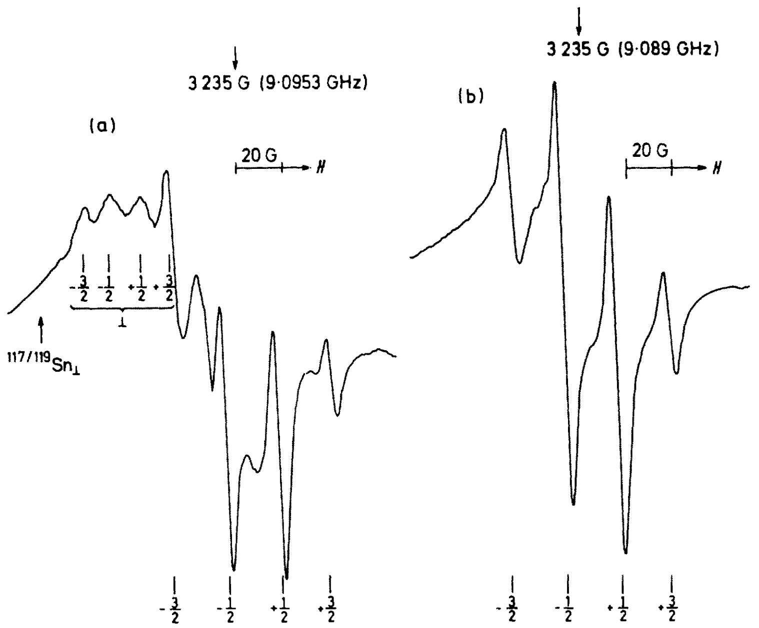


Figure 3. First derivative *X*-band e.s.r. spectra for (*a*) $SnMe_3Cl$ and (*b*) $SnMe_2Cl_2$ in $CFCl_3$ after exposure to ^{60}Co γ-rays at 77 K, showing features assigned to the parent cation, $SnMe_3Cl^+$, and for $SnMe_2Cl_2$, the formation of methyl radicals

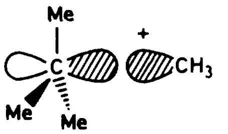
$SnMe_3Cl^+$ cations. Irradiation of $SnMe_2Cl_2$ solutions at 4 K gave no methyl signals, but these ' grew-in ' strongly in the range 40—70 K.

Finally a few other stannanes were arbitrarily selected for study. $SnPh_3Cl$ gave a cation which is thought to have its semi-occupied molecular orbital (s.o.m.o.) centred on one of the benzene rings. This will be considered further in a forthcoming report on substituted aromatic radical cations. $SnBu^n_3(OMe)$ gave butyl radicals together with a species closely similar to the $SnMe_4^+$ cation with two equivalent protons [$A(^1H) = 14$ G] showing that the s.o.m.o. is the $Sn{-}CH_2CH_2CH_2CH_3$ σ bond. Spectra for $SnBu^n_3H^+$ cations were too poorly defined for analysis, whilst that for $SnBu^n_3(O_2CMe)$ was dominated by features due to n-butyl radicals. These results will not be considered further.

Structure.—Stannane and $SnMe_4$ have T_d symmetry, and electron loss is expected to occur from the triply-degenerate t_2 orbitals. There are two types of distortion that satisfy the Jahn–Teller theorem, namely to D_{2d} or C_{3v} symmetry. However, in our view, this restriction to D_{2d} and C_{3v} symmetry only really applies to the initial vibrational pathway leading from T_d to lower symmetry. Ultimately, the cations will select any reduced symmetry that removes orbital degeneracy and gives an energy minimum. Thus the appearance of species with C_{2v} symmetry is also expected. A C_{3v} distortion fits the results for SnH_4^+ (I), for $SnMe_4^+$, and for CMe_4^+. This involves stretching of a unique Sn–ligand bond leading to a s.o.m.o. (8*a* orbital for $SnMe_4$) which is, essentially, one of the Sn–ligand σ orbitals, as indicated in (II). For $H_3Sn{-}H^+$ the SnH_3 unit stays strongly pyramidal ($p:s$ ratio *ca.* 2.9), the spin density being greater on the SnH_3 unit than on hydrogen. We calculate from the coupling constants *ca.* 80% on tin and *ca.* 34% on hydrogen. These results were obtained using the atomic parameters listed by Morton and Preston (Table). Had the alternative set of atomic parameters been used,[16] the total spin density would have been even greater than the value of 114% obtained. Such high values (Table) are frequently found for heavy-atom radicals, and probably reflect the inadequacy of the atomic data and of this simplified type of calculation However, it is also possible that there is a small reduction in the effective radius of the 1*s* hydrogen orbitals, induced by the positive charge, so that the estimated spin densities become too large. Such changes are far more important for hydrogen, with its single orbital bearing all the effect, than for other atoms.

This C_{3v} distortion is not observed for $SnMeH_3^+$ but is postulated for $SnMe_4^+$. There is, however, a major difference between the two sets of data, since, for $H_3Sn{-}H^+$ the tin orbital is *ca.* sp^3 hybridised, whilst for $Me_3Sn{-}Me^+$ it is almost pure 5*p*. The spin density has shifted concomitantly, away from tin. We previously argued from the magnitude of the ^1H hyperfine coupling that the methyl group must also have undergone extensive flattening. Thus from the tin coupling, the spin density on tin must be *ca.* 18%, with presumably slight delocalisation onto the three equivalent methyl groups. This gives a value of *ca.* 75% on the unique methyl. A planar methyl group would then give a proton coupling of *ca.* (−) 16 G. Hence the observed coupling of *ca.* 13.5 G, which is almost certainly negative, suggests near planarity for the $-CH_3$ unit, since the magnitude of the coupling falls on bending. From our rough estimate of the ^{13}C coupling we obtain *ca.* 70% $2p_z$ occupancy (Table) with only *ca.* 6.7% 2*s* occupancy, suggesting that the group is indeed nearly planar.

The results for $Me_3Sn{-}CMe_3^+$ make an interesting contrast, and help to establish why this cation is more reluctant to yield $^\bullet CMe_3$ radicals than the ethyl and isopropyl derivatives. In this case, the ^1H coupling of *ca.* 7.6 G is considerably reduced from the normal value of *ca.* (+) 22 G for $^\bullet CMe_3$. If the unit were planar, this would give a spin density of only 34% which is certainly too low. As with methyl, the magnitude of the proton coupling falls on bending, so more extensive bending is indicated in this case. Unfortunately, there is some ambiguity over the interpretation of the ^{13}C features. The analysis given by Kochi and co-workers[9] gives $A_\perp(^{13}C) = 187$ G. The small increase in the tin coupling (Table) and in $\Delta g_\perp$ relative to $SnMe_4^+$ suggests that the spin density on tin is slightly increased, a reasonable value being *ca.* 25—30%. If



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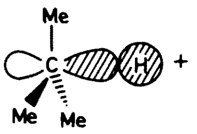
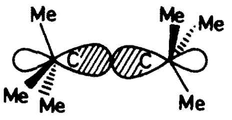


(VI)

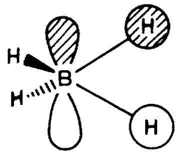
we assume $a_p^2 \geqslant 0.5$ for carbon, we calculate from their $A_\perp$ value, a value of $\geqslant$202 G for A_{iso} which gives $\geqslant$18% *s* character, with a total spin density $\geqslant$68% and a *p* : *s* ratio $\leqslant$2.8. This result is possible, but the relaxation of the $SnMe_3$– moiety to almost complete planarity with virtually no relaxation for the $^{-}CMe_3$ unit seems to us to be unlikely.

An alternative is that the ^{13}C multiplet shown in Figure 2(*b*) is for cations containing ^{117}Sn and ^{119}Sn isotopes rather than non-magnetic isotopes. [This requires that the ^{13}C features for the central lines fall under the main $^{117/119}Sn$ satellite lines. The previous theory requires the presence of another satellite due to (^{13}C + $^{117/119}Sn$) outside the main features. We have searched for such features, but have found nothing.] The alternative requires that this line (for ^{13}C + $^{117/119}Sn$) is fortuitously almost isotropic, in order to account for its high intensity. Just such a situation was recently described for $[PtH(CN)_4]^{2-}$ complex ions.[17] In that case, $A_\perp(^{13}C) \approx 90$ G, and $A_\parallel(^{13}C)$ must be close to 140 G to provide such an intense feature. This gives $A_{iso} \approx 107$ G corresponding to *ca.* 10% 2*s* character and $2B \approx 33$ G, corresponding to *ca.* 54% 2*p* character. In this case, the total spin density is 64%, and the *p* : *s* ratio is 5.4, suggesting considerable flattening. In view of our inability to find the extra ^{13}C feature required by the interpretation of Walther *et al.*,[9] and these structural implications, we favour the alternative interpretation given herein.

The most marked difference between SnH_4^+ (C_{3v}) and $SnMe_4^+$ is the complete loss of 5*s* character in the s.o.m.o. for the latter. We suggest that the difference can be understood in terms of a greater stretching of the unique Sn–C bond relative to the Sn–H bond. Moving along the bond-breaking coordinate, both the $-SnL_3$ (L = H or Me) unit and, for $SnMe_4^+$, the $-CH_3$ unit must move towards planarity. Since $SnMe_3^+$ cations are more stable than SnH_3^+ this is understandable. However, $^{\bullet}CMe_3$ radicals are more stable than $^{\bullet}C_2H_5$ radicals, so it seems surprising that the dissociative process has proceeded less extensively in this case. This is almost certainly a steric effect. As the two units begin to flatten there will be strong methyl-group repulsions which will oppose the flattening. Hence the bond-stretching process, which would relieve the pressure, cannot occur so readily since, as shown for $Me_3Sn{-}Me^+$ cations it is dependent upon, and concomitant with the move towards planarity. An argument of this sort has also been used by Kochi and co-workers [9] to explain their results. It is interesting to compare these results with those for the effectively C_{3v} cations $Me_3C{-}Me^+$, $Me_3C{-}H^+$,[18] and $Me_3C{-}CMe_3^+$.[18,19] According to the interpretation of the e.s.r. parameters offered by Iwasaki and co-workers,[18] and to their INDO m.o. calculations, the CMe_3 groups in (V) and (VI) are almost planar [as we had originally guessed might be the case for the Me_3C– groups in $Me_3C{-}CMe_3^+$ cations [19]]. However, for the $Me_3C{-}CMe_3^+$ cation (VII) their results indicate a smaller tendency towards planarity, and this is also supported by their calculations. Once again, it seems that steric interactions oppose the movement towards planarity, as was originally suggested by Wang and Williams.[20] It is noteworthy that the experimental and calculated proton coupling for the unique methyl group in (III) are close to zero. This shows that there is little or no flattening of this group and supports our contention that the large coupling for the methyl protons of $Me_3Sn{-}Me^+$ cations must be negative and indicative of a considerably flattened unit.



(VII)



(VIII)

The species with effective C_{2v} symmetry all appear to have the structure indicated in (I). This is the $2a_1$ structure postulated for the $SiMe_4^+$ cation, which has two strongly-coupled sets of methyl protons and two weakly-coupled sets.[21] In contrast, our results and calculations for the BH_4 radical support the alternative $^2B_1$ structure indicated in (VIII).[22] Our reason for insisting on the a_1 orbital for SnH_4^+ (I) and the other C_{2v} species is the large 5*s* admixture indicated by the magnitude of the isotropic hyperfine coupling. This is the only one of the three orbitals derived from the t_2 set that can be hybridised in this way. In the absence of ^{29}Si coupling for $SiMe_4^+$ cations, we cannot make a clear distinction between these alternative s.o.m.o.s. We have studied the e.s.r. spectrum for $Si(CD_3)_4^+$ cations with great care, and conclude that the ^{29}Si coupling must be small, since it seems that the expected ^{29}Si features were hidden in the wings of the main line. In that case, it is probable that the structure is similar to that postulated for BH_4. On the other hand, it must be borne in mind that the extent of *s*-orbital admixture may increase on going down the Periodic Table, just as it does in the series $^{\bullet}CH_3$, $^{\bullet}SiH_3$, and $^{\bullet}SnH_3$.[16]

Unfortunately we cannot be sure of the structures adopted by $SnMe_3H^+$ and the more stable form of $SnMe_2H_2^+$ (III). The results given in the Table do not accord well with any of the expected trends. Thus, for species (III), it is tempting to select the effective C_{3v} limiting structure, $Me_2HSn{-}H^+$. However, because of the expected flattening of the Me_2HSn– unit, with an increase in the 5*p*-orbital content, we expect an increase in the spin density on the unique hydrogen, relative to $H_3Sn{-}H^+$, rather than the marked decrease observed. Good m.o. calculations are required to give a proper understanding of the structure for these low-symmetry species.

The $Me_3Sn{-}SnMe_3^+$ *Cation*.—Our results for this ion suggest that, in contrast with the $Me_3C{-}CMe_3^+$ ion, the two $-SnMe_3$ units must be almost planar. Clearly, in this case with the two large tin atoms, steric repulsions between the six methyl groups will be far less significant than in the case of $Me_3Sn{-}CMe_3^+$ cations. Again we have looked for ^{29}Si satellites in the spectrum for $Me_3Si{-}SiMe_3^+$ ions to no avail, so it is impossible to gauge the extent of flattening experienced by the $-SiMe_3$ units. Walther *et al.*[9] have shown that the tin coupling in the cation $Me_3Sn{-}GeMe_3^+$ is also small which suggests that the Me_3Sn group is effectively planar in this ion also.

Comparison with Corresponding Anions.—The anion SnH_4^- has been formed by electron addition to stannane in neopentane [23] and in tetramethylsilane.[24] Evidence for the formation of $SnMe_4^-$ was obtained in studies of the irradiated pure material,[25] and also for all the methylated stannane radical anions for solutions in tetramethylsilane.[24] In all cases, a trigonal-bipyramidal structure is postulated, with two strongly-coupled protons in the axial sites for SnH_4^-, $SnMeH_3^-$, and $SnMe_2H_2^-$, and one methyl and one proton in these sites for $SnMe_3H^-$. The proton coupling constants were almost isotropic , in the range 127—140 G. Tin coupling constants in the region of 2 000 G show that, in all cases, very extensive *s–p* mixing occurred for the tin orbitals. Thus the C_{2v} structures for the cations have e.s.r. spectra which are qualitatively very similar to those for the corresponding anions. However, for the cations, it is the two ' equatorial ' ligands which are close together, that exhibit strong hyperfine coupling, whereas for the anions it is the two ' axial ' ligands which couple strongly.

Aspects of Mechanism.—The most significant aspect of these results is the extreme readiness with which the parent cations dissociate to give alkyl radicals. Indeed, it is remarkable that for $SnMe_3Et^+$ and $SnMe_3Pr^{i+}$ this reaction is fast at 77 K. These results nicely confirm conclusions based on liquid-phase mechanistic studies.[10]

The relative stability of the t-butyl derivative links with its modified structure, as stressed above. Because of steric resistance to the progress of the pyramidal $-CMe_3$ unit towards planarity on going along the minimum-energy dissociative pathway, there is a greater barrier to dissociation. However, the bond is still extremely weak. The remarkable reversibility of the dissociation process leads to a misleading idea of the strength of the Sn–C bond. We suggest that this is exaggerated by the inability of the $SnMe_3^+$ and $\cdot CMe_3$ fragments to separate, thereby facilitating the effectively unimolecular back-reaction.

When methyl groups are replaced by chlorine the loss of methyl is facilitated, presumably because of the ability of the chlorine ligands to form π bonds with tin, thereby delocalising the positive charge. It seems that this is more effective than hyperconjugative delocalisation by the methyl substituents.

Experimental

Stannane was prepared by the reduction of tin(IV) chloride with lithium aluminium hydride in anhydrous diethyl ether and purified by repeated passage through a trap cooled to −112 °C.[26] [$^2H_4$]Stannane was prepared similarly, using lithium aluminium deuteride. Methylstannane was obtained by the method of Flitcroft and Kaesz.[27] Sodium tetrahydroborate was added to a solution of $K[SnCH_3(O_2)]$ prepared according to Pfeiffer and Lehnardt,[28] which was then added to a well stirred solution of 6 mol dm^{-3} hydrochloric acid. The crude product of methylstannane was fractionated on a vacuum line. Dimethyl- and trimethyl-stannane were prepared by the reduction of the corresponding bromides with lithium aluminium hydride.[29] Dibromodimethylstannane was prepared by direct reaction of tin metal and methyl bromide at 395 °C [30] and bromotrimethylstannane was formed by reaction between bromine and tetramethylstannane.[31] $Sn^{13}CH_3(CH_3)_3$ was prepared from $^{13}CH_3I$ and $SnMe_3Cl$ *via* the Grignard reagent. $^{13}CH_3I$ was 99.9% from MSD Isotopes. $SnMe_3Et$ was similarly prepared suing C_2H_5I. $SnMe_3Bu^t$ was prepared from $LiBu^t$ and $SnMe_3Cl$ by a standard procedure. Other organotin compounds were kindly supplied in a pure state by Professor A. G. Davies.

Dilute solutions in purified, degassed $CFCl_3$ were frozen either as small beads, or in quartz capillary tubes, and irradiated with ^{60}Co γ-rays at 77 K. E.s.r. spectra were measured on Varian (Leicester) or JEOL (Hiroshima) spectrometers at 77 K. Samples were both pulse-annealed, with recooling to 77 K for measurement, or continuously annealed in a variable-temperature insert.

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